ORGANIC REACTIONS IN THE GAS PHASE

Part I: Decomposition of Isomeric Cis 6, 7-dimethyl-2, 3-diazabicyclo[3.2.0]hept-2-enes in the Gas Phase

Part II: The Wall-less Reactor

Part III: Thermal Isomerization of Cyclopropenes

Thesis by

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ABSTRACT

Part I: Decomposition of Isomeric Cis-6, 7-dimethyl-2, 3-diazabicyclo[3.2.0]hept-2-enes in the Gas Phase

The thermal decomposition of the isomeric cis 6, 7-dimethyl-2, 3-diazabicyclo[3.2.0]hept-2-enes was studied. In order to account for the products observed, dual pathways for the decomposition are proposed. The formation of isomeric cis 2, 3-dimethyl-bicyclo[2.1.0] pentanes is explained by a mechanism involving a diradical intermediate. The formation of 2, 3-dimethylpenta-1, 4-dienes is best explained by a stereospecific retro-1, 3-dipolar cleavage to an acyclic diazo compound which loses nitrogen to form a carbene. The absence of a thermal "Di-π-methane" pathway is indicated from the products.

Part II: The Wall-less Reactor

A wall-less reactor was constructed based on one designed previously at Kent State. The reactor was modified and used to study the unimolecular decomposition of strained hydrocarbons. Cyclopropane was found to isomerize to propylene with a rate law of log k = 14.6 - 65.1 kcal per mole/θ over the temperature range of 936 to 1026°K. The wall-less reactor was also used to study the isomeri-

zation of 3,3-dimethylcyclopropene (see abstract of Part III).

Part III: Thermal Isomerization of Cyclopropenes

The thermal rearrangement of 3,3-dimethylcyclopropene (6) was studied in the wall-less reactor over a temperature range of 608 to 668°K. The rate law for the isomerization was found to be $\log k = 12.6 - 36.2$ kcal per mole/θ. 6 isomerized to 86.2% 3-methyl-1-butyne, 12.9% 1-methyl-1,3-butadiene and 0.9% 3-methyl-1,2-butadiene. The data were in accord with published results of the isomerization of 6 in a static thermal reactor.

The thermal rearrangement of 1-methylcyclopropene (14) was investigated by entering the energy surface for the reaction by two routes: thermal isomerization of the cyclopropene and pyrolysis of a vinylcarbene precursor, 3-methyl-3-vinyldiazirine (12). The acyclic C_4H_6 products from both reactions are identical, however the proportions vary greatly. Greater than 99% of the product from the diazirine is the cyclopropene, and the remainder of the products is 1,3-butadiene, 2-butyne and 1,2-butadiene in the ratio of 1:0.6:0.2, respectively. The products from the isomerization of 1-methylcyclopropene are the same but in the ratio of 5:93:2, respectively.

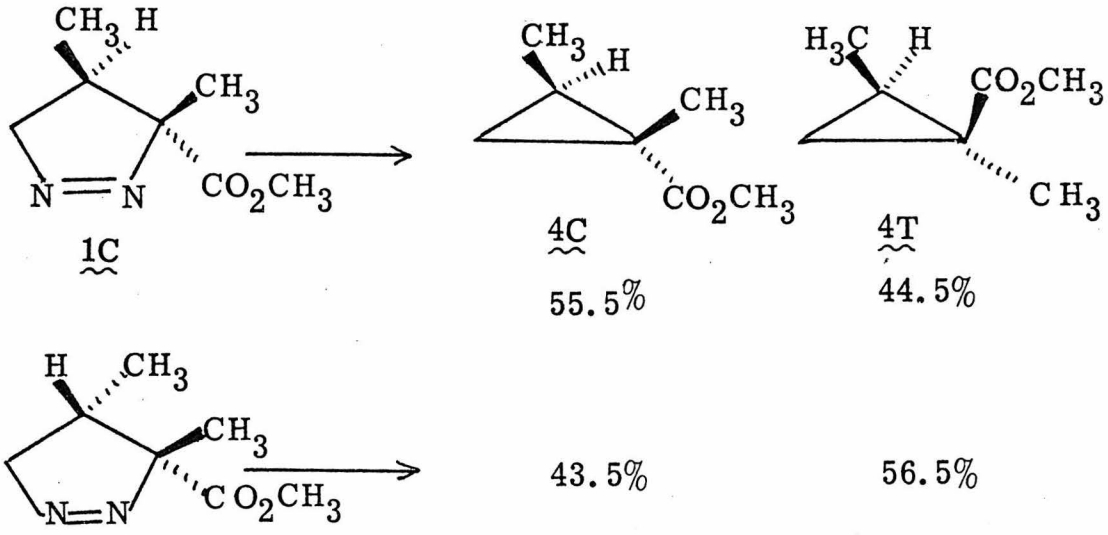
From the data it is concluded that two intermediates exist for the isomerization, a planar vinylcarbene and a 90° rotamer, designated a diradical.

TABLE OF CONTENTS

INTRODUCTION

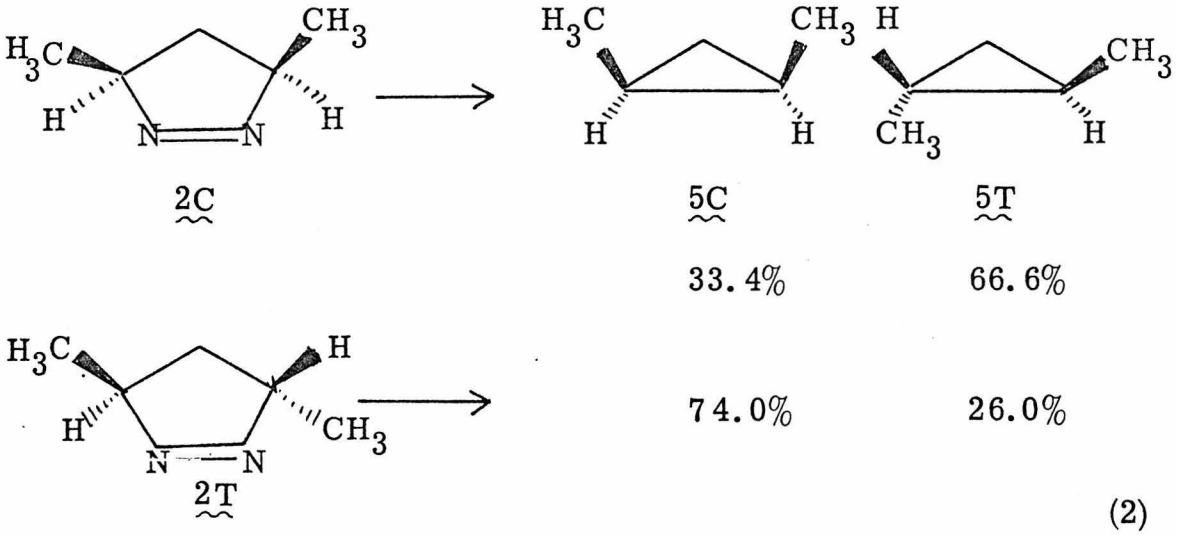
History of Pyrazoline Decompositions

The first report of a pyrazoline decomposing to give cyclopropane products dates back to 1888.[1] From 1932[2] to 1960,[3] it was generally accepted that the stereochemistry of the pyrazoline was retained in the major cyclopropane decomposition product. All experimental studies were in accord with this postulate. Then in 1962, van Auken and Rinehart found an isomeric pair of pyrazolines (1C) and (1T), which gave cyclopropane products exhibiting only a slight preference for retaining the stereochemistry of the pyrazoline precursor.[4]



(1)

From 1962 to the present, the stereochemistry of the thermal decompositions of pyrazolines have received a great deal of study. Much of this interest was prompted by the results of experiments conducted by Crawford's research group starting in 1965.[5] It was found that pyrazolines alkylated on the C-3 and C-5 carbon atoms decomposed thermally to give cyclopropane products with inverted stereochemistry at the two labeled carbons.[5b, c]

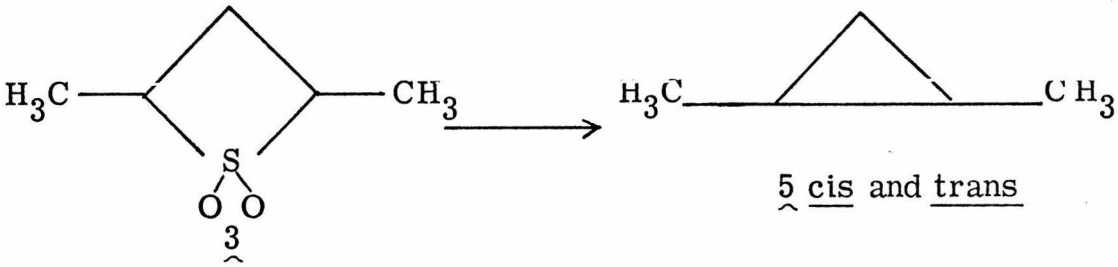


(2)

The cis 1-pyrazoline (2C) gave mainly trans cyclopropane (5T), while the trans 1-pyrazoline gave predominately cis cyclopropane (5C). See Equation 2.

A list of 1-pyrazolines and their cyclopropane thermal decomposition products is shown in Table I. The cyclopropane products are divided into two categories. Those in which the stereochemistry of the precursor is retained at the C-3 and C-5 carbon atoms and those in which it is inverted. A large number of thermal gas phase pyrazoline decompositions give as the major product the cyclopropane with the inverted stereochemistry at C-3 and C-5. It is clear from this data, that stereochemical results are dependent upon degree and types of substitution.

This phenomenon of forming cyclopropanes with a net inversion of stereochemistry is not limited to pyrazolines. Other compounds which extrude stable molecules such as N_2 or SO_2 give similar results, for example, the sulfone 3.[14] The results of studies of this general



(3)

class of reactions are given in Table II. Selectivity shows a general decrease with increasing temperature.

Several possible theories were advanced to explain these results. These are discussed below in light of experimental evidence and recent theoretical calculations.

Table I: Stereochemistry of Pyrazoline Thermolyses in Gas Phase

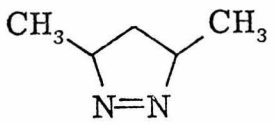
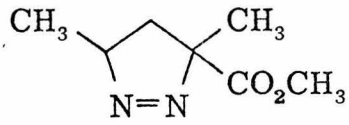
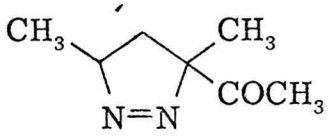
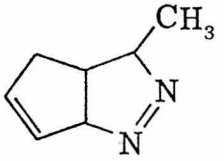
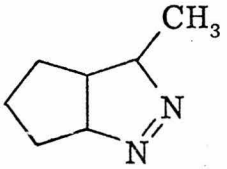
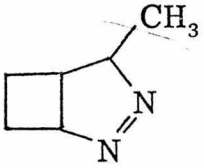
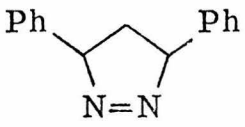
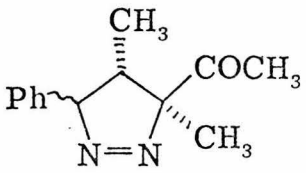
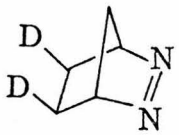
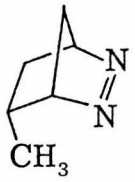
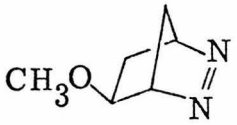
Compounds		Cyclopropane products[a] Retained	Inverted	Ref.
	trans	26[d]	74	5b, c, h
	cis	33	67	5b, c, h
	cis methyls	26	74	7
	trans	17	83	7
	cis methyls	36	64	6
	trans	22	78	6
	exo	38	62	5i
	exo	10	90	8a
	endo	24	76	8a
	exo	21	79	8c
	endo	37	63	8c
	trans[c]	91	9	9

Table I (Cont'd)

	trans [c]	99	1	10
	cis [c]	55	29, 16 [b]	10
	exo	25	75 [b]	11a
	endo	43	57 [b]	11a
	exo	63	37 [b]	12b
	endo	6	94 [b]	12b
	endo	41	59 [b]	13

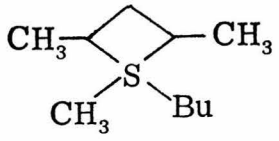
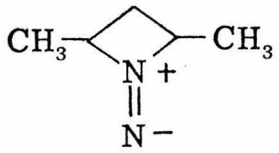
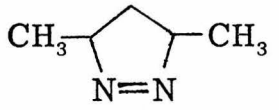
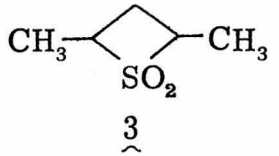
[a] Normalized to 100%.

[b] Doubly inverted.

[c] Injection port pyrolysis may not be occurring in the gas phase.

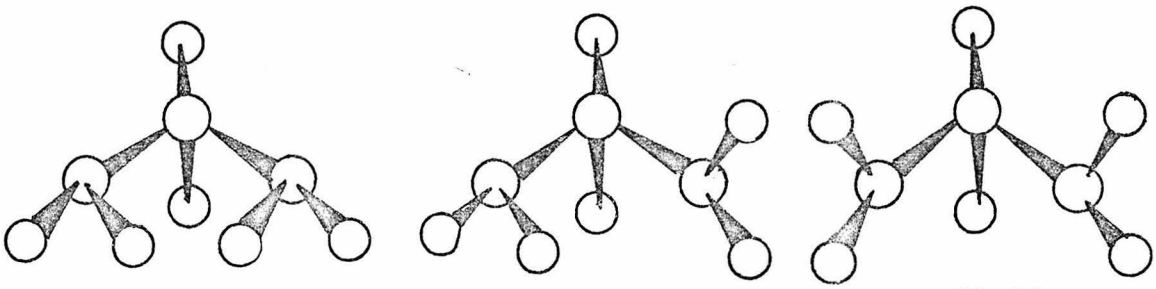
[d] 62% doubly inverted.

Table II: Stereochemistry of Cyclopropanes Formed in Extrusion Reactions

Compound		Temp. °C conditions	% cis	% trans	% Other	Reference
 7	cis	-78	2.1	22.9	~75	14
	trans	-78 liquid phase	22.2	2.8	~75	14
 6	cis	58	15.6	84.4	<0.3	15
	trans	58 liquid phase	68.5	31.5	<0.3	15
 2T	cis	220	33.2	66.1	0.7	5b, c
	trans	220 gas phase	72.6	25.4	2.0	5b, c
 3	cis	350	33.8	40.1	26.1	14
	trans	350 gas phase	39.2	32.9	27.9	14

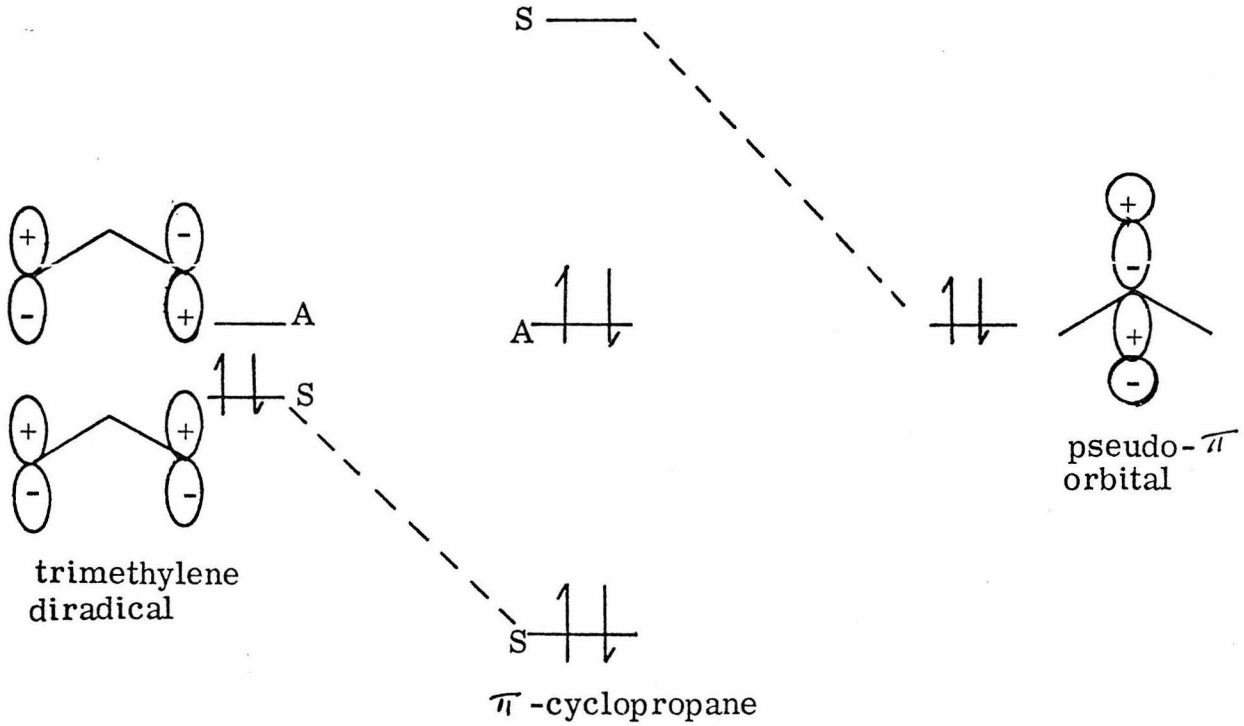
A π-Cyclopropane Intermediate in the Decomposition of Pyrazolines

1. π-Cyclopropane. In 1968, Hoffmann carried out extended Hückel calculations on the trimethylene diradical, the suspected intermediate in cyclopropane isomerizations.[16] He investigated the total energy of this system with respect to the three most important degrees of freedom of the molecule; the central C—C–C bond angle and the rotations of the terminal methylene groups out of the plane defined by the three carbon atoms. These calculations led to the prediction that there exists an energy minimum for the trimethylene diradical at what Hoffmann called the 0, 0 π-cyclopropane. The central bond angle is calculated to be 125°; the diradical lobes are predicted to be perpendicular to the plane defined by the three carbon atoms. Furthermore, Hoffmann stated that the 0, 0 conformer was at least 8 kcal per mole more stable than the 90, 90 conformer.



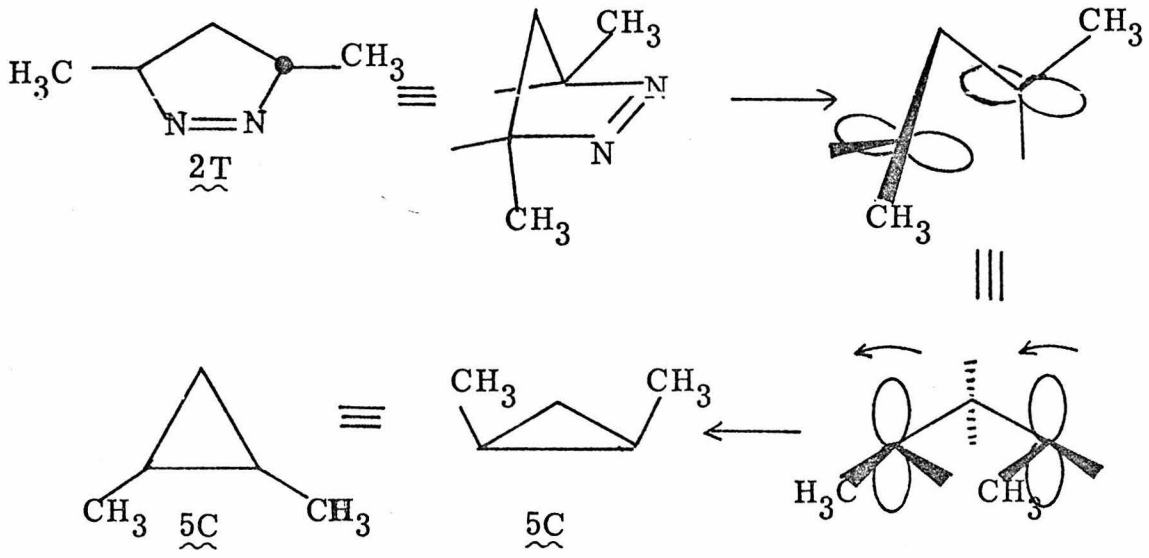
0, 0 0, 90 90, 90

It was also found from the calculations that the easiest passage to and from the ground-state cyclopropane is via a conrotatory motion of the terminal carbons.[17] The electrocyclic rule (disrotatory for a 4n + 2 electron system) predicts disrotatory closure if the system is treated as a simple two-electron problem. However, the C–H orbitals of the C-2 carbon atom are strongly mixed into the symmetric orbital of the pseudo-π system, and the mixing results in an increase in energy of the symmetric orbital, leaving the non-interacting anti-symmetric orbital as the highest occupied molecular orbital of the system.



Because of this effect, the π-cyclopropane resembles an allylic anion (4 π electrons). The ground state of the cyclopropane and the π-cyclopropane now correlate in the C_2 mode. Therefore, a conrotatory ring closure is predicted.

The pyrazoline precursor of π-cyclopropane has a C-C-C carbon bond angle of 109°, making the predicted intermediate readily accessible. The one net inversion of the cyclopropane products formed on the pyrazoline decompositions is explained by conrotatory closure. Using 2T as an example, it was proposed that loss of nitrogen from the configuration of the pyrazoline shown in Scheme I, leads directly to the π-cyclopropane which closes as predicted to give cis-1, 2-dimethylcyclopropane.



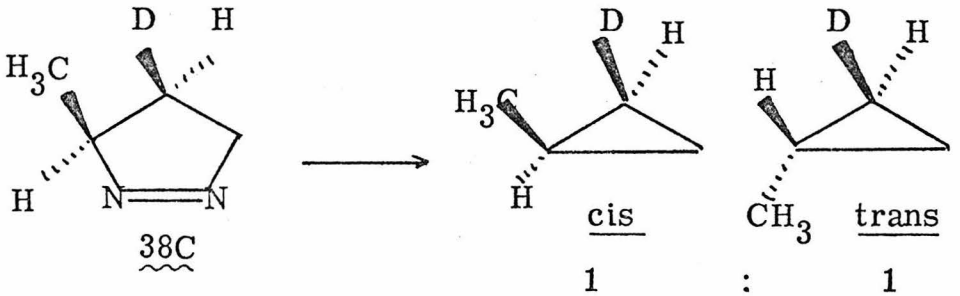
Scheme I

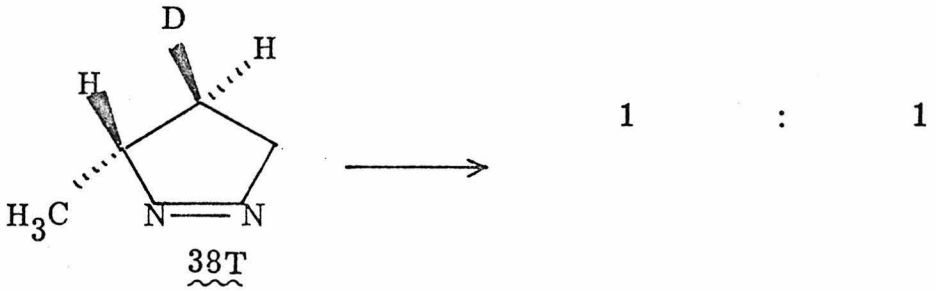
It should be pointed out, that the loss of nitrogen can be concerted or else involve fast sequential C–N bond breaking without bond rotations to give the intermediate shown. Note also that the π-cyclopropane has a plane of symmetry.

Although the cis cyclopropane is the major product from the trans pyrazoline, some trans cyclopropane is also formed. This is either because the tendency for conrotatory rotation to form the ring is not absolute and the minor product arises from a disrotatory closure, or else a second mechanism, which is only slightly less favored, is competing with π-cyclopropane formation and gives the products in a random ratio (a freely rotating 1,3 diradical, for example).

2. Evidence for π-cyclopropane. The extrusion reactions listed in Table II, all of which give the singly inverted cyclopropane as the major cyclopropane product, have been postulated as proceeding through a π-cyclopropane intermediate. It seems unlikely that this data can be explained by a mechanism involving sequential carbon-heteroatom bond cleavage followed by the necessary rotations, given the varied nature of the extruded molecules. A common intermediate free of nitrogen or sulfur dioxide can best explain these data.

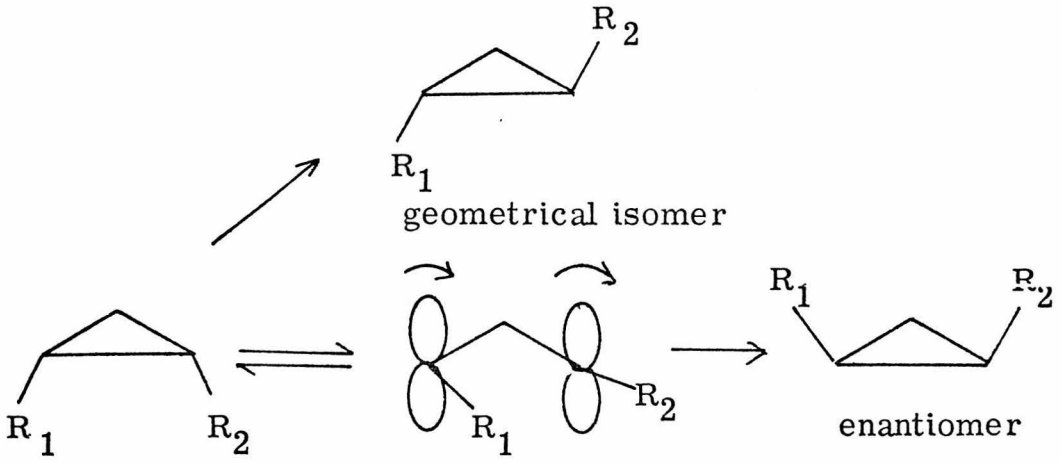
The observation that both cis and trans 4-deuterio-3-methyl-1-pyrazoline (38C and 38T) decompose thermally to an equimolar mixture of cis and trans 1-deuterio-2-methylcyclopropane seems to imply the intermediacy of a π-cyclopropane which has the required plane of symmetry.



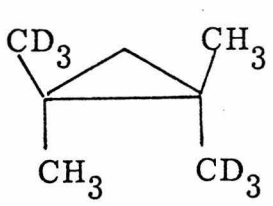


A freely rotating trimethylene diradical could explain these results, but not the single inversion observed in C-3 and C-5 alkyl labeled pyrazolines.

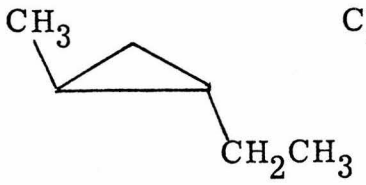
3. Evidence against π-cyclopropane. If π-cyclopropane closes in a conrotatory fashion to give a cyclopropane then, by the principle of microscopic reversibility, a cyclopropane should open in a conrotatory manner. Therefore an optically active cyclopropane should open to π-cyclopropane (which has a plane of symmetry) which can close in either of two directions; it can give back the starting cyclopropane or its mirror image. Geometrical isomerization can only occur through a disrotatory ring closure, a less favored process. Thus, it is predicted that racemization will be much faster than the geometrical isomerization of an optically active cyclopropane.



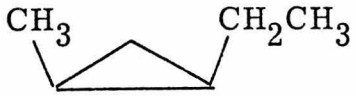
This type of experiment has been carried out by Bergman (compound 39)[50] and Berson (compound 40).[49] In both cases isomerization was competitive with racemization. No evidence for a π-cyclopropane was found.



40

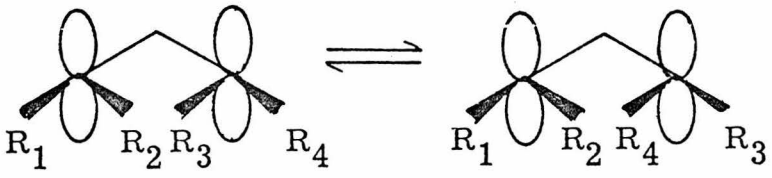


39T



39C

Hoffmann had predicted that the conrotation from the π-cyclopropane to the cyclopropane should proceed over a barrier of at most 1 kcal per mole, whereas interconversion of π-cyclopropane structures (41 ⇌ 42), a process which leads to geometrical isomerization by



41 ⇌ 42

rotation of a single methylene group through the destabilized 0, 90 conformer, should require 10 kcal per mole. His predictions are clearly not borne out by the results of Bergman[50] and Berson.[49]

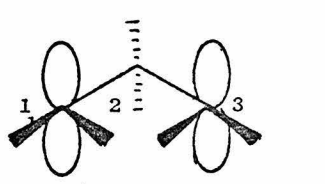
Recent, more sophisticated calculations by Salem [51] and Goddard [52] have cast further doubt on the π-cyclopropane intermediate. These calculations predict there is no such barrier and no energy well for the diradical.

The most convincing argument against the π-cyclopropane mechanism comes from the study of the pyrolyses of fused bicyclic pyrazolines carried out in the Bergman research group. [8a-c] White, Condit and Bergman synthesized several bicyclic pyrazolines; 2,3-diazabicyclo[3.2.0]hept-2-ene (14), the isomeric 4-methyl-2,3-diazabicyclo[3.2.0]hept-2-enes (7A and 7S) and isomeric 4-methyl-2,3-diazabicyclo[3.3.0]oct-2-enes (8X and 8N), and looked at their photochemical and thermal decompositions.

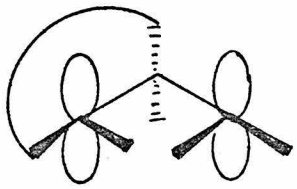
The rational for studying these molecules was to provide evidence for or against the π-cyclopropane intermediate mechanism.

The π-cyclopropane has a rigidly specified geometry. They hoped to alter this geometry by constructing an azo compound in which the possible π-cyclopropane intermediate would be highly strained. In this way the careful balance between a mechanism which gave products of only one stereochemistry (the π-cyclopropane) and another mechanism which gave products of random stereochemistry would be tipped toward the randomizing process.

In the unstrained π-cyclopropane substituents on the C-1 and



unstrained π – △

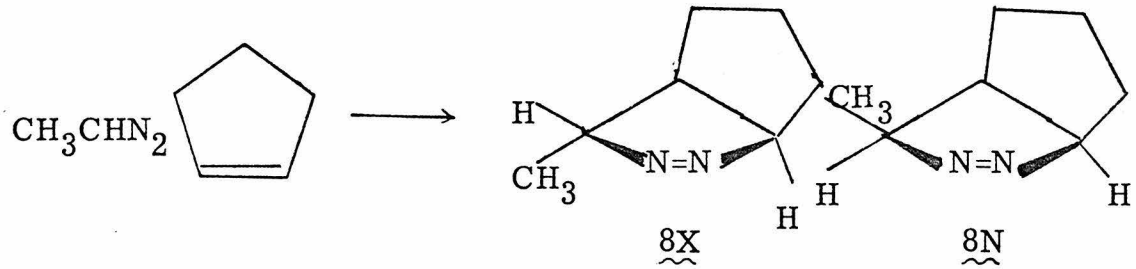


strained π – △

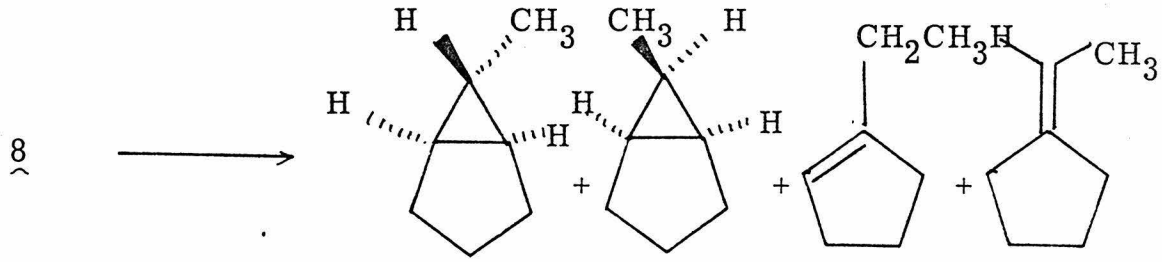
C-2 carbon atoms are pointing in opposite directions. If these carbon atoms were tied together by a two or three carbon atom bridge, a great deal of strain would be necessary to attain the π-cyclopropane conformation. Thus this mechanism would predict that upon such substitution, the energy of the π-cyclopropane would be greatly increased and the randomizing mechanism would take over. However, if one observes the same amount or more of the singly inverted cyclopropanes from these strained pyrazolines, then this would be strong evidence against a π-cyclopropane intermediate.

Decomposition of 8X and 8N was carried out thermally and photochemically. The results of these studies are shown in Table III. In all cases only four products were found.

The thermal decomposition of the two isomers gave predominant inversion of configuration at the methyl substituted carbon, but with greater inversion in the exo case (8X) than was observed in the thermal decomposition of cis 3, 5-dimethyl pyrazoline.[5b, c] (See Table I)



8X 8N



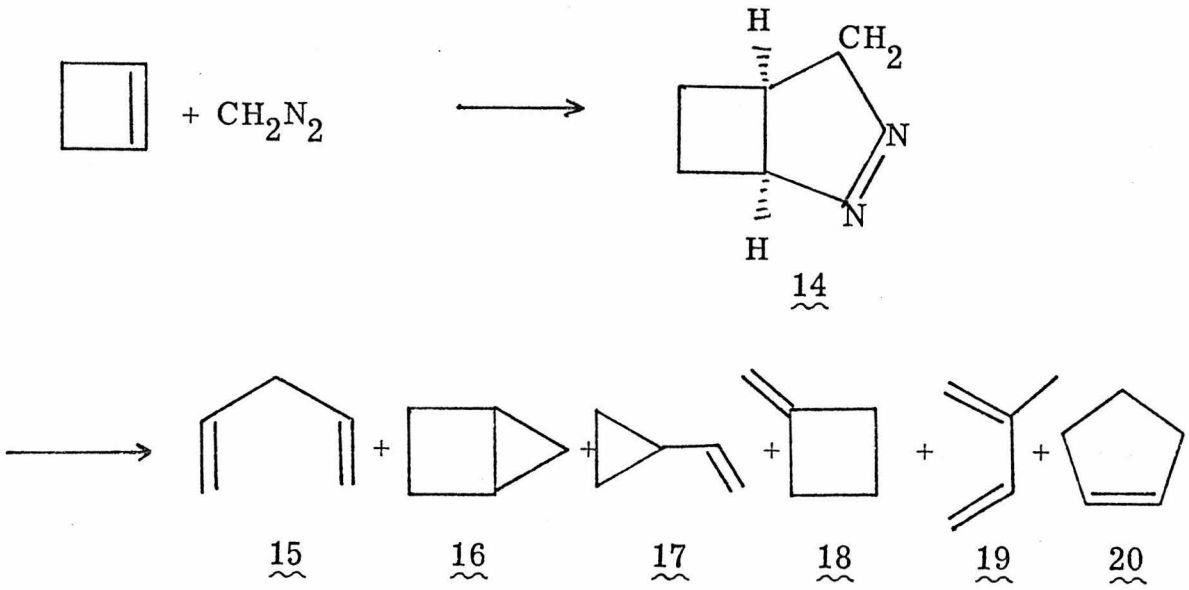
9X 9N 11 10

Table III: Products Formed in the Thermal and Photochemical Decomposition of endo- and exo-4-methyl-2,3-diazabicyclo[3.3.0]oct-2-enes (8N and 8X) [8a]

Substrate	Decomposition conditions	Products %[e] 9X	9N	10	11
8N	a, 260°	67.2	21.2	6.3	5.3
8X	a, 260°	8.1	72.8	8.1	11.0
8N	b, 260°	65.8	22.2	6.8	5.2
8X	b, 260°	7.5	74.1	8.0	10.4
8N	c	29.8	61.0	3.4	5.8
8X	c	62.2	21.3	7.5	9.0
8N	d	59.4	40.6	Trace	Trace
8X	d	68.9	31.1	Trace	Trace

[a] Gas phase, flow system, atmospheric pressure with N_2 carrier gas, contact time 70 sec. [b] Same as a, except tube packed with glass helices. [c] Direct irradiation with an Ultra-Violet Products 305 mμ lamp, pyrex filter, pentane solvent, c = 0.14 M, 25°. [d] Same as c, except benzophenone sensitizer present in concentration sufficient to absorb >98% of the incident light, pyrazoline concentration 0.014 M. [e] All products were stable to the thermolysis and photolysis conditions employed, except in the case of the olefins in the photosensitization experiments. Control experiments under condition d, however, showed that no more than 2% olefins could have been formed as kinetic product from either 8N or 8X in the presence of benzophenone.

2,3-Diazabicyclo[3.2.0]hept-2-ene[18] (14) which does not have a label on one of the carbon adjacent to the nitrogens gave rise to 6 products (88%), (15-20) in the proportions listed in Table IV, page 18.



The formation of the diene as the major product (69-75%) was totally unexpected. The bicyclopentane accounted for only 15% of the reaction mixture.

Anti and Syn 4-methyl-2,3-diazabicyclo[3.2.0]hept-2-enes[18] (7A and 7S, respectively) were decomposed thermally in the heated injector port of a vapor phase chromatograph. The products are listed in Table V and were found in the percentages shown. Again, a large amount of diene was found in the product mixture.

Table IV: Products Formed on Decomposition of 2,3-Diazabicyclo[3.2.0]heptene-2 (14) and 4-pentenal p-toluenesulfonylhydrazone lithium salt (26) [8b]

Starting material	Conditions	Products %						
		15	16	17	18	19[d]	20[d]	Other
14	297°, gas phase [a]	72.0	15.1	5.9	2.1	2.5	2.3	
14	267°, gas phase [b]	75.3	14.5	6.1	1.9	2.1	0.2	
14	290°, gas phase [b]	73.5	15.4	6.0	2.2	2.7	0.3	
14	339°, gas phase [b]	69.5	17.1	6.3	2.7	3.3	1.0	
14	389°, gas phase [b]	64.7	15.9	6.5	3.6	4.1	5.2	
14	321°, gas phase [b, c]	71.2	16.7	6.1	2.7	2.9	0.3	
14	hν, cyclohexane, λ >3000 nm	25.5	62.1	9.4	0	1.3	0	
14	hν, cyclohexand, acetophenone	10.3	89.7	trace	trace	trace	trace	
26	251°, tetraglyme [b]	92.2	0	3.8	0	0	0	4.0[e]
26	335°, tetraglyme [b]	88.7	0	6.0	0	0	0	5.5[e]

Table IV (cont'd):

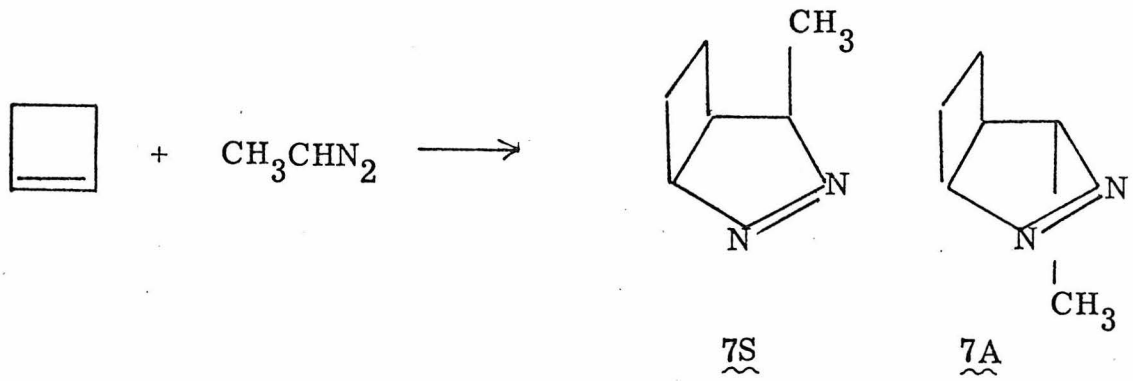
[a] Flow system, atmospheric pressure, contact time = ca. 20 sec.

[b] Pyrolysis carried out in injector port of Hewlett-Packard glc instrument equipped with electronic digital integrator. Percentages are reproducible to ± 0.2 absolute %; where zero percentages are listed, ≥ 0.1% was detectable.

[c] Injector port packed with glass chips.

[d] Compound 19 is probably formed from thermal rearrangement of 1-methylcyclobutene. The small amounts of 20 observed probably arise from thermolysis of 16; kinetic studies reported earlier (C. Steel, R. Zand, P. Hurwitz and S. G. Cohen, J. Amer. Chem. Soc., 96, 679 (1964)) are consistent with slight conversion of 16 to 19 under our pyrolysis conditions. Appropriate control experiments demonstrated that all the other products are stable to the pyrolysis conditions.

[e] Mainly piperylenes, which Kirmse and Grassman have indicated[33] are formed in a competing cationic pathway.



7S 7A

The syn isomer (7S) gave only a single diene, cis 1, 5-hexadiene and predominantly the anti bicyclopentane at temperatures low enough to prevent the equilibration of the syn and anti bicyclopentanes (equilibrium ratio of anti:syn equals 2.1:1).

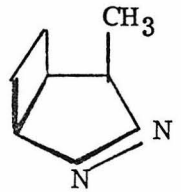
The anti isomer (7A) gave a single diene also, trans 1, 5-hexadiene and mostly the syn bicyclopentane at low temperature. Again, the thermal decomposition of the two isomers gave predominantly inversion of configuration at the methyl substituted carbon.

Connecting C-3 and C-4 of a 1-pyrazoline with even a two carbon atom bridge changed the preference for single inversion very little in 7A and 7S compared with that of 3, 5-dialkyl substituted monocyclic pyrazolines (see Tables I and V).

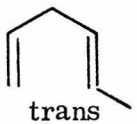
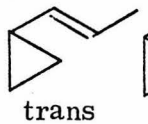
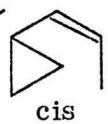
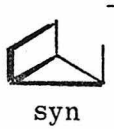
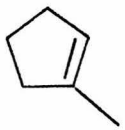
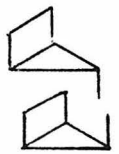
An alternative mechanism to the one involving a π-cyclopropane must be sought to explain these results.

Table V: Product Compositions from Injection Port Pyrolysis of

anti



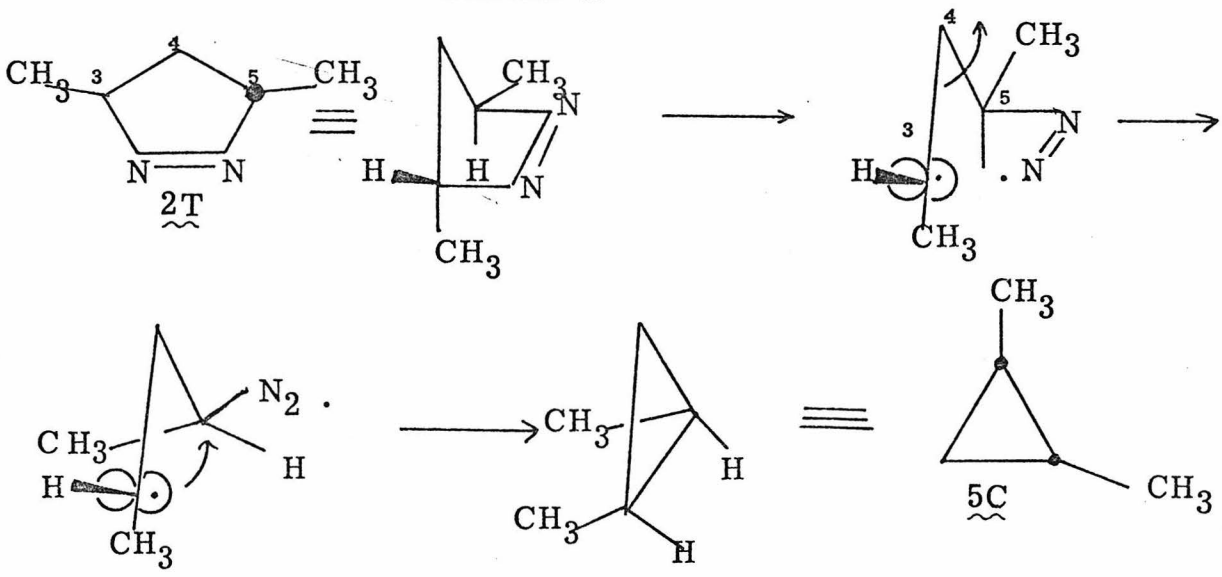
syn

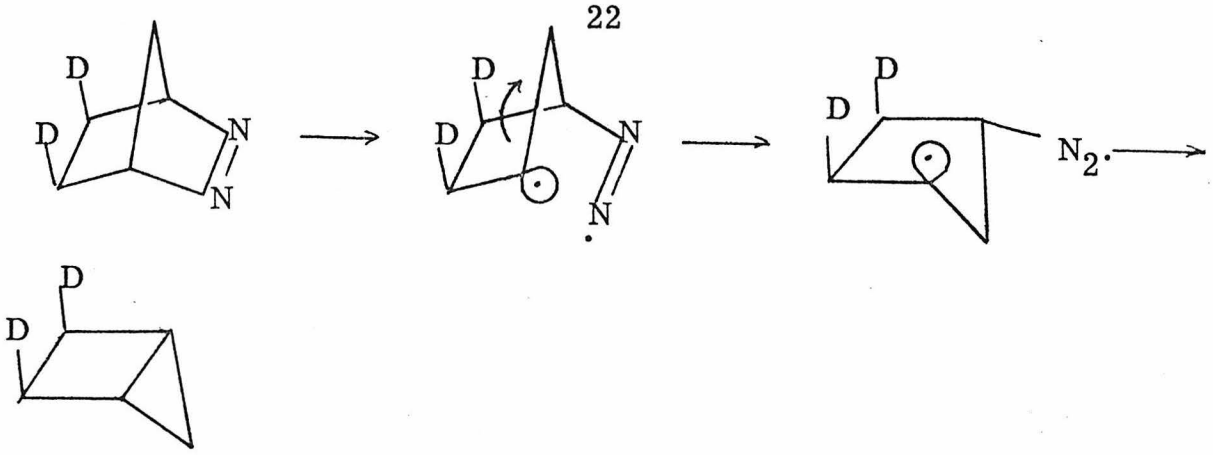
pyrazoline	Temp. °C	 trans	 cis	 trans	 cis	 anti	 syn		anti / syn	
syn (7S)	256	0	12.4	0	0.8	54.5	31.7	0	1.7	
	313	0	12.7	0.1	1.1	53.5	26.8	0.5	2.0	
	352	0	12.6	0.1	1.3	52.0	26.1	2.3	2.0	
	395	0	12.2	0.1	1.5	45.1	24.1	9.9	1.9	
	438	0	12.4	0.1	1.6	30.6	14.1	31.4	2.2	
anti (7A)	233	57.0	0	2.4	0.1	8.0	31.9	0	0.25	
	250	56.5	0	2.9	0.1	8.2	31.3	0	0.3	
	302	52.5	0	4.0	0.3	20.2	19.1	0.2	1.0	
	354	46.1	0	4.1	0.3	24.3	19.1	1.1	1.3	
	400	45.4	0	4.2	0.4	24.1	16.4	3.7	1.5	
	460	41.2	0	4.2	0.4	20.8	10.1	16.6	2.1	

Sequential Carbon-Nitrogen Bond Cleavage Mechanism

A second possibility, which accounts for the singly inverted stereochemistry of the product cyclopropanes, is the assumption that only one carbon nitrogen bond breaks in the initial transition state to give a diradical (or a zwitterion). This is followed by a rotation of the carbon containing the nitrogen fragment (C-5) about its carbon-carbon bond axis. After a single 180° rotation about this axis, the radical center at C-3 carries out a backside displacement of N_2, now in a good position to be a leaving group, at C-5 to give a product of the correct stereochemistry (see Scheme II). This mechanism was postulated by Roth and Martin to explain the double inversion of stereochemistry observed in the thermal decomposition of bicyclic azo compounds [11] (see Table I). This mechanism is illustrated for the bicyclic and the monocyclic cases.

Scheme II





1. Evidence for this mechanism. A good deal of the evidence for this mechanism comes from recent studies of the thermal decomposition of straight chain azo compounds.

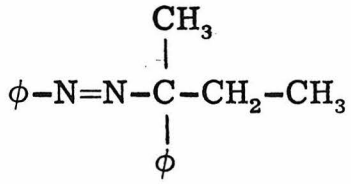
Pryor and Smith[54] have found that the pyrolysis of 43 was dependent on the solvent viscosity in contrast to the pyrolysis of azocumene which showed no solvent dependence. In azocumene both possible radical fragments are benzylic, where as in 43 one possible radical is much more stable than the other. The viscosity effect was attributed to a cage recombination of radicals from breaking only a single C-N bond.

$$p\mathrm{NO_2}\phi\text{–N=N–C}\phi_3 \qquad \text{solvent separated radicals}$$

$$\underset{\underset{\mathrm{p\,NO_2}\phi\text{–N=N}\cdot \quad \cdot\mathrm{C}\phi_3}{43}}{\longrightarrow} \quad \nearrow \quad \underline{\qquad\qquad\qquad\qquad}$$

$$\mathrm{p\,NO_2}\phi\cdot \; + \mathrm{N_2} + \cdot\mathrm{C}\phi_3$$

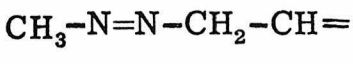
Porter, Landis and Marnett[58] have found that the rate of racemization of optically active 44 on photolysis as well as the quantum yield depends on the viscosity of the solvent.



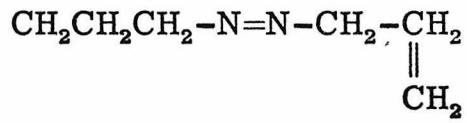
44

A mechanism similar to one proposed for 43 is involved. The free benzylic radical inverts in the solvent cage and recombines with the nitrogen containing fragment to give racemized starting material.

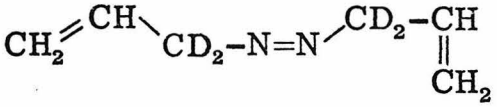
Crawford and Takagi have studied the decomposition of azo compounds 45, 46 and 47, and have come up with substantial support for the sequential bond cleavage mechanism for acyclic azo compounds in the gas phase.[55, 56]



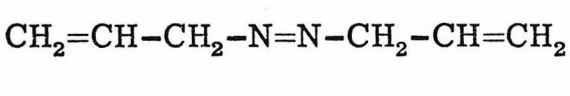
45



46



47-D$_4$



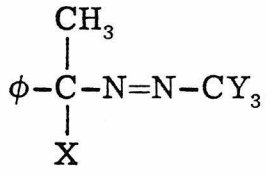
47

The compounds 45 and 46 both decompose with an activation energy of 35-36 kcal per mole which is 12 kcal per mole less than for azoethane (E act = 48.5 kcal per mole).[55] The 12 kcal per mole represent the greater stability of an allyl radical compared to an ethyl radical. Compound 47 decomposes with an activation energy of 36.1 kcal/mole, the same activation energy as for 45 and 46. This suggests that the mechanism of decomposition is by single bond cleavage as the rate determining step because the replacement by a second allyl group in 47 should decrease the activation energy by at most 12 kcal per mole compared to 45 or 46, if both bonds were breaking simultaneously.

When 47-D_4 was partially decomposed and the starting material was recovered, an increase was found in the amount of deuterium in the vinylidene positions.[56] This can best be accounted for by single bond cleavage followed by rearrangement of the free allyl radical in the solvent cage and then recombination with the nitrogen containing radical.

Seltzer and co-workers have reported solution phase deuterium isotope effects for azo compounds which suggest that if one possible radical is very much more stable than the other possible radical, sequential cleavage occurs.[57] However, if the radicals are identical, hence of equal stability, simultaneous cleavage occurs. A mechanism

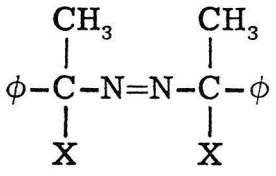
intermediate between the two occurs for radicals which are more closely matched in their stability.



54, X = Y = H

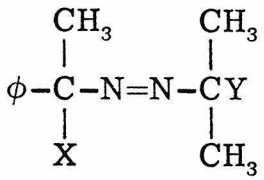
54-D_1, X = D, Y = H

54-D_3, X = H, Y = D



55, X = Y = H

55-D_2, X = Y = D



56, Y = X = H

56-D_X, X = D, Y = H

56-D_Y, X = H, Y = D

$$\left(\frac{k_H}{k_D} = \right) \frac{k\ 54}{k\ 54\text{-}D_1} = 1.13 \qquad \frac{k\ 55}{k\ 55\text{-}D_2} = 1.27$$

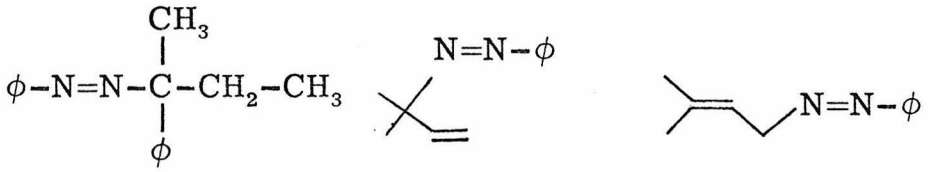
$$\frac{k\ 54}{k\ 54\text{-}D_3} = 0.97 \qquad \left(\frac{k_H}{k_D} = 1.13 \text{ per D}\right)$$

$$\left(\frac{k_H}{k_D} = 0.99\right)$$

$$\left(\frac{k_H}{k_D} = \right) \frac{k\ 56}{k\ 56\text{-}D_x} = 1.15$$

$$\left(\frac{k_H}{k_D} = \right) \frac{k\ 56}{k\ 56\text{-}D_y} = 1.04$$

Compound 54 is an example of sequential bond cleavage,[57a] 55 an example of simultaneous cleavage,[57b] and 56 an example of the mechanism intermediate between the other two.[57c]



58

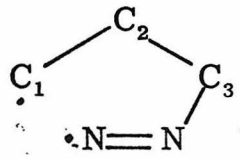
59

60

Porter et al. have used CIDNP to show that the initial reaction step involves a reversible formation of $R_1\cdot$ and $\cdot N{=}N\,R_2$ from azo compounds 58, 59 and 60 in which R_1 is more stable than R_2.[53]

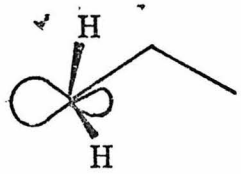
The sequential bond cleavage mechanism also finds support in the study of radical displacement reaction. The only examples of radical displacement reactions found in the literature in which the stereochemistry of the attacked center is known, involve the attack of chlorine or bromine radicals on substituted cyclopropane.[61] The displacement center always has its stereochemistry inverted. While these examples are not exactly similar to the pyrazoline case, the results do make the assumption of inversion of stereochemistry at the attacked carbon in this mechanism for the decomposition of pyrazoline a reasonable one.

An important assumption in this mechanism is that in the intermediate 48 of Scheme II the nitrogen containing carbon must rotate about the C_2-C_3 bond axis faster than the methylene radical center rotates about the C_1-C_2 bond axis.



48

Free rotation about C_1-C_2 would give the same product distribution from both cis and trans 3, 5-disubstituted-1-pyrazolines. No experimental evidence exists to support this contention, however Salem has performed calculations that suggest that the most stable conformation of the n-propyl primary radical is as shown in figure 49. The radical lobes are perpendicular to the plane of the three carbon atoms.[51]

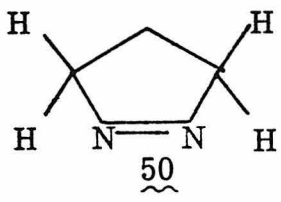


49

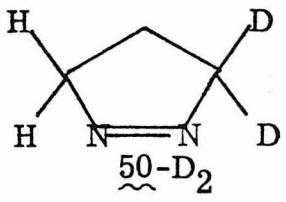
The sequential bond cleavage mechanism can be expanded to explain Crawford's observation on the thermal behavior of trans 3, 5-dimethyl-1-pyrazoline (see below). Predominance of doubly inverted over noninverted trans cyclopropane in the product can be explained by a single 180° rotation about the C_1–C_2 bond axis in 48 in the time it takes for a single 180° rotation to occur about the C_2–C_3 axis, putting the nitrogen fragment in a good position to be a leaving group. Rotation about C_2–C_3 must still be faster than rotation about C_1–C_2 in order for the singly inverted product to predominate.

2. Evidence against sequential bond cleavage. All of the pyrazoline decomposition data cannot be accommodated in the sequential carbon-nitrogen bond cleavage mechanism.

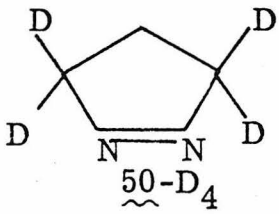
For example, the effect on the decomposition rate of increasing deuterium substitution in 50 has been looked at by Crawford.[5g]



50



50-D_2

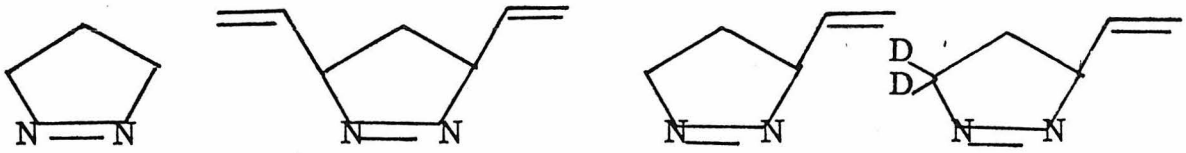


50-D_4

$k_{rel.}$ = 1 : 1/1.19 : 1/1.40

The data areconsistent either with the simultaneous cleavage mechanism assuming a k_H/k_D of 1.1 per deuterium or with sequential cleavage mechanism if a larger k_H/k_D of 1.2 per deuterium is assumed in 50-D_4.[56]

Crawford has studied the effects of increasing vinyl substitution on C-3 and C-5 positions of 1-pyrazoline;[61] the deuterium isotope effect in the decomposition of 51 has also been studied.[5g]



50 52C and T 51 51-D_2

The activation energy for the decomposition of 51 was found to be 32.2 kcal per mole, 10.2 kcal per mole less than that found for 50. The activation energy for decomposition of 52C and 52T was found to be 22.2 and 25.1 kcal per mole, respectively. Increasing vinyl substitution on 50 resulted in a lowering of the activation energy by 10 kcal per mole per vinyl group. The data aredifferent from that obtained in acyclic azocompounds, where substitution of a second vinyl group did not lower the activation energy further. 51-D_2 exhibited a total secondary deuterium isotope effect of 1.21 (k_H/k_D = 1.1 per D).

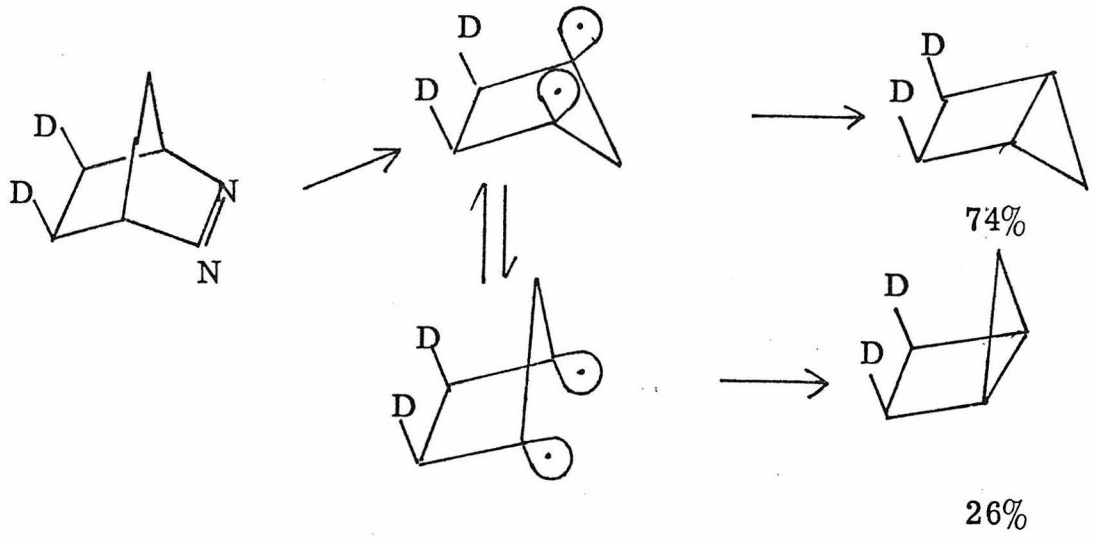
The data on 50, 51 and 52 can best be explained by a simultaneous cleavage of the two carbon-nitrogen bonds.

The observation that both cis and trans 4-deuterio-3-methyl-1-pyrazoline (38C and T)[5d] gave identical ratio of cis and trans 1-deuterio-2-methyl cyclopropanes (53C and T) (see above) is taken as evidence against the sequential bond breaking mechanism. Assuming a preference for initial cleavage at the carbon containing the methyl group (to give the most stable radical), the sequential cleavage mechanism predicts a predominance of 53C from 38C, and 53T from 38T.

The sequential bond cleavage mechanism cannot explain the cases in which the pyrazolines decompose to give cyclopropanes which have the same stereochemistry of the precursors (non-inversion).[63, 64]

The Recoil Mechanism

The third mechanism specifically proposed to explain the double inversion occurring in the bicyclo[2.2.1] azo compounds is the recoil mechanism of Allred and Smith.[12] These authors invoke Newton's Third Law which states that for every action there is an opposite and equal reaction. As the nitrogen molecule moves away from the monocycle (the action), the two carbons to which the nitrogens were attached move in the opposite direction (the reaction) and invert (see Scheme III).



Scheme III

The mechanism is illustrated for exo-5, 6-dideuterio-2, 3-diazabicyclo[2.2.1]heptene.[11a] There must be some crossover between the two diradical conformations which explains the presence of the non-inverted isomer.

The recoil mechanism has been used to explain the double inversion of bicyclo[2.2.1] pyrazolines, and as such it was not intended to explain single inversion at the carbons adjacent to the nitrogens. However, evidence that it does intervene in monocyclic systems comes from Crawford's study of optically active trans 3, 5-dimethyl-1-pyrazoline.[5h] This pyrazoline decomposed to give a trans 1, 2-dimethylcyclopropane which was 24% optically pure; the isomer with the doubly inverted carbon atoms was in excess. Exactly

the same results were obtained by Clarke who studied the decomposition of optically active trans 3-ethyl-5-methyl-1-pyrazoline.[47] However, these results can be explained in an extension of the sequential carbon-nitrogen bond breaking mechanism, as was discussed previously.

Furthermore, the recoil mechanism has been attacked on theoretical grounds by Collins et al.[48]

Concerted Formation of Cyclopropanes from Pyrazolines

A concerted mechanism was proposed to explain the single inversion of stereochemistry in cyclopropanes coming from the decomposition of pyrazolines.

Assuming hyperconjugation is a relatively weak phenomenon and the central methylene group does not interact significantly with the breaking bonds, then the nitrogen extrusion is the microscopic reverse of a hypothetical 2+2 cycloaddition of N_2 to a cyclopropane. Such a reaction is predicted by the Woodward-Hoffmann rules[17] to be a "$\sigma^2s + \sigma^2a$" process; i.e., to proceed in a suprafacial sense with respect to one of the developing fragments and an antarafacial sense with respect to the other. The transition state is visualized as depicted in Scheme IV.

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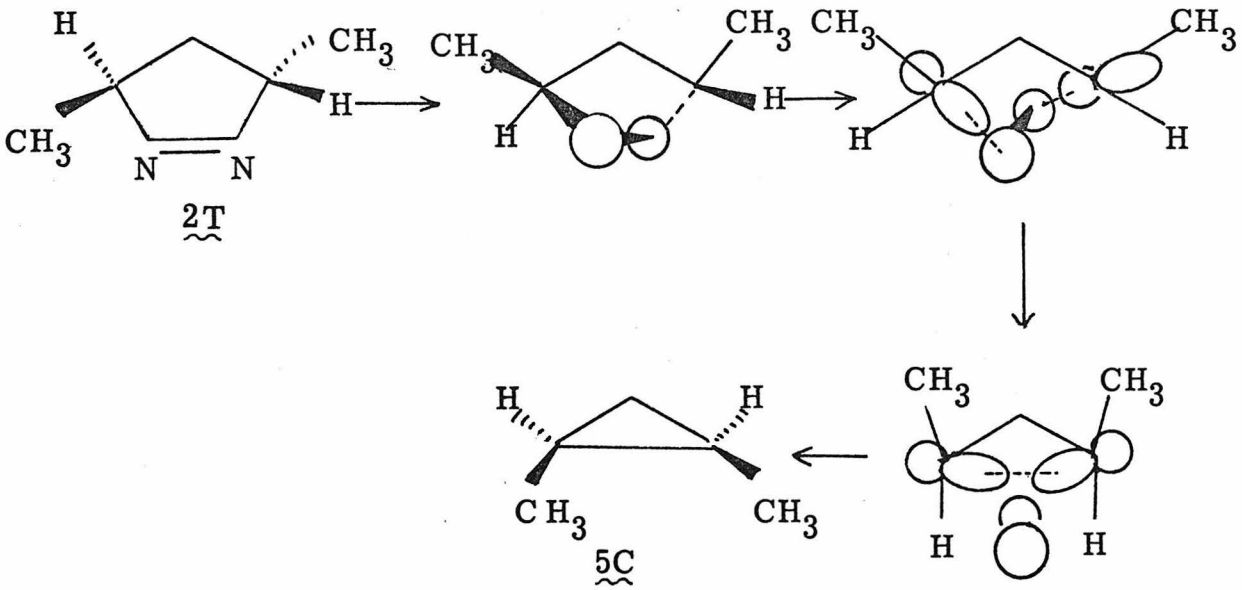


Scheme IV

The concerted mechanism has been rejected by most workers for two reasons.[46] First, Crawford has provided evidence for the existence of at least one intermediate after the rate-determining step in the pyrolysis of 4-deuterio-4-methyl-1-pyrazoline.[5c] Here Crawford finds a large isotope effect on the cyclopropane to propylene ratio, but little effect on the overall decomposition rate of the pyrazoline. This result indicates that the rate-determining step is the formation of an intermediate common to both the propylene and cyclopropane reaction pathways. If the cyclopropane formation was concerted (and thus distinct from the formation of propylene), the overall rate constant for the disappearance of pyrazoline would be

the sum of the two rate constants for the competing reaction pathways. If one of these individual rate constants decreases (decrease in propylene formation), while the other stays the same, the overall rate constant for the disappearance of pyrazoline must decrease. This was not observed, therefore cyclopropane formation appears not to be concerted.

The other evidence is from inspection of molecular models. To attain the $\sigma^2s + \sigma^2a$ transition state for the decomposition of a pyrazoline is very difficult due to geometric restraints.

Summary of the Mechanisms Proposed to Explain Pyrazoline Decomposition Data

No one of the mechanisms which have been discussed will adequately explain all of the 1-pyrazoline decomposition data. The best mechanism for the formation of singly inverted cyclopropanes is probably the sequential carbon-nitrogen bond cleavage mechanism. In its expanded form it can also explain doubly inverted cyclopropanes. The non-inverted cyclopropanes arise from simultaneous cleavage of the carbon-nitrogen bonds. Seltzer and others have shown that in azo compounds albeit in solution the whole spectrum of sequential to simultaneous bond cleavages can occur, which is in agreement with the proposed mechanism for gas phase decompositions.

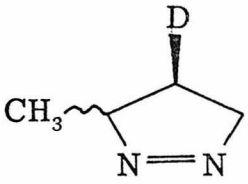
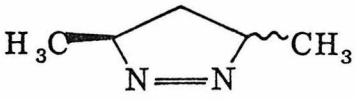
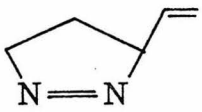
Still there are problems. Simultaneous cleavage appears to occur when the potential radicals are of equal stability (i.e., they are identical); sequential cleavage occurs when radicals are greatly different in stability. Three important exceptions to this (and to the mechanism suggested) are found in Table VI. However, until a new theory is proposed which is in better agreement with experimental data, the mixed mechanism of sequential C–N bond cleavage with a component of simultaneous cleavage appears to be the best alternative to π-cyclopropane.

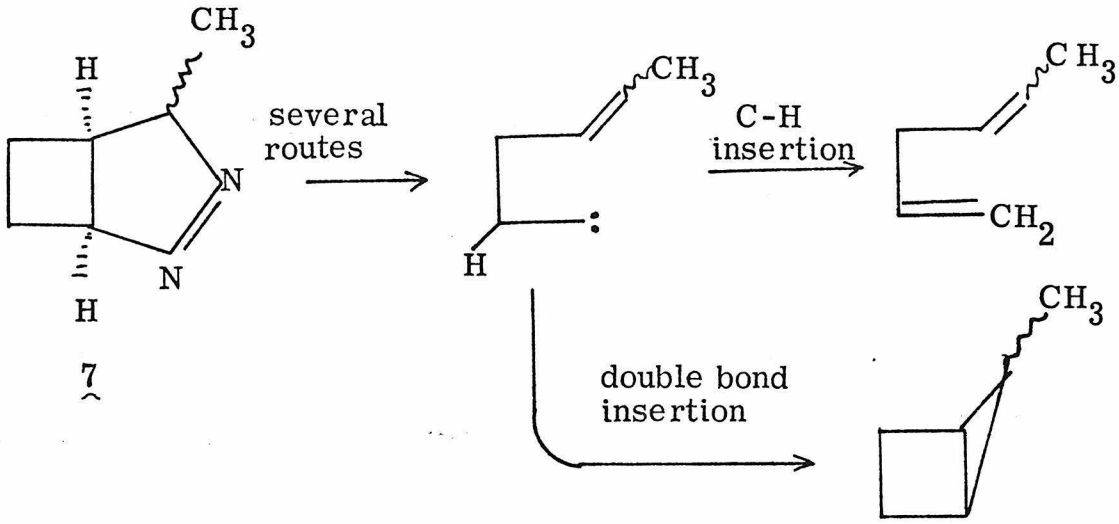
Purpose of This Study

The presence of 1,4-dienes as the major products from 14 and and its 4-methyl derivatives, 7A and 7S (see Tables IV and V), was unexpected and indicates that the decomposition of bicyclic pyrazolines is somewhat more complex than for simple monocyclic pyrazolines.

One of several possible mechanisms for the formation of these dienes involves a 1-diazo-4-hexene (57) coming from 7 by several possible routes. 57 can lose nitrogen to give a carbene which, in addition to insertion into the carbon-hydrogen bond of the adjacent carbon atom, can also insert into the remote double bond to give bicyclopentane products (see Scheme V).

Table VI: Exceptions to Proposed Mechanism

Pyrazoline	Mode of decomposition based on experimental evidence and stereochem. of major cyclopropane product (if known)	Stabilities of R_1 versus R_2
 38C	simultaneous singly = non-inverted	$R_1 > R_2$
38T	simultaneous singly = non-inverted	
 2T	sequential singly inverted	$R_1 = R_2$
 51	simultaneous	$R_1 > R_2$



Scheme V

If a fair amount of the bicyclopentanes derived from 7A or 7S are formed in this manner, grave doubts arise about the significance of the stereochemistry of the major 5-methylbicyclopentane observed.

In order to assess how much of the bicyclopentanes arises from the hypothetical carbene and to understand how the dienes are formed in 14 and its 4-methyl analog (7), I synthesized two isomeric dimethyl derivatives of 14, namely syn and anti 6, 7-dimethyl-2, 3-diazobicyclo[3. 2. 0]hept-2-ene (28 and 27, respectively), and looked at the products of their thermal decomposition reactions.

Evidence indicating the mechanism of the formation of 1, 4-dienes and the bicyclopentane products can be derived from the

decomposition of 27 and 28 as will be discussed later.

Studies of Reactions of Compounds Related to the Thermal Decomposition of 14, 7, 27 and 28

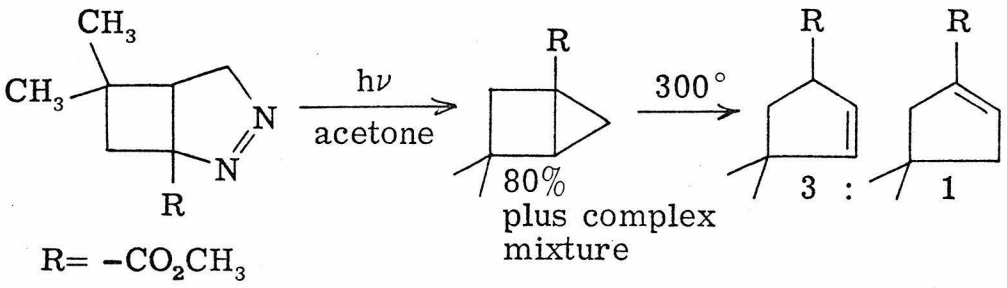
Several substituted derivatives of 14 have been synthesized and were used in thermal and photochemical studies.

For the bicyclic pyrazolines which were used in thermal or photolytic studies, no stereochemical information as to the nature of the intermediate, if any, or the mode of decomposition is available (see Table VII).[24-26] Also, many of the products are unidentified and both means of decomposition, thermochemical and photochemical, were not always explored in many cases.

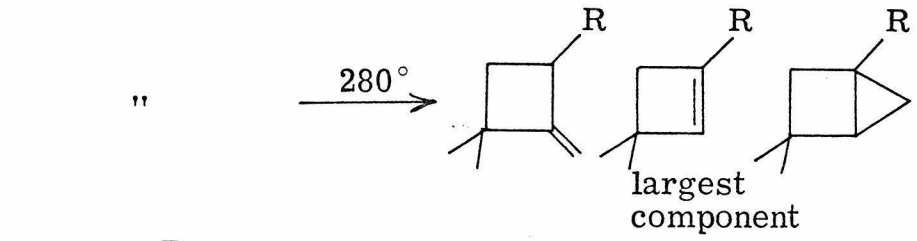
Many of the products are similar to those of monocyclic pyrazolines; bicyclopentanes from closure of a hypothetical diradical intermediate , methylenecyclobutenes and 1-methylcyclobutenes from a hydrogen shift in the intermediate. The presence of 1,4-dienes and unidentified products in some bicyclic pyrazolines shown in Table VII again suggests that the decomposition pathways are more complex than with the monocyclic pyrazolines and that additional processes must be occurring.

In this general area of chemistry, the addition of carbenes and carbenoids to substituted cyclobutenes, which might generate diradical

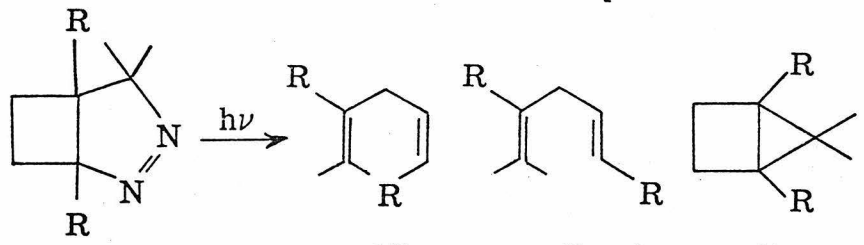
Table VII



R= $-CO_2CH_3$

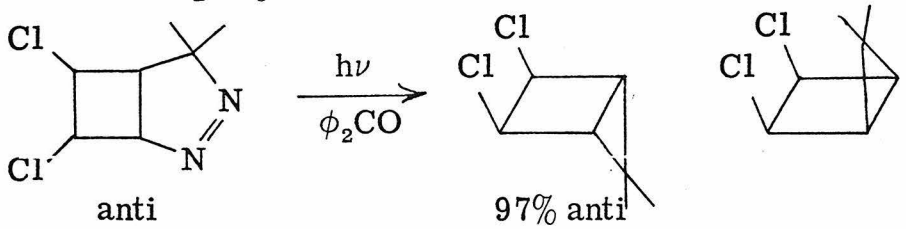


Ref 24



R= $-CO_2CH_3$

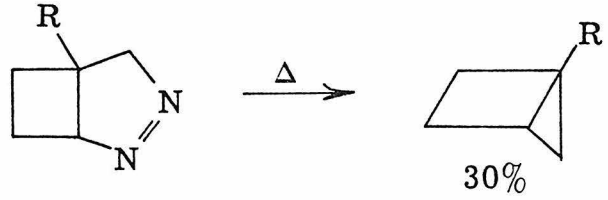
Ref 25



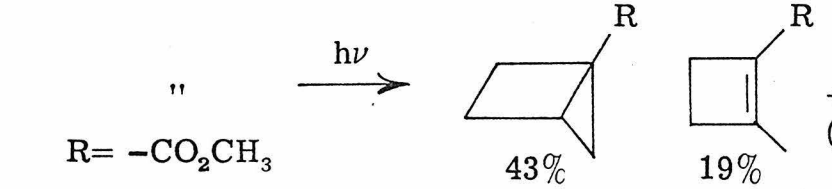
anti

syn

80% syn Ref 25



+ 5 others



R= $-CO_2CH_3$

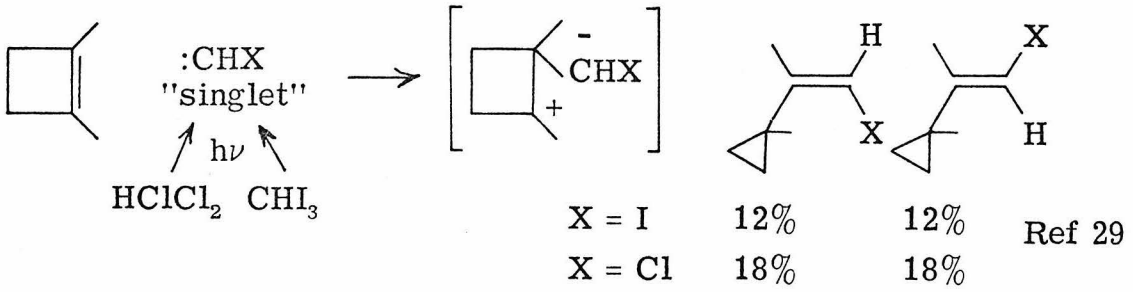
+ 2 others
(7 and 12%)

Ref 26

intermediates similar to those generated in pyrazoline decompositions, has been reported to give dienes, bicyclopentanes, and vinyl carbenes as well as others [27-29] (see Table VIII).

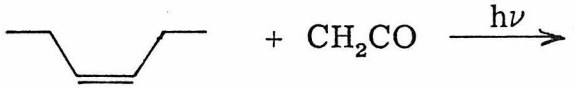
Photolysis of diazomethane in the presence of cyclobutene gave products consistent with the direct formation of bicyclopentane via a concerted reaction between the singlet carbene and the cyclobutene.[27-28] However, the mercury sensitized photolysis of diazomethane in the presence of cyclobutene gave vinylcyclopropane as the major product (88%) and no bicyclopentane.[27] If this reaction is presumed to go through the triplet diradical, it is very difficult to reconcile the data with the observation that benzophenone-sensitized photolyses of a bicyclic pyrazoline in Table VII resulted in predominant formation of bicyclopentanes, since this reaction is also presumed to proceed via a triplet intermediate. Furthermore, while Frey maintains that singlet carbene addition to cyclobutenes gives bicyclopentanes and triplet addition gives vinylcyclopropanes,[27, 28] other workers have found that the singlet addition of "CHX" (X = I, Cl) to 1, 2-dimethyl-cyclobutene gives yields of up to 36% vinylcyclopropane.[29] A dipolar intermediate was postulated in the addition, but a 1, 3 diradical was not ruled out.

Table VIII

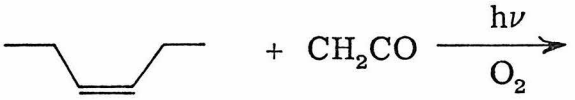


X = I 12% 12% Ref 29

X = Cl 18% 18%

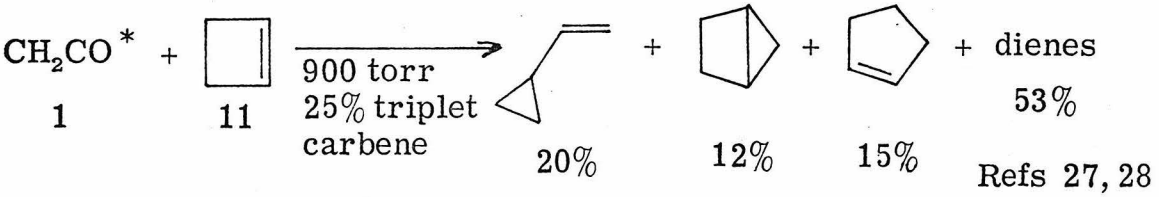


mainly cis-cyclopropane but always some trans postulated to arise from triplet carbene

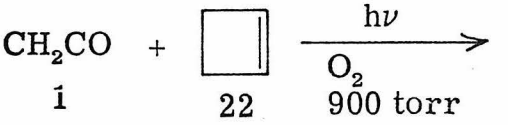


drastic reduction in the amount of trans-cyclopropane

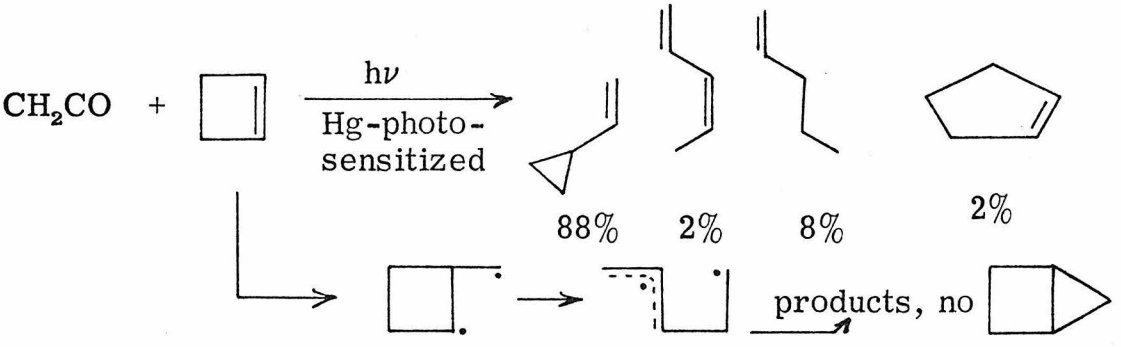
Ref 28



Refs 27, 28



no vinylcyclopropane Ref 28



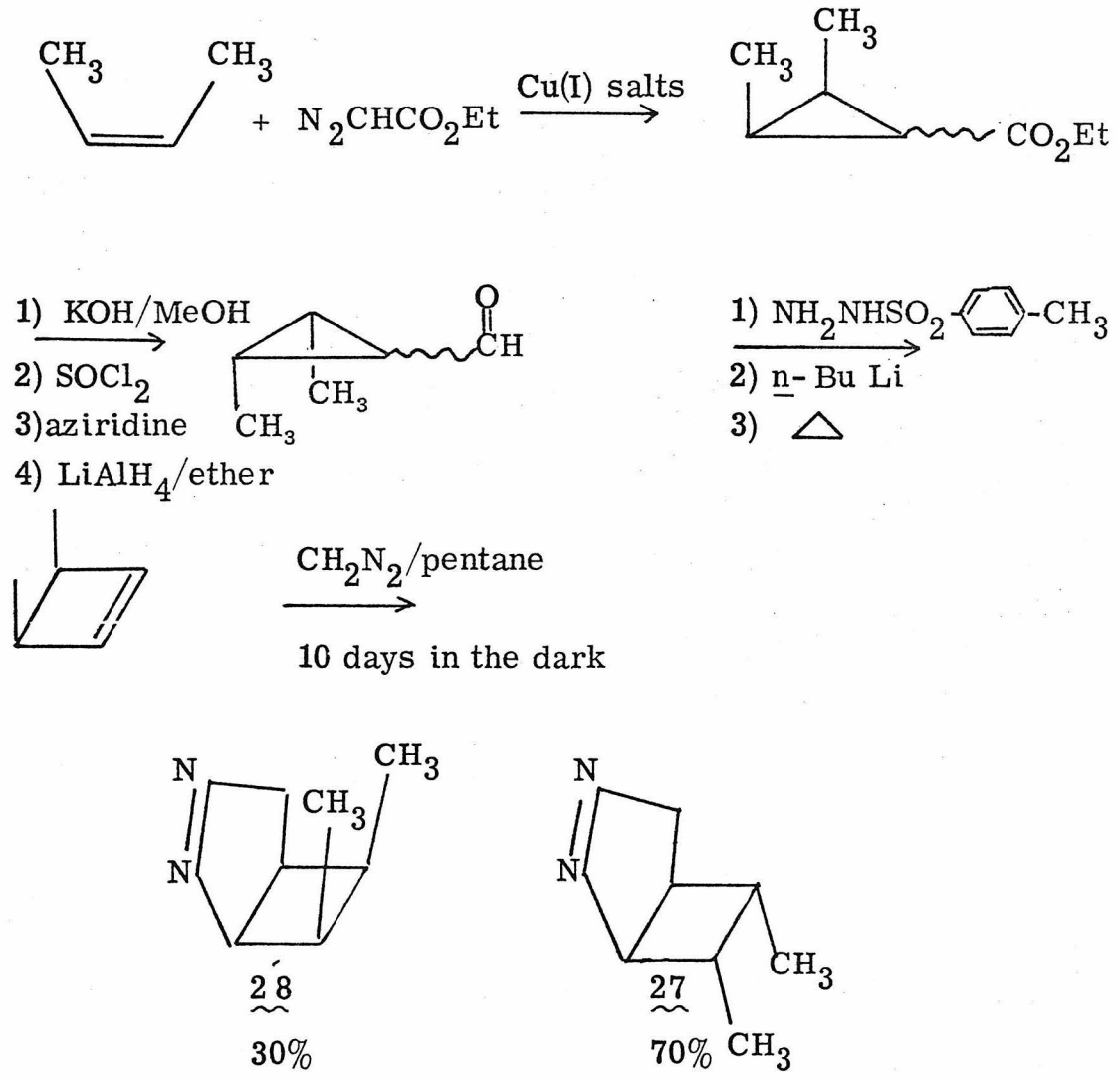
Ref 27

* If CH_2N_2 is substituted for CH_2CO, the same results are obtained.

RESULTS

Pyrazoline Synthesis

The isomeric syn and anti cis 6, 7-dimethyl-2, 3-diazabicyclo-[3.2.0]hept-2-enes (28 and 27) were prepared by the route outlined in Scheme VI.



Scheme VI

2, 3-Dimethyl-1-carbethoxy cyclopropane was formed in 29% yield by the catalyzed [(triphenyl phosphite) copper(I) chloride[30]] decomposition of diazoacetate[30] in the presence of cis-2-butene (J. T. Baker Chemicals) at 0°. Attempted conversion of the product directly to the cis 2, 3-dimethyl-1-formyl-cyclopropane by the use of the reducing agent, Red-Al[32] ($NaAlH_2$-$(OCH_2CH_2OCH_3)_2$) failed (vpc and nmr evidence). The ester group was therefore hydrolyzed to the acid by KOH in methanol and water in 82% yield. The recrystallized acid was converted to cis 2, 3-dimethyl-1-chloroformyl cyclopropane by refluxing in $SOCl_2$ (1:1 mole ratio). The yield was nearly quantitative. The acid chloride was converted to the amide by stirring with aziridine in triethyl amine and ether at -60°. The amide was reduced to the aldehyde with $LiAlH_4$ at -50° without isolation of the amide or aldehyde. Cis 2, 3-dimethyl-1-formyl-cyclopropane was converted to the corresponding tosylhydrazone by refluxing the ethereal solution of the aldehyde with a 1:1 mole ratio of p-toluenesulfonhydrazide. Cis 2, 3-dimethylcyclopropane-1-carboxaldehyde p-toluenesulfonyl hydrazone was purified by recrystallization from methanol and water. Yield from cis 2, 3-dimethyl-1-carboxyl cyclopropane was 19%. Overall yield from diazoacetate was 4. 5%.

Later work on aldehyde syntheses led to the discovery of an improved pathway to cis 2, 3-dimethyl-1-formylcyclopropane.

The ester, cis 2,3-dimethyl-1-carbethoxy cyclopropane was reduced directly to the corresponding alcohol. The alcohol was then oxidized to the aldehyde with ceric ammonium nitrate in water and distilled to give a 60% yield based on the alcohol.[35]

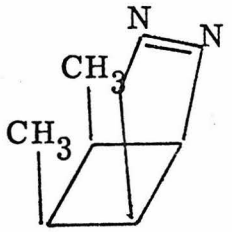
The tosylhydrazone was converted to its lithium salt with n-butyllithium and decomposed at 150° in diethyl carbitol to cis 2,3-dimethyl-1-cyclobutene-2,4-hexadiene, and acetylene and cis 2-butene. The cyclobutene, unseparated from the other products, was condensed into an ethereal solution of diazomethane. The 1,3-dipolar addition was slow; after 13 days at room temperature, 87% of the cyclobutene was consumed and two products (7:3) ratio were observable gas-liquid chromatography (glc).

Identification of pyrazoline isomers. The major product was identified as the anti 1,3 dipolar cycloadduct (27) and the minor product as the syn isomer (28). Identification was made by the incremental addition of a $Eu(fod)_3$[38] solution in CCl_4 to a mixture of the two isomers in an nmr solution of CCl_4. It was observed that as increments of the nmr shift reagent were added, the methyl doublets of one isomer shifted further than those of the other isomer. Since $Eu(fod)_3$ complexes with the heteroatoms present in the molecule and the amount of shift of a group is a function of the distance from that group to the point of complexation (closer groups shift further), it was deduced that the

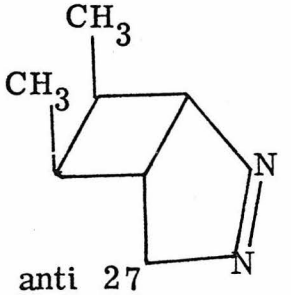
isomer with the faster shifting methyl groups was the syn isomer. See Figure 1.

Further proof of the assignment of the stereochemistry was provided by their gas-phase thermolysis. The syn isomer 28 at 254°C gave only the endo 2,3-dimethylbicyclo[2.1.0]pentane (34), whereas, the anti pyrazoline (27) decomposed to give only the exo 2,3-dimethylbicyclo[2.1.0]pentane (32).

Isomers (27) and (28) were separated in greater than 95% purity by preparative vpc on a glass column to prevent decomposition. A second purification on the same column gave samples of syn and anti bicyclopyrazolines of greater than 99% purity. Total overall yield was 2.5%.



syn 28

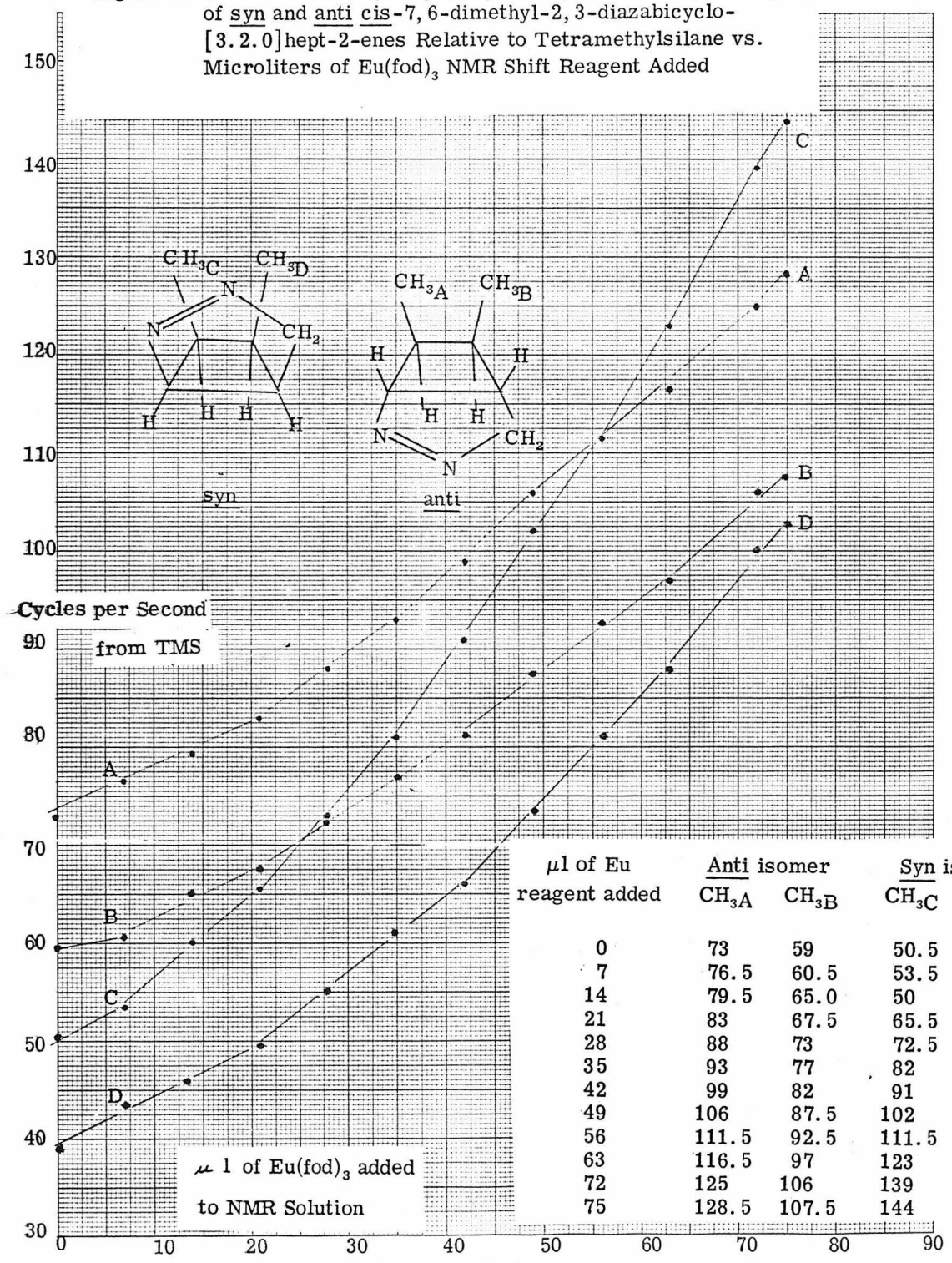


anti 27

Identification of Flow Tube Pyrolysis Products

Decompositions were carried out in two different systems. The first one used was a flow reactor. It was used primarily for preparative work and consisted of a 0.5" O.D. quartz tube heated to 280-320°. Nitrogen gas carried the volatized pyrazolines through the

Figure 1: Chemical Shifts (in Cycles per Sec) of the Methyl Groups of syn and anti cis-7, 6-dimethyl-2, 3-diazabicyclo-[3.2.0]hept-2-enes Relative to Tetramethylsilane vs. Microliters of $Eu(fod)_3$ NMR Shift Reagent Added

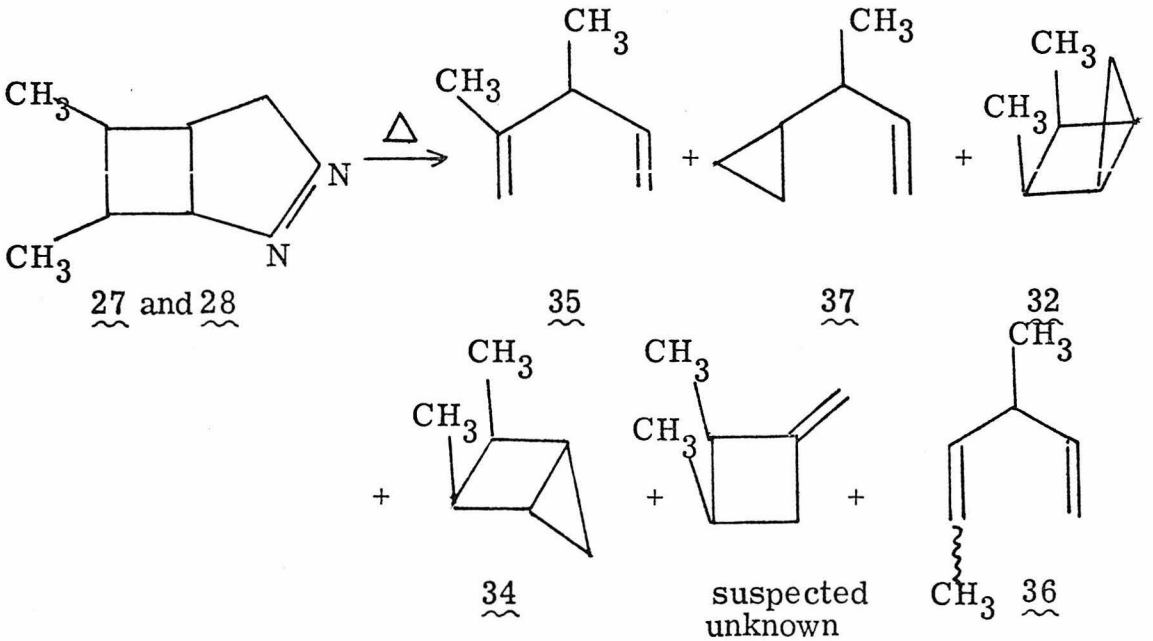


μl of Eu reagent added	Anti isomer CH_3A	Anti isomer CH_3B	Syn isomer CH_3C	Syn isomer CH_3D
0	73	59	50.5	39
7	76.5	60.5	53.5	43.5
14	79.5	65.0	50	46
21	83	67.5	65.5	49.5
28	88	73	72.5	55
35	93	77	82	61
42	99	82	91	66
49	106	87.5	102	73.5
56	111.5	92.5	111.5	81
63	116.5	97	123	88
72	125	106	139	100
75	128.5	107.5	144	103

12" tube; residence time in the tube was around 70 sec.

The second system, which was used primarily for quantitative work, consisted of the heated injection port, into which the pyrazoline was introduced via a syringe, of a Hewlett-Packard gas chromatography instrument equipped with an electronic digital integrator. The temperature range utilized was from 280° to 380°. Contact time was 2-5 seconds.

Products of the decomposition were isolated by preparative gas chromatography.[40] As in the parent case (14), thermal decomposition of each gave rise predominantly to diene, but also to cyclopropane and bicyclopentane products (Table IX). With regard to the latter, both dimethylbicyclopentanes[39] 32 and 34 (Scheme VII) were formed at 300°,



27 and 28 35 37 32

34 suspected unknown 36

Scheme VII

Table IX: Products Formed in the Thermal Decomposition of syn- and anti-6,7-dimethyl-2,3-diazabicyclo[3.2.0]hept-2-enes.[8c]

Starting material and conditions	Products, %				
	32	34	35	37	Other[d]
27, flow system[b], 278°	13.1	<1	56.8	23.2	6.8
28, flow system[b], 278°	<1	10.1	52.8	28.4	8.6
27, flow system[b], 300°	8.2	6.4	54.2	21.6	9.7
28, flow system[b], 300°	5.2	9.6	50.5	21.7	12.9
27, injector port[c], 280°	20.3	0.3	45.5	24.4	8.3
27, injector port[c], 305°	19.0	3.8	43.6	22.0	10.4
27, injector port[c], 342°	15.6	9.2	40.2	20.7	12.2
27, injector port[c], 378°	15.7	11.5	36.0	17.3	12.8

[a] all pyrolyses carried out in the gas phase. [b] quartz tube; contact time 70 sec. [c] injector port of a Hewlett-Packard 5750 gas chromatograph equipped with electronic digital integrator. Percentages reproducible to ± 1 %. [d] tentatively assigned as cis-2,3-dimethyl-1-methylenecyclobutane.

but control experiments showed that the two isomers interconvert thermally at this temperature. At 278°, where only very slow interconversion occurs, 27 gave rise to <1% 34 and 28 produced <1% 32. The diene product proved to be 35; less than 0.1% of 36[42] was detectable in the reaction mixture. Spectral data obtained on 35 were identical upon comparison with that of an independently synthesized sample.[41] 37 was prepared independently by the addition of methylene to 3-methyl-1, 4-pentadiene.[43] 36 was prepared by the $Rh(Cl)_3(H_2O)_3$ catalyzed addition of ethylene to 1, 3-pentadiene.[36] 32 and 34 were characterized by comparison with nmr and ir of samples synthesized independently by Berson and co-workers.[39] The unknown is believed to be mainly cis 2, 3-dimethyl-1-methylene-cyclobutane (nmr evidence).

From inspection of Table IV, there appear to be two types of products: those whose relative abundance increases with increasing decomposition temperature (the bicyclopentanes (32) and (34), and the methylenecyclobutane), and those whose relative abundance decreases with increasing temperature (the allylcyclopropane (37) and the 1, 4-pentadiene (35)).[44] This is indicative of a dual pathway decomposition which will be discussed later.

Although when 27 and 28 are decomposed under identical conditions in a quartz tube (first four experiments in Table IX) they both give 35 and 37 as major products, the ratio of 35:37 is

slightly different depending on the stereochemistry of the starting pyrazoline. The syn pyrazoline (28) gives 35 and 37 in the ratio of 2.1:1 while the anti isomer (27) decomposes to give 35 and 37 in the ratio of 2.5:1. This observation will be discussed later.

DISCUSSION

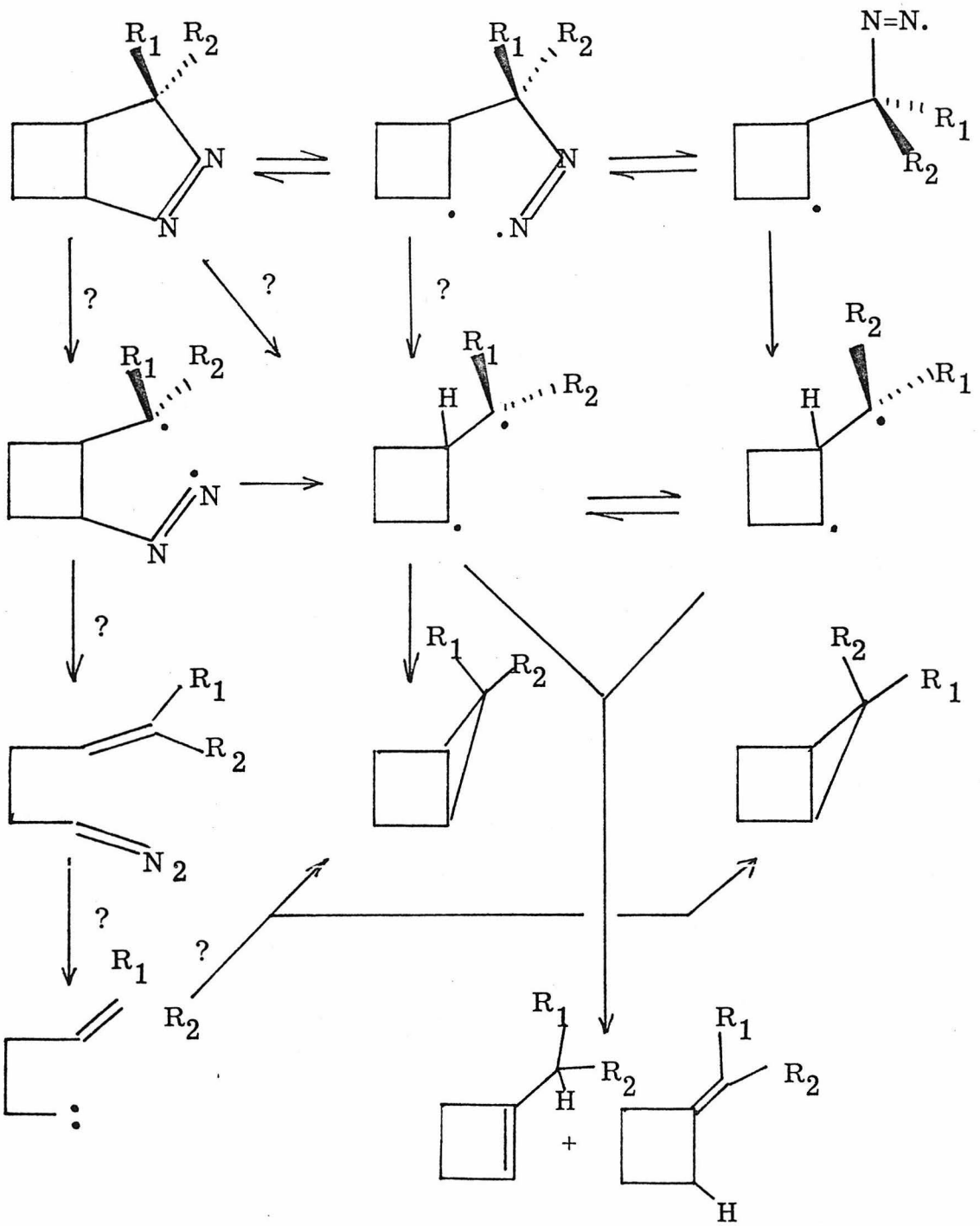
Mechanism for the Formation of Bicyclopentanes from 14

The various mechanisms for the formation of bicyclopentanes from 14 and 7 are presented in Scheme VIII. In light of the results obtained in the decomposition of 27 and 28, the bicyclopentanes probably could not arise by the addition of a carbene to a remote double bond (see Figure 2). The bicyclopentanes from 27 and 28 retain the stereochemistry of their precursors. This would not be expected if they were coming from a carbene. Several ways are presented in Scheme VIII for the formation of the carbene. These will be discussed in the next section.

Formation of Diene Products

The formation of 1, 4-dienes as a major product in the thermal decompositions was unexpected. See Tables IV, V and IX. Three mechanisms can be proposed. One possibility, which could explain their presence and that of vinylcyclopropane, is that the diradical (21), a potential initial intermediate, is in equilibrium with an isomeric "di-π-methane" intermediate[65] formally written as the diradical (22).

Scheme VIII : Mechanisms for the Formation of Bicyclopentanes



hydrogen shift products

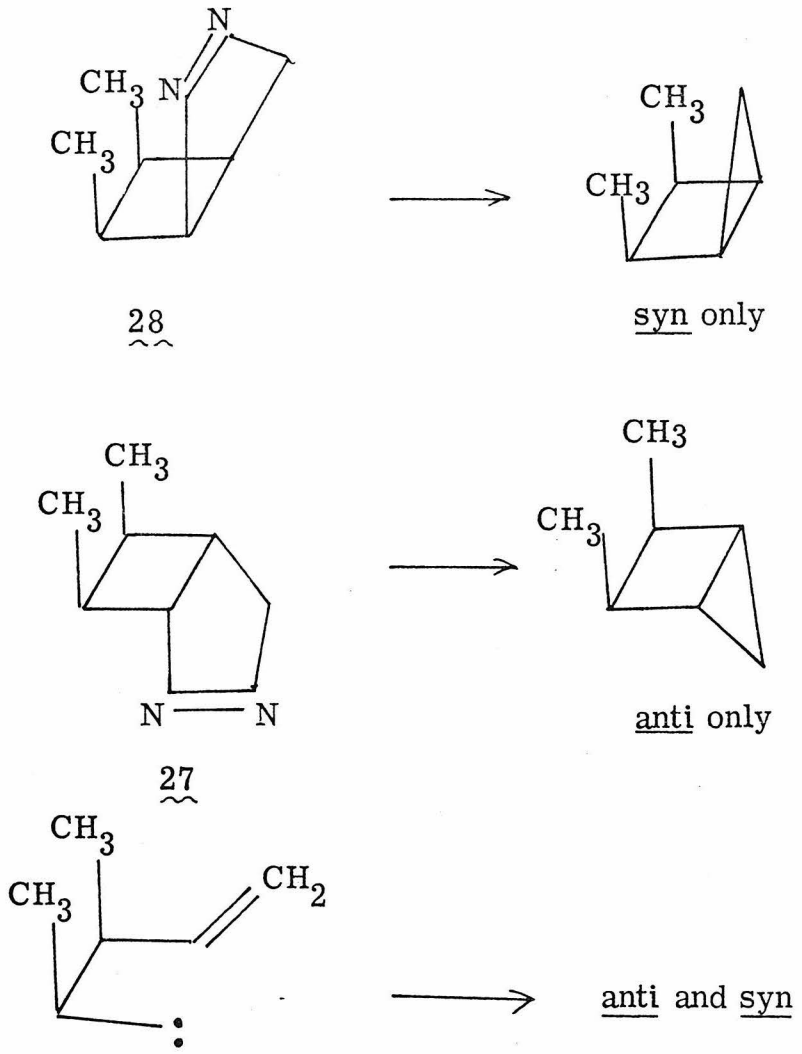
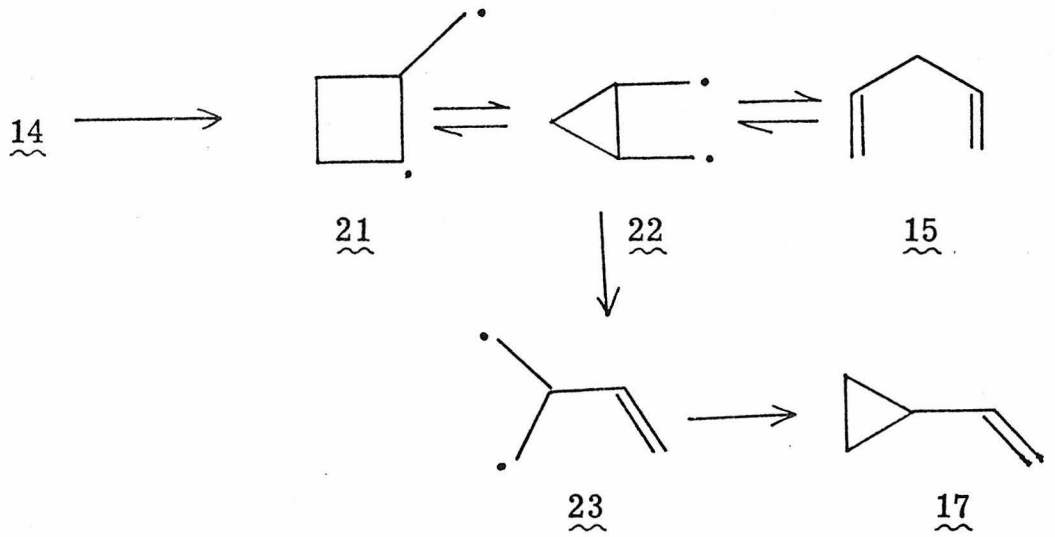
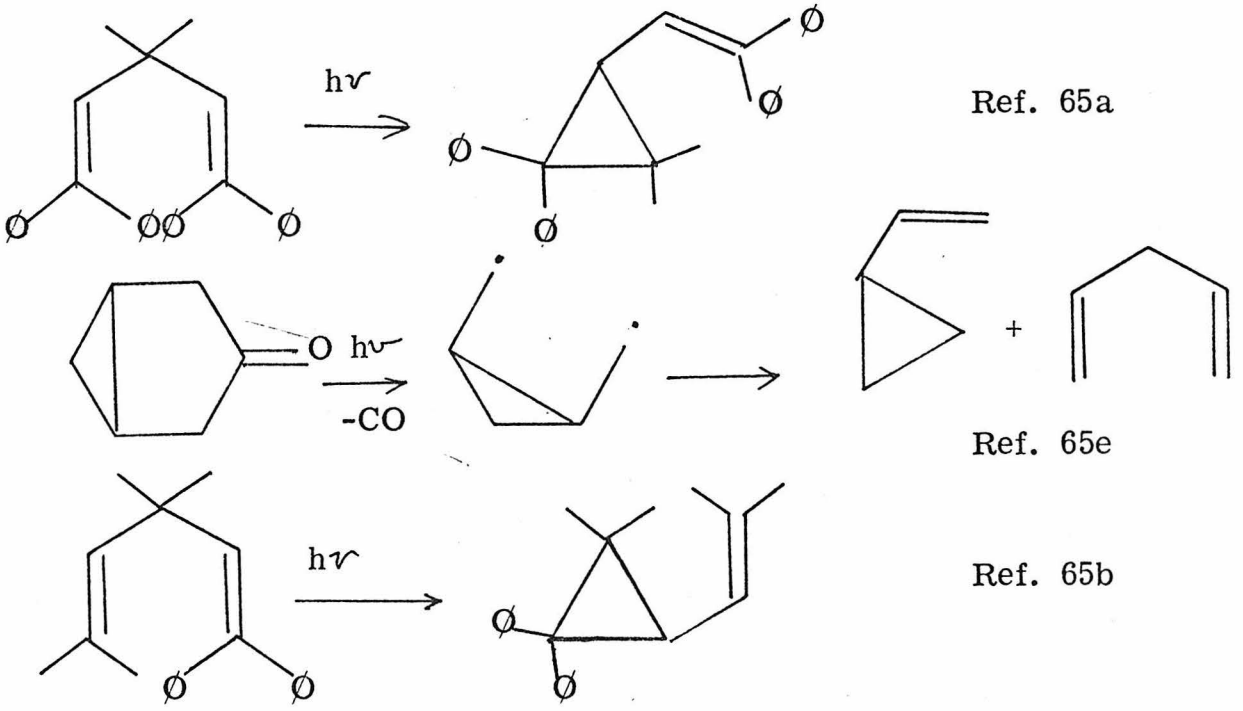


Figure 2 : Bicyclopentanes from Isomeric Cis 6,7-dimethyl-2,3-diazabicyclo [3.2.0] hept-2-ene



Di-π-methane intermediates were postulated to occur in the following irradiation reactions.[65]

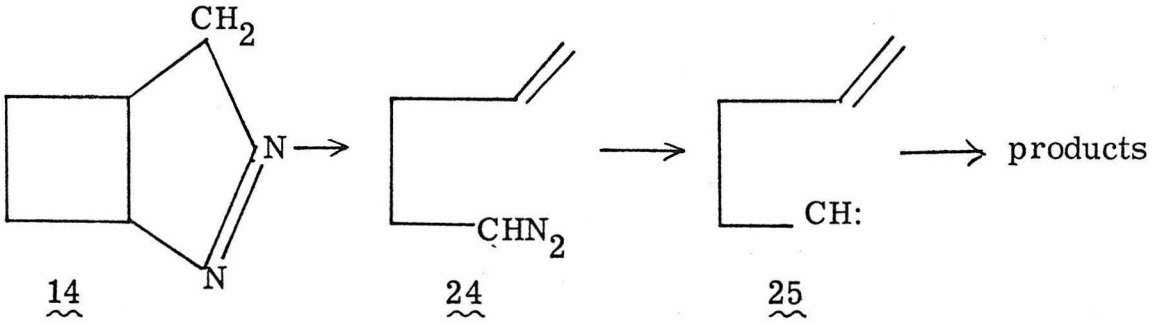


Ref. 65a

Ref. 65e

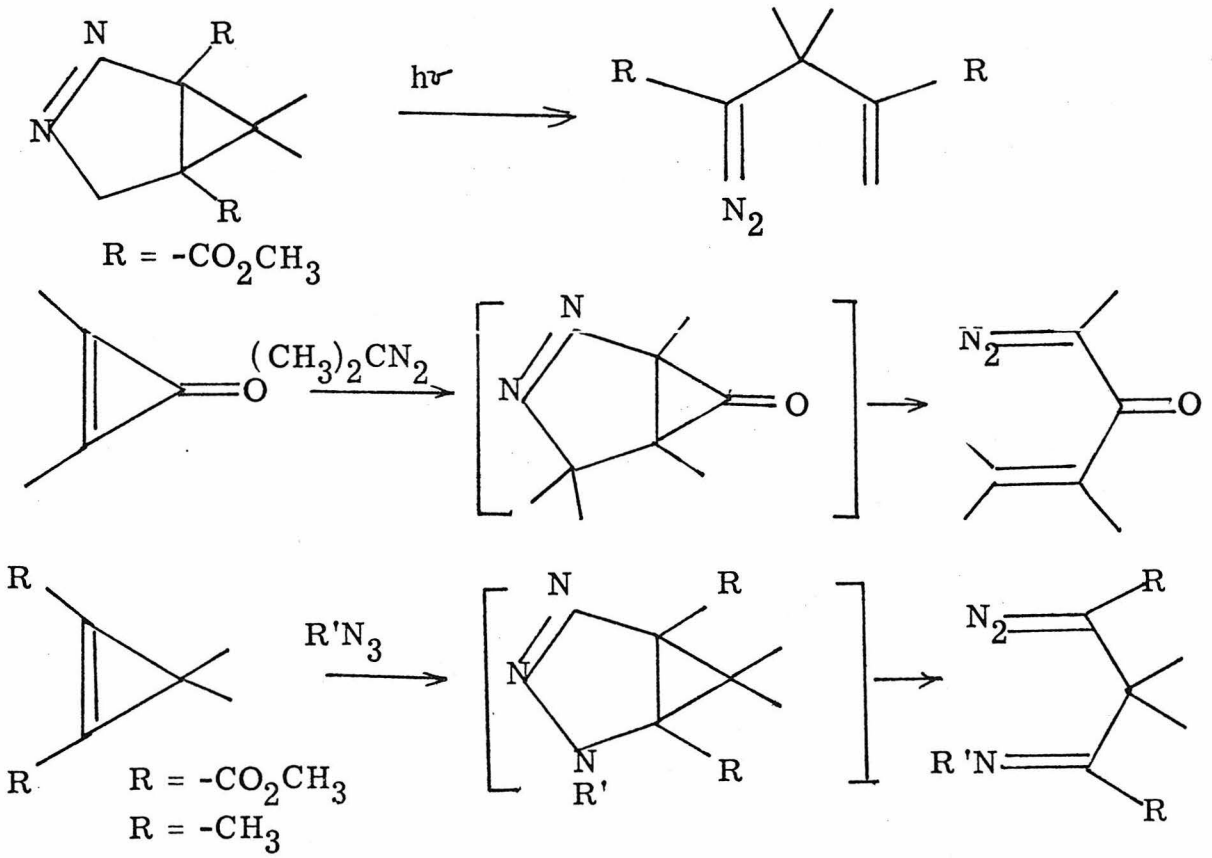
Ref. 65b

A second possibility is that 14 may undergo a reverse 1,3 dipolar addition to the diazo compound (24), which decomposes via carbene (25) to 15 and 17.



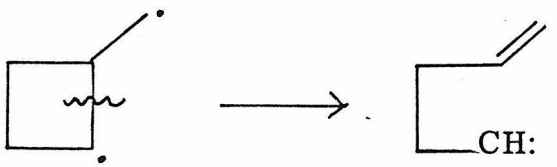
14 24 25

Similar retro-1,3-dipolar reactions have been reported in systems where the diazo compounds have been isolated.[66]



Ref. 66

The third mechanistic alternative is the direct formation of 25 from 21 by scission of the cyclobutane carbon-carbon bond.



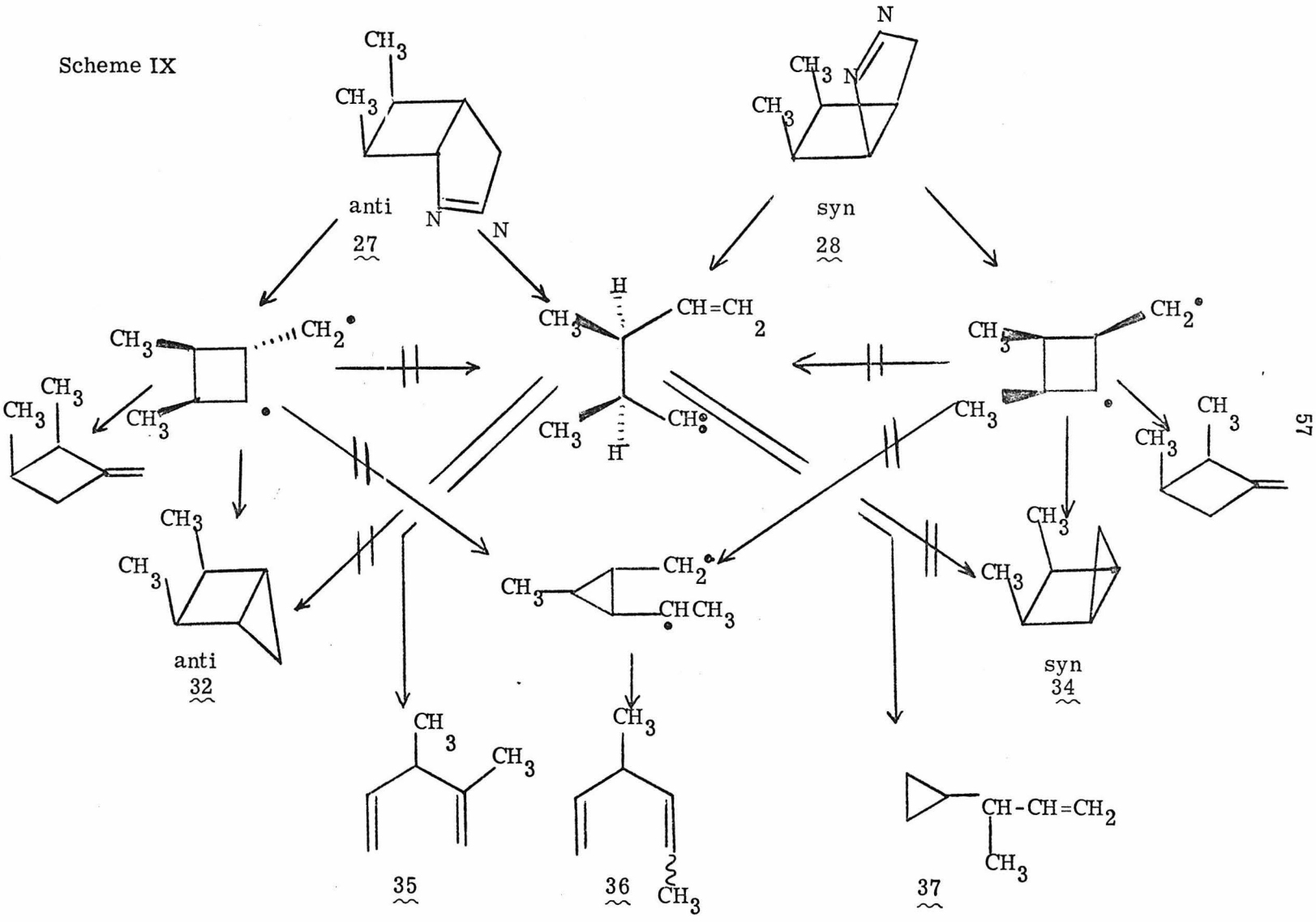
21 25

The study of the products from the thermal decomposition of 27 and 28 strongly suggests that the second mechanism is operating (see Scheme IX). The diene expected from the di-π-methane pathway 37 was not found to be a product.

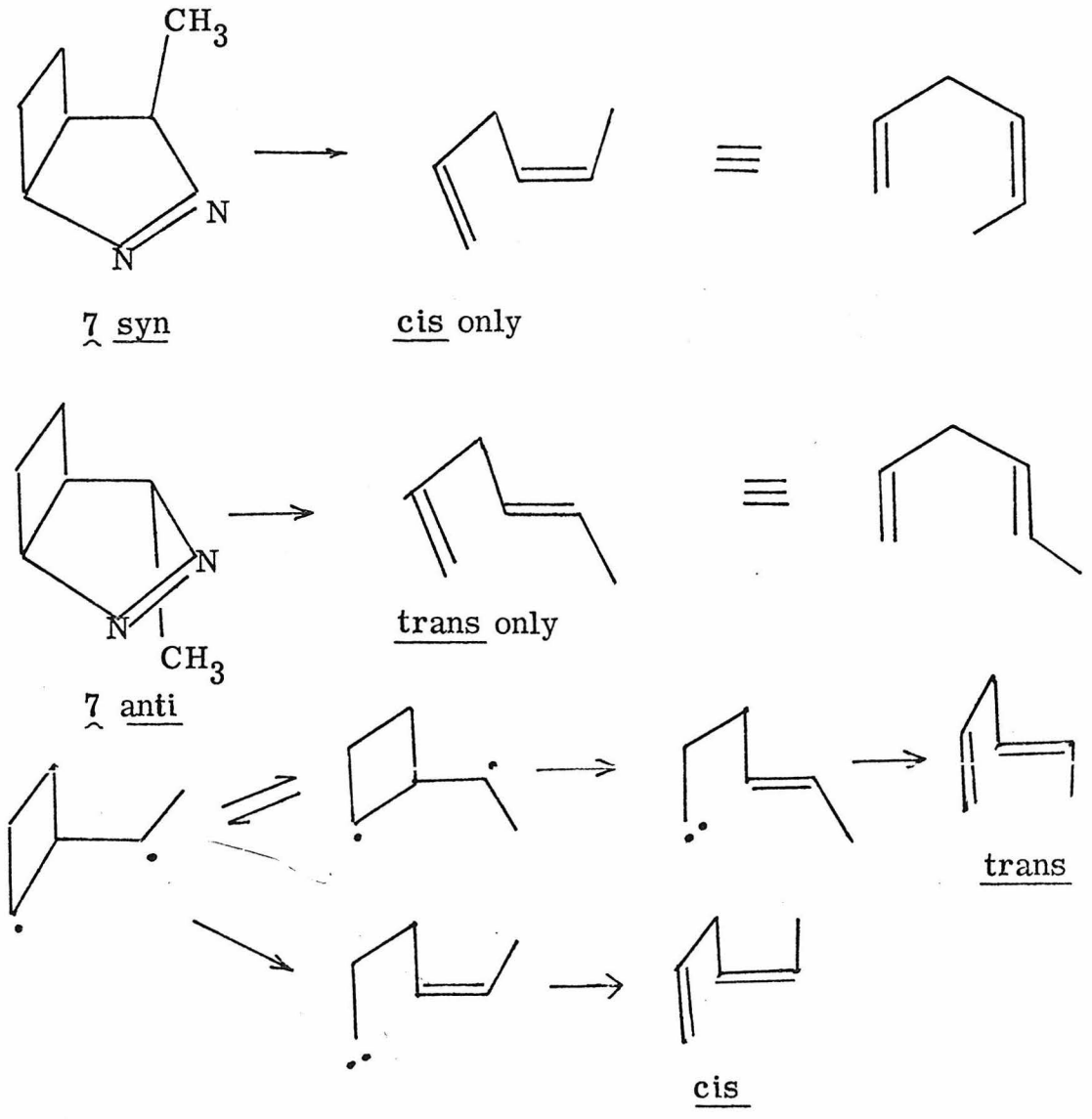
The diene 35 expected by insertion of the carbene 30 into the carbon-hydrogen bond of the adjacent carbon atom is found to be the major product both from 27 and 28. The cyclopropylbutene 37 can be formed by insertion in the β carbon-hydrogen bond.

The dual pathway (carbene and diradical) seems to be further supported by the appreciable temperature dependence of the azo compound product distribution (Table IX); as the temperature was raised, the percentage of "carbene-derived" products 35 and 37 decreased with respect to the "diradical-derived" products 32, 34 and unknown. A plot of the yield ratio [(32, 34 and unknown/35 + 37)] versus 1/T was linear and gave ΔE_{act} = 5.2 kcal/mole, and a $\Delta\Delta S$ = 3.4 e.u. Thus the third possibility is eliminated.

Scheme IX



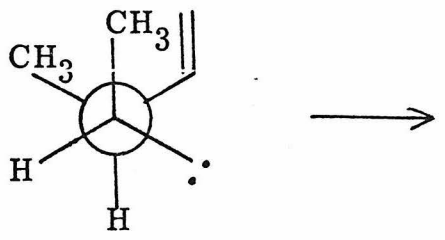
Further evidence for the preference of the second mechanism over the third was obtained in the study of the isomeric 4-methyl-2,3-diazabicyclo[3.2.0]hept-2-enes. See Scheme X.

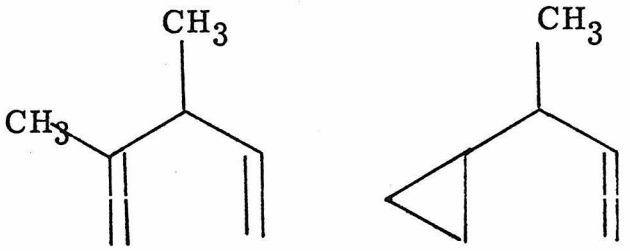


Scheme X

The concerted retro-dipolar addition would be expected to give only a single diene isomer, whereas the diradical intermediate should lead to isomeric dienes. Since anti 7A gave only trans 1, 4-hexadiene, and syn 7S gave only cis 1, 4-hexadiene, a retro-dipolar addition is strongly implied.

The ratio of 35 to 37 is slightly lower coming from 28 than from 27 (see Table IX). This probably has to do with the conformation in which the carbene is generated. However, examination of Fischer projections of the carbenes derived from pyrazolines 27 and 28 predicts the opposite trend .

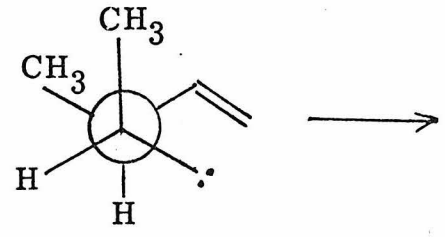




35 37

2.1 : 1

carbene from 28 (syn)



2.5 : 1

carbene from 27 (anti)

The increased steric hindrance caused by the newly formed double bond pointing toward the α-CH_3 group in the carbene derived from 28 should cause a greater preference for insertion into the carbon-hydrogen bond of the carbon adjacent to the carbene (giving rise to 35).

The steric hindrance is less in the carbene derived from 27 and hence more of 37 should be seen from insertion into the carbon-hydrogen bond of the α-methyl group.

The effect may be caused by some non-obvious steric hindrance leading to the observed results.

EXPERIMENTAL

General

Infrared spectra were obtained on a Perkin-Elmer 257 Grating Infrared Spectrophotometer in 0.2 mm solution cells with solvent as reference. Nuclear magnetic resonance spectra were obtained on a Varian A-60A, except where noted in the text. Ultraviolet spectra were obtained on a Cary 14 Spectrophotometer. Melting points were determined on a Thomas Hoover capillary apparatus and are uncorrected.

Preparative vapor phase chromatography (VPC) and all analytical VPC on 1/4 inch columns were accomplished on a Varian Aerograph Model 90P. Analytical VPC on 1/8 inch columns was performed on a Hewlett-Packard Model 5750 Research Chromatograph with flame ionization detector. The signal was automatically integrated by a Hewlett-Packard 3370A digital integrator and recorded on a Hewlett-Packard 7127A Strip-Chart recorder. All 3/8 inch and 1/4 inch columns were operated with a He carrier flow rate of 60 ml/min. All 1/8 inch columns were made of stainless steel tubing.

Preparation of diazoacetate.[30] Ethyl diazoacetate was prepared by the method of Moser, except the diazoacetate was not

distilled. The pentane was stripped on a rotary evaporator until the weight of the remaining solution approximated the theoretical yield (228 g on Moser's scale) or until the condensing pentane took on a yellowish tinge. NMR (CCl_4/pentane): δ 1.75 (t, J = 7 cps, $\underline{CH_3}-CH_2-$), δ 4.15 (q, J = 7 cps, $CH_3-\underline{CH_2}-CO$), δ 4.60 (s, $N_2=\underline{CH}-CO_2$). IR (CCl_4/pentane: 3115 (m), 2960 (s), 2920 (s), 2880 (s), 2105 (s), 1700 (s). Yield was 70% of theoretical based on NMR evidence.

Preparation of 2,3-dimethyl-1-carbethoxy cyclopropane. This compound was prepared by the method of Doering and Mole. One-half ℓ of cis 2-butene (J. T. Baker Chemical Co.) was condensed into a 2 ℓ 3-neck round bottom boiling flask cooled in a dry ice acetone bath. The flask was equipped with a 500 ml pressure equalizing dropping funnel, magnetic stirrer, and dry ice acetone condenser to which was attached another condenser cooled by a Forma Bath to -15°C. The last condenser was vented to the atmosphere through a Drierite-filled drying tube and an oil-type bubbler.

After the cis butene was condensed in, a water-ice-salt bath was substituted for the dry ice acetone bath and 4 g (0.01 m) of catalyst (triphenyl phosphite)-copper(I) chloride [16] (see below) was added to the cis 2-butene. 70 g (0.6 m) ethyl diazoacetate in pentane solution (~50 m per cent) was added dropwise to the stirred butene solution.

The reaction was followed by the use of infrared spectroscopy. The diazo band at 2100 cm^{-1} slowly disappeared. The time needed for completion of the reaction varied between 44 hr and 23 hr from run to run.

The cis-butene was distilled off by heating the reaction flask in warm tap water and condensing the butene in a dry ice-acetone cooled flask. The remaining material was stripped of residual butene on a rotary evaporator at 1/3 atmosphere. The product was distilled at 5 torr to give 5 fractions. The first three fractions, collected between 35° and 51°C, were combined to give 25 g of 95.7% pure product. The yield from ethyl diazoacetate was 29%. The major side reactions are the formation of diethyl maleate and fumarate, which are higher boiling than the desired product. IR (CCl_4): 3000-2880, 1720, 1315, 1165, 1090, 1045, cm^{-1} in agreement with literature values.

The NMR of 2,3-dimethyl-1-carbethoxy cyclopropane revealed a 2 H quartet at 4.02 δ (J = 7 Hz) and a complex of 12 H between 1.83 δ and 2.55 δ. The major product and the side reaction products were also analyzed by GLC using a 15' × 1/8" column containing UCW98 as the liquid phase and 100-120 mesh chromosorb P as a solid support. The cyclopropane ester elutes before the diethyl maleate and fumarate.

Preparation of (triphenyl phosphite)copper(I) halide.[30] 15.5 g (0.05 m) of triphenyl phosphine were mixed with 9.5 g (0.05 m) of Cu(I)

in benzene. The mixture was allowed to stir for 48 hr or until all solids dissolved.

The solution was filtered by gravity and stripped to ~100 ml. Addition of 60°-90° ligroin caused the oiling out of the catalyst. This oil can be refrigerated to give crystals or used as is after decanting the benzene and ligroin.

Preparation of 2,3-dimethyl-1-carboxyl cyclopropane. 13.2 g (0.093 m) of the ester were dissolved in 140 ml of methanol (1 m of ester per 1.5 ℓ of methanol) in a 500 ml one-neck round-bottom boiling flask equipped with a pressure equalizing 250 ml dropping funnel. The flask was cooled in a water ice and salt bath. 26 g of KOH (0.465 m) (molar ratio of ester to KOH is 1:5) was dissolved in enough water to give a 10 M solution. This solution was cooled in ice and then added slowly over the period of 0.5 hr.

The dropping funnel was replaced by a water cooled condenser and the solution was refluxed for 3 hr using a steam bath as heat source.

The reaction was followed by IR; each aliquot was washed with CH_2Cl_2 and the organic layer washed with brine, dried, and stripped on a rotary evaporator. The reaction was complete when no carbonyl absorption could be detected in the IR.

The reaction was worked up as follows. The solution was washed twice with ethyl ether. The ethyl ether washings were combined and extracted with saturated NaCl solution. The brine solution was then combined with the water solution. The water solution was slightly acidified with aqueous HCl; it was then extracted twice more with ethyl ether. The ethyl ether was separated from the water phase and washed once with brine. The combined ethyl ether solutions were dried overnight with anhydrous Na_2SO_4.

The ether solution was evaporated to dryness on a rotary evaporator to give either crystals or an oil. The oil was cooled in a refrigerator overnight to give crystals which were then recrystallized from hot ligroin. Yield on the basis of ester was 82%.

NMR ($CDCl_3$): δ 12.64 (s, $-CO_2\underline{H}$), δ 0.85-1.58 (m, 3 H), δ 1.08 (d, J = 5 cps, $C-C\underline{H}_3$). IR ($CHCl_3$): 2500-3400, 1690, 1462, 1450, 1320, 1200, 1090 cm^{-1}.

Preparation of cis 2,3-dimethyl-1-chloroformyl cyclopropane. 33 g of the acid (0.293 m) were mixed with 38.4 g of thionyl chloride (0.323m) (molar ratio of acid to thionyl chloride is 1:1.10) in a 100 ml one-neck round-bottom flask equipped with a reflux condenser and magnetically stirred. The reaction was end o thermic. The mixture was stirred for 1 hr at room temperature and then heated to reflux for 1 hr. The reaction was followed by IR. The C=O stretch of the acid at

1690 cm^{-1} was gradually replaced by C=O stretch of the acid chloride at 1780 cm^{-1}. After cooling, excess $SOCl_2$ was removed in vacuo. The yield of crude product was nearly quantitative. NMR (neat): δ 1.1-1.8 (m, 3 ring H), δ 1.0 (d, J = 5.5 cps, $-C\underline{H}_3$)

Preparation of cis 2,3-dimethyl-1-formyl-cyclopropane via the intermediacy of an aziridine amide.[31] Triethylamine and aziridine were stirred in dried ethyl ether cooled to -50° to -60°C. The molar ratio of triethyl amine to aziridine to acid chloride is 1:1:1. The amount of ether used was in the ratio of 1.5 ℓ of ether per mole of acid chloride. The largest reaction run was on 38.4 g of the acid chloride reacting with 12.8 g of aziridine in 425 ml of ether. The acid chloride, in a solution of ethyl ether, was added over the period of 1 hr. The reaction was run under a nitrogen atmosphere using ether distilled from $LiAlH_4$. After addition of the acid chloride the solution was stirred for 1 hr at -50°C and then allowed to slowly warm to room temperature. The ethereal solution was separated from the precipitated triethylammonium chloride by means of diatomaceous earth and a sintered glass funnel (fine pores). The precipitate was washed with ethyl ether to recover all the amide.

The ethereal solution of the amide was transferred to a new vessel and cooled under a nitrogen atmosphere to -50°C in a dry ice-acetone bath. A slurry of $LiAlH_4$ in ethyl ether was added through an

addition funnel over the period of 0.5 hr. The solution was stirred 15 min at -50°, 30 min at 0° and 30 min at room temperature. Solid Na_2SO_4 and saturated Na_2SO_4 solution were added to hydrolyze the $LiAlH_4$ and the intermediate. The ethereal solution of the aldehyde was decanted and the precipitate washed three times with ether. The combined washings and the ether solution were dried overnight over anhydrous Na_2SO_4.

An NMR spectrum of the aldehyde in ethereal solution showed doublets at δ 9.1 (J = 4 Hz) and 9.7 ppm (J = 4 Hz) corresponding to anti and syn aldehydes (ca. 4:1 ratio). The doublet at 9.1 δ is the larger peak and is presumably the anti isomer. Normally the aldehyde was not isolated; the ether solution produced in the $LiAlH_4$ reduction was used directly in the tosylhydrazone preparation (vide infra).

(cis 2,3-dimethylcyclopropyl)-carbinol. 54.6 g (0.38 moles) of cis 2,3-dimethyl-1-carbethoxy cyclopropane were dissolved in 200 ml of anhydrous ethyl ether. A 500 ml 3-neck round bottom boiling flask equipped with a mechanical stirrer and reflux condenser was charged with 10.6 g (0.28 moles) of lithium aluminum hydride (LAH) in 100 ml of anhydrous ether. The solution of the ester in ether was added through the dropping funnel to the stirred suspension of LAH in ether, which was cooled to 0°C, under an inert nitrogen atmosphere over a period of 4 hr. After the addition was complete,

the reduction was carefully quenched by adding a saturated aqueous solution of sodium sulfate until the suspension was light gray in color. After a few hours stirring, the mixture had turned completely white, at which time the ethereal solution was suction filtered and the residue on the filter was washed with more ether. Removal of the solvent (ethyl ether and ethanol) at atmospheric pressure left a residue that was 96% by weight the desired alcohol, (cis 2, 3-dimethyl-cyclopropyl)-carbinol. NMR (D_2O): δ 4.58 (s, CH_2–OH), δ 3.59-3.20 (m, CH_2OH), δ 0.77-δ 0.13 (m, 3 ring H), δ 0.85-1.15 (m, $-(CH_3)_2$).

Improved synthesis of cyclopropylcarboxaldehyde from cyclopropylcarbinol.[35] To 8.07 g (0.112 mole) of cyclopropylcarbinol was added a solution of 136.5 g (0.241 mole) of ceric ammonium nitrate (G. Frederick Smith Chemical Co.) in 250 ml of water. The cloudy, deep red solution was heated on a steam bath until colorless (15 min). The solution was cooled, saturated with sodium chloride, and transferred to a separatory funnel. Water (400 ml) was added, and the solution was extracted four times with 50 ml portions of dichloromethane. The combined dichloromethane layers were dried overnight over a mixture of magnesium sulfate and sodium bicarbonate. The volume of the solution was reduced to 50 ml by distillation through a 30 cm Vigreux distillation column. 4 ml of bromobenzene were added to the residue and this solution was distilled through a 20 cm

Vigreux column into a receiver flask cooled in an ice-acetone bath. A quantity of 5.8 g of material was obtained, boiling point 97-99° (760 mm) which was 84.0% (by weight) (0.03 mole) the desired aldehyde, and 16% dichloromethane. The yield was 61.3%. Analysis of product was by NMR and vapor phase chromatography on a 6' × 1/8" column maintained at 35°C and packed with 10% UCW98 on chromosorb W. NMR (CCl_4): δ 1.0 (d first order, J ≃ 6 cps, 4 H), δ 1.3-1.8 (m, 1 H), δ 8.93 (d, J = 5.5 cps, C–C<u>H</u>O).

<u>Cis 2,3-dimethylcyclopropane-anti-1-carboxaldehyde p-toluene-sulfonyl hydrazone</u>. To the dried ethereal solution of the aldehyde was added tosylhydrazide and the solution was refluxed for 6 hr. Tosylhydrazide was added in the mole ratio of 1:1 on the basis of maximum aldehyde obtainable from the acid chloride. The reaction was followed by disappearance of the carbonyl band in the IR. After the reaction had gone to completion, the ether was stripped and a viscous yellow solution obtained. This crystallized upon standing in the refrigerator. The tosylhydrazone was recrystallized twice by dissolving in the minimum amount of methanol necessary and then adding water until crystallization began. The overall yield of tosylhydrazone (based on starting carboxylic acid) was 19%. NMR (acetone-D_6): δ 7.8 (d, J = 8 cps, 2 H_{Ar}), δ 7.3 (d, J = 8 cps, 2 H_{Ar}), δ 6.8 (d, J = 6.5 cps, <u>anti</u> –CH–C<u>H</u>=N), δ 6.1 (d, J = 6.5 cps, <u>syn</u>

-CH-CH=N), δ 2.32 (s, $-CH_3$), δ 1.15-0.80 (m, 3 ring H), δ 9.0 (s, $-(CH_3)_2$). Ratio of anti to syn by NMR is 5:3.

Preparation of cis 3,4-dimethyl-1-cyclobutene. One gram of the tosylhydrazone was dissolved in 30 ml of diethyl carbitol (dried over $LiAlH_4$ and distilled) contained in a 50 ml three neck round bottom flask equipped with a magnetic stirring bar, a reflux condenser, a rubber septum and a nitrogen flush inlet. N-butyllithium (Alpha Inorganics) in hexane was added in a 25% mole excess through the septum into the stirred solution under a nitrogen atmosphere, with cooling by an ice-salt bath. Sufficient n-butyllithium was added to cause the solution to assume a yellow tinge, the color of the n-butyllithium in hexane. A salt precipitate formed.

The nitrogen flow was discontinued and the system was evacuated at low pressure (high vacuum pump), carefully at first, to remove the volatiles, mainly butane and hexane. Next, a trap and drierite filled drying tube was introduced between the condenser and a water aspirator. The trap was cooled to -78° in a dry ice-acetone bath and the diethyl carbitol solution was heated to the boiling point (approximately 160°) at a reduced pressure of 100 torr for one hr. Decomposition of the lithium salt of cis 2,3-dimethylcyclopropane-anti-1-carboxaldehyde p-toluenesulfonylhydrazone took place and the product, cis 3,4-dimethyl-1-cyclobutene, was condensed in the cooled

trap.

The material in the trap was vacuum transferred to a gas bulb after two freeze-thaw cycles using liquid nitrogen as the cold source and dry ice-acetone as the hot source. Material in the trap was warmed gradually to 50° to effect total transfer.

The product was vacuum transferred to gas bulb equipped with a serum cap. A gas tight syringe was used to sample products by withdrawal through the cap. The products were analyzed on a 22' by 1/4" O.D. dibutyltetrachlorophthalate (DBTCP) column at 100° and a helium flow rate of 1 ml per second. The order of elution of products and impurities is; air (1.7 min), cis 2-butene (3.6 min), hexane (8.2 min), cis 3,4-dimethyl-1-cyclobutene (8.7 min), and 2,4-hexadiene (19.3 min). Percentage of carbene intermediate going to acetylene and cis 2-butene was 18.7%, to the cyclobutene was 67%, to the hexadiene was 14.3%. NMR of cis 3,4-dimethyl-1-cyclobutene (CCl_4): δ 0.98 (d, J_{ab} = 7 cps, 6 H_a), δ 2.98 (m, 2 H_b), δ 6.07 (s, 2 H_c).

Preparation of nitrosomethylurea. Prepared by the method of F. Arndt. Into a tared one-liter one-neck round bottom flask equipped with a reflux condenser was placed 200 grams of 24% methylamine (1.55 mole), 155 ml of concentrated HCl (until solution was acid to methyl red) and water to bring the total weight to 500 grams. To this

was added 300 grams of urea (5 moles). The solution was boiled gently for 2.75 hr and vigorously for 0.5 hr. The solution was cooled to room temperature, 110 grams of 95% $NaNO_2$ (1.51 mole) were dissolved in, and the whole was cooled to 0° in an ice-salt bath.

A mixture of 600 grams of ice and 100 grams (1 mole) of concentrated H_2SO_4 was placed into a three-liter beaker which was surrounded by an efficient freezing mixture of ice, salt and water. The cold methylurea-nitrite solution was run in slowly with mechanical stirring at such a rate that the temperature did not exceed 0°.

The nitrosomethylurea rose to the surface as a crystalline, foamy precipitate which was filtered out at once with suction and pressed well on the filter. The crystals were stirred to a paste with 50 ml of water, sucked as dry as possible on suction filter and dried in a vacuum desiccator to a constant weight in a freezer. Crystals can be stored indefinitely in the freezer. The yield was 115 grams or 65% of the maximum. NMR (acetone-D_6): δ 3.15 (s, $C\underline{H}_3$), δ 3.52 (broad s, $N\underline{H}_2$).

Preparation of diazomethane from nitrosomethylurea. The procedure of P. Condit was used. Fifty-six grams of KOH were dissolved in 30 ml of water contained in a 200 ml unscratched flask which were cooled in an ice-salt bath. Thirty ml of diethyl ether were added to the magnetically stirred solution of KOH. Eight grams of

nitrosomethylurea were added cautiously; rapid addition caused excessive frothing. The generation of diazomethane was run in the hood because of its toxicity. During the course of the reaction a yellow gas, diazomethane, formed above the yellow colored ether layer. A polyethylene cap was placed lightly over the mouth of the flask. The solution was stirred for 0.5 hr in an ice-salt bath and then cooled in a dry ice-acetone bath. If the aqueous layer froze, the decantation of the ether layer into another unscratched 200 ml conical flask containing pellets of KOH for drying the ether was easily facilitated. If the aqueous layer did not freeze, as was more often the case, care was taken to prevent the transfer of the aqueous layer. The aqueous layer was washed twice with 20 ml portions of ether. The ether solutions were combined.

Preparation of 6, 7-dimethyl-2, 3-diazabicyclo[3.2.0]hept-2-ene. The 3, 4-dimethyl-1-cyclobutene was vacuum transferred from the gas bulb into a 50 ml 3-neck round bottom flask equipped with a rubber septum and a stopcock; the middle neck was connected to the vacuum line via a stopcock.

The 200 ml flask containing the diazomethane was fitted with a two-hole rubber stopper containing a drying tube and a glass tube extending below the surface of the liquid. The glass tube was connected by rubber tubing to the stopcock of the flask containing the cyclobutene.

The flask of diazomethane was cooled in a dry ice-acetone bath to -78°.

The flask of cyclobutene was closed off and removed from the vacuum line. A dry ice-acetone bath was substituted for the liquid nitrogen bath. The flask was pressurized slightly by the introduction of nitrogen through the septum via a syringe. The flask containing cyclobutene was connected to the flask of diazomethane in ether. The stopcock was cracked. Care was taken to make sure that no ether solution was sucked back into the flask of cyclobutene. The cyclobutene was allowed to warm up gradually and the volatile material was bubbled slowly into the ether solution of CH_2N_2. Finally, when no more material transferred in this fashion, a stream of dry N_2 was introduced to waft the remaining material into the ether solution. If this failed to effect total transfer, ether was introduced and the remaining material was pipetted into the ether solution of CH_2N_2.

The solution was transferred to a darkened pressure bottle which had previously been cooled gradually to -78° in a dry ice-acetone bath. The pressure bottle was stoppered and placed in the dark. Every three days, the bottle was opened with care and the reaction was monitored. If a peak corresponding to 3, 4-dimethyl-1-cyclobutene appeared on a 22' DBTCP column, another portion of CH_2N_2 was prepared as before and added to the pressure bottle.

After 13 days at room temperature, more than 87% of the cyclobutene had reacted. The resulting pyrazolines could be made quite pure by prolonged stripping on a rotary evaporator because of their low volatility. The pyrazolines could be stored at low temperatures in darkened vessels indefinitely.

Analysis of the pyrazolines was carried out on a 15% UC-W 98 glass column, 10' by 1/4". A glass column was used because the pyrazolines decomposed on a stainless steel one. This column was suitable for preparative gas chromatography of the syn and anti isomers which were formed, in greater than 95% isomeric purity.

Determination of the stereochemistry of syn and anti 6, 7-dimethyl-2, 3-diazabicyclo[3.2.0]hept-2-ene. The reaction of cis 3, 4-dimethyl-1-cyclobutene and diazomethane yielded two isomers in a 7:3 ratio. The major product was identified as the anti 1, 3 dipolar cyclo adduct and the minor product as the syn dipolar adduct.

The identification was made by observing the larger shifts of the methyl groups in the syn isomer than the anti isomer when both are complexed with $Eu(fod)_3$ in CCl_4 (fod is the abbreviation for tris 1, 1, 1, 2, 2, 3, 3-heptafluoro-7, 7-dimethyl-4, 6-octanedione). The complexation was done on a mixture of the two isomers by adding increments of a standard solution of $Eu(fod)_3$ in CCl_4 and taking an NMR after each addition. It was found that the resonance of the

methyls of the syn isomer shifted farther down field than those of the anti isomer; in all cases the methyl groups closer to the nitrogen-nitrogen double bond shifted farthest.

Also, at the temperature where the interconversion of the syn and anti 2,3-dimethyl-bicyclo[2.1.0]pentanes is slow, the anti pyrazoline gave rise to anti bicyclopentane, and the syn pyrazoline gave rise to syn bicyclopentane, exclusively in both cases. NMR of anti isomer (CCl_4): δ 0.95 (d, J = 7 cps, 3 H), δ 1.22 (d, J = 7 cps, 3 H), δ 1.8-2.5 (m, 3 H), δ 4.36 (m, 2 H), δ 4.66 (m, 1 H). Partial NMR of syn isomer (CCl_4): δ 0.56 (d, 3 H, J = 7 cps), δ 0.85 (d, J = 7 cps, 3 H). IR of anti isomer (CCl_4): 2860-2960, 1715, 1450, 1360, 1220 cm^{-1}.

Flow pyrolysis of 6,7-dimethyl-2,3-diazabicyclo[3.2.0]hep-2-ene. The first pyrolysis system used was a 12" by 0.5" O.D. quartz tube heated in the temperature range of 270° to 320° in a tube oven. A U-shaped glass tube was connected to the quartz tube at one end and equipped with a rubber septum at the other. This served as a vaporization chamber for the pyrazoline. Vaporization was accomplished by directing a flow (10 ml per 12-14 sec) of dry N_2 through the septum via a syringe across the pyrazoline. The U-shaped tube was heated by immersion in an oil bath heated to 100° when runs were undertaken for quantitative results and by a heat gun when large

amounts of pyrazoline were pyrolyzed only for the sake of product analyses. In all runs, the joint connecting the U tube and the quartz tube was heated intermittently with a heat gun to prevent condensation of the pyrazoline.

The pyrazoline, which was introduced via a syringe through the septum, was pyrolyzed neat or as a 5-10% solution in pentane (pentane did not interfere with the products on the gas chromatographic column used for the analysis).

The products (32-37) were collected in a trap cooled in liquid N_2 and then vacuum transferred to a more suitable container. Analysis and preparative gas chromatography were conducted on a 10' by 1/4" O.D. UC-W 98 stainless steel column at 65° and a helium flow rate of 10 ml per 12.5 sec. Characterization was by NMR and IR spectroscopy (see below).

After the identification of most (88%) of the products had been accomplished, later pyrolyses were carried out in the heated injector port (270°-380° range) of a Hewlett-Packard gas chromatograph instrument equipped with an electronic digital integrator and analyzed on a 10' by 1/8" O.D. 20% SE-30 column. The advantage gained here was the smaller amount of material required (1/2 microliter versus 5 microliters in the quartz system) and the elimination of the product collection before analysis, not to mention the increased accuracy of the

integrations. For spectral data on 3-cyclopropyl-1-butene and 3-methyl-1, 4-hexadiene, see following procedures. NMR of 2, 3-dimethyl-1, 4-pentadiene (CCl_4): δ 5.78 (d, d, d, J_{cg} = 6.5, J_{eg} = 9.5, J_{gf} = 17.5, 1 Hg), δ 5.08 (sym m, 1 vinyl H), δ 4.83 (sym m, 1 vinyl H), δ 4.70 (q, J_{bd} = 0.7 cps, $C(CH_3) = C\underline{H}_2$), δ 2.79 (first-order pentet, J_{cg} = 6.5 cps, J_{ac} = 7 cps, 1 doubly allylic H), δ 1.68 (d, J_{bd} = 0.7 cps, allylic, $C\underline{H}_3$), δ 1.12 (d, J_{ac} = 7 cps, $-CH-C\underline{H}_3$). IR (CCl_4): 3060, 2960, 2900, 2850, 1625, 1445, 1360, 985, 905, 885 cm^{-1}. NMR of <u>endo cis</u> 2, 3-dimethylbicyclopentane (CCl_4): 0.65 (d, J = 6 cps, $-(CH_3)_2$), δ 0.1-0.4 (m, 2 H), δ 1.35-1.83 (m, 2 H), δ 2.30-2.70 (m, 2 H). NMR of <u>exo cis</u> 2, 3-dimethylbicyclopentane (CCl_4): δ 1.64 (m, 2 H), δ 1.03 (d, J = 6 cps, $-(C\underline{H}_3)_2$), δ 1.55 (m, 2 H), δ 1.72 (m, 2 H). NMR's of isomeric bicyclopentanes agree with those published.[24] NMR of 2, 3-dimethyl-1, 4-pentadiene agrees with a commercial sample (Chemical Samples Co.).

<u>Preparation of 3-methyl-1, 4-hexadiene</u>.[42] Into a test tube, the mouth of which had been joined to a 7 mm O.D. glass tube was placed 190 ml of absolute ethanol, 0.407 grams of $RhCl_3(H_2O)_3$ and 5.7 grams of mixed geometric isomers of 1, 3-pentadiene. Ethylene was condensed into the glass tube, which was cooled in liquid nitrogen, directly from the lecture bottle. Approximately 5 ml of ethylene at that temperature were introduced. The tube was placed into a nitrogen

cooled stainless steel cylindrical bomb; the bomb was sealed and placed in an oil bath, and heated to 60°-70° for 20 hr without agitation. Prior to opening, the bomb was cooled in liquid nitrogen.

The product solution was filtered to remove the catalyst. The product, 3-methyl-1,4-hexadiene, was easily separated from unreacted 1,3-pentadiene by preparative gas chromatography on a 10' by 1/4" 20% SE-30 stainless steel column at 65° and a helium flow rate of 10 ml/12.5 sec. The NMR was identical with that of 3-methyl-1,4-hexadiene synthesized by N. F. Cywinski.[41] The 3-methyl-1,4-hexadiene was shown to be stable under the pyrazoline pyrolysis conditions. NMR (CCl_4): δ 1.03 (d, J_{ac} = 7 cps, 2 H_a), δ 1.62 (m, 3 H_b), δ 2.73 (broad sextet, J = 6 cps, 1 H_c), δ 4.87 (m, 1 H_d), δ 4.95 (m, 1 H_e), δ 5.37 (m, 2 H_f), δ 5.62 (d, d, d, J_{ge} = 17.5, J_{gd} = 9.5, J_{gc} = 6.5 cps, 1 H_g). IR ($CHCl_3$): 3080, 3019-2850, 1638, 1455, 1415, 1379, 1370, 1250 cm^{-1}. NMR in agreement with literature.[27]

Preparation of 3-cyclopropyl-1-butene.[41,43] To a hot rapidly stirred solution of 0.6 grams of cupric acetate monohydrate in 20 ml of glacial acetic acid was added 10.5 grams (0.15 mole) of zinc dust. After about 30 sec all of the copper had deposited on the zinc. The couple was allowed to settle for 30 to 60 sec and then as much of the acetic acid as possible was decanted, taking care not to loose the silt-like couple. The dark reddish gray couple was then washed with one

20 ml portion of glacial acetic acid, followed by four 35 ml portions of absolute ether. The last washing was itself extracted with water and the pH of the water was found to be 6-7 pH units as indicated by pH paper.

The 100 ml round-bottom boiling flask used for the preparation of the zinc-copper couple was equipped with a reflux condenser, a dropping funnel, and a magnetic stirring bar. The solvent, 35 ml of ether, was added followed by a few ml of diiodomethane. The reaction started immediately as indicated by bubbles rising from the couple. While the stirred solution was kept at reflux by the heat of the reaction or by slight warming, a mixture of 6 grams (0.075 mole) of 3-methyl-1,5-hexadiene and the remainder of the 28 grams of diiodomethane (0.105 mole total) in ten ml of ether was added dropwise over a period of 1.5 hr. The reaction mixture was stirred at reflux for 20-30 hr. To prevent the loss of solvent during this period a Formabath set at -10° was used to cool the reflux condenser. Reaction was monitored by gas chromatography.

At the end of the reaction, the mixture was a dark brown-purple in color. The ether solution was separated from the zinc by suction filtration first through a coarse then a fine pored sintered glass funnel. The zinc was washed on the filter with ether to remove as much of the product as possible.

The combined ether solutions were washed in a separatory funnel containing ice and 1 N HCl. The ethereal solution was separated, washed a second time with ice-HCl acid, washed three times with water, and dried over K_2CO_3.

The water washings greatly reduced the volume of the organic layer by virtue of the large amounts of water used (200 ml per wash), and the solubility of ether in water (7.5 grams per 100 ml). This greatly concentrated the product in the organic phase. The organic phase, after drying, was vacuum transferred to separate the product from polymeric material. The yield was 1.2 grams of which 43% was the desired product (0.5 grams); the rest was ether and unreacted starting material. The overall yield was only 7%. This was ample amount to, after preparative gas chromatography on a 10' by 1/4" O.D. 20% SE-30 column at 65° and a helium flow rate of 10 ml per 12.5 sec, take an NMR and do a stability study of the product under the reaction conditions used to decompose the pyrazolines. NMR (CCl_4): δ 0.06 (m, 2 H_a), δ 0.40 (m, 3 H_b), δ 1.05 (d, J_{dc} = 5.5 cps, 1 H_c), δ 1.40 (m, 1 H_d), δ 4.90 (m, 1 H_e), δ 5.02 (m, 1 H_f), δ 5.82 (d, d, d, J_{gf} = 17.5, J_{gc} = 10, J_{gd} = 6 cps, 1 H_g). IR ($CHCl_3$): 3080, 3000, 2985, 2935, 2885, 1640, 1455, 1369 cm^{-1}.

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64. (a) For references to a number of examples of the di-π-methane rearrangement, see H. E. Zimmerman and P. Mariano, J. Amer. Chem. Soc., 91, 1718 (1969). For other examples and mechanistic studies, see (b) H. E. Zimmerman and A. A. Baum, ibid., 93, 3646 (1971); (c) H. E. Zimmerman and A. C. Pratt, ibid., 92, 6259 (1970); (d) W. G. Dauben and W. A. Spitzer, ibid., 92, 5817 (1970); (e) for an example in which apparent di-π-methane products were formed from an independent precursor, see L. D. Hess and J. N. Pitts, ibid., 89, 1973 (1967).

65. M. Franck-Neumann and C. Buchecker, Tetrahedron Lett., 2659 (1969).

Part II

INTRODUCTION

The Wall-less Reactor Concept

"The extent to which the surface of the vessel enters into the reaction mechanism of thermal decompositions is one of the most prominent and puzzling questions which cannot yet be satisfactorily answered even after thirty years of rather intensive research."[28] This quotation by Rice and Herzfeld appeared in a review article published in 1951, but it could very well apply to the present state of knowledge concerning the role of the surface in gas-phase reactions.

In recent years, new techniques have been developed for studying various aspects of gas-phase reactions under completely homogeneous conditions. Some of these involve mass spectroscopic techniques,[1] molecular beam interactions,[2] flash photolysis,[3] and shock tube investigations.[4] However, the most widely used method for determining the effect of heterogeneity on gas-phase thermal reactions still remains the study of the effect on the rate and product distribution of a reaction by varying the surface to volume ratio or by changing the surface material of the reactor.

Because of surface effects it is almost impossible to define a set of conditions under which a pyrolysis reaction has been carried out.

The nature and area of the surface remains a variable.

In 1968, D. A. Hutchings [5] designed, constructed and tested a homogeneous (wall-less) reactor for the pyrolysis of hydrocarbons. In principle, the wall-less reaction encompasses a flowing stream of hydrocarbon inside a protective cylinder of inert flowing gas. No contact of the hydrocarbon to be pyrolyzed is permitted with the containing surface. The hydrocarbon, maintained at a low temperature, enters the reactor through a tube. By mixing with a zone of superheated gas, it quickly heats up to the temperature of the gas. Laminar flow is maintained throughout except in the zone of mixing. The flow is downward to avoid turbulence due to gravity effects. A cooled sampling tube, mounted on a three dimensional microscope stage permitting movement in any part of the reaction zone, is used to collect samples of the pyrolysate before lateral diffusion can move any of the hydrocarbon to the wall. Plug flow is maintained over the significant range since the length of movement on the gas is only one to three times that of the diameter of the tube.

Reactions Suitable to the Wall-less Reactor

Hutchings first used the reactor in the study of the pyrolysis of neopentane. He found [6] that the decomposition of neopentane was first-order from 650°-850° with an activation energy of 80.5 kcal/mole

and an A factor of $10^{16.9}$. This was in contrast to earlier results at lower temperatures which indicated reaction order of 3/2 and an energy of activation of between 51.5 and 60 kcal/mole [7, 8, 9] which was well below the C–C bond energy in neopentane which is approximately 80 kcal/mole.

Since that time, the reactor has been used by Professor J. E. Taylor's research group to study the isomerization of cyclopropanes,[25] and the pyrolysis of ethane.[26]

Many other reactions are suitable for study in the wall-less reactor. Compounds which exhibit a surface dependence in their decomposition or isomerization could be studied in the wall-less reactor where conditions are homogeneous. For example, the effect of the surface is especially great in the thermal decomposition of t-buyl and t-amyl chlorides as was found out by Bearley, Kistiakowsky and Stauffer.[12] Similar effects were found in the pyrolysis of 1,1,1-trichloroethane by Barton and Onyon.[13] The decomposition of dimethyl-triazine gave a 12% higher rate value in the first run than in succeeding runs.[18]

The thermal decomposition of acetaldehyde at 380-400° in a silica vessel appears to be a purely surface reaction yielding several products in addition to methane and CO. If the decomposition is carried out at 500° or higher only methane and CO are formed and the rate of

reaction is almost independent of the surface to volume ratio.[24, 14, 22] The reaction order at lower temperatures is 3/2 while at higher temperatures it is first order which presents evidence for a heterogeneous and homogeneous mechanism in the decomposition.

Any gaseous decomposition reaction which has a "long" induction period is conceivably surface dependent. To initiate reaction the gas has to be brought up to temperature and then the steady-state concentration of radicals must be attained. On the basis of the original Rice-Herzfeld theory[19] the steady-state concentration would take only a fraction of a second to attain. However, if the steady-state concentration is dependent on a diffusion process from the wall, the time for induction will be much longer. The decomposition of ethylene oxide, a free radical process, has been carefully studied and shows a well-marked induction period[16] and a surface dependence.

Some gaseous decomposition reactions show a marked dependence on the influence of the inert gas. The wall-less reactor can be used to exclude all other surface effects except that of the carrier gas which can be varied. Hydrogen has a pronounced effect of increasing the rate of thermal decomposition of ethylene oxide,[16] dimethyl ether,[21] methyl ethyl ether,[15] methyl propyl ether[15] and diethyl ether[17] in surface reactions. While CO_2, CO, He, N_2, CH_4, Ar and Ne have no effect at all.

A large effect on the rates of the thermal decompositions of phosphine [11, 23] and sulfuryl chloride [20] is exhibited when the surface to volume ratio is changed, making these two compounds likely candidates for further study using a wall-less reactor.

Many cis ⇌ trans isomerizations of olefins appear to be surface dependent. Examples are the interconversion of cis and trans 1, 2-difluoroethene and cis and trans 1, 2-dichloroethene. [27, 32]

Limitations of the Wall-less Reactor

The wall-less reactor is restricted to the study of reactions which exhibit first-order rate equations. This encompasses a wide variety of reactions including reversible and irreversible isomerizations, and irreversible decompositions. A second restraint is that the measurements must be made in the temperature range where first-order rate constants are greater than 1×10^{-3} per sec. The first restraint arises from that fact that absolute concentrations of reactant or products cannot be known. Only the relative ratio of reactant concentration to product concentrations is available to the experimenter. The second restraint arises out of the inherent residence time limitation for a molecule in the wall-less reactor.

DESIGN OF ORIGINAL APPARATUS

General

The wall-less reactor, which I constructed for use in the Bergman group, was originally based on one designed by D. A. Hutchings and J. E. Taylor of Kent State University. The reactor underwent some modification during the course of my research. I will begin by first explaining, in detail, the original wall-less reactor I constructed, and then discuss the subsequent modifications.

A drawing of area surrounding the reaction zone of the wall-less reactor is presented in Figure 1. In principle, the reactor consists of a stream of hydrocarbon (1A) entering the reactor through a cooled tube (called the nozzle, 1Q), that is kept at a low enough temperature to prevent any reaction prior to the point of heat up (1T). Upon entrance into the reaction zone (1U), the hydrocarbon is very quickly heated up to reaction temperature by mixing with the preheated blanket gas flowing through tube (1W) in a vertically downward direction. All gas streams are assumed to be laminar. This outer stream of gas is of sufficient thickness that a significant concentration of neither reactant or product contacts the reactor wall within the chosen reaction time. Quenching of the reaction and collection of a sample is brought about by means of the probe (1X), also a cooled tube, through which a

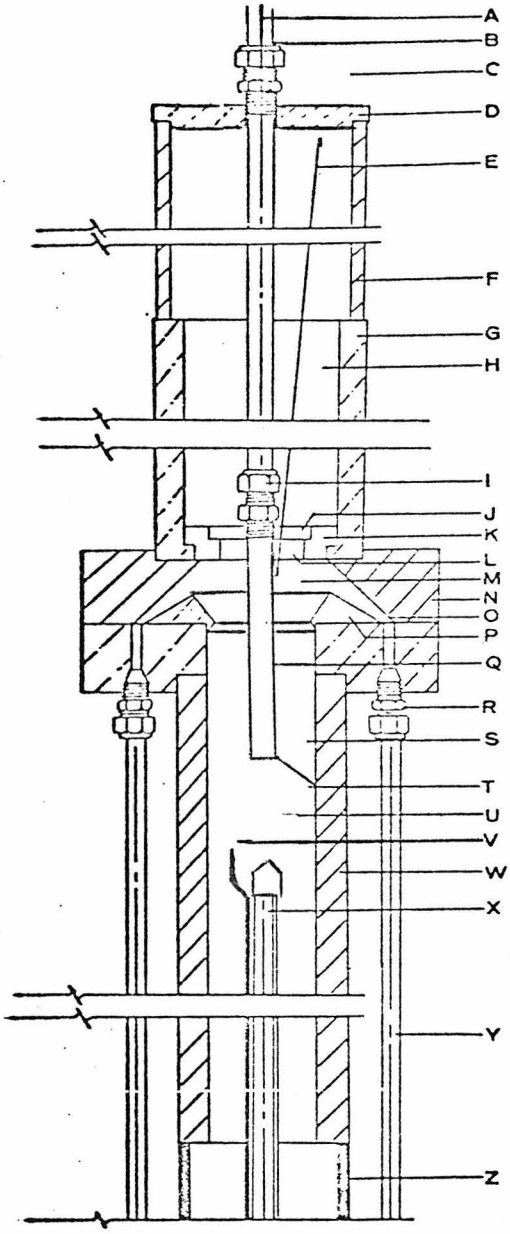


Figure 1: Original Wall-less Reactor

sample of the reaction mixture can be withdrawn by a syringe for analysis on a vapor-phase chromatograph. The whole apparatus shown in Figure 1 is contained in a three-zone Lindberg-Hevi-Duty furnace, model number 54847-A, 10,000 watts (2D of Figure 2).

All materials shown in Figure 1 are constructed of stainless steel unless otherwise specified. The nitrogen used for the blanket gas, which comes from 5 foot cylinders, is metered by rotameters and enters the oven via tube 1Y (3/8 in O.D.). From there it flows to a mixing chamber 1M formed by pieces 1N and 1P (which are bolted together), and then into tube 1W, the actual reaction tube. Tube 1W has an inner diameter (ID) of 1.5 in (3.81 cm), an outer diameter of 2.375 inches, and a length of 12.5 inches.

Tube 1Z is the exhaust tube and leads to the open air (2.375 in O.D., 2.060 in I.D., length 18 in). Exhaust hydrocarbons are sucked out of the room or into a hood by means of an exhaust fan, the suction tube of which is placed about 3 inches from the end of the exhaust tube (1Z).

1V is a chromel-alumel thermocouple encased in a stainless steel sheath (1/16 in O.D.) filled with a ceramic insulator to prevent short circuits between sheathing and wires (trade name of thermocouple is Conax SS6K).

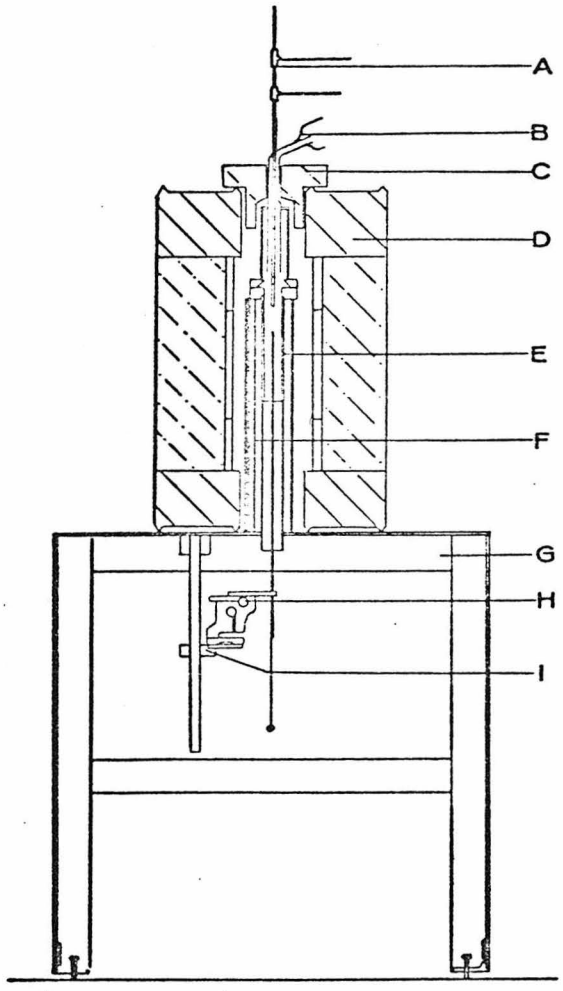


Figure 2: Wall-less Reactor Enclosed in Oven

The nozzle (1Q), which has an O.D. of 3/8", is fitted through swagelock fittings (1B and 1I, stainless steel, 3/8 in swagelock and 3/8 in pipe fitting, Crawford part number 600-1-6-316) which have been bored out to accept the nozzle. These swagelocks are screwed into plates (1D and 1 J-K-L). 1 J-K-L is now a single piece of metal. Pieces 1D, 1 J-K-L, 1I, 1B and 1Q can be removed (after loosening bolts holding plate 1D to piece 1 G-F) as a single unit for nozzle repair or modification. The section of the nozzle (1Q) between plate 1D and 1 J-K-L is wrapped with layers of pyrex glass wool and asbestos tape to provide better insulation between the cool nozzle and the rest of the reactor. Piece 1 G-F is bolted to piece 1N.

The reactor shown in Figure 1 is mounted on a heavy duty aluminum table (2G) by means of three stainless steel rods (2F). Attached to the underside of the table is a three-way microscope stage (2H) to which the probe assembly (1X) is fixed for manipulation. See Figure 3. The probe, when it is detached from the microscope stage, can be removed from inside the reactor for cleaning and repair work.

The sampling probe. The sampling probe consists of three tubes. See Figures 4 and 5. The inner tube (4B, 0.022 in OD, 4 ft in length) through which the sample is withdrawn, is cooled by air (4E) blown into the divider tube 4D. The air exits through tube 4F. The inner tube 4B is press-fitted (or welded) into stainless steel cone (4A),

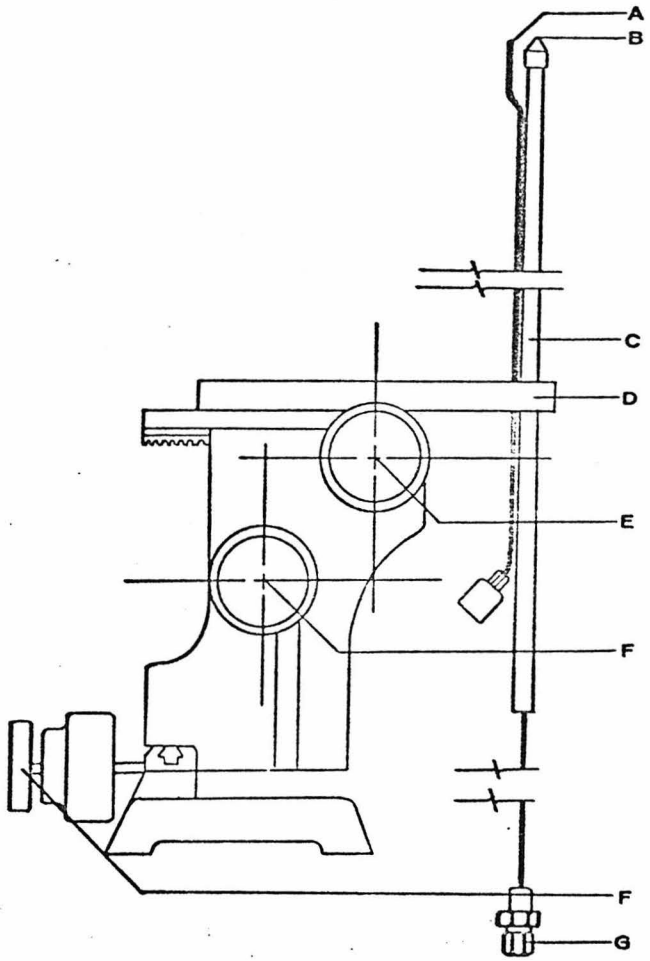


Figure 3: Microscope Stage with Sampling Probe Attached

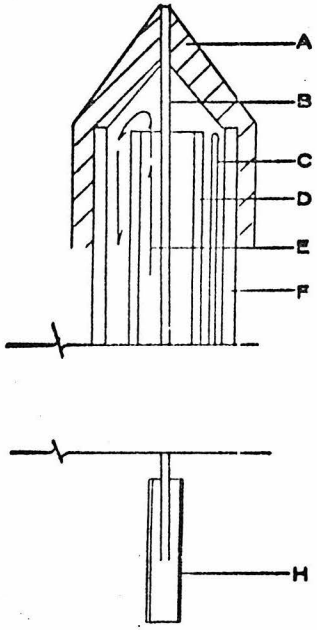


Figure 4: Tip of Probe (above)

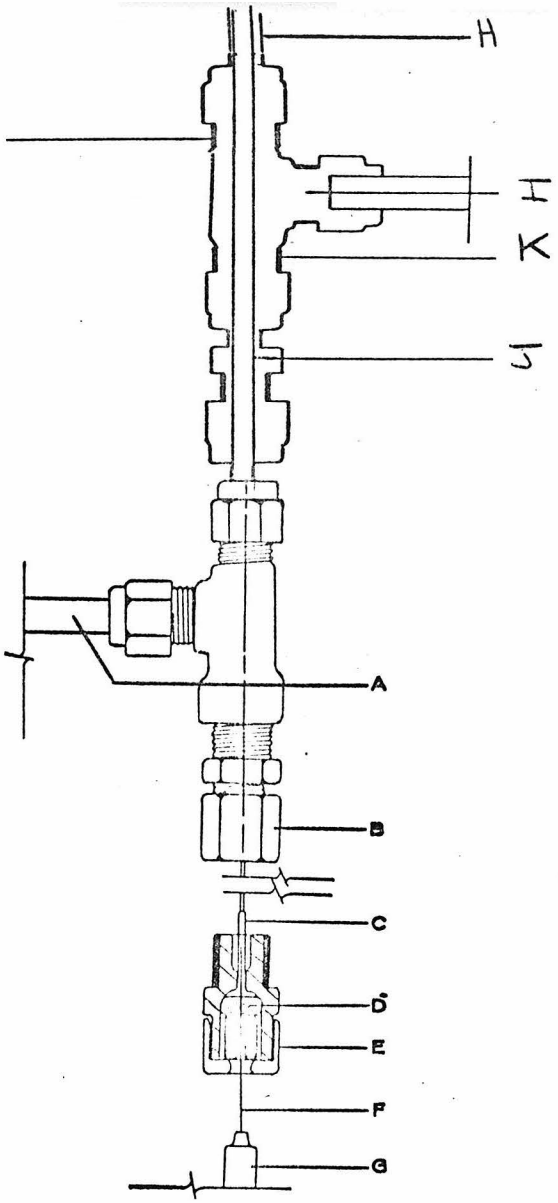


Figure 5: Design of Probe Outside of Oven (right)

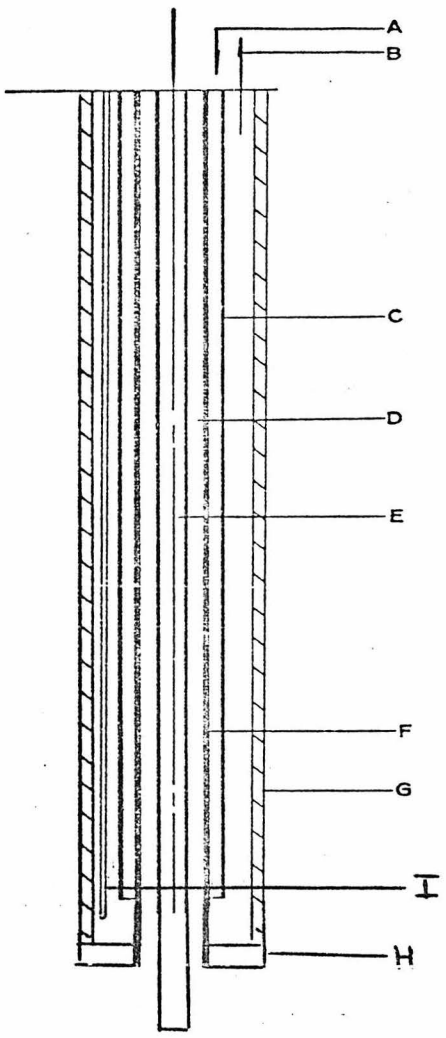
which is in turn press-fitted (or welded) over a 32 inch piece of 1/4 O.D. stainless steel tubing (4F) to form a cooling jacket (all junctures must be air tight). A 1/8 in O.D. tube (4D) with a 0.01 in wall thickness serves as a divider to permit air flow over the entire length of the cooling jacket.

The temperature at the tip of the probe is monitored by a 0.040 in O.D. chromel-alumel stainless steel sheathed thermocouple (4C, Conax SS4K) which is placed inside the cooling jacket. Entry into the probe for the thermocouple is gained by cutting out a hole in the base of tube 5H (tube 4F of Figure 4), close to where it is attached to 5K (Figure 5). Temperatures 500°C below the reaction zone temperature can be maintained at the tip of the probe.

The other end of tube 4B is attached to a Conax 1/16 in thermocouple fitting (5D). Samples are withdrawn from the thermocouple fitting by using a gas tight syringe (5G).

A minor modification made was to wrap the sampling probe with asbestos paper in order to provide better insulation between the cold probe and hot reactor.

Original nozzle design. The nozzle consists of four concentric tubes (see Figures 6 and 7). A hydrocarbon stream enters the reactor through a 1/16 in O.D. hydrocarbon inlet tube (6E). A cooled nitrogen



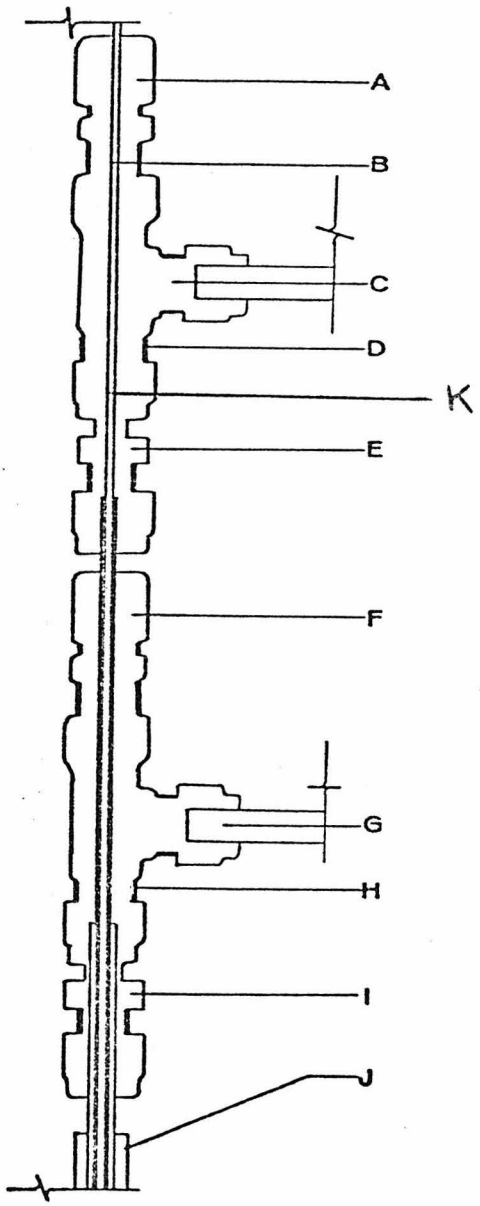


Figure 6: Tip of Nozzle (left)

Figure 7: Design of Nozzle Assembly Outside of Oven (right)

stream, called the diluent, enters the reaction zone through tube (6F) (1/16 in O.D.). A piece of 3/8 inch O.D. tubing (6G), that has had three inches of its length turned down to an outside diameter of 0.325 inches is joined to the 1/8 inch tube (6F) by means of a donut shaped plug (6H) to form a cooling jacket for the diluent and hydrocarbon streams. A divider tube (6C), which allows the cooling air (in 6A, out 6B) to flow through the entire length of the nozzle, is formed from a 3/16 inch O.D. piece of tubing.

The other end of the nozzle is outside of the furnace (see Figure 7). The diluent nitrogen stream enters via 7C. The cooling air stream enters via 7G and exits at 7J. 7D and 7H are Crawford fittings number 400-3-4TFT-316; 7E and 7I are Crawford fittings number 400-R-6-316. A chromel-alumel, stainless steel sheathed thermocouple (6F, Conax SS4-K) is inserted into tube (7J) all the way down to the tip of the nozzle in order to monitor the temperature inside the nozzle. By loosening the swagelock fitting on 7A, it is possible to remove only the hydrocarbon delivery tube (7B) for replacement or cleaning without opening the oven.

MODIFICATION

Sample delivery system. The sample delivery system is of two types. The one used depends on whether the material to be pyrolyzed is a liquid at room temperature and pressure or a gas. Discussion of the liquid delivery system will be first.

The original wall-less reactor designed by D. A. Hutchings, utilized a complicated motor driven syringe for the delivery of liquids and gases. The sample was drawn up by the syringe and injected into a stream of nitrogen gas. The rate of flow of the nitrogen gas was dependent on how often the syringe was discharged into the stream. To achieve a desired total velocity, both the rates of nitrogen gas flow and syringe discharge must be taken into consideration. Another problem is noncontinuous input of material into the sample delivery system, since a syringe must be refilled before it can be discharged.

A simple bubbler type delivery system was designed to improve Hutchings' methods (see Figure 8). Nitrogen gas (Linde-High Purity Dry Grade), which was passed through air purifying filters (Koby Jr. air purifier and flow equalizer) and a flow equalizer, and then metered on an appropriate rotometer, is directed through a glass frit (8A, coarse porosity) into a pure sample of the liquid hydrocarbon (8B) to be pyrolyzed and then to the reactor. In this manner, hydrocarbon

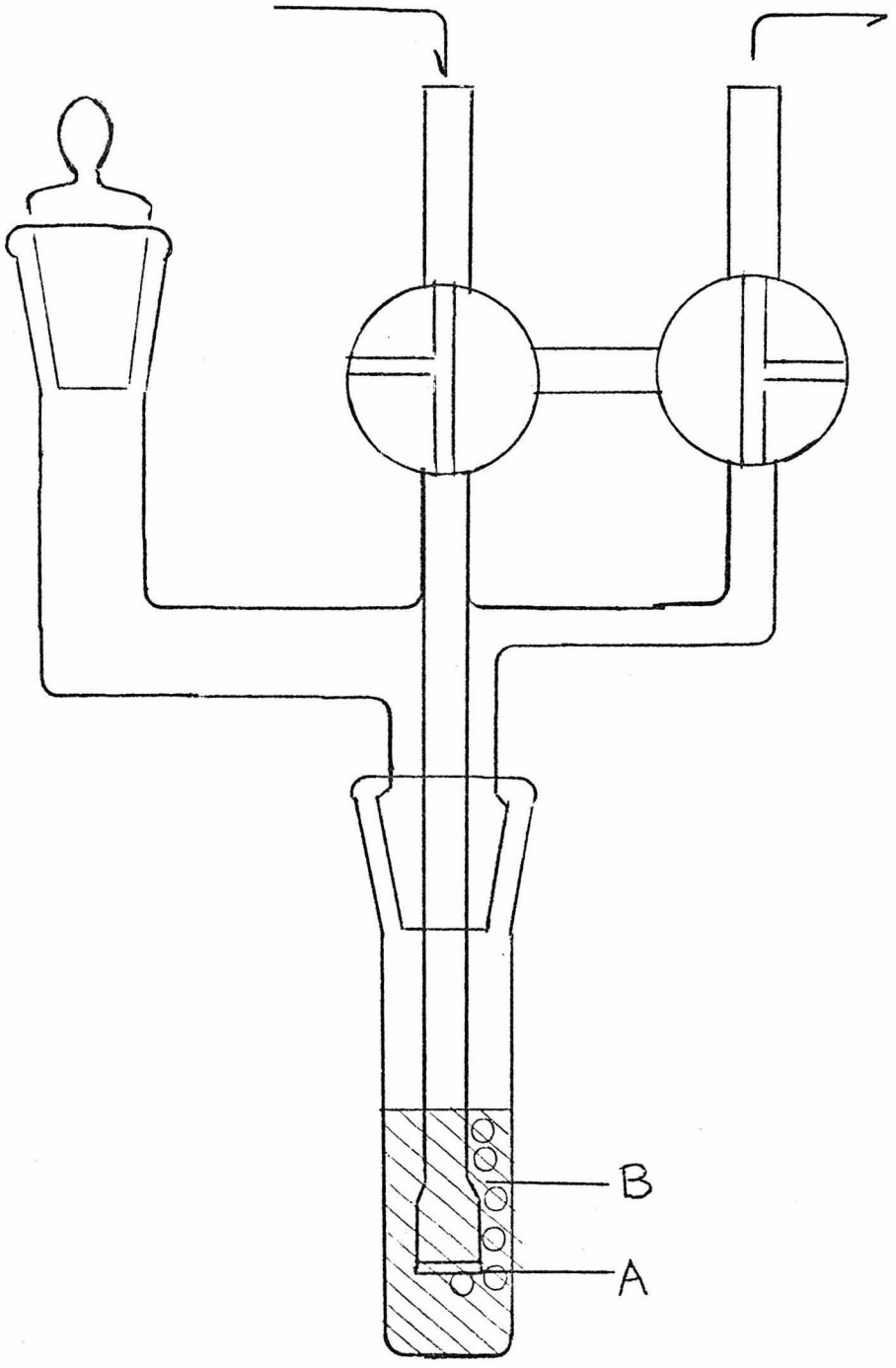


Figure 8: Simplified Liquid Delivery System

delivery is continuous, and its concentration in the stream is uniform over the period of a pyrolysis run.

The method for the introduction of gases was also simplified. A lecture bottle containing the hydrocarbon to be pyrolyzed is plugged into the nozzle gas line before metering. The hydrocarbon and nitrogen both contribute to the total back pressure (back pressure is defined as the pressure on the upstream side of the rotameter). Thus the fraction of hydrocarbon in the center stream can be varied from 0-100%.

Nozzle design modifications. The most troublesome problem that had to be solved in the wall-less reactor before it could be used for kinetic studies was the control of the temperature in the reaction zone. The problem arises because there are two cold fingers, one 3 feet long (the probe) and the other 1 foot long (the nozzle), placed inside another larger tube, through which hot gases are flowing. At times these cold fingers are a single cm apart, at other time 15 cm apart. The goal was to control temperature in the reaction zone, over its 14 cm length, to ±1 °C. Many variations, mostly involving nozzle modifications, were tried. These are discussed below.

A. The first nozzle modification was directed toward solving another problem, but did assist in temperature control (see Figure 9). Four stainless steel screens (9H) (two 100 mesh and two 25 mesh) were placed around the nozzle extending to the inner walls of the reaction

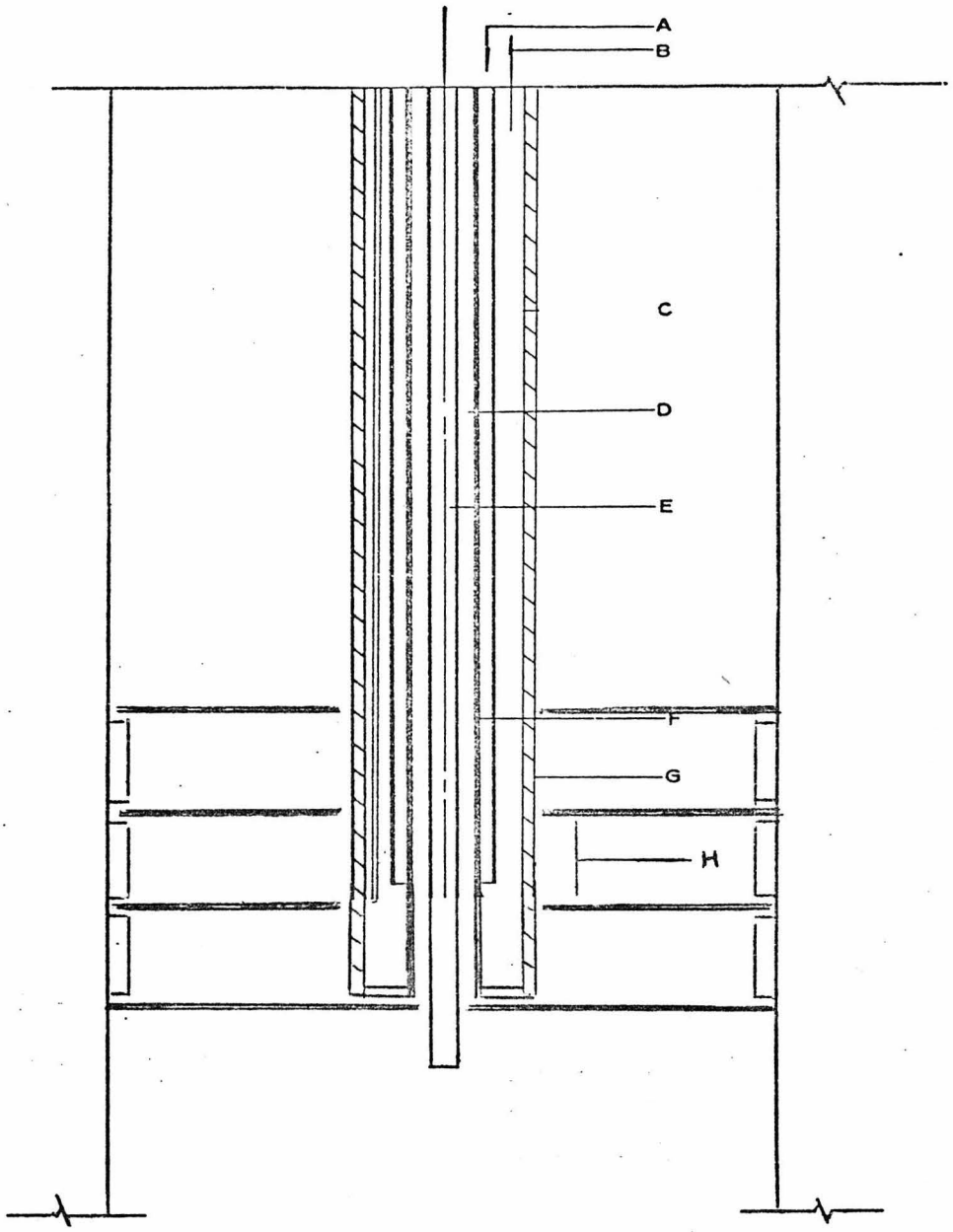


Figure 9: Tip of Nozzle with Screens Inside Reaction Zone

tube.[10] The first was placed at the tip of the nozzle with the hydrocarbon tube extending through a hole in its center. The others were set 1 cm apart further up the nozzle. The portion of the nozzle above the screens was packed with quartz wool (9C, Arthur H. Thomas Co.). The purpose of the screens and quartz wool was to even out pressure variations in the blanket gas, thus ensuring plug flow. The increase in temperature control probably occurred because steel, being a better conductor of heat than nitrogen, decreased the temperature gradient between the cool nozzle and the hot wall of the reaction tube.

B. Next, it was decided to increase the temperature in the two cold fingers. If the internal temperature of the probe and nozzle were raised from 300° to only 100°C below the temperature of the reactor, temperature variations in the reaction zone should be moderated, hopefully without undue reaction in the probe or nozzle. This modification helped with temperature control, but resulted in actual physical harm to the reactor. More frequent replacement or cleaning of the probe and nozzle was required. This probably was caused by surface catalyzed reactions, which did not require the higher temperatures of the homogeneous reaction, taking place on the metal surfaces inside the nozzle or probe. This modification was abandoned.

C. The diluent stream of cool nitrogen (6D of Figure 6) was eliminated as suggested by Professor Taylor. The nozzle was

redesigned (see Figure 10) along the lines of the probe. The hydrocarbon delivery tube (10C, still 1/16 in O.D.) extended 3 mm beyond the stream lined cooling jacket (10A, now with a 0.3125 in O.D. with the last three inches turned down to a 0.2865 in O.D.). The central hydrocarbon tube was welded to the nozzle assembly which necessitated cooling down the oven and disassembling the reactor everytime the nozzle clogged (a very frequent occurrence). The screens and the quartz wool were retained from the old nozzle. Unfortunately, the new nozzle design did not markedly increase temperature control.

In order to provide better insulation between the nozzle and the hot blanket gases, a quartz sleeve was designed to fit over the nozzle. This design was unsuccessful. The coefficient of expansion with heat is not similar for quartz and stainless steel. Upon heating up the reactor after the placement of the sleeve, it was observed that the sleeve cracked and broke.

This nozzle design was also ultimately abandoned. First, it was inconvenient to constantly cool down and heat up the reactor every time the nozzle had to be cleaned or repaired. Second, the nozzle began to direct the stream of hydrocarbon away from the center of the reaction zone towards the wall. Removal of the 3 mm of hydrocarbon tube (9C) extending beyond the cooling jacket did not remedy the situation. The only plausible explanation was that strains caused by temperature gradients within the nozzle when the

Figure 11: Detail of Nozzle Tip Heater

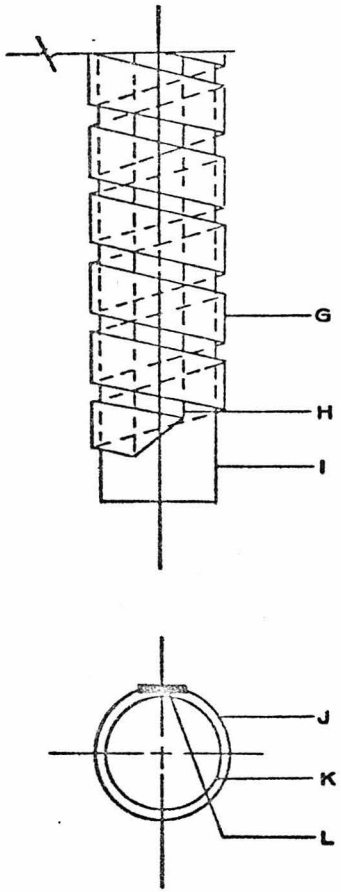
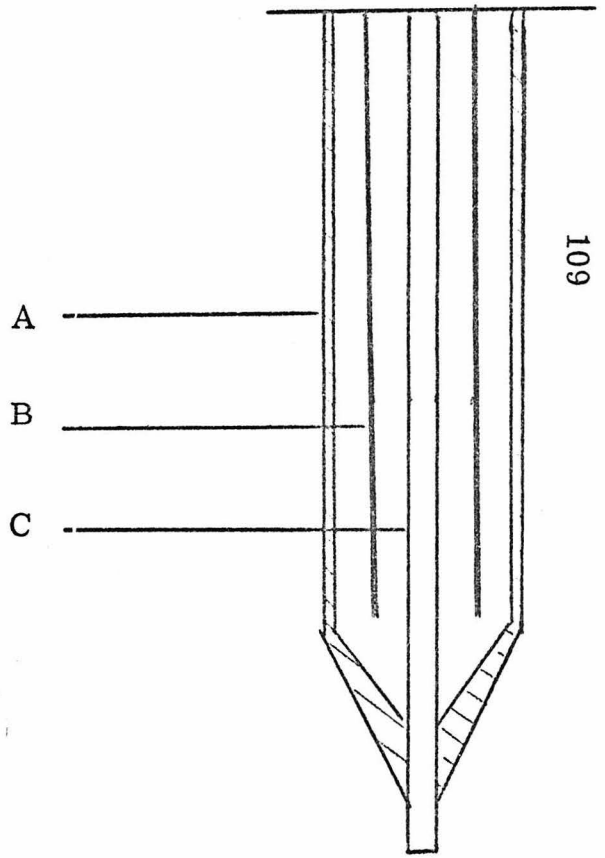


Figure 10: Modified Nozzle Tip



reactor was heated, caused the nozzle to behave in this erratic manner.

D. The use of the previous nozzle was resumed (see Figure 6), but without any cool nitrogen diluent flowing into the reactor from 6D. The hydrocarbon tube, detached from the cooling jacket except outside of the reactor, was in a more strain-free situation in the previous nozzle design. It was also decided to install a nozzle heater (see Figures 11 and 12). The heater consists of 1/16 in by 0.008 in nichrome V ribbon (Driver-Harris Company). The nozzle was first wrapped with asbestos paper (Arthur H. Thomas Co.) to insulate it from a lead ribbon extending to its tip. The lead ribbon was wrapped with more asbestos paper and the nichrome ribbon was wound about the asbestos covered nozzle at a 1/16 inch spacing. Leads, which extend to the nozzle heater from outside the oven through holes in plates (12D and 12 J-K-L) consist of 5 or 6 folded lengths of resistance ribbon. Leads and heater are fashioned from one continuous ribbon of nichrome V. The leads are insulated from plates (10D and 10 J-K-L) by ceramic thermocouple insulators, which are covered with a cement capable of with standing high temperatures (Briskeat, Briscoe Mfg. Co.) in order to make the feed through air tight.

Electricity to operate heater is provided by a variac (0-135 volt range, 5 amps). Best temperature control with the current

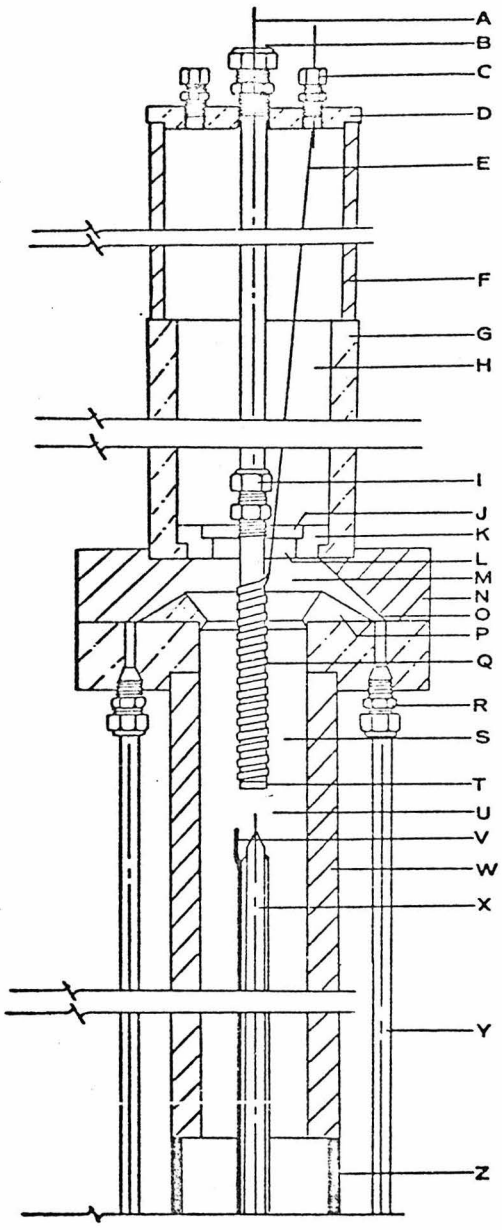


Figure 12: Wall-less Reactor with Nozzle Heater

apparatus is obtained with variac settings from 20 to 35 volts.

Temperature control with this system proved to be very good, however an unexplained difficulty arose. In studying the isomerization of cyclopropane to propylene, a series of parallel Arrhenius rate plots were obtained when only a single variable was changed. That variable was change in the voltage supplied to the heater from the variac. In other words, if a series of rate constant determinations at various temperatures with a variac setting of 20 volts was carried out, and results were plotted in an Arrhenius rate plot (logarithm of rate constant versus inverse of the temperature) a straight line was obtained, which paralleled a similar line obtained by doing another series of rate constant determinations but at a variac setting of 35 volts, for example. The differences in the intercepts are slight.

E. The problem of parallel Arrhenius plots disappeared after the last nozzle modification. Ten screens, packed tightly together, ranging in mesh from 25 to 100, were placed at the tip of the nozzle extending to the reactor wall.

Temperature control in the reaction zone is now to $\pm 1\,^{\circ}C$. (The first cm after the hydrocarbon enters the reaction zone is discarded in rate determinations.) All rate constants, regardless of variac settings, lie on the same Arrhenius rate plot.

Probe modifications. The probe remained relatively unchanged in its physical appearance, except for the wrapping with asbestos paper, already mentioned.

It was found to be beneficial to keep the internal temperature of the probe constant to ± 5 °C over a pyrolysis run. This was done by gradually decreasing the flow of cooling air to the probe as more and more of the probe was withdrawn from the oven, i.e., as residence time of the hydrocarbon was increased.

Placement of the exterior probe thermocouple. It is difficult to know the exact temperature that the hydrocarbon experiences as it flows from nozzle to probe the problem arises out of the design of the probe. At present the thermocouple is attached to the probe for support. The tip of thermocouple is located at some distance from the tip of the probe and its movement is coupled to that of the probe. Ideally one would like to know the temperature with the probe positioned in the center of the hydrocarbon stream at all points along the stream. One can place the thermocouple in the center of the stream equidistant from nozzle and probe and read a temperature. This will probably be the highest temperature reading, since upstream or downstream the thermocouple is getting closer to either of the two cold fingers. If one moves the probe vertically in the stream, the thermocouple is no longer equidistant from the cold sources and the influence of one is

felt more strongly than the other. Furthermore, if the thermocouple resides in the stream during sampling, it acts as a hot surface, and data can not longer be said to have been obtained under homogeneous conditions. Therefore if the movement of the thermocouple remains coupled to that of the probe, it must lie off to one side of probe at a fixed distance above or alongside the probe tip. This position is not without problems. First,the thermocouple continues to feel the effect of the cool probe. Second, one can not take both the temperature in central gas stream and sample the gas stream without a horizontal movement of the probe. Thus the conditions under which temperatures are taken (thermocouple in the center of the hydrocarbon stream, probe to one side) are different than when a sample is taken (probe in the center of the hydrocarbon stream). Also, the change in the temperature gradient in the region between probe and nozzle, caused by gradually withdrawing more of the length of the probe from the reactor (to increase residence time of hydrocarbon) cannot be gauged.

At present the tip of the thermocouple is located 13 mm to one side of and 10 mm above the tip of the probe. This arrangement is to decrease the effect of the cold probe on the readings of the thermocouple. However, the disparity between conditions for temperature reading (probe at wall) and sampling is at a maximum. After experimenting with the thermocouple positioned 2 mm, 3.5 mm, 7.0 mm

and 12.0 mm from, and 12.0 mm from and 10 mm above the tip of the probe, it was concluded that correcting for the first effect is more important than the second. Even so, the fundamental problem has not been solved.

The answer lies in decoupling the movement of the thermocouple and probe. So that with the probe in position for sampling, the thermocouple tip can range over the whole length of the central hydrocarbon stream from nozzle to probe, recording the temperature at all points, and then be removed before the sample is withdrawn. The actual mechanics of the solution will be rather complex.

TECHNIQUES

Preparation for Sampling

Before a successful kinetic run can be carried out, constancy of temperature in the reaction zone must be attained. The two end zone heaters of the Lindbergh Hevi-Duty furnace provide little control over the small 17 cm reaction zone deep inside the central heater. (It is suggested the end heaters be set at 5.00 and left.) The most delicate control is provided by the nozzle heater. A voltage between 25 and 35 supplied to the heater provides the most uniform temperature in the reaction zone. All testing for uniformity of temperature must be done with the blanket gas and the central hydrocarbon stream flow rates at the settings to be used for the kinetic run. (If the sample to be pyrolyzed is in limited supply, pure nitrogen can be used for temperature control studies.)

The volume flow rates of the central hydrocarbon stream and the blanket gas must be set so that their linear velocity is matched. This is determined by comparing the cross sectional area of hydrocarbon delivery tube to that of the blanket gas tube. The ratio of these two numbers determines the ratio of the setting for the volume flow rate of the two streams.

$$\frac{\frac{\pi[(D_{I.L.})^2 - (D_{O.S.})^2]}{4}}{\frac{\pi D_{I.S.}^2}{4}} = \frac{D_{I.L.}^2 - D_{O.S.}^2}{D_{I.S.}^2} = 1246 \qquad (1)$$

$D_{I.L.}$ = inner diameter of reaction tube

$D_{O.S.}$ = outer diameter of hydrocarbon tube

$D_{I.S.}$ = inner diameter of hydrocarbon tube

Therefore, if the volume flow rate of the blanket gas is 124.6 cm^3/sec, the flow rate of the hydrocarbon stream must be 0.1 cm^3/sec, and the total volume flow rate is 124.7 cm^3/sec.

It has been found experimentally that the central hydrocarbon's linear velocity can be set less than that of the blanket gas, without any bad effects. However, if the linear velocity of the hydrocarbon stream is faster than that of the blanket gas, the hydrocarbons shoot out of the nozzle in a jet, causing turbulence and decreasing the actual residence time of the hydrocarbon. See Table 1.

Sampling. When good temperature control has been achieved, and the blanket gas and central gas stream flow rates have been appropriately set, sampling can begin. When determining a rate, several samplings are taken along the center of the hydrocarbon stream at intervals of about 1 cm. When studying decompositions it is also necessary to sample along a horizontal line intersecting the

Table 1: % Cyclopropane in the Reaction Mixture as a Function of the Volume Flow Rate of the Central Hydrocarbon Stream. Temp = 723 °C. Exactly Matched Flow Rates are 0.1 cc/sec for Central Hydrocarbon Stream to 124.6 cc/sec for Blanket Gas.

Flow rate of blanket gas (cm^3/sec)	Flow rate of central stream (cm^3/sec)	% Δ in reaction mixture	Distance from nozzle
124.6	0.089	81.03	5.0 cm
124.6	0.122	82.42	5.0 cm
124.6	0.165	85.48	5.0 cm
124.6	0.197	87.27	5.0 cm

hydrocarbon stream. This is because the rates of diffusion out of the central stream for the decomposition products are greater than those for the reactant. This will be discussed more fully later. In order to get the most accurate results, the probe must be recentered each time it is moved vertically. The tip of the probe is aligned by sight with the center of the hydrocarbon inlet tube. This visual sighting represents a starting point and several samples are taken about this point until the region of greatest concentration of hydrocarbon is found.

TREATMENT OF DATA

Fundamental Equations

Only unimolecular reactions can be studied in the wall-less reactor. These include irreversible isomerizations, reversible isomerizations, and irreversible decompositions. The fundamental rate laws for each reaction are given below:

1. Irreversible isomerizations (2)

$$A \xrightarrow{K_b} B,$$

$$A \xrightarrow{K_c} C,$$

$$A \xrightarrow{K_d} D, \text{ etc.}$$

$\ln A_o/A = K_t t$ $\quad A_o$ = initial concentration of A

$K_t = K_b + K_c + K_d$ $\quad A$ = concentration of A at time t

$B:C:D = K_b:K_c:K_d$ if $B_o = C_o = D_o = 0$

$A = A_o - B - C - D$

2. Reversible isomerizations (3)

$$A \underset{K_a}{\overset{K_b}{\rightleftharpoons}} B$$

$$\ln \frac{A_o - A_c}{A - A_c} = (K_b + K_a)t$$

$A = A_0 - B$ $\quad A_c$ = equilibrium conc of A

B_c = equilibrium conc of B

$K_b A_c = K_a B_c$

3. Irreversible decompositions (4)

$$A \xrightarrow{K} B + C$$

$\ln A_0/A = Kt$

$A_\circ = A + (\text{reacted A})$

It is apparent that only the time and the ratio of the concentration of unreacted A to reacted A + unreacted A must be known. No knowledge of absolute concentrations is necessary. No other information is necessary except the values A_c and B_c in case 2.

Determination of Residence Time

Determination of the residence time of a species inside of the reaction zone follows from the ideal gas law, and two observable facts; the volume rate of flow of gas at room temperature into the reaction zone (see Tables 2-4 for calibration data for all rotameters used) and the temperature inside of this zone. The ideal gas law states:

$$PV = nRT \qquad (5)$$

If a gas at room temperature T_L undergoes a heating to a new temperature T_H without an increase in pressure, the volume increases.

$$\frac{V_L}{T_L} = \frac{nR}{P} = \frac{V_H}{T_H} = \text{constant} \tag{6}$$

or

$$V_L \cdot \frac{T_H}{T_L} = V_H$$

Taking the derivative with respect to time (to obtain a volume flow rate):

$$\frac{\partial V_H}{\partial t} = \frac{T_H}{T_L} \frac{\partial V_L}{\partial t} \tag{7}$$

Thus if an amount of gas metered at T_L is heated to $T_H = XT_L$, then the volume flow rate at $T_H = X\partial V_L/\partial t$.

The time it values for a species to travel from point A to point B in the reactor is equal to:

$$\text{time to travel from point A to point B} = \frac{\pi(D/2)^2 \cdot d_{AB}}{\frac{T_H}{T_L} \cdot \frac{\partial V_L}{\partial t}}$$

D = diameter of reactor tube

d_{AB} = distance between point A and point B

Table 2: Calibration Data on Rotameter A (Chem No. 1355) Used in Connection with the Wall-less Reactor.

Back pressure on rotameter is 10 psi of nitrogen at 26°C

Position of light ball	Position of heavy ball	Flow rate (26°C) in cm^3/sec
.20		.0845
.35		.0851
.50		.0940
.70		.103
.90		.105
.98		.109
1.35		.125
1.42		.127
1.60		.134
1.78		.143
1.95		.148
2.30		.167
2.35		.170
2.73		.188
2.75		.193
2.95		.198
2.98		.204
3.25		.217
3.45		.222
3.55		.233
3.88		.257
3.90		.259
4.30	0.4	.282
4.50		.290
5.15	1.0	.337
5.65		.366
5.85	1.50	.391
6.30	1.65	.419
6.90		.473
7.50		.518
8.15	2.75	.580
8.60	3.10	.622
8.95	3.30	.656

Table 3: Calibration of Rotameter B (Chem No.
Used in Connection with the Wall-less Reactor.

Back pressure on rotameter is 12 psi at 26°C

Position of light ball	Position of heavy ball	Flow rate (26°C) in cm^3/sec
0.60		.156
0.80		.175
1.00		.179
1.45		.242
2.00		.291
2.70		.348
3.35		.406
3.95		.462
4.45		.533
4.85		.598
5.45		.685
5.85	0.05	.737
6.15		.792
6.55	0.1	.850
7.05	0.25	.945
7.50	0.80	1.026
8.15	1.10	1.162

Table 4: Calibration Data for Rotameter C (Chem No. 17812)
Used in Connection with the Wall-less Reactor.
Back pressure on rotameter is 25 psi (26 °C) of nitrogen

Position of light ball	Position of heavy ball	Flow rate (26 °C) in cm^3/sec
1.00		1.13
2.10	.55	3.46
2.20	.55	3.79
3.10	.90	6.17
4.05	1.25	9.28
4.10	1.30	9.48
5.00	1.60	12.3
5.00	1.60	12.2
6.00	1.95	15.2
6.00	1.95	14.9
7.05	2.30	18.2
7.10	2.35	18.0
8.10	2.70	20.9
8.15	2.75	20.8
8.60	2.90	22.7
9.45	3.20	25.1
10.10	3.40	27.4
10.70	3.65	28.7
11.20	3.80	30.4
11.50	3.95	31.6
11.80	4.05	32.1
12.70	4.35	34.7
12.95	4.45	35.4
13.60	4.70	37.3
14.00	4.85	38.8
14.50	5.00	40.3
14.95	5.15	41.2
15.80	5.45	43.1
16.15	5.55	44.6
16.50	5.70	44.6
16.95	5.90	47.3
17.75	6.10	49.3
18.00	6.20	49.8

Table 4 (Cont'd):

18.95	6.50	53.8
20.10	6.95	54.35
21.00	7.20	58.1
21.25	7.30	59.1
22.10	7.55	61.6
22.30	7.65	61.7
23.20	7.95	64.5
23.20	7.90	64.9
23.95	8.20	66.4
24.00	8.20	65.8
24.95	8.55	68.5
25.05	8.55	70.0
	9.00	73.5
	10.00	81.7
	11.00	90.4
	12.00	100.3
	13.00	106.8
	14.00	114.9
	15.00	123.4
	16.00	131.6
	17.00	141.5
	17.95	154.6
	19.00	159.74
	20.00	164.7
	21.00	169.8
	22.00	182.9
	23.00	190.5
	24.05	200.9
	25.00	207.5

Determination of the Ratio of Product Concentration to Reactant Concentration

The accuracy of the micromanipulator is ±0.1 mm with some reduction in accuracy due to length of the probe. It is possible to make a concentration map of both reactant and product(s) at any level in the reactor. In order to prepare such a map, a series of samplings is taken at equal increments along a line which lies in a plane that is perpendicular to the hydrocarbon stream and at a fixed distance from the nozzle tip. From these maps, information regarding the diffusion and symmetry properties of the hydrocarbon stream can be determined. Figures 13 to 21 are cross-sectional maps of the type described above taken during the isomerization of cyclopropane. (Because the thermocouple is located 13.5 mm away from the tip of the probe, it is only possible to sample slightly more than half of a diameter of the reaction tube. Since these distributions are symmetrical the half not sampled is simply the mirror image of the half sampled.) These data are proof that laminar flow of the hydrocarbon stream with minimal diffusion through the inert blanket gas stream is taking place. Figures 13,16 and 19 are of cyclopropane pyrolysis data taken with the nozzle 4 cm away from the probe, but at different temperatures; 989°K, 993°K and 1004°K, respectively.

Most of the material is located in a stream with roughly a diameter of 1.2 cm. (Had a sample been taken at the exit of the nozzle, all of the hydrocarbon would be located in a stream of diameter 0.12 cm, the I.D. of hydrocarbon tube.) This is evidence for some lateral diffusion. Figures 14, 17 and 20 are of data taken at 70 cm from the nozzle. The data show that the central stream has widened further to about 1.6 cm. The last series of data (Figures 15, 18 and 21) were taken at a distance of 10.3 cm away from the nozzle. The central stream is roughly 2.2 cm in diameter, but there is a considerable amount of material located 1.6 to 1.8 cm from the center of the stream. This represents the upper limit of the permissible residence time of the reactor for the pyrolysis of cyclopropanes, since the radius of the reactor tube is only 1.905 cm. In other words, any data for the pyrolysis of cyclopropanes taken at a vertical distance representing less than 0.30 sec of residence time, can be assumed to have been taken under completely wall-less conditions. (The vertical distance traveled by cyclopropane can be altered by increasing or decreasing the rate of flow of the blanket gas. The 0.30 sec represents the extreme upper limit for the residence time.) This is the reason that all reactions studied must have relatively fast unimolecular rate constants on the order of 10^{0} to 10^{-3} per sec.

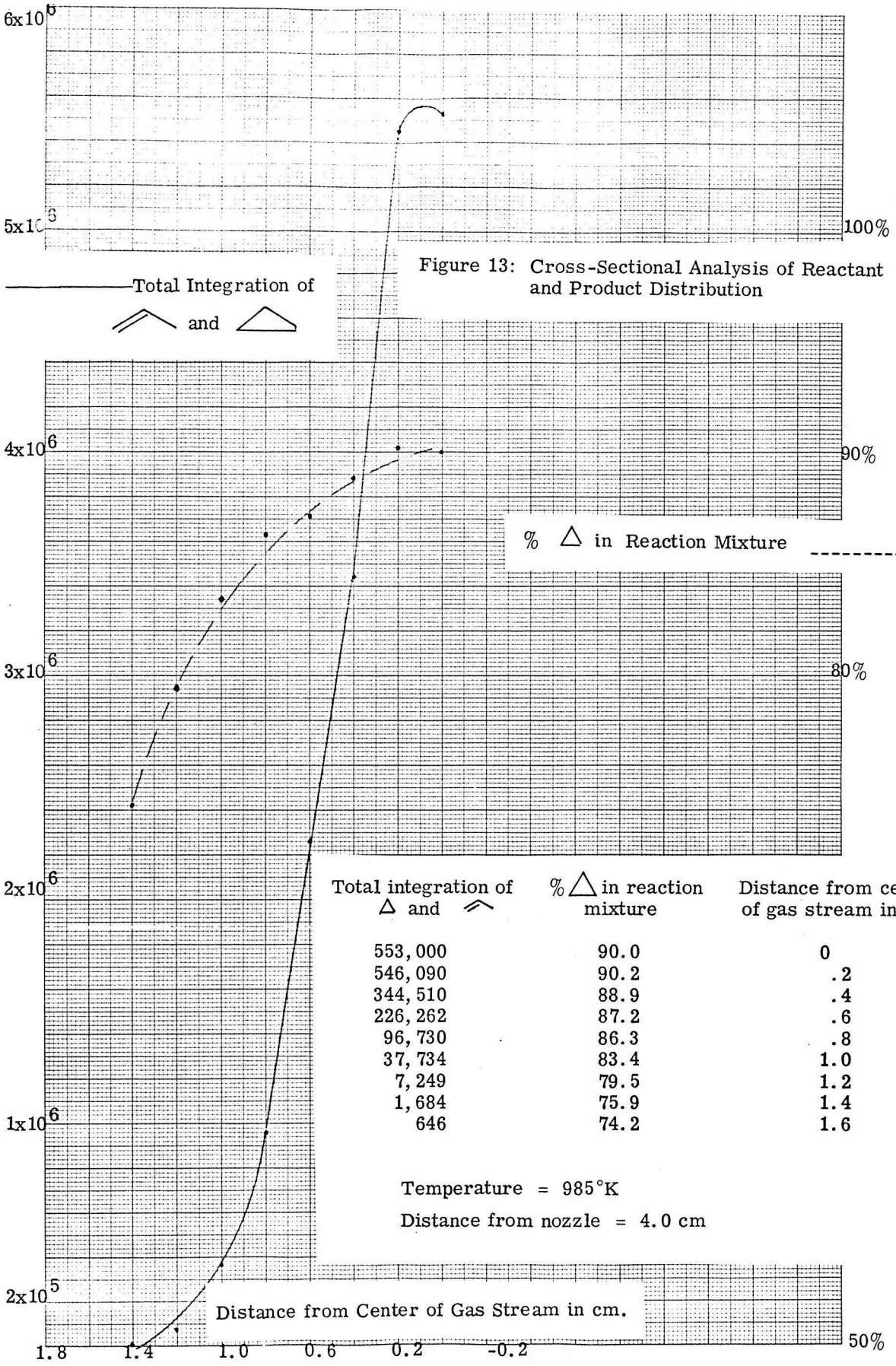


Figure 13: Cross-Sectional Analysis of Reactant and Product Distribution

Total integration of △ and ⩥	% △ in reaction mixture	Distance from center of gas stream in cm.
553,000	90.0	0
546,090	90.2	.2
344,510	88.9	.4
226,262	87.2	.6
96,730	86.3	.8
37,734	83.4	1.0
7,249	79.5	1.2
1,684	75.9	1.4
646	74.2	1.6

Temperature = 985°K

Distance from nozzle = 4.0 cm

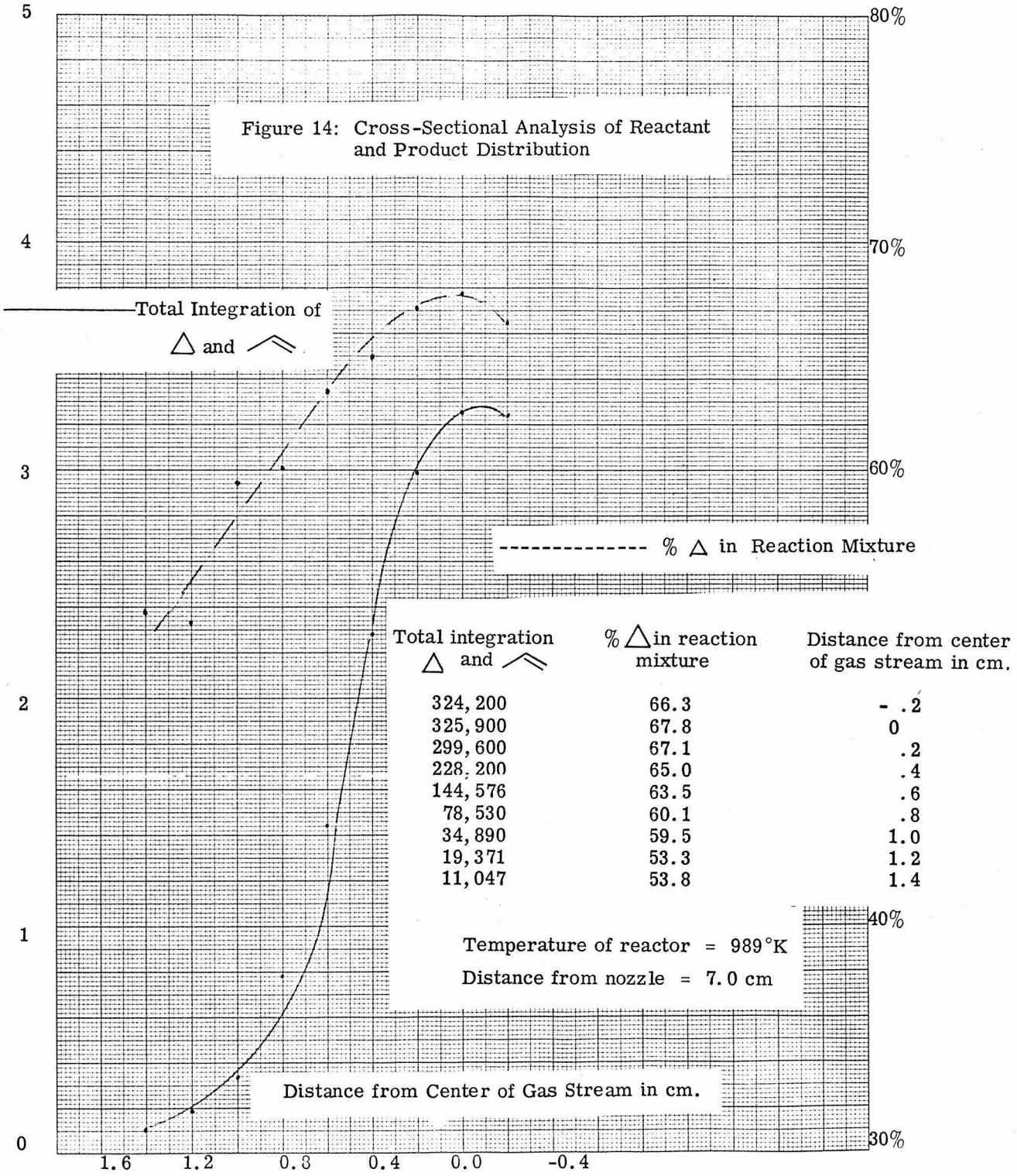


Figure 14: Cross-Sectional Analysis of Reactant and Product Distribution
Total Integration of △ and ⩥
---------- % △ in Reaction Mixture
Total integration △ and ⩥
% △ in reaction mixture
Distance from center of gas stream in cm.
324,200 66.3 - .2
325,900 67.8 0
299,600 67.1 .2
228,200 65.0 .4
144,576 63.5 .6
78,530 60.1 .8
34,890 59.5 1.0
19,371 53.3 1.2
11,047 53.8 1.4
Temperature of reactor = 989°K
Distance from nozzle = 7.0 cm
Distance from Center of Gas Stream in cm.
5
4
3
2
1
0
80%
70%
60%
40%
30%
1.6
1.2
0.8
0.4
0.0
-0.4

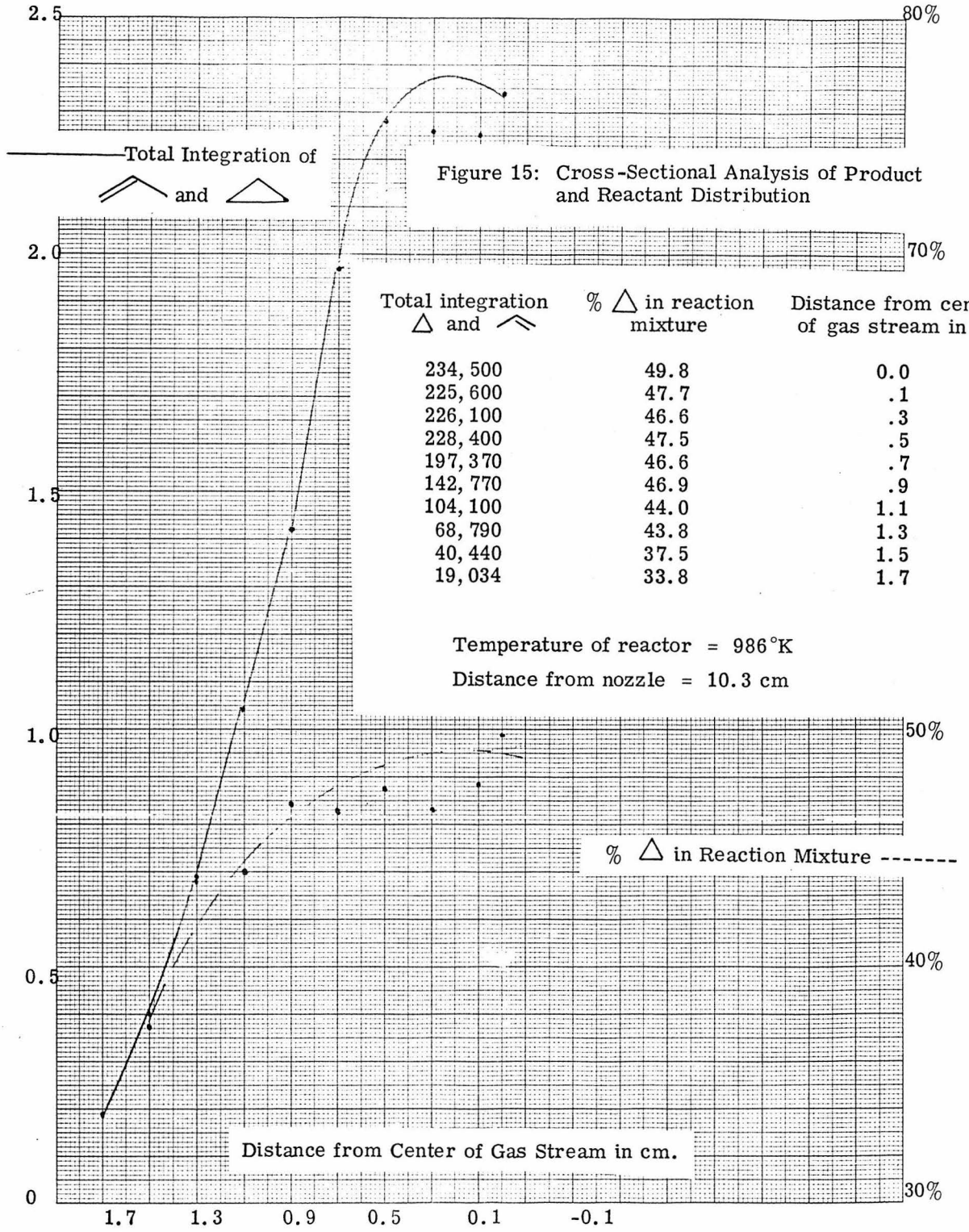


Figure 15: Cross-Sectional Analysis of Product and Reactant Distribution

Total integration △ and ⩘	% △ in reaction mixture	Distance from center of gas stream in cm.
234, 500	49.8	0.0
225, 600	47.7	.1
226, 100	46.6	.3
228, 400	47.5	.5
197, 370	46.6	.7
142, 770	46.9	.9
104, 100	44.0	1.1
68, 790	43.8	1.3
40, 440	37.5	1.5
19, 034	33.8	1.7

Temperature of reactor = 986°K

Distance from nozzle = 10.3 cm

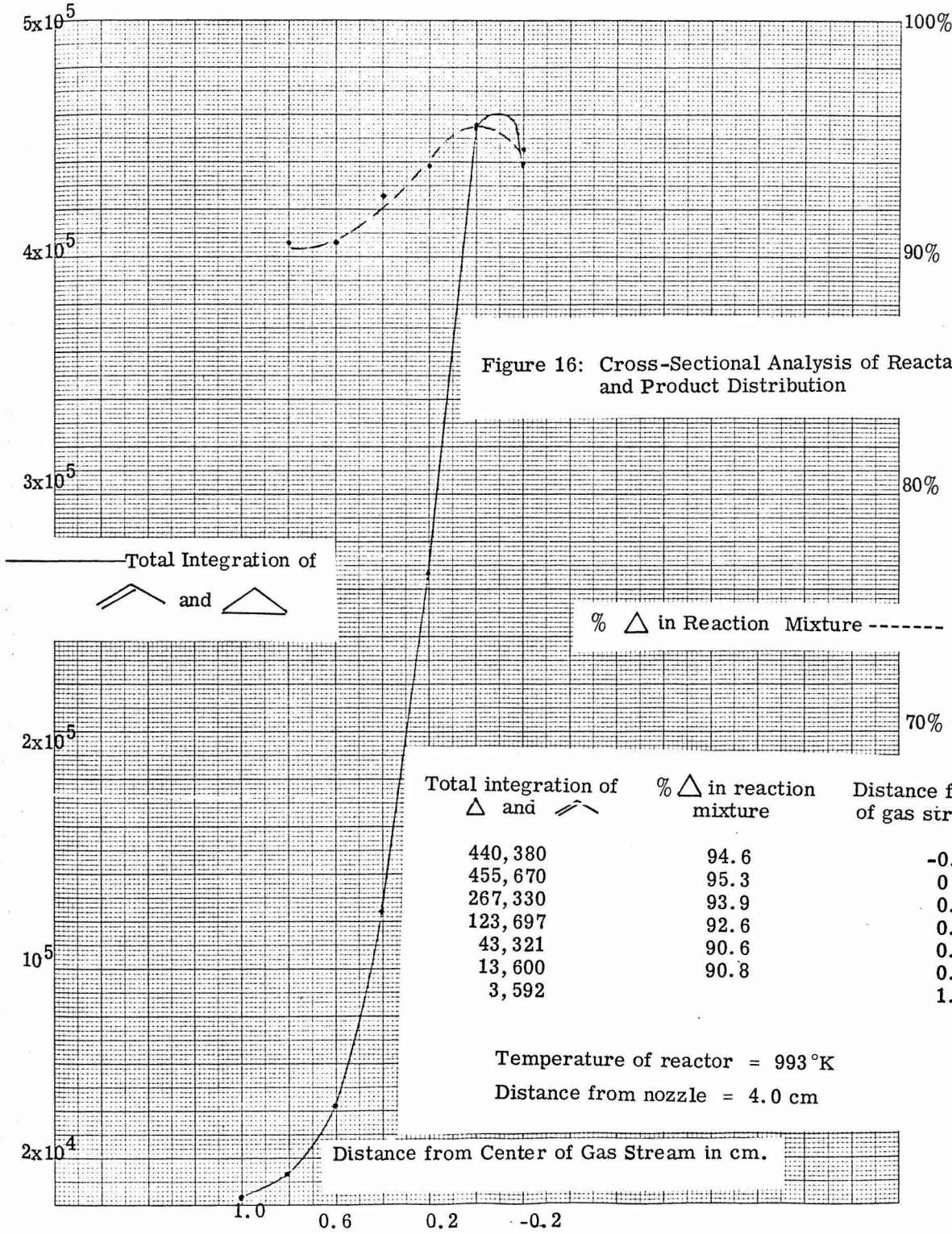


Figure 16: Cross-Sectional Analysis of Reactant and Product Distribution

Total integration of △ and	% △ in reaction mixture	Distance from center of gas stream in cm.
440,380	94.6	-0.2
455,670	95.3	0
267,330	93.9	0.2
123,697	92.6	0.4
43,321	90.6	0.6
13,600	90.8	0.8
3,592		1.0

Temperature of reactor = 993 °K

Distance from nozzle = 4.0 cm

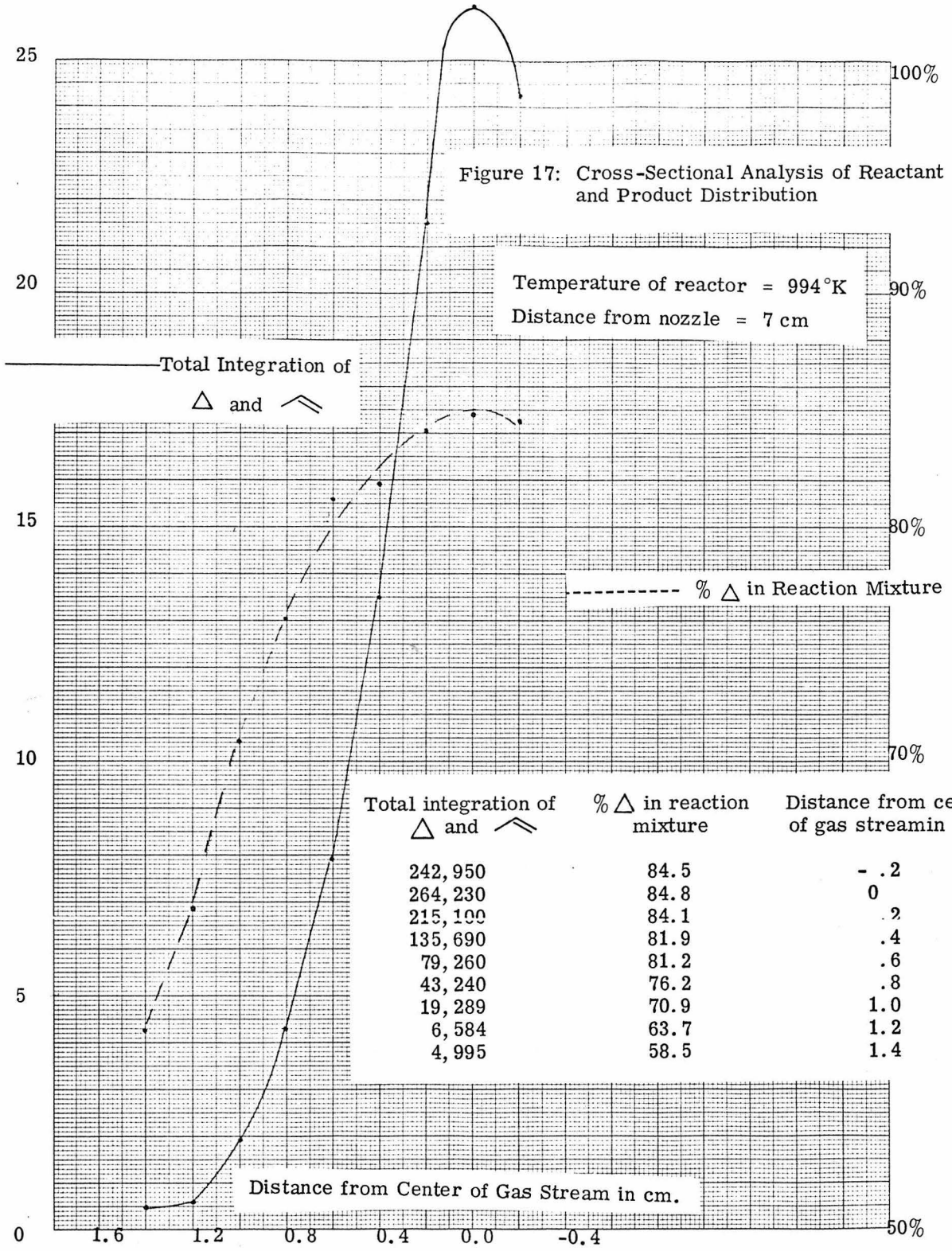


Figure 17: Cross-Sectional Analysis of Reactant and Product Distribution

Total integration of △ and ⩥	% △ in reaction mixture	Distance from center of gas streamin cm.
242,950	84.5	- .2
264,230	84.8	0
215,100	84.1	.2
135,690	81.9	.4
79,260	81.2	.6
43,240	76.2	.8
19,289	70.9	1.0
6,584	63.7	1.2
4,995	58.5	1.4

Total integration of △ and ⩥	% △ in reaction mixture	Distance from center of gas stream in cm.
15,085	43.3	1.8
15,534	45.0	1.6
23,820	49.4	1.4
42,500	60.5	1.2
60,750	63.7	1.0
92,033	65.3	.8
109,230	65.9	.6
129,800	67.6	.4
158,010	68.6	.2
178,180	69.7	0

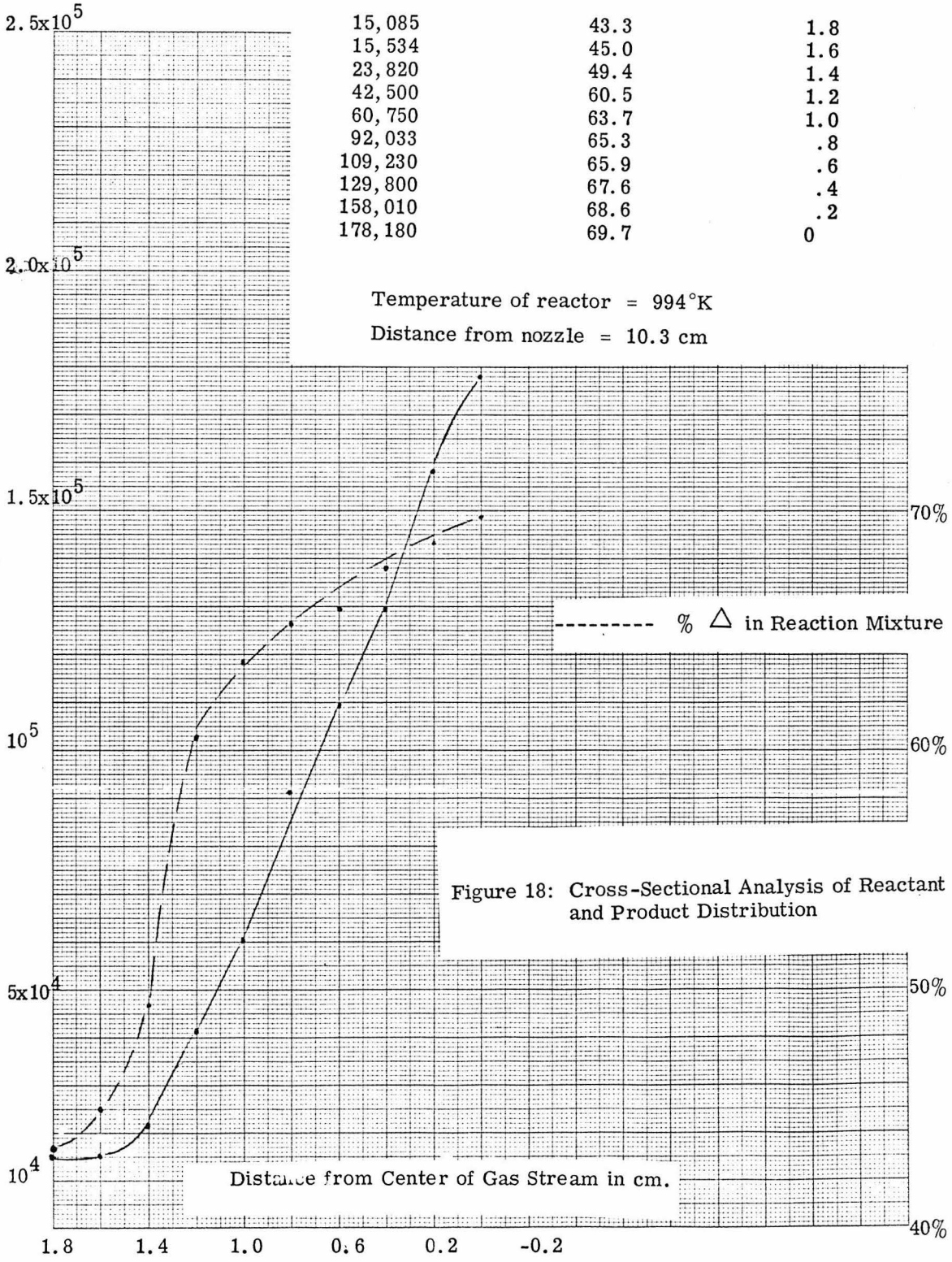


Figure 18: Cross-Sectional Analysis of Reactant and Product Distribution

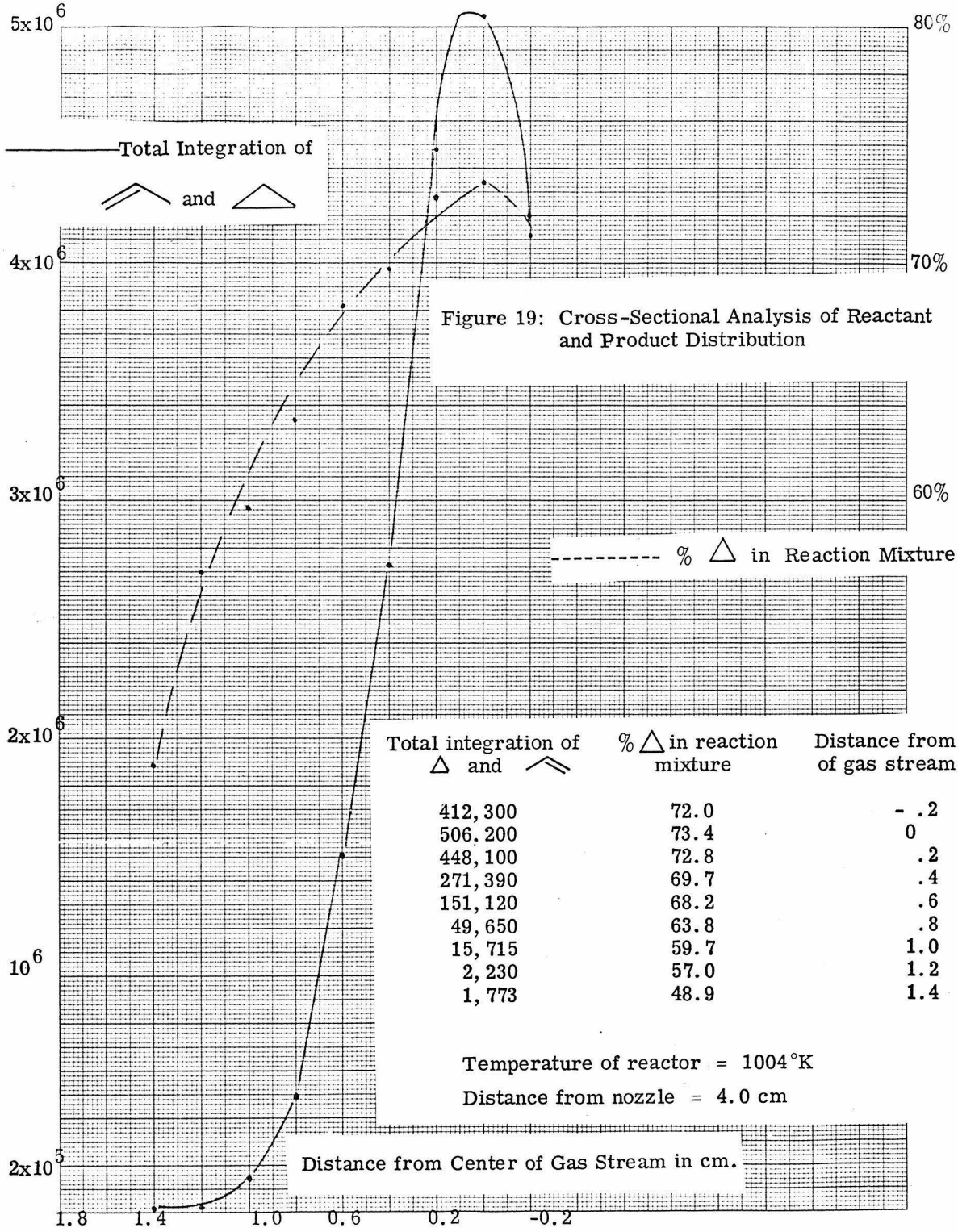


Figure 19: Cross-Sectional Analysis of Reactant and Product Distribution

Total integration of △ and ⩥	% △ in reaction mixture	Distance from center of gas stream in cm.
412,300	72.0	- .2
506,200	73.4	0
448,100	72.8	.2
271,390	69.7	.4
151,120	68.2	.6
49,650	63.8	.8
15,715	59.7	1.0
2,230	57.0	1.2
1,773	48.9	1.4

Temperature of reactor = 1004°K

Distance from nozzle = 4.0 cm

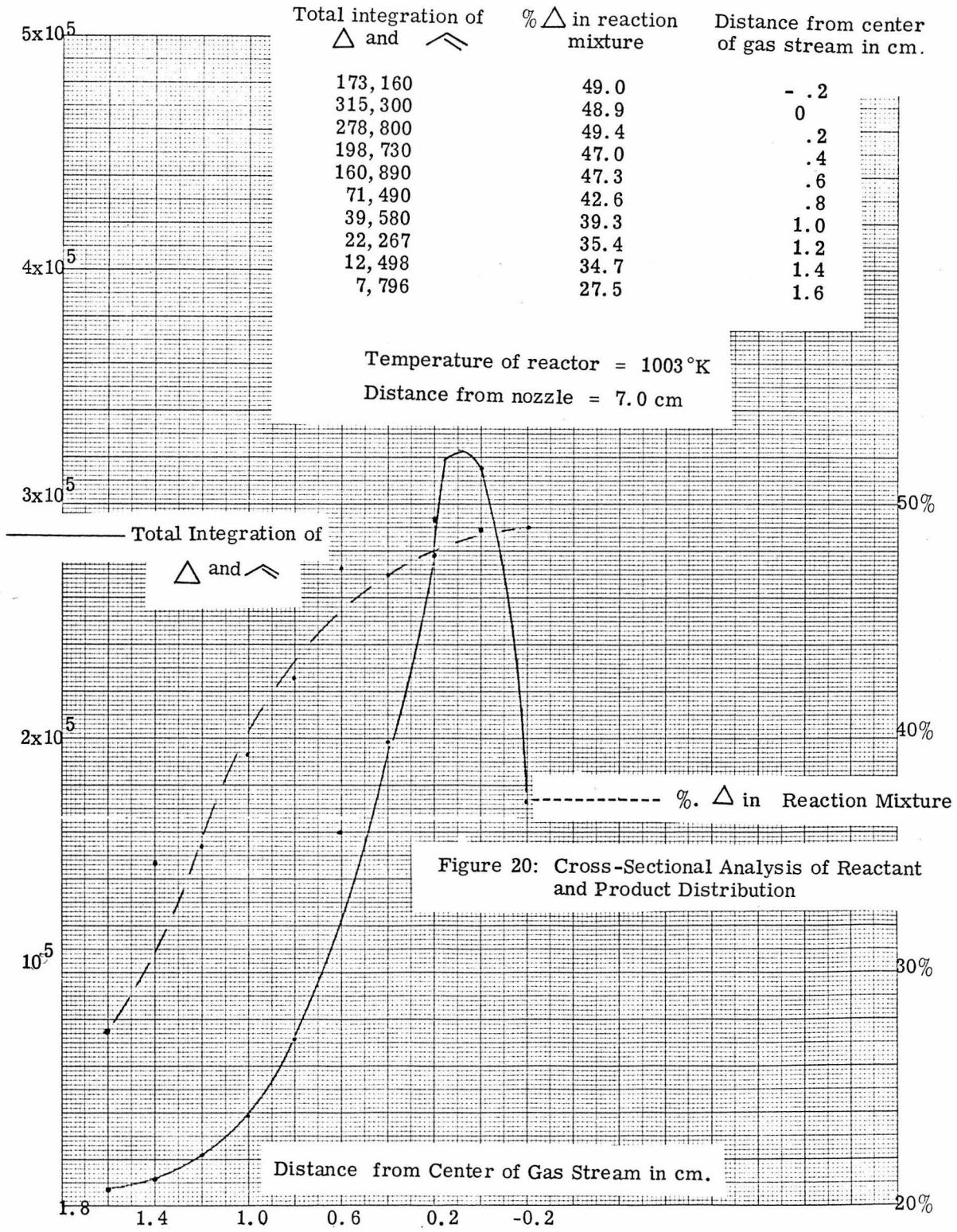


Figure 20: Cross-Sectional Analysis of Reactant and Product Distribution

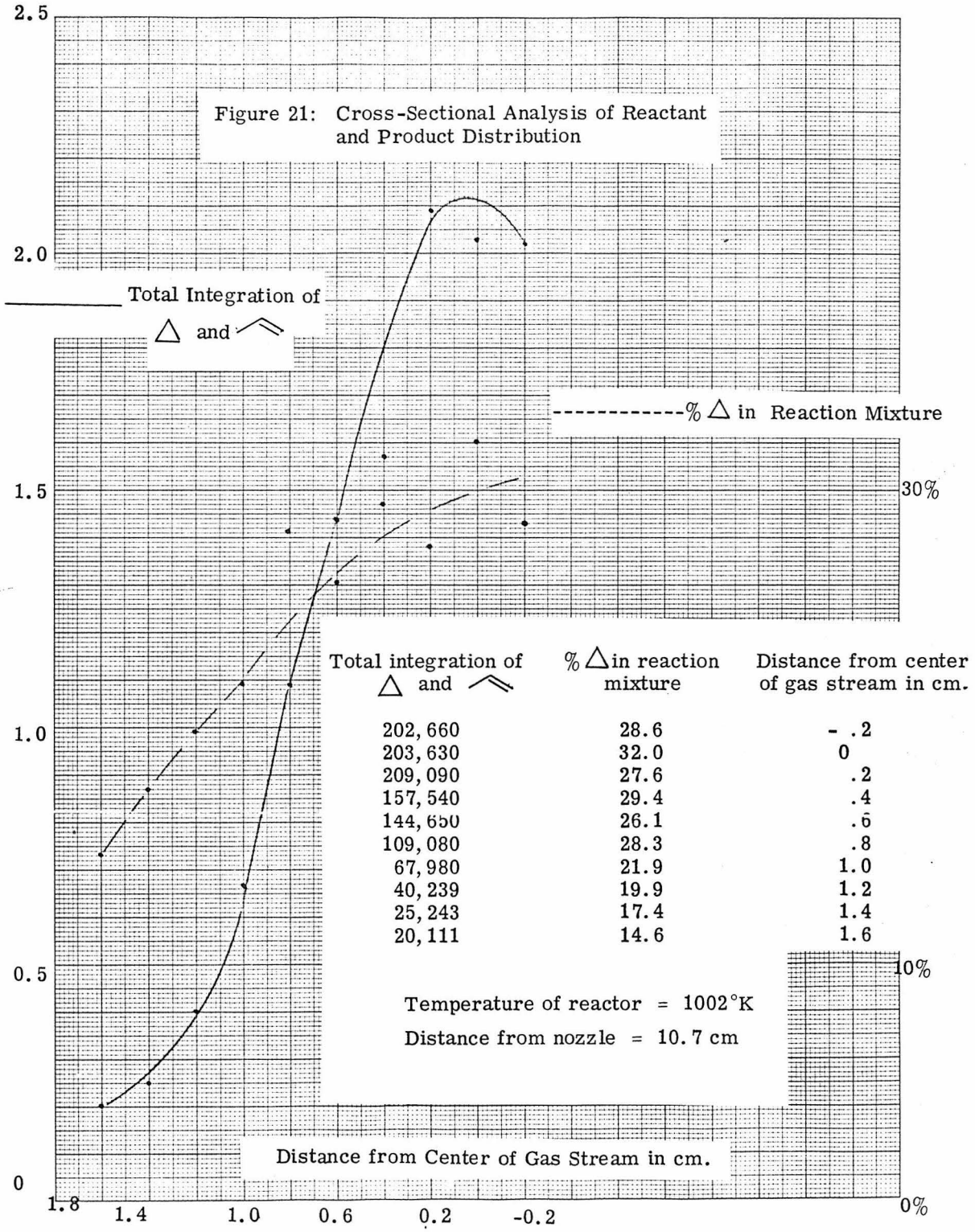


Figure 21: Cross-Sectional Analysis of Reactant and Product Distribution

Total integration of △ and	% △ in reaction mixture	Distance from center of gas stream in cm.
202,660	28.6	- .2
203,630	32.0	0
209,090	27.6	.2
157,540	29.4	.4
144,650	26.1	.6
109,080	28.3	.8
67,980	21.9	1.0
40,239	19.9	1.2
25,243	17.4	1.4
20,111	14.6	1.6

While 0.30 seconds represents the upper limit of residence time for the cyclopropane isomerization to propylene, it does not represent the upper limit for other reactions. Graham's Law states that the rate of diffusion of a gas through a small orifice is inversely proportional to its density (and to its molecular weight assuming ideal gas behavior).

$$\frac{\text{rate of diffusion of molecule B}}{\text{rate of diffusion of molecule A}} = \frac{\text{M.W. (A)}}{\text{M.W. (B)}} \qquad (9)$$

M.W. = molecular weight

Thus a molecule heavier than cyclopropane will diffuse to the wall slower than cyclopropane, whereas a molecule lighter than cyclopropane will diffuse faster. Total permissible residence time will be dependent on the diffusion of the lightest product to the wall. For example, in the pyrolysis of neopentane, the major products are isobutylene and methane. Since methane is lighter than cyclopropane, total residence time is determined by methane's diffusion to the wall and will be less than 0.3 sec. On the other hand, the pyrolysis of 3,3-dimethylcyclopropene gives only C_5H_8 hydrocarbons, which makes the allowable time for study of the reaction some number greater than 0.30 sec (that number is found experimentally).

From inspection of Figures 13 to 21, it is observed that the ratio of cyclopropane to propylene decreases as one moves away from the center of the stream. This is because a cyclopropane molecule, which diffuses out of the central stream, has traveled a longer distance than a molecule remaining in the central stream, and has had a greater probability of reacting.

From these cross-sectional maps of reactant and product distributions, the ratio of reactant to product is calculated by rotating the map along its central axis of symmetry (the center of the hydrocarbon stream) and generating a volume. Mathematically, this is achieved by using the following equation for each reactant and product at each vertical sampling distance from the nozzle.

$$\text{Total count volume} = \sum_{x=0}^{1.6} (R_{x+2}^2 - R_x^2)\pi \times \text{integration at } R_x \qquad (10)$$

R_x = radius at X mm from center of stream

R_{x+2} = radius at X + 2 mm from center of stream

X increases by increments of 2 mm

For example using the data found in Figure 13, the first three numbers in this series are:

$$[(.2)^2 - (0)^2)]\pi\ 553,000 +$$

$$[(.4)^2 - (.2)^2]\pi\ 546,090 +$$

$$[(.6)^2 - (.4)^2]\pi\ 344,510 +, \text{ etc.}$$

The equation breaks down the generated volume into a series of concentric cylinders (of wall thickness 0.2 cm) each with decreasing heights. The outer cylinders, due to their larger circumference, count more heavily in proportion to their radii than do the internal cylinders. Therefore the two dimensional figures are not always proportionately representative of concentrations.

This sampling procedure and mathematical treatment must be followed for all decompositions studied. But when products and reactant have the same molecular weight and, hence, the same rates of diffusion out of the stream, it is only necessary to sample at the point of highest concentration in the central hydrocarbon stream at any vertical distance from the nozzle. Data for the cyclopropane isomerization and the cyclopropene isomerization (see below), were taken using the latter method.

RESULTS

Cyclopropane Isomerization

The first reaction studied in our version of the wall-less reactor was the irreversible isomerization of cyclopropane to propylene. The reason this system was selected, beside the fact that the reaction is fairly non-complicated having only a single product, is that it is known to have a very small or no surface effect.[34] This was important in that data obtained on the wall-less reactor could be checked against published data on this system.

1. Pyrolysis conditions. Undiluted cyclopropane (Matheson Company Inc.), 99.92% pure, made up the central hydrocarbon stream. One cc samples of the reactant and product mixture were analyzed on a 20 ft by 1/8 in copper column which was packed with 2% Silicon Oil as the liquid phase on Chromosorb P, and maintained at room temperature. Retention times of cyclopropane and propylene were 3.12 min and 4.31 min, respectively. Nine rate constants were found spanning a temperature range of 936°K to 1025°K. See Figures 22 to 30. Voltages supplied by the variac to the nozzle heater were in the range of 25-35 volts.

T (seconds)	log $[\Delta]_o/[\Delta]$
0.000	0.0028
0.029	0.0048
0.058	0.0073
0.087	0.0096
0.116	0.0127
0.146	0.0158
0.175	0.0200
0.195	0.0230

Run 1 936.9 °K

Wall-less reactor

k_{obs} = 0.237

by least-squares analysis

Empirical correlation coefficient = .9919

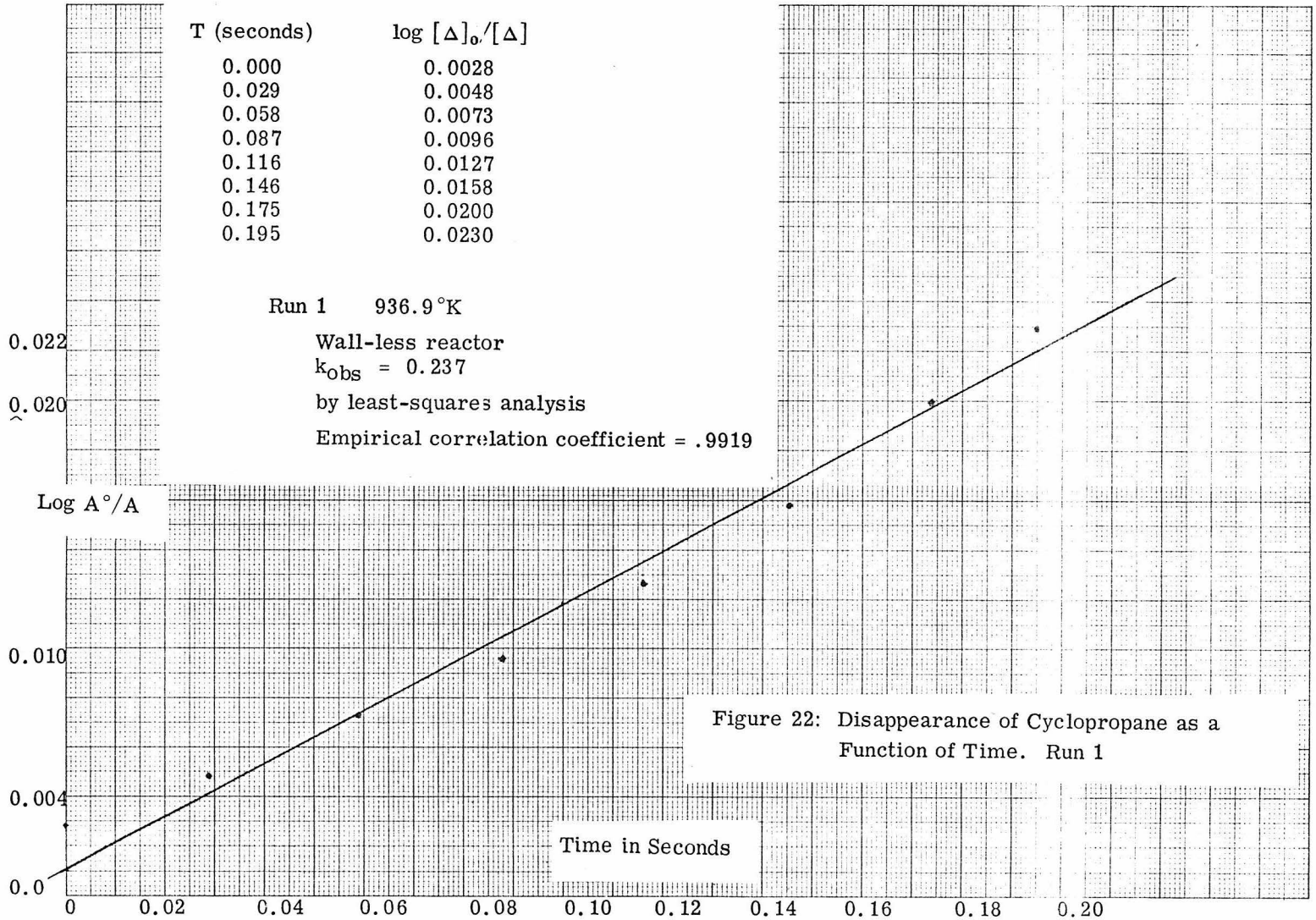


Figure 22: Disappearance of Cyclopropane as a Function of Time. Run 1

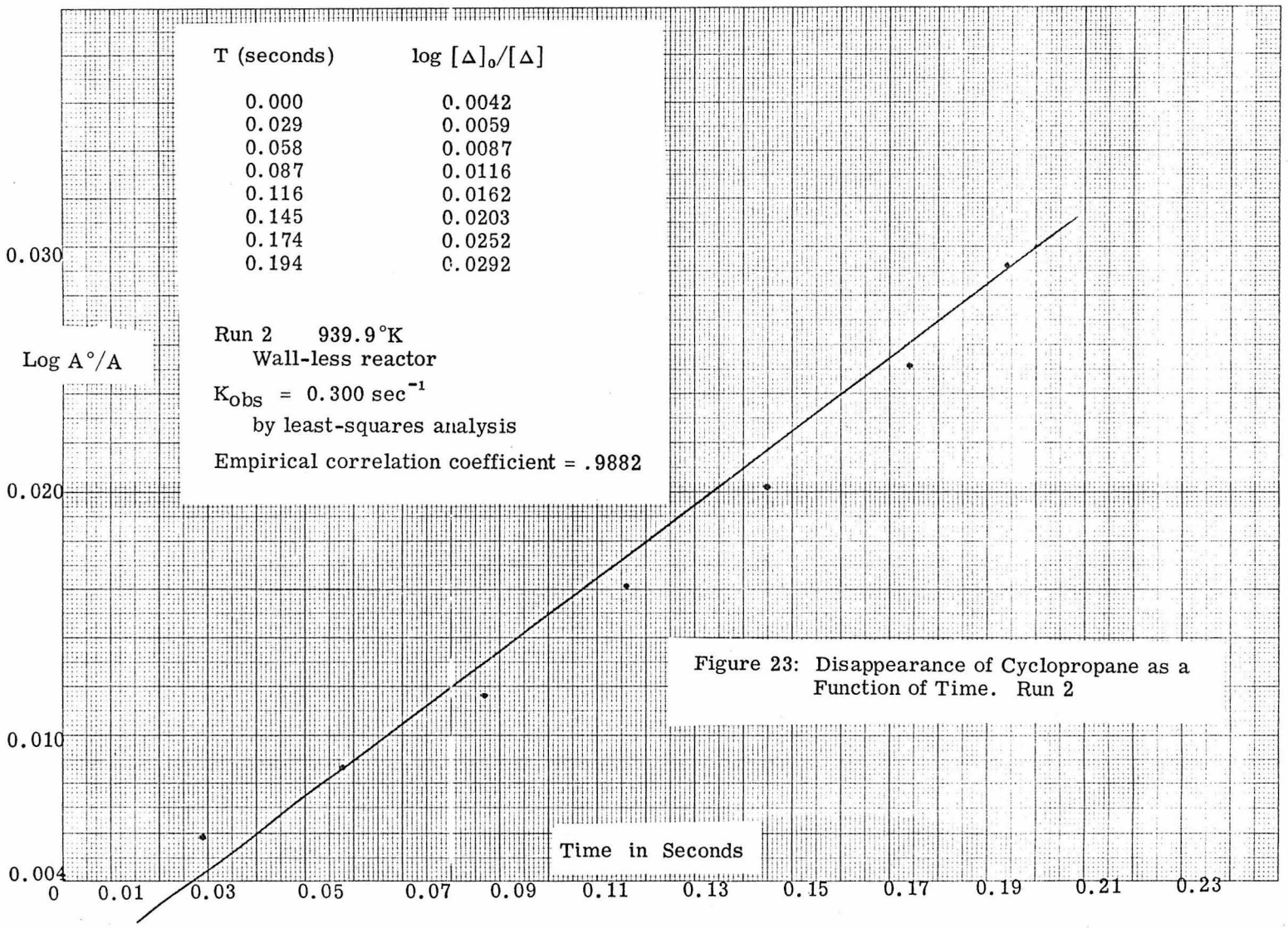


Figure 23: Disappearance of Cyclopropane as a Function of Time. Run 2

T (seconds)	log $[\Delta]_o/[\Delta]$
0.000	0.0089
0.028	0.015
0.057	0.022
0.085	0.029
0.113	0.036
0.142	0.046
0.170	0.048
0.190	0.061

Run 3 963.0°K
Wall-less reactor

k_{obs} = 0.607 sec^{-1}
by least-squares analysis

Empirical correlation coefficient = 0.9918

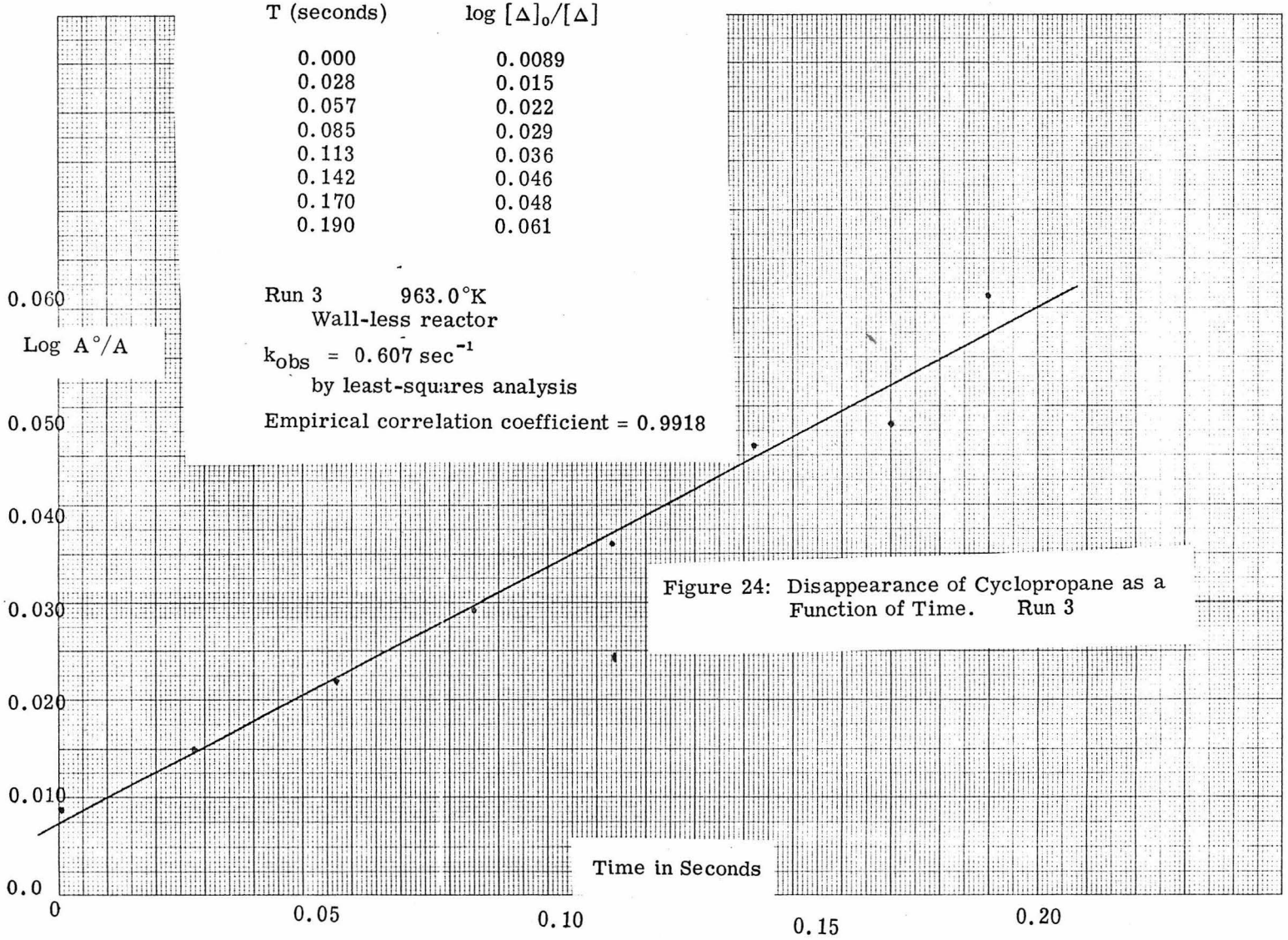


Figure 24: Disappearance of Cyclopropane as a Function of Time. Run 3

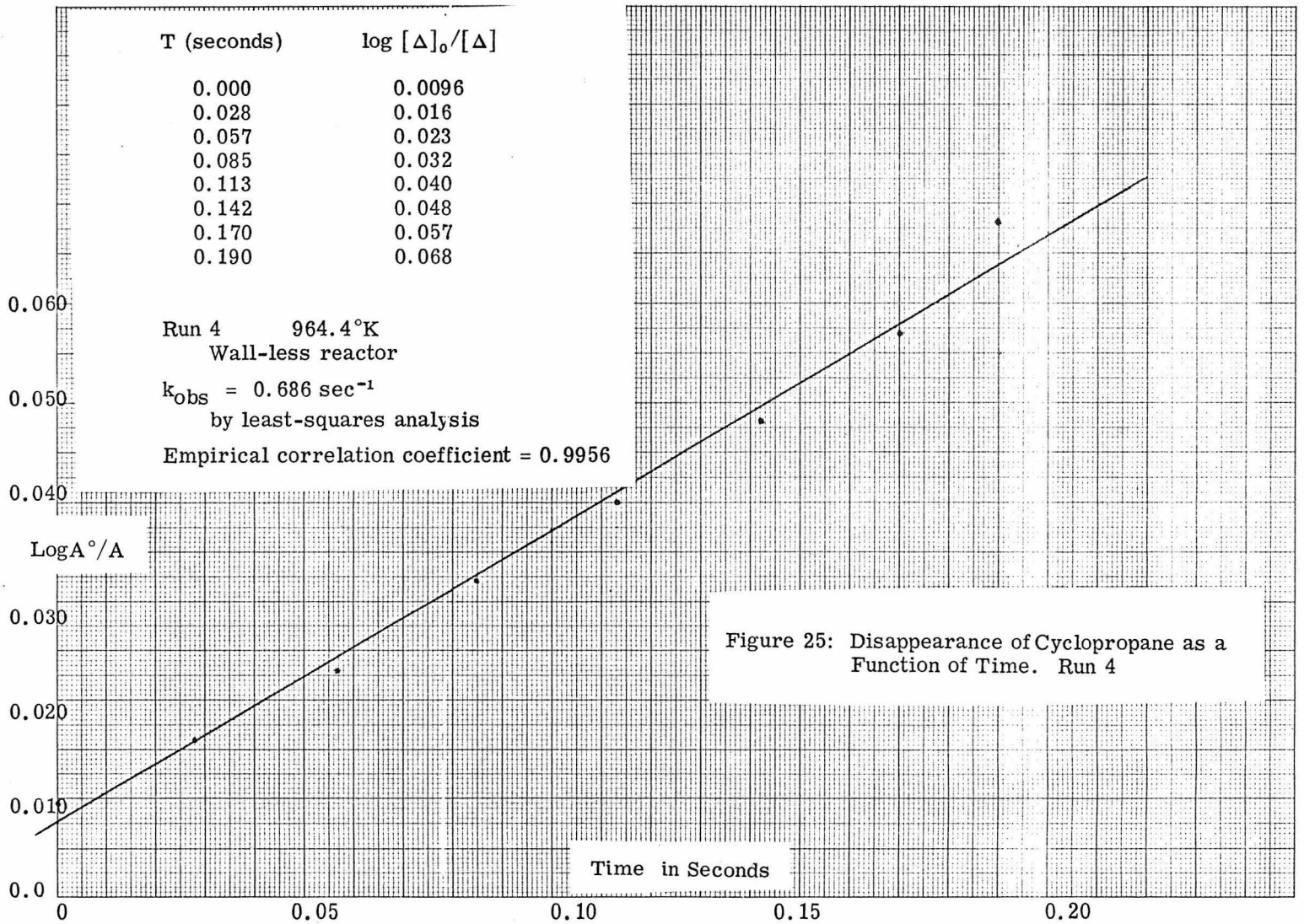


Figure 25: Disappearance of Cyclopropane as a Function of Time. Run 4

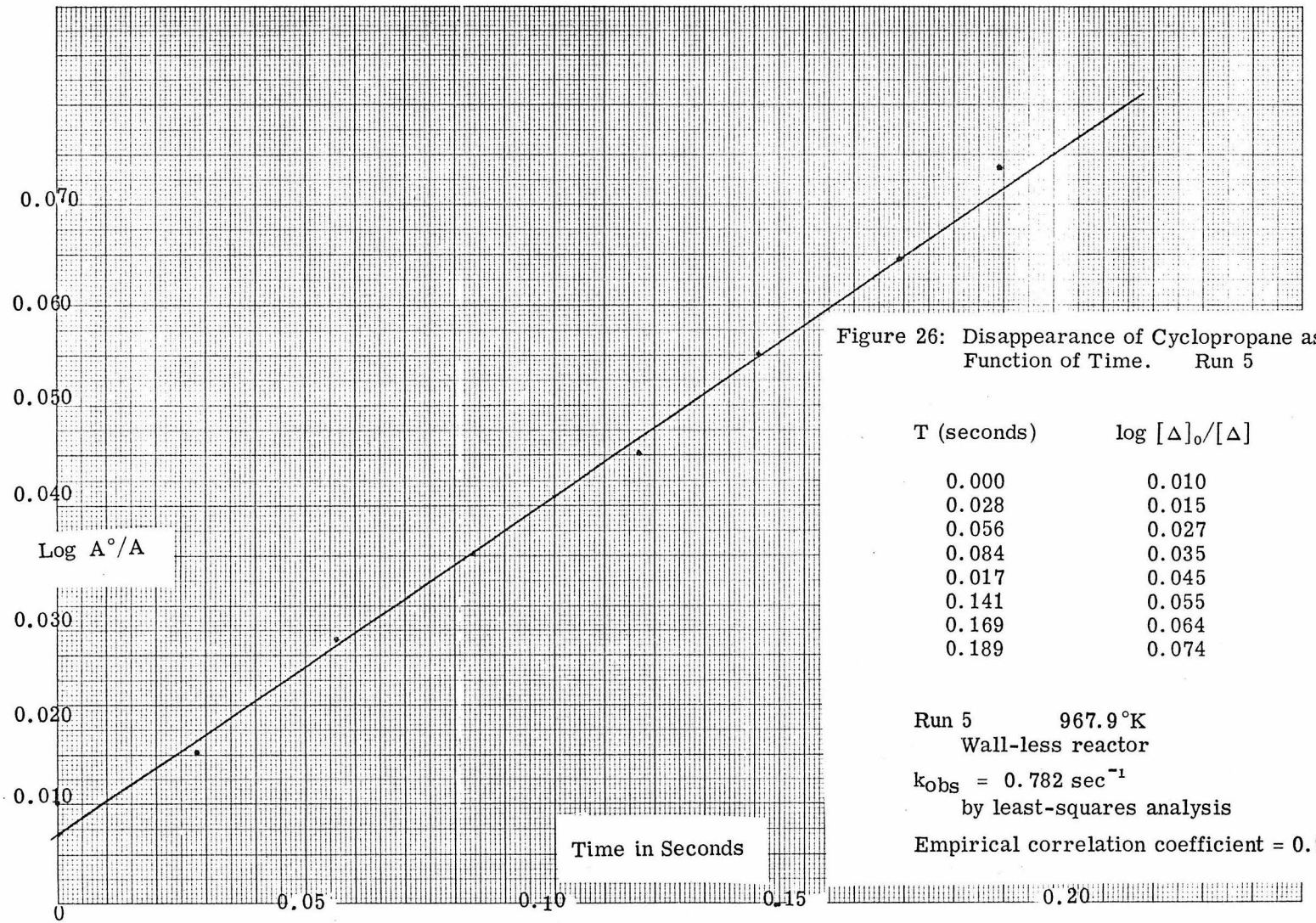


Figure 26: Disappearance of Cyclopropane as a Function of Time. Run 5

T (seconds)	log $[\Delta]_o/[\Delta]$
0.000	0.010
0.028	0.015
0.056	0.027
0.084	0.035
0.017	0.045
0.141	0.055
0.169	0.064
0.189	0.074

Run 5 967.9°K
Wall-less reactor

$k_{obs} = 0.782\ sec^{-1}$
by least-squares analysis

Empirical correlation coefficient = 0.9973

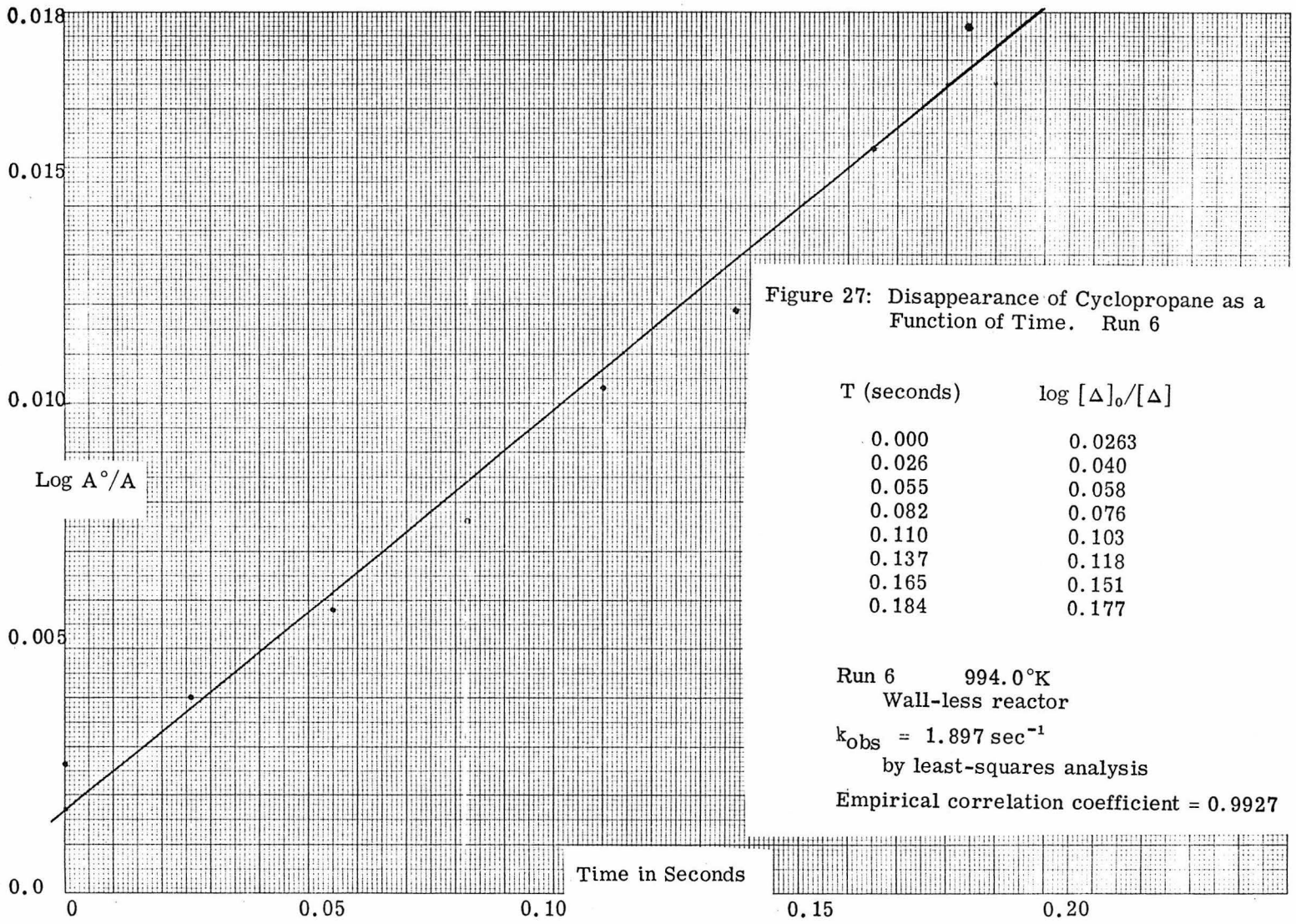


Figure 27: Disappearance of Cyclopropane as a Function of Time. Run 6

T (seconds)	$\log [\Delta]_o/[\Delta]$
0.000	0.0263
0.026	0.040
0.055	0.058
0.082	0.076
0.110	0.103
0.137	0.118
0.165	0.151
0.184	0.177

Run 6 994.0°K
Wall-less reactor

$k_{obs} = 1.897\ sec^{-1}$
by least-squares analysis

Empirical correlation coefficient = 0.9927

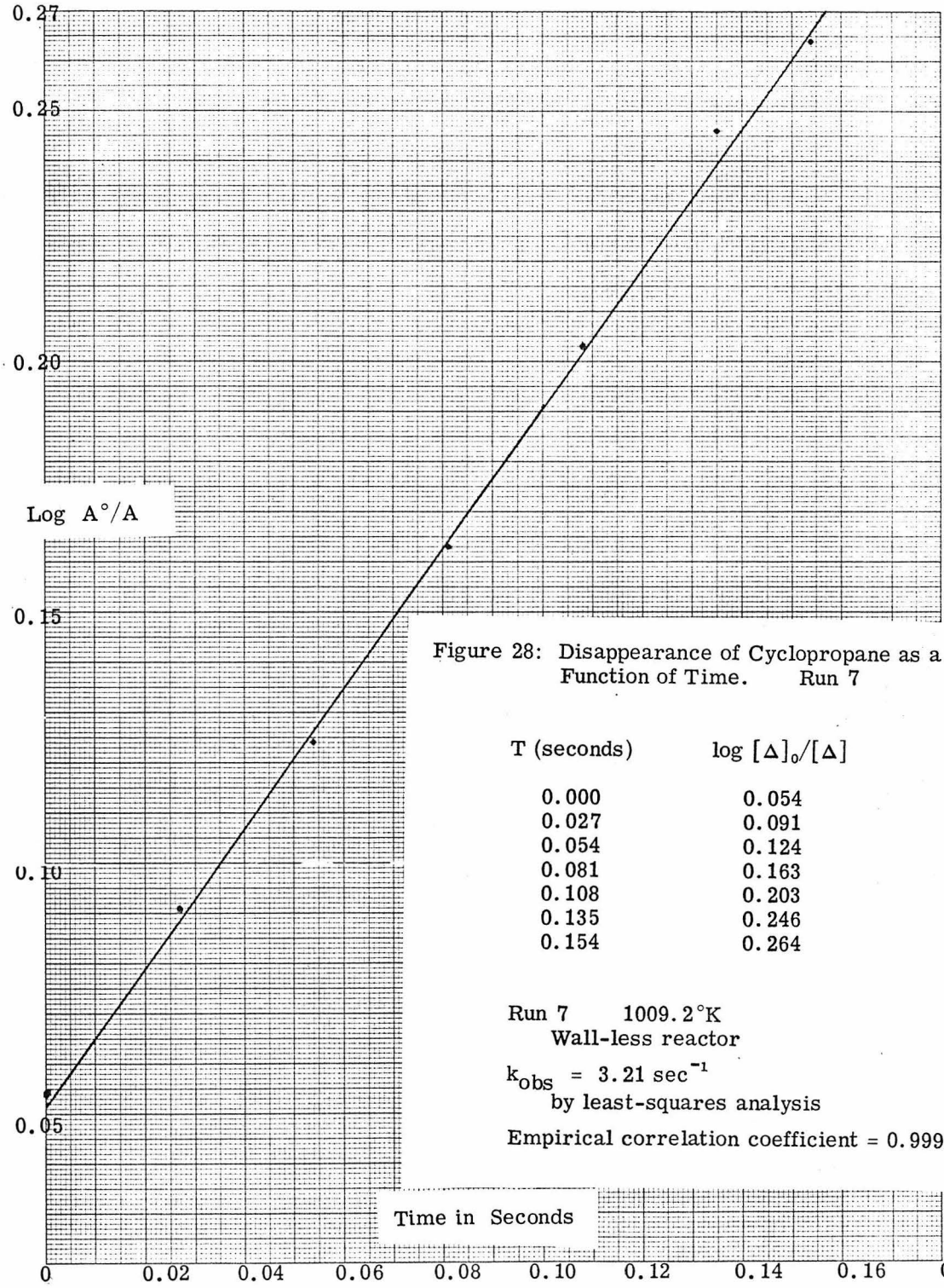


Figure 28: Disappearance of Cyclopropane as a Function of Time. Run 7

T (seconds)	$\log [\Delta]_0/[\Delta]$
0.000	0.054
0.027	0.091
0.054	0.124
0.081	0.163
0.108	0.203
0.135	0.246
0.154	0.264

Run 7 1009.2°K
Wall-less reactor

$k_{obs} = 3.21 \text{ sec}^{-1}$
by least-squares analysis

Empirical correlation coefficient = 0.9992

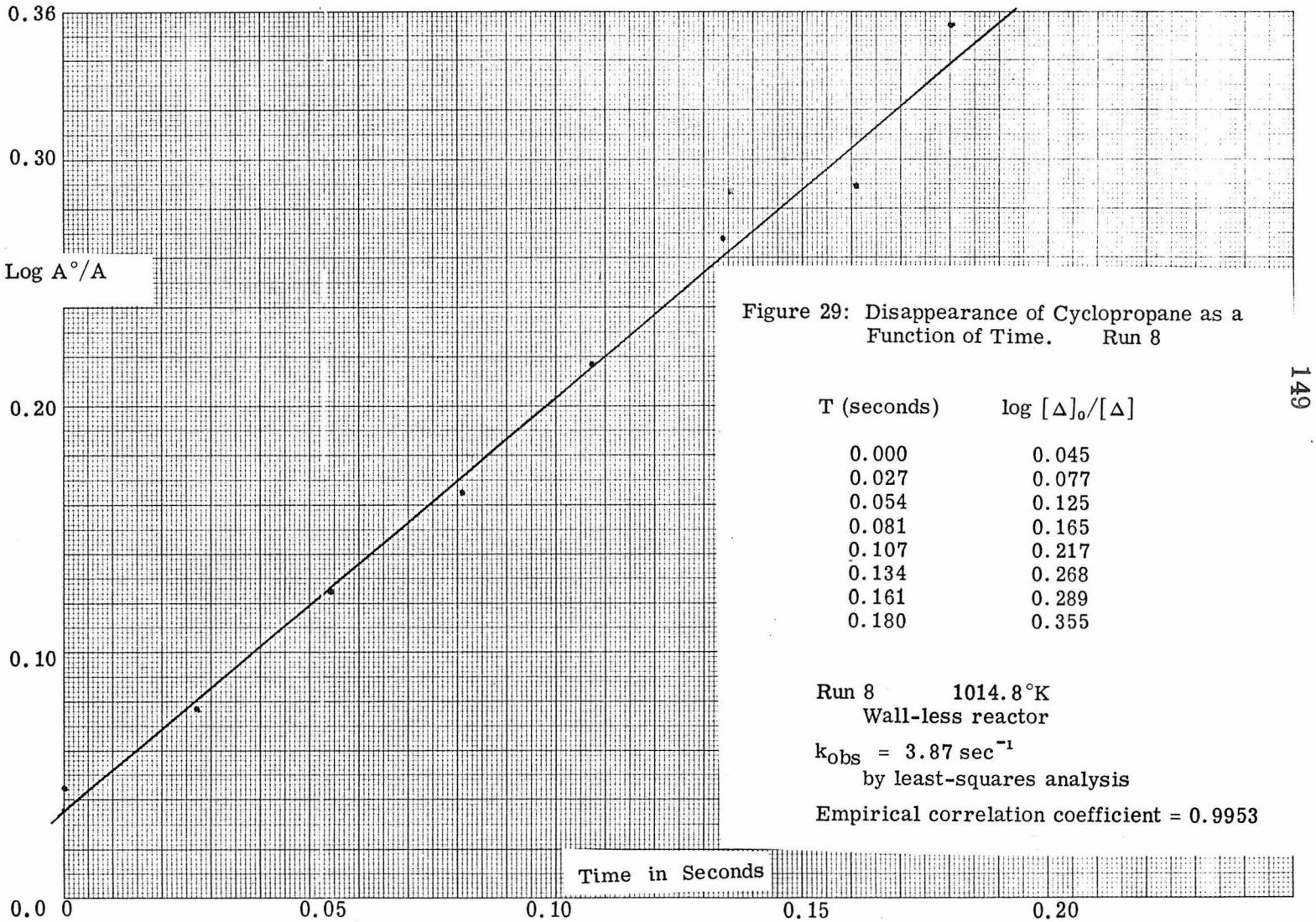


Figure 29: Disappearance of Cyclopropane as a Function of Time. Run 8

T (seconds)	log $[\Delta]_o/[\Delta]$
0.000	0.045
0.027	0.077
0.054	0.125
0.081	0.165
0.107	0.217
0.134	0.268
0.161	0.289
0.180	0.355

Run 8 1014.8°K
Wall-less reactor

k_{obs} = 3.87 sec^{-1}
by least-squares analysis

Empirical correlation coefficient = 0.9953

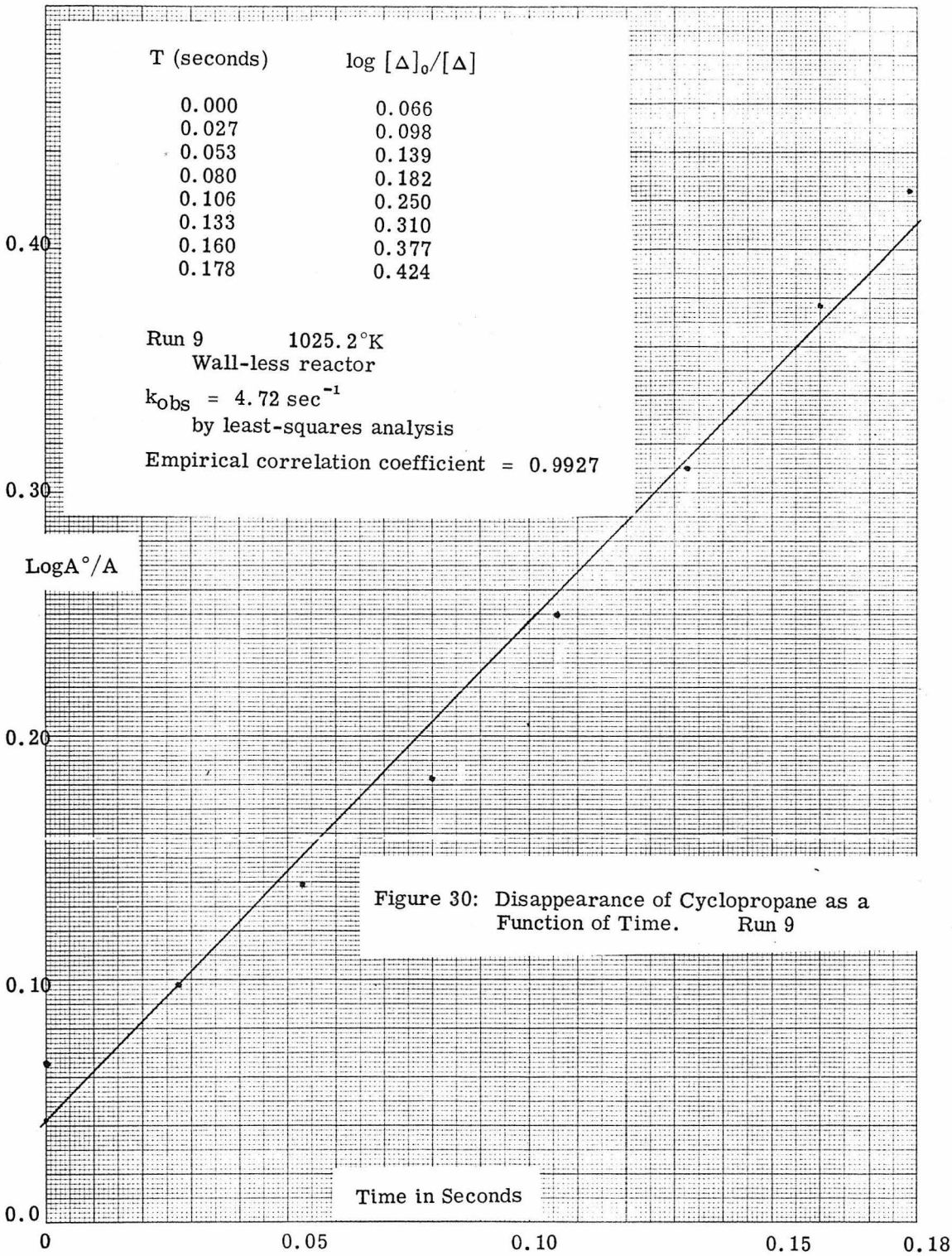
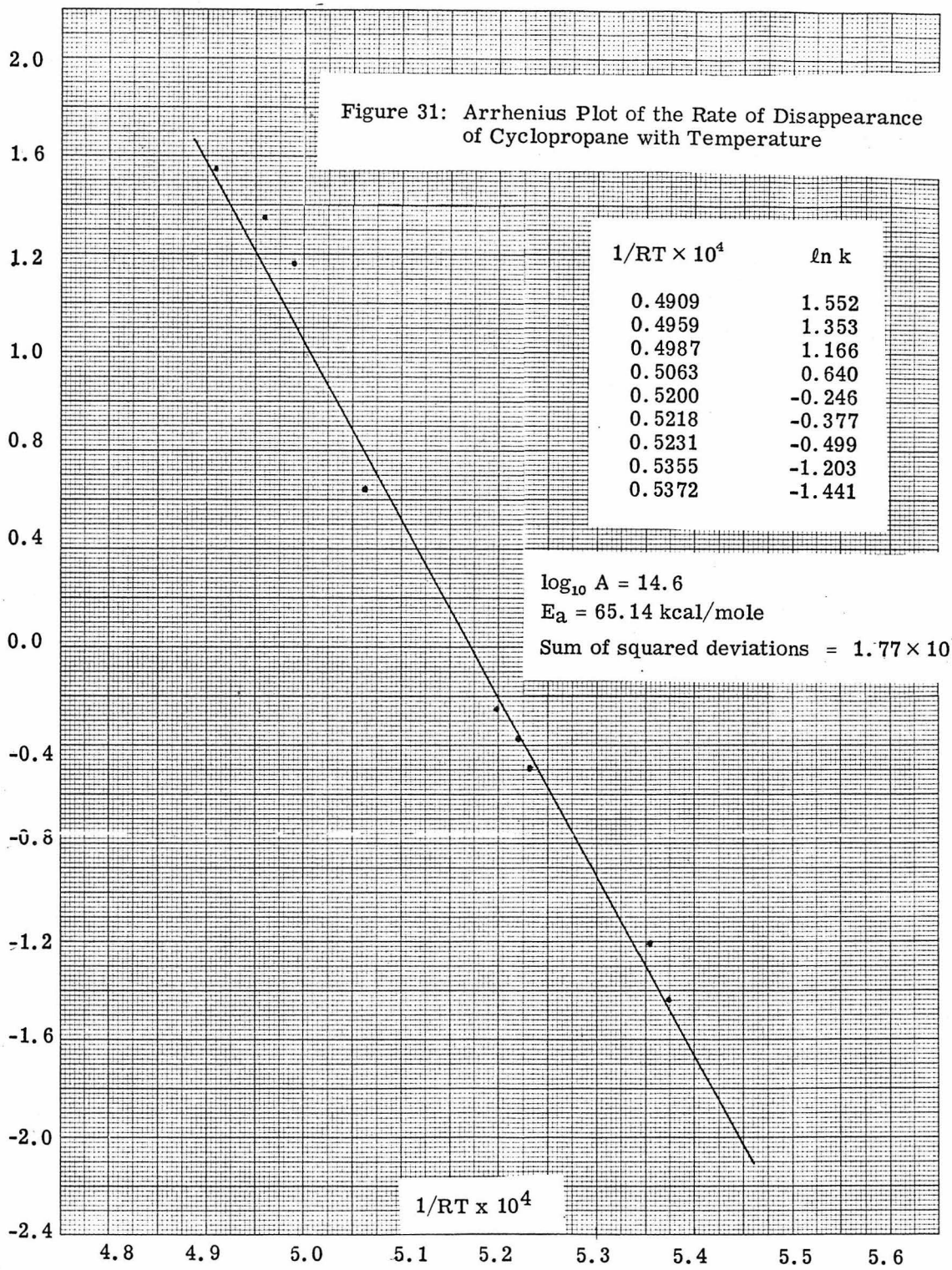


Figure 30: Disappearance of Cyclopropane as a Function of Time. Run 9

Figure 31: Arrhenius Plot of the Rate of Disappearance of Cyclopropane with Temperature



$1/RT \times 10^4$	$\ell n\ k$
0.4909	1.552
0.4959	1.353
0.4987	1.166
0.5063	0.640
0.5200	-0.246
0.5218	-0.377
0.5231	-0.499
0.5355	-1.203
0.5372	-1.441

$\log_{10} A = 14.6$

$E_a = 65.14$ kcal/mole

Sum of squared deviations $= 1.77 \times 10^{-5}$

2. Results of cyclopropane pyrolysis. From the nine rate constants was calculated the following rate law governing the cyclopropane isomerization; $\log k = \log 10^{14.6} - 65.1/\theta$. (For a partial discussion of the suspected 1,3 diradical intermediate, see Part I of this thesis.) This compares favorably with the results of other investigators who used more conventional reactors, and with the results of a similar, recently published study by Taylor's group. See Table 5.

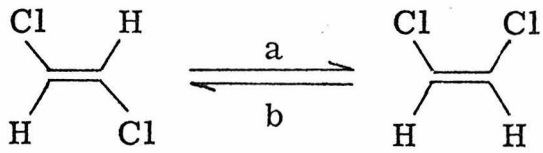
Table 5:

log A	E	Conditions	System	References
15.17	65	772 ± 29 °K	Static	29
14.89	65.2	753 ± 40 °K	Static	30
15.45	65.6	750 ± 57 °K	Static	31
14.6	65.1	981 ± 45 °K	Wall-less	This work
14.3	64.0	966 ± 36 °K	Wall-less	25

With the data obtained for cyclopropane isomerization, a degree of confidence in the results of the wall-less reactor was established.

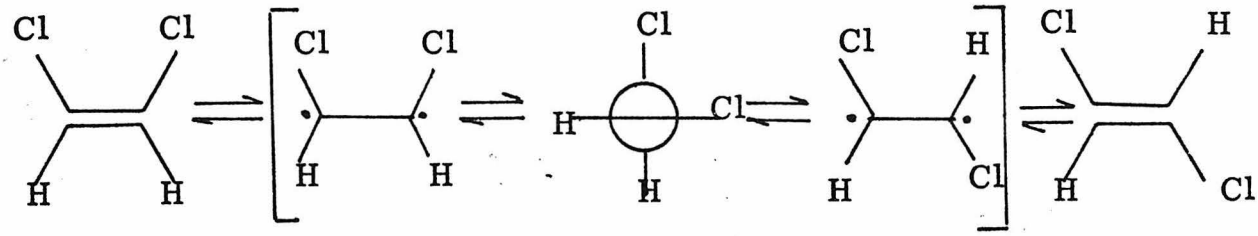
Reversible isomerization of 1, 2-dichloroethene. The reversible isomerization of cis and trans 1, 2-dichloroethene is a very surface dependent reaction,[27, 32] making it an ideal reaction to study under completely homogeneous conditions (See Table 6). As late as 1941, an activation energy of 16 kcal/mole was reported for this

Table 6: Experimentally Derived Rate Data on the Thermal Isomerization of 1, 2 Dichloroethene



Path	log A	E	Conditions	System	Reference
a	12.69	41.9	560-608 °K 200-270 mm Hg	Static	35
b	2.32	16.0	473-523 °K 40 mm of Hg	Static	27
a	12.68	55.3	806-846 °K 39 mm of Hg	Flow	32
b	12.76	56.0			
a	12.26	52.7	1050-1350 °K	Shock tube	33
b	12.35	53.4			

isomerization. An activation energy of approximately 55 kcal/mole would be more in keeping with the energy necessary to break one bond of a carbon-carbon double bond with electron withdrawing substituents in order for the isomerization to take place.



The best numbers obtained to date,[32] were found by extrapolating data, which showed a surface effect, to a zero surface to volume ratio. Because this common procedure for reactions exhibiting a surface effect was used, the data are suspect. We felt a reinvestigation of this system under homogeneous conditions was warranted.

1. Conditions for this study. Aldritch cis and trans dichloroethenes were subjected to two fractional distillations. The middle portion in each case was used in the second distillation. The middle portions of the subsequent distillations were used in the pyrolyses. The cis isomer was analyzed on a 15 ft by 1/8 in stainless steel column packed with 15% DEGS on Chromosorb WAW maintained at 70°C and was found to be 99.7% pure (retention time was 6.2 min).

The trans isomer analyzed under the same conditions was found to be 99.6% pure (retention time was 3.3 min). The purified isomers were stored in the dark over a small amount of pyro-catechol. Pyrolyses were carried out over the temperature range of 885°K to 950°K. The temperatures at the tips of the probe and nozzle were maintained 350° and 320°, respectively, below the temperature in the reaction zone. Introduction of the isomers was by bubbling pure, dry nitrogen through a sample of each.

2. Results of the study of the isomerization of 1, 2-dichloroethenes. The data obtained from the study of the isomerization of 1, 2-dichloroethene were puzzling. The equilibrium ratio of the cis isomer to the trans isomer is approximately 54:46. From the rate equations for this type of reaction are drawn the following conclusions.

$$\underline{\text{cis}} \underset{K_t}{\overset{K_c}{\rightleftharpoons}} \underline{\text{trans}}$$

$$\frac{d[\underline{\text{cis}}]}{dt} = -K_c[\underline{\text{cis}}] + K_t[\underline{\text{trans}}]$$

$$\frac{d[\underline{\text{trans}}]}{dt} = -K_t[\underline{\text{trans}}] - K_c[\underline{\text{cis}}]$$

at equilibrium $\frac{d[\underline{\text{cis}}]}{dt} = \frac{d[\underline{\text{trans}}]}{dt} = 0$

and therefore $\frac{K_c}{K_t} = \frac{[\underline{\text{trans}}]e}{[\underline{\text{cis}}]e} = \frac{46}{54} = \frac{1}{1.17}$

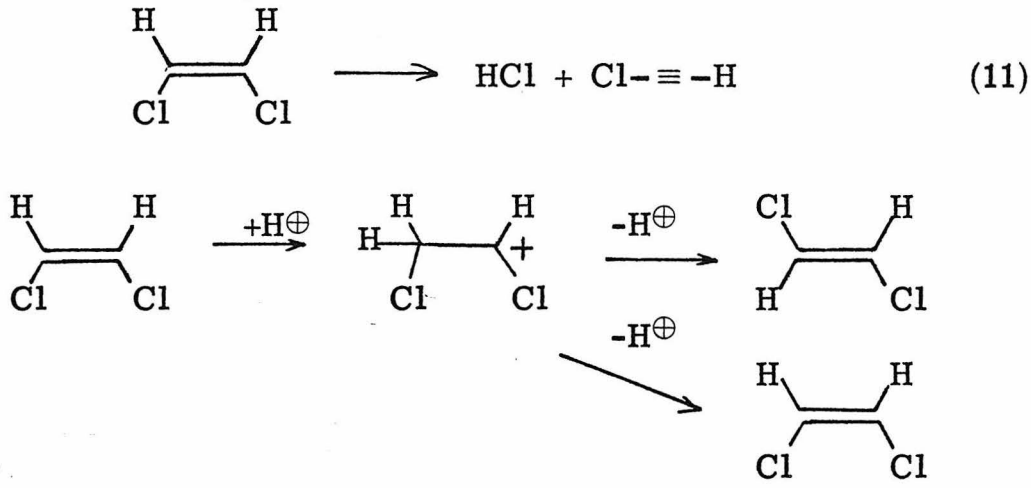
This means that the rate of approach to the equilibrium concentrations of cis and trans starting with the all cis isomer should be slightly slower than the rate of approach to equilibrium starting with the all trans isomer. However, this was not found to be the case. The cis isomer reached its equilibrium concentration much faster than did the trans isomer. Typical raw data are found in Table 7.

After 0.26 seconds the cis isomer had equilibrated, whereas for the same residence time only 10% of the trans isomer had become cis. The same trend was observed at 942°, 928°, 899° and 885°K. Calculation of $(K_c + K_t)$ at 941.6°K starting from the pure cis isomer gives a value of 20.5 per second. Calculation of $(K_c + K_t)$ at 942.4°K starting from the pure trans isomer gives 3.15 per second.

The data can best be explained in following way. The cis dichloroethene must be undergoing a side reaction. This side reaction most likely is the trans elimination of HCl to give chloroacetylene. The trans isomer does not eliminate because it has the wrong orientation of leaving groups. The side reaction probably occurs in the relatively warm reactor nozzle (515°-600°K). The large amounts of acid formed then undergo a bimolecular reaction with the remaining cis dichloroethene in the reactor catalyzing the cis $\rightleftharpoons$ trans isomerization.

Table 7: Raw Data for the Isomerization of Cis and Trans Dichloroethene at 910°K.

Time	% Cis in reaction mixture	Time	% Trans in reaction mixture
0.000	99.5	0.000	99.5
0.080	94.2	0.075	97.7
0.095	92.1	0.090	97.4
0.110	89.2	0.105	95.6
0.125	86.1		
0.140	80.4	0.135	96.1
0.155	76.4	0.150	
0.170	72.1	0.165	94.5
0.185	67.8		
0.200	65.0	0.196	92.3
0.229	58.7	0.225	90.8
0.259	57.5	0.255	89.9
0.289	55.5	0.285	88.1
0.319	56.0	0.314	84.1



The pyrolysis starting from pure trans has very little acid present and therefore, undergoes a slower, unimolecular conversion to the cis isomer. Preferential polymerization of the cis isomer in the nozzle or equally warm probe is ruled out as a possible mechanism, because the cis isomer does approach and hold its equilibrium concentration.

There is evidence for this hypothesis. Early investigators have noticed the production of HCl in kinetic studies of the cis ⇌ trans isomerization of this compound.[27,35] A new peak in the VPC was observed (retention time of 1.35 min) which could be chloroacetylene. The nozzle probe and probe thermocouple underwent accelerated corrosion during this study probably due to the effect of the eliminated HCl.

Attempts to neutralize the HCl by adding ammonia gas or triethylamine to the central hydrocarbon stream did not improve the results.

Finally, the study was abandoned. This fascinating, highly surface catalyzed reaction is worthy of further investigation. Improved cooling of the nozzle and probe or replacement of these stainless steel parts with parts fashioned out of quartz glass may provide a solution to this problem.

The pyrolysis of 3,3-dimethylcyclopropene. A discussion of the results of this study is found in Part III of this thesis.

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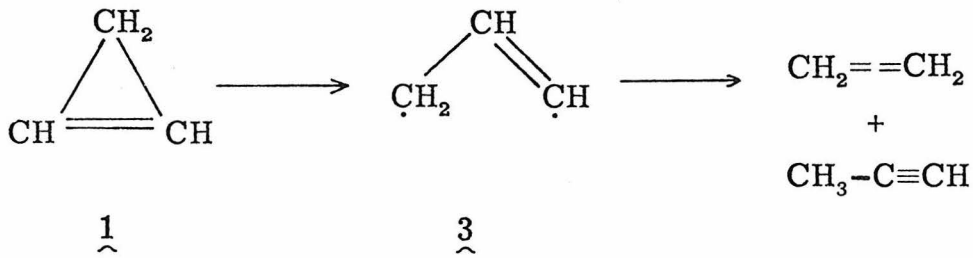
PART III

INTRODUCTION

In 1960 Wiberg and Bartley[1] found that cyclopropene (1) on passage through a heated quartz tube was converted almost quantitatively to methylacetylene (2). In 1968 Srinivasan reinvestigated this system and looked at the kinetics of the reaction.[2] He found that allene was also produced in the thermolysis of 1. From the kinetics of the reaction he found an activation energy of 35.2 kcal per mole and a frequency factor of $10^{12.13}$. A similar rate law (log k = 11.4 - 34.7/θ) was found for the pyrolysis of 1-methylcyclopropene.[2]

The simplest mechanism which can be postulated to explain these results is that one of the carbon-carbon single bonds of cyclopropene is stretched to the breaking point to give a diradical (3), from which the observed products arise by 1, 2 hydrogen shifts in either of two directions.



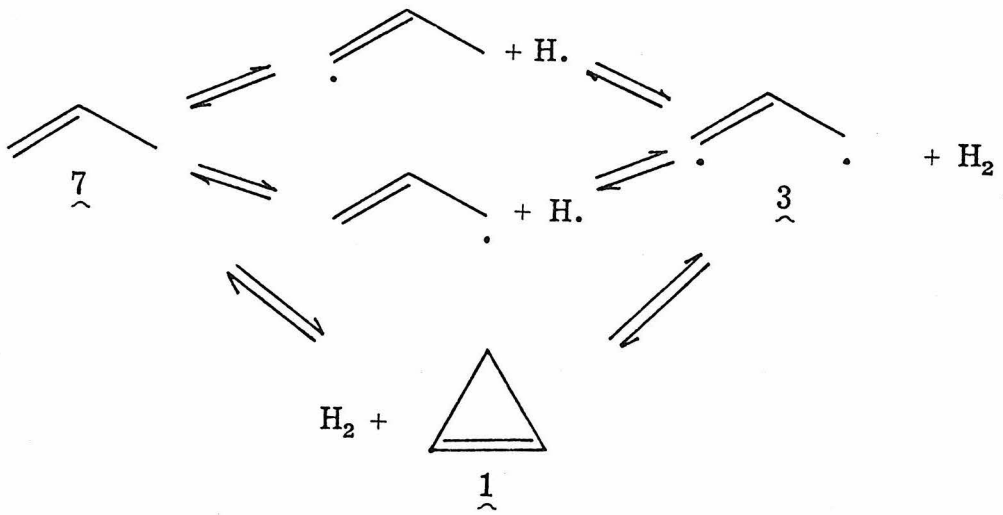
1 3

This mechanism is analogous to that proposed for the thermal isomerization of cyclopropane; the single product, propylene, comes about by a 1, 2 hydrogen shift from the 1, 3 trimethylene diradical intermediate. (See Part I of this thesis for a discussion of the intermediate in cyclopropane isomerizations.)

Thermochemical Analysis and Its Implications

The mechanistic picture does not remain simple for cyclopropene isomerizations when a thermochemical analysis is carried out on the possible conformers of 3. The methods of Benson and O'Neal were used to estimate ΔH_f^0 for 1 and 3 (cf. the simple thermochemical cycle illustrated in Scheme I). The heat of formation of propylene is +4.88 kcal per mole.[3] The heat of formation of the diradical 3 can be estimated as that of propylene plus the energy necessary to remove one vinyl and one allylic C–H bond and reform hydrogen from the atoms.[4] The assumption was made that the energy necessary to remove the last hydrogen from the monoradicals shown in Scheme I was the same as the energy required if that were the first hydrogen removed.

The ΔH_f^0 of cyclopropene 1 is 66.6 kcal/mole[5] and that of the diradical 3 is calculated to be 96.4 kcal/mole. The difference ($\Delta H^0 = \Delta H_f^0(3) - \Delta H_f^0(1) = 29.8$ kcal/mole) represents an estimate of



$$\Delta H_f^0(3) = \Delta H_f^0(7) - \Delta H_f^0(H_2) + \text{vinyl C–H bond energy} + \text{allylic C–H bond energy}$$

$$\Delta H_f^0(3) = 4.9 - 104 + 108 + 87.5 = 96.4 \text{ kcal/mole}$$

Scheme I

the cyclopropene thermodynamic C–C bond energy. The energy of activation for the ring opening to a diradical intermediate can be estimated from the energy for 1 → 2 isomerization. This number[2] (35 kcal/mole) suggests that the barrier to reclosure of 3 is ≤ 5 kcal/mole (Figure 1).

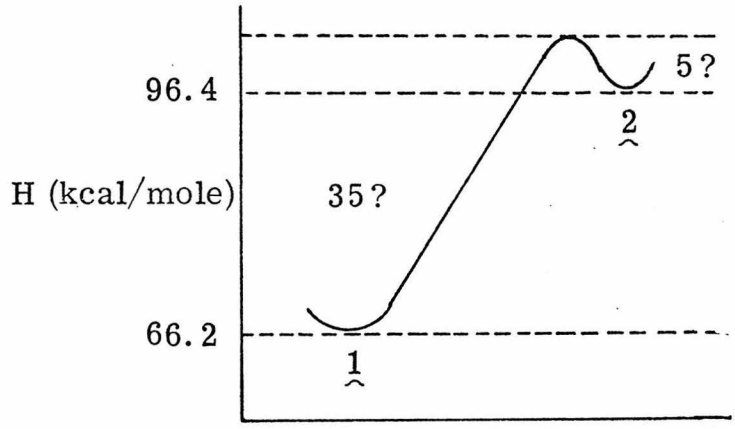
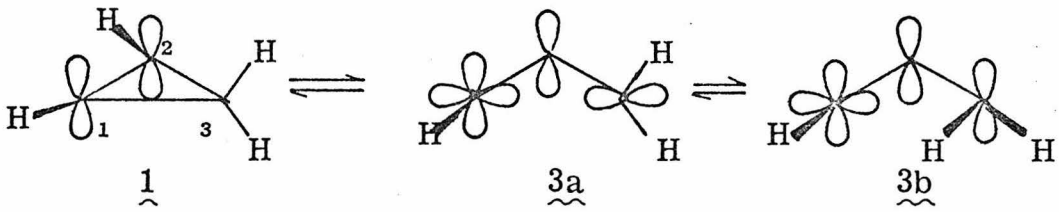


Figure 1: Possible Reaction Coordinate Diagram for Cyclopropene Ring Opening

This value of 5 kcal is interesting when one considers that Benson's parallel calculations on the cyclopropane isomerization gave a ring closure of 8-9 kcal/mole from a diradical intermediate to a molecule which contains 27 kcal/mole less strain energy (S.E.) than cyclopropene. (The S.E. of cyclopropene is 55 kcal/mole,[6] while that of cyclopropane is 28 kcal/mole.[6]) Of course, all the strain energy of the 3-membered ring may not be present in the transition state. Nevertheless, the smaller barrier to ring closure in cyclopropene is perplexing.

The question as to whether the assumption that the C–H bond energy at C-1 in $\underset{\sim}{3}$ is truly allylic[7] in the calculation of ΔH_f^o ($\underset{\sim}{3}$) casts some doubt on the reliability of this exercise.

If the reaction proceeds as depicted below, allylic stabilization is present only in 3b and not in 3a.



1 3a 3b

Intermediate 3a can be formed by simply stretching the C-1, C-3 single bond in cyclopropene. 3b can be formed by a 90° rotation of C-3 following, or during, ring opening. On the basis of allylic stabilization one would predict 3b to be more stable than 3a, although it is more geometrically distant from 1 (in that it requires a rotation as well as C–C bond cleavage), unless there is a large unanticipated stabilization of 3a by 1,3 overlap of the orbitals which formed the C–C single bond. By assuming an allylic resonance energy of 12 kcal/mole [7] in 3b, the heat of formation of 3a (which does not have allylic resonance) is calculated to be 108 kcal/mole (96 + 12 kcal/mole), which makes ΔH^{0} for the ring opening (108-67 = 39 kcal/mole) larger than $\Delta H^{\ddagger}$ (35 kcal/mole). Therefore 3a cannot be an intermediate by this analysis.

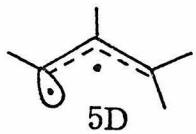
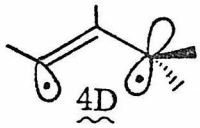
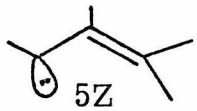
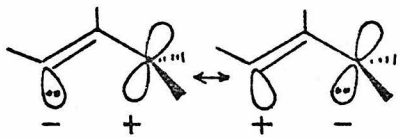
Assumptions in the thermochemical analysis restrict its value. These include the structure of the intermediate, the accuracy with which the activation barrier to ring opening of 1 is known, the magnitude of the allylic resonance energy in the diradical 3, and the ability of the 3a ⇌ 3b rotation to compete with other processes (such as H-shift) which may occur. It is possible that ring cleavage and rotation are synchronous, in which case the low activation barrier is explained by partial allylic stabilization. On the other hand, if ring opening and H-shift are concerted then the model used is inapplicable.

Hartree-Fock Calculations of Transients Found in Cyclopropene Isomerizations

More sophisticated calculations on possible intermediates in cyclopropene isomerizations were recently carried out by Salem and Stohrer using the Hartree-Fock Hamiltonian.[9] Several low lying states with the geometries of 3a and 3b were found with only a 15 kcal per mole spread in their energies. These are given below in Table I.

The energy difference between the 4D and 5Z singlets (identical to 3a and 3b, respectively) was found to be 6 kcal per mole which is in fair agreement with the value estimated from the simple thermodynamic analysis (see below). It was found that the geometry of the ground state in conformation 5 was the triplet state as was

Table I: Energies of Possible Intermediates in the Isomerization of Cyclopropenes

Geometry	Energy (kcal per mole)	Electronic state
 5D	-7.0	triplet
 4D	1.5	triplet
 5Z	0	singlet
4D	5.8	singlet
5D	8.4	singlet
 4Z	> 80	singlet

first predicted by Hoffmann.[10] The other conformation in which all substituents are not in the plane of the cyclopropenyl carbons (4D) was also predicted to have a triplet electronic ground state.

Salem also has looked at the energies necessary to transform the geometries of 4 and 5 into one another by a rotation of the methylene. He has charted the energies of the various states as a function of the degrees of rotation of the methylene and the amount of double bond

character in one bond (which changes with respect to the other bond in the three-carbon fragment).

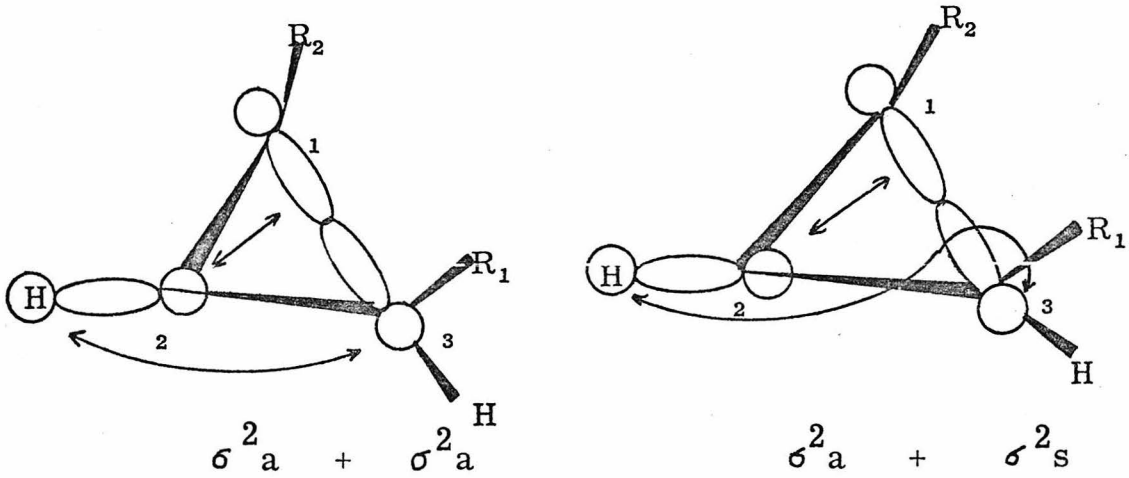
Salem concludes from his calculations that "if 5Z is created (from a vinyl carbene precursor) any additional energy which can push it over to cyclopropene via 4D can also make it leak onto the excited surface(at a pointwhere vertical separation is only 6 kcal per mole). If such a passage does occur, the reactivity of the vinyl carbene should be particularly sensitive to temperature, mode of generation, isotopic substitution, etc. Dual chemistry from two different states should be observed, but may be difficult to distinguish from dual chemistry due to two different exits on the ground surface. Thus, the ground pathway 5Z to 4D should ultimately lead to reclosure to cyclopropene or intramolecular hydrogen shift to methylacetylene. On the other hand, the transformation of 5Z to 5D could be responsible for the hydrogen shift leading to allenes (or 1,3 dienes if the cyclopropene has a 3-methyl group)."[9]

Salem's calculations, in short, predict that more than one intermediate is possible in the cyclopropene isomerizations and that one can enter the energy surface at points other than that at which the cyclopropene enters. Furthermore, product distributions should vary if one enters the system at these different points.

Concerted Mechanisms

Distinct concerted pathways which are allowed by the Woodward-Hoffmann rules [11] can be postulated for the formation of 1,3 dienes and acetylene and for the racemization of optically active cyclopropenes (see below).

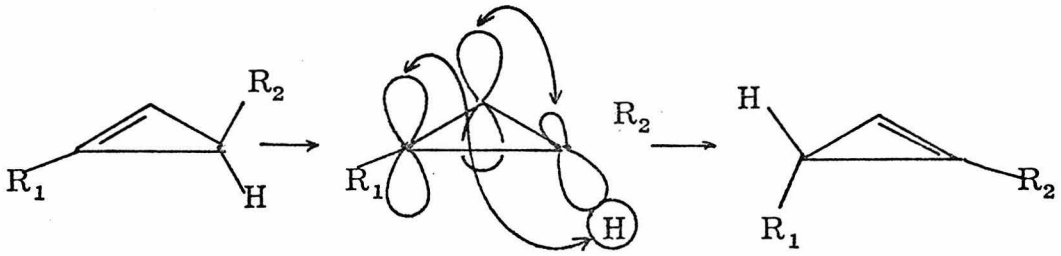
1. Formation of acetylenes. Acetylenes can be formed by an allowed $\sigma^2a + \sigma^2s$ process which transfers the hydrogen at C-2 to the opposite face of the C-3 carbon atom. This allowed process is clearly sterically less feasible than its electronically forbidden suprafacial alternative, $\sigma^2a + \sigma^2a$.



$\sigma^2a + \sigma^2a$ $\sigma^2a + \sigma^2s$

Scheme II

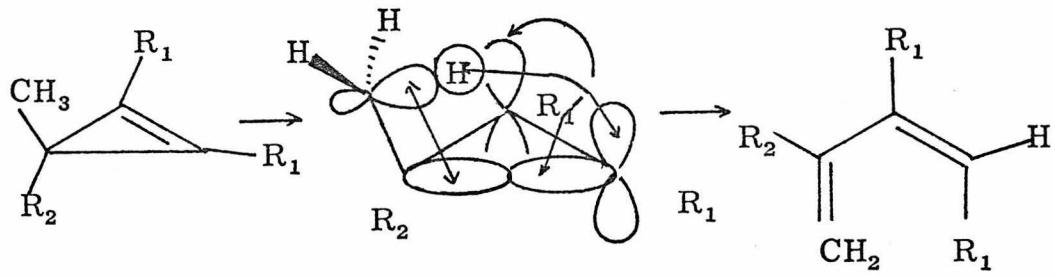
2. Racemization of optically active cyclopropenes. A $\sigma^2a + \pi^2s$ transition state can be envisioned to explain the racemization of optically active cyclopropanes. The racemization scheme shown below is that for a 1,3 hydrogen shift; a similar transition state can be envisioned if an alkyl group instead of hydrogen is shifted.



$\sigma^2a + \pi^2s$

Scheme III

3. Formation of dienes. The only allowed transition state is the $\sigma^2s + \sigma^2s + \pi^2s$ shown for a 3-methyl substituted cyclopropene. This concerted reaction predicts that the former vinyl substituents will end up in a trans orientation on the new double bond.



$\pi^2_s + \sigma^2_s + \sigma^2_s$

Scheme IV

Purpose of Study

In addition to some doubts about the validity of the activation energies found for the isomerization of cyclopropenes by Srinivasan, the low values found for log A factors also caused a good deal of concern. These values, 12.13 and 11.4 for cyclopropene and 1-methylcyclopropene,[2] respectively, are much less than were anticipated for a reaction of a cycle going to non-cyclic products.[12] Normally, a positive entropy of activation ($\log_{10} A > 13$) is expected which reflects the increased flexibility of transition state over the

starting cycle.

Srinivasan reported a surface dependence in the rates of isomerization of 1 and 1-methylcyclopropene. Low A factors and activation energies are often the result of surface catalyzed reactions (see Table 6 of Section II of this thesis for an Example). It was decided to reinvestigate the kinetics of a cyclopropene isomerization under completely homogeneous conditions, i.e., pyrolyses were carried out in the wall-less reactor. 3,3-Dimethylcyclopropene (6) was the cyclopropene selected for this study. 6 was reported to have a surface dependence in its isomerization.[13]

The second part of this study is concerned with the generation of a vinylcarbene from a source other than a cyclopropene. The decomposition products from the vinylcarbene precursor were to be compared with the isomerization products from the corresponding cyclopropene. It was necessary that the carbene precursor be amenable to reaction in the gas phase and have a $\Delta G^{\ddagger}$ less than that of the cyclopropene. 3-Vinyl-3-methyl diazirine[14] was found to meet these criteria and the thermal gas phase decomposition was studied. It was predicted that if the vinylcarbene from the diazirine was identical to the intermediate or the first intermediate generated from the cyclopropene, then the products and their relative ratios from both carbene precursors should be identical. If the vinylcarbene from the diazirine

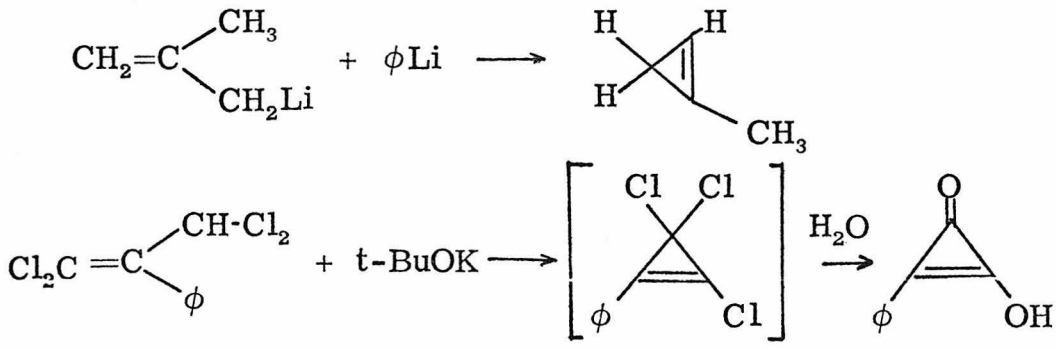
is a secondary intermediate in the cyclopropene isomerization, it is predicted that the products may be similar in structure but not in their relative ratios. If the decomposition products from the diazirine do not resemble the cyclopropene isomerization products, it is concluded that the diazirine derived vinylcarbene is not an intermediate and some other mechanism (possibly a concerted one) is operating in the cyclopropene thermolysis.

BACKGROUND

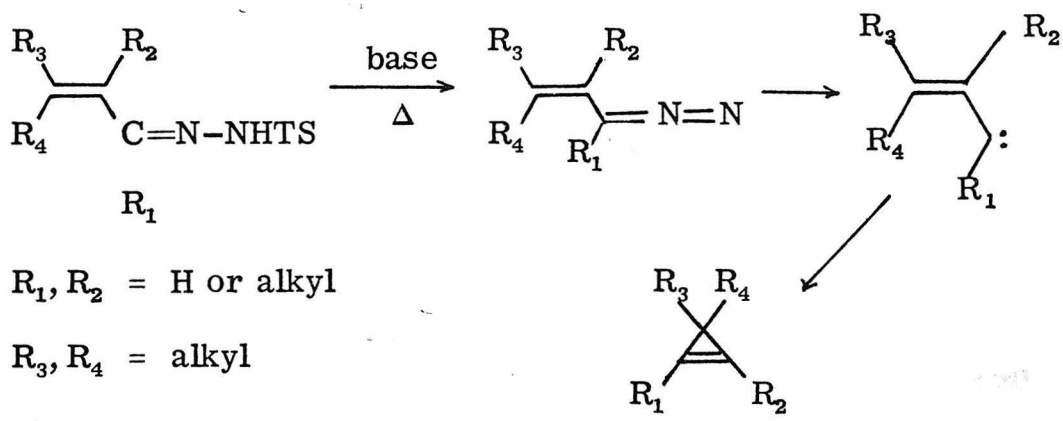
Generation of Potential Intermediates in Cyclopropene Isomerizations by Alternative Reactions

Potential vinylcarbenes have been generated in several ways. In most cases the only products isolated are cyclopropenes.

Cyclopropenes result from the reaction of allylchloride (or alkyl substituted allyl chlorides) with strong bases such as organolithiums [8, 15-18], sodium amide [19, 20] or potassium tertiary butoxide. [21]

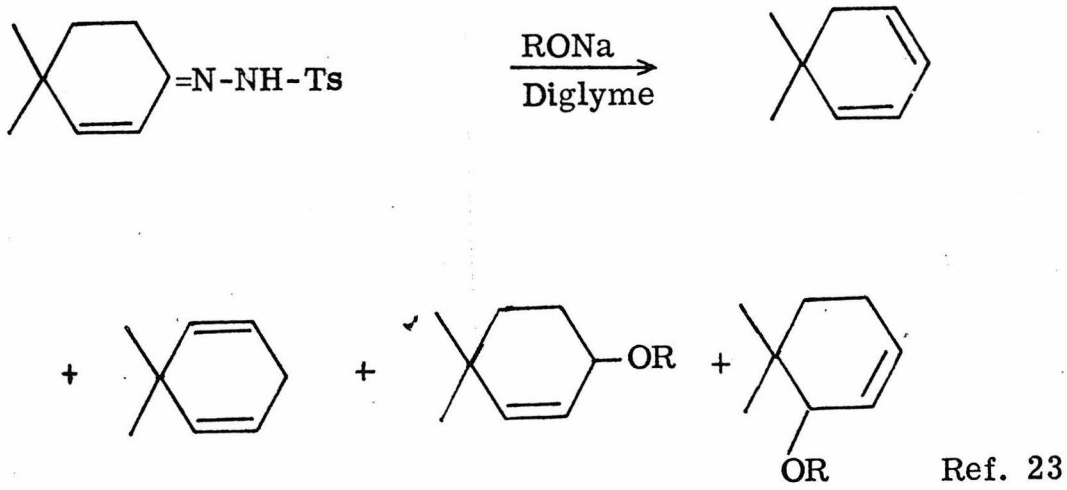


The base-induced pyrolysis of tosyl hydrozones of α,β-unsaturated aldehydes and ketones is a convenient route to alkyl cyclopropenes. [13, 17, 22] The alkenylcarbenes are likely intermediates generated from the transient diazoalkenes.



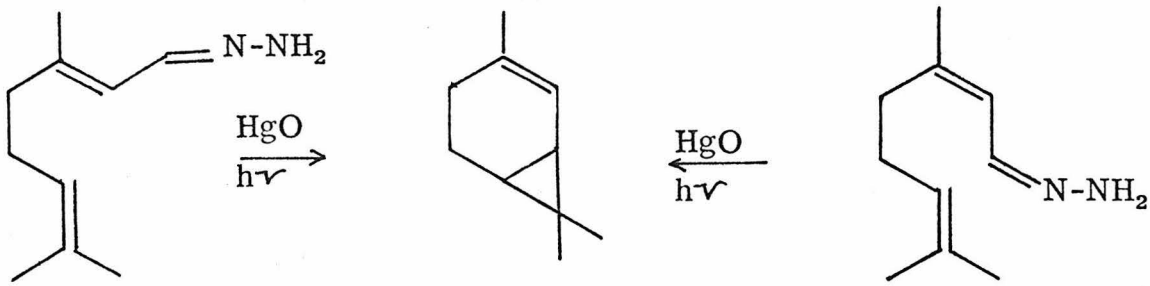
If R_3 or R_4 is hydrogen, pyrazole formation becomes the major reaction path.[22]

One case of a thermally generated vinylcarbene not forming a cyclopropene is reported by Kirmse and Ruetz.[23] This is probably because the expected cyclopropene would be highly strained.

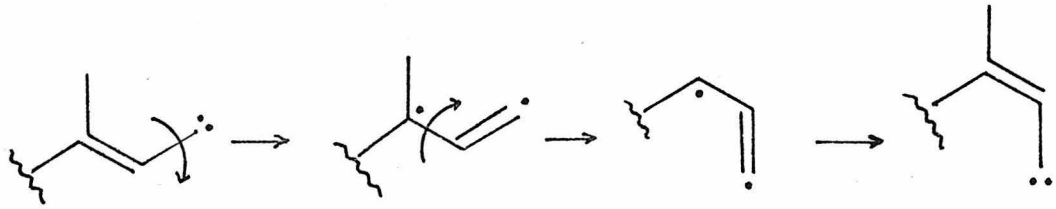


Ref. 23

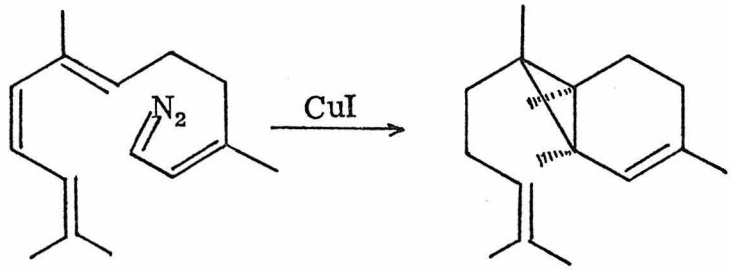
A photochemically generated vinylcarbene has been found which preferentially adds to a remote double bond;[24] the hydrazones from



both double bond isomers give the same product. This presumably means that the intermediate can rotate about its bonds without being converted to the cyclopropene.

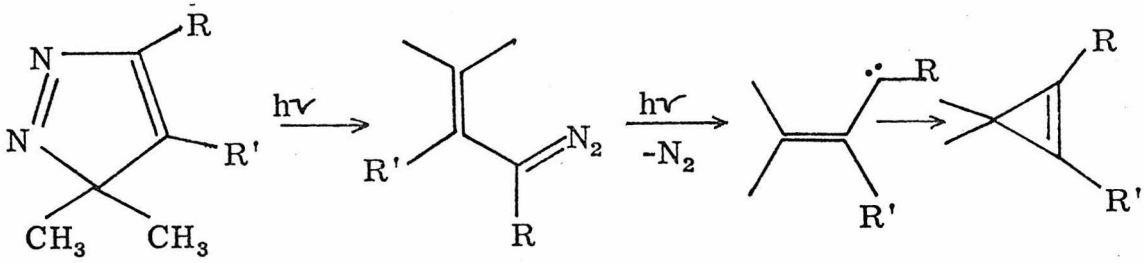


Other intramolecular additions of the vinylcarbene to a remote double bond have been reported by Corey and Achiwa in the transition metal catalyzed decompositions of α,β-unsaturated diazo compounds. Catalysts include cupric fluoroborate,[25] cuprous iodide[25, 26] and mercuric iodide.[26]



Ref. 25

Efforts to prepare the 1,3 diradical intermediate directly from pyrazolenines (26) have been unsuccessful, because pyrazolenines are thermally more stable than the corresponding vinyl diazo compounds.[22] Diazo intermediates have been observed in the photolysis of pyrazolenines.[27-32] Again, further reaction of the diazo intermediates leads only to cyclopropenes.



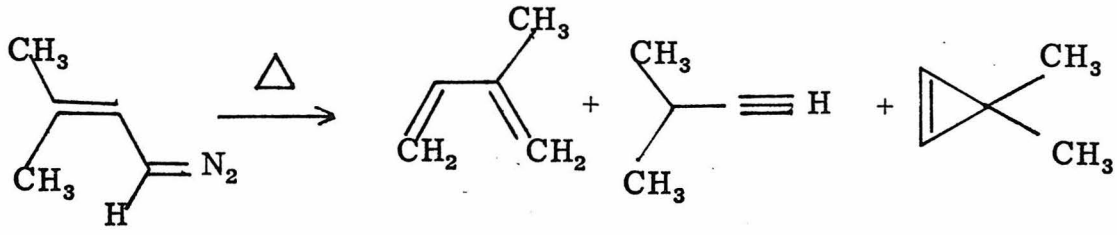
26

The flash vacuum pyrolyses of pyrazoles which give cyclopropene products probably also involve a diazo intermediate as well as a pyrazolenine.[33]

Although the fate of most vinylcarbenes (generated from precursors other than cyclopropenes) is ring closure to give cyclopropenes, Closs has observed small amounts of diene products in his preparation of cyclopropenes from pyrolysis of the sodium salts of α,β-unsaturated tosylhydrazones which he ascribes to a vinylcarbene.[22]

Prompted by this report, T. H. Morton has synthesized and studied the pyrolysis of precursor to the vinylcarbene expected from 3,3-dimethyl-cyclopropene (6). The relative ratio of the products

found in this study are shown in Table II.



27 10 9 6

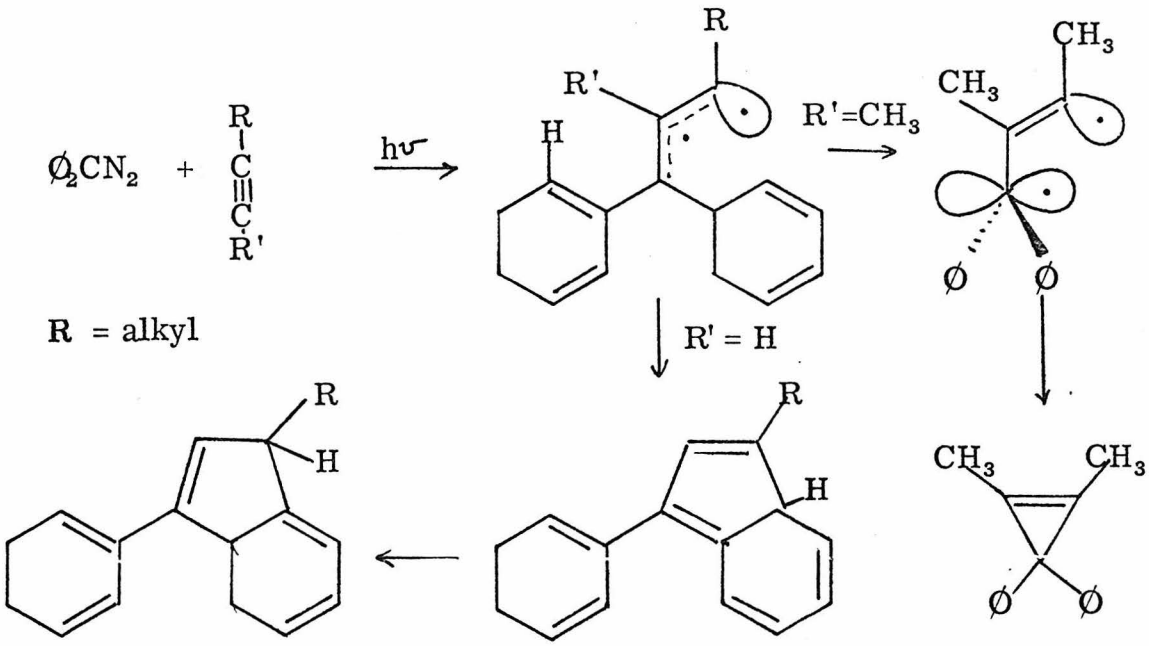
Table II: Product Distribution from Pyrolysis of Isobutenyldiazomethane

Temperature of flow tube	Isopropene 10	Isopropyl-acetylene 9	6
447°K	2.6	1	125
449°K	2.3	1	45

Again, a cyclopropene was the main product of the vinyl diazo compound. The ratio of acyclic products to one another were greatly different from that observed in the pyrolysis of 6 (see below). If the product ratio accurately reflects the true course of the decomposition of isobutenyldiazomethane, then the singlet vinylcarbene cannot be the primary intermediate in the decomposition of 3,3-dimethylcyclopropene (6).

Hendrick, Baron and Jones[34] have observed chemistry indicative of a vinylcarbene analgous to Salem's 5D upon the addition of

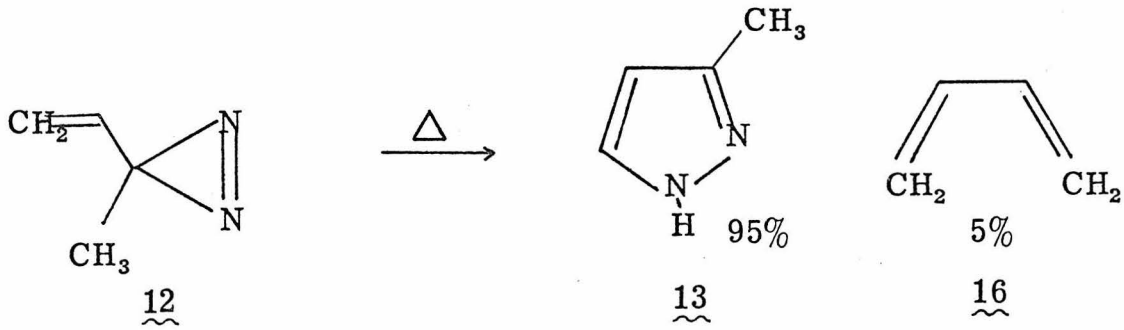
triplet diphenyl carbene to 1-butyne. No cyclopropene products were found; instead only phenyl indenes were produced. This is in keeping with Salem's predictions for 5D. Neither the direct nor the sensitized irradiation of the corresponding cyclopropenes produced any indene products. The authors conclude that the cyclopropenes are not intermediates and that the indenes arise as shown in the scheme below.



Curiously the irradiation of diphenyldiazomethane in the presence of 2-butyne produced a cyclopropene as the major product (75%). A methyl-phenyl hydrogen steric interaction which is lacking in the intermediate from 1-butyne causes a rotation in the planar carbene to

give a species analogous to 4D which closes up, as predicted by Salem, to a cyclopropene.

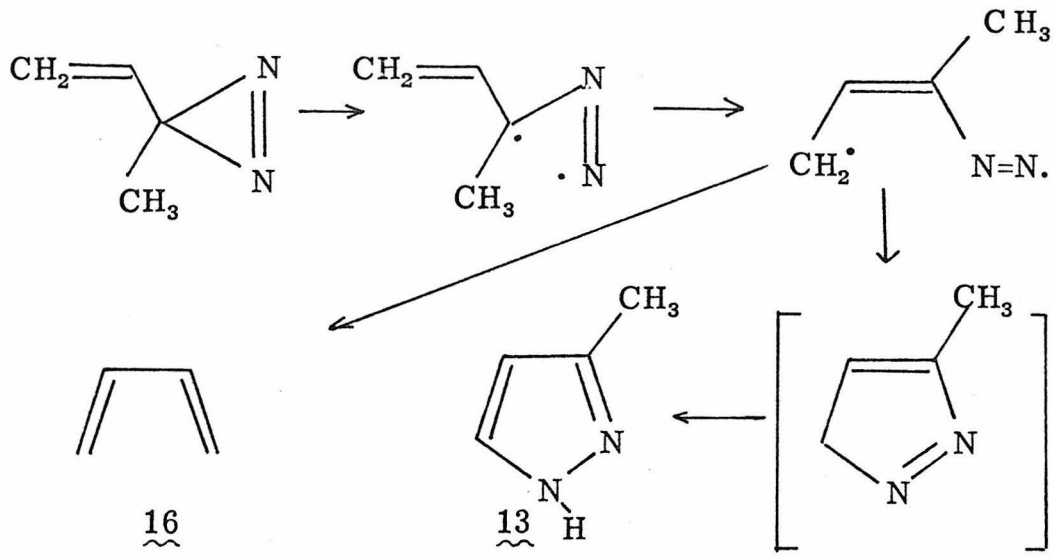
In 1967, Schmitz reported the synthesis of 3-vinyl-3-methyldiazirine (12).[14a] 12 is a potential vinylcarbene precursor by loss of



12 13 16

nitrogen. However, he also noted that after seven days in dichloromethane, 12 isomerized to 3-methylpyrazole (13) without loss of nitrogen.

Liu and Toriyama looked at the kinetics of the isomerization in a variety of solvents.[14b] They found the following rate law for the reaction: $\log K = 13.7 - 25.6$ kcal per mole/θ. Over the temperature range of 40-80°C, the rate of isomerization of 12 did not vary significantly in going from very non-polar to very polar solvents. They also noted that a small amount of what they presumed to be butadiene (5%) was also formed. They postulated a mechanism which involves breaking of a carbon-nitrogen single bond to give a diradical, which rearranges and closes up to a pyrazolenine (see Scheme V). The

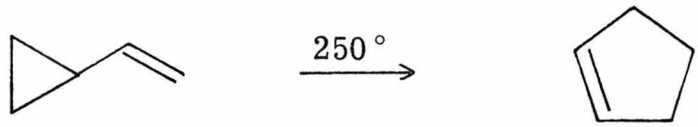


Scheme V

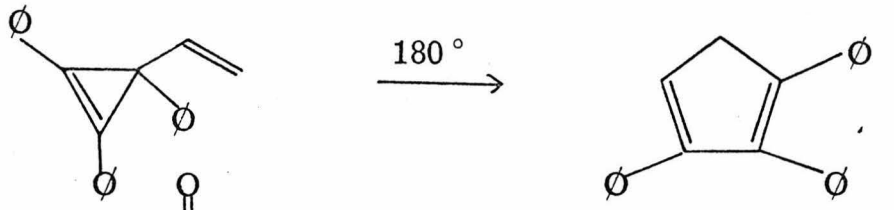
pyrazolenine rearranges quickly to a pyrazole, a well documented isomerization for pyrazolenines with unsubstituted methylenes.[22] No mechanism was offered for the formation of 1,3-butadiene.

Cyclopropene Isomerizations

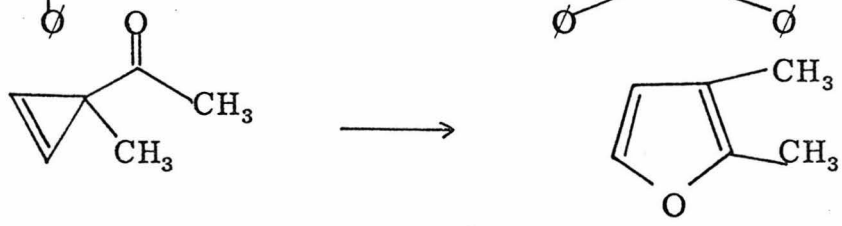
One class of reaction which gives some indication as to the course of unimolecular cyclopropene ring cleavage reactions is the ring expansion of cyclopropene containing double bond substituents at C-3.[35,36] As shown in examples below, there is a parallel with the vinylcyclopropane to cyclopentene rearrangement which is believed



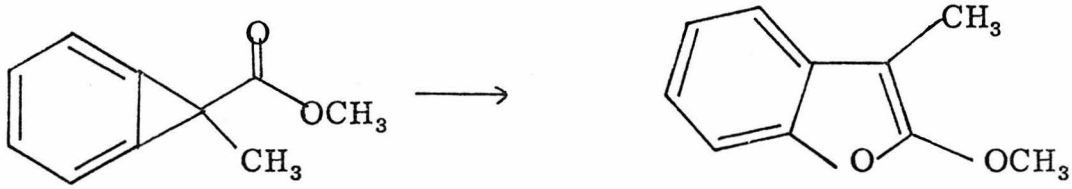
Ref. 66



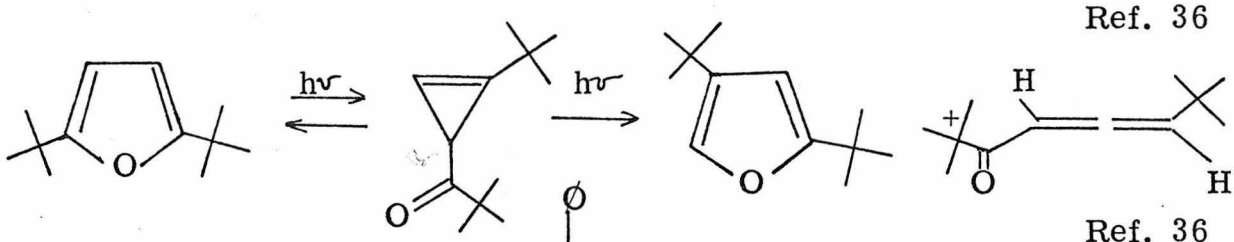
Ref. 35



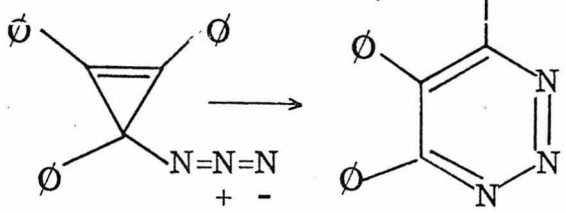
Ref. 36

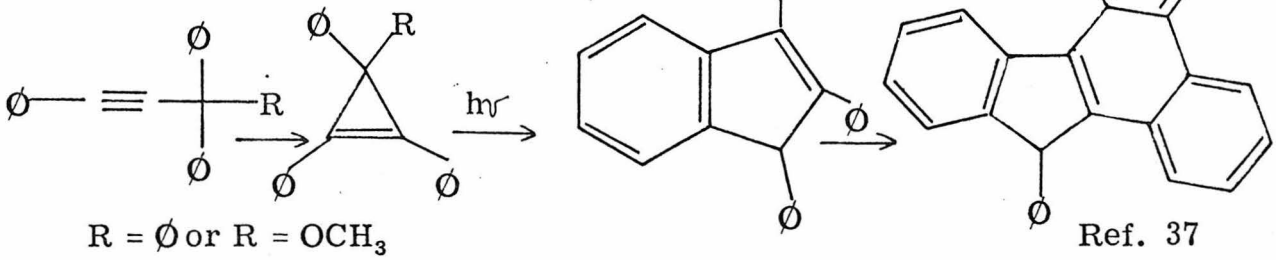


Ref. 36



Ref. 36



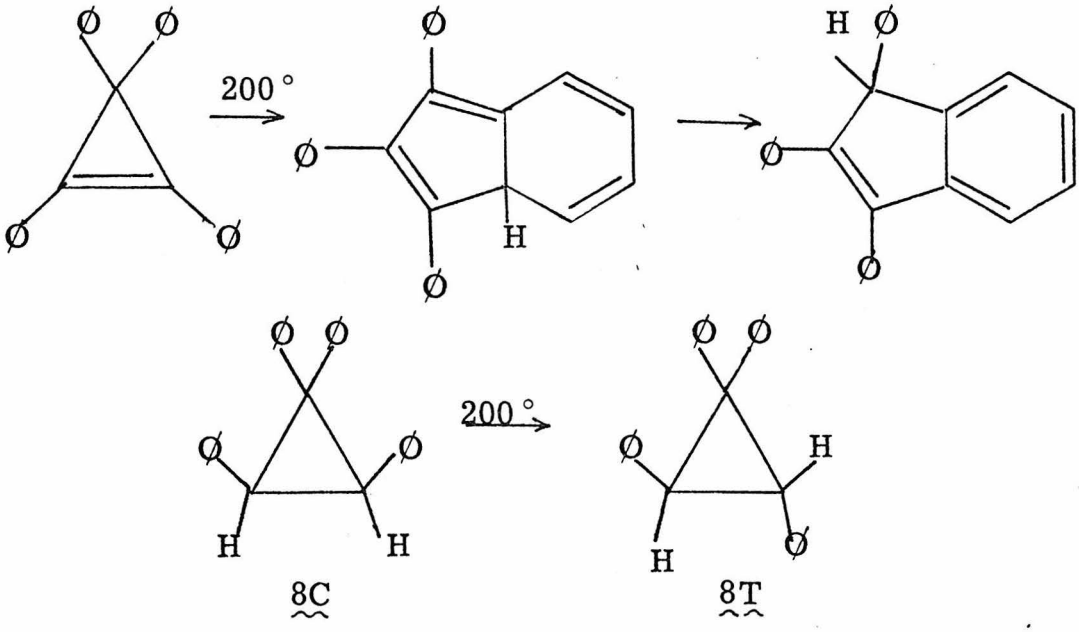


$R = \emptyset$ or $R = OCH_3$

Ref. 37

to go via a stepwise mechanism. However nothing is known about the mechanisms of these cyclopropene ring expansions, so the presence of transients discussed in the introduction cannot be ruled out as possible intermediates.

An interesting related study was carried out by Battiste et al. on the pyrolysis of tetraphenylcyclopropene in diphenylether at 176-206°C.[38]

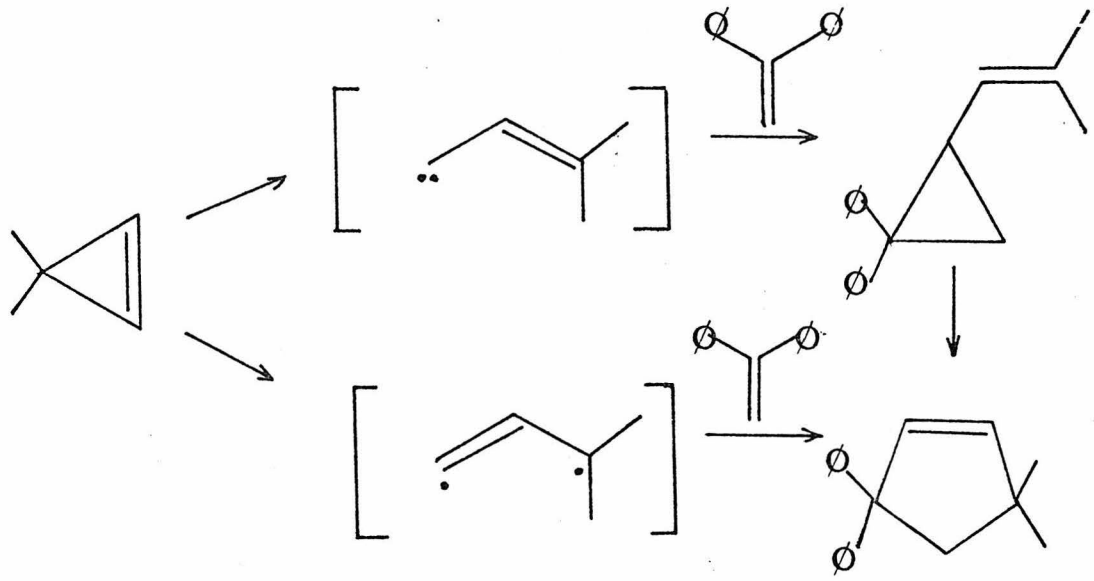


8C 8T

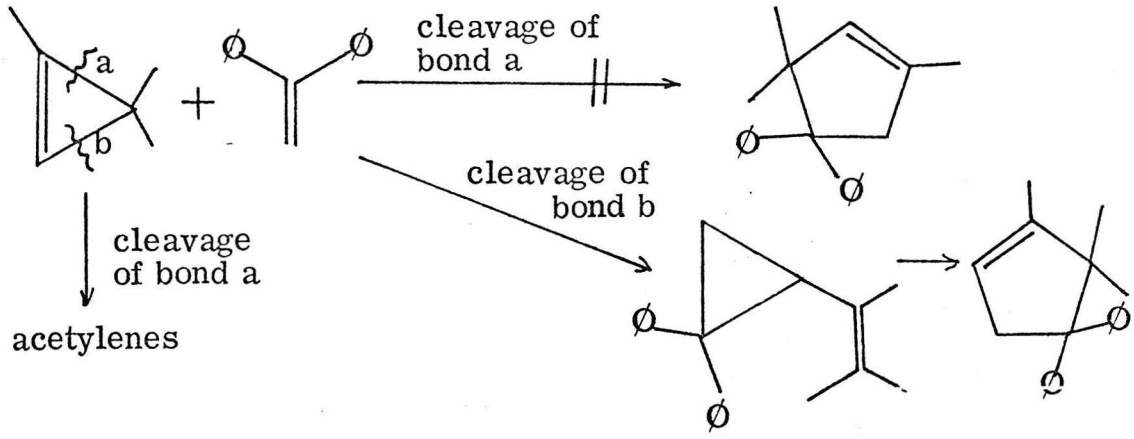
A rate law of $\log K = 14.0 \pm 0.5 - 40 \pm 1/\theta$ was found for this isomerization. This is very surprising because the activation energy is slightly larger than that observed for alkyl cyclopropenes. In the isomerization of 8C to 8T the activation energy was found to be 26 kcal per mole less than that observed for the isomerization of the 1, 2-dideuterio cyclopropanes (38.4 versus 64 kcal per mole,

respectively[15, 40]). In the cyclopropane ring opening, each phenyl group stabilizes the incipient 1, 3 diradical by 12-13 kcal per mole,[39] whereas in the cyclopropene ring opening, the phenyl groups slightly destabilize the intermediate. This is a most unexpected and unusual result if the intermediate in the cyclopropene isomerization is diradical-like in nature.

Attempts have been made to trap the intermediate in the cyclopropene isomerization. Closs decomposed 3, 3-dimethylcyclopropene (6) in a sealed tube with 1, 1-diphenyl ethylene as solvent at 250°.[41] The product, 3, 3-diphenyl-5, 5-dimethylcyclopentene, was that expected for the addition of a vinyl carbene, similar to 3b, to the double bond followed by a vinylcyclopropane to cyclopentene rearrangement[66] (see above), or by the 1, 3 addition of a diradical intermediate, similar to 3a, to give the cyclopentene directly.



The experiment was repeated with a different cyclopropene, 1, 3, 3-trimethylcyclopropene.[41] The only addition product found was 2, 3, 3-trimethyl-4, 4-diphenylcyclopent-1-ene. This was unexpected because it indicates that the least substituted single bond (bond b) in the cyclopropene was breaking to form the intermediate which adds to the ethylene. In cyclopropane isomerizations, the bond with the most alkyl substituents breaks preferentially because alkyl groups stabilize radicals. However, the major products (mainly acetylenes) can be rationalized by cleavage of the most substituted single bond (bond a).

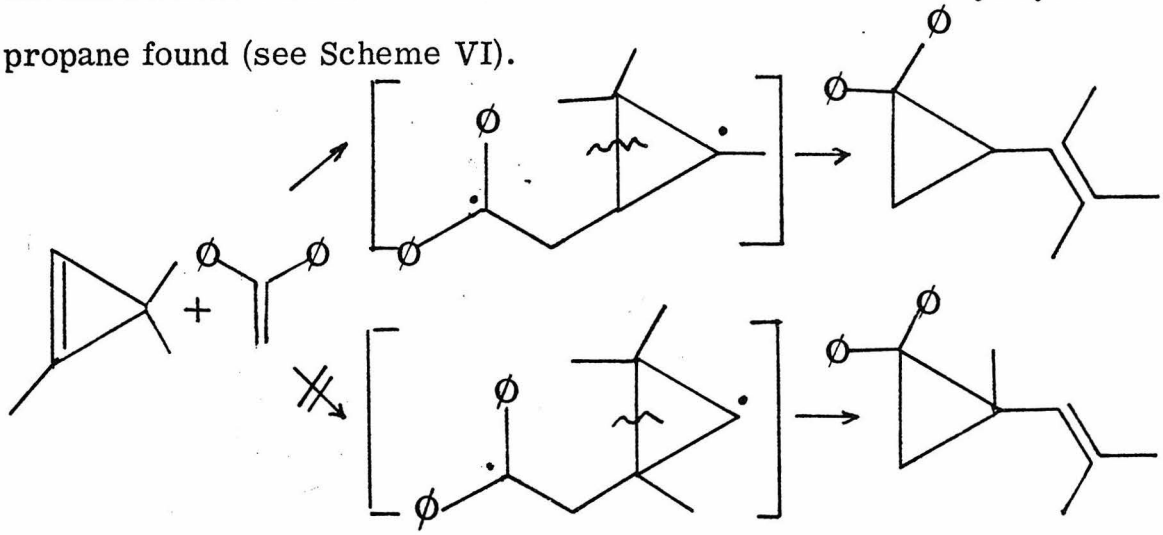


When the pyrolysis temperature was lowered, Closs isolated the vinylcyclopropane responsible for the only cyclopentene observed.

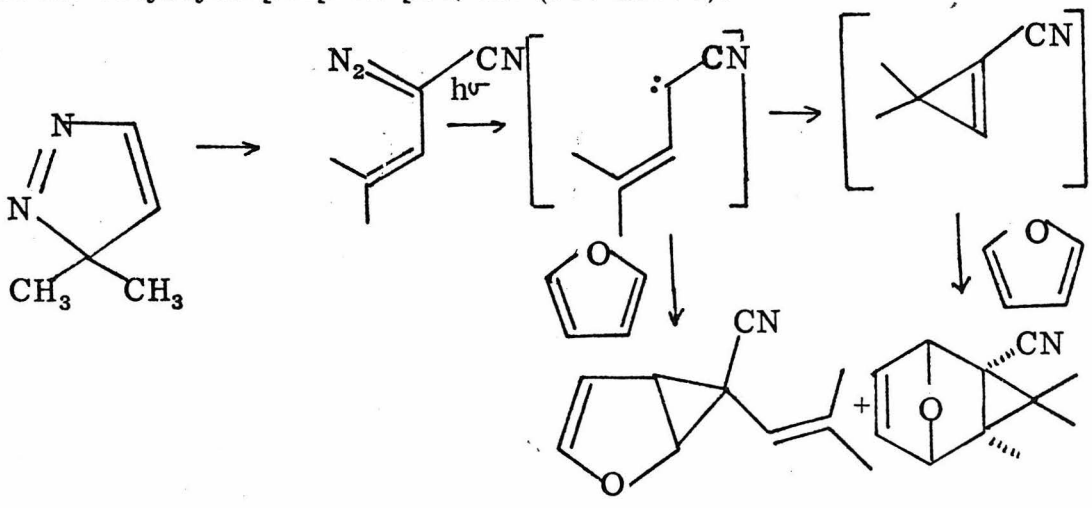
The data can be explained in the following way. Cleavage of the most substituted bond gives an intermediate which has a very favorable reaction pathway to acetylenic products by a 1, 2 hydrogen shift. Cleavage of the least substituted bond has no favorable pathway

to acetylenes; it either closes up or reacts with a molecule of 1,1-diphenylethylene.

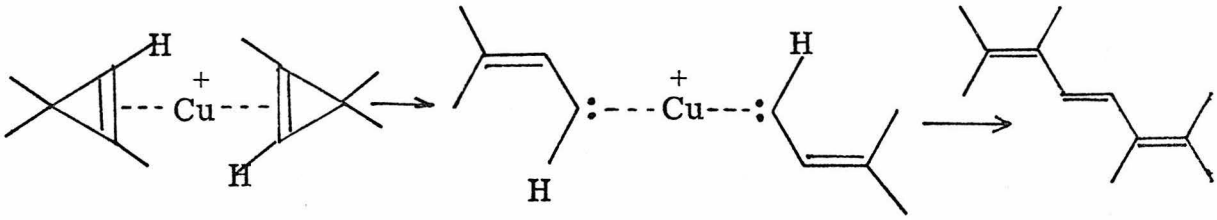
Closs chooses to explain the data by an alternative mechanism.[41] Formation of a tertiary radical over a secondary radical in the intermediate leads to the exclusive formation of the vinyl cyclopropane found (see Scheme VI).



The photochemical reaction of a pyrazolenine in the presence of furan leads to products which could come about by trapping of the cyclopropene and the vinylcarbene intermediate.[42] However, the data could be explained by Closs' alternative mechanism for the formation of the vinylcyclopropane product (see above).



Stechl has reacted 1, 3, 3-trimethyl and 1, 2, 3, 3-tetramethyl-cyclopropenes in the presence of cuprous chloride in acrylonitrile.[67] The major products are 1, 3, 5-trienes which can arise through catalyzed dimerization of the vinylcarbenes as shown in the scheme below.



No intermolecular addition to double bonds was reported.

A fair amount of kinetic data is to be found in the literature on the thermal isomerizations of cyclopropenes both in solution and in the gas phase.

T. H. Morton of the Bergman research group has synthesized 3, 3-dimethyl-cyclopropene (6) and has looked at the kinetics of the gas-phase reaction in a static system over the temperature range of 450-504°K.[13] 6 isomerized to 90% isopropylacetylene (9), 10% isoprene (10), and 0.1% gem-dimethylallene (11) with a rate law of log K = 13.9 - 38.5 kcal per mole/θ. These numbers represent an improvement over those reported by Srinivasan for cyclopropene and 1-methylcyclopropene.

However, in a packed reactor the cyclopropene polymerized even after numerous attempts to condition the reactor. No meaningful rate data were obtained.

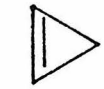
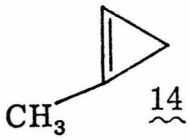
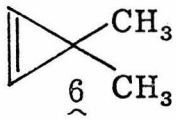
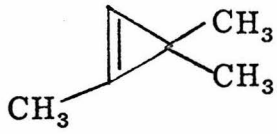
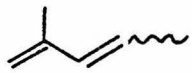
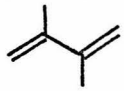
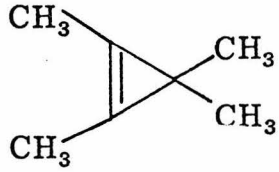
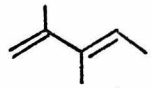
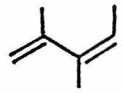
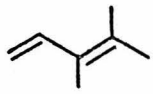
In any case, Morton did show that the ratio of 9:10 coming from 6 was different than the ratio from isobutenyldiazomethane (27) (9:1 and 1:2.6 from 6 and the diazo compound, respectively). He interpreted these results as evidence that the transients from cyclopropene and the diazo compound enter the C_5H_8 energy surface at different points; the vinyl carbene from 27 is an intermediate in the isomerization of 6 but is not the primary one.

At the same time Morton was carrying on his studies on 6, R. Srinivasan published a comprehensive study of methyl substituted cyclopropenes including 6[43] the results of which are shown in Table III along with the results of his earlier studies.[2]

Contrary to Morton's results, he found no surface dependence on the rate of the isomerization of 6. However, the activation energy he found for this cyclopropene was 2 kcal per mole lower than Morton's value.

He also reported the peculiar result that increasing methyl substitution raised the activation energy for cyclopropene isomerization. Again, this effect is opposite to what is known for cyclopropanes. Increasing methylsubstitution in cyclopropanes decreases the activation

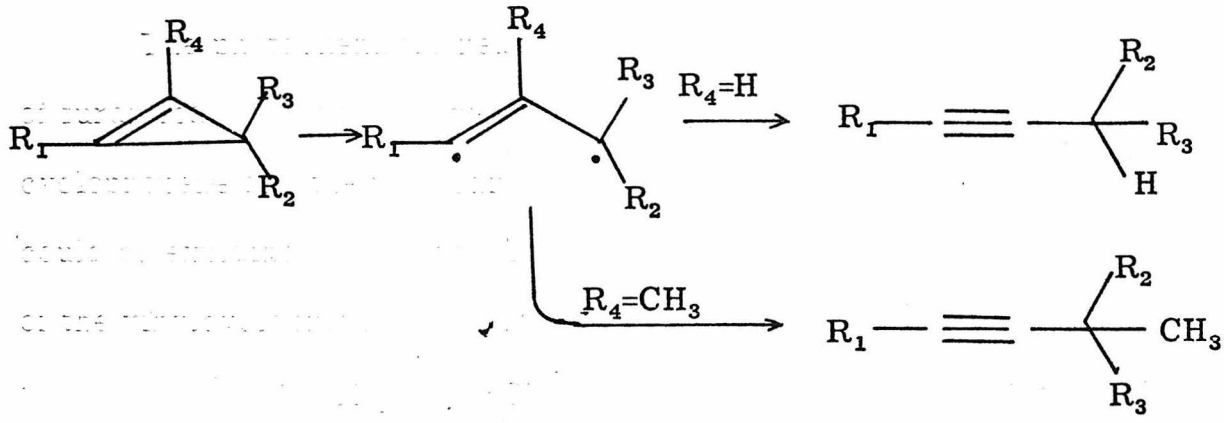
Table III: Kinetic Parameters for the Isomerization of Methyl Substituted Cyclopropenes [2, 43]

	log A	Activation energy	Products	
	12.13	35.2±1.30	$CH_3C{\equiv}CH$	
			$CH_2{=}CHCH{=}CH_2$	3.6-7.8%
 14	11.4	34.6±0.70	$CH_3C{\equiv}CCH_3$	89.6-94.2%
			$CH_2{=}C{=}CHCH_3$	1.8-3.1%
 6	13.0±0.4	36.6±0.85	$CH_2{=}CH{-}C(CH_3){=}CH_2$	10%
			$(CH_3)_2CHC{\equiv}CH$	90%
	13.4±0.6	39.0±1.35		71%
				21%
			5 minor products	7%
	12.5±0.8	39.97±2.0	 trans	85%
			 cis	5%
				10%

energy for the isomerization.[44]

In the cyclopropenes with carbon-carbon single bonds which are differentially substituted, the major products can be rationalized by breaking the most substituted bond.

Srinivasan explained these results by postulating a diradical intermediate in the formation of acetylenes, and a concerted mechanism for the formation of dienes. The sharp rise in the activation energy in going from 6 to tri- and tetra-methyl substituted cyclopropenes is explained by the shutting down of the diradical mechanism since an unfavorable 1, 2 methyl shift is necessary to give acetylenic products.



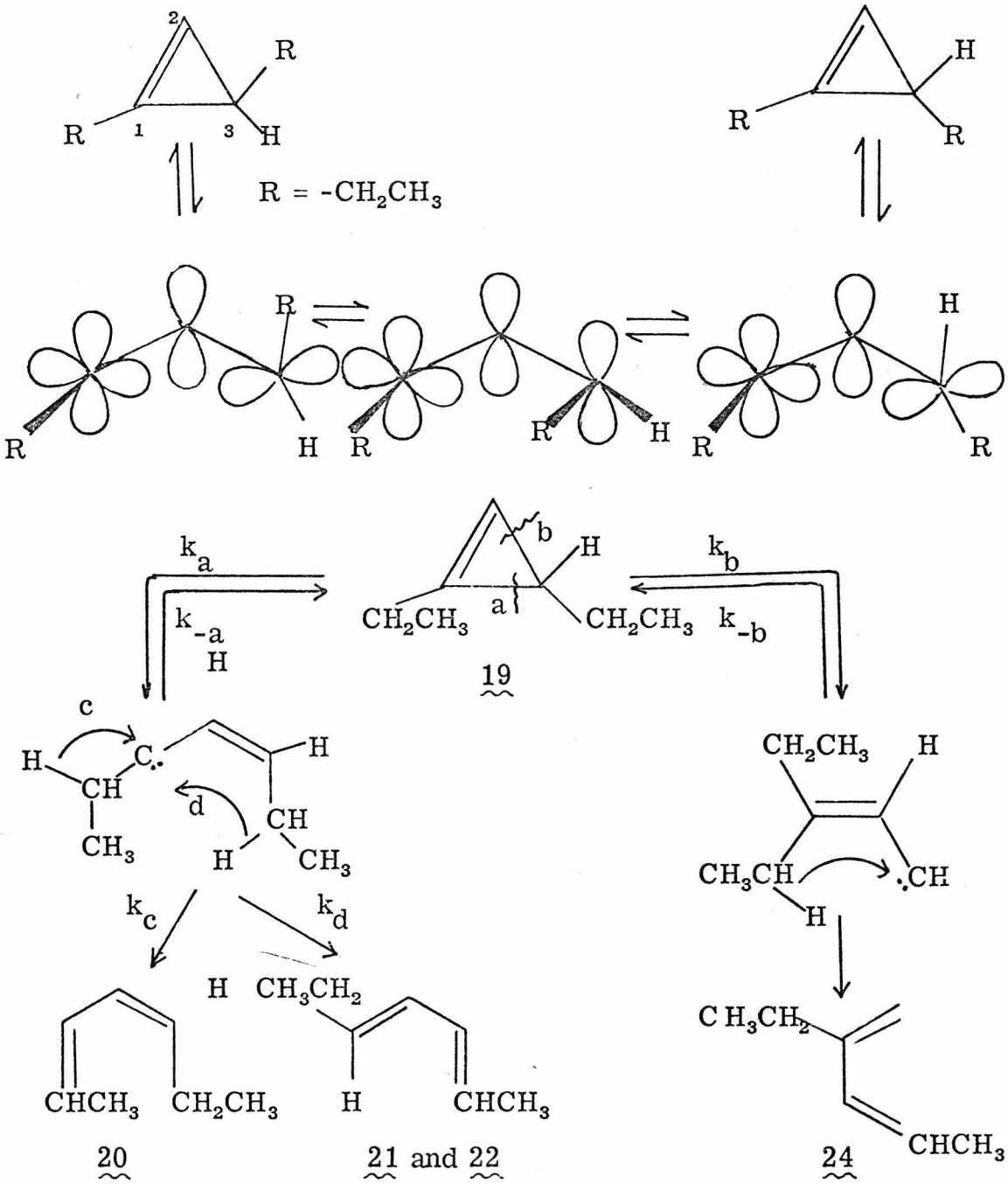
However, the most likely allowed concerted reaction which gives dienes predicts that tetramethylcyclopropene should isomerize to only cis 1, 2-dimethyl-1, 3-pentadiene (see Introduction). Since mostly the trans isomer is found, the concerted mechanism must be

of a most unusual type if this is the true reaction pathway leading to the 1,3 diene products (products were found to be stable under the reaction conditions).

It is interesting that 1,3,3-trimethylcyclopropene does not isomerize to any 4-methyl-2-butyne. Breaking the most substituted single bond gives a diradical intermediate which can give rise to this acetylene.

York, Bergman, Dittmar and Stevenson have synthesized an optically active cyclopropene, 1,3-diethylcyclopropene (19), and have studied the rates of racemization and isomerization of this compound over the temperature range of 160 to 191 °C.[45] The rate law for the racemization is log K = 11.8-32.6 kcal per mole/θ, while that for isomerization to acyclic products is log K = 10.4-32.2 kcal per mole/θ. The products derived from 19 are 33% 3-heptyne (23) and 67 % the isomeric 2,4-heptadienes (20, 21, 22) all of which could be rationalized as arising from breaking the most substituted carbon-carbon single bond of 19 (see Scheme VII). No 2-ethyl-1,3-pentadiene (24) was observed, the product expected from breaking the least substituted double bond.

The rate of racemization was 8-9 times that for isomerization to the acyclic products over the temperature range of the study. In order for racemization to occur, the cyclopropene 19 must pass

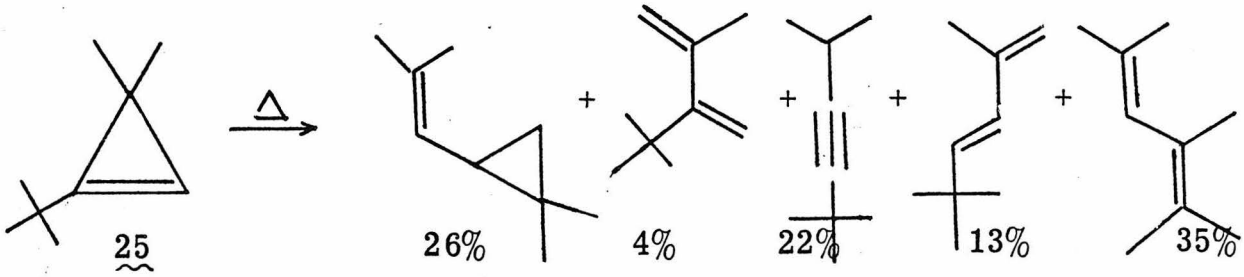


Scheme VII

through an intermediate which has a plane of symmetry. All states which have the conformation of 3a (the diradical) do not have the necessary plane of symmetry; only the vinylcarbene conformer (3b) does (see Scheme VII). The preference of the vinylcarbene generated in this study to close in preference to forming acyclic products is in keeping with the observed behavior of other vinylcarbenes.[8, 22]

The authors state that the racemization is probably not a concerted process involving an alkyl shift. They base this claim on the fact that neither 1- and 3-methylcyclopropene[2] (H shift process), nor 1,3- and 3,3-dimethylcyclopropene[43] (alkyl shift) are observed to interconvert thermally.

Streeper and Gardner have synthesized 1-t-butyl-3,3-dimethylcyclopropene (25) and have looked at the kinetics of the isomerization of 25 in benzene over the temperature range of 150 to 195°C.[68] 25 isomerized to the 5 products shown below with a rate law of log K = 9.0-29.8 kcal per mole/θ. 96% of the products can be rationalized by



breaking the most substituted single bond. In contrast to Srinivasan's study on 1,3,3-trimethylcyclopropene, an acetylene was found to be a major product from 25. Most of the products could only have been formed via a carbene.

RESULTS

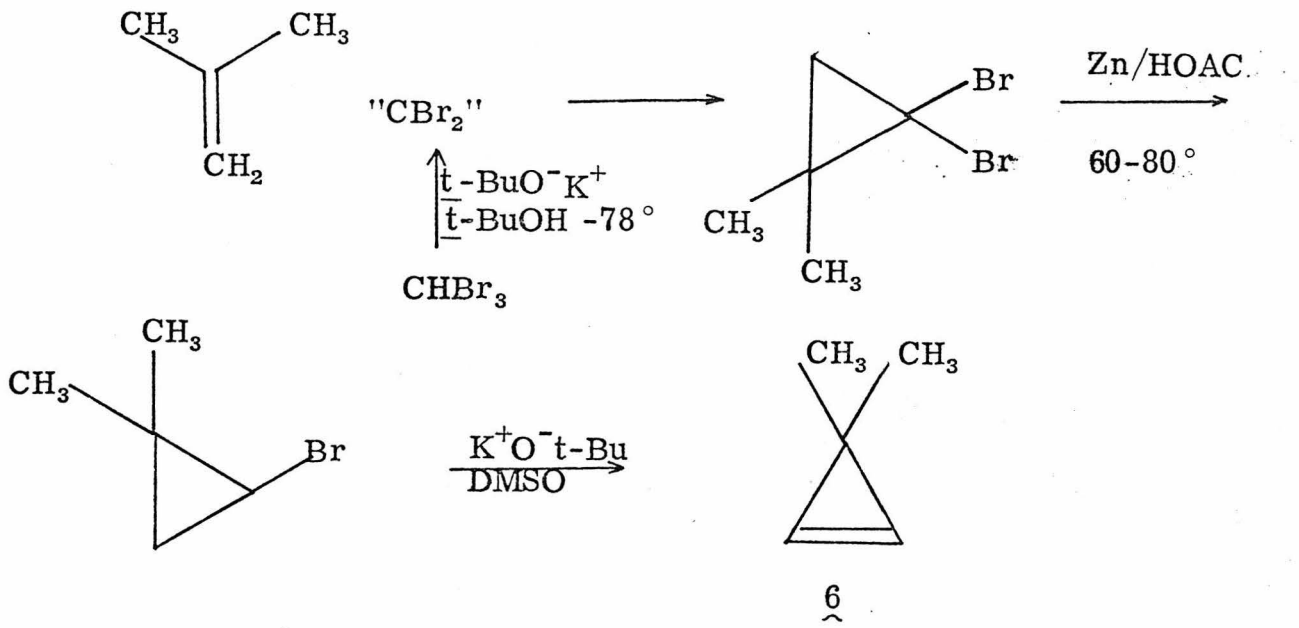
Synthesis of 3,3-Dimethylcyclopropene (6)

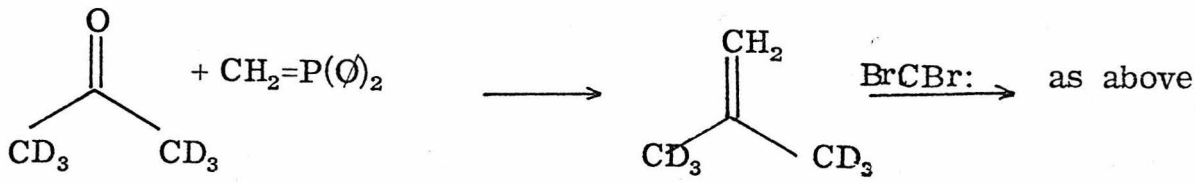
6 was prepared in the straightforward manner depicted in Scheme VIII. This method of preparation of cyclopropenes was developed by Dr. J. R. Stevenson in these laboratories, and details are presented in the Experimental section of Part III of this thesis. Also, described in the experimental section is the preparation of 3,3-di(trideuteromethyl)cyclopropene and the deuteration of the vinyl sites of 6 by a base catalyzed exchange developed by Dr. T. H. Morton[13] (see Scheme VIII).

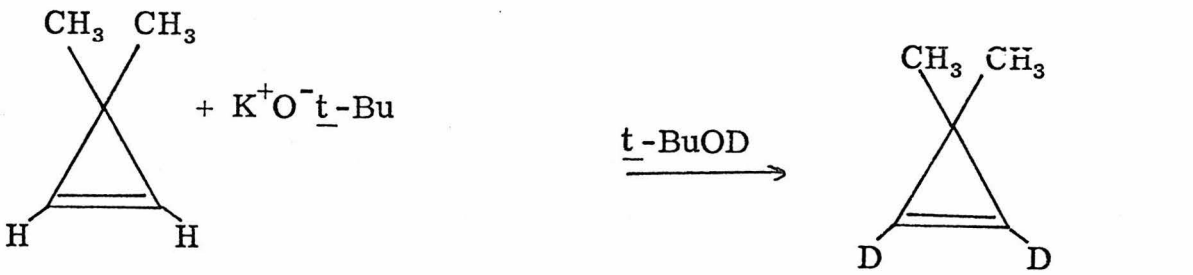
6 synthesized in this manner was found to be 99.4% pure. The impurities were 0.5% 1,1 dimethylcyclo propane, 0.1% isoprene (10) and 0.06% isopropylacetylene (9). 6 was used without further purification in the kinetic studies.

Kinetic Study of the Gas-Phase Isomerization of 6 in the Wall-less Reactor

The isomerization of 6 was studied in the wall-less reactor (see Part II of this thesis) over a temperature of 608 to 668°K. The rate law for the isomerization was found to be log K = 12.6-36.2 kcal per mole/θ based on 9 runs (see Figures 2 to 11). 6 isomerized to


CH3
CH3
CH2
"CBr2"
t-BuO⁻K⁺
t-BuOH -78°
CHBr3
Br
Br
CH3
CH3
Zn/HOAC
60-80°
CH3
CH3
Br
K⁺O⁻t-Bu
DMSO
CH3
CH3
6


O
+ CH2=P(Ø)2
CD3
CD3
CH2
CD3
CD3
BrCBr:
as above


CH3
CH3
+ K⁺O⁻t-Bu
H
H
t-BuOD
CH3
CH3
D
D

Scheme VIII

86.2% 9, 12.9% 10 and 0.9% gem-dimethylallene (11) (see Table VIII). The products and reactants were analyzed on a 22 ft by 1/8 in column packed with $\beta\beta'$-ODPN as the liquid phase. Ratio of products did not vary significantly over the temperature range used in this study. Residence time of the hydrocarbons in the reactor was 0.35 seconds.

Table VIII: Product Distribution from 3,3-Dimethylcyclopropene (6)

Temperature °C	Products %			Ref.
	9	10	11	
374	.9	12.9	86.2	This work
373	.8	12.9	86.3	This work
372	.9	12.9	86.2	This work
386	.9	12.9	86.3	This work
362	.8	12.6	86.6	This work

Preparation and Purification of 3-n-butyldiazirine [46-48]

3-n-butyldiazirine was prepared by the general method of Schmitz [46] as modified by Frey [47, 48] for the synthesis of diazirines from aldehydes (see Scheme IX). Details and spectral data on this new compound are found in the Experimental section of this thesis.

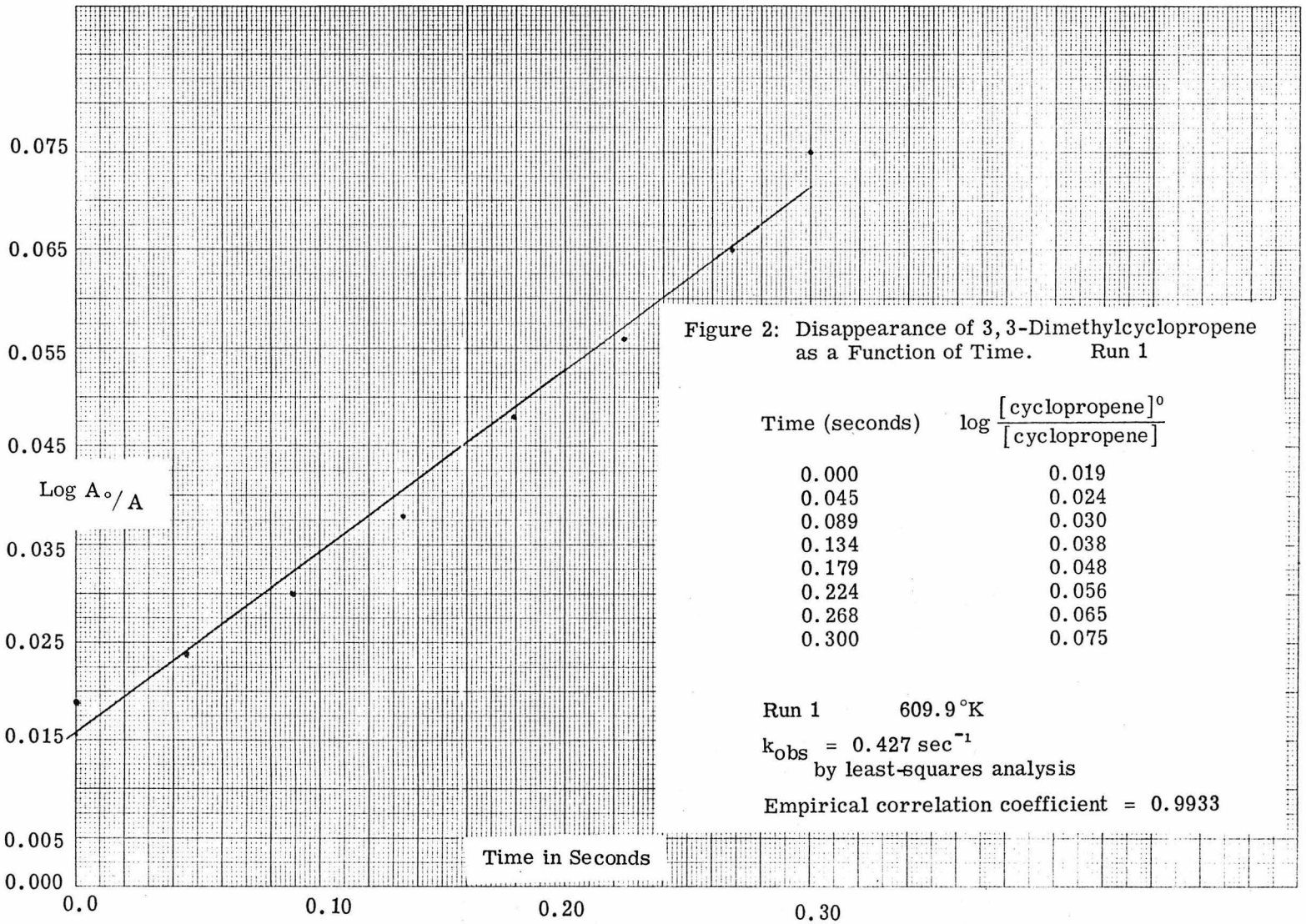


Figure 2: Disappearance of 3,3-Dimethylcyclopropene as a Function of Time. Run 1

Time (seconds)	$\log \frac{[\text{cyclopropene}]^0}{[\text{cyclopropene}]}$
0.000	0.019
0.045	0.024
0.089	0.030
0.134	0.038
0.179	0.048
0.224	0.056
0.268	0.065
0.300	0.075

Run 1 609.9 °K

$k_{obs} = 0.427\ sec^{-1}$ by least-squares analysis

Empirical correlation coefficient = 0.9933

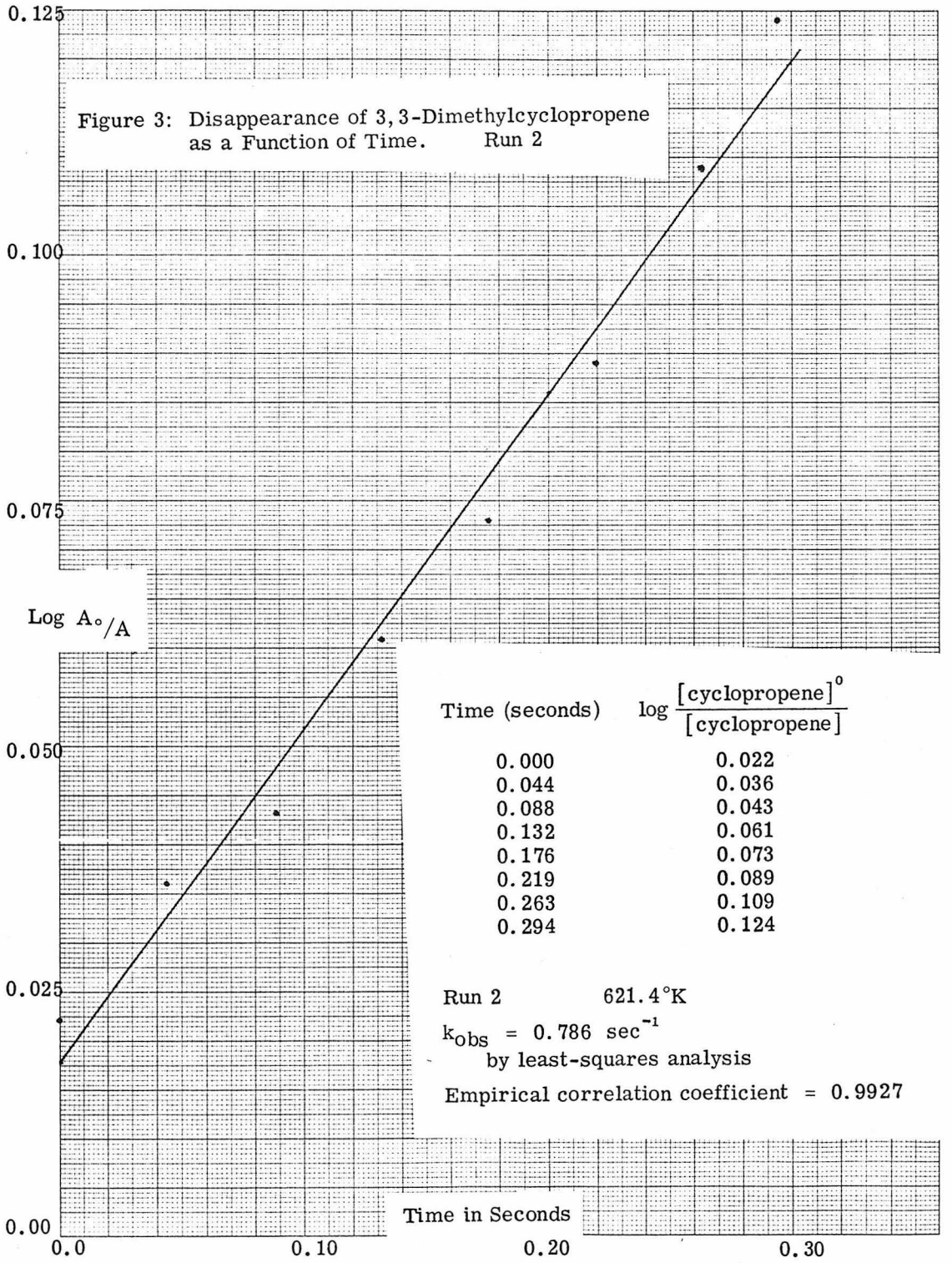


Figure 3: Disappearance of 3,3-Dimethylcyclopropene as a Function of Time. Run 2

Time (seconds)	$\log \frac{[\text{cyclopropene}]^{\circ}}{[\text{cyclopropene}]}$
0.000	0.022
0.044	0.036
0.088	0.043
0.132	0.061
0.176	0.073
0.219	0.089
0.263	0.109
0.294	0.124

Run 2 621.4°K

k_{obs} = 0.786 sec^{-1}
by least-squares analysis

Empirical correlation coefficient = 0.9927

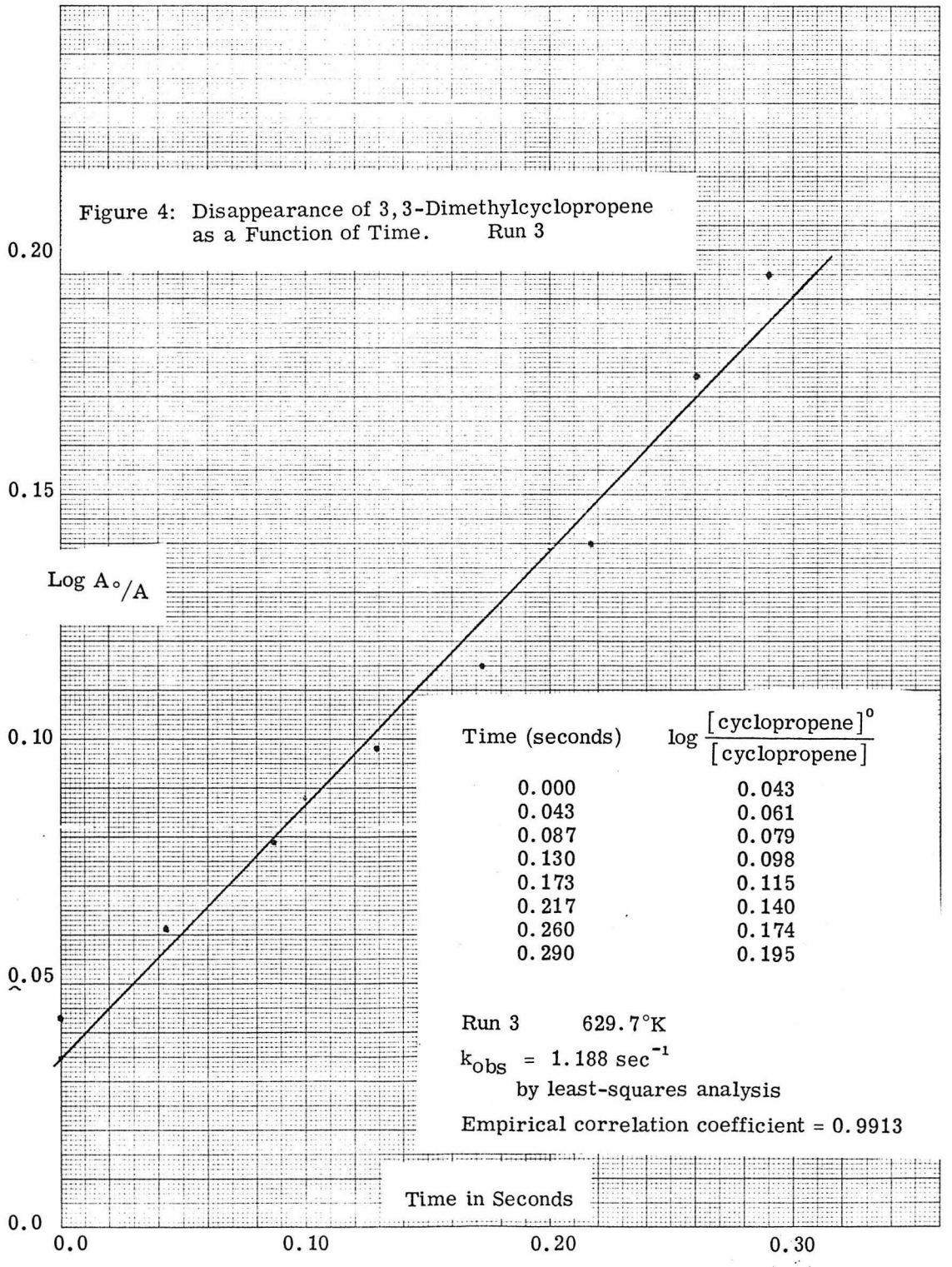


Figure 4: Disappearance of 3,3-Dimethylcyclopropene as a Function of Time. Run 3
0.20
0.15
Log A∘/A
0.10
0.05
0.0
0.0
0.10
0.20
0.30
Time in Seconds
Time (seconds)
log [cyclopropene]∘ / [cyclopropene]
0.000 0.043
0.043 0.061
0.087 0.079
0.130 0.098
0.173 0.115
0.217 0.140
0.260 0.174
0.290 0.195
Run 3 629.7°K
k_{obs} = 1.188 sec^{-1}
by least-squares analysis
Empirical correlation coefficient = 0.9913

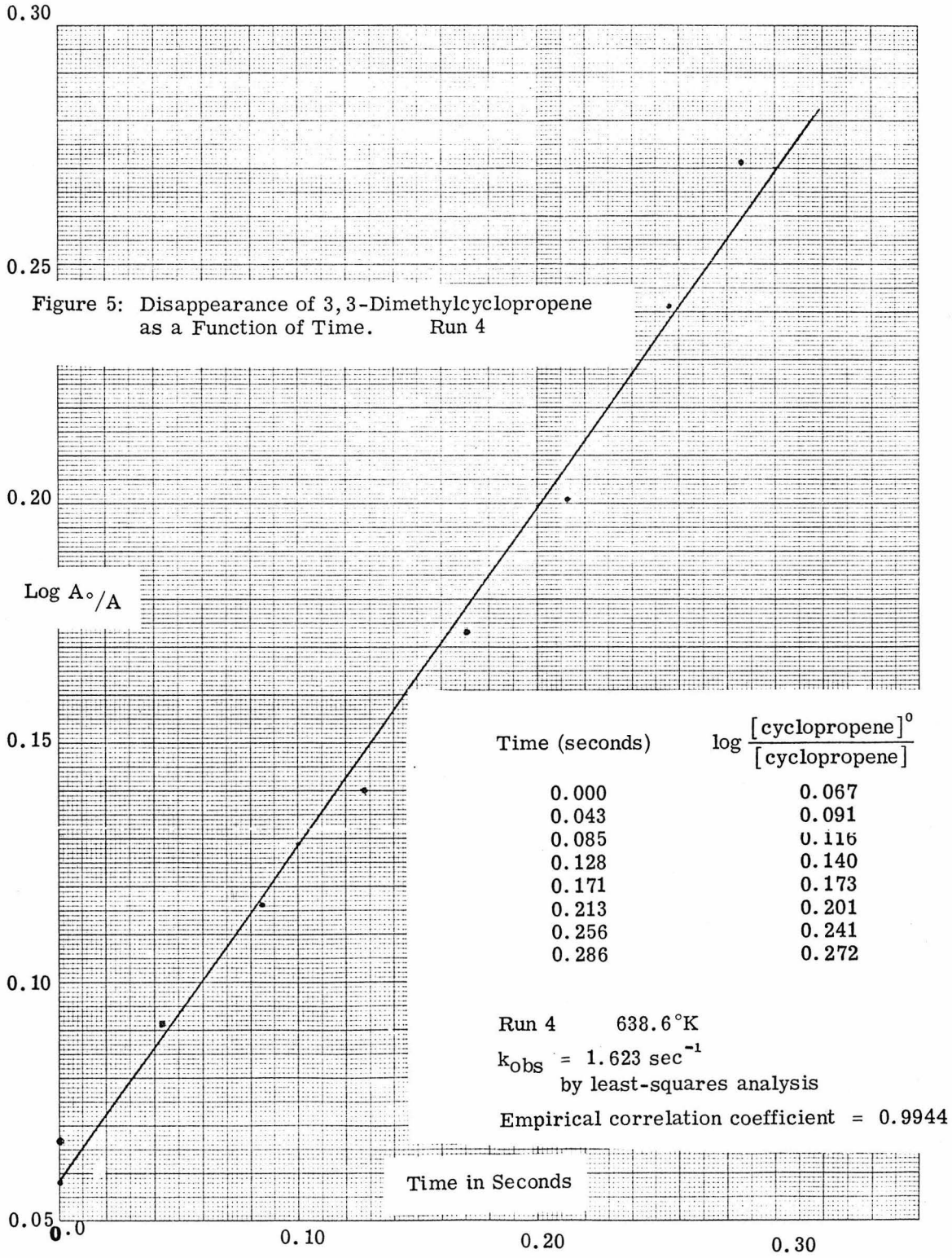


Figure 5: Disappearance of 3,3-Dimethylcyclopropene as a Function of Time. Run 4

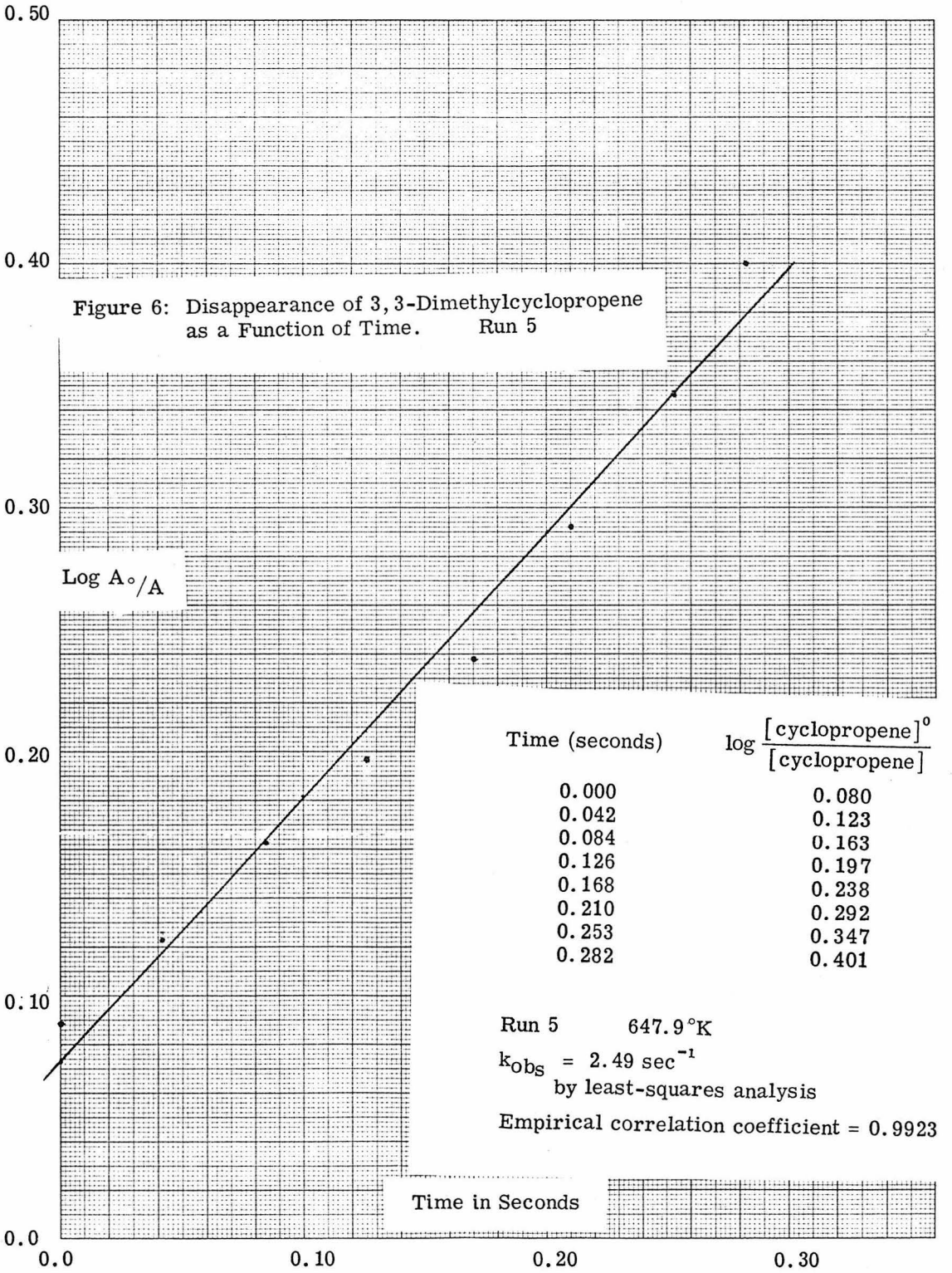


Figure 6: Disappearance of 3,3-Dimethylcyclopropene as a Function of Time. Run 5

Time (seconds)	$\log \frac{[\text{cyclopropene}]^{\circ}}{[\text{cyclopropene}]}$
0.000	0.080
0.042	0.123
0.084	0.163
0.126	0.197
0.168	0.238
0.210	0.292
0.253	0.347
0.282	0.401

Run 5 647.9°K

k_{obs} = 2.49 sec^{-1}
by least-squares analysis

Empirical correlation coefficient = 0.9923

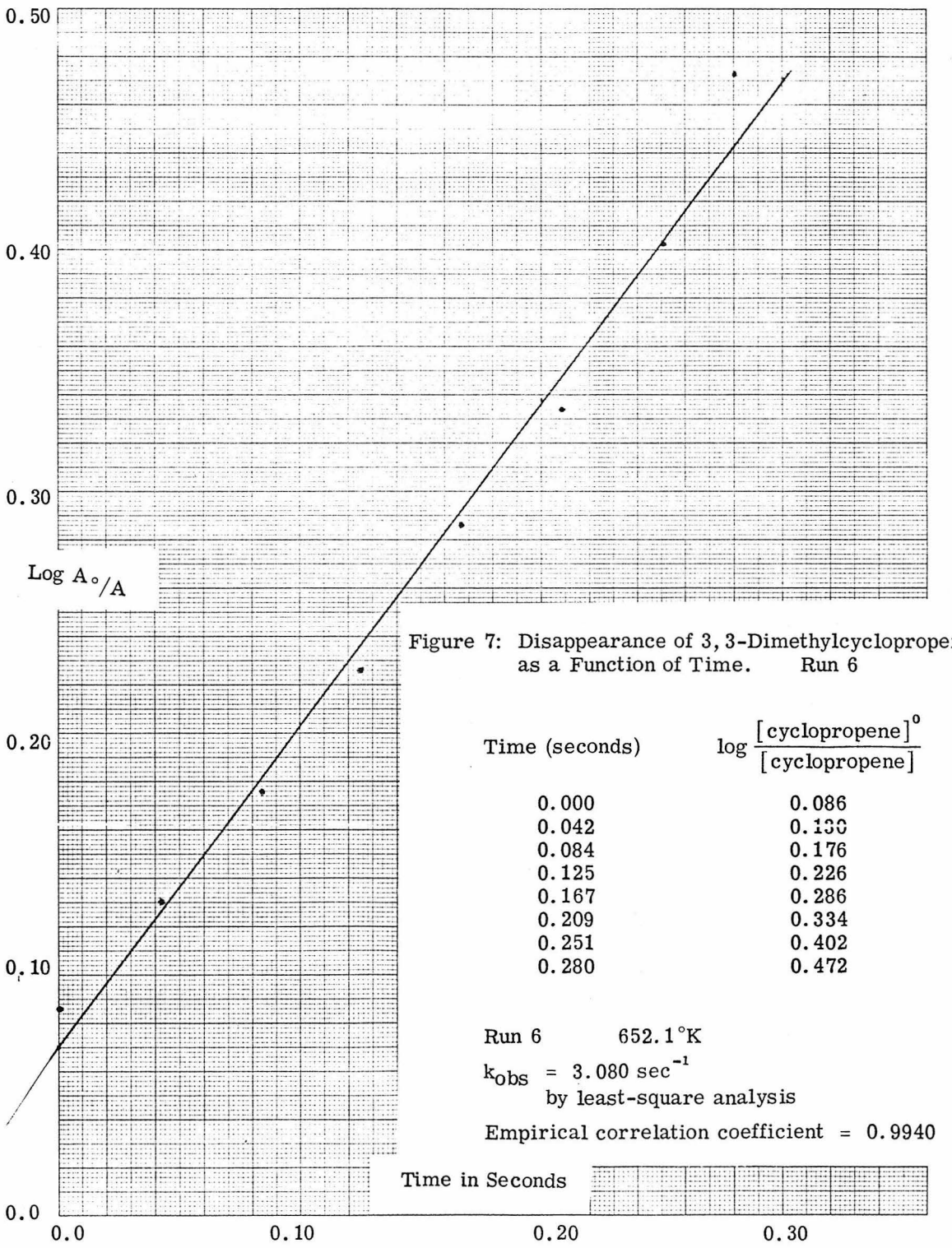


Figure 7: Disappearance of 3, 3-Dimethylcyclopropene as a Function of Time. Run 6

Time (seconds)	$\log \frac{[\text{cyclopropene}]^{\circ}}{[\text{cyclopropene}]}$
0.000	0.086
0.042	0.130
0.084	0.176
0.125	0.226
0.167	0.286
0.209	0.334
0.251	0.402
0.280	0.472

Run 6 652.1°K

k_{obs} = 3.080 sec^{-1}
by least-square analysis

Empirical correlation coefficient = 0.9940

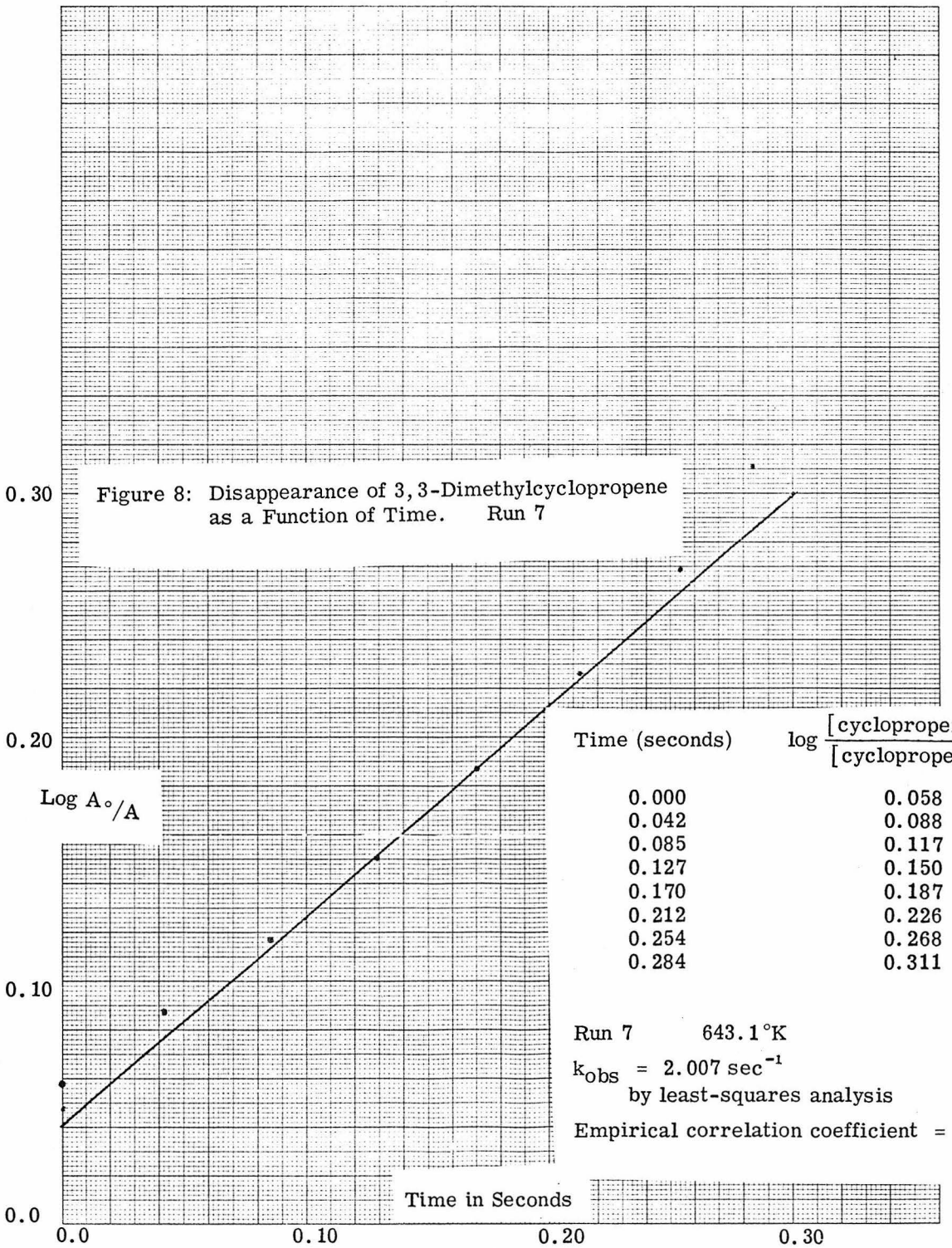


Figure 8: Disappearance of 3,3-Dimethylcyclopropene as a Function of Time. Run 7

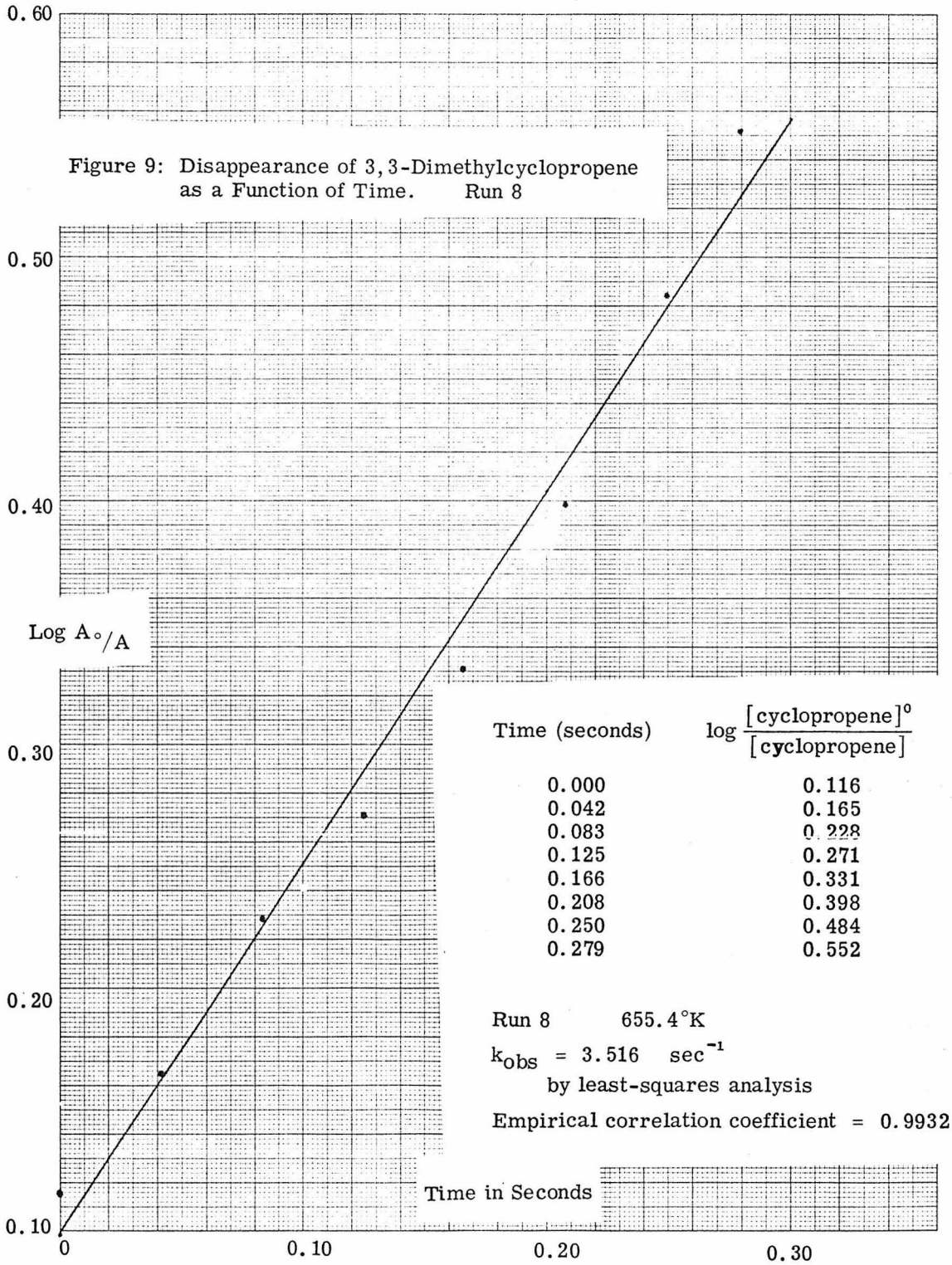
Time (seconds)	$\log \frac{[\text{cyclopropene}]^0}{[\text{cyclopropene}]}$
0.000	0.058
0.042	0.088
0.085	0.117
0.127	0.150
0.170	0.187
0.212	0.226
0.254	0.268
0.284	0.311

Run 7 643.1°K

$k_{obs} = 2.007\ sec^{-1}$
by least-squares analysis

Empirical correlation coefficient = 0.9949

Figure 9: Disappearance of 3,3-Dimethylcyclopropene as a Function of Time. Run 8



Time (seconds)	$\log \frac{[\text{cyclopropene}]^0}{[\text{cyclopropene}]}$
0.000	0.116
0.042	0.165
0.083	0.228
0.125	0.271
0.166	0.331
0.208	0.398
0.250	0.484
0.279	0.552

Run 8 655.4°K

k_{obs} = 3.516 sec^{-1}

by least-squares analysis

Empirical correlation coefficient = 0.9932

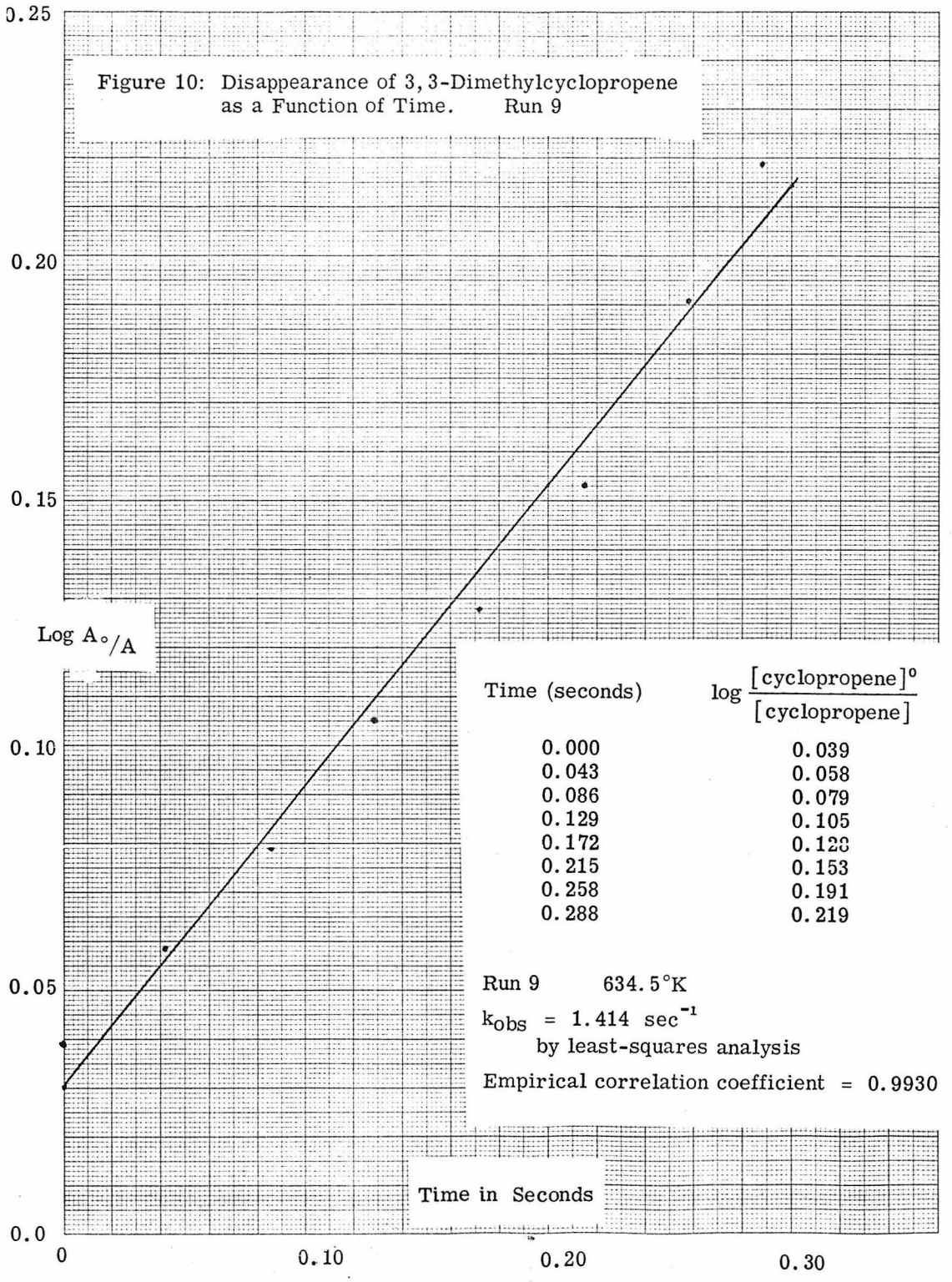


Figure 10: Disappearance of 3,3-Dimethylcyclopropene as a Function of Time. Run 9

Time (seconds)	$\log \frac{[\text{cyclopropene}]^{\circ}}{[\text{cyclopropene}]}$
0.000	0.039
0.043	0.058
0.086	0.079
0.129	0.105
0.172	0.128
0.215	0.153
0.258	0.191
0.288	0.219

Run 9 634.5°K

k_{obs} = 1.414 sec^{-1}

by least-squares analysis

Empirical correlation coefficient = 0.9930

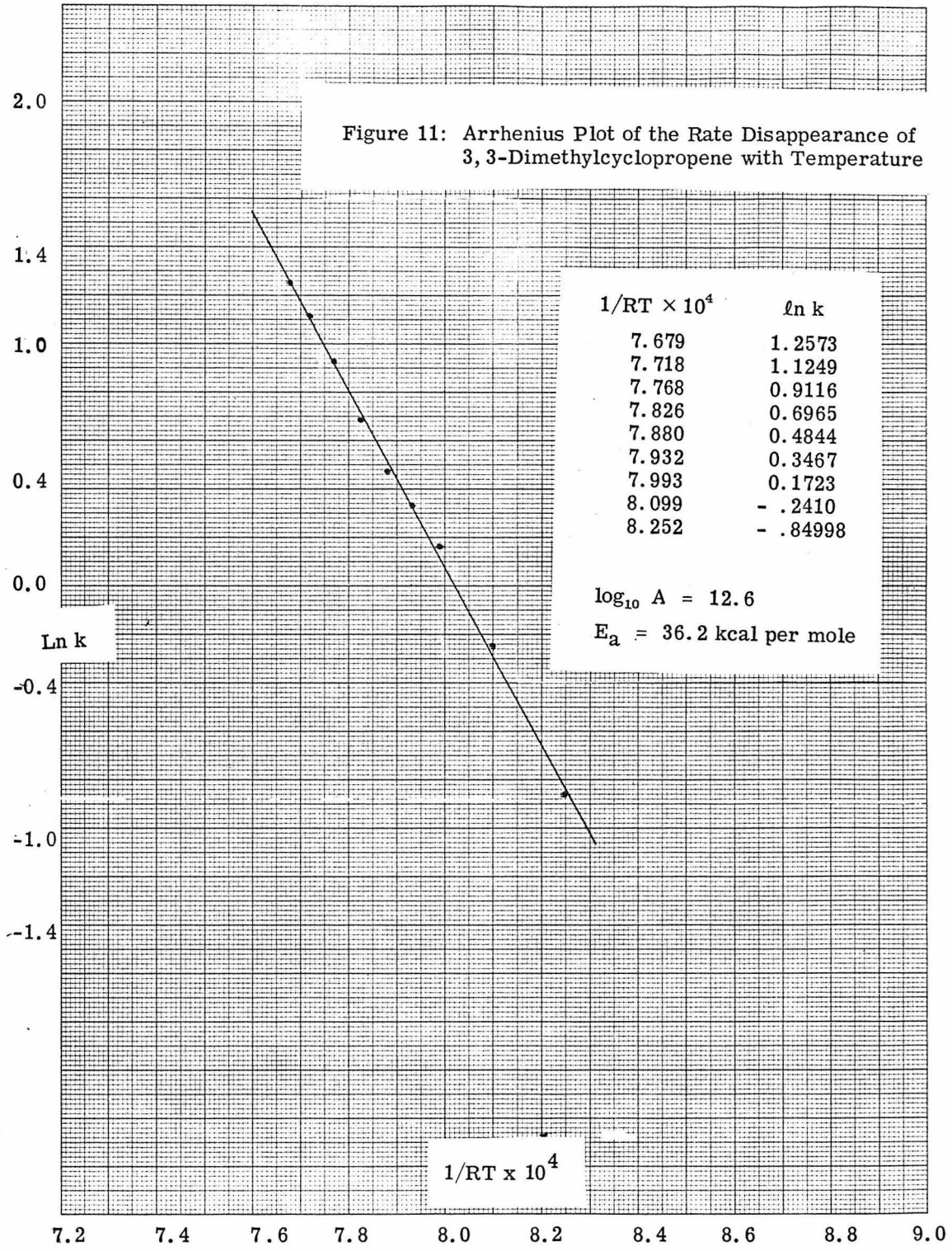
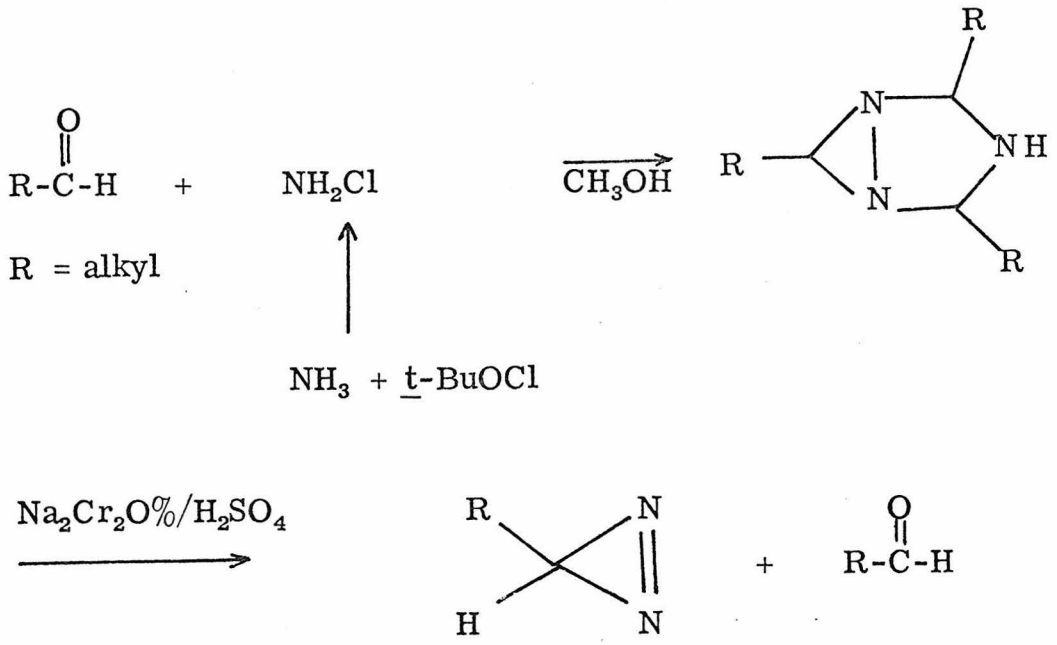


Figure 11: Arrhenius Plot of the Rate Disappearance of 3, 3-Dimethylcyclopropene with Temperature

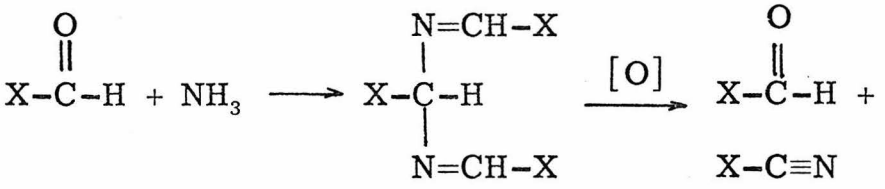


Scheme IX

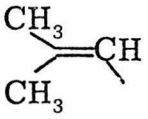
Oxidation of the fused diaziridine, formed from the aldehyde and chloroamine,[47, 48] to the diazirine was carried out with a solution of sodium dichromate in 2 N H_2SO_4. The diazirine was freed from the aldehyde by bubbling through[9] saturated sodium hydrogen sulphite solution followed by drying over potassium hydroxide pellets. The diazirine formed in this manner was found to be greater than 99% pure by VPC analysis.

Attempted Synthesis of 3-Isobutenyldiazirine

The synthesis of 3-isobutenyldiazirine was attempted using the method described for the synthesis of diazirines from aldehydes. The method failed. An imine of unknown structure formed from the reaction of senecialdehyde and ammonia. Oxidation of the imine with a solution of sodium dichromate in 2 N H_2SO_4 yielded β,β-dimethylacrolein and starting aldehyde as the only products. The proposed reaction scheme shown below is based on analogous behavior of aromatic aldehydes.[49]



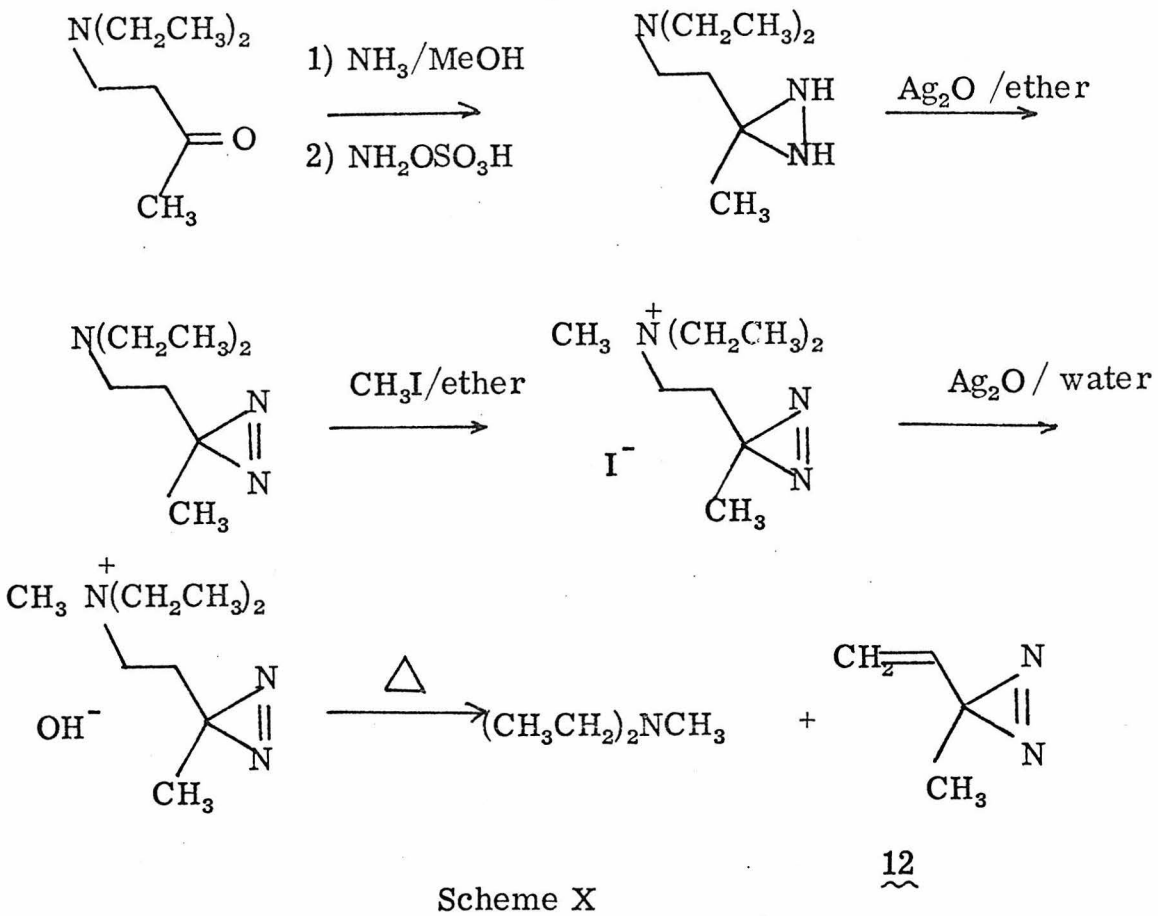
X = Aryl[49]

X = 

X = R_2CH or R_3C[50]

Preparation and Purification of 3-Vinyl-3-methyldiazirine (12)

12 was synthesized by the method of Schmitz as depicted in the scheme below.[14a] Details of the procedures and spectral data are found in the experimental section.



12

Scheme X

The Hoffmann elimination was carried out by dropwise addition of an aqueous solution of the quaternary ammonium salt to a flask heated to 105°C. The volatiles were swept out of the reaction flask and condensed into cooled traps. The contents of the traps were washed with 1 N HCl. The organic phase was separated and was found to be almost completely 12 free of diethylmethylamine. Samples of 12 for pyrolysis were purified by preparatory VPC on a 22 ft by 3/8 in glass column packed with 20% by weight Carbowax 1500 on Chrom

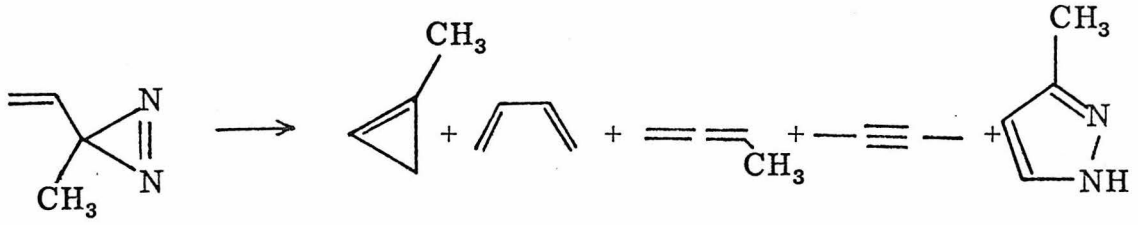
WAW, 60-80 mesh. The column was maintained at 25°; the injector port and collector were kept at 50° and 55°, respectively. The low temperatures and the glass column were used to prevent the isomerization of 12 to 3-methylpyrazole. This isomerization without loss of nitrogen is very facile in the liquid phase.[14] Samples of 12 were diluted with spectral quality benzene and stored at -40°.

Pyrolysis of 3-Vinyl-3-methyldiazirine (12) and Identification of Products

The thermal gas-phase reaction of 12 was studied in three flow systems: (1) 20% solutions of 12 in benzene were injected through a rubber septum into the heated, quartz lined injector port of a Hewlett-Packard vapor phase chromatograph (Model 5750) and the pyrolysate was VPC analyzed immediately afterwards; (2) 20% solution of 12 in benzene were volatilized by a stream of He gas and directed through a heated quartz tube. The pyrolysate was condensed in traps cooled in liquid nitrogen; (3) this system was similar to the second except the quartz tubing was replaced by teflon tubing. Packing of the teflon tube with teflon helices permitted a study of the dependence of the product distribution from the decomposition of 12 on the surface to volume ratio. Isooctane was used as an internal standard when analysis was by VPC; the residual hydrogens in commercial benzene-D_6 were used

as an internal standard when the reaction mixture was analyzed by NMR.

C_4H_6 products were identified by comparing their retention times on a VPC column with those of authentic samples. Only 1-methylcyclopropene was produced in sufficient quantity to be identified in the reaction mixture by NMR.

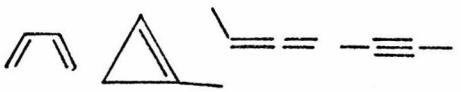
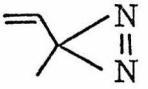


12 14 16 17 18 13

Results of the thermal reaction of 12 in a heated teflon tube, a heated quartz tube and a quartz lined injector port of a gas chromatograph are given in Tables IV, V and VI, respectively.

The pyrolysis of 12 in an unpacked teflon tube gave a fairly constant ratio of the three acyclic C_4H_6 products to one another over the temperature range of 89 °C to 230 °C (see Table IVa). The ratio of 1-methylcyclopropene to 1, 3-butadiene (16) reached a maximum between 122-143 °C. Isomerization of 1-methylcyclopropene did not become an important factor until temperatures in excess of 250 °C were used (see Table VII, Runs 1-3). The percentage of 12 going to C_4H_6 products steadily increased with increasing temperature.

Table IVa: Pyrolysis of 12 in a Heated Teflon Tube [a, b]

Temp. °C	Ratio of products [c] 			% unreacted  12	% of 12 going to C_4H_6 [d]
89	1	45.2	0.13	0.48		
103	1	156	0.17	0.56		
111	1	210	0.20	0.67		
116	1	301	0.14	0.67	4.2	10.4
122	1	379	0.18	0.65		
143	1	368	0.19	0.75		12.5
164	1	194	0.17	0.67		
198	1	199	0.19	0.57		13.4
230	1	76	0.10	0.50		
266	1	55	0.14	2.4		16.6
268	1	47	0.10	2.2		

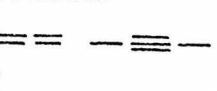
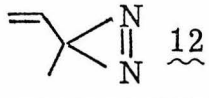
[a] Flow system, atmospheric pressure, contact time = 14-18 sec.

[b] Surface to volume ratio of 4.5:1.

[c] Ratio determined by combination of digital integrator printout of Hewlett-Packard VPC Model 5750 and triangulation of peaks on recorder presentation.

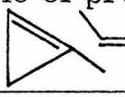
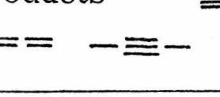
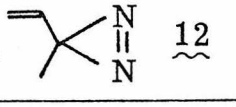
[d] Internal standard was isooctane.

Table IVb: Pyrolysis of 12 in a Heated Teflon Tube [9] Packed with Teflon Helices [b]

Temp. °C	Ratio of products [c]				% unreacted [d]	% of 12 going
				 12		to C_4H_6 [d]
122	1	186	.09	.50	31	11
204	1	87	.08	.26	–	15
264	1	13	.03	.44	–	11

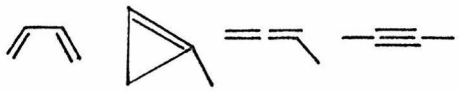
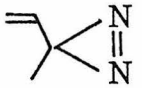
[a] Flow system, atmospheric pressure, contact time = 8-10 sec. [b] Surface to volume ratio of 24.6:1. [c] Ratio determined by combination of digital integrator printout of Hewlett-Packard VPC Model 5750 and triangulation of peaks on recorder presentation. [d] Internal standard was isooctane.

Table V: Pyrolysis of 12 in a Heated Quartz Tube [a, b]

Temp. °C	Ratio of products [c]				% unreacted [d]	% of 12 going
				 12		to C_4H_6 [d]
89	1	36	.13	.55		
112					17	16
123					4.1	21

[a] Flow system, atmospheric pressure, contact time = 14-18 sec. [b] Surface to volume ratio of 4.5:1. [c] Ratio determined by combination of digital integrator printout and triangulation of peaks. [d] Internal standard was residual hydrogens in benzene-D_6. Analysis by NMR.

Table VI: Pyrolysis of 12 in a Heated Quartz Lined Injector Port[a] of a Vapor Phase Chromatograph[b]

Temp. °C	Ratio of products[c] 				% unreacted  12	% of 12 going to C_4H_6[d]
146	1	86	.27	.42	9.6	4.6
170	1	41	.38	.45	1.3	2.7
192	1	32	.30	.50	–	2.1
202	1	34	.30	.39	–	1.8
210	1	51	.22	.47	–	3.7
250	1	30	.29	.81	–	4.0
295	1	17	.29	3.2	–	8.1

[a] Total residence time was 0.05 to 0.03 sec. Surface to volume ratio was 1 cm^2: .006 cm^3. Helium carrier gas.

[b] Hewlett-Packard Model 5750 equipped with electronic digital integrator.

[c] Ratio determined by combination of digital integrator print-out and triangulation of recorder presentation.

[d] Internal standard was isooctane.

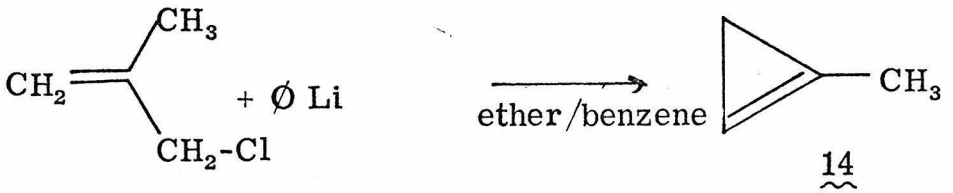
Pyrolysis of 12 in a packed teflon tube gave slightly different results than those obtained in the unpacked tube (see Table IVb). The ratio of 1-methylcyclopropene to 1,3-butadiene (16) declined at a faster rate. The percentage of 12 going to C_4H_6 products started to decrease after 204°C.

Pyrolysis of 12 in a heated quartz tube gave a C_4H_6 product distribution very similar to that obtained with the teflon tube (see Table V). The percentage of 12 going to C_4H_6 products was slightly higher.

Pyrolysis of 12 in a heated quartz lined injector port gave very low conversions of 12 to C_4H_6 products, possibly because of the high surface to volume ratio.

Synthesis and Study of the Pyrolysis of 1-Methylcyclopropene (14)

1-Methylcyclopropene was synthesized by the method of Magid and co-workers,[18] except commercial phenyllithium was used.



14

The solution of 14 was concentrated by a trap to trap distillation. The final solution of 20% 14 in ether was used as is in all thermal isomerization studies shown in Table VII except one. This solution contained <1% of acyclic impurities 16-18.

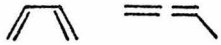
The solution of 14 used in run No. 4 of Table VII was generated by the pyrolysis of a 20% solution of 12 in benzene by passage through a teflon tube heated to 142°C. The small amounts of acyclic products from 12 (<1%) were corrected for in determining the product distribution in the second pyrolysis.

Products were identified previously (see above). All products were stable under the reaction conditions.

The major acyclic product from 14, in contrast to the vinylcarbene results, is 2-butyne (18). This is in agreement with the results of Srinivasan's study of the isomerization of 14[2] (see Table III).

The ratio of products seems somewhat erratic. A surface dependence on the isomerization of 14 has been reported. The systems used in our study of 14 were not conditioned in any special way. In the following calculations of the rate constants, Srinivasan's product distribution was used (see Table III).

Table VII: Pyrolysis of 1-Methylcyclopropene (14) in Three Pyrolysis Systems

Run Number	Temperature conditions	Products, %[e] 	% unreacted[d] 14
1	190, a	– – –	99.9
2	249, a	14.4 – 85.6	98.7
3	335, a	9.0 2.1 88.9	6.2
4	267, b	28.7 1.2 70.1	26.2
5	250, c	17.8 12.2 69.9	14.2
6	310, c	22.9 2.8 74.3	11.0
7	360, c	17.1 6.3 76.6	1.6

[a] Flow system, atmospheric pressure, contact time = 14-18 sec. Quartz tube, surface to volume ratio of 4.5:1.

[b] Flow system, atmospheric pressure, contact time 35 sec. Teflon tube, surface to volume ratio of 4.5:1.

[c] Flow system, contact time 0.05 to 0.03 seconds. Quartz lined injector port of Hewlett-Packard VPC Model 5750, surface to volume ratio of 166:1.

[d] Ether was internal standard.

[e] Determined by combination of digital integrator printout and triangulation of peaks on recorder presentation.

DISCUSSION

Surface Dependence on the Kinetics of the Isomerization of 3,3-Dimethylcyclopropene (6)

Pyrolysis of 6 under completely homogeneous conditions at high temperatures yielded results which agreed closely with those obtained under more conventional conditions. It appears that Srinivasan's data on 3,3-di-, tri- and tetra-alkyl substituted cyclopropenes are reliable.[43] In contrast, the kinetics of the isomerization of minimally substituted cyclopropenes has been found to have a surface dependence by several investigators.[2,45] Judging from the low A values and activation energies as well as wide variations in the product distributions further investigation appears to be warranted in these systems.

Mechanism of Cyclopropene Isomerization

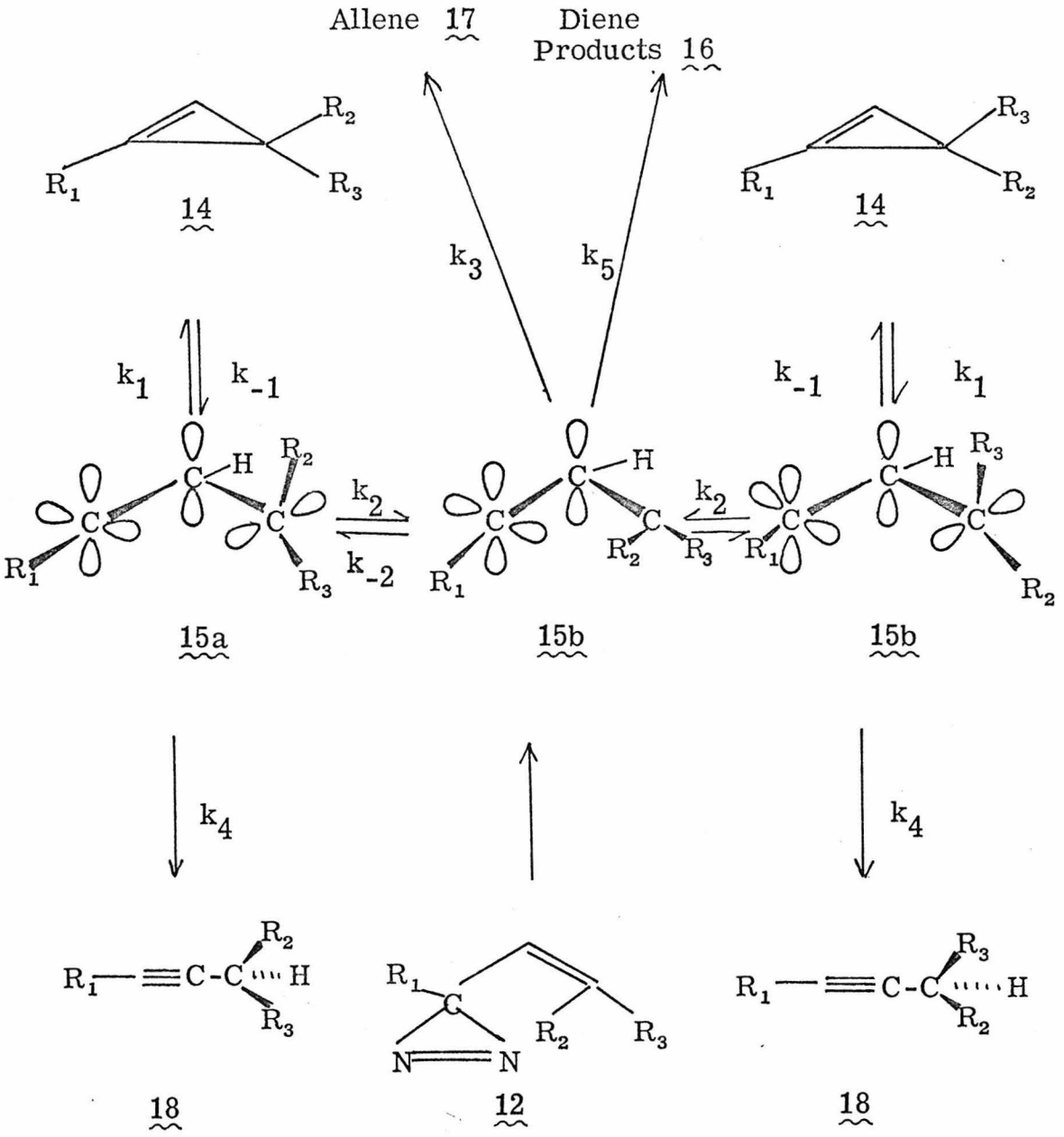
It is quite clear that the product distribution (but not the products) from 1-methylcyclopropene (14) is different from that of the vinylcarbene (15) expected from 3-vinyl-3-methyldiazirine (12). This result is similar to that observed by Morton in his study of the thermal isomerization of 3,3-dimethylcyclopropene (6) and the corresponding vinylcarbene precursor, 3-methyl-1-diazo-2-butene.[13] This seems to

indicate that the reaction pathways of cyclopropenes and their corresponding vinylcarbenes cross. The nature of this crossing will be discussed and a free energy surface will be calculated in the remainder of this section.

It is possible that due to fortuitous circumstances the reaction pathways of 12 and 14 do not cross. For example, 14 may be isomerizing through a series of concerted mechanisms (evidence from other studies of cyclopropenes tends to rule out this alternative mechanism[2,43]). However, it seems rather unlikely that both 14 and 12 should react to give the same acyclic products unless their reaction pathways cross.

From the data, all mechanisms in which the three products, 1,3-butadiene, 1,2-butadiene and 2-butyne, come from intermediates arising after the joining of the reaction pathways of 12 and 14, can be eliminated. These mechanisms predict identical product distributions.

The most economical mechanism which fits the data is the one shown in Scheme XI. This mechanism involves two intermediates, the diradical (15a) which has the conformation of 3a and a vinylcarbene (15b) which has the conformation of 3b. The secondary intermediate from 14 is the primary intermediate from the decomposition of 12. The acetylene is formed from the diradical 15a; the dienes from the vinylcarbene 15b.


Allene 17
Diene Products 16
14
14
k3
k5
k1
k-1
k-1
k1
k2
k-2
k2
15a
15b
15b
k4
k4
18
12
18

Scheme XI

The kinetic scheme can be generalized for all cyclopropene thermal rearrangements. The values for the individual rate constants in the scheme can be calculated from the experimental data derived from the studies of a cyclopropene isomerization and the decomposition of the precursor to the corresponding vinylcarbene.

The following is an analysis based on Scheme XI for the isomerization of 1-methylcyclopropene.

The following kinetic expressions may be written, based upon a steady state approximation for each intermediate:

$$\frac{d[\underset{\sim}{15a}]}{dt} = k_1[\underset{\sim}{14}] + k_{-2}[\underset{\sim}{15b}] - (k_{-1} + k_2 + k_4)[\underset{\sim}{15a}] = 0 \qquad (1)$$

and

$$\frac{d[\underset{\sim}{15b}]}{dt} = k_2[\underset{\sim}{15a}] - (k_3 + k_5 + k_{-2})[\underset{\sim}{15b}] = 0 \qquad (2)$$

Therefore

$$[15b] = \frac{k_2}{k_3 + k_5 + k_{-2}}[\underset{\sim}{15a}] \qquad (3)$$

$$[\underset{\sim}{15a}] = \frac{k_1[\underset{\sim}{14}] + k_{-2}[\underset{\sim}{15b}]}{k_{-1} + k_2 + k_4} \qquad (4)$$

Substituting for $[\underset{\sim}{15b}]$ in last expression

$$[\underset{\sim}{15a}] = \frac{k_1[\underset{\sim}{14}]}{k_{-1} + k_2 + k_4 - \frac{k_{-2}k_2}{k_3 + k_5 + k_{-2}}} \tag{5}$$

Now

$$\frac{d[\underset{\sim}{17}]}{dt} = k_3[\underset{\sim}{15b}] \qquad \frac{d[\underset{\sim}{18}]}{dt} = k_5[\underset{\sim}{15a}] \tag{6}$$

$$\frac{d[\underset{\sim}{16}]}{dt} = k_4[\underset{\sim}{15b}] \tag{7}$$

Then in the thermal rearrangement of $\underset{\sim}{14}$

$$\frac{[\underset{\sim}{17}]}{[\underset{\sim}{18}]} = \overline{B} = \frac{k_3}{k_4}\frac{[\underset{\sim}{15b}]}{[\underset{\sim}{15a}]} =$$

$$\frac{k_3 k_2}{k_4(k_3 + k_5 + k_{-2})} = \frac{k_2}{k_4}\left(\frac{1}{1 + \frac{k_{-2}}{k_3} + \frac{k_5}{k_3}}\right) \tag{8}$$

Similarly,

$$\frac{[\underset{\sim}{16}]}{[\underset{\sim}{18}]} = \overline{C} = \frac{k_5}{k_4}\frac{[\underset{\sim}{15a}]}{[\underset{\sim}{15b}]} =$$

$$\frac{k_5 k_2}{k_4(k_3 + k_5 + k_{-2})} = \frac{k_2}{k_4}\left(\frac{1}{1 + \frac{k_{-2}}{k_5} + \frac{k_3}{k_5}}\right) \tag{9}$$

In the pyrolysis of $\underset{\sim}{12}$, k_1 may be neglected since once $\underset{\sim}{14}$ is formed it does not isomerize.

$$\frac{d[15a]}{dt} = k_{-2}[15b] - k_{-1} + k_2 + k_4[15a] \tag{10}$$

Making the steady state assumption that $\frac{d[15a]}{dt} = 0$ and neglecting $k_4 \ll k_{-1}$ (because most of diradical goes to 14) the equation simplifies to:

$$[15a] = \frac{k_{-2}[15b]}{k_{-1} + k_2} \tag{11}$$

Rearranging

$$\frac{[15b]}{[15a]} = \frac{k_{-1} + k_2}{k_{-2}} \tag{12}$$

Therefore in the pyrolysis of 12

$$\frac{[17]}{[18]}_{\text{from } 12} = E = \frac{k_3}{k_4}\frac{[15a]}{[15b]} = \frac{k_3(k_1 + k_2)}{k_4(k_{-2})}$$

$$= \frac{k_3}{k_{-2}}\left(\frac{k_{-1}}{k_4} + \frac{k_2}{k_4}\right) \tag{13}$$

Similarly,

$$\frac{[16]}{[18]}_{\text{from } 12} = D = \frac{k_5}{k_4}\frac{[15a]}{[15b]} = \frac{k_5}{k_4}\left(\frac{k_{-1} + k_2}{k_{-2}}\right)$$

$$= \frac{k_5}{k_{-2}}\left(\frac{k_{-1}}{k_4} + \frac{k_2}{k_4}\right) \tag{14}$$

Designating the following ratio with symbols

$$\frac{k_3}{k_5} = W, \quad \frac{k_4}{k_2} = X, \quad \frac{k_5}{k_{-2}} = Y, \quad \frac{k_{-1}}{k_4} = Z, \quad \frac{k_3}{k_{-2}} = V \tag{15}$$

and noting $WY = V$

$$\overline{C} = \frac{1}{X}\left(\frac{1}{1 + \frac{1}{Y} + \frac{1}{W}}\right) = \frac{YW}{X}\left(\frac{1}{WY + W + Y}\right) \tag{16}$$

$$D = Y\left(Z + \frac{1}{X}\right) \tag{17}$$

$$\overline{B} = \frac{1}{X}\left(\frac{1}{1 + \frac{1}{V} + \frac{1}{W}}\right) = \frac{YW}{X}\left(\frac{1}{YW + 1 + Y}\right) \tag{18}$$

$$E = V\left(Z + \frac{1}{X}\right) \tag{19}$$

Substituting the experimentally determined values [43, 51]

$$\overline{C} = \frac{1}{15} \qquad D = \frac{1}{0.6} \qquad Z = 285 = \frac{k_{-1}}{k_4}$$

$$\overline{B} = \frac{1}{35} \qquad E = \frac{0.4}{1}$$

$$W = \frac{k_3}{k_5} = .67$$

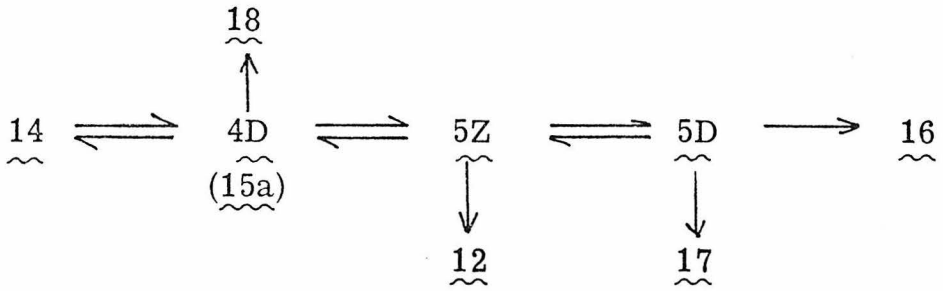
$$X = \frac{k_4}{k_2} = .08$$

$$Y = \frac{k_5}{k_{-2}} = .0053$$

$$V = \frac{k_3}{k_{-2}} = .0035$$

The implication of these results is that the necessary hydrogen shifts to give acyclic products occur more slowly than interconversion of the intermediates. The vinylcarbene (15b) reverts back to the diradical (15a) 190 times faster than it rearranges to 1,3-butadiene. The diradical (15a) closes to 1-methylcyclopropene 285 times faster and rotates to the vinylcarbene (15b) 12.5 times faster than it is converted to 2-butyne. The results of this analysis are in keeping with the observed preference of vinylcarbenes (generated both from cyclopropenes and other acyclic sources) to close up to cyclopropenes faster than they form acyclic products.[8, 22, 45] The observation that optically active 1,3-diethylcyclopropene racemizes faster than it isomerizes is also consistent with these results.

In terms of Salem's calculations on possible transients in cyclopropene isomerizations, 15a corresponds to 4D, and 15b corresponds to the singlet 5Z. Salem invokes another intermediate, 5D, which comes from 5Z and leads to the butadienes. Addition of another intermediate does not change the overall implications of the mechanism (see Scheme XII). It is probably best left out since it is not



Scheme XII

required to understand the data presently available. The differences of the energies of Salem's transients are very slight, and some questions about the exact ordering of the energies have been raised. Valence bond calculations are currently underway to help clarify this aspect of the problem.[65]

Using Scheme XI with only two intermediates and the W, X, Y and Z values derived from the analysis above, a free energy diagram can be constructed along the reaction coordinate for the thermal rearrangement of 14 at 475°K (see Figure 12). $\Delta\Delta G^{\ddagger}$ for the products can be derived from their ratios in lieu of good kinetic data on rates of their appearance.[2] The free energy, $\Delta G^{\ddagger}$, for the isomerization of 14, is calculated from the kinetic parameters of Srinivasan,[2] $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S$ where $\Delta H^{\ddagger} = Ea - RT$ and $T\Delta S = TR \ln \frac{h}{kT} A$. Therefore $\Delta G^{\ddagger} = 35$ kcal per mole at 475°C. From the value of Z, the barrier height for ring opening of 14 to the diradical is calculated to be 35 - 5

= 30 kcal per mole which is in good agreement with the thermochemical analysis presented in the Introduction. From the value of X it is concluded that the energy difference for 15a going to vinylcarbene 15b versus giving 2-butyne (18) is $\Delta\Delta G$ = 2.4 kcal per mole. Thus the $\Delta G^{\ddagger}$ for opening to the carbene is found to be 32.3 kcal per mole which is in agreement with the value of York et al.[45]

The increase in activation energy in going to more highly substituted cyclopropenes[43] can be explained by an increase in the energy necessary to form the acetylenes. When this pathway becomes unfavorable, formation of dienes takes over and the height of the barrier leading to dienes becomes the free energy necessary to isomerize the cyclopropene.

The mechanistic picture I have drawn here must be qualified. The analysis excludes any concerted reactions. For example, the data could be explained by a more complicated scheme. The bulk of the acetylene may be formed from the cyclopropene in a concerted reaction, while that from the diazo compound may arise through a carbene. All intermediates common to both the cyclopropene and diazirine are assumed to be in the same electronic and vibrational states.

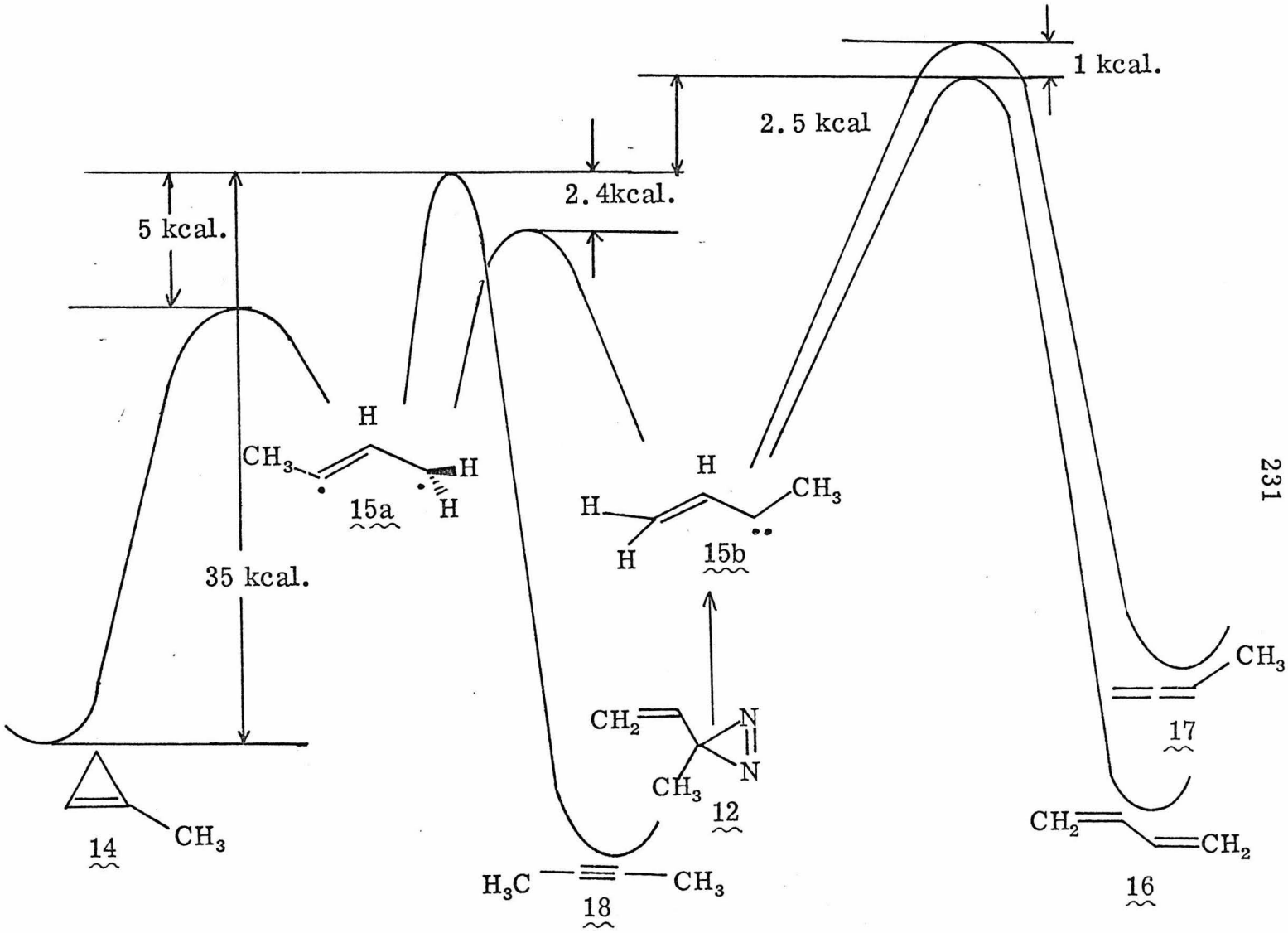


Figure 12 : Free Energy Diagram for the Thermal Rearrangement of 1-Methylcyclopropene at 475 °K

EXPERIMENTAL

General

See Part I of this thesis.

Preparation of triphenylmethylphosphonium iodide (prepared by method of Wittig).[53] A solution of 55 g (0.21 mole) of triphenylphosphine dissolved in 45 ml of dried benzene (distilled from $LiAlH_4$) was placed in a pressure bottle, the bottle cooled in an ice-salt bath, and 42 g (0.29 mole) of methyl iodide was added. The bottle was sealed, allowed to stand for 2 days at room temperature, and was reopened. The white solid was collected by suction filtration with the aid of 500 ml of hot benzene, and was dried in a vacuum desiccator heated to 100° over phosphorus pentoxide. The yield was 83.7 g (86%), melting point 183-185°.

Preparation of D_6-isobutylene from D_6-acetone. A 500 ml three-neck round-bottom flask was fitted with a reflux condenser, an addition funnel, a mechanical stirrer, and a gas inlet tube. A gentle flow of N_2 was maintained through the apparatus throughout the reaction. A solution of n-butyllithium in hexane (Alpha Inorganics) (0.13 mole total) and 200 ml of anhydrous dimethoxy ethane was added to the flask. The solution was stirred and 43 g (0.11 mole) of triphenylmethylphosphonium iodide was added cautiously over a 5 min

period. The solution was stirred for 4 hr at room temperature.

The reflux condenser was cooled to -5°. The flask was connected through the condenser to a collection vessel for the isobutylene. The collection vessel was cooled to -78° in a dry ice-acetone bath. 6.4 g (0.11 mole) of D_6-acetone were added slowly dropwise. The solution became colorless and a white precipitate formed. The mixture was heated to 40° and the volatile isobutylene was distilled out of the reaction vessel into the cold collection vessel. The reaction flask was stirred overnight. The NMR of D_6-isobutylene showed no resonance for the methyl hydrogens (1.7 δ in the protio case). The vinyl hydrogen resonance appeared at 4.6 δ.

Preparation of 1,1-dibromo-2,2-dimethylcyclopropane.[54]

67 g (1.7 moles) of potassium metal were dissolved, under nitrogen, in 1570 ml of t-butanol (freshly distilled from $LiAlH_4$) at reflux with mechanical stirring in a 3 liter three neck flask. When the dissolution was complete, the t-butanol was removed by atmospheric distillation. Final traces of t-butanol were removed by evacuating the vessel at low pressures (1-0.1 torr) and heating to 150° for 2 hr. Nitrogen was readmitted and the vessel was cooled to room temperature. The above procedure was used for D_6-isobutylene because dibromocarbene reacts with t-butanol by dehydrating it. Connate isobutylene (non-deuterated) will contaminate the deuterated isobutylene

from the Wittig reaction. The t-butanol was not distilled from the K^+O^-Bu when non-deuterated cyclopropane was desired, but was removed later in the washing and by rotary evaporation.

800 ml of n-pentane were added with continuous stirring, and the solution was cooled in dry ice-acetone bath. A reflux condenser filled with dry ice-acetone was fitted on the flask and 81 grams (1.45 mole) of isobutylene (commercial or from the Wittig reaction) were poured in. With continued stirring, 320 grams of bromoform (1.28 moles) were added dropwise over 2 hr. The mixture was left stirring overnight and allowed to reach room temperature. The next day, the entire mixture was dumped into 2 liters of water and the lower organic phase separated and its volume reduced on a rotary evaporator until no more solvent would come over. The material was washed again and rotary evaporated again; this procedure was repeated four more times to free the product from pentane, isobutylene, and t-butanol. The material was quite pure by VPC on a 5' by 1/4" 3% SE 30 column (injector at 145° and column at 85°). Retention time was 3 min. The yield was 80% (239 grams). NMR, in CCl_4, consisted of a singlet at 1.4 δ (methyl groups), and a shoulder (singlet) 1 1/2 cps downfield from this peak (ring protons). The NMR of the 1,1-dibromo-2,2-di (1,1,1-trideuteromethyl)cyclopropane had only the "shoulder", mentioned above, at 1.4 δ.

Preparation of 1-bromo-2, 2-dimethylcyclopropane. 128 grams of 1, 1-dibromo-2, 2-dimethylcyclopropane (0.56 mole) were added to a mixture of 1.1 liter of glacial acetic acid to which 12 g of zinc dust had been added and magnetically stirred at 80°. Immediately the zinc dust conglomerated into small clumps and settled to the bottom of the flask. 150 grams of zinc dust were added in small amounts over the next 3 hr. The reaction was monitored by VPC using the column and conditions mentioned in the preparation of the dibromocyclopropane. When no further change in reactant concentration was observed, the mixture was removed from the bath and washed repeatedly with water to remove the acetic acid. The lower phase was found to be pure by VPC except for a few per cent of 1, 1-dimethylcyclopropane. The retention time of the monobromocyclopropane was 2 min on the column mentioned previously under the same conditions. The 43.5 g collected from the organic phase were dried over anhydrous magnesium sulfate and distilled at aspirator pressure. The first portion showed the presence of a persistent dimethylcyclopropane impurity. The second cut (bp lit [53] = 107°-108°) was 19.5 g which was found to be pure by VPC. The boiling point was found to be 70-71° at 170 torr. The yield of monobromide free from impurities was 0.13 mole (23%). The NMR in CCl_4 consisted of a quartet of peaks at 2.75 δ of equal spacing and

height J = 4-5 Hz for the proton geminal to the bromine, a singlet at 1.3 for the methyl cis to bromine, a singlet at 1.2 δ for the methyl trans to the bromine, and a multiplet from 1.1 δ to 0.5 δ for the remaining ring protons.

Preparation of 3,3-dimethyl-1-cyclopropene. 16 grams (0.11 moles) of 1-bromo-2,2-dimethylcyclopropane free from dimethylcyclopropane impurities, dissolved in 35 ml dimethylsulfoxide (freshly distilled from calcium hydride) were added at once to a 1 liter three necked flask equipped with a pressure equalizing dropping funnel and charged with 30 g (0.27 moles) of potassium tert-butoxide from a freshly opened bottle (Alpha Inorganics, free from t-butanol) and 250 ml dimethylsulfoxide (freshly distilled from calcium hydride). The liter flask was connected to a 100 ml pear shaped flask filled with glass helices cooled in a 1/2 pint dewar filled with dry ice-acetone. The pear shaped flask was in turn connected to a trap cooled in liquid nitrogen. The system protected by a drying tube was evacuated by a water aspirator through the trap, cooled in liquid nitrogen. After a few minutes magnetic stirring, the stopcock to the aspirator was cracked and reclosed. Immediate frothing resulted, and a clear liquid began to collect in the cold trap. When frothing had subsided, the stopcock was again cracked, and this procedure was continued for 0.5 hr until continuous suction on the reaction mixture yielded no more

bubbles. The contents of the cold traps were vacuum transferred into a vacuum stopcock gas flask and vacuum transferred back and forth between gas flasks five times to free the product from t-butanol and other nonvolatile impurities. Yield was 3.8 g (0.056 moles), 52% yield, 99% pure by VPC on the β,β'-ODPN column. NMR (CCl_4): δ 7.31 (septet, J = 0.8 cps, ring vinyl protons), δ 1.13 (triplet, J = 0.8 cps, methyl protons), nearly identical to published spectrum.[17] IR (CCl_4): 2970, 2940, 2930 cm^{-1} (s), 2880 cm^{-1} (m), 2865 cm^{-1} (s), 1625 cm^{-1} (s, possible shoulder at 1615 cm^{-1}).

Pyrolysis of 3,3-dimethylcyclopropene. 3,3-Dimethylcyclopropene was pyrolyzed in the wall-less reactor over a temperature range of 608 to 658°K. Volume flow rate of blanket gas to the reactor at room temperature was 124.6 cm^3 per sec. This gave a total maximum residence time of 0.35 sec. Nozzle and probe were maintained 250 to 260° below the temperature of the reactor. Consequently no reaction took place in the delivery or collection systems.

Products were analyzed on a 25 ft by 1/8 in stainless steel column with 20% β,β'-ODPN on 100/120 mesh Chromosorb P. Products were previously identified and their order of elution determined by T. H. Morton.[13] Retention times with column maintained at 25°C were 5.36, 6.25, 13.31, 14.46 and 15.56 min for 1,1-dimethylcyclopropane, 6, 11, 10 and 9, respectively. With the column at 80°C all of the

products were grouped together with a retention time of 6.60 min, while 6 eluted after 4.30 min. Determination of relative concentrations was by means of an electronic digital integrator (see Experimental of Part I of this thesis). Reproducibility was to within 0.5%.

Attempted synthesis of 1,3-dimethylcyclopropene. An attempt was made to synthesize 1,3-dimethylcyclopropene from trans 2,3-dimethyl-1-bromocyclopropane using the same conditions and apparatus as in the synthesis of 3,3-dimethylcyclopropene (see above). 1.8 grams (0.012 mole) of trans 2,3-dimethyl-1-bromocyclopropane dissolved in 3.0 ml of dry dimethylsulfoxide were added at once to 5.0 g of potassium tert-butoxide in 29 ml of dimethylsulfoxide. Trapping and purification of product was carried out as before (see above). The product was identified by NMR as 2-methyl-1-methylenecyclopropane. NMR (CCl_4): δ 5.2-5.4 (m, 2H), δ 1.0-1.4 (m, 2H), δ 1.12 (d, J = 4.5, CH_3-C), δ 0.5-0.7 (m, 1H).

Attempted synthesis of 3-ethylcyclopropene from 1-butene. The attempted synthesis of 3-ethylcyclopropene was identical to that of 3,3-dimethylcyclopropene (see above), except that after the formation of potassium tert-butoxide, the excess tert-butanol was removed by distillation at atmospheric pressure and then under reduced pressure (1-.01 mm for 2 hr). Two isomeric dibromides were obtained from which three isomeric mono-bromides resulted. These

were 1-bromo-2, 2-dimethylcyclopropane (in all probability derived from the dibromide formed by the addition of dibromocarbene to isobutylene; the isobutylene could have arisen by the dehydration of tert-butyl alcohol by dibromo carbene), and the cis/trans isomers of 1-bromo-2-ethylcyclopropane. The mixture of mono-bromides was dehydrobrominated as before to give four products. These were: 3, 3-dimethylcyclopropene, ethylidenecyclopropane, 3-ethylcyclopropene (this compound was extremely labile and disappeared as the NMR of the reaction mixture was taken), and 1-ethylcyclopropene. The ratio of products by NMR was 18:21:3.5:18, respectively. After 5 days at room temperature the ratio was 18:29:0:10, respectively. The 3-ethylcyclopropene had disappeared completely, while the ethylidene cyclopropene absorptions grew at the expense of 1-ethylcyclopropene. NMR of 3, 3-dimethylcyclopropene (CCl_4): δ 7.31 (septet, J = 0.8 cps, ring vinyl protons), δ 1.13 (triplet, J = 0.8 cps, $\underline{CH_3}$). NMR of ethylidenecyclopropene (CCl_4): δ 5.63 (quintet, quartet, J = 2 cps, J = 6 cps, vinyl H), δ 1.77 (d, quintet J = 6 cps, J = 1.5 cps, $\underline{CH_3}$), δ 0.97 (m, 4H). Partial NMR of 3-ethylcyclopropene (CCl_4): δ 7.26 (m, 2 vinyl H). Partial NMR of 1-ethylcyclopropene (CCl_4): δ 6.42 (first-order quartet, J = 1.5 cps, 1 vinyl H), δ 2.42 (first-order quartet, J = 8 cps, $-\underline{CH_2}-CH_3$).

Deuteration of 3,3-dimethyl-1-cyclopropene. The vinyl positions of 3,3-dimethyl-1-cyclopropene were deuterated using a modification of the method of Dorko and Mitchell.[55] Tert-butyl alcohol-D_1 was prepared by the method of Young and Guthrie[56] from t-butyl borate[57] as follows:

25 grams (0.4 mole) of orthoboric acid, 135 g of t-butyl alcohol (1.8 mole), and 100 ml of benzene were refluxed for one week with a Vigreux column connected to a Barret trap to permit drainage of the water removed from the refluxing mixture as the azeotrope. After 16-1/2 ml of water had been drained from the trap, no more water was observed to come over. The reflux was stopped, and excess t-butyl alcohol and benzene were cautiously removed on a stream bath followed by rotary evaporation at aspirator pressure. The residue was a clear liquid standing over a white solid. NMR of the supernatant showed a 1.3 ppm and a smaller singlet at 1.4 ppm (it was not possible to separate the integral; the ratio of the heights was 4:1, respectively). No signal indicative of a hydroxyl proton was detected, and the two singlets were attributed to t-butyl borate and t-butyl boroxin, respectively.[56]

To the mixture of borate and boroxin was added 18 g (0.9 mole) of D_2O (Columbia, 99.7%), and the mixture was refluxed for 8 hr on a steam bath. The supernatant was distilled at atmospheric pressure at

81°. The NMR showed no indications of hydroxylic protons. Yield was 32 g (0.43 mole) of t-butyl alcohol-D_1 (36% of maximum yield).

0.5 gram (0.013 mole) of potassium metal were dissolved in 5.5 g of t-butanol-D_1 (0.07 moles, vacuum transferred from the t-butanol-D_1 described above stored over sodium wire), and the solution was introduced into a gas flask equipped with a micro magnetic spin bar. The solution was frozen in liquid N_2 and the gas flask was evacuated. 0.8 gram of cyclopropene (0.012 mole) were vacuum transferred into the gas flask, and the mixture was allowed to reach room temperature. After stirring for one week, the mixture was chilled in ice and the cyclopropene was vacuum transferred out of the flask. The cyclopropene was freed from t-butanol impurity by vacuum transfer back and forth several times between gas flasks.

1-Methylcyclopropene. A solution of 2.75 g (0.30 mole) of β-methylallyl chloride in 50 ml of anhydrous ether was added over a period of 30 min at room temperature to a stirred solution of 39.1 ml of 2.3 M phenyllithium in ether/benzene (Alpha Inorganics). The mixture was stirred for an additional 30 min.

The reaction mixture was freed from the benzene and most of the ether by a vacuum distillation (1 mm of pressure) through a trap cooled by dry ice-acetone to a second trap cooled by liquid nitrogen. The contents of the second trap (about 2.5 ml) were analyzed by NMR

and were found to be about 20% cyclopropene, 1% benzene and 80% ether. This material was used as is in the 1-methylcyclopropene thermolysis studies. NMR of 1-methylcyclopropene (benzene D_6): δ 6.44 (m, 1 vinyl H), δ 1.96 (d, J = 1 cps, $\underline{CH_3}$), δ 1.18 (d, J = 2 cps, $-CH_2-$). NMR (CCl_4): δ 6.40 (m, 1 vinyl H), δ 2.13 (d, J = 1 cps, $C\underline{H_3}$), δ 0.83 (d, J = 2 cps, $-C\underline{H_2}-$). IR (CCl_4): -C=C- stretch at 1780 cm^{-1} in agreement with literature value.[19]

1-Hydroxy-3-methyl-2-butene. A 2-liter three-neck round bottom boiling flask, equipped with a mechanical stirrer and a reflux condenser, was charged with 31 g (0.82 mole) of lithium aluminum hydride (LAH) and 200 ml of anhydrous ethyl ether. The suspension was cooled in an ice-salt bath as 64 g (0.75 mole) of 3,3-dimethyl-acrylic acid (Aldrich) were added under an inert, dry nitrogen atmosphere over a period of 2 hr. After the addition of LAH was completed, the reduction was carefully quenched by the dropwise addition of a saturated aqueous solution of sodium sulfate (approx. 125 ml) until the suspension was light gray. After a few hours of stirring, the mixture had turned completely white. At which time the ethereal solution was suction filtered and the residue on the filter was washed with more ether. Removal of the solvent under reduced pressure on a rotary evaporator left 50 g of a pale yellow liquid. VPC on a 6 ft by 1/8 in column, which was packed with UCCW 982 on

Chromosorb W, 60/80 mesh and maintained at 45°C with a helium flow rate of 1 cc/sec, showed the presence of three peaks. The largest peak (retention time 11 min) proved to be the desired alcohol. Assuming 8 9% purity from the VPC, this corresponds to a yield of 45 g (0.5 moles) of 3-methyl-2-buten-1-ol (85% of theoretical yield) IR (neat film): 3400-3350 (s), 2960 (s), 2910 (s), 2860 (s), 1670 (m). NMR (CCl_4): δ 5.3 (first-order triplet J = 7 cps, $C\underline{H}-CH_2OH$), δ 4.0 (d, J = 7 cps, $C\underline{H_2}OH$), δ 3.2 (s, $CH_2O\underline{H}$) δ 1.6 (broad singlet $-C\underline{H_3}$ cis), 1.5 (d, J = 1 cps, $C\underline{H_3}$ trans).

Senecialdehyde. Several syntheses of senecialdehyde were undertaken. All of these involved the oxidation of the corresponding alcohol, 1-hydroxy-3-methyl-2-butene. The best results were obtained with pyridinium dichromate. The oxidations by chromic anhydride intercalated in graphite were test reactions using this new reagent. As such, the reactions were not worked up. Oxidation with Ce(IV) ions resulted in the oxidation of the double bond and rearrangement of the alcohol.

Attempted synthesis of senecialdehyde from 2-methyl-4-hydroxy-2-butene.[58] The method of Trahonovsky and Young using cerium(IV) (see above) was tried on 2-methyl-4-hydroxy-2-butene with the following modification; sodium bicarbonate was not used in the drying step. Workup as for the cyclopropylcarboxaldehyde and

distillation yielded only two products. The major product (3 ml) was identified as the rearranged alcohol by its NMR and IR, 3-methyl-3-hydroxy-1-butene and the minor product (1 ml) as acetone. The alcohol presumably resulted from a rearrangement via an allylic cation and then solvolysis at the position of highest positive charge density. The acetone probably arose from oxidation of double bond of the reactant. NMR of 3-methyl-3-hydroxy-1-butene (CCl_4): δ 1.28 (s, $(C\underline{H}_3)_2C$), δ 3.63 (s, $\underline{H}O-C$), δ 4.93 (m, $\underline{H}_a\underline{H}_bC=C$), δ 5.8 (d, d J = 10.5, J = 17.5 cps, $H_c-C = CH_2$).

Senecialdehyde. Pyridinium dichromate was prepared by the method of Coates and Corrigan.[59] A solution of 1 pound (4.6 moles) of chromic anhydride in 300 ml of water was added slowly over the period of 1 hr to a mechanically stirred solution of 400 g (5.1 moles) of pyridine and 40 ml of water. The suspension was cooled and suction filtered to yield 725 g (1.9 moles) of orange crystals of pyridinium dichromate (83%).

15 grams (0.175 moles) of 1-hydroxy-3-methyl-2-butene were dissolved in 300 ml of CH_2Cl_2. To this solution 150 g of pyridinium dichromate (0.4 moles) were added gradually over the period of 1 hr with vigorous mechanical stirring. The progress of the reaction was monitored by VPC on a 6 ft by 1/8 in column, which was packed with UCW 982 on Chromosorb P, 60/80 mesh, maintained at 45°C, and had

a He flow rate of 1 cc/sec through it. The alcohol had a retention time of 8 min, while the product aldehyde had a retention time of 6.5 min. After addition was complete, the reaction mixture was permitted to stir for 45 min. At this time, reaction was shown to be complete by VPC. The reaction mixture was permitted to stand without stirring for 5 hr. A solution of product in methylene chloride separated from a black tarry emulsion and was decanted off. The black tar was washed five times with 50 ml portions of methylene chloride. The combined washes and the original reaction solvent, which had a brownish tinge, were washed with 50 ml of 2 N HCl saturated with sodium chloride. The brownish, hazy solution of senecialdehyde in dichloromethane was clarified and lightened by suction filtration through alumina. The volume of the solution was reduced to 150 ml by distillation of the methylene chloride at atmospheric pressure. The resulting solution of senecialdehyde was dried over anhydrous sodium sulfate and distilled under reduced pressure to give 8.1 g of senecialdehyde, 63% of theoretical. Boiling point 54°C/36 mm. IR (CH_2Cl_2): 2960 (s), 2890 (m), 2860 (m), 1675 (s), 1665 (s), 1585 (s). NMR (CCl_4): δ 9.8 (d, J = 8 cps, C<u>H</u>O), δ 5.8 (d, q, J = 8 cps, J = 1 cps, C<u>H</u>–CHO), δ 2.15 (d, J = 1 cps, C<u>H</u>$_3$ <u>cis</u>), δ 1.95 (d, J = 1 cps, C<u>H</u>$_3$ <u>trans</u>.

Senecialdehyde.[60] In a 100 ml single-neck round bottom boiling flask, equipped with a reflux condenser and a magnetic stirring bar, was placed 2.58 g (0.03 mole) of 1-hydroxy-3-methyl-2-butene, 25 ml of o-xylene, and 10 g (.02 mole) of chromic anhydride intercalated in graphite ("Seloxcette", Alpha Products). The reaction mixture was heated to 118 °C with stirring. The reaction progress was followed by NMR and after 6 days of stirring at 118 °C the ratio of aldehyde to alcohol was 5:1.

Senecialdehyde.[60] In a 300 ml single-neck round bottom boiling flask; equipped with a reflux condenser and a magnetic stirring bar, was placed 7.6 g (0.088 mole) of 1-hydroxy-3-methyl-2-butene, 175 ml of dichloromethane, and 70 g (.14 mole) of chromic anhydride intercalated in graphite (Seloxcette, Alpha Products). The reaction mixture was heated to reflux with stirring. The reaction progress was followed by NMR, and after 7 days 5 hr the reaction was terminated, at which time it was 85% complete.

Chloroamine.[46] 250 ml of a 10 N methanolic ammonia at -40 °C were placed in a 500 ml three-neck round bottom boiling flask, that was equipped with a mechanical stirrer and a dry ice-acetone reflux condenser. Maintaining the temperature at -40 °C, 30 ml of tert-butyl hypochlorite (0.25 mole)[61] in 30 ml of tert-butyl alcohol were added dropwise to the stirred solution over the period of 1 hr. The yield of

chloroamine, which was determined by titration of iodide, was found to be 60-80% of theoretical.

2,4,6-Tri-n-butyl-1,3,5-tri-azabicyclo[3.1.0]hexane.[46] To the freshly prepared, stirred solution of chloroamine (see above) at -30°C, was added three times the molar amount of pentanal in 2 min. The reaction mixture was permitted to stir for 1 hr at -30° and for another hour without the bath. The MeOH was removed under reduced pressure on a rotary evaporator. The reduced solution was suction filtered to remove the ammonium chloride salts which precipitated out of the solution. The salts were washed on the filter with anhydrous ether, and the solution was refiltered. The remaining solvents were completely removed under reduced pressure on a rotary evaporator, to give a residue which crystallized. The crystals were yellow and tended to darken upon standing. The material was recrystallized twice from petroleum ether to give 17.3 g of slightly yellow crystals (36% of theoretical yield). Melting point 62-64°C. IR (CCl_4): 3300, 2940, 2880, 1478, 1380, 1220 cm^{-1}.

3-n-Butyl-diazirine.[46-48] In a 500 ml 3-neck round bottom boiling flask equipped with an addition funnel, a nitrogen gas inlet and and outlet leading to two traps, the first of which was cooled by dry ice-acetone and the second by liquid nitrogen, was placed a solution of 9.3 g of sodium dichromate in 100 cc of 2 N sulfuric acid. 6.9 grams

of bicyclodiaziridine (see above) in 200 cc of 2 N H_2SO_4 were added to the dichromate solution at 40°C and a stream of nitrogen gas was bubbled through the reaction mixture. The reaction vessel was warmed to 80° and the diazirine was swept out in the stream of nitrogen and condensed in the traps. The dichromate solution changed color over the period of 1 hr from orange to brown to green.

The crude diazirine was freed from the aldehyde by bubbling through a saturated solution of sodium bisulfite, dried over potassium hydroxide pellets and collected at -78° as a colorless, mobile liquid. It had infrared peaks at 1595 and 985 cm^{-1}, characteristic of the diazirine ring. The yield was 0.39 g, which is 15% of theoretical yield. The retention time on a 10 ft by 3/8 in glass column, which was packed with 20% UCW98 on Chromosorb WAW-DMCS, injector = 155°C, column = 75°, He flow = 1 cm^3/sec, was 8 min. After scrubbing with sodium bisulfite solution, purity by VPC was calculated to be greater than 99%. Note well, an attempt was made to pyrolyze 3 μl of n-butyldiazirine in the heated (320°C) injector port of a Varian 90-P VPC. A syringe with a metal plunger and a ground glass cylinder was used. Either because of the type of syringe (syringes with teflon coated plungers and smooth fire-polished walls are strongly recommended) or the intense heat of the injector block, the syringe exploded when the needle was touched to the hot septum. NMR (CCl_4): δ 1.1-0.6

(m, 3H) δ 1.5-1.1 (m, 7H).

Attempted Synthesis of 3-isobutenyldiazirine. An attempted synthesis of 3-isobutenyldiazirine was carried out using the method of Schmitz for the formation of diazirines from aldehydes (see above). Senecialdehyde (27) was prepared as described above . 27 reacted with an ammonia to form an imine of unknown structure (NMR evidence). The unpurified imine was oxidized with sodium dichromate as before to give β,β-dimethylacrolein and starting aldehyde. NMR of imine (CCl_4): δ 1.90 (d, J = 1.5 cps, $-(\underline{CH_3})_2$) δ 5.99 (d, septet J = 10 cps, J = 1.5 cps, $(CH_3)_2-C=C\underline{H}-$), δ 9.91 (d, J = cps, $-C\underline{H}=N-$) NMR of β,β-dimethylacrolein (CCl_4): δ 2.00 (d, J = 1.5 cps, $-C\underline{H_3}$) δ 2.10 (broad singlet, $-C\underline{H_3}$), δ 5.13 (septet, J = 1.5 cps, $(CH_3)_2-C=C\underline{H}-CN$). VPC isolated β,β-dimethylacrolein gave a parent peak of 81 atomic mass units in the mass spectrometer.

4-Diethylamino-2-butanone.[62] In a 3 l round-bottom flask equipped with a reflux condenser were placed 176 g (1.60 moles) of diethylamine hydrochloride, 68 g (2.26 moles) of paraformaldehyde, 600 ml (8.1 moles) of acetone, 80 ml of methanol, and 0.2 ml of concentrated HCl. The mixture was heated for 12 hr at a moderate to vigorous rate of reflux. The solution (light-yellow), in which a small amount of gelatinous solid remained, was cooled, and a cold solution of 65 g (1.63 moles) of sodium hydroxide in 300 ml of water was added.

The mixture was extracted with three 200 ml portions of ether; the combined extracts were washed with two 150 ml portions of saturated sodium chloride solution, and the washes re-extracted with two 150 ml portions of ether.

The combined ether solutions were dried with 80 g of anhydrous sodium sulfate for 12 hr, filtered and then distilled under reduced pressure through a 20 cm Vigreux distilling column. After the solvent and a small forerun (acetone and methanol) had been distilled, 150-174 g (66%-76%) of 4-diethylamino-2-butanone was collected as a light lemon yellow liquid, boiling point 63-67°/7 mm (75-77°/15 mm, 72-75°/10 mm). NMR (CCl_4): δ 0.95 (q, J = 7.0 cps, $-(CH_2-C\underline{H}_3)_2$), δ 2.06 (s, $-CO-C\underline{H}_3$), δ 2.84-2.45 (m, 4H), δ 2.43 (t, J = 7 cps, $-(C\underline{H}_2-CH_3)_2$.

3-Methyl-3-[β-diethylamino-ethyl]diaziridine.[14a] Thirty-five ml of liquid ammonia were added to 130 ml of methanol, cooled to -50° C, that was contained in a 300 ml 3-neck round-bottom boiling flask equipped with a mechanical stirrer and dry ice/acetone condenser. 0.1 mole (14.3 g) of 4-diethylamino-2-butanone were added to the solution. Over the period of 1 hr, freshly prepared 0.1 moles (11.4 g) of hydroxylamine-0-sulfonic acid[63] were added in small portions to the mechanically stirred, cooled solution (-50°C). The mixture was then permitted to stir in the cold bath for three more hr, and then was

allowed to warm up to room temperature over night. A precipitate of ammonium sulfate formed which was removed by suction filtration. The yield was determined by tritation with iodine.

The solution of the diaziridine in methanol was condensed on the rotary evaporator and distilled at reduced pressure through a 20 cm Vigreux distillation column to give a 56% yield of isolated diaziridine. Boiling point 0.4 torr 63-64°, 1.2 torr 72-73°C. Purity by titration with iodine was 98%.

3-Methyl-3-[β-diethylamino-ethyl]diazirine.[14a] To 16.1 g of 3-methyl-3-[β-diethylamino-ethyl]diaziridine in 250 ml of anhydrous ether, was added 19.1 g of freshly prepared silver oxide.[64] The mixture was stirred (magnetic stir bar) for 3 hr at room temperature. The reduced silver was removed by vacuum filtration and washed on the filter with anhydrous ether. The combined ether solutions were condensed on the rotary evaporator, and distilled under reduced pressure through a 20 cm Vigreux column to give 11.2 g (71%) of the isolated diazirine. Boiling point $_{17}$ 62-63°C, $_{19}$ 65-66°C.

Methyl iodide salt of 3-methyl-3-[β-diethylamino-ethyl]-diazirine. To 4 g of the diazirine in 5 ml of anhydrous ether, was added 8.0 g of methyl iodide. The mixture was cooled in ice for 30 min and then permitted to stand overnight at room temperature. White crystals of the salt precipitated out of the solution. (The

diazirine must be dry; otherwise a yellow oil will form instead of the white precipitate. This oil darkens with time, but may be used as is in the Hoffmann elimination, the next step of the procedure.) The precipitate in ether was diluted by adding more ether. The salt was isolated by suction filtration and dried in a high-vacuum desiccator. The salt was recrystallized from absolute ethanol to yield 7.5 g (97%). Melting point 143° with evolution of gas.

3-Methyl-3-vinyl-diazirine. 6.0 grams of the methyl iodide salt of 3-methyl-3-[β-diethylamino-ethyl]diazirine were dissolved in 80 cc of water. 4.0 grams (23.5 mmole) of silver oxide, freshly prepared from silver nitrate, were added to the solution. Although an instantaneous color change occurred in the silver oxide, the mixture was permitted to stir (magnetic stir bar) for 1 hr. The solution was separated from the grayed silver iodide by suction filtration, and reduced on a rotary evaporator (connected to a high vacuum pump) to 8 cc without permitting the solution to be warmed over 25°C.

The Hoffmann elimination was carried out by the dropwise addition of the reduced solution of the quarternary base from a pressure equalizing dropping funnel into a preheated (100-105°C), preevacuated (90-100 torr) 100 ml 3-neck round-bottom boiling flask connected to two cold traps. The cold trap nearest the reaction

vessel was cooled by ice water, and the other trap by a dry ice-acetone mixture. The volatile product was trapped in the second, coldest trap, while the water was collected in the first trap. Only after the reaction was over, and the reaction vessel had cooled, was the vacuum broken and the diazirine collected. The contents of both traps were collected and the liberated diethylmethylamine was neutralized with 15.5 cc (84% of theoretical) of 1 N HCl. (Note, aqueous phase must be checked to make sure it is acidic.) The diazirine was removed by pipetting and stored at -40°C to prevent its decomposition. (Note well, this reaction and all handling of the diazirine should be carried out in a hood, behind a safety shield to guard against explosions.) The original investigators [14a] suggested immediate dilution with methylene chloride to prevent explosions, however neat solutions were stored at -40°C without mishap.

3-Methyl-3-vinyl diazirine was a water insoluble light red oil. IR (CCl_4): 3080, 3030, 2950, 2930 and 1600 cm^{-1}. NMR (CCl_4): δ 1.2 (s, $C\underline{H}_3$–C), δ 5.1 (m, ABC spectrum, $\underline{H}_2C$=CH–C). UV (cyclohexane): 218 mμ (log ϵ = 3.35), 355 mμ (log ϵ = 1.78). NMR (benzene-D_6): δ 5.00 (m, ABC spectrum, $\underline{H}_2C$=C$\underline{H}$–C), δ 0.80 (s, $C\underline{H}_3$–C).

Preparation of 3-methyl-3-vinyl-diazirine for thermolyses. The neat solutions of the vinyldiazirine were prepared twice on a Varian 90-P VPC using a 22 ft by 1/4 in glass column packed with 20% by weight of Carbowax 1500 on a solid support of acid-washed Chrom W 60-80 mesh.

The injector port, which was pyrex glass lined, was kept at 40°C, the column was maintained at room temperature and the detector at 50°C. This was to prevent the formation of large amounts of 3-methyl-pyrazole (13).

The average shot size was 25 μl of neat diazirine. (Note well, the use of syringe with bare metal plungers and ground glass cylinders is discouraged. An explosion occurred in just such a syringe. It is recommended that "Hamilton gas-tight" syringes be used which have teflon covered plungers and smooth, fire polished cylinder walls.) After 150-200 μl of diazirine were prepared and collected in dry ice cooled traps, the diazirine was diluted to six times its volume with spectroquality benzene (which was dried and its purity checked by vapor phase chromatography prior to its use). These solutions in benzene were used as is or with a small amount of isooctane of known weight, added as an internal standard.

Pyrolysis of 3-vinyl-3-methyldiazirine (12) and identification of products. 12 was pyrolyzed in three different reactor systems. The first consisted of a 27 cm by 1 cm I.D. quartz tube (total volume of 21.2 cm^3, total internal surface area of 27.3 cm^2) enclosed in a tube oven. 20% solutions of 12 in benzene were pyrolyzed in a stream of He (flow rate at room temperature of 1 cm^3 per sec) at atmospheric pressure by passage through the tube heated over the range of 60-260° C. The reaction mixture was condensed in two liquid nitrogen cooled traps after pyrolysis. Residence time was 14-18 seconds.

The second system was similar to the first except a teflon tube of the same dimensions as the quartz tube was used. The teflon system was also used in a study of the surface dependence of the product distribution from 12. The surface to volume ratio was increased by a factor of 3.2 by packing the tube with pieces of teflon.

The last system used was the quartz lined injector port of a Hewlett-Packard Model 5750 Research Chromatograph (see Experimental section of Part I for details). The quartz liner was 12 cm long and 0.025 cm in diameter (total volume of .006 cm^3, area of the surface is 1 cm^2) and was heated over the range of 146-295°C. 5 μl of 20% solutions of 12 in benzene were injected through a septum into the heated injector port. The flow of He through the injector port was 7cc per minute at room temperature. Total residence time was

calculated to be .05 to .03 seconds.

The reaction mixture was vacuum transferred out of the traps into ampoules which were sealed and stored in liquid nitrogen until mixture was to be analyzed. The pyrolysate was analyzed on a 25 ft by 1/8 in stainless steel column packed with 20% β,β-ODPN on Chromosorb P NAW 100/120 mesh and maintained at room temperature. Products were identified by comparison of their retention time with authentic samples. Retention times were 1220, 1320, 1590, 5060 and 6614 seconds for 1,3 butadiene, 1-methylcyclopropene, 1,2 butadiene, 2-butyne and 12, respectively. In some runs an internal standard, isooctane, was used which eluted with a retention time of 2200 seconds. Benzene stayed on the column for 8 hr.

In some runs on systems one and two benzene-D_6 was used as the solvent and the reaction mixture was vacuum transferred into NMR tubes.

The small amount of protons remaining on the benzene rings were used as an internal standard to calculate how much diazirine was decomposing to C_4H_6 hydrocarbons since the major product 3-methylpyrazole (13) being fairly non-volatile, condensed out of the pyrolysate before reaching the two cooled traps. 3-Methylpyrazole (13) was identified by its NMR. NMR (CCl_4): δ 2.25 (singlet $-C\underline{H}_3$), δ 6.00 (m, 1 vinyl H), δ 7.42 (m, 1 vinyl H).

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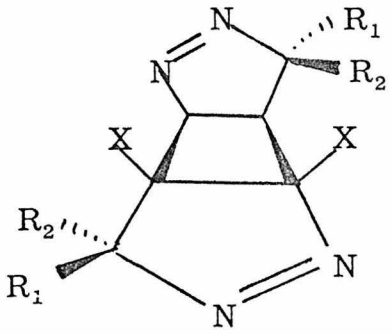
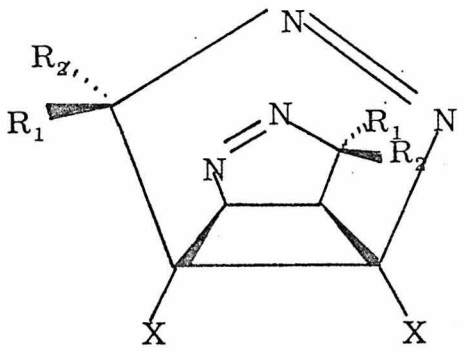
PROPOSITION I

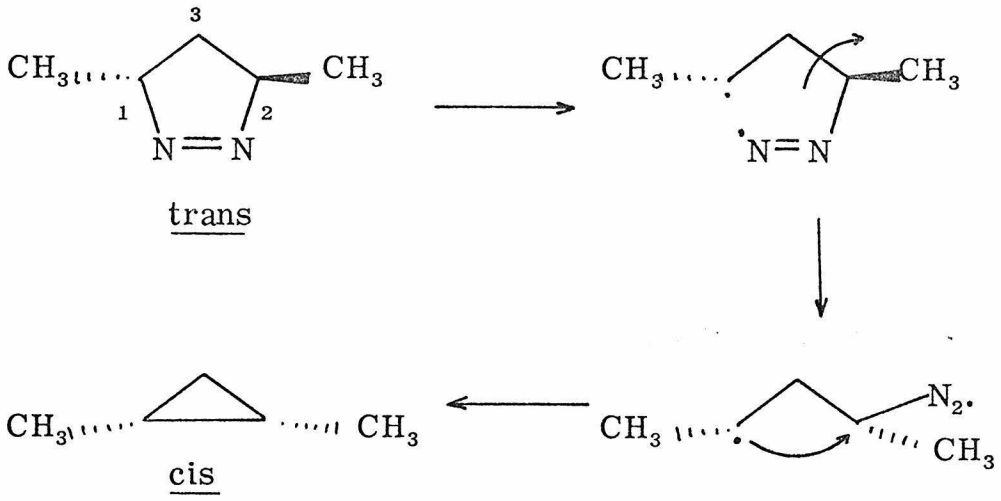
A. In Part I of this thesis, the mechanisms proposed to explain the data obtained from studies of the decompositions of 1-pyrazolines were discussed. In particular, from the study of thermal decomposition of 2,3-diazabicyclo[3.2.0]hept-2-ene and its methyl derivatives, evidence against the intermediacy of the π-cyclopropane was found.[1] Almost by default, the sequential carbon-nitrogen bond cleavage mechanism was invoked to explain the data. It is proposed that 3,4,8,9-tetraazatricyclo-[5.3.0.$0^{2,6}$]3,8-decadiene (1, bipyrazoline) and suitably labeled derivatives be synthesized to provide evidence for this mechanism (see below).





$X=R_1=R_2=H$,	1A	$X=R_1=R_2=$ H,	1S
X=D, $R_1=R_2=H$,	1A-D_2	X=D, $R_1=R_2=H$,	1S-D_2
$R_1=CH_3$, $X=R_2=H$,	2XAX	$R_1=CH_3$, $X=R_2=H$,	2XSX
$R_1=CH_3$, $R_2=H$, X=D,	2XAX-D_2	$R_1=CH_3$, X=D, $R_2=H$,	2XSX-D_2
$R_1=X=H$, $R_2=CH_3$,	2NAN	$R_1=H=X$, $R_2=CH_3$,	2NSN
$R_1=H$, X=D, $R_2=CH_3$,	2NAN-D_2	$R_1=H$, X=D, $R_2=CH_3$,	2NSN-D_2

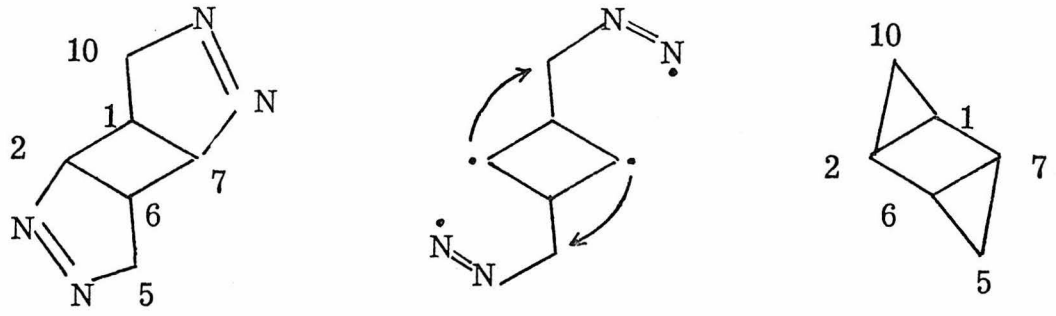
By the sequential bond cleavage mechanism a whole series of specific events must take place (see Scheme I below) if the cyclopropane is to be formed with only an inversion of stereochemistry at one carbon. After cleavage of the first carbon-nitrogn bond, a rotation of 90° must occur about the C-2, C-3 bond axis before a rotation about the C-1, C-2 bond axis occurs. The radical center then attacks the carbon containing the nitrogen fragment from the backside.



Scheme I

It is hoped that in the pyrolysis of 1-D_2 + 2-D_2 one can disrupt this pathway by generating a second alkyl radical so situated that it can attack the nitrogen containing fragment from the backside as soon as it is formed without a rotation, or else induce decomposition by backside attack on the

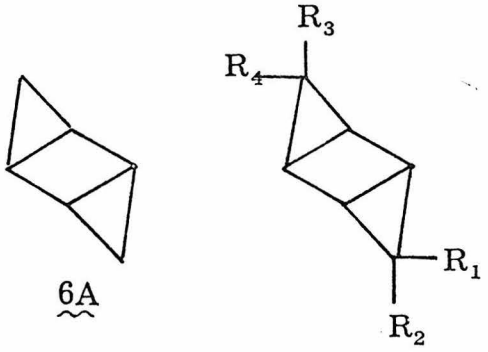
pyrazoline. The two radicals that can be formed from a bipyrazoline are identical except in their orientation with respect to the carbon containing the nitrogen fragment. This is illustrated for anti 1.



anti tricyclohexane (6)

The orientation is correct for the radical center at C-2 (generated from the pyrazoline fused to the cyclobutane at carbon atoms 2 and 6) to attack the nitrogen fragment on C-10 (which was part of the second pyrazoline ring) from the backside. Thus the expected formation of a bond between C-2 and C-5 may not be realized in this pyrazoline system.

Based on previous work bicyclic pyrazolines,[1c] 1A or 2A are expected to give initially anti tricyclohexane (6A) or isomeric anti 3,6-dimethyltricyclohexanes (7A), respectively.



6A

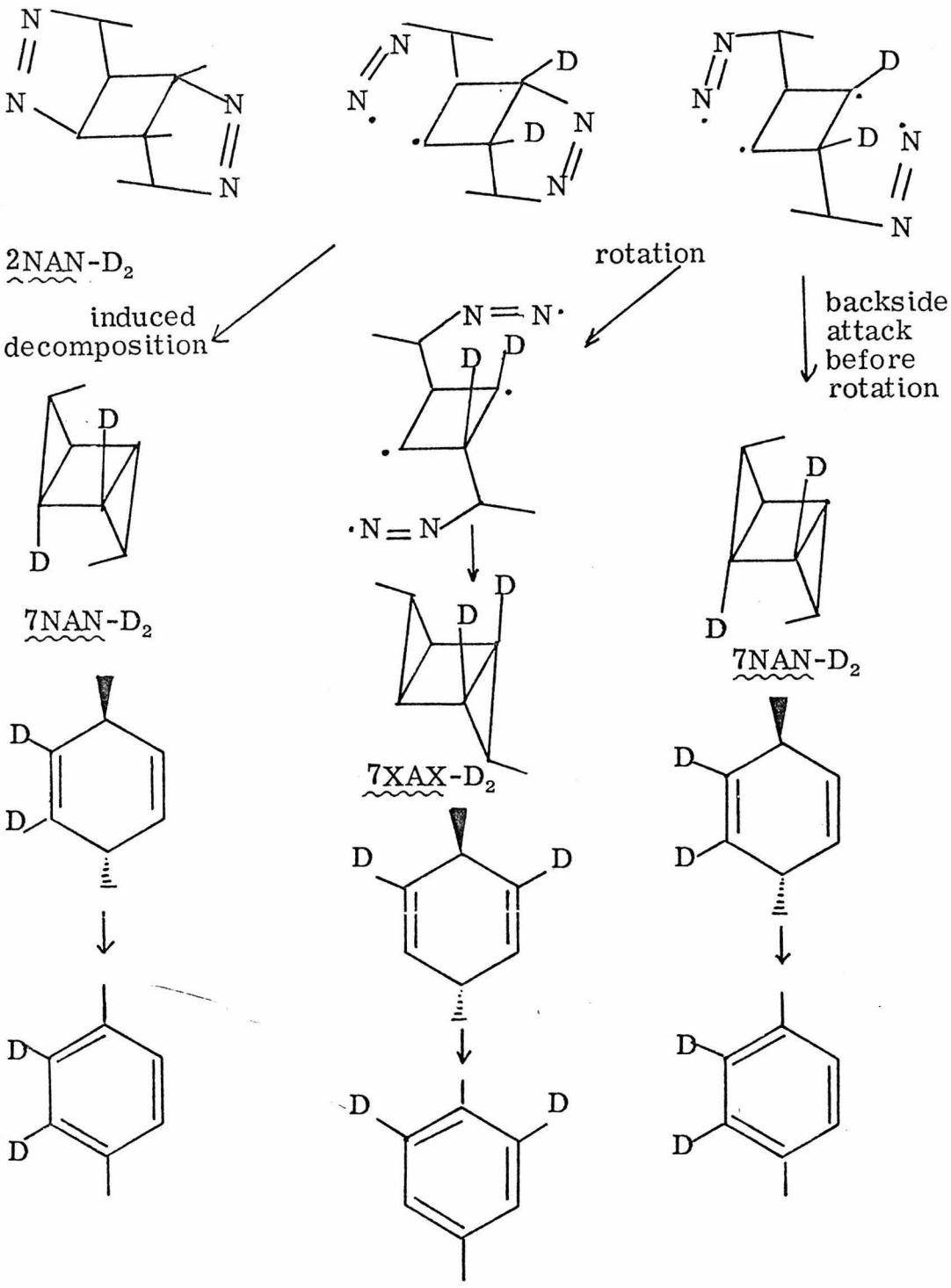
$R_1=R_3=CH_3$,	$R_2=R_4=H$,	7NAN
$R_1=R_3=H$,	$R_2=R_4=H$,	7XAX
$R_1=R_4=H$,	$R_2=R_3=CH_3$,	7XAN

Similar products are expected from 1S or 2S, except the initial tricyclohexanes will be in the syn conformation, 6S and 7S, respectively. It is expected that syn and anti 7 (or 6) will interconvert reversibly at high enough temperatures. Irreversible isomerization to 1,3 cyclohexadienes is also expected under more forceful conditions. However, 6 was found to be stable for two hr at 100°C, but after three hr at 150°, 50% of the orginal 6 was converted to 1,3 cyclohexadiene.[2]

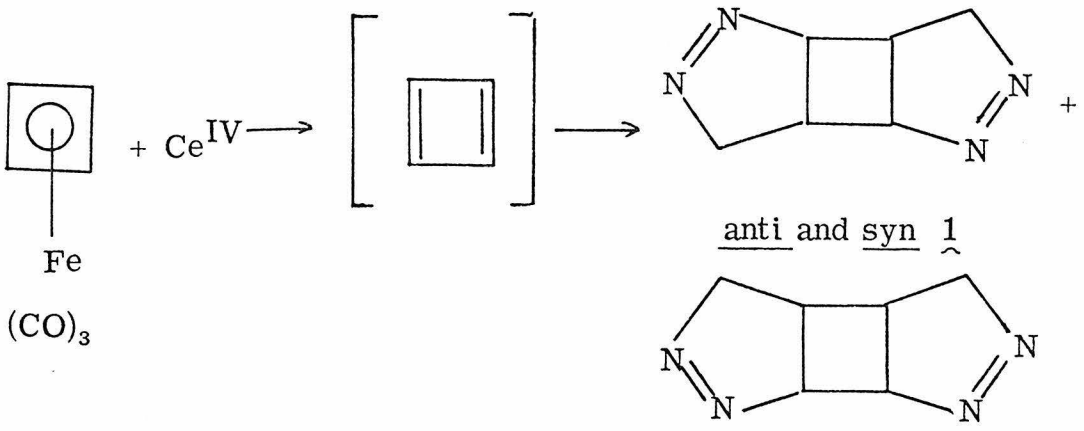
In Scheme II, the decomposition of 2NAN-D_2 by the two pathways is illustrated. If the bipyrazolines can be decomposed at low enough temperatures, so that the tricyclohexanes survive with their stereochemistry intact, it is expected that 2NAN-D_2 will give 1,2 dideuterio 7NAN if attack precedes rotation. On the other hand, if the two halves of the molecule decompose independently by the normal sequential cleavage mechanism, 1,5 dideuterio 7XAX is expected to be the major product.

However, from inspection of Scheme II, it is clear that even if the tricyclohexanes do not survive the reaction conditions, the deuterium label in the cyclohexadienes will still be able to delineate the two alternative mechanisms; backside attack after rotation will give 1,5-dideuterio trans 3,6-dimethylcyclohexa-1,4-diene while backside attack before rotation will give 1,2 dideuterio trans 3,6 dimethylcyclohexa-1,4-diene.

1 could presumably be synthesized by two 1,3 dipolar additions of diazomethane to cyclobutadiene.

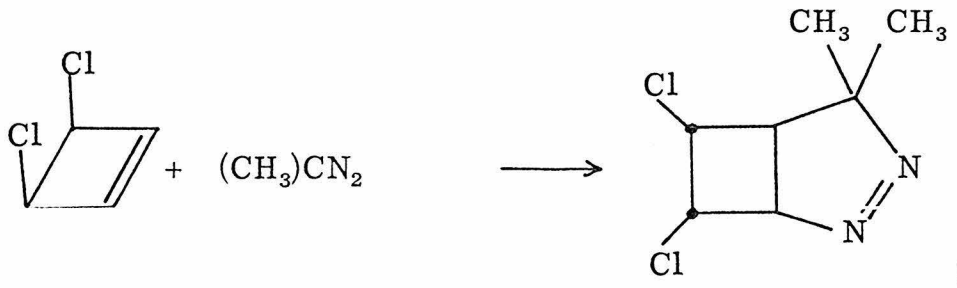

2NAN-D2
induced decomposition
rotation
backside attack before rotation
7NAN-D2
7XAX-D2
7NAN-D2

Scheme II



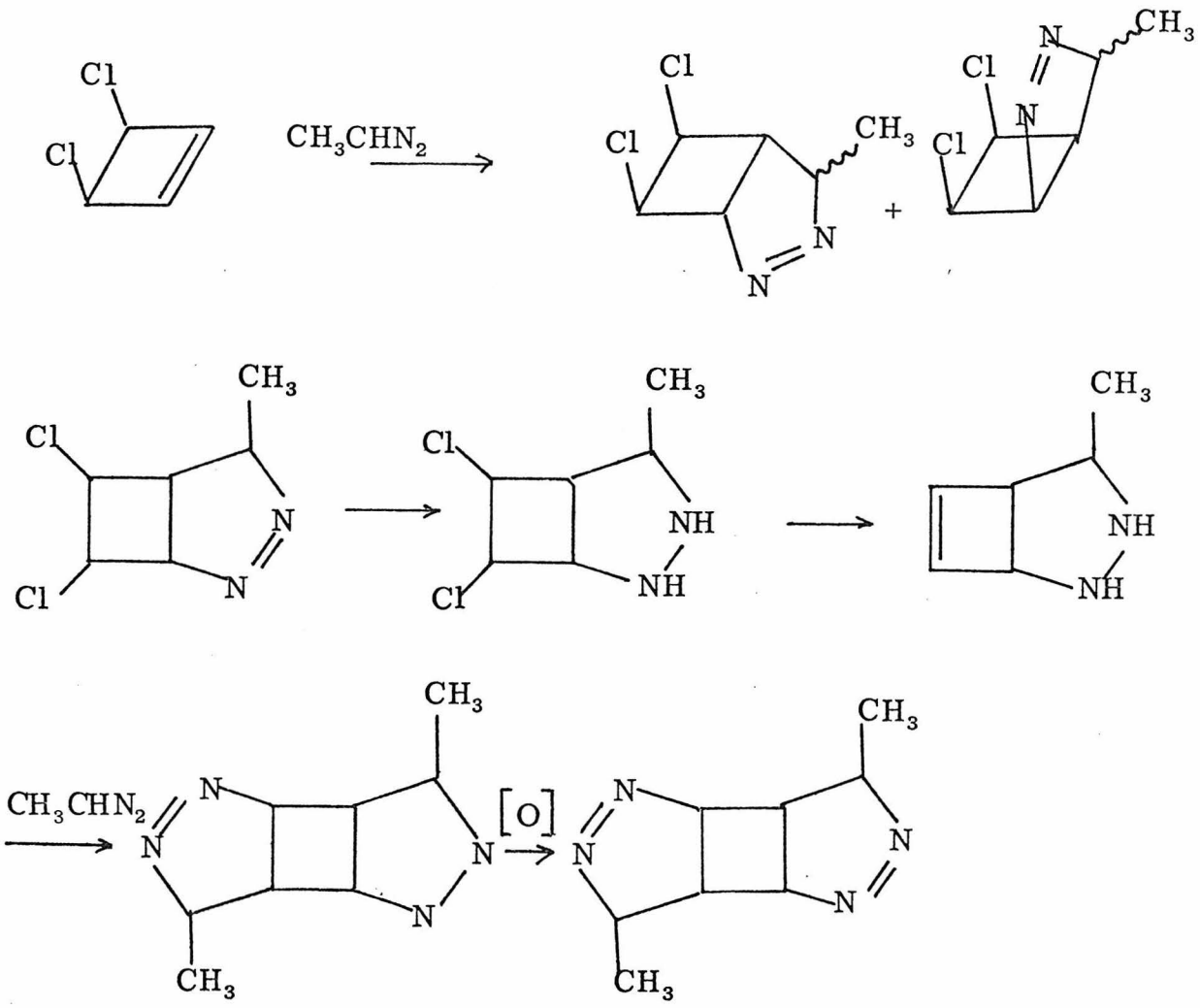
Pettit has shown that cyclobutadiene is a reactive ene.[3] Other substituted diazomethanes can be used in this reaction, however as many as 16 isomers of 2 could be formed.

A second route to 1 and 2 involves forming the pyrazoline skeleton one ring at a time, and separating the isomers in two stages.



Ref. 4

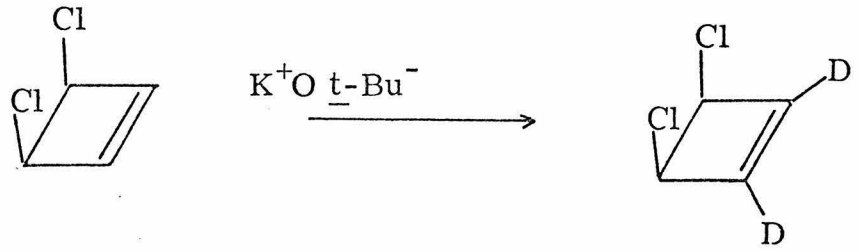
3 was prepared as shown by Franck-Neumann.[4] If diazoethane is used instead, this route provides an intermediate in the formation of 2 (see below).



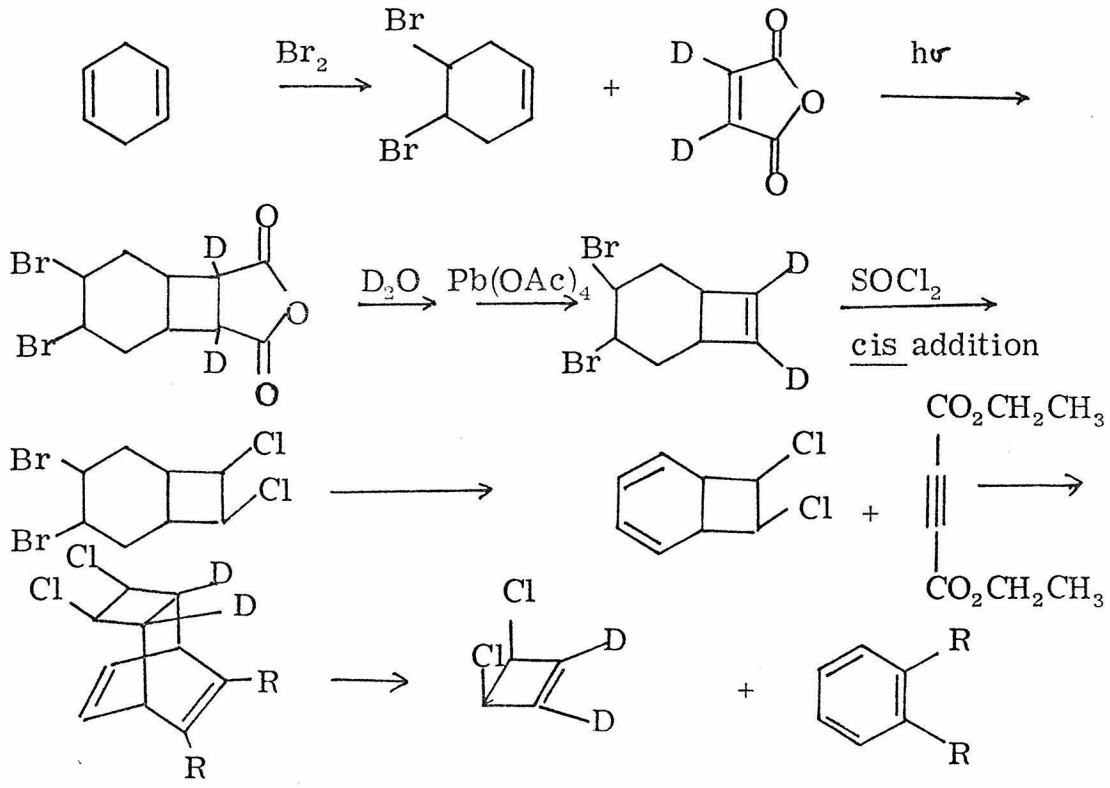
Azo compounds can be reduced catalytically or by diimine. Sodium borohydride and palladium-charcoal have been used to reduce pyrazolines.[2] 1, 2 Dichlorides have been converted to double bonds with Zn, Mg, iodide ions, phenyllithium, phenylhydrazine, or lithium aluminum hydride.[18] Oxidation of cyclic hydrazines to pyrazolines has been accomplished with oxygen,[5] cupric acetate,[5] silver oxide and mercuric oxide.[2,6]

Stereochemistry of isomers of 5 can be determined by the coupling constants of hydrogens at C-4 and C-5 [1b, 7] and by the coupling constants at hydrogens C-5 and C-6. Also, analogous behavior of 5 to 3 upon photolysis is expected (see Table III, Part I). [4] Stereochemistry of highly symmetric endo, anti, endo 2 (EAE 2) and endo, syn, endo 2 (ESE 2) can be determined by NMR signals and by knowing the stereochemistry of 5.

2-D_2 can be synthesized from labeled 4 as shown below.

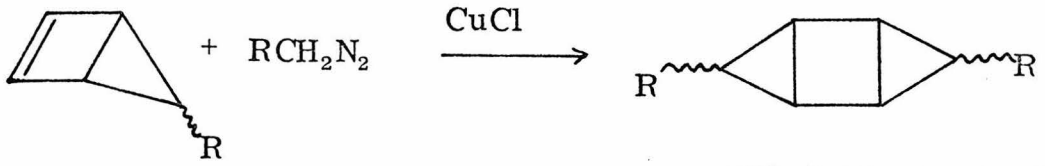


If this fails, a more roundabout route is available.



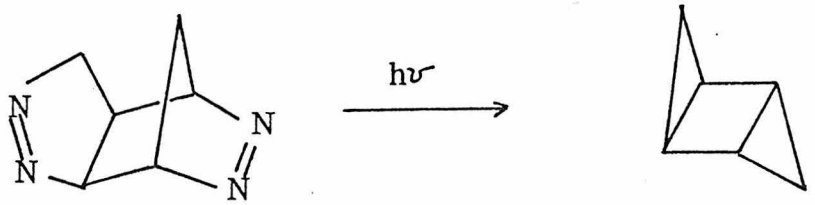
The Diels-Alder followed by a reverse Diels-Alder in the last two steps is the conventional method for synthesis of 3.[8]

Products can be synthesized independently by the method of Baldwin who prepared the parent compound 6 in 85% yield, by the reaction of diazomethane with bicyclopentene in the presence of cuprous chloride.[19]



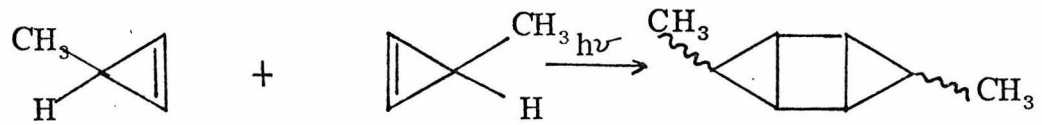
85% yield, R = H, (6)
R = CH_3, (7)

Allred and Hinshaw's synthesis of 6 can be utilized.[2]



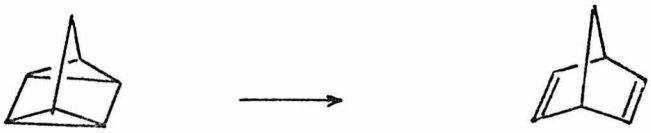
6

Photochemical dimerization of cyclopropenes have been shown to lead to tricyclo[3.1.0.$0^{2,4}$]hexanes.[9]

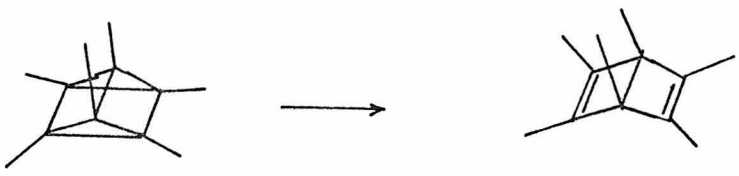


B. 1 may be a precursor to a new, interesting [10] annulene.

The internal cyclobutane ring of 1 may be cleaved to two ethylenes by reaction with an appropriate transition metal catalyst. Precedent is found for this reaction in the reversion of quadricyclene to norbornadiene in the presence of rhodium, palladium or platinum complexes,[10a] the isomerization of prismanes to Dewar benzenes by rhodium,[10b] and in the isomerization of cubane to syn bicyclobutadiene with a rhodium catalyst.[10c]

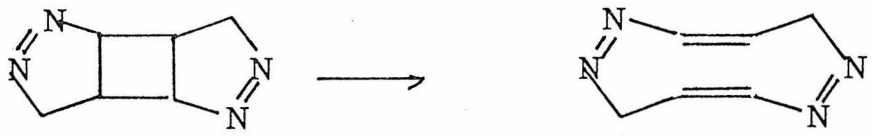


Ref. 10a

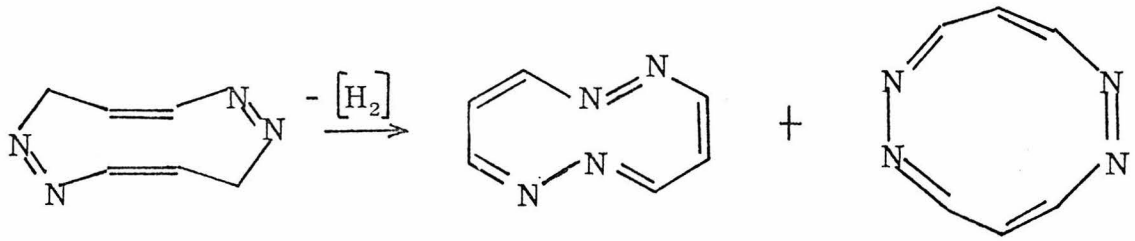


Ref. 10b

Ref. 10c

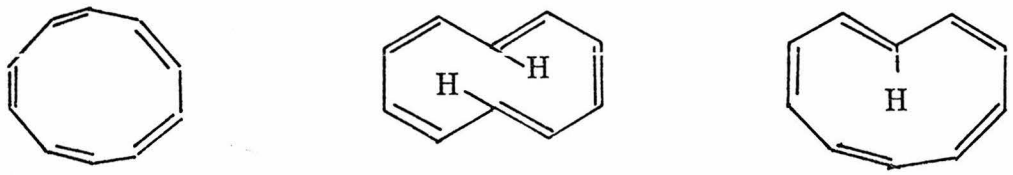


Oxidation of the tetraene to pentaene could lead to the stable [10] annulene (12).



di-trans 12 all cis 12

So far all attempts to isolate the all-carbon [10] annulene (13) analogous to 12 at room temperatures have proved fruitless, although [10] annulenes are predicted to be aromatic by the Hückel rule.[11] Attainment of planarity in [10] annulene is very unfavorable. Di-trans 13 has no bond angle strain but the 1, 6 hydrogens interact extensively. The all cis 13 in the planar configuration has a high degree of bond angle strain (internal angles = 144°).



all cis 13 di-trans 13 mono-trans 13

Mono-trans 13 appears to be the most stable based on experimental evidence, but inspection of models shows that it's planar form has both bond angle strain and steric interactions.

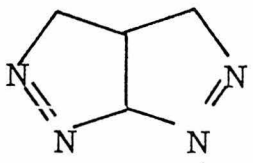
It is predicted that 12 should exist primarily in the di-trans

configuration since the 1, 6 hydrogen interaction will be alleviated.

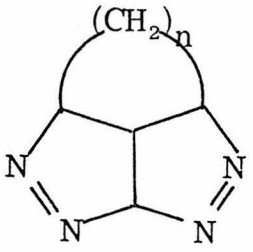
Physical properties of 12 can be determined by NMR and X-ray crystallography. These analytical tools should aid in ascertaining the aromaticity of 12 and in the determining of the planarity and nature of the double bonds (localization versus delocalization) in 12.

Friedel-Crafts acylation and nitration and electrophilic substitution experiments should also help in the determination of degree of aromaticity.

C. Bipyrazolines such as derivatives of 8, in which one of the carbon-carbon bonds is shared by each pyrazoline ring would be expected to have an interesting chemistry.

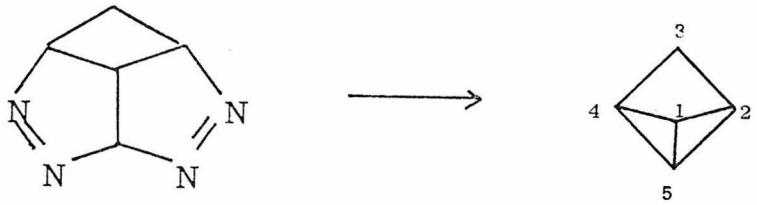


8



n = 1, 9 n = 3, 11
n = 2, 10

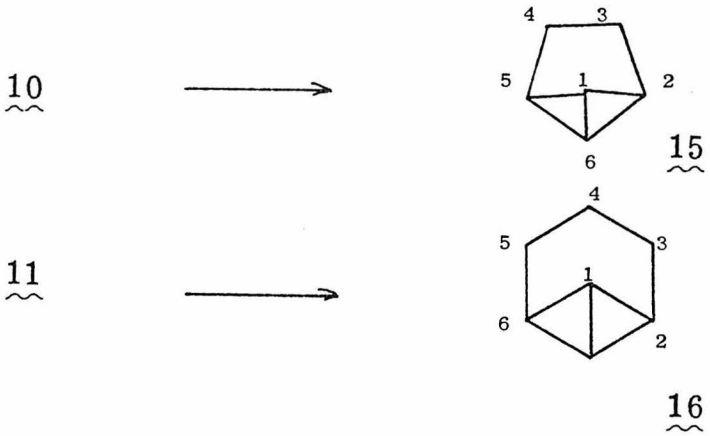
Decomposition of 9 by light or heat may lead to tricyclo-[2.1.0.$0^{2,5}$]pentane (14), an interesting molecule from a theoretical viewpoint because of its high degree of strain.



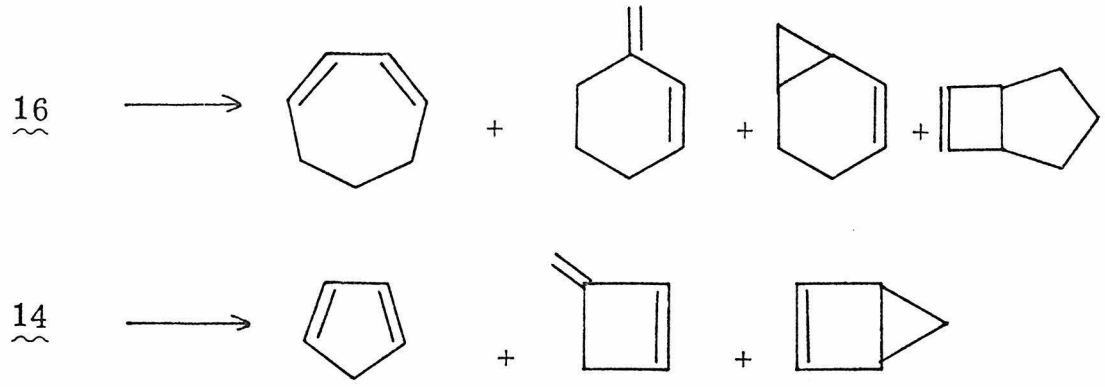
9 14

The parent compound has not been synthesized although the 1, 5 dimethyl-3-keto derivative is known.[12]

Similarly 10 and 11 might be expected to give tricyclo-[3.1.0.$0^{2,6}$]hexane (15) and tricyclo[4.1.0.$0^{2,7}$]heptane (16), respectively.

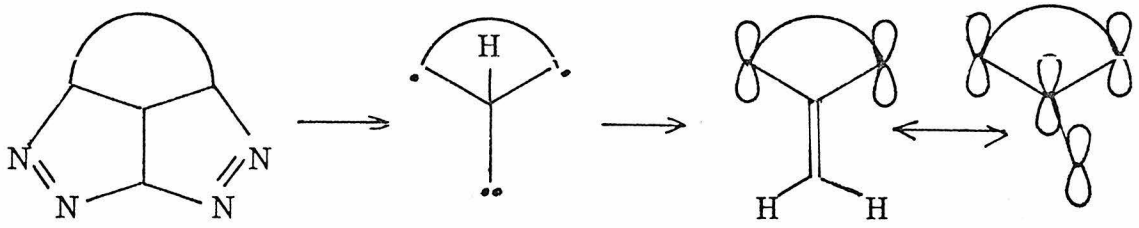


The isomerization of 14 and 15, both thermal and catalytic, should be interesting in light of the current research on the isomerization of bicyclobutane derivatives.[13] The rhodium and silver catalyzed reactions of 16 (and derivatives of 16) have resulted in a wide variety of products. The analogous products expected from 14 are shown below.

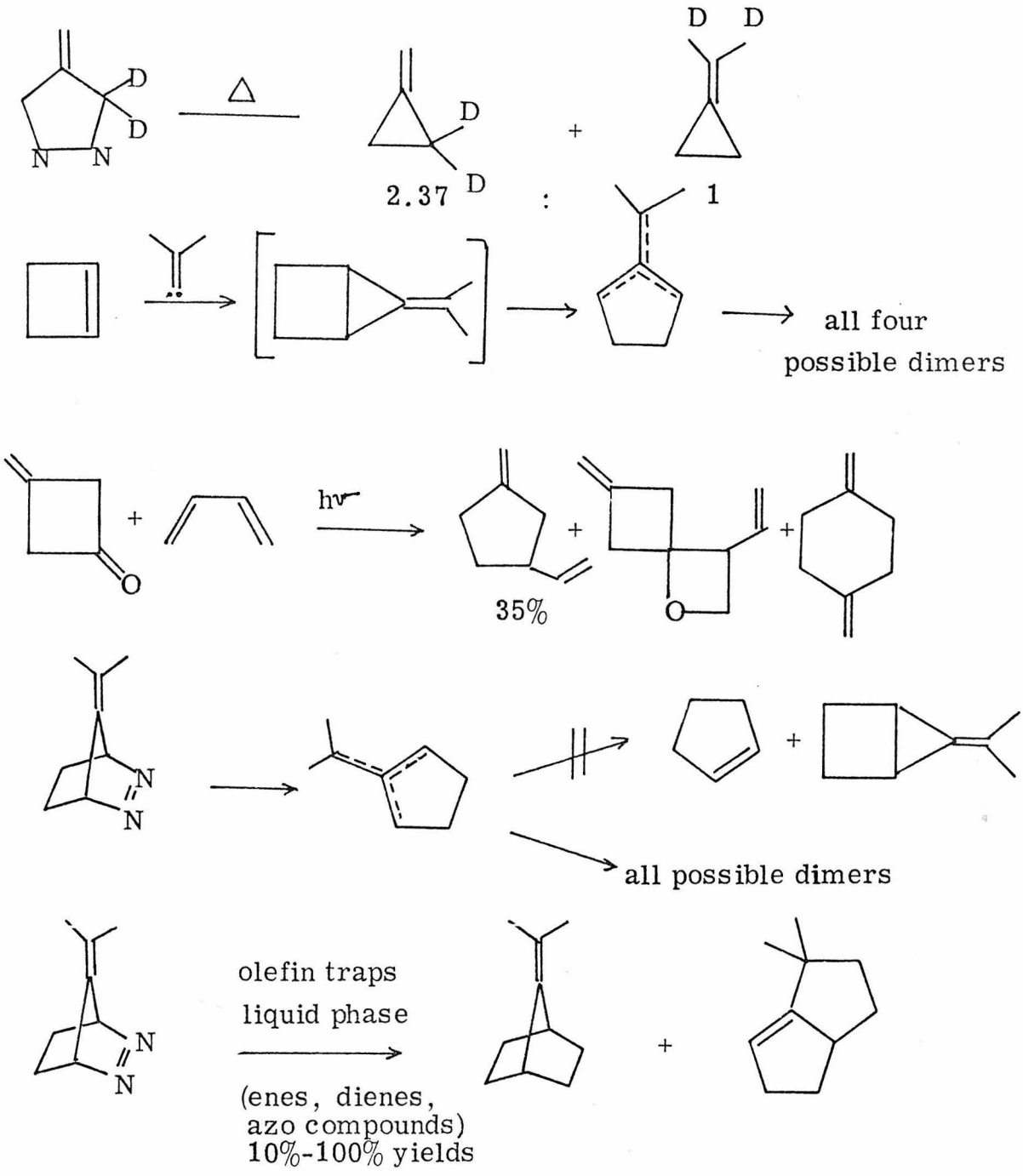


Product distribution from bicyclobutanes and derivatives of 16 show a marked dependence on transition metal catalyst, pH, solvent and substituents.

An alternative pathway is available to the decomposition of 9-11. Loss of N_2 will result in a diradical-carbene which may rearrange to a trimethylene methane diradical by a carbene insertion into a C–H bond.

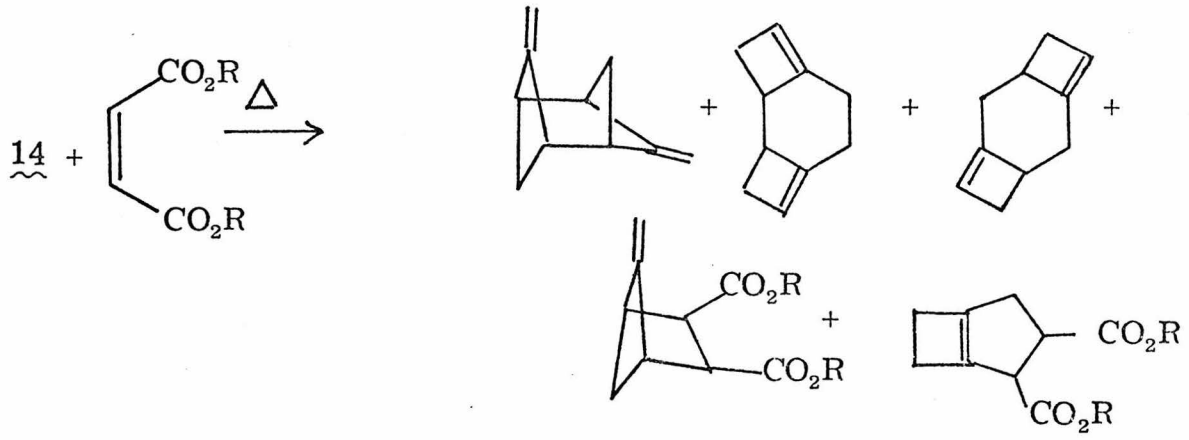


Typical reactions of trimethylenemethanes generated by other methods are dimerizations, formation of methylenecyclopropanes and addition to double bonds.[14]

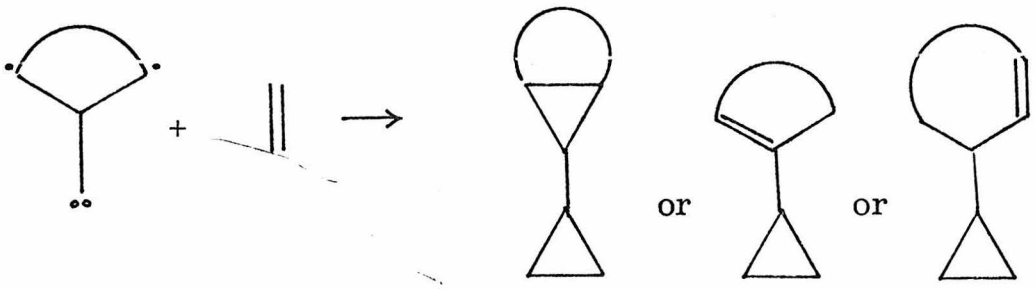


The last example above which decomposes thermally to a bridged trimethylenemethane has been shown by Berson to give dimers and add to a variety of double bond compounds rather than close to a strained

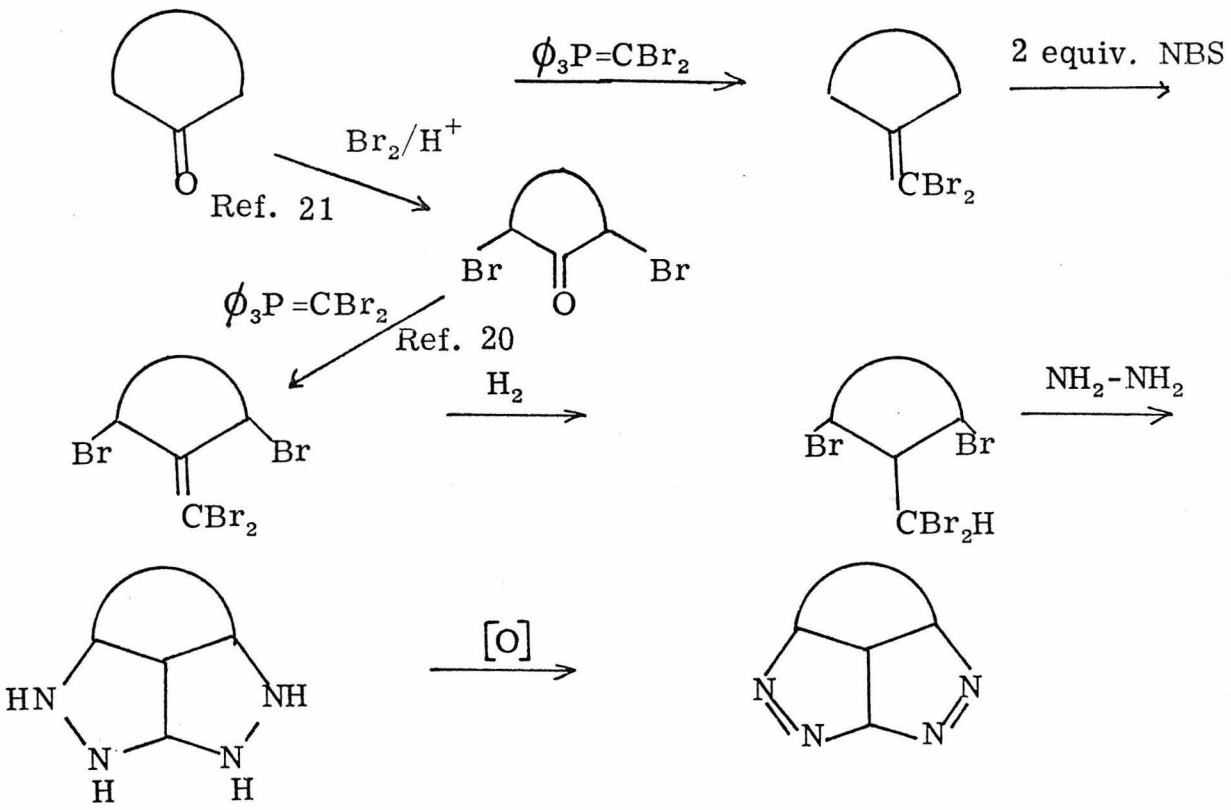
methylenecyclopropane. Decomposition of 14-16 in the presence of maleate and fumarate esters or fumaronitrile, compounds shown to be good traps for Berson's bridged trimethylenemethane,[15a] might compete with dimerization and lead to interesting compounds.



Another set of compounds that might be generated from 14-16 is by trapping of the diradical-carbene with an olefin.



The syntheses of 9, 10 and 11 are all based on the same general sequence of reactions.



The Wittig reaction has been used to prepare dibromo- and dichloro-methylenes from cyclohexanone [16a, c] and benzaldehyde. [16b] Wittig reaction on cyclobutanone derivatives are also known. [16d] Allylic brominations of vinyl halides have been carried [17b, c] out. There are examples in the literature of allylic brominations of methylenecyclobutanes. [17a] The reagents used for the oxidation to pyrazolines are listed in Part A of Proposition I. 1, 1, 3, 3, 3-Pentachloropropene has been prepared from trichloroethanal via the Wittig reaction. [20] 2, 6-Dibromo- and 2,6-dichlorocyclohexanones, and 1,1,3-trichloro-2-chloromethylpropene are known compounds. [20, 21]

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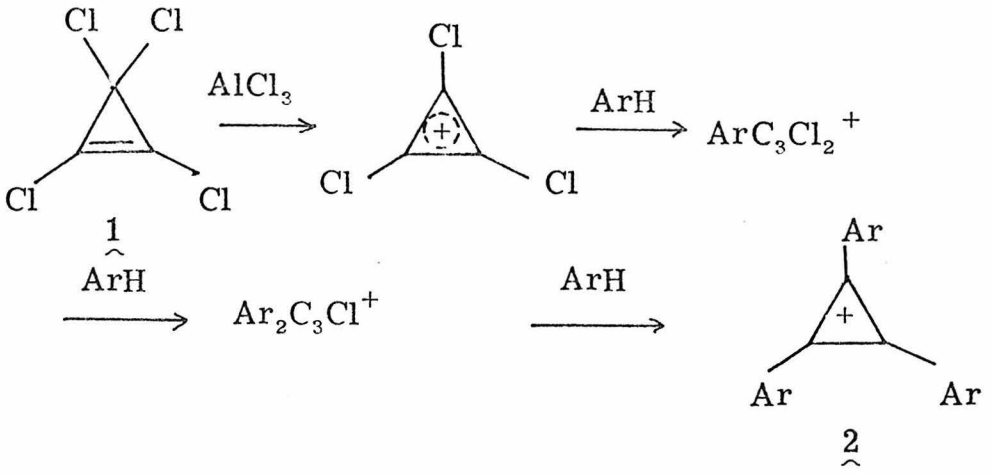
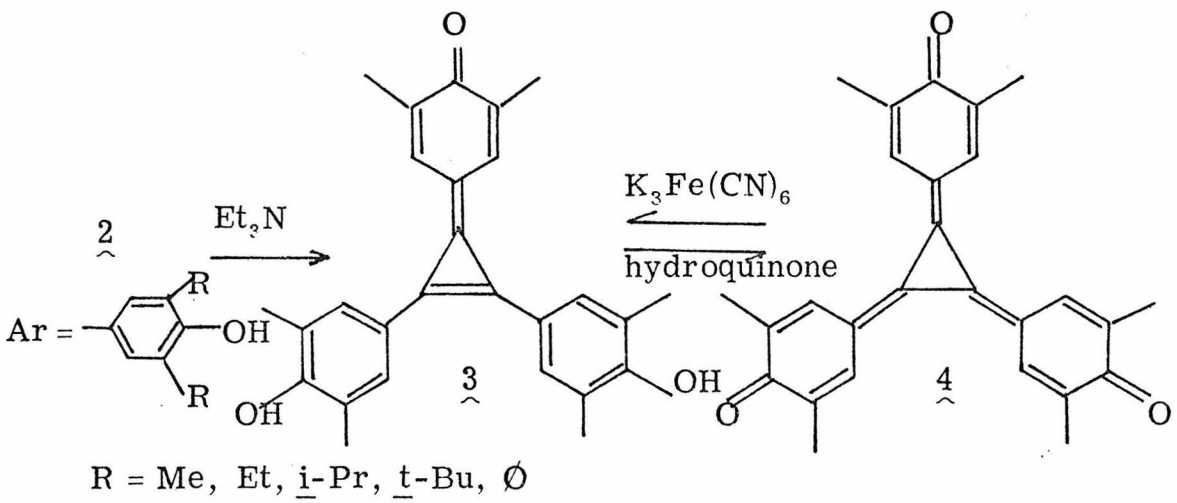
PROPOSITION II

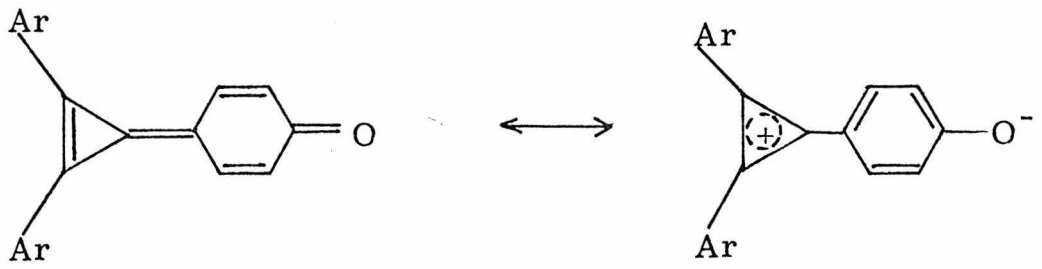
In 1970 R. West published the first of a series of papers on a new class of compounds, the highly symmetric triquinocyclopropanes.[1a] The preparation of these compounds was the culmination of work which started with the synthesis of trichlorocyclopropenium ion (1).[1b] It was found that this 2π aromatic ion will take part in Friedel-Crafts type reactions with benzenes and activated aromatic hydrocarbons to give successive aryl substitution which leads eventually to triarylcyclopropenium ion (2).[1c]



In particular, it was found that when phenols substituted in the 2 and 6 position were reacted with 1, the initial products are tris(hydroxyphenyl) cyclopropenium ions. These lose protons to form quinocyclopropenes 3 when treated with bases such as triethylamine. Oxidation of 3 with aqueous potassium hexacyanoferrate(III) solution gives triquinocyclopropanes (4).[1a]

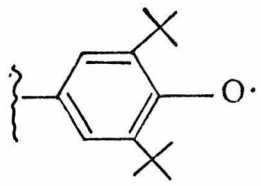


Diarylquinocyclopropenes (3) are isolated as brightly colored solids which change color as they are heated to their decomposition temperature (approx. 250°). In solution 3 are acid-base indicators. Diarylquinocyclopropenes are highly polar. The electronic spectra of these compounds show a bathochromic shift from polar to non-polar solvents which can be explained as resulting from a transition to an excited state that is less polar than the ground state. Such a ground state may have an ionic form involving the cyclopropenium ion.

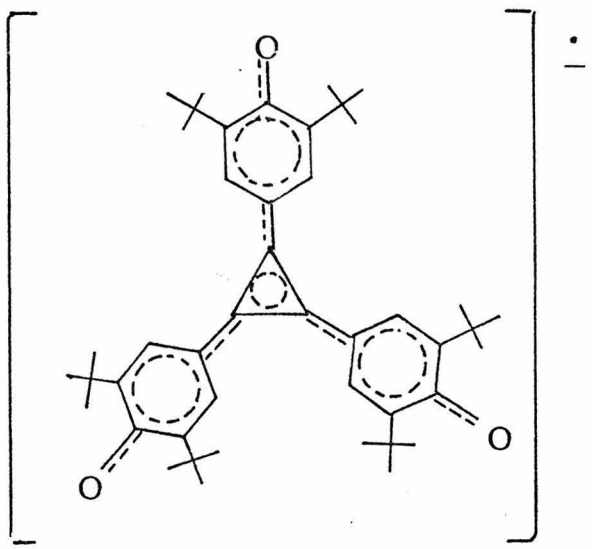


The triquinocyclopropanes(4)of West are purple compounds with zero dipole moment, hence they are soluble in non-polar solvents.

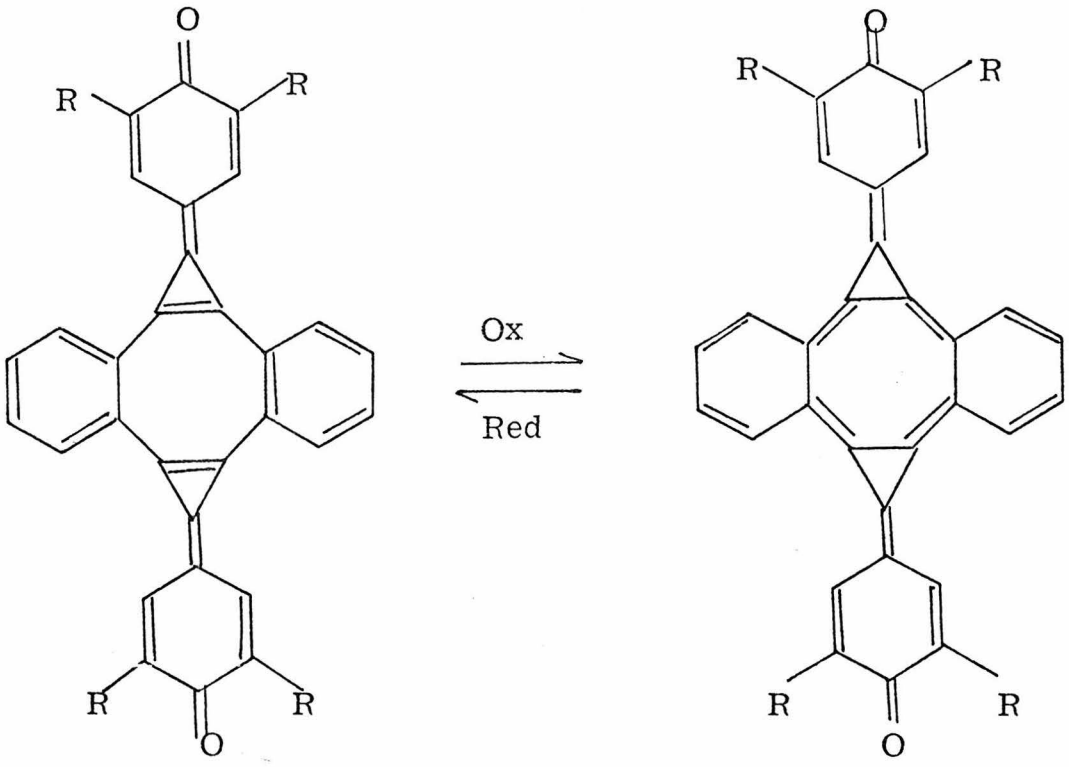
The IR consists of 6 bands. Stability of analogs of 4 increases with the bulk of the R groups on the phenol; 4 in which all R are t-butyl is stable to 250°C. ESR and magnetic studies show that the products are paired electron species (singlet ground state), but at temperatures near that which they decompose a thermally populated species which gives an ESR spectrum indicative of a phenoxyl radical is observed.



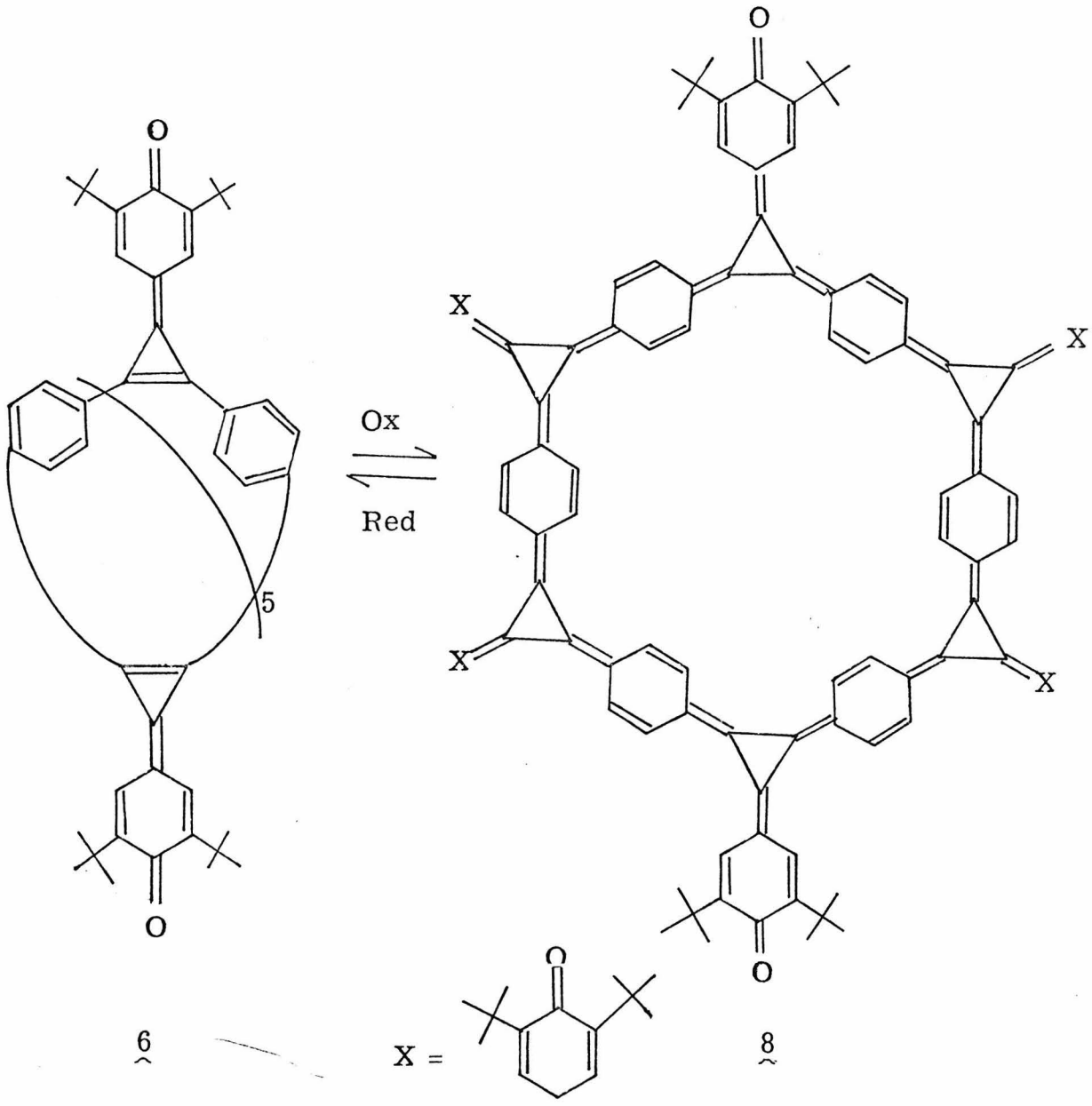
The anion radical of derivatives of 4 are generated by treatment of 4 with sodium-potassium alloy. The ESR spectrum of the anion radical of 4 where R = t-Bu consists of 7 lines which indicates the unpaired electron is totally delocalized.[1d]



It is proposed that two novel diarylquinocyclopropenes (5 and 6) and the corresponding triquinocyclopropanes (7 and 8) be synthesized and their physical properties be noted and compared with known members of this class of compounds.



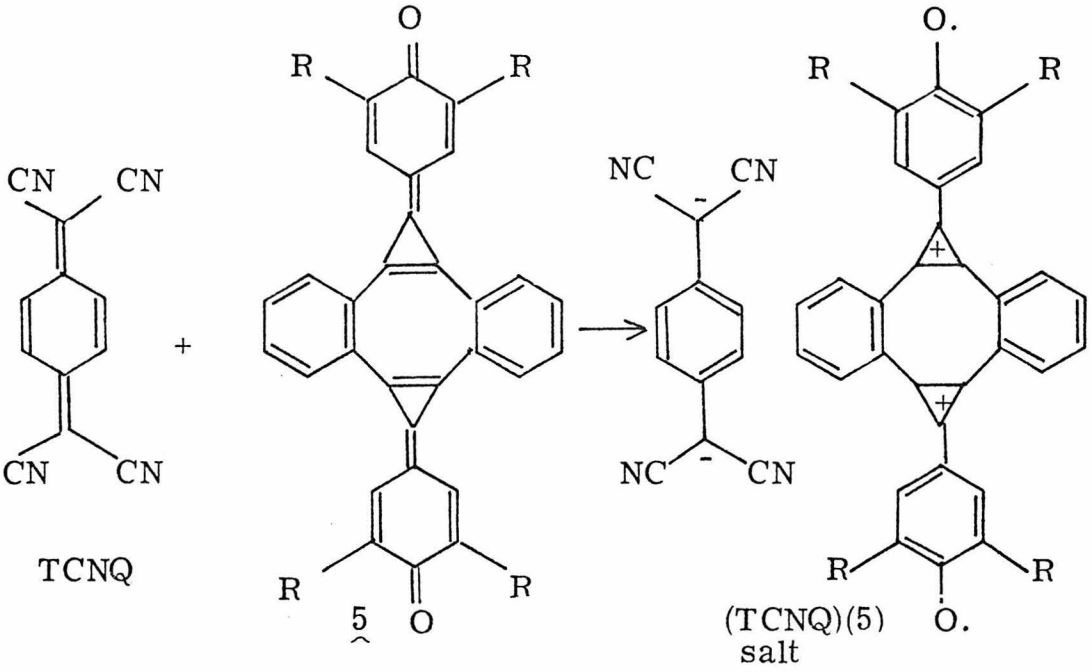
5 7



6 8

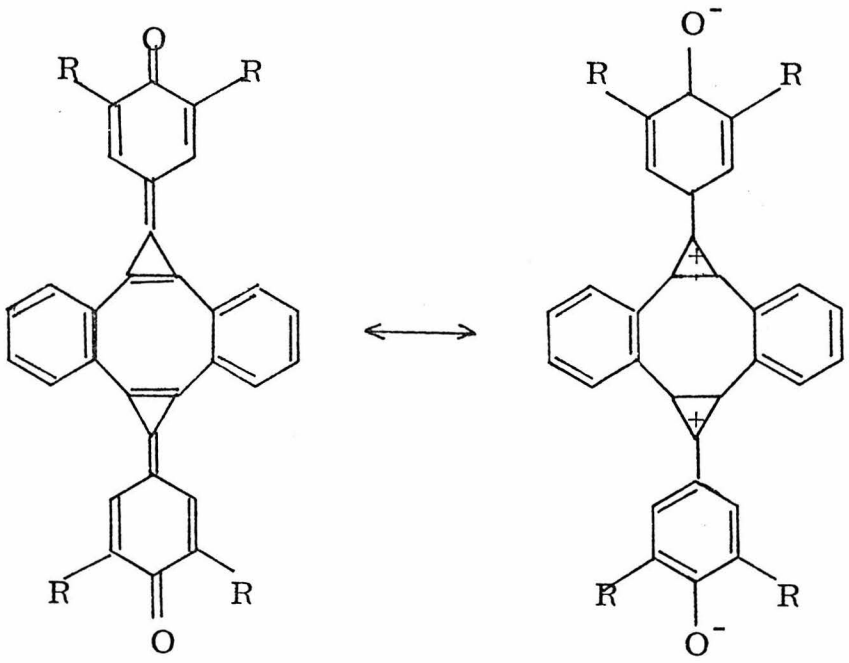
Compounds 5-8 because they are highly conjugated are expected to show an intense electronic absorption throughout the visible region of the spectrum. Possibly they can be used as dyes or potential sensitizers.

The geometry of 5 suggests that it may make an excellent π-donor in a charge transfer complex. Recently crystals of a charge transfer complex of tetrathiofulvalene (TTF) and tetracyanoquinodimethane (TCNQ) were found to be superconductors at 58°K.[2]

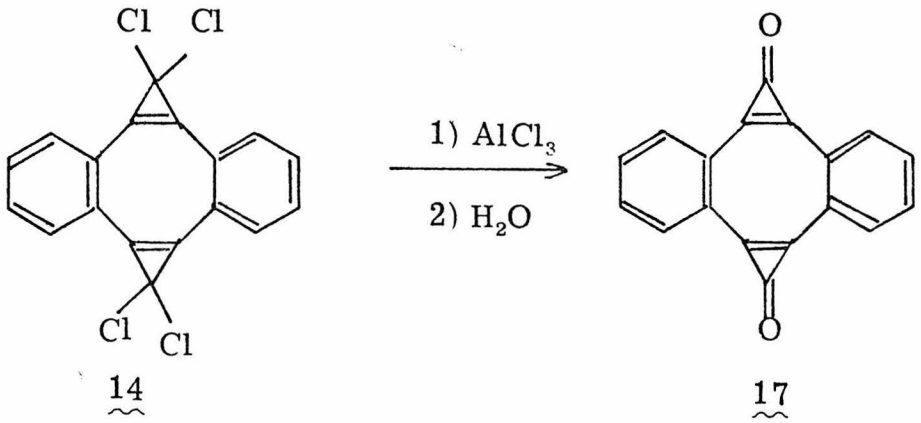


Most metals have been cooled to within a few degrees of absolute zero to become superconductors, and the highest temperature at which superconductivity has been found for compounds of several metals is 20.8°K. Any class of organic compounds that superconduct at liquid nitrogen temperatures would be a significant advance beyond superconductors cooled with liquid helium.

Like other diarylquinocyclopropenes, 5 is expected to have a large amount of ionic character.[1a] This can be exploited in forming the charge transfer complex. The geometry of 5 and TCNQ are such that maximum amount of electrostatic attraction is possible.



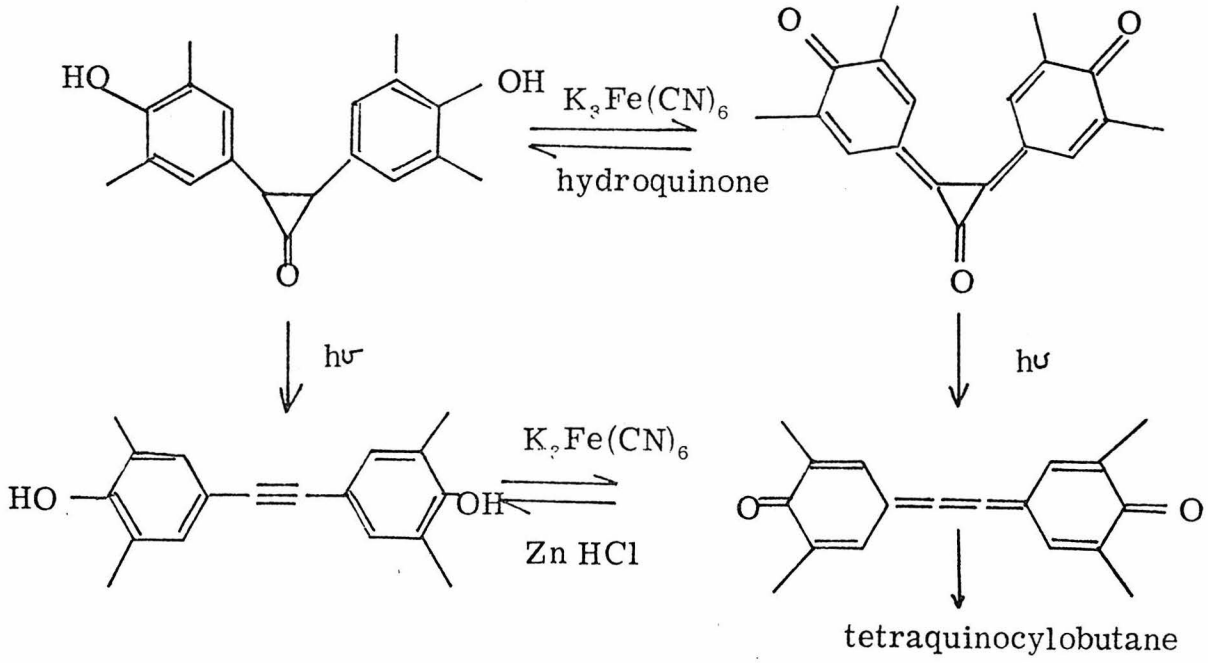
Another bonus from this study may be the synthesis of new cyclopropenones. The reaction of 14 with $AlCl_3$ to form the dication followed by quenching with water should give the diarylcyclopropenone 17, in analogy to the known chemistry of other diarylcyclopropenones.[1e]



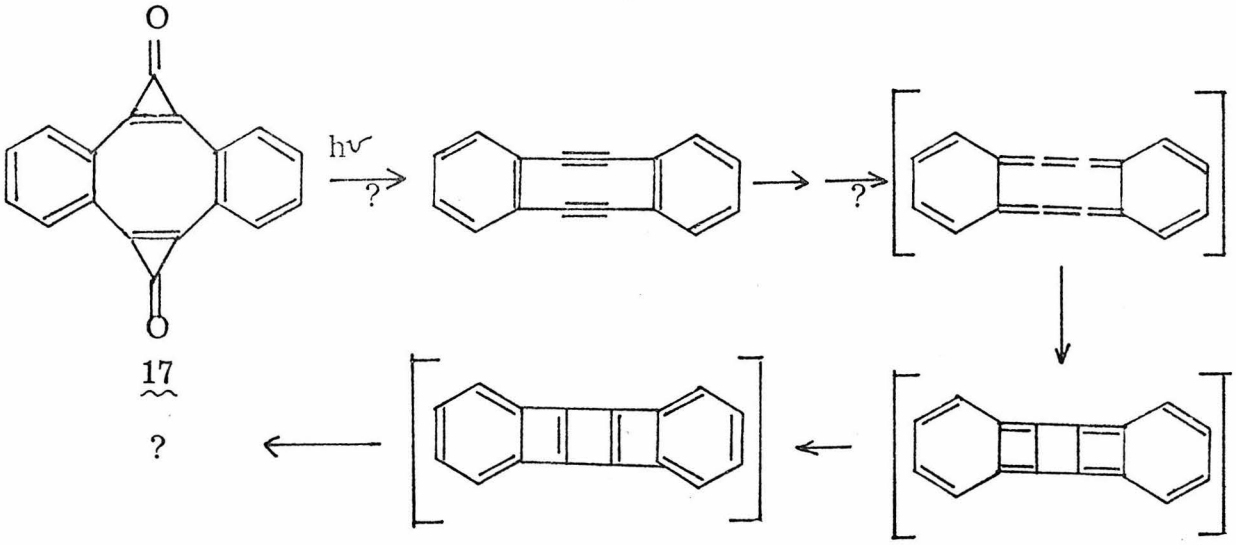
14 17

Similarly, from the cyclic diaryldichlorocyclopropene precursor to 6 may be isolated the corresponding cyclic cyclopropene.

Photolysis of simple diarylcyclopropenones results in the formation of diphenylacetylenes in excellent yields, which can be oxidized to diquinoethylene.[1e] Diquinoethylenes can also be obtained from the thermal decomposition of diquinocyclopropanone.



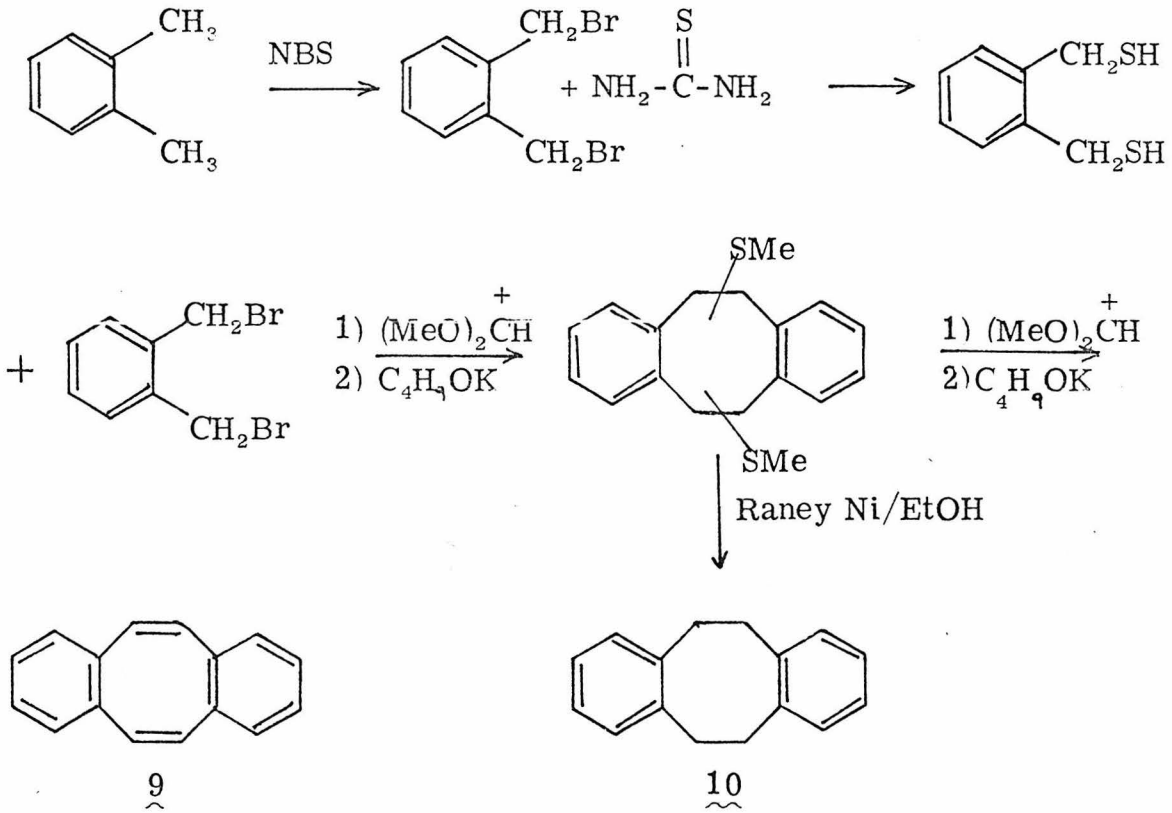
Diquinoethylenes dimerize thermally to give tetraquinocyclobutane.[1e] The photochemistry and oxidation of 17, although because of steric interactions it may not be completely analogous to simple diarylcyclopropenones, may be equally as interesting.



17

?

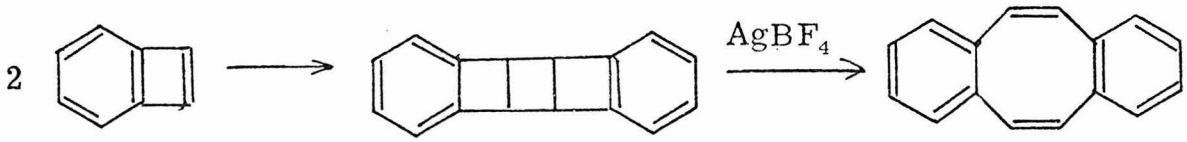
The synthesis of 5 procedes through a dichloro dibenzocycloocta-tetraene which can be obtained in several ways.



9

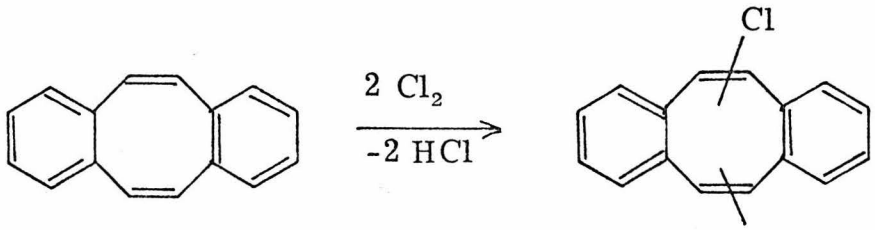
10

All of the above reactions have been carried out by Boekelheide et al. except derivatives of meta or para xylenes were used instead of ortho xylene.[3a, b] Boelkelheide obtained [2.2] metacyclophanes, [2.2] metaparacyclophanes and [2.2] metacyclophane-1,9-diene by this method. If the reaction sequence is successful for dibromoxylene as a starting material, an added bonus from this study will be a new means of obtaining dibenzocyclooctatetraene (9) currently available only from the dimerization of benzocyclobutadiene.[4]



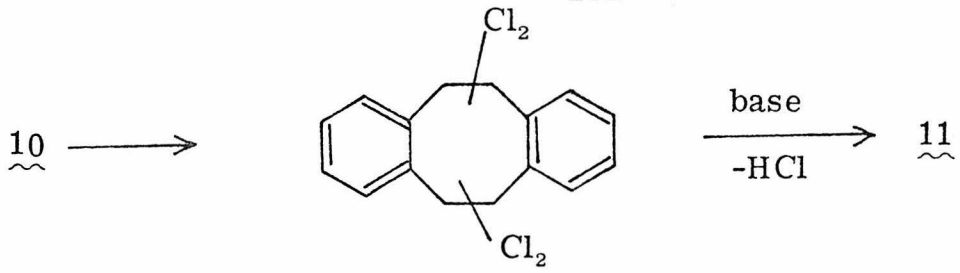
9

Addition of two moles of Cl_2 to the double bonds of 9 followed by loss of two moles of HCl should result in the necessary dichloride 11.

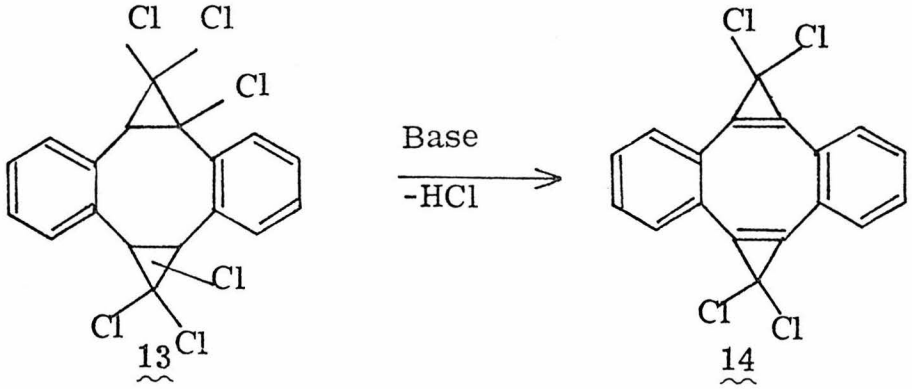


9 11

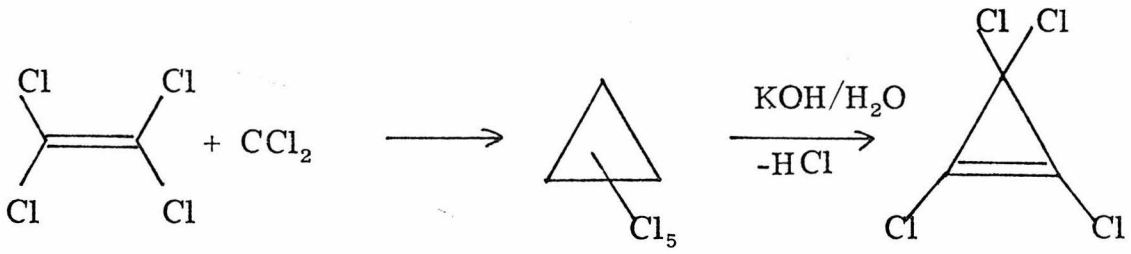
On the other hand, allylic chlorination of 10 will lead to the tetrachloride 12. Precedent is found in the allylic halogenation of [2.2] paracyclophane which gives all 4 possible tetrahalo [2.2] paracyclophanes.[5]



Addition of dichlorocarbene to 11 followed by base elimination of HCl should result in the formation of 14.

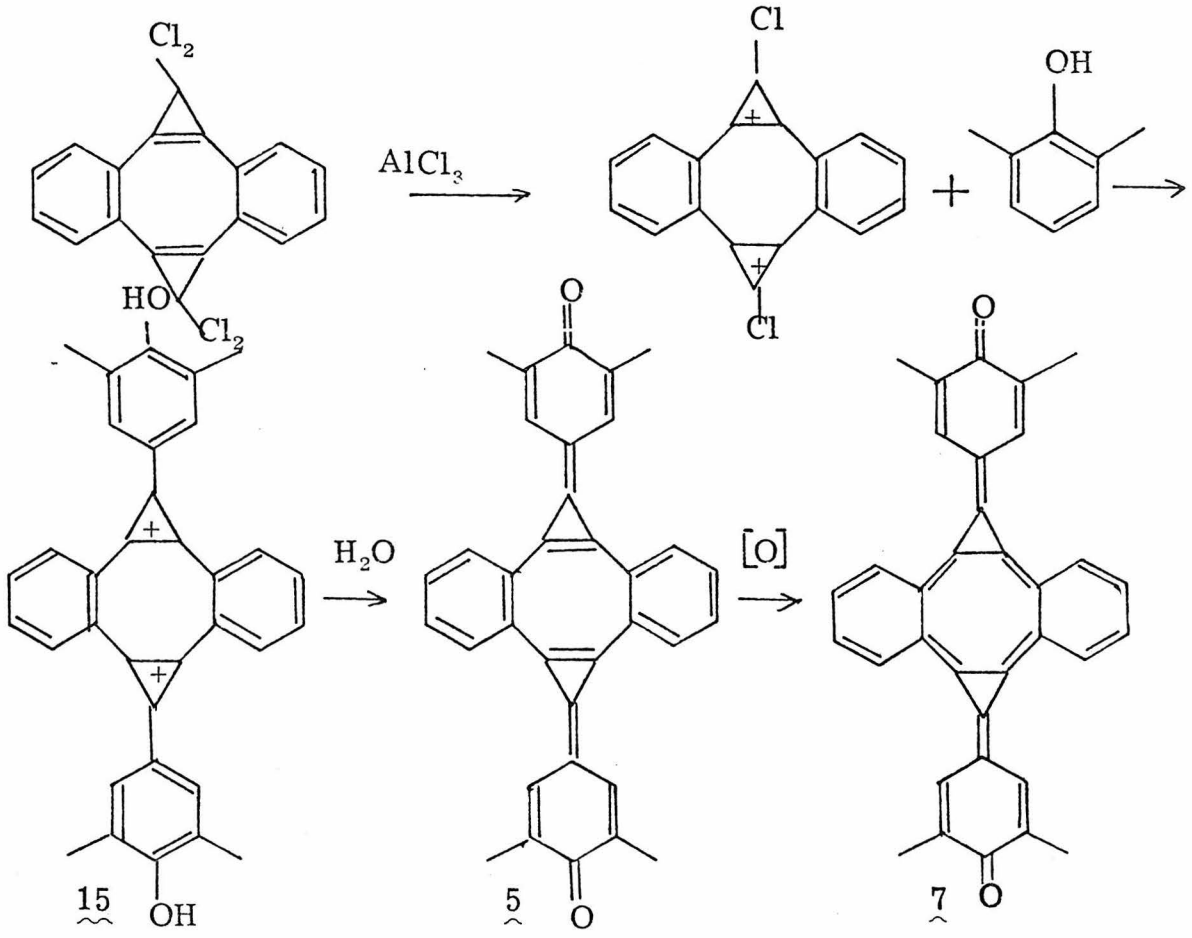


Precedent is found in the preparation of tetrachlorocyclopropene. The sodium salt of trichloroacetic acid was decomposed in dry glyme in the presence of trichloroethylene to give pentachlorocyclopropane which eliminated HCl in an aqueous KOH solution.[6]

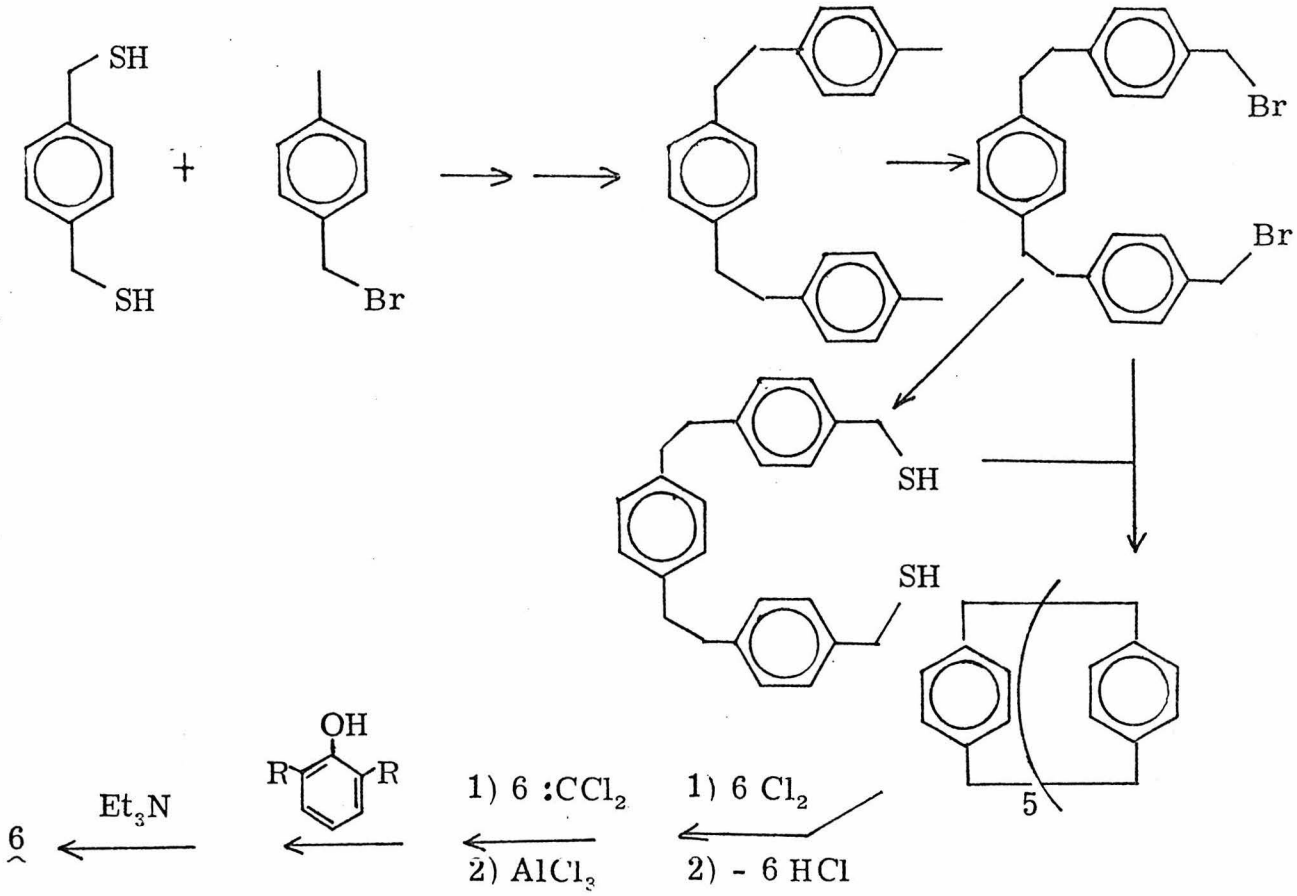


Successful additions of dihalocarbene to phenylsubstituted ethylenes have been carried out.[7]

Once the 3, 3 dichloro-1, 2-diphenyl substituted cyclopropenes are synthesized, the triquinocyclopropanes are formed by reaction with aluminum trichloride in the presence of 2, 6 substituted phenols followed by quenching with H_2O. The reaction between cyclopropenium cation and the aromatic ring is viewed as a Friedel-Crafts alkylation involving electrophilic substitution on the ring. Oxidation of the methylene cyclopropene with $K_3Fe(CN)_6$ should lead to 7. Substituents on phenol can be aryl or alkyl.[1a] The last sequence of steps is the method of West for preparing triquinocyclopropanes from 1, 2-diphenyl-3, 3-dichlorocyclopropene.[1c]



The synthesis of 8 is similar to that of 7. The method of Boekelheide is used to construct a skeleton of para substituted benzene rings linked by dimethylene bridges.[3a, b]



The key intermediate 16 is treated as 10 was before to give 6 and 8.

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1. (a) R. West and D. C. Zecher, J. Amer. Chem. Soc., 92, 155 (1970); (b) S. W. Tobey and P. West, ibid., 86, 1459 (1964); (c) R. West, D. C. Zecher, and W. Goyert, ibid., 92, 149 (1970); (d) R. West and D. C. Zecher, ibid., 92, 161 (1970); (e) D. C. Zecher and R. West, ibid., 89, 153 (1967).

2. W. D. Metz, Science, 180, 1041 (1973) and references therein.

3. (a) R. H. Mitchell and V. Boekelheide, J. Amer. Chem. Soc., 96, 1547 (1974); (b) V. Boekelheide, P. H. Anderson, and T. A. Hylton, ibid., 96, 1558 (1974).

4. R. Pettit and W. Merk, ibid., 89, 4487 (1969).

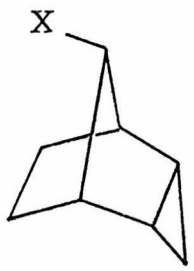
5. D. J. Cram, Record of Chem. Prog., 20, 71 (1959).

6. S. Tobey and R. West, Tetrahedron Lett., 1179 (1963).

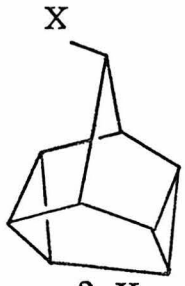
7. J. H. Davis, unpublished results.

PROPOSITION III

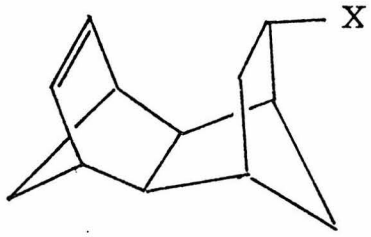
The efficiency of cyclopropane rings and double bonds in providing anchimeric assistance to the solvolysis of various compounds has received a great deal of attention of late.[1] The degree of assistance of a group depends on its orientation with respect to the reaction center. Examples of various systems which have been studied and their relative rates of solvolysis are given in Table I.



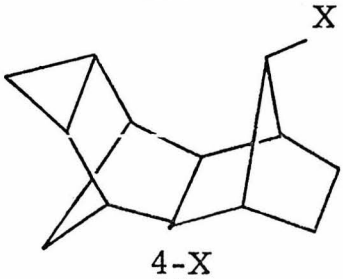
1-X



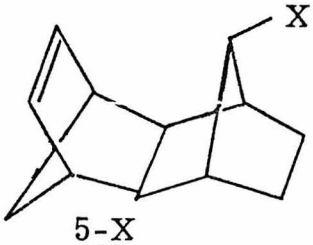
2-X



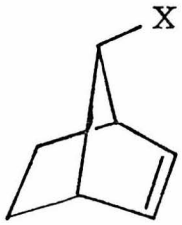
3-X



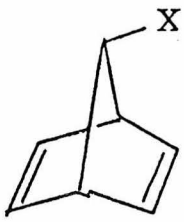
4-X



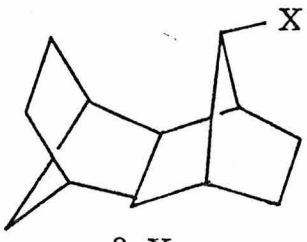
5-X



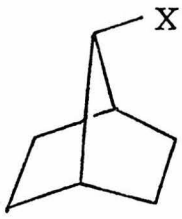
6-X



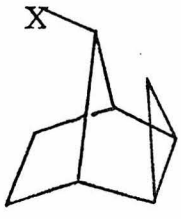
7-X



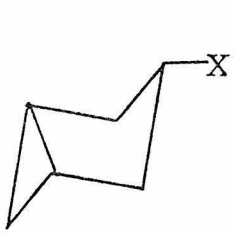
8-X



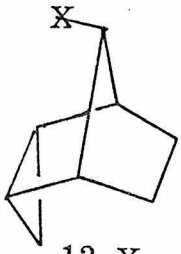
9-X



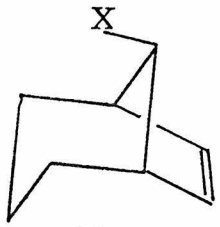
10-X



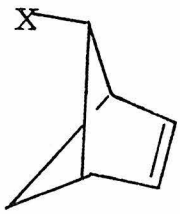
11-X



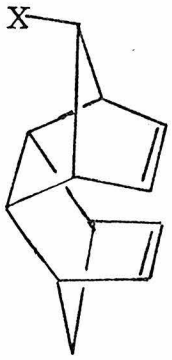
12-X



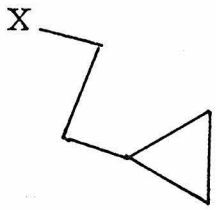
13-X



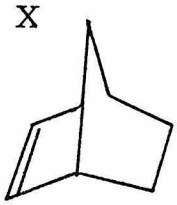
14-X



15-X



16-X



17-X

X = leaving group; tosylate (TsO), brosylate (BsO), acetate (AcO), dinitrobenzoate (DNBO), etc.

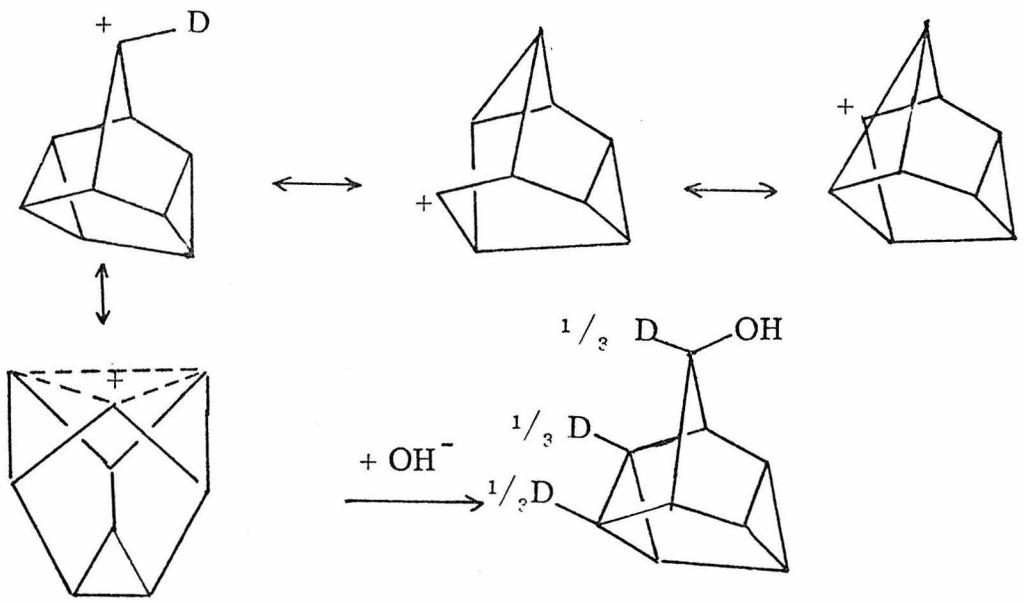
Table I: Relative Solvolytic Rates of Some Esters

Compound	1	2	3	4	5	6	7	8
Rel K (25°)	10^{14}	10^{12}	$10^{13.3}$	$10^{8.2}$	$10^{10.6}$	$10^{11.1}$	10^{14}	$10^{3.6}$
Ref.	1a, b	1c	1ℓ	1d	1e	1f	1f	1g
	9	10	11	12	13	14	15	17
	10^{0}	$10^{0.4}$	10^{8}	$10^{2.4}$	$10^{8.3}$	$10^{14.7}$	$10^{14.4}$	10^{6}
	1f	1k	1a, b	1b	1i	1j	1n	1f

From inspection of Table I, one can see that increasing rigidity of the system increases the rates of solvolysis (compare 1-X, 11-X and 16-X; in 16-X there is no neighboring group assistance compared to ethylbrosylate [1m]). Orientation of the cyclopropane ring is very important (compare 1-X and 10-X, and 1-X and 12-X). Participation of the π lobes of double bonds seems to be a sensitive function of puckering of the five-membered ring in the bicyclo [X.2.1] series, e.g., 13-X, 6-X and 14-X. The rate is always greater when the leaving group and the neighboring group which lends anchimeric assistance are on opposite sides of the methano bridge (compare 17-X and 6-X and 1-X and 12-X). This can be explained in terms of an intramolecular displacement reaction involving nucleophilic attack by the electrons of the neighboring group from the back side.

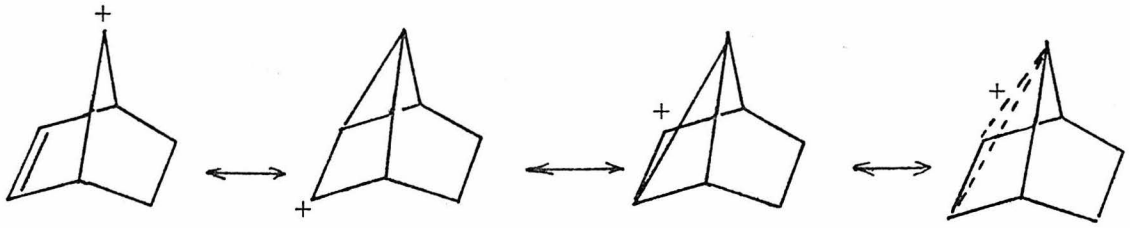
Large rate enhancements are observed even if the group lending assistance is located 4 bonds (5 atoms) from the reaction site if the stereochemical arrangement is correct, e.g., 3-X, 4-X and 5-X.

Of equal interest are the electron sufficient non-classical carbonium ions which are intermediates in these reactions. In these ions the positive charge is delocalized over three(or more) carbon atoms, for example, the ion derived from 2-X consists of the following resonance forms.



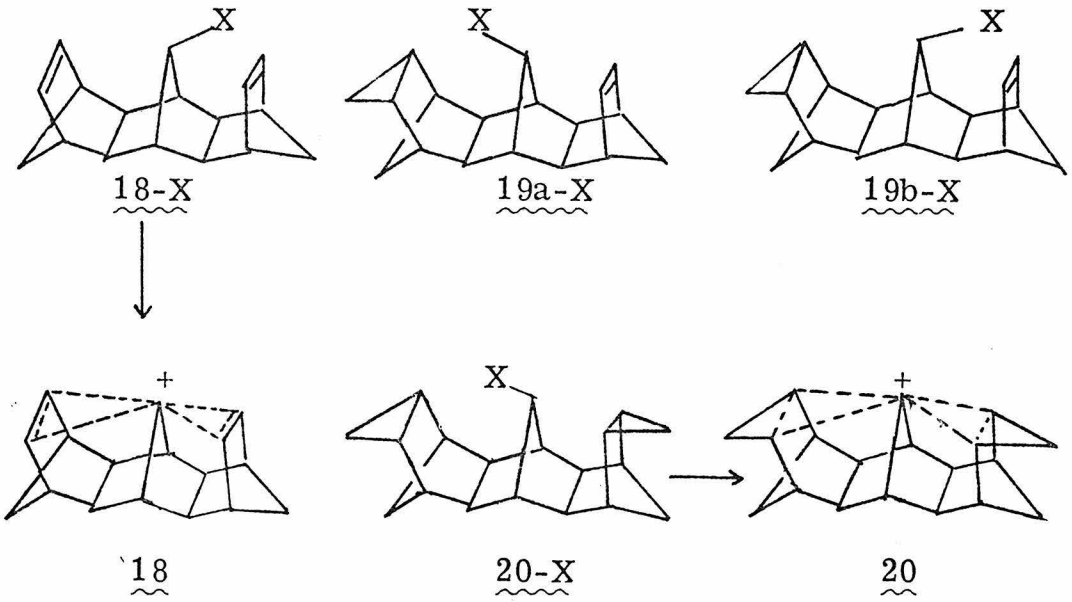
When 2-X was labeled with D on the carbon containing X and solvolyzed to 2-OH, the label was found to be equally distributed over the three equivalent positions.[1c]

Similar resonance forms can be written for the delocalization of cations containing double bonds.



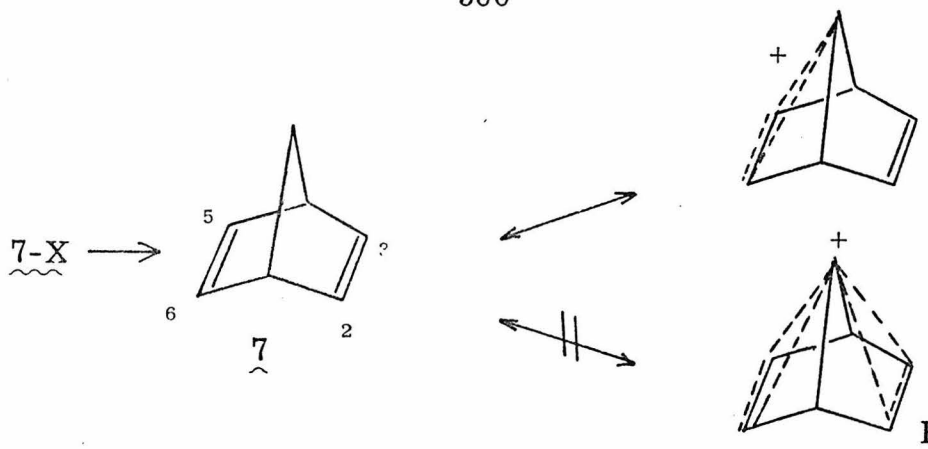
It is proposed that 4 new compounds 18-X, 19a-X, 19b-X and 20-X be synthesized and their rates of solvolysis and the new class of

cationic intermediates expected be studied. This study should provide additional information about the phenomena of delocalized non-classical carbonium ions.



The non-classical carbonium ions from 18-20-X are expected to delocalize the charge over 5 carbon atoms. Other compounds have been studied which possess the potential for this extended delocalization.

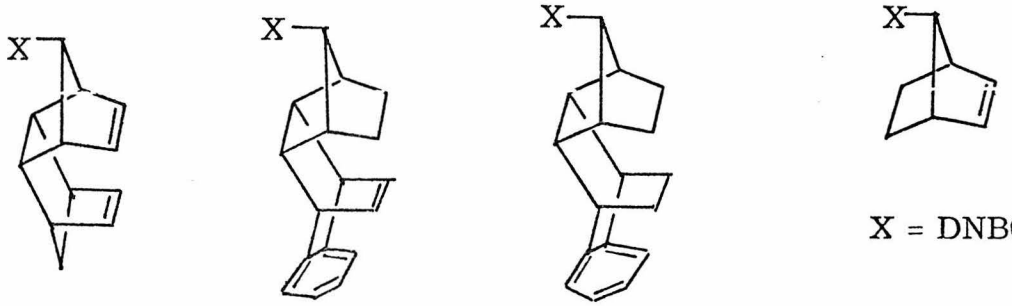
The cation derived from 7 has been examined in SO_2 by NMR. The 2 and 3 protons were found not to be identical to the 5 and 6 protons, thus it is concluded that there is an interaction between the charged carbon and a single double bond in this molecule.[2]



Ref. 2

The cations 18-20 and 15 are examples of species endowed with laticyclic topologies comprised of more than two ribbons.[3] Using the extended Hückel rules of Hoffmann, it is predicted that cation 18 should be more stable than 15.

In fact, 15 and 21 have been studied by Allred and Hinshaw,[1h] and Paquette and Dunkin,[4] respectively. It has been found that there is no enhancement of the rates of solvolysis of 21-X over a suitable model compound (22-X).[4]



	15-X.	21-X	22-X	6-X
$k_{rel.}^{(100°)}$	1.2	2.1	2.3	0.006

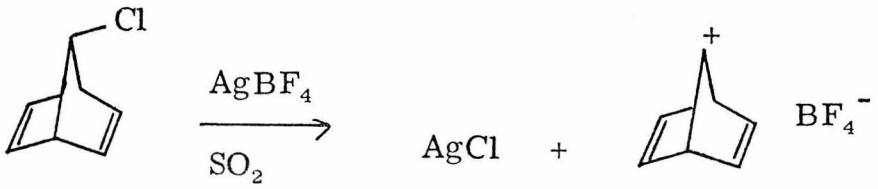
Enhancement of solvolysis rates of 15-X over 6-X is explained by a puckering effect in five-membered ring (see above).

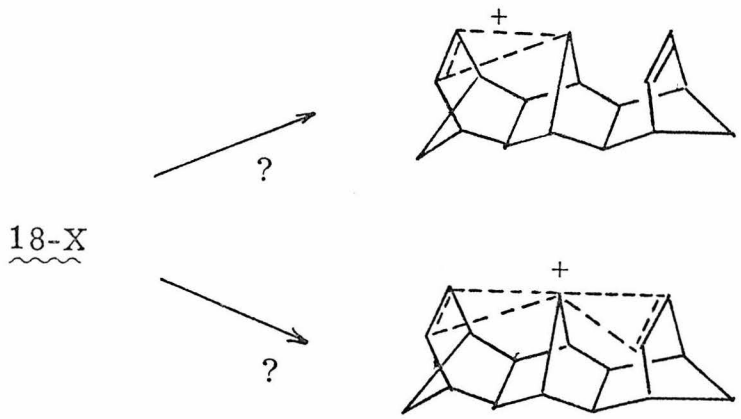
Based on Winstein's study of the rates of solvolysis of 5-OBs and Battiste's study of 4-OBs, it is predicted that 18-X should solvolyze faster than 20-X. The π orbitals of the double bonds in 18-X and 5-X are oriented directly toward the reaction center which makes them suitable to lend assistance to the developing carbonium ion center. The cyclopropyl rings of 4-X and 20-X have their σ orbitals directed into the cavity region between the bridges. Similarly 19a-X should solvolyze faster than 19b-X.

Solvolysis rates may be accelerated in 18-20-X compared with 4 and 5-X due to a lessening of steric hindrance between the leaving group and the double bond or cyclopropyl ring through ionization.

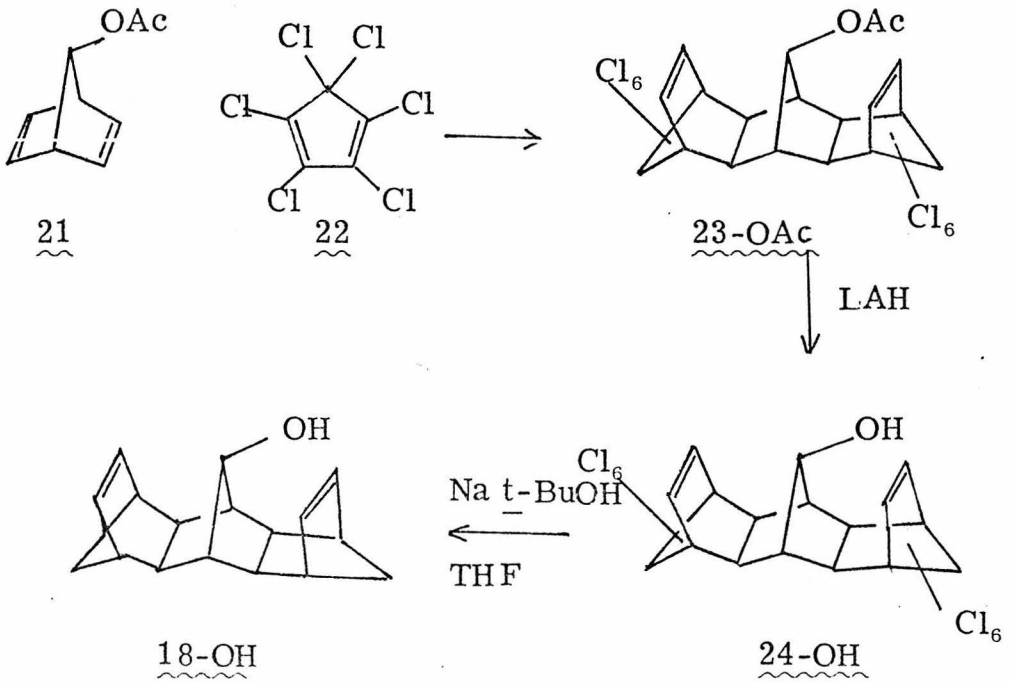
Based on the product distributions from the studies of 5-OBs and 4-OBs, extensively rearranged products from the solvolysis of 18-20-X are expected.

Using the method of Storey et al.[2] it might be possible to observe the NMR of 18, 19 or 20 in SO_2 if the corresponding chlorides can be synthesized. The question of delocalization over five centers as opposed to three can be answered.



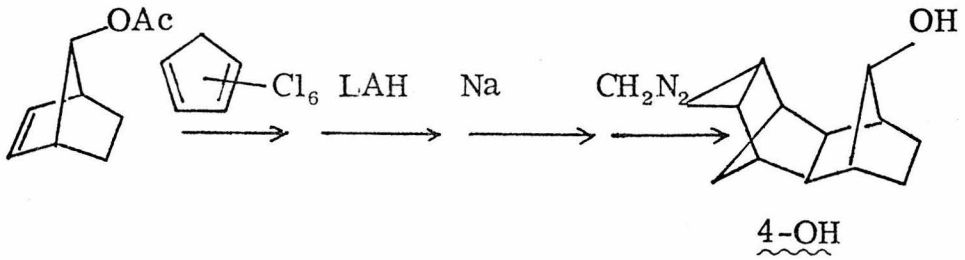


The proposed syntheses of 18-X, 19a-X, 19b-X and 20-X starts with commercially available norborndienyl acetate 21 (Chemical Samples Co.). Reaction of 2 moles of hexachlorocyclopentadiene with 20 should give the bis Diels-Alder adduct, which is converted to the alcohol 23 by $LiAlH_4$ reduction. Dechlorination of 24 with sodium-t-butyl alcohol-tetrahydrofuran should lead to the alcohol 18-OH, a key intermediate.



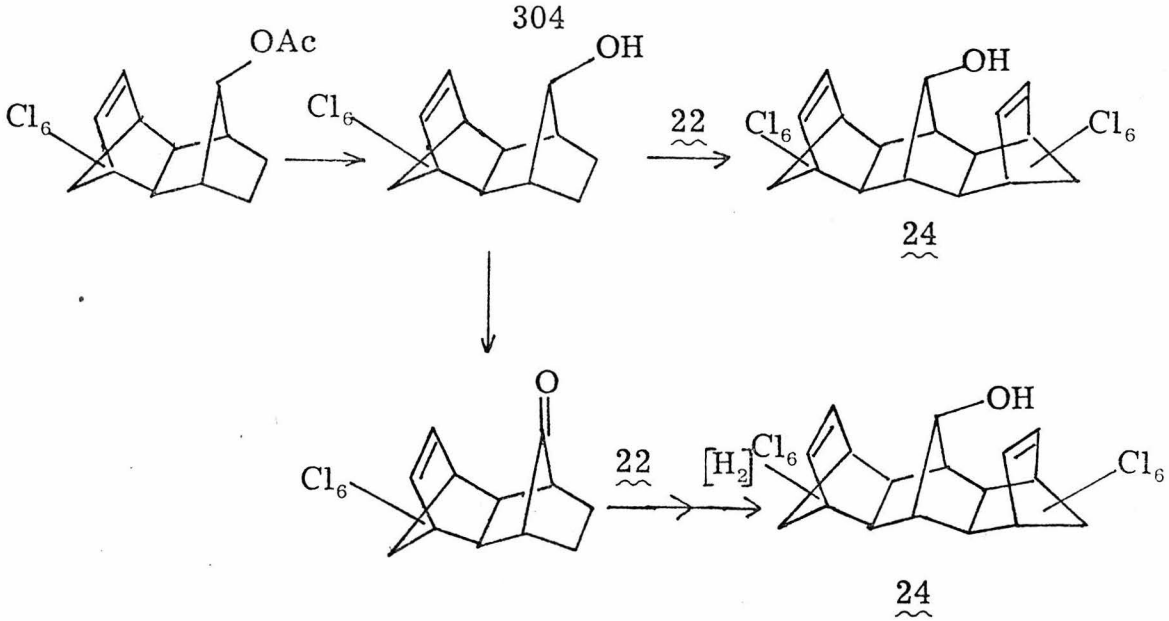
Cyclopropanation of one or both double bonds with CH_2N_2–CuCl should give rise to 19a-OH and 19b-OH, and 20-OH, respectively.

The proposed scheme finds precedent in the synthesis of 4-OH starting from anti-norbornenylacetate.[1d] The stereochemistry of Diels-Alder reaction is as shown.



4-OH

Complications can arise in the Diels-Alder reaction. Addition of a second mole of hexachlorocyclopentadiene (22) could be thwarted by steric hindrance of the acetate group. If a second mole of 22 does add it may add with the wrong orientation. If only a mono-adduct forms with 21, the steric hindrance to second addition of a mole of 22 arising from the acetate group may be decreased by reduction to a hydroxyl group with $LiAlH_4$ or $NaBH_4$ with LiCl. Should this fail, oxidation of the mono-adduct to the ketone followed by a Diels-Alder addition of 22 and a regeneration of the alcohol by oxidation of the ketone with $LiAH_4$ or $NaBH_4$ will lead to 24.



18-OH, 19a-OH, 19b-OH and 29-OH are converted to corresponding 3, 5-dinitrobenzoates, tosylates or broxylates by reaction with the appropriate acid chlorides.

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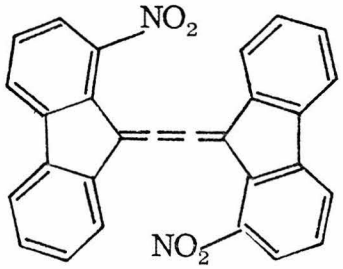
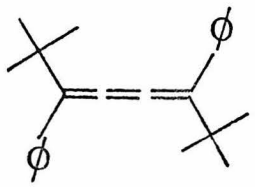
PROPOSITION IV

It is proposed that the kinetics of the cis/trans isomerization of a 1, 2, 3-butatriene be studied in the gas phase using a wall-less reactor.

To date, limited kinetic data are available on this class of compounds. In 1954 Kuhn and Scholler studied the cis/trans isomerization of 1 and found an activation energy of 19.5 kcal per mole for the transformation of the trans isomer into the cis.[1]



1T



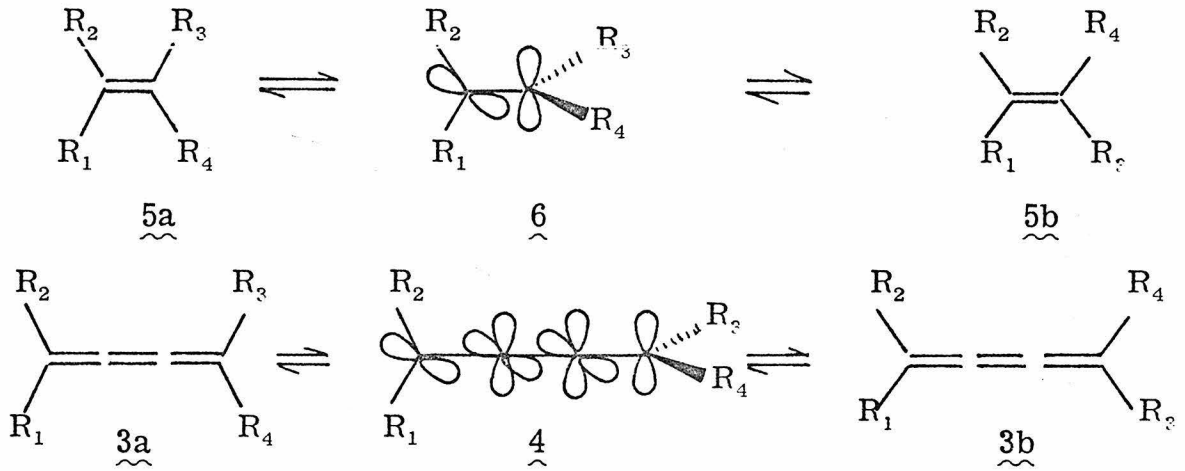
2T

In 1966 Kuhn et al. looked at the isomerization of 1, 4 di-t-butyl-1, 4-diphenylbuta-1, 2, 3-triene (2) and estimated 30 kcal per mole for the activation energy based on NMR studies of samples of 2 at elevated temperatures.[2]

While a paucity of experimental knowledge exists about the cis/trans isomerizations of 1, 2, 3-butatrienes, a great many theoretical studies on barriers to rotation in this system are to be found in the literature.

Calculations	Rotational barrier kcal/mole	Ref.
MINDO/2	32.3	3
Extended Hückel	40.7	4
Extended Hückel	21.8	4
Hückel	40.8	4
Hückel	39.1	4
Hückel	54.6	4
Hartree-Fock	40.0	4
Hartree-Fock	56.5	4

The lower activation energy for isomerization in 1, 2, 3-butatrienes compared to simple olefins is immediately obvious by examination of the transition state for the isomerization which can be thought of as arising from breaking one of the double bonds of 3 and rotating the fragments of the double bond by 90° (see Scheme I).



Scheme I

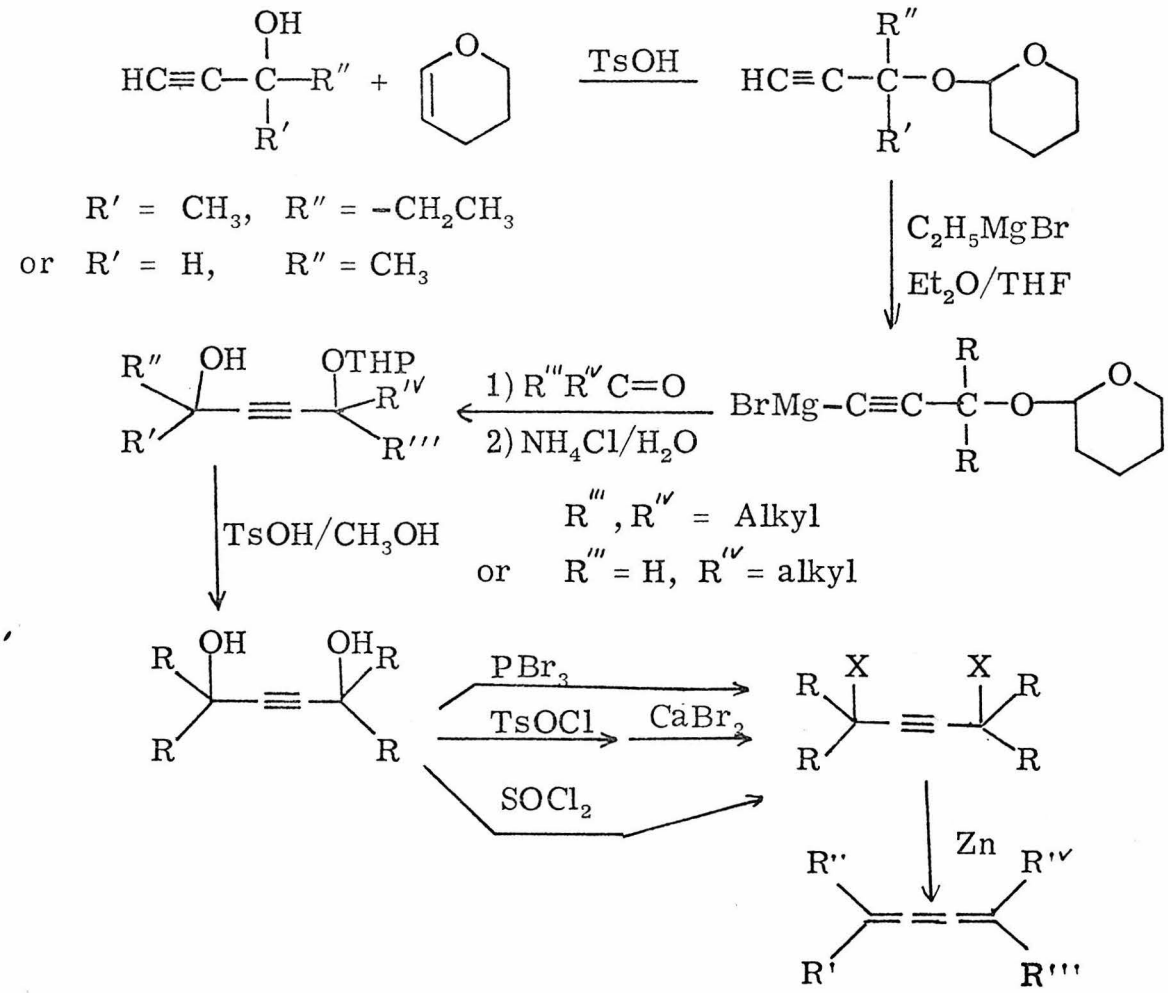
From simple Hückel theory, the energy difference between the transition state for isomerization of ethylene and ethylene itself is $2\alpha-(2\alpha + 2\beta) = -2\beta$ (the transition state (6) consists of two orthogonal p orbitals which do not overlap). However, the transition state for the isomerization of 1, 2, 3-butatriene can be visualized as two allylic systems orthogonal to each other, each containing 3π electrons. On the other hand, the 1, 2, 3-butatriene consists of a butadiene-like arrangement of orbitals perpendicular to an ethylenic arrangement of orbitals. The π-energy difference between 4 and 3 is much less than the difference calculated for 6 and 5.

π energy of 4 - π energy of 3 =

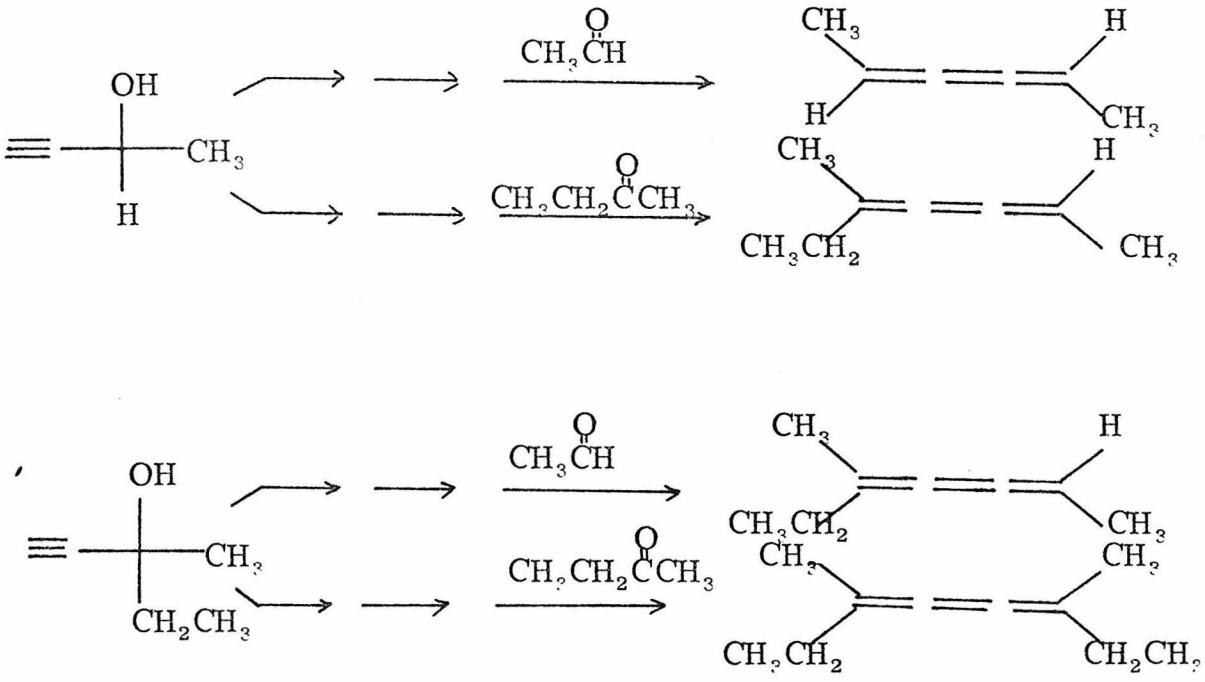
$$2\alpha + 4(\alpha + 1.414\beta) - 2(\alpha + \beta) - 2(\alpha + 0.618\beta) - 2(\alpha + 1.618\beta) = 6\alpha + 5.656\beta - 6\alpha - 6.472 = -8.16\beta$$

To carry this analysis to its limits, if one assumes that 2β equals 65 kcal per mole, the experimental activation energy found for the thermal isomerization of trans 1, 2-dideuterioethene,[5] then the anticipated activation energy for the isomerization of a similarly substituted 1, 2, 3-butatriene should be $0.816 \times \beta = 0.816\ (32.5) = 26.6$ kcal per mole which is in fair agreement with more sophisticated calculations.

The synthesis of cis/trans isomers of 1, 2, 3-butatrienes suitable for this study follows from known reaction sequences that give cumulenes.



This reaction sequence has been successfully utilized for the synthesis of 1, 2, 3-butatrienes starting with propargyl alcohol.[6] Condensation with ketones or aldehydes have resulted in the formation of 1, 1-dialkyl or 1-alkyl 1, 2, 3-butatriene, respectively. 3-Hydroxy-1-butyne and 3-hydroxy-3-methyl-1-pentyne are known compounds. Reaction with simple ketones or aldehydes should give cis/trans isomers of 1, 2, 3-butatriene.

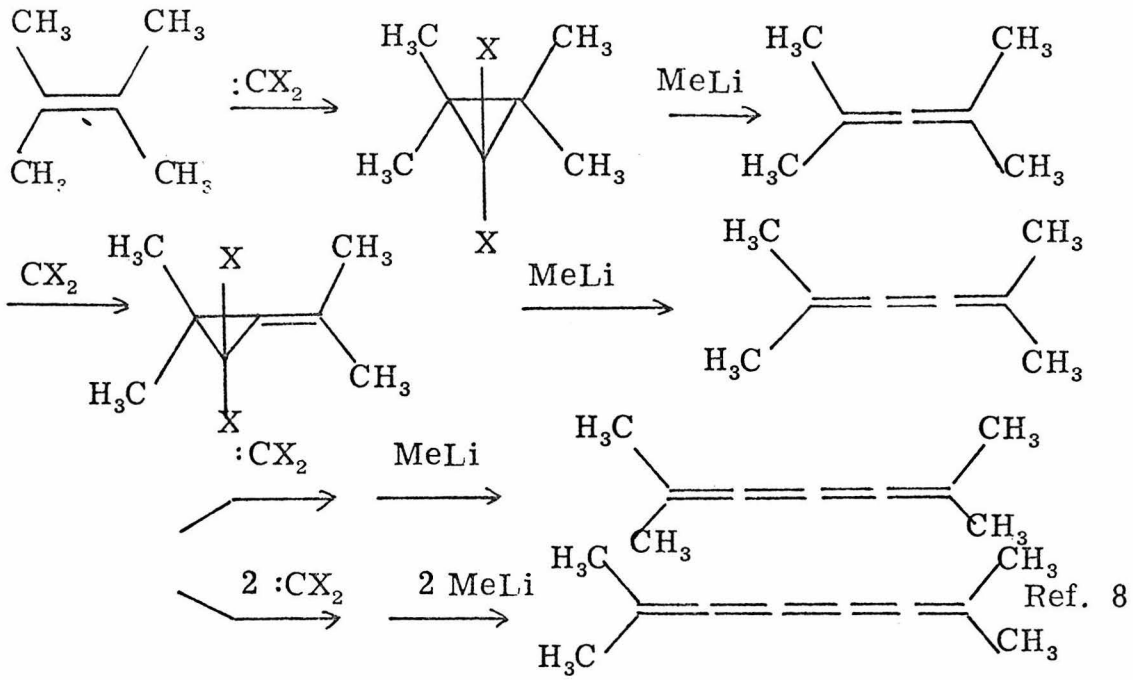


Tetraaryl-1, 2-3-butatrienes have been prepared by the above reaction scheme starting with diphenyl propargyl alcohols and reacting with diaryl ketones.[11] Therefore derivatives of propargyl alcohol as starting material should cause no problems.

These cumulenes should be reasonably stable; tetraalkyl- and 1, 4-dialkyl-1, 2, 3-butatrienes are known (see below).

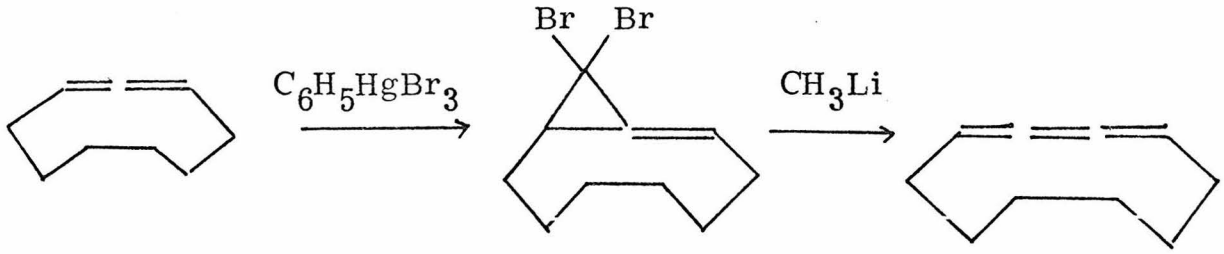
Skattebøl has designed a synthesis of 1, 2, 3-butatrienes starting with allenes.[8] Dibromo or dichloro carbene is added to an allene to give a methylene cyclopropane. Treatment with the base, methyllithium at -78°C results in the formation of cumulenes. The allenic substrates

themselves are generated from the addition of dihalocarbenes to simple olefins.



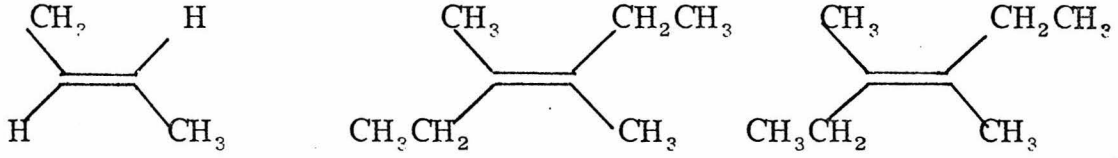
Ref. 8

1, 2, 3-Cyclodecatriene has been synthesized by this method. [9]

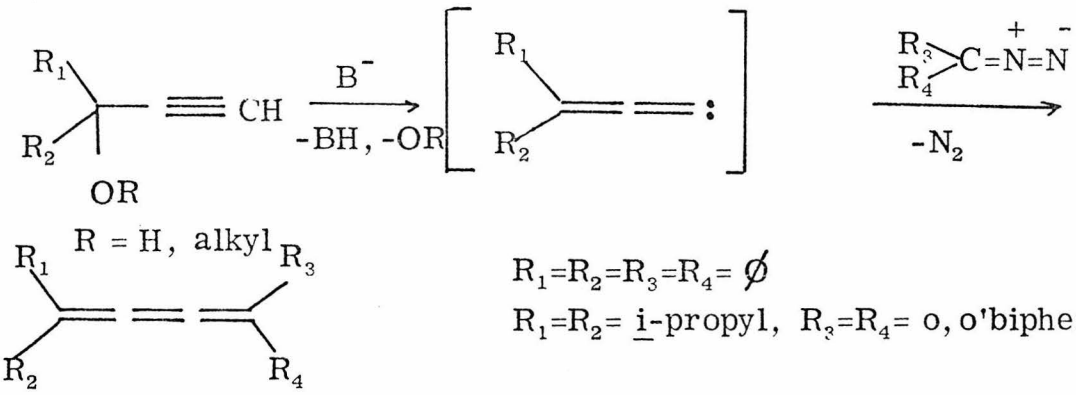


Ref. 9

It should be possible to substitute other olefins as substrates in this reaction (see below).



A third method involves the treatment of substituted propargyl alcohols with base in the presence of substituted diazomethanes.[7]



$R_1=R_2=R_3=R_4=\phi$

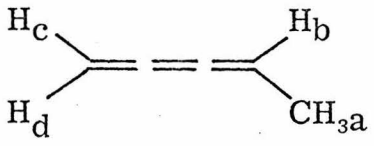
$R_1=R_2=$ i-propyl, $R_3=R_4=$ o, o'biphenylene

Ref. 7

Reaction of simple alkyl derivatives of the propargyl alcohol and the diazomethane have not been attempted.

Separation and purification of cis/trans isomers will be by preparative vapor phase chromatography at low temperatures.

Assignment of stereochemistry will be based on NMR coupling constants. From the NMR of known cis/trans isomers of 1, 2, 3-butatrienes (mainly alkoxy derivatives) it has been found that $J_{d,b}$ is always greater



than $J_{c,b}$ and that $J_{a,c}$ is greater than $J_{d,a}$.[12] Thus, for all proposed cis/trans isomers containing at least one cumulenic proton, stereochemistry is assignable. For tetraalkyl substituted 1, 2, 3-butatrienes assignment

of stereochemistry will be more difficult, but there is one example in the literature in which the stereochemistry of a tetrasubstituted 1, 2, 3-butatriene was determined by UV spectra.[10]

In all cases in which the cis/trans isomers of a 1, 2, 3-butatriene are known, the trans isomer is more abundant at the equilibrium concentrations.[13]

Substantial differences exist in the IR spectra of cis/trans isomers of 1, 4-diphenyl-1, 4-di-t-butyl-1, 2, 3-butatrienes which may be exploited in assigning stereochemistry to other tetrasubstituted 1, 2, 3-butatrienes.[14]

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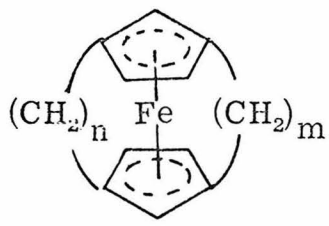
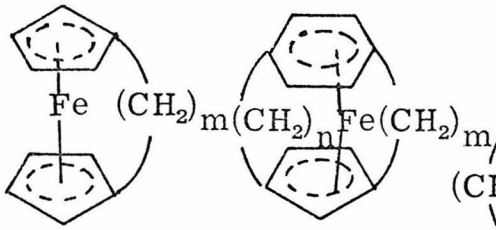
PROPOSITION V

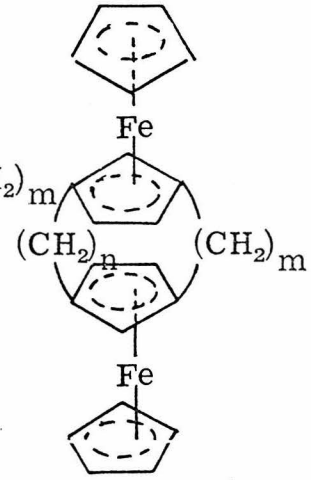
Ferrocene has been found to have an extensive chemistry. One of the more recent aspects of this is the preparation of some ferrocenophanes (1) analogous to paracyclophanes (2) but differing radically because of the existence of a transition metal between the two rings. The presence of the "sandwiched in" metal in a stable compound makes ferrocene chemistry unique. The research proposed here should serve to extend the knowledge in this area of chemistry.



1a



1b 2



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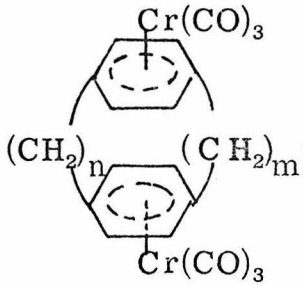

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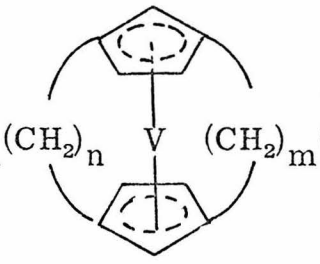

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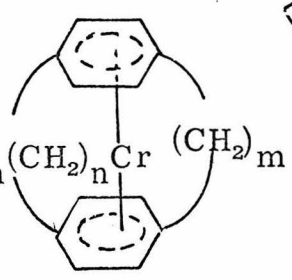


6

Part A

It is proposed that structures of general formula 1a and 3 be synthesized and studied as to their physical properties.

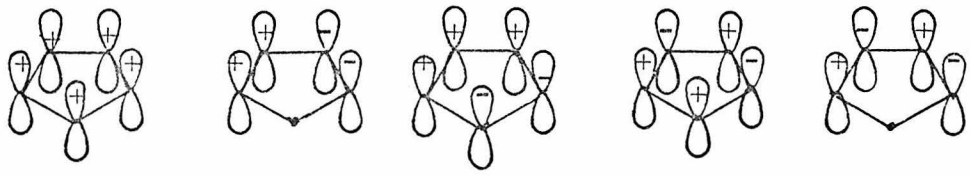
The general question one would hope to be able to answer from such a study is: What is the effect of decreasing the number of methylene groups between the two rings? This has the effect of forcing the two aromatic rings together with the metal atom between them as in 1a, or with no atom between the rings as in 3.

The specific questions one would hope to answer from this study are dealt with individually below.

(1) How is the bonding between the aromatic ring and the transition metal affected as m and n are decreased? Is the overall stability of the π-complex increased or decreased?

A qualitative understanding of the bonds in ferrocene can be derived by consideration of the symmetry properties of the ring and metal orbitals from which molecular orbitals (MO's) are constructed.[1]

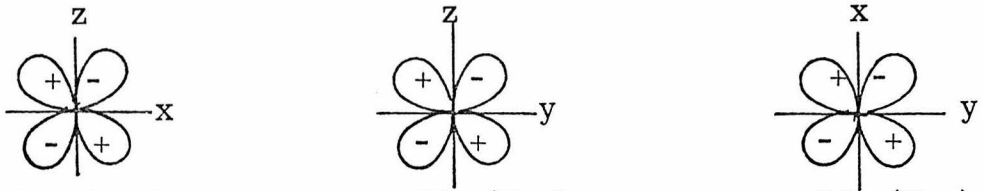
The five molecular orbitals of cyclopentadienyl (cp) anion fall into three groups which differ in their symmetry properties with respect to rotation about the molecular axis perpendicular to the rings and passing through their centers. The MO's and symmetry designations are shown. The order of increasing energy is A_1, E_1 and E_2.

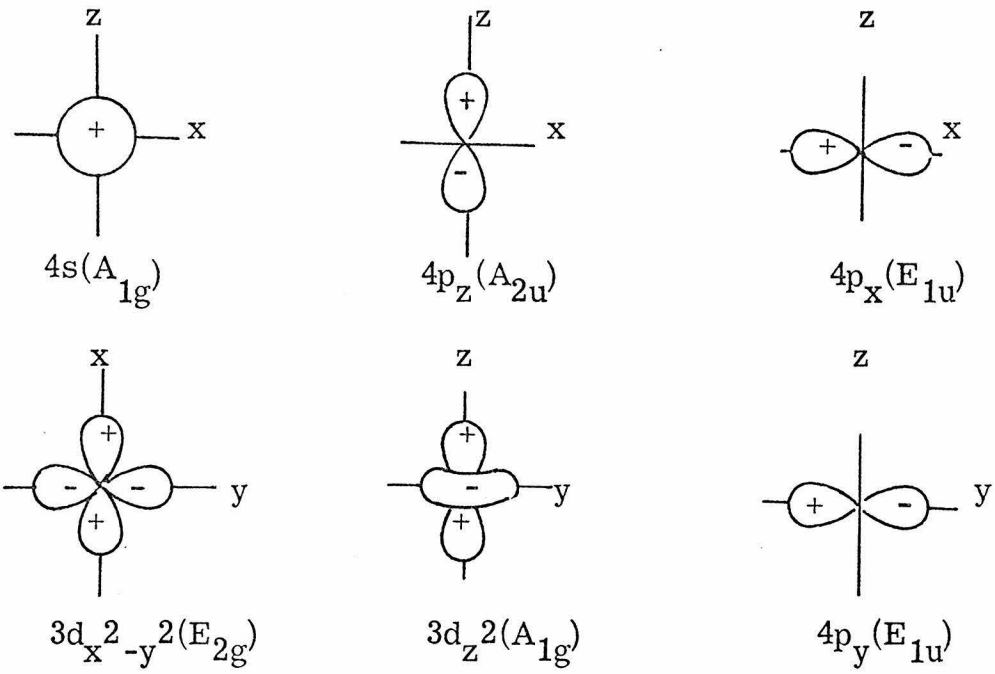


$\psi_1(A_1)$ $\psi_2(E_1)$ $\psi_3(E_1)$ $\psi_4(E_2)$ $\psi_5(E_2)$

It is possible to form linear combinations of these localized molecular orbitals (assuming no interaction between them) to give a set of ten new MO's which encompass both rings. Combination is along the molecular axis and the rings are parallel to one another arranged in an antiprismatic structure with D_5d symmetry point group. The symmetry designations are $A_{1g}(\psi_1 - \psi_1)$, $A_{1u}(\psi_1 + \psi_1)$, $2E_{1g}(\psi_2 + \psi_2)$ and $(\psi_3 + \psi_3)$, $2E_{1u}(\psi_2 - \psi_2)$ and $(\psi_3 - \psi_3)$, $2E_{2g}(\psi_4 - \psi_4)$ and $(\psi_5 - \psi_5)$ and $2E_{2u}$ $(\psi_5 + \psi_5)$ and $(\psi_4 + \psi_4)$.

The metal orbitals are shown below with their symmetry designations.





The MO's of ferrocene are listed below.

A_{1g} (CpA_{1g} - 4s)

A^1_{1g} (CpA_{1g} - $3dz^2$)

E_{1g} (CpE_{1g} - $3d_{xz, yz}$)

E_{2g} (CpE_{2g} - $3d_{xy, x^2-y^2}$)

E_{1u} (CpE_{1u} - $4p_{x, y}$)

A_{2u} (CpA_{2u} - $4p_z$)

The relative contribution of these MO's is not the same.[1] Twelve electrons are assigned to strongly bonding metal-ring hybridized orbitals, probably the $(CpA_{1g} - 4s)^2$, $(CpE_{1g} - 3d_{xz, yz})^4$, $(CpA_{2u} - 4p_z)^2$ and the $(CpE_{1u} - 4p_{x, y})^4$ of the remaining six electrons, four occupy the weakly bonding E_{2g} levels, while two are placed in a non-bonding

$3d_z2$ orbital. The importance of CpA_{1g} - $3d_z2$ overlap is very small.

The distance of the carbons to the iron in ferrocene is 2.05 Å which is equal to the sum of their covalent radii, .77 Å and 1.26 Å for carbon and 12 coordinate iron, respectively.[2] The distance between the rings is 3.32 Å.[3] [3.3] ferrocenophane has been synthesized and can be shown to be "compressed". The average C-2 - C-2′ distance is 3.01 Å, the average among C-1 - C-1′ and C-3 - C-3′ distances is 3.09 Å, and the C-4 - C-4′ and C-5 - C-5′ distance is 3.36 Å, the angle of tilt between the ring is 9°.[4] The [3.3.3] ferrocenophane is even more compressed.

When the rings are pushed closer together greater overlap between the metal orbitals and those of the aromatic rings can occur which may strengthen the bonding interaction. If so the splitting of the bonding and antibonding MO's should increase. This difference should be detectable in the electronic spectra by shifting of bands toward shorter wavelength.

On the other hand, once formed the aromatic character of the ring may be decreased in compressed sandwich compounds by deviation of the ring from planarity. D. J. Cram has proposed that in [2.2] paracyclophane the benzene rings are no longer planar.[5] The effect of loss of aromaticity of the rings may destabilize the ferrocene and decrease its reactivity toward electrophilic aromatic substitution. It would be interesting to study reaction rates as the value of m and n

decreases in 1a.

(2) What are the effects on the spectral properties (electronic, IR and NMR) of forcing two rings together? The anticipated effect on the electronic spectra has been mentioned previously.

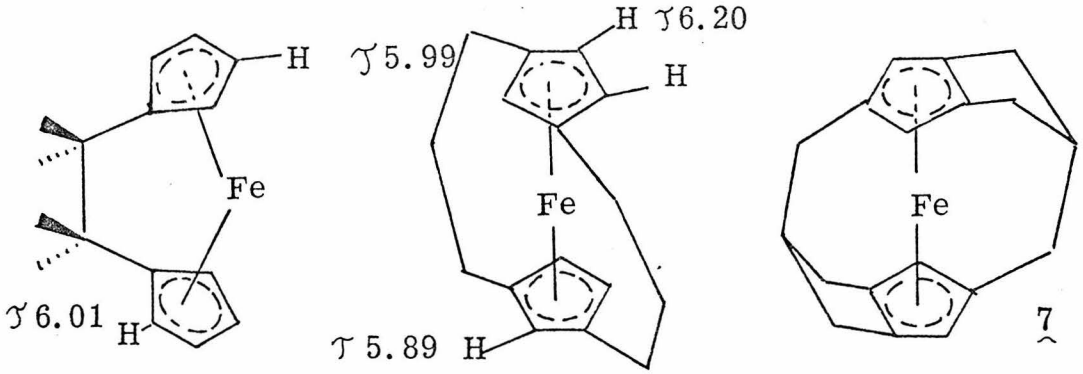
NMR has proved to be a useful tool in studying tilting of the ferrocene rings and the proximity of the ring hydrogens to the central atom.

The [3.3] ferrocenophane (1a, m = n = 3)[6] and the [m] ferrocenophanes (1a, m = 2 - 5)[7] have been synthesized and studied. The NMR's of these compounds are presented in Table I.

Table I: NMR's of Some Ferrocenes (Fn) and Some Ferrocenophanes (Fnp)

Ferrocene (Fn)	Chemical shifts at ring protons, τ			
	2	3	4	5
Parent	6.00	6.00	6.00	6.00
Methyl Fn	6.07	6.07	6.07	6.07
[3]Fnp	6.14	5.99	5.99	6.14
[2]Fnp	6.01	5.46	5.46	6.01
[3.3]Fnp		6.20	5.89	6.20
[3.3]Fnp	6.43		6.14	6.14
[3.3.3]Fnp			6.04	6.04
[3.3.3]Fnp		6.37		6.37

The higher τ values for H's α to substituent are a combination of the inductive effect of the alkyl substituent and result of tilting the rings so that the α-H's are closer to the iron atom.



A compound which should prove interesting for study is 7. This compound is as yet unknown (possible synthesis is described later) but the strain should be only slightly greater than it is in [3.3.3] or [3.3] ferrocenophane. The rings should be parallel in 7 because of the symmetrical distribution of restraining bridges. The NMR of the 2, 4 hydrogens of 7 should have values greater than 6.37 τ. The NMR's of [2.4] (and [2.3] ?) ferrocenophane should also be of interest because of the very large tilt angles of the rings.

The infrared spectra of ferrocene shows several bands which would be a significance in a study of bridged ferrocenes. They are: the C–H stretch (3085 cm^{-1}), antisymmetric C–C stretch (1411 cm^{-1}), antisymmetric ring breath (1108 cm^{-1}), C–H bend (parallel 1002 and perpendicular 811 cm^{-1}), antisymmetric ring tilt (492 cm^{-1}) and the ring-metal bend (170 cm^{-1}).[1] The bands should be sensitive to ring tilt, ring deformation from planarity and the proximity of the rings to one another.

(3) What is the interannular electronic affects in the bridged and non-bridged metal complexes? How are these effects changed as m and n decreases?

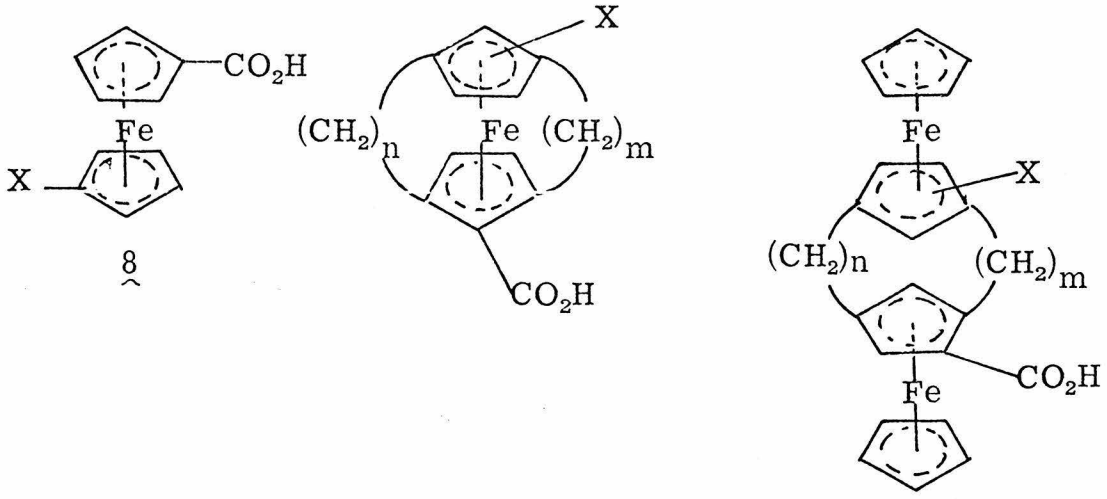
The effect upon each other of two components connected via a ring is termed the transannular effect. Transannular effects have been studied in a number of compounds and they usually exhibit themselves as steric and/or electronic effects.

From the study of substitution in ferrocene, it is apparent that the electronic effects of a substituent were transmitted from one ring to another; the introduction of an electron withdrawing group on one ring can deactivate the other ring. For example, many reactions give exclusively or nearly exclusively monosubstitution: dimethylaminomethylation, formylation, N-phenylcarbamylation, and N,N-diphenylcarbamylation.[8] The question can be asked: if electron withdrawing groups withdraw electron density from the ring to which they are not bonded presumably making it less attractive to electrophilic reagents, then would not this effect be enhanced by forcing the rings into greater proximity by shorter bridges? Conversely, electron releasing groups should activate each ring toward further electrophilic substitution and this effect will be enhanced by decreasing the value of m and n in $\underset{\frown}{1}$ and $\underset{\frown}{5}$.

Another probe one might use in answering question (3) is to look for the effect on pK_a in changing the length of the bridges (changing the value of m and n) connecting the two rings in a series of ferrocene acids.

If the rings in ferrocene are viewed as electron releasing, shorter bridges should decrease the acid strength by destabilizing the negatively charged conjugate base.

Further insight may be gained by using heteroannular substituted ferrocene acids which are bridged. The length of the bridge and the nature of the substituent can both be variables. A study of this type has been carried out on the unbridged acids.[8] The results are given in Table II. This study is complicated because each of the rings must be trisubstituted which is difficult to attain because of steric and electronic factors, nevertheless, [3.3.3] and [3.3] bridged ferrocenophanes have been acylated.[6] Presumably other aromatic electrophilic substitutions can be carried out, or the acetyl group can be modified.



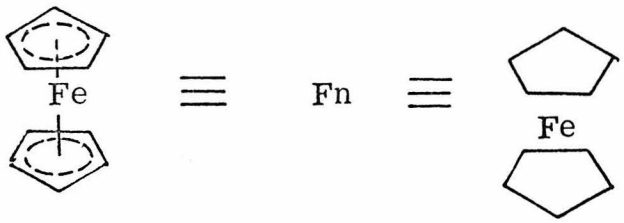
8

Table II: pK_a Values of Heteroannularly Substituted Ferrocenoic Acid (8)

Substituent	pK_a 68% MeOH	pK_a 50% EtOH
$-C_4H_9$	6.52	
$-C_2H_5$	6.43	6.34
$-CH_2-\phi$		6.25
$-H$	6.29	6.11
$-CO-\phi$		5.90
$-CH(OH)-\phi$		5.34
$-CO-CH_3$	6.08	5.76
$-CO_2C_3H_7$	5.95	
$-CO_2CH_3$	5.91	

Synthesis of Ferrocenophanes

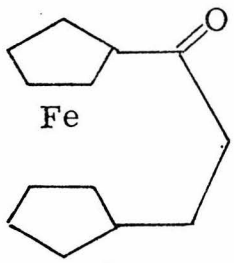
A. [3.3] and [3.3.3] ferrocenophanes



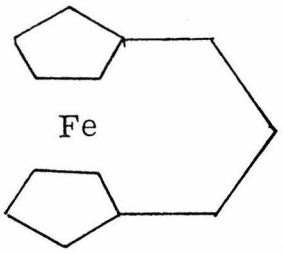
$$Fn + CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{AlCl_3} Fn-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[2.\ CO(OC_2H_5)_2]{1.\ NaH}$$

$$Fn-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow[2.\ NaOH,\ then\ H_2PO_4]{1.\ H_2,\ PtO_2,\ HOAc} Fn-CH_2-CH_2-CO_2H$$

$$(CF_3CO)_2O \xrightarrow[CCl_4]{}$$



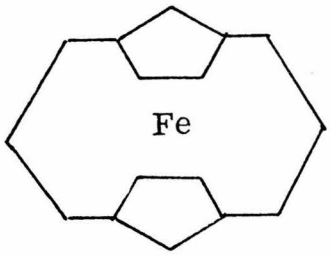
$$\xrightarrow[AlCl_3]{LAH}$$



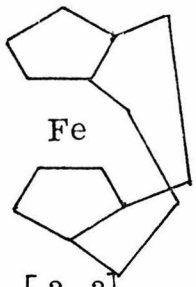
Ref. 6

9 50% yield from Fn 10

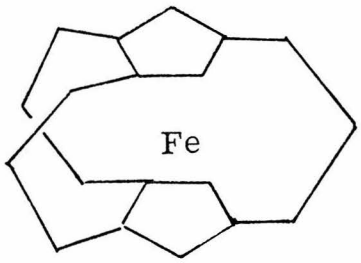
The sequence of steps was repeated to give the following ferrocenophanes.



[3.3]
19% yield from acetylated 10

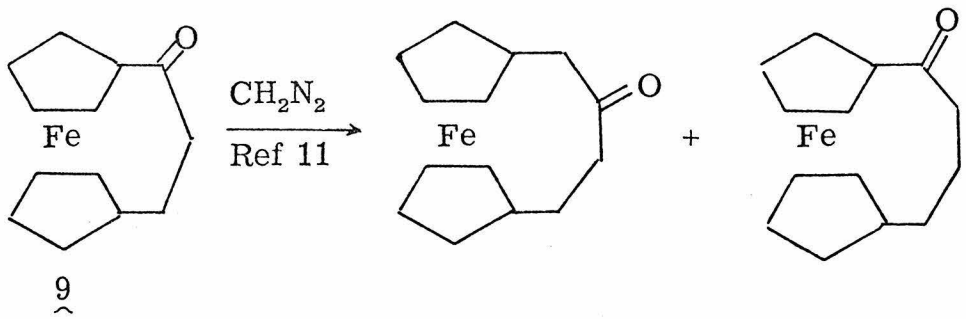


[3.3]
46% yield from acetylated 10



[3.3.3]

B. Proposed synthesis of [4.4] and [4.3] ferrocenophanes from 11.



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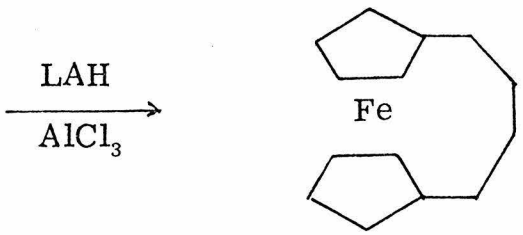
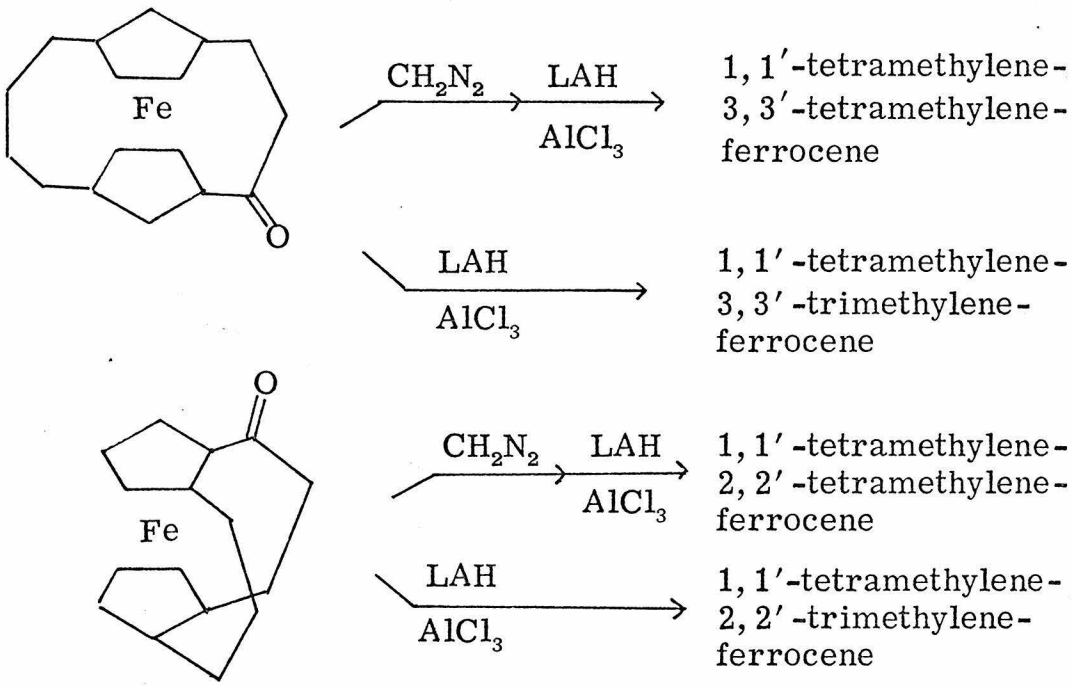
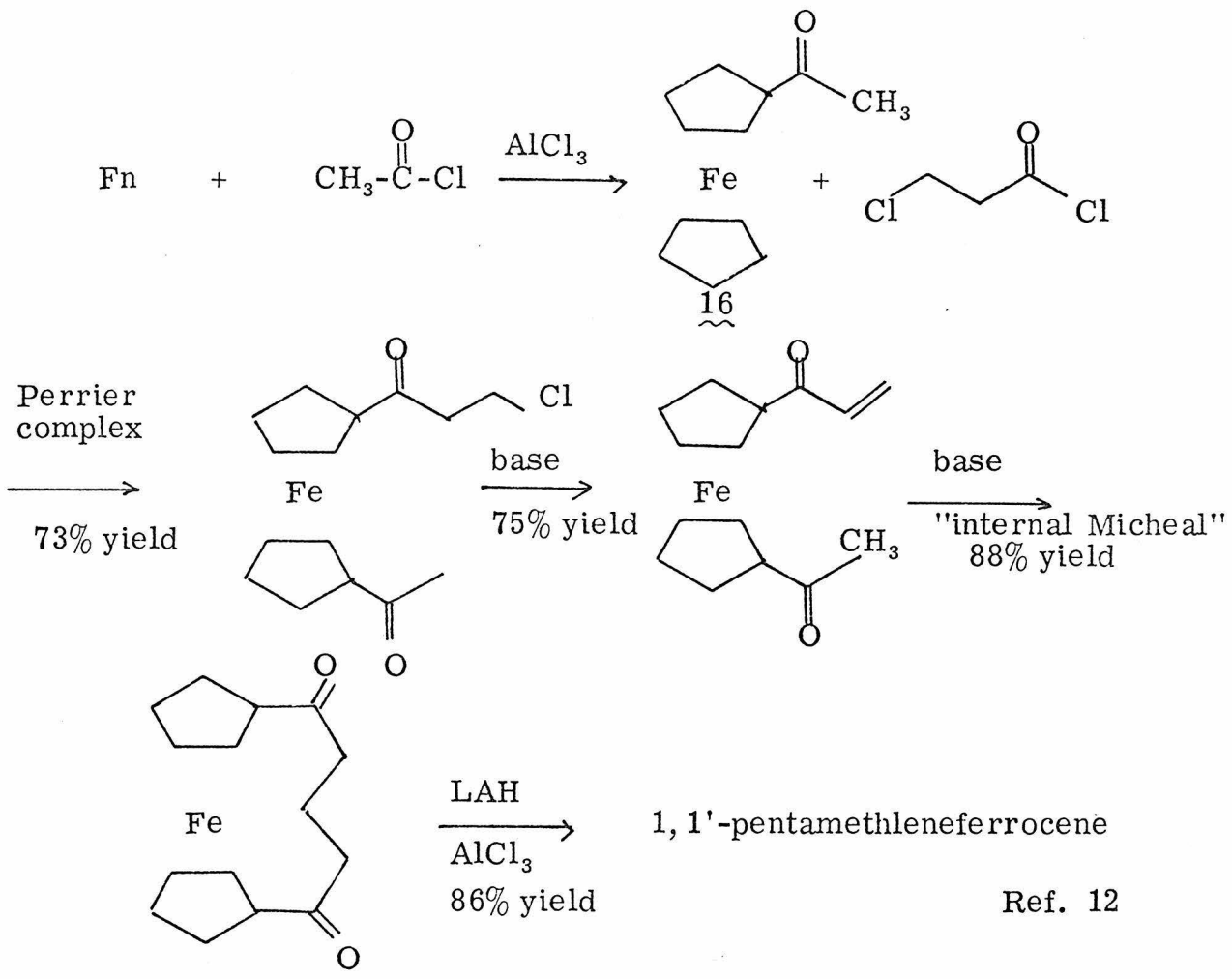


11, 80% yield from 9

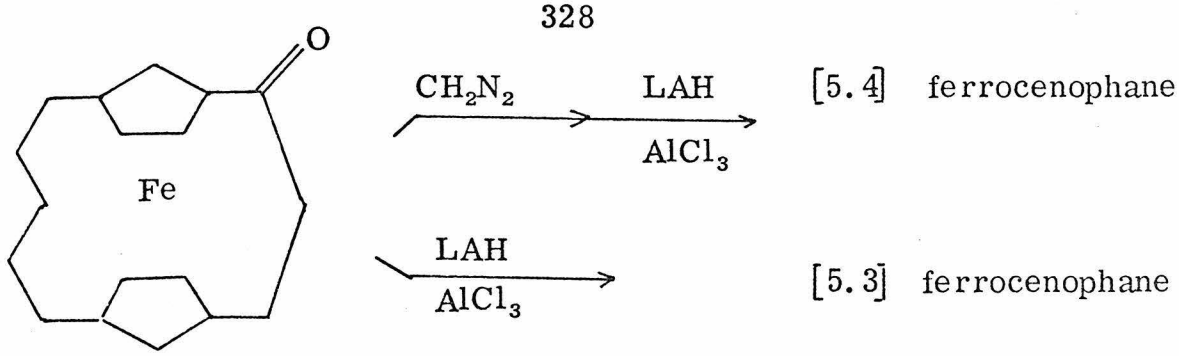
Repeat the sequence shown on the previous page for building the three-membered bridge



C. Synthesis of [5.X] ferrocenophanes (X = 3, 4 or 5)

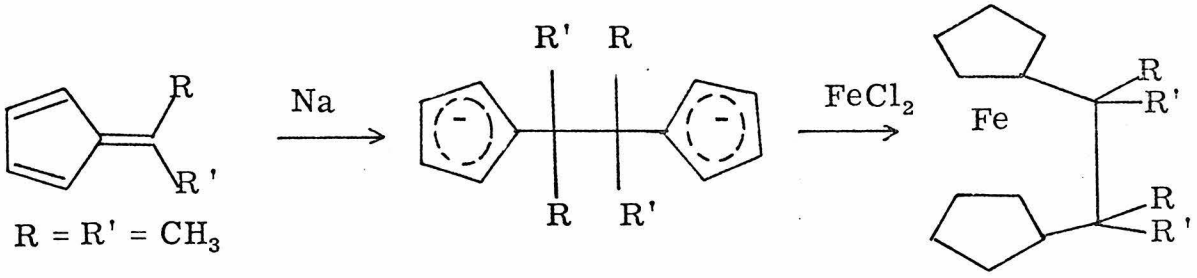


I propose that the above sequence of steps be repeated for the synthesis of [5.5] ferrocenophanes. Synthesis of [5.3] and [5.4] ferrocenophanes should be possible by repetition of the steps leading to the three carbon bridged ketone. This would then be followed by treatment with CH_2N_2 and LAH with $AlCl_3$, or omitting the CH_2N_2 and treatment only with LAH and $AlCl_3$.



D. [2.X] ferrocenophanes

The first 2 carbon bridged ferrocenophanes were prepared from fulvenes. The yield was subsequently increased from a few per cent to 70%.[10]



R = R' = CH_3

R = H, R' = 3-heptyl

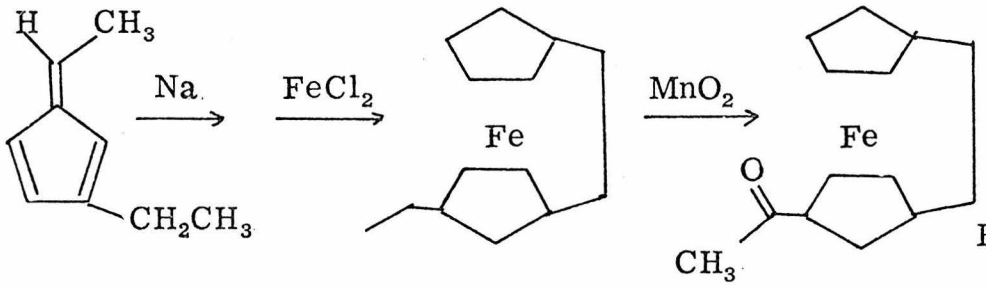
Acetylation with CH_2COCl and $AlCl_3$ failed[13] because of the presumed coordination of three filled non-bonding orbitals of Fe atom, which are projected away from the tilted aromatic rings, with the Lewis acid. This causes drainage of the electron density from the rings which are then deactivated towards electrophilic attack.[13]

Acylation can probably be accomplished by other routes. HF, H_3PO_4, $SnCl_4$, BF_3 and other Lewis bases, known to monoacylate ferrocenes with acid anhydrides could be tried with [2] ferrocenophane.

Methods of acylation which do not rely upon the use of Lewis acids are available. Acylation has been accomplished by MnO_2 oxidation of ethylferrocene,[16] and methylmagnesium iodide treatment of cyanoferrocene.[17]

$$\text{Fn} + \underline{\text{n}}\text{-butyllithium} \longrightarrow \text{Fn-Li} \xrightarrow{\text{tributylborate}} \text{Fn-B(OH)}_2 \xrightarrow{\text{CuCN}}$$

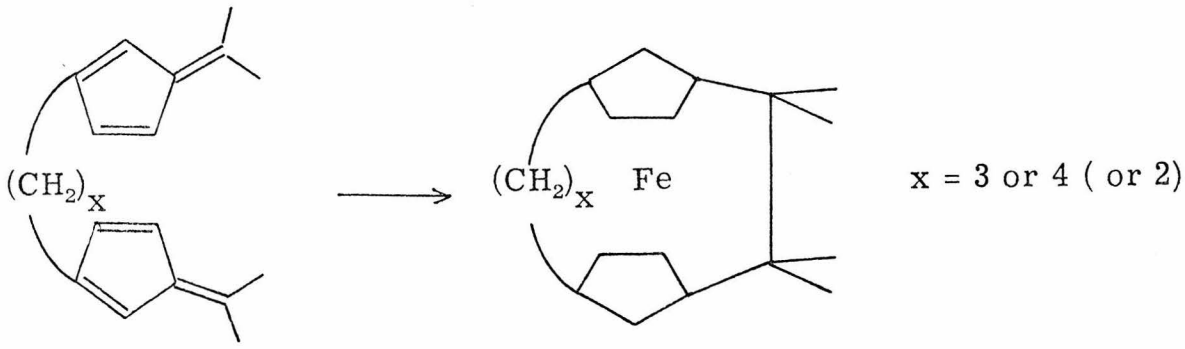
$$\text{Fn-CN} + \text{CH}_2\text{MgI} \longrightarrow \text{Fn-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-CH}_3 \quad (\underset{\sim}{16}) \qquad \text{Ref. 17}$$



Ref. 16

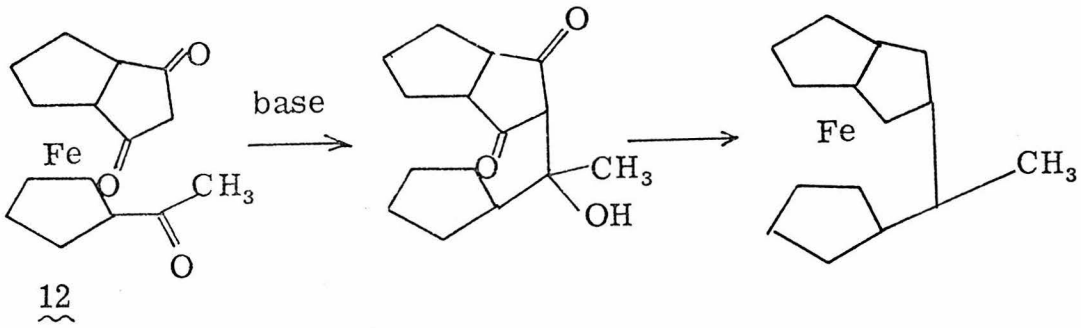
Ring closure to [2.4] and [2.3] ferrocenophanes can be accomplished by bridging methods identical to the formation of [3.4] and [3.3] ferrocenophane except starting from the aceylated [2] ferrocenophanes instead of acetylated [3] ferrocenophanes.

Another possibility is that [2.X] ferrocenes can be obtained from fulvenes connected by an alkyl bridge. The high yield obtained with fulvenes tends to encourage this approach.

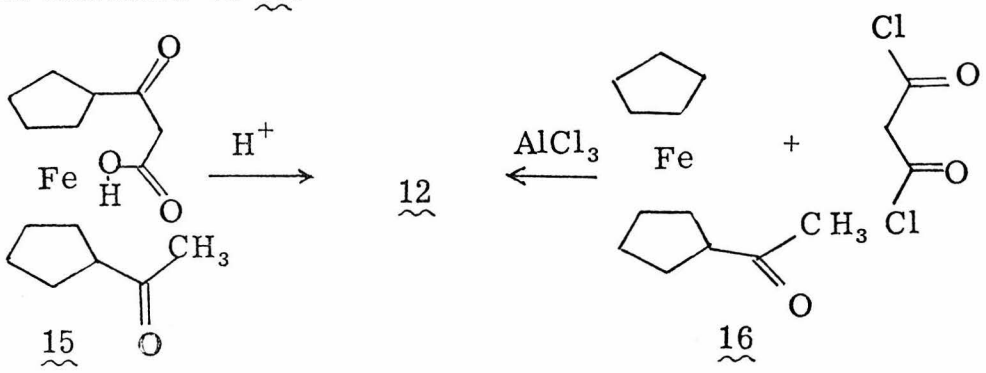


E. Proposed synthesis of 7

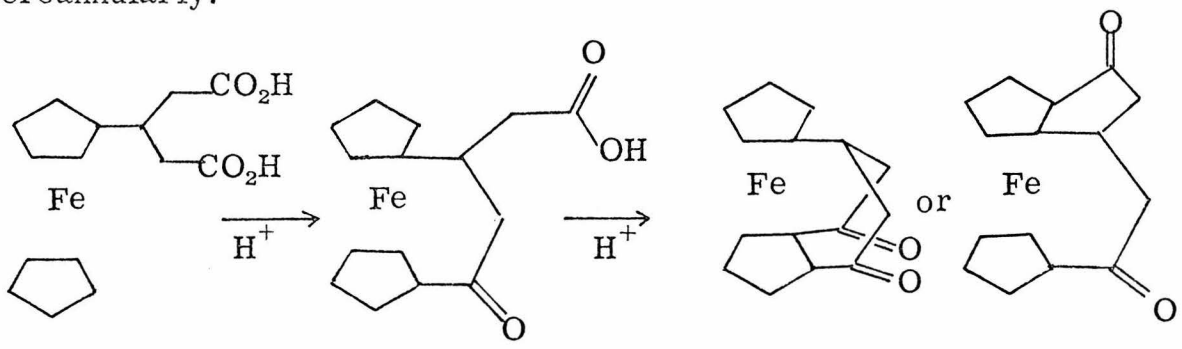
Intramolecular condensation of 12 should lead to the formation of the bridged compound.



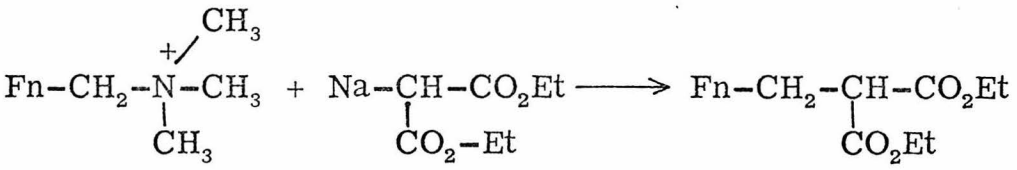
12 can be prepared by intraannular cyclizations of 15or by addition of the diacid chlorides to 16.



The bridges can be made by the acid catalyzed cyclization of the substituted β ferrocenyl propionic acid shown below. This reaction makes use of the tendency of the β ferrocenyl propionic acids to cyclize heteroannularly.



The acid has been prepared from the ester.[18]



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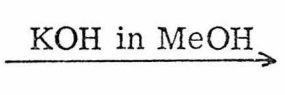
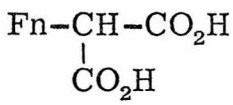




Ref. 18

67% yield from 14

F. Proposed synthesis of intermolecularly bridged ferrocenophanes (3).

There are no known syntheses of compounds of the general structure 3. Some known compounds which may serve as convenient

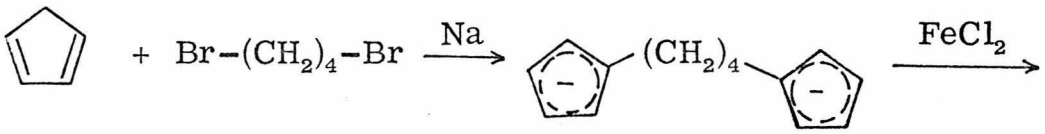
starting materials are listed below.

$Fn-CH_2-CH_2-Fn$ Ref. 15

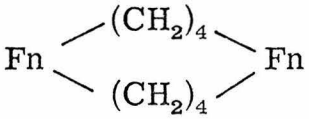
$Fn-CH=CH-CO-Fn$ Ref. 23

$Fn-C(CH_3)(C_2H_5)-C(CH_3)=C-Fn$ Ref. 24

These possible precursors can be reduced to the saturated compounds by various known reactions. The $Fn-(CH_2)_n-Fn$ can probably be obtained from a mixture of 13 and cyclopentadiene. 13 and $FeCl_2$ has been shown to give intermolecularly bi-bridged ferrocenophanes in low yields ($< 1\%$).[25]



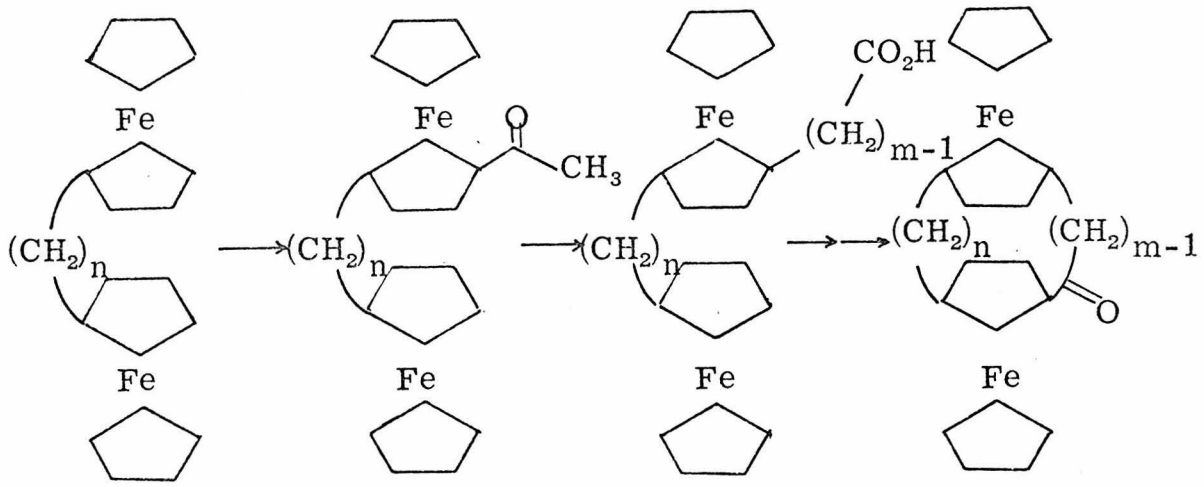
13



plus polymers Ref. 25

If the ratio of 13 to cyclopentadiene is sufficiently low, the amount of polymers formed should be greatly decreased. This approach to synthesis of intermolecularly mono-bridged ferrocenophanes should be applicable to cases in which n = 2, 3 and 5.

If one applies known cyclization reactions to these compounds many side-products are possible and probable.

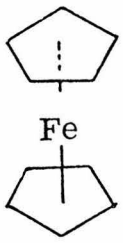


n = 2, 3, 4, or 5

3

Part B

The extensive organic chemistry of ferrocene suggests some exciting possibilities for the synthesis of unusual cyclic organic compounds. Ferrocene strongly activates its rings to a large number of aromatic electrophilic substitution reactions as well as to reactions proceeding through a lithiated or mercurated intermediate compound. These properties can be made use of to synthesize compounds which are inaccessible through other means. The crux of the problem is to liberate the preformed organic molecule from the iron atom. A reaction that does just that has been found.[19]



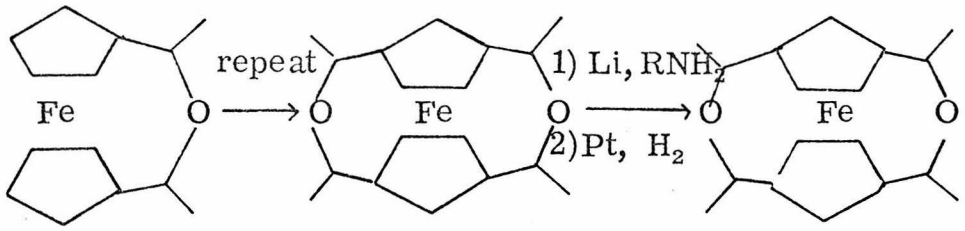
$\xrightarrow[4\text{-}6\ \text{min.}]{\text{Li, EtNH}_2}$

53% yield (distilled)
71% yield (by adduct with maleic anhydride) Ref. 19

The generalized synthetic scheme is shown below.

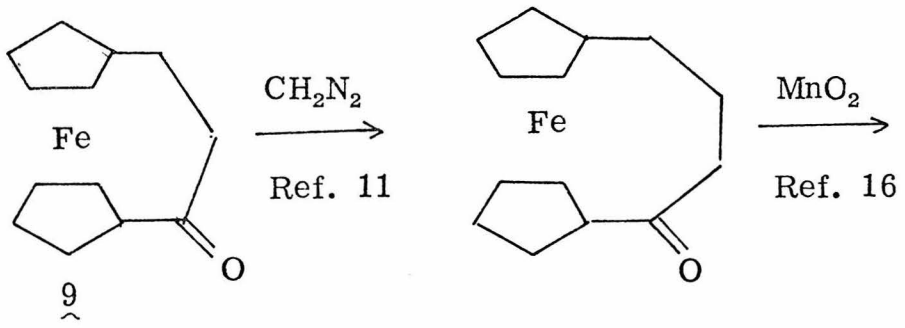
$$\text{Fn} \xrightarrow{\text{chemistry}} \text{substituted Fn} \xrightarrow{\text{Li, EtNH}_2} \text{substituted cyclopentadiene} + \text{Fe}^{\circ}$$

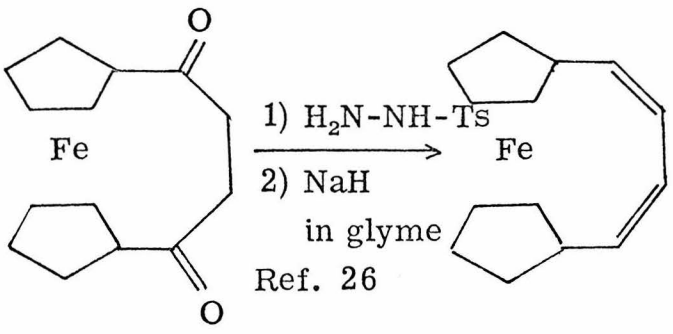
1. The synthesis of a new crown ether

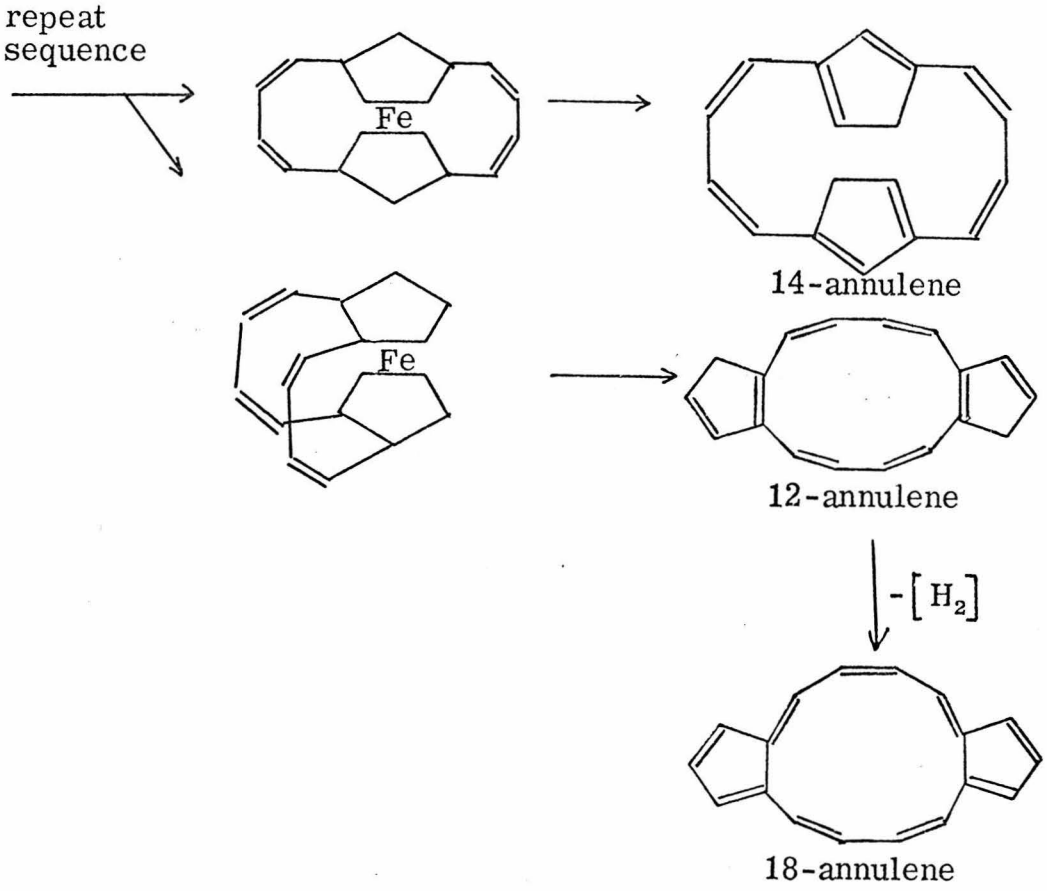


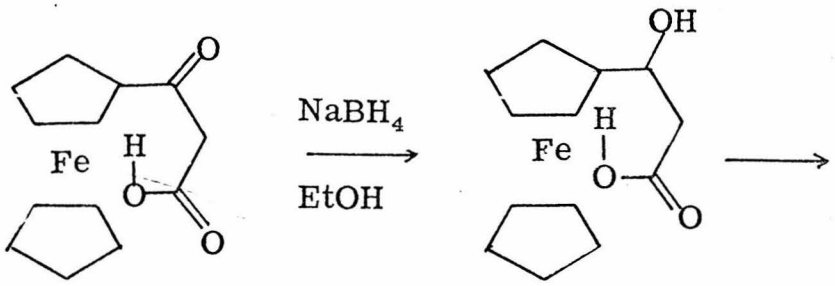
Ref. 21

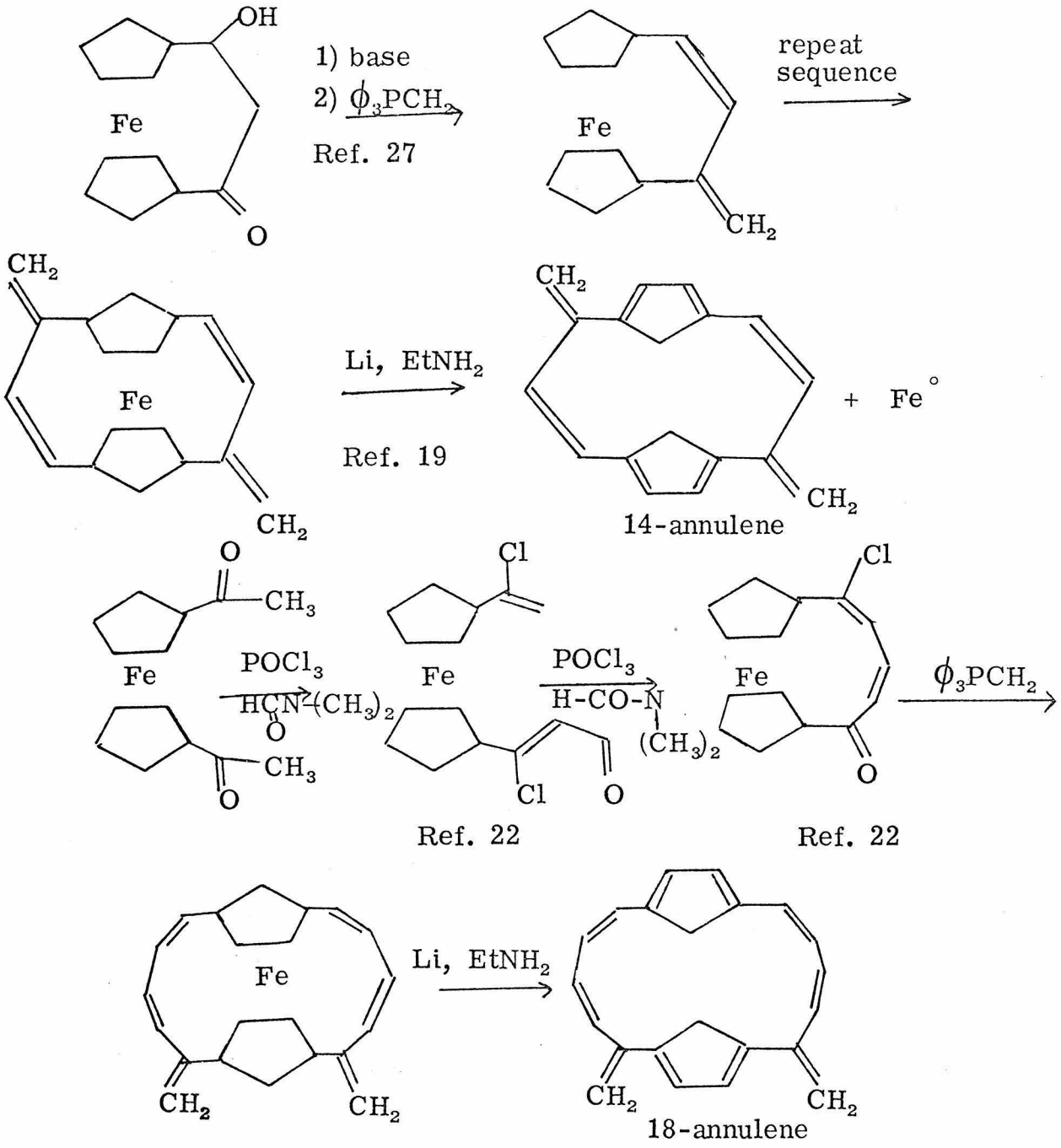
2. Syntheses of non-benzenoid aromatic annulenes






repeat
sequence
Fe
14-annulene
Fe
12-annulene
-[H2]
18-annulene


O
Fe
H
O
O
NaBH4
EtOH
OH
Fe
H
O
O


OH
Fe
O
1) base
2) ϕ_3PCH_2
Ref. 27
repeat sequence
Fe
CH_2
CH_2
Fe
CH_2
Li, $EtNH_2$
Ref. 19
CH_2
+ Fe°
CH_2
14-annulene
O
CH_3
Fe
O
CH_3
$POCl_3$
$HCN(CH_3)_2$
Cl
Fe
Cl
O
$POCl_3$
H-CO-N
$(CH_3)_2$
Ref. 22
Cl
Fe
O
ϕ_3PCH_2
Ref. 22
Fe
CH_2
CH_2
Li, $EtNH_2$
CH_2
CH_2
18-annulene

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PROPOSITION VI

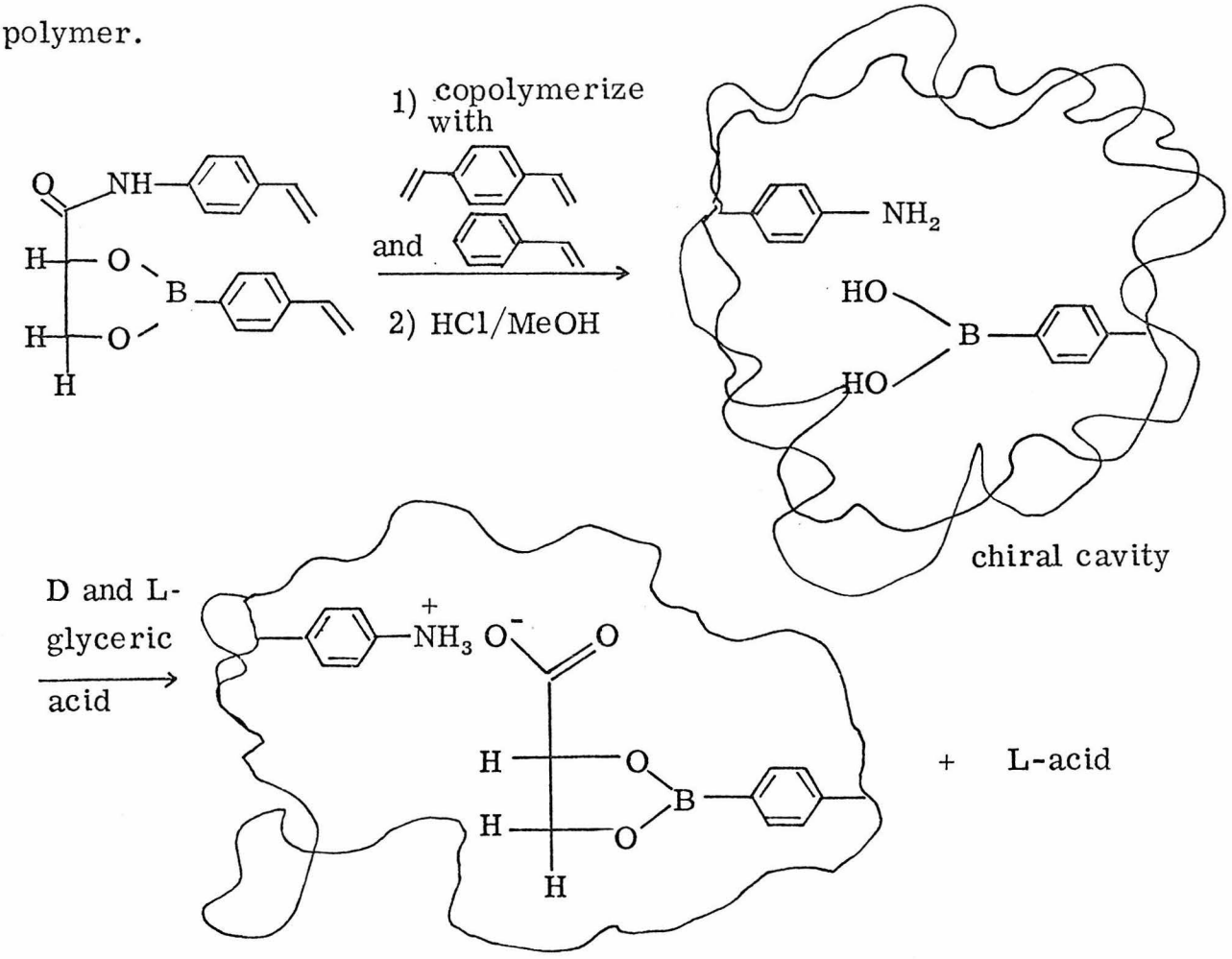
It is proposed that zeolites with chiral cavities be synthesized, and their potential utility as resolving agents of racemic mixtures of organic compounds be studied.

The most commonly used method for the separation of a racemic mixture of organic compounds is reaction of the mixture with an optically active reagent to form two diastereomeric complexes which can be separated on the basis of different physical properties.[1] Usually this involves the formation of diastereomeric salts by the reaction of an acidic functional group on one chiral compound with a basic functional group on the other chiral compound.

Recently, however, some investigators have concerned themselves with finding systems that differentiate between enantiomers on the basis of their individual three-dimensional shapes. In the two examples which will be discussed this has involved the formation of chiral cavities into which one enantiomer fits better than the other.

In 1973, Wulff, Sarhan and Zabrocki designed a highly cross-linked polystyrene which contained chemically bound units of D-glyceric acid (see Scheme 1).[2] The glyceric acid was bound through its acid function to an aniline unit by an amide linkage and through its hydroxyl groups by the formation of a boronic acid diester. The D-glyceric acid was then

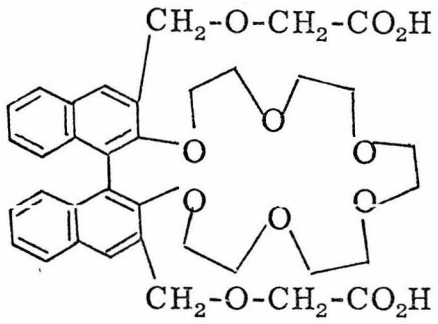
"clipped out" of the polymer by reaction with HCl and removed from the polymer.



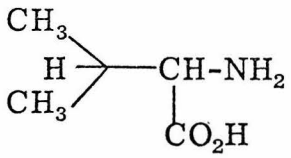
The authors felt that the cavity where the D-acid had resided was more disposed to rebind a D-form rather than an L-form of the acid if a 1:1 mixture of the enantiomers was brought into contact with the polymer. Appropriate experiments showed that the polymer did, in fact, show a slight preference for complexing with the D-form over the L (resolving factor of 1.034).

This pseudo-enzyme system was easily and irreversibly "denatured" by physical forces that changed the shape of the cavity such as heat and polymer swelling in certain solvents.

Cram et al. has designed a polymer containing macrocyclic crown ethers that have chiral cavities by virtue of the restricted rotation about the napthyl linkage (see below).[3a] Because the functional groups which bind the substrate (simple amino acids) are all located on a single cycle of 20 atoms, deformations due to heat and solvent caused polymer swellings are much less. A column packed with bound units of a single antipode of 1 was used to resolve a racemic mixture of (R) and (S) valine. Heating of the macrocycle to temperatures (205°; 200 hr) at which the binapthyl group inverts results in loss of all resolving ability.[3b]



1



valine

In contrast to organic polymers the structural frameworks of zeolites are known to be stable at very high temperatures (650°C).[4] The introduction of chiral cavities into zeolites follows from the studies of Barrer and Denney.[5] These workers in their pioneering research on

zeolite synthesis have introduced the use of large organic cations to replace or partly replace the alkali metal cations such as Na^+ which are normally present in classical zeolite syntheses. Zeolites are hydrous aluminosilicates of calcium, sodium and other metals in which as much as half the total volume consists of cavities that are as much as 11 Å in diameter. The Group Ia and IIa metals are present as counterions to the negatively charged aluminate units in the zeolite skeleton which consists of tetrahedral Al and Si atoms connected by σ's. The positively charged metals are not bound tightly to the zeolite and may be exchanged, for example, a zeolite containing Na^+ counterions may exchange these for Ca^{++}ions in the ratio of 2 for 1.[4]

Replacement of several alkali metal ions by bulky organic cations of unit charge in the syntheses of zeolites has been found to increase the silicon-aluminum ratio in order to preserve electrical neutrality and has promoted unusual structural designs.[8] Organic cations that have been used are quaternary ammonium salts such as tetramethylammonium hydroxide (TMAH). In addition to preserving electrical neutrality in zeolites, other TMAH molecules have been shown to be trapped in the cavities of the zeolites.[6]

It is proposed that quaternary ammonium salts with optically active groups be used in the syntheses of a novel class of zeolites. The optically active hydroxides are expected to cause chiral cavities to be formed to accommodate the bulk of the molecules as the zeolite crystallizes out of

solution. Furthermore, it is expected that zeolites with chiral cavities will selectively adsorb one member of an enantiomeric pair. Thus, columns (vapor phase or column chromatography) packed with zeolites may be used to resolve racemic mixtures as the mixture passes through it.

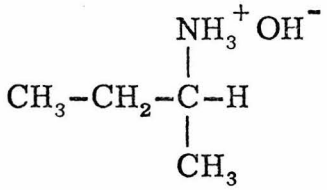
The use of zeolites to select molecules on the basis of shape is not new. For example, n-pentane is much more easily accommodated in zeolites with cavities of a certain size than is isopentane (by a factor of 35:1).[7] This research is proposed to fine adjust this selection process so that enantiomers can be distinguished by the zeolite in the same way that a right-handed nut selects a right-handed screw over a left-handed one.

The synthesis of zeolites with organic counterions is rather straightforward.[5,6] Sodium hydroxide, sodium aluminate, sodium silicate, a quaternary ammonium salt and water are heated at reflux for a few days till crystals of the zeolite fall out of solution. The zeolite is collected on a filter and dried at 120°. Occluded TMAH is released by heating to 350°C. Quaternary ammonium salts are broken down at these temperatures according to the equation:

$$(CH_3)_4\overset{+}{N}\overset{-}{O}H \xrightarrow[\Delta]{} (CH_3)_3N + CH_3OH$$

Occluded water (zeolitic water) and TMA ions acting as counterions are not released until the zeolite is heated to 650°C.

It is proposed that first syntheses be attempted with optically active sec-butylammonium hydroxide.



After appropriate heat treatment of the resulting zeolite, a VPC column will be prepared with this zeolite. Resolution of a racemic mixture containing an asymmetric center with a H, $-CH_3$ and $-CH_2CH_3$ and one other group will be attempted.

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