PART I

THERMAL REARRANGEMENTS OF SMALL RING HYDROCARBONS

PART II

PHOTOSENSITIZED REARRANGEMENTS OF SMALL RING HYDROCARBONS — NONVERTICAL ENERGY TRANSFER

Thesis by
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In Partial Fulfillment of the Requirements
For the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California
1966
(Submitted September 9, 1965)

ACKNOWLEDGMENT

I would like to express my appreciation to Dr. George S. Hammond for his kind attention and guidance of my work. I would also like to thank his exceptional group of students for many interesting and inspiring discussions. In particular, I would like to thank Donald Valentine, Kenneth Servis and F. Guy Moses for discussions pertinent to this work.

I offer my heartfelt thanks to my parents for their encouragement and support during my education, and to Dr. Glen A. Russell for his interest and help in my undergraduate education.

The monetary support of my education by the National Science Foundation, the Texaco Company and the Des Moines Register and Tribune Company is gratefully acknowledged.

ABSTRACT

PART I

The thermal rearrangements of _cis_- and _trans_-1, 2-divinylcyclobutane, _cis_- and _trans_-8-vinylbicyclo(4, 2, 0)-2-octene, _trans_-1, 2-dimethyl-1, 2-divinylcyclobutane and _trans_-1-isopropenyl-2-methyl-2-vinylcyclobutane have been studied in detail. The kinetic parameters indicate that the rearrangements of the _cis_ isomers occur by way of a concerted transition state while the _trans_ isomers rearrange through a diradical intermediate. Optically active _trans_-1, 2-divinylcyclobutane undergoes racemization as well as rearrangement, and produces 4-vinylcyclohexene having a trace of residual optical activity. Consequently we infer that the rates of ring closure in the intermediate are of the same order of magnitude as the rates of internal rotation about single bonds.

We have also studied the rates for the reversible isomerization of _cis_- and _trans_-1, 2-diphenylcyclopropane. Here the concerted mechanism is not possible for the _cis_ isomer; both isomers appear to go through a diradical intermediate.

PART II

We have observed the reversible photosensitized isomerization of _cis_- and _trans_-1, 2-diphenylcyclopropane. In contrast to the direct irradiation of diphenylcyclopropane, which gives several products, the sensitized reaction is very clean, giving only _cis_-_trans_ isomerization.

Comparison of the product ratios from the photosensitized decomposition of 3, 5-diphenyl-1-pyrazoline with the intercepts of Stern-Volmer plots for the sensitized isomerization of diphenylcyclopropane indicates that the same rotationally equilibrated species, 1, 3-diphenyltrimethylene, is produced in both cases. Apparently the triplet state of the diradical undergoes *cis*-*trans* equilibration before ring closure, while the singlet state, produced by either thermal decomposition or direct irradiation of the pyrazoline, does not. We infer from this that the rate of spin inversion is slower than the rate of internal rotation.

The quantum yields for the reaction with many different sensitizers were measured, and the rate constants for the energy transfer step calculated from these. These rate constants show an approximate correlation with the triplet energy of the sensitizer.

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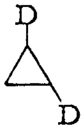
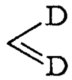
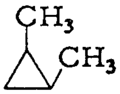
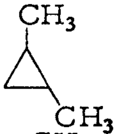
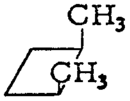
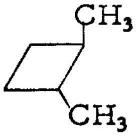
PART I

THERMAL REARRANGEMENTS OF SMALL RING HYDROCARBONS

INTRODUCTION

Substantial research has been done on the products and rates of thermal rearrangement of small ring cycloalkanes and alkylcycloalkanes. As examples the following rearrangements and their activation parameters are shown.

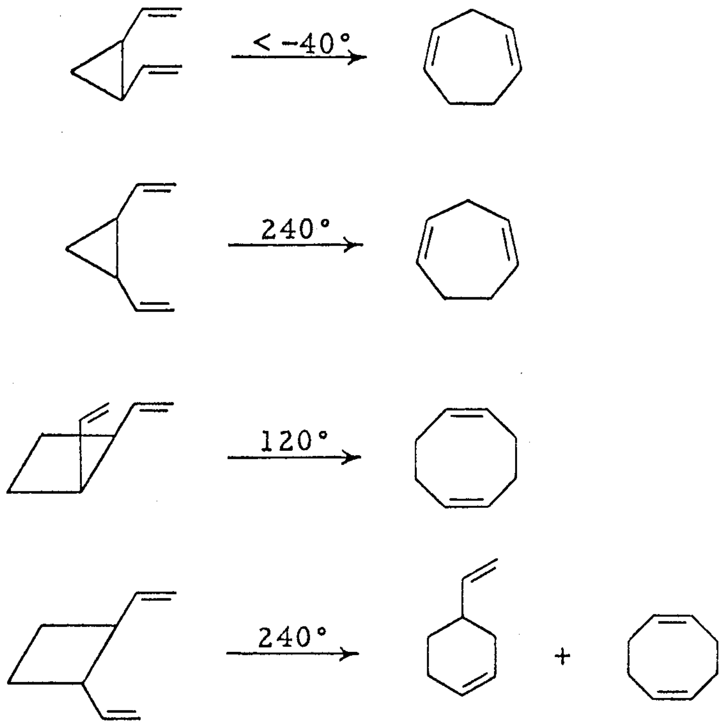
Reactant	Products	$\Delta H^{\ddagger}$(kcal/mole)	$\Delta S^{\ddagger}$(e.u.)	$\Delta F^{\ddagger}$(kcal/mole)
		63.7	13.2	53.9 (21)
		64.0	2.4	62.3
		58.0	7.6	52.5
		58.7	5.5	54.7 (22)
		59.0	8.6	52.8

These rearrangements are all first order and certainly unimolecular, as evidenced by their complete insensitivity to added catalysts, inhibitors and radical trapping agents. Since cis-trans isomerization has a lower activation enthalpy than hydrogen migration in the cyclopropane cases or breakup to ethylenes in the cyclobutane cases, these rearrangements are believed to go through diradical intermediates where only one bond is broken. The enthalpies of activation are much lower than that for the decomposition of ethane to two methyl radicals

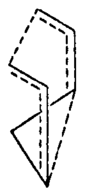
(83.3 kcal/mole), indicating that relief of strain helps the reaction. Furthermore, a large positive entropy of activation as is observed, would be expected for a reaction leading from a constrained small ring to a relatively loose diradical.

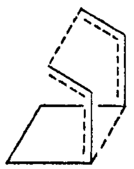
Frey, et al. (15), have studied the thermal rearrangements of vinylcyclopropane to cyclopentene and isopropenylcyclopropane to 1-methylcyclopentene. The enthalpies of activation for both reactions are 48.5 kcal/mole; the entropies of activation for both reactions are +1 e.u. It is clear from the lower enthalpy of activation (compared to 1,2-dideuterocyclopropane) that the transition state is stabilized by allylic resonance. Thus the transition state, which is probably very close to the intermediate, must have some diradical character. However, the smaller value for the entropy of activation, in the absence of information about the entropy change in going from a vinylmethylene group to an allylic radical, makes it necessary to consider the possibility of a "virtual" diradical intermediate rather than a "true" diradical intermediate. A true diradical is characterized simply by the absence of significant bonding between the two carbons to which radical character is attributed; in a virtual diradical some bonding will remain. Another way of looking at this is to say that the reaction is nearly or "partially" concerted.

It is futile to search the literature for rate studies on the thermal rearrangements of small ring 1,2-divinylcycloalkanes. For this reason it is difficult to make meaningful statements about the mechanisms of the reactions. Substantial differences have been found between the thermal rearrangements of cis- and trans-1,2-divinylcycloalkanes. Vogel (1) and Doering (6) have shown that the following rearrangements occur at the temperatures indicated.



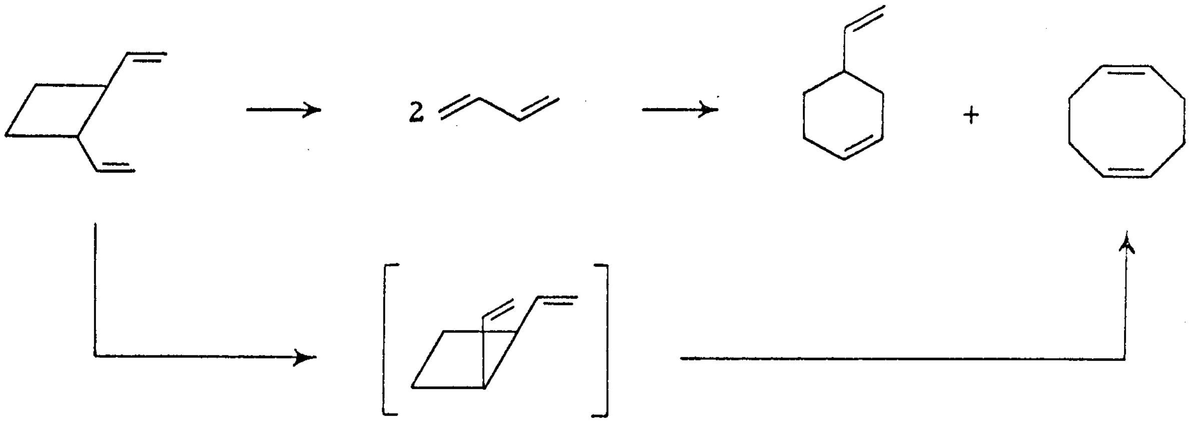
On the basis of the much lower temperatures required and the clean rearrangement to a single product with the cis isomers, a concerted transition state has been postulated, with bonds being broken and formed at the same, or nearly the same time.





The rearrangement thus occurs through a classical "no-mechanism" pathway similar to that proposed for the Cope rearrangement (2). Vogel (1) has suggested that the determining factor in the question of whether a given divinylcycloalkane will readily undergo this kind of rearrangement is simply the difference in strain energy between the reactants and products. Thus the relatively unstrained cis-1, 2-divinylcyclopentane will not rearrange to the highly strained cyclonona-1, 5-diene; in fact the reverse reaction occurs.

The mechanisms for the rearrangements of small ring trans-1, 2-divinylcycloalkanes are uncertain. Vogel (1) has proposed that trans-1, 2-divinylcyclobutane thermally rearranges by the mechanism shown below. We shall show that this is incorrect.



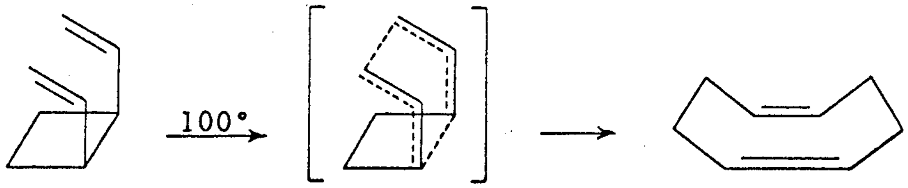
The mechanism for the thermal rearrangement of trans-1, 2-divinylcyclopropane is not clear. It has been proposed (2) that the rearrangement occurs through a "diradical" species to give either cis-1, 2-divinylcyclopropane (which would rearrange instantly under the conditions of its formation to 1, 4-cycloheptadiene) or directly the concerted transition state leading to 1, 4-cycloheptadiene. Although the nature of this "diradical" has never been discussed, it is unlikely that it can be a true diradical, since one would expect a true diradical to close more easily to a five-membered ring than either a three- or a seven-membered ring. No 4-vinylcyclopentene was observed in the products, even though it is stable under the conditions of its formation and analysis. Thus the intermediate in the rearrangement may be a virtual diradical, characterized by the existence of a significant amount of bonding between the two carbon atoms to which radical character is attributed. Thus the molecule cannot get into the proper orientation leading to 4-vinylcyclopentene.

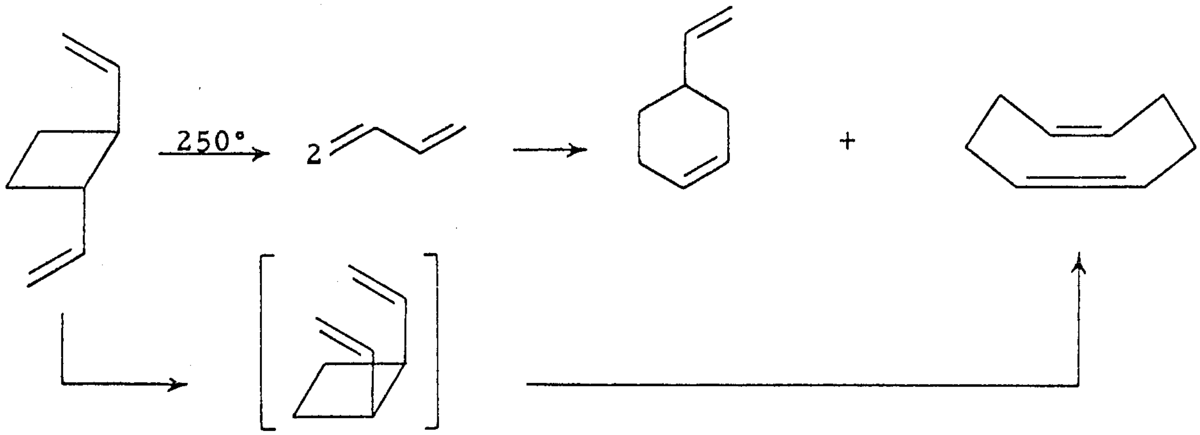
The purpose of the experiments done for this thesis is to shed some light on the question of the nature of the intermediates involved in thermal rearrangements of small ring 1, 2-divinylcycloalkanes and to give an insight into the details of the mechanisms involved.

RESULTS

Preliminary Mechanistic Study

Vogel (1) has reported the following mechanisms for the thermal isomerizations of *cis*- and *trans*-1, 2-divinylcyclobutane.





The mechanism for the rearrangement of *cis*-1, 2-divinylcyclobutane to *cis*, *cis*-1, 5-cycloöctadiene involves concerted bond breaking and bond formation. It is a classical "no-mechanism" (2) Cope rearrangement. The mechanism for the rearrangement of *trans*-1, 2-divinylcyclobutane, on the other hand, requires at least two concurrent steps, since the thermal dimerization of butadiene gives much less 1, 5-cycloöctadiene than is actually observed in the rearrangement of *trans*-1, 2-divinylcyclobutane (3). Since Vogel gives no evidence requiring this mechanism, we may suppose it was intended to be sufficient to explain the data but not to be the only possible mechanism.

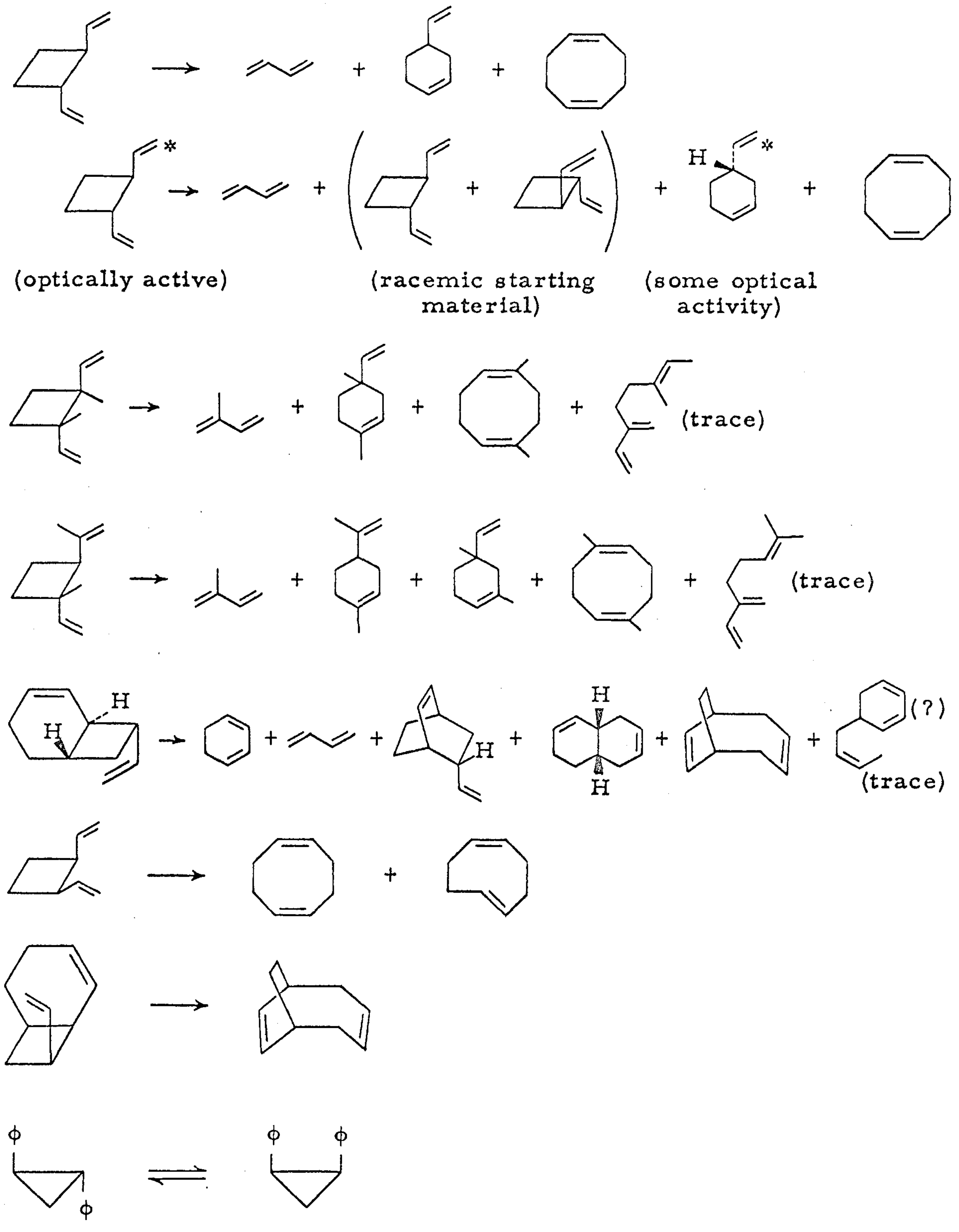
The following experiments prove that Vogel's mechanism is incorrect for the rearrangement of trans-1, 2-divinylcyclobutane.

1. When 1, 3-butadiene and trans-1, 2-divinylcyclobutane are passed through a hot pyrex tube in streams of nitrogen under identical conditions, the divinylcyclobutane is about 50% rearranged while only a fraction of a percent of dimers are found with butadiene. (Since some dimers are present in the commercial butadiene used for this experiment, it is not certain that any dimers were formed in the hot tube.)
2. The ratio of butadiene produced to other products formed when trans-1, 2-divinylcyclobutane is heated in sealed tubes does not depend on the extent of the rearrangement.
3. When optically active trans-1, 2-divinylcyclobutane is rearranged, the 4-vinylcyclohexene produced is optically active.

Thermal Rearrangements

We have studied the thermal rearrangements shown in Figure I. All the cyclobutane substrates were prepared by photosensitized dimerization or cycloaddition reactions of the appropriate starting materials. (See the Experimental section for details.) The cyclopropanes were prepared by conventional methods which are described in the Experimental section. Identification of all products was done by comparison of the v. p. c. elution times with those of authentic samples.

Figure I


*
(optically active)
*
H
(racemic starting material)
(some optical activity)
(trace)
H
H
H
H
H
(?)
(trace)
ϕ
ϕ
ϕ
ϕ

Structure proofs of the products from rearrangement of the isoprene dimers and the cyclohexadiene-butadiene adducts were done by Dr. R. S. H. Liu (4). The structures of the trace products have not been proved. They are based on an analogous rearrangement of 1-methyl-2-vinylcyclobutane which will be discussed later.

All thermal rearrangements were run with neat liquids in very small sealed tubes in an oil bath. Various changes in the conditions were made (amount of oxygen present, pressure in the tube, kind of glass used in the tube and presence or absence of solvent). None of these changes affected the reactions in any way. There were no side reactions other than those indicated by trace products and no loss of material to 5% accuracy.

The Kinetics of the Rearrangements

To provide an insight into the mechanisms of these rearrangements, the kinetics of the loss of starting material for all the reactions in Figure I were studied at different temperatures. Furthermore, trans-1, 2-divinylcyclobutane was partially resolved by asymmetric hydroboration (5) and the kinetics of the loss of optical activity of the total solution were studied. Figures II through IX show representative plots of ℓn (fraction of starting material remaining) vs. time. It is obvious that all the data give an excellent fit with first-order kinetics.

Variation of the Product Distribution with Temperature

Table I gives the product distributions at the various temperatures

Figure II

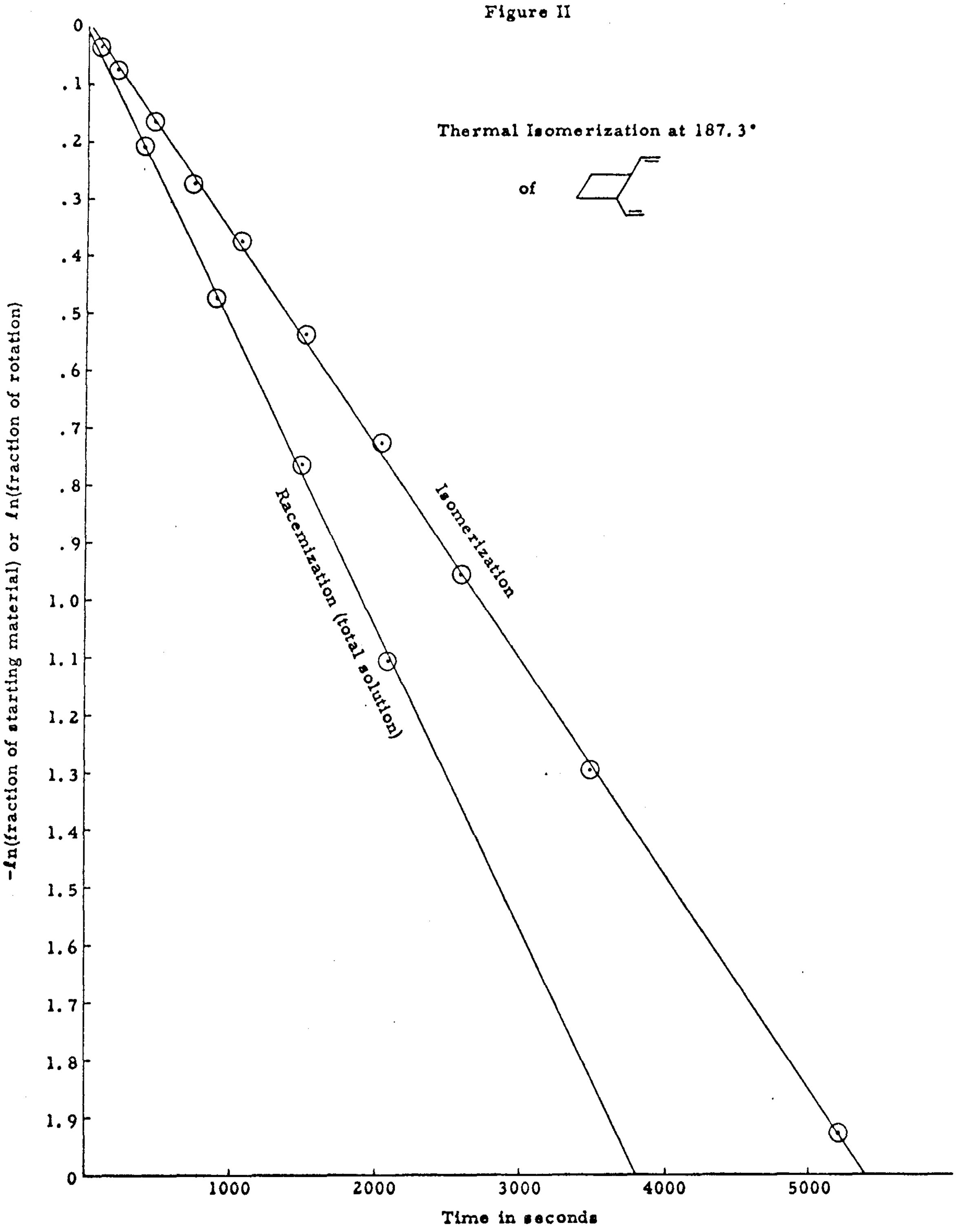
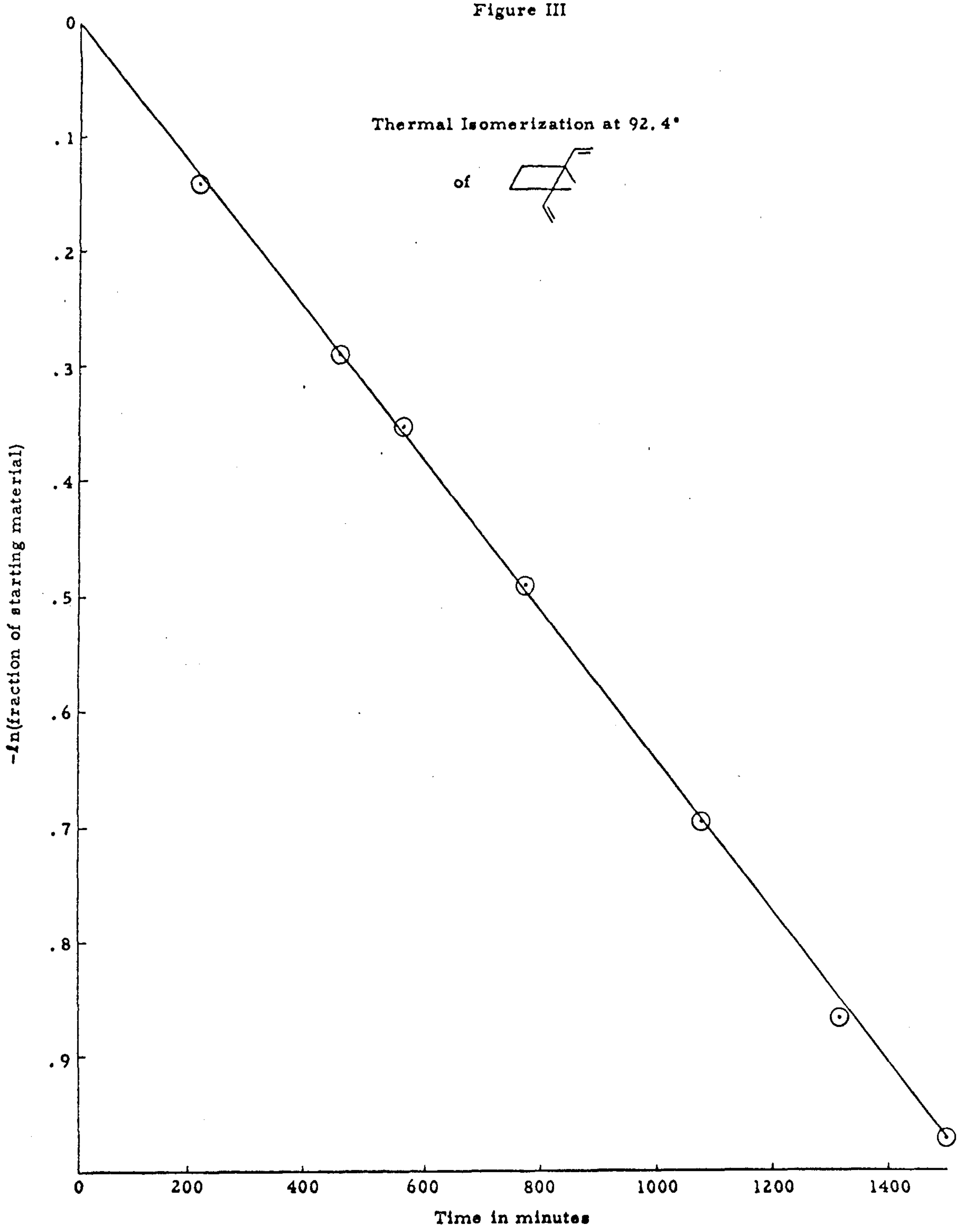

Thermal Isomerization at 187.3°
of
Isomerization
Racemization (total solution)
-ℓn(fraction of starting material) or ℓn(fraction of rotation)
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
0
1000
2000
3000
4000
5000
Time in seconds

Figure III



Thermal Isomerization at 92.4° of

Figure IV

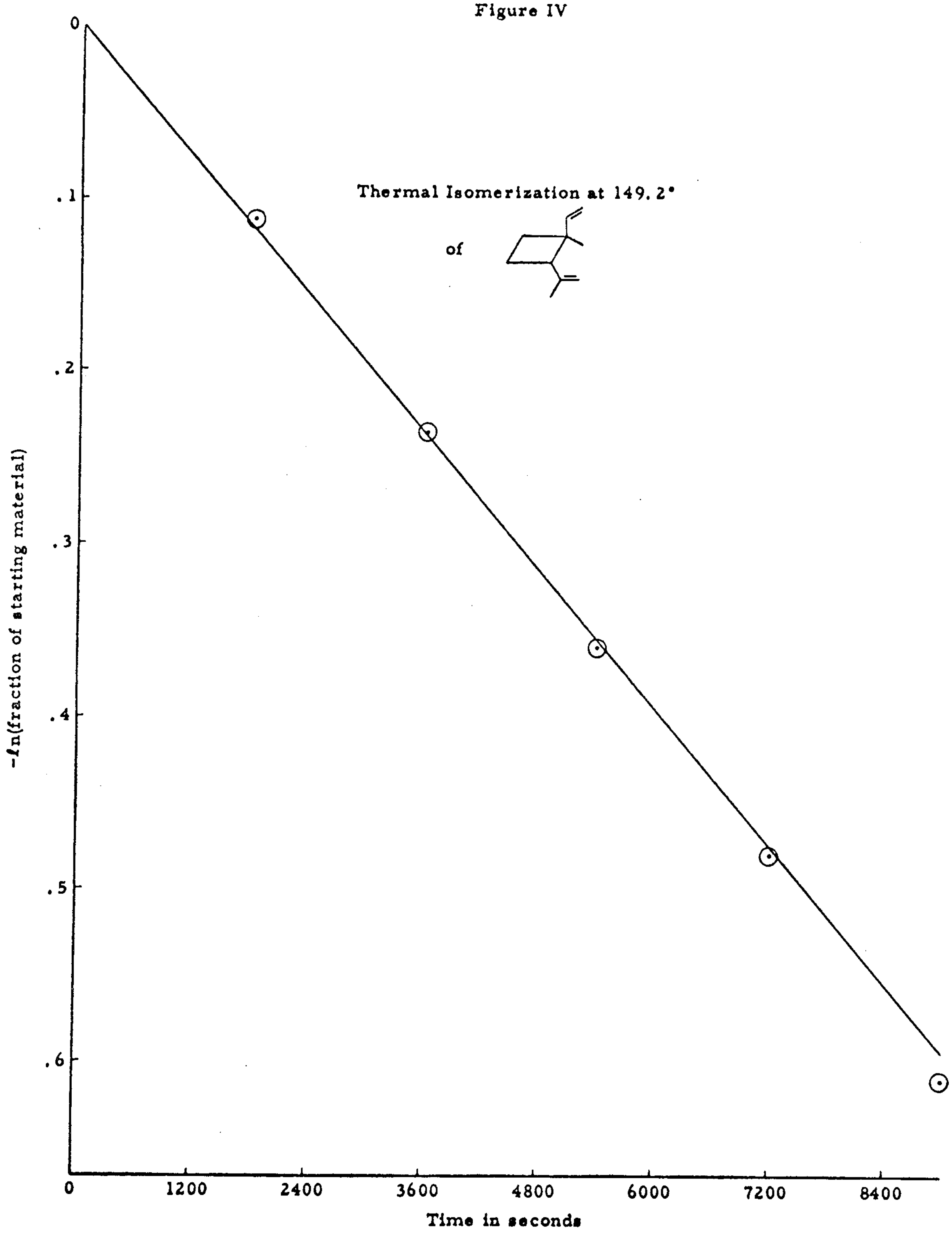
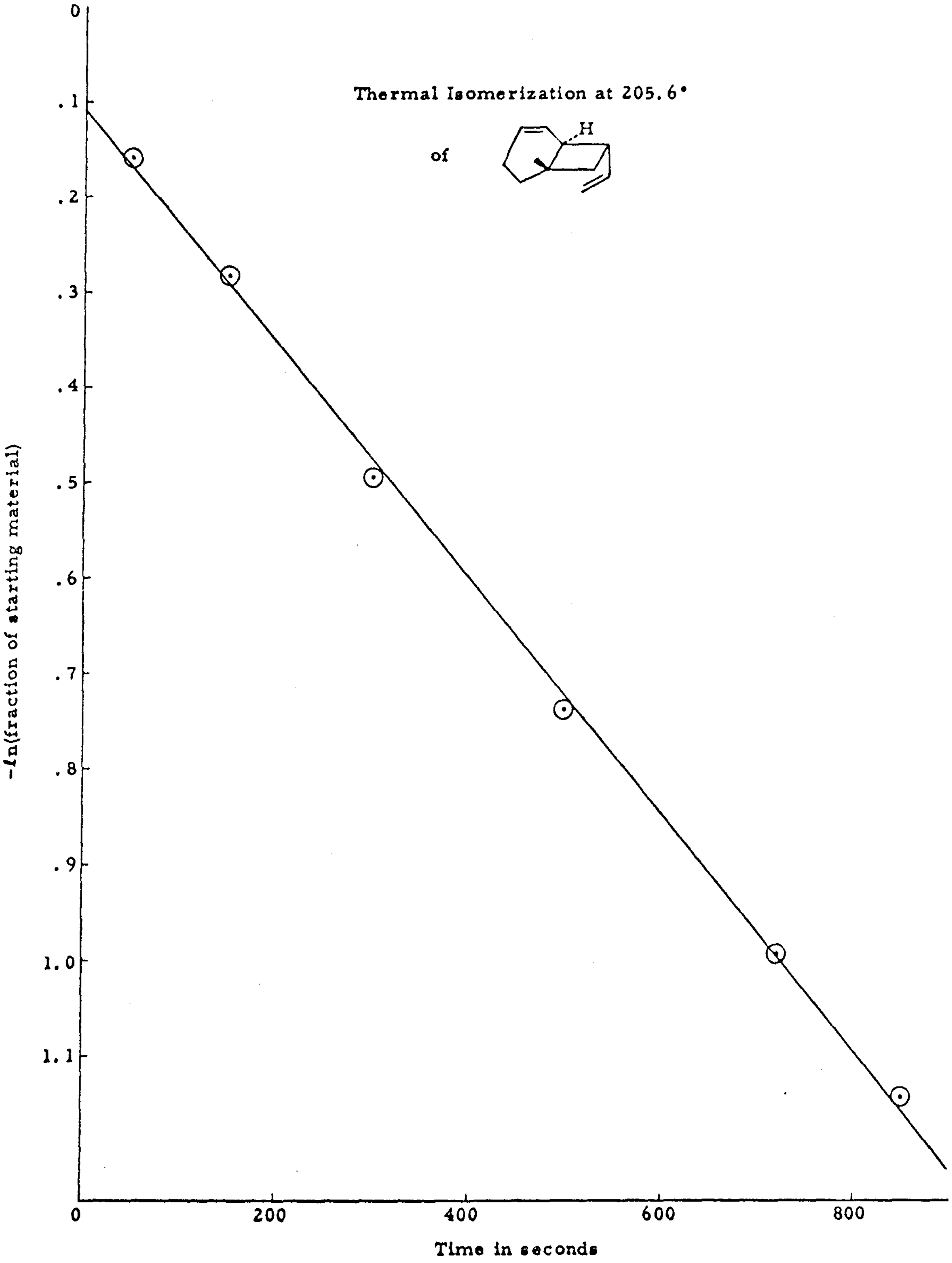
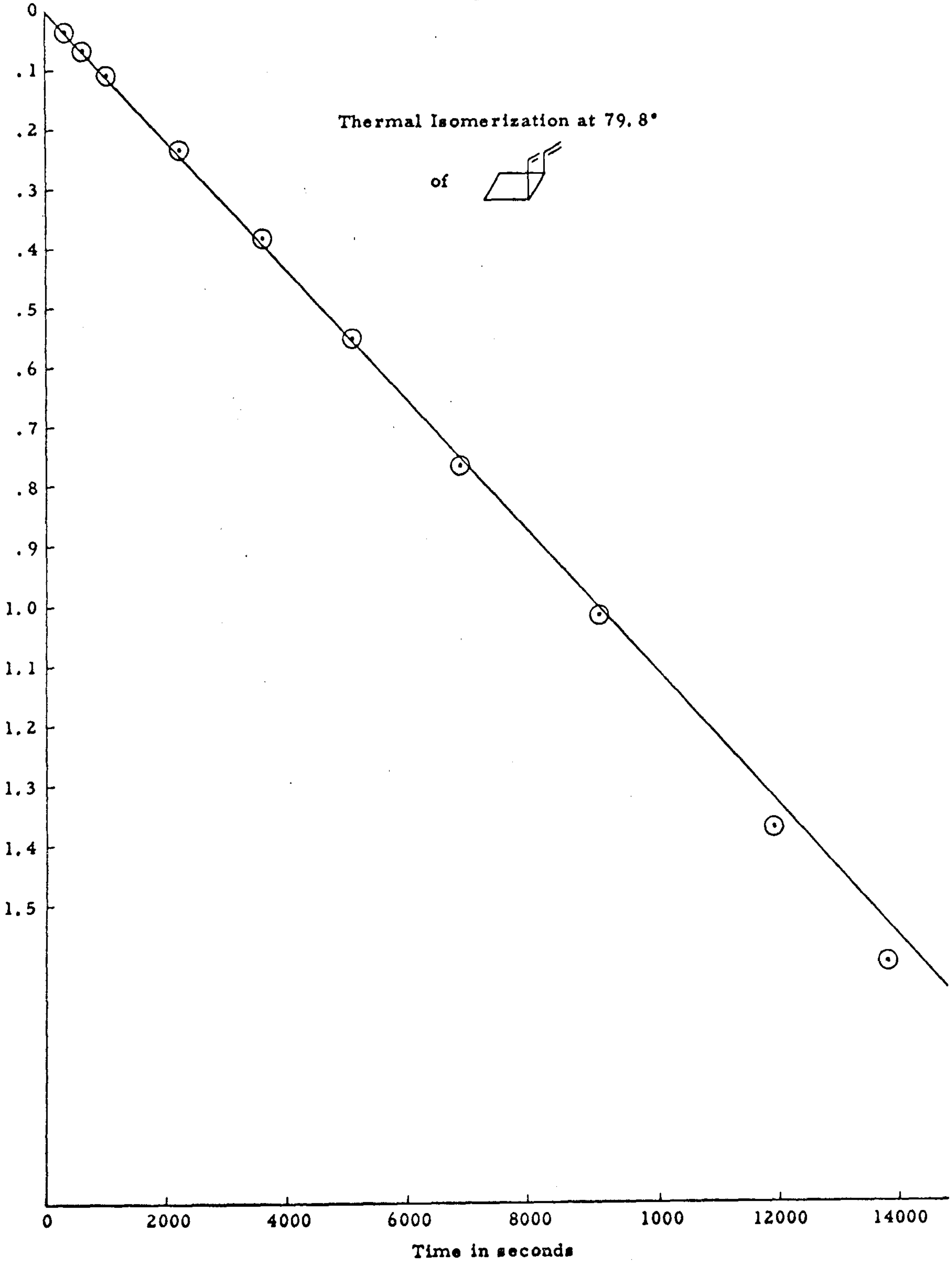

Thermal Isomerization at 149.2°
of
0
.1
.2
.3
.4
.5
.6
−ℓn(fraction of starting material)
0
1200
2400
3600
4800
6000
7200
8400
Time in seconds

Figure V



Thermal Isomerization at 205.6° of

Figure VI



Thermal Isomerization at 79.8° of

Figure VII

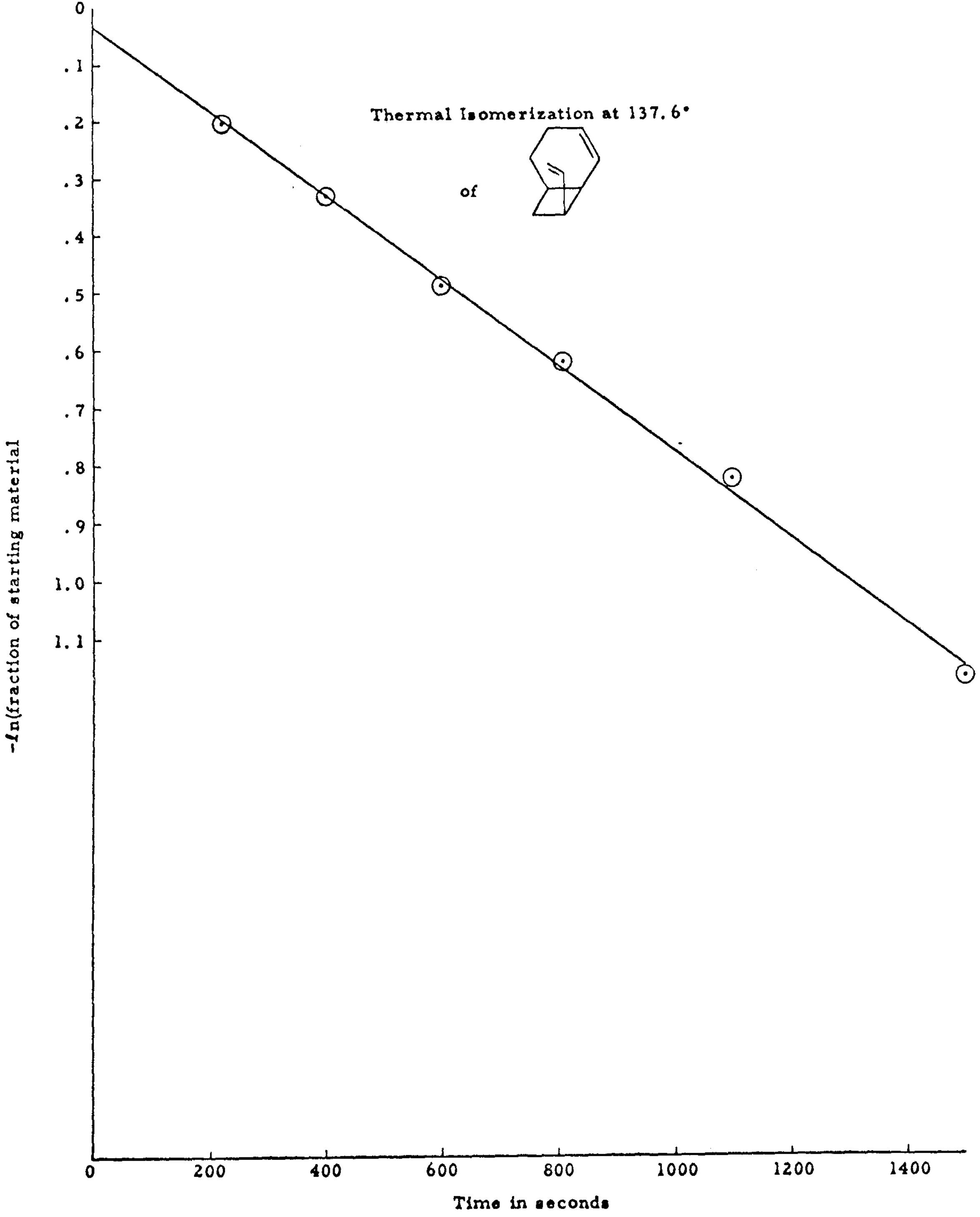

Thermal Isomerization at 137.6°
of
-ln(fraction of starting material
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
1.1
0
200
400
600
800
1000
1200
1400
Time in seconds

Figure VIII

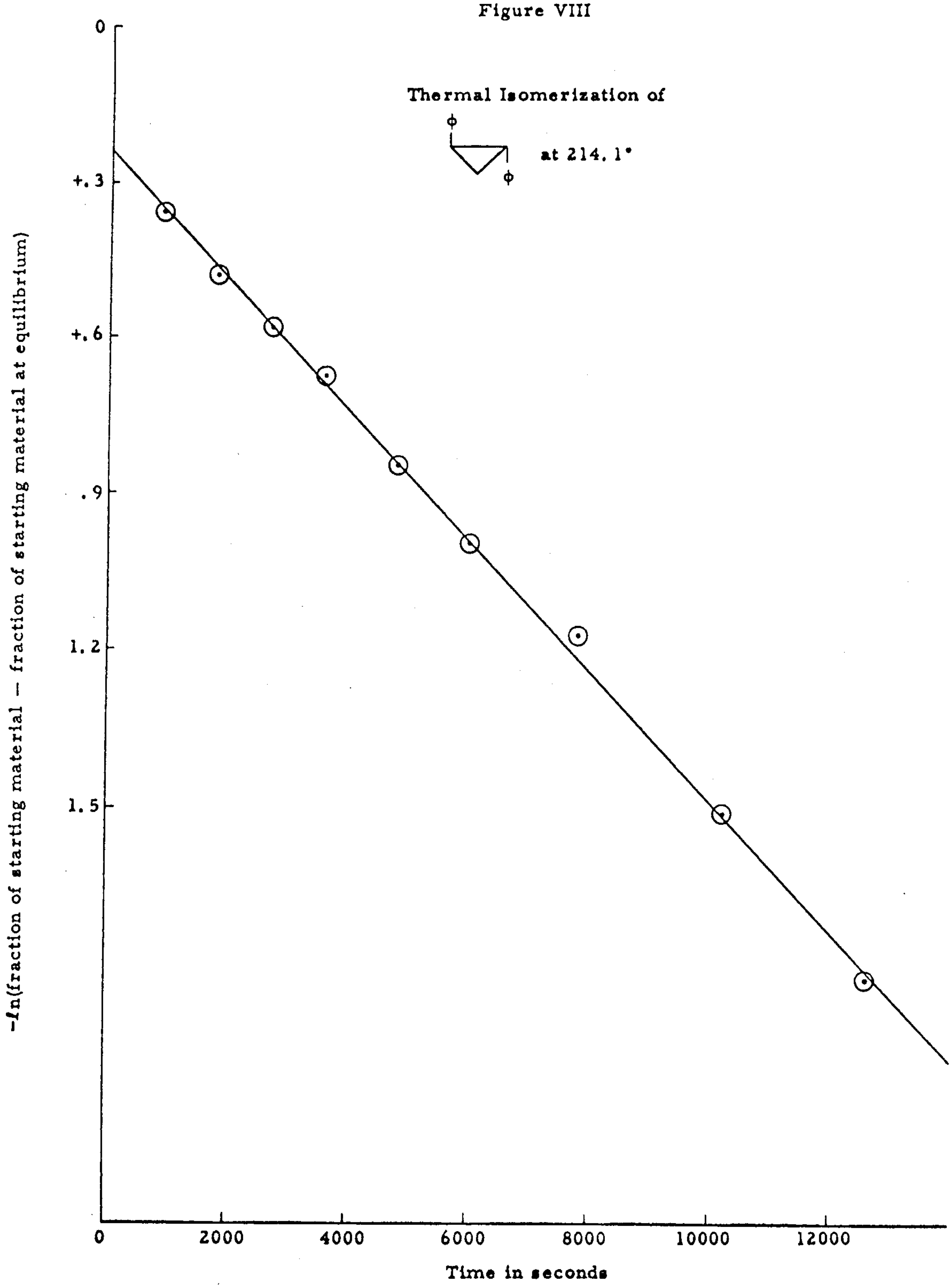

Thermal Isomerization of
ϕ
ϕ
at 214.1°
-ln(fraction of starting material — fraction of starting material at equilibrium)
0
+.3
+.6
.9
1.2
1.5
0
2000
4000
6000
8000
10000
12000
Time in seconds

Figure IX

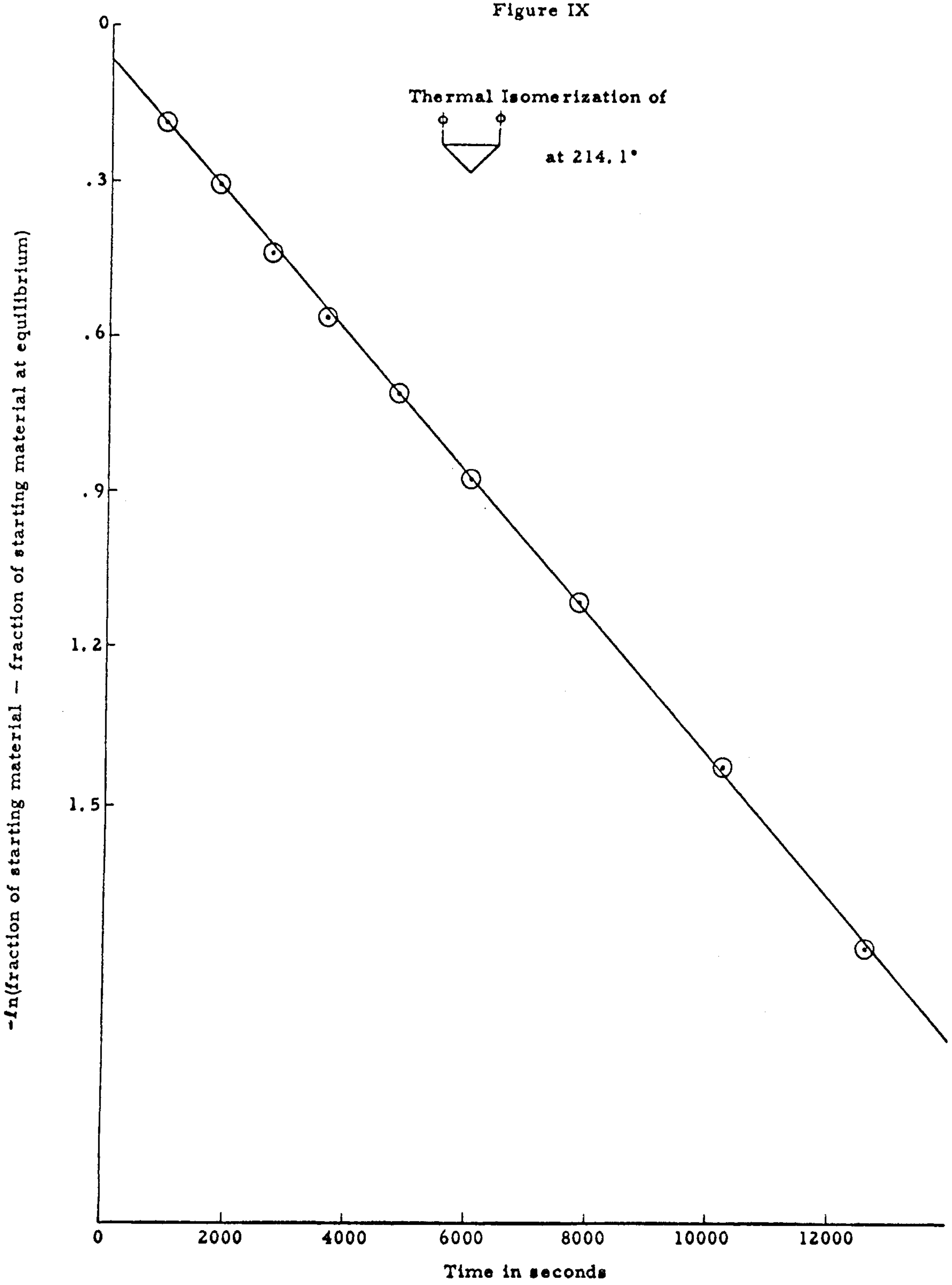
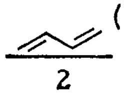
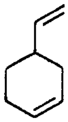
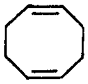
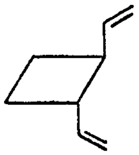
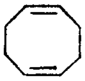
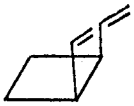

Thermal Isomerization of
at 214.1°

Table I

Variation of Product Distributions with Temperature

Substrate	Temperature °C	Products		
		 (a)		
	139.3	3.5%	71.3%	25.2%
	153.9	3.8%	70.4%	25.7%
	175.2	4.8%	69.3%	25.8%
	187.3	6.1%	68.2%	25.6%
	210.3	7.0%	67.5%	26.3%

		 cis-trans	 cis-cis
	65.4	1.5%	98.5%
	79.8	2.0%	98.0%
	96.8	2.5%	97.5%
	108.5	3.0%	97.0%

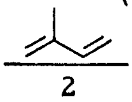
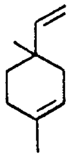
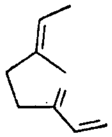
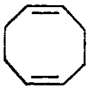
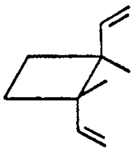
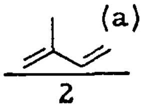
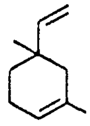
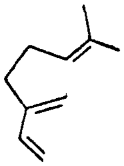
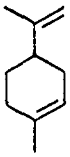
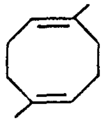
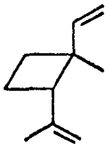
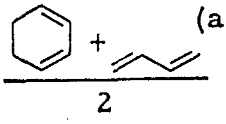
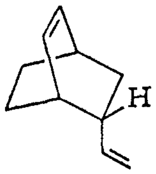
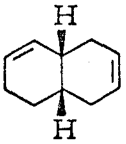
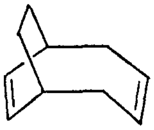
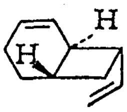
		 (a)			
	92.4	14.5%	72.9%	5.4%	7.2%
	109.2	16.0%	71.9%	5.0%	7.1%
	121.9	17.1%	70.0%	4.3%	8.6%
	135.7	18.0%	69.5%	3.9%	8.6%

Table I (continued)

		Products				
Hydro-carbon	Temper-ature	 (a)				
	135.7	11.1%	32.1%	1.3%	45.7%	9.8%
	149.2	12.2%	33.8%	0.7%	41.0%	12.3%
	161.3	12.5%	31.4%	1.2%	39.1%	15.8%
	176.8	14.0%	30.7%	1.1%	35.4%	18.8%

		 (a)	 (b)		
	179.7	5.3%	≈20%	48.4%	46.7%
	193.0	5.9%	≈20%	46.5%	47.6%
	206.5	5.1%	≈20%	46.9%	47.0%

a. The amount of these products, unseparated on the v. p. c. where two were found, was divided by two to show what percentage of starting material was used to form them.

b. Variation of this product with temperature was not measured since it was discovered later unseparated from starting material. It was assumed to be constant with temperature to show the relative variation of the other products. All the rates were corrected for this additional product.

that the reactions were run. All products were stable under the conditions of the analysis, and the product distributions were invarient with time or extent of conversion of the starting material.

Table II gives the optical rotation of the 4-vinylcyclohexene produced at different temperatures from optically active trans-1, 2-divinylcyclobutane. The rotation of the 4-vinylcyclohexene did not change upon prolonged heating at the highest reaction temperature.

In Figure II it can be seen that loss of optical activity of the total solution is faster than loss of starting material. After 50% rearrangement of optically active trans-1, 2-divinylcyclobutane, the starting material remaining was isolated. It was partially racemized, just as Figure II would lead one to expect. The difference between the rate of racemization of the total solution and the rate of isomerization at different temperatures gives a measure of the amount of the enantiomer of the starting material produced at different temperatures. Since the 4-vinylcyclohexene produced had a small rotation in these experiments, all the data were corrected so that only the activity due to trans-1, 2-divinylcyclobutane appears.

Variation of the Rate Constants with Temperature

The measured rate constants for these reactions can be fitted into the Eyring kinetic treatment,

$$\ln \frac{k}{T} = \ln \frac{\kappa}{h} + \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{R} \left(\frac{1}{T}\right)$$

Figures X through XVII show Eyring plots for all the reactions studied.

Table II

Optical Rotation of 4-Vinylcyclohexene Formed at Various Temperatures

Temperature °C	Rotation of Product[a]
176.3°	0.124° ± .002°
192.9°	0.076° ± .002°
204.5°	0.054° ± .002°

a. Starting material had a rotation of 2.0°.

Figure X

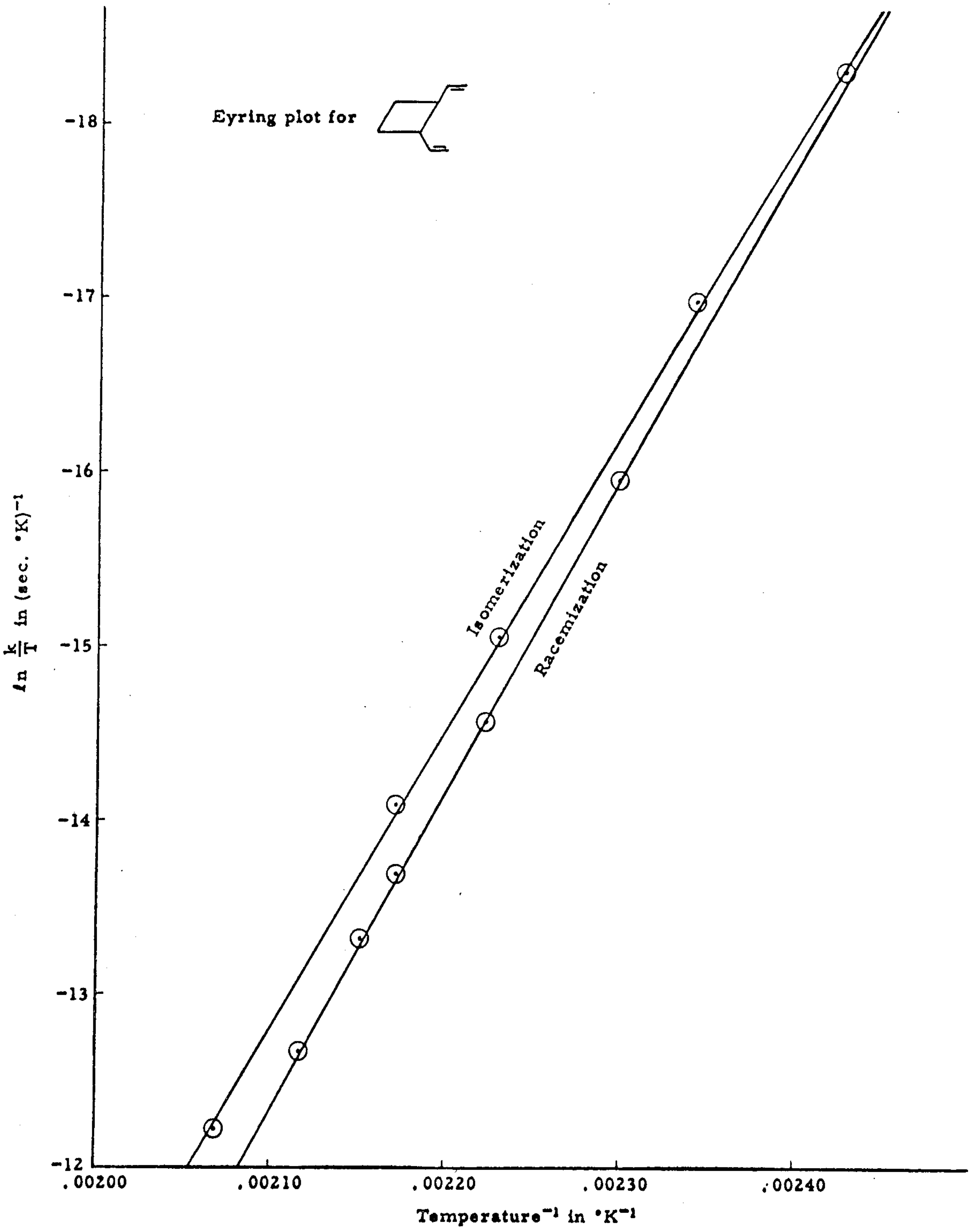

Eyring plot for
-18
-17
-16
-15
-14
-13
-12
$\ln \frac{k}{T}$ in (sec. °K)$^{-1}$
Isomerization
Racemization
.00200
.00210
.00220
.00230
.00240
Temperature^{-1} in °K^{-1}

Figure XI

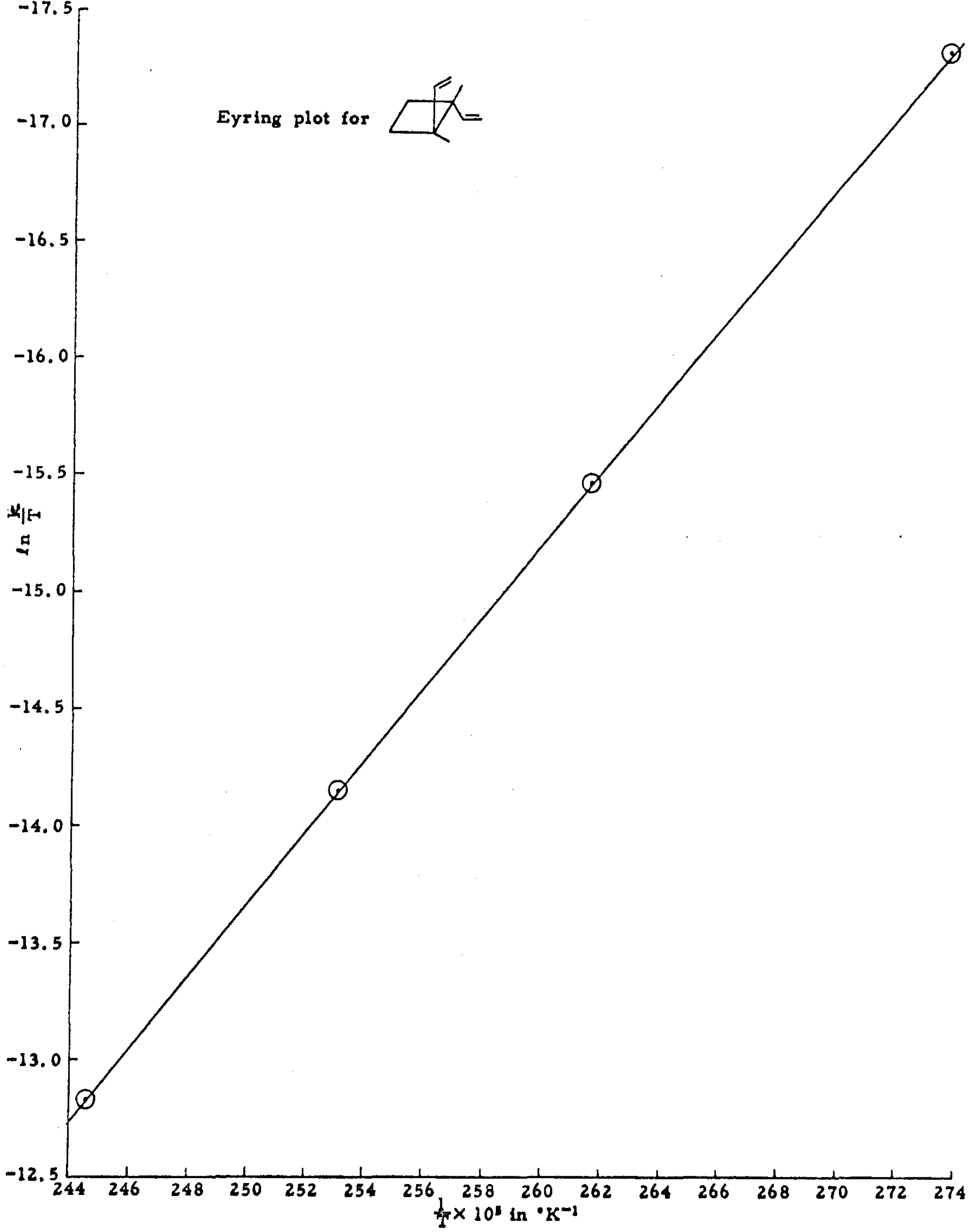

Eyring plot for
-17.5
-17.0
-16.5
-16.0
-15.5
-15.0
-14.5
-14.0
-13.5
-13.0
-12.5
ln k/T
244
246
248
250
252
254
256
258
260
262
264
266
268
270
272
274
1/T × 10⁵ in °K⁻¹

Figure XII

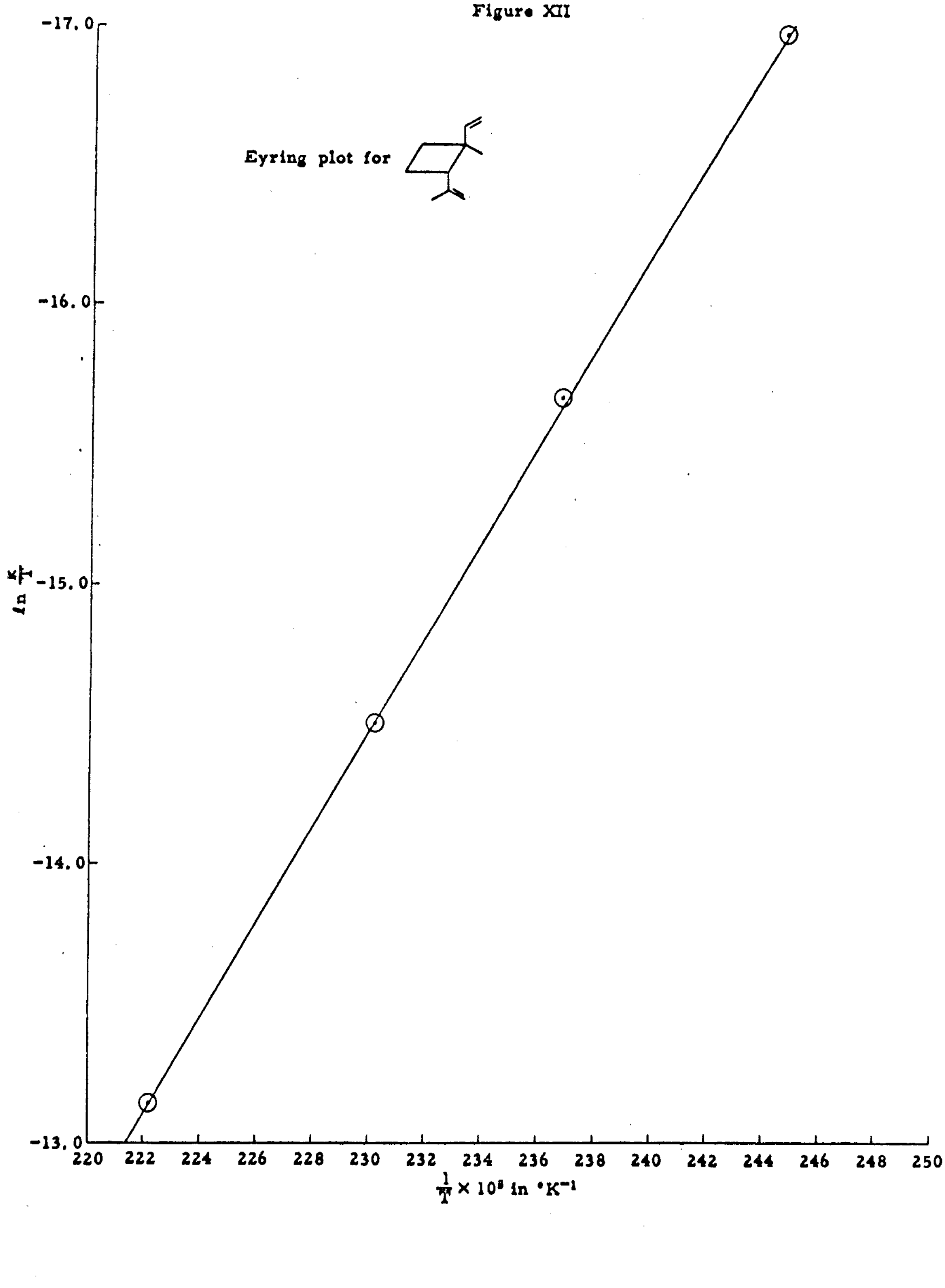

Eyring plot for
-17.0
-16.0
-15.0
-14.0
-13.0
$\ln \frac{k}{T}$
220
222
224
226
228
230
232
234
236
238
240
242
244
246
248
250
$\frac{1}{T} \times 10^5$ in °K^{-1}

Figure XIII

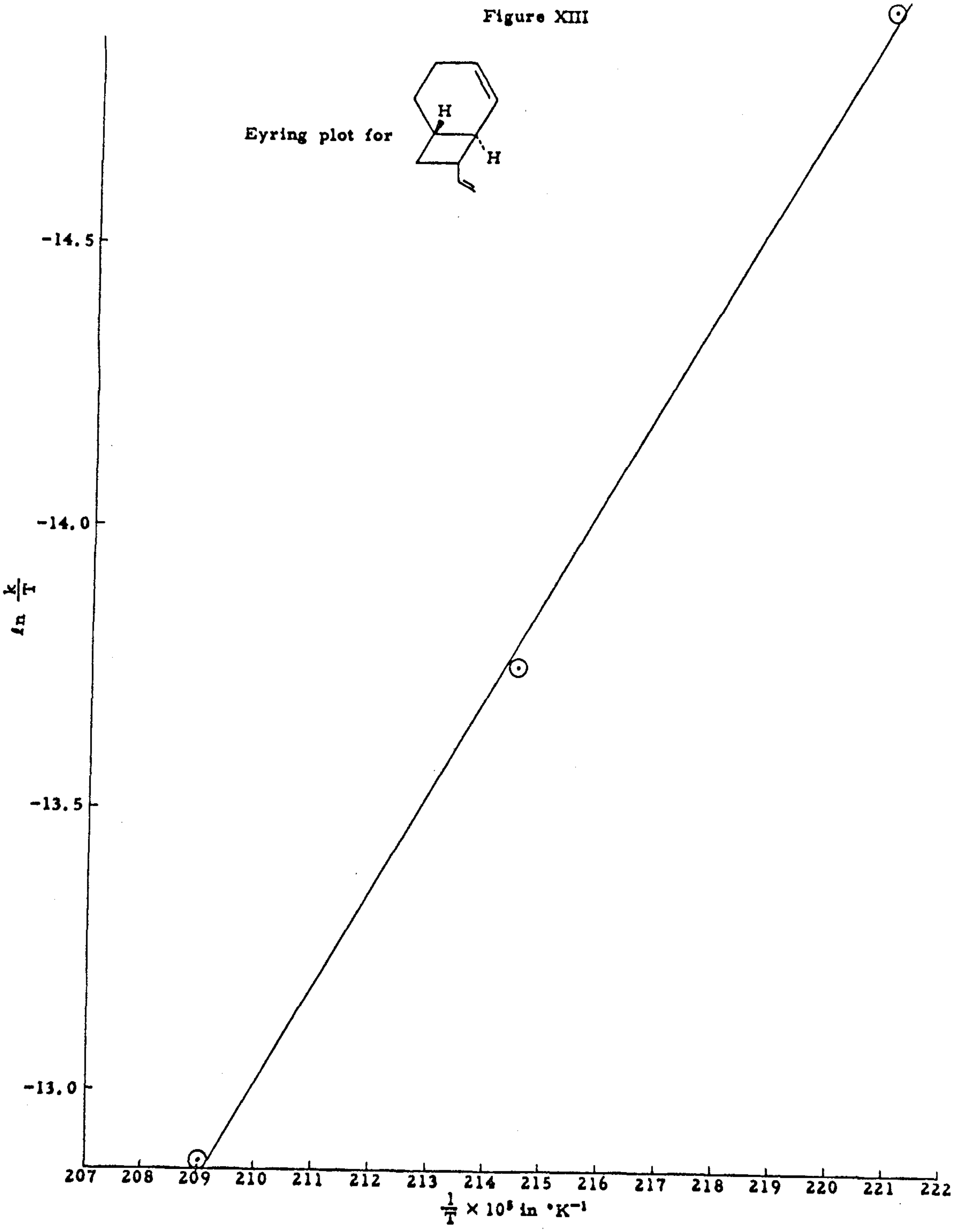
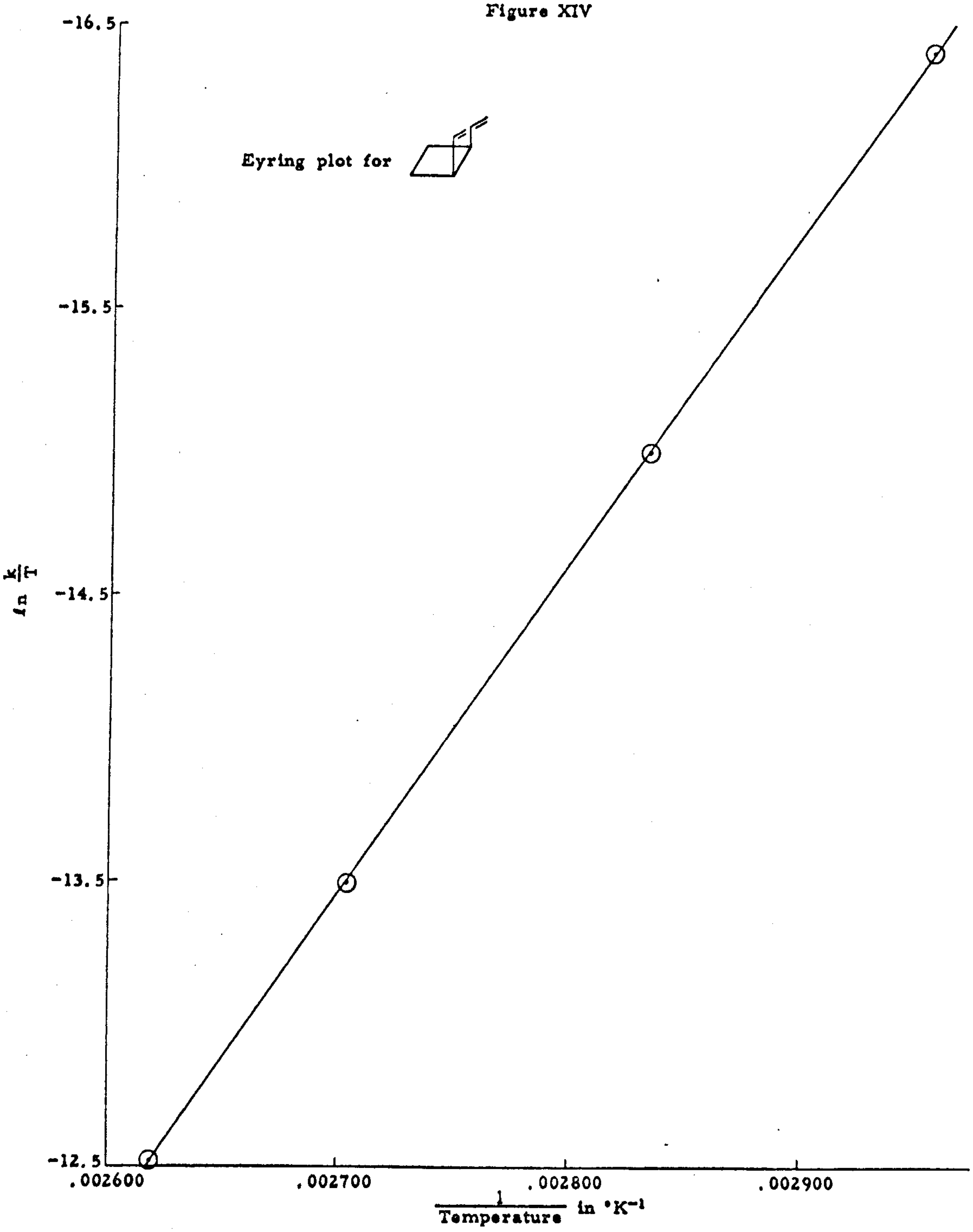

Eyring plot for
H
H
-14.5
-14.0
-13.5
-13.0
ln k/T
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
1/T × 10⁵ in °K⁻¹

Figure XIV


Eyring plot for
-16.5
-15.5
-14.5
-13.5
-12.5
$\ln \frac{k}{T}$
.002600
.002700
.002800
.002900
$\frac{1}{\text{Temperature}}$ in °K^{-1}

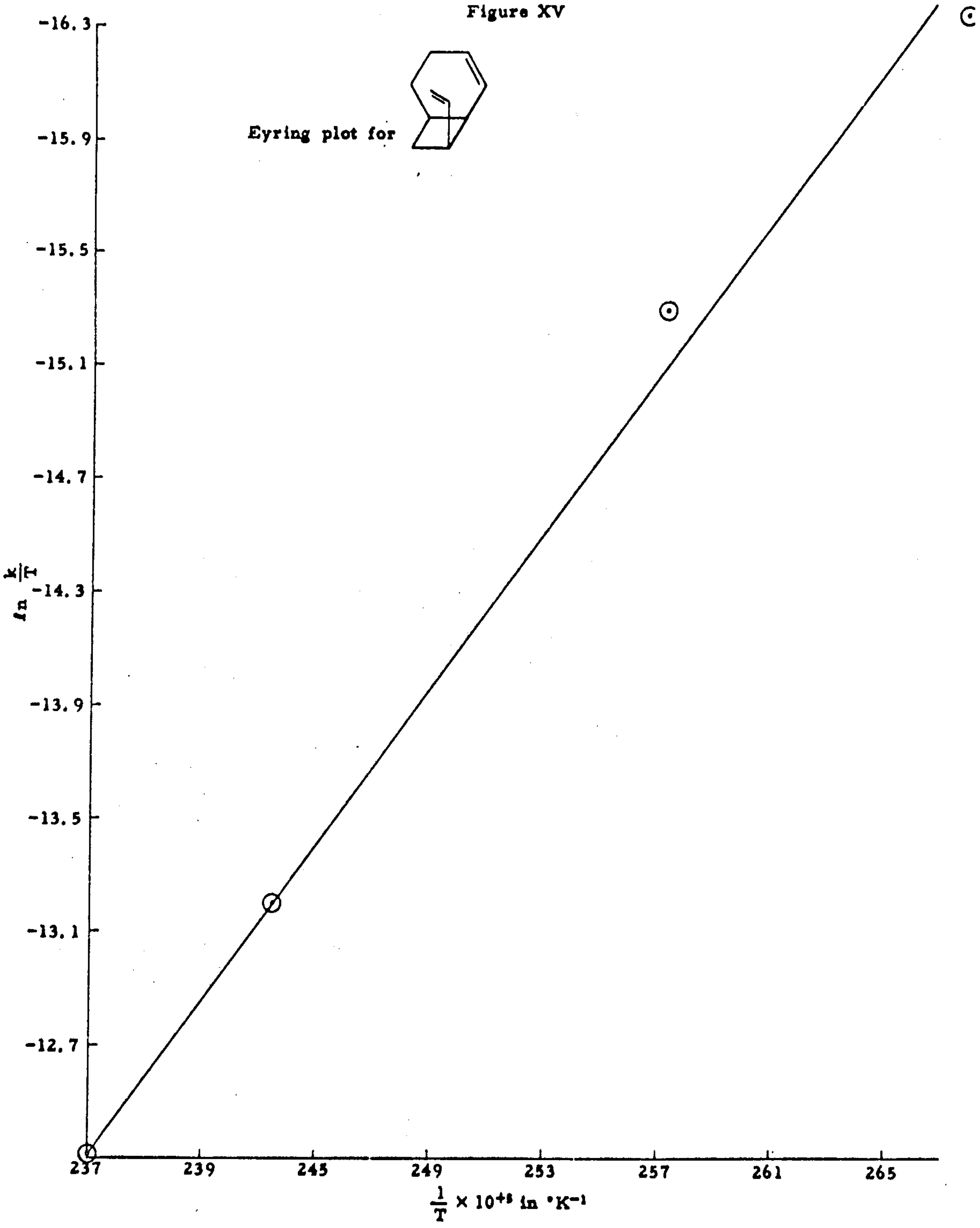


Figure XV

Eyring plot for

Figure XVI

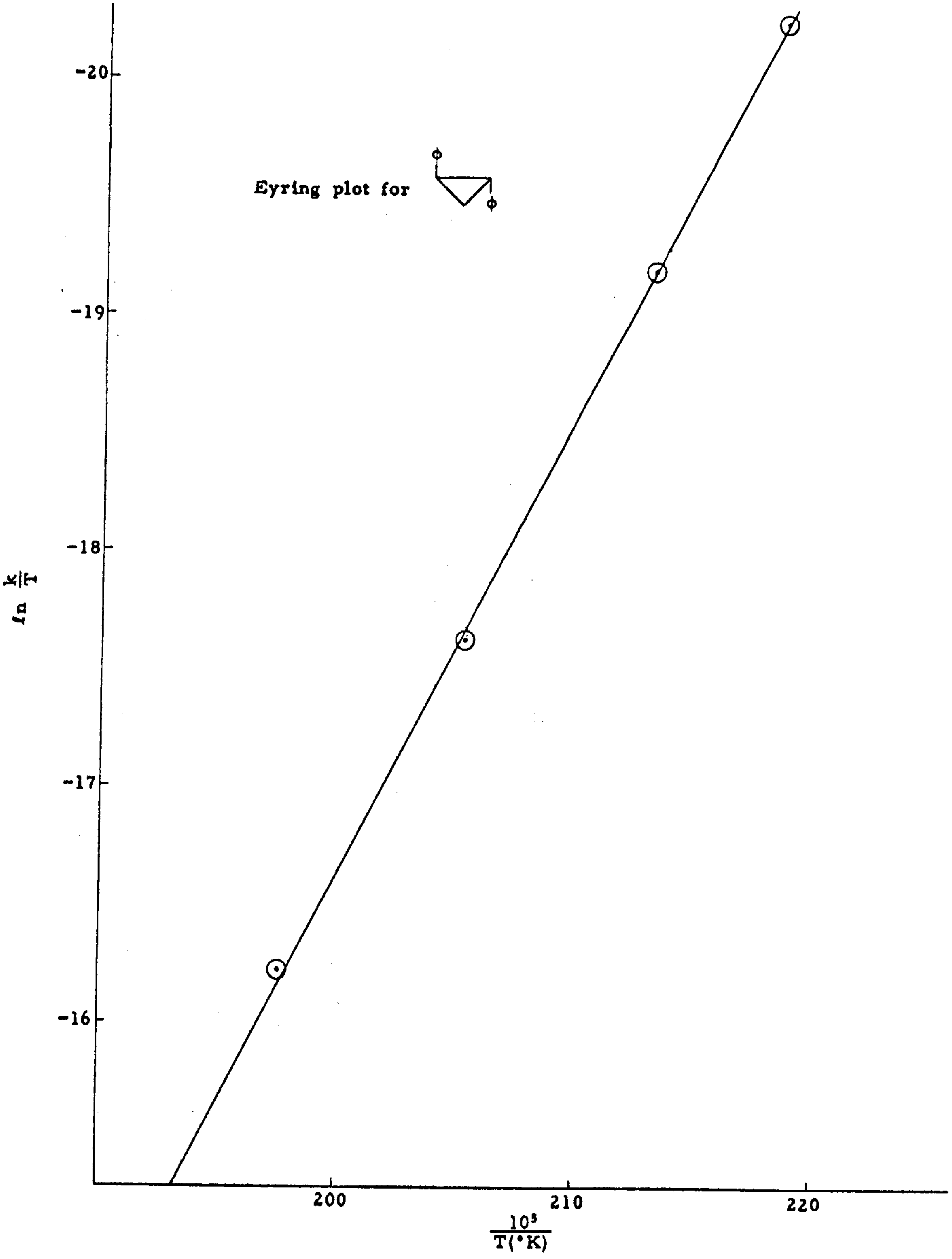

Eyring plot for
ϕ
ϕ
-20
-19
-18
-17
-16
ln $\frac{k}{T}$
200
210
220
$\frac{10^5}{T(°K)}$

Figure XVII

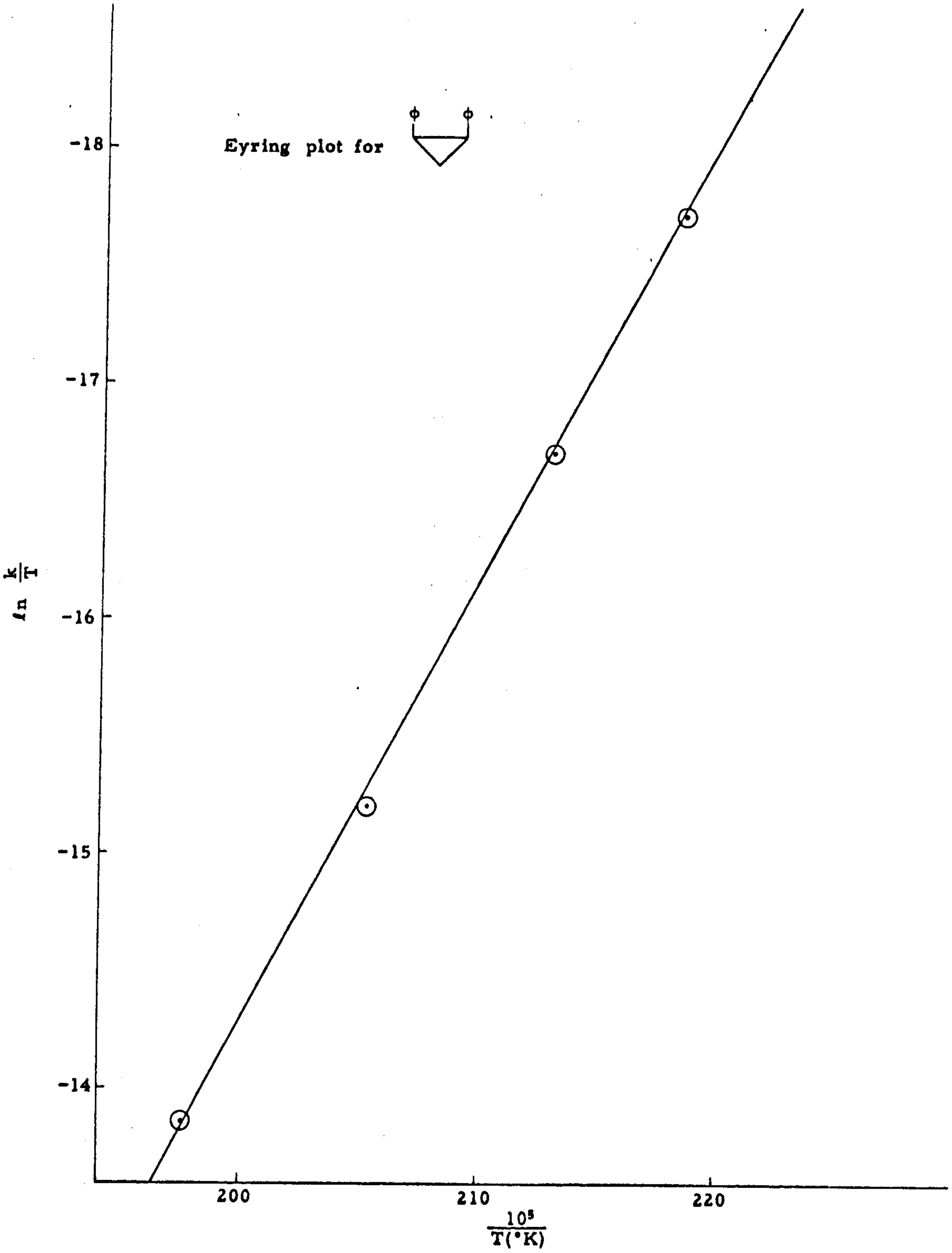


Table III gives the rate constants for these reactions at different temperatures and the activation parameters calculated from these rate constants. The fit to the Eyring plots was excellent. The standard deviation of the enthalpies of activation is 0.5 kcal per mole; the standard deviation of the entropies of activation is one e.u.

The Equilibrium between *cis*- and *trans*-1, 2-Diphenylcyclopropane

The equilibrium constant for *cis*- and *trans*-1, 2-diphenylcyclopropane was measured at different temperatures by heating the substrate for at least ten half lives. Figure XVIII is a plot of the logarithm of the equilibrium constant vs. temperature^{-1}. From this plot we calculate that the *cis* isomer has an enthalpy content of 1.6 ± 0.1 kcal/mole *more* and an entropy content of 1.6 ± 0.5 e.u. *less* than the *trans* isomer. Table IV shows the value of the equilibrium constant measured at different temperatures.

Table III

Variations of Reaction Rate with Temperature

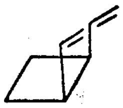
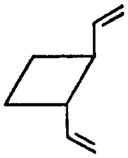
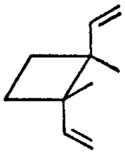
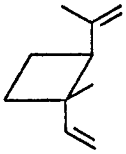
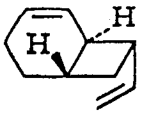
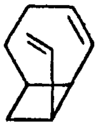
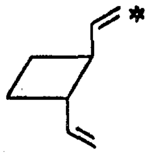
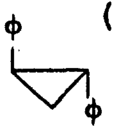
Substrate	T°C	κ sec^{-1} for disappearance of starting material	ΔH‡ $\frac{\text{kcal}}{\text{mole}}$ (a)	ΔS‡ e.u. (a)
	65.4	$2.55 \pm 0.06 \times 10^{-5}$	23.1	-11.7
	79.8	$1.09 \pm 0.05 \times 10^{-4}$		
	96.8	$5.12 \pm 0.15 \times 10^{-4}$		
	108.5	$1.39 \pm 0.05 \times 10^{-3}$		
	139.3	$4.66 \pm 0.16 \times 10^{-6}$	34.0	-1.2
	153.9	$1.85 \pm 0.03 \times 10^{-5}$		
	175.2	$1.32 \pm 0.06 \times 10^{-4}$		
	187.3	$3.58 \pm 0.09 \times 10^{-4}$		
	210.3	$2.40 \pm 0.08 \times 10^{-3}$		
	92.4	$1.08 \pm 0.02 \times 10^{-5}$	30.9	+2.9
	109.2	$7.21 \pm 0.25 \times 10^{-5}$		
	121.9	$2.77 \pm 0.12 \times 10^{-4}$		
	135.7	$1.08 \pm 0.02 \times 10^{-3}$		
	135.7	$1.72 \pm 0.21 \times 10^{-5}$	34.2	+3.1
	149.2	$6.59 \pm 0.16 \times 10^{-5}$		
	161.3	$2.14 \pm 0.04 \times 10^{-4}$		
	176.8	$8.70 \pm 0.10 \times 10^{-4}$		
	179.7	$1.48 \pm 0.05 \times 10^{-4}$	34.5	-1.5
	193.0	$4.92 \pm 0.23 \times 10^{-4}$		
	206.5	$1.23 \pm 0.47 \times 10^{-3}$		

Table III (continued)

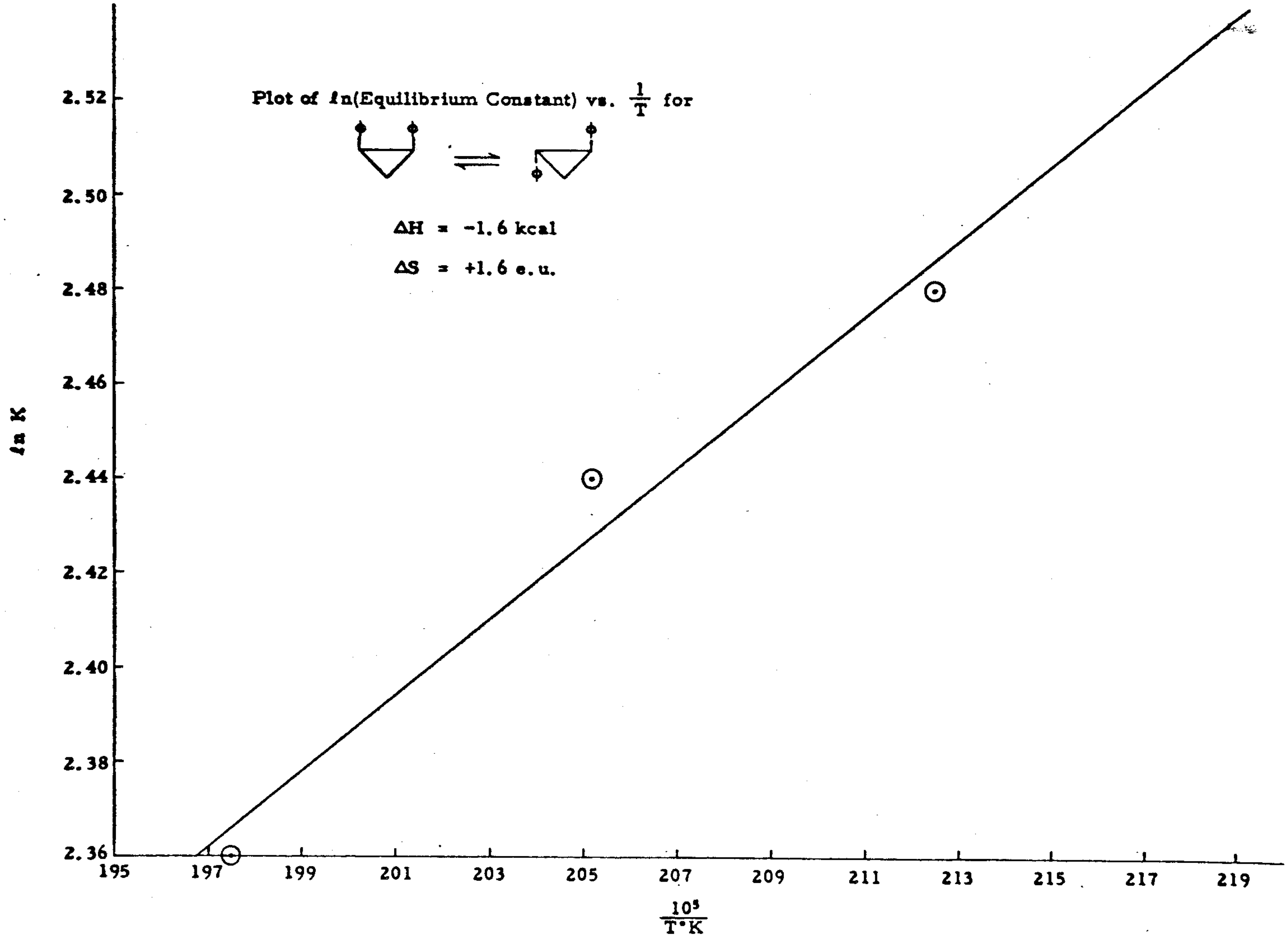
Substrate	T°C	κ sec^{-1} for disappearance of starting material	$\Delta H^{\ddagger}$ $\frac{\text{kcal}}{\text{mole}}$ (a)	$\Delta S^{\ddagger}$ e. u. (a)
	100.6	$2.90 \pm 0.14 \times 10^{-5}$	27.7	-6.5
	115.8	$8.77 \pm 0.57 \times 10^{-5}$		
	137.6	$7.46 \pm 0.38 \times 10^{-4}$		
	148.4	$1.87 \pm 0.11 \times 10^{-3}$		
	161.8	$5.23 \pm 0.10 \times 10^{-5}$	36.3*	+4.6*
	176.8	$2.16 \pm 0.05 \times 10^{-4}$		
	187.2	$5.21 \pm 0.06 \times 10^{-4}$		
	191.4	$7.79 \pm 0.09 \times 10^{-4}$		
	198.6	$1.50 \pm 0.05 \times 10^{-3}$		
 (b)	184.9	$1.11 \pm 0.07 \times 10^{-5}$	37.2	-1.2
	197.4	$3.23 \pm 0.08 \times 10^{-5}$		
	214.1	$1.34 \pm 0.05 \times 10^{-4}$		
	233.0	$5.55 \pm 0.07 \times 10^{-4}$		
 (b)	184.9	$1.01 \pm 0.06 \times 10^{-5}$	38.9	-2.6
	197.4	$2.87 \pm 0.11 \times 10^{-5}$		
	214.1	$1.34 \pm 0.03 \times 10^{-4}$		
	233.0	$5.29 \pm 0.17 \times 10^{-4}$		

*These values are for loss of optical activity of the total solution.

a. Calculated from the least squares lines from Figures X-XVII.

b. These rates are the rates of approach to equilibrium. Thus they are the sum of $k_1 + k_2$ described on p. 51. The activation parameters were calculated from these sums and the equilibrium data shown in Figure XVIII and Table IV.

Figure XVIII



Plot of ln(Equilibrium Constant) vs. $\frac{1}{T}$ for

ΔH = −1.6 kcal

ΔS = +1.6 e.u.

Table IV

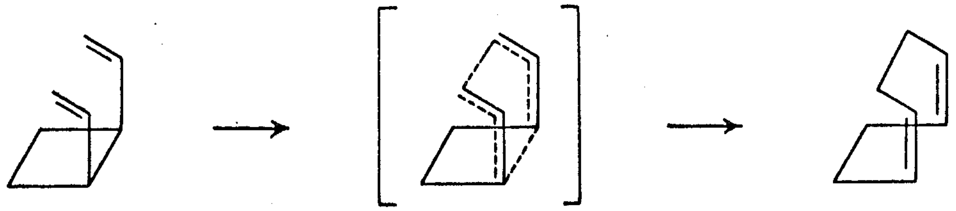
Variation of Equilibrium Constant with Temperature for _cis_ ⇄ _trans_-1, 2-Diphenylcyclopropane

Temperature (°K)	Equilibrium Constant (K) (_cis_ ⇄ _trans_)	ΔH	ΔF
470.5°	12.0	$-1.6\ \frac{\text{kcal}}{\text{mole}}$	+1.6 e.u.
487.2°	11.5		
506.1°	10.6		

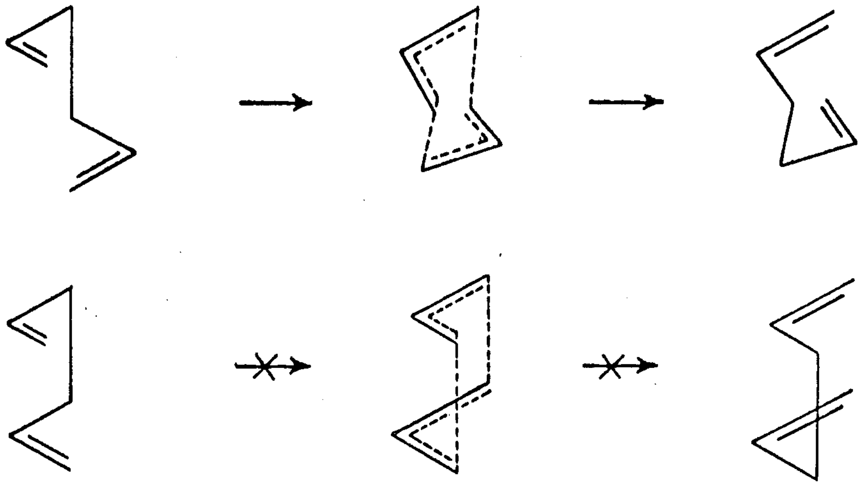
DISCUSSION

The Mechanism of the Thermal Rearrangement of cis-1, 2-Divinylcyclobutane

It is immediately apparent that cis-1, 2-divinylcyclobutane rearranges by a different mechanism than trans-1, 2-divinylcyclobutane. The cis isomer gives one major product, while the trans isomer gives three, counting the enantiomer of the starting material. Furthermore, the activation parameters for the two reactions are very different, the cis isomer being characterized by a much lower enthalpy of activation and a large negative entropy of activation. Obviously the concerted mechanism proposed by Vogel (1) is appropriate for the rearrangement of cis-1, 2-divinylcyclobutane; the large negative entropy of activation indicates the system becomes more constrained in the transition state.

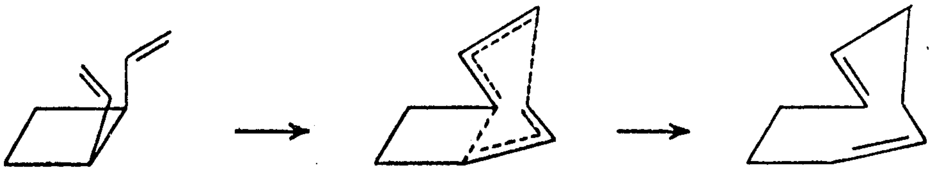


This is an example of a six center Cope rearrangement (2). Doering and Roth (6) have shown that, other things being equal, a four center transition state is more favorable than a six center transition state in the Cope rearrangement.



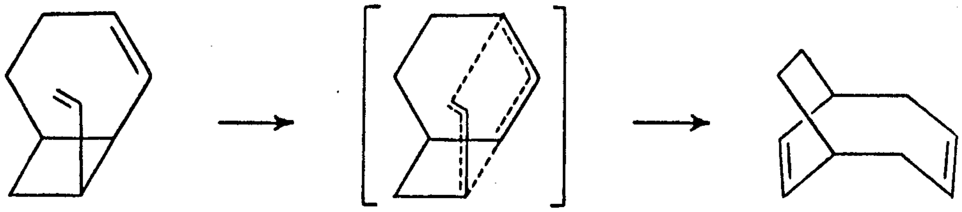
Thus the rearrangement of *cis*-1, 2-divinylcyclobutane is an example of a Cope rearrangement where the geometry of the starting material has made the six center transition state more favorable than the four center transition state.

The minor side product from *cis*-1, 2-divinylcyclobutane is of interest. Although its structure has not been proved, the fact that attempted isolation by preparative v. p. c. gave a mixture of *cis*, *cis*-1, 5-cycloöctadiene and the unknown product indicates that the later may be *cis*, *trans*-1, 5-cycloöctadiene. This could arise from a four center rather than six center transition state as shown below in rather distorted geometry.

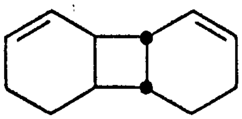


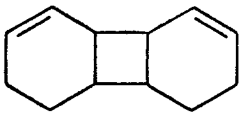
(*cis*, *trans*)

The one other rearrangement studied which appears to go through the concerted mechanism is that of the cis adduct of cyclohexadiene and butadiene. This rearrangement also gives only one product and has both a large negative entropy of activation and a lower enthalpy of activation than the trans isomer.



It must be noted that the absolute value of the activation entropy for this rearrangement is only about half as large as that for cis-1,2-divinylcyclobutane and that the enthalpy of activation is larger as well. This is reasonable in light of the rearrangements of the cyclohexadiene dimers



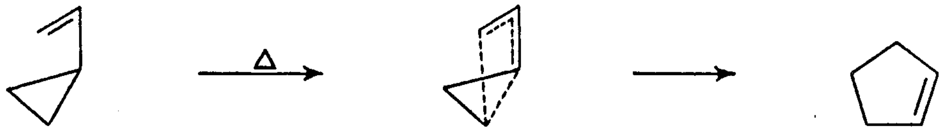


studied by Dr. Donald Valentine (7, 8). Dr. Valentine found no mechanistic difference between the cis- and trans-cyclohexadiene dimers in their thermal rearrangement. Evidently the cyclohexane rings hold the double bonds far enough apart to render the concerted rearrangement impossible. In the adduct of cyclohexadiene and butadiene the steric constraint of one cyclohexane ring makes the concerted mechanism less favorable but still possible, thus accounting for the larger enthalpy of activation. Since the starting material is more constrained than cis-1, 2-divinylcyclobutane, the absolute value of the entropy of activation is correspondingly smaller.

The Mechanism of the Rearrangement of trans-1, 2-Divinylcyclobutane

The rearrangements of trans-1, 2-divinylcyclobutane, the trans isoprene dimers and the trans adduct of cyclohexadiene and butadiene all show certain similarities in their products and activation parameters. Since trans-1, 2-divinylcyclobutane has been most extensively studied, the mechanism of its rearrangement will be discussed first. It will then be shown that the remaining cyclobutane rearrangements will also be accommodated by this mechanism.

We have demonstrated earlier that the mechanism proposed by Vogel for the rearrangement of trans-1, 2-divinylcyclobutane is unsatisfactory. Frey, et al. (9), has investigated the related rearrangement of vinylcyclopropane. He proposes that this goes through a concerted four center transition state.

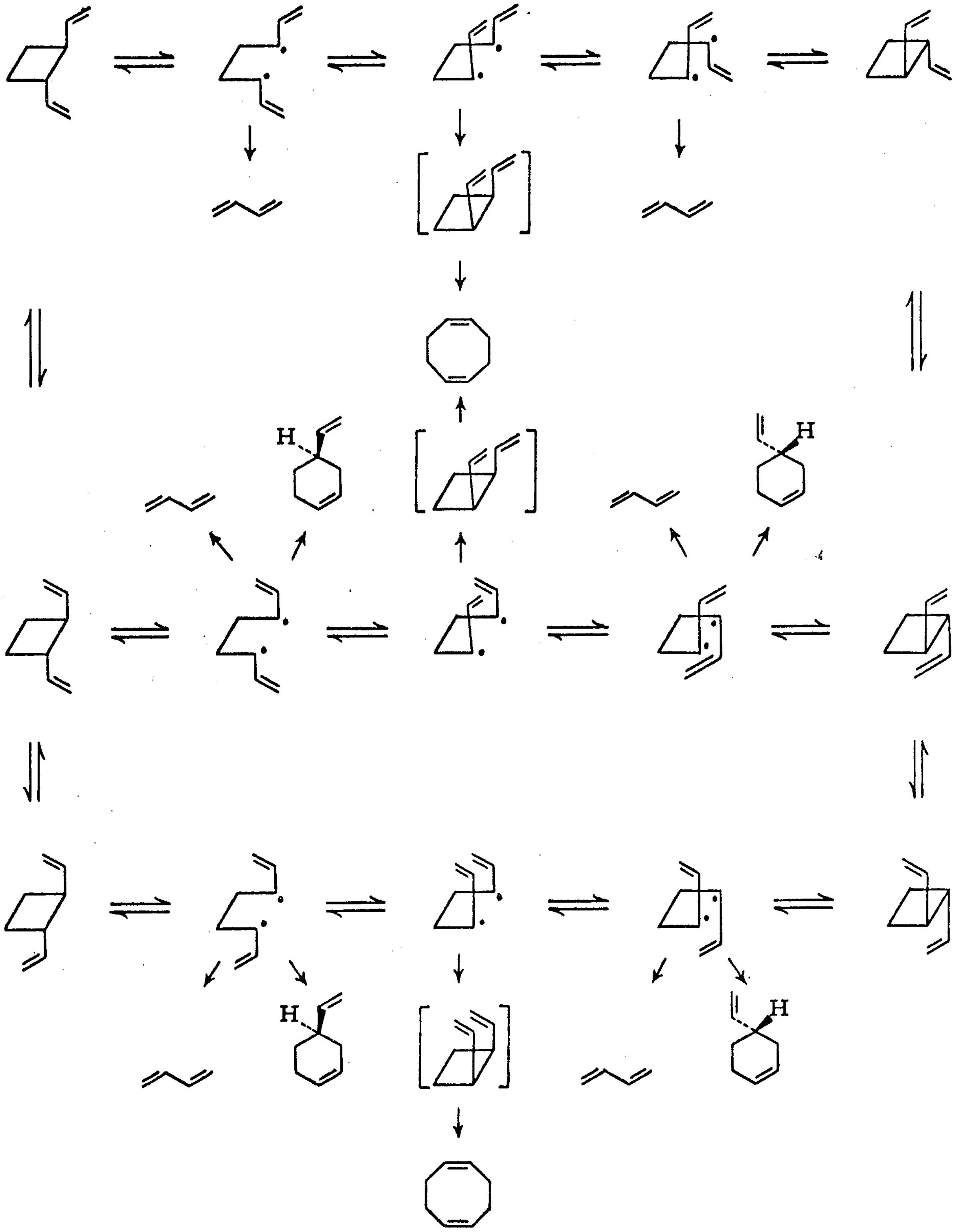


As evidence for this mechanism he offers the normal pre-exponential factor for the reaction $10^{13.5}$, which corresponds to an activation entropy of one e. u. It seems likely that the constrained 4-center transition state would require a rather large negative activation entropy, but in any case, this kind of mechanism could account for the production of optically active 4-vinylcyclohexene from optically active trans-1, 2-divinylcyclobutane; in fact, it would lead to complete retention of configuration. The mechanism cannot, however, account for the multiplicity of products nor the loss of optical activity of the starting material in the rearrangement of optically active trans-1, 2-divinylcyclobutane. Rather than postulate parallel mechanisms, we will discard Frey's mechanism in favor of a single mechanism which will explain all the data. This mechanism involves breaking the bond between the 1- and 2-carbon atoms to produce a diradical species which can rotate freely and then close or break up to products. Since allylic radicals are known to retain their geometrical configuration in the diradicals derived from thermal addition of 1, 1-dichloro-2, 2-difluoroethylene to piperylene (10) and in free radical chlorination reactions (11), three separate diradical species could be produced, depending on the configuration of the starting material. The mechanism in its entirety is shown in Figure XIX.

The origin of the 1, 5-cyclooctadiene is not clear. We have indicated in Figure XIX the possibility that the diradical intermediate could close to cis-1, 2-divinylcyclobutane which would rearrange instantly under the conditions of its formation to give 1, 5-cyclooctadiene.

The activation enthalpy for this mechanism can be roughly estimated from the strength of an aliphatic carbon-carbon bond (12) (85 kcal/mole), the strain energy of the cyclobutane ring (13) (24 kcal/mole),

Figure XIX



and the resonance energy of the allyl radical (14) (12 kcal/mole) to be equal to 85 − 24 − 2 × 12 = 37 kcal/mole. This agrees quite well with the observed value for the enthalpy of activation. Moreover, this mechanism predicts a small positive activation entropy for going from the cyclobutane ring to the less constrained diradical. Unfortunately, neither measurement of the isomerization of the racemate nor measurement of the loss of optical activity from optically active starting material will give the true rate of the bond breaking step. It is clear that measurements of the loss of optical activity will be more nearly equal to the rate of the bond breaking step, since an additional product (the enantiomer of the starting material) is being measured. The kinetics for loss of optical activity are shown in Figure XX. Figure XXI shows the kinetics for rearrangement of the racemate.

The only way in which k_1 itself (the bond breaking step) can be isolated is to study the product distribution from the thermal decomposition of the hitherto unknown compound, (+) trans-3, 6-divinyl-1-pyridiazine. The product ratios of this decomposition will give the ratios k_3/k_2 and k_2/k_{-1} needed to isolate k_1 from the kinetic expression in Figure XX.

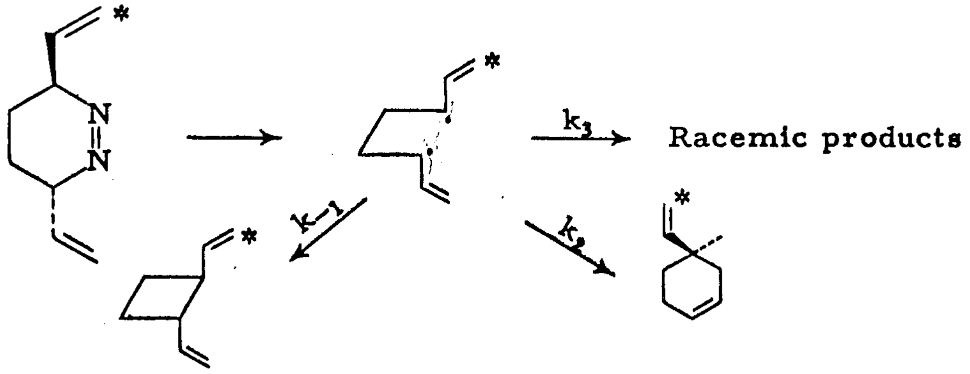
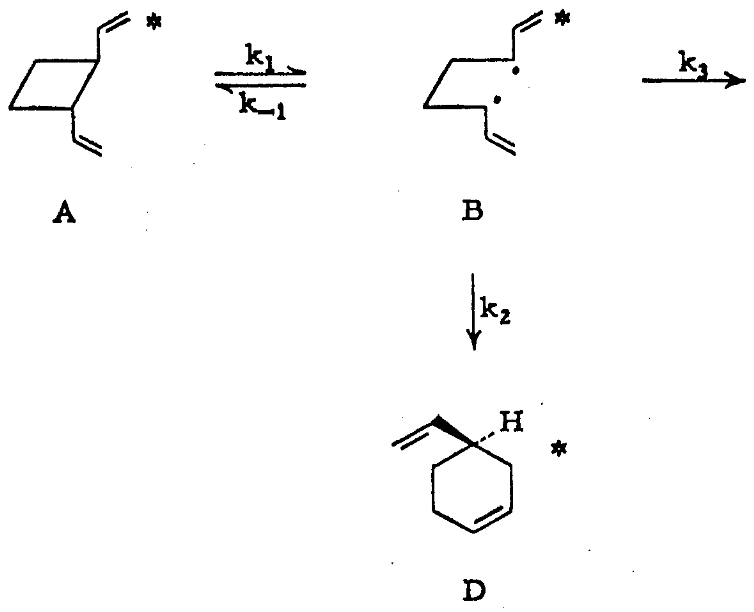


Figure XX



Racemic products

C

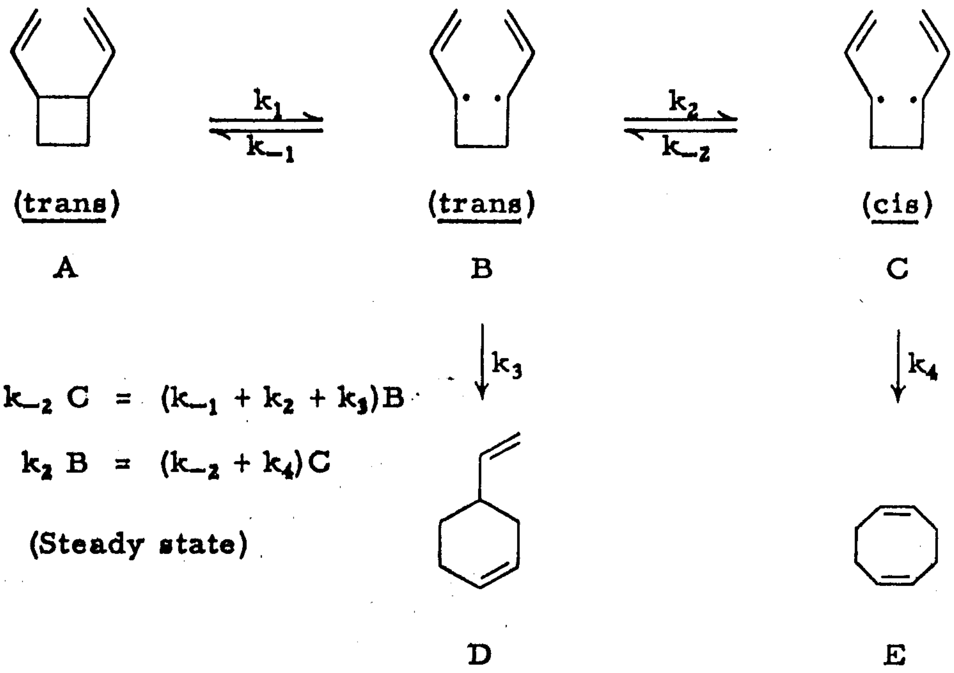
$$k_1\ A = (k_{-1} + k_2 + k_3)B$$

(Steady state)

$$-\frac{dA}{dt} = k_1\ A - k_{-1}\ B = k_1 - \left(\frac{k_{-1}\ k_1}{(k_{-1} + k_2 + k_3)}\right) A$$

$$-\frac{dA}{dt} = \left(\frac{k_1\ k_2 + k_1\ k_3}{k_{-1} + k_2 + k_3}\right) A = k_1 \left(\frac{1 + \frac{k_3}{k_2}}{1 + \frac{k_3}{k_2} + \frac{k_{-1}}{k_2}}\right)$$

Figure XXI



$$k_1 A + k_{-2} C = (k_{-1} + k_2 + k_3)B$$

$$k_2 B = (k_{-2} + k_4)C$$

(Steady state)

$$-\frac{dA}{dt} = k_1 A - k_{-1} B$$

$$k_1 A = k_{-1} + k_2 + k_3 - \left(\frac{k_2 k_{-2}}{k_{-2} + k_4}\right) B \quad \text{(Steady state)}$$

$$-\frac{dA}{dt} = k_1 \; 1 - \left(\frac{k_{-1}}{k_{-1} + k_2 + k_3 - \dfrac{k_2}{1 + \dfrac{k_4}{k_{-2}}}}\right) A$$

The execution of these experiments will be left as an exercise for the reader.

Since the rates of loss of optical activity are more nearly equal to the rate of the bond breaking step than the rates of isomerization of the racemate, we shall use the activation parameters derived from the rates of loss of optical activity as an approximation to the activation parameters for the bond breaking step. The value of +4 e. u. for the activation entropy agrees well with the diradical mechanism.

The appearance of optically active 4-vinylcyclohexene from optically active trans-1, 2-divinylcyclobutane is particularly interesting. It indicates that the intermediate diradical is not completely equilibrated. Since we do not know the absolute rotation of either the starting material or the product, we do not know the extent of the stereospecificity of the reaction. We would guess, however, that it is small. The optical rotation of 4-vinylcyclohexene produced at higher temperatures is smaller, indicating that the rate of ring closure increases less rapidly with temperature than the rate of internal rotation. Probably the rates of ring closure are only slightly smaller than the rates of internal rotation, and the activation energy for ring closure is about one kcal/mole higher than the barrier to rotation. This value of one kcal/mole was approximated by plotting the logarithm of the optical rotation of the 4-vinylcyclohexene against the reciprocal temperature at which it was formed. Bartlett has observed that the barrier to ring closure is one kcal/mole higher than the barrier to rotation in the diradical formed by thermal addition of 1, 1-dichloro-2, 2-

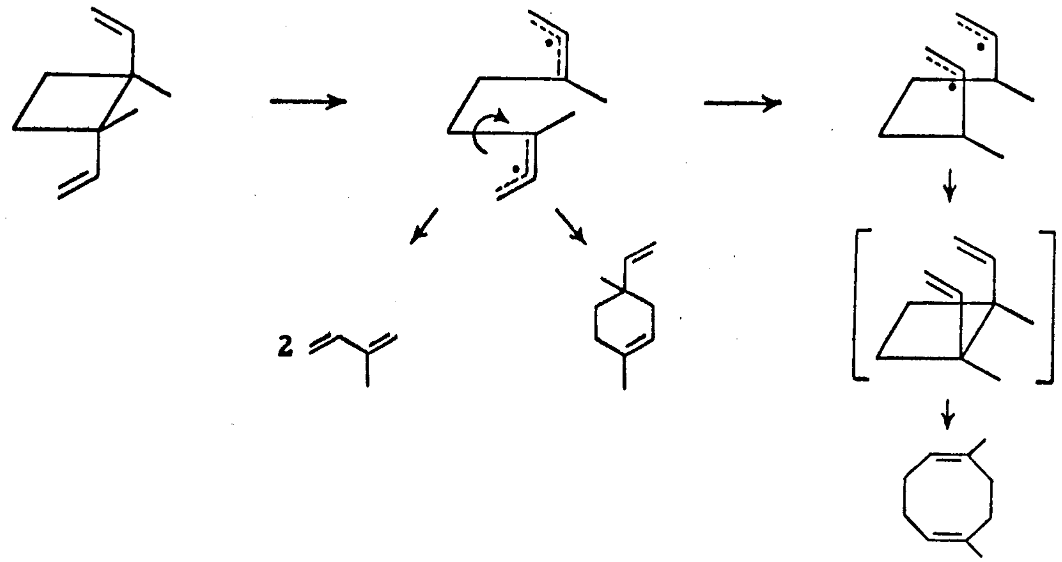
difluoroethylene to 2, 4-hexadiene (10).

Finally, the diradical mechanism with an incompletely equilibrated diradical will account for the variation in the product distribution with temperature, since 1) the steps leading from the diradical to products will have different activation parameters and 2) at higher temperatures the more equilibrated diradical will favor products which are more than one internal rotation away from the starting material.

The Rearrangements of the Isoprene Dimers and *trans*-8-Vinylbicyclo(4, 2, 0)-2-octene

The diradical mechanism proposed for the rearrangement of *trans*-1, 2-divinylcyclobutane will accommodate the rearrangements of the title compounds very well. The activation parameters for these rearrangements are all nearly equal to those found for the rearrangement of *trans*-1, 2-divinylcyclobutane. The enthalpy of activation for *trans*-1, 2-divinyl-1, 2-dimethylcyclobutane is somewhat lower (about three kcal/mole) than the other *trans* compounds, probably reflecting the increased strain in the transition state due to opposition of methyl and vinyl groups. Not much importance can be attributed to the remaining small differences in the activation parameters of the *trans* rearrangements, since 1) the experimental precision is too low and 2) the rate of disappearance of the starting material is only approximately equal to the bond breaking rate (see Figure XXI).

The products of these rearrangements are nicely explained by the diradical mechanism.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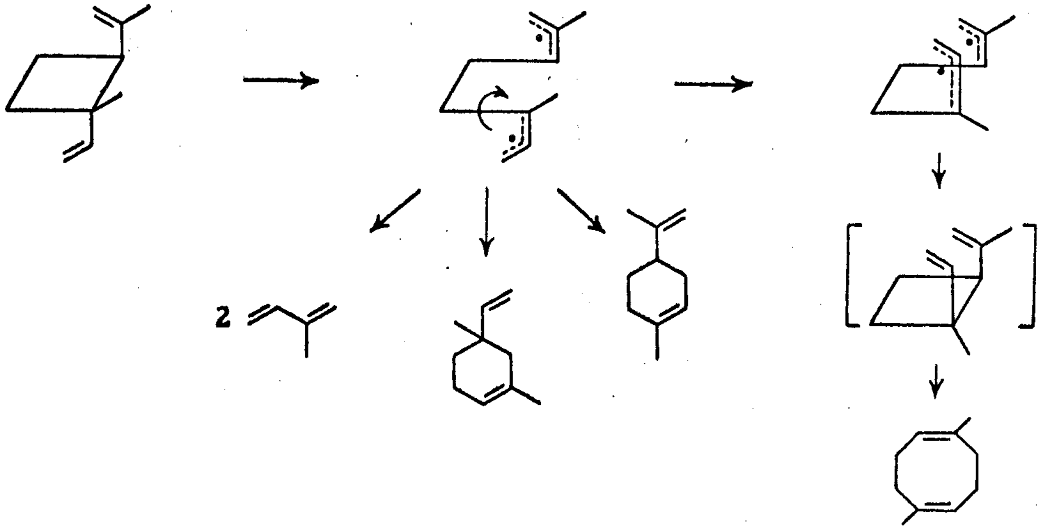
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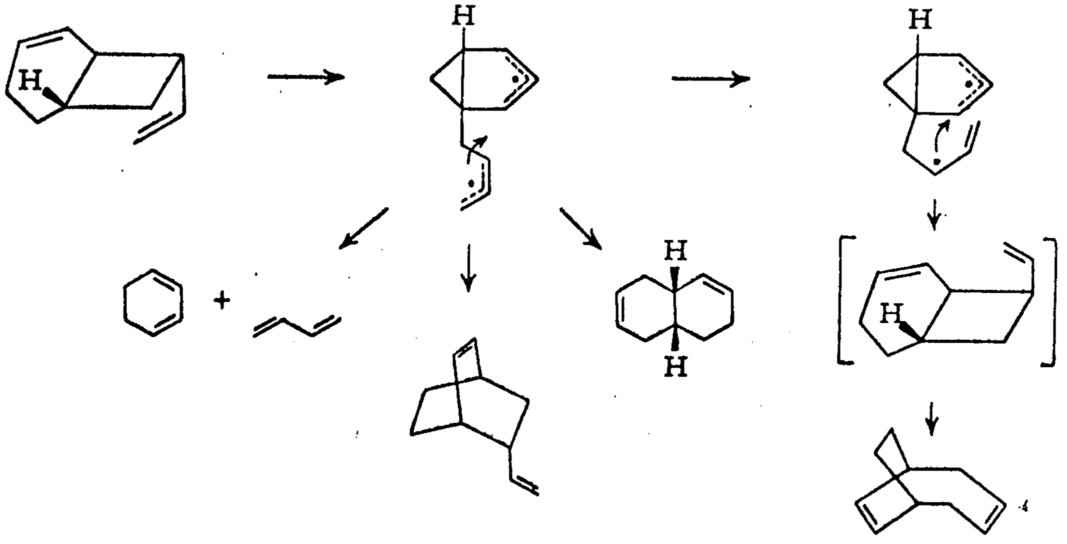
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H
H
+
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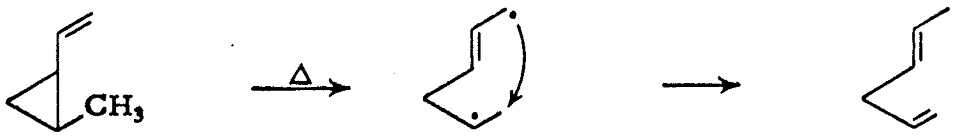
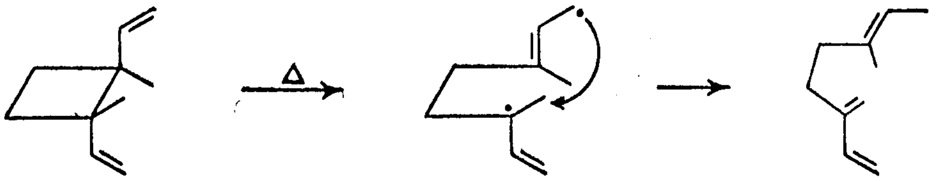
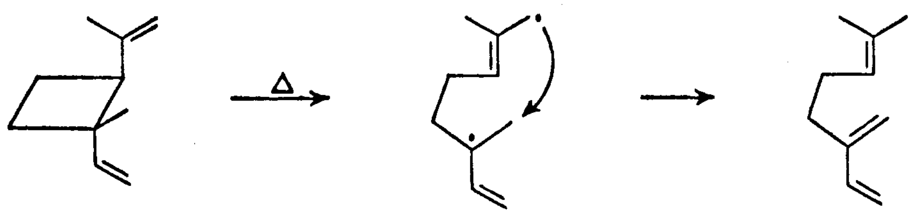
H

Rearrangement of the optically active isoprene dimer trans-1, 2-divinyl-1, 2-dimethylcyclobutane might shed some light on the question of the origin of the 1, 5-cycloöctadienes produced in these rearrangements. This follows since the steric barrier from introduction of two methyl groups should be similar for closure to either a cis or a trans four-membered ring. If the decrease in the yield of the enantiomer of the starting material were approximately equal to the decrease in the yield of cycloöctadiene (compared to the rearrangement of trans-1, 2-divinylcyclobutane), this fact could be used as evidence that the diradical closes to cis-1, 2-divinylcyclobutane which immediately rearranges by a concerted mechanism to cycloöctadiene.

It is interesting to speculate on the structures of the unidentified trace products from rearrangement of the isoprene dimers. The v. p. c. elution times of these trace products indicate they are probably isomers of the starting material, but their elution times do not correspond to any of those of the thermal dimers of isoprene. Probably they arise via the hydrogen abstraction mechanism discovered by Frey (15) for the thermal isomerization of 1-methyl-2-vinylcyclopropane.







Although the above drawings do not indicate it, this rearrangement, at least in the case of methyl vinyl cyclopropane, occurs only in the cis isomer by way of a concerted seven-membered ring transition state, characterized by an enthalpy of activation about 12 kcal lower than that for the trans isomer and an entropy of activation of -11 e.u. The trans isomer gives the same products, but has an entropy of activation of nearly zero. Apparently it rearranges by way of a diradical to the cis isomer which undergoes the concerted hydrogen migration rearrangement very rapidly at the more elevated temperatures needed for the trans-cis rearrangement.

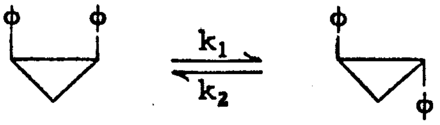
Comparison of the Thermal Rearrangements of trans-1, 2-Divinylcyclobutane and trans-1, 2-Divinylcyclopropane

Doering has reported (16) that trans-1, 2-divinylcyclopropane gives no 4-vinylcyclopentene when heated; the sole product is 1, 4-cycloheptadiene. (4-Vinylcyclopentene is stable under the conditions of the rearrangement.) If this rearrangement goes through a true diradical intermediate, similar to the one proposed for the rearrangement of trans-1, 2-divinylcyclobutane and characterized simply by the absence of significant bonding between the two carbon atoms to which radical character is attributed, there must be a surprisingly large barrier to closure of the diradical to a five-membered ring. This is unlikely, since it is generally supposed that closure to five-membered rings is more favorable than closure to either three-membered or seven-membered rings. Thus the absence of 4-vinylcyclopentene is simultaneously an argument for the existence of a "true" diradical intermediate in the rearrangement of trans-1, 2-divinylcyclobutane (since 4-vinylcyclohexene is a major product) and an argument against a "true" diradical intermediate in the rearrangement of trans-1, 2-divinylcyclopropane. A possible, although speculative, intermediate in the rearrangement of trans-1, 2-divinylcyclopropane is a "virtual" diradical, where some bonding remains between the two "radical" centers, thus allowing cis-trans isomerization but not ring expansion. (The cis-1, 2-divinylcyclopropane produced isomerizes instantly to 1, 4-cycloheptadiene by a concerted mechanism under these conditions.)

The Reversible Isomerization of cis- and trans-1, 2-Diphenylcyclopropane

The reversible thermal isomerization of cis- and trans-1, 2-diphenylcyclopropane is very clean, giving no side products. Since there is a measurable amount of both the cis and trans isomer present at equilibrium, a first order plot of the rate of approach to equilibrium (Figures VIII and IX) will give the sum of the rate constants for the forward and reverse reactions. Combined with measurements of the equilibrium constant at the same temperatures, this sum will give the rate constant for either reaction. Table III shows the sum of $k_1 + k_2$

(see below) measured with both the <u>cis</u> and <u>trans</u> isomer as starting material. The close agreement of these sums with either isomer as starting material indicates the measurements are internally consistent. Since the <u>cis</u> isomer has "farther to go" to reach equilibrium, the rates measured starting with the <u>cis</u> isomer should be more accurate, and they were used to calculate the activation parameters.



A B

$$-\frac{dA}{dt} = (k_1 + k_2)A - k_2 A_o$$

$$\frac{B_e}{A_e} = \frac{A_o - A_e}{A_e} = \frac{k_1}{k_2} \qquad \frac{A_o}{A_e} = 1 + \frac{k_1}{k_2} = \frac{k_1 + k_2}{k_2}$$

$$\therefore \; -\frac{dA}{dt} = (k_1 + k_2)A - (k_1 + k_2)A_e$$

$$\frac{dA}{A - A_e} = (k_1 + k_2)dt$$

$$-\ln\left(\frac{A - A_e}{A_o - A_e}\right) = (k_1 + k_2)t$$

The above expression can be transformed into the expression used for the graphs shown in Figures VIII and IX by the addition of $-\ln(k_1/k_1 + k_2)$ to both sides of the equation. The slopes of the lines in Figures VIII and IX then equal $k_1 + k_2$.

$$-\ln\left(\frac{A - A_e}{A_o - A_e}\right) - \ln\left(\frac{k_1}{k_1 + k_2}\right) = -\ln\left(\frac{A}{A_o} - \frac{A_e}{A_o}\right) = (k_1 + k_2)t - \ln\left(\frac{k_1}{k_1 + k_2}\right)$$

$$y = m\,x + b$$

The activation parameters for the reversible isomerization of 1, 2-diphenylcyclopropane are just what would be expected. The strain energy of the cyclobutane and cyclopropane rings is thought to be similar (17), and the resonance energy of the benzyl radical is approximately that of an allyl radical (18). Thus the activation parameters should be similar to those for trans-1, 2-divinylcyclobutane. Our values of the activation parameters agree well with those measured independently by Rodewald and DePuy (19). They found the rate for the reaction = $10^{11.2 \pm 0.5}$ exp (-33, 530 ± 1070/RT). It was not specified whether this expression was for the sum of the forward and reverse reactions or just for the isomerization from cis- to trans-1, 2-diphenylcyclopropane.

From the evidence available it is impossible to say whether the intermediate in this isomerization is a "true" or a "virtual" diradical, since products with a five-membered ring would not be expected in either case. However, Morris (20) found that less than 1% (and perhaps none) of the products from thermal isomerization of 1-phenyl-2-vinylcyclopropane was 4-phenylcyclopentene. This again, as in the rearrangement of trans-1, 2-divinylcyclopropane, points to an intermediate where some bonding remains between the two radical centers. Thus it would not be surprising if thermal isomerization of 1, 2-diphenylcyclopropane gave a similar intermediate.

The thermal decomposition of trans-3, 5-diphenyl-1-pyrazoline gives the same products as thermal isomerization of 1, 2-diphenylcyclopropane. (See Part II of this thesis for details.) Assuming the decomposition of the pyrazoline gives the same intermediate, it will be shown in Part II that this intermediate is not fully equilibrated, and that internal rotation and decay to products have comparable rates, just as in the case of trans-1, 2-divinylcyclobutane.

EXPERIMENTAL

Materials

cis- and trans-1, 2-Divinylcyclobutane were prepared by photosensitized dimerization of butadiene. This method has been reported in detail elsewhere (4). Their rearrangement products were identified by other workers (1) and checked by comparison of the v. p. c. elution times of commercial samples with those of the rearrangement products. Optically active trans-1, 2-divinylcyclobutane was prepared by Brown's (5) method of partial asymmetric hydroboration.

α-Pinene (43. 7 g, $[\alpha]_D^{27} = -23.0°$, distilled from Oregon balsam fir oil) was placed in a 500 ml round-bottomed flask with 120 ml of diglyme which had been distilled under vacuum from lithium aluminum hydride. Sodium borohydride (4. 35 g) was added and the mixture was cooled in ice water and stirred with a magnetic stirrer. When cool, 22 g of freshly distilled boron trifluoride etherate was added and the reaction mixture stirred in ice water for four hours. trans-1, 2-Divinylcyclobutane (35 g) was added and the mixture stirred in an ice bath for four more hours. Then 10 ml of water was added to destroy the excess sodium borohydride and the mixture was distilled under vacuum into a dry ice condenser until the volume of the pot was reduced by one half. The distillate was dried and redistilled through a spinning band column. This distillate was purified further by preparative gas chromatography on a Carbowax column and finally a bulb-to-bulb distillation gave 9. 7 g of trans-1, 2-divinylcyclobutane having

$[\alpha]_D^{27} = 2.0°$. This material was diluted with pure racemic divinylcyclobutane to give material with full scale deflection on the 0.1° scale of a Bendix Ericsson Type 143 A Automatic Polarimeter with 4 cm path length in the polarimeter cell.

***trans*-1,2-Divinyl-1,2-dimethylcyclobutane and *trans*-1-methyl-1-vinyl-2-isopropenylcyclobutane** were prepared by photosensitized dimerization of isoprene by Dr. R. S. H. Liu (4). Dr. Liu also purified the starting materials and proved the structures of their rearrangement products.

***cis*- and *trans*-8-Vinylbicyclo(4,2,0)-2-octene** were prepared by photosensitized cycloaddition of 1,3-cyclohexadiene to 1,3-butadiene by Dr. R. S. H. Liu (4). Dr. Liu also purified the starting materials and proved the structures of the products of their rearrangement. The *trans* isomer was not completely pure; it contained some of its own rearrangement products. For this reason the line in Figure V does not go through zero.

***cis*- and *trans*-1,2-Diphenylcyclopropane** were prepared by the method of Beach *et al.* (24). Benzalacetophenone (240 g) was dissolved in 600 ml of ethanol and 135 ml of hydrazine hydrate was added. The solution was refluxed without a condenser on a steam bath for one hour. The ethanol was then stripped off on a steam bath at a pressure of 20 torr. One g of potassium hydroxide pellets was added and the mixture was heated to 150° in an oil bath. Moderately vigorous nitrogen evolution started and the temperature of the solution rose to about

200°. After 30 minutes the reaction ceased and the products were distilled under vacuum at one torr pressure. V.p.c. analysis on a column of silicone grease showed the products to be 45% *cis*-1,2-diphenylcyclopropane and 55% *trans*-1,2-diphenylcyclopropane. The isomers were separated by fractionation on a 3 foot spinning band column at one torr. They were then recrystallized from 95% ethanol and dried under vacuum. Their melting points and n.m.r. spectra corresponded exactly with those reported elsewhere (23). V.p.c. analysis showed both isomers to be better than 99.9% pure.

Equipment and Procedures

Preliminary Vapor Phase Rearrangements. — The rearrangements in the vapor phase at one atmosphere pressure were run in a Pyrex flow tube 8 mm in diameter and 2 feet long. The tube was equipped with a thermocouple well, an inlet for the nitrogen stream, a septum for admitting the starting material and a dry ice condenser to capture the products. About 1 foot of the tube was wrapped with nichrome wire and asbestos. The temperature in the tube was controlled by varying the voltage applied to the nichrome wire. The flow rate of nitrogen was such that the average residence time was about 1 second.

Rearrangement Rate Measurements. — Small tubes 1 mm in diameter and 40 to 50 mm in length containing 10 to 50 microliters of neat starting material were frozen, evacuated to one torr and sealed with a torch. The tubes were stored at −30° when not in use. The tubes were wired with 24 guage copper wire onto 1 foot long pieces of 14 guage copper wire. These were then hung over the edge of an insulated four liter beaker filled with peanut oil well stirred with a Lightning stirring motor. The temperature of the bath was maintained at the desired point by a variac controlled constant running 1000 watt heating coil and an on-off 50 watt heating coil controlled by a thermoregulator thermometer. The variation in the temperature of the bath was less than 0.1°. The temperature of the bath was measured with a set of total immersion precision thermometers calibrated by the National Bureau of Standards. When total immersion of the thermometers was impossible, stem corrections were made. The reaction was quenched by swirling the tube in a water bath at room temperature. Since very thin walled tubes were used, the quenching time was less than 1% of the total time of the fastest run.

In preliminary experiments the volume of free space in the tube and thus the pressure in the tube was varied systematically to check for pressure effects. None was found. The material of the tube was changed from Pyrex to soft glass to investigate possible wall effects. None was found. Another variation involved addition of cyclohexane as an internal standard to check the possibility that material was destroyed in side reactions such as polymerization since nonvolatile materials would not be detected in the analysis. No loss of material or change in the rate was found. All the products of the rearrangements were found to be stable at the highest reaction temperatures.

Analytical Procedure. — Analyses of all the products of cyclobutane rearrangements were carried out on a Loenco model 15 B gas chromatograph equipped with a 6 foot column of 10% carbowax 20 M on firebrick at a temperature of 75° with a helium flow rate of 60 ml per minute. Analyses of the cyclopropane rearrangements were done on a Loenco model 72 dual flame gas chromatograph with 6 foot columns of Dow Corning Hi Vac silicon grease (10%) on firebrick at a temperature of 175° with a helium flow rate of 60 ml per minute. Integrations of peak areas were done by an automatic disk integrator. In all cases blanks were run of unheated starting material. All the data were treated by least squares. The standard deviation of the enthalpies of activation was 0.1 kcal/mole; the standard deviation of the entropies of activation was one e.u.

Racemization Rate Measurements. — The optically active trans-1,2-divinylcyclobutane was sealed in 1 ml portions in 13 by 125 mm test tubes. These were heated for various lengths of time in the oil bath described above. Since large tubes were used, time zero was taken at 200 seconds. After quenching the reaction by swirling the tubes in a water bath at room temperature the rotation of the contents of the tube was measured on a Bendix Ericsson Type 143 A Automatic Polarimeter with a 4 cm path length in the polarimeter cell. The 4-vinylcyclohexene produced was separated by preparative gas chromatography and its rotation was measured. (See Table III.) The rotation of the recovered starting material was also measured and found to have decreased from 2.0° to 1.2°. The optically active 4-vinylcyclohexene was sealed in a tube (degassed) and left for eleven hours at 200°. At the end of this time its rotation was unchanged.

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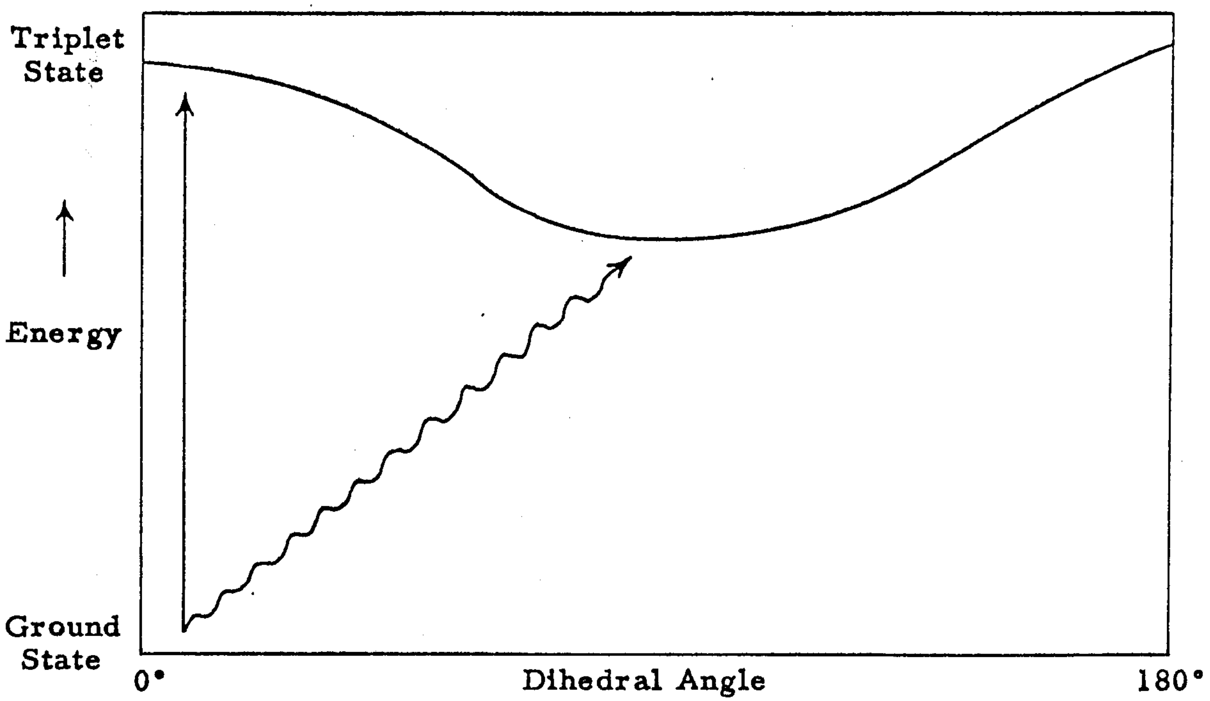
PART II

PHOTOSENSITIZED REARRANGEMENTS OF SMALL RING HYDROCARBONS – NONVERTICAL ENERGY TRANSFER

INTRODUCTION

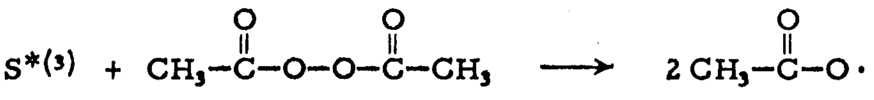
Recent investigations in organic photochemistry have shown that triplet energy transfer is an important process in many reactions (1). Some organic molecules, such as benzophenone, have high probabilities of intersystem crossing from the initially formed excited singlet state to the lower energy triplet state upon absorption of light. Other molecules, such as butadiene, have negligible intersystem crossing efficiencies. Through triplet energy transfer from a benzophenone triplet to a butadiene ground state, the butadiene triplet state can be generated. Since the triplet states of most organic molecules are many orders of magnitude longer lived than the excited singlet states, many new intermolecular reactions between excited triplets and the ground states of the same or a different substrate are possible through the use of triplet energy transfer. Generally these photosensitized triplet reactions have higher quantum yields, are much cleaner and give fewer and sometimes different products than excited singlet reactions with the same substrates. Thus when 1, 3-butadiene is irradiated for several weeks, a small amount of perhaps a dozen products is formed along with a great deal of polymer. On the other hand, when a small amount of benzophenone is added, a good yield of <u>cis</u>- and <u>trans</u>-1, 2-divinylcyclobutane is obtained along with a trace of 4-vinylcyclohexene.

Triplet energy transfer from high energy sensitizers to conjugated dienes and similar molecules, producing triplet states of the latter, is well understood (3). The rate of the transfer appears to be diffusion controlled, and it has been assumed that the Franck-Condon principle holds for the reaction. The triplet state of the diene or olefin can be understood in terms of simple molecular orbital theory, and there are spectroscopic processes analogous to the various transitions involved. Somewhat less well understood is the fact that sensitizers with triplet energies less than that of the acceptor can also effect the same reactions. This phenomenon has been investigated in some detail with stilbene and isoprene as substrates. It has been found that the rate of the energy transfer falls off rapidly from diffusion controlled as the sensitizer triplet energy is lowered (4), but not as rapidly as would be expected if the transfer were occurring from vibrationally excited states. Furthermore, it has been inferred in the case of cis-stilbene that energy transfer from low energy sensitizers gives directly a twisted triplet state of stilbene which is intermediate in geometry between the transoid and cisoid forms of the triplet. The fact that the triplet species derived from this reaction can be quenched by azulene in the same way as the triplets derived from the high energy sensitizers unequivocally demonstrates that the low energy sensitizer does not merely deliver vibrational excitation to the stilbene (5). Similar observations have been made with isoprene (6). These observations have necessitated the postulate that these low energy transfers involve some sort of transformation of the acceptor during the transfer which does not conform to the Franck-Condon principle. The diagram on the following page shows the essential points of the hypothesis.

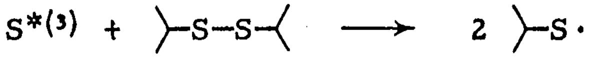


Excitation from the ground state to the first excited triplet state according to the Franck-Condon principle must be along the vertical arrow (straight line). This is the known spectroscopic transition of the substrate, since the Franck-Condon principle holds for spectroscopic measurements. However, there may be a lower energy path to a twisted triplet available to the system (wave line). This is called "nonvertical" excitation.

This thesis deals with another kind of nonvertical excitation: the transfer of triplet energy to carbon-carbon sigma bonds. The following two related photosensitized reactions have been known for several years.



$$S^{*(3)} + CH_3-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-CH_3 \longrightarrow 2\,CH_3-\overset{\overset{O}{\|}}{C}-O\cdot \qquad (7)$$



(8)

Only recently the former reaction has been carefully investigated by Mr. F. G. Moses (9). He has concluded that the energy transfer probably occurs with concurrent stretching of the oxygen-oxygen bond. In other words, the Franck-Condon principle is not obeyed. Moreover, the data are nicely explained by an extended Franck-Condon principle in which only the minimum motion of nuclei occurs. Thus all the energy from a high energy sensitizer is transferred; the extra energy ends up overcoming the repulsive forces between the partially dissociated unpaired radicals.

Triplet energy transfers to sigma bonds could have wide importance in both chemistry and microbiology. The transfer of energy to disulfide bonds in particular could prove important to the microbiologist working with protein substances.

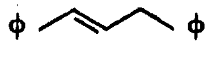
RESULTS AND DISCUSSION

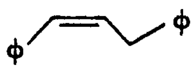
Introduction

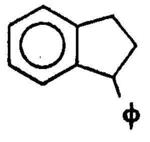
We have observed that the reversible isomerization of *trans*- to *cis*-1,2-diphenylcyclopropane occurs when a degassed benzene solution of *trans*-1,2-diphenylcyclopropane and a sensitizer of triplet energy between 40 and 75 kcal/mole is irradiated with light absorbed by the sensitizer alone. The reaction is very clean, with the only product being the other isomer. With carefully filtered light, the reaction can be run to the photostationary state without difficulty or loss of material. The reaction appears to go by transfer of energy from the triplet state of the sensitizer with conservation of spin, giving the ground state of the sensitizer and an excited triplet species of the diphenylcyclopropane. The evidence for the preceding statement is the following.

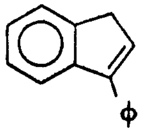
1. 1,2-Diphenylcyclopropane will quench sensitizer triplets; moreover each triplet quenched leads to a corresponding amount of isomerization predicted by the decay ratio of the intermediate. This will be discussed in more detail later.

2. Direct irradiation of 1,2-diphenylcyclopropane, producing the singlet excited state, leads to a number of products, shown below, which are not seen in the sensitized reaction (10).

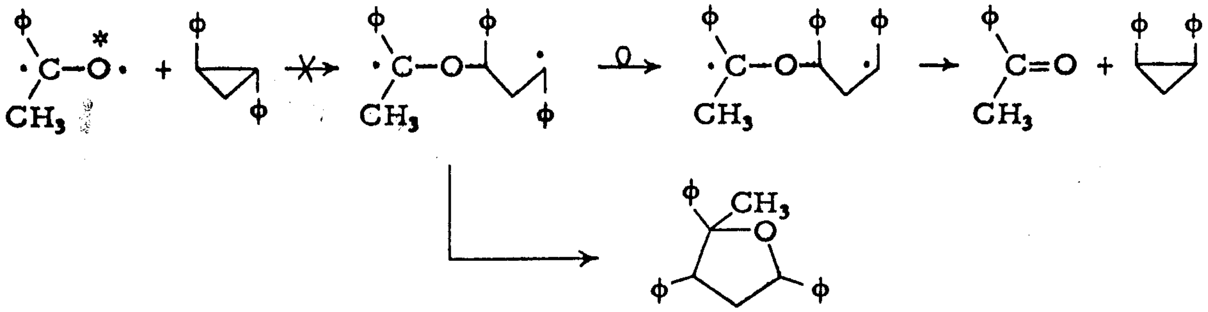




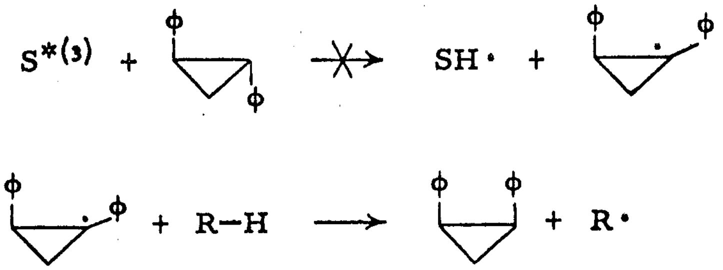




3. There are no cyclic ethers formed when ketones are used as sensitizers, ruling out mechanisms such as:



4. Aromatic hydrocarbons such as naphthalene and triphenylene are effective sensitizers for the reaction, ruling out mechanisms involving hydrogen abstraction.



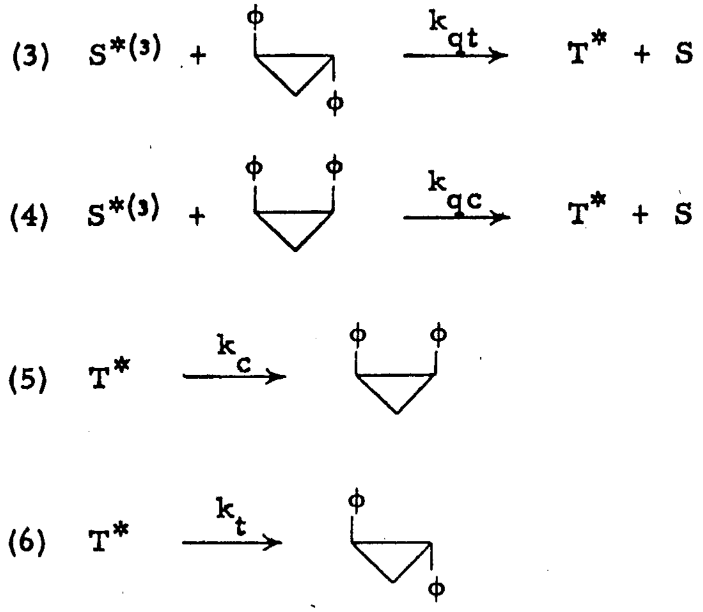
$$R\cdot + SH\cdot \longrightarrow RH + S$$

The mechanistic steps postulated for the reaction are as follows:

$$(1)\quad S + h\nu \longrightarrow S^{*(1)} \xrightarrow{a^{\ddagger}} S^{*(3)}$$

$$(2)\quad S^{*(3)} \xrightarrow{kd} S$$

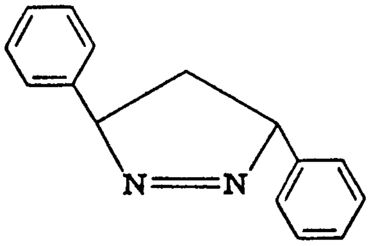
[‡] Here a is the fraction of excited sensitizer molecules which cross over to the triplet manifold (11).



Steps 1 and 2 have been examined and discussed in much detail by others (4, 11). This mechanism would be expected to give a linear plot of (moles of product)$^{-1}$ vs. (concentration of substrate)$^{-1}$. Plots for both cis- and trans-1, 2-diphenylcyclopropane as substrates and triphenylene as sensitizer are shown in Figures I and II.

It will be shown in the remaining parts of the Results and Discussion section of this thesis that all the experimental evidence agrees with the above mechanism.

Experiments with trans-3, 5-Diphenyl-1-pyrazoline



(I)

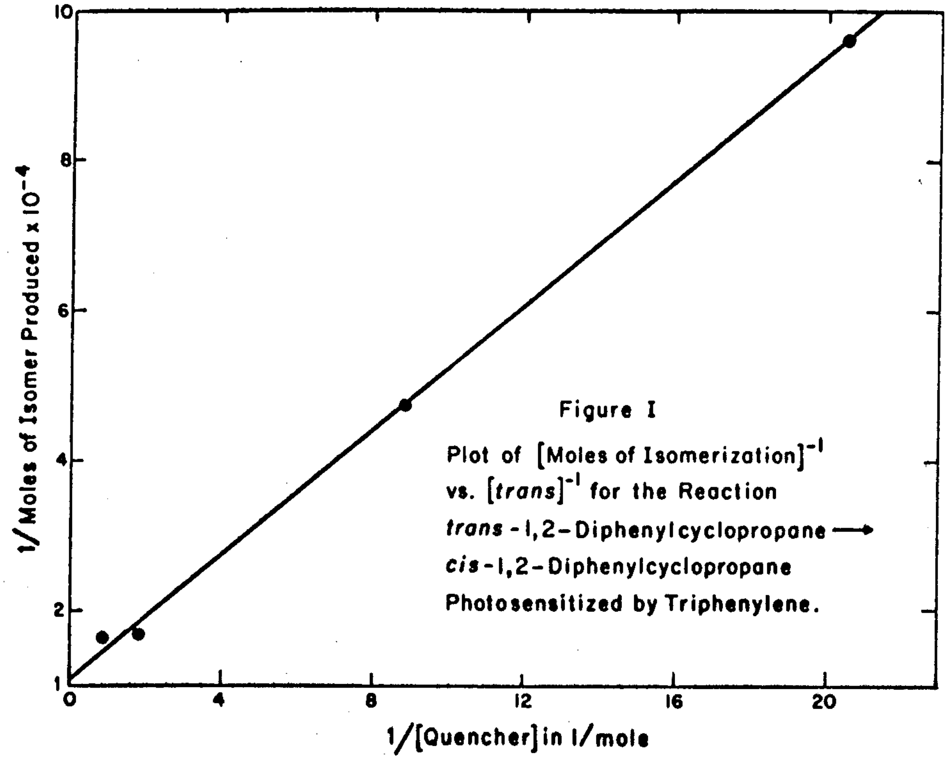


Figure I

Plot of [Moles of Isomerization]$^{-1}$ vs. [*trans*]$^{-1}$ for the Reaction *trans*-1,2-Diphenylcyclopropane ⟶ *cis*-1,2-Diphenylcyclopropane Photosensitized by Triphenylene.

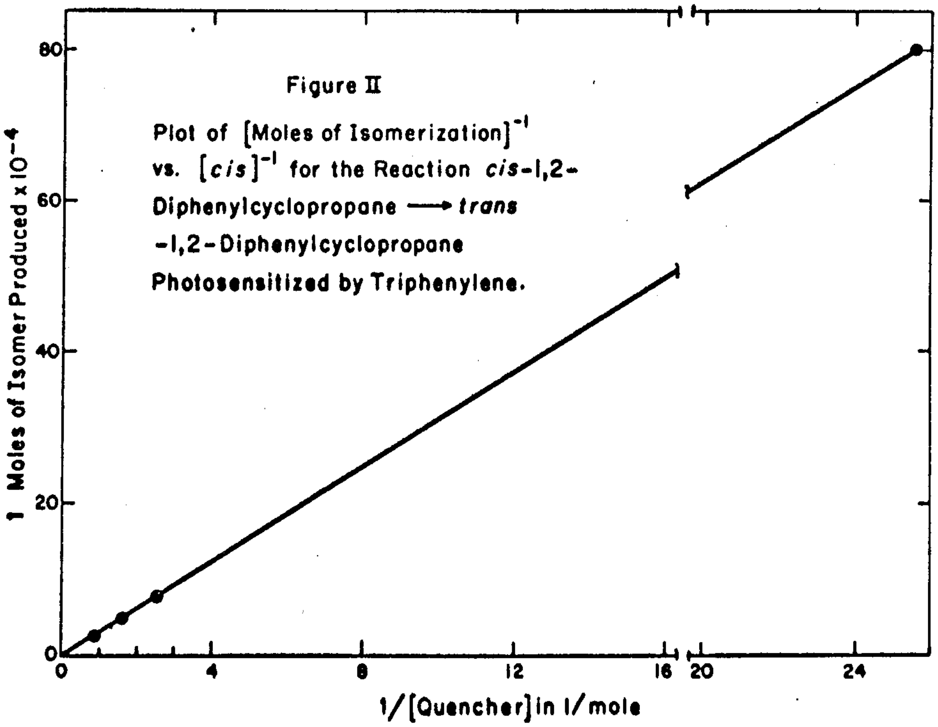


Figure II

Plot of [Moles of Isomerization]$^{-1}$ vs. [*cis*]$^{-1}$ for the Reaction *cis*-1,2-Diphenylcyclopropane ⟶ *trans*-1,2-Diphenylcyclopropane Photosensitized by Triphenylene.

Overberger and Anselme have reported that I decomposes upon heating or irradiation with ultraviolet light to give 100% trans-1, 2-diphenylcyclopropane (12). To check this, I was refluxed in benzene until nitrogen evolution ceased (one hour). Analysis of the solution by v. p. c. showed two lower boiling compounds (molecular weight estimated at 150 from elution times), 10. 8% and 4. 4% of the total area of the trace and two compounds corresponding precisely in elution times to cis- and trans-1, 2-diphenylcyclopropane. Taken by themselves, there was 8. 9% of the cis isomer and 91. 1% of the trans isomer. When a solution of I was injected into the v. p. c. at temperatures above 150° C, the only products observed were cis- and trans-1, 2-diphenylcyclopropane. The percentage of the trans isomer out of the total isomers at different temperatures of the inlet is shown in Table I. There was no loss of material in these decompositions.

A solution of I in benzene, degassed and under nitrogen, was irradiated until nitrogen evolution ceased under conditions described in the Experimental section. Analysis of the solution by v. p. c. indicated 7% of the products consisted of five incompletely separated lower boiling materials with the remaining material consisting of a mixture of 10. 0% cis- and 90. 0% trans-1, 2-diphenylcyclopropane. Again there was no unaccounted for material.

Solutions of I were irradiated in the presence of various sensitizers. The absorption spectrum of I indicates that light of longer wavelength that 3650 Å will be at least partially absorbed. Therefore only sensitizers which absorb light strongly at 3660 Å were used with

TABLE I

Thermal Decomposition of 3, 5-Diphenyl-1-pyrazoline

Temperature (°C)	% trans-1, 2-Diphenylcyclopropane(a)
80°(b)	90.0%
150°(c)	85.5%
160°(c)	85.2%
185°(c)	83.7%
250°(c)	83.3%
315°(c)	80.9%

(a)The remaining material was cis-1, 2-Diphenylcyclopropane.

(b)Refluxing benzene.

(c)These temperatures were achieved by injecting the pyrazoline into the v. p. c. at different injector temperatures. The products were stable under these conditions, indicating low residence times in the injector. Therefore, the average temperature of decomposition (column temperature 185°) may be different from the value given.

the 3660 Å filter system. The samples were irradiated just long enough to decompose all the pyrazoline and then stopped to avoid photosensitized change of the product ratio. The time of irradiation needed to accomplish this was determined separately for each sensitizer as described in the Experimental section. The products of the photosensitized reaction consisted of about 10% of three incompletely separated lower boiling materials (one of these had an elution time identical to one of the products from direct irradiation) and 90% cis- and trans-1, 2-diphenylcyclopropane. Table II shows the isomer ratios of the cyclopropanes produced with different sensitizers. The method for determining the extent of reaction is found in the Experimental section.

Discussion of the Pyrazoline Experiments

Overberger, et al. (13), has reported that cis- (II) and trans- (III) 3, 5-bis(p-methoxyphenyl)-1-pyrazoline give different distributions of cis- and trans-1, 2-bis(p-methoxyphenyl)cyclopropane when heated or irradiated. His results, taken from the communication, are shown on the following page.

DECOMPOSITIONS OF II AND III

	% of cyclopropanes[c, d]			
	Thermal[a]		Photolytic[b]	
	cis	trans	cis	trans
II (cis)	43.0	57.0	57.2	42.8
III (trans)	6.7	93.3	0.7	99.3

[a] In toluene at 100°

[b] In THF at 13°; a second set was carried out in benzene with comparable results. Corrections were made for isomerization of the cyclopropanes under the reaction conditions.

[c] In all cases quantitative yields of cyclopropanes were obtained; no olefins were found.

[d] Percentages were calculated by comparison of the areas under the methoxy peaks in the n.m.r. spectra of the resulting cyclopropanes (cis τ 6.52; trans 6.39). These values are averages of two separate decompositions and are accurate to within ±1.5%.

It is evident that this result agrees well with our results with trans-3,5-diphenyl-1-pyrazoline. The most economical explanation of all the data is that trans-3,5-diphenyl-1-pyrazoline decomposes to a singlet diradical when heated or irradiated directly. Internal rotation, and thus cis-trans equilibration, of this singlet diradical is slower than ring closure to products. Thus when the temperature is raised, the rate of internal rotation increases more than the rate of ring closure and the ratio of products is more nearly that of a completely equilibrated diradical. When a solution of the pyrazoline and a sensitizer

TABLE II

Photochemical Decomposition of 3, 5-Diphenyl-1-pyrazoline

Sensitizer	E_t[a] $\left(\frac{\text{kcal}}{\text{mole}}\right)$	Extent of Reaction[b]	% *trans*-1, 2-Diphenyl-cyclopropane[c]
None	—	Complete	90.0%
Anthracene	42.7	None	—
3-Acetyl pyrene	45.5	None	—
Benzanthrone	47[d]	None	—
Pyrene	48.7	None	—
Fluorenone	53.3	None	—
Benzil	53.7	None	—
1-Naphthyl phenyl ketone	57.5	Nearly complete	65%
Michler's ketone	61.0	Complete	63.1%
4-Methylbenzophenone	68.5	Complete	63.4%
Triphenylmethyl phenyl ketone	70.8	≈ 50%	82%
Acetophenone	73.6	Nearly complete	66%

(a)See Table III for references.

(b)See Experimental for details.

(c)The remaining material was *cis*-1, 2-diphenylcyclopropane.

(d)Determined by Dr. Angelo Lamola.

of triplet energy greater than 55 kcal/mole is irradiated with light absorbed only by the sensitizer, triplet energy transfer occurs, probably giving the triplet state of the pyrazoline which then splits off nitrogen to give the triplet diradical. [Triplet energy transfer to azo compounds has been well documented by Hammond and Fox (14).] This triplet diradical cannot close to diphenylcyclopropane until spin inversion has taken place; apparently the process of spin inversion is slow compared to internal rotation, and the diradical has time enough to equilibrate or nearly equilibrate before spin inversion and ring closure occurs. Although photosensitized decomposition of the cis isomer of the pyrazoline would be needed to prove that the triplet diradical is truly equilibrated, Overberger's work with the bis(p-methoxyphenyl)pyrazoline would lead one to expect a trans rich mixture of the cyclopropanes from the equilibrated diradical. Furthermore, Figure III indicates that at infinitely high temperature the product ratio would be that which is found with the photosensitized decomposition of the pyrazoline. Further support for a 63/37 ratio of trans/cis diphenylcyclopropane from the equilibrated diradical will be given in the Quantum Yield section.

This work is the first conclusive evidence that spin inversion can be slower than internal rotation in a diradical. It has been found that singlet methylene adds stereospecifically to cis- and trans-2-butene, while triplet methylene, produced either by collisional deactivation of singlet methylene by an inert gas (15) or by photosensitized decomposition of diazomethane (16), gives nearly the same

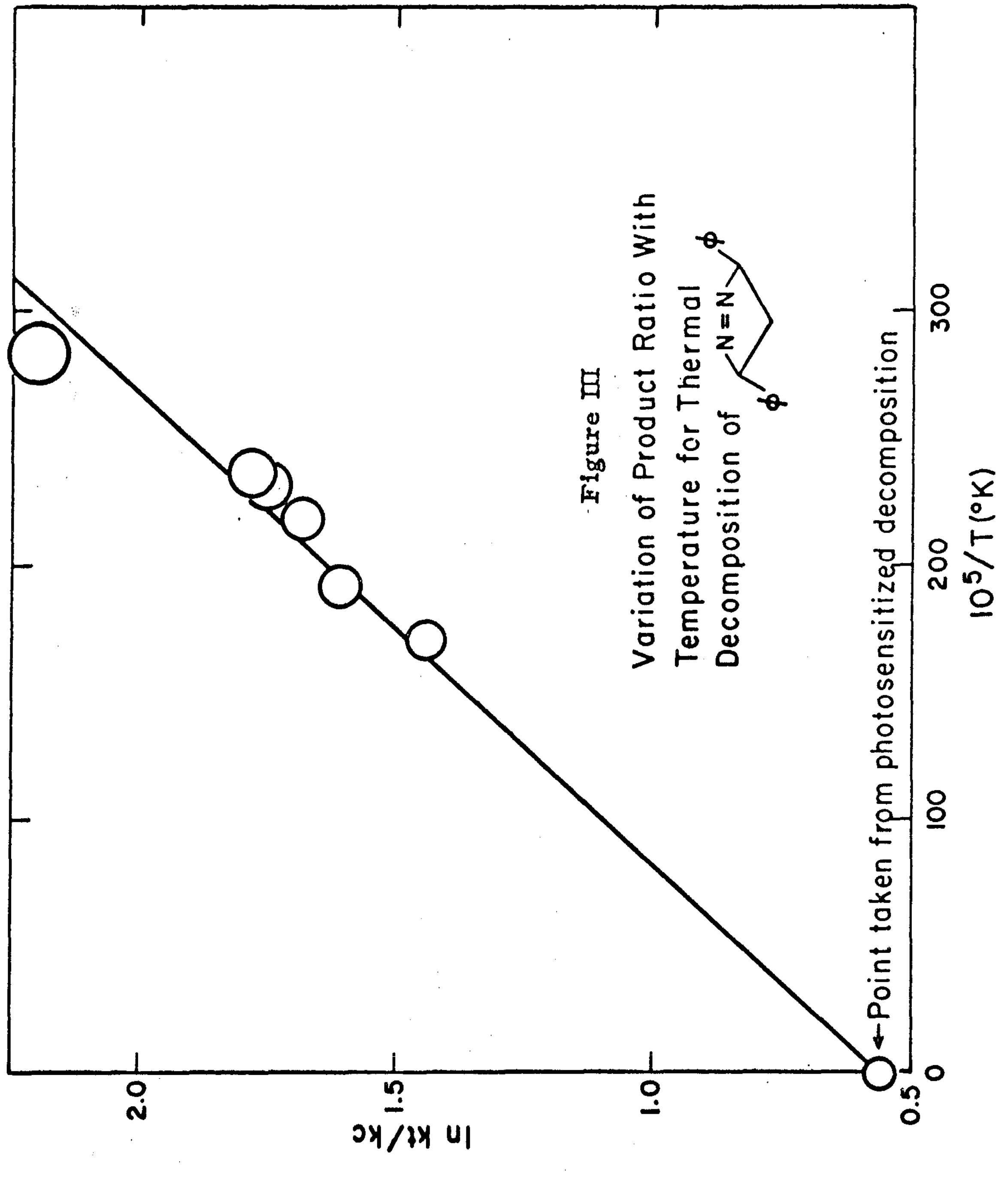


Figure III

Variation of Product Ratio With Temperature for Thermal Decomposition of stereochemical mixture of dimethylcyclopropanes with either starting material. However, it is felt that when singlet methylene adds to an olefin, both the new bonds of the cyclopropane are formed at the same time; thus no diradical intermediate is present and no conclusions about the rate of spin inversion can be drawn.

Photostationary States of the *cis*- and *trans*-1, 2-Diphenylcyclopropane System

The photostationary state compositions of the photosensitized reversible isomerization of *cis*- and *trans*-1, 2-diphenylcyclopropane with several different sensitizers were measured. They are shown in Table III. Since the reaction is slow with most sensitizers, the value for the photostationary state was determined by irradiating two mixtures of the *cis* and *trans* isomers differing by 5% in their composition and finding that both mixtures tended to converge on each other. Determination of these starting mixtures was by trial and error.

When properly filtered light is used, the photosensitized isomerization of diphenylcyclopropane is very clean, with no side reactions occurring. However, when only Pyrex filters are used (as was the case in the measurements of photostationary states), enough light is absorbed by the diphenylcyclopropanes to give some of the singlet reaction. This singlet reaction produces enough quenchers (probably the 1, 3-diphenylpropenes) to stop the photosensitized reaction after a few percent isomerization. The fact that the reaction did apparently stop indicates that the contribution of the direct reaction

TABLE III

Photostationary State Compositions of the
<u>cis</u>-<u>trans</u> Isomerization of 1, 2-Diphenylcyclopropane

Sensitizer	% cis$^{(c)}$	$\frac{k_q \text{ trans}}{k_q \text{ cis}}^{(a)}$	$E_t^{(b)} \left(\frac{\text{kcal}}{\text{mole}}\right)$
Acetophenone	81%	7.92	73.6
Isobutyrophenone	80%	7.44	73.1
p-Methylbenzophenone	75%	5.58	68.5
Fluorenone	67%	3.72	53.3
Mesityl naphthyl ketone	80%	7.44	57 (estimated)
2-Acetonaphthone	70%	4.34	59.3
1-Naphthyl phenyl ketone	76%	5.89	57.5
3-Acetyl pyrene	63%	3.16	45.5*
Naphthalene	48%	1.71	60.9
1, 4-Di-t-butyl-naphthalene	48%	1.71	60 (estimated)
1, 2, 3, 4, 7, 8, 9, 10-octahydro-1, 4, 7, 10-octamethylnaphthacene	65%	3.45	60 (estimated)
Biphenyl	83%	9.07	65.3*
Hexaphenylbenzene	75%	5.58	69**
Chrysene	72%	4.78	56.6*
Pyrene	72%	4.78	48.7
Anthracene	76%	5.89	42.7*
1, 2, 3, 4-Dibenzanthracene	65%	3.45	50.8*
Phenanthrene	71%	4.56	62.2

Table III (continued)

[a] Calculated from the expression $\frac{k_q \underline{\text{trans}}}{k_q \underline{\text{cis}}} = \frac{65}{35} \frac{[\underline{\text{cis}}]}{[\underline{\text{trans}}]}_{\text{P.S.S.}}$. See Experimental section.

[b] $T_1 \rightarrow S_0$. Unstarred values are taken from the unpublished results of Dr. W. G. Herkstroeter, Dr. A. A. Lamola and Dr. G. S. Hammond. Starred values are taken from reference 25. The double starred value was determined by Mrs. Lelia Coyne.

[c] These values were gotten by bracketing the photostationary state by two samples differing by 5%. The error is probably ±3%.

was not enough to change the product ratio. Thus the values in Table III can be trusted, even though they were run with improperly filtered light. The error is probably ±2-3%.

Table III also contains the ratio k_{qt}/k_{qc} calculated from the photostationary state ratio of isomers and the results of the 3, 5-diphenyl-1-pyrazoline experiments. This calculation is based on the mechanism shown on page 68, where T^* is a rapidly equilibrated mixture of the trans and cis excited states of the diphenylcyclopropane. At the photostationary state

$$\text{Rate } \underline{\text{cis}} \rightarrow \underline{\text{trans}} = \text{Rate } \underline{\text{trans}} \rightarrow \underline{\text{cis}}$$

so we can write

$$k_{qc}[S^{*(3)}]\,[\underline{\text{cis}}]k_t = k_{qt}[S^{*(3)}]\,[\underline{\text{trans}}]k_c$$

which can be rearranged to

$$\frac{[\underline{\text{cis}}]}{[\underline{\text{trans}}]}_{\text{P.S.S.}} = \frac{k_{qt}}{k_{qc}} \; \frac{k_c}{k_t}$$

The value of k_c/k_t is determined by the product ratio from the photosensitized decomposition of 3, 5-diphenyl-1-pyrazoline.

Figure IV shows the Saltiel plot (5) of the triplet energy of the sensitizer vs. [cis]/[trans] at the photostationary state. There is no a priori reason to expect any order in this plot, and indeed, none is found. Therefore the triplet energy is not the determining factor in the question of how much a given sensitizer will prefer to react with

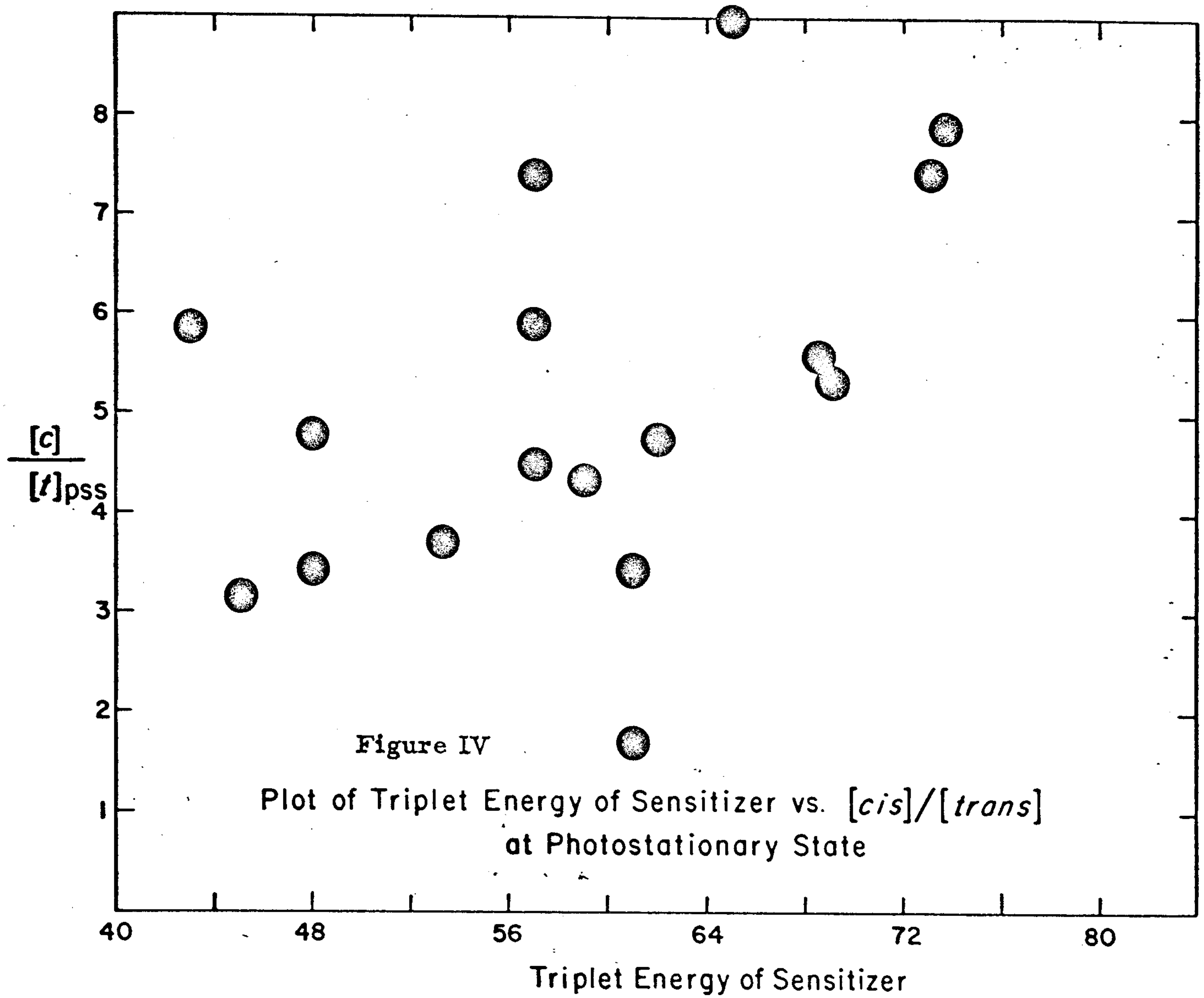


Figure IV

Plot of Triplet Energy of Sensitizer vs. [*cis*]/[*trans*] at Photostationary State one isomer rather than the other. It is clear from Figure IV that all the sensitizers used prefer to react with the *trans* isomer rather than the *cis*. It is not clear why this should be so. One possibility is that the sensitizer must approach the substrate with intimate contact with a phenyl ring, and that the steric crowding of the nearby second phenyl ring in the *cis* isomer makes the reaction less favorable.

Quantum Yields

The quantum yields for the photosensitized isomerization of 1, 2-diphenylcyclopropane were measured with various sensitizers. They are shown in Table IV. The measurements were made with carefully filtered light so that there was no interference from side reactions caused by the direct process. The actinometer used for all the quantum yield measurements was the benzophenone sensitized dimerization of 1, 3-cyclohexadiene. The precision in these measurements was low, with errors ranging from ±10% for most of the sensitizers for which more than one measurement was made to ±25% for the worst behaved sensitizer (*p*-methylbenzophenone). This error was due partly to scatter in the actinometry and partly to the difficulty in measuring small percentages of isomerization. Fortunately, the variation in the quantum yields with different sensitizers was very large, and an error of ±25% will not affect the conclusions drawn from these measurements.

With several sensitizers the variation of the quantum yield with the concentration of the substrate was measured. For these

TABLE IV

Quantum Yields for the Photosensitized Isomerization of 1, 2-Diphenylcyclopropane

Sensitizer	Conc. of Sensitizer (M)	Substrate	Conc. of Substrate (M)	Light (Å)	Temp. (°C)	$\phi^{(a)}$	
Aceto-	.62	trans[(c)]	.527	3660(F)[(d)]	27°	.333	Fig. V
phenone	.62	trans	.105	3660(F)	27°	.256	
$E_t^{(b)}$ = 73.6	.62	trans	.0414	3660(F)	27°	.171	
	.50	trans	.103	3660(F)	31°	.229	
	1.0	trans	.104	3660(F)[(d)]	31°	.225	Fig. XII
	.088	trans	.105	3130(IF)[(d)]	31°	.316	
	.090	trans	.0126	3130(IF)	31°	.162	
	.10	trans	.104	3130(OB)[(d)]	31°	.306	
	.10	trans	.104	3130(OB)	31°	.324	
	.62	cis[(e)]	.533	3660(F)	27°	.234	Fig. VI
	.62	cis	.103	3660(F)	27°	.0864	
	.62	cis	.053	3660(F)	27°	.0576	
p-Diacetyl-	.092	trans	.104	3660(F)	31°	.22	
benzene	.062	trans	.105	3130(IF)	31°	.29	
E_t = 67.7							
Pripio-	.079	trans	.105	3130(IF)	31°	.26	Fig. XI
phenone	.080	trans	.0126	3130(IF)	31°	.14	
E_t = 74.6	.075	trans	.104	3130(OB)	31°	.30	
Isobutyro-	.07	trans	.105	3130(IF)	31°	.22	Fig. IX
phenone	.07	trans	.0126	3130(IF)	31°	.078	
	.07	trans	.104	3130(OB)	31°	.19	

Table IV (continued)

Sensitizer	Conc. of Sensitizer (M)	Substrate	Conc. of Substrate (M)	Light (Å)	Temp. (°C)	$\phi^{(a)}$	
Cyclopropyl phenyl ketone E_t = 74.4	.07 .07	<u>trans</u> <u>trans</u>	.105 .0126	3130(IF) 3130(IF)	31° 31°	.20 .076	Fig. X
Benzyl phenyl ketone E_t = 72 (est.)	.05	<u>trans</u>	.105	3130(IF)	31°	.064	
2,4,6-Trimethylacetophenone E_t = 73 (est.)	.07	<u>trans</u>	.105	3130(IF)	31°	<.005	
m-Nitroacetophenone E_t = 60.1	.10	<u>trans</u>	.105	3130(IF)	31°	<.005	
4-Acetylbiphenyl E_t = 60.6	.10	<u>trans</u>	.105	3130(IF)	31°	<.005	

Table IV (continued)

Sensitizer	Conc. of Sensitizer (M)	Substrate	Conc. of Substrate (M)	Light (Å)	Temp. (°C)	$\phi^{(a)}$
9-Acetyl-fluorene E_t = 61 (est.)	.10	<u>trans</u>	.105	3130(IF)	31°	< .005
Benzaldehyde* E_t = 72.2	.10	<u>trans</u>	.105	3130(IF)	31°	< .005
Triphenylmethyl phenyl ketone E_t = 70.8	.10	<u>trans</u>	.104	3660(F)	31°	$<5\times10^{-5}$
1-Naphthyl phenyl ketone E_t = 57.5	.01	<u>trans</u>	.107	3660(F)	31°	1.0×10^{-3}
Michler's ketone(f) E_t = 61.0	.01	<u>trans</u>	.107	3660(F)	31°	$<3\times10^{-5}$
Fluorenone E_t = 53.3	.012	<u>trans</u>	.107	3660(F)	31°	5.8×10^{-4}

Table IV (continued)

Sensitizer	Conc. of Sensitizer (M)	Substrate	Conc. of Substrate (M)	Light (Å)	Temp. (°C)	$\phi^{(a)}$	
2-Acetonaphthone E_t = 59.3	.041	*trans*	.107	3660(F)	31°	1.8×10^{-4}	
Benzil E_t = 50.1	.050	*trans*	.107	3660(F)	31°	3.8×10^{-4}	
p-Methylbenzophenone E_t = 68.5 (est.)	.10	*trans*	.507	3660(F)	31°	4.9×10^{-3}	Fig. XVI
	.10	*trans*	.640	3660(F)	31°	6.1×10^{-3}	
	.10	*trans*	.276	3660(F)	31°	8.4×10^{-3}	
	.05	*trans*	.378	3660(F)	31°	5.0×10^{-3}	
	.05	*trans*	.185	3660(F)	31°	3.2×10^{-3}	
	.05	*trans*	.141	3660(F)	31°	5.1×10^{-3}	
	.05	*trans*	.136	3660(F)	31°	6.1×10^{-3}	
	.05	*trans*	.173	3660(F)	31°	3.0×10^{-3}	
	.05	*trans*	.179	3660(F)	31°	2.8×10^{-3}	
Acridine** E_t = 45.3	.0015	*trans*	.107	3660(F)	31°	$<7\times10^{-6}$	
Carbazole* E_t = 70.1	.042	*trans*	.107	3660(F)	31°	$<2\times10^{-5}$	
Triphenylene E_t = 66.6	.01	*trans*	.105	3130(IF)	31°	.082	
	.01	*trans*	.104	3130(OB)	31°	.12	
	.01	*trans*	.104	3130(OB)	31°	.09	
	.01	*trans*	.104	$>3000^{(g)}$	31°	.058	

Table IV (continued)

Sensitizer	Conc. of Sensitizer (M)	Substrate	Conc. of Substrate (M)	Light (Å)	Temp. (°C)	$\phi^{(a)}$
Triphenylene E_t = 66.6	.001	<u>trans</u>	.0516	3130(SF)$^{(i)}$	26°	.093
	.001	<u>trans</u>	.105	3130(SF)	26°	.136 } Fig. VII
	.001	<u>trans</u>	.330	3130(SF)	26°	.292
	.001	<u>cis</u>	.0492	3130(SF)	26°	.018
	.001	<u>cis</u>	.0825	3130(SF)	26°	.029 } Fig. VIII
	.001	<u>cis</u>	.309	3130(SF)	26°	.106
Naphthalene E_t = 60.9	.12	<u>trans</u>	.176	3130(SF)$^{(h)}$	28°	9.4×10^{-5}
1,4-Di-<u>t</u>-butylnaphthalene E_t = 60 (est.)	.066	<u>trans</u>	.176	3130(SF)	28°	3.8×10^{-3}
2,6-Di-<u>t</u>-butylnaphthalene E_t = 60 (est.)	.066	<u>trans</u>	.176	3130(SF)	28°	3.8×10^{-3}
Naphthalene + <u>p</u>-methylbenzophenone E_t = 60.9	.123(N) .051(M) for all runs	<u>trans</u>	.107	3660(F)	31°	2.5×10^{-3}
		<u>trans</u>	.107	3660(F)	31°	2.5×10^{-5}
		<u>trans</u>	.107	3660(F)	31°	1.6×10^{-3}
		<u>trans</u>	.0508	3660(F)	31°	4.4×10^{-4} } Fig. XIII
		<u>trans</u>	.212	3660(F)	31°	2.3×10^{-3}

Table IV (continued)

Sensitizer	Conc. of Sensitizer (M)	Substrate	Conc. of Substrate (M)	Light (Å)	Temp. (°C)	$\phi^{(a)}$	
1,4-Di-*t*-butyl-naphthalene + *p*-methylbenzophenone E_t = 60 (est.)	.123(D)	*trans*	.105	3660(F)	31°	3.8×10^{-4}	
	.051(M)	*trans*	.105	3660(F)	31°	4.8×10^{-4}	
	for all	*trans*	.0555	3660(F)	31°	1.4×10^{-4}	Fig. XV
	runs	*trans*	.216	3660(F)	31°	2.0×10^{-3}	
1,2,3,4,7,8,9,10-Octahydro-1,4,7,10-octamethylnaphthacene + *p*-methylbenzophenone E_t = 60 (est.)	.021(O)	*trans*	.104	3660(F)	31°	6.7×10^{-4}	
	.051(M)	*trans*	.104	3660(F)	31°	1.7×10^{-4}	
	for	*trans*	.104	3660(F)	31°	2.9×10^{-4}	
	all	*trans*	.0655	3660(F)	31°	1.2×10^{-4}	Fig. XIV
	runs	*trans*	.204	3660(F)	31°	5.3×10^{-4}	
2,2'-Binaphthyl** E_t = 55.9	.02	*trans*	.104	3130(OB)	31°	$< 10^{-4}$	

Table IV (continued)

Sensitizer	Conc. of Sensitizer (M)	Substrate	Conc. of Substrate (M)	Light (Å)	Temp. (°C)	$\phi^{(a)}$
Biphenyl** + p-methyl-benzophenone $E_t = 65.5$	.15(B) .10(M)	<u>trans</u>	.104	3660(F)	31°	2.8×10^{-3}
Chrysene** $E_t = 56.6$	.010	<u>trans</u>	.107	3660(F)	31°	4.3×10^{-4}
Fluoranthene** $E_t = 53.0$	.002	<u>trans</u>	.107	3660(F)	31°	4.3×10^{-4}
1,2,5,6-Dibenzanthracene** $E_t = 52.3$	.003	<u>trans</u>	.107	3660(F)	31°	1.3×10^{-4}
1,2-Benzanthracene** $E_t = 47.2$	.003	<u>trans</u>	.107	3660(F)	31°	1.1×10^{-4}
Pyrene $E_t = 48.7$	.005	<u>trans</u>	.107	3660(F)	31°	$< 7 \times 10^{-6}$
Anthracene** $E_t = 42.7$	—$^{(j)}$	<u>trans</u>	.107	3660(F)	31°	5.6×10^{-4}

Table IV (continued)

Sensitizer	Conc. of Sensitizer (M)	Substrate	Conc. of Substrate (M)	Light (Å)	Temp. (°C)	$\phi^{(a)}$
9,10-Dibromo-anthracene** E_t = 40.2	.003	trans	.107	3660(F)	31°	8.5×10^{-4}
Bromobenzene E_t = 73.2	neat(k)	trans	.104	3130(OB)	31°	.010

(a) The actinometer used for all runs was the dimerization of 1,3-cyclohexadiene (.25 M) photosensitized by benzophenone (.1 M). The quantum yield for this actinometer for up to 40% conversion is 0.90, according to Mr. George Vesley, unpublished results. The largest error in the determination of the quantum yield was the scatter in the actinometry. The error is estimated to be ±15%.

(b) $T_1 \rightarrow S_0$ in kcal/mole. The unstarred values are taken from the unpublished results of Dr. W. G. Herkstroeter, Dr. A. A. Lamola and Dr. G. S. Hammond.

*These values are taken from reference 24.

**These values are taken from reference 25.

(c) trans-1,2-Diphenylcyclopropane.

Table IV (continued)

[d]3660(F) = Hanovia L 679A 450-watt medium-pressure mercury arc lamp filtered by Corning C.S. O-52 and C.S. 7-37 filters, used with the "merry-go-round" described in the Experimental section.

3130(IF) = Hanovia L 679A 450-watt medium-pressure mercury arc lamp filtered by Baird-Atomics 3rd order interference filters. Centered at 3000 Å, used with the "merry-go-round."

3130(OB) = A collimated beam from Westinghouse SAH-800c 800-watt medium-pressure mercury arc lamp filtered by a Corning C.S. 7-54 glass filter, 2.5 cm of 0.45 M $NiCl_2$ in water, 2.0 cm of 0.005 M K_2CrO_4 in water, and 2.0 cm of 0.005 M potassium biphalate in water (quartz solution holders).

[e]<u>cis</u>-1,2-Diphenylcyclopropane.

[f]4,4'-Bis(dimethylamino)benzophenone.

[g]Hanovia 450-watt lamp filtered by 1 cm .01 M potassium biphalate. The actinometer for this run was a solution of 1,3-cyclohexadiene with an identical concentration of triphenylene as the sample tube.

[h]3130(SF) = Hanovia 450-watt lamp with solution filters of 1 cm of .5 M cobaltous sulfate and 1.6 M nickelous sulfate in water and 0.5 cm of .015 M potassium biphalate, in a quartz holder described in the Experimental section.

[i]The same set up as (h) except replace 0.5 cm of .015 M potassium biphalate by 2 mm Pyrex.

[j]Anthracene dimerizes under these conditions. At the beginning of the reaction A = 2; at the end of the reaction A = .9.

[k]Neat bromobenzene has an absorbance of .8 at 3130 Å, probably the $S_0 \rightarrow T_1$ band, from which the value for E_t was taken.

measurements all the tubes were run under identical conditions to eliminate any relative error due to scatter in the actinometry. According to the mechanism on page 68 we can write

$$\frac{1}{\phi_{c \to t}} = \frac{1}{a}\left(\frac{k_t + k_c}{k_t}\right)\left(1 + \frac{k_d}{k_{qc}[\underline{cis}]}\right)$$

and

$$\frac{1}{\phi_{t \to c}} = \frac{1}{a}\left(\frac{k_t + k_c}{k_c}\right)\cdot\left(1 + \frac{k_d}{k_{qt}[\underline{trans}]}\right).$$

Thus a Stern-Vollmer plot of ϕ^{-1} vs. (concentration of substrate)$^{-1}$ will be linear with an intercept determined by the decay ratio of the excited state of the substrate. The sum of the intercepts^{-1} with both the cis and the trans isomer as substrates will equal unity if the same species or a rapidly equilibrated species is produced from either substrate; the sum will be less than unity if different species are produced which do not have time to equilibrate before they decay to the ground state. Furthermore, the intercept for the Stern-Vollmer plot can be predicted from the photosensitized decomposition of 3, 5-diphenyl-1-pyrazoline if we assume that the same excited species is involved in both the pyrazoline decomposition and the photosensitized isomerization of diphenylcyclopropane.

Figures V through XIV show Stern-Vollmer plots of the data in Table IV. The square points at the intercepts are taken from the photosensitized decomposition of 3, 5-diphenyl-1-pyrazoline. In

Figures XIII through XVI the slopes of the lines are so large that the error in the intercept is too large to allow similar conclusions. Furthermore, these experiments were done with p-methylbenzophenone present to absorb the light. The presence of the p-methylbenzophenone allowed use of the more intense 3660 Å light source, which made the experiments more convenient. Since the naphthalene triplets quench the benzophenone triplets at a diffusion controlled rate, the diphenylcyclopropane sees only naphthalene triplets. The quantum yields for the isomerization of trans-1, 2-diphenylcyclopropane sensitized by naphthalene in the presence and absence of p-methylbenzophenone are different by a factor of ten, while the lifetime of the naphthalene triplet remained nearly unchanged. Therefore it seems likely that there are systematic difficulties in the runs in the presence of p-methylbenzophenone, and that runs with more than one sensitizer should not be trusted if other measurements conflict.

The fact that the same intercept is observed in Figures V through XII for all sensitizers indicates the excited species of the substrate is independent and free from the sensitizer when the decay to ground state occurs. It is very likely that sensitizers as different as triphenylene and acetophenone would give different decay ratios if a complex of the sensitizer and substrate excited state were decaying to the ground state.

The sum of the intercepts^{-1} in Figures V through VIII equals unity within 5%. Thus we are dealing with the same or a rapidly equilibrated excited species produced from either cis- or trans-1, 2-

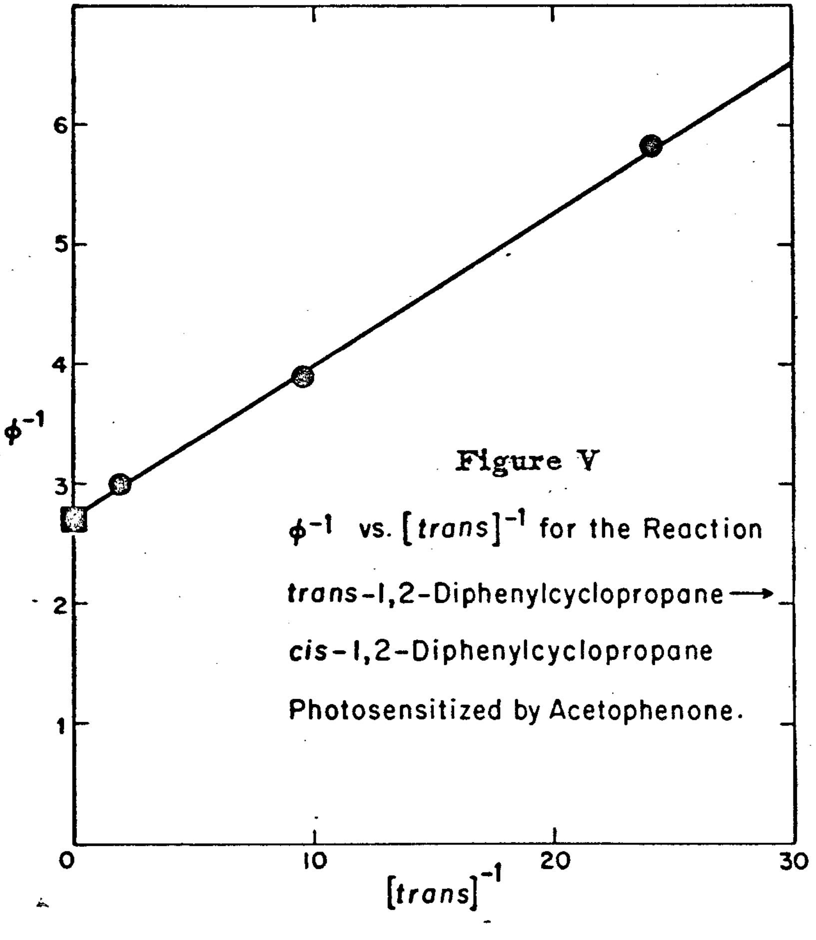


Figure V

ϕ^{-1} vs. $[trans]^{-1}$ for the Reaction *trans*-1,2-Diphenylcyclopropane → *cis*-1,2-Diphenylcyclopropane Photosensitized by Acetophenone.

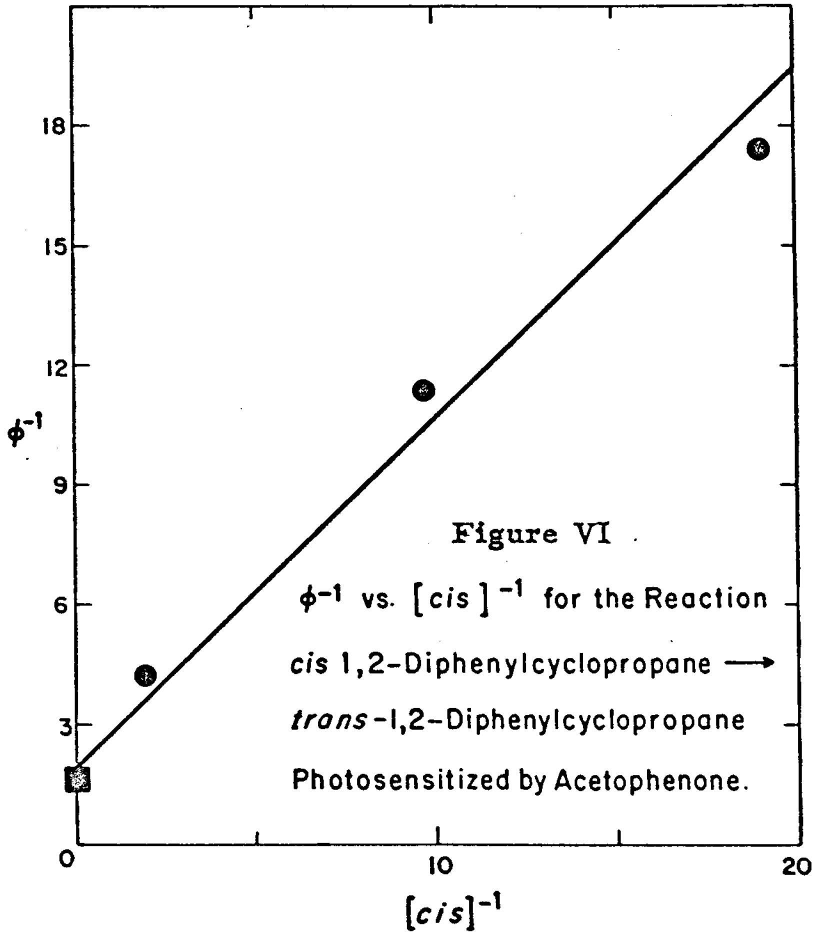


Figure VI

ϕ^{-1} vs. $[cis]^{-1}$ for the Reaction *cis* 1,2-Diphenylcyclopropane → *trans*-1,2-Diphenylcyclopropane Photosensitized by Acetophenone.

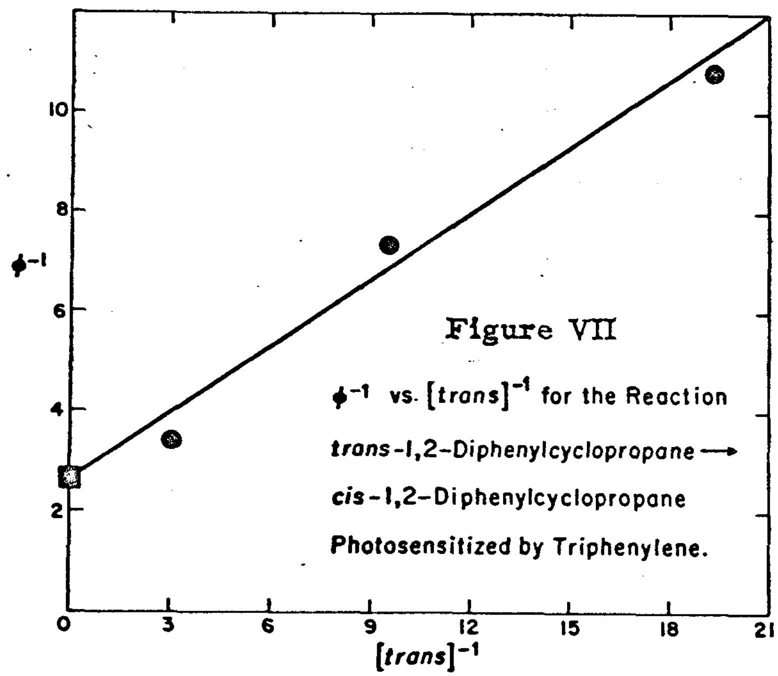


Figure VII

ϕ^{-1} vs. [*trans*]$^{-1}$ for the Reaction
trans-1,2-Diphenylcyclopropane ⟶
cis-1,2-Diphenylcyclopropane
Photosensitized by Triphenylene.

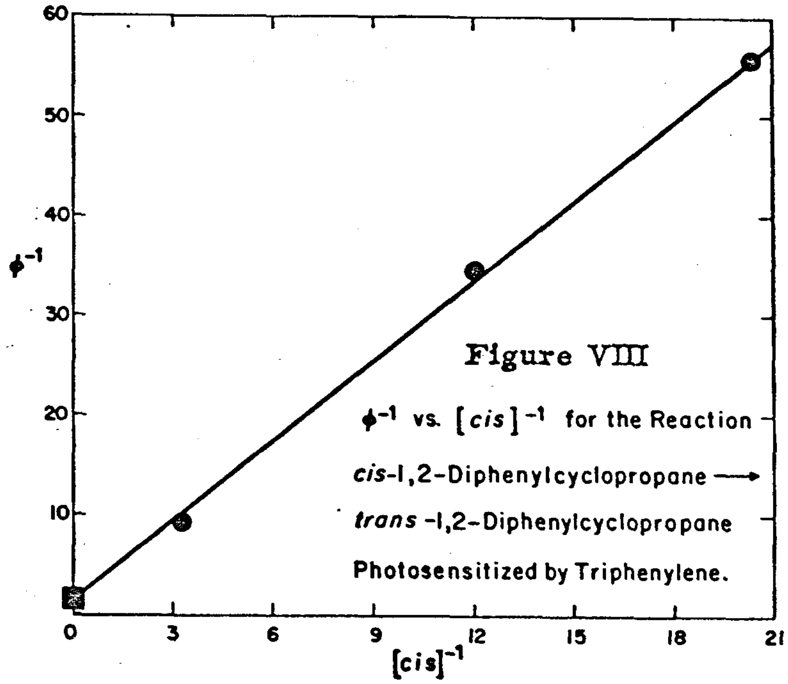


Figure VIII

ϕ^{-1} vs. [*cis*]$^{-1}$ for the Reaction
cis-1,2-Diphenylcyclopropane ⟶
trans-1,2-Diphenylcyclopropane
Photosensitized by Triphenylene.

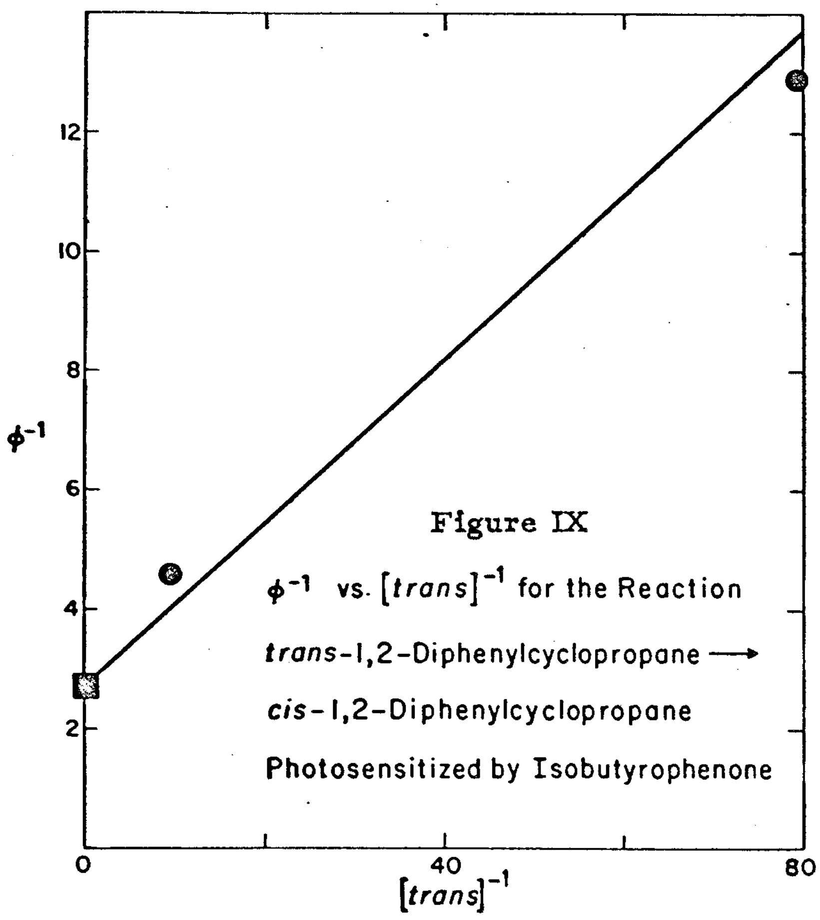


Figure IX

ϕ^{-1} vs. $[trans]^{-1}$ for the Reaction

trans-1,2-Diphenylcyclopropane ⟶

cis-1,2-Diphenylcyclopropane

Photosensitized by Isobutyrophenone

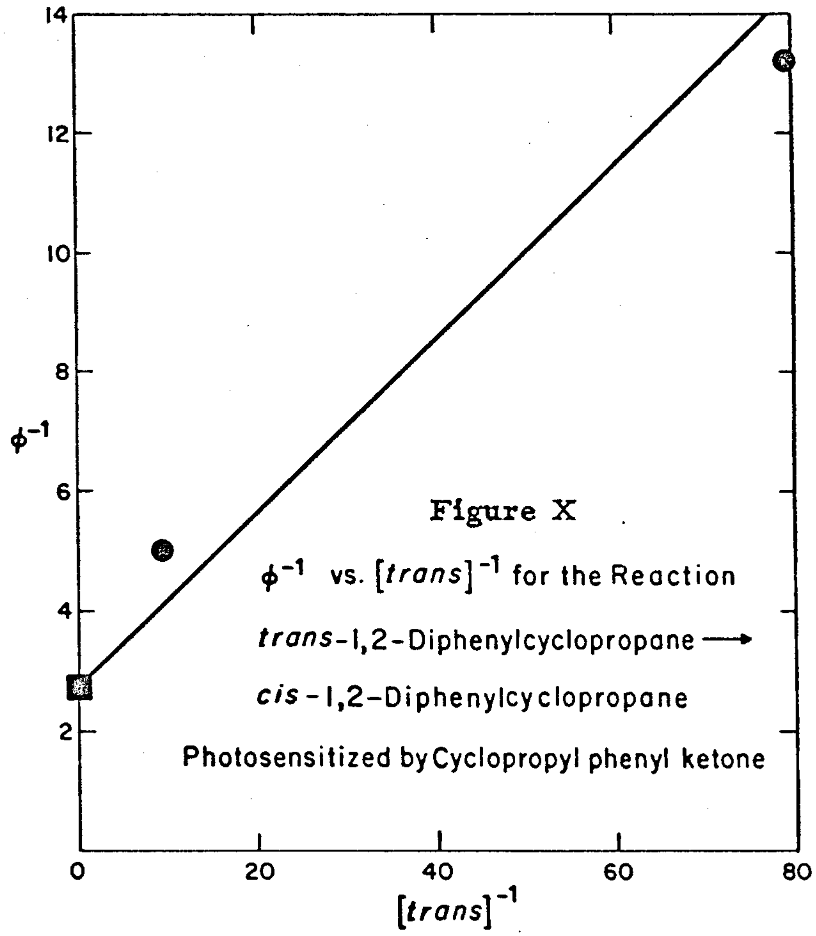


Figure X

ϕ^{-1} vs. $[trans]^{-1}$ for the Reaction

trans-1,2-Diphenylcyclopropane ⟶

cis-1,2-Diphenylcyclopropane

Photosensitized by Cyclopropyl phenyl ketone

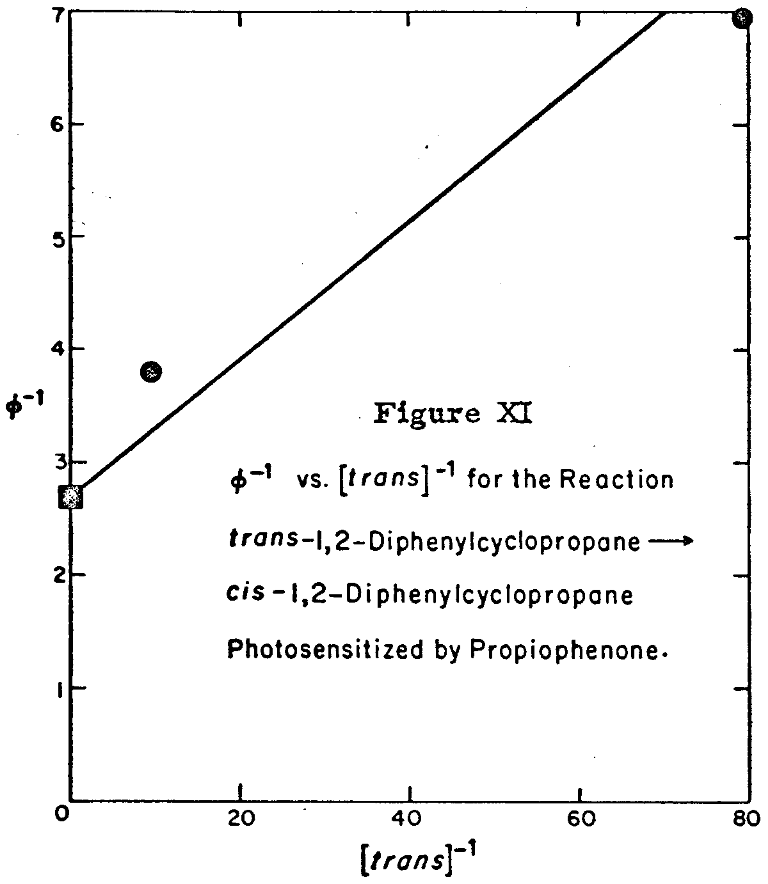


Figure XI

ϕ^{-1} vs. $[trans]^{-1}$ for the Reaction
trans-1,2-Diphenylcyclopropane ⟶
cis-1,2-Diphenylcyclopropane
Photosensitized by Propiophenone.

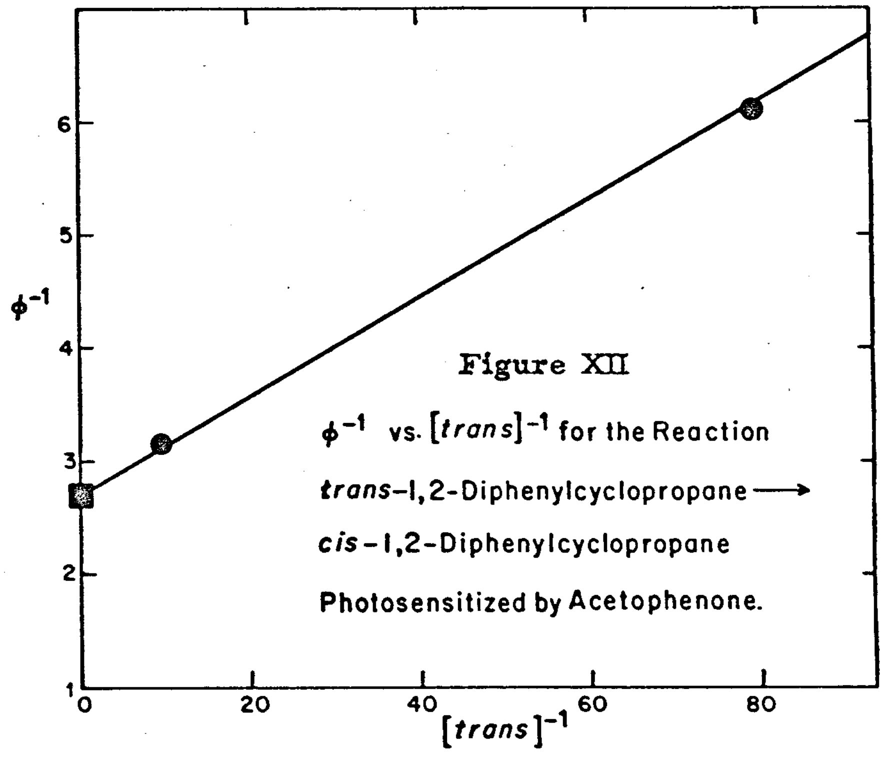


Figure XII

ϕ^{-1} vs. $[trans]^{-1}$ for the Reaction
trans-1,2-Diphenylcyclopropane ⟶
cis-1,2-Diphenylcyclopropane
Photosensitized by Acetophenone.

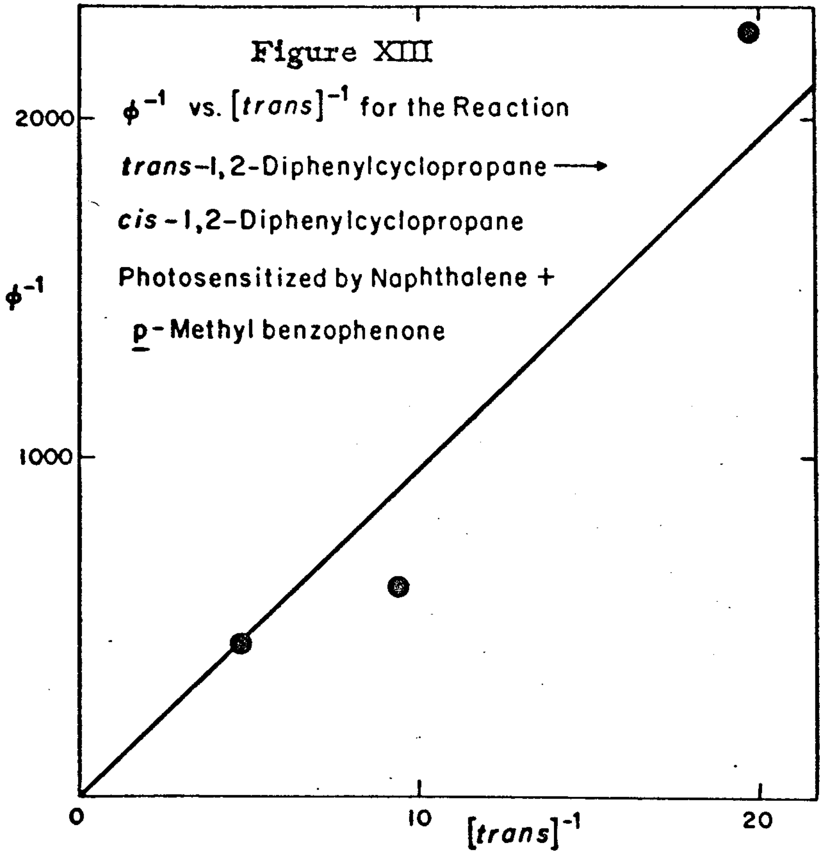


Figure XIII

ϕ^{-1} vs. $[\mathit{trans}]^{-1}$ for the Reaction

trans-1,2-Diphenylcyclopropane ⟶

cis-1,2-Diphenylcyclopropane

Photosensitized by Naphthalene +

p-Methyl benzophenone

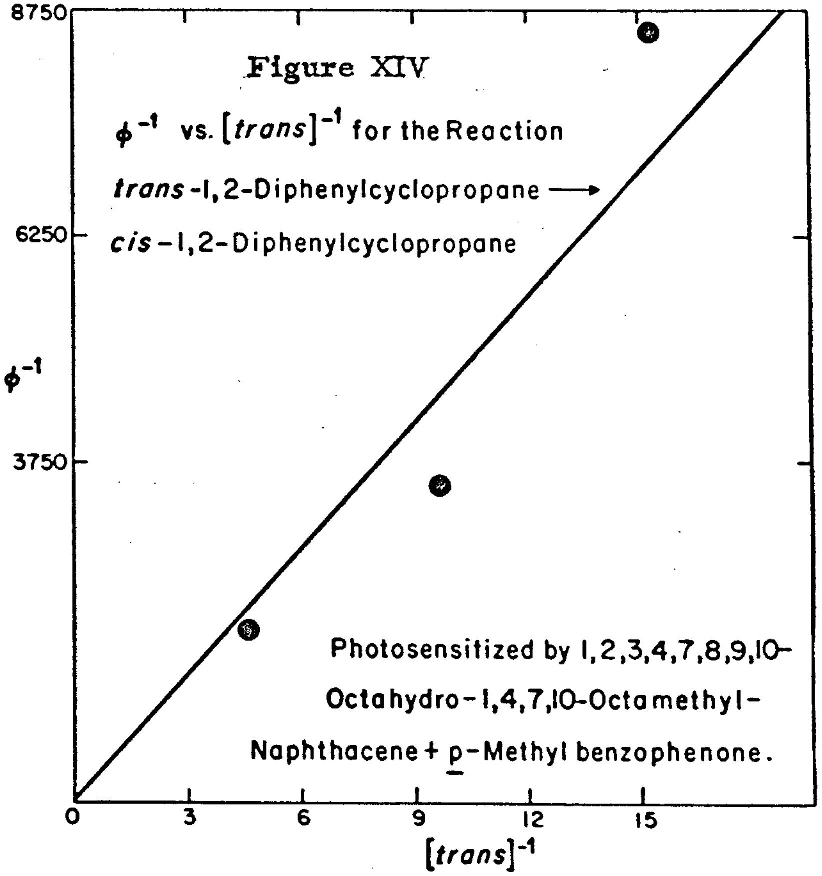


Figure XIV

ϕ^{-1} vs. $[\mathit{trans}]^{-1}$ for the Reaction

trans-1,2-Diphenylcyclopropane ⟶

cis-1,2-Diphenylcyclopropane

Photosensitized by 1,2,3,4,7,8,9,10-Octahydro-1,4,7,10-Octamethyl-Naphthacene + p-Methyl benzophenone.

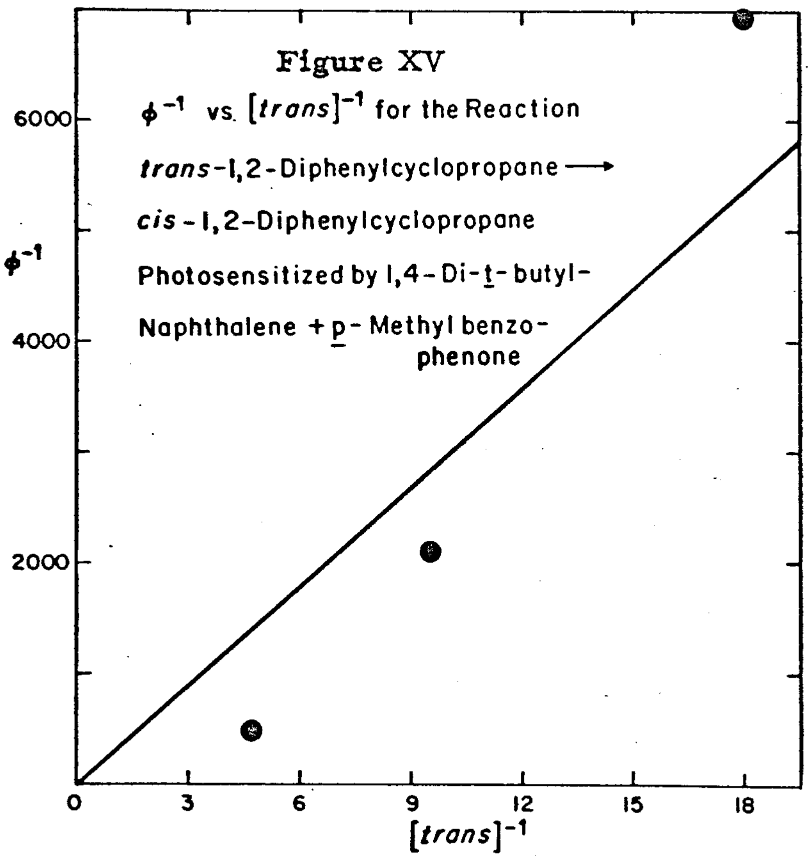


Figure XV

ϕ^{-1} vs. $[trans]^{-1}$ for the Reaction

trans-1,2-Diphenylcyclopropane ⟶

cis-1,2-Diphenylcyclopropane

Photosensitized by 1,4-Di-t-butyl-Naphthalene + p-Methyl benzophenone

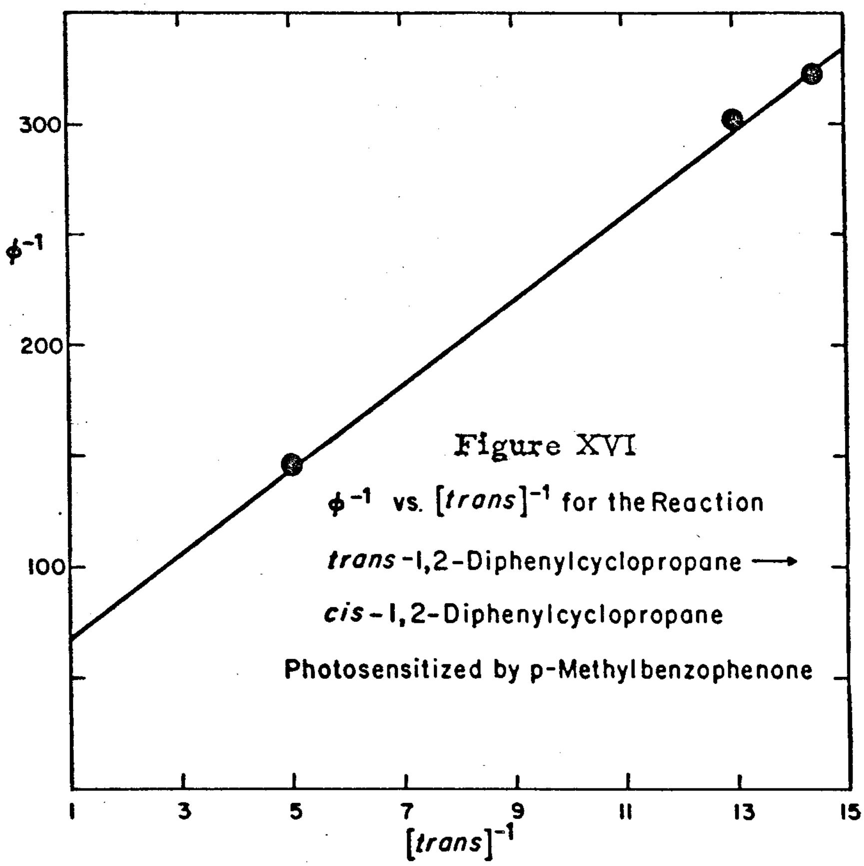


Figure XVI

ϕ^{-1} vs. $[trans]^{-1}$ for the Reaction

trans-1,2-Diphenylcyclopropane ⟶

cis-1,2-Diphenylcyclopropane

Photosensitized by p-Methylbenzophenone

diphenylcyclopropane. Finally, the data agree very well with the postulate that the same species is produced from the photosensitized decomposition of 3, 5-diphenyl-1-pyrazoline and photosensitized isomerization of diphenylcyclopropane. Thus it seems almost certain that the intermediate in this reaction is simply the triplet state of 1, 3-diphenyltrimethylene, since this is almost certainly the species produced in the photosensitized decomposition of 3, 5-diphenyl-1-pyrazoline.

Flash Spectroscopic Measurements

The lifetimes of a number of sensitizer listed in Table V were measured by the method developed by Dr. W. G. Herkstroeter (4). The main purpose of these measurements was to obtain triplet lifetimes which could be used to extract the quenching constants from the quantum yield measurements. This will be discussed in the section on Quenching Constants. With triphenylene further experiments were run to quantitatively determine the quenching of the triplet lifetime by the addition of cis- and trans-1, 2-diphenylcyclopropane to the solutions. The results of these experiments are also shown in Table V along with the quenching constants k_{qt} and k_{qc} calculated from the data. These are found simply by the expression

$$\alpha' - \alpha = k_q[\text{quencher}]$$

where alpha is the decay constant of the triphenylene triplet in the absence of diphenylcyclopropane and alpha' is the decay constant in the

TABLE V

Flash Spectroscopy Measurements

Sensitizer(a)	Quencher	Conc. (M)	α(sec^{-1})(d)	k_q $\frac{\text{liters}}{\text{mole sec}}$	Comment
Triphenylene	—	—	5.0×10^3	—	Substrates zone-refined.
	trans(b)	1.08	70×10^3	$6.5\pm1\times10^4$	
	cis(c)	1.04	15×10^3	$1.0\pm.5\times10^4$	
	—	—	2.5×10^3	—	
	cis	1.3	14.2×10^3	$9.0\pm.5\times10^3$	Substrate recrystallized from ethanol.
	—	—	2.7×10^3	—	
	trans	.25	9.6×10^3	$2.7\pm.5\times10^4$	Substrated treated with Br_2 in CCl_4, then recrystallized from ethanol.
2-Acetonaphthone			2.5×10^3(e)		
1-Naphthylphenyl ketone			7.6×10^3		
Benzophenone			5.0×10^4		
Naphthalene			2.8×10^4		
1,4-Di-t-butylnaphthalene			1.7×10^4		

Table V (continued)

Sensitizer[a]	Quencher	Conc. (M)	$\alpha(\mathrm{sec}^{-1})$[d]	k_q $\frac{\mathrm{liters}}{\mathrm{mole\ sec}}$	Comment
2, 6-Di-*t*-butylnaphthalene			2.7×10^3		
Naphthalene + *p*-methylbenzophenone			1.4×10^4		
1, 4-Di-*t*-butylnaphthalene + *p*-methylbenzophenone			1.9×10^4		
1, 2, 3, 4, 7, 8, 9, 10-Octahydro-1, 4, 7, 10-octamethylnaphthacene + *p*-methylbenzophenone			1.3×10^4		

[a] Concentration of the sensitizer was 4×10^{-5} M in all cases except benzophenone which was 2×10^{-2} M.

[b] *trans*-1, 2-Diphenylcyclopropane.

[c] *cis*-1, 2-Diphenylcyclopropane.

[d] Taken from the computer analysis of three separate pictures (cf. Experimental).

[e] This number and those which follow it were used in the calculation of quenching constants from the quantum yields.

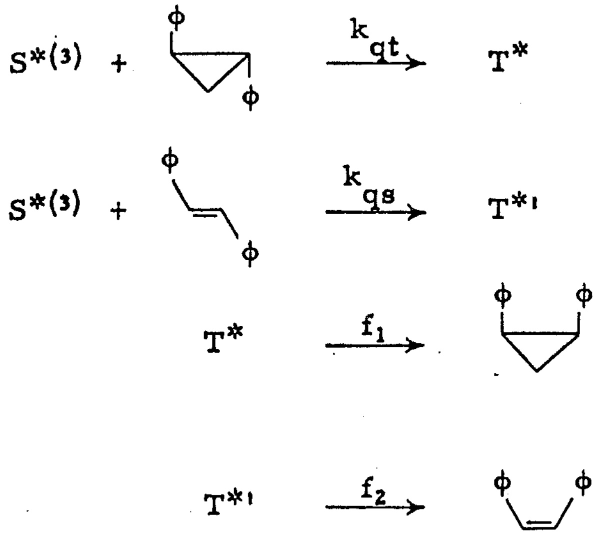
presence of diphenylcyclopropane. The exact details of this method can be found in the thesis of Dr. W. G. Herkstroeter (4).

Comparison of the triplet lifetimes measured by Dr. Herkstroeter and by the author shows that the method is reproducible to within at least ±50% when the same solvent purification methods (see the Experimental section) are used. Therefore, we have used Dr. Herkstroeter's triplet lifetimes in the Quenching Constants section of this thesis. The error of ±50% will not markedly affect the conclusions which are drawn from the data.

The fact that the lifetimes of the 2, 2'-binaphthyl and fluoranthene triplets are not changed by the addition of <u>trans</u>-1, 2-diphenylcyclopropane indicates the substrate is free from adventitious quenchers which have triplet energies of 56 kcal/mole or less. Furthermore the flash experiments with triphenylene and <u>trans</u>-1, 2-diphenylcyclopropane which was purified by the bromine treatment (see the Experimental section) indicate that all triphenylene triplets quenched lead to isomerization; therefore the substrate, as far as we can determine, is pure. This was shown by the fact that when a sensitizer triplet was quenched (measured by flash photolysis) it leads to a corresponding amount of product (the amount fixed by the decay ratio of the intermediate) as measured by the quantum yield. This was not true for the <u>cis</u> isomer, where the bromine treatment was omitted. This point will be discussed further in later sections.

Competition Experiments

A number of photosensitized isomerizations of trans-1, 2-diphenylcyclopropane were run in the presence of a small amount of trans-stilbene. The ratio of the amount of diphenylcyclopropane isomerized to the amount of stilbene isomerized allows us to calculate the relative quenching constants of the two substrates. The results of these measurements are shown in Table VI. The mechanistic steps which will be important are



where f_1 and f_2 represent the fraction of the excited states that decay to each of the products. The value of f_1 is determined by the ratio of products from the photosensitized decomposition of 3, 5-diphenyl-1-pyrazoline; the value of f_2 is simply the quantum yield for the isomerization of stilbene with high energy sensitizers (3). We can write

TABLE VI

Competition Experiments between trans-1, 2-Diphenylcyclopropane[(a)] and trans-Stilbene[(b)]

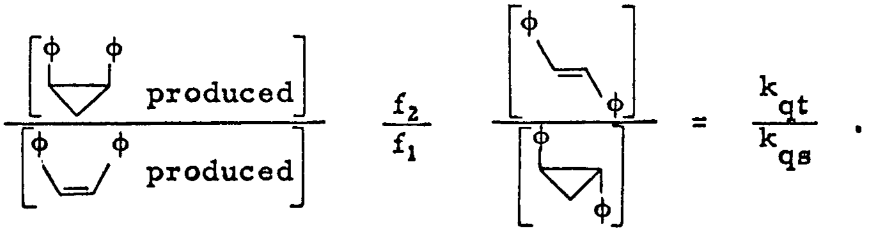
Sensitizer	Moles cyclopropane isomerized / Moles stilbene isomerized[(c)]	k_{qt}[(d)] $\frac{\text{liters}}{\text{mole sec}}$
Acetophenone	5.0	2.2×10^7
Propiophenone	1.8	8.0×10^6
Isobutyrophenone	2.5	1.1×10^7
p-Diacetyl benzene	1.2	5.6×10^6
Benzyl phenyl ketone	2.5	1.1×10^7

[(a)] 2.0 M.

[(b)] 8.0×10^{-4}.

[(c)] Corrected for blank and back reactions.

[(d)] Calculated on the basis of the quenching constant for trans-stilbene equals 7×10^9. The absolute error for these numbers is probably ±30%. The relative error is about ±15%, depending on the extent of conversion of the stilbene. See the Experimental section for explanation of the large error.



Dr. W. G. Herkstroeter (4) has shown that k_{qs} for a sensitizer of triplet energy larger than 70 kcal/mole = 7×10^9 and is independent of the sensitizer used. Since small amounts of quenching impurities do not affect the results, this method is inherently more accurate than any other for determining the quenching constants. Unfortunately, to achieve good precision with this method the rate constants for the two competing processes can differ by only 10^3 or less. In this case, this is only true when the alkyl phenyl ketones are used as sensitizers. Moreover, the accuracy of these experiments suffered from three other factors:

1. There was only time to do one set of runs with one mixture of trans-stilbene and trans-1,2-diphenylcyclopropane.

2. The trans-1,2-diphenylcyclopropane used contained about 0.024% cis-1,2-diphenylcyclopropane for which a correction had to be made.

3. The trans-stilbene could not be seen in the analysis (being buried under the trans-1,2-diphenylcyclopropane peak), so the back reaction correction for stilbene (which was large since the concentration of stilbene was so low) had to be made by comparison to an identical sample which was run to the photostationary state in stilbene (see the Experimental section for details). Thus the error in these

runs is probably between ±20 to 50%. Even so, these are the most inherently accurate values for the quenching constants because of the large uncertainty in the lifetime of the triplet with the other sensitizers.

Quenching Constants

Of particular interest are the quenching constants k_{qt} and k_{qc} in the mechanism on page 68. The values for these constants with variation of the sensitizer are needed to gain an insight into the mechanism of the energy transfer step. Tables VII and VIII give the values of k_{qt} and k_{qc}. These were determined in three different ways.

1) Flash Spectroscopy

The difference in the triplet lifetime of a sensitizer in the presence and absence of diphenylcyclopropane is a direct measurement of the quenching constant times the concentration of the quencher, provided that the quencher is pure. We have already shown in the section on Flash Spectroscopy that this is true for the trans isomer of diphenylcyclopropane. The precision in the measurement of a triplet lifetime by this method is probably ±10%. Two difficulties limit the scope of this method. The first is that the sensitizer being studied must have a lifetime greater than 10^{-4} if accurate results are to be obtained; thus most $n-\pi^*$ triplets cannot be used. The second difficulty is that if the quenching constant of a given sensitizer is less than 10^3 ℓ mole^{-1} sec^{-1} it is difficult or impossible to get a high

TABLE VII

Rate Constants (liters/mole sec) for the Reaction $S^{*(3)}$ + trans-1, 2-Diphenylcyclopropane → $S + T^{*(3)}$

Sensitizer	$E_t\left(\frac{kcal}{mole}\right)$	(a) Rate constant from single quantum yield	(a) Rate constant from variation of quantum yield with conc. of substrate (see page 116)	(a) Rate constant from flash spectroscopy	(a) Rate constant from competition with stilbene
Acetophenone	73.6	8.0×10^7 (d)	1.1×10^8 (Fig. V)	—	2.2×10^7
		8.0×10^7	3.1×10^8 (Fig. XII)	—	
		2.7×10^8			
		3.4×10^8			
p-Diacetyl benzene	67.7	7.3×10^7 (e)	—	—	5.6×10^6
		1.7×10^8			
Propiophenone	74.6	2.3×10^8 (e)	2.2×10^8 (Fig. XI)(e)	—	$8 \quad \times 10^6$
Isobutyrophenone	73.1	5.2×10^7 (e)	9.6×10^7 (Fig. IX)(e)	—	1.1×10^7
Cyclopropyl phenyl ketone	74.4	—	7.1×10^7 (Fig. X)(e)	—	—

Table VII (continued)

Sensitizer	$E_t\left(\frac{\text{kcal}}{\text{mole}}\right)$	(a) Rate constant from single quantum yield	(a) Rate constant from variation of quantum yield with conc. of substrate (see page 116)	(a) Rate constant from flash spectroscopy	(a) Rate constant from competition with stilbene
Benzyl phenyl ketone	72 (b)	1.1×10^{7}(e)	—	—	1.1×10^{7}
1-Naphthyl phenyl ketone	57.5	1.9×10^{2}	—	—	—
Fluorenone	53.3	4.3×10	—	—	—
2-Acetonaphthone	59.3	9	—	—	—
Benzil	53.7	1.7×10^{2}	—	—	—
p-Methyl benzophenone	68.5	$4.9\times10^{+3}$	7.0×10^{3}	—	—
		$7.2\times10^{+3}$		—	—
		$9.6\times10^{+3}$			
		$6.5\times10^{+3}$			
		$4.2\times10^{+3}$			
		$6.5\times10^{+3}$			
		$7.0\times10^{+3}$			

Table VII (continued

Sensitizer	$E_t\left(\frac{\text{kcal}}{\text{mole}}\right)$	(a) Rate constant from single quantum yield	(a) Rate constant from variation of quantum yield with conc. of substrate (see page 116)	(a) Rate constant from flash spectroscopy	(a) Rate constant from competition with stilbene
Triphenylene	66.6	7.1×10^{3}	3.1×10^{4}	6.5×10^{4}	—
		1.2×10^{4}		2.7×10^{4}	—
		8.0×10^{3}			
		4.6×10^{3}			
Naphthalene	60.9	1.0×10^{4}	$3.9\times10^{2\,(c)}$	—	—
		$9.4\times10^{2\,(c)}$			
1, 4-Di-t-butylnaphthalene	60 (est)	$2.0\times10^{3\,(f)}$	$1.7\times10^{2\,(c)}$	—	—
		$2.0\times10^{2\,(c)}$			
2, 6-Di-t-butylnaphthalene	60 (est)	$3.2\times10^{2\,(f)}$	—	—	—
1, 2, 3, 4, 7, 8, 9, 10-Octahydrol, 4, 7, 10-Octamethylnaphthacene	60 (est)	$2.3\times10^{2\,(c)}$	—	—	—
		$5.9\times10^{(c)}$			
Biphenyl	65.3	7.6×10^{2}	—	—	—

Table VII (continued)

Sensitizer	$E_t\left(\frac{\text{kcal}}{\text{mole}}\right)$	Rate constant from single quantum yield	(a) Rate constant from variation of quantum yield with conc. of substrate (see page 116)	(a) Rate constant from flash spectroscopy	(a) Rate constant from competition with stilbene
Chrysene	56.6	1.8×10	—	—	—
Fluoranthene	53.0	1.8×10	—	—	—
1, 2, 5, 6-Dibenzanthracene	52.3	2.1	—	—	—
1, 2-Benzanthracene	47.2	0.6			
Anthracene	42.7	$8^{(f)}$	—	—	—
9, 10-Dibromoanthracene	40.2	$5.8\times10^{2\,(f)}$	—	—	—

(a) For details of these methods see Experimental.

(b) Estimated by Mr. Donald Valentine.

(c) p-Methyl benzophenone present to absorb the light. These points were not used in Figure XVII.

Table VII (continued)

[d] Using the value of $k_d = 5.0 \times 10^6$ taken from the thesis of Dr. William M. Hardham and the author's value of $k_d = 5.0 \times 10^4$ for the benzophenone triplet.

[e] Based on the assumption that the lifetime of the sensitizer triplet is the same as that of the acetophenone triplet. For the other sensitizers values of the lifetime were taken from Table V of the thesis of Dr. W. G. Herkstroeter.

[f] The intersystem crossing ratio for these compounds has not been measured. They are estimated to be equal to that for naphthalene.

TABLE VIII

Rate Constants for the Reaction

$S^{*(3)}$ + cis-1,2-Diphenylcyclopropane → S + $T^{*(3)}$

Sensitizer	$E_t\left(\frac{\text{kcal}}{\text{mole}}\right)$	Rate constant from variation of quantum yield with conc. of substrate	Rate constant from flash spectroscopy
Triphenylene	66.6	3.0×10^3 (Fig. VIII)	9.0×10^3 (Table V)
Acetophenone	73.6	9.1×10^6 (Fig. VI)	

enough concentration of quencher to change the lifetime of the sensitizer triplet more than 10%. For these reasons this technique was only used with triphenylene as the sensitizer.

2) Competition Experiments

This method, which has been discussed fully in the section on Competition Experiments, is the most inherently accurate method. Some allowance for error will have to be made since there was only time for one set of runs, but it is unlikely that this exceeds 50%. Comparison of the values obtained by this method with those obtained from the quantum yields leads to a disagreement with the work of Dr. W. M. Hardham about the lifetime of the acetophenone triplet. This will be discussed later.

3) Quantum Yields

A value for the quenching constant can be found from a single determination of the quantum yield by the expression

$$\frac{1}{\phi_{t \rightarrow c}} = \frac{1}{a}\left(\frac{k_t + k_c}{k_c}\right)\left(1 + \frac{k_d}{k_{qt}[\underline{\text{trans}}]}\right)$$

if we assume that 1) $(k_t + k_c)/k_c$ is independent of the sensitizer and measured by the photosensitized decomposition of 3, 5-diphenyl-1-pyrazoline (we have shown that this is a good assumption in the Quantum Yield section) and that 2) the value of k_d can be taken directly from flash spectroscopic measurements. This second assumption will be the main cause of error in the quenching constants. However, we have shown in the section on Flash Spectroscopy that through careful solvent preparation techniques and identical degassing conditions our values of triplet lifetimes compare well to those found by Dr. Herkstroeter. The probable error in the quenching constants calculated by this method is estimated to be ±50%. The values for a (intersystem crossing ratio) were determined by Dr. A. A. Lamola.

The quenching constants can also be obtained from a Stern-Vollmer plot of ϕ^{-1} vs. (concentration of substrate)$^{-1}$ since the slope of the line divided by the intercept equals k_d/k_q. This is essentially the same method as the single quantum yield, and the same two assumptions are used. The only difference is that k_d/k_q now comes from a graphical average of the separately determined quantum yields.

The Choice of Points for Figure XVII

Figure XVII is a plot of k_{qt} vs. the triplet energy of the sensitizer used. Where there is a choice of values for k_{qt} determined by different methods, some of which are inherently more accurate than others, a simple average of the values is not the best choice. For that reason the values of k_{qt} with the alkyl phenyl ketones as sensitizers were taken from the competition experiments whenever possible. Two interesting points concerning the lifetimes of alkyl phenyl ketone triplets are brought to light through comparison of the quenching constants obtained from the quantum yields and those obtained from the competition experiments. Dr. W. M. Hardham found that the lifetime of the acetophenone triplet was 10^2 shorter than that of the benzophenone triplet (17). We have measured the benzophenone triplet lifetime

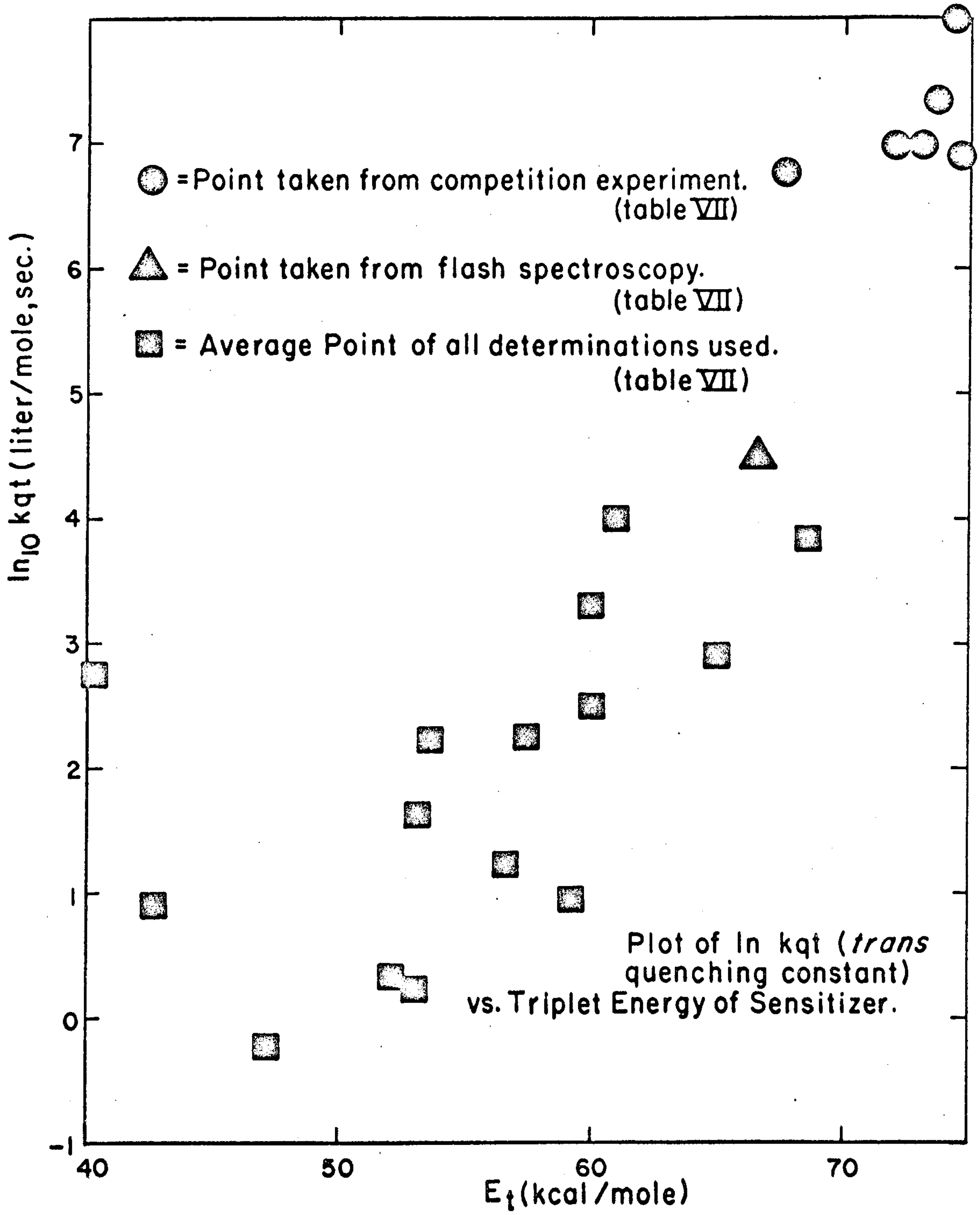

= Point taken from competition experiment. (table VII)
= Point taken from flash spectroscopy. (table VII)
= Average Point of all determinations used. (table VII)
Plot of ln kqt (*trans* quenching constant) vs. Triplet Energy of Sensitizer.
$\ln_{10} kqt$ (liter/mole, sec.)
7
6
5
4
3
2
1
0
-1
40
50
60
70
E_t(kcal/mole)

Figure XVII

and found that the decay constant equals 5.0×10^4. This would make the decay constant of the acetophenone triplet = 5×10^6. If the value of k_{qt} from the competition experiment with stilbene (using k_q for stilbene = 5.0×10^9 as Dr. Hardham did) is plugged into the expression

$$\frac{1}{\phi_{t \rightarrow c}} = \frac{1}{a} \left(\frac{k_c + k_t}{k_c} \right) \left(1 + \frac{k_d}{k_{qt} [\underline{trans}]} \right)$$

and the decay constant calculated, the value of k_d obtained is about 10^6. Thus our value for the lifetime of the acetophenone triplet, although smaller, is within the combined error limits of this work and Dr. Hardham's work. The acetophenone triplet may have a much shorter lifetime than the benzophenone triplet because of $\pi - \pi^*$ state mixing from the additional phenyl group in benzophenone.

The second fact involving triplet lifetimes is that the quenching constants as measured by the competition method are all nearly equal. The quantum yields with the alkyl phenyl ketones, on the other hand, show a wide variation. This means that the lifetimes of the different alkyl phenyl ketones investigated also vary widely. This variation is somewhat surprising. It cannot be attributed to impurities in the sensitizer since benzyl phenyl ketone, which is a solid and much easier to purify than the liquid ketones, has one of the lowest quantum yields.

The remaining points in Figure XVII with the exception of that for triphenylene, were taken from single quantum yield determinations and were averaged when more than one determination was made with a given sensitizer. With triphenylene, determinations of the quenching constant and quantum yield were made with samples of diphenylcyclopropane purified by different means. Since impurities in the diphenylcyclopropane will raise the value of k_{qt} from flash spectroscopic measurements and lower the value from quantum yield measurements, the two values of k_{qt} should converge when the substrate is pure. This was found to be the case for trans-1,2-diphenylcyclopropane but not for cis-1,2-diphenylcyclopropane, where the bromine treatment was omitted for the flash measurements (see Experimental for details). The convergent value for k_{qt} with triphenylene was used in Figure XVII.

Examination of Figure XVII indicates that there is a rough correlation between the $\ln\ k_{qt}$ and the triplet energy of the sensitizer. The scatter of the points along the line extends over two orders of magnitude, showing that other factors than the triplet energy of the sensitizer are of great importance in determining the rate of energy transfer.

The only point in Figure XVII which falls well off the line is that for 9,10-dibromoanthracene, which has an energy transfer rate much larger than expected for such a low energy sensitizer. This point is calculated on the basis of an estimated intersystem crossing ratio of 40%. If the intersystem crossing ratio is actually as high as 100%, the rate constant will still lie almost within the error square in Figure XVII. If the intersystem crossing ratio is very low, the rate constant will actually be much larger. This raises the intriguing possibility that the presence of the heavy bromine atoms facilitates triplet energy transfer. Heavy atom effects are known to facilitate spin forbidden electronic transitions (18).

Speculation on the Mechanism of the Energy Transfer Step

Mr. Ronald Cole has shown (19) that when an optically active sensitizer is used to effect the isomerization of trans-1, 2-diphenylcyclopropane one enantiomer is consumed faster than the other and that the unreacted starting material is optically active. This shows that there is steric repulsion when a sensitizer triplet is brought close enough to a molecule of diphenylcyclopropane to effect energy transfer. This quite straightforward kind of barrier to the reaction will not depend only on the energy of the triplet, but also on the shape and size of the sensitizer. Thus we would expect to find substantial differences in the quenching constants with different isoenergetic triplets. This is borne out by scatter in Figure XVII.

We would guess that the energy required to go from the ground state of 1, 2-diphenylcyclopropane to the triplet state diradical (T^* on page 68) with no nuclear motion and retention of the ground state geometry (that is, to a σ^* state) is more than the energy available from most, if not all, of the sensitizers used. This is because the two p orbitals on carbon atoms 1 and 2 which contain the unpaired electrons in the diradical will repel each other when brought into intimate contact. Since the carbon atoms 1 and 2 are close enough together in the ground state to give bonding overlap of their electronic orbitals, there should be a substantial amount of repulsion in the triplet diradical with ground state geometry. For this reason we feel that carbon atoms 1 and 2 must move apart during the energy transfer. In other words, the Franck-Condon principle is not obeyed.

The most economical explanation of our data and also the work of Mr. F. Guy Moses on the related nonvertical energy transfer to acetyl peroxide is based on two postulates.

1) All of the energy of the sensitizer is transferred during the reaction. That is, the sensitizer does not find itself in a high vibrational state after the transfer.

2) Although the Franck-Condon principle per se is not obeyed, a modified Franck-Condon principle will be obeyed, where the minimum amount of nuclear motion occurs during the electronic transfer.

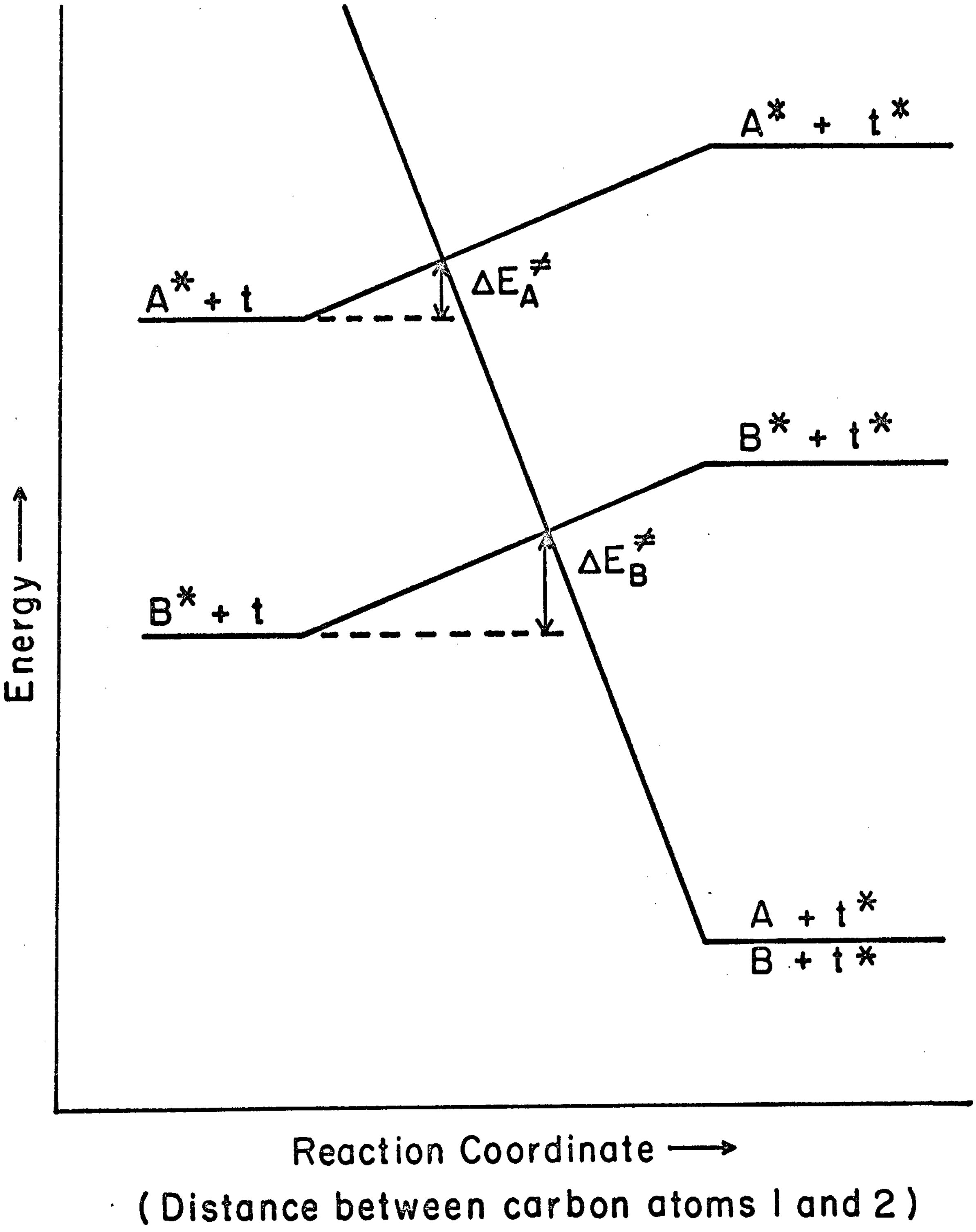
Both of the above postulates are good ones. Mr. F. Guy Moses has shown that in the photosensitized decomposition of acetyl peroxide the product ratio varies in a systematic way with the triplet energy of the sensitizer, with high energy sensitizers giving more of the primary decarboxylation products. This is interpreted to mean that all of the energy is transferred to the 0-0 bond, with minimum motion of the two oxygen atoms away from each other. The excess energy of the sensitizer is used to overcome the repulsion between the two unpaired oxygen radicals. Thus the higher energy sensitizers produce "hotter" acetyl radicals which give more of the primary decarboxylation products.

The same kind of a mechanism can be used for the energy transfer to diphenylcyclopropane. It can be most easily understood with the help of Figure XVIII. The reaction coordinate in this figure is simply the distance between the two phenyl bearing carbon atoms in the diphenylcyclopropane. As the energy transfer begins the cyclopropane bond begins to stretch. This costs something in energy, and this cost is depicted by the uphill line leading away from the starting materials in Figure XVIII. Eventually this line intersects the steep downhill line representing the potential curve of the dissociative σ^* state + the sensitizer ground state. These are the products of the reaction. The energy transfer thus occurs with minimum nuclear motion and with all of the available energy of the sensitizer being transferred.

It is clear from the geometry of Figure XVIII that the activation energy in this model for the reaction is proportional to the triplet energy of the sensitizer. Even if better potential functions are chosen for Figure XVIII this proportionality will still be approximately correct.

It should be pointed out that Figure XVIII is a potential energy diagram. The barrier to the reaction in this figure is an enthalpy of activation barrier. There will also be an entropy of activation, or probability factor in collision kinetics terms, depending on the sensitizer under consideration. This may be quite large and may vary greatly with different sensitizers, since some sensitizers may require very specific orientation of the reactants in order for the transfer to take place. This could be another reason for the roughness of the

Figure XVIII



correlation in Figure XVII. It is apparent that the variation of the rate of energy transfer with temperature must be studied to define the mechanism of the reaction more clearly.

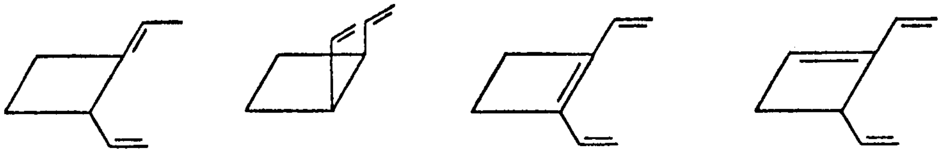
Although we favor the mechanism described above, we must admit that other possible mechanisms can be imagined. For example, the data in Figure XVII will also be satisfied by a mechanism where there is no normal energy of activation and the rate of the transfer is governed solely by a probability factor, with higher energy sensitizers having larger probability factors.

The Effect of the Electronic Structure of the Sensitizer Triplet on the Quenching Constant

It was felt that the electronic structure of the sensitizer triplet ($n-\pi^*$ or $\pi-\pi^*$) might make a difference in the size of the quenching constant. This was tested by measuring the relative quantum yields of the isomerization of trans-1, 2-diphenylcyclopropane with quinoline as the sensitizer in dry pentane and in methanol. In dry pentane the quinoline triplet is $n-\pi^*$; in methanol it is $\pi-\pi^*$ (20). The ratio of the quantum yield in methanol to the quantum yield in pentane was 20:1. Unfortunately, it was impossible to measure the lifetimes of these two kinds of quinoline triplets by flash spectroscopy; the absorption of the triplets was too weak to give accurate measurements. Thus the quenching constants cannot be calculated from the quantum yields. However, the fact that the quantum yield in pentane is smaller than that in methanol is in line with the known fact that $n-\pi^*$ triplets have shorter lifetimes than $\pi-\pi^*$ triplets. Apparently there is no large change in the quenching constant with different electronic structures in the sensitizer triplet.

The Photosensitized Isomerization of trans-1, 2-Divinylcyclobutane

The quantum yields for the isomerization of trans-1, 2-divinylcyclobutane with various sensitizers were measured in pentane. The only sensitizers which would effect reaction were acetophenone and benzophenone, having quantum yields for total production of products of 0. 5 and 2. 0 respectively. Both sensitizers produced some seven or more incompletely separated products on the v. p. c. in different ratios. Triphenylene, naphthalene, biphenyl, anthracene, 9, 10-dibromoanthracene and fluorenone would not effect measurable reaction. p-Diacetylbenzene gave a trace of one product. The experiment was capable of measuring a quantum yield as low as 10^{-2}. It is known that the C—H bonds in cyclobutane are more labile to free radical abstraction than those of cyclopropane (21). It is also known that benzophenone triplets are capable of abstracting hydrogen atoms from hydrocarbons such as toluene (22). It seems likely that this photosensitized reaction is proceeding through a mechanism involving hydrogen abstraction to give a radical species which can then reabstract hydrogen from the solvent or undergo further loss of hydrogen. Some of the products (none of the products has been identified, but all of them have similar molecular weights to the starting material as estimated by their v. p. c. elution times) might be



The question of why sensitizers such as triphenylene and naphthalene will not effect the isomerization of <u>trans</u>-1, 2-divinylcyclobutane by the same mechanism as that for <u>trans</u>-1, 2-diphenylcyclopropane cannot be answered without much more experimental data. The activation parameters for the thermal rearrangements of the two compounds are quite similar (see Part I of this thesis), showing that the combined strain and resonance effects on the formation of a thermal diradical are similar. If future experiments indicate that the decisive factor in the photosensitized rearrangement is the presence of the cyclopropane ring rather than the phenyl group, it may become necessary to postulate an intermediate in the rearrangement having the properties of an excited molecular state of the whole system including the cyclopropane ring.

EXPERIMENTAL

Materials

Substrates

trans-1,2-Diphenylcyclopropane was prepared as described in the Experimental section of Part I of this thesis. It was further purified for all the experiments except the early flash spectroscopic measurements and the photostationary state measurements by treatment with bromine in carbon tetrachloride for five minutes followed by distillation and three recrystallizations from 95% ethanol and water at -20°. A final distillation under vacuum with an apparatus which allowed no contact of the vapor or liquid with the stopcock grease removed all traces of solvent. The material was stored frozen in sealed degassed tubes until used.

cis-1,2-Diphenylcyclopropane was prepared as described in the Experimental section of Part I of this thesis. The bromine treatment was omitted. The main criterion of substrate purity was whether a 0.1 M solution of the substrate and a sensitizer of sufficiently low reactivity such that quenching of the sensitizer triplets by the substrate would be negligible would show the same triplet lifetime, measured by flash spectroscopy, as an identical solution without the substrate. As shown in the Flash Spectroscopy Section, this was true for the *trans* isomer but not for the *cis* isomer. V.p.c. analysis showed both materials to be 99.98% pure, with the only impurity being the other isomer of the substrate.

trans-1, 2-Divinylcyclobutane was prepared by photosensitized dimerization of butadiene. This method has been described in detail elsewhere (2). It was purified by preparative gas chromatography at room temperature on a freshly made six foot column of 20% diethylene glycol succinate (DEGS) which had been baked out at 200° for three days with a fast stream of helium before use. Its absorption spectrum showed only end absorption starting at 2300 Å. A 0. 1 M solution of the substrate did not change the lifetime of the triphenylene triplet in flash spectroscopy measurements.

Sensitizers

Acetophenone (Matheson, Coleman and Bell, Reagent Grade) was recrystallized once from 95% ethanol and water, twice from freshly distilled pentane which had been treated with H_2SO_4 until the acid layer was colorless, dried under high vacuum until it had melted at room temperature and distilled at one torr through a still which allowed no contact of either vapor or liquid with the stopcock grease. It was stored frozen under nitrogen until used.

Naphthalene was obtained pure from Dr. W. G. Herkstroeter. It had been purified by zone melting.

1, 4-Di-*t*-butylnaphthalene was obtained pure from Mr. Ronald Cole. It had been recrystallized twice from heptane.

2, 6-Di-*t*-butylnaphthalene was obtained pure from Mr. Ronald Cole. It was sublimed at 80° and 0. 1 torr before use.

1,2,3,4,7,8,9,10-Octahydro-1,4,7,10-octamethylnaphthacene was obtained pure from Mr. Ronald Cole. It had been recrystallized twice from heptane.

p-Diacetylbenzene (Eastman Kodak, Reagent Grade) was sublimed under high vacuum before use.

Propiophenone was obtained pure from Dr. Donald Valentine.

Isobutyrophenone was obtained pure from Dr. Donald Valentine.

Cyclopropyl phenyl ketone was obtained pure from Dr. Donald Valentine.

2,4,6-Trimethylacetophenone (Matheson, Coleman and Bell) was distilled under reduced pressure.

Benzyl phenyl ketone (Matheson, Coleman and Bell, Reagent Grade) was recrystallized once from ethanol and water, twice from petroleum ether that had been passed through an alumina column and dried under high vacuum.

4-Acetylbiphenyl was obtained pure from Dr. Jack Saltiel and sublimed under high vacuum before use.

2-Acetylfluorene (Matheson, Coleman and Bell, Reagent Grade) was sublimed under high vacuum before use.

m-Nitroacetophenone (Aldrich, Reagent Grade) was purified by zone melting.

Benzaldehyde (Matheson, Coleman and Bell, Reagent Grade) was distilled under reduced pressure before use.

Triphenylene (Aldrich, Reagent Grade) was purified by zone melting.

2, 2'-Binaphthyl was commercially zone refined by James Hinton, Ph. D.

Triphenylmethyl phenyl ketone was obtained pure from Dr. A. A. Lamola. It had been recrystallized twice from petroleum ether.

Biphenyl was obtained pure from Dr. A. A. Lamola. It had been recrystallized twice from petroleum ether.

1-Naphthyl phenyl ketone was obtained pure from Dr. Albert Fry. It had been recrystallized twice from heptane.

Michler's ketone (4, 4'-bis-dimethylaminobenzophenone) was obtained pure from Dr. A. A. Lamola. It had been recrystallized twice from methanol.

Fluorenone was obtained pure from Dr. W. G. Herkstroeter. It had been purified by recrystallization followed by zone melting.

Carbazole was obtained pure from Dr. W. G. Herkstroeter.

Benzil was obtained pure from Dr. W. G. Herkstroeter. It had been purified by zone melting.

Fluoranthene was commercially zone refined by James Hinton, Ph. D.

1, 2, 5, 6-Dibenzanthracene was obtained pure from Dr. W. G. Herkstroeter.

1, 2-Benzanthracene was obtained pure from Dr. W. G. Herkstroeter.

2-Acetonaphthone was obtained pure from Dr. W. G. Herkstroeter. It had been purified by zone melting.

Chrysene was obtained pure from Dr. W. G. Herkstroeter.

Pyrene was obtained pure from Dr. R. S. H. Liu. It had been recrystallized twice from petroleum ether.

Acridine was obtained pure from Dr. W. G. Herkstroeter.

Anthracene (Eastman Kodak, Fluorescent Grade) was used without further purification.

9, 10-Dibromoanthracene was obtained pure from Dr. Donald Valentine. It had been recrystallized three times from carbon tetrachloride and sublimed under high vacuum.

Bromobenzene (Matheson, Coleman and Bell) was stirred with H_2SO_4 for three weeks, with fresh acid added each week. It was then distilled from P_2O_5 under reduced pressure.

p-Methylbenzophenone (Aldrich, Reagent Grade) was recrystallized twice from ethanol and water and twice from distilled petroleum ether. It was dried under high vacuum.

3-Acetylpyrene was obtained pure from Dr. W. G. Herkstroeter.

Benzanthrone was obtained pure from Dr. A. A. Lamola.

Quinoline (Eastman Kodak, Synthetic) was distilled at atmospheric pressure from zinc dust and then distilled under high vacuum.

Solvents

Benzene (Matheson, Coleman and Bell, Analytical Reagent) was stirred three times with H_2SO_4 for two days and then distilled from P_2O_5.

Pentane (Practical Grade) was treated three times with fuming sulfuric acid, neutralized with sodium bicarbonate in water and distilled from P_2O_5.

Vapor Phase Chromatography Equipment

All v. p. c. measurements were made with a Loenco Model 70 dual flame gas chromatograph with independently heated column oven, detector oven and injector block. The helium flow rate was always 60 ml/min. The columns used for all analyses were hand packed in six foot lengths of $\frac{1}{4}$ inch aluminum tubing. The packing material consisted of two feet of 10% diethylene glycol succinate (at the injector end), two feet of 10% Dow Corning Hi-Vac silicone grease and two feet of 10% silicone gum rubber, all on Chromasorb W. The column oven temperature was 185° for all analyses except those for the competition experiments and the actinometry, where the temperature was 150°. The detector oven was at 190° for all analyses.

For the analyses of the products formed in experiments with trans-1, 2-divinylcyclobutane six foot columns of 10% Carbowax 20 M on Chromasorb P were used at a temperature of 50°. The detector temperature was 100°.

3, 5-Diphenyl-1-pyrazoline Experiments

Materials

3, 5-Diphenyl-1-pyrazoline. — The method of Overberger and Anselme (12) was used to prepare 3, 5-diphenyl-1-pyrazoline. Benzaldehyde (106 g) was slowly added with stirring to 66 g of 97% hydrazine in 60 ml of anhydrous ether. The bottom layer was discarded. Yellow mercuric oxide (300 g) was added in small quantities with stirring. The mixture was stirred three hours and then filtered through anhydrous sodium sulfate. Styrene (35 g) in 90 ml of ether was then dripped slowly into the ether solution with stirring. The mixture was allowed to sit overnight. The volume of the solution was reduced to 100 ml on a rotary flash evaporator with a water asperator. The solution was cooled and the crystals filtered and washed with cold ether. Yield: 10 g. The yield was low because of poor stirring of the solution when the mercuric oxide was added. The material was recrystallized from methanol, dried under vacuum and stored in a sealed bottle in a dark freezer. The material was shining white plates which melted with decomposition at around 100° depending on the rate at which the melting block was heated. The n. m. r. spectrum of the material indicated it was the pure trans isomer.

Solvents. — The solvent for all these experiments was Eastman Kodak Spectro Grade benzene used without purification.

Preparation of Samples. — The solutions of 3, 5-diphenyl-1-pyrazoline in benzene (all 0. 05 M) were degassed in two different ways:

a) The samples for refluxing and direct irradiation were degassed by bubbling a stream of Matheson prepurified dry nitrogen through them for one hour.

b) The 0.25 ml samples for photosensitized decomposition were placed in 8 mm tubes 3 inches long, degassed by three freeze thaw cycles at 10^{-4} torr and sealed. The samples for photosensitized decomposition contained enough sensitizer to give an absorbance of two at 3660 Å. There was no particular attempt to get better than ±50% accuracy in the amount of sensitizer or the volume of solution used, since only the product ratio was of interest.

Decomposition and Analysis

Thermal Decompositions. — For the sample refluxed in benzene, 5 ml of the stock solution (0.05 M) was contained in a 25 ml flask equipped with a 6 inch water cooled condenser closed with a Tygon tube leading to an inverted water filled cylinder. This was immersed in a 90°C oil bath until gas evolution ceased (one hour). The solution was then analyzed by v.p.c. with a 6 foot, $\frac{1}{4}$ inch aluminum column packed with 10% Ucon Polar oil on Chromasorb P. For thermal decompositions in the v.p.c. the column was maintained at 185°C and the injector temperature was varied. One microliter samples of the stock solution were injected. The products *cis*- and *trans*-1,2-diphenylcyclopropane were stable under these conditions except when the inlet temperature was at 315° when about 2% isomerization of *trans*- to *cis*-1,2-diphenylcyclopropane was observed.

Direct Irradiation. — The same equipment was used for the direct irradiation that was used for the decomposition in refluxing benzene, except that the flask was immersed in a 31°C water bath and irradiated with a 450 watt Hanovia mercury arc lamp in a water cooled Pyrex well until gas evolution ceased.

Photosensitized Decomposition. — Three duplicate tubes were made for each sensitizer. These were irradiated for periods of time ranging from one to four days on the merry-go-round with the 3660 Å filters described in the Quantum Yield part of the Experimental section. After irradiation 2.0 microliters of solution were injected into the v.p.c. and both the total area and ratio of areas of the diphenylcyclopropane isomers were measured. The solution was then shaken with 50% conc. HCl in water to convert the remaining 3,5-diphenyl-1-pyrazoline to the tautomeric 3,5-diphenyl-2-pyrazoline. This tautomer will not decompose under the conditions of the v.p.c. analysis, and thus does not interfere. Two microliters of the solution were then analyzed again. If the total area and the ratio of the isomers remained unchanged, the reaction had gone to completion. Material balance for the reaction was checked by running 2.0 µl of a stock solution of trans-1,2-diphenylcyclopropane through the v.p.c. under the same conditions. The sensitizers which are labeled "no reaction" in Table II were irradiated four days, the maximum time needed to achieve complete reaction with the higher energy sensitizers.

Photostationary State Experiments. — Stock solutions of various mixtures of cis- and trans-1,2-diphenylcyclopropane were weighed out to give a total solution concentration of 0.1 ± 0.02 M in diphenylcyclopropanes. An appropriate amount of sensitizer was weighed out in a 1 ml volumetric flask and the appropriate stock solution added. These solutions were then placed in 4 mm tubes 3 inches long, degassed by three freeze thaw cycles at 10^{-3} torr and sealed. The tubes were placed around a 450 watt medium pressure Hanovia mercury arc lamp in a 31° water bath and irradiated 24 hours. Both the stock solutions and the irradiated tubes were analyzed by v.p.c.

Quantum Yield Experiments. — All materials were prepared as described above except the substrate for the acetophenone sensitized isomerization of *cis*-1,2-diphenylcyclopropane. This was further purified by treatment with bromine in carbon tetrachloride followed by high vacuum distillation and three recrystallizations from distilled ethanol and water. The material was then dried under high vacuum for 4 hours.

All glassware except the sample tubes was cleaned with alcoholic KOH, rinsed with distilled water followed by reagent grade absolute methanol, dried 4 hours or more in a 120° oven and flushed with pure dry nitrogen while still hot from the oven. The sample tubes for the quantum yields consisted of either 13 × 125 mm Pyrex culture tubes attached with a constriction to a grease trap to prevent stopcock grease from flowing down into the tube during the degassing procedure and opening with a 14-20 standard taper ground glass female joint, or a similar tube with a bottom of 13 mm quartz tubing attached to the upper Pyrex by a graded seal. The tubes were made from new glass and were clean as they came from the glass blower's annealing oven.

An appropriate amount of each sensitizer was weighed into a 5 or 10 ml volumetric flask. This was either filled to the mark with a stock solution of the substrate in benzene or the appropriate amount of substrate was weighed into the volumetric and then pure benzene was added. The substrate (trans-1, 2-diphenylcyclopropane) was all from one purification batch which was stored frozen in several sealed degassed tubes until just before use. Enough sensitizer was used in all cases to give an absorbance between one and five at the wavelength used. Aliquots of 3.22 ml were then measured into the sample tubes with a spring loaded syringe. The tubes were then degassed by freeze thaw cycles with liquid nitrogen as the coolant. Two cycles were done at 10^{-4} torr with the forepump followed by three cycles at better than 10^{-6} torr with the oil diffusion pump. This procedure is identical with the degassing procedure used by the author and Dr. W. G. Herkstroeter for flash spectroscopic measurements. The tubes were then sealed while frozen with the vacuum stopcock open at a pressure of better than 10^{-6} torr. The sealed tubes were stored frozen in the dark until used.

Two kinds of apparatus were used for the irradiations. The first of these is the optical bench. It is described in detail elsewhere (23). Briefly, the light from a Westinghouse (SAH-800c) 800 watt medium pressure mercury arc lamp is collimated with mirrors and the beam passed down the bench. The two sample tubes are held in the beam by a Beckman D. U. cell holder. The filters (described below) are placed between the lamp and the samples. The samples and filters are cooled by an air blower. With the filters in place the temperature of the samples reaches a steady state of 31 ± 3°. The second apparatus is the "merry-go-round" designed by Mr. F. G. Moses. This consisted of a turntable which revolves around the light source (Hanovia L679A 450 watt medium pressure mercury arc lamp) contained in a quartz cooling well at the center of the turntable. Four sets of glass filters can be placed in a holder around the quartz well. The turntable has room for 30 sample tubes all in equivalent positions. The windows through which the light passes to reach the samples were machined to have less than 0.5% variation in their areas. Various filter combinations were used. Below is the code for the filters shown in Table IV.

<u>3660 F</u>

This was a combination of Corning C. S. 7-37 and 0-52 glass filters used in the "merry-go-round" for 3660 Å light. The transmission characteristics of this filter combination can be found elsewhere (11).

<u>3130 IF</u>

This was a Baird Atomics interference filter (used with the "merry-go-round") centered at 3000 Å with a transmittance of 10% at 3000 Å, 0% a5 2850 Å, 3% at 3130 Å and 0% at 3300 Å.

<u>3130 OB</u>

This was a filter train used with the optical bench consisting of a Corning C. S. 7-54 glass filter, 2.5 cm of 0.5 M $NiCl_2$ in water, 2.0 cm of .0005 M K_2CrO_7 in water and 2.0 cm of .005 M potassium biphthalate in water with quartz solution holders in all cases. The transmission characteristics of this filter combination can be found elsewhere (11).

3130 SF

This consisted of an inner solution (nearest to the lamp) of 1 cm of 14 g of cobaltous sulfate and 46 g of nickelous sulfate in 100 ml of water and an outer solution of 0.5 cm of 0.015 M potassium biphthalate in water. The solution holder was of quartz and was used with the "merry-go-round." Its transmission characteristics were nearly identical with those of the 3130 OB filter train.

3000 SF

This was a filter solution of 2 cm of .005 M potassium biphthalate in water in a Pyrex holder, used with the "merry-go-round." It passed light of any wavelength longer than 3000 Å. This filter was used with only one run with triphenylene as sensitizer. The actinometric solution for this run had exactly the same concentration of triphenylene so the light absorbed should have been the same in both the sample solution and the actinometer solution. From the large deviation of the value of the quantum yield obtained in this way, it was concluded that this method is unsatisfactory.

The sample tubes were irradiated for different lengths of time, but the conversions were always kept below 1% except in the cases of triphenylene and the alkyl phenyl ketones. There the conversions were as high as 5%. Even at 5% conversion the back reaction correction was negligible compared to the errors involved. A back reaction correction (11) was made for one sample which went to 20% conversion.

Actinometry

Materials. — 1,3-Cyclohexadiene (Aldrich Chemical Company) was degassed and sealed into a bulb-to-bulb distillation apparatus with several take off bulbs. The cyclohexadiene was distilled into the take off bulbs, sealed off and removed from the system. These bulbs were then stored in a dark freezer until used.

Hexadecane was purified by high vacuum distillation by Mr. George Vesley. V.p.c. analysis showed it was pure.

Preparation of Actinometry Samples. — All glassware was prepared as described in the Quantum Yield Experiments part of the Experimental section. Identical tubes were used for the actinometer solutions and the sample solutions. In a typical preparation of the actinometer solution 0.4402 g of hexadecane were weighed directly into a 100 ml volumetric flask. Then about 1 g of benzophenone and 2 g of 1,3-cyclohexadiene were added. The volumetric was filled to the mark with benzene, stoppered and sealed with Teflon tape and stored frozen in a dark freezer until used. Identical aliquots of 3.22 ml of the actinometer solution were measured into the reaction tubes with a spring loaded syringe. The same setting on the syringe was used for the actinometer solutions and the sample solutions. The accuracy of this spring loaded syringe was one part in one thousand, measured by weighing samples of water. The tubes were then placed on rubber, one-holed stoppers attached to a high vacuum pump, frozen in liquid nitrogen and degassed by three freeze thaw cycles. They were then sealed at the constriction with the solution frozen and the stopcock open to the vacuum at a pressure of 10^{-3} torr or better. The sealed tubes were stored frozen in the dark until use.

Actinometry Irradiation Procedures. — In all the irradiation systems described under Quantum Yield Experiments except the optical bench two or three actinometer tubes were run at all times the sample tubes were run. When a run lasted 24 hours, three sets of actinometer tubes were run 8 hours each. Thus all variation of the light intensity was measured. With the optical bench the sample tube and its corresponding actinometer tube were interchanged every 4 hours during the 30 hour run. The actinometers were never irradiated to dimerize more than 40% of the cyclohexadiene. Mr. George Vesley has shown that under these conditions the quantum yield for the reaction is independent of the amount of conversion and equal to 0.90 ± 0.02.

Actinometry Analytical Procedures. — The v.p.c. columns described above were used at a temperature of 150°. The conversion factor N for the expression

$$\frac{\text{moles} \quad \text{dimers}}{\text{moles hexadecane}} = N \; \frac{\text{area dimers}}{\text{area hexadecane}}$$

was determined by analysing a known mixture of hexadecane and 1,3-cyclohexadiene dimers prepared by the photosensitized dimerization of cyclohexadiene and purified by Dr. Donald Valentine. This conversion factor was within 2% of the ratio of the number of carbon atoms in the two substances, as would be expected with a flame detector. Under these v. p. c. conditions the dimers are incompletely separated and their areas were integrated together. The integrations were done either by an automatic disk integrator or by cutting out the peaks and weighing them.

Flash Spectroscopic Experiments. — For the first flash spectroscopic measurement listed in Table V of the quenching constant with triphenylene, the bromine treatment of *trans*-1, 2-diphenylcyclopropane was omitted. For the remaining measurements the materials were purified as described under Substrates.

All glassware was cleaned as described under Quantum Yield Experiments except the flash cells. These were rinsed carefully with methanol after use and brought to the glass blower for reconstruction. They were clean when received from the glass blower's annealing oven.

Stock sensitizer solutions were made a concentration of 10^{-3} M in 50 ml volumetric flasks. The appropriate amount of diphenylcyclopropane was weighed out into a 25 ml volumetric and filled to the mark with benzene. The substrate solutions and the blank solutions (identical 25 ml volumetrics containing only benzene) were poured through a 30 ml syringe used as a funnel into the flash cells. Then 1. 5 ml of the stock sensitizer solution was added through the 30 ml syringe and washed down with 1. 5 ml of benzene to give a total volume of 28 ml per flash cell. The flash cells were then degassed as described under

Quantum Yield Experiments and sealed. The exact details of the design of the flash cells and the procedures and equipment for taking and analysing the flash pictures can be found elsewhere (4). Briefly, the flash cell is a cylinder of glass 15 mm in diameter and about 1 foot long. It is placed in an enclosure with two 1 foot tubes containing zenon parallel to it. A one microfarad capacitor charged to about 18, 000 volts is discharged through the zenon tubes, producing an intense flash of light lasting for a few microseconds, which populates the triplet state of the sensitizer. A steady monitoring beam of light passing down the flash cell, through a monochromator and onto a phototube records the absorption of the sensitizer molecules in the triplet state. The decay of this absorption is read out on an oscilloscope and a slide picture of the oscilloscope trace is taken. This is projected onto a large piece of paper and traced with a pencil with graphical averaging being done by eye. The data from this paper are fed to the computer which breaks the curve of the trace down into first and second order exponential decay constants. The first order decay constant is taken as the triplet lifetime.

Competition Experiments. — The *trans*-stilbene used in these experiments was commercially zone refined by James Hinton, Ph. D.

trans-Stilbene (8.0×10^{-4} M) and *trans*-1, 2-diphenylcyclopropane (2.0 M) were weighed into a 5 ml volumetric flask which was filled to the mark with benzene. Enough sensitizer to absorb at least 90% of the light at 3660 Å was weighed out into a 4 mm Pyrex tube 3 inches long. Then 0.25 ml of the solution of stilbene and diphenylcyclopropane was added. The tubes were degassed by three freeze thaw cycles at 10^{-3} torr and sealed. The tubes were stored frozen in the dark until use.

The tubes were irradiated for 5 minutes with the 3660 F filter system in the "merry-go-round." A duplicate tube with each sensitizer was irradiated for 1 hour to establish the photostationary state for the stilbene isomers. Ten microliters of both tubes were analyzed on the v.p.c. and the absolute area of the 5 minutes was compared to the area of the 1 hour tube. The difference between these (about 50%) allowed us to calculate the back reaction correction for the stilbene isomerization. The blank reaction correction for the cis-diphenylcyclopropane impurity was determined by analysis of ten microliters of the starting solution under the same v.p.c. conditions.

trans-1,2-Divinylcyclobutane Quantum Yields. — trans-1,2-Divinylcyclobutane was purified as described under Substrates. The preparation of samples and irradiation procedures were identical to those described under Quantum Yields, and the actinometry was the same. The solvent was pentane. The analysis is described under Vapor Phase Chromatography Equipment.

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PROPOSITIONS

or

ASTOUNDING TALES OF FANTASY AND SCIENCE FICTION

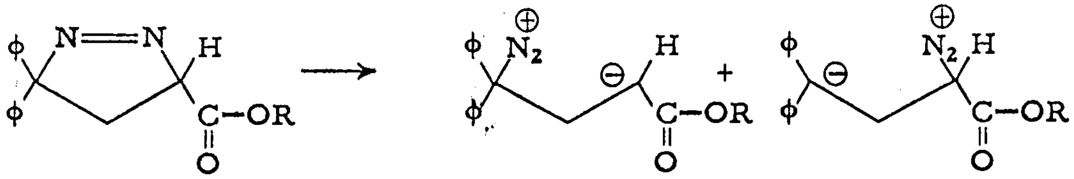
PROPOSITION I

Decomposition experiments with appropriate substituted optically active 3, 5-diphenyl-1-pyrazoline are proposed in order to 1) elucidate the mechanism of pyrazoline decompositions and 2) to provide information about the relative rates of ring closure in zwitter ions and diradicals.

* * * * * * * *

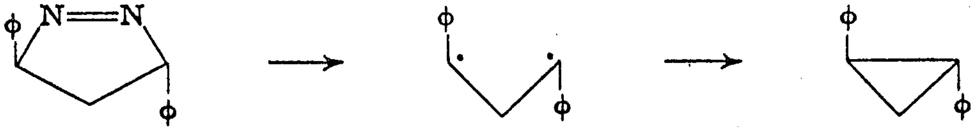
A considerable amount of work has been done on both the thermal and photochemical decompositions of 3, 5-substituted-1-pyrazolines (1, 2, 3). Unfortunately, the mechanism or mechanisms of the decomposition are still not well understood. Some workers in this field have claimed that the thermal decomposition of 1-pyrazolines to the corresponding cyclopropanes is a non-stereospecific process, while others (working with the same pyrazolines) have claimed it is a stereospecific one. The photochemical decomposition has been found to be essentially stereospecific in the two examples referenced (1, 2), while the author found a non-stereospecific reaction when he repeated the work of reference 1 (this thesis). Thus the mechanisms proposed for the reaction, mostly on the basis of the products of the reaction, cannot be trusted.

Walborsky and Pitt (3) have postulated, on the basis of the stereochemistry of the products, that I decomposes thermally by way of an ionic intermediate, II or III, with III being favored.



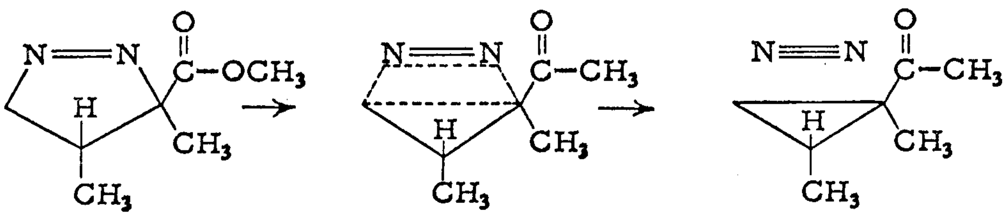
I II III

Overberger (1), on the other hand, postulated that IV decomposes thermally as well as photochemically by way of a diradical intermediate, V, on the basis of the stereospecificity of the reaction and because radical e.s.r. signals were seen in the low temperature photolysis of IV.



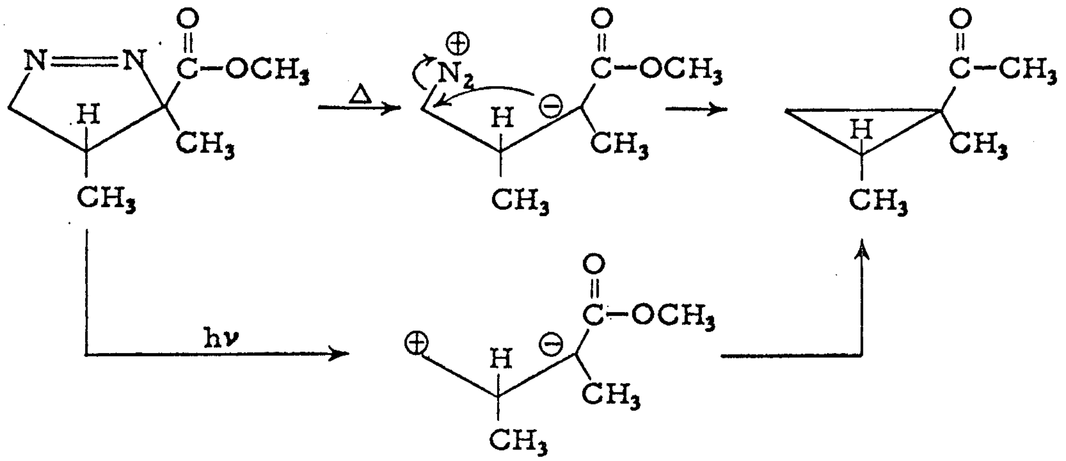
IV V

Still another photochemical mechanism has been postulated by van Auken and Rinehart (2) for the decomposition of VI. They found more stereospecificity in the photochemical decomposition of VI than in the thermal decomposition, implying (to them) a concerted transition state, VII.



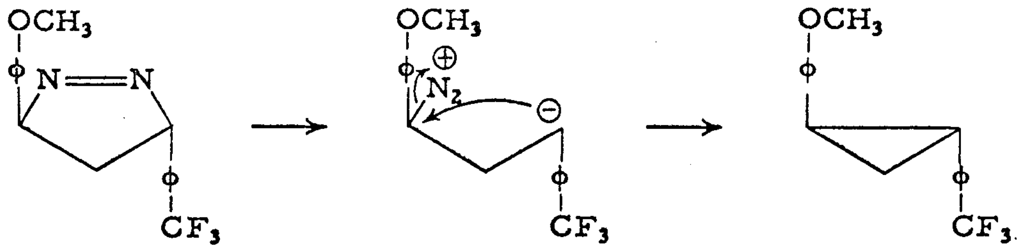
VI

A more likely explanation of their data is that the photochemical decomposition gives a zwitter ion intermediate in which the nitrogen has already departed, thus accounting for the more rapid ring closure than in the thermal decomposition, where the carbanion may have to displace the nitrogen during the ring closure, thus possibly giving more time for internal rotation before ring closure.

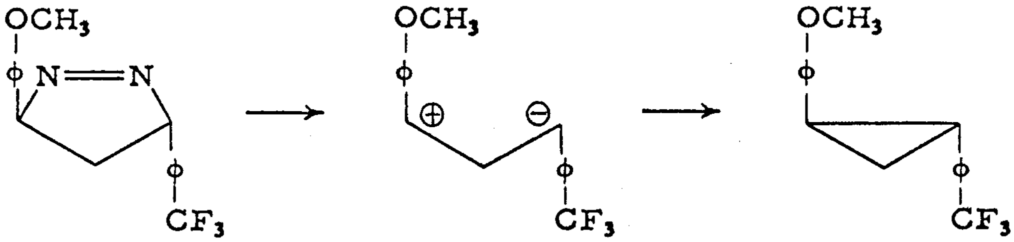


We propose to study the solution decomposition of optically active *trans*-3-(*p*-trifluoromethylphenyl)-5-(*p*-methoxyphenyl)-1-pyrazoline thermally, with direct irradiation and with photosensitized irradiation. The following mechanisms of decomposition are predicted.

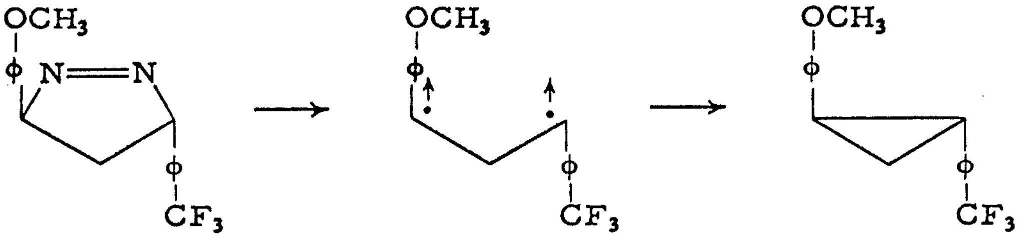
Thermal



Direct Irradiation



Photosensitized Irradiation



The ratio of optically active cyclopropane produced to racemic products will give the ratio of ring closure to internal rotation (if there is only one optically active center in the molecule). It is unlikely that the rate of internal rotation will change much with the three intermediates shown above. Thus we predict that the ratio will be largest for direct irradiation, smaller for thermal decomposition and smallest for the photosensitized decomposition.

We can further predict the ratio should become smaller with increasing solvent polarity if the intermediate species is a zwitter ion, since solvation will probably affect the rate of ring closure more than the rate of internal rotation. The effect of different solvents on the diradical intermediate will probably be negligible.

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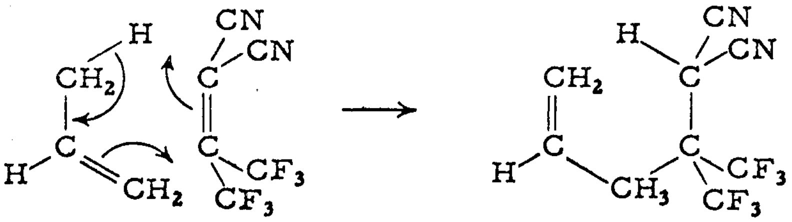
PROPOSITION II

It is proposed that 1, 1-di(trifluoromethyl)-2, 2-dicyanoethylene may prove to be a reactive enough dipolariphile to provide a general method of:

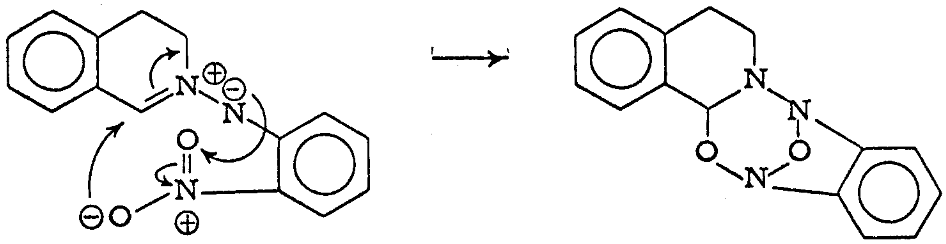
1. Production of dihydro 1, 3, 2-dioxazoles.
2. Reduction of organic acids to aldehydes.
3. Two carbon chain insertions into amides.

* * * * * * * *

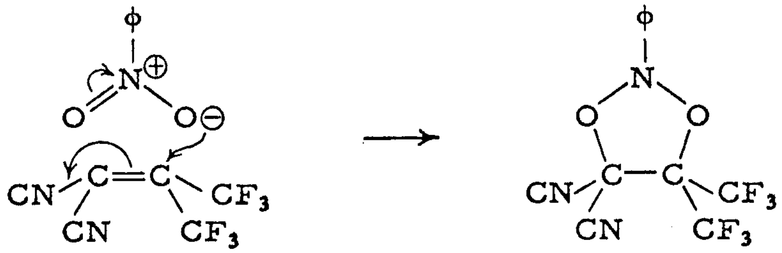
Dipolar additions to olefins generally proceed more readily when the olefin is polarized. Thus, for example, $(CH_3)_2S{=}CH_2$ will add to 1, 1-diphenylethylene but not to stilbene (1). Additional reactivity can be expected if the olefin is electron poor. 1, 1-Di(trifluoromethyl)-2, 2-dicyanoethylene (I) is a newly discovered olefin with both high polarizability and a low electron density (2). It is extremely reactive. It is nearly as reactive in Diels-Alder reactions as TCNE, it undergoes cycloadditions to olefins to form four-membered rings with great ease and it will add to olefins such as propylene as shown below.



We propose that (I) will be reactive enough to undergo addition reactions with very weak 1, 3-dipoles such as the nitro group and the carboxylate group. It is known that the nitro group can act as a 1, 3-dipole with strong acceptors. Grashey found the following reaction (3).

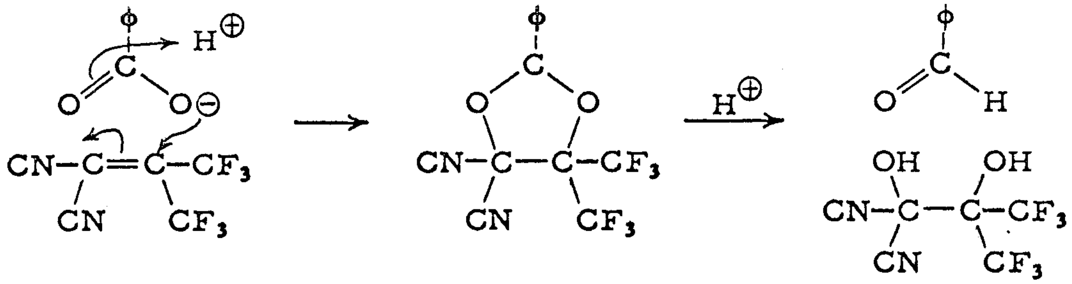


It may be possible to produce substituted dihydro 1, 3, 2-dioxazoles by the reaction of (I) with nitrobenzene or even nitromethane.

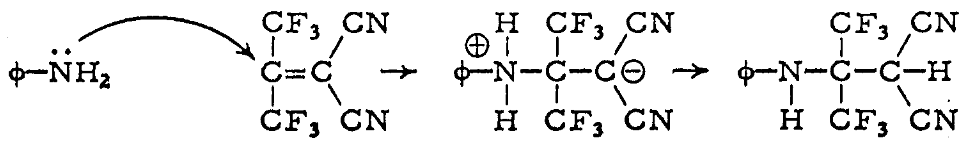


These interesting compounds would be well worth having, since their chemistry is little known. Their thermal decomposition would probably provide many hours of fascinating experiments.

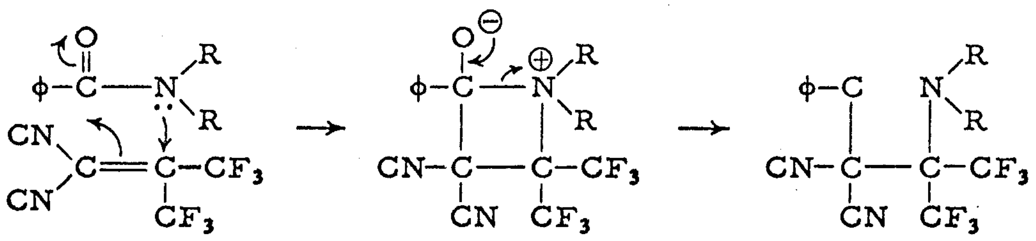
With the even weaker 1, 3-dipole, $-CO_2^{\ominus}$, one might be able to accomplish the following general reduction of acids to aldehydes.



(I) is also very reactive toward nucleophiles. An adduct is very readily formed with aniline.



This implies that the following chain expansion of amides might be possible.



Although there is little precedence for these reactions, the unusual nature of (I) might make them possible.

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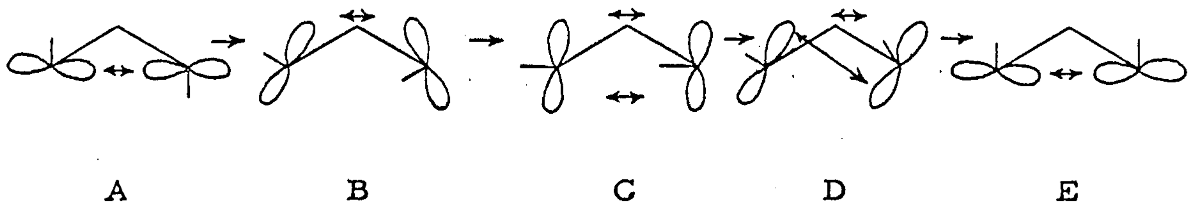
PROPOSITION III

The absence of cyclopentene products in the thermal isomerization of <u>trans</u>-1, 2-divinylcyclopropane and <u>trans</u>-1-vinyl-2-phenylcyclopropane implies that the intermediate in the rearrangement is a "virtual" diradical, in which there is some bonding at all times between the initial radical centers. It is proposed that generation of the diradical intermediate in the triplet state will lead to 4-substituted cyclopentenes as the major products.

* * * * * * * *

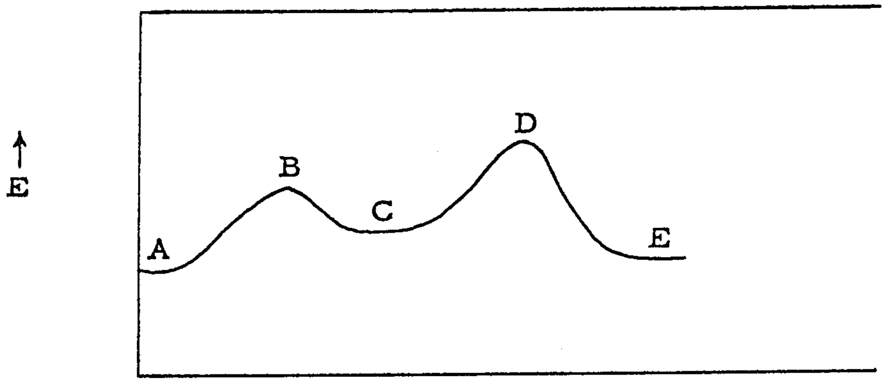
The thermal isomerization of <u>trans</u>-1, 2-divinylcyclopropane gives no 4-vinylcyclopentene (1). The only product is 1, 4-cycloheptadiene, presumably arising from a concerted rearrangement of the transiently formed <u>cis</u>-1, 2-divinylcyclopropane. Furthermore, the thermal isomerization of 1-vinyl-2-phenylcyclopropane gives no 4-phenylcyclopentene (2). On the other hand, <u>trans</u>-1, 2-divinylcyclobutane gives 4-vinylcyclohexene as the major product when heated (3). All three of these rearrangements are presumed to go through a diradical intermediate. Clearly this can be a "true" diradical, that is, one where there is no bonding between the radical centers, only in the case of divinylcyclobutane. From present ways of thinking it seems very likely that a "true" diradical derived from divinylcyclopropane would prefer to close to a five-membered ring rather than to either a three- or seven-membered ring. Therefore we must postulate that the intermediate in the thermal isomerization of either divinylcyclopropane or vinyl phenyl cyclopropane is a "virtual" diradical in which some bonding remains at all times between the two initial radical centers (carbon atoms 1 and 2). This bonding must allow rotation in order to get cis-trans isomerization but must make the two ends of the alyllic radicals nonequivalent. Without specifying the nature of this bonding, we can predict that the thermal racemization of optically active 1-vinyl-2, 2'-diphenylcyclopropane (easily prepared by asymmetric hydroboration) will be at least 100 times faster than formation of the product, 4, 4'-diphenylcyclopentene (4).

The nature of the bonding in the "virtual" diradical is of interest. It is fairly easy to imagine that this might consist of simple overlap of the two pi orbitals which contain the odd electrons, as illustrated below. As internal rotation occurs, giving cis-trans isomerization, it may be possible to have enough bonding overlap, indicated by the double arrows, to hold the two radical centers together, although not necessarily at the cyclopropane bond distance. This implies, of course, that a slight displacement of the 1 and 2 carbon atoms in a cyclopropane ring relieves strain more effectively than a corresponding displacement in a cyclobutane ring.



Following is a possible energy diagram for the species shown above.

True Diradical



Now clearly the "virtual" diradical bonding shown above will not be possible, because of the Pauli exclusion principle, if the spins of the diradical electrons are unpaired (the triplet state). Therefore we propose to photosensitize the isomerization of <u>trans</u>-1, 2-divinylcyclopropane and <u>trans</u>-1-vinyl-2-phenylcyclopropane to give the triplet diradical intermediate. We predict that the major product will then be 4-vinyl- or 4-phenylcyclopentene.

A further interesting experiment with this system would be the thermal decomposition of <u>trans</u>-3-phenyl-5-vinyl-1-pyrazoline (easily prepared by 1, 3-dipolar addition of phenyl diazomethane to butadiene in ether). Presumably this will produce the diradical species with the two radical centers enough separated to be a "true" diradical, and again the major product should be 4-phenylcyclopentene.

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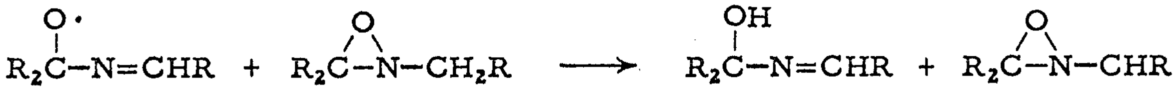
PROPOSITION IV

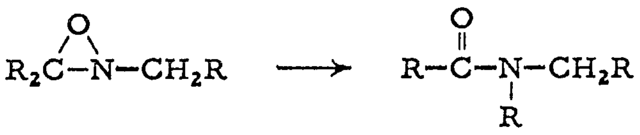
Some experimental tests are proposed to establish the mechanism of the thermal rearrangement of oxaziranes to amides.

* * * * * * * *

The mechanism of the thermal rearrangement and/or decomposition of substituted oxaziranes is not well understood. There seem to be two competing mechanisms. When a concentrated solution of the oxazirane or the oxazirane itself is allowed to sit at room temperature the mixture discolors and an oily dark mixture of decomposition products is obtained (1). This has been postulated as due to the radical chain reaction shown below.

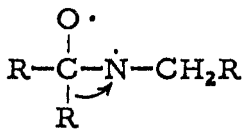


In dilute solutions or in the vapor phase, the predominant mode of reaction is a unimolecular rearrangement to the corresponding amide.

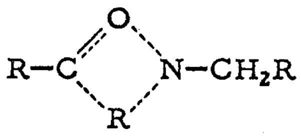


Emmons (2) has suggested this is because the chain reaction becomes improbable under these conditions. However, Shinzawa and Tanaka (1) found that 2, 3-diphenyl oxazirane also decomposes to a dark brown oil having a strong aldehyde band in the IR when left at room temperature in a concentrated solution. Clearly the proposed radical chain mechanism is impossible here, since there are no α hydrogens to be abstracted. It is not possible to write a mechanism for the decomposition of 2, 3-diphenyl oxazirane without further data. The reaction should be studied under carefully controlled conditions with the usual radical chain reaction techniques and a careful product analysis should be done in order to determine the mechanism of the decomposition.

It is not known whether the unimolecular rearrangement of oxaziranes occurs by way of diradical intermediate (I) or through a concerted transition state (II). The small pre-exponential factor (3×10^{11})

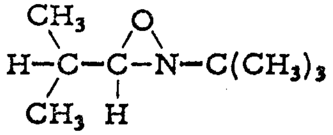


I

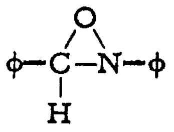


II

which was found in the thermal rearrangement of 2, 3-diphenyloxazirane (III) indicates that the transition state is more constrained than the starting material, arguing for a concerted rearrangement. However, the activation energy for the rearrangement of (III) is about 15 kcal/mole less than that for (IV). (The activation energy for the



IV

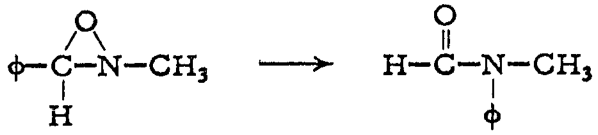


III

rearrangement of (IV) was estimated from the fact that 13% of the starting material was unrearranged after 2 hours at 250°.) This could be easily attributed to resonance stabilization of the diradical intermediate; it is more difficult to attribute this fact to an enhanced migratory aptitude of the R group in the concerted transition state in light of fact that Emmons (2) found very little difference in the relative migratory aptitudes of the R groups in 3, 3-disubstituted oxaziranes.

We propose the following thermal rearrangements of oxaziranes in order to pin down the mechanism a little better.

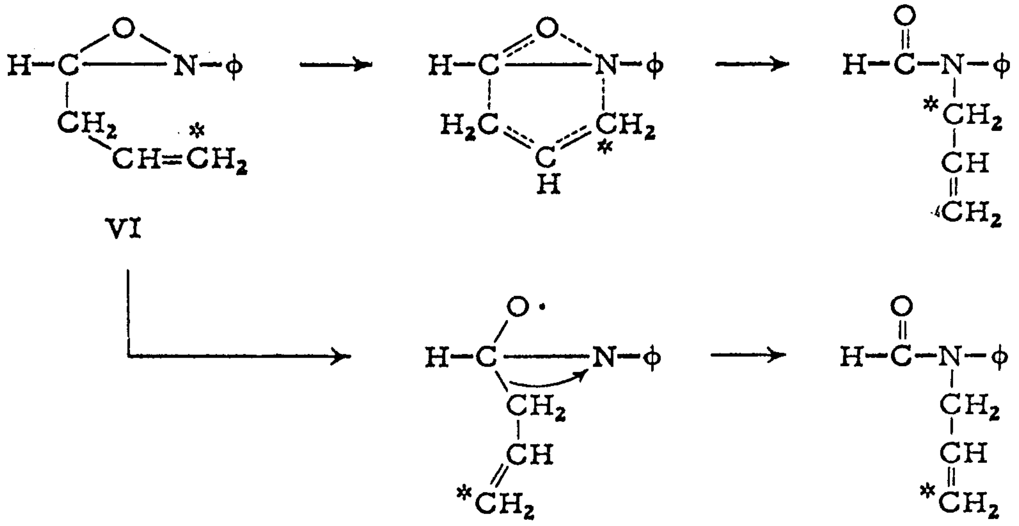
(1)



V

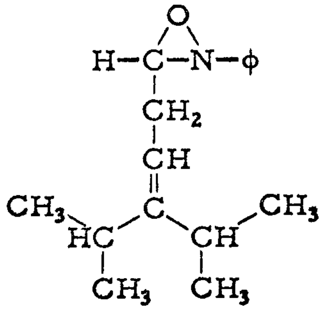
If the activation parameters for (V) are very similar to those for (III), we can conclude that the concerted mechanism probably obtains. If on the other hand, the activation energy is substantially higher for (V) than for (III), either the diradical mechanism or a concerted mechanism with considerable charge separation might obtain. The latter possibility could be detected by varying the substituents on the N-bonded phenyl group.

(2)



VI

If the concerted mechanism obtains, we would expect to find a substantially lower activation energy for (VI) and all of the carbon 14 on the carbon bonded to nitrogen. If the diradical obtains, we might expect to find some of the carbon 14 on the terminal position. The result of this experiment cannot be unambiguously predicted, but coupled with other data it might prove very enlightening. One might be able to force the rearrangement through a pathway involving no alyllic rearrangement by substituting the terminal carbon with bulky groups, as in (VII).



VII

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1. Kinko Shinzawa and Ikuzo Tanaka, J. Phys. Chem., **86**, 1205 (1964).
2. W. D. Emmons, in "Heterocyclic Compounds with Three- and Four-Membered Rings," Part One, Chapter IV, Part IV, 1964, John Wiley and Sons, Inc., London, and references therein.

PROPOSITION V

An interesting molecular rearrangement is proposed.

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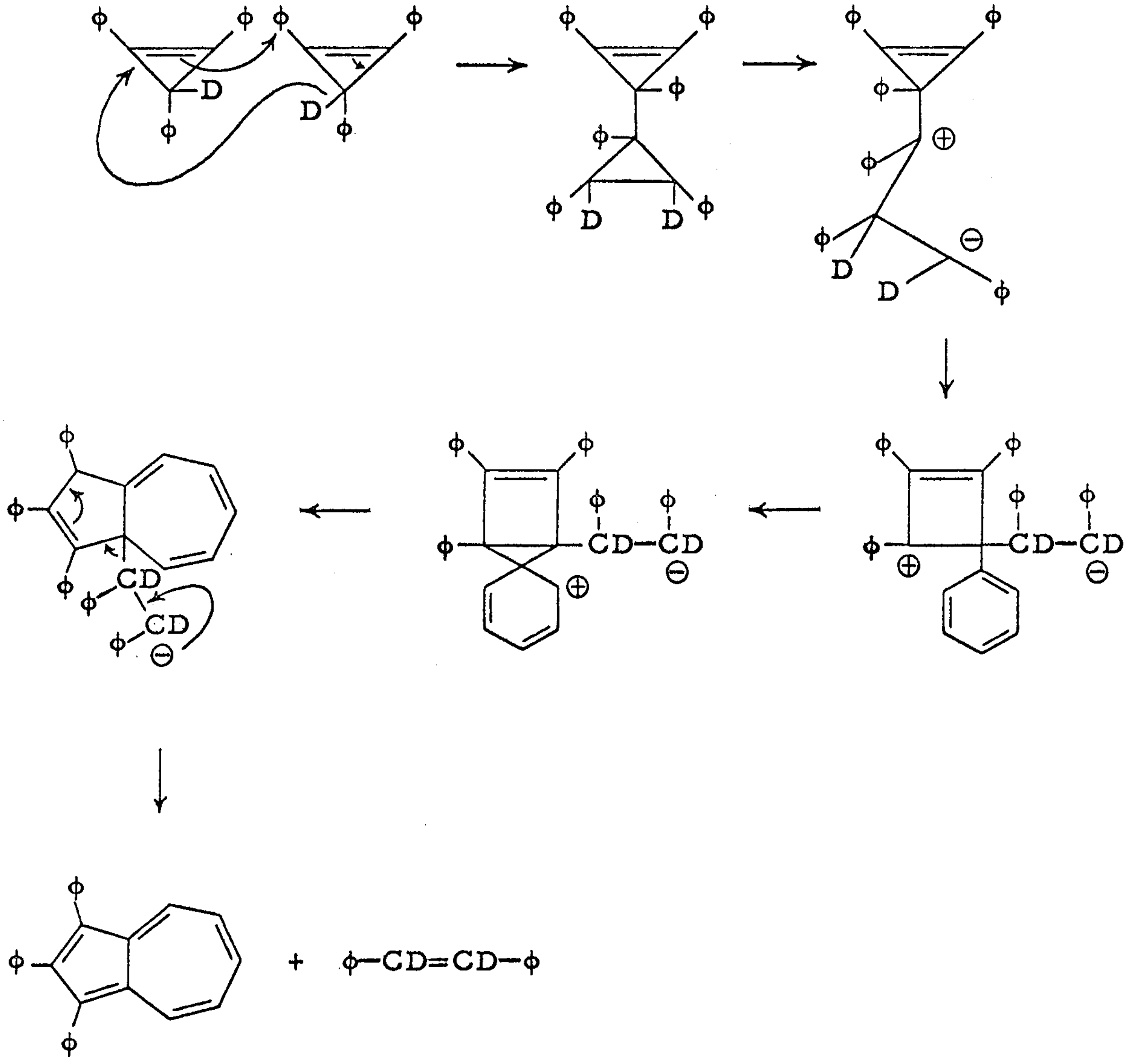
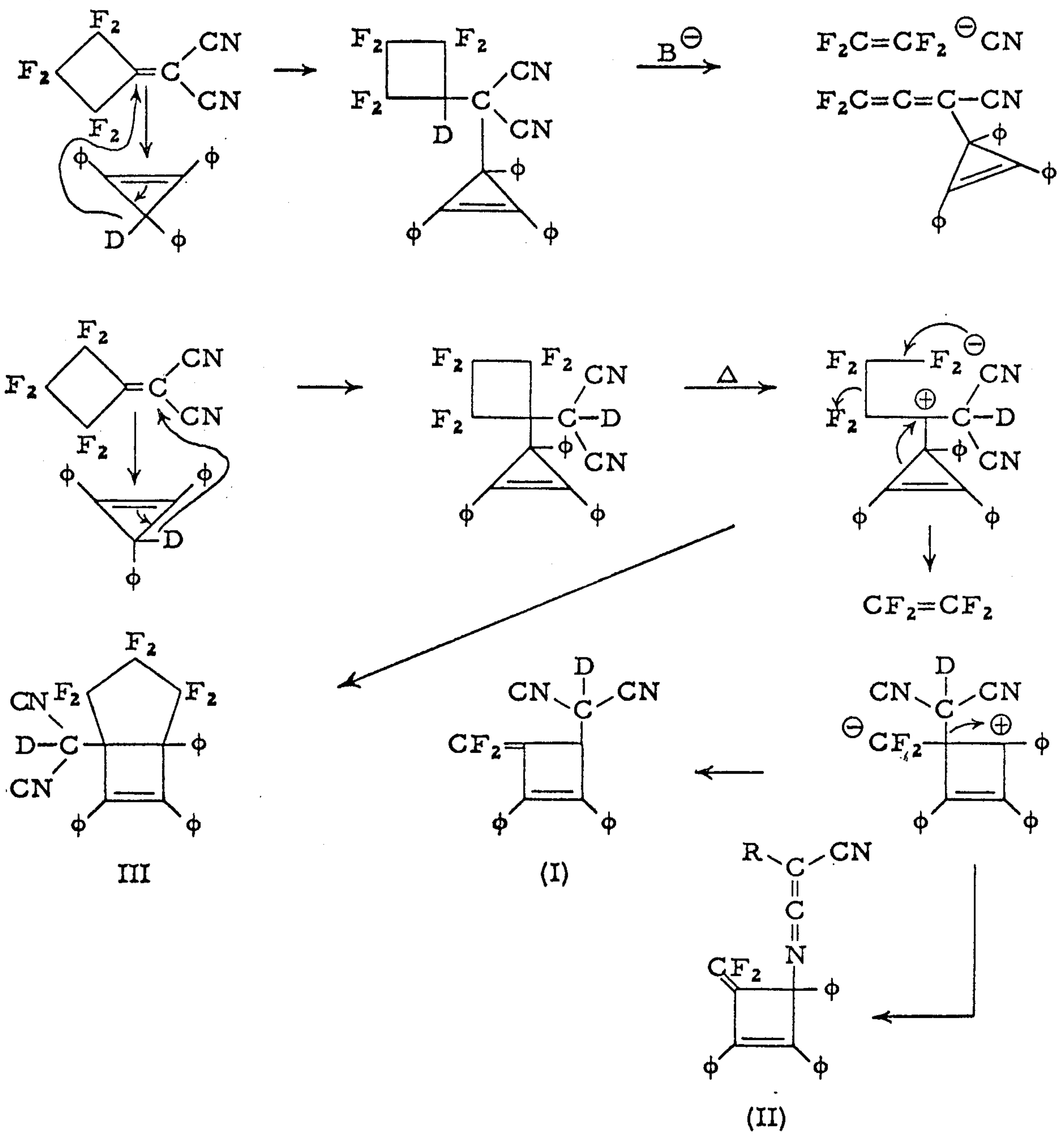
Breslow (1) has suggested the following mechanism may obtain in the thermal dimerization and rearrangement of triphenylcyclopropene.



We propose that the following thermal reactions may occur between triphenylcyclopropene and dicyanomethylene perfluorocyclobutane (2). The intermediate in the second reaction should be quite capable of sustaining a zwitter ion because of the stabilization of the negative charge by the fluorene atoms.

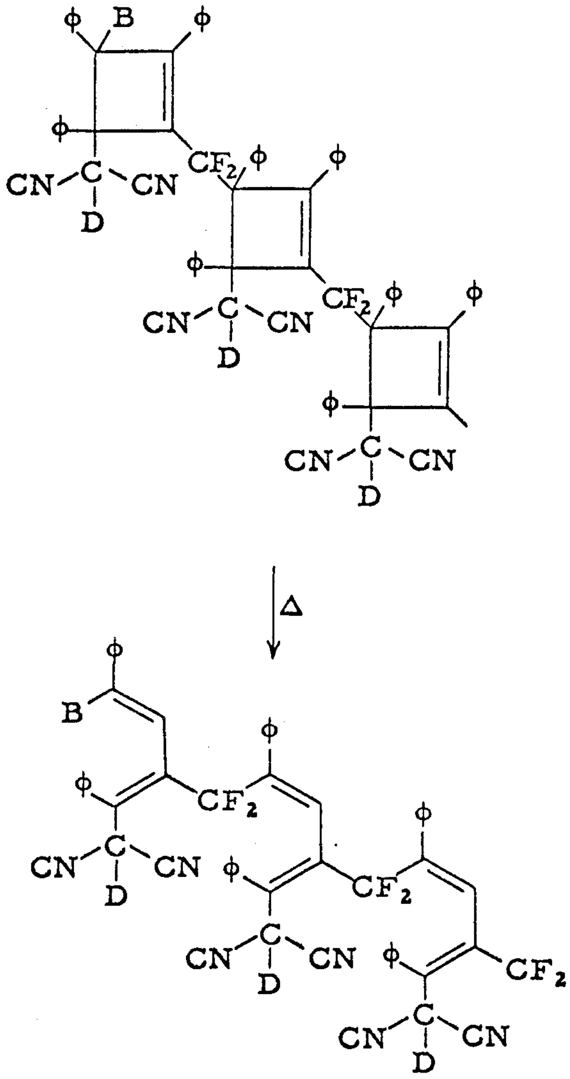


III

(I)

(II)

Products (I) and (II) of the reaction might undergo facile anionic polymerization to give the polycyclobutane structure below, which when heated could open to the polybutadiene structure, providing many opportunities for further cross linking.



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Proposition VI

It is proposed that the rearrangement of the product of 2-methyl pyridine N-oxide with acetic anhydride to 2-acetoxymethyl pyridine proceeds through a caged ion pair.

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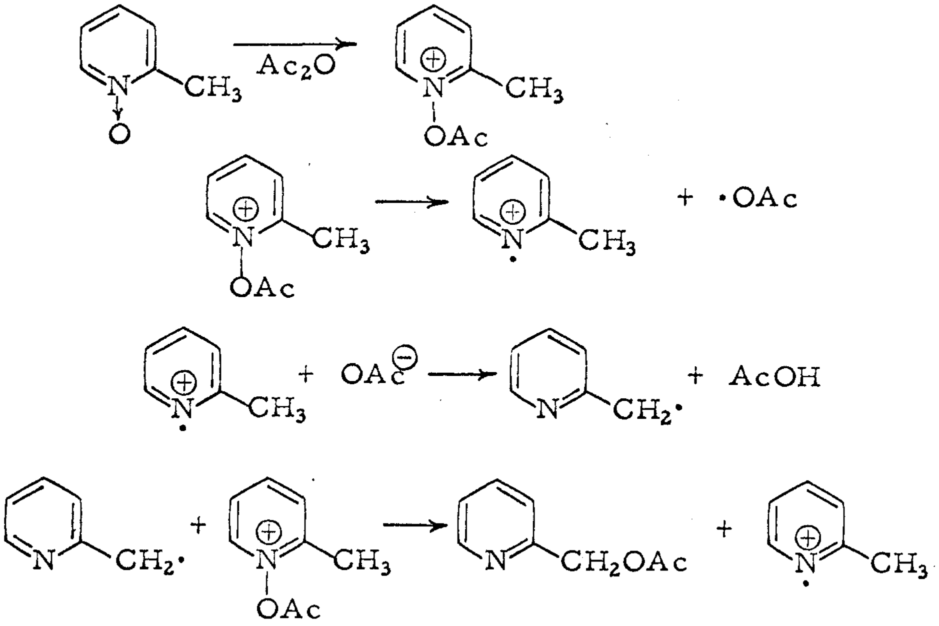
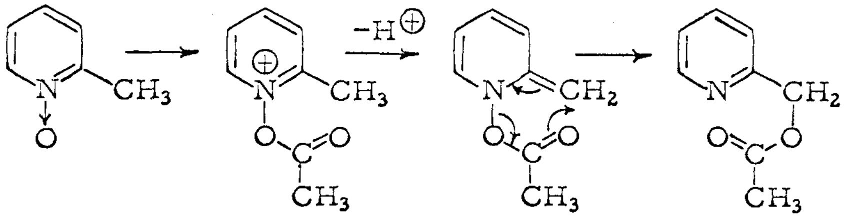
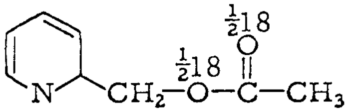
When 2-methyl pyridine N-oxide is heated with acetic anhydride an exothermic reaction occurs after an induction period at about 120° (1). The mixture turns brown and about a 75% yield of 2-acetoxymethyl pyridine can be isolated. When styrene is added, polymerization of the styrene occurs (2). These facts suggest the mechanism:



However, when scavengers were added the polymerization of styrene was stopped but the yield of 2-acetoxymethyl pyridine was unchanged (3). This favors the ionic mechanism shown below with perhaps a few percent of a competing radical mechanism.

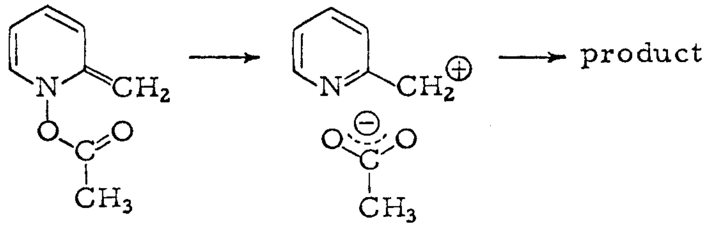


When all three oxygens of the acetic anhydride are labeled with O^{18} the product has the label distribution shown below (4):



This was given as proof that the intermediate product breaks up to a radical pair which recombines before escape from the cage but not before total equilibration of the two oxygens of the acetoxy radical.

It is clear that the data will be satisfied equally well by a mechanism involving an ion pair in the solvent cage.



These two possibilities could probably be distinguished by addition of a sufficient concentration of a scavenger to eat up the radicals in the cage, if they are produced.

Furthermore, the induction period for the reaction is curious, since there is no apparent reason for it with any of the mechanisms given. It is proposed that this reaction could be cleaned up and studied more easily by using a dipolar aprotic solvent such as dimethyl sulfoxide or hexamethyl phosphoramide. In these solvents the N-oxide is a much more effective nucleophile, allowing the reaction to be run at a lower temperature and probably much more cleanly. However, if the final step consists of competing radical and ionic bond scission, as may be the case, the solvent change might make the ionic rearrangement more favorable.

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(3) V. J. Traynelis and R. F. Martello, J. Am. Chem. Soc., **80**, 6590 (1958).

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