PART I
PHOTOSENSITIZED ISOMERIZATIONS

PART II
PHOTOSENSITIZED DIMERIZATIONS

Thesis by

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"Es irrt der Mensch,
so lang' er strebt..."

Goethe

"Zumindest hat dieser
Mensch versucht..."

Turro

ABSTRACT

PART I

cis $\rightleftarrows$ trans isomerization of the piperylenes (1,3-pentadienes), the 1,2-dichloroethylenes, and the 2-pentenes occurs in the presence of photosensitizers, mainly carbonyl compounds. The results form a coherent pattern if it is assumed that the key step is transfer of triplet excitation, which occurs on every collision between carbonyl triplets and a second molecule provided that transfer is exothermic. Endothermic transfers may occur but only with reduced efficiency.

PART II

Butadiene, cyclopentadiene, and cyclohexadiene are dimerized by irradiation in the presence of various photosensitizers. The relative yields of butadiene dimers are dependent upon the photosensitizer employed; however, the relative yields of cyclic diene dimers shows no corresponding dependence. The results are consistent with the assumption that energy transfer to the two conformers of butadiene produces two stereoisomeric, non-interconvertible triplets.

Introduction

Interest in the scope and mechanisms of photoreactions has surged in the last several years. The influx of literature in the field is reflected by recent reviews.[1] Somewhat belated employment by the photochemist of the powerful tools of the spectroscopist has allowed the direct investigation of transient species formerly relegated to the realm of unverifiable speculation. Moreover, careful study of photoreactions by physical organic chemists is beginning to provide new kinds of information concerning excited states which are not readily accessible by spectroscopic techniques. Excellent reviews[2] of molecular photochemistry and electronic excited states of molecules, written by spectroscopists in a language palatable to organic chemists, have facilitated the alliance of spectroscopists and organic photochemists. A brief survey of the results and methods of spectroscopy is necessary for a complete understanding and appreciation of mechanistic organic photochemistry.

Photochemistry and Spectroscopy

Electronically Excited Molecules.

In accordance with the Pauli and Aufbau principles[3] most polyatomic organic molecules possess ground state electronic configurations in which all of the bonding molecular orbitals are filled with two spin-paired electrons. Such a configuration is termed a ground singlet state, S_o. Absorption of a quantum of ultra-violet or visible radiation by the molecule promotes an electron from an occupied molecular orbital (MO) to a vacant antibonding MO; two electrons become *orbitally* unpaired. However, unless the electrons remain *spin-paired* the transition is highly forbidden and the corresponding absorption can occur only with extremely low intensity. Nearly all absorption bands observed in ordinary absorption spectroscopy are the result of singlet-singlet transisitons, i.e., $S_o \longrightarrow S_n$. The Pauli principle places no spin restrictions for most excited configurations, so the radiationless spin inversion (intersystem crossing) may occur producing a second excited state, T_1, a triplet.

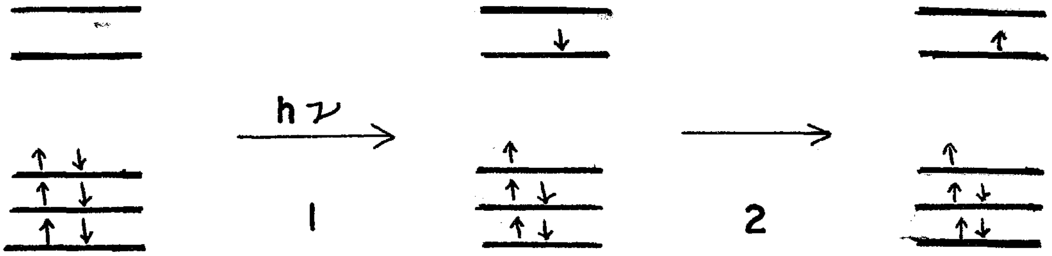

Figure 1

Other processes which may typically occur after electron excitation are shown in Figure 2. Absorption, *1*, of a quantum of light excites the molecule from its ground state, S_o, to an upper vibrational level of the excited singlet state, S_2. The Franck-Condon principle[4] states

Molecular Excited States

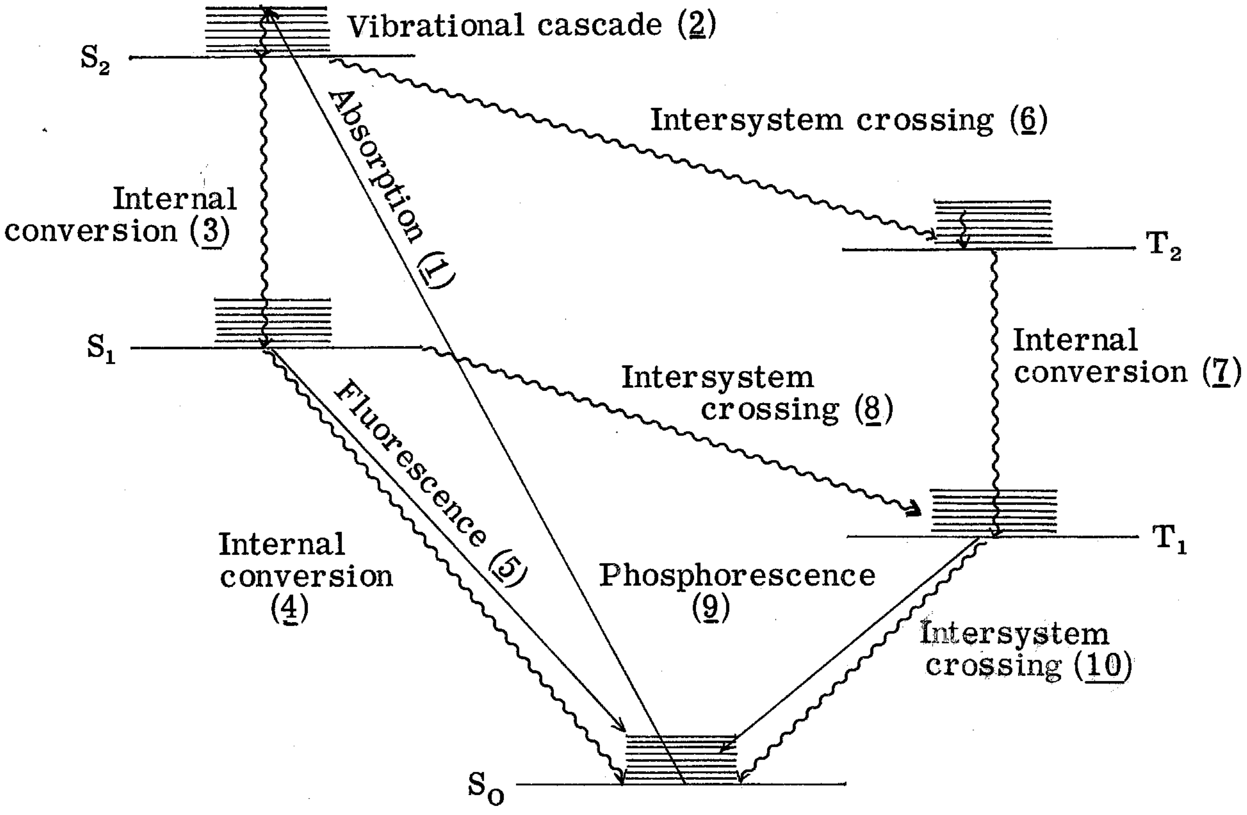

Figure 2

that nuclear motions (which occur in about 10^{-10} - 10^{-12} sec.) are slow compared to the time necessary for electron excitation (10^{-15} sec.), so that the geometry of the excited molecule immediately before and after absorption *is identical. It is important* to point out that rapid vibrational relaxation of excited states, 2, may produce nuclear geometries quite different from that of the ground state. Internal conversion, radiationless transition between states of like multiplicity, 3, to the S_1 state usually occurs within 10^{-11} sec. In condensed phases the S_1 state is invariably populated very shortly after electronic excitation to any upper excited singlet state[5]. From S_1 several paths are available for stabilization of the excess electronic energy. Fluorescence, 5, (radiative transition to S_o) usually occurs with 10^{-8} - 10^{-9} sec., while internal conversion to S_o, 4, takes about 10^{-9} - 10^{-10} sec.[5] The longest lived S_1 states possess radiative lifetimes in the order of 10^{-7} sec. Radiationless transition between states of different multiplicity, intersystem crossing, 8, to produce T_1 must therefore occur at a rapid rate to compete with other modes of deactivation of S_1. From T_1 the molecule may decay to S_o by either phosphorescence, 9, in a time usually greater than 10^{-5} sec., or undergo intersystem crossing, 10, to S_o. Forbiddenness caused by spin inversion causes the rate of the latter two processes to be slowed down (lifetimes of corresponding states increased) with respect to other modes of deactivation which do not involve a change in multiplicity.

For example, the absorption corresponding to promotion of a π -bonding election to π *-antibonding orbital ($\pi \longrightarrow \pi^*$) in formaldehyde possesses an extinction maximum at 1700A with ϵ max = 20,000. Another absorption corresponding to promotion of a n nonbonding electron on oxygen to a π * orbital ($n \longrightarrow \pi^*$) occurs at 2900 A with ϵ max = 20 (See Figure 3).

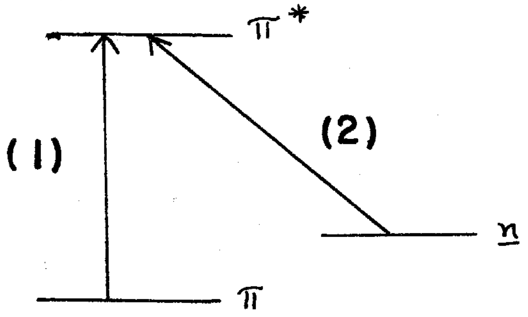

Figure 3

Transition (1) produces a singlet excited state symbolized by $^1(\pi, \pi^*)$ and has a lifetime of roughly 5 x 10^{-9} sec. Transition (2) produces a $^1(n, \pi^*)$ state which has a lifetime of roughly 5 x 10^{-6} sec. The triplet states corresponding to these two transitions are symbolized as $^3(\pi, \pi^*)$ and $^3(n, \pi^*)$, respectively. In general, the non-bonding lone pair n electrons of a carbonyl are the least strongly bonded in the molecule, so that the $^1(n, \pi^*)$ state will be the S_1 state for these compounds. Transition to the latter state is forbidden, and accordingly it possesses a long radiative lifetime.

In closing we should define the important quantity Φ, the quantum yield, which is the measure of the efficiency of a photochemical reaction.

$$\Phi \equiv \frac{\text{rate of formation of products or disappearance of reactants}}{\text{rate of absorption of light by the system}}$$

Energy Transfer. An important process in organic photochemistry involves transfer of electronic excitation from one molecule to another[6]. Consider Figure 4 in which a simplified energy level diagram of the sensitizer (S) and the acceptor (A) is represented.

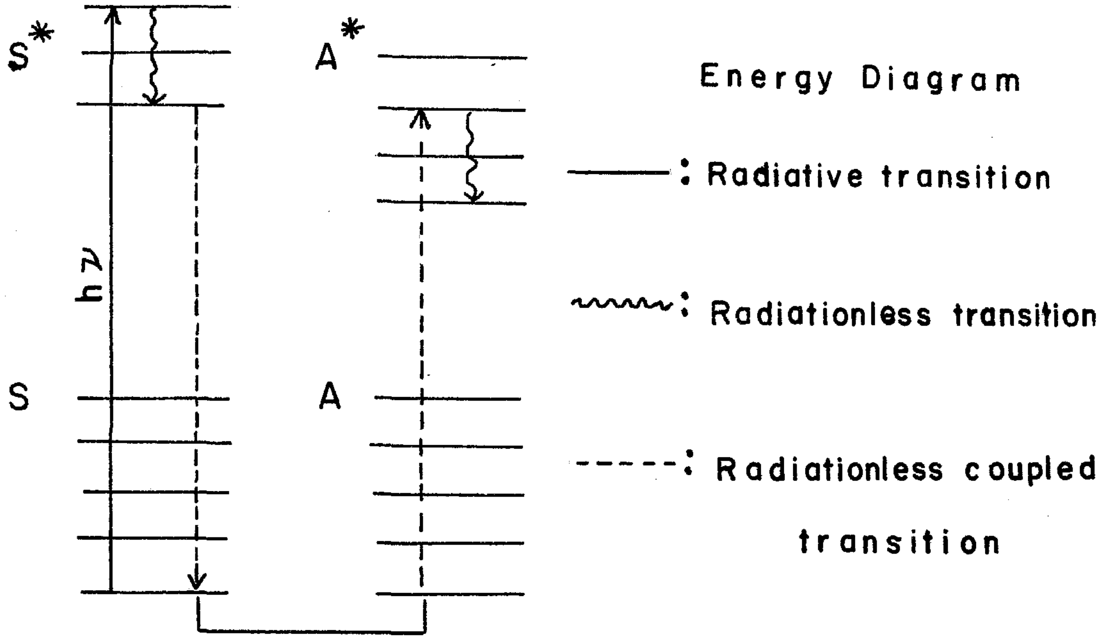

Figure 4

If an excited molecule (S*) exists in the neighborhood of another molecule (A) and the energy difference for a possible deactivating process in the sensitizer molecule corresponds exactly to that for a possible absorption transition in A, then with sufficient energetic coupling between these molecules, both processes may occur simultaneously. The net result is given in equation 2.

$$S \xrightarrow{h\nu} S^* \qquad (1)$$

$$S^* + A \longrightarrow A^* + S \qquad (2)$$

The molecule A may undergo a photochemical reaction, even though it does not absorb the exciting radiation.

$$A^* \longrightarrow \text{Products} \qquad (3)$$

Obviously, the longer a molecule persists in an excited state the greater the probability that it will encounter another molecule capable of accepting its excitation energy. In addition to being the lowest excited states in most molecules, triplet states possess lifetimes several orders of magnitude greater than excited singlet states. Triplets therefore are likely candidates to transfer energy to suitable acceptors.

At 90° K in alcohol/isopentane solution, Terenin and Ermolaev detected triplet-triplet energy transfer[7]. These workers found that many donor substances are capable of exciting certain acceptors to triplet states. For instance, irradiation of a glassy solution containing naphthalene and benzophenone in which the latter absorbs all of the light, produces a high yield of naphthalene phosphorescence.

$$(C_6H_5)_2C{=}O \longrightarrow (C_6H_5)_2C{=}O(S^*) \longrightarrow (C_6H_5)_2C{=}O(T)$$

$$(C_6H_5)_2C{=}O(T) \; + \; C_{10}H_8 \longrightarrow (C_6H_5)_2C{=}O \; + \; C_{10}H_8(T)$$

$$C_{10}H_8(T) \longrightarrow C_{10}H_8 \; + \; h\nu$$

A major requirement for the occurrence of energy transfer is that the <u>donor triplet excitation energy be higher than the corresponding energy of the acceptor</u>. Since relatively high concentrations (0.1 M) of acceptor and donor were required to detect such induced excitation it was assumed that energy transfer from triplet levels does not occur over distances much greater than molecular diameters[8].

<u>Energy Transfer in Solution</u>. Evidence for the production of triplet states in solution has come from several independent sources:

(a) flash photolytic determination of absorption spectra of triplets;

(b) phosphorescence spectra of molecules in solution;

(c) energy transfer from the triplet state of one molecule to another;

(d) kinetic analysis of photoreduction reactions.

Although phosphorescence of most compounds is rarely observed in solution (α -diketones being notable exceptions) due to the existence of faster, non-radiative paths to the ground state, flash techniques permit the direct observation of triplet species in solution[9]. This elegant technique for the detection of transient species in solutions employs an extremely intense flash of light of short duration which excites a large number of molecules to upper singlet states. Usually a significant number of these excited molecules decay to a long-lived triplet state. A second spectrophotometric flash then determines the triplet-triplet absorption spectrum of the molecule. Porter[9] has reported a large number of such experiments. These workers have concluded that energy transfer from donor to acceptor occurs at a diffusion controlled rate, when the latter molecule possessed a $S_o \longrightarrow T_1$ transition which is lower in energy than the initially excited molecule.

Backstrom and Sandros[10] have come to the same conclusion during their study of the quenching of the solution phosphorescence of biacetyl. Energy transfer occurs at the diffusion controlled rate when the $S_o \longrightarrow T_1$ transition of the acceptor is lower than that of the $T_1 \longrightarrow S_o$ emission of biacetyl. As the $S_o \longrightarrow T_1$ transition of the quencher becomes slightly greater than the energy for the $T_1 \longrightarrow S_o$

emission of biacetyl, the efficiency of energy transfer decreases due to reversible transfer from quencher to biacetyl. When the triplet energy of the quencher becomes much greater than that of biacetyl, the efficiency of energy transfer falls off drastically.

Hammond and co-workers[11] have analyzed the kinetic data for the photoreduction of benzophenone by benzhydrol and concluded that the triplet state of the ketone is the chemically active species in this reaction.

Similar analysis for the photoreduction of 2-acetonaphthone by tributyltin hydride leads to a similar conclusion.[12] From measurements of the rate of quenching relative to the rate of hydrogen abstraction, it was also concluded that the rate of quenching of ketone triplets by naphthalene and certain metal chelates was close to diffusion controlled. More direct evidence for the intermediacy of triplets in the photoreduction has been produced by the measurement of the rate constants for triplet decay, hydrogen abstraction, and triplet quenching of benzophenone and 1-naphthaldehyde[13]. Here again the rate of quenching of ketone triplets by metal chelates was found to occur at the diffusion-controlled rate.

Finally, the photosensitized decomposition of 1-iodonaphthalene to give iodine has led to similar conclusions to those stated above[12a].

The above results demonstrate several important points:

(a) the excited state involved in the photoreductions of aromatic ketones is the triplet state;

(b) irradiation of carbonyl compounds produces triplets in high yield;

(c) energy transfer from carbonyl triplets to suitable acceptors occurs at the rate of diffusion when the transfer is exothermic.*

Most of the results discussed above involve carbonyl compounds as energy donors. There is no reason to expect that only carbonyl compounds are capable of transferring triplet excitation in solution. Indeed, recent results[14] have shown that sensitization by non-carbonyl compounds can occur, although usually with lower efficiency than that observed with carbonyl compounds. For example, these authors observed energy transfer from many unsubstituted aromatic molecules to substituted naphthalenes.

The work of Schenck[15] while woven in a different mechanistic framework, has demonstrated the synthetic utility of sensitized photoreactions. Photosensitized addition of maleic anhydride to itself and to a large number of unsaturated compounds is only one example of a set of reactions with enormous potential synthetic scope.

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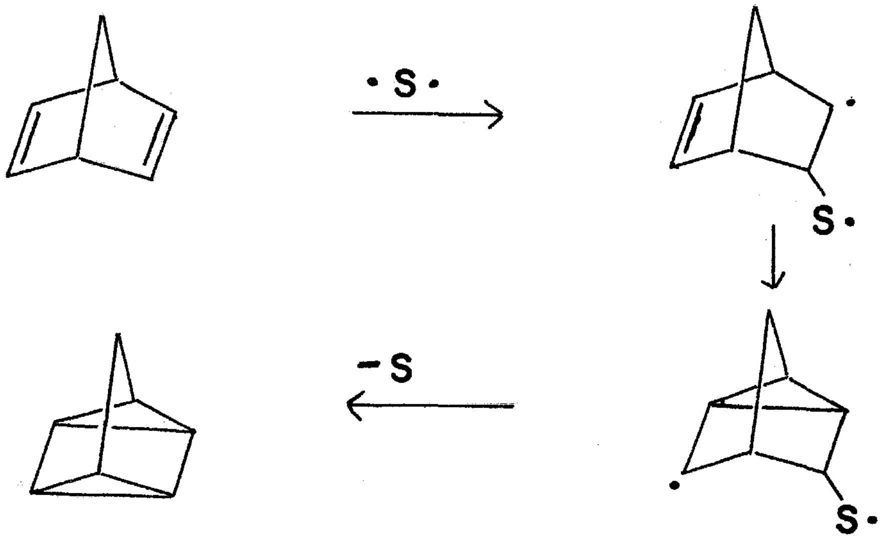
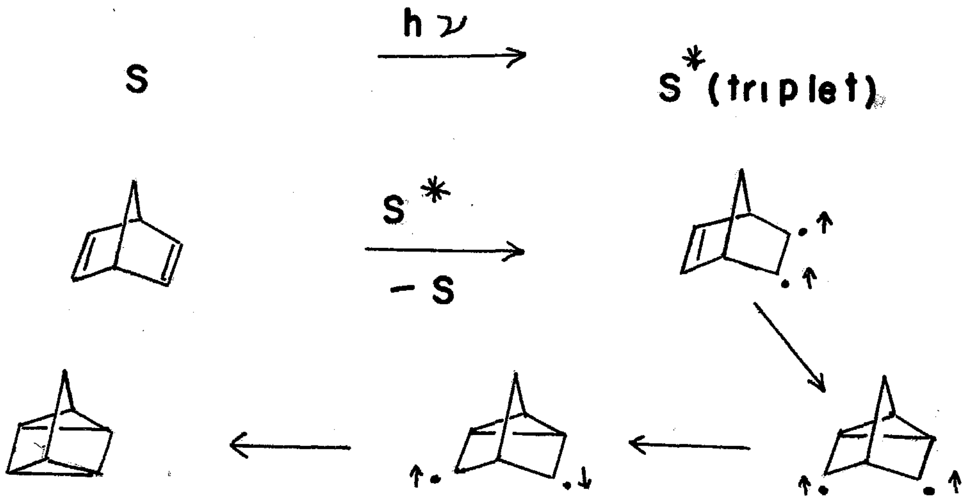
*By exothermic transfers is meant, coupled transitions occurring between the sensitizer and acceptor in which Franck-Condon excitation occurs and for which E_t (sensitizer) $>$ E_t (acceptor).

Schenck[16] has long advocated a radical addition-elimination mechanism to account for these photosensitized reactions. The following mechanism for the photosensitized isomerization of norbornadiene[17] is typical.

$$\mathrm{S} \xrightarrow{h\nu} \cdot\mathrm{S}\cdot \text{ (radical)}$$



Although many of the sensitizers (notably carbonyl compounds) used in these photoreactions show "radical-like" character in their excited states, we feel that a large body of the photosensitized reactions which occur in solution can be more satisfactorily explained on the basis of physical energy transfer from sensitizer to acceptor. Thus, the above mechanism proposed by Schenck would be replaced by the following one.

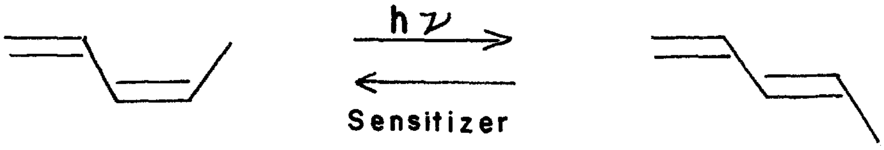


The work reported here was performed in order to obtain evidence for the role of triplets in solution photochemistry, to establish a theoretical scheme which will lead to a better understanding of mechanistic organic photochemistry, and to establish triplets as useful intermediates in organic chemistry. The study of energy transfer is of general importance to such areas as photosynthesis[18], scintillations[19a], radiation protection[19b] and photochromism[20]. Furthermore, triplet-triplet transfer permits studies of the photochemistry of the triplet state without the intermediacy of the singlet state.

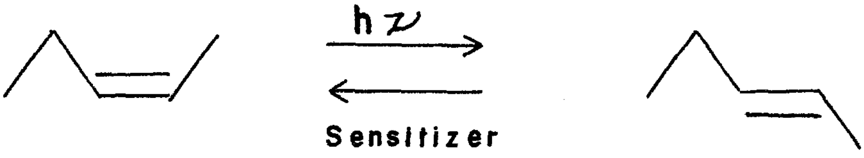
Experimental Results

Although many examples of photochemical *cis*-*trans* isomerizations (lg) and a few scattered reports of photosensitized isomerizations[35] appear in the literature, only recently have the detailed mechanisms of these reactions received adequate attention[22]. The role of triplet states in these reactions has often been suspected but no definitive experiments have been performed to substantiate this hypothesis.

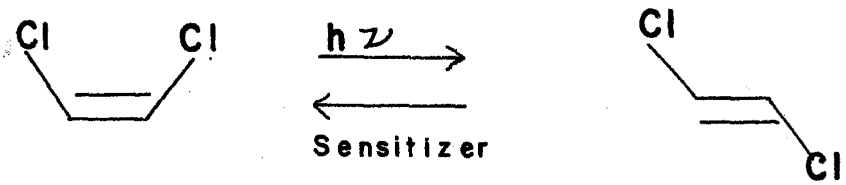
The *cis* ⇄ *trans* interconversion of the piperylenes (1,3-pentadienes), 2-pentenes, and 1,2-dichloroethylenes was chosen as convenient chemical processes for the detection of energy transfer from the triplet states of various sensitizers to unsaturated molecules.



cis-Piperylene *trans*-Piperylene



cis-2-Pentene *trans*-2-Pentene



cis-Dichloroethylene *trans*-Dichloroethylene

The results presented here hopefully provide strong evidence that triplets play an important role in photochemical cis-trans isomerizations.

Benzene solutions containing sensitizer and acceptor were irradiated with a high pressure mercury arc. Vapor phase chromatography (vpc) was used to follow the course of isomerization. Two kinds of measurements were employed to characterize these cis-trans interconversions; (a) determination of the photostationary mixtures produced by prolonged irradiations and (b) measurement of the quantum yields, at low conversion, for the cis ⟶ trans and trans ⟶ cis processes.

Prolonged irradiation of the piperylenes in the presence of different sensitizers* produces different photostationary mixtures as shown in Table I. A revealing pattern of the variation is given in Figure I in which the % trans isomer at the photostationary state is plotted against the triplet excitation energy (energy corresponding to the $0 \longrightarrow 0$ phosphorescence band) of the sensitizer.

The photostationary mixture of piperylenes produced by any given sensitizer is not dependent upon solvent as seen from Table II. *Likewise, variation of the concentration of piperylene has little effect on the photostationary*

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*Direct irradiation of cyclohexane solutions of cis- or trans- piperylene produces cis-trans isomerization, and intramolecular addition to produce 3-methylcyclobutene[21a].

mixture of isomers as shown in Table III. On the other hand, variation of the concentrations of sensitizers had a striking effect on the photostationary mixture of piperylenes, as shown in Table IV.

Quantum Yields. The results of quantum yield measurements were made with 0.20 M solutions of *cis* or *trans*-piperylene and are given in Table VI. These measurements were repeated at about a ten-fold decrease in the intensity of the exciting radiation, and at a slightly lower concentration of piperylene. The results of these measurements are given in Table V.

Dichloroethylenes and 2-Pentenes. Prolonged irradiation of the dichloroethylenes and 2-pentenes produces mixtures of *cis-trans* isomers which, at least for the latter compounds, appear to be close to photostates since similar compositions are obtained starting with either isomer. Benzil, fluorenone and 2-acetonaphthone are extremely inefficient as sensitizers. The data for these systems are presented in Tables VII and VIII.

Table I

Isomerization of cis and trans piperylene

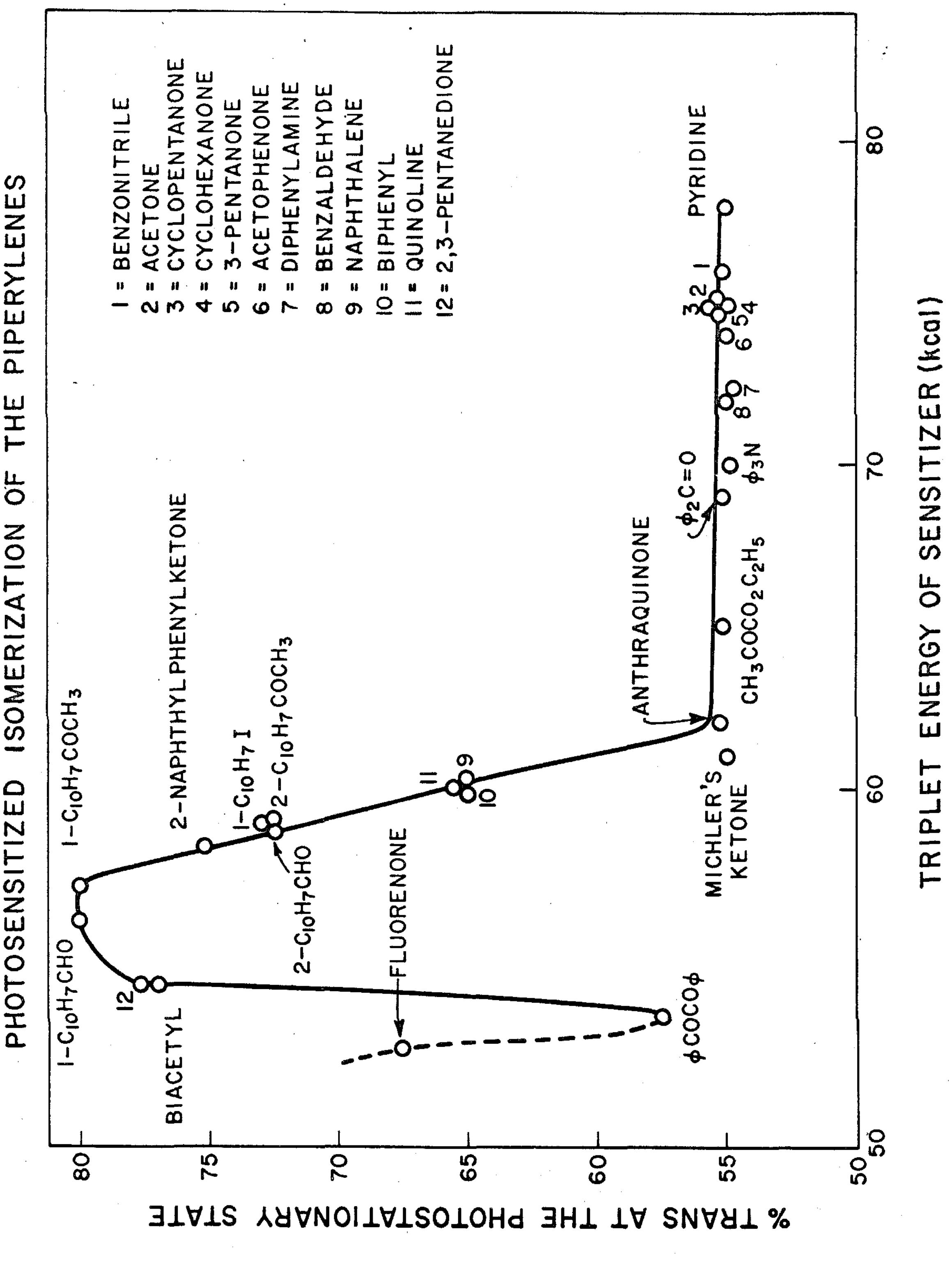
Sensitizer[a]	% trans from trans	% trans from cis	E_t^d of Sensitizer kcal
Benzonitrile[b]	-	55	78
Acetone[c]	-	57	74
Butanone[c]	-	57	74
3-Pentanone[c]	-	57	74
Cyclopentanone[c]	59	57	74
Cyclohexanone	59	58	74
2-Methylcyclohexanone[c]	59	57	74
Benzoic acid	-	55	78
Ethylbenzoate	-	57	?
Acetophenone	55	53	74
p-Hydroxybenzaldehyde	-	55	-
o-Methoxybenzaldehyde	-	55	-
Benzaldehyde	55	53	74
Diphenyl amine[b]	-	55	72
Pyridine[b]	-	55	?
Triphenylamine[b]	-	55	70
Benzophenone	57	56	69
Ethyl pyruvate	58	54	65
Biphenyl[b]	-	74	65
Anthraquinone	57	57	62
Michler Ketone	56	56	61
Naphthalene[b]	-	74	60
1-Iodonaphthalene	79	73	60
Quinoline[b]	-	74	60
2-Naphthaldehyde	72	71	59
2-Acetonaphthone	72	72	59
2-Naphthyl phenyl ketone	76	74	58
1-Nitronaphthylene	75	74	58
β-Naphthyl	75	76	58,54
1-Acetonaphthone	79	79	57
Biacetyl	77	77	55
2,3-Pentanedione	77	76	55
9-Fluorenone	69	67	53
Benzil	58	56	54
Dibenzylacetone[b]	100[a]	9[a]	53
Benzanthrone[b]	81[a]	30[a]	?
3-Acetylpyrene[b]	80[b]	27[b]	?
o-Hydroxybenzaldehyde	No reaction		70
2,4-Dihydroxybenzaldehyde	No reaction		
2-Hydroxyl-4 methoxy-benzophenone			

a. Unless specified, sample irradiated for 5-10 hours.

b. Sample irradiated for 3-5 days.

c. E_t assigned on the basis of the value measured for diisopropyl ketone

d. E_t is the triplet energy available for transfer from sensitizer based on the 0 → 0 band for phosphorescence. These values were taken mainly from two sources: G.N. Lewis and M. Kasha, J. Am. Chem. Soc., 66, 2100 (1944), and W. G. Herkstroeter, unpublished results.



PHOTOSENSITIZED ISOMERIZATION OF THE PIPERYLENES

Table II

Solvent Effects on the Isomerization of *cis*-Piperylene in the Presence of Three Sensitizers; (% *trans* at the Photostationary State.)

Solvent	Benzophenone	2,3-Pentanedione	2-Acetonaphthone
Ethanol	0.57	0.62	0.63
Pentane	0.57	0.68	0.63
Chlorobenzene	0.54	0.64	0.61
Benzene	0.54	0.66	0.64
Acetonitrile	0.54	0.66	0.63

Table III

Dependence of Photostationary State Composition on Piperylene Concentration

Sensitizer (0.1N)	$(\text{trans})_0^a$	% trans^b	$(\text{cis})_0^a$	% trans^b
Benzophenone	10^{-1}	55	10^{-1}	54
	10^{-2}	55	10^{-2}	56
	10^{-3}	54		
2-Acetonaphthone	10^{-1}	72	10^{-1}	72
	10^{-2}	76	10^{-2}	76
	10^{-3}	75		
Fluorenone	10^{-1}	71	10^{-1}	70
	10^{-2}	73	10^{-2}	72
	10^{-3}	75		

a. Initial concentration of pure piperylene

b. % at photostationary state

Table IV

Effect of Sensitizer Concentration on Photostationary Mixture of Piperylenes[a]

Sensitizer	Concentration of Sensitizer[b]	cis/trans
Benzophenone	1	0.80
	10^{-1}	0.80
	10^{-2}	0.80
	10^{-3}	0.80
	10^{-4}	0.80
Fluorenone	1	0.17
	10^{-1}	0.32
	10^{-2}	0.49
	10^{-3}	0.66
2-Acetonaphthone	1	0.37
	10^{-1}	0.41
	10^{-2}	0.62
	10^{-4}	0.78

a. Starting with pure <u>trans</u>-piperylene

b. Concentration in moles per liter

Table V

Quantum Yields for the Isomerization of the Piperylenes at Reduced Intensity[a]

Sensitizer[b]	$\Phi_{t \to c}$	$\Phi_{c \to t}$
Benzophenone	0.37	0.42
	0.39	0.50
	0.35	
2-Acetonaphthone	0.27	0.45
	0.29	0.39
	0.26	
Fluorenone	0.28	0.49
	0.31	0.45
	0.30	
Benzil	0.23	0.42
	0.24	0.42
	0.21	0.42
	0.23	0.42

a. concentration of piperylene 0.10-0.05N

b. concentration of sensitizer 0.1N

Table VI

Quantum Yields for the Photosensitized Isomerization of cis- and trans- Piperylene

Sensitizer	$\Phi_{t \rightarrow c}$	$\Phi_{c \rightarrow t}$
Benzophenone	0.39 ± 0.01	0.53 ± 0.02
	0.41 ± 0.01	0.58
Benzaldehyde	0.36 ± 0.01	0.53 ± 0.03
	0.30 ± 0.01	0.57
	0.36	0.56
2-Acetonaphthone	0.35 ± 0.01	0.53 ± 0.01
	0.34	0.55
	0.32	
1-Naphthaldehyde	0.39 ± 0.01	0.64
	0.36 ± 0.03	
	0.38 ± 0.03	
Acetophenone	0.32 ± 0.01	0.67 ± 0.02
	0.32 ± 0.01	0.56
Benzil	0.24 ± 0.01	0.55 ± 0.01
Fluorenone*	0.51 ± 0.03	0.71
	0.30 ± 0.02	0.75 ± 0.03
Michler's Ketone*	0.59	0.84
	0.51	0.91
		0.54
Biacetyl*	0.42	0.85
	0.41	

*It appears that quantum yields of isomerization by "yellow" sensitizers are consistently high. This was later shown to be due to absorption of 4000Å light not sensed by the actinometer. For measurements of quantum yields with a$_o$ Corning 737 filters (narrow band of transmission at 3660A) see Table VII.

Table VII

Photosensitized Isomerization of 2-Pentenes

Sensitizer	Starting Material	trans/cis after 8 days of irradiation
Acetone	cis-2-pentene	1.7
Acetone	trans-2-pentene	1.9
2-Acetophenone	cis-2-pentene	3.6
2-Acetophenone	trans-2-pentene	3.9
Benzophenone	cis-2-pentene	6.1
Benzophenone	trans-2-pentene	6.6
Benzil	cis-2-pentene	0.8
Fluorenone	cis-2-pentene	0.2

Table VIII

Photosensitized Isomerization of trans-1,2-Dichloroethylene

Sensitizer	cis/trans in photostationary mixtures
Acetone	2.1
Acetophenone	3.1
Benzophenone	4.5
Benzil	4.1
Fluorenone	2.5
2-Acetonaphthone	very slow isomerization

Discussion

Dependence of Photostationary Compositions of Piperylenes on Sensitizer. Inspection of the data in Table I and Figure I reveals several striking results:

(a) use of various sensitizers gives photostationary mixtures whose compositions differ dramatically;

(b) dibenzalacetone, acetopyrene and benzanthrone, whose triplet state are less than 53 kcal above their ground states are extremely inefficient as sensitizers, in marked contrast to the high efficiency exhibited by other carbonyl compounds;

(c) sensitizers whose triplet excitation energies are above 60 kcal give the same results;

(d) sensitizers whose triplet excitation energies are below 60 kcal give a variety of results.

It is significant that a plot of the % trans isomer in the photostationary mixtures against E_t of the sensitizer produces an inflection point near 59-60 kcal (see Figure I), since the latter value corresponds closely to the energy found for the $S_o \longrightarrow T_1$ absorption of butadiene[21]. The failure of carbonyl compounds whose E_t is less than 53 kcal to function as efficient sensitizers characterizes the $S_o \longrightarrow T_1$ transition of the piperylenes as requiring more than 53 kcal., the approximate location of the minimum in Figure I. The cause of the second ascent of the curve at energy below 53 kcal is not clear, but a similar behavior is observed in other systems[22].

Measurements of the effect of cis- piperylene as a quencher of the photoreduction of benzophenone by benzhydrol[23] have led to the conclusion that excitation transfer from ketone to diene occurs on every collision. Since the studies cited in the introduction of this section indicate that the major requirement for diffusion controlled transfer is that the process be exothermic, the fact that sensitizers that have E_t greater than 60 kcal produce the same photostationary mixture of isomers is of special significance. The postulate which most easily accomodates this result is the view that <u>all of these sensitizers transfer energy to the piperylenes at every collision</u>. The composition of the photostationary mixtures is therefore dependent only on the decay processes of the piperylene triplets.

The pattern of the variation of compositions of photostationary mixtures produced by sensitizers with 53 kcal $< E_t <$ 60 kcal can be explained by the following simple hypothesis:

> If the energy of the ground vibrational level of the T_1 state of the sensitizer is less than the energy of the $0 \longrightarrow 0$ component of the $S_o \longrightarrow T_1$ transition of the acceptor, excitation transfer will be an endothermic process and will become measurably inefficient.

There is no reason to expect that transfer processes involving the <u>cis</u> and <u>trans</u> dienes to decrease at the same rate. Sensitizers possessing E_t between 53 and 60 kcal establish stationary states in which the trans isomer predominates. These data indicate that transfer to the trans isomer becomes inefficient more rapidly than does transfer to the cis isomer. Therefore, if energetics were the only controlling factor we would conclude that the $S_o \longrightarrow T_1$ transition of the trans diene lies at a slightly shorter wavelength than the same transition of the cis isomer.

Finally a point is reached where the triplet levels of the sensitizers are lower than the triplet levels of both dienes (E_t of the sensitizer less than 53 kcal) and isomerization occurs inefficiently if at all.

Dependence of Photostationary Mixtures on Solvent. The lack of a solvent effect on the photostationary states produced by a given sensitizer is perhaps surprising. The position of $S_o \longrightarrow S_1$ absorption for many carbonyl compounds shows marked dependence upon solvent[24]. These shifts can be interpreted as arising from Franck-Condon excitation of a molecule and the different energetics due to the variation in solvating power of the solvent for the ground state and the excited states of a molecule. Since there is no solvent effect on the photostationary compositions, even for sensitizers whose E_t falls in a region which is very sensitive to the energy available for transfer, we might conclude that (a) solvent does not participate in energy transfer, and (b) that electronic and nuclear configuration of the sensitizer triplet is similar to that of the ground state. Since correlation of E_t values derived from phosphorescence spectra show peculiar solvent dependence at times[25] it is not clear what type of solvent effect is to be expected for transfer of triplet excitation.

It should be pointed out that no solvent effect is to be expected for benzophenone since energy transfer to each isomer is highly exothermic. The lowest triplet state of 2-acetonaphthone probably has the (π, π*) configuration. Solvent shifts are not large for absorption bands due to (π, π*) singlet-singlet transitions, so perhaps only a small solvent shift is to be expected for the (π, π*) triplet.

This leaves 2,3-pentanedione as the only sensitizer for which a change of solvent might be expected to shift significantly the energy for the $S_o \longrightarrow T_1$ transition. Since 2,3-pentanedione abstracts hydrogens from alcohols, a characteristic reaction of n, π* triplet states[11,23], the lack of a solvent effect here is perhaps significant. A pertinent experiment is to seek the effect of solvent on phosphorescence spectra in solution at room temperature for benzil and 2,3-pentanedione. Measurements of the solvent dependence of the photostationary composition of <u>cis</u>-<u>trans</u> isomers produced by endothermic energy transfer from benzophenone (vide infra) should help to elucidate this problem, also.

The data in Table III show that there is only a slight dependence of the photostationary mixtures of piperylenes on the diene concentration. However, the effect of variation of sensitizer concentration of the photostationary states of the piperylenes is quite striking. These experiments are preliminary in nature and need to be better documented by approaching the photostationary state starting from each isomer, but a trend is quite clear. As the concentration of sensitizer is lowered, for sensitizers possessing E_t less than 60 kcal, the mixture of piperylenes becomes more like that of a sensitizer possessing E_t greater than 60 kcal.

In order to explain these results an examination of the kinetics of the photosensitized isomerization is in order. The two following mechanisms are proposed:

I	Reaction	Rate[#]	
	$B \longrightarrow B^*$	I	(1)
	$B^* \longrightarrow B$	$k_d [B^*]$	(2)
	$cP + B^* \longrightarrow B + T$	$k_{qc} [B^*] [cP]$	(3)
	$tP + B^* \longrightarrow B + T$	$k_{qt} [B^*] [tP]$	(4)
	$T \longrightarrow cP$	$k_1 [T]$	(5)
	$T \longrightarrow tP$	$k_2 [T]$	(6)

[#] The efficiency of triplet formation is assumed to be unity. Since the sum of the quantum yields for isomerization for many sensitizers approaches one, intersystem crossing must be nearly quantitative.

II

Reaction	Rate	
$B \longrightarrow B^*$	I	(7)
$B^* \longrightarrow B$	$k_d \, [B^*]$	(8)
$cP + B^* \longrightarrow B + T$	$k_{qc} \, [B^*] \, [cP]$	(9)
$tP + B^* \longrightarrow B + T$	$k_{qt} \, [B^*] \, [tP]$	(10)
$T + B \longrightarrow cP + B + E$	$k_{rc} \, [T] \, [B]$	(11)
$T + B \longrightarrow tP + B + E$	$k_{rt} \, [T] \, [B]$	(12)
$T \longrightarrow cP$	$k_1 \, [T]$	(13)
$T \longrightarrow tP$	$k_2 \, [T]$	(14)

where B is the sensitizer, cP is cis-piperylene, tP is trans-piperylene and T is triplet piperylene.

Mechanism I predicts the following equations if the steady state approximation for (B*) and (T) is used.

$$\frac{1}{\phi_{t \rightarrow c}} = \frac{k_1 + k_2}{k_1} \left[1 + \frac{kd}{k_{qt} \, [tP]_o} \right] \qquad (15)$$

$$\frac{1}{\phi_{c \rightarrow t}} = \frac{k_1 + k_2}{k_2} \left[1 + \frac{k_d}{k_{qc} \, [cP]_o} \right] \qquad (16)$$

$$\frac{k_1 + k_2}{k_1} = 1 + \frac{k_{qc} \, [cP]_s}{k_{qt} \, [tP]_s} \qquad (17)$$

where subscript o refers to the concentration of piperylene at time equal zero and subscript s refers to the concentration of piperylene at the photostationary condition.

Similarly, mechanism II predicts the following relationships

$$\frac{k_{qt}\,[tP]_s}{k_{qc}\,[cP]_s} = \frac{k_{rt}\,[B] + k_2}{k_{rc}\,[B] + k_1} \qquad (18)$$

$$k'\,\frac{[tP]_s}{[cP]_s} = \frac{k_{rt}\,[B]}{k_{rc}\,[B] + k_1} + \frac{k_2}{k_{rc}\,[B] + k_1} \qquad (19)$$

where

$$k' = \frac{k_{qt}}{k_{qc}} \qquad (20)$$

When $k_{rt} = 0$ then equation 19 after rearrangement becomes

$$\frac{k'\,[tP]_s}{[cP_s]} = \frac{k_2}{k_1} + \frac{k_2}{k_{rc}\,[B]} \qquad (21)$$

Similarly, when $k_{rc} = 0$ we have

$$\frac{k'\,[tP]_s}{[cP]_s} = \frac{k_{rt}\,[B]}{k_c} + \frac{k_2}{k_1} \qquad (22)$$

Examination of the data in Table IV show that $\frac{tp}{cp}$ increases with decreasing concentration of sensitizer for fluorenone and 2-acetonaphthone, but the data do not yield a linear plot as predicted by equation 21. Apparently neither extreme case applies[26a], but mechanism II is probably operating when the triplet energy of the sensitizer is close to that of the piperylenes. Backstrom[10] has come to a similar conclusion that reversible energy transfer occurs between biacetyl and quenchers whose triplet energies are slightly higher than that of the diketone.

Mechanism I, however, in which energy transfer occurs irreversibly from sensitizer to diene, probably applies for diffusion controlled energy transfer to both isomers of the diene. This is in agreement with the fact that the composition of the photostationary mixture of piperylene isomers is independent of benzophenone concentration. Furthermore, equations 15, 16 and 17 can be simplified for the limiting case of diffusion controlled energy transfer. Under these conditions k_{qt} is equal to $k_{qc} >> k_d$, and the rate of the reverse energy transfer is zero. Equations 15 and 16 simplify to 23 and 24 , respectively

$$\frac{1}{\phi_{t \rightarrow c}} = \frac{k_1 + k_2}{k_1} \qquad (23)$$

$$\frac{1}{\phi_{c \rightarrow t}} = \frac{k_1 + k_2}{k_2} \qquad (24)$$

Equation 17 becomes

$$\frac{k_1 + k_2}{k_2} = 1 + \frac{[cP]_s}{[tP]_s} \tag{25}$$

or

$$\frac{k_1 + k_2}{k_1} = 1 + \frac{[tP]_s}{[cP]_s} \tag{26}$$

Combining the four above equations we have

$$\frac{1}{\Phi_{t \rightarrow c}} = 1 + \frac{[tP]_s}{[cP]_s} \tag{27}$$

$$\frac{1}{\Phi_{c \rightarrow t}} = 1 + \frac{[cP]_s}{[tP]_s} \tag{28}$$

Table IX presents a comparison of the value of the lefthand sides of the two above equations calculated from the data in Table V with the value of the righthand sides as calculated from the data in Table I with benzophenone as sensitizer.

Table IX

Comparison of Quantum Yield and Photostationary State Measurements with Benzophenone as Sensitizer

$\frac{1}{\Phi}$		$1 + \frac{cP}{tP}$	$1 + \frac{tP}{cP}$
$c \rightarrow t$	$t \rightarrow c$		
1.8	2.6	1.8	2.3

The near equality of the values predicted by equation 27 and 28 is confirmatory evidence that benzophenone transfers energy according to mechanism I.

On the basis of the simple mechanism I, the relative rates of transfer to cis and trans isomers contain no concentration units

$$-\frac{d\,[\text{cis}]}{d\,[\text{trans}]} = \frac{k_{qc}\,[\text{cis}]}{k_{qt}[\text{trans}]} \qquad (29)$$

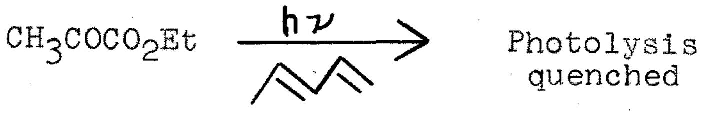
It should be pointed out that the quantum yields were measured under non-competitive conditions, i.e., only one isomer was present. Under these circumstances the sensitizer may transfer energy to this isomer with close to unit efficiency, even though transfer does not occur on the first encounter. Thus, the quantum yields are quite similar for different sensitizers. However, in the competitive situation, i.e., both isomers present as in the case of the stationary state mixtures, one sees the consequences of inefficient transfer even at high concentrations of diene, because the isomer to which transfer is more efficient will accept the excitation if the other isomer fails to quench the donor after the initial encounter.

There are several complications to both mechanisms presented above which cannot be fully elucidated by the above chemical methods and measurements. For instance, while charge transfer complexes between sensitizer and acceptor are excluded for the ground states by spectrophotometric measurements, relatively strong complexes between *excited* sensitizer and ground state acceptor might exist. This possibility can only be properly examined by a technique such as flash photolysis, which can also reveal whether *two or more piperylene triplets are formed during these isomerizations*.

It should be noted also that *cis*-*trans* isomerization can be used to understand the mechanism of unsensitized reactions. Consider a system in which a photochemical intermediate transfers triplet energy with a quencher such as one of the piperylenes, with consequent isomerization of the latter; *the presence of a triplet intermediate in the original photoreaction can then be presumed.* Induced *cis-trans* isomerization therefore provides a straight forward chemical means of following such excitation interchanges.

For example, ethyl pyruvate is decomposed by 3130 Å radiation.[26c] In the presence of cis-piperylene (which does not absorb at this wavelength) the photolysis is dramatically quenched. Furthermore, a photostationary mixture of piperylenes is produced and is precisely that predicted for a sensitizer possessing E_t greater than 60 kcal. The $S_o \longrightarrow T_1$ excitation energy of ethyl pyruvate has been measured recently in these laboratories[34] and was found to be 65 kcal.

$$CH_3COCO_2Et \xrightarrow{h\nu} 2\ CH_3CHO + CO \qquad (30)$$

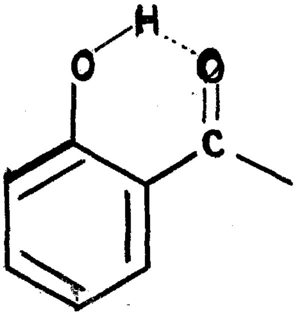


$$CH_3COCO_2Et \xrightarrow{h\nu} \text{Photolysis quenched} \qquad (31)$$

Similar phenomena have been observed for photosensitized reactions in the gas phase[26d].

Results with o-Hydroxycarbonyl Compounds. Although carbonyl compounds are in general the most efficient sensitizers found for isomerization of the piperylenes, they are by no means unique. Examination of Table I shows that aromatic amines, hydrocarbons, halides, nitriles and nitro-compounds can also induce isomerization, but usually at reduced efficiency.

The inefficiency of some of the sensitizers listed in Tables I and II can be partially explained by feeble light absorption of the sensitizers, and partially by lack of sufficient triplet energy. Such is not the case, however, for o-hydroxyaroyl compounds. These compounds possess extremely intense absorption bands in the region of 3360 Å, and probably possess $S_0 \longrightarrow T_1$ transition energies around 65-69 kcal[26b]. A special path for extremely rapid annihilation of triplets must be available for these compounds (if they form triplets at all in solution). Three such compounds, o-hydroxybenzaldehyde, o-hydroxybenzophenone and 2-hydroxy-4methoxy-benzophenone were found to be completely inactive as sensitizers for the isomerization of the piperylenes. In contrast, p-hydroxybenzophenone and o-methoxy benzaldehyde were very effective sensitizers. The excited state appears to be incapable of transferring energy due to the presence of an internal hydrogen bond.



The presence of such a structure may inhibit energy transfer by any of several processes:

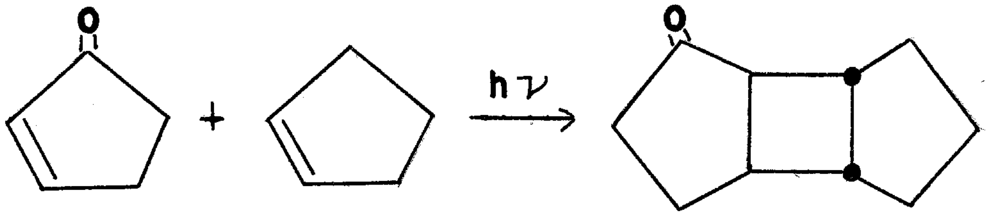
(a) favor the $S_1 \longrightarrow S_0$ degradation relative to intersystem crossing, i.e., $S_1 \longrightarrow T_1$;

(b) disturb the usual relationship between (π, π*) and (n, π *) states, producing a species of very low energy or very short lifetime;

(c) cause special chemical implementation of the $S_1 \longrightarrow S_0$ process (i.e., tautomerization), which requires only breaking of a hydrogen bond to create a facile path for energy dissipation by reverse tautomerization.

A process formally analogous to (c) has been proposed to explain the failure of certain ortho-substituted benzopheneone to undergo the usual photoreduction reactions[27].

Endothermic Energy Transfer*. The sensitized isomerization of unconjugated alkenes was expected to be endothermic (E_t for ethylene is about 80 kcal) and presumably inefficient. This expectation was confirmed; extremely long irradiation times were required to achieve photostationary mixtures of the 2-pentenes and the dichloroethylenes. However the data in Tables X and IX show that the relationship between decreasing energy of the sensitizer triplets and the trans/cis ratio at the steady state is adequately explained by the hypothesis that endothermic transfer to each isomer becomes inefficient at different rates. The fact that fluorenone and benzil sensitize these isomerizations at all (Franck-Condon excitation transfer is endothermic by nearly 20 kcal for these sensitizers) is very surprising. These reactions are further complicated by the fact that addition of the sensitizer to the olefinic compounds and other reactions frequently occur. The following are representative examples[28, 29].



(32)

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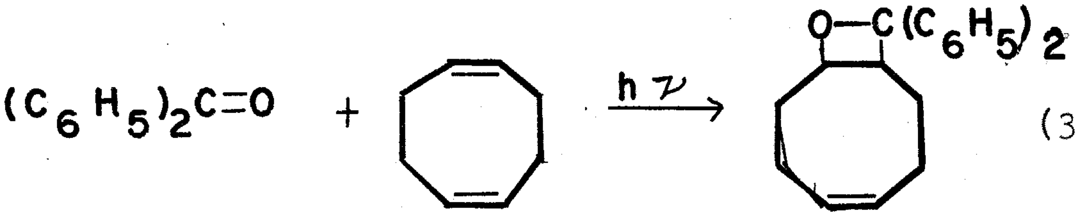
*Endothermic transfers refer to the Franck-Condon excitation from sensitizer to acceptor for which E_t (acceptor) > E_t (donor).

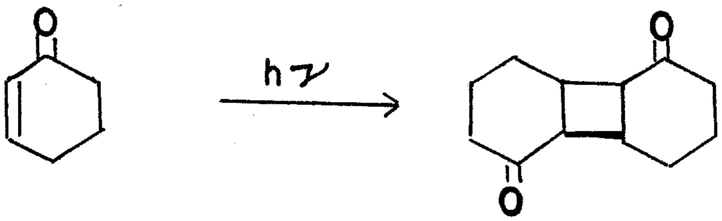


(33)

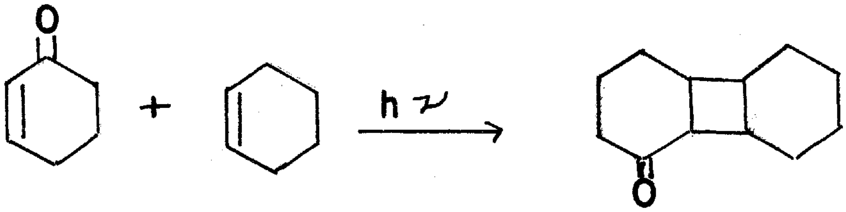
$$(C_3H_7)CH=CH_2+(CH_3)_2C=O \xrightarrow{h\nu} \text{Saturated alcohols} \qquad (34)$$

The reasons why these additions are favored over simple energy transfer is not clear, but it is certainly reasonable that chemical processes may begin to compete when the transfer process becomes very slow.

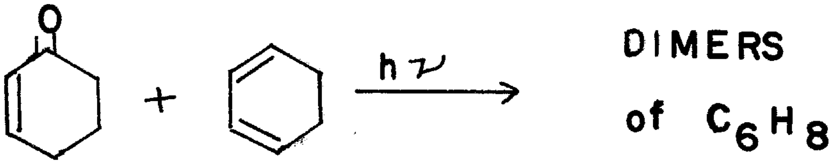
Correlation of the relationships of these reactions to simple energy transfer is even more confusing after consideration of the following reactions[29].



(35)



(36)



(37)

The three above equations show that cyclohexenone:

(a) dimerizes efficiently in the absence of other unsaturated compounds;

(b) undergoes exclusive addition in the presence of excess olefin;

(c) exclusively transfers energy to cyclohexadiene with consequent dimerization of the latter compound[30].

It seems remarkable that in the last case there is no evidence for the addition of diene triplets to cyclohexenone[29].

Possible Mechanisms for Endothermic Transfer. Needless to say, considerable work is required to unravel the details of the addition reactions and to establish their relationship to inefficient "endothermic" transfer processes. Two of many possible mechanisms for extremely endothermic transfer are outlined below.

Mechanism I

$$S \longrightarrow S^* \qquad (38)$$

$$S^* + S^* \longrightarrow S^{**} + S \qquad (39)$$

$$S^{**} + Q \longrightarrow S + Q^* \qquad (40)$$

Mechanism II

$$S \longrightarrow S^* \qquad (41)$$

$$S^* + Q \longrightarrow S^{*}\text{-----}Q \qquad (42)$$

$$S^* + S\text{----}Q \longrightarrow 2S + Q^* \qquad (43)$$

In the first mechanism two sensitizer triplets collide to produce an ill-defined dimer capable of dissociation into a species which transfers two quanta of energy[31]. The second mechanism invokes formation of a sensitizer-acceptor complex (probably similar to the biradical supported by Schenck)[15], which accepts energy from a second excited sensitizer molecule and then decomposes to yield unexcited sensitizer and excited quencher. The first of these two mechanisms has received recent support from the detection of delayed fluorescence which occurs at <u>shorter</u> wavelengths that the exciting radiation[32]. Triplet-triplet annihilation has also been proposed to explain the mechanism of certain "endothermic" reactions which are important in photosynthesis[31].

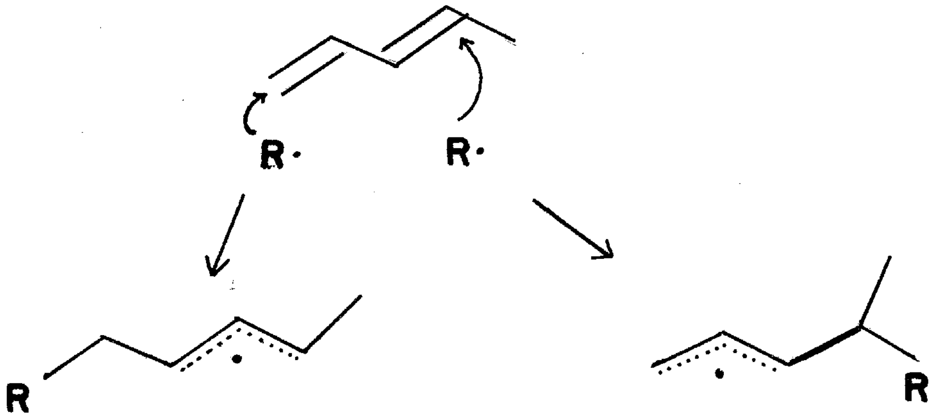
A final mechanism might invoke non-vertical, non-Franck-Condon excitation of the acceptor with production of a distorted, low-energy form of the acceptor by a sort of tunnelling effect[33].

Each of the above mechanisms predicts reduced efficiency of energy transfer and makes predictions concerning experimentally verifiable relationships between such quantities as the quantum yield of energy transfer and light intensity. Also, flash photolysis should prove to be a powerful tool in resolving the role of the species hypothesized above in endothermic energy transfer.

Conclusion

The above results provide cogent support for the intermediacy of triplet states in photosensitized isomerizations. The most persistent opposition to energy transfer in these reactions has been due to the theories of Schenck, et al[15,35], who would advocate a radical addition, isomerization and radical dissociation mechanism for these isomerizations. Such a process is very unlikely for the case of piperylene from our present knowledge of the mode of attack of radicals on conjugated dienes and the stability of allylic radicals[30]. Either attack at the 4-position of piperylene, or attack at the 1-position followed by isomerization of the resultant allylic species is demanded by the radical mechanism. Attack at the 4-position is expected to be negligible in analogy to other radical additions to dienes, and attack at the 1-position is not expected to lead to efficient isomerization due to the stability of the allylic unit. If the allylic radicals produced by dissociation possess excess vibrational energy, isomerization might be expected to occur, but such a process would require a significant modification of Schenck's present position.

Also, a radical addition-dissociation mechanism obviously cannot adequately satisfactorily account for the remarkable effects on photostationary mixtures produced by different sensitizers. Finally, the "radical" addition of (n, π *) and (π , π *) triplets is expected to be quite different[23], yet the quantum yields for isomerization of the piperylenes (see Table VI) are high for sensitizers with lowest (n, π *) triplet states (e.g. benzophenone) and high for (π , π *) triplet states (e.g. 2-Acetonaphthone). It is clear that the transfer process is only a function of the triplet energy of the sensitizer in these cases.



Experimental Part

PURIFICATION OF STARTING MATERIALS FOR QUANTUM YIELDS

Benzene - Mallinckrodt - reag. Thiophene free was washed 3 times with conc. H_2SO_4, then 2 times with water, dried over $CaCl_2$, $MgSO_4$ and then distilled from Na. The first 100 ml distilled was discarded and the next 1800 ml (BP = 80°) collected and stored in a brown bottle over sodium wire. For the data given in Table V the benzene was purified by preparative vapor phase chromatography followed by washing with H_2SO_4 and distillation.

Acetophenone - Matheson-Coleman and Bell - 180 ml. reag. material. Distilled under reduced pressure the fraction boiling 35-36° at 1-2mm was collected and stored in a dark bottle.

Benzophenone - Matheson, Coleman and Bell - reag. recrystallized from hot hexane. m.p. 47-48°.

2-Acetonaphthone - Eastman Kodak - White Label - recrystallized from hot ligroin. m.p. 53°.

9-Fluorenone - Matheson, Coleman and Bell - reagent- recrystallized from hot ligroin. m.p. 83-84°.

Benzil - Matheson, Coleman and Bell - reag. recrystallized from Pet ether 30-60°. m.p. 95°.

Biacetyl - Matheson, Coleman and Bell - reag. distilled at atmospheric pressure. b.p. 89-90°.

Benzaldehyde - Matheson, Coleman and Bell - reag. chlorine free. b.p. 31-2°/1-2mm.

1-Naphthaldehyde - Eastman Kodak - White Label - distilled; b.p. 84-88°/1-2mm.

Michler's Ketone - (p,p'-tetramethyldiaminobenzophenone) recrystallized twice from methanol washed with Pet ether 30-60°; m.p. 171-171.5 light yellow powder.

Benzhydrol - Matheson, Coleman and Bell - reag. recrystallized 3 times from benzene-hexane (2X Norite) washed with Pet ether (30-60°) air dried. m.p. 66.5-67.5°.

trans-piperylene - Matheson, Coleman and Bell - technical - distilled b.p. 38-42°. The technical mixture consisted of about 62% trans and 38% cis. The trans-isomer was easily purified by preparative vapor chromatography on a 6 ft. 3/8 in. $AgNO_3/CH_2OHCH_2OH$ column in the Megachrom. Distilled immediately prior to use. b.p. 41.5°.

cis-piperylene - Matheson, Coleman and Bell - technical - distilled b.p. 38-40°. Contained 62% trans-isomer. Pure cis was obtained by refluxing the mixture of isomers with an excess of maleic anhydride. The trans-isomer was completely eliminated by this procedure but another impurity had to be removed by preparative vapor chromatography on β,β^1-oxydiproprionitrile, and was then redistilled. b.p. 42.5°

cis-2-pentene - Phillips Petroleum, Technical, was distilled, (b.p. 36°) and then separated from trans-2-pentene by vapor chromatography on $AgNO_3/Et(OH)_2$ and then redistilled. b.p. 36.5-37°.

trans-2-pentene - Distilled. b.p. 36-7°. Phillips Petroleum Tech. Separated from cis-2-pentent by preparative vapor chromatography on $AgNO_3$/ethylene glycol and then redistilled. b.p. 36°.

trans-Dichloroethylene - Matheson, Coleman and Bell reag. was distilled. b.p. 47-48°. This material was purified of traces of cis-dichloroethylene by preparative vapor chromatography on Apiezon J at 45°, 5 psi.

Measurement of Photostationary Mixtures

Piperylenes. The standard following procedure was used for the study of photostationary states. Stock solutions 0.25 M in sensitizer were prepared. A 5.0 ml sample stock solution was added to a 25 ml vol. flask and diluted to about 20-22 ml with solvent. Sufficient *cis*- or *trans*-piperylene to make the final concentration of diene 0.2 M (0.50 ml) was then added to the volumetric flask and the sample diluted to volume. A 2.0 ml sample of the resulting solution was added to a constricted 13 x 100 mm pyrex test tube, which was then frozen and degassed three times. The tubes were then photolyzed at 25-30° on a rotating turn table at the center of which was placed a 450-watt Hanovia high pressure mercury lamp. Samples were removed periodically and analyzed by vpc on a 10 ft by 1/4 in column packed with a 60:40 mixture of 25% saturated solution of silver nitrate solution in ethylene glycol and 25% oxydipropionitrile (column A). The photostationary mixture was attained when the *cis*/*trans* ratio of the sample which initially contained pure *cis*-piperylene was nearly identical to the *cis*/*trans* ratio of the sample initially containing pure *trans*-piperylene. Absorption measurements of the irradiated solutions were made on a DU spectrophotometer to determine the consumption of sensitizer. For nearly all carbonyl compounds used as sensitizers (benzil being one of the notable exceptions) a photostationary mixture of piperylenes was usually reached before 3-5% consumption of sensitizer had occurred.

cis and trans-2-Pentene and cis- and trans-Dichloroethylene. The procedure for the measurement of the photostationary states of the above two sets of isomers was similar to that described above for the piperylenes, except that the samples were not degassed, and were usually strapped to the inner jacket of the Hanovia quartz immersion reactor. *cis*- and *trans*-2-Pentene are easily separable on a 10 ft by 1/4 in column packed with 25% saturated silver nitrate dissolved in ethylene glycol (column N). The 1,2-dichloroethylenes are separated satisfactorily by either a 12 ft. by 1/4 in. column packed with 35% Apiezon J (column Q) or a 12 ft. by 1/4 in. column packed with 25% oxydipropionitrile (column X).

Quantum Yield Determinations

General Procedure. An enclosed 800-watt medium pressure mercury arc, previously described[11], was used for the measurement of quantum yields. Corning C57-51 or C37-37 filters were employed to isolate the 3660Å mercury line. Complete absorption of the light by the sample was checked by making periodic readings on an Eppley Laboratory thermopile. In all cases this reading indicated that less than 1% of the light was being transmitted.

Preparation and Irradiation of Samples. The irradiation cells were 15 by 125 mm pyrex test tubes which had been fused to a 12/30 standard taper joint and were provided with a constriction for sealing. A 4.0 ml sample of the solution to be irradiated was added to the cells which were then connected to a vacuum line, then frozen and degassed three times to 10^{-3} mm. These tubes were then irradiated for various periods of time, sufficient to produce 1-5% isomerization.

An actinometer consisting of 0.05 M benzophenone and 0.10 M benzhydrol[11] was irradiated simultaneously with the other samples.

The amount of isomerization produced by irradiation was determined by analytical vpc on a Loenco model 15 B chromatograph provided with a flame ionization detector. A 4.8 ft. by 1/8 in. column A packed with 2.5 ml of oxydipropionitrile at the inlet side and 2.3 ml of saturated silver nitrate in ethylene glycol (column B) was used for these analyses. Standard solutions of cis or trans-piperylene were prepared to calibrate peak areas.

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26. a An equation analogous to 22 applies to the photosensitized isomerization of the stilbenes; J. Saltiel, personal communication.

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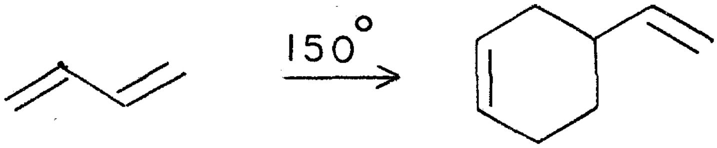
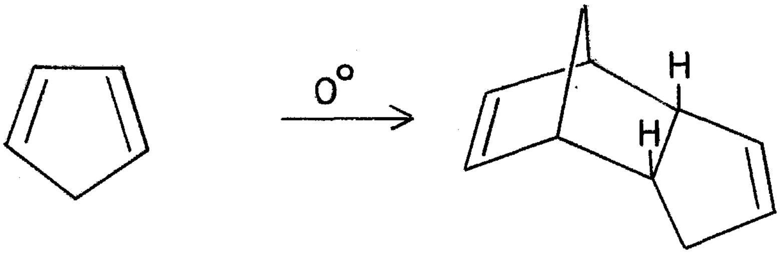
Experimental Results

Diels-Alder dimerization of conjugated dienes to produce cyclohexenes is well known.[1,2,3,4] The following examples are representative of the reaction.



(1)



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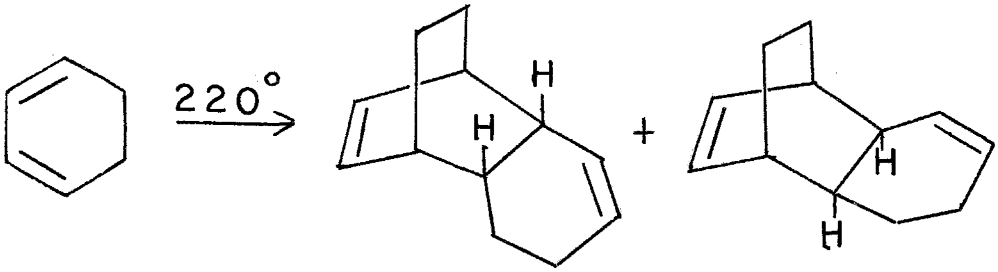
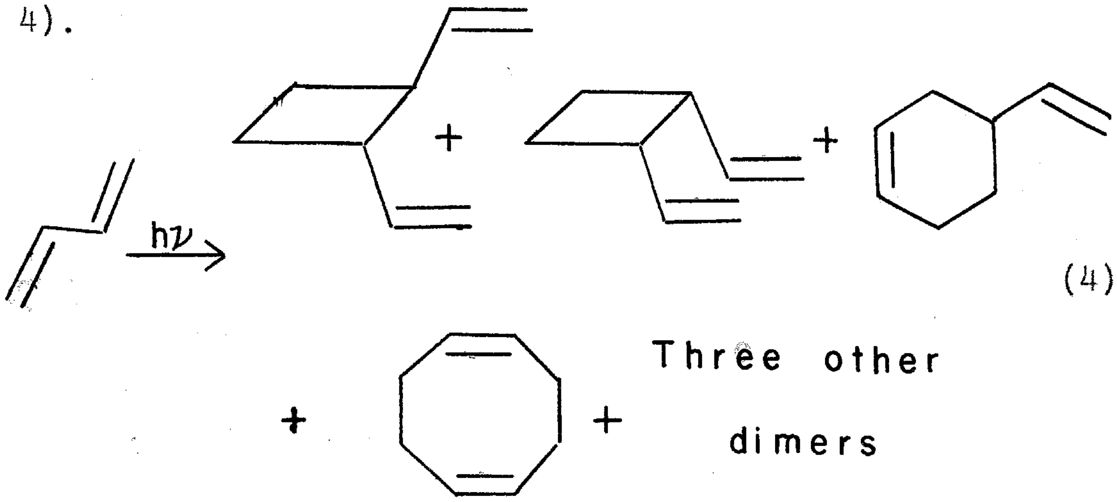


(3)

The thermal dimerization of 1,3-butadiene is the only one of the above reactions in which detectable quantities of cyclobutane or cyclooctadienes are formed[2]. Evidence has been obtained for the production of triplet states of dienes in solution by the process of energy transfer from various photochemically excited carbonyl compounds[5,6]. Photosensitized dimerization of the three above dienes produces significant amounts of cyclobutanes in the dimer mixtures*.

Structure Proofs

Butadiene Dimers. Direct dimerization of isopentane solutions of butadiene results in the formation of one minor and six major dimers. Four of these have been identified tentatively by comparison of their retention times on vapor phase chromatograms with known dimers (see equation 4).



(4)

The photosensitized dimerization of butadienes in various solvents or in the neat liquid produces three dimers as shown in equation 5.

Although the direct irradiation of certain substituted butadienes leads to the formation of cyclobutenes in good yields[7], irradiation of butadiene itself does not

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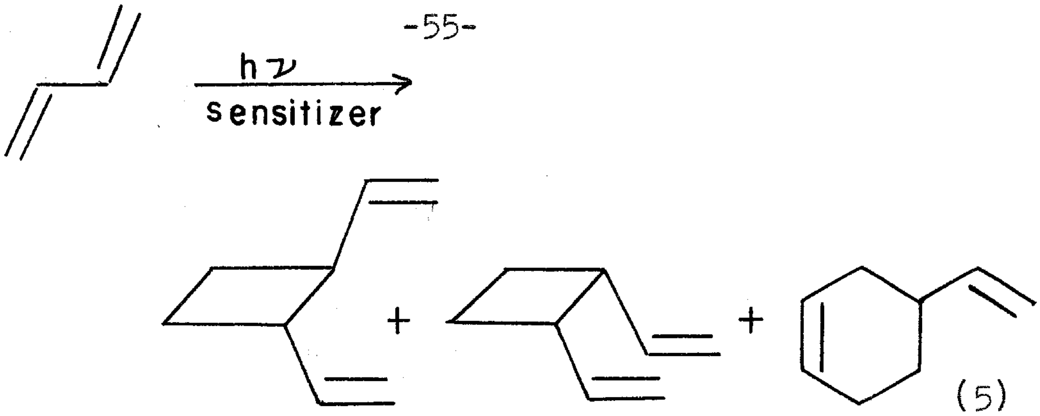
* The photosensitized dimerization of perdeuterated butadiene has been used as the method of choice for the synthesis of perdeuterated cis, cis-cyclooctadiene-1,5[4,b]



1 2 3 (5)

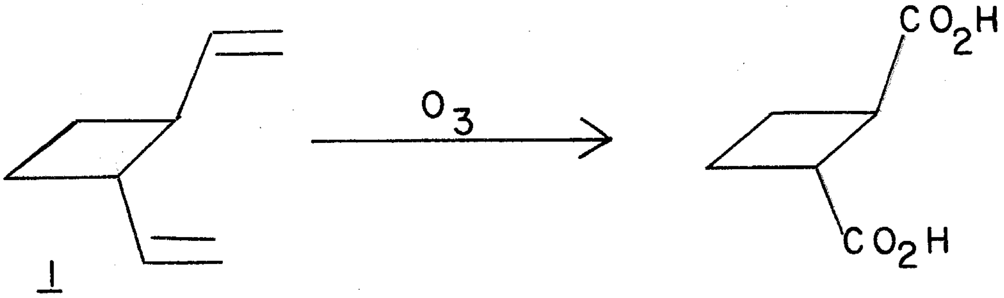
produce detectable amounts of isomeric monomers. Furthermore, no evidence for the formation of cyclobutene was found when dilute or concentrated solutions of butadiene were irradiated in the presence of photosensitizers. Since butadiene exists mainly in the s-_trans_ configuration under the conditions of these experiments, the geometric requirements favoring cyclobutene formation, i.e., attainment of the s-_cis_ configuration, are not met, and the quantum yield for ring closure is low.

The three products, 1, 2, and 3 were separated by preparative vapor phase chromatography (v.p.c.). The physical constants and infrared spectra of these dimers agree exactly with those reported in the literature.[2,8] The nuclear magnetic response (nmr) spectrum of 1 shows resonance at 5.9 to 5.3 ppm* and a series of overlapping doublets from 4.80 to 4.50 ppm, due to six vinyl protons as a complex multiplet, two allylic cyclobutane protons

---

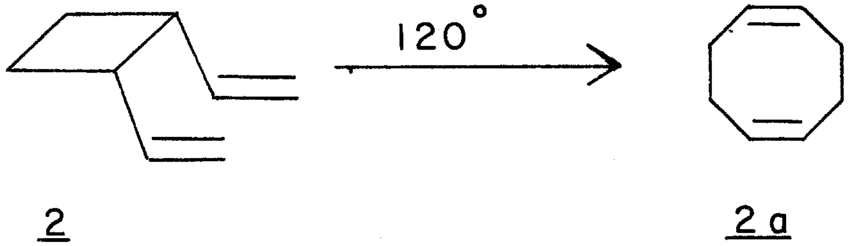
* All nmr resonances reported are relative to an external sample of tetramethylsilane at 60 mc, unless specified differently.

as a broad band centered at 2.4 ppm, and four methylene cyclobutane protons as a complex broad multiplet centered at 1.6 ppm. Ozonolysis of 1 produces trans-1,2-divinylcyclobutane dicarboxylic acid.[2]



(6)

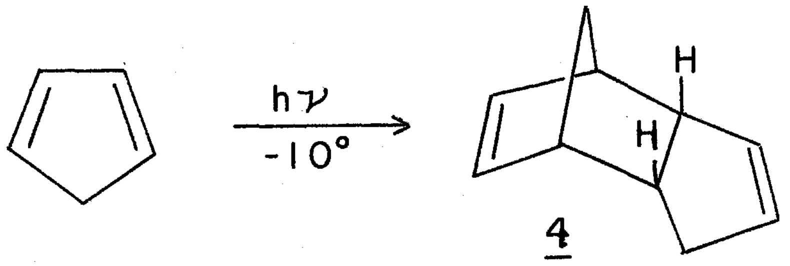
The n.m.r. spectrum of 2 shows resonances at 6.20 to 5.30 ppm and 5.00 to 4.50 ppm due to six vinyl protons, at 3.00 to 2.50 ppm due to two allylic cyclobutane protons and at 2.0 to 1.3 ppm due to four methylene protons. Compound 2 undergoes thermal isomerization to cis, cis-1,5-cyclooctadiene[8] at 120°.



(7)

Compound 3 is identical in all respects to a sample of authentic 4-vinylcyclohexene.

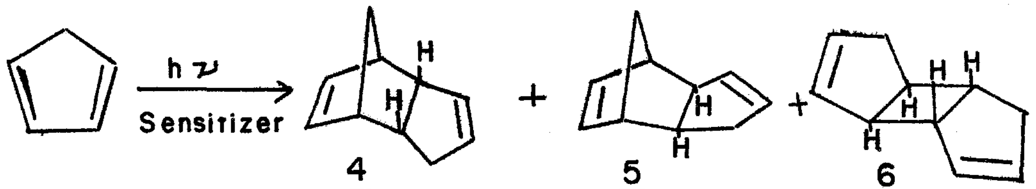
Cyclopentadiene Dimers. Direct irradiation of cyclopentadiene produces only the thermal dimer, endo-dicyclopentadiene, 4. Irradiation of cyclopentadiene



4

(8)

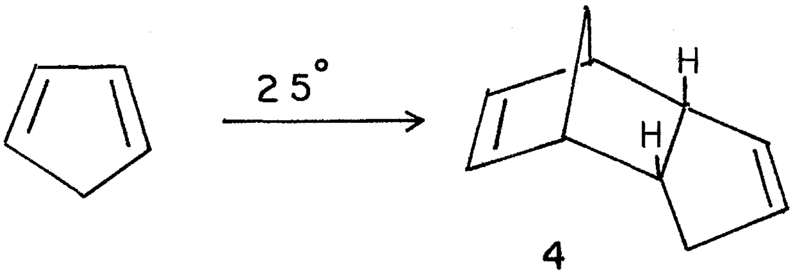
containing acetophenone, benzophenone, fluorenone, mesityl oxide, acetone, benzil or 2,3-pentanedione with a Hanovia 450-watt, quartz immersion apparatus produces *endo*-dicyclopentadiene, 4, *exo*-dicyclopentadiene, 5, and *trans*-$(5.3.0.0.^{2,6})$-tricyclo-2,8-decadiene, 6, in approximately equal amounts *(after correction for the thermal dimerization)*.



4 5 6

(9)

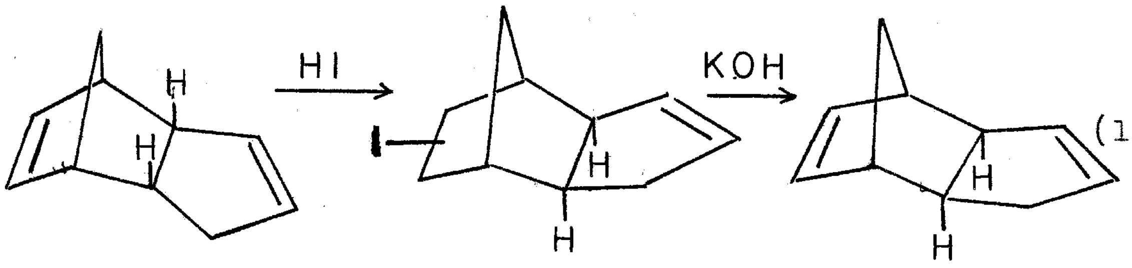
The three dimers were separated by preparative v.p.c. Compound 4 is identical in all respects to a sample of *endo*-dicyclopentadiene prepared by thermal dimerization of cyclopentadiene.



4

(10)

Compound 5 is identical in all respects to a sample of *exo*-dicyclopentadiene prepared by the method of Bartlett and Goldstein[9], equation 11.



(11)

4 5

The gross structure of compound 6 was shown to correspond to any one of the four isomers of the tricyclodecadiene, 7, from its n.m.r. spectrum in carbon tetrachloride.

cis and trans cis and trans

7

The n.m.r. spectrum* shows of 6 a sharp peak in the vinyl region at 5.70 ppm (four protons), a broad band centered at 3.0 ppm due to absorption by two tertiary allylic protons, and a pair of overlapping doublets at 2.45, 2.35 and 2.90 ppm due to absorption of six methylene ring protons. The location of the double bonds and the stereochemistry of 6 was established by reference to the cyclopenteneone photodimers 8 and 9 prepared by Eaton[10].

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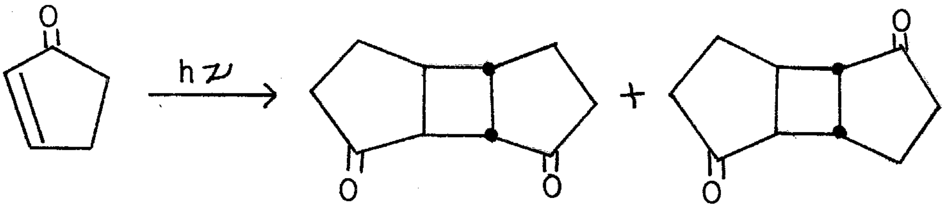
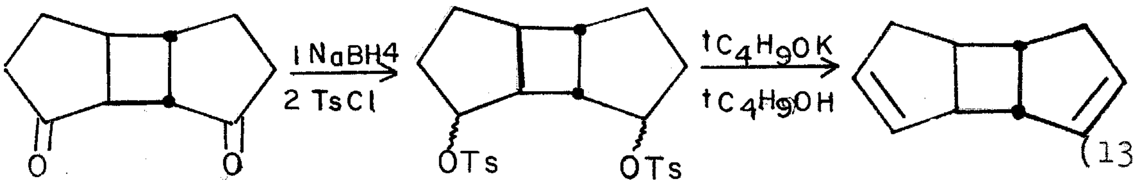
* Relative to an internal standard of tetramethylsilane



8 9

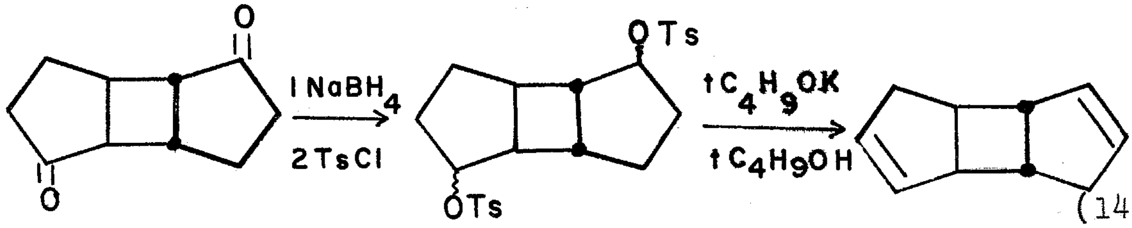
(12)

Both 8 and 9 were converted to dienes by reduction to the alcohol followed by tosylation and elimination.



(13)

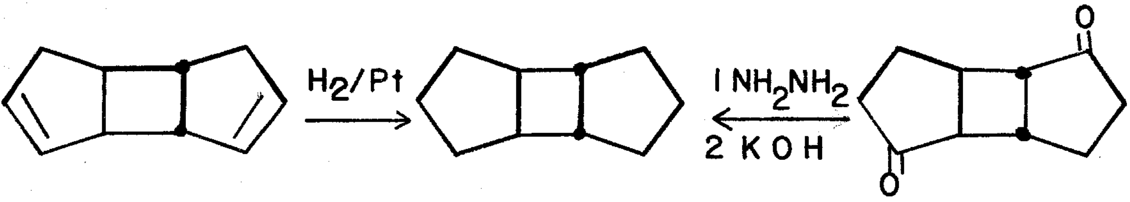
8 10s 6



(14)

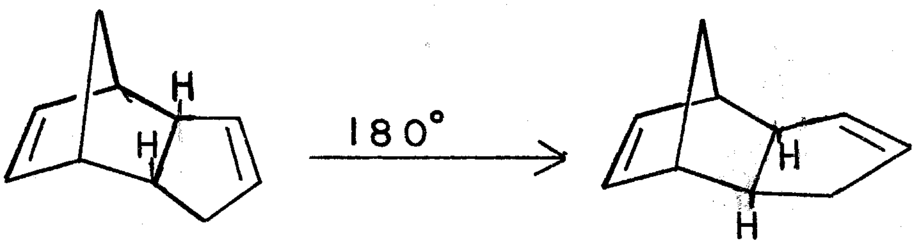
9 10a 11

The diene derived from the *syn*-*trans*-dione, 8, was identical to the photodimer, 6. The diene, 11, had significantly different infrared and n.m.r. spectra, and a longer retention time in vapor chromatograms. Catalytic hydrogenation of 6 gave a hydrocarbon identical with that obtained by Wolff-Kischner reduction of 9[10].



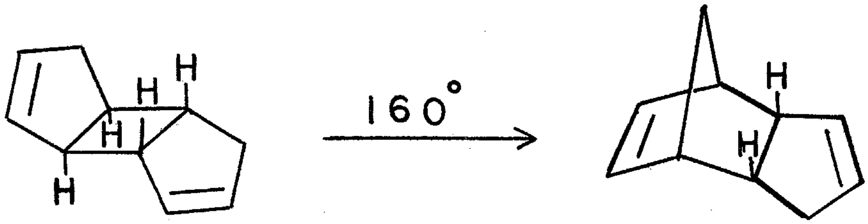
6 9 (15)

endo-Dicyclopentadiene, 4, is converted to exo-dicyclopentadiene, 5, at 180°.



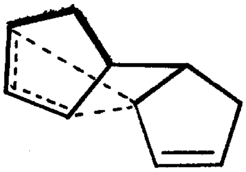
4 5 (16)

At slightly lower temperatures the diene, 6, is converted smoothly to endo-dicyclopentadiene, 4.

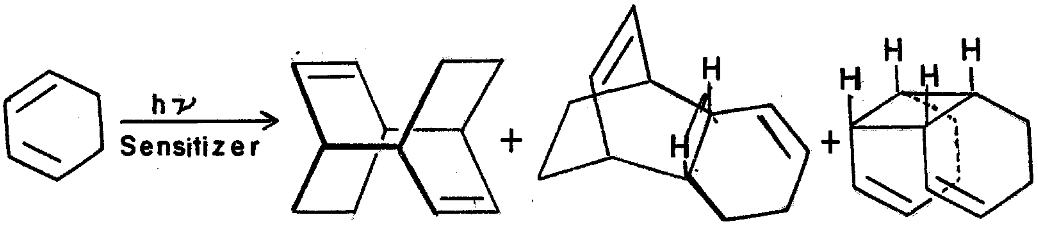


6 4 (17)

Although the rearrangement given in equation 16 is complicated by slow polymerization and cracking, the cyclobutane, 6, appears to be converted nearly quantitatively to endo-dicyclopentadiene. The smoothness of the latter reaction argues for a concerted mechanism, via a transition state similar to many of those proposed for Cope rearrangements[39]. The mechanism of the conversion of *endo*- to *exo*-dicyclopentadiene is not known, and merits further study to establish whether the isomerization occurs by an external or an internal rearrangement[37].

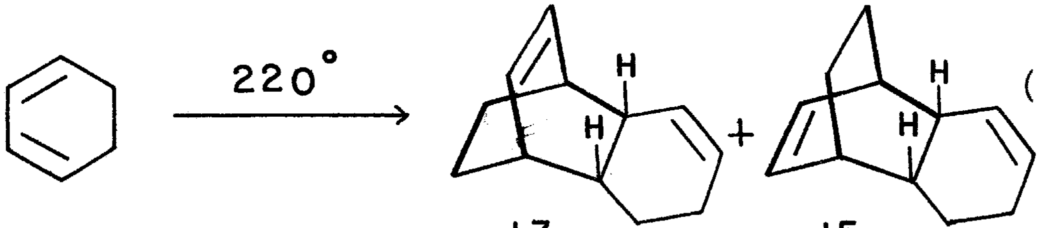


Cyclohexadiene Dimers. Irradiation of isopentane solutions of cyclohexadiene containing various carbonyl compounds with a Hanovia 450-watt lamp produces *anti*-$(4.2.2.2.^{5,8})$-2,9-dodecadiene, *exo*-dicyclohexadiene, 13, and *syn*-*cis*-$(6.4.0.0.^{2,10})$-tricyclo-dodecadiene, 14.



12 13 14 (18)

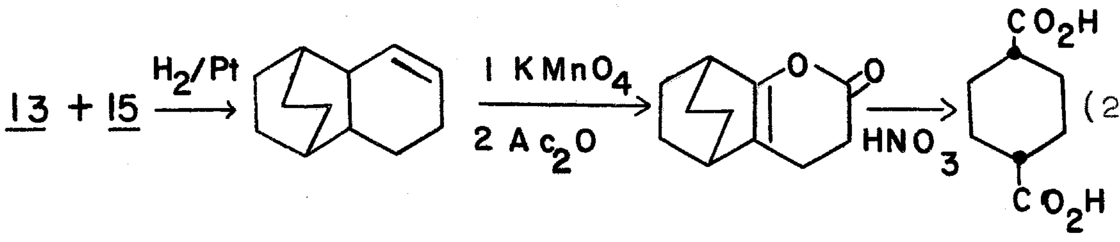
The thermal dimerization of cyclohexadiene at 220°[4,12] produces 78% *endo*-dicyclohexadiene, 15, and 22% *exo*-dicyclohexadiene, 13, Alder and Stein[4] assigned a structure to the thermal dimers of cyclohexadiene on the basis of the



(19)

13 15

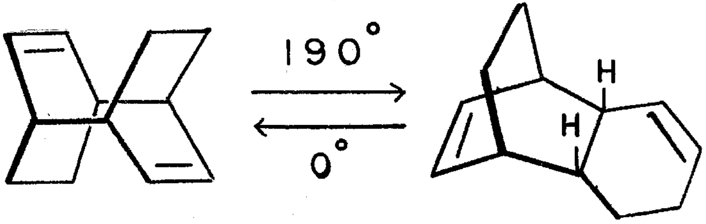
credible degradative scheme given in equation 20; however, this study gives no information concerning the stereochemistry of the products.



(20)

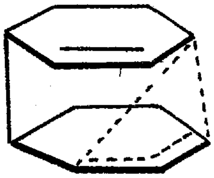
The major product of the thermal dimerization has been tentatively assigned endo stereochemistry on the basis of the Alder rule[12]. These assignments hang on somewhat shaky ground, for if the Alder rule should be wrong (or if the kinetically controlled isomer is the minor one isolated under the somewhat severe reaction conditions), all the assignments will be reversed. exo-Dicyclohexadiene produced by the thermal dimerization was found to be identical to the photodimer, 13, by comparison of retention times on a Golay chromatographic column.

Compound 12 possesses an exceedingly simple n.m.r. spectrum consisting of a sharp singlet at 5.75 ppm due to four vinyl protons, a singlet at 2.50 ppm assigned to four tertiary allylic protons and a broad set of multiplets from 2.20 to 1.50 ppm assigned to eight saturated ring protons. Surprisingly, 15 undergoes rearrangement to 12 under very mild conditions. The reaction is smoothly and quantitatively reversed by heating 12 to 190°.



12 15 (21)

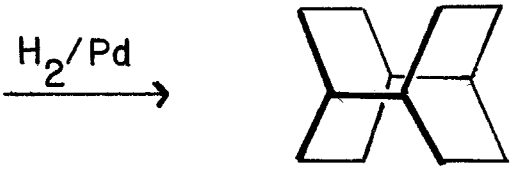
The fact that these rearrangements are smooth and quantitative implies that they proceed by way of a concerted mechanism and a transition state such as 16.



16

Hydrogenation of 12 produces a saturated hydrocarbon, 17.

12

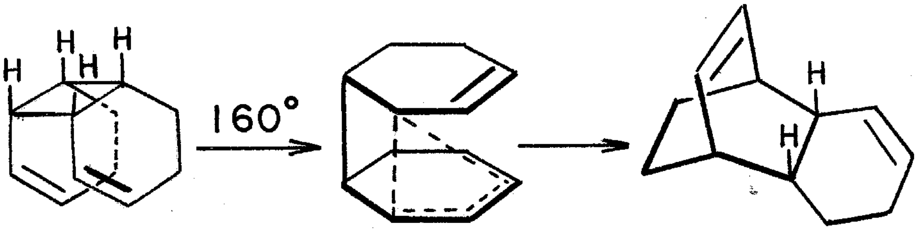


17 (22)

The latter possesses a n.m.r. spectrum consisting of essentially two bands in the saturated region of absorption at 2.25 and 1.55 ppm with a ratio of intensities of 1:4, respectively. The relative simplicity of the infrared spectrum of 12 and 17 also indicates a highly symmetrical structure.

The gross structure of 14 was deduced from its n.m.r.

spectrum, which shows a slightly split doublet in the region of vinyl proton absorption (four protons) at 5.80 ppm, a broad band centered at 2.9 ppm, assigned to two tertiary allylic protons and a broad multiplet centered at 1.8 ppm assigned to eight methylene ring protons. The tentative assignment of structure to 14 is based on analogy to other sensitized dimerizations mentioned above in which structures containing 1,2-divinylcyclobutane unit are produced with the complete exclusion of 1,3-divinylcyclobutane units[13]. The *cis*-stereochemistry is consistent with the smooth, quantitative conversion of 14 to 13 at 150-180°.



14 17 13 (23)

A kinetic study of the remarkable thermal isomerizations described above and determination of the energetics, equilibrium constants and inter-relationships of the potential energy surfaces connecting these $C_{12}H_{16}$ compounds is of considerable interest. Such studies and more rigorous establishment of the assigned structures are in progress[11].

Variation in the Composition of Products. The composition of the product mixtures produced by photosensitized dimerization of butadiene varies considerably as the sensitizer is changed (Table I). On the other hand relative yields of dimers are independent of sensitizer for the photosensitized dimerization of 1,3-cyclohexadiene and cyclopentadiene. The simple theory of sensitization by transfer of excitation from the lowest triplet states of the sensitizer to the diene[6] does not directly predict a variation in the relative yields of dimers as observed for isoprene and butadiene[13]. The variation in the composition of product mixtures from butadiene is given in Table I in which the percentages of the three products produced by different sensitizers are given, along with the relative quantum yields for dimerization. Figure 1 shows the pattern of the variation when the sum of the yields of the two cyclobutanes produced is plotted against the $S_o \longrightarrow T_1$ excitation energies of the various sensitizers.

Temperature showed a significant effect on the relative yields of butadiene dimers as shown in Tables II and III. Table IV shows the corresponding effect of temperature on the relative yields of cyclohexadiene dimers. A tenfold increase in the intensity of exciting radiation has little effect on the composition of the mixture of butadiene dimers as shown by the data given in Table V. Similarly, the composition of the mixture of butadiene dimers was little affected by change in solvent, concentration of sensitizer or concentration of butadiene, as seen from the data in Tables VI, VII and VIII.

The composition of product mixtures at several temperatures for the photosensitized dimerization of cyclohexadiene, together with the quantum yields for dimerization at two intensities, is given in Table IV.

Examination of the above data reveals several significant features of these dimerizations:

(a) high selectivity is exhibited in dimer formation since only three of many possible dimers are produced in each instance;

(b) although a large variation is found in the composition of the mixture of butadiene dimers as the sensitizer is changed, there is no corresponding variation in the composition of the mixture of dimers produced from cyclic dienes;

(c) the quantum yield for dimerization of cyclic dienes is about 100 times greater than that for butadiene[15];

(d) 1,3-divinylcyclobutanes are not formed;

(e) an increase in temperature produces rather large increases in the amount of 4-vinylcyclohexene relative to the divinylcyclobutanes for butadiene dimerization, but a 60° increase in temperature does not affect the relative yields of cyclohexadiene dimers.

The above results can be explained by assuming that stereoisomeric *cis* and *trans*-triplets result from excitation of s-*cis* and s-*trans*-butadiene, respectively.

Table I

Dimerization of Butadiene by Various Sensitizers

	Relative Yields of Dimers[d]			
Sensitizer[a]	% 1	% 2	% 3	Φ[c] (x 10^{-3})
Benzophenone[b]	81	18	2	1.0
Dicyclopropylketone[b]	78	20	2	0.1
9,10-Dibromoanthracene	78	19	3	0.02
Acetophenone[b]	78	19	3	1.0
Michler ketone	80	17	3	1.0
Xanthone[b]	78	19	3	0.4
Benzaldehyde	80	16	4	0.5
Anthraquinone	77	19	4	0.4
4-Acetylfluorenone	78	18	4	0.3
2-Cyclohexeneone[b]	81	15	4	-
Ethyl phenylbyloxalate	76	19	5	0.3
4-Acetylbiphenyl	77	17	6	0.3
Flavone	75	18	7	0.02
2,2'-Dimethyl-1,1'-dianthraquinone	74	19	7	0.1
o-Dibenzoylbenzene	76	16	8	0.5
2-Acetonaphthone[b]	76	16	8	1.0
Phenanthroquinone	73	17	10	0.01
Duroquinone	72	16	12	0.02
2-Naphthylphenyl ketone	71	17	12	0.2
2-Naphthaldehyde	72	16	12	0.2
Anthracene	75	10	15	0.01
1-Acetonaphthone	63	17	20	0.2
Eosin	60	17	23	-
1-Naphthaldehyde	62	15	23	0.6
β-Naphthil	57	15	28	0.1
Benzanthrone	55	10	35	0.03
Biacetyl	52	13	35	0.4
Fluorenone	44	13	43	1.0
Benzil	44	10	45	0.2
Benzoquinone	~51	~ 6	~43	0.02
3-Acetylpyrene	43	12	45	0.01
Anthranthrone	45	7	48	0.03
1,3,5-Triacetylbenzene	45	7	48	0.04
Pyrene	~30	~10	~60	0.02
Acenaphthylenequinone	~30	~10	~60	0.04
Camphorquinone	30	7	63	0.01

a. Unless specified, sensitizer ~0.1 M in ether.

b. Sensitizer ~0.1 M in benzene.

c. Quantum yield of dimerization relative to benzophenone, for which $\phi_d \cong 0.004$. The reactions were carried to less than 1% completion.

d. Reaction run to less than 1% conversion.

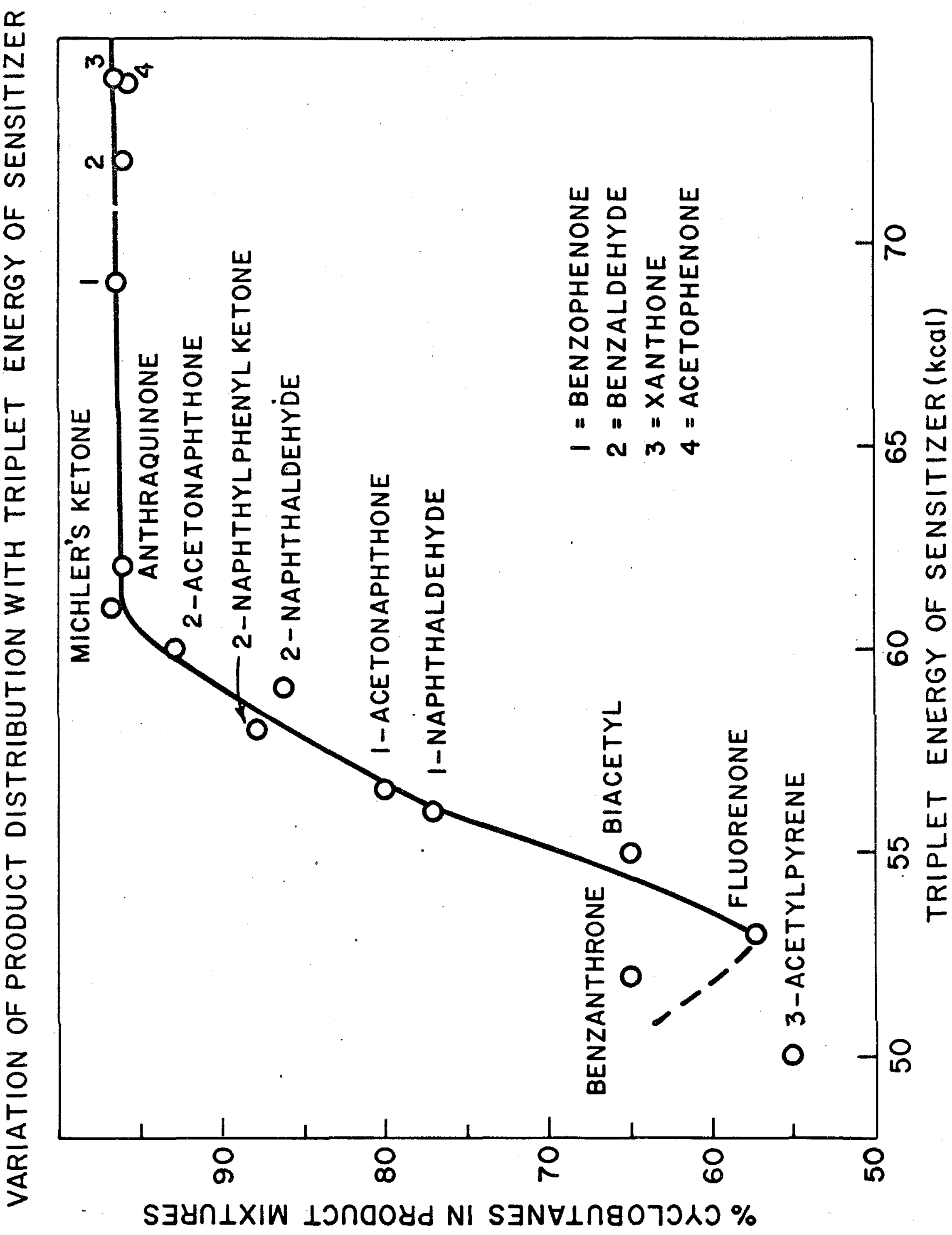

VARIATION OF PRODUCT DISTRIBUTION WITH TRIPLET ENERGY OF SENSITIZER
% CYCLOBUTANES IN PRODUCT MIXTURES
50
60
70
80
90
TRIPLET ENERGY OF SENSITIZER (kcal)
50
55
60
65
70
MICHLER'S KETONE
ANTHRAQUINONE
2-ACETONAPHTHONE
2-NAPHTHYLPHENYL KETONE
2-NAPHTHALDEHYDE
1-ACETONAPHTHONE
1-NAPHTHALDEHYDE
BIACETYL
BENZANTHRONE
FLUORENONE
3-ACETYLPYRENE
1
2
3
4
1 = BENZOPHENONE
2 = BENZALDEHYDE
3 = XANTHONE
4 = ACETOPHENONE

Figure I

Table II

Temperature Effects on the Dimerization of Butadiene

A. Benzene Solutions[a]

Sensitizer[b]	T	Relative Yields of Dimers[d]			
		% 1	% 2	% 3	% 2a[c]
Benzophenone	0°	81	18	1-2	0
	25°	78	19	4	<1
	55°	69	12	8	10
Acetophenone	0°	82	18	1-2	0
	25°	76	21	4	<1
	55°	76	5	7	12
Xanthone	0°	82	16	2	0
	25°	78	19	4	<1
	55°	76	5	7	12
Michler's Ketone	0°	82	18	1-2	0
	25°	82	15	3	<1
	55°	78	2	8	12
2-Acetonaphthone	0°	78	16	6	
	25°	73	18	9	0
	55°	69	5	14	12
2-Naphthaldehyde	0°	60	24	16	0
	25°	62	17	21	<1
	55°	65	6	19	11
Biacetyl	0°	54	14	32	
	25°	53	15	33	

a. Approximately 50% butadiene.

b. Approximately 0.1 N.

c. Produced from thermal isomerization of *cis*-1, 2-divinylcyclobutane.

d. Reactions run to 10-50% completion.

Table III

Ether Solutions[a]

Sensitizer[b]	T	Relative Yields of Dimers[d]		
		% 1	% 2	% 3
Benzophenone	0°	80	18	2
	25°	76	17	7
Michler's Ketone	0°	80	15	2
	25°	76	17	6
	60°	69[c]	15[c]	8[c]
2-Acetonaphthone	0°	77	16	7
	25°	75	16	8
Fluorenone	0°	54	13	33
	25°	54	14	32

a. Approximately 50% butadiene.

b. Approximately 0.1 N.

c. About 8% of 1,5 cyclooctadiene formed in this experiment.

d. Reactions run to 10-30% completion.

Table IV

Temperature and Sensitizer Effects on the Photosensitized Dimerization of 1,3-Cyclohexadiene[b].

Sensitizer[a]	T	Relative Yields of Dimers			
		%12[c]	%13[c]	%14	Φ
Benzophenone	0°	61	22	17	-
	25°	62	22	16	0.97[d]
	50°	62	23	15	1.0[e]
Fluorenone	0°	60	24	16	
	25°	58	23	19	0.40[d]
	50°	58	23	19	0.35[e]
Biacetyl	0°	60	21	19	0.75
	25°	60	21	19	-
	50°	61	21	18	-
2-Acetonaphthone	0°	58	23	19	0.90[d]
	25°	58	23	19	1.2[e]
	50°	58	23	19	-

a. 0.1 N in ether.

b. 25% in ether.

c. Percentages estimated from two incompletely resolved peaks.

d. Intensity ~ 2.3×10^{16} photons per second at 3660 Å.

e. Intensity ~ 2.2×10^{15} photons per second at 3660 Å.

Table V

Intensity Effects on the Dimerization of Butadiene.

Sensitizer[a]	Intensity[b]	Relative Yields of Dimers %1	%2	%3
Benzophenone	x1	77	19	4
	x10	75	19	6
Acetophenone	x1	76	19	4
	x10	77	19	4
Benzil	x1	49	14	37
	x10	46	14	38
Fluorenone	x1	47	14	41
	x10	43	13	45
2-Naphthaldehyde	x1	68	17	15
	x10	66	17	16
Michler's Ketone	x1	79	19	3
	x10	76	19	6
Xanthone	x1	81	18	5
	x10	76	18	7

a. Ether solutions, except for starred sensitizers which were run neat. Temperature was 28-32°.

b. Intensity of x1 is ~ 5 x 10^{15} photons 1 sec. (Corning 751 filter).
x10 is ~ 5 x 10^{16} photons 1 sec. (unfiltered light).

Table VI

Effect of Solvent on the Dimerization of Butadiene

Sensitizer	Solvent	Relative Yields of Dimers %1	%2	%3
Benzophenone	Benzene	77	19	4
	Ether	77	17	6
	Acetonitrile	79	18	3
	neat	86	12	2
Michler's Ketone	Benzene	78	19	3
	Ether	79	19	3
	neat	82	14	4
2-Acetonaphthone	Benzene	73	18	9
	Ether	73	18	9
	Acetonitrile	76	17	7
	neat	82	14	4
Fluorenone	Benzene	47	13	40
	Ether	44	13	43
	Acetonitrile	40	14	48
	neat	48	9	43

Table VII

Effect of Decreasing Concentration of Sensitizer on Butadiene (Dimerization)

Sensitizer	Concentration	Relative Yields of Dimers %1	%2	%3
Fluorenone in Ether	0. 1 N	48	12	40
	0. 01 N	46	14	40
	0. 001 N	45	13	42

Table VIII

(Variation of Concentration of Butadiene)

A. Direct Irradiation

Percentage Butadiene[a]	Relative Yields of Dimers						
	%1	%2	%P_1	%3	%P_2	%P_3	%2a
10%	24	17	33	12	3	4	7
30%	25	20	28	15	< 1	4	8
60%	26	21	23	18	< 1	3	8

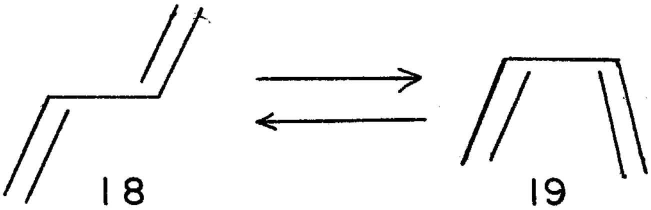
a. Isopentane solution.

B. Sensitized Dimerization

Sensitizer	% Butadiene[a]	Relative Yields of Dimers		
		%1	%2	%3
Benzophenone	5	78	19	3
	50	81	18	2
	100	86	12	2
2-Acetonaphthone	5	73	15	12
	50	75	16	8
	100	82	14	4
Fluorenone	5	47	14	39
	50	44	13	43
	100	48	9	43
Biacetyl	5	55	10	35
	50	52	13	36

a. Ether solution.

Effect of Sensitizer on the Composition of Butadiene Dimer Mixtures. The marked effect of variation of sensitizer on the composition of butadiene dimers is quite striking. The following discussion offers an explanation of these results. The energy separation between the s-cis and the s-trans-forms of 1,3-butadiene has been estimated to be 2.6 kcal at 300° K[16]. This figure leads to an estimate of about 4% of the s-cis-conformer, 19, and 96% of the s-trans-conformer, 18, in mobile equilibrium at room temperature[16b].



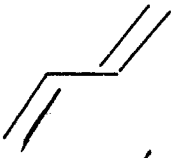
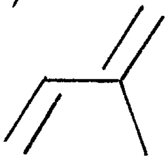
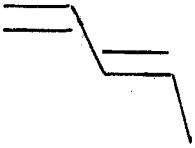
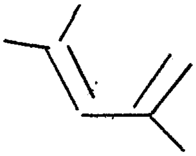
(23)

Both Raman and ultra-violet absorption spectroscopy[16c] indicate that butadiene exists mainly as the s-trans-conformer at ordinary temperatures. Table X gives the extinction coefficients, λ_{max}, and the $S_0 \longrightarrow T_1$ excitation energies of representative 1,3-dienes. 1,3-dienes in the s-trans-configuration characteristically absorb more intensely and at shorter wavelengths than the corresponding s-cis-analogues.

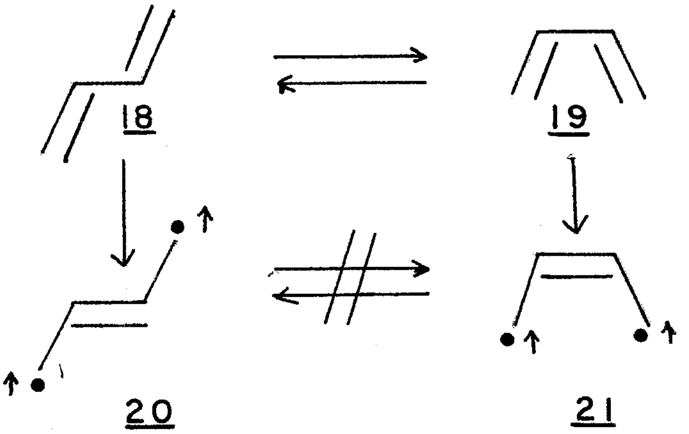
Attempts to determine the population of the conformations in 1,3-butadiene[17,18] by chemical methods all lead to the conclusion that at 25° the s-trans conformer predominates by more than 95%.

Table IX

Extinction Coefficient and λ_{max} of s-*cis* and s-*trans* - 1,3 Dienes.

Compound	Probable conformation	ϵ_{max} (21a)	λ_{max} (21a)	E_t(Kcal) (20)
	s-*trans*	21,000	217	59.7
	s-*trans*	24,000	222	60.0
	s-*trans*	23,000	222	-
	s-*cis*	3,400	239	58.3
	s-*cis*	8,000	256	53.5
	s-*cis* (?)	8,500	228	-

Examination of Figure 1 shows that all sensitizers possessing triplet excitation energies greater than 60 kcal give the same results, while those having excitation energies of less than 60 kcal give a variety of results. It is significant that 60 kcal is precisely the *energy required for the $S_0 \longrightarrow T_1$ transition of the s-trans butadiene*[20]. This behavior is reminiscent of that observed in the sensitized *cis-trans* isomerization of 1,3-pentadiene[5], and the photosensitized dimerization of isoprene[13]. The following discussion involves arguments similar to those offered by Hammond and Liu[13]. In the case of photosensitized isomerization the result can be accommodated by the assumption that the substrate systems can undergo two or more transitions[6]. The two transitions involved in the case of butadiene involve Franck-Condon excitation of the s-*trans* and s-*cis* forms to produce the non-interconvertible stereoisomeric *trans*- and *cis*-triplets, 20 and 21, respectively.*



(24)

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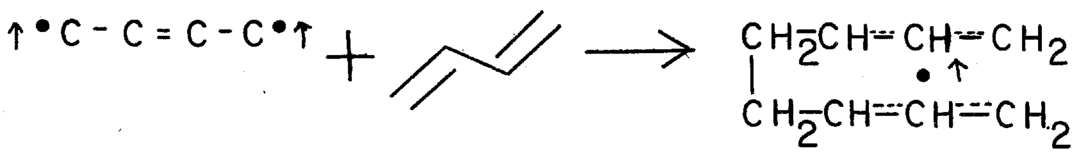
*Evidence for stereoisomeric triplet states of α-diketone has recently been reported[21b]. Although the terminology is somewhat different, Havinga has discussed the photoisomerization of calciferol and related compounds in terms of stereoisomeric excited states[21c].

The data in Tables I, II, and III can be interpreted as follows: the triplet, 20, produced by excitation of 18 reacts predominately to yield cyclobutanes, while the triplet 21, derived by excitation of 19 reacts to give relatively large yields of 4-vinylcyclohexene. Since high energy sensitizers transfer excitation to either s-*cis* or s-*trans*-butadiene on every collision, 20 is overwhelmingly produced, and greater than 90% of the mixture of products contains the cyclobutane unit. When the energy of the sensitizer falls below 60 kcal, transfer to produce *trans* triplets begins to become inefficient and relatively large amounts of *cis* triplets are formed. The latter give relatively large amounts of 4-vinylcyclohexene. Sensitizers having less than 53 kcal excitation energy cannot transfer energy efficiently to either isomeric form of the diene. Under such circumstances transfer probably does not involve Franck-Condon excitation of the acceptor and follows rules which we do not at present completely understand.

The carbon skeleton of cyclic dienes is rigidly held in the cisoid configuration. Only the *cis* triplet can be formed and the major portion of the products contain cyclohexene structures; furthermore, no dependence of the composition of products produced on the nature of the sensitizer is observed.

The regularity with which dimers are formed containing the unit C=C-C-C-C=C, makes it seem probable that the dimerization proceeds in two steps.



(25)

$$\longrightarrow \quad \text{Products}$$

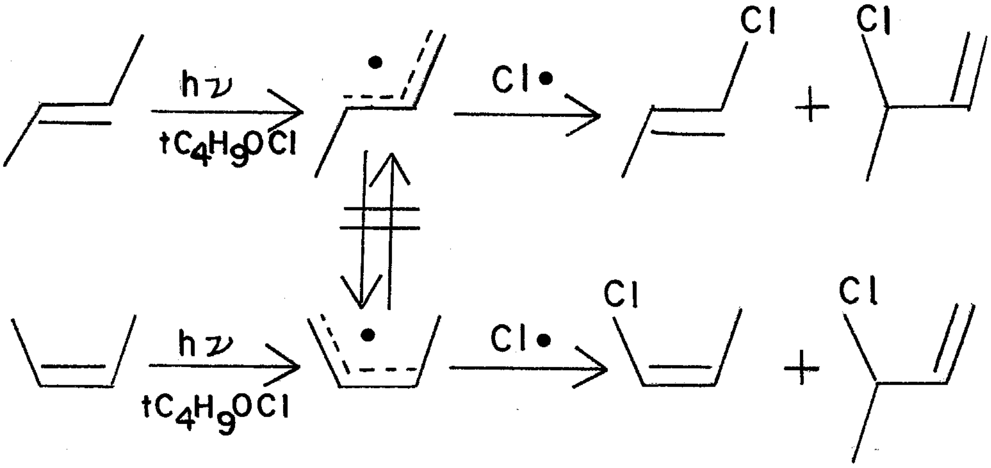
Such a process is analogous to the addition of radicals and polymerization of butadiene[25,27] which apparently involves the resonance stabilized unit, 22.

$$M_x^{\bullet} + C=C-C=C \longrightarrow M_x-C-C\overset{\cdots}{-}\overset{\bullet}{C}\overset{\cdots}{-}C \qquad (26)$$

$$\underline{22}$$

This may mean that the direction of addition of a triplet to a molecule of diene is guided by the same factor, i.e., stabilization of the allylic units, which controls the point of attack of radicals to conjugated dienes.[27]

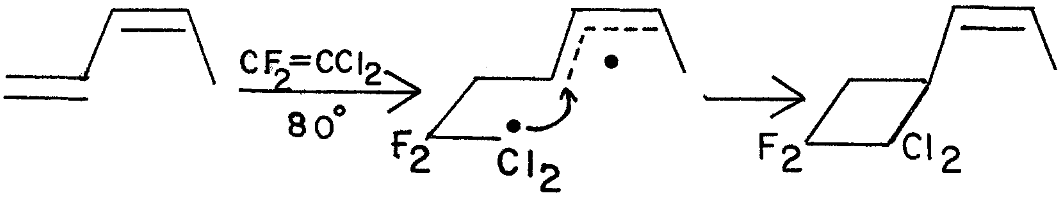
It seems quite likely that the steric configuration of biradicals formed by combination of cis and trans triplets with s-cis and s-trans diene molecules is maintained. This conclusion is derived from the results of several recent investigations. Walling has shown that allylic radicals are capable of maintaining steric integrity (in the absence of excessive bulky substituents) by demonstrating that complete retention of cis-trans stereochemistry is observed during the photochlorination of cis and trans-2-butene by tert-butyl hypochlorite[28].



(27)

(28)

Bartlett[29] has confirmed this hypothesis by demonstrating that the addition of 1,1-difluoro-2,2-dichloroethylene (1122), to dienes produces adducts whose stereochemistry had the same geometry as the parent diene from which they were derived. The addition of 1122 to cis and trans-1,3-pentadiene (piperylene) which is believed to occur via a biradical intermediate occurs at the 1,2-position due to the steric repulsion of the C-4 methyl group, and the stereochemistry of the remaining double bond is maintained.



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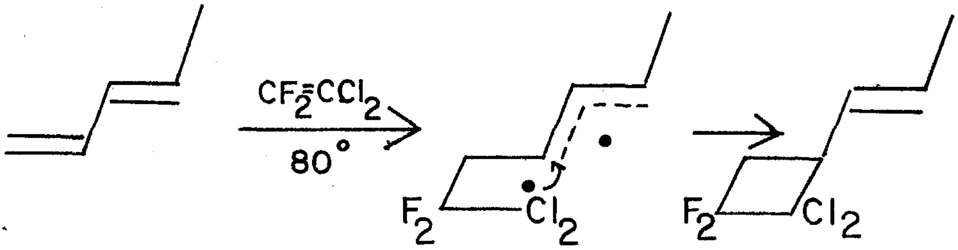
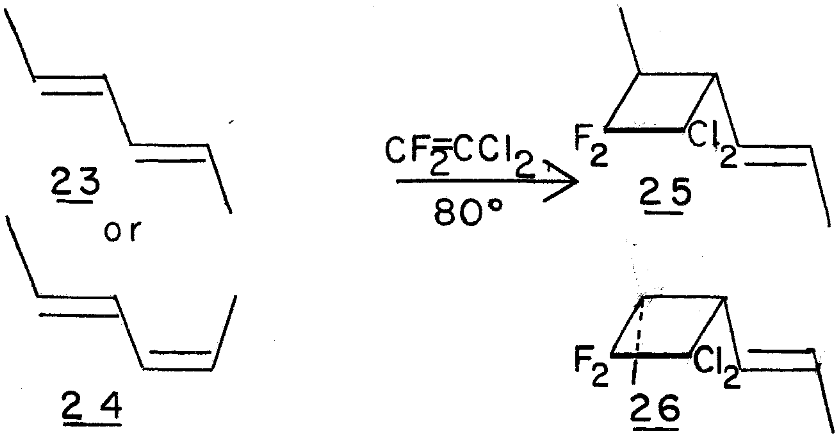


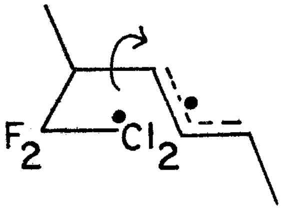
(30)

A more revealing example is the addition of 1122 to <u>trans</u>, <u>trans</u>-2,4-hexadiene, <u>23</u>, and to <u>trans</u>, <u>cis</u>-2,4-hexadiene, <u>24</u>. *These two reactions produce a nearly equilibrated* mixture of the two isomeric adducts, <u>25</u> and <u>26</u>.

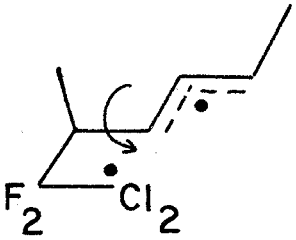


(31)

Rotation about the 2,3-bond occurs during the process, but the isomerization of the allylic system does not occur.



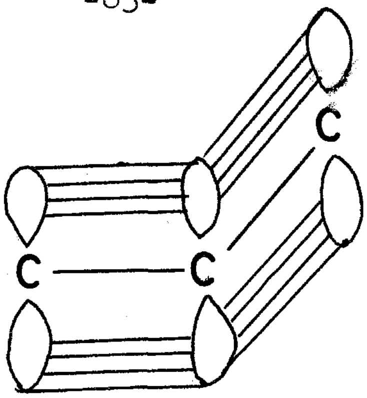
from 23



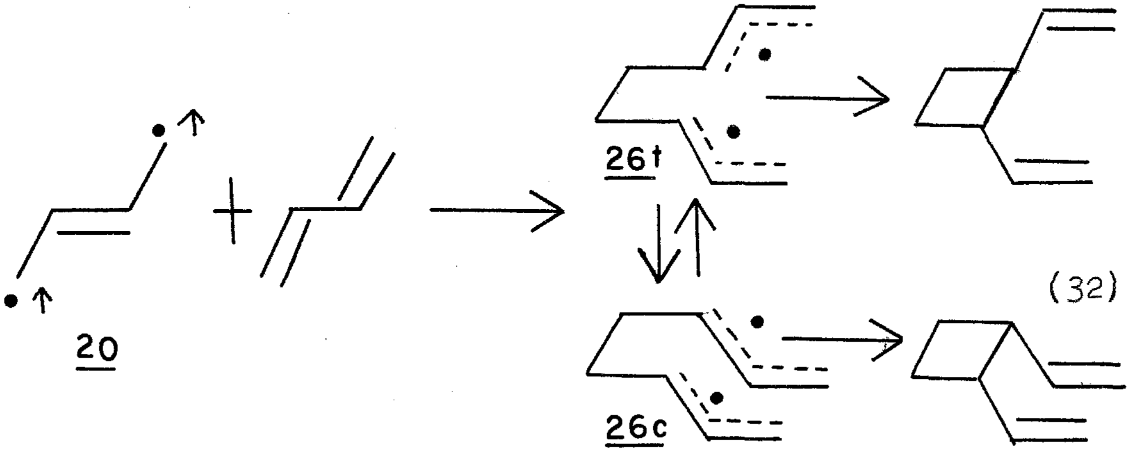
from 24

As a final example, the addition of benzenethyl radicals to butadiene and 1,3-pentadiene exhibits similar stereospecificity. Examination of the configuration of the 1,2-adducts formed by the addition of benzenethyl radicals followed by rapid reaction with oxygen, showed that these adducts had the same geometry as the compound from which it was derived,[29b] indicating that the intermediate radicals are configurationally stable and do not isomerize.

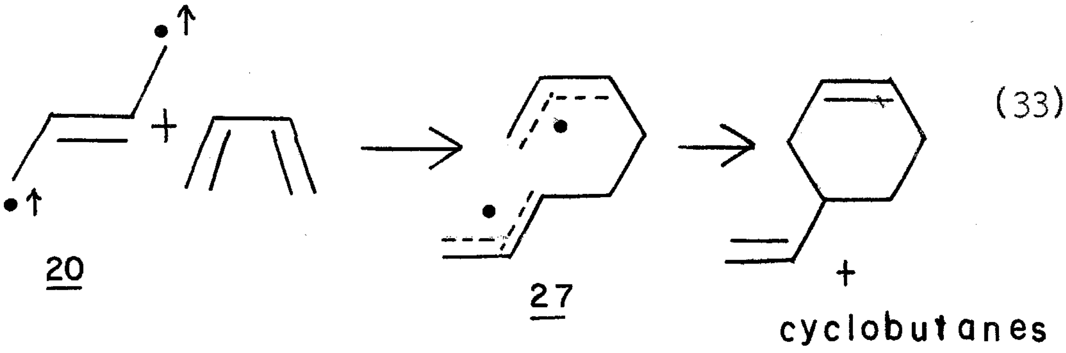
It is somewhat surprising that only very recent experiments have documented the stability of the allylic unit toward isomerization. Simple molecular orbital calculations[21] predict that the allyl radical, should possess considerable resonance stabilization. Since rotation about a C-C bond will destroy this stabilization in the transition state, a substantial barrier to rotation is expected.



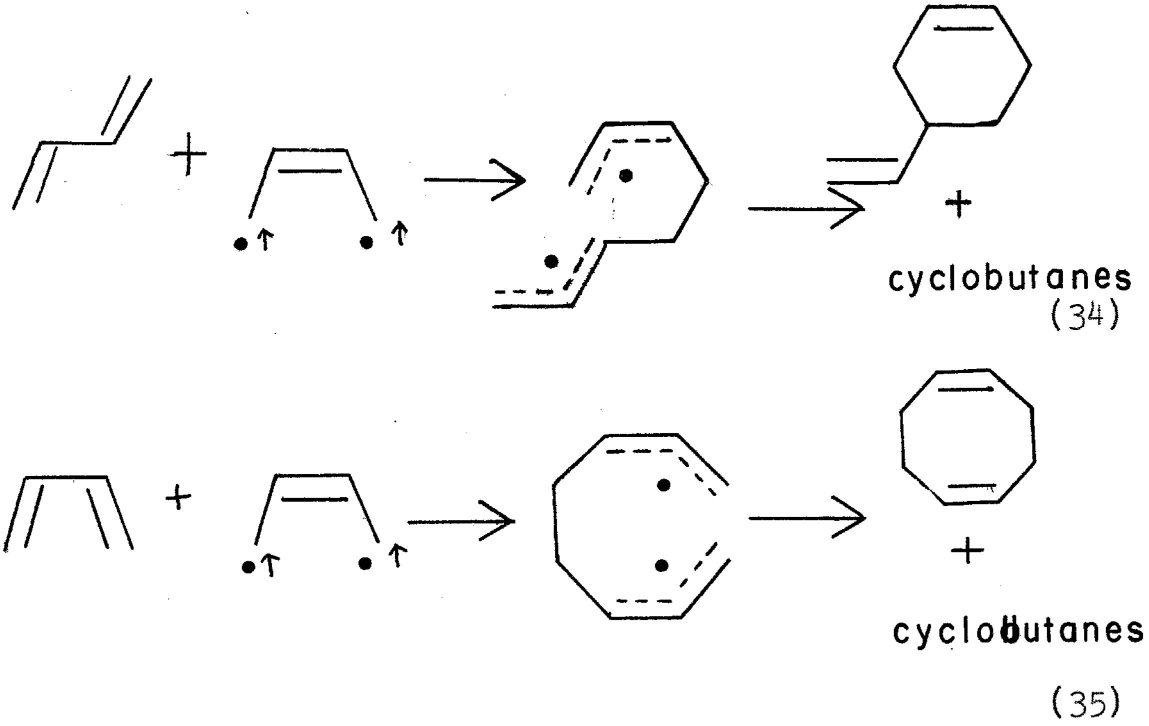
The assumption that triplet addition also occurs without disruption of the steric relationships within either partner of the diallylic biradical leads to the formulation of the four paths for dimerization, shown in Figure II.



(32)



(33)



(34)

(35)

Figure II

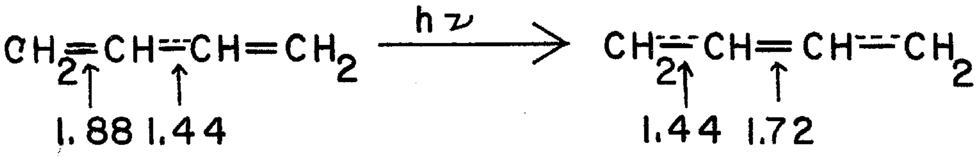
The reaction shown in equation 32 is probably predominant when high energy sensitizers are used. With low energy sensitizers (E < 60 kcal) reaction shown in equation 34 probably is the principal path. The reaction shown in equation 33 may make a very small contribution (due to the small amounts of s-_cis_-butadiene present) which could become increasingly significant as the reaction temperature is increased. Reaction equation 35 should be insignificant under all circumstances.

The following equations include all of the steps considered significant to account for the dimerization (neglecting radiationless transitions and reaction equation 35.

From the data in Table IX we expect that the energy for the $S_o \longrightarrow T_1$ transition for 18 will be different than the corresponding transition for 19[19]. The energy of the $0 \longrightarrow 0$ component of the $S_o \longrightarrow T_1$ transition of 1,3-butadiene is 59.6 kcal. Since this figure undoubtedly arises from overwhelming light absorption by s-*trans*-butadiene, it is probable that the lowest triplet state of simple s-*trans*-dienes lies about 60 kcal above their ground states. Furthermore, the corresponding energy for the $S_o \longrightarrow T_1$ transition of 1,3-cyclohexadiene is 53.5 kcal, which is probably representative of those of s-*cis* dienes in general.

Simple molecular orbital calculations[21] for linear butadiene predict that the first excited state, which is (π, π^*) results from excitation of an electron which is antibonding between carbon atoms 2 and 3 to an orbital which is bonding between these centers.[21a] Therefore, the lowest excited states of 1,3-butadiene and related conjugated dienes are expected to have large barriers to rotation about the central bond. Bond order calculations for linear ground state and excited state butadiene emphasize this prediction.

Bond Orders for Butadiene



$$CH_2 \underset{\underset{1.88}{\uparrow}}{=} CH \underset{\underset{1.44}{\uparrow}}{\overset{-\,-}{-}} CH = CH_2 \xrightarrow{h\nu} CH_2 \underset{\underset{1.44}{\uparrow}}{\overset{-\,-}{-}} CH \underset{\underset{1.72}{\uparrow}}{=} CH \overset{-\,-}{-} CH_2$$

With the above facts in mind let us now attempt to interpret the data for the photosensitized dimerizations and formulate a mechanism which is in satisfactory agreement with the results.

$$S \xrightarrow{h\nu} S^* \qquad (36)$$

$$S^* + t \xrightarrow{k_1} t^* + S \qquad (37)$$

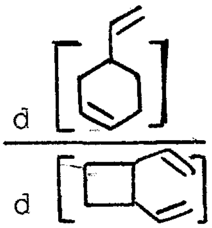
$$S^* + c \xrightarrow{k_2} c^* + S \qquad (38)$$

$$c^* + t \xrightarrow{k_3} \text{cyclohexene and cyclobutanes} \qquad (39)$$

$$t^* + c \xrightarrow{k_4} \text{cyclohexene and cyclobutanes} \qquad (40)$$

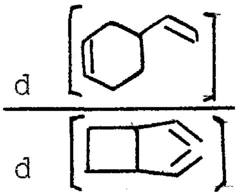
$$t^* + t \xrightarrow{k_5} \text{cyclobutanes} \qquad (41)$$

In the above scheme S is the sensitizer, S* the excited sensitizer, t the s-trans isomer, c the s-cis isomer, t* the trans triplet, and c* the cis triplet. From the steady state assumption for c* and t*, the yield of 4-vinylcyclohexene relative to that of the cyclobutanes is expected to vary with the concentration of s-cis and s-trans butadiene as follows (see Appendix I for derivation).



$$= \frac{k_3 + \frac{k_4\ k_2}{k_1}\ [c]}{\frac{k_5 k_2}{k_1}\ t} \qquad (42)$$

Since high energy sensitizers transfer energy to each isomer at the rate of diffusion, $k_1 = k_2$. Furthermore, if the rate constants k_3, k_4 and k_5 are approximately equal, then



$$= \frac{2\,[c]}{[t]} \qquad (43)$$

From equation 43 and Table X, an estimate of the expected increase in cyclohexene with an increase in temperature can be made and compared with that predicted from an energy difference of 2.6 kcal (assumed to be independent of temperature) between the s-*cis* and s-*trans* forms.

Table X

Increase in the Mole Percentage of s-*cis*-Butadiene with Temperature

% *cis*	T (Kelvin)
4	300°
9	400°
16	500°

The percentages of s-*cis* butadiene at 0° and 55° from the data in Table X is extrapolated to be 2.5% and 5.2% respectively. From equation 43 we expect the relative amount of cyclohexene to increase by a factor of 4.2 in going from 0° to 55°. From the experimental values given in Tables II and III it is found that the corresponding factor is 4.4, in good agreement with the calculated value.

Since a ten-fold change in intensity of exciting radiation had no significant effect on the composition of the product mixtures of butadiene or cyclohexadiene dimers, mechanisms involving reaction of two triplets to produce dimers (the rate of which should be dependent on the square of the light intensity) can properly be eliminated from consideration.

Photosensitized Dimerization of Cyclic Dienes. Reasoning similar to that above for the probable paths for the dimerization of butadiene, leads to the formulation of the three reactions shown in Figure III for the dimerization of cyclohexadiene.

Finally, the reactions shown in Figure IV account for the observed products from the dimerization of cyclopentadiene.

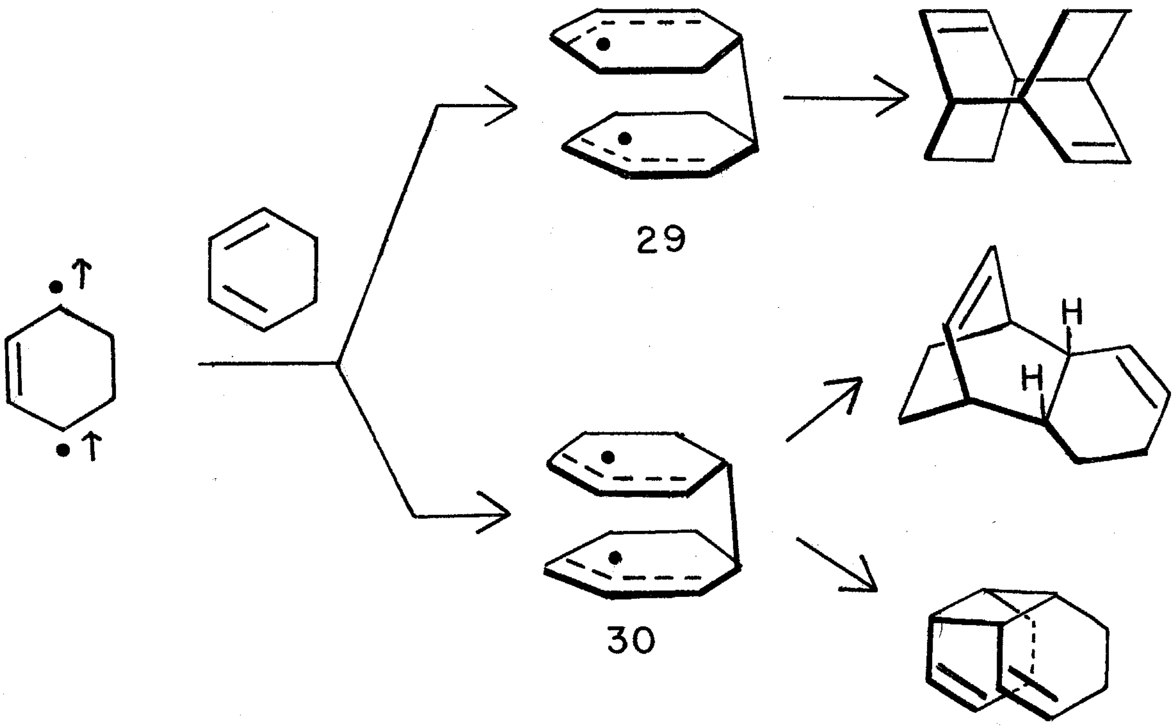


Figure III

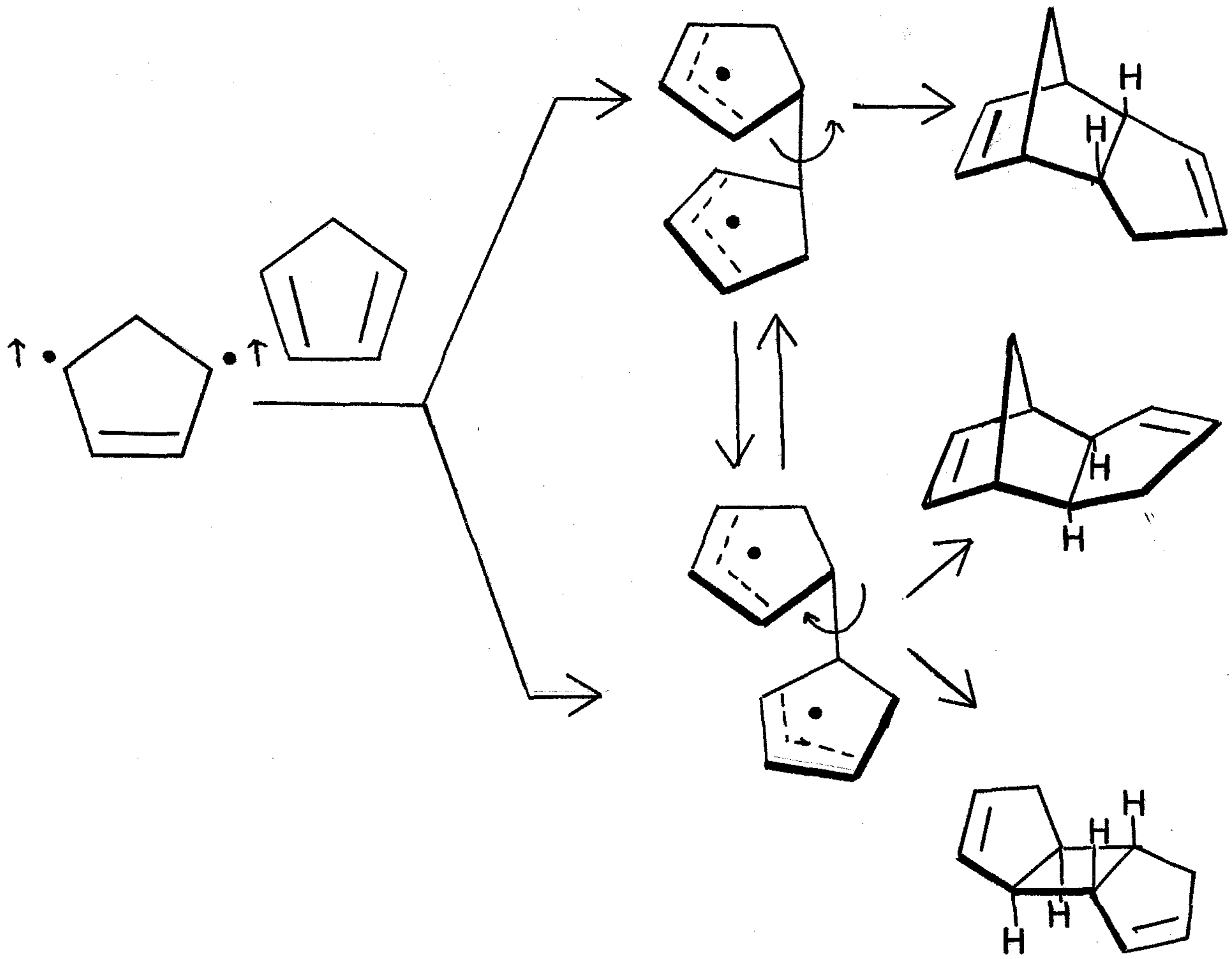
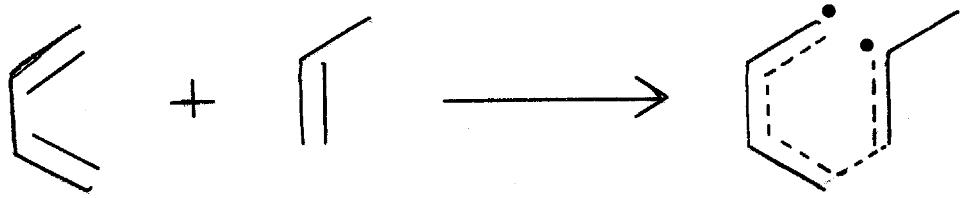


Figure IV

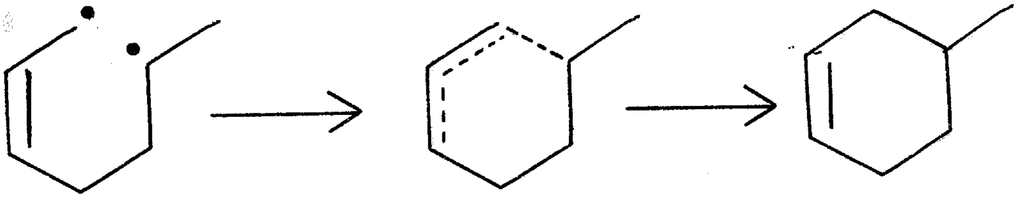
CONCLUSIONS

Intermediates or transition states analogous to 27, 30, and 31 have been proposed for the Diels-Alder reaction[32], the retro-Diels-Alder reaction[33,34] and the isomerization of dicyclopentadienes.[33] In particular the mechanism of the Diels-Alder reaction has been the subject of much debate.[35] In general, recent interpretations have favored one of two extremes in formulating the reaction path:

(a) a two-step process involving a noncyclic intermediate (biradical) B in which the transition state A is higher in energy than C[32]



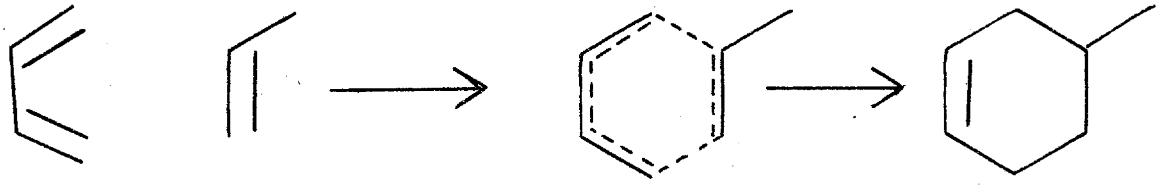
A



B

C

(b) a one step, more or less concerted process with two partial bonds formed in the transition state, D[37]



D

A hypothetical energy profile for paths (a) and (b) is given in Figure V.

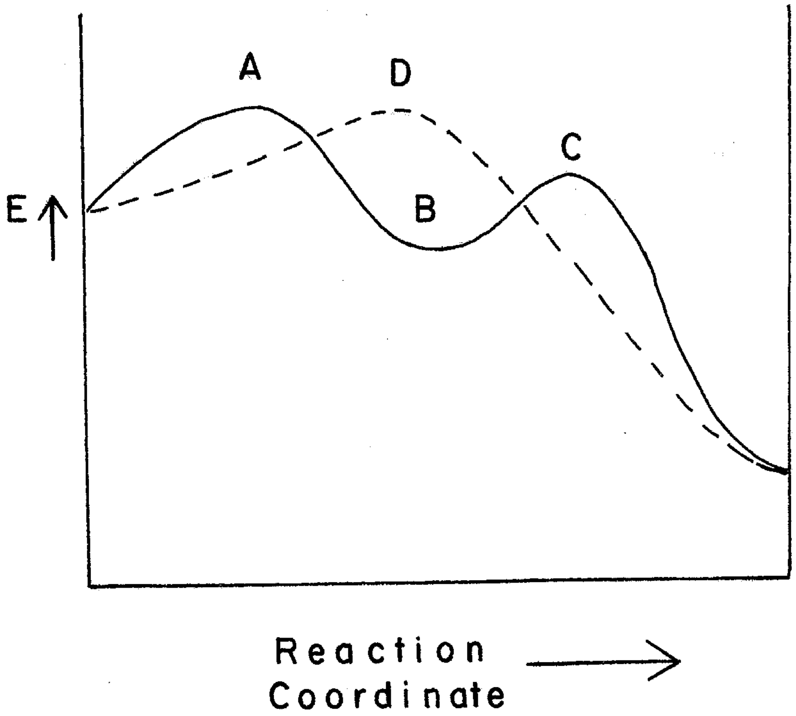


Figure V

The state of electron pairing in B is of significance in the mechanistic description of path (a). The authors favoring the open chain biradical[32] have not explicitly considered the multiplicity of this species, but recently it has been termed a singlet[36]. The one-step mechanism (b) demands that electrons remain spin paired at all times.[33]

The dienes studied in this report undergo Diels-Alder reaction nearly exclusively when carried out thermally, but their photosensitized dimerizations yield varying amounts of cyclohexenes and significant yields of cyclobutanes. Since the photoreactions very probably involve triplet biradical intermediates, our results provide evidence against the intermediacy of open chain triplet biradicals in the Diels-Alder reaction, but have no bearing on the possible involvement of spin paired intermediates in this reaction.

The results given in this thesis strongly support the notion that the triple state of conjugated open chain dienes, such as butadiene, can exist as cis or trans isomers, which possess a substantial barrier to interconversion. Aside from its theoretical interest, the photosensitized dimerization of butadiene offers an attractive synthetic route for the preparation of 1,2-divinylcyclobutanes.

Finally, Schenck's radical addition-elimination mechanism fails badly in explaining the nature of the variation of relative yields of butadiene dimers with change of sensitizer and corresponding lack of variation for cyclic dienes.

EXPERIMENTAL

Butadiene. Matheson, Coleman and Bell (MC&B), Instrument Grade was used directly for preparative dimerizations. The diene was purified by preparative vapor phase chromatography on the Megachrom apparatus for use in the study of various effects on the relative yields of dimers. This procedure eliminated the necessity of correcting for the small amount of 4-vinylcyclohexene in the butadiene.

Cyclopentadiene, was prepared immediately before use by cracking dicyclopentadiene, MC&B, practical, at 172°. The fraction boiling at 40-42° was collected for use.

1,3-Cyclohexadiene, Columbia or Aldrich, reagent, was distilled and the fraction boiling at 80-82° was collected for immediate use.

Sensitizers, were all reagent grade or the best quality commercially available. See the experimental section of Part I, this thesis, for further purification procedures employed.

Preparative Dimerizations and Characterization of Products Dimerization of 1,3-Butadiene. Instrument grade 1,3-butadiene (80-100 g) was irradiated in a Hanovia Type S 200-watt immersion apparatus equipped with a 2800 Å cut-off filter. The lamp housing was cooled with ethylene glycol-ice water and the entire reactor was surrounded by a one gallon dewar flask filled with dry ice. The sensitizer

(5-15 g.) was added and the solution irradiated. The course of the reaction was followed by periodic sampling and analysis by vapor phase chromatography at 75° employing a six ft. by 1/4 in. column packed with 35% Carbowax 20M (column K). Three new peaks, 1, 2 and 3, appeared in the vapor chromatograms. In the presence of 2,3-pentanedione, for example, the reaction went to near completion in about 80 hours, while the reaction is only 12% complete at 40 hours in the presence of benzophenone or acetophenone. A typical workup procedure is the following one. 80 ml. of 1,3-butadiene containing 15 ml of 2,3-pentanedione was irradiated for 80 hours at which time only 4% unreacted butadiene remained, as indicated by vapor phase chromatographic (vpc) analysis. The diketone was removed by passage of the mixture through an alumina column and the eluent heated under reflux at 120° for three hours to convert *cis*-1,2-divinylcyclobutane to *cis*, *cis*-1,5-cyclooctadiene (vide infra). The resulting mixture was then fractionated through a spinning band column. The fractions obtained were 15 g. of *trans*-1,2-divinylcyclobutane, b.p. 111-113°, n_d^{25} 1.4430; 12 g. of 4-vinylcyclohexene, b.p. 128°, n_d^{25} 1.4620; and 2 g. of *cis*, *cis*-1,5-cyclooctadiene, b.p. 150-155°, n_d^{25} 1.4930.

Rearrangement of cis-1,2-Divinylcyclobutane. Pure *cis*-1,2-divinylcyclobutane purified by preparative vapor chromatography on a six ft. by 1/4 in. column K. Twenty g.

of the pure material was heated in a sealed tube for 18 hours at 120°. Analysis by vpc of the reaction product showed that the starting material was completely gone and only one new peak appeared in the trace. The infrared spectrum, boiling point and index of refraction of this compound agreed exactly with those reported in the literature for _cis_, _cis_-1,5-cyclooctadiene.

Ozonalysis of trans-1,2-Divinylcyclobutane. Two g. of the diene was dissolved in 100 ml. of ethyl acetate and ozonized for 6 hours at -78°. The ozonide was decomposed by adding a solution prepared from 6 ml. of 30% hydrogen peroxide and 80 ml. of water followed by heating of the resultant solution on a steam bath for several hours. Upon concentration and cooling, an oil formed. The oil was extracted with ether, the extract dried and then concentrated to yield yellow crystals. After two recrystallizations from benzene-ethyl acetate, white crystals m.p. 127° (lit. 129°) were obtained. Neutralization equivalent: Found, 68-and 75. Calc. for $C_6H_8O_4$, 72.

Dimerization of Cyclopentadiene. In a typical run 10-20 g. of sensitizer was added to 140 g. of freshly cracked cyclopentadiene, and the resulting solution was irradiated in a Hanovia 450 watt immersion apparatus cooled in a similar manner to that described above for dimerizations of butadiene. The temperature of the reaction mixture was maintained at -10° or lower in order to minimize the thermal dimerization. The reaction was usually complete after 24 hours of irradiation as shown by disappearance of monomer in the vpc analysis. The reaction mixture was distilled under vacuum yielding 130 g. of material boiling at 32-40° at mm. Vapor phase chromatographic analysis on a 12 ft. by 1/4 in. column X showed the products to consist of three peaks practically equal in area (after corrections for the thermal dimerization). Freshly distilled dimers were separated into two fractions at 90° by preparative vpc on a Megchrom apparatus, equipped with eight 6 ft. by 5/8 in. columns packed with 35% Apiezon J. The two separated fractions consisted of a mixture of two stereoisomers, *exo*-dicyclopentadiene, 5, and *endo*-dicyclopentadiene, 4, and pure *trans*-tricyclo-(5,3,0,0,^{2,6})-3,9-decadiene, 6. The two stereoisomers were separated by preparative vpc employing a single 6 ft. by 5/8 in. column X in the Megachrom. The *endo*-dicyclopentadiene produced in the photodimerization has b.p. 170-172°, n^{25}_{D}, 1.5080 and infrared and n.m.r. spectra identical to those of an authentic sample prepared by the method of Bartlett and Goldstein[9]. *trans*-Tricyclo-(5,3,0,$0^{2,6}$)-3,9-decadiene has b.p. 170-2°, n^{25}_{D}, 1.5080 maxima.

Hydrogenation of trans-Tricyclo-(5,3,0,$0^{2,6}$)-3,9-decadiene, 13. A 0.5 g. sample of the dimer, 6, contaminated with about 20% of *endo*-dicyclopentadiene was dissolved in 5 ml of 95% ethanol and then placed in a 25 ml hydrogenation flask. Platinum dioxide (50 mg.) was added and the mixture was treated with hydrogen gas (uptake 170 ml.). The mixture was then filtered and concentrated. Analysis by vpc on column X at 80° showed that the diene had been completely converted and a compound of considerably shorter retention time was detected. This compound was obtained pure by preparative vpc. The material did not decolorize a solution of bromine in carbon tetrachloride or an aqueous solution of potassium permanganate. The infrared and n.m.r. spectra of the saturated material were identical to those of the hydrocarbon produced by Wolff-Kischner hydrogenation of trans-tricyclo-(5,3,0,$0^{2,6}$)-3,8-decandione[10].

trans-Ditosyloxytricyclo-(5,3,0,$0^{2,6}$) -3,8-decane. Tricyclo (5,3,0,$0^{2,6}$)-3,8-decandione was prepared by the method of Eaton[10]. A 10.0 g. sample was dissolved in 250 ml. 95% ethanol and cooled in an ice bath. A solution of 5.0 g. sodium borohydride in 20 ml of 0.1N. aqueous sodium hydroxide was then added slowly. An exothermic reaction occurred and the mixture became cloudy. After two hours stirring and cooling, the mixture was concentrated to 50 ml. and diluted with 20 ml. of cold water. The alcohol was exhaustively extracted with ether and methylene chloride. The extracts were combined, dried and concentrated until crystals appeared. The crystals were filtered and dried, m.p. 193-4°, yield 8.0 g. Anal. Calc. for $C_{10}H_{16}O_2$: C 71.50; H, 9.54. Found: C, 71.88; H, 9.66. The spectrum of a potassium bromide pellet showed a broad alcohol band at

3,200 cm.$^{-1}$. The diol (1.0 g.) was dissolved in pyridine (15 ml.) and cooled in an ice bath. A solution of 3.0 g. of tosyl chloride dissolved in 15 ml. pyridine was added to the stirred solution. After five hours of stirring the mixture was left overnight in the refrigerator. The mixture was then poured into cold 1N sulfuric acid and crystals appeared. The crystals were washed with pentane and then recrystallized from hexane; m.p. 158-159° (decomp); yield, 1.8 g. Anal. Calcd. for $C_{17}H_{24}SO_5$: C, 60.50; H, 5.88; S, 13.54. Found: C, 59.44; H, 5.88; S, 13.54.

trans-Tricyclo-$(5,3,0,0^{2,6})$-3,8-decadiene. Potassium was dissolved in freshly distilled tert-butyl alcohol (20 ml.) under nitrogen. A 1.5 g. sample of the tosylate was added slowly to the solution and the mixture was heated under reflux overnight. Cold water (100 ml.) was added to the cooled solution. The mixture was filtered and the aqueous filtrate was extracted 3 times with pentane. The extract was dried and concentrated to yield 80 mg. of product. The product was obtained pure by preparative vapor chromatography on column X. The pure material had a retention time longer than that of the tricyclodiene produced in the photoreaction, and could be separated from the latter.

trans-Ditosyloxytricyclo-$(5,3,0,0^{2,6})$-3,9-decane. Tricyclo $(5,3,0,0^{2,6})$-2,9-decanedione was separated from the mixture of cyclopentenone photodimers according to the method of Eaton[10] and reduced with sodium borohydride by the procedure described above for the preparation of the isomeric diol. The diol was purified by continuous extraction with ether in a Soxhlet apparatus; m.p. 168-170°. Anal. Calcd; for $C_{10}H_{16}O_2$; C, 71.50; H, 9.54. Found: C, 71.16; H, 9.68. The tosylate of this diol was prepared as described above. The crude tosylate was extracted three times with benzene and then recrystallized from hexane, m.p., 119-120°. Anal. Calcd. for $C_{17}H_{24}SO_5$: C, 60.50; H, 5.88; S, 13.45. Found: C, 60.58; H, 6.12; S, 12.60.

trans-Tricyclo-$(5,3,0,0^{2,6})$-3,9-decadiene. Four g. of the tosylate was added to a refluxing solution of four g. of potassium in 35 ml. of tert-butyl alcohol (under nitrogen). The mixture was analyzed after five hours by vpc on column X and a product was found retention time identical to that of the tricyclodecadiene produced in the photodimerization of cyclopentadiene, the yield calculated from the vpc data was 0.6 g. The material was obtained pure by preparative chromotography on column X. It possessed infrared and n.m.r. spectra identical to those of the tricyclic dimer.

Thermal Rearrangement of the Dicyclopentadiene. A sample of 10 ml of the tricyclododecadiene, 6, (90% contaminated with about 10% endo-dicyclopentadiene, 4, in 10 mg of benzene was heated for five hours in a Wood's metal bath at 165-175°. A sample of 50% endodicyclopentadiene in benzene was heated simultaneously. Analysis of the heated samples was made by analytical vpc on a 10 ft. by 1/4 in. column X, at 80°. The sample of 4 showed about 1% conversion to exo-dicyclopentadiene, 5. The cyclobutane, 6, was converted to about 35% of 4 and less than 1% of 5. Heating a sample of 4 at 180-185° for 16 hours produced a mixture of about 70% of 4 and 30% of 5, with a few percent cracking also occurring.

Dimerization of 1,3-Cyclohexadiene. A 2.0 gm. sample of sensitizer was added to a solution of 1,3-cyclohexadiene (23 g.) in 110 ml. of isopentane. The resulting solution was irradiated in a Hanovia type S 200 watt immersion apparatus equipped with 2800 Å cutoff filter and a reflux condenser. The mixture was purged continuously with nitrogen. The progress of the reaction was followed by vpc employing column Q at both 32° and 160°. The analysis at the lower temperature showed the diene to be contaminated with benzene and cyclohexene. The cyclohexadiene peak decreased to zero after four hours but the concentration of impurities remained constant. At the higher temperature three product peaks appeared in the relative yield of 61:22:17, in order of increasing retention time. The bulk of the solvent was removed by distillation and then 10 g. of material boiling at 50-52° at 1-2 mm. was collected. The three products were obtained pure by preparative vpc after several cycles on Apiezon J.

Determination of the Relative Yields of Dimers. The following standard procedure was followed for the study of the effects produced by variation of sensitizer, concentrations, temperature and solvent. Stock solutions 0.5 to 0.25 M of all sensitizers in reagent solvents were used.

If the solubility of the sensitizer was low, saturated solutions were employed. Nearly equal volumes of the stock sensitizer solution and neat butadiene were added to a constricted 13 x 100 mm pyrex test tube, which had been previously cooled to -78°. The solution was then frozen at the temperature of liquid nitrogen, evacuated and sealed. The sealed tubes were then placed on a rotating turntable, at the center of which was a 450-watt immersion lamp. The entire apparatus was immersed in an insulated water bath. Irradiations were usually conducted for 12-40 hours. The tubes were then opened and analyzed immediately by vpc on a 10 ft. x 1/8 in. column packed with 35% Apiezon J (column Q) at 60-80°. For analysis of mixtures produced at low conversions a Loenco model 15 B vpc provided with a flame ionization detector was employed. For conversions greater than 5% either a Loenco model 15 B or a Loenco model 70 Hi-Flex Program vpc was used. The relative areas under the peaks were measured with a disc integrator. Sensitivity changes were made when possible in order to maximize the heights of the peaks produced on the chromatogram.

A 10 ft. x 1/8 in. column Q and a 12 ft. x 1/4 in. column packed with 25% oxydipropionitrile (column X) were used to analyze the dimers of cyclohexadiene and cyclopentadiene, respectively.

<u>Direct Irradiation of the Dienes</u>. Blank analysis of solutions of the dienes which were irradiated under identical conditions to the samples containing photosensitizers, showed

less than 1-2% conversion to dimeric material after prolonged irradiation during which time sensitized reaction was virtually at completion. Irradiation of isopentane solutions of butadiene for three weeks in an evacuated, sealed quartz tube produced very little dimerization and polymerization.

Determination of Quantum Yields. The enclosed 800-watt photochemical reactor previously described[5,24] was employed for the measurements of quantum yields. The photolysis cells were similar to those previously described.[5]

Butadiene. A stock solution of 3.20 gm of butadiene in 25 ml of ether was prepared. To 5.0 ml of this stock solution was added to 5.0 ml of a 0.1 M solution of sensitizer, and 4.0 ml of the resulting solution was added to a constricted 15 x 150 mm pyrex test tube, frozen, evacuated and sealed. Measurements made with the Beckman DU Spectrophotometer indicated that all of the samples, except that containing biacetyl as sensitizer (which showed 50% transmission) transmitted less than 1% at 3660 Å. The samples were irradiated through a Corning 751 filter and ferricoxalate actinometry was used to monitor the intensity.[38] Analyses of the irradiated samples were made by vpc with a Loenco Model 15 B chromatograph, provided with a flame ionization detector. A standard solution of trans-1,2-divinylcyclobutane was used to calibrate the concentrations of dimers formed.

Cyclohexadiene. A procedure similar to that employed for butadiene was used for the measurement of quantum yields for cyclohexadiene dimerization. To a 1.0 ml sample of cyclohexadiene and 3.0 ml of 0.1 M solution of sensitizer were added to a photolysis cell and treated as described above. In another experiment the intensity was decreased about ten times by replacing the Corning filter with a combination of a Corning 052 plus a Corning 737 filter. Ferrioxalate actinometry was used to monitor the intensity. Measurements of the amounts of dimers produced were made by analytical vpc as described above. A standard sample of the three photodimers of cyclohexadiene was used to calibrate the peak areas.

Thermal Isomerizations. Thermal isomerizations of dimers was conducted according to the following procedure. A 10-20 mg sample of substrate was heated in a 3 x 75 mm evacuated and sealed tube. Analysis and identification of products were made by vpc as described above. For example, 10 mg of the tricyclododecadiene 12 was added to a 3 x 50 mm tube, evacuated and sealed. The tube was then heated in a Wood's metal bath at 220° for eight hours. Analysis by vpc on a 300 ft. x 0.01 in. column Q indicated that complete conversion to endo-dicyclohexadiene 15 had occurred. Injection of equal volumes of the heated material and a standard sample of 13, produced nearly equal areas in the chromatograms, indicating that little polymerization or other side reactions had occurred.

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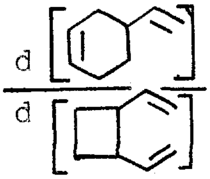
APPENDIX I

From equations 37-41

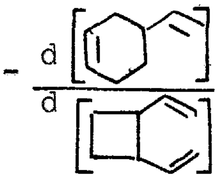


$$= \frac{k_3 \left[c^*\right] \left[t\right] + k_4 \left[t^*\right] \left[c\right]}{k_5 \left[t^*\right] \left[t\right]} \qquad (41a)$$

$$\frac{d\ c^*}{d\ t^*} = \frac{k_1 [c]}{k_2 [t]} = \frac{c^*}{t^*}$$

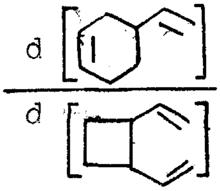
thus $t^* = \dfrac{k_2 c^* t}{k_1 c}$

from (43) and (45)



$$= \frac{k_3 t c^* + \frac{k_4 k_2}{k_1} c^* t}{\frac{k_5 k_2}{k_1} \frac{t^2 c^*}{c}} \qquad (41b)$$

whence



$$= \frac{k_3 + \frac{k_4 k_2 \left[c\right]}{k_1}}{\frac{k_5 k_2}{k_1} \left[t\right]} \qquad (42)$$

Propositions
or
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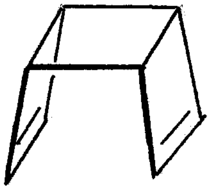
I

The preparation and properties of the tricyclodiene, 1, have been recently described[1]

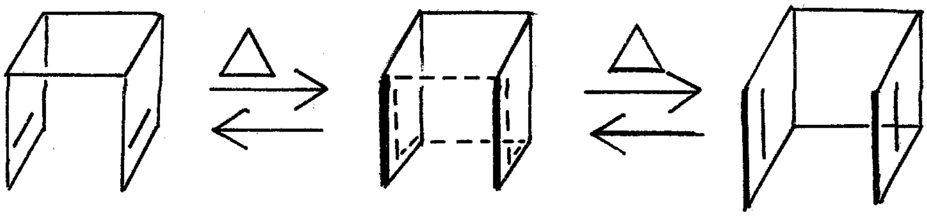


1

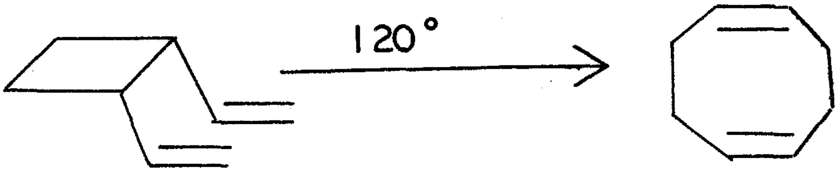
The n.m.r. and infrared spectra of 1 are consistent with the assigned structure. The compound possesses the interesting feature that a Cope rearrangement will produce a molecule which is (in the absence of labelling) identical in all respects to 1.

$$\underline{1} \xrightleftharpoons{\Delta} \underline{1}$$

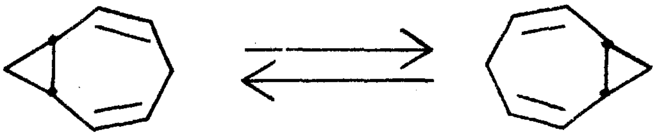
The geometry of 1 is favorable for such a rearrangement to occur. In fact, 1,2-divinyl-cyclobutane, 2, the most stable conformation of which is not favorable for Cope



rearrangement, undergoes smooth conversion to cis, cis-1,5-cyclooctadiene at 120° [3].



It is proposed that 1 be prepared labelled with deuterium. Heating of the deuterated compound to 100-150° should produce scrambling of the label. Furthermore, the n.m.r. spectrum of unlabelled 1 at 100° should be quite different from the spectrum at room temperature. A similar phenomenon has recently been reported for 3,4-homotropilidene, 3, whose n.m.r. spectrum at 180° C. indicates that the hydrogens are shifting their positions very rapidly.[2]

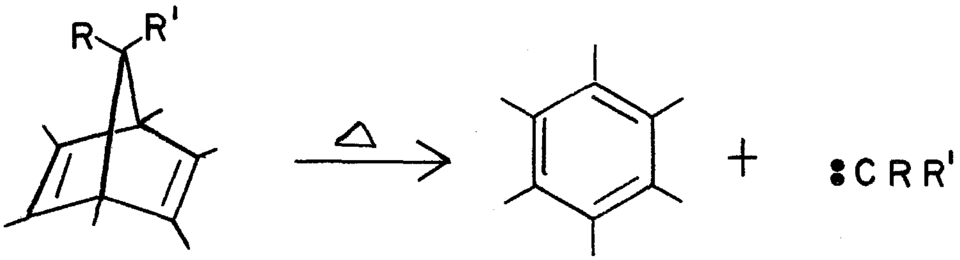


References

1. M. Avram, et al., Chem. Ber., 92, 1088 (1959)
2. W.v.E. Doering and W. R. Rogh, Angew Chem., 75, 27 (1963)
3. E. Vogel, Ann., 615, 1 (1958)

II

There are several reports in the literature of bicyclic compounds which decompose thermally to formally extrude methylenes.[1,2] The intermediacy of these methylenes has not been confirmed. It is proposed that methylene fragments will result from the thermal decomposition of appropriately substituted norbornadienes, under conditions which allow trapping of the methylene.



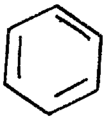
7,7-Substituted tetraphenylcyclopentadienes are readily available[3]. Relief of steric strain due to bulky phenyl groups and resonance stabilization gained by aromatization will provide driving force for the extrusion of methylene.

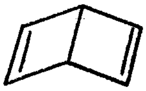
References

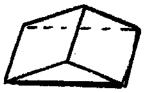
1. E. T. McBee, et al., J. Am. Chem. Soc., 77, 387 (1955)
2. W. von Doering, et al., J. Am. Chem. Soc., 84, 1224 (1962)
3. A. Allen, Chem. Revs., 62, 635 (1962)

III

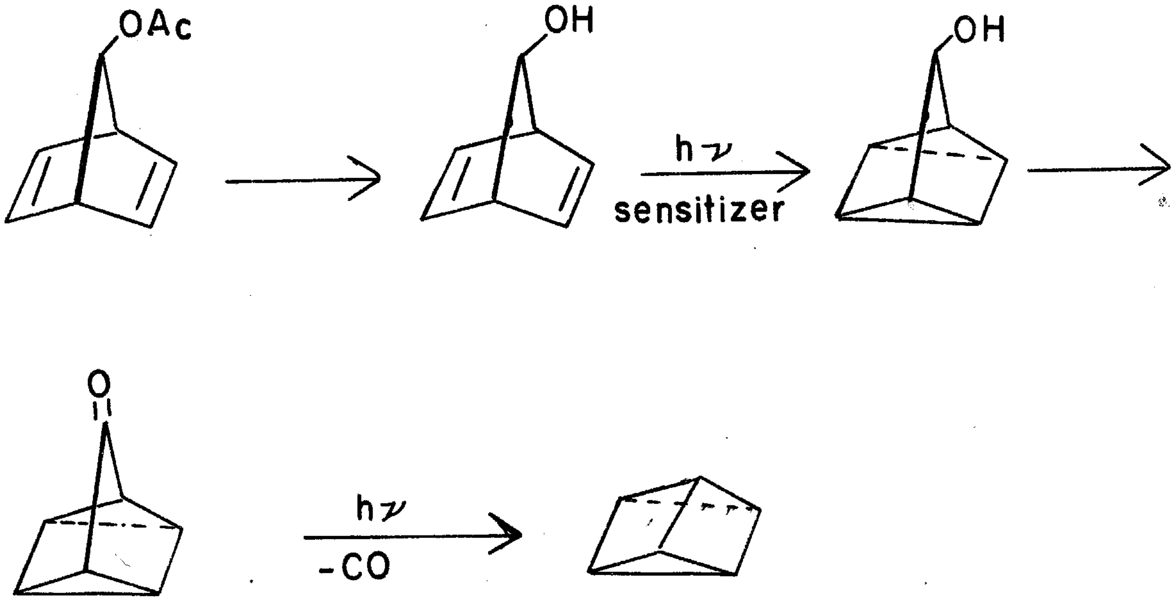
Benzene, 1, Dewar benzene, 2, and prisbane, 3, represent an interesting family of isomers.



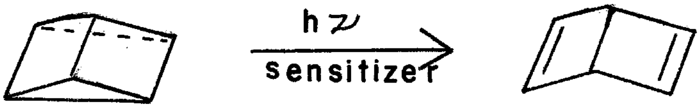




The following synthesis[1] of 2 is proposed from the readily available material 4.



The sensitized isomerization of 2 to 3 should provide a method of preparation of Dewar benzene[2].



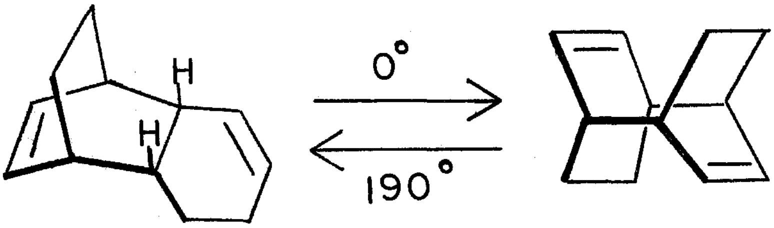
A study and comparison of the thermodynamic properties and reactions of 2 and 3 with those of benzene will offer insight to the relationships of the potential energy surfaces involved in these reactions.

References

1. P. R. Story, *J. Org. Chem.*, 26, 287 (1961)
2. Quadricyclene is isomerized to norboradiene by several sensitizers.

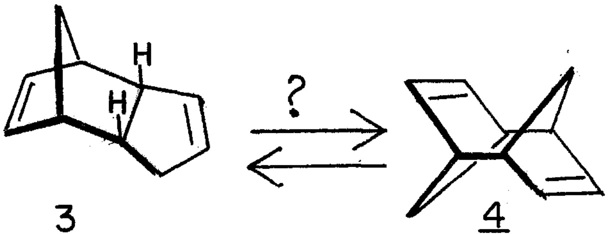
IV

endo-Dicyclohexadiene, 1, rearranges to the tricyclododecadiene, 2, at room temperature.[1]

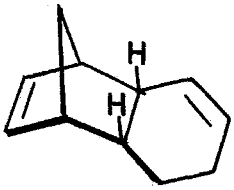


15 12

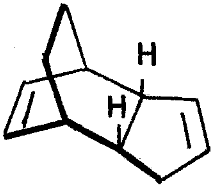
It is of interest to determine if a similar reaction occurs with endo-dicyclopentadiene, 3.



3 4



5



6

If the intermediacy of 4 in this reaction is real, it can be demonstrated by racemization of optically active 3, under conditions which do not allow isomerization by an external mechanism.[2]

A study of the racemization and dissociation of 3 may provide information concerning the relationship of these two reaction pathways and the Diels-Alder reaction[3].

Similar studies of compounds 5 and 6 will give further information concerning the energetics and potential energy surfaces involved in these reactions.

References

1. This thesis, Part II.
2. See ref. 34, Part II, this thesis
3. See ref. 37, Part II, this thesis

V

If aqueous 1 M Cr(II) perchlorate, also 1 M with respect to perchloric acid, is shaken with benzyl chloride an aqueous solution of Cr(III) $CH_2C_6H_5(H_2O)$ is formed.[1] This compound slowly decomposes in the absence of oxygen to bibenzyl.

$$2\ \mathrm{Cr(III)}\ CH_2C_6H_5(H_2O)_5 \xrightarrow{H_2O} 2\ \mathrm{Cr(III)}(H_2O)_6 + C_6H_5CH_2CH_2C_6H_5$$

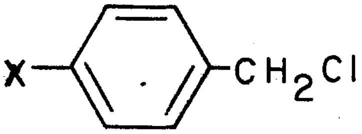
In the presence of chloride ion, however, toluene, instead of bibenzyl is formed. This discrepancy has been explained by assuming that the presence of chloride ion favors electron transfer by bridging with chloride, producing the following reaction.

$$\mathrm{Cr(III)}\ Cl\cdots\cdots CH_2C_6H_5 \longrightarrow \mathrm{Cr(III)}\ Cl^{2+}$$

$$+\ C_6H_5CH_2(—) \xrightarrow{H_2O} C_6H_5CH_3$$

This mechanism can be easily verified by running the reaction with labelled chloride ions and then determining the extent of corporation of labelled chloride in the $\mathrm{Cr(III)}Cl^{2+}$ produced. Furthermore, kinetic measurements should be made to determine the order of the reaction with respect to substrate, chloride ion and chromous ion.

Chromous ion is known to reduce by remote attack on systems possessing extensive conjugation.[2] It is of interest, therefore, to prepare appropriately substituted benzyl chlorides for which the probability of remote attack would be favored. Representative substrates are given below.



X = $-CO_2Me$, $-CH=CH-CO_2Me$, etc.

Finally, Cr(2,2-dipyridyl)$_3^{2+}$, which must react through an outer sphere complex, should be substituted for Cr(II) in these reactions to determine if an inner sphere complex is required for these reductions.

References

1. F. A. L. Anet and E. Leblanc, J. Am. Chem. Soc., 79, 2649 (1957)

2. H. Taube, J. Am. Chem. Soc., 77, 4481 (1955) and later papers.