I. SYNTHESIS AND DECOMPOSITION OF SEVERAL 2,3-DIAZABICYCLO[3.1.0] HEX-2-ENES

II. WAVELENGTH EFFECTS IN PIPERYLENE PHOTOISOMERIZATION

Thesis by

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Our discussion will be adequate if it has as much clearness as the subject matter admits of, for precision is not to be sought for alike in all discussions.

Aristotle

It's all in the mind, you know.

John Lennon

ACKNOWLEDGMENTS

It has been a very great pleasure to be associated with George S. Hammond and his research group. His enthusiasm for ideas, discussion and argument, and his perceptive view of many chemical problems have been a source of amazement, amusement and challenge.

I am grateful to Robert G. Bergman for many discussions and suggestions concerning the work described in Part I of this thesis.

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ABSTRACT

Part I

The synthesis and characterization of several methyl substituted 2, 3-diazabicyclo[3. 1. 0]hex-2-enes are described. The thermal and photochemical decomposition of stereochemically labeled pyrazolines has been shown to afford mixtures of hydrocarbon products with a high degree of stereoselectivity. The nature of the products from _exo_- and _endo_-4-_exo_-6-dimethyl-2, 3-diazabicyclo-[3. 1. 0]hex-2-ene suggests that carbene intermediates are formed, and multiple mechanisms for decomposition are proposed to account for the observation that the product distributions obtained are temperature dependent. A formal 1, 3-dipolar cycloreversion to afford an acyclic diazo compound, which decomposes to a carbene under the reaction conditions, is proposed to compete with formation of diradical intermediates.

Part II

Initial quantum yields of _trans_ → _cis_ and _cis_ → _trans_ isomerization of _trans_- and _cis_-1, 3-pentadiene have been determined in pentane solutions for four excitation wavelengths in the range 236-254 nm. The photoisomerization efficiency was found to decrease markedly when high energy excitation was employed. Analysis of the data suggests that contributions of _s_-_cis_ conformations may only be important for 254 nm excitation and that the bulk of the diminution in isomerization quantum yield as the initial excited state energy content is increased must be accounted for in terms of enhanced radiationless decay probabilities. Several possible mechanisms are discussed.

This thesis is dedicated to the memory of Peter A. Leermakers, teacher and friend.

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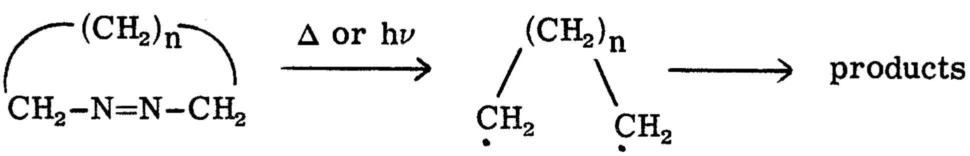
PART I

INTRODUCTION

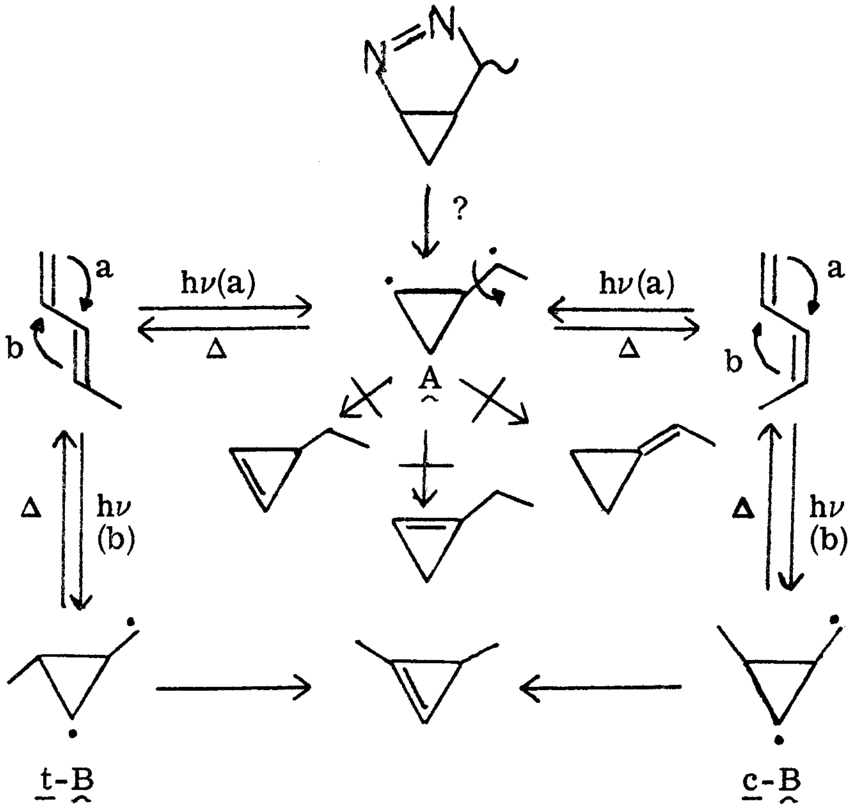
The pyrolytic and photolytic decomposition of cyclic azo compounds has frequently been used to generate short-lived 1, ω-diradicals. Although the precise nature of these intermediates is still a subject of active inquiry, particularly in the case of the "trimethylene" diradical,[1-3] the generality of the pattern of ring-closed and radical disproportionation products (Scheme 1) is well established.[4-18] Similarly, the elimination of molecular nitrogen from 2, 3-diazabicyclo[3. 3. 0]oct-2-ene derivatives[19, 20] and trans-9, 10-diazabicyclo[6. 3. 0]undec-9-ene,[21] probably affords diradical intermediates.



n = 1, ref. 4-15; n = 2, ref. 16, 17; n = 4, ref. 18

Scheme 1

In the present study, the synthesis and decomposition of several compounds containing the 2, 3-diazabicyclo[3. 1. 0]hex-2-ene skeleton have been accomplished. This work was initiated to evaluate the reactivity of "cyclopropyl methylene" diradicals, e. g., **A** in Scheme 2, which had been proposed[22, 23] as intermediates in the direct photoexcitation of acyclic, conjugated dienes. Scheme 2 illustrates the mechanisms proposed by Srinivasan[22] for the observed formation of 1, 3-dimethylcyclopropene and by Saltiel[23] for the cis-trans isomerization of the isomeric 1, 3-pentadienes on direct irradiation at 253. 7 nm. Cyclization of the (singlet) excited diene according to path b affords diradicals **B**, which suffer either



Scheme 2

collapse to starting material or hydrogen migration toward the exocyclic radical center, yielding 1, 3-dimethylcyclopropene. Excited state cyclization according to path a gives diradical **A** which can either revert to the initial diene isomer or rotate about the exocyclic C–C bond and then collapse to diene of opposite geometry.

A major drawback of the mechanistic scheme proposed by Saltiel and Srinivasan is the restricted reactivity of diradical **A**. Possible products of hydrogen migration were not observed. It seems unlikely that diradical **A** would decay exclusively by rotation and subsequent collapse, while the related diradicals **B** exhibit measurable decay to hydrogen migration products.

Unfortunately, unambigous answers to the questions raised by the suggestions of Srinivasan and Saltiel can not be derived from the results of the present study. However, the research reported here provides notable and interesting exceptions to the generally observed decomposition modes of cyclic and bicyclic azo compounds.

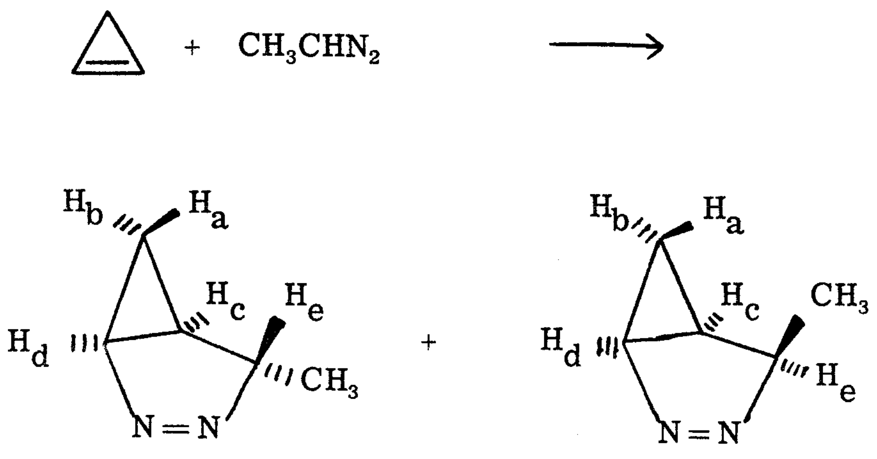
A preliminary report of this work has been accepted for publication: D. F. Eaton, R. G. Bergman, and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 0000 (1972).

RESULTS AND DISCUSSION

Synthesis and Characterization of Pyrazolines

Several reports[24-33] in the literature describe 1,3-dipolar cycloaddition reactions of diazoalkanes and cyclopropenes (or hetero analogs). In many of the cases[24-28] the products isolated are secondary ones derived by decomposition of the initially formed bicyclic Δ^1-pyrazoline.

In the present study, the reaction of diazoethane and cyclopropene was found to proceed rapidly and essentially quantitatively at low temperature (-78°), affording a glpc separable mixture of *exo*- and *endo*-4-methyl-2,3-diazabicyclo[3.1.0]hex-2-ene, **3** and **4**, respectively (Scheme 3). The gross structural assignments are supported by mass spectral, ultraviolet, infrared, and nmr evidence, as well as by the method of synthesis.



3 **4**

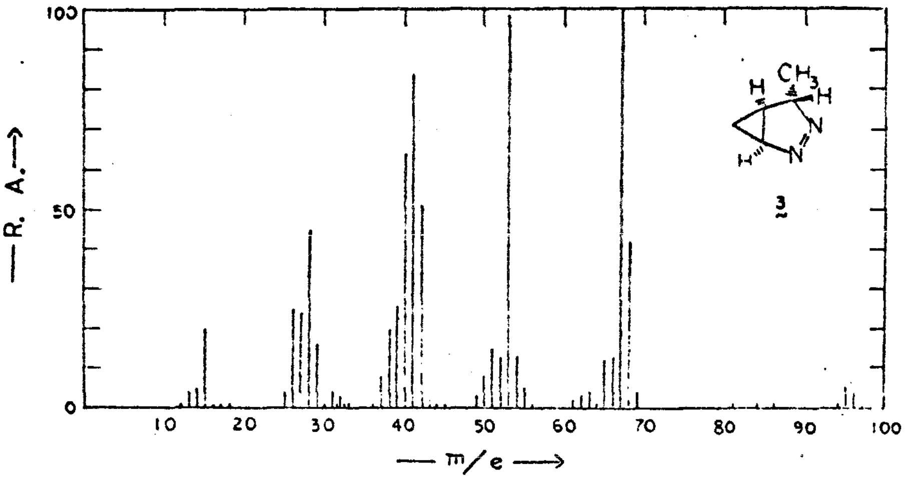
Scheme 3

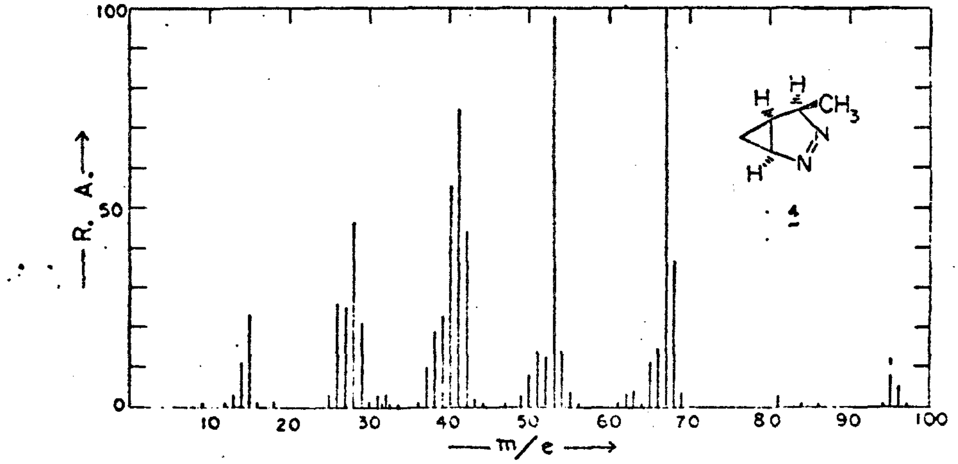
The mass spectra of **3** and **4** are shown in Figure 1. Both **3** and **4** exhibit molecular ions at m/e 96, appropriate for $C_5H_8N_2$. The observed M^++1 peaks were found to be _ca._ 7-8% of the parent, in reasonable agreement with that expected (6.3%) from the known natural abundances of ^{13}C, ^{2}H, and ^{15}N. The mass patterns found for both **3** and **4** are strikingly similar to those of _cis_- and _trans_-1,3-pentadiene[34] (Figure 1c), suggesting that the initially formed pyrazoline ions rapidly decay to species (M^+-N_2) which are similar, or identical, to the ion(s) formed from the dienes.

Figure 2 shows the infrared spectra of pyrazolines **3** and **4**. The absorptions near 1515 cm^{-1} are assigned to –N=N– stretching modes. The band positions are at slightly lower frequencies than those observed for other cyclic azo compounds: e.g., 1555 cm^{-1} for _trans_-9,10-diazabicyclo[6.3.0]undec-9-ene,[35] and 1540 cm^{-1} for 2,3-diazabicyclo[3.2.0]-hept-2-ene.[36] Conversely, the absorptions at 1030 and 3065 cm^{-1}, assigned as cyclopropyl ring deformations and C–H stretching, respectively, are shifted to slightly higher frequencies than are normally observed (1010 and 3050 cm^{-1}) for simple _cis_-dialkyl substituted cyclopropanes[37] and are also higher than those found for bicyclo[3.1.0]hex-2-ene (1020 and 3055 cm^{-1}).[38]

Pyrazolines **3** and **4** exhibit ultraviolet maxima in _n_-hexane solutions at 328 nm (ϵ 335 l $mole^{-1}$ cm^{-1}) and 330 nm (ϵ 149 l $mole^{-1}$ cm^{-1}), respectively. In addition to these $\pi^* \leftarrow n$ transitions, intense $\pi^* \leftarrow \pi$ transitions are found at shorter wavelengths.

Figure 1. Mass spectra of: a) *exo*-4-methyl-2, 3-diazabicyclo[3. 1. 0]hex-2-ene (**3**); b) *endo*-4-methyl-2, 3-diazabicyclo[3. 1. 0]hex-2-ene (**4**); and c) *trans*-1, 3-pentadiene (ref. 34).


100
50
0
— R. A. →
10
20
30
40
50
60
70
80
90
100
— m/e →
CH$_3$
H
H
N
N
H
3


100
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CH$_3$
N
N
H
4

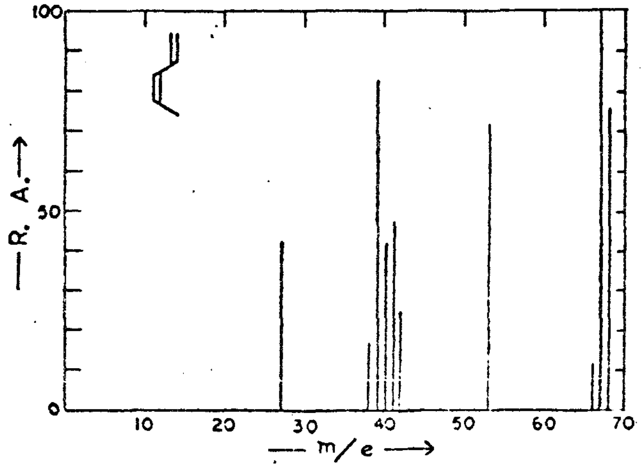

100
50
0
— R. A. →
10
20
30
40
50
60
70
— m/e →

Figure 2. Infrared spectra (as liquid films).

a) *exo*-4-methyl-2, 3-diazabicyclo[3. 1. 0]hex-2-ene (**3**); and b) *endo*-4-methyl-2, 3-diazabicyclo[3. 1. 0]hex-2-ene (**4**).

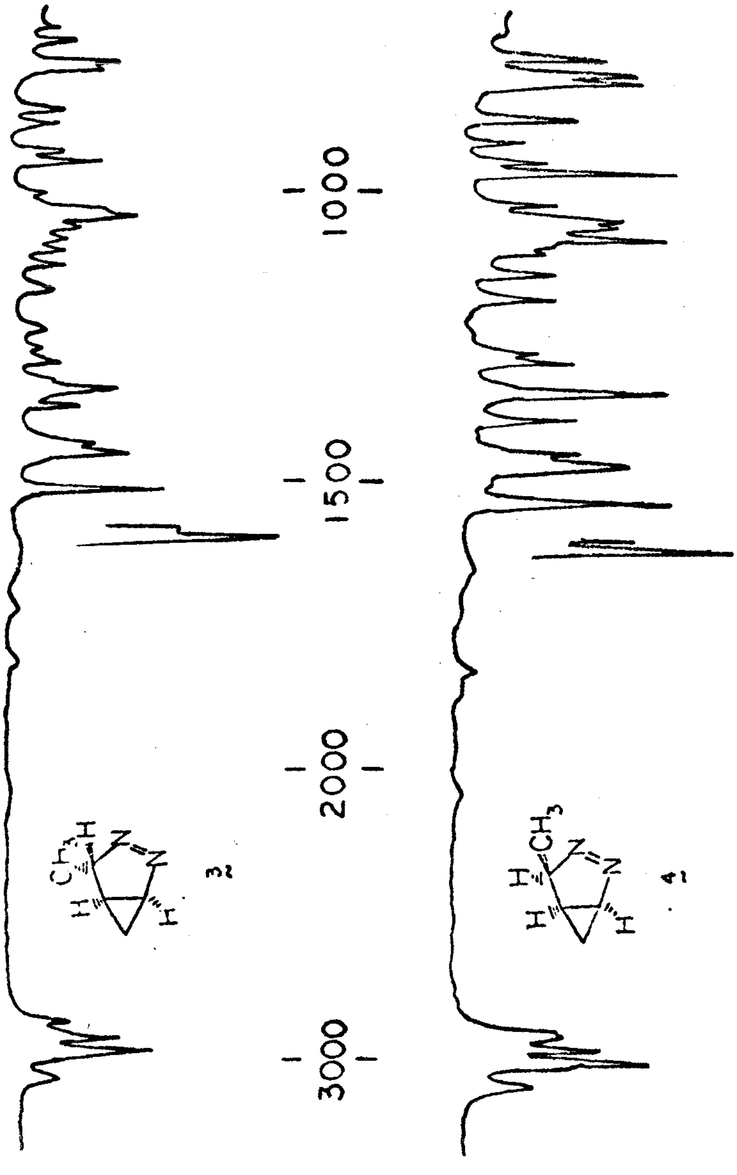

1000
1500
2000
3000
3
4

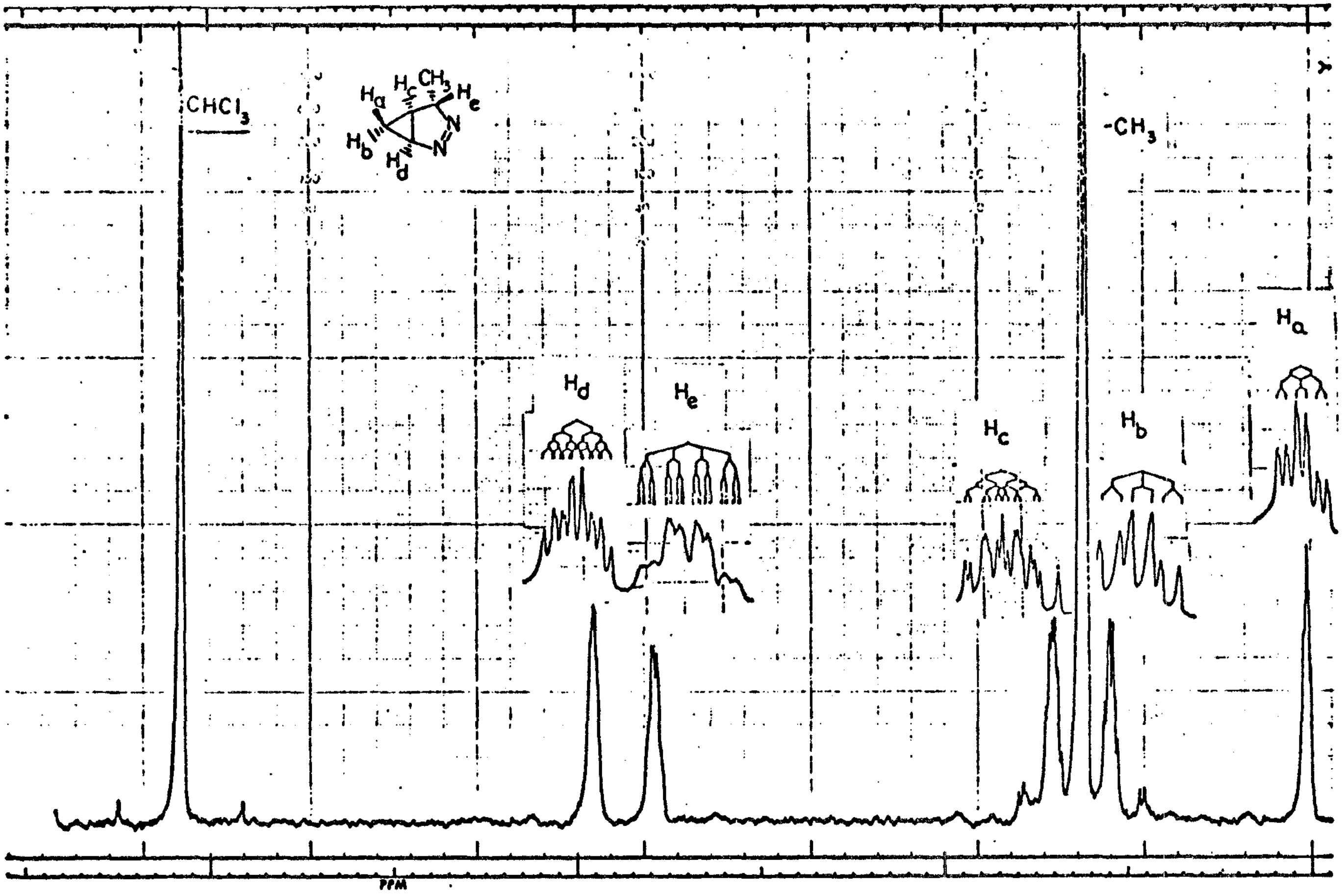
Figure 3 shows the 220 MHz nmr spectra of pyrazolines 3 and 4. Table 1 lists the observed chemical shifts; protons are labeled as in the structures given in Scheme 1. The proton assignments are based upon both the chemical shift data and the coupling constant analysis (*vide infra*). Examination of the chemical shift values reveals several general conclusions. First, the azo linkage exerts a strong shielding effect on protons H_a in both 3 and 4. The chemical shift of H_a is identical to the *endo*-C-6 proton in bicyclo[3.1.0]hex-2-ene.[38] The cyclopropane ring also appears to exert some shielding: the *endo*-methyl group in 4 appears at higher field than the *exo*-methyl of 3. Similarly, H_e appears at higher

Table 1. Observed Chemical Shifts of Protons in 3 and 4

3		4	
Proton	Chemical shift[a]	Proton	Chemical shift[a]
H_a	-0.19	H_a	-0.17
H_b	1.14	H_b	0.89
$-CH_3$	1.33	$-CH_3$	1.47
H_c	1.54	H_c	1.60
H_e	4.24	H_d	4.62
H_d	4.66	H_e	4.74

[a] Chemical shifts are reported as δ values downfield from TMS in ppm and are for CCl_4 solutions containing $CHCl_3$ as internal standard.

Figure 3. 220 MHz nmr spectra (CCl_4--1% $CHCl_3$). a) *exo*-4-methyl-2, 3-diazabicyclo[3. 1. 0]hex-2-ene (**3**) and b) *endo*-4-methyl-2, 3-diazabicyclo[3. 1. 0]hex-2-ene (**4**).


CHCl3
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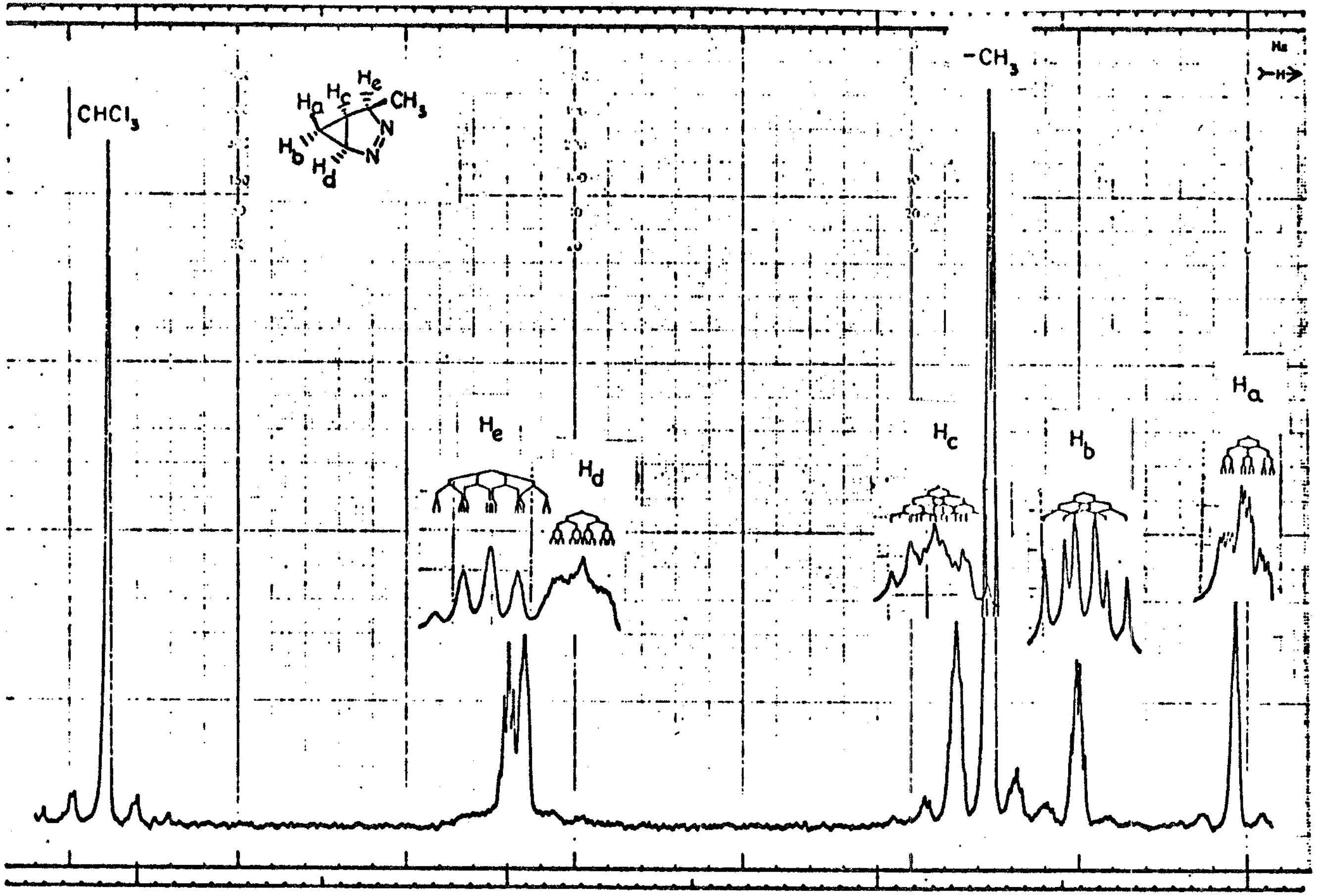
Hc
CH3
He
Hb
Hd
N
N
-CH3
Hd
He
Hc
Hb
Ha
PPM


CHCl$_3$
H_a
H_b
H_c
H_d
H_e
CH$_3$
N
N
$-CH_3$

field when it is stereochemically *endo* with respect to the cyclopropane ring (**3**) than when it is *exo*, as in **4**. Both H_c and H_d are essentially unaffected by the stereochemistry at C-4. In pyrazoline **3**, H_b is at somewhat lower field than it is in **4**. The presence of the *endo*-methyl group seems to be responsible for this shift: similar shifts are noted in methyl-substituted bicyclo[3.1.0]hex-2-enes.[19]

Table 2 lists the coupling constants derived from a pseudo-first order analysis of the splitting patterns of the 220 MHz nmr spectra of **3** and **4**. From the values of $J_{c,e}$ and the Karplus

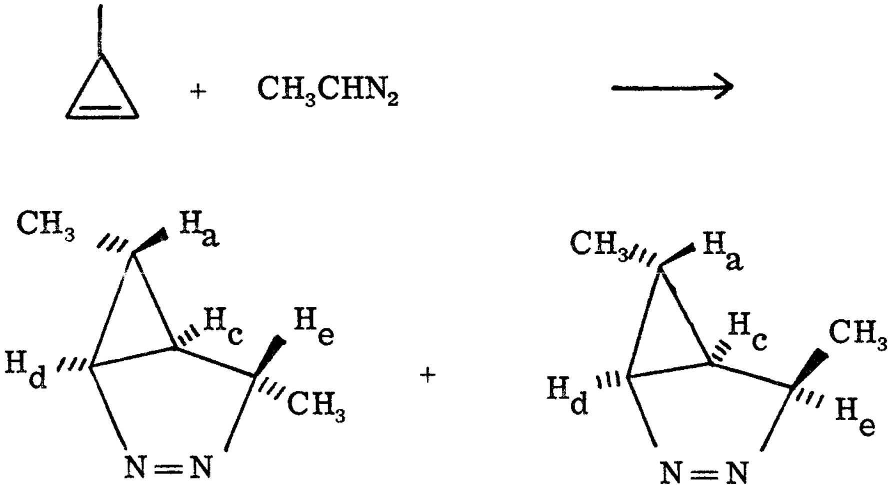
Table 2. Derived H-H Coupling Constants for **3** and **4**

3		**4**	
Proton pair	J(Hz)	Proton pair	J(Hz)
a, b	5.2	a, b	5.2
a, c	5.2	a, c	5.2
a, d	2.4	a, d	2.0
a, e	~0.5	a, e	1.0
b, c	7.7	b, c	7.9
b, d	7.7	b, d	7.9
b, e	~0.4	b, e	0
c, d	4.7	c, d	4.9
c, e	1.3	c, e	6.5
d, e	3.0	d, e	1.3
e, $-CH_3$	7.5	e, $-CH_3$	7.3

relation[39a] it is possible to unequivocally establish the stereochemistry of 3 and 4 at C-4. In pyrazoline 3 the coupling constant for H_c-H_e is found to be 1.3 Hz. Application of the Karplus relation[39a] implies that the dihedral angle between H_c and H_e is approximately 65°. Thus H_e must be stereochemically *endo* to the bicyclic system. The value of $J_{c,e}$ found for 4 is 6.5 Hz. The calculated dihedral H_c-H_e angle is 20°, strongly suggesting that in pyrazoline 4 H_e is oriented *exo* to the bicyclic system.

Of some note is the profusion of long-range[39b] H-H couplings found (Table 2), particularly in 3. Proton e is strongly coupled to H_d (J = 3.0 in 3, J = 1.3 in 4), and weakly coupled with both bridge-head cyclopropyl protons in 3, but only coupled to H_a in 4. An examination of molecular models serves to clarify the geometry of the systems. Long-range W paths[39b] are found for both H_a and H_b with H_e in 3. The geminal angle H_a-C-H_b is nearly bisected by a W-path plane through H_e in 3, which gives rise to the two long-range couplings. In pyrazoline 4, however, the *exo* orientation of H_e eliminates the W-path[39b] to H_b, and appears to render the path to H_a more favorable.

The synthesis and characterization of the pyrazolines formed by reaction of diazoethane and 3-methylcyclopropene (Scheme 4) are entirely analogous to the mono-methyl system. *Exo*-4-*exo*-6-dimethyl-2,3-diazabicyclo[3.1.0]hex-2-ene (5) and *endo*-4-*exo*-6-dimethyl-2,3-diazabicyclo[3.1.0]hex-2-ene (6) were the only pyrazoline products formed. No evidence for the formation of



5 Scheme 4 6

pyrazolines with an endo-C-6 methyl group was found, which suggests that in the transition state for the formation of C-6-endo-methyl products there is significant strain induced by interaction of the 1, 3-dipole with the incipient endo-methyl group.

Evidence supporting the gross pyrazoline structure is gained from the infrared, ultraviolet and mass spectra of 5 and 6 (see Experimental). An unambiguous assignment of the stereochemistry at C-4 rests on the 100 MHz nmr spectra. Table 3 lists the observed chemical shifts for both 5 and 6, and Table 4 shows the results of the coupling constant analysis. The coupling constant values for $J(H_c-H_e)$ suggest that the dihedral H_c-H_e angles are approximately 60° in 5 and 22° in 6, establishing the stereochemistry as indicated in Scheme 2 for both 5 and 6. The exo-methyl stereochemistry at C-6 is assigned on the basis of the nmr resonances of H_a in 5 and 6, which appear at high field, and on the

Table 3. Chemical Shifts of Protons in 5 and 6

5		6	
Proton	Chemical shift[a]	Proton	Chemical shift[a]
H_a	-0.02	H_a	0.09
CH_3 (C-6)	0.82	CH_3 (C-6)	1.00
CH_3 (C-4)	1.14	CH_3 (C-4)	1.37
H_c	*ca.* 1.1[b]	H_c	*ca.* 1.3[b]
H_e	4.02	H_d	4.28
H_d	4.21	H_e	4.61

[a] Chemical shift in δ units downfield from TMS, for CCl_4 solutions containing 2% $CHCl_3$ as internal reference.

[b] H_c is obscured by the C-4 methyl resonance.

Table 4. Derived H-H Coupling Constants for 5 and 6

5		6	
Proton pair	J(Hz)	Proton pair	J(Hz)
CH_3(C-6), a	6.0	CH_3 (C-6), a	5.8
CH_3(C-5), e	7.3	CH_3 (C-4), e	7.1
a, c	5	a, c	1.8
a, d	1.8	a, d	1.2
c, d	4.6	c, d	4.4
c, e	2.4	c, e	7.1

fact that the coupling constants $J(H_a-H_c)$ and $J(H_a-H_d)$ are smaller than those expected for *cis*-cyclopropyl H–H couplings.[40]

Decomposition of Pyrazolines

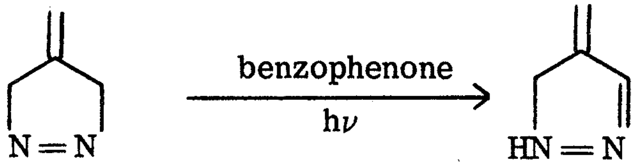
Pyrazolines 3, 4, 5 and 6 are smoothly decomposed under pyrolytic and photolytic conditions. No epimerization was observed under any of the decomposition conditions employed.

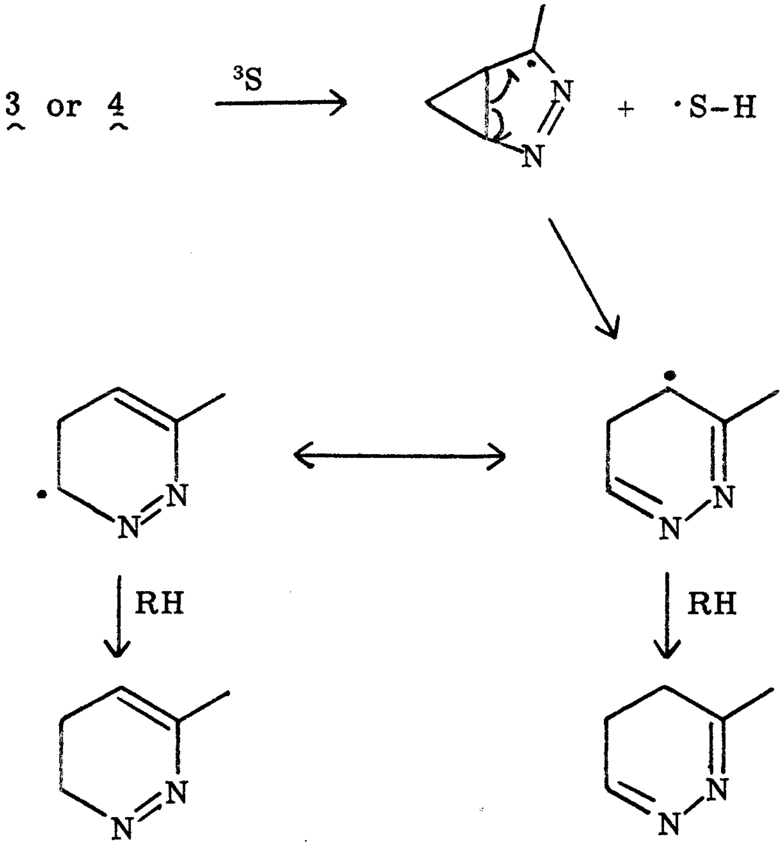
Pyrolysis of 3 in the range 119°-173° results in the formation of *trans*-1, 3-pentadiene (7, 98%) and *cis*-1, 3-pentadiene (8, 2%). Decomposition of 4 under identical conditions affords 7 (3%) and 8 (97%). The absolute yield of dienes is 86%. Pyrazoline disappearance is first-order through at least three half-lives. At 119°, the rate constant for disappearance of 3 was determined to be 4.8×10^{-4} sec^{-1} and that for the disappearance of 4 was 1.6×10^{-5} sec^{-1}. The ratio of the rate constants at 119° is then $k_3/k_4 = 30$.

Direct irradiation of 3 in pentane solutions at 313.0 nm yields the isomeric 1, 3-pentadienes in the same ratio found in the thermal decomposition. The quantum yield for pyrazoline disappearance was found to be 0.86; the diene appearance quantum yield, however, is only 0.3. Similarly, irradiation of 4 yields dienes in the thermal ratio. The quantum yield of disappearance of 4 is 0.73, and the diene appearance yield is 0.2.

Blue fluorescence (λ_{max} 430 nm) with an onset at 365 nm (~78 kcal/mole) was observed from a degassed pentane solution of a 3:2 mixture of 3 and 4. Emission occurred at both room temperature and 77°K. Several fluorescent bicyclic azo systems are known.[41] 2,3-Diazabicyclo[3.1.0]oct-2-ene fluoresces in isooctane solution at room temperature with a quantum yield of 0.2.[41a] The emission is assigned to the $\pi^* \rightarrow n$ transition. 2,3-Diazabicyclo[2.2.1]hept-2-ene exhibits $\pi^* \rightarrow n$ emission only in the vapor phase; the quantum yield of fluorescence is 0.01.[41a]

Decomposition of pyrazolines 3 and 4 could also be effected by a variety of triplet sensitizers and by naphthalene, as a singlet sensitizer.[41c] Singlet sensitization of 3 produced 7 and 8, again in the ratio 7:8 = 98:2, while 4 gave 7:8 = 3:97 under identical conditions. Irradiation of triplet sensitizers, in the presence of pyrazolines 3 and 4, under conditions in which the sensitizers absorbed better than 98% of the incident radiation, caused efficient pyrazoline disappearance, but no diene products were observed. The Michler's ketone sensitized decomposition of a mixture of pyrazolines 3 and 4 could be conveniently monitored by nmr. The integral of the C-4 methyl doublet smoothly decreased with time. Concomitant appearance of new resonances, and the infrared spectrum of the solution at the end of the irradiation (vide infra) suggest that the ketone sensitizer may act on the pyrazolines as indicated in Scheme 5. The mechanism outlined in Scheme 5 is qualitatively similar to one proposed in order to account for the benzophenone sensitized decomposition of 4-methylene-1-pyrazoline:[42]





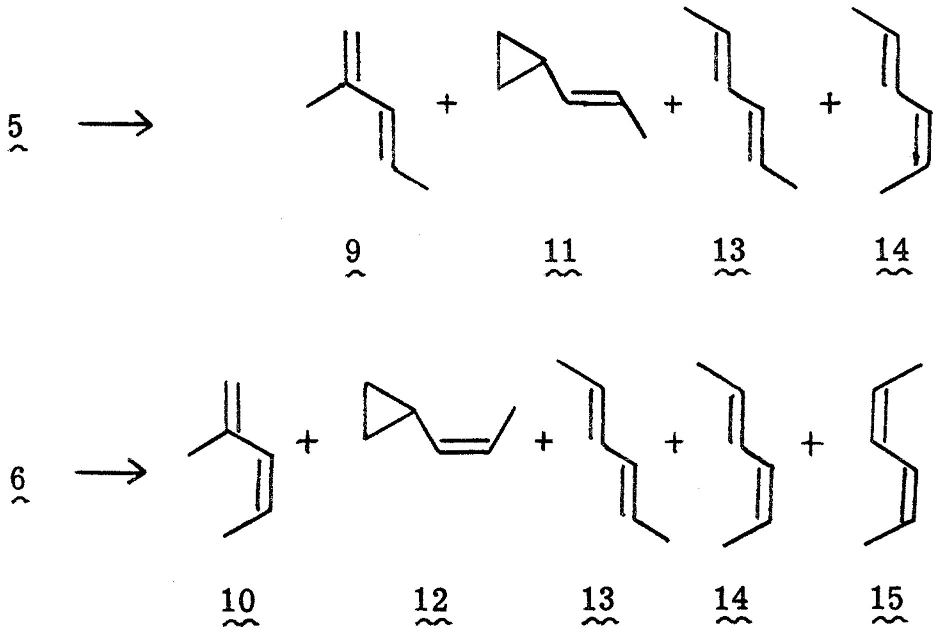
Scheme 5

The nmr spectrum of the irradiated Michler's ketone-pyrazoline mixture showed, inter alia (see Experimental), a broad peak at δ 7.2, which suggests that a proton attached to the carbon of an imine group may be present, and multiplets in the allylic region. In addition, a singlet at δ 1.45 may be assigned to an allylic methyl group. The infrared spectrum exhibited a strong absorption at 1730 cm^{-1}, which may be interpreted as being an imine C=N stretching mode in a cyclic system. Also, absorptions near 2840

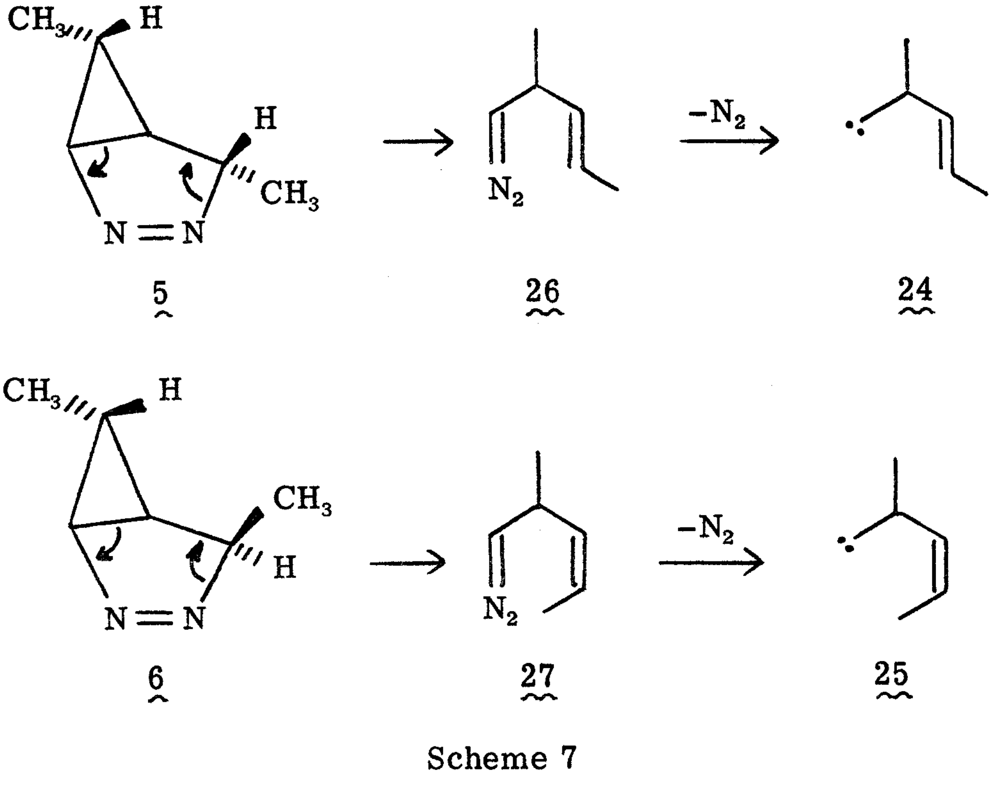
cm^{-1} are assigned as imine C–H stretching. While the evidence cited is far from conclusive, it appears to support the mechanism outlined in Scheme 5 in a qualitative sense.

The high product stereoselectivity found in the thermal and (direct) photochemical decomposition of pyrazolines 3 and 4, and the large difference in the pyrolysis rates, are difficult to rationalize within the context of a diradical mechanism for pyrazoline decomposition. The possibilities of intervention of diradicals will be discussed later.

Dimethyl-substituted pyrazolines 5 and 6 were prepared, and decomposed under pyrolytic and photolytic conditions, in order to determine the fate of an additional stereochemical label in the 2,3-diazabicyclo[3.1.0]hex-2-ene system. Decomposition of 5 and 6 afforded mixtures (71% isolated yield) of the following C_6H_{10} hydrocarbons: 2-methyl-*trans*-1,3-pentadiene (9), 2-methyl-*cis*-1,3-pentadiene (10), *trans*- and *cis*-1-cyclopropylpropene (11 and 12, respectively), and *trans, trans*-, *cis, trans*-, and *cis, cis*-2,4-hexadiene (13, 14 and 15, respectively). Scheme 6 illustrates the transformations found for both epimeric pyrazolines. The nature of the decomposition products strongly suggests the intervention of carbenes 24 and 25, which may arise as shown in Scheme 7. (However, see pages 42-53 for a modification of this view). Carbene intermediates 24 and 25 can account for all of the observed hydrocarbon products by conventional carbene reactions: (a) 1,2-hydrogen migration toward the carbene center leads to the observed



Scheme 6



Scheme 7

2-methyl-1, 3-pentadiene products 9 and 10; (b) carbene insertion into the C–H bonds of the adjacent methyl group gives vinylcyclopropanes 11 and 12; and (c) either vinyl or methyl migration toward the carbene center produces the isomeric 2, 4-hexadienes, 13, 14 and 15.[43]

Table 5 lists the product distributions obtained from pure 5 and 6 on thermolysis at several temperatures (sealed tubes in degassed n-pentane solutions, or by direct injection into the heated injection port of a vapor phase chromatograph), and on direct irradiation at 313.0 nm in pentane solutions. Also, shown in Table 5 is the product distribution obtained on pyrolysis of an alternate precursor (23) to carbenes 24 and 25 (vide infra). The strong dependence of the product distribution on pyrolysis temperature is graphically shown in Figure 4. The product distributions did not vary with the extent of conversion.

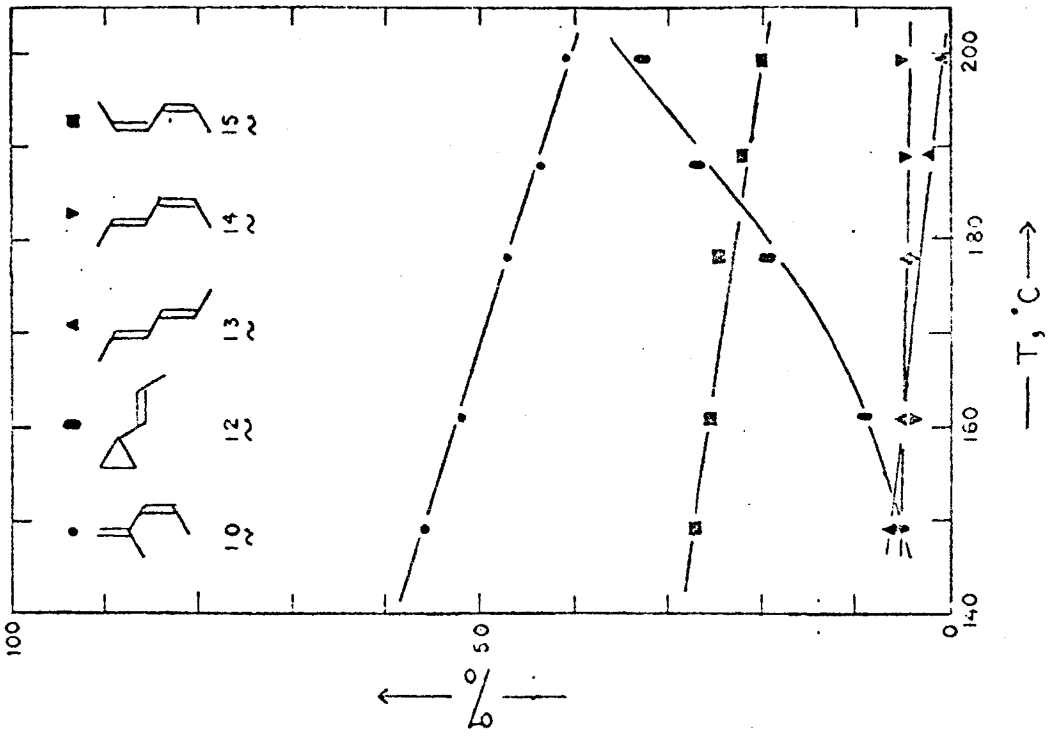
In order to more accurately assess the inherent reactivity of carbenes 24 and 25, the tosylhydrazone sodium salt precursor 23 was prepared by the synthetic route outlined in Scheme 8. Details of the methods are given in the Experimental section. Decomposition of 23 as a suspension in tetraglyme by direct injection into the hot glpc inlet port[44] afforded a mixture of hydrocarbons 9-15. The distribution of products under these conditions is listed in Table 5. No significant change in the product distribution was observed in the temperature range 180-240°.

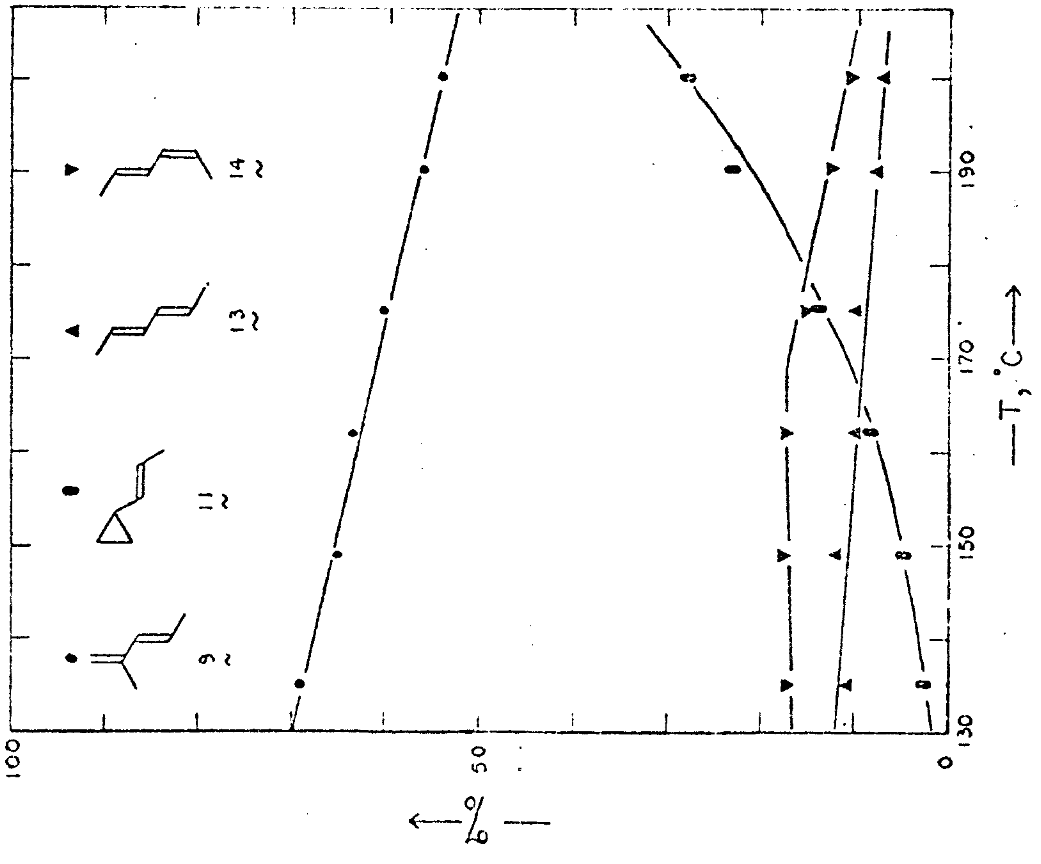
Table 5. Product Distributions Observed on Decomposition of 5, 6 and 23

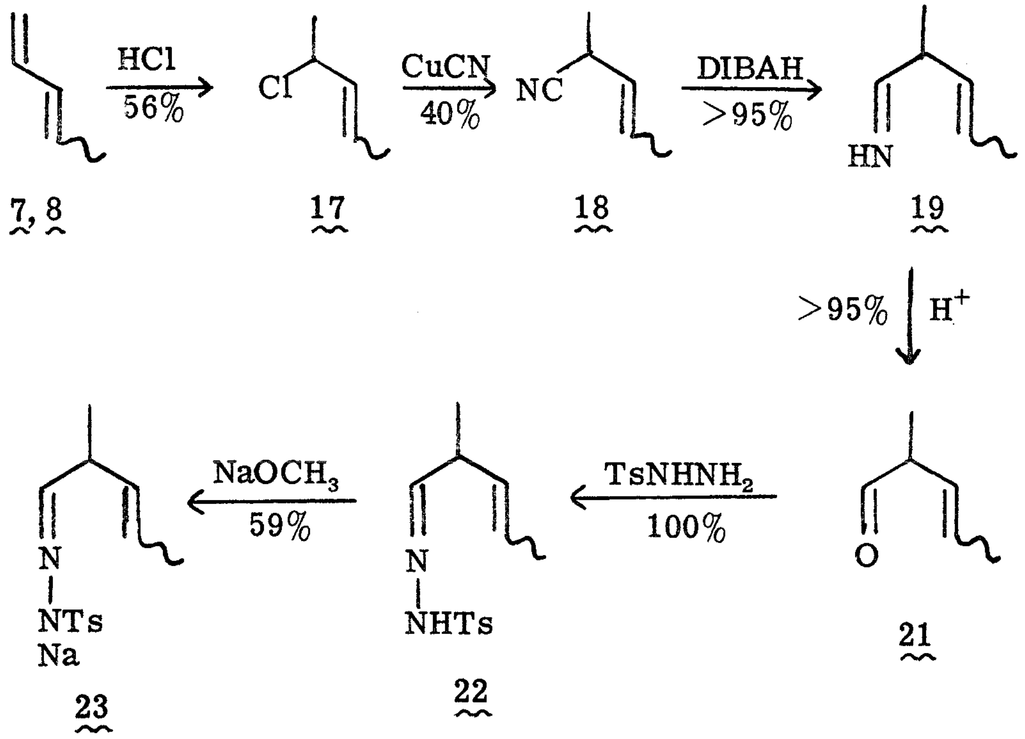
Compound	Decomposition Conditions	Products,[a] %						
		9	10	11	12	13	14	15
5	Δ, 135°	69.3	–	2.8	–	10.4	17.4	–
	Δ, 149°	65.1	–	4.9	–	12.3	17.7	–
	Δ, 162°	63.8	–	9.0	–	9.6	17.5	–
	Δ, 175°	60.4	–	14.4	–	10.0	15.3	–
	Δ, 190°	56.4	–	23.4	–	7.8	12.8	–
	Δ, 200°	54.1	–	28.1	–	6.9	11.0	–
	hν, 313 nm	57.7	–	5.8	–	15.0	21.5	–
6	Δ, 149°	–	55.9	–	4.9	6.3	5.8	27.1
	Δ, 161°	–	51.9	–	9.0	5.3	3.5	25.3
	Δ, 178°	–	47.2	–	19.5	4.4	4.3	24.6
	Δ, 188°	–	43.6	–	27.1	2.3	4.8	22.2
	Δ, 199.5°	–	41.1	–	33.0	0.7	5.3	19.9
	hν, 313 nm	–	47.6	–	23.5	4.6	12.4	11.9
23	Δ, 180°	61.6	13.2	3.6	0.6	9.9	8.3	2.8
	Δ, 200°	61.6	13.3	3.6	0.5	9.7	8.8	2.6
	Δ, 240°	63.2	10.6	4.3	0.8	9.8	9.2	2.1

[a] Products are stable to the reaction conditions employed.

Figure 4. Product distributions obtained on decomposition of (a) pyrazoline **5**, and (b) pyrazoline **6** at several temperatures.


10
12
13
14
15
100
50
0
% →
140
160
180
200
— T, °C →


9
11
13
14
100
50
0
% →
130
150
170
190
— T, °C →



Scheme 8

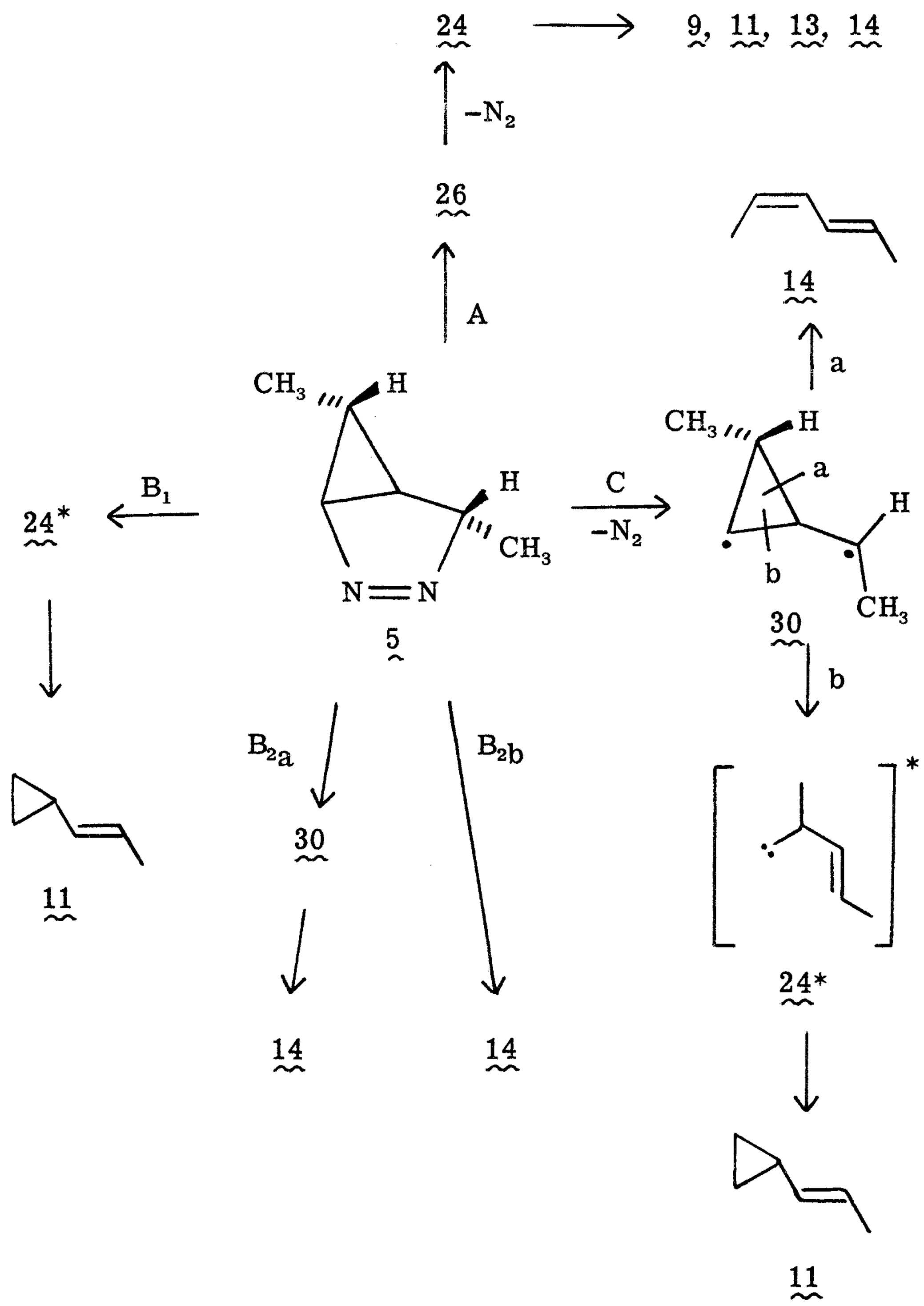
As noted for the triplet sensitized photochemical decomposition of mono-methyl pyrazolines 3 and 4, benzophenone sensitization of 5 or 6 resulted in only pyrazoline disappearance. No diene products were found, even after complete destruction of starting material.

Rate data for the decomposition of pyrazolines 5 and 6 were not directly obtained. However, estimated decomposition half-lives were obtained at several decomposition temperatures (see Experimental). The approximate value for the disappearance rate of 5 at 119° is 2×10^{-3} sec^{-1}, which is four times the value observed for the mono-methyl analog, 3 (4.8×10^{-4} sec^{-1}). At 147.5°, the estimated ratio of half-lives, $\tau_{1/2}(5)/\tau_{1/2}(6)$, is 1/13. This ratio implies a rate ratio at 147.5° of $k_5/k_6 = 13/1$, which is lower than the ratio k_3/k_4 (at 119°): 30/1.

Mechanistic Considerations

The marked dependence of the product distributions from both 5 and 6 on the decomposition temperature can be best rationalized by invoking multiple pathways for the loss of pyrazoline. A detailed analysis of the data allows several inferences concerning these mechanistic alternatives.

The mechanistic alternatives which will be discussed are summarized in Scheme 9, for the decomposition of 5. A similar scheme could be drawn for 6. Path A is a formal retro-1,3-dipolar addition reaction, affording a ring-opened diazo compound, which is not isolated under the reaction conditions. Loss of nitrogen from 26 produces carbene 24, which decays to products. Path B_1 is visualized as a direct route from 5 to a carbene, 24^*, without the intermediacy of diazo compound 26. The carbene 24^* is thought to be formed in a non-equilibrium geometry which may result in a higher fraction of C–H insertion than is observed from the carbene 24 derived from diazo compound 26. Paths B_2 (a and b) are, respectively, diradical and concerted routes to hexadiene products. Path C involves initial diradical formation followed by partitioning to a carbene with initial non-equilibrium geometry (24^*) and to hexadienes.


24
9, 11, 13, 14
$-N_2$
26
14
A
a
CH_3
H
H
CH_3
N
N
5
B_1
24*
C
$-N_2$
CH_3
H
a
H
b
CH_3
30
b
11
B_2a
B_2b
30
*
24*
14
14
11

Scheme 9

The discussion which follows is based on several major assumptions. The primary one is that the Path A component of the pyrazoline decomposition can be accounted for in terms of the observed product distribution obtained from the temperature-independent decomposition of the tosylhydrazone sodium salt 23. Further it is assumed that the product distribution from 23 can be meaningfully dissected into parts which represent the products of decomposition of the isomeric diazo compounds 26 and 27 and the derived carbenes 24 and 25. Finally, it is suggested that any differences found between the observed product distributions from pyrazolines 5 and 6 and the estimated contributions due to the assumed Path A reaction component represent real mechanistic alternatives for the decomposition of the pyrazolines.

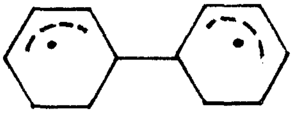
Path A Diazo Compound Formation

Of primary importance is the observation that the decomposition of the epimeric pyrazolines proceeds with a high degree of stereoselectivity (c.f., Schemes 4 and 5, and Table 5). If the not unreasonable assumption is made that in carbenes 24 and 25, as derived from the tosylhydrazone precursor 23, a similar geometrical selectivity obtains (that is, the initial geometry about the remote C–C double bond is retained in the olefinic products), then an estimate of the natural decay characteristics of the diazo compounds 26 and 27 can be made. The carbene precursor 23 is estimated by nmr to be a mixture of 18-23% *cis*-23 and 77-82% *trans*-23. This estimate is based on careful integration of the vinylic protons and vinyl methyl resonances of synthetic intermediates **18** and **21**. It is further assumed that formation of the isomers of 2, 4-hexadiene occurs largely by vinyl migration toward the carbene center rather than *via* methyl migration,[45] and that the vinyl migration is governed by the relative thermodynamic stabilities of the hexadiene products.[46] An ancillary assumption is that the total amount of *cis, cis*-2, 4-hexadiene is derived from *cis*-**23**. From the data in Table 5 and the assumptions above, the product distributions from **26** and **27** are estimated. Table 6 lists the results of this analysis.

Table 6. Estimated Product Distributions from Diazo Compounds **24** and **25**

Carbene	Product, %						
	9	**10**	**11**	**12**	**13**	**14**	**15**
24	77.7	–	4.5	–	11.9	5.9	–
25	–	63.9	–	2.4	1.4	19.7	12.5

Comparison of the estimated distributions of Table 6 with the observed pyrazoline distributions (Table 5) indicates that at none of the temperatures of decomposition of **5** or **6** does the observed distribution correspond to the estimated one. In particular, it is noted that the yield of *cis, trans*-2, 4-hexadiene (**14**) from **5**, and of *cis, cis*-2, 4-hexadiene (**15**) from **6** is substantially greater than the estimated yield. Also, at elevated temperatures, the amounts of a biradical such as VII, indicated below, as an intermediate in the thermal isomerization of II and IV to I and III respectively. It is



VII

possible that such a species is formed in both thermal and γ radiation processes, in the latter case from VI by electron capture. Alternatively VI may ring close prior to neutralization to give the same I:III distribution as VII. These alternative radiation chemical processes are represented by reactions [9'] and [9''] respectively. D_2^+ is the representation for a cationic Diels-Alder species produced by ring closure of intermediate VI. Lacking evidence, these proposed possible reaction pathways are only conjecture.

If an electron scavenger S is added to the diene, additional reactions become possible.

$$e^- + S \rightarrow S^- \qquad [11]$$

$$CHD^+ + S^- \rightarrow CHD^3 + S \qquad [7a]$$

$$(CHD)_2^+ + S^- \rightarrow \text{thermal dimers} \qquad [9a]$$

Since reaction [10] proceeds from CHD^3 with 100% efficiency as

Table 7. Deviations of the Decomposition of Pyrazolines 5 and 6 from a Diazo Compound Mechanism

		Product, %[a]						
Compound	T(°C)	9	10	11	12	13	14	15
5	135	-8.3	–	-1.6	–	-1.5	+11.5	–
	149	-12.6	–	+0.4	–	+0.4	+11.8	–
	162	-13.9	–	+4.5	–	-2.6	+11.6	–
	175	-17.3	–	+9.9	–	-1.9	+9.4	–
	190	-21.7	–	+18.9	–	-4.1	+6.9	–
	200	-23.6	–	+23.6	–	-5.1	+5.1	–
	[hν]	-20.0	–	+0.7	–	+3.1	+15.6	–
6	149	–	-8.0	–	+2.5	+4.9	-13.9	+14.6
	161	–	-8.6	–	+7.3	+4.0	-16.3	+13.7
	178	–	-16.7	–	+17.1	+3.0	-15.4	+12.1
	188	–	-20.3	–	+24.7	+0.9	-14.9	+ 9.7
	199.5	–	-22.8	–	+30.6	-0.7	-14.4	+7.4
	[hν]	–	-16.3	–	+21.1	+3.2	-7.3	-0.6

[a] The values listed are: % product observed (at temperature T) minus the calculated product % based on only a diazo mechanism. See Tables 5 and 6.

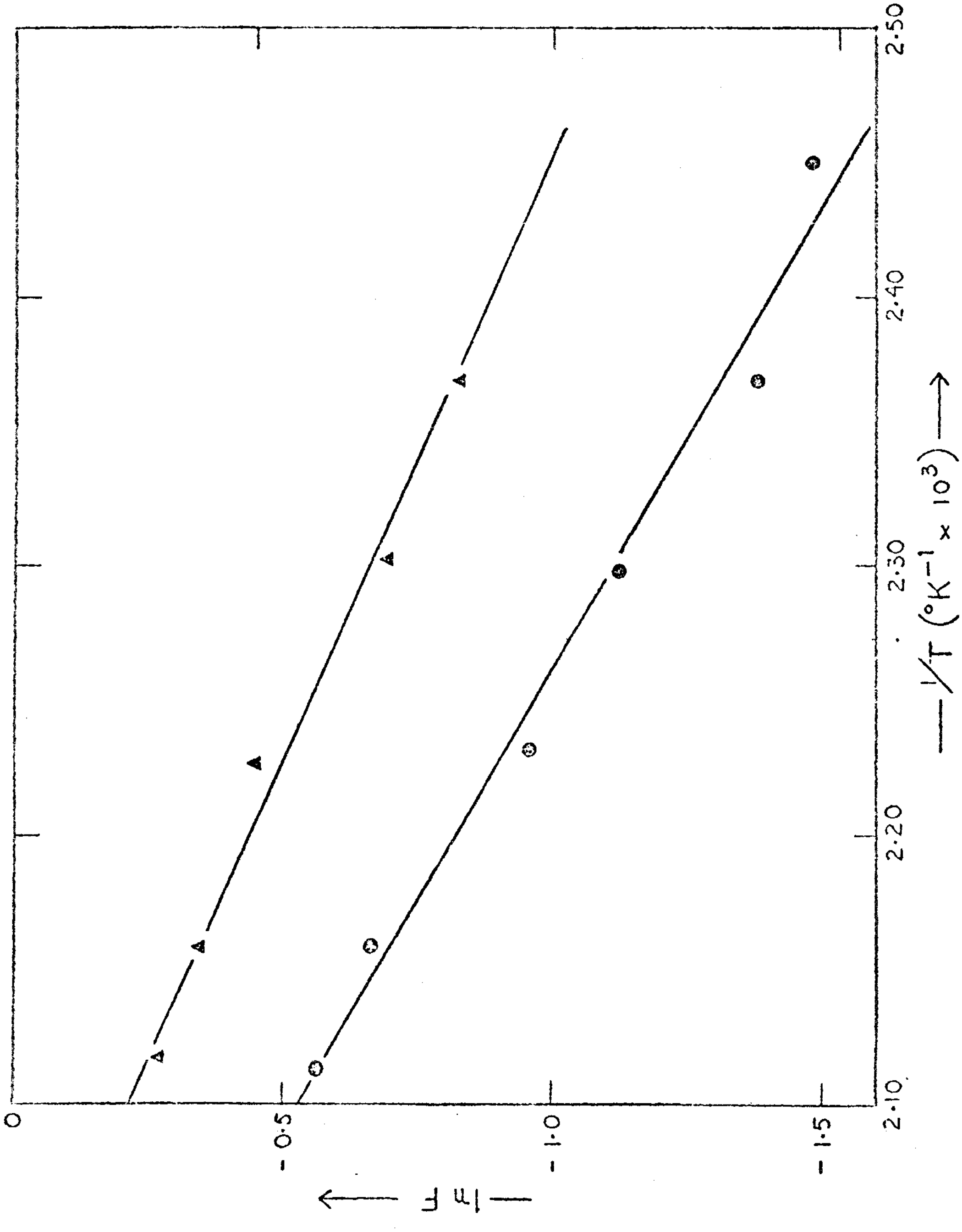
Table 8. Fraction of Pyrazoline Decomposition that does not Procede *via* Diazo Intermediates

Compound	T(°C)	Sum[a], %	Fraction[b]
5	135	22.9	0.229
	149	25.2	0.252
	162	32.6	0.326
	175	38.5	0.385
	190	51.6	0.516
	200	57.4	0.574
	[hν]	39.4	0.394
6	149	43.9	0.439
	161	49.9	0.499
	178	64.3	0.643
	188	70.5	0.705
	199.5	75.9	0.759
	[hν]	48.6	0.486

[a] Sum of the absolute values of the deviations from a diazo compound mechanism: Table 7.

[b] Ratio of the "Sum" column to the observed yield (by definition 100%) at each temperature.

Figure 5. Arrhenius plot for the decomposition of pyrazolines **5** (●) and **6** (▲): ℓn F *vs.* 1/T (°K), where F is the estimated fraction of decomposition which proceeds *via* diazo compounds **26** and **27**.


0
- 0·5
- 1·0
- 1·5
- ln F →
2·10
2·20
2·30
2·40
2·50
1/T (°K⁻¹ × 10³) →

A least-squares treatment of the data gives the kinetic parameters: E_a(diazo) - E_a(other paths) = -5.8 kcal/mole for 5, and -4.6 kcal/mole for 6; the calculated activation entropy differences (high energy path minus diazo path) are 11 eu (5) and 9.2 eu (6). The least-squares correlation coefficients for the data were 0.9901 (5) and 0.9941 (6).

The treatment outlined above, while perhaps seriously handicapped by the many assumptions made, serves to emphasize two main points. First, the component of the pyrazoline decompositions which affords diazo compounds 26 or 27 is a lower energy pathway because of compensating effects: the activation energy for this path is lower than for alternative routes, but the entropy change along the reaction coordinate for the path leading to diazo compound is less positive than the change along other paths. Second, the plots shown in Figure 5 are linear, suggesting that the mechanistic alternatives to the diazo derived reaction component are of similar energies, or that they arise from a common intermediate. Deviation from the observed linearity is demanded if the paths leading to excess cyclopropylpropene and the appropriate 2, 4-hexadiene isomer are radically different.

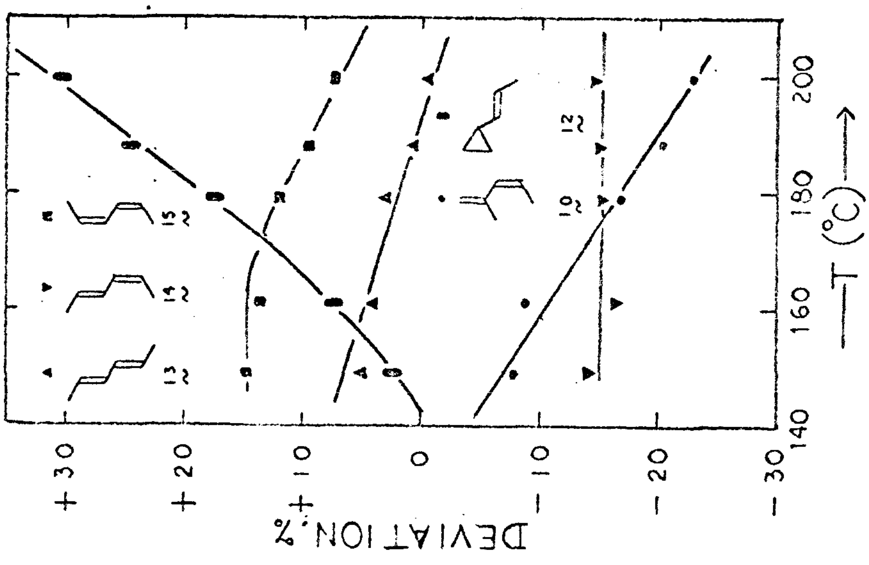
Although the kinetic treatment employed above gives some insight into the energetics of the pyrazoline decompositions, no information as to the nature of the "high energy" intermediate(s) is obtained. The lower energy paths have been assumed to involve, exclusively, thermally equilibrated diazo compounds. The sense of "thermally equilibrated" is that the diazo compounds formed by ring opening of the pyrazolines possess lifetimes sufficiently long to allow collisional stabilization to an equilibrium geometry before nitrogen loss to yield carbenes occurs. That is, the diazo intermediates are geometrically relaxed before they collapse to carbenes, so that the initial geometry of the carbenes derived by this route is nearly the same for all decomposition temperatures and leads to a distribution of products which is similar for all conditions. This view is supported by the observation that the distribution of products obtained on pyrolysis of the tosylhydrazone salt is essentially, if not entirely, temperature independent in the range examined.

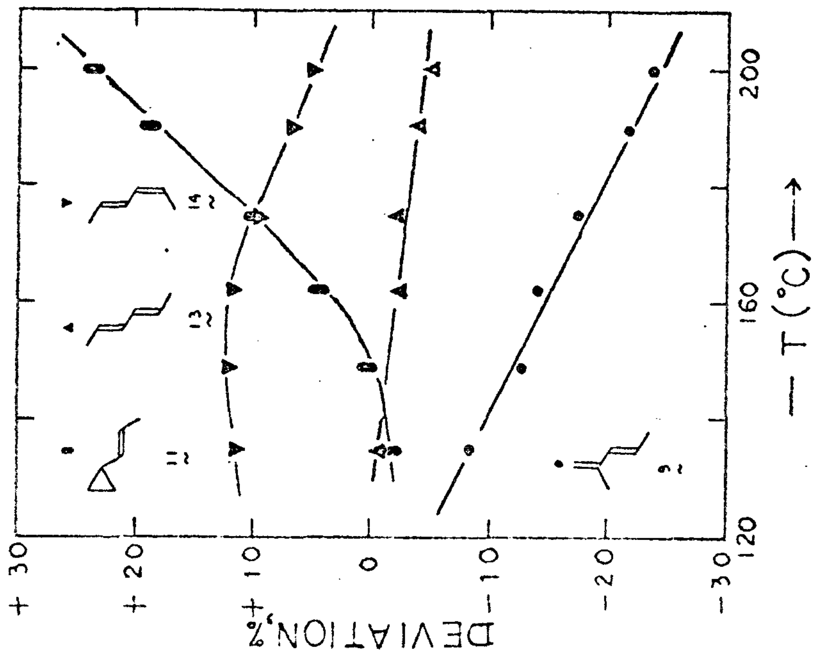
It has been assumed, in the treatment outlined above, that the decay characteristics of the diazo compounds and carbenes derived from the pyrazoline decompositions are those of the diazo compounds and carbenes presumably generated by pyrolysis of the tosylhydrazone precursor 23. If these assumptions were entirely correct, then the deviations from the diazo derived product distribution (as estimated above), for all products which arise only from the relaxed intermediate, would be expected to parallel one another as a function of the decomposition temperature. Conversely, those products which can be obtained by more than one path would not be expected to deviate from the estimated diazo component in a parallel fashion. A graphical representation, as a function of temperature, of the calculated deviations from the component of the reaction which represents the intermediacy of diazo compounds, for both 5 and 6, is shown in Figure 6; the figure is drawn from the data listed in Table 7.

For the decomposition of pyrazoline **5**, Figure 6(a) indicates that at elevated temperatures, the deviations of the observed yields of *cis, trans*-2, 4-hexadiene (**14**) and 2-methyl-*trans*-1, 3-pentadiene (**9**) from the estimated yields of products from diazo compound **26** are roughly parallel, but that they diverge near the low temperature limit of the experimental conditions. Similarly, the deviation found for *trans, trans*-2, 4-hexadiene (**13**) is roughly parallel over most of the temperature range studied. The deviation of the yield of *trans*-1-cyclopropylpropene (**11**) from the expected yield is, however, clearly not parallel. The implication of these results is that **11** and, at low decomposition temperatures, **14** arise, at least in part, by pathways that do not involve the thermally equilibrated diazo compound **26**. Moreover, product **9**, and probably **13**, arise for the most part from **26**.

Similar analysis of Figure 6(b) indicates that, for the decomposition of **6**, product **12** and, at low temperatures, **15**, are formed, at least in part, *via* paths which do not involve ring opening to **27**, while products **10** and **13** are derived largely from this intermediate. The formation of *cis, trans*-2, 4-hexadiene (**14**) from **6** appears to be anomalous: the deviation of the observed yield from the calculated one is constant over the temperature range studied. (Similarly, the deviation found for the yield of **13** from **5** was not strictly parallel to the calculated one.) The possibility that **14** may arise from **6** by

Figure 6. Deviations of the observed product distribution from (a) pyrazoline 5 and (b) pyrazoline 6 from the estimated contribution of diazo intermediates 26 and 27, as a function of decomposition temperature. See text.


DEVIATION,%
+30
+20
+10
0
−10
−20
−30
140
160
180
200
T (°C)
13
14
15
10
12

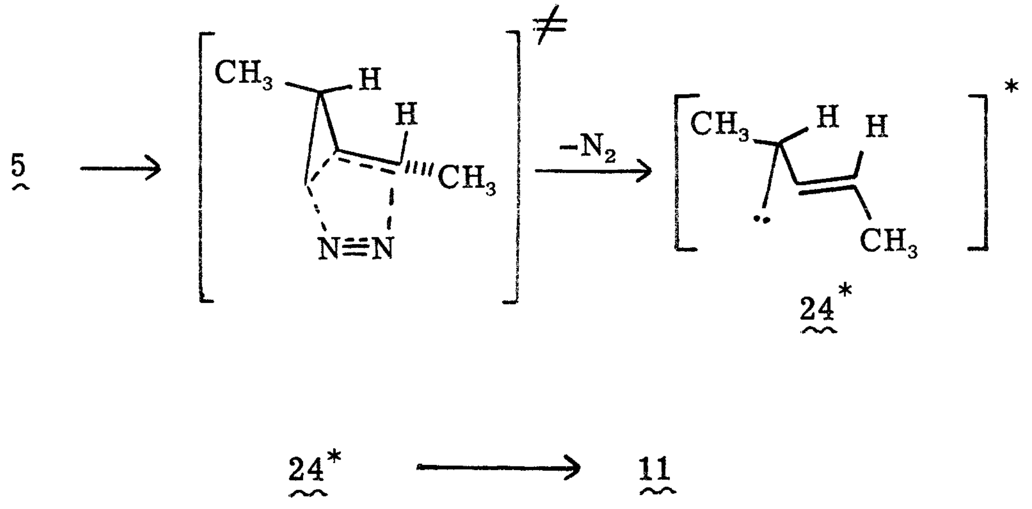

DEVIATION,%
+30
+20
+10
0
−10
−20
−30
120
160
200
T (°C)
11
13
14
9

paths other than ring opening to 27 (and that 13 may arise from 5 in part by other mechanisms) cannot be dismissed.

Several mechanistic interpretations of the dependence of the pyrazoline product distribution on the decomposition temperature are possible. The data and calculations presented above suggest that in addition to a decomposition path which proceeds *via* thermally equilibrated diazo compounds 26 and 27, either one or two other mechanistic alternatives must be invoked in order to fully rationalize the experimental observations. The ensuing discussion will consider, first, the possibility that two pathways, in addition to the relaxed carbene path, are involved in the pyrazoline decomposition, and, second, that only one other intermediate exists along the reaction coordinates connecting reactants and products.

Path B_1 Non-Equilibrium Carbene Formation

Of the two possible alternatives to diazo compound intermediates, the one which may lead to cyclopropylpropenes (11 and 12) is first considered. The most economical route to these products is envisioned as proceeding *via* direct formation of a highly energetic carbene, without the intermediacy of ring-opened diazo compounds 26 and 27, followed by rapid and preferential insertion of the carbene center into a C–H bond of the adjacent methyl group. This mechanism is shown in Scheme 10 for the decomposition of 5. The carbene 24* is supposed to be formed, initially, in a non-equilibrium geometry in which the carbene center and the alpha-methyl group are in relatively fortuitous proximity: at least they are presumed to be



Scheme 10

in relative positions which are (mechanistically) significantly different from the equilibrium geometry considered in the discussion of the Path A mechanism.

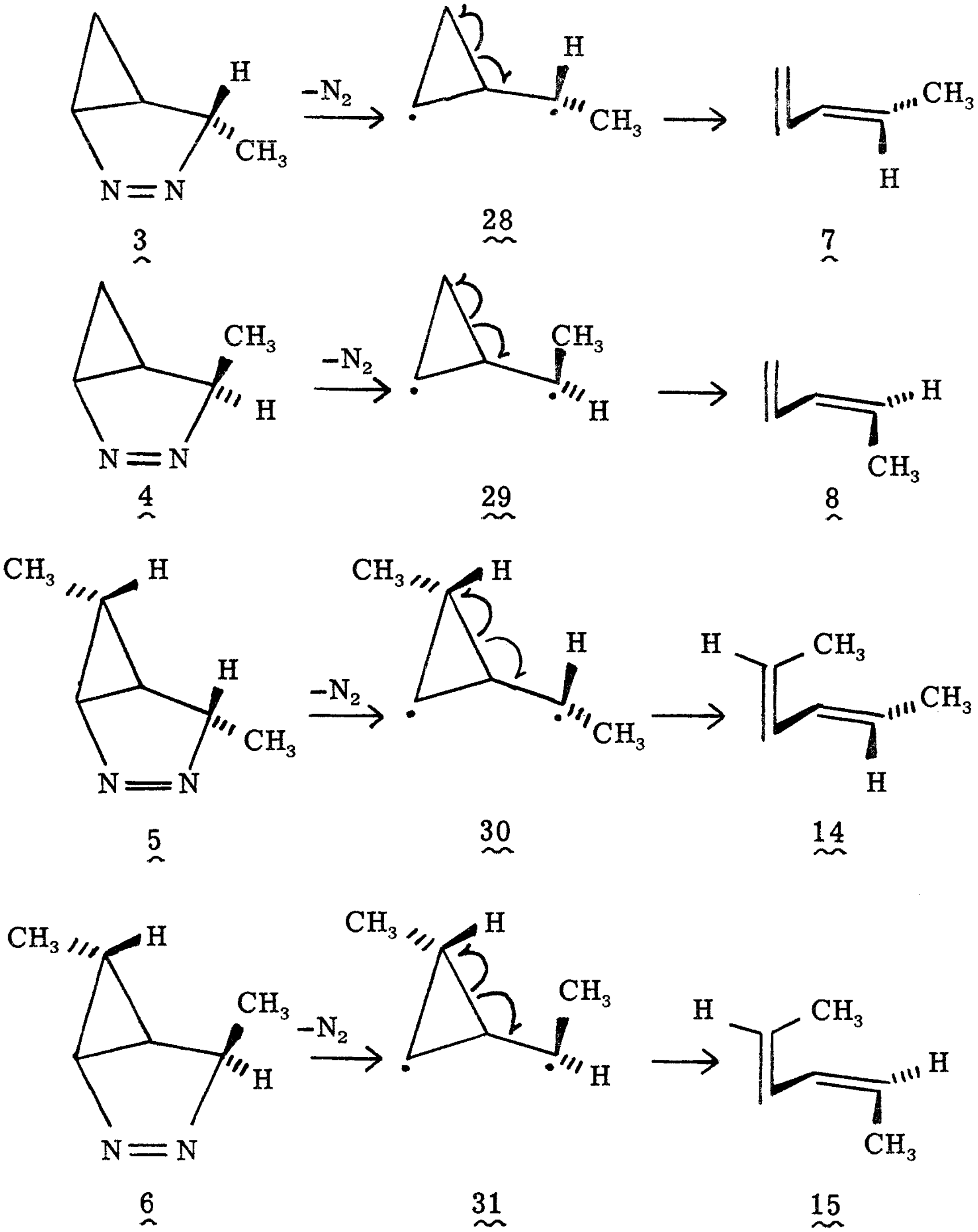
In general, the reactions of carbenes are strongly exothermic.[47] Therefore, the transition state for the insertion of a carbene center into a C–H bond might be expected to reflect the geometry of the initial carbene and to be largely independent of the relative stabilities of the various possible products.[48] In addition, Gutsche[49] has recently shown that the relative probabilities of intramolecular carbene insertion into various C–H bonds of a norbornyl-substituted *o*-tolyl carbene are governed not only by the geometric proximity of the carbene center and the C–H bond with which it reacts, but also by the angle of approach of the carbene toward the bond. A C–H bond which is disposed in such a way as to allow a perpendicular approach of the electrophilic carbene is more likely to suffer attack by the carbene than is a C–H bond, at approximately the same initial distance from the divalent center, which does not allow such a favorable perpendicular approach. It is suggested, therefore, that quite small differences in the initial geometry of the carbene 24*, relative to the thermally equilibrated geometry of 24, can induce substantial changes in the reactivity of 24*.

Reactive carbenes which can react intramolecularly are in general extremely difficult to trap intermolecularly,[50] suggesting that the unimolecular reaction rates may be competitive with bimolecular collisions with solvent or other trapping reagent. Similarly, the reactions of carbenes which are not capable of intramolecular decay (e. g. methylene) are rather unselective toward the mode of intermolecular trapping. In the liquid phase methylene attacks primary, secondary and tertiary C–H bonds with nearly the same efficiency.[51] It appears that the intramolecular reactions of reactive carbenes can be extremely rapid, and may be expected to be competitive with thermal equilibration of the initially generated species with the environment. Conversely the generation of carbenes 24 and 25 *via* decomposition of the sodium salt of the tosylhydrazone 23 presumably occurs through initial formation of diazo compounds 26 and 27, which are supposed to become thermally equilibrated with the surroundings before collapse to the carbenes.

Path B_{2a} Diradical Intermediates

An intermediate which can, in principle, be formed during the decomposition of pyrazolines 5 and 6, and which can lead to formation of the isomeric 2, 4-hexadienes is a diradical. Within the context of the present study, the diradicals which are generated by decomposition of 5 and 6 (or from 3 and 4) are required by the nature of the products observed to decay with a high degree of stereoselectivity. Scheme 11 illustrates the processes which must occur in order to account for the experimental observations. The specificity of the overall observed changes is so high that the intermediacy of diradicals 28-31 seems, on the surface, unlikely. However, a realistic estimate of the activation energy necessary to break the cyclopropane C–C bond is difficult to make. The transformation, diradical to diene, is estimated (*vide infra*) to be approximately 75 kcal/mole exothermic (for the parent, unsubstituted diradical collapsing to butadiene). Also, the development of favorable pi bonding character at the various centers would appear to be likely without severe distortion of the initial diradical geometry. Thus, the energy necessary for scission of the C-5–C-6 bond may be quite low.

In order to rationalize the presumed inversion of initial pyrazoline stereochemistry at C-6, it is necessary to invoke selective rotation about the C-1–C-6 bond, concomitant with scission of the C-5–C-6 bond. This rotation may be facilitated by effective buttressing of the two *endo*-substituents at C-4 and C-6. Molecular


H
CH3
N=N
3
-N2
H
CH3
28
CH3
H
7
CH3
H
N=N
4
-N2
CH3
H
29
H
CH3
8
CH3
H
H
CH3
N=N
5
-N2
CH3
H
H
CH3
30
H
CH3
CH3
H
14
CH3
H
CH3
H
N=N
6
-N2
CH3
H
CH3
H
31
H
CH3
H
CH3
15

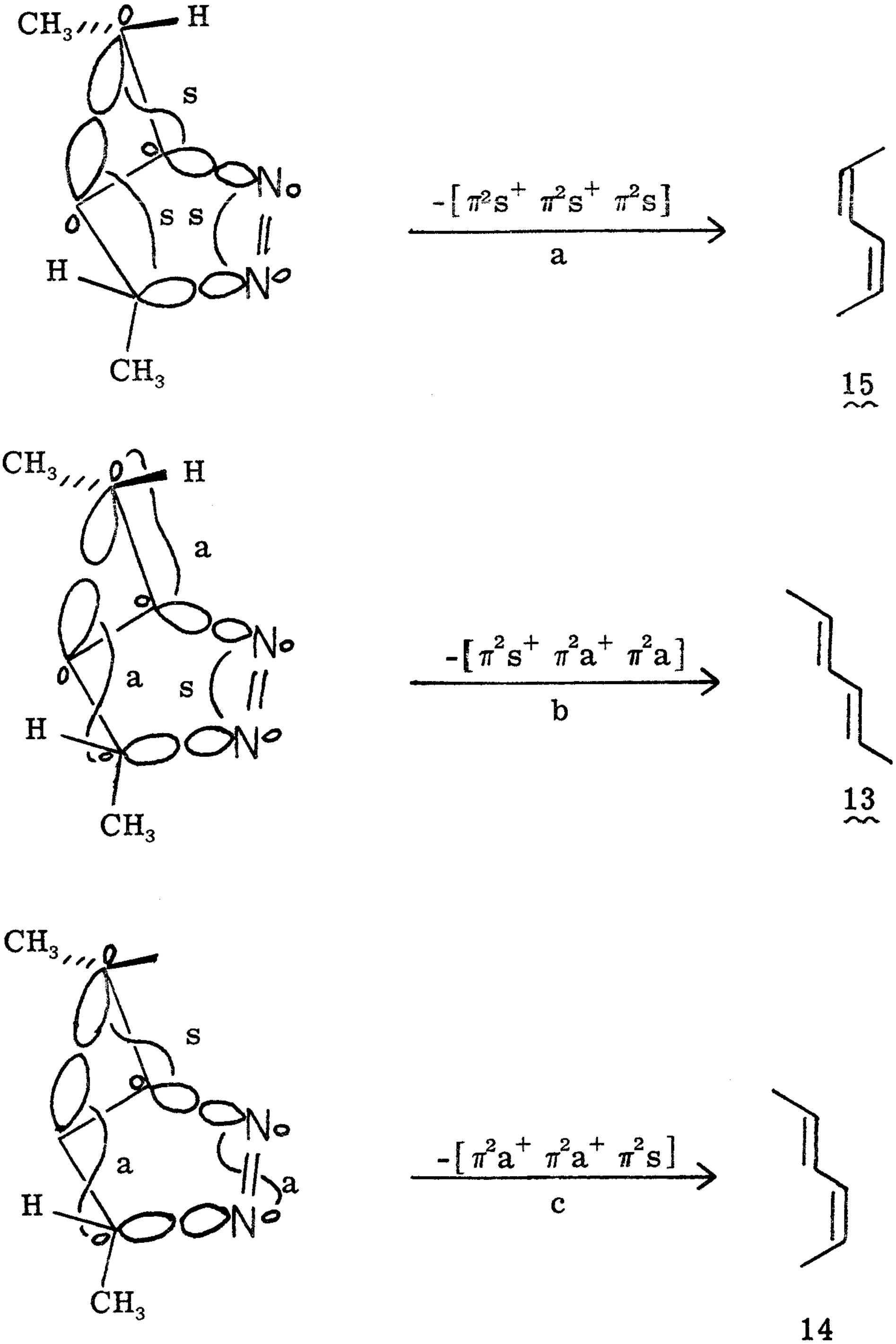
Scheme 11

models indicate that these two groups are nearly within van der Waals radii of one another.

Path B_{2b} Concerted Decomposition

An alternate mechanism for the formation of the 2, 4-hexadienes is a formally concerted rearrangement. The treatment of Woodward and Hoffmann[52] predicts that six electron, [2 + 2 + 2]-cycloadditions (or cycloreversions) are symmetry allowed thermal reactions if the process occurs either totally suprafacially, or with two antarafacial components and one suprafacial one. In the present system, the consequences of the three allowed thermal cycloreversions are shown in Scheme 12, for pyrazoline 5. Similar treatment of the decomposition of 6 indicates that, for the processes a, b and c, the products are 14, 14 and 15, respectively.

The treatment of Woodward and Hoffmann[52] suggests that, for [2 + 2 + 2] thermal retrogressions in systems with initial cyclohexane conformations, the development of favorable overlap between incipient π bonds is most rapid in the totally suprafacial allowed mode. Thus, this mode is expected to be most favored in these systems. In the present system, the initial geometry is radically different from the geometry considered by Hoffmann and Woodward. An examination of molecular models suggests that in the [3. 1. 0] pyrazoline system, either allowed odd-s thermal process contributes approximately equally to the development of favorable overlap early on the reaction coordinate. Thus, no choice can be made between the alternatives on prima-facie evidence.



15

13

14

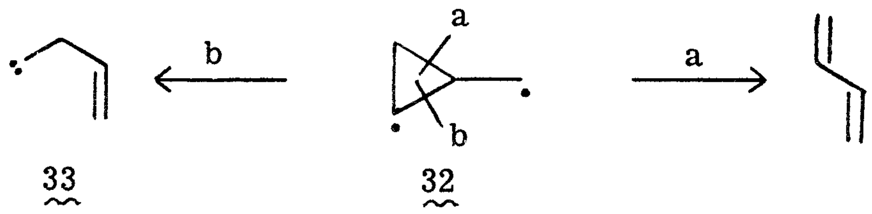
Scheme 12

The least likely allowed path would appear to be (c) of Scheme 12. In order to accommodate the required antarafacial elimination of nitrogen, a large twisting motion must occur in the five-membered ring. One consequence of this motion would be a considerable diminution of the π-bond order in the N–N double bond.[53b] In the only reported study of a [2+2+2] reversion in a suitably labeled cyclic azo system, Berson and Olin[53] find that the *trans* elimination of nitrogen does not occur. Rather, the results (of the thermal reaction) are compatible with the allowed, totally suprafacial mode. The photochemical nitrogen elimination, however, is not so conveniently analyzed.

In the present system, the analysis of the product data given previously suggested that, from pyrazoline **5**, *cis, trans*-2, 4-hexadiene (**14**) was formed in excess of the amount predicted for a simple mechanism requiring initial diazo compound formation, while **6** gave excess *cis, cis*-2, 4-hexadiene (**15**). That is, those products formed are the ones predicted by (c) of Scheme 12. The most reasonable conclusion is that these products are not formed by an orbital symmetry allowed path. However, it is apparent from the nature of the products of the decomposition of the epimeric pyrazolines that, even in the transition state for formation of diazo compounds **26** and **27**, there is substantial *endo*-directed rotation about the C-4–C-5 bond, and therefore a concomitant puckering of the five-membered ring. Thus, some of the extrasymmetric[53b] inhibition to path (c) of Scheme 12 may be overcome by allowing the orbital symmetry allowed path to partition from the path which leads to diazo compounds fairly late along the reaction coordinate.

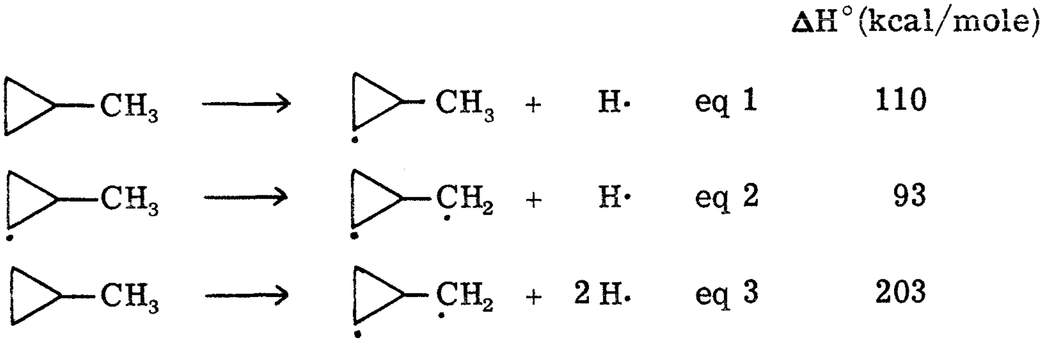
Path C. Diradical Partitioning

As alluded to previously, there is, in principle, a third possibility which may rationalize the deviations that are observed in the decomposition of pyrazolines **5** and **6** from the product distribution predicted from consideration of only a simple mechanism proceeding *via* diazo compounds. Diradicals of type **32** can, in theory, decay by either homolytic scission according to path a (Scheme 13), affording butadienes, or as in path b, which yields a carbene, **33**. Application of Bensons's[54] group additivity method for estimation of thermochemical parameters allows a rough estimate of the enthalpy difference between diradical **32** and carbene **33** to be made. The method used is outlined below.



Scheme 13

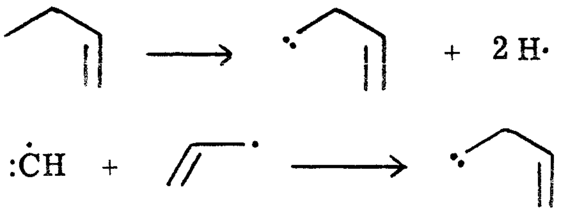
The enthalpy of the reaction (eq 3) is derived from eq 1 and eq 2 using Hess' law. The enthalpy of reaction 1 can be estimated



to be 110 kcal/mole from the (estimated) values: ΔH_f° of the cyclopropyl radical (61 kcal/mole),[55] ΔH_f° of methylcyclopropane (5.7 kcal/mole) and the known standard heat of formation of the hydrogen atom (52.1 kcal/mole). Estimation of the enthalpy change for eq 2 rests on an assumed bond dissociation energy of 93 kcal/mole for a cyclopropyl carbinyl C–H bond; this value is the mean of the literature values for the allyl and ethyl C–H bond dissociation energies.[56] The calculated enthalpy of the reaction depicted in eq 3 is 203 kcal/mole.

The standard state heat of formation of methylene is estimated to be 89 kcal/mole.[57] The enthalpy of the reaction shown in eq 4 is estimated to be 199 kcal/mole from a calculated heat of formation of 1-butene of -0.2 kcal/mole, the (spectroscopically) estimated heat of formation of :$\dot{\mathrm{C}}$H from methylene[58] (92 kcal/mole), the known[59] heat of formation of the allyl radical (40.5 kcal/mole) and an estimated enthalpy for the hypothetical reaction shown in eq 5.

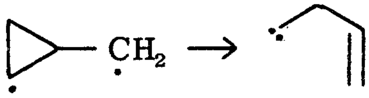
ΔH° (kcal/mole)



eq 4 199

eq 5 -74.5

From the above data, the standard state enthalpies of formation of diradical 32 and carbene 33 can be estimated: $\Delta H_f^\circ(32) = 104.7$ kcal/mole, and $\Delta H_f^\circ(33) = 94.9$ kcal/mole. Thus, the reaction (eq 6) is exothermic by approximately 10 kcal/mole.



32 33

$\Delta H^\circ = -10$ kcal/mole eq 6

Alternatively, the enthalpy of the change depicted in eq 6 may be more simply estimated by considering the strain energy released (27 kcal/mole)[60] by opening of the cyclopropane ring, the energy required to break the cyclopropyl C–C bond[61] (65 kcal/mole), and the energy gained (59 kcal/mole) by the formation of the new C–C double bond.[62] The value calculated in this manner is -22 kcal/mole, in reasonable agreement with the value calculated from estimated heats of formation.

The calculations described above suggest that formation of diradicals (i. e. **28**-**31**) during the course of decomposition of pyrazolines **3**-**6** may also be a source of energetic carbenes such as **24***. The carbene formed in this manner would initially contain 10-22 kcal/mole of excess energy, and, by arguments similar to those given above for the direct formation of **24*** from **5**, the energetic carbene would have an initial geometry which may favor enhanced insertion into a C–H bond of the adjacent methyl group.

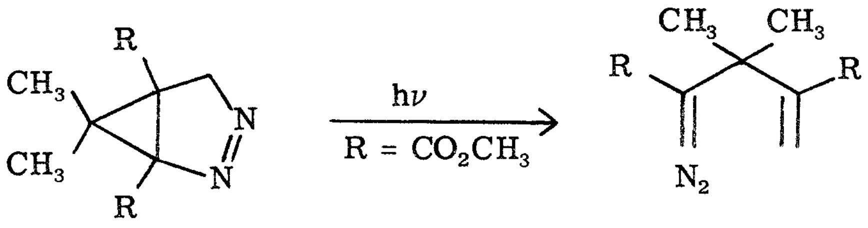
A distinct advantage of the proposed intermediacy of diradicals which can partition between paths leading to diene products and to a carbene is the fact that only one initial intermediate need be formed on decomposition of the pyrazolines **5** or **6**. That is, the initial energy content of the diradical may determine both the degree of partitioning to and the geometry of the carbene which is derived from it, thus accounting for all the observed energy (temperature) dependence of the pyrazoline decomposition. This interpretation is consistent with, but not demanded by the Arrhenius treatment of the data discussed previously.

Comparison to Related Systems and Conclusions

The results reported here and the interpretations given are supported by several reports in the literature concerning the decomposition of cyclic and fused bicyclic azo compounds.

Precedents can be found in the literature for path A decompositions, particularly those initiated photochemically. Franck-Neumann[33] has reported that photolysis of 1, 5-dicarbomethoxy-

6, 6-dimethyl-2, 3-diazabicyclo[3. 1. 0]hex-2-ene, 34, leads to the ring-opened diazo compound 35 as the only isolated product:



34 35

Several simple Δ^1-pyrazolines also afford decomposition products which can be viewed as resulting from formal retro-1, 3-dipolar additions. Rinehart and van Auken[63] found small amounts of methyl tiglate among the photolysis products of cis- and trans-3, 4-dimethyl-3-carbomethoxy-Δ^1-pyrazoline, and McGreer et al.[4] found 4-10% of methyl methacrylate from photolytic decomposition of cis- and trans-3, 5-dimethyl-3-carbomethoxy-Δ^1-pyrazoline. Crawford and Mishra[6] recovered 1.4% 2-methylpropene from the thermolysis products of 4, 4-dimethyl-Δ^1-pyrazoline. None of the workers reports isolation of products derived from secondary reaction of the diazo compounds that are necessarily formed as a consequence of the pyrazoline cleavage.

Recent work by Bergman and co-workers[20, 64, 65] indicates that pyrolysis of 2, 3-diazabicyclo[3. 1. 0]hept-2-enes proceeds through both a diradical and a carbene path,[64, 65] but that the decomposition of the next higher homolog, 2, 3-diazabicyclo[3. 3. 0]-

oct-2-ene probably occurs only by initial diradical formation.[20] Comparison of the results of the present study to those of Bergman *et al.* allow several interesting conclusions. First, the preferred mode of decomposition of the three homologous bicyclic pyrazolines seems to be a delicate function of the inherent ring strain of the systems. No retrograde dipolar addition is observed from the [3.3.0] pyrazoline. A substantial portion of the decomposition of both the [3.2.0] and [3.1.0] systems proceeds *via* carbenes, but much lower temperatures are needed for decomposition of the [3.1.0] pyrazoline than for the [3.2.0]. The distributions of products obtained on pyrolysis of both 2,3-diazabicyclo[3.2.0]hept-2-enes studied by Bergman are temperature dependent. As the decomposition temperature was increased, the percentage of diradical-derived products increased at the expense of the carbene product yield.[64, 65] Linear Arrhenius plots were obtained for both the parent 2,3-diazabicyclo[3.2.0]hept-2-ene (the calculated parameters are: E_a(diradical) - E_a(carbene) = 3.3 kcal/mole and $\Delta\Delta S^{\ddagger}$ (diradical minus carbene) = 3.2 e.u.)[64] and the 6,7-dimethyl-2,3-diazabicyclo-[3.2.0]hept-2-ene system (ΔE_a = 5.2 kcal/mole, $\Delta\Delta S^{\ddagger}$ = 3.4 e.u.)[65] The activation energy differences observed by Bergman and co-workers are similar to those found in the present study, but the activation entropy differences are significantly lower than those calculated for the [3.1.0] pyrazolines.

It seems reasonable to conclude that the decomposition mechanisms of the homologous pyrazolines are qualitatively similar. Although no definitive choice can be made among the various paths originally outlined in Scheme 9, it is suggested that the most attractive alternatives for the dual decomposition routes are those represented as A and C. However, partitioning of the diradical 30 (derived from 5), path C, as the sole route to products, is only scorned because of the precedent reported by Franck-Neumann.[33]

Thermolysis of pyrazolines 3 and 5 is more facile than the decomposition of the epimers 4 and 6. This is in qualitative agreement with the mechanistic requirement that an endo-directed rotation occurs in the (presumed) rate determining ring-opening to the appropriate diazo compounds. Such a rotation would seem to be more hindered in those pyrazolines (4 and 6) in which the C-4 methyl group is oriented endo to the bicyclic system than it would be when the bulky group is positioned exo, as in 3 and 5.

Photolysis of pyrazolines 5 and 6 yields product distributions (Table 5) which do not strictly correspond to any one of the thermal distributions. Pyrazoline 5 affords trans, trans- and cis, trans-2, 4-hexadiene (13, and 14, respectively) in relatively larger amounts than are found under any of the thermal conditions. In particular, the yield of 14 is considerable. These results are compatible with increased diradical formation on photo-excitation, relative to the amount which may be generated thermally. However, if a similar photochemical path obtains for pyrazoline 6, it is necessary to invoke preferential partitioning of the initially formed diradical **31** to a carbene, **25***, which does not possess an equilibrium geometry, since direct irradiation of **6** affords moderate yields of C-H insertion product **12** in addition to substantial amounts of **14**. The photochemical yield of *cis, cis*-2, 4-hexadiene, **15**, is lower than the thermal yields. Comparison of the photochemical product distributions of both **5** and **6** to the estimated distribution obtained from the intermediate diazo compounds **26** and **27** (Table 6) supports the qualitative conclusions suggested above.

The results of the present study strongly implicate carbene intermediates in the decomposition, both thermal and photochemical, of alkyl-substituted derivatives of the 2, 3-diazabicyclo[3. 1. 0]hex-2-ene skeleton. The observation that such intermediates participate in the thermolysis of these pyrazolines is unique. It is also of interest that stabilizing groups, such as carbomethoxy (c. f. reference 33), are apparently not required to render the formal 1, 3-dipolar cycloreversion path favorable. The general requirements for this mechanism are suggested to be a labile C–N bond, and a relatively weak internal C–C bond, such as those found at the ring fusion in the present system and in the pyrazolines studied by Bergman.[64, 65]

The interesting, but unexpected, chemistry observed in this study necessarily complicates any attempt to assess the inherent reactivity of diradicals such as **28**-**31**. Thus the results reported here do not allow any definitive assessment of the suggestion of Saltiel[23] concerning the involvement of "cyclopropyl methylene" diradicals in the photochemical *cis*-*trans* isomerization of acyclic, conjugated dienes. However, several of the tentative conclusions of this research may be germane. First, if diradicals **28**-**31** are intermediates in the decomposition of pyrazolines **3**-**6**, the data presented argue strongly that the lifetimes of such diradicals are very short, perhaps significantly short on the scale of bimolecular collision. Further, these diradicals may decay by collapse to carbene species as well as to dienes. No such carbene products have been reported in the photochemistry of simple dienes.

EXPERIMENTAL

General

Infrared spectra were obtained on a Perkin Elmer 257 Grating Infrared Spectrometer. Nuclear magnetic resonance spectra were measured on a Varian A-60A Spectrometer. Ultraviolet spectra were measured on a Cary 14 Recording Spectrometer. Melting points were obtained on a Thomas-Hoover Capillary Melting Point Apparatus and are uncorrected. GC-MS experiments were performed by West Coast Technical Service, San Gabriel. A Hewlett-Packard 700 (flame ionization detection) equipped with a Model 7127A strip chart recorder was employed for all analytical glpc. Preparative glpc was accomplished on a Varian Aerograph Model 90P. A list of glpc columns used in this study is given below. Experimental conditions used are stated at the appropriate points in this section.

Glpc Columns

Column A:	22' × 1/8" SS 25% β, β'-oxydipropionitrile on Chromosorb W (60/80 mesh), NAW
Column B:	Tandem column: Column A plus 15' × 1/8" SS 25% β, β'-oxydipropionitrile / 5% $AgNO_3$ on Chromosorb W (60/80)
Column C:	12' × 1/8" SS 10% UC-W98 on Chromosorb W (80/100), HMDS treated
Column D:	6' × 1/8" SS 10% UC-W 98 on Chromosorb W (80/100), HMDS

Column E: 20' × 3/8" Cu 25% β, β′-oxydipropionitrile on Chromosorb P (60/80)

Column F: 10' × 3/8" glass 25% UC-W98 on Chromosorb W DMCS AW (60/80)

Column G: 6' × 1/8" SS 30% Carbowax 20M on Chromosorb W (60/80)

Column H: 10' × 3/8" Al 30% Carbowax 20M on Chromosorb W

Photolysis Apparatus[66]

The merry-go-round apparatus for isolation of the 253.7, 313.0 and 360.0 nm mercury lines has been previously described.[67] Actinometry performed at these wavelengths followed the procedure of Hatchard and Parker.[68] Irradiations other than quantum yield runs were conveniently performed in phosphor-coated, circular lamp apparatus provided by Ultraviolet Products Corp. Several phosphor coatings are available which provide ultraviolet radiation at 254, 305 or 365 nm.

Materials

Solvents

Hydrocarbon solvents (*n*-pentane, *n*-hexane, cyclohexane, Phillips 99 mol % grade) were stirred over P_2O_5 and distilled. The distillate was passed through a column containing 10% $AgNO_3$ on acid washed alumina according to the procedure of Murray and Keller,[69] and finally again distilled, through a 24" Vigreaux. Only the middle fraction was retained. Solvents were stored in tightly capped, solvent rinsed bottles under nitrogen. Hydrocarbons treated in this way showed a maximum optical density of 0.02 at 220 nm in a 1.0 cm quartz cell, *versus* air.

Benzene (Matheson, Coleman and Bell) was either used as received or further purified by photolysis (305 nm) of a chlorine stream passing through the solvent. Distillation through a Vigreaux column afforded benzene essentially free of saturated hydrocarbons or alkyl substituted benzene as evidenced by glpc (Column A, room temperature, N_2 carrier 12 ml/min, and 60°, N_2 12 ml/min). *Diethyl ether* (Mallinckrodt) was distilled from lithium aluminum hydride just prior to use. *Ethanol* (U.S. Chemical Industries) was used as received. *Tetraglyme* (bis[2-(2-methoxyethoxy)-ethyl]ether) (Matheson, Coleman and Bell) was distilled from sodium hydride, bp 152-153°/30 mm. *Benzene-d_6* (Volk), *1,4-dioxane* (Matheson, Coleman and Bell) and *methylene chloride* (Matheson, Coleman and Bell) were used as received.

Sensitizers

Naphthalene (Eastman) was recrystallized from ethanol and sublimed at 50°/0.05 mm; mp 79.6-80.1°. *Benzophenone* (Eastman) was recrystallized from diethyl ether and sublimed at 42°/0.05 mm; mp 48.0-48.6°. *Acetone* (Matheson, Coleman and Bell, spectrograde) was used as received. *Michler's ketone* (4,4′-bis-dimethylaminobenzophenone) (J. T. Baker) was purified by sublimation; mp 173.5-175.0°. *Acetophenone* (Matheson, Coleman and Bell) and *m-methoxyacetophenone* (Matheson, Coleman and Bell) were vacuum distilled by Dr. R. G. Weiss.

Pyrazolines

N-ethyl-N-nitrosourea, **1**, was prepared as described for N-nitroso-N-methylurea,[70] but aqueous ethylamine was used in place of methylamine. Concentrated hydrochloric acid (~35 ml) was added to 50 g of 33% aqueous ethylamine (Matheson, Coleman and Bell) (0.36 mol) until the mixture was acid to methyl red. The total weight of material was brought to 125 g by the addition of distilled water. Urea (75 g, 1.25 mol) was added and the mixture gently refluxed for 2.75 hr, followed by 15 min of vigorous reflux. The solution was cooled to room temperature, 27.5 g sodium nitrite (0.40 mol) was added and the mixture further cooled to 0°, and finally siphoned slowly into a 1 liter beaker containing 150 g ice and 25 g concentrated sulfuric acid at 0-5°. The resulting amorphous precipitate was filtered by suction and washed with 10 ml of cold water, dried and stored in a vacuum desiccator at 0°. The yield of **1** was 23.3 g (56% based on ethylamine).

Diazoethane, **2**. Pentane solutions of diazoethane were prepared by the method of Turro.[71] N-ethyl-N-nitrosourea (**1**) (5.0 g, 42 mmol) was added over 15 min to a stirred mixture of pentane (40 ml) and aqueous potassium hydroxide (12.5 g in 25 ml water) at 0°. After complete dissolution, stirring was stopped, the phases were allowed to separate, and then the system was held at -78° until the aqueous layer was completely frozen. The orange organic layer containing **2** was decanted and dried over potassium hydroxide pellets.

Exo- and *endo*-4-methyl-2,3-diazabicyclo[3.1.0]hex-2-ene, **3** and **4**, respectively. Cyclopropene was generated according to the procedure of Closs.[72] A three-necked flask equipped with magnetic stirring, nitrogen inlet, additional funnel and a 16-inch condenser packed with glass helices (1/8") was charged with 12 g (0.3 mol) sodium amide (Fischer Scientific) and 20 ml mineral oil. The resulting suspension was stirred and heated to 80°. The glass-packed condenser was cooled to ~0-5° by a constantly circulating ethylene glycol/water mixture (0°). A section of Pyrex tubing led from the top of the condenser to below the liquid level of a side-arm flask equipped with a drying tube and containing a freshly prepared solution of diazoethane, **2**. This solution was kept at -78° with a Dry Ice/acetone bath. Allyl chloride (Matheson, Coleman and Bell; 23.0 g, 0.3 mol) was added to the sodium amide suspension over a three-hour period. At the end of the addition, heating was continued for 1-1/2 hr while a slow stream of nitrogen was passed through the system. After this time the diazoethane color was no longer noticeable, and the flask was removed from the apparatus and allowed to warm to room temperature. Flash evaporation of the solvent (30°) yielded 2.0 g (50% based on **2**, 7% based on allyl chloride)[73] of a mixture of **3** and **4** (59:41 by glpc, Column C, 85°) as a pale yellow oil. The nmr spectrum (CCl_4--2% CH_2Cl_2) of the mixture showed a pair of doublets (3H) at $\delta \sim 1.5$ and 1.3 in an integrated ratio of 3:2 (high field:low field) with a common splitting of *ca.* 7 Hz. The spectrum also showed complex absorptions of δ 4.9-4.0 (2H), 1.9-0.7 (2H) and -0.2 (1H). The infrared spectrum (liquid film) exhibited absorptions at 3070, 3065, 1515, 1514, 1040 and 1038 cm^{-1} *inter alia*.

Separation of **3** and **4** was effected by preparative glpc (Column F, 60°, He carrier, 60 ml/min). Glass glpc columns were found to be necessary, as the pyrazolines appeared to decompose on metal surfaces during the chromatographic time. The shorter retention fraction (R_t ~35 min) was identified unequivocally as *exo-4-methyl-2,3-diazabicyclo[3.1.0]hex-2-ene* (**3**) on the basis of its 220 MHz nmr spectrum (see Results and Discussion). The 60 MHz spectrum (CCl_4--2% $CHCl_3$) showed: δ 4.66 (1H, 8 line symmetrical pattern, further split), 4.24 (1H, broadened doublet of quartets, J = 7.3, 3.0, ~1 Hz), 2.8-0.9 (2H, complex mult.), 1.33 (3H, d, J = 7.3 Hz), -0.19 (1H, d of d of d, J = 5, 5, 2.5 Hz). The infrared spectrum (liquid film) of **3** is shown in Figure 2 (Results and Discussion). The mass spectrum (see Results and Discussion) showed: m/e 96 (M^+, 4%), 68 ($M^+ - N_2$, 42%) and 67 (base). Pyrazoline **3** exhibited an $\pi^* \leftarrow n$ absorption maximum at λ_{max}^{hexane} 328 nm (ε 335).

The longer retention product (R_t ~42 min) was assigned the *endo*-methyl configuration (**4**) on the basis of its 220 MHz nmr spectrum (see Results and Discussion). The 60 MHz spectrum (CCl_4--2% $CHCl_3$) exhibited absorptions at: δ 5.0-4.5 (2H, complex mult.), 1.60 (1H, mult.), 1.47 (3H, d, J = 7.3 Hz), 0.89 (1H, mult.),

-0.17 (1H, mult.). The infrared spectrum (liquid film) is shown in Figure 2; ν_{max}^{film}:3065, 1514, 1038, 1026 cm^{-1}. The mass spectrum (see Results and Discussion) exhibited: m/e 96 (M^+, 5%), 68 (M^+-N_2, 37%), 67 (base), and the ultraviolet $\pi^* \leftarrow n$ maximum was observed at λ_{max}^{hexane} 330 nm (ϵ 149).

Exo-4-exo-6-dimethyl-2,3-diazabicyclo[3.1.0]hex-2-ene (5) and endo-4-exo-6-dimethyl-2,3-diazabicyclo[3.1.0]hex-2-ene (6) were prepared analogously to pyrazolines 3 and 4. The procedure of Binger et al.[74] was employed to generate 3-methylcyclopropene, which was condensed into a pentane solution of diazoethane as before, except that the gas was passed through a sulfuric acid trap (12 g con. H_2SO_4 in 80 ml H_2O), to remove the ammonia by-product, and then through a drying tube before condensation into the diazoethane solution. Lithium amide was prepared by the addition of lithium wire (1.9 g, 0.27 mol, Lithium Corp. of America) to 100 ml of liquid ammonia in a three-necked, 200 ml round bottom flask, equipped with a Dry Ice condenser and overhead stirring, and cooled in a Dry Ice/acetone bath. A small amount (~20 mg) of ferric nitrate was added to the flask, after persistence of the deep blue color characteristic of the solvated electron was noted, as a catalyst. After two hr of stirring the ammonia was allowed to evaporate, leaving 5.8 g (0.25 mol) of grey lithium amide. The Dry Ice condenser was replaced by a nitrogen inlet and the system was flushed with dry nitrogen for 15 min. The apparatus was then reassembled as described for the preparation of 3 and 4. The reaction flask was charged with 30 ml 1, 4-dioxane and 5 drops of water,[75] and the mixture was brought to reflux. 1-Chloro-2-butene (23.0 g, 0.26 mol, Matheson, Coleman and Bell) was added dropwise over 2.5 hr, and heating was then continued another four hr. The diazoethane solution was prepared as before, using 10.0 g (0.085 mol) N-ethyl-N-nitrosourea. At the end of the reaction (judged by the disappearance of the diazoethane color), the gas trap was allowed to warm to room temperature and the solvent was flash evaporated (30°), leaving 2.6 g of a clear oil. The yield of 5 and 6 was 28% based on N-ethyl-N-nitrosourea and 8% based on crotyl chlorides. Final purification was accomplished by preparative glpc (Column F, 70°, He carrier 60 ml/min). The peak of shorter retention time (48 min) was tentatively identified as 5. The 60 MHz nmr spectrum (CCl_4--2% $CHCl_3$) showed absorptions at δ 4.4-3.9 (2H, mult.), 1.14 (4H, a 3H doublet, J = 7.3 Hz and a 1H mult.), 0.82 (3H, d, J = 6.0 Hz) and -0.02 (1H, five-line pattern, J = 6.0, ~5 Hz). Other spectral characteristics observed were m/e: 110 (M^+, 1%), 82 (M^+-N_2, 3%), 67 (base); ir: ν_{max}^{film}: 3066, 3052, 1517 cm^{-1}; ultraviolet: $\lambda_{max}^{CCl_4}$ 326 (ϵ 435). The glpc peak of longer retention time (53 min) was tentatively assigned structure 6 on the basis of the following spectral characteristics. Nmr (60 MHz, CCl_4--2% $CHCl_3$) δ 4.61 (1H, five line pattern, J = 6, 7.1 Hz), 4.28 (1H, broadened d, J = 4.5 Hz), 1.37 (3H, d, J = 7.1 Hz), ~1.3 (1H, mult.), 1.00 (3H, d, J = 6 Hz), 0.09 (1H, mult.); infrared: ν_{max}^{film}: 3062, 1524 cm^{-1}; ultraviolet: $\lambda_{max}^{CCl_4}$: 332 (ϵ 467); m/e 110 (M^+, 2%), 82 (M^+-N_2, 14%), 67 (base).

Stereochemical assignments in 5 and 6 are based on coupling constants deduced from 100 MHz nmr spectra. (See Results and Discussion).

Pyrazoline Product Identification

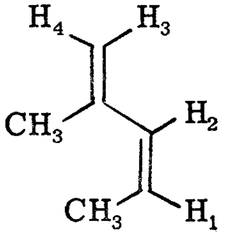
Preparative pyrolyses were done in a flow system at (approximately) atmospheric pressure. The compound being pyrolyzed was held at 80° while a 45 cc/min stream of nitrogen was bubbled through the liquid. Vapors were carried into the heated (260°) quartz tube (contact time 1 min) and finally trapped at -78° in a U-tube packed with glass helices. Volatile products were vacuum transferred and final separation was effected by preparative glpc (Column E, room temperature, He carrier 55 ml/min).

Pyrolysis of 1.0 g (10.4 mmol) of a 60:40 mixture of pyrazolines 3 and 4 afforded 0.21 g (40%) of a mixture of *trans*-1,3-pentadiene (7, 64%) and *cis*-1,3-pentadiene (8, 36%). The infrared and nmr spectra of isolated 7 and 8 were identical with those of authentic samples (Chemical Samples Co.).

Preparative pyrolysis of 1.18 g (10.7 mmol) of a crude mixture of 5 and 6 gave 0.63 g (71%) of a mixture of products. Analytical glpc (Column A, room temperature, N_2 15 ml/min) showed six peaks: A (R_t 12.0 min, 12.4%), B (R_t 15.8 min, 39.3%), C (R_t 18.7 min, 19.8%), D (R_t 22.6 min, 16.2%), E (R_t 24.9 min, 6.4%), F (R_t 26.8 min, 5.8%). In addition, a long retention time peak (70 min) was noted and identified as crotyl chloride (a contaminant from the pyrazoline synthesis). Peak F was also found to be an impurity present in the original pyrazoline mixture and was not further characterized.

Preparative glpc (Column E, room temperature, He carrier 55 ml/min) afforded samples of all products. Retention times under these conditions were: A, 24 min; B, 32 min; C, 38 min; D, 45 min; E, 50 min; and F, 53 min. GC-MS indicated that products A-E were C_6H_8 isomers ($M^+ = 82$).

Product A was identified as 2-methyl-*cis*-1, 3-pentadiene (10) on the basis of the following spectral characteristics and independent synthesis (*vide infra*). Nmr (CS_2--1% TMS):



10

δ 5.78 (H_2, d, $J_{1,2} = 11.7$ Hz), 5.49 (H_1, d of q, $J_{1,2} = 11.7$, $J_{1,\,CH_3(C_4)} = 6.5$ Hz), 4.88 (H_3 or H_4, broad s), 4.75 (H_3 or H_4, broad s), 1.82 (C_2-methyl, s), 1.77 (C_4-methyl, d, $J_{1,\,CH_3} = 6.5$ Hz). The H_1, H_2 and C_4 methyl patterns appear as an ABX_3 system in which $J_{A,X}$ is zero. The nmr spectrum of product A also showed resonances *ca.* 0.9 δ which may be attributed to the presence of 2, 4-dimethylbicyclo[1. 1. 0]butanes. If this analysis is correct, an upper limit of 2-3% can be placed on the amount of bicyclobutanes produced by decomposition of pyrazolines **5** and **6**. The infrared spectrum (CS_2) of product A showed absorptions at 3100, 3030, 1650, 1008, 906, 758 and 686 cm^{-1}. The ir and nmr spectra of product A are identical (except for the nmr resonance near 0. 9 δ) to those of authentic **10** (*vide infra*).

Product B was identified as *2-methyl-trans-1, 3-pentadiene* (**9**). The nmr and ir spectra and glpc characteristics of isolated B were identical to those of authentic **9** (Aldrich).

Product C exhibited the same ir and nmr spectra and glpc characteristics as authentic *trans, trans-2, 4-hexadiene* (**13**) (Chemical Samples Co.).

Product D was found to be a mixture of *cis, trans-2, 4-hexadiene* (**14**, 55%) and *cis-1-cyclopropylpropene* (**12**, 45%). The nmr spectrum ($CDCl_3$--1% TMS) showed resonances at δ 6. 5-4. 5 (mult.), 1. 8-1. 2 (methyl doublets plus mult.) and 0. 8-0. 2 (mult.). The nmr spectrum of authentic **14** (Chemical Samples Co.) and **12** (*vide infra*) could be overlaid, generating the spectrum of product D. The ir spectrum of D showed a *trans*-substituted double bond (995 cm^{-1}) and two maxima in the region characteristic of *cis*-substitution about a double bond:[76] 711 and 707 cm^{-1}. A band at 1028 cm^{-1} is assigned to the cyclopropane skeletal deformation[77] of **12**. The infrared spectra of authentic samples of **12** and **14** correspond to the spectrum of D.

Product E was identified as *cis, cis*-2, 4-hexadiene (**15**) by comparison of its ir and nmr spectra with those of an authentic sample (Chemical Samples Co.).

2-Methyl-cis-1, 3-pentadiene (**10**). An authentic sample of **10** was prepared by benzophenone sensitized *trans* → *cis* isomerization of 2-methyl-*trans*-1, 3-pentadiene (**9**). Irradiation (365 nm) of 2.1 g (25 mmol) **9** in 120 ml diethyl ether containing 1.37 g benzophenone (0.063 *M*) effected clean conversion to **10**. The photostationary state under these conditions is estimated by graphical extrapolation of the time dependence of the photolysis to be $(\mathbf{9}/\mathbf{10})_{pss} = 2.57$. The photolysis was monitored by glpc (Column A, room temperature, N_2 15 ml/min) over 48 hr. The solvent was then removed by distillation and the remaining material was vacuum transferred to effect separation of the benzophenone. The residual clear oil (1.9 g) contained 2.9% ether, 22.1% **10**, 73.5% **9** and 1.4% unidentified material. Preparative glpc (Column E, room temperature, He 55 ml/min) afforded a pure (98%, Column A) sample of **10**. Nmr ($CDCl_3$--1% TMS): δ 5.80 (1H, d, J = 11.7 Hz), 5.50 (1H, d of q, J = 11.7, 6.5 Hz), 4.88 (1H, s), 4.76 (1H, s), 1.84 (3H, s), 1.76 (3H, d, J = 6.5 Hz). The infrared spectrum of **10** showed $\nu_{max}^{CS_2}$: 3103, 3030, 2990, 2955, 2935, 2880, 1795 (w), 1785 (w), 1650 (s), 1383 (m), 1259 (m), 1047 (w), 1015 (w), 980 (m), 906 (s), 775 (s) and 687 (s), in good agreement with the published spectrum.[78]

Nmr spectra of *cis*-1-cyclopropylpropene (**12**) and *trans*-1-cyclopropylpropene (**11**) were provided by Dr. P. Condit.[79] The spectrum of authentic **12** was identical to those portions of the spectrum of D which were not attributable to **14**. Samples of **11** and **12** for glpc comparison to the products of pyrazoline decomposition were prepared by reaction of cyclopropanecarboxaldehyde (**16**) with ethylidene triphenylphosphorane. Cyclopropanecarboxylic acid chloride (Matheson, Coleman and Bell) was converted to **16** by the procedure of Brown.[80] Addition of 1.8 g (24 mmol) **16** to a benzene solution of ethylidene triphenylphosphorane (prepared from 11.1 g (30 mmol) ethyl triphenylphosphonium bromide and 15 ml of 2 *M* phenyl lithium) at 45° under nitrogen caused rapid disappearance of the orange-red color and formation of a heavy precipitate. Stirring was continued for 1 hr, and the volatiles were then distilled from the mixture. Glpc (Column A, room temperature, N_2 15 ml/min) showed two peaks, R_t 19.0 min (30.1%) and 22.8 min (69.9%). The minor component was determined to be *trans*-1-cyclopropylpropene (**11**) by glpc peak enhancement (Column A) during co-injection of an authentic sample of **11** provided by Dr. Condit. Similarly, the longer retention component was found to show peak enhancement when co-injected with authentic *cis*-1-cyclopropylpropene (**12**).

It was later found that all the olefinic products could be efficiently separated analytically on Column B at room temperature (N_2 12 ml/min). Table 9 lists the observed retention times of the materials under these conditions. Co-injection of authentic samples

Table 9. R_t (min)[a] of Decomposition Products of 5 and 6

Compound	R_t
10	30.0
9	38.4
13	44.4
11	47.6
14	55.2
12	61.2
15	64.8

[a] Column B, room temperature, N_2 12 ml/min.

with a pyrolyzed mixture of 5 and 6 containing all olefinic products established the assignments shown in Table 9.

Carbene precursor 23

4-Chloropent-2-ene (cis and trans) (17). Chlorides 17 were prepared substantially as described by Henne *et al.*[81] Piperylene (Matheson, Coleman and Bell, Technical) was distilled from lithium aluminum hydride prior to use; bp 41.5-42°/amb. Gaseous hydrogen chloride (J. T. Baker) was passed through neat piperylene (48.3 g, 0.71 mol) at 0°. The reaction was monitored by glpc (Column D, 50°, N_2 50 ml/min): piperylene R_t 0.9 min, 17 R_t 5.4 min. After 18 hr glpc indicated 70% conversion of starting material. The mixture was washed once with water, twice with 5% sodium bicarbonate, once with saturated sodium chloride and then dried over sodium sulfate. Distillation afforded 41.6 g (56%) 17, bp 50-51°/135 mm (lit.[81] 45-47°/110 mm). Nmr ($CDCl_3$--1% TMS): δ 6.7-5.3 (2H, vinyl, mult.), 4.7-4.3 (1H, allylic, d of q plus other, J = 6.7, 6.7 Hz), 1.68 (3H, vinyl methyl, d, J = 5.0 Hz), 1.55 (3H, d, J = 6.7 Hz). The other resonances in the allylic region are presumably from the minor (*cis*) isomer. Infrared, ν_{max}^{film}: 3050 (m), 3010 (s), 2995 (s), 2945 (m), 2890 (m), 1680 (m), 1465 (s), 1390 (m), 975 (s), 755 (m) and 655 (s) cm^{-1}.

4-Cyanopent-2-ene (*cis* and *trans*) (18) were prepared from chlorides 17 following methods in the literature for this[82] and similar[83] systems. Dried (140°, 3 hr) cuprous cyanide (14.3 g, 0.16 mol; Baker and Adamson), 17 (15.6 g, 0.15 mol), and potassium iodide (100 mg) were heated at 110° until refluxing ceased (1 hr). Diethyl ether (50 ml) was added to the cooled reaction mixture and solids were removed by suction filtration. The ether was flash evaporated and the residual oil distilled, affording 5.6 g (0.06 mol, 40%) 18, bp 52-54°/25 mm. The nmr spectrum ($CDCl_3$--1% TMS) of 18 showed δ 6.15-5.14 (2H, vinyl, mult.), 3.50-3.05 (1H, allylic, broad five line pattern), 1.73 (3H, vinyl methyls, pair of doublets, J = 6.1 and 6.2 Hz), and 1.37 (3H, allylic methyl, d, J = 7.0 Hz). Infrared, ν_{max}^{film}: 3050, 2265 (nitrile[84]), 1455, 968, 730 cm^{-1}.

2-Methylpent-5-ene-1-imine (*cis* and *trans*), 19, were prepared by diisobutylaluminum hydride[85] reduction of 18. Standard solutions of diisobutylaluminum hydride (**20**, Texas Alkyls) were prepared in tared volumetric flasks under argon. Dried benzene was used as solvent. To a cooled (0°), stirred solution of **18** (1.0 g, 10.5 mmol) in 30 ml dry benzene was added 20 ml of 0.555 *M* **20** in benzene. Stirring was continued for 10-15 min, and the reaction mixture was poured into 100 ml of cold (5°) 7.5% potassium hydroxide (aqueous). The mixture was extracted twice with diethyl ether and the combined organic portions were washed once with water and once with brine, and then filtered through Celite and dried over magnesium sulfate. Attempted isolation of product afforded only polymerized material. In practice, **19** was hydrolyzed (*vide infra*) immediately after work up. However, spectral data for **19** were obtained by partial concentration of an aliquot of the synthetic mixture, addition of CCl_4, further concentration followed by addition of more CCl_4 and repetition of the cycle until it was judged that ether was no longer present. The nmr spectrum of a sample of **19** treated in this way showed absorptions at δ 7.4 (1H, d, J = 4.5 Hz), 5.6-5.2 (2H, mult.), 3.4-3.1 (1H, mult.), 1.69 (3H, d, J = 5.5 Hz), and 1.0 (3H, d, J = 7 Hz). The resonance of the =N–H proton may be near δ 4.1, as a broad singlet, but the assignment is only tentative. The infrared spectrum of **19** exhibited maxima at 3330, 3045, 1683, 1662, 1465, 982 and 780 cm^{-1}.

2-Methylpent-3-enal (*cis* and *trans*), **21**, was prepared by acid catalyzed hydrolysis of imines **19**. The ether extract of **19**, prepared as described above, was concentrated by flash evaporation to a volume of 50 ml and poured into 20 ml of water containing sufficient oxalic acid (Mallinckrodt) to be only weakly acid to pH paper. The mixture was stirred for 30 min, the ether layer was separated and the aqueous portion extracted with ether. The combined ether portions were washed once with saturated sodium chloride and dried over magnesium sulfate. Flash evaporation of solvent afforded 0.82 g **21** (8.4 mmol, 80% based on nitriles **18**). Final purification of **21** was accomplished by preparative glpc (Column H, 130°, He 40 ml/min). The nmr spectrum ($CDCl_3$--1% TMS) of **21** showed: δ 9.55 (1H, aldehyde, d, J = 1.5 Hz), 5.8-5.1 (2H, vinyl, mult.), 3.3-2.8 (1H, allyl, overlapping d of q, J = 6.5, 6 Hz), 1.71 (3H, vinyl methyl, two doublets, J = 5 Hz), 1.19 (3H, allylic methyl, d, J = 6.5 Hz). Infrared, ν_{max}^{film}: 3040, 2730, 1728, 1455, 973, 725 cm^{-1}. Analytical glpc (Column G, 140°, N_2 20 ml/min) of the crude reaction mixture indicated the purity of isolated **21** to be 90%. The major impurity was found to be 2-methylpent-2-enal by nmr ($CDCl_3$-1% TMS): δ 9.39 (1H, s), 6.42 (1H, t, J = 7 Hz), 2.33 (2H, broad pentet, J = 7, 7 Hz), 1.71 (3H, s), 1.10 (3H, t, J = 7 Hz) and ir, ν_{max}^{film}: 2715, 1690 cm^{-1}.

2-Methylpent-3-enal(*p*-toluenesulfonylhydrazone), **22**.

p-Toluenesulfonylhydrazide (Eastman; 51 mg, 0.29 mmol), and **21** (27 mg, 0.28 mmol) were stirred at room temperature in diethyl ether (15 ml) in the presence of Linde 5 Å molecular sieves.[86] The disappearance of **21** was monitored by glpc (Column G, 140°, N_2 20 ml/min). After 8 hr the mixture was suction filtered and the solvent removed, yielding 82.3 mg (0.28 mmol, 100%) 22 as a viscous, clear oil which rapidly yellowed on standing and which could not be crystallized. The nmr (CCl_4--1% TMS) showed no aldehyde resonance at δ 9.55, but exhibited: δ 8.76 (1H, N–H, broad s), 7.5 (4H, arom., A_2B_2), 7.05 (1H, imine H, d, J = 5 Hz), 5.25 (2H, vinyl, mult.), 2.90 (1H, allylic, mult.), 2.58 (3H, arom. methyl, s), 1.6 (3H, vinyl methyl, d, J = 5 Hz), 1.0 (3H, allylic methyl, d, J = 7 Hz). The infrared spectrum of 22 showed $\nu_{max}^{CCl_4}$: 3220 (broad, s), 3050 (m), 2985 (m), 2950 (m), 2760 (w), 1610 (m), 1510 (w), 1465 (m), 1372 (m), 1335 (m), 1318 (sh), 1305 (sh), 1200 (sh), 1180 (s, split band), 1135 (w), 1108 (m), 980 (m), 805 (s), 720 (m), and 680 (m) cm^{-1}. The infrared spectrum contains absorptions which can be assigned to N–H stretching of the amine function, imine C–N stretching and C–H stretching, N–N stretching, aromatic modes, alkene C–C and C–H modes and sulfonyl modes.[87]

Sodium(2-methylpent-3-enal p-toluenesulfonylhydrazide), 23, was prepared by treating 0.45 g 22 (1.7 mmol) with 0.092 g (1.7 mmol) sodium methoxide (Matheson, Coleman and Bell) in methanol. Addition of diethyl ether to the mixture caused formation of a white precipitate. Centrifugation of the mixture, decantation of the solvent and drying at 40°/25 mm afforded 0.248 g (1.0 mmol, 59%) 23. D_2O (Columbia Organic, 1 ml) was added to 25 mg (0.1 mmol) 23. The precipitate which formed was taken up in $CDCl_3$. The nmr spectrum of this material was substantially the same as that of 22 (the N–H resonance was not present), indicating that no double bond migration had occurred during the formation of 23. Heating a sample of 23 in a melting point capillary caused slow decomposition and coloration in the range 130-170°.

Pyrolysis of 23. A suspension of 10 mg 23 in 50 μl tetraglyme was introduced in 4 μl portions into the heated (180-240°) injector port[44] of an analytical vpc (Column B, room temperature, N_2 12 ml/min). The product distributions obtained by this method are shown in Table 5 (Results and Discussion).

Analytical Pyrazoline Decompositions

The general pyrolysis procedure is outlined below. Freshly purified (preparative glpc, Column F) pyrazolines were used in all runs. For vapor phase decompositions 1.0 μl of material was placed in a pre-constricted Pyrex tube (6 × 30 mm, or 13 × 100 mm) and sealed after three freeze-pump-thaw cycles at $\sim 5 \times 10^{-4}$ torr. Pyrolysis was accomplished by immersing the tube in a heated oil bath for a known time (15 sec-15 min). Temperature variations were ±0.7°. The pyrolyzed tubes were quenched in ice water, and then opened after freezing one end in liquid nitrogen. An aliquot (25 μl) of a stock solution of *n*-nonane (Aldrich) (0.04 *M* in benzene or pentane) was added and analysis was done by glpc (Column A, room temperature, N_2 15 ml/min for 3 and 4; Column B, room temperature, N_2 12 ml/min for 5 and 6). Solution measurements were made similarly, except that stock solutions containing 3 or 4 (*ca.* 0.02 *M*) and *n*-nonane (0.04*M*) in pentane, or containing 5 or 6 (0.3 *M*) and *n*-pentane (0.05 *M*) in benzene were employed.

Pyrolyses were done over approximately three pyrazoline half-life periods. No change in product distribution was observed in this range at constant temperature. Kinetic data for pyrazolines 3 and 4 are shown in Table 10. Estimated half-lives for pyrazolines 5 and 6 at several temperatures are listed in Table 11.

Table 10. Disappearance of 3 and 4 at 119°

Compound	t (min)	moles decomposed (x 10^5)	C_i/C_t [a]
3	9.0	1.32	1.29
3	13.0	1.72	1.49
3	27.0	2.58	2.24
4	9.0	0.11	1.036
4	19.0	0.13	1.044
4	65.0	0.17	1.059

[a] Ratio of initial pyrazoline concentration to that at time t.

Direct irradiations were done in 6 × 30 mm Pyrex tubes (305 nm) or, for quantum yield runs, in 13 × 100 mm Pyrex tubes (313.0 nm). Stock solutions containing pyrazoline and internal standard were used. Initial pyrazoline concentrations were such that 99.9% of the incident radiation was absorbed. Quantum yields

Table 11. Estimated $\tau_{1/2}$ for 5 and 6 at Several Temperatures

Compound	T (°C)	$\tau_{1/2}$ (sec)[a, b]
5	118.5	350
5	147.5	90
5	170	14
6	147.5	1200
6	170	150

[a] Estimated from glpc data, using integrated areas of pyrazoline peaks.

[b] Initial concentrations: 5, 0.145 *M*; 6, 0.138 *M*.

for disappearance of 3 and 4 were extrapolated to zero time; pyrazoline disappearance was (pseudo-) first-order up to 20% decomposition.

Photosensitized Decompositions

Stock solutions of pyrazoline and sensitizer were prepared, and samples for irradiation were made up by adding measured aliquots of the stock solutions to Pyrex or quartz tubes. All tubes were thoroughly degassed and sealed. Sensitizers employed for decomposition of 3 and 4 were: benzophenone, acetophenone, *m*-methoxyacetophenone, Michler's ketone, benzene and naphthalene. In each case the sensitizer concentration was sufficient to absorb 99% of the light at the wavelength of irradiation. Pyrazoline concentrations were ca. 0.01 M. Photosensitized decomposition of 5 and 6 employed only benzophenone as sensitizer.

Analyses were performed on columns A and C, or B and D.

The Michler's ketone sensitized decomposition of a benzene-d_6 solution of 3 and 4 was monitored by nmr. Clean disappearance of pyrazoline resonances was noted. Concomitant appearance of new resonances was noted at δ 7.2 (broad singlet), 3.6 (triplet?), 2.7 (multiplet), 2.5 (multiplet), 1.45 (s) and others near 1.8. No decrease (or increase) in the Michler's ketone resonances was observed during 36 hr of irradiation. At the end of the photolysis the tube was opened and an infrared spectrum of the contents was recorded, versus a reference of benzene-d_6 containing the same concentration of Michler's ketone as used in the photolysis. The prominent features of the spectrum are bands at 2840, 1730 (s) and a split band at 780 and 790 cm^{-1}.

Pyrazoline Emission Spectra

Emission studies were performed on an Aminco-Bowman Spectrophotofluorimeter in degassed 13 × 100 mm Pyrex or 5 × 100 mm quartz tubes. 2.77 mg of a freshly purified mixture of 3 and 4 was dissolved in EPA (Matheson, Coleman and Bell, Spectroquality) and diluted to 10.0 ml with EPA. The final pyrazoline concentration was 2.9×10^{-4} M. 1.0 ml of this solution was further diluted with EPA to give a final concentration of 5.8×10^{-5} M. Spectra were run at room temperature and 77°K, both with and without the rotating can in operation. EPA blank spectra were taken under identical conditions.

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73. Closs[72] reported the yield of cyclopropene generated from allyl chloride and sodium amide to be 6-10%. We have obtained 6-7% yields of *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene[24] from the addition of cyclopropene, generated by Closs' method, to cyclopentadiene, suggesting that the dipolar addition of cyclopropene to diazoethane proceeds essentially quantitatively.

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83. *Organic Synthesis*, Coll. Vol. 3, p. 852 (note 1).

84. K. Nakanishi, *op. cit.*, p. 28.

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PART II

INTRODUCTION

The dependence of photochemical reactivity on the initial energy content of the system has received little attention from organic photochemists. The experimental difficulties inherent in such a study are at least partly responsible for the dearth of reports in this fundamental area. A reliable "monochromatic" radiation source which can be used over the entire range of wavelengths of interest to organic photochemists (200-400 nm) and a calibrated actinometric analytical method appropriate to the same excitation region are required for any systematic approach to the problem. As a complement to the difficulty of the problem is the historical fact that there were many equally interesting phenomena which could be examined with greater ease.

In spite of the problems, the number of reports of wavelength dependence on photochemical reactivity is increasing.[1-23] Taken as a whole, the available literature suggests several general considerations which may obtain, alone or in combination, in an energy dependent photochemical system. First, electronic states of different multiplicities can exhibit vastly different reactivity patterns.[3-5, 15] Second, initial photoproducts may themselves undergo reactions initiated by light of wavelengths other than those responsible for the primary process.[20] Third, non-interconvertible excited states may be populated to different extents by excitation with light of varying energy. This situation obtains, for example, when several ground state conformers, with different absorption characteristics, exist in equilibrium.[8] Weakly interacting bichromophoric systems, in which the initial excitation is quasi-localized in one or another of the light-absorbing centers can also exhibit energy dependent photoreactivity patterns.[9, 14, 18, 21] Fifth, upper electronic states produced by optical absorption may decay by quite different paths than those observed for lower levels as a consequence of the possible differences in the electron distributions in the various states.[6] Lastly, there can be significant participation of molecular vibrations in the decay of the initially formed excited state. Reaction can sometimes occur from, or be accelerated by participation of, upper vibrational levels populated by initial excitation.[6, 10, 17, 22, 23] The extent of vibrational participation is dependent on both the vibrational quantum number of the excited level and the character of the molecular motions associated with the progression into which excitation occurs.[10]

The interesting experimental results of Becker and coworkers[10] have indicated that the consequences of both electronic and vibrational factors can be manifested quite explicitly in photochemical unimolecular reactions. Hammond has discussed, in a qualitative fashion, the relation of these factors to photochemical systems.[24]

Hammond[24] has applied the theory of Robinson and Frosch[25] to the decay of excited states via photochemical paths. An expression for the absolute rate constant for the process $A^* \rightarrow B$ is developed in direct analogy to the method of Robinson, eq 1.

$$k_{A^* \rightarrow B} = \frac{2\pi \beta_{el}^2 \sum_n \langle \phi_{nB} | \phi_{0A^*} \rangle^2}{\hbar \alpha} \qquad \text{(eq 1)}$$

β_{el} is the matrix element coupling the electronic parts of the wavefunctions of the initial and final states. It is a measure of the electronic interactions of the "reactant" and "product" states, and, in order for β_{el} to be finite, spatial overlap of the initial and final wavefunctions is required. The Franck-Condon factor, $\langle \phi_{nB} | \phi_{0A^*} \rangle$, is a measure of the degree of overlap of vibrational wavefunctions. ϕ_{nB} are the vibrational wavefunctions of the levels of product B to which decay of excited A initially occurs, and ϕ_{0A^*} is the vibrational wavefunction of the zeroth level of A^*. It seems reasonable that the vibrational overlap factor in eq 1 could be modified to include the m vibrational levels of excited A so as to allow application of the expression to photoreactions which proceed from these upper levels. The parameter α is the interaction energy derived from coupling between vibrational modes of the product B and the environment. If eq 1 is expanded to include contributions of the upper vibrational levels of A^*, then an additional environmental term is necessary.

While the parameters in eq 1 will allow no quantitative treatment of the energy dependence of photochemical reactivity, they provide a convenient framework for the discussion of the possible origins of observed effects.

Photochemistry of Acyclic 1,3-Dienes

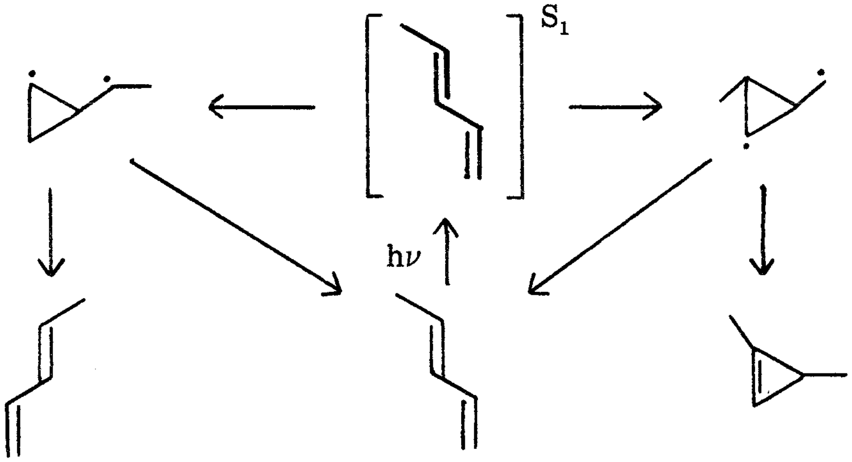
The photochemistry of simple conjugated dienes has been reviewed by several authors.[8, 26-28] The first electronic transition in butadiene and in alkyl substituted butadienes has been the subject of many studies.[29-37] The absorption is $\pi^* \leftarrow \pi$ in nature, and it is a singlet transition. A detailed analysis of the spectra of simple conjugated dienes has not been carried out.

The first transition in linear conjugated dienes exhibits very little resolvable vibronic structure. The absorption maxima are in the range 210-250 nm, but a definitive assignment of the O′–O band has not been possible from spectral evidence since fluorescence has not been observed from any simple dienes. However, several lines of evidence suggest that the O′–O transition may lie at wavelengths considerably removed from the traditional long-wavelength side of the absorption maximum. First, a weak, but long, tail is observed in the absorption spectra of simple dienes in solution (*vide infra*). Also, several steroidal dienes are known to fluoresce in rigid matrices at 77°K.[38] Lumisterol and ergosterol, *s-cis* polycyclic dienes, exhibit fluorescence spectra in EPA glasses which are mirror images of the absorption spectra, but the fluorescence is considerably red-shifted from the absorption origin, suggesting that either a very weak long wavelength O′–O band is present which does not appear in the absorption spectrum under normal analytical conditions, or that significant geometric changes occur in the excited state within the fluorescence life time.

The observed photoreactions of acyclic 1, 3-dienes on direct irradiation in solution are rich and varied. Formation of bicyclo[1. 1. 0]butane, cyclobutene and the dimers cis- and trans-1, 2-divinylcyclobutane, 1, 5-cyclooctadiene, and 2-vinylbicyclo[3. 1. 0]-hexane has been observed during irradiation of butadiene in an inert solvent at 253. 7 nm.[28, 39, 40] Alkyl substituted dienes also yield ring closure products on singlet excitation.[41] Substitution of a methyl group at the 2-position (e. g. isoprene) favors internal cyclization to cyclobutene products, while 1-substituted systems cyclize at a lower rate than the parent butadiene.[41] In addition to cyclobutene formation, Srinivasan[42] has observed 1-ethyl-3-methylcyclopropene from the 253. 7 nm photolysis of the isomeric 2, 4-hexadienes. Diradical intermediates were proposed (vide infra).

Geometrical photoisomerization has been observed to compete efficiently with valence isomerization, in both the 2, 4-hexadiene[42, 43] and 1, 3-pentadiene[43] systems. Unlike the triplet sensitized isomerization of the 2, 4-hexadienes,[44] which proceeds via common triplet state intermediates and leads to net isomerization at both termini of the conjugated system, the singlet state isomerization does not involve a single intermediate: isomerization occurs only at one terminus or the other, but not at both.[43]

Srinivasan[42] and Saltiel[43] have postulated that "cyclopropylmethylene" diradicals are formed via excited state cyclization of the diene singlet, and that the diradicals either revert to ground state diene or suffer hydrogen migration which leads to cyclopropene products:



In the present study, the dependence of the initial quantum yields for cis → trans and trans → cis photoisomerization of the isomeric 1, 3-pentadienes have been determined at four excitation wavelengths in the range 236-254 nm in n-pentane solutions. The results are discussed with reference to possible mechanisms of isomerization of acyclic conjugated dienes and also within the context of current theories of radiationless decay of excited states.

RESULTS AND DISCUSSION

The ultraviolet spectra of cis- and trans-1, 3-pentadiene in n-pentane solution in the range 220-270 nm are shown in Figure 1. The observed maxima are: 223.5 nm (trans) and 223 nm (cis), in agreement with the reported values.[32] The striking features of the spectra are the two crossing points at approximately 230 and 250 nm. The molar extinction coefficient of trans-1, 3-pentadiene at the absorption maximum (2.65×10^4 l mole^{-1} cm^{-1}) is slightly higher than that observed for the cis isomer (1.92×10^4 l mole^{-1} cm^{-1}). However, the trans compound shows considerable long wavelength absorption: $\epsilon_{270\text{ nm}} = 2$ l mole^{-1} cm^{-1}; at 270 nm the extinction coefficient of cis-piperylene is only 0.2 l mole^{-1} cm^{-1}. Figure 2 shows the long wavelength absorption of the two isomers.

The molecular origin of the long absorption tail is not at all clear. Several possible interpretations will be discussed later.

The observed initial quantum yields of geometric isomerization of the pure (>99.5%) dienes are listed in Table 1. The excitation wavelengths examined were isolated by the use of a high intensity monochromator and a 2.5 kw high pressure mercury-xenon source, with the exception of 253.7 nm, which was obtained with a conventional merry-go-round apparatus.[45] In Figure 1, the vertical ties indicate the wavelengths employed. Actinometry was performed using a minor modification of the uranyl oxalate procedure of Pitts.[46]

Figure 1. Ultraviolet spectra of 1, 3-pentadienes:

trans-1, 3-pentadiene (————) and

cis-1, 3-pentadiene (—— —— ——), in n-pentane.

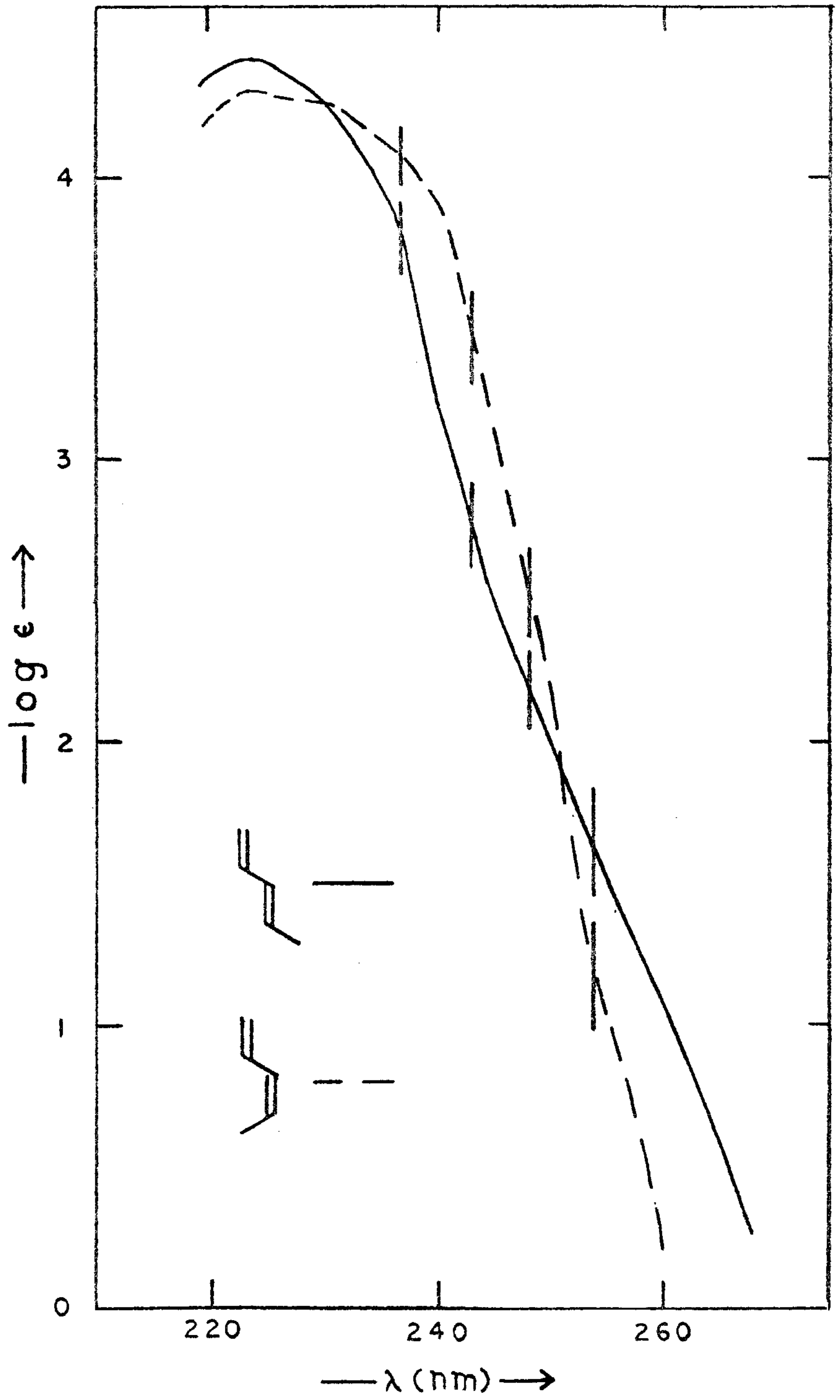

—log ε →
4
3
2
1
0
220
240
260
— λ (nm) →

Figure 2. Long wavelength absorption of trans-1, 3-pentadiene (————) and cis-1, 3-pentadiene (— — —), in n-pentane.

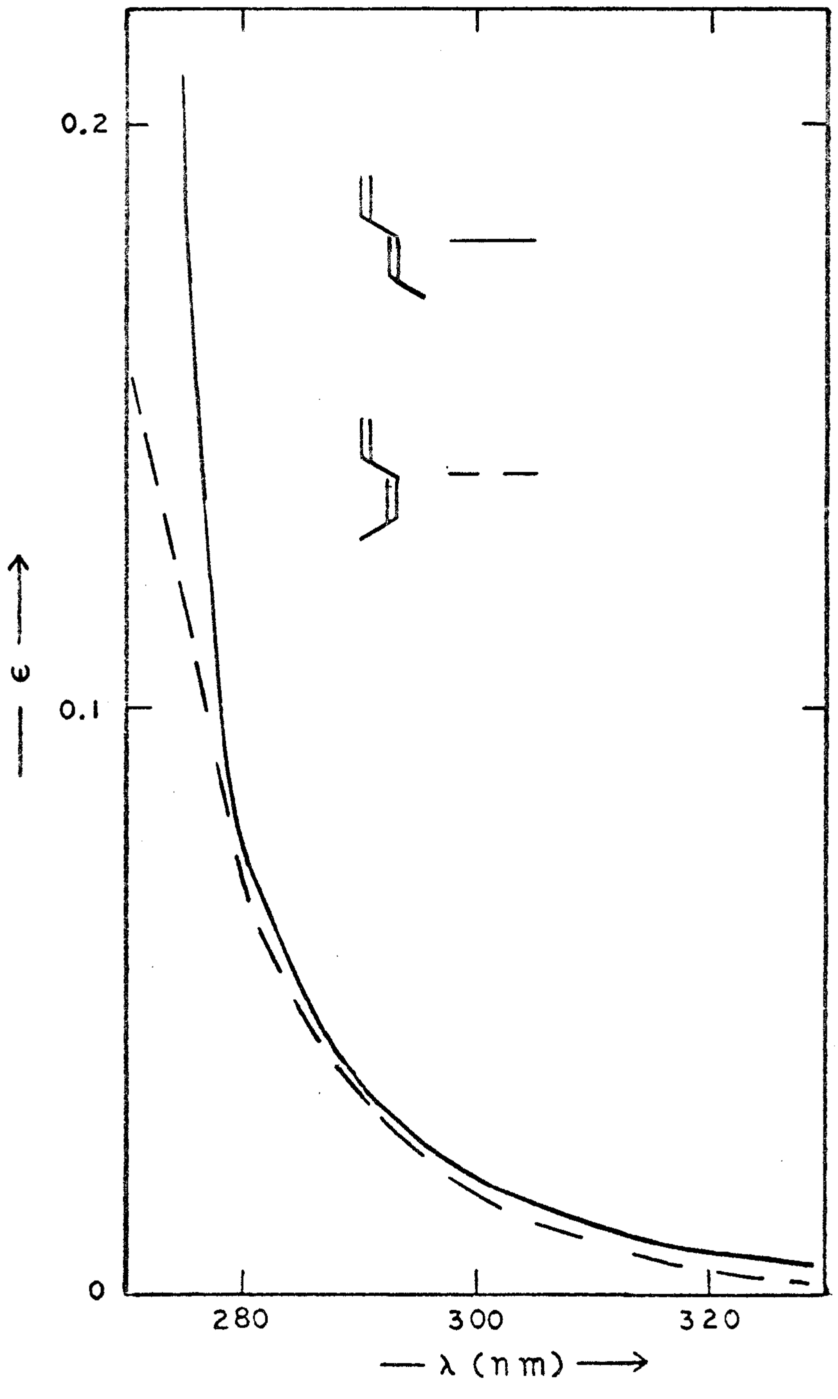

0.2
0.1
0
ε
280
300
320
λ (nm)

Table 1. Quantum Yields[a] of Cis-Trans Isomerization of Piperylenes at Several Excitation Wavelengths

λ(nm)[b]	$\phi_{c\rightarrow t}$	$\phi_{t\rightarrow c}$
253.7	$0.085_4 \pm 0.004$	$0.093_4 \pm 0.008$
247.5	$0.097_5 \pm 0.002$	$0.092_3 \pm 0.003$
242.9	$0.067_3 \pm 0.006$	$0.039_8 \pm 0.005$
236.6	$0.036_1 \pm 0.004$	$0.020_5 \pm 0.001$
(253.7	0.091	0.11_5)[c]

[a] Initial yield: <4% conversion; n-pentane solution, diene 0.1 M.

[b] See text for bandwidths.

[c] Values of Saltiel et al., Ref. 43.

Complete experimental details are given in the Experimental section. The errors given in Table 1 are experimentally observed reproducibility figures; inherent errors of the analytical methods are ±10%.

The radiative output of the optical train and monochromator utilized in the experiments reported here is an approximately triangular distribution of wavelengths about the maximum. The excitation wavelengths listed in Table 1 are the observed maxima; the practical bandwidth at one half intensity was 3-6 nm, depending on the wavelength (c. f. Experimental).

The quantum yields listed in the table were determined from a number of runs for which the total number of quanta absorbed by the substrate was nearly the same. Thus any possible contribution of quantum yield dependence on intensity of the incident light was probably eliminated.

As an approximate internal check on the quantum yields listed in the table, the relative intensities of the incident radiation were estimated by integration of the area under a spectroscopically determined intensity *versus* wavelength curve for the monochromator output. The curves were determined by monitoring the excitation output of the primary monochromator with an automatic scanning monochromator equipped with a photomultiplier tube. The phototube output was displayed on a strip chart recorder. The relative monochromator output data were corrected for variations in the phototube sensitivity as a function of the wavelength of the incident light and for approximate changes in grating efficiency (in the analyzing monochromator) with wavelength. The relative intensity data calculated in this manner were then compared with the same data measured chemically using uranyl oxalate actinometry. Table 2 shows the results of the calculations and the comparison to the experimentally determined values. The agreement between the calculated and observed values is an indication that the quantum yields listed in Table 1 do not simply reflect analytical errors, but are in fact true variations with wavelength of excitation.

Table 2. Calculated and Observed Relative Intensities of Excitation Output of Monochromator

λ (nm)	I (calc.)[a]	I (obs.)[b]
236.6	1.0	1.0
242.9	3.2	3.7
247.5	4.3	3.8

[a] See text.

[b] Uranyl oxalate actinometry.

If it is assumed that the photoisomerization process at each wavelength can be described by the kinetic scheme shown below (eqs 2-7), then, under steady state illumination, the photostationary state ratio, P, of cis diene to trans can be derived to be eq 8.

Process

$c \xrightarrow{h\nu} c^*\,(S_1)$ $\quad I_a$ (eq 2)

$c^* \longrightarrow c$ $\quad k_{ic}[c^*]$ (eq 3)

$c^* \longrightarrow t$ $\quad k_{ct}[c^*]$ (eq 4)

$t \xrightarrow{h\nu} t^*\,(S_1)$ $\quad I_a'$ (eq 5)

$t^* \longrightarrow t$ $\quad k_{ic}'\,[t^*]$ (eq 6)

$$t^* \longrightarrow c \qquad k_{tc}[t^*] \qquad \text{(eq 7)}$$

$$P = \frac{[c]}{[t]}\bigg|_{pss} = \frac{\epsilon_t \cdot \phi_{tc}}{\epsilon_c \cdot \phi_{ct}} \qquad \text{(eq 8)}$$

Cis-1, 3-pentadiene is abbreviated c, and t stands for the trans isomer. The absorption rates I_a are given by eqs 9:

$$I_a = I \cdot \epsilon_c \cdot [c]_{pss} \qquad I_a' = I \cdot \epsilon_t \cdot [t]_{pss} \qquad \text{(eqs 9)}$$

where I is the incident light intensity (E/min), the ϵ are the appropriate molar extinction coefficients, and the diene concentrations are the photostationary state values. The quantum yields which appear in eq 8 are defined by eqs 10:

$$\phi_{tc} = \frac{k_{tc}}{k_{ic}' + k_{tc}}$$

$$\phi_{ct} = \frac{k_{ct}}{k_{ic} + k_{ct}} \qquad \text{(eqs 10)}$$

in which k_{ic} and k_{ic}' represent the rate constants for decay of the excited states c* and t^* via internal conversion (or other non-isomerization paths), and k_{tc} and k_{ct} are the rate constants which pertain to geometric isomerization.

From the observed isomerization quantum yields and the extinction coefficients for absorption at the various wavelengths of excitation, photostationary state ratios, P, may be calculated from eq 8. The calculations are listed in Table 3.

The photostationary state ratio calculated for irradiation at 253.7 nm (2.88, % c at pss = 74.2) is in good agreement with the only reported[47] value at the same wavelength of excitation: P = 2.6; % c at pss = 73.

The photostationary state ratios listed in the table may be compared with the (room temperature) equilibrium ratio of 0.187 (*cis*:*trans*), which represents 15.7% *cis*-1,3-pentadiene. This value has been extrapolated from the (vapor phase) data of Egger and Benson determined by the iodine or nitric oxide technique in the range 120-230°C.[48] The photostationary state ratio determined using high energy (>60 kcal/mole) triplet sensitizers is 0.82 (45% *cis*).[49]

Table 3. Calculated[a] Photostationary State Ratios

λ (nm)	ϵ_t [b]	ϵ_c [b]	P[a]	% c_{pss} [c]
243.7	42.6	16.2	2.88	74.2
247.5	162	224	0.69	40.8
242.9	604	1180	0.30	23.1
236.6	6910	10600	0.37	27.0

[a] Equation 8; errors *ca.* ±15%.

[b] $1\ mole^{-1}\ cm^{-1}$.

[c] Percent *cis* at photostationary state; from P.

The data shown in Table 1 and the calculations listed in Table 3 indicate several general conclusions. First, the isomerization of trans-1, 3-pentadiene to the cis isomer is roughly five times more efficient at 253. 7 nm that at the shortest wavelength examined (236. 6 nm), but the quantum efficiency of cis to trans isomerization decreases by only a factor of 2. 5 over the same range of wavelengths. The general trends, however, of decreased isomerization efficiency at higher excitation energy are observed for both isomeric dienes. Also, while the quantum yields at 247. 5 nm are nearly the same as those at 253. 7 nm for both isomers, the calculated photostationary state ratios at these wavelengths are strikingly dissimilar: at 253. 7 nm the predicted stationary state clearly favors the cis isomer, but at 247. 5 nm the mixture is calculated to be trans rich. In this case, the sole contributing factor to the variation in stationary state ratio is the change in the relative magnitudes of the extinction coefficients of the isomeric dienes at the two wavelengths. For the other wavelengths examined, the calculated photostationary state ratios reflect changes in both the isomerization efficiencies and the appropriate extinction coefficients.

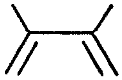
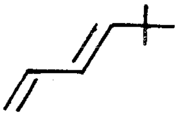
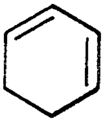
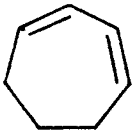
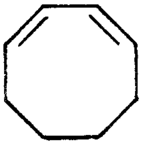
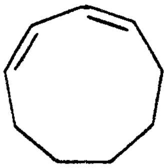
These observations suggest that the wavelength dependence may be manifested through the operation of two independent phenomena: (1) at long wavelengths the isomerization process is more efficient than at short waves, and (2) the isomerization at long wavelengths, particularly in the case of the trans isomer, is dominated by contributions of s-cis conformers.

The preferred conformation of linear 1, 3-dienes is the *anti*, or *s*-*trans* conformation.[54] However, for the simplest conjugated diene, butadiene, it is estimated[55] that at room temperature approximately 2% of the molecules exist in the *s*-*cis* conformation. Srinivasan has postulated[41] that photochemical cyclobutene formation occurs from the excited state produced when light is absorbed by the *s*-*cis* conformer of the diene. In agreement with this idea is the observation[56] that *trans*-1, 3-pentadiene closes to 3-methylcyclobutene ten times more efficiently than the *cis* isomer closes, when irradiated at 253.7 nm. That is, since it is expected that fewer *cis*-1, 3-pentadiene molecules will exist in the *s*-*cis* habit than will *trans*, the probability of absorption by a molecule with the proper orientation for ring closure will be significantly lower in the case of *cis*-1, 3-pentadiene, assuming that the quantum yields for cyclization are similar for both the *s*-*cis* *trans* and *s*-*cis* *cis* species, and also assuming that the *s*-*cis* and *s*-*trans* conformers do not interconvert in the excited state. For the case of *trans*-1, 3-pentadiene, Fonken[57] has suggested that "the *s*-*cis* conformation is attainable with no greater difficulty than in butadiene." That is, roughly 2% of the ground state *trans*-1, 3-pentadiene molecules may be in the *s*-*cis* conformation. For the *cis* geometric isomer, the data of Srinivasan cited above suggest that at most 0.2% of the molecules can exist in the *s*-*cis* conformation.

Table 4 lists the ultraviolet maxima of several 1, 3-dienes for which the conformation about the single bond joining the two olefinic units can be known with some certainty. Although it is difficult to separate substituent effects on the position of the absorption maximum from conformational effects, several general conclusions appear valid. The absorption maximum of *s-cis* dienes lies at longer wavelength than the maximum of a substitutionally equivalent *s-trans* species, and the molar extinction coefficient of the *s-cis* conformer is in general lower than that of the *s-trans* diene. The data listed for the *t*-butyl substituted butadienes[50] are particularly informative. The trends noted for the cyclic conjugated dienes probably reflect both the *s-cisoid* conformation and the variations in ring strain throughout the series, as well as, for the larger cycles, contributions due to the presence of *cis, trans* geometric isomers as impurities.

The data in Table 4 indicate that for the case of the isomeric 1, 3-pentadienes the *s-cis* conformers can be expected to absorb at longer wavelengths than the *s-trans* species, and that the extinction coefficient of the *s-cis* conformers can be estimated to be near 7×10^3 l mole^{-1} cm^{-1} at the maximum, roughly 236-245 nm. Furthermore, as a model, it is assumed that approximately 2% of the *trans*-1, 3-pentadiene molecules exist in the *s-cis* conformation, but that only 0. 2% of the *cis*-piperylene molecules can attain the *syn* conformation about the central bond.

Table 4. Ultraviolet Maxima of Several 1, 3-Dienes

Compound	λ_{max} $(\epsilon)^{a}$	Ref.
	217 (21, 000)	37
	226 (21, 400)	37
	224 (26, 900)	50
	236 (6, 800)	50
	256 (7, 940)	51
	248 (7, 420)	51
	228 (5, 500)	52
	220 (2, 520)	53

[a] Wavelength in nm; extinction coefficient in l mole^{-1} cm^{-1}.

Given these assumptions the quantum yield data (Table 1) at 253.7 nm and the extinction coefficients at that wavelength suggest that, unless the inherent isomerization efficiencies of the s-cis trans and s-cis cis dienes are markedly different, some, but not all of the long wavelength isomerization can be attributed to s-cis conformers. That is, if the 253.7 nm absorption of cis-1,3-pentadiene ($\epsilon = 16.2$) was entirely due to the presence of s-cis conformers, then one might predict that the extinction coefficient of trans-piperylene at 253.7 nm would be nearly 162 l mole^{-1} cm^{-1}. This is clearly not the case. Furthermore, since the observed quantum yields of isomerization at an excitation wavelength of 247.5 nm are, within experimental error, the same as those at 253.7 nm, while the extinction coefficients (cis, 224; trans, 162) at the shorter wavelength have changed drastically from the values at 253.7 nm, it seems unreasonable that s-cis conformers can contribute in any significant sense to either the absorption or isomerization processes at wavelengths other than 253.7 nm. The bulk of the diminution in quantum yield for both cis- and trans-1,3-pentadiene must then be the result of some other factor, or combination of factors.

A precise definition of the term "radiationless decay" is rather elusive. Direct measurement of the yields of radiationless transitions in a photochemical system is not possible, with the exception of those processes known as intersystem crossing between the lowest lying singlet state and the triplet manifold where chemical methods can give quantitative estimation of the quantum yield. The general procedure for the determination of internal conversion yields is to sum the yields of all other photophysical and photochemical decay paths open to the excited state and then to attribute any deviation from unit efficiency to radiationless decay to the initial ground state.

Implicit in a discussion of the importance of non-radiative processes to the decay of metastable excited states is a knowledge of the alternate decay paths available to the initial state. At the present time, the available theoretical treatments of photochemical reactivity do not describe in detail how specific rearrangement modes can be favored over others, or how the various molecular degrees of freedom are coupled to produce the required molecular motions. However, the treatment given by Hammond[24] and summarized as eq 1 (Introduction) suggest that several factors contribute to the decay of the initial state, and that these factors are similar for both internal conversion steps and for decay promoted by molecular rearrangement. That is, the absolute rates of the various decay paths depend on electronic, vibrational and environmental terms. Furthermore, photochemical reactions, in particular isomerization and rearrangements, may be thought of as a special case of the general radiationless decay problem. It is apparent, however, that rearrangements necessitate, a priori, changes in nuclear configuration relative to the geometry of the initial state, and that these changes require highly anharmonic vibrations as well as, in some cases, specific rotational motions, so that it will be extremely difficult to judge rates of these changes in relation to other processes since a detailed knowledge of the upper vibrational levels of the product is not in general available.

The current theories of radiationless transitions have in common the prediction that the rates of radiationless decay should decrease as the energy separation between the two states being considered increases. There are, however, a substantial number of examples in the literature which seem to contradict this generality. In order to rationalize this apparent discrepancy between theory and fact, Noyes and co-workers[6] have suggested that isomerization of the parent system in the excited state to a thermodynamically unstable molecule followed by thermal decay of the new isomer back to the ground state of the initial species can be an effective route for the dissipation of excitation energy by an electronically excited state.

In the present system the observations demand that the energy which is initially deposited in the diene chromophore by absorption must be more efficiently dissipated, *via* paths which do not lead to *cis*-*trans* isomerization, when the initial energy content of the system is high than when the initial excitation derives from light of long wavelengths. In view of the currently accepted theories of radiationless transitions, it may therefore be necessary to postulate that the "energy wastage" derives from increased efficiency of formation of unstable intermediates as the excitation energy is increased. Such a process could be manifested as an increased yield of cyclobutene products during irradiation at short wavelengths, or it could reflect increasingly efficient diradical formation as proposed by Srinivasan at 253.7 nm.[42]

However, it was argued earlier (vide supra) that cyclobutene formation may in fact derive from excitation of s-cis conformers, which were thought to absorb competitively with the predominant s-trans conformers only at long wavelengths. At higher excitation energies, then, cyclobutene formation may not occur. The point is moot in the absence of quantum yield data for cyclobutene formation as a function of excitation wavelength.

The case for formation of cyclopropyl methylene diradicals (c.f. Introduction) is equally tenuous. However, it seems clear that increased yields of the diradical proposed by Saltiel,[43] which would presumably lead to increased isomerization yields at higher excitation energies, is incompatible with the observations reported here.

An alternative explanation for the observed decrease in isomerization yield with increased excitation energy could invoke rapid decay via solute-solvent interactions in which the density of "acceptor modes" is greater for excitation of the diene with high incident energies than for longer wavelength irradiation. However, this effect may be countered by increased Franck-Condon factors for diene isomerization when short wavelength excitation is employed.

It is attractive to propose that the upper vibrational levels of an excited state may play an important role in radiationless decay mechanisms, particularly in systems which do not fluoresce, for which it is apparent that the initial excited state does not survive long enough to emit--i.e., internal conversion to the ground state is faster than it is for fluorescent molecules. Thus, internal conversion can become competitive with vibrational relaxation processes, and the effect of varying the initial energy content of the system may be manifested.

The precise nature of the factors which operate in the 1,3-pentadiene system can certainly not be elucidated on the basis of the preliminary results reported here. The strong wavelength dependence observed is of interest and suggests that further studies on simple photochemical systems will be informative.

EXPERIMENTAL

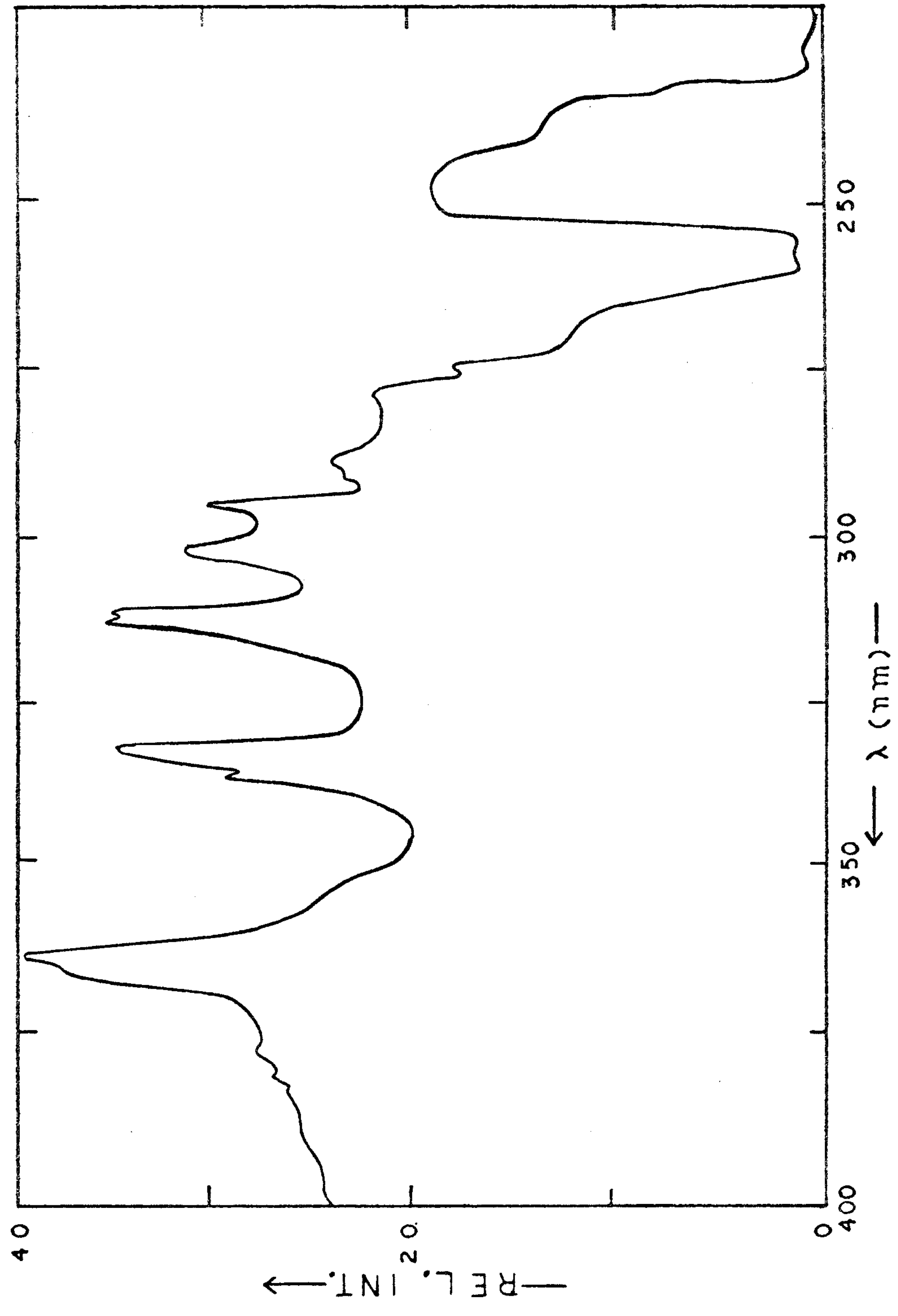
Light Source

An optical bench consisting of a 2.5 kilowatt dc mercury-xenon arc lamp (Hanovia 929-B9U) and a Bausch and Lomb quarter-meter, uv blazed (2500 Å) diffraction grating monochromator (B. & L. cat. #33-86-01) was employed for isolation of wavelengths other than 253.7 nm. The monochromator was equipped with variable exit and entrance slits. The reciprocal linear dispersion of the grating was 3.2 nm/mm, and the exit beam had an f-number of 3.5. A Supracil-quartz-windowed water filter was used to remove infrared radiation. Supracil lenses (Oriel Optics, Stamford, Conn.) were employed throughout the optical train.

The lamp is powered by a Westinghouse DC Arc Welding power source operated at 50 volts and 50 amperes. The power supply was kindly loaned by the Jet Propulsion Laboratories and Dr. E. Laue. The lamp housing is aluminum and is provided with a high speed fan at the base and a reversed blower at the top to force cooling air across the lamp envelope.

Figure 3 shows the spectral distribution of the Hanovia source. The distribution was determined by scanning the polychromatic, collimated beam with a motor-driven half-meter Jarrel-Ash grating monochromator equipped with an EMI-9558 QB photomultiplier tube. The phototube output was displayed on a Hewlett-Packard 7101B strip chart recorder. The spectrometer wavelength

Figure 3. Spectral distribution of Hanovia source. Relative intensity in arbitrary units versus wavelength in nm.


40
20
0
400
350
300
250
λ (nm)
REL. INT.

drive was calibrated with a mercury pencil arc, but the distribution shown in the figure was not corrected for phototube response.

The half-meter Jarrel-Ash spectrometer was also employed, with the Bausch and Lomb monochromator on line, to record the purity and band width of the radiative output of the Bausch and Lomb instrument at the irradiation wavelengths used in this study. Table 5 lists the observed spectral purity and band pass for these

Table 5. Spectral Characteristics of Radiative Sources

λ (nm)[a]	Purity (%)[b]	Band pass (nm)[c]	I ($E/min \times 10^8$)[d]
236.6	97	3.0	1.5 - 2.0
242.9	96	6.3	6.0 - 6.4
248.1	98	5.0	5 - 6
253.7	–	9[e]	3.01[f]

[a] Wavelength at intensity maximum.

[b] Integrated area of major band relative to extraneous output area at $\lambda < 300$ nm.

[c] Band width at half-height.

[d] Uranyl oxalate actinometry; ranges of observed values over several days.

[e] Baird Atomic third order 254 nm interference filter. Spectral purity and band pass of merry-go-round apparatus not determined.

[f] 254 nm merry-go-round; ferri-oxalate and uranyl oxalate actinometry.

wavelengths. Also listed are the observed absolute intensities of the radiative output, as determined by chemical actinometry (*vide infra*). The intensities are corrected for long-wavelength radiation (e.g. second order scattering from the grating), but the spectral purities listed are not corrected in this way. In general the long-wavelength contribution was *ca.* 10% of the measured intensity. Since output intensity decreases as the spectral band width is narrowed by adjusting the entrance and exit slit widths, in practice a compromise was necessary. The intensities listed in the table are the optimum values obtained at an arbitrary spectral purity of *ca.* 95%.

Irradiations at 253.7 nm were carried out in a conventional merry-go-round apparatus.[45]

Actinometry

For irradiations at wavelengths other than 253.7 nm, light intensities were determined by uranyl oxalate actinometry.[58-60] A minor modification of the procedure given by Pitts *et al.*[46] was used to analyze irradiated aliquots of the actinometer. A detailed description of the procedure used is given in the Appendix.

For actinometric runs on the optical bench, both quartz and Pyrex tubes were used in order to apply a correction to the calculated light intensities at short wavelengths. Such a correction is desirable because of the stray light of wavelengths which are absorbed by the actinometer but not by the diene substrate. The corrections applied to calculated intensities are small. In general, it was found that better than 90% of the light was at wavelengths below 290 nm.

The actinometer solution, prepared and stored in the dark, was 5×10^{-3} $\underline{M}$ in $H_2C_2O_4$, 1×10^{-3} $\underline{M}$ in UO_2SO_4 and 0.2 $\underline{N}$ in H_2SO_4. After irradiation of the actinometer an aliquot of standard oxidant, Ce(IV), is added to an aliquot of the irradiated solution and a blank. The concentration of the cerium(IV) is sufficient that, after oxidation of all oxalate in the blank, a slight excess of cerium remains. Differential absorption spectroscopy is used to determine the excess of Ce(IV) in the irradiated mixture relative to the blank. The loss of oxalate caused by photosensitized oxidation can then be calculated from optical density data. $Ce(SO_4)_2$, prepared according to Smith and Fly,[61] in 0.2 $\underline{N}$ H_2SO_4 solutions at a concentration of ca. 0.01 $\underline{M}$, was used as the oxidant. The broad band absorption of Ce(IV) exhibits a maximum at 320.0 nm (ϵ 5.41×10^3 l mole^{-1} cm^{-1}). Beer's law is obeyed over the concentration range sufficient for adequate transmittance in a 1.0 cm cell.

Quantum yields for oxalate loss at the wavelengths used in the present study are given in Table 6. The values are interpolated from the data of Forbes.[58, 59]

Actinometry runs at 253.7 nm in the merry-go-round apparatus were done using both ferri-oxalate[62] and uranyl oxalate. The intensities calculated by the two methods were within experimental error (± 6%) of one another.

Table 6. Quantum Yields for Uranyl Oxalate Actinometry

λ (nm)	ϕ (oxalate ion loss)
236.6	0.580
242.9	0.603
248.1	0.606
253.7	0.600

Materials

All irradiations and ultraviolet spectra reported were done in n-pentane (Phillips) purified by passage through a 10% silver nitrate on alumina column according to Murray and Keller.[63] Cis- and trans-1,3-pentadiene were obtained from Chemical Samples Co. The dienes were bulb to bulb distilled from lithium aluminum hydride prior to use.

Irradiation Procedure

Irradiations were performed in 13 mm (OD) matched quartz tubes. 3.0 ml of a stock diene solution (ca. 0.1 M) was introduced into each of several tubes via a calibrated syringe. The tubes were thoroughly degassed by three freeze-pump-thaw cycles at 5×10^{-4} torr. Irradiations at 253.7 nm were performed in the merry-go-round apparatus.[45] For photolyses using the optical bench apparatus, tubes were positioned in the collimated, monochromatic exit beam of the Bausch and Lomb monochromator. Analysis of the light which passed through the solution indicated that only wavelengths greater than 260 nm were not absorbed by the substrate. Irradiation times were of the order of 12-30 hours. Conversions were lower than 4%. The total number of photons absorbed by the substrate was similar for all runs at all wavelengths. Actinometry was performed, as described above, in duplicate, at least three times during a given run.

At the end of a run, the tube was opened and a 1.0 ml aliquot was taken. To the aliquot of irradiated solution was added 1.0 ml of a solution of n-nonane (Aldrich) in pentane as internal standard. The solution was then analyzed by glpc (tandem column of 22' × 1/8" stainless steel 25% β, β'-oxydipropionitrile on Chromosorb W (60/80), NAW plus 15' × 1/8" SS 25% β, β'-oxydipropionitrile/5% silver nitrate on Chromosorb W (60/80), NAW, operated at room temperature, N_2 carrier 12 ml/min) on a Hewlett-Packard F. & M. 700 flame ionization vapor phase chromatograph. Relative peak areas of dienes and internal standard were measured by disc integration or by the cut-out and weigh method. Retention times of the materials under the analysis conditions were: trans-1, 3-pentadiene, 16 min, cis-1, 3-pentadiene, 22 min, and n-nonane, 29 min. Inherent errors of the analysis procedures are ±6-8%.

APPENDIX

URANYL OXALATE ACTINOMETRY

References

W. G. Leighton and G. S. Forbes, *J. Amer. Chem. Soc.*, **52**, 3139 (1930).

F. P. Brackett and G. S. Forbes, *ibid.*, **55**, 4459 (1933).

J. N. Pitts, Jr., J. D. Margerum, R. P. Taylor, and W. Brim, *ibid.*, **77**, 5499 (1959).

Preparation of Solutions

Uranyl oxalate ($UO_2C_2O_4$): 0.42478 g uranyl sulfate (UO_2SO_4) and 0.67262 g sodium oxalate ($Na_2C_2O_4$, primary standard grade) are dissolved in 0.2 *N* H_2SO_4 and diluted to 1.0 ℓ in the dark. The solution is 5.004×10^{-3} *M* in oxalate dianion and 1.011×10^{-3} *M* in uranyl ion. Store in a dark room.

Ceric sulfate ($Ce(SO_4)_2$): Ceric sulfate is prepared from ammonium hexanitratocerate according to the procedure of Smith and Fly (*Anal. Chem.*, **21**, 1233 (1949)). Approximately 5.5 g $(NH_4)_2Ce(NO_3)_6$ is dissolved in 15 ml water and treated with 100 ml 15 *N* NH_4OH. The resulting precipitate is washed with six portions of water (25 ml each) until neutral to pH paper. The precipitate is then dissolved in hot 2 *N* sulfuric acid (125 ml) and washed into a 1.0 ℓ volumetric flask. The solution is cooled and brought to approximately 950 ml. The cerium concentration is then determined spectrophotometrically by dilution of an aliquot and measurement of the optical density at 320.0 nm versus 0.2 N H_2SO_4 in a 1.0 cm cell. The extinction coefficient of Ce(IV) at this wavelength is 5.41×10^3 l $mole^{-1}$ cm^{-1}. The concentration of cerium is then adjusted until it is slightly greater than twice the (molar) concentration of oxalate in the actinometer solution. The use of commercial ceric sulfate is not recommended, since it is contaminated by ammonium nitrate which limits the stability of standardized cerium solutions.

2 N H_2SO_4: 56 ml concentrated sulfuric acid is diluted to 1.0 ℓ with water.

Procedure

Two 3.0 ml aliquots of actinometer solution are irradiated for 30 min or 60 min, depending on the wavelength of excitation: 30 min for 253.7 merry-go-round, and for 248 and 242 nm on the optical bench; 60 min for 236 nm. At the end of the irradiation, a 1.0 ml aliquot is pipetted into a 10.0 ml volumetric flask. 1.0 ml of the standard Ce(IV) solution and 1.0 ml 2 N H_2SO_4 are added and the solution brought to the mark with water. Both irradiated samples and an unirradiated blank are treated in this way. The solutions are then incubated at 80°C for 10 min and allowed to cool in the dark. The optical densities of the irradiated samples are determined at 320.0 nm *versus* a reference of the unirradiated blank.

Calculations

The measured light intensity is given by:

$$I = \frac{3 \times (OD) \times (10^{-2})}{2 \times t \times \phi \times A \times \epsilon}$$

where

OD = measured optical density at 320.0 nm vs. unirradiated blank. 1.0 cm path.

3 = volume of irradiated actinometer solution (ml).

10^{-2} = volume of dilution in liters.

2 = conversion factor to convert from moles cerium analyzed to moles oxalate photolyzed:

$$2\,Ce(IV) + C_2O_4^{=} \rightarrow 2\,Ce(III) + 2\,CO_2$$

t = time of irradiation (min)

ϕ = quantum yield of oxalate loss

A = fraction of incident light absorbed by actinometer solution (0.999)

ϵ = extinction coefficient of cerium(IV) at 320.0 nm (5.41×10^3 l mole^{-1} cm^{-1})

The formula reduces to

$$I = \frac{OD}{t \times \phi} \times (2.773 \times 10^{-6} \text{ Einsteins/min})$$

The quantum yields for photosensitized oxalate decomposition are:

λ (nm)	ϕ	λ (nm)	ϕ
208	0.48	278	0.58
(237)	(0.58)	302	0.57
(243)	(0.60)	313	0.56
245	0.61	335	0.53
(248)	(0.61)	366	0.49
254	0.60	405	0.56
265	0.58	436	0.58

The values in parentheses are interpolated from the other data (due to Leighton and Forbes, and Brackett and Forbes).

Comments

The procedure discussed here is an improved version of one due to Pitts. The sensitivity of the method is only half of that of the conventional ferri-oxlate procedure (largely because the extinction coefficient of Ce(IV) at the analysis wavelength is only half that of the phenanthroline-Fe(II) complex used in the analysis of the ferrioxalate procedure). Also, the success of the method outlined here depends critically on the concentration of Ce(IV): if the concentration is less than sufficient to oxidize all the oxalate in the unirradiated blank, the results will be meaningless; if the concentration is significantly greater than twice the oxalate concentration of the blank then the optical densities measured for the blank and irradiated samples will be so large as to render differential absorption techniques invalid. Considerable care must be exercised when one uses the uranyl oxalate actinometer, and one should always check the integrity of freshly prepared solutions by comparing intensities measured by uranyl oxalate actinometry to those obtained using ferri-oxalate actinometry at a wavelength at which quantum yields are known for both systems.

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