PHOTOSENSITIZED REACTIONS OF CONJUGATED DIENES

Thesis by

Robert Shing-Hei Liu

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To My Parents

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ABSTRACT

Conjugated dienes are shown to undergo photosensitized dimerization reaction, photosensitized cross addition reaction, and photosensitized inter- or intramolecular addition to olefins. Structures of isoprene, piperylenes, 2,3-dimethylbutadiene dimers, butadiene-1,3-cyclohexadiene, 1,3-cyclohexadiene-cyclopentene cross adducts, and myrcene photoisomers have been assigned (some in parts). The mechanism of the dimerization reaction, which is closely related to the other reactions, has been studied in detail with isoprene as the representative system. It was found that in order to explain the results consistently, several postulates are necessarily invoked. They include the non-interconvertible stereoisomeric triplets of conjugated diene, the unusual stable nuclei configuration of diene triplets, new assignments of the O-O components of singlet-triplet transition of dienes, and "nonvertical" energy transfer from sensitizer to diene molecules. Evidence is presented in support of the mechanism in which only one diene triplet is involved in such a bimolecular reaction.

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INTRODUCTION

The field of photochemistry seems to have received a stimulus in the recent decade. New reactions and even new classes of reactions are being brought forth at a torrid pace. Playing a significant role in this rapid surge of photochemistry is the study of photochemical reactions of conjugated dienes. Although the study is still actively pursued by many research groups, the reports in the past few years have been so numerous and mechanistic studies have been in sufficient detail, that it is now possible to categorize photochemical reactions of conjugated dienes. Before plunging into a review of the reactions, the processes of excitation and deactivation with butadiene as the representative system will be summarized briefly.

Conjugated dienes absorb only in the ultraviolet region. The O-O component of the singlet-singlet transition of 1,3-butadiene, for example, is at 2170 Å (1); therefore, the first excited singlet state is about 132 kcal/mole above the ground state. The forbidden singlet-triplet transitions can normally be observed only under special conditions, e.g. in solvents with heavy atoms or under high oxygen pressure. In the case of butadiene, λ_{max} of the longest wavelength absorption band is at 4800 Å, which was assigned as the O-O component by Evans (2). The spectroscopic triplet state is, therefore, 60.0 kcal/mole above the ground state. A simple energy diagram of butadiene is shown in Figure I.

In Figure I, ways to populate the excited states and paths of

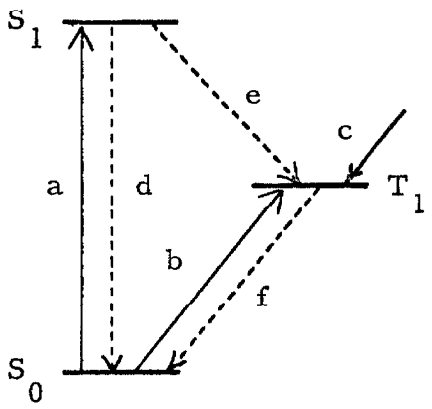


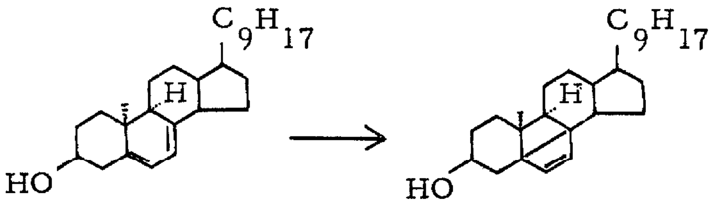
Fig. I

relaxation to the ground state are also indicated. Paths (a) and (b) are the allowed and forbidden absorptions; path (c) is the energy transfer step. Path (d) is radiationless deactivation following internal conversion from the excited singlet (S_1) to the ground state; paths (e) and (f) represent radiationless deactivation following intersystem crossing from an excited state (S_1 or T_1) to a state (T_1 or S_0) of different multiplicity. Emission from the excited states is not included in the figure, since there is no evidence in the literature for emission from dienes. Any of the following excited states may conceivably undergo chemical reactions: (1) the excited singlet state, S_1, (2) the triplet state, T_1, (3) a vibrationally excited ground state formed after conversion from S_1 to S_0 (path d), (4) a vibrationally excited triplet state formed after crossing from S_1 to T_1 (path e), or (5) a vibrationally excited ground state formed after crossing from T_1 to S_0. Molecules in state (5) are quite different from those in state (3), since "cooler" molecules are produced by crossing from T_1 than from S_1.

Of all the known photochemical reactions of dienes, only a few have been studied in sufficient detail that one can unequivocally assign the state in which reaction occurs. It will, nevertheless, be interesting to examine each type of reaction closely.

Photochemical reactions are generally brought about by direct irradiation and conjugated dienes are no exception. Theoretically, it is evident from the diagram that under such conditions reactions could take place in any one of the five states. However, from the study of cyclization of myrcene (this thesis), intersystem crossing of dienes appears to be an inefficient process; therefore, by direct irradiation, only states (1) and (3) are important. More recently, photosensitized reactions of dienes have attracted much attention (3, 4, 5). In these cases the initial excited species of diene is believed to be the triplet state (T_1) (3, 4); therefore, reaction can take place only in states (2) and (5). Since photosensitized reactions are of prime interest in this work and will be discussed in detail later, only results from direct irradiation will be reviewed in this section.

One of the better known and the most thoroughly studied reactions of conjugated dienes is formation of cyclobutenes. Windhaus et al. (5) first observed that pyrocalciferol and isopyrocalciferol isomerize upon irradiation to give photo-products of unknown structure. Dauben et al. (6) later were able to make definitive structural assignments of the photoproducts (reactions 1 and 2) and thus established the first examples of cyclobutene formation via irradiation.



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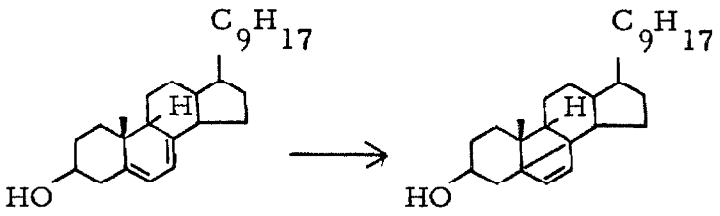

(2)

Numerous reports of such reactions have been published since. Representative are the works of Srinivasan, Crowley, and Dauben et al., who obtained corresponding cyclobutenes from simple dienes such as 1,3-butadiene (10), isoprene (8), 2,3-dimethylbutadiene (8,9), myrcene (9), 1,3-cycloheptadiene (11a), 1,3-cyclooctadiene (8), and dicyclohexenyl (9). In some instances, other minor products were also produced. Recently Dauben and Coates (11b) showed by an unambiguous degradation that photolevopimaric acid also contains the cyclobutene group.

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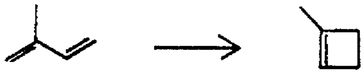

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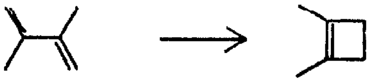

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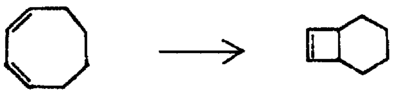

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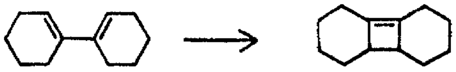

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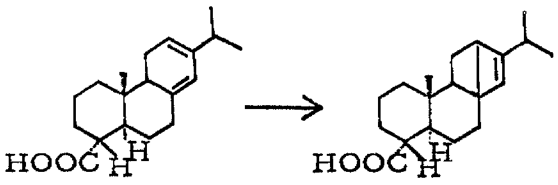
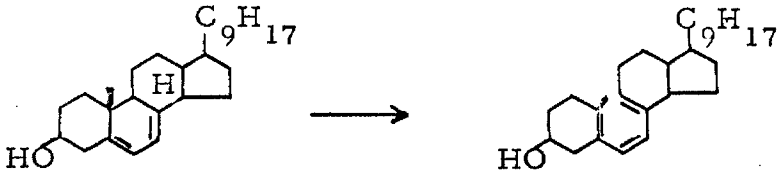


(10)

In the case of 2,3-dimethylbutadiene, reaction proceeds both in the vapor phase and in solution. In the vapor phase, it was shown that the quantum yield of the reaction is independent of oxygen and nitric oxide and the possibility of triplet intermediates is dismissed. Also noteworthy is the fact that yields increase with the pressure of inert gas in the system. This was taken as indication that formation of cyclobutenes involves singlet states of dienes to produce products in vibrationally excited ground states. The inert gas serves the purpose of stabilizing "hot" cyclobutenes by removing excess vibrational energy. By contrast, reactions 8 (12) and 9 (13) can also be sensitized. Obviously, under the latter experimental conditions, singlet states cannot be exclusively responsible for formation of cyclobutene.

Ergosterol and lumisterol, the 9,10-anti-analog of pyrocalciferol and isopyrocalciferol, behave differently upon irradiation (14). Instead of bond formation, bond cleavage occurs to give trienes.



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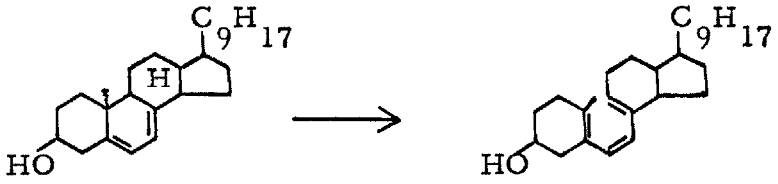
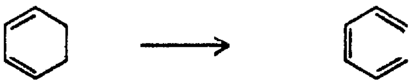


(12)

In general, compounds with the 1,3-cyclohexadiene structure appear to prefer the fission reaction rather than cyclobutene formation. Reports in the literature are numerous. Representative examples are the isomerization of 1,3-cyclohexadiene (15, 16), α-phellandrene (15), 5,6-dimethyl-1,3-cyclohexadiene (17), and palustric acid (11) (reactions 13-16).



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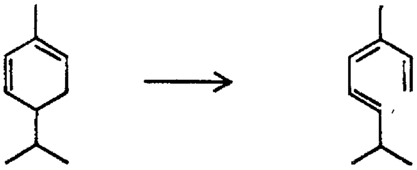

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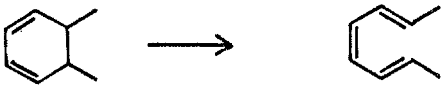

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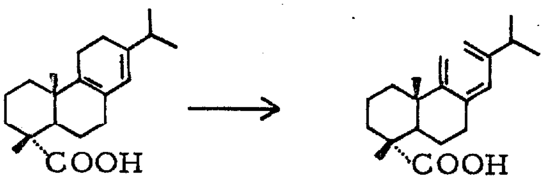


(16)

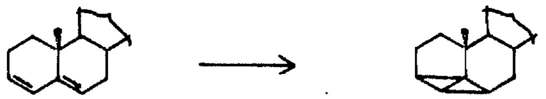
In the vapor phase, the efficiency of reaction (12) was shown to be independent of the pressure of inert gas introduced (18). Since singlet states are too short-lived to be quenched through collision, Srinivasan (18) interpreted the results to mean that the reactant and the product formed initially are in excited singlet states.

The factors controlling the course of reaction of 1,3-cyclohexadienes (valence isomerization or ring-opening) have been of interest to several research groups (19). It is agreed that ring-opening is the general reaction. Valence isomerization occurs only when the conformation of the ground state molecule is specially favored for bond formation between the end carbon atoms of the diene unit. It is interesting to note the result recently reported by Fonkon and Mehrotra (20) that irradiation of bicyclo[4, 4, 0]-1, 3-decadiene leads to two products (reaction 17). If both products are

(17)

indeed primary photoproducts, this would be the first example of simultaneous formation of cyclobutene and hexatriene products.

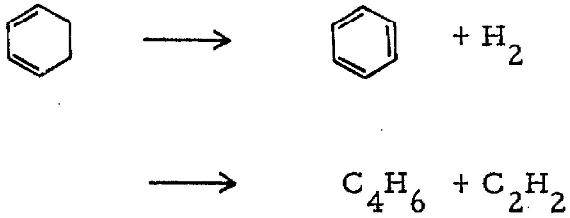
Formation of bicyclobutane is probably a general reaction of dienes constrained in transoid configuration(s). On irradiation of $\Delta^{3,5}$-cholestadiene, Dauben and Willey (21) isolated a monomeric, saturated hydrocarbon, which, they believe, has a structure containing the bicyclobutane moiety. Bicyclobutane has also been



(18)

isolated as a minor product on direct irradiation of butadiene in solution (10). Again, results of inert gas quenching experiments in the vapor phase led Srinivasan (10) to postulate that the formation of bicyclobutane arises from the singlet state of butadiene.

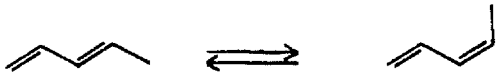
Dienes in their respective singlet states have been suggested as intermediates in all the reactions discussed above. Reaction in vibrationally excited ground states (state 3) is almost an unknown process in solution. In the vapor phase, "hot" molecules have been suggested as the reactive intermediates for reactions whose quantum yields decrease with increase of inert gas pressure, the function of which is to remove excess energy from the "hot" molecules. For dienes, as exemplified by 1,3-cyclohexadiene (18) and butadiene (22), fragmentation is the typical reaction under such conditions.



(19)

$$\begin{aligned} &\longrightarrow CH_2{=}C{=}CH{-}CH_3 \\ &\longrightarrow C_2H_4 + C_2H_2 \qquad (20) \\ &\longrightarrow CH_2{=}CH{-}C{\equiv}CH + H_2 \end{aligned}$$

Besides the reactions discussed above, dienes also participate in other photochemical reactions. Examples are: <u>cis-trans</u> isomerization of piperylenes (8), cycloaddition of butadiene (23), and hydrogen migration of 4-methyl-1,3-pentadiene (24). However, generality and mechanistic studies of these types of reactions are yet to be investigated.



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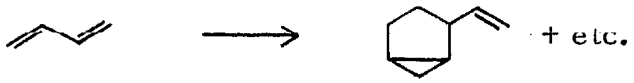

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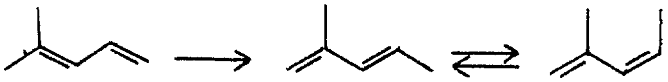
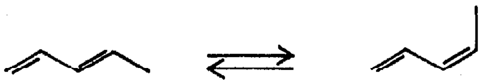


(23)

Since diene singlets do not cross efficiently to triplet states, studies of triplet state reactions of dienes generally involve indirect excitation of diene molecules by means of triplet excitation transfer from sensitizer to substrate. An ideal substrate for sensitized reactions is one having a large separation between excited singlet and triplet states so as to bracket the corresponding energy level of the sensitizer. If this requirement is satisfied, an appropriate filter system can insure that light will be absorbed exclusively by the sensitizer and thus exclude the possible complication of singlet state substrate reactions. Conjugated dienes with the two lowest excited states separated by more than 70 kcal/mole satisfy this condition.

At the time this work was initiated, several photosensitized reactions of conjugated dienes were reported in the literature. These include the sensitized isomerization of the piperylenes (3) and the sensitized dimerization of butadiene (4) and cyclopentadiene (5). The dimerization reactions are of particular interest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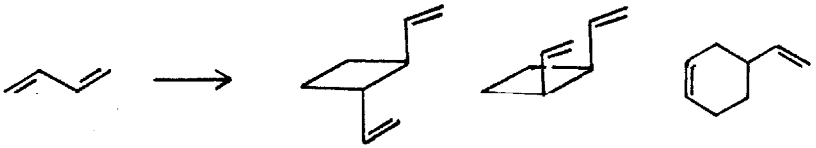
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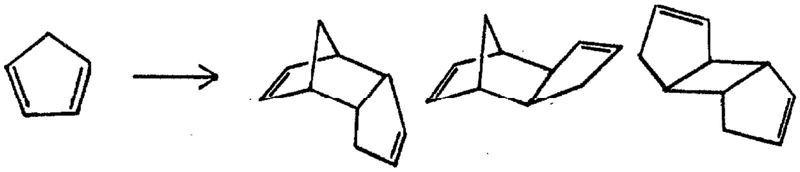

(25)

here. In the case of butadiene, the product composition is dependent upon the sensitizer employed (4) (Table I), but such dependence was not observed with cyclopentadiene (5). This work was started with the objective of seeking satisfactory explanations for these contrasting results.

Table I. Butadiene Dimer Compositions (4)

Sensitizer	trans	cis	cyclohexene
Benzil	49 %	8 %	43 %
2, 3-Pentanedione	44	12	42
Acetophenone	82	14	4
β -Acetonaphthone	76	17	7

A word must be said about the two mechanisms that have been proposed to explain photosensitized reactions. The first is the energy transfer mechanism (25), in which one believes that reaction of the substrate is preceded by a discrete step involving transfer of triplet energy from a donor (excited sensitizer) to the substrate. The necessary conditions for the triplet energy transfer process are: (1) the excess energy of the donor must be higher than the energy required for the transition (of whatever nature) in the acceptor, and (2) there must be actual contact between the donor and acceptor molecules.

The second mechanism was originally proposed by Schönberg (26) and is currently vehemently advocated by Schenck. This mechanism has recently been discussed in detail by Schenck and Steinmetz (27). The complete scheme is repeated here:

$$
\begin{array}{lcl}
\text{Sens} + h\nu & \rightarrow & \text{Sens}^1 \\
\text{Sens}^1 & \rightarrow & \text{Sens} + h\nu \\
\text{Sens}^1 & \rightarrow & \text{Sens}^3 \\
\text{Sens}^1 & \rightarrow & \text{Sens} \\
\text{Sens}^1 + \text{A} & \rightarrow & .\text{Sens-A}. \\
\text{Sens}^3 & \rightarrow & \text{Sens} + h\nu \\
\text{Sens}^3 + \text{A} & \rightarrow & .\text{Sens-A}. \\
.\text{Sens-A}. & \rightarrow & \text{Sens} + \text{A} \\
.\text{Sens-A}. + \text{B} & \rightarrow & \text{Sens} + \text{AB} \\
\text{Sens}^1 + \text{Q} & \rightarrow & \text{Sens} + \text{Q} \\
\text{Sens}^3 + \text{Q} & \rightarrow & \text{Sens} + \text{Q}
\end{array}
$$

In this mechanism the reactive species is a diradical with the sensitizer bonded to the substrate. According to Schenck, all sensitized reactions can be explained by this mechanism.

At the present moment, there is no evidence in the literature to establish unequivocally the mechanism of sensitized reactions. There are indications, however, that the energy transfer mechanism is the preferred one, and most reaction courses are more clearly visualized and can be more easily understood in terms of the energy transfer mechanism. The approach in the present discussion will center attention on the energy transfer mechanism. However, a discussion of "prejudice" against the Schenck mechanism will also be presented.

RESULTS

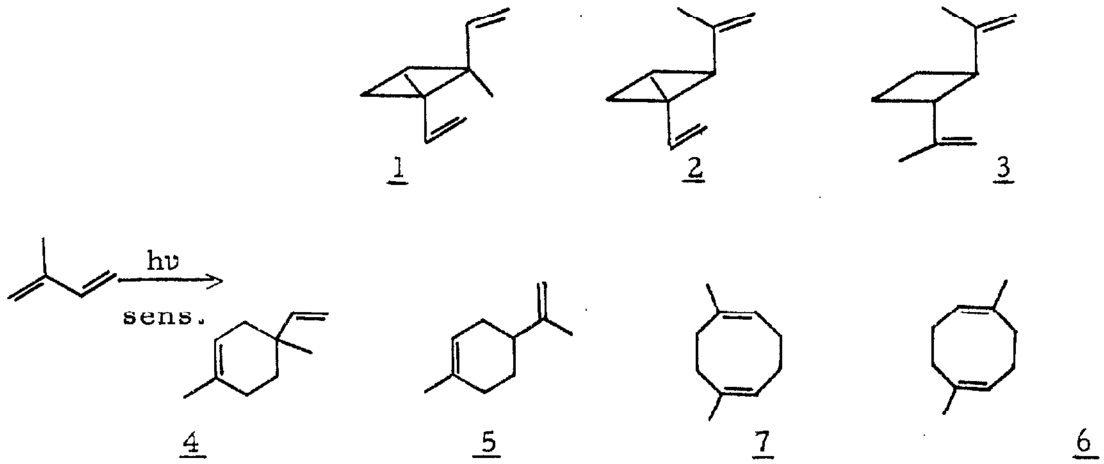
I. Separation and Identification of Dimers of Isoprene

Photosensitized dimerization of isoprene leads to formation of seven products, 1, 2, 3, 4, 5, 6, and 7. An eighth product may have been formed but never amounted to more than 1% of the mixture of dimers. Pure or nearly pure samples of the seven photodimers were obtained by preparative vapor chromatography. Structural assignments have been made, largely on the basis of n.m.r. spectra.

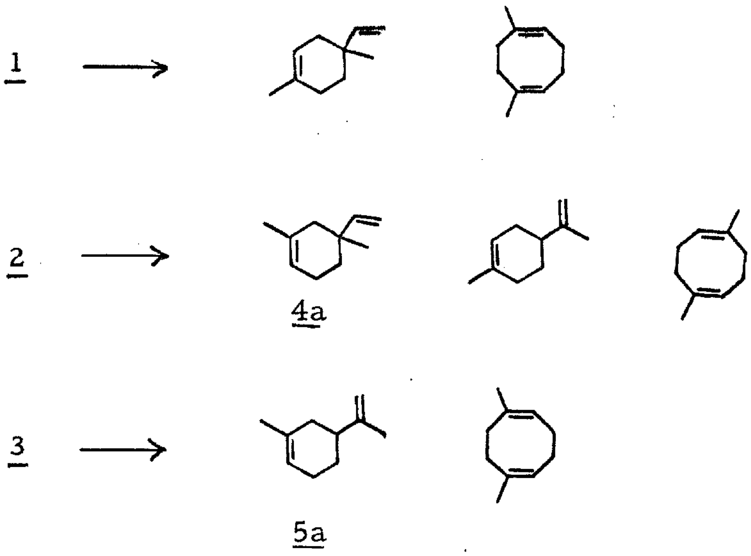
Eighteen cyclodimers of isoprene can be formulated. Structures may be grouped as twelve cyclobutanes, four cyclohexenes, and two cyclooctadienes. All of the cyclobutanes contain two terminal vinyl protons ($CH_2=C$) plus zero to two other vinyl protons. Each cyclohexene contains only one vinyl group, and one or two other vinyl protons. These key features, which are reflected in the n.m.r. spectra, together with the observed thermal rearrangements of the cyclobutane products, lead to rapid reduction of the problem of structural assignments.

Detailed description of the n.m.r. spectra, and other information which led to eventual assignment of structures have already been published (28). To avoid repetition, detailed argument will not be presented here, except that the final assignments will be summarized.

Among the seven photodimers, three possess the cyclobutane structure. They are *trans*-1,2-dimethyl-1,2-divinylcyclobutane, 1, *trans*-1-isopropenyl-2-methyl-2-vinylcyclobutane, 2, and *trans*-1,2-diisopropenylcyclobutane, 3. The two dimers with cyclohexene structures are 1,4-dimethyl-4-vinylcyclohexene, 4, and 1-methyl-4-isopropenylcyclohexene (dipentene, or limonene), 5. The remaining two are cyclooctadienes, 2,4-dimethyl-1,5-cyclooctadiene, 6, and 2,5-dimethyl-1,5-cyclooctadiene, 7.



The observed thermal rearrangements (29) of the cyclobutane dimers are:



Dimerization of isoprene was also studied by Trecker *et al.* (30) with benzil as sensitizer. Similarly, they reported formation of seven dimers. However, they failed to recognize the presence of diisopropenylcyclobutane in the product mixture, and instead reported to have isolated a mixture of dipentene and diprene, 5a.

No products of low boiling point could be detected in the product mixtures; therefore, compounds such as methylcyclobutene, methylbicyclobutane are not formed in the sensitized reactions.

II. Dependence of Product Composition upon Sensitizer

Thirty sensitizers in all were used to study their effects upon the distribution of isoprene dimers. The choice of sensitizers is such that their energies are evenly separated. Thirteen of them have triplet energies greater than 60 kcal/mole, eleven between 50 and 60 kcal/mole, and six less than 50 kcal/mole. Structures of these sensitizers are quite different, including 19 ketones, 3 aldehydes, 3 α-diketones, 4 aromatic hydrocarbons, and 1 halohydrocarbon.

All sensitizers give product mixtures containing the seven photodimers, although with varying amounts. Table II contains the complete results, where the dimer compositions are expressed as the sum of percentages of cyclobutane and cyclooctadiene dimers (denoted as Σ from here on). The reason for such a choice will become evident in the discussion section. Table III shows percentages of individual dimers of ten randomly chosen sensitizers.

Several other compounds were also used as sensitizers. Both _cis_ and _trans_ stilbenes formed an adduct with isoprene accompanied by very inefficient formation of isoprene dimers. Eosin is almost insoluble in isoprene. Solution of acridine in isoprene turned green after irradiation, and 1-amino-4-nitronaphthalene apparently initiated polymerization of isoprene upon irradiation. Both α- and β-naphthils are efficient sensitizers for the reactions, and the composition of dimers formed (Σ = 57, 58, respectively) agrees with the postulate that these sensitizers exist as an

Table II. Dependence of Composition of Isoprene Dimers on Sensitizer

	Sensitizers	E_T(kcal/mole)$^{(32)}$	Σ^*
1	cyclopropylphenylketone	74.7	92
2	propiophenone	74.6	93
3	acetophenone	73.6	92
4	1,3,5-triacetylbenzene	73.3	92
5	benzaldehyde	71.9	90
6	o-dibenzoylbenzene	68.7	92
7	benzophenone	68.5	93
8	thioxanthone	65.5	92
9	anthraquinone	62.4	91
10	flavone	62.0	90
11	Michler's ketone	61.0	91
12	2-acetylfluorene	60.8	91
13	acetylbiphenyl	60.6	90
14	β-naphthylphenylketone	59.6	81
15	β-naphthaldehyde	59.5	76
16	β-acetonaphthone	59.3	81
17	α-naphthylphenylketone	57.5	75
18	α-acetonaphthone	56.4	66
19	α-naphthaldehyde	56.3	60
20	biacetyl	54.9	52
21	2,3-pentanedione	54.7	49
22	benzil	53.7	45
23	9-fluorenone	53.3	43
24	1,2,5,6-dibenzanthracene	52.3	38
25	pyrene	48.7	36

Table II. (continued)

	Sensitizers	E_T(kcal/mole)(32)	Σ*
26	benzanthrone	47	35
27	3-acetylpyrene	45	51
28	9, 10-dimethyl-1, 2-dibenzanthracene	44.4	58
29	anthracene	42.5	87
30	9, 10-dibromoanthracene	40.2	94

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* Sum of percentages of 1, 2, 3, 6, and 7.

Table III. Selected Examples of Isoprene Dimer Composition

	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>, <u>7</u>
cyclopropyl-phenylketone	28.0	30.5	8.0	5.4	2.9	23.3
benzophenone	29.0	30.1	9.0	4.7	2.1	25.2
thioxanthone	28.6	26.0	8.0	5.2	3.2	28.9
flavone	26.2	28.3	5.8	7.8	3.9	28.1
β-acetonaphthone	26.3	27.2	9.3	14.5	4.5	18.2
α-acetonaphthone	19.6	19.5	8.7	27.0	7.7	17.4
9-fluorenone	12.7	11.7	4.6	42.5	14.6	14.1
pyrene	12.1	12.4	2.1	45.4	18.4	9.5
4-acetylpyrene	13.5	15.3	6.4	36.6	12.3	15.7
9,10-dibromo-anthracene	30.8	33.8	7.9	3.6	2.1	21.8

equilibrium mixture of stereoisomers which have different triplet energies (31). Azulene failed to sensitize the reaction.

III. Quantum Yield of Dimerization of Isoprene

In determination of quantum yield of the dimerization reaction, a method which requires neither an independent actinometer solution nor a monochromatic light source was adopted. This method involves determination of the yields of dimers after irradiation of solutions containing isoprene of varying concentration for the same period of time (33).

Quantum yield (Φ) of the reaction and concentration of diene are related in the way shown in equation 13 (for details, see Discussion section).

$$\frac{1}{\Phi} = \frac{1}{a} + \frac{1}{a}\frac{k_d}{k_r}\frac{1}{[D]} \qquad (13)$$

In equation 13, a represents efficiency of intersystem crossing of sensitizer, D is diene, and k_d, k_r are, respectively, constants of deactivation to the ground state and reaction to form dimers.

Putting

$$\Phi = \frac{\text{total dimers formed } (D_2)}{\text{total quanta absorbed } (T)}$$

one can rewrite equation 13:

$$\frac{T}{D_2} = \frac{1}{a} + \frac{1}{a}\,\frac{k_d}{k_r}\,\frac{1}{[D]}$$

or

$$\frac{1}{D_2} = \frac{1}{aT} + \frac{1}{aT}\,\frac{k_d}{k_r}\,\frac{1}{[D]}$$

The concentration of diene, [D], is known, and amounts of dimers, D_2, formed can be measured. From the value of the intercept of a plot of $\frac{1}{D_2}$ versus $\frac{1}{[D]}$, the total light quanta (T) absorbed by the samples can be calculated. Studies were made with three sensitizers, benzophenone (a = 1.00), β-acetonaphthone (a = 0.85), and fluorenone (a = 0.92) (32a). The results are listed in Table IV, and the plots shown on page 78 . In the case of benzophenone as sensitizer, total quanta absorbed were also calibrated with the benzophenone-benzhydrol actinometer. Results from both methods agreed reasonably well.

It is difficult to estimate the accuracy of the numbers determined by this method. The relative errors between the points within a run are probably small, and up to the accuracy of v.p.c. analysis. However, the absolute values of quantum yield may be less accurate because of the larger error involved in obtaining values of intercepts.

Table IV. Yields of Dimers by Varying Concentration of Isoprene

a. Benzophenone as sensitizer (0.1M)

Conc. of Isoprene [D] M	$\frac{1}{[D]}$	Dimer Yield D_2 (moles)	$\frac{1}{D_2}$
9.22	0.109	7.65×10^{-4}	1.31×10^{3}
6.25	0.160	5.86	1.71
3.91	0.259	4.09	2.44
3.12	0.320	3.42	2.92
2.92	0.340	3.26	3.07
2.81	0.356	3.14	3.18

Intercept = 4.95×10^{2}

T = 2.02×10^{-3} einstein

At 10M $1/D_2 = 1.25 \times 10^{3}$ $D_2 = 8.00 \times 10^{-4}$ moles

$\Phi = 0.40$

Total quanta (T) determined by benzophenone-benzhydrol actinometer = 2.39×10^{-3} einstein

b. β-Acetonaphthone as sensitizer (0.05M)

Conc. of Isoprene [D] M	$\frac{1}{[D]}$	Dimer Yield D_2 (moles)	$\frac{1}{D_2}$
8.99	0.111	2.07×10^{-3}	4.83×10^{2}
6.66	0.150	1.66	6.02
4.66	0.215	1.32	7.58
3.33	0.300	0.910	1.10×10^{3}
2.66	0.376	0.760	1.30

Intercept = 1.28×10^{2}

T = 9.1×10^{-3} einstein

At 10 M, $1/D_2 = 4.46 \times 10^{2}$ $D_2 = 2.24 \times 10^{-3}$ moles

$\Phi = 0.25$

Table IV. (continued)

c. Fluorenone (0.05M) as sensitizer

Conc. of Isoprene [D] M	$\frac{1}{[D]}$	Dimer Yield D_2 (moles)	$\frac{1}{D_2}$
8.99	0.111	4.63×10^{-3}	2.16×10^{2}
6.66	0.150	3.75×10^{-3}	2.66×10^{2}
4.66	0.215	2.82×10^{-3}	3.54×10^{2}
3.33	0.300	2.07×10^{-3}	4.83×10^{2}
2.66	0.376	1.74×10^{-3}	5.75×10^{2}

Intercept = 6.33 x 10

$T = 1.72\times10^{-2}$ einstein

At 10M $1/D_2 = 200$ $D_2 = 5.0 \times 10^{-3}$

$$\Phi = \frac{5.0 \times 10^{-3}}{1.72\times 10^{-2}} = 0.29$$

IV. Effect of Azulene on Dimerization of Isoprene

Azulene conveniently possesses a "window" in its absorption spectrum in the region 3550-4200 Å ($\epsilon < 50$) (34). Therefore, using light of wavelength in this region and with solutions of sufficiently high concentration of sensitizer relative to that of azulene, study of the effect of azulene upon the dimerization reaction without introducing the complication of internal filtering is possible.

With benzophenone as sensitizer, the study was carried out in two ways: first, with a constant concentration of azulene and varying amounts of isoprene; then, with a constant concentration of isoprene, but varying amounts of azulene. The highest concentration of azulene used was 1×10^{-2} M while the benzophenone concentration was 2×10^{-1} M. Under these experimental conditions and together with the use of a filter system which allows transmission of light near 3660 Å only, at most one per cent of light was absorbed by azulene. Results are listed in Tables V and VI. The plots are shown on pages 80, 81. When biacetyl was used as sensitizer, a uranium filter glass was used which permits transmission of light of wavelength above 3350 Å. Therefore, in these runs azulene absorbed part of the light, especially in the long wavelength region where the extinction coefficient is high. However, internal filtering should not affect dimer composition. Results are listed in

Table V. Quantum Yield (Φ) of Dimerization of Isoprene with Constant Concentration of Azulene (5×10^{-3}M)

[D]	Φ	$\frac{1}{[D]}$	$\frac{1}{\Phi}$
7.28	0.299	0.137	3.34
5.63	0.234	0.178	4.28
4.47	0.216	0.224	4.63
3.64	0.162	0.275	6.17
3.14	0.141	0.350	7.09
2.48	0.117	0.403	8.54
2.15	0.107	0.465	9.35

Sensitizer: benzophenone (0.1M)

Table VI. Quantum Yield (Φ) of Dimerization of Isoprene with Varying Concentrations of Azulene

[Az]M	Φ	$1/\Phi$
10×10^{-3}	0.206	4.86
7.6	0.230	4.34
5.2	0.249	4.01
2.6	0.289	3.46
1.1	0.289	3.36
0	0.326	3.07

Sensitizer: benzophenone (0.1M)

Concentration of isoprene = 6.86M

Table VII.

Solutions of isoprene (2M) and benzophenone in hexadecane (η = 3.34 cp.) were irradiated with or without azulene (5 x 10^{-3}M). Quantum yields of dimerization under these conditions are 0.121 and 0.098, respectively. Corresponding values with isopentane (η = 0.223 cp) as solvent are 0.122 and 0.101 (extrapolated from Figure IX).

V. Variation of Sensitizer Concentration and Isoprene Concentration

Effect of concentration of sensitizer on product composition was studied with several low-energy sensitizers. With the exception of biacetyl, the range of sensitizer concentration was rather small, generally limited by solubility of sensitizers. Results are tabulated in Table VIII. Table IX contains results of study of the effect of concentration of isoprene upon product composition. Apparently, there are no significant differences among the compositions of dimers.

VI. Physical Methods to Study Diene Triplets

Experiments designed to induce phosphorescence from dienes and to detect diene triplets by flash photolysis were performed. The results will be presented in connection with discussion on nature of diene triplets. Direct singlet-triplet absorption spectra of dienes were taken using solvents containing heavy atoms. The results agree with the values reported by Evans (2) and Kellogg (35) in their studies of singlet-triplet absorption enhanced by high pressure oxygen. It was found that solutions of

Table VII. Effect of Azulene on Dimer Composition

conc. of sensitizer = 0.100M

Sensitizer	[Az]M	Σ
benzophenone	5×10^{-3}	$95.6 \pm 0.7^{*}$
benzophenone	---	$92.6 \pm 0.4^{*}$
biacetyl	5×10^{-3}	$54.5 \pm 1.0^{**}$
biacetyl	---	$48.7 \pm 1.6^{**}$

* Average value of 8 samples

** Average value of 6 samples

Table VIII. Dimer Composition by Varying Concentration of Sensitizers

Sensitizer	Conc. (M)		Σ (%)
β-acetonaphthone	0.500		80
	0.125		80
	0.032		80
biacetyl	40%[*]		51
	20%		52
	5%		52
	0.100		
fluorenone	0.1500		43
	0.0375		41
	0.0075		42
pyrene	0.230		37
	0.086		36
	0.020		36
	0.010		36
benzanthrone	saturated[**]		35
	0.015		35
	0.0076		36
9,10-dibromoanthracene	0.0600		94.4[†]
			94.2
		Ave.	94.3
	0.0180		95.7
			96.0
			95.9
		Ave.	95.9

[*] Percentage by volume

[**] ~ 0.03 M

[†] Repeated analysis of the same sample.

Table IX. Dimer Composition by Varying Concentration of Isoprene

a. Benzophenone as sensitizer
conc. = 0.100M
solvent: isopentane

[D] M	Σ
7.28	92
5.63	92
4.47	92
3.64	93
3.14	93
2.48	92
2.15	93
1.98	93

b. Biacetyl as sensitizer
conc. = 0.100 M
solvent: benzene

[D] M	Σ
9.13	50
6.65	49
4.75	50
3.66	49

isoprene in ethyl iodide (1M) absorb weakly in the long wavelength region (λ_{max} = 4770, 4430, 4150 Å). Intensity of these absorptions increased by eight times when a four-to-one mixture of isoprene and methylene iodide was used. The singlet-triplet absorption of myrcene in ethyl iodide is structureless, and therefore not informative.

VII. Photosensitized Dimerization of Piperylenes, 2,3-Dimethylbutadiene, and Other Dienes

Piperylenes:-- Irradiation of commercial mixture of piperylenes (trans:cis ~3:1) in the presence of photosensitizers gives at least 15 products as shown by v.p.c. analysis. The composition of product mixtures again varies with choice of sensitizer. In the case of benzophenone or any other high-energy sensitizer, three products are predominant (8, 52%; 9, 22%; 10, 8% of total amounts of dimers). They were isolated by preparative v.p.c. method. The yields of these three dimers decrease when low-energy sensitizers are used. Therefore, by analogy to other dimerization reactions and from consideration of their n.m.r. spectra,* these compounds have been assigned with the following structures: trans-1,2-

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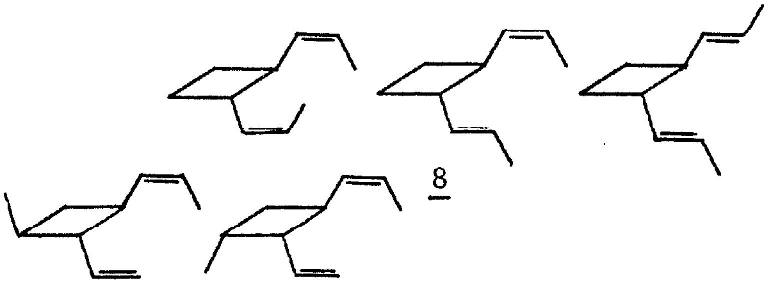
* Detailed description of the n.m.r. spectra has been published elsewhere (28).

dipropenylcyclobutane, 8; *trans*-1-methyl-3-propenyl-2-vinylcyclobutane, 9; and *trans*-1,2-dimethyl-3,4-divinylcyclobutane, 10. The extremely complicated structures of the n.m.r. spectra of these compounds indicate that the isolated fractions were probably mixtures of stereoisomers as shown in the drawings.



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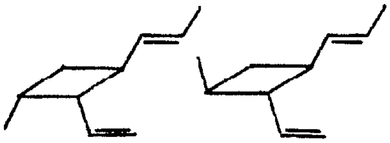

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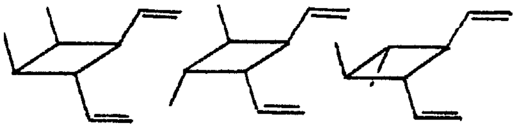

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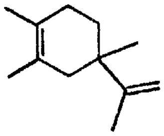
No attempts have been made to identify the other dimers.

2,3-Dimethylbutadiene

Irradiation of the diene with sensitizers leads to formation of dimers (11 - 17). Sufficient quantities of the four major products (12, 13, 15, 17) were isolated for spectral measurements, which provided information for preliminary structural assignments. Sensitizers of energy less than 60 kcal/mole give larger amounts of 15 in product mixtures, and lesser amounts of all other six dimers (Table X). Such variation immediately suggests that 15 is probably a cyclohexene derivative. The structure, 1,2,4-trimethyl-4-*iso*propenylcyclohexene, is the only possible structure of 2,3-dimethylbutadiene dimers containing cyclohexene rings. Indeed, the n.m.r. spectrum of 15 agreed with such structure. It consists of a multiplet centered at τ 5.13 (relative area 2.0), a broad band between τ 7.80-8.55 superimposed by two singlets at τ 8.16 and 8.33 (relative area 15.0), and a singlet at τ 8.95 (relative area 3.1). The n.m.r. spectrum of compound 17 consists of only two singlets centered at τ 7.67 and 8.35 of ratio 7.0 to 11.5. Obviously no vinyl protons are present in 17. However, its infrared spectrum shows weak absorption due to carbon-carbon



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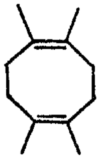
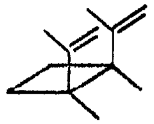


17

double bond (6.10 μ). Based on this information, compound 17 has been assigned the structure 1,2,5,6-tetramethyl-1,5-cyclooctadiene. The n.m.r. spectra of 12 and 13 both showed low-field to high-field proton ratio of ~ 1:4. By analogy with results of other diene systems, the following structures are tentatively assigned.

Table X. Composition of 2,3-Dimethylbutadiene Dimers (in percentages)

Sensitizer	11	12	13	14	15	16	17
acetophenone	2.4	15	36	4.5	27	5.0	9.3
benzophenone	2.5	16	36	3.0	27	5.1	9.0
β-acetonaphthone	2.9	16	34	4.6	35	3.0	5.7
biacetyl	0.9	8.1	20	3.6	59	2.1	6.8
pyrene	0.4	4.2	13	4.3	70	1.0	7.5



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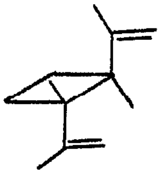


13

1, 2-Dimethylcyclobutene was not detected in product mixtures of these sensitized reactions.

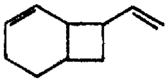
2, 5-Dimethyl-2, 4-hexadiene: No reaction could be detected (by v.p.c. and n.m.r. methods) after prolonged irradiation of the diene in the presence of benzophenone.

3-Methylenecyclohexene: 3-Methylenecyclohexene prepared by the procedure of Bailey (35) was irradiated with photosensitizers. Product mixtures contain at least three dimers as shown by v.p.c. The products seem to be quite unstable. So far they have not been isolated successfully.

VIII. Photosensitized Cycloaddition of Mixed Dienes

Photosensitized cross addition of mixed dienes has been studied. The system investigated in most detail is the butadiene-1,3-cyclohexadiene system. Irradiation of a mixture of the two dienes in the presence of sensitizer gives in addition to the corresponding dimers of the two dienes three new products (18, 19, 20) in the ratio 43: 6: 1. The two major components have been isolated by preparative v.p.c. method.

The n.m.r. spectrum of 18 shows low-field signals in the region of τ 3.9-5.4 of relative area 5.00, and high-field signals in the region of τ 7.0-8.9 of relative area 8.92. 7-Vinylbicyclo-[4.2.0]-5-octene, a, and 5-vinylbicyclo[2.2.2]-2-octene, b, are the only two structures of cross adducts between butadiene and cyclohexadiene with proton ratio 5 to 9. Compound 18 cannot be a bicyclo[2.2.2]octene because its n.m.r. spectrum does not have the low-field signals of two protons in the region τ 3.5-4.0, where signals of vinyl protons in bicyclo[2.2.2]octenes are generally observed* (e.g. in the parent compound, such absorption appears as a multiplet centered at τ 3.8). By elimination, 18 probably has the gross structure of a. The n.m.r. spectrum of 19 shows signals between τ 3.9-5.3 and 6.6-8.8. of relative area 5.00 and 8.82. For the same reason, 19 probably has the gross structure of a.



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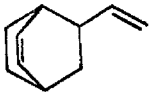

b

Both compounds 18 and 19 undergo facile thermal rearrangement. Rearrangement of 19 at 120° leads to formation of one new

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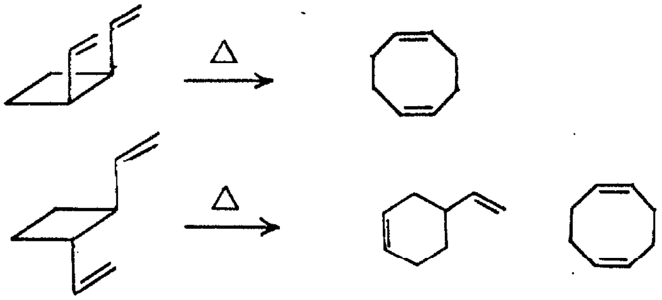
* Such correlation was first observed by D. Valentine.

compound, while rearrangement of *18* gives three new products, one of which is identical with the thermal product from *19*. Activation parameters of these rearrangements have been measured by C. DeBoer (41) (Table XI). Distribution of products and activation parameters of these rearrangements are reminiscent of those observed for the 1,2-divinylcyclobutanes. In the latter cases, it

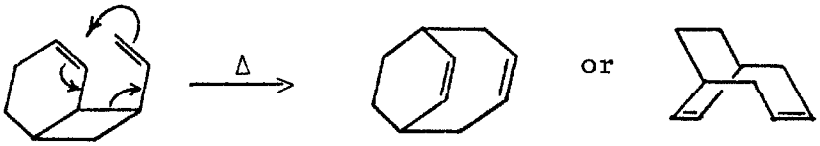


was reported that the *cis*-isomer rearranges solely to 1,5-cyclooctadiene; while the *trans*-isomer gives 4-vinylcyclohexene in addition to the cyclooctadiene. Activation parameters of these reactions were also reported (29) (Table XI). The difference in entropy of activation of rearrangement of the two divinylcyclobutanes was attributed by Hammond and DeBoer (29) to the difference in mechanisms in operation. They believe that *cis*-divinylcyclobutane rearranges in a concerted manner, while the *trans*-isomer proceeds through a less rigid diradical intermediate. By analogy, one would expect that in *19* the substituents at 1 and 8 positions are *cis* to each other, and in 18, *trans*; and compound *19*

Table XI. Activation Parameters of Thermal Rearrangements of Four Compounds. (41)(29)

Compound	ΔH^{*} (kcal/mole)	ΔS^{*} e.u.
18	34.5	- 1.8
19	27.7	- 6.5
cis-1,2-divinyl-cyclobutane	23.1	-11.7
trans-1,2-divinyl-cyclobutane	34.0	- 1.2

rearranges by way of a concerted mechanism giving a product with the structure bicyclo[4.2.2]-3,7-decadiene, 21. Indeed, the n.m.r. spectrum of the thermal product derived from 19 agrees with this structure. Therefore, the rearrangement of 19 can be formulated as follows.*



19

21

The three thermal products derived from 18 are formed in the ratio 45:40:15. Hydrogenation of the major product gives *cis*-decalin exclusively; therefore, it probably has the structure *cis*-bicyclo-[4.4.0]-2,8-decadiene, 22. Its n.m.r. spectrum agrees with the assignment. The second most abundant material is identical with 21, by comparison of v.p.c. retention time and n.m.r. spectrum with the product from thermal rearrangement of 19. The minor product probably is 5-vinylbicyclo[2.2.2]octene, 23, because its n.m.r. spectrum shows a band of complicated structure (2 protons) between τ 3.5-4.0, a region characteristic of signals of vinyl protons in bicyclo[2.2.2]octenes (*vide supra*) in addition to signals of

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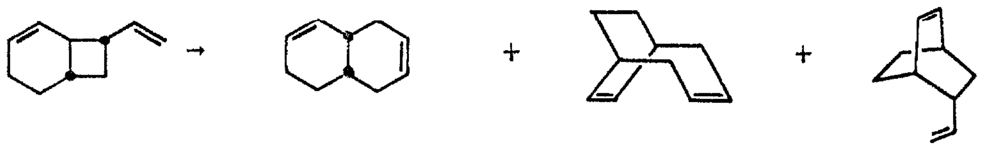
* Information at hand is not sufficient for speculation of stereochemistry of the ring junction in 19.

three vinyl protons at slightly higher field. The structure of 18* and its rearrangement can be formulated as follows.



18 22 21 23

The third product was not isolated.

Product distribution of cross adducts has been examined by varying relative amounts of dienes, and by employing sensitizers of different triplet excitation energies (benzophenone, biacetyl, and fluorenone). Formation of cross adducts is generally accompanied by simultaneous formation of dimers. Only when the concentration of one diene is much lower than the other (for butadiene, less than 1/20 of cyclohexadiene; for cyclohexadiene, less than 1/50 of butadiene), then the corresponding dimers are not observed.(41a).

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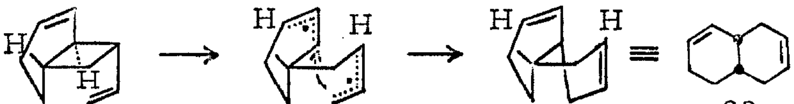
[*] Assignment of trans ring junction in 18 is an attempt to incorporate the result of exclusive formation of 22 with no trans isomer. This result can be rationalized by assuming that minimum movement of the allyl radical in the intermediate is a requirement in closure of the diradical from trans ring fused 18. Under similar conditions, the cis ring fused compound might be expected to lead to the trans isomer of 22.



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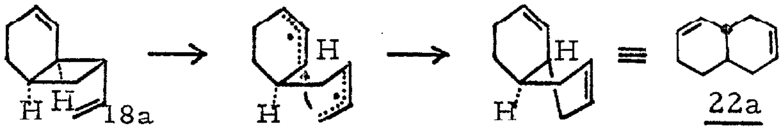

22a

Relative yields of the three cross adducts remain the same under most conditions (Table XII). However, with solution of concentration of cyclohexadiene less than 1 per cent of butadiene and with fluorenone as sensitizer, a new product, X, is formed as shown by v.p.c.[*] The yield of the new product relative to other cross adducts increases as the amount of cyclohexadiene is further decreased. Unfortunately, this compound was formed in too small quantities for isolation.

Other diene mixtures were studied only in preliminary forms. In the case of mixtures of 1,3-cyclohexadiene and 3-methylenecyclohexene, at least one cross adduct was formed; and butadiene 3-methylenecyclohexene mixture gave at least four cross adducts on irradiation. These products have not been isolated.

IX. Photosensitized Intermolecular Addition of Diene Triplet to Olefin

A number of cross additions of diene triplets to olefins were carried out with very limited success. No cross adducts were obtained when solutions containing cyclopentadiene, isoprene, or 1,3-cyclohexadiene and sensitizer in olefins such as cyclohexene,

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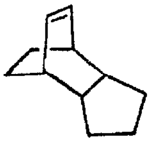
[*] Another new product might have been formed; but the amount formed is less than one-fourth of X.

Table XII. Distribution of Cross Products of Butadiene and 1,3-Cyclohexadiene (Solvent: benzene)

Sensitizers	Dienes (%)		Products (%)		
	C_4H_6	C_6H_8	<u>18</u>+<u>19</u>	<u>20</u>	<u>X</u>
acetophenone	36	4	98	2	-
	20	20	98	2	-
benzophenone	90	10	97	3	-
	50	50	98	2	-
	99	1	98	2	-
biacetyl	36	4	98	2	-
	20	20	98	2	-
fluorenone	95	5	98	2	-
	99	1	98	2	~0.3
	99.5	0.5	97	2	~1

norbornene, and 1, 5-hexadiene were irradiated with light only absorbed by the sensitizer. However, irradiation of a solution of 15:1 cyclopentene–1, 3-cyclohexadiene mixture containing 0.02M β-acetonaphthone led to formation of three new compounds in addition to the photodimers of cyclohexadiene. The new compounds were formed in the ratio 4:2:1. The major component was isolated by v.p.c. in sufficient amount to permit measurement of its n.m.r. and infrared spectra. A mixture of the major product and the second most abundant material was also isolated. Features of the spectra* of the mixture are similar to that of pure material, and hydrogenation of the mixture gave a single product having v.p.c. retention time identical with that of the product from hydrogenation of the major product. Consequently, it is believed that the compounds are the two stereoisomers of tricyclo[5. 2. 2. $0^{2,6}$]-8-undecene, 24. The minor component has not been isolated in sufficient amount for identification.



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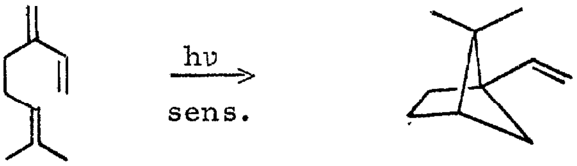
* Details of the n.m.r. spectra have been published (37).

X. Photosensitized Intramolecular Addition of Diene Triplet to Olefin

A much more promising situation was encountered when intramolecular cycloaddition of a diene unit to a double bond was attempted. Myrcene, containing the two necessary function groups and being readily available, was the first compound studied.

Irradiation of a 2 per cent solution of myrcene in n-hexane or benzene containing benzophenone, β-acetonaphthone, or fluorenone leads to formation of a single product with a quantum yield of 0.05 in the case of benzophenone (37). For reasons outlined below, the product is believed to be 5,5-dimethyl-1-vinylbicyclo[2.1.1]hexane, 25.



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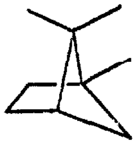
The photoproduct is easily isolated and purified by fractional distillation through spinning band column, or by preparative v.p.c. The structure is clearly indicated by the n.m.r. spectrum. The low-field signals are multiplets of ABC pattern characteristic of vinyl groups (relative area 3.0). Two strong, unsplit signals at τ 8.86 and 9.25 have relative areas of 3.1 and 2.9. The signals obviously belong to two isolated methyl groups and have chemical shifts virtually identical with those of the corresponding methyl groups in 26 (τ 8.89 and 9.30). A doublet with total area 1.1 is centered at τ 9.03 with a coupling constant of 0.8 cps. This signal is probably the most definitive of the spectrum. Structures 25 and 27 are the only products of internal cycloaddition which would have



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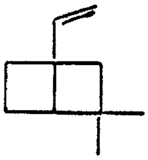
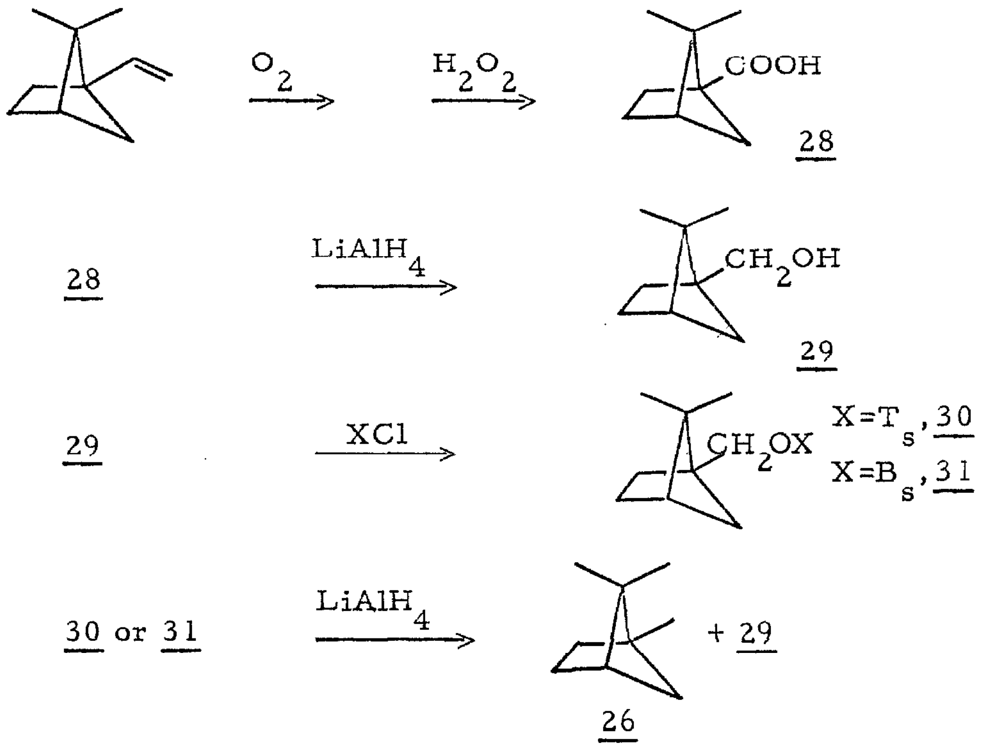


27

intact vinyl groups. There is no precedent for the expectation that any of the single protons of 27 would absorb at very high field. On the other hand, the spectra of bicyclo[2.1.1]hexane (38) and its derivatives (39) have high field signals (τ 9.13 in the parent compounds and 9.11 in 26 (39)) attributed to the *endo* protons on methylene bridges. A slightly distorted A_2B_2 group (relative area 2.0) centered at τ 7.69 must include the *exo*-methylene and bridgehead protons.

The assignment was confirmed by degradation of the photoproduct to known compound. Ozonization of the photoproduct followed by oxidative work-up gave a solid of low melting point, the n.m.r. spectrum of which agrees with the structure 28. The acid, 28, was reduced by lithium aluminum hydride to give another low melting solid with strong camphor-like odor. Its n.m.r. spectrum agrees with the structure 29. From the alcohol, 29, both the tosylate, 30, and brosylate, 31, were prepared. Reaction of 30 or 31 with lithium aluminum hydride followed by hydrolysis gave a a product mixture of two compounds in 5: 1 ratio. The minor product is identical with the alcohol, 29. The n.m.r. spectrum of the major product is identical with the reported spectrum of 26 (39).



The hydrocarbon 25, on heating, reverts to myrcene. Activation energy of this rearrangement is 35 kcal/mole (40).

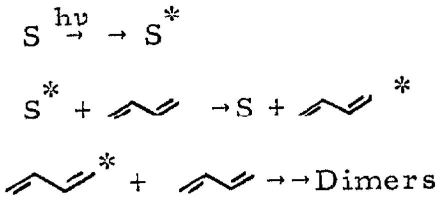
Several attempts were made to generalize such reaction. The hydrocarbon, 2-phenyl-1,4-pentadiene,was synthesized.

However, irradiation of this compound with or without sensitizer did not give any new product as shown by n. m. r. Preliminary results on irradiation of 3-methyl-1,4,6-heptatriene with sensitizer show that besides a rapid reaction, possibly the *cis-trans* isomerization, three new products are formed at a slower rate. These have not been isolated and characterized.

DISCUSSION

The mechanisms of all the photosensitized reactions studied in this work have many points in common. In the following discussion the mechanism of the dimerization reaction will be considered in detail. For other cycloaddition reactions, only points characteristic of the reactions will be mentioned.

In their discussion of the mechanism of photosensitized dimerization of butadiene and cyclopentadiene, Hammond and Turro (4, 5) proposed the following simple scheme, where asterisks represent triplet states.



The three equations of the scheme represent, in the language of the energy transfer mechanism, the three essential steps of a photosensitized reaction. These include excitation of sensitizer followed by intersystem crossing to the triplet state, energy transfer from the excited sensitizer to substrate, and reaction of the excited substrate. However, it is obvious, as recognized by Hammond and Turro, that without further modifications, this scheme fails to account for the observed variation of butadiene dimer composition when different sensitizers were used.

Results of the present study show that such variation also occurs in isoprene, 2,3-dimethylbutadiene, and piperylenes (42). Isoprene has been used as the model system for conjugated dienes and has been studied in most detail. It is believed that not only can a successful explanation for the variation of dimer composition now be offered, but also as a result of this work, the mechanism of the sensitized dimerization reaction, the energy transfer process, and the nature of the diene triplets are better understood. Furthermore, perhaps as a bonus, the present study has opened synthetic routes to compounds which would otherwise be difficult to prepare.

Nature of the Diene Triplets and Mechanism of Energy Transfer

Results show that the variation of composition of the seven dimers of isoprene follows the pattern that any change which increases the yield of 1, also increases the yields of 2, 3, 6, and 7, and decreases the yields of 4 and 5, the two derivatives of cyclohexene. Apparently the variation involves two parameters; i.e., there is one precursor which reacts to give predominantly cyclobutanes and cyclooctadienes and another which reacts to give relatively large amounts of cyclohexenes. The pattern of variation is shown in Figure II, in which the percentages of the total yield represented by the sum of yields of 1, 2, 3, 6, and 7 is plotted against the S_0-T_1 excitation energies of the sensitizers. Sensitizers having relatively high triplet energies all give the same results; those having excitation energies of 60 kcal/mole or less give a variety of results. A minimum shows up near 50 kcal. With sensitizers of energies less than 50 kcal, more cyclobutanes and cyclooctadienes are again formed, resulting in a rise on the left side of the curve. This behavior is reminiscent of that observed in the studies of photosensitized cis-trans isomerization of unsaturated compounds (43). In the latter cases, the results have been partially explained by the assumption that the substrate system can undergo two or more transitions. It is not immediately obvious that a similar explanation applies to dienes such as butadiene and isoprene. However, reflection shows that there should be two transitions originating from the s-trans and s-cis forms of the dienes. Furthermore, the lowest excited states of the dienes should have large barriers to rotation about the central bonds. The last conclusion follows from the fact that excitation involves promotion of an electron from an orbital which is antibonding between carbon atoms 2 and 3 to an orbital which is bonding between those centers (44). It was reported by Evans (2) that the longest wave-

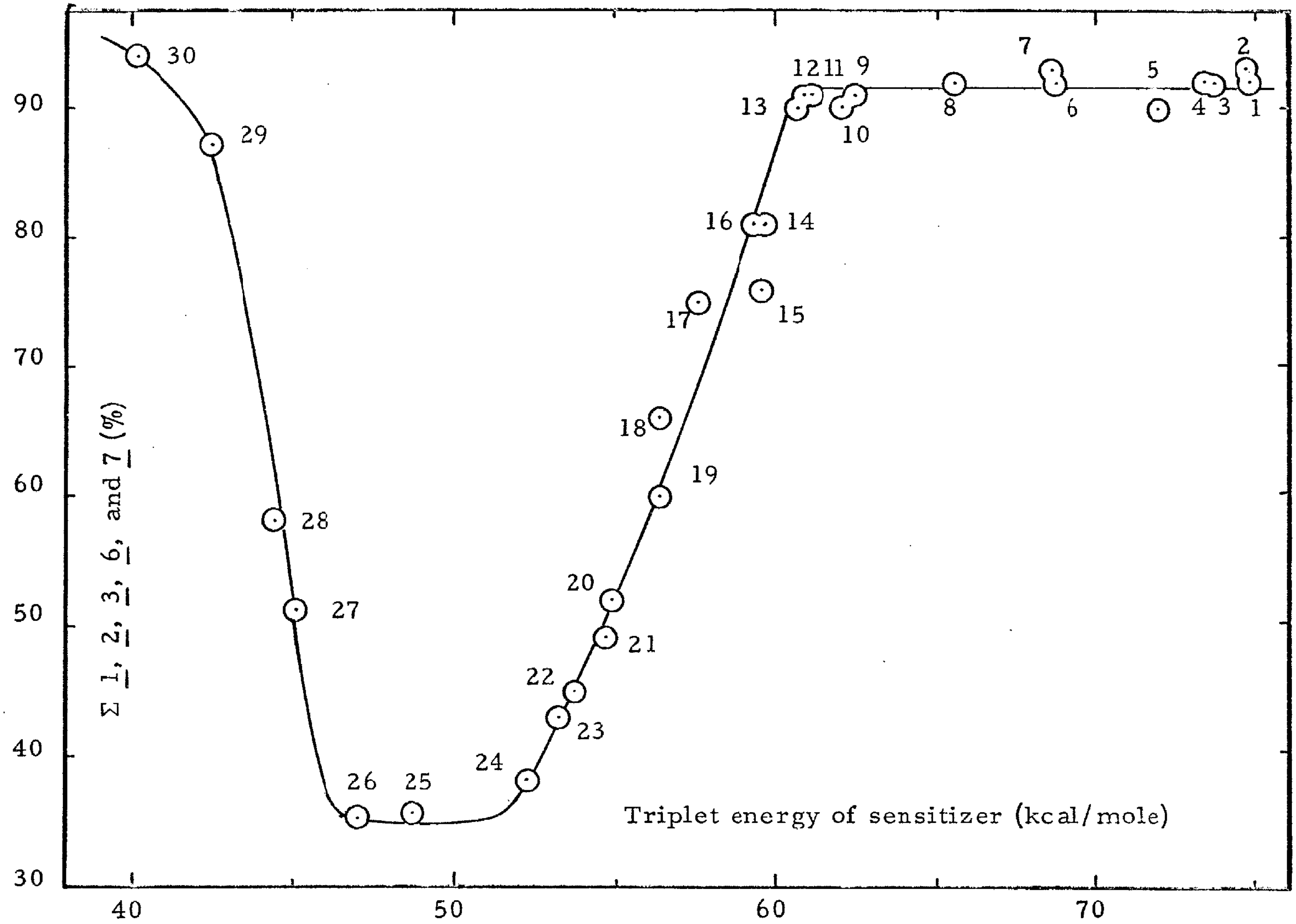


Figure II. Isoprene dimer composition vs triplet energy of sensitizer length absorption observable in butadiene and isoprene occurs at 20,830 cm^{-1} (59.6 kcal/mole) and 21,000 cm^{-1} (60.0 kcal), respectively, and these bands were assigned to the S_0-T_1 transitions. These transitions undoubtedly arise from light absorption by molecules in trans configurations. The corresponding transition of 1,3-cyclohexadiene occurs at 18,350 cm^{-1} (52.5 kcal).* This lower value of transition energy is probably typical of cis-1,3-dienes. The data of Figure II are consistent with the assumption that high energy sensitizers (>60 kcal) transfer their triplet excitation indiscriminately to the dienes at rates comparable to the rate of collision of molecules in solution. Since in the ground state isoprene is predominantly in the transoid configuration (45), a correspondingly excess number of trans-triplets are produced which in turn react with isoprene to give cyclobutanes and cyclooctadienes. When the energy of the sensitizer falls below 60 kcal, transfer to produce trans-triplets becomes inefficient, and relatively large amounts of cis-triplets are produced, thus giving larger quantities of cyclohexenes on reaction with isoprene.

With sensitizers of energies lower than 50 kcal, energy cannot be transferred efficiently to either isomeric form of the diene. A severe drop in the rate of reaction would be expected,

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* A value of 53.5 was originally reported by Evans. This number is a redetermined value by Kellogg (35).

and eventually, with sensitizers of sufficiently low energies (5-6 kcal "endothermic"), energy transfer to the diene molecules might be expected to be so inefficient that for practical purposes the reaction could no longer be sensitized. This does not agree with our experimental results completely. The reaction proceeds even with sensitizers of energy as low as ∼40 kcal, although at a somewhat reduced rate; furthermore, the dimer composition again becomes rich in cyclobutanes and cyclooctadienes as indicated on the left side of the curve. A mere consideration of excitation energies of isoprene isomers to their respective spectroscopic triplets is insufficient to account for these observations. Additional explanation must be offered to explain the apparent "endothermic" sensitized reaction, or more appropriately the apparent "endothermic" transfer of triplet excitation to the dienes.

"Endothermic" energy transfer is not entirely a new observation. Sandros and Bäckström (46), in their study of quenching of biacetyl phosphorescence, noticed that compounds with triplet energies as much as 6 kcal higher than that of the donor can still quench biacetyl phosphorescence albeit with reduced efficiency. Their results are reproduced in Figure III. The solid line marks the triplet energy of biacetyl. Points to the right of the line correspond to compounds with higher triplet energies than the donor;

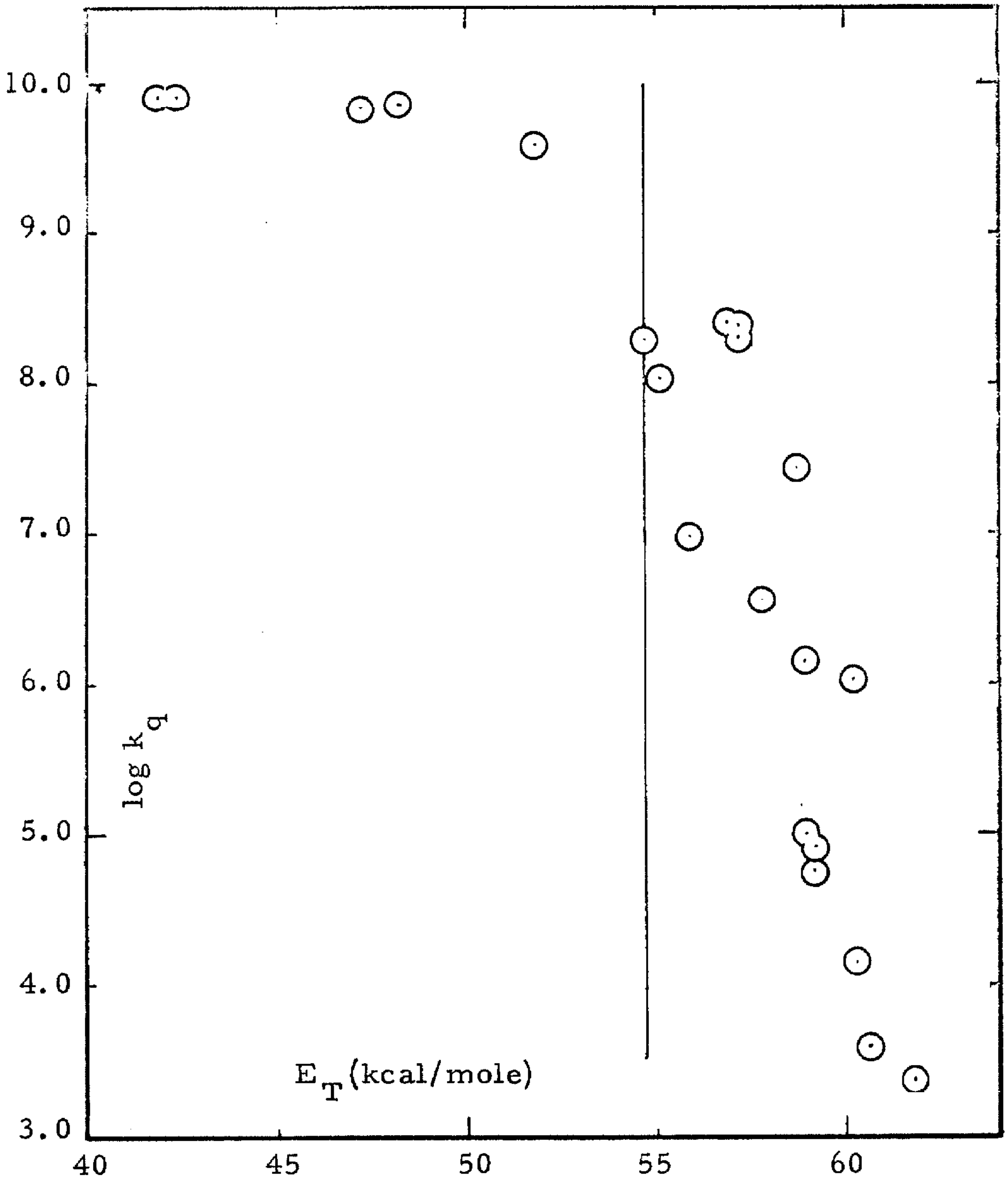

Fig. III. Rates of quenching of biacetyl triplet (k_q) vs. triplet energies (E_T) of quenchers.

thus, for these cases, the quenching process is "endothermic." Quenching rates apparently drop sharply in this region. Since the quenching process cannot be attributed to reactions involving biacetyl triplets and these carefully chosen inert quenchers, they believe that, similar to low-energy quenchers (points on the left side of the line), physical processes of energy transfer are responsible for the quenching, except that under such circumstances the acceptors are being excited from higher vibrational levels of the ground state. In all cases, they believe, the coupled transitions of donors and acceptors obey the Franck-Condon principle. Such a mechanism of "endothermic" energy transfer is not, however, applicable to the diene systems. Particularly, it fails to account for the fact that sensitizers of energy as low as 40 kcal (e.g. 9,10-dibromoanthracene) can still sensitize the reaction. To be consistent with the dimer composition, such sensitizers would have to excite transoid diene molecules with 20 kcal per mole of vibrational energy more efficiently than to excite cisoid molecules with 10 kcal of vibrational energy. It is absurd first to suspect the possibility of having such hot molecules at room temperature, and then to hope that trans triplets can be formed more efficiently with such energy differences. However, the possibility of "endothermic" energy transfer processes with energies of donor and acceptor closely matched is not excluded.

During the course of this work, "endothermic" sensitized reactions were also observed in many systems in these laboratories. Such a process has been studied in exhaustive detail in the stilbene system by J. Saltiel (47,48). Photosensitizers with energies lower than that required for spectroscopic transitions of the stilbene isomers were found capable of initiating the isomerization reaction. Data on the photostationary compositions demand a low-energy excitation path which was described as excitation of cis-stilbene molecule in its ground state directly to the trans-triplet (or some form resembling it) (48). Obviously, such an excitation process does not obey the Franck-Condon principle. The term "non-vertical" excitation has been used for processes as such. Figure IV describes this process together with relative energy levels of the ground state stilbenes and their respective spectroscopic triplets. Reflection on relative energy levels of the cisoid and transoid forms of diene* and their respective

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*Various approaches have been used to estimate distribution of transoid and cisoid butadiene at room temperature. Results obtained do not agree exactly although all works suggest that cisoid diene is present only in minor quantity. Temperature dependence study of infrared spectrum of butadiene vapor indicates transoid diene is more stable by 1.7±0.5 kcal/mole (49). Chemical method using the assumption of retention of configuration of allyl radical gives values of 93-97% of transoid diene at room temperature (50). Raman spectroscopy study indicates presence of minor amount of cisoid diene (51); while micro-wave (52) and electron diffraction (53) techniques failed to detect cis-diene. Calculation by Aston and Szasz arrived at the result of trans-butadiene being more stable by 2.3 kcal/mole (54). There were no similar detailed studies on spectroscopic triplets points out immediately (see Fig. V) that such

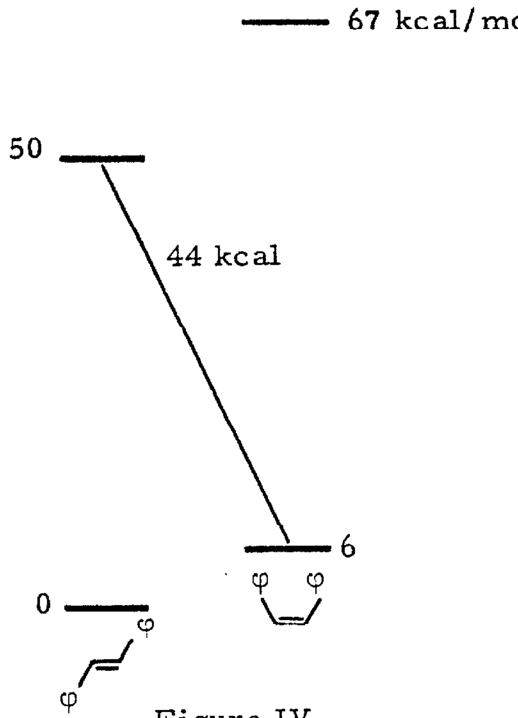

Figure IV

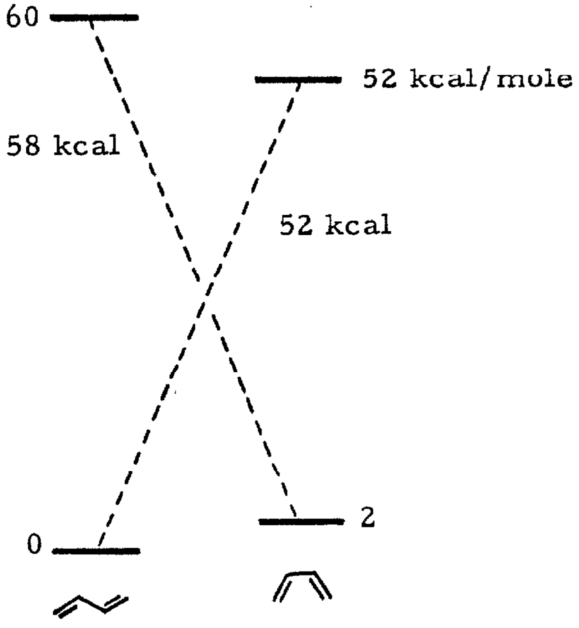

Figure V

"non-vertical" excitation is not energetically feasible in the diene system, although not excluding "non-vertical" excitation of a different nature.

It is well known that for molecules whose equilibrium nuclear positions in the excited state are considerably different from that of the ground state, the 0-0 transition, or even a transition to higher vibronic levels, is often too weak to be observed because of limitations ascribed to the Franck-Condon principle. The acyclic dienes

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isoprene. The only related work is the infrared measurement at room temperature giving the result that trans-isoprene is predominant at room temperature (45). The value used here (2 kcal) is a reasonable estimated value.

can hardly be considered as rigid molecules. This, plus the fact that singlet-triplet transition is itself a highly forbidden process, gives reason to suspect that the observed absorption by Evans (2) and others (35) is due to transitions to higher vibronic levels with the 0-0 component much too weak to be seen. Our results, particularly from the experiment with biacetyl as sensitizer, strongly support this suspicion. The 0-0 phosphorescence band of biacetyl is at 5210 Å (32), with a corresponding triplet energy 54.9 kcal. This value is conveniently between the spectroscopic triplet state energies of the isomeric dienes. Biacetyl was found to be an efficient sensitizer giving product mixture containing 52% of cyclobutane and cyclooctadiene dimers. Table VIII shows that this composition is <u>independent</u> of the concentration of biacetyl used. If the 0-0 separation between the <u>trans</u>-triplet and its ground state were 60 kcal, it is expected that <u>trans</u>-triplets of isoprene will transfer excitation reversibly to unexcited biacetyl molecules at a much faster rate than the corresponding process from the <u>cis</u>-triplets, the latter being energetically unfavorable. Consequently, in solutions containing high concentrations of biacetyl, fewer <u>trans</u>-triplets would survive to undergo dimerization; the product mixture therefrom should contain less cyclobutanes and cycloctadienes than in a solution of low biacetyl concentration. Obviously, this is not in agreement with the experimental results.

The biacetyl result and other results obtained in this work can be consistently explained by assuming the absorption of 60 kcal corresponds to excitation to high vibrational levels of the triplet state, and the 0-0 energy difference is significantly lower. For reasons to be clarified, it is asserted here that the 0-0 transition in transoid isoprene is at least 20 kcal lower than the assigned value of 60 kcal, and in cisoid isoprene ~ 13 kcal lower than the value assigned for 1,3-cyclohexadiene (52.5 kcal), taken as typical for a cis-1,3-diene. Furthermore, it is proposed that the low-energy path of forming diene triplet is the direct excitation of ground state isomeric molecules to lower or even to the lowest vibrational level of the corresponding triplets. Such an excitation process is also "non-vertical." One rule will be imposed on this process, which is in agreement with the present knowledge of rates of energy transfer, that its rate is slower than those when the Franck-Condon principle is not violated. All excitation paths and relative energy levels are described in Figure VI in the form of idealized potential curves. Solid lines are transitions which obey the Franck-Condon principle, and should, in principle, include excitation of diene molecules at excited vibrational levels as well as the zero vibrational level. Dotted lines represent excitations which do not obey the Franck-Condon principle.*

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* Present results cannot exclude a non-vertical process of exciting, e.g., cisoid diene to lower vibrational level of trans-triplet. However, there are no obvious advantages to introducing processes as such.

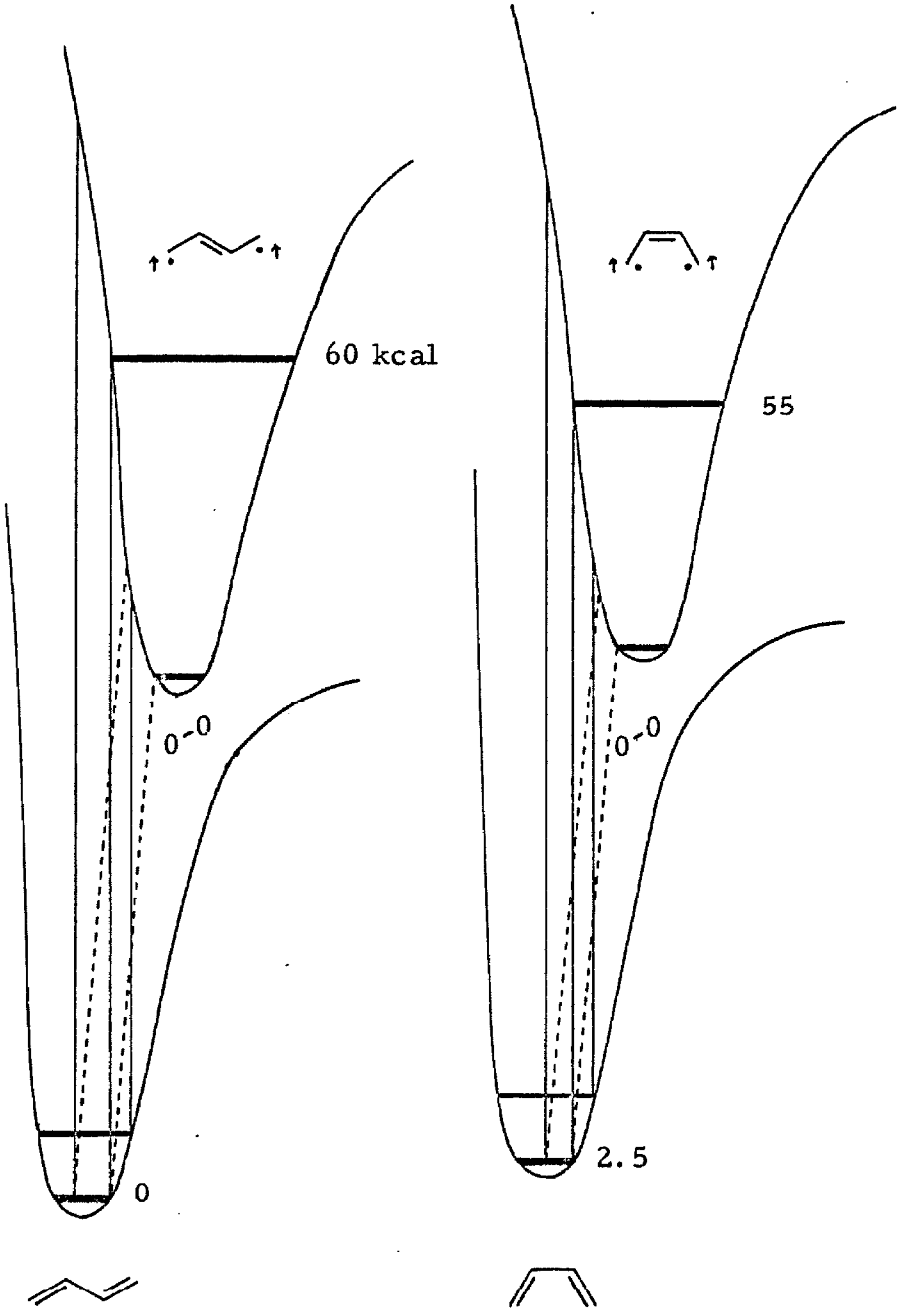


Fig. VI. Energy diagram of butadiene

——— , vertical excitation

. . . . , non-vertical excitation

The estimation of the 0-0 transition energy of the trans-triplet being lower than 40 kcal is demanded by the result that 9, 10-dibromoanthracene (E_T = 40.2 kcal) can sensitize the reaction, giving almost exclusively products produced by the trans-triplets. The presence of cyclohexene dimers, coupled with the apparent difference of dimer compositions of 9, 10-dibromoanthracene and anthracene, its closest neighbor, indicates that cis-triplets are still produced, but rather inefficiently. It is interesting to note the results of studies of the effect of sensitizer concentration upon dimer composition (Table VII). In most cases, variation of concentration of sensitizer showed no influence upon dimer composition (e.g., β-acetonaphthone, biacetyl, pyrene, benzanthrone); however, the results of 9, 10-dibromoanthracene seem to indicate increase of cyclobutane and cyclooctadiene dimer yields when a higher concentration of sensitizer was used. Such variation is reminiscent of results of photosensitized isomerization of stilbenes (43, 47), that for low-energy sensitizers photostationary compositions depend upon the concentration as well as the energy of the sensitizers. This result is also what would be expected for the biacetyl experiment, had the 0-0 component of singlet-triplet absorption of isomeric dienes had values as high as reported by Evans (2). A plausible explanation for this observed variation is that cis-triplets, and not the trans, can transfer triplet excitation reversibly to ground state 9,10-dibromoanthracene molecules. Such an explanation immediately suggests that the 0-0 component of the S_0-T_1 transition of cisoid isoprene has a value close to 40 kcal/mole, and that of transoid is lower. It will be interesting to see whether sensitizers with even lower triplet energies can produce a product mixture void of cyclohexene dimers.

In an attempt to obtain direct information concerning the 0-0 transition energies of dienes and the properties of the triplets, several experiments were carried out to detect diene triplets. Phosphorescence spectra normally provide direct information in regard to position of the 0-0 component in singlet-triplet absorption. However, not a single case of diene has been reported to phosphoresce. This, among other possible reasons, may only reflect inefficiency of intersystem crossing in dienes. Attempts, therefore, were made to induce phosphorescence of isoprene by populating the triplet state via energy transfer from benzophenone triplets. Failure to detect any emission provides no useful information except that radiationless deactivation of diene triplets to the respective ground states is probably a fast process. Similar negative results were obtained in flash photolysis studies. Employing a flash-photoelectric apparatus, no triplet-triplet absorption from either isoprene or benzophenone was detected from 4000 to 6000 Å.

Isoprene was present in sufficient amount to quench rapidly all benzophenone triplets. Failure to observe absorption by diene triplets may be due to short lifetimes of the triplets (a minimum lifetime of 10 μsec is required for detection of triplet-triplet absorption on the above flash apparatus). The result is also interpretable if diene triplets only absorb in the ultraviolet region or if the extinction coefficients in the visible are small. Both of these experiments actually proved only one trivial point, i.e., benzophenone triplets were quenched by diene molecules.

It remains to examine possible structures of diene triplets in their equilibrium position, to see whether the assumption that vertical excitation leads to "hot" triplet is justified. Because of redistribution of electron density following excitation, the equilibrium carbon-carbon bond distances in an excited molecule will very likely be different from those in a ground state molecule. However, on this ground alone, one would not expect vertical excitation to lead to triplets with high vibrational energy as required by the experimental results. The positions of the nuclei at equilibrium in the excited state must be quite different from those of the ground state so that absorption may lead to "hot" triplets. Perhaps the best noted example that a molecule has a vastly different nuclear geometry in the excited state is ethylene (55). In its ground state, the most stable structure is with the methylene groups lying in the same plane to ensure maximum overlap of the π electrons; but in the excited state (singlet or triplet state), the most stable structure is one with the methylene groups perpendicular to each other, thus minimizing repulsion between the unpaired electrons. Excitation by absorption leads to high-vibrational (tortional) levels of the excited state. According to calculation, the perpendicular and the planar triplets of ethylene have an energy difference of as much as 110 kcal/mole (55). Electronic repulsion should also be important in determining nuclei configurations of dienes in excited states; but here the effect of this contribution is obscured because of the complication of resonance energy. Among possible structures of diene triplets, the two that are believed most probable are consistent with information about diene triplets obtained from photochemical studies. One is with both methylene groups perpendicular to the plane formed by the π electrons of C_2-C_3 carbon atoms (Fig. VIIa). In such a structure, the two unpaired electrons are essentially localized at the end methylene groups. With the two electrons far apart, electronic repulsion energy should be at a minimum; however, this gain is accompanied by a loss of resonance energy. The second possibility is one with only one end methylene in the perpendicular position, and the remaining end

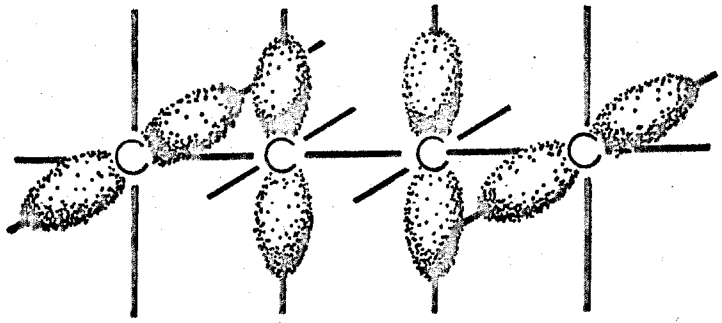


Figure VIIa

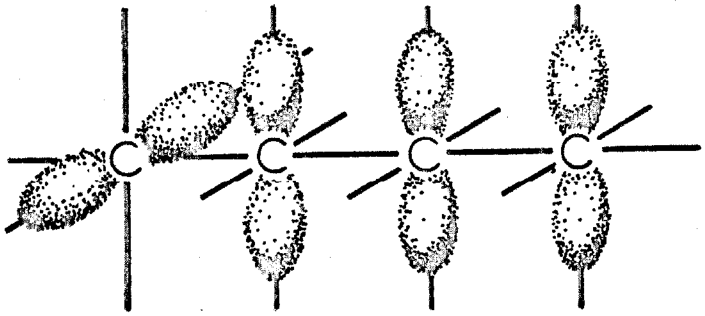


Figure VIIb

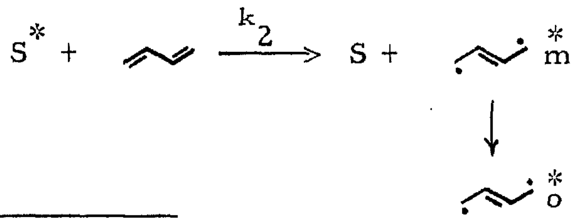
methylene group lying in the same plane as the π electrons of the central carbon atoms, thus to form an allyl radical (Fig. VIIb). Greater repulsive energy is expected for such a structure; however, the allyl radical should provide resonance stabilization. Due to lack of knowledge of the relative importance of the contributions of these two factors, one cannot indicate a preference between the two structures. It is pertinent to mention that both of these structures can readily account for the observation of cis-trans isomerization of piperylenes when irradiated in the presence of photosensitizers (3).

A word must be said about the apparent inconsistency between the results of Sandros and Bäckström (44) and those reported here concerning the rates of triplet energy transfer when the energy of the donor is slightly greater or equal to that of the acceptor. According to the results and interpretation presented here, the rate of energy transfer should be the same for donor-acceptor pairs of equal energies or for pairs with the donor of slightly higher energy, and both equal to the rate of collision. Results of Sandros and Bäckström seem to suggest that the donor must have at least ~3 kcal excess energy to ensure maximum rate of energy transfer. The difference can be rationalized by consideration of the difference in structure of acceptors involved in these studies. All the quenchers used by Sandros and Bäckström are rigid molecules whose 0-0 transitions are well defined by their phosphorescence spectra. With such quenchers, it is conceivable, as clearly demonstrated by these authors in one case, to have reversible energy transfer from the excited quencher molecule to ground state sensitizer. Values of the observed quenching constants should then be smaller than the actual values. The data reported by them were not corrected for the reversible process. In the case of dienes, because of rapid deactivation to lower vibrational levels, reversible energy transfer from diene triplets is not possible. Since the reversible energy transfer process is important only when the energies of the donor and acceptor are closely matched, only in this region is the "inconsistency" noticed.

Scheme of the Photosensitized Dimerization of Conjugated Dienes

The complete scheme of the photosensitized dimerization with incorporation of the discussed background knowledge and postulates regarding stereoisomeric diene triplets, nature of the "non-vertical" excitation processes, and relative rates of energy transfer from sensitizers of varying triplet energies to dienes will now be presented. It is necessary to describe the reaction by a minimum of eleven steps.[*]

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



(2)

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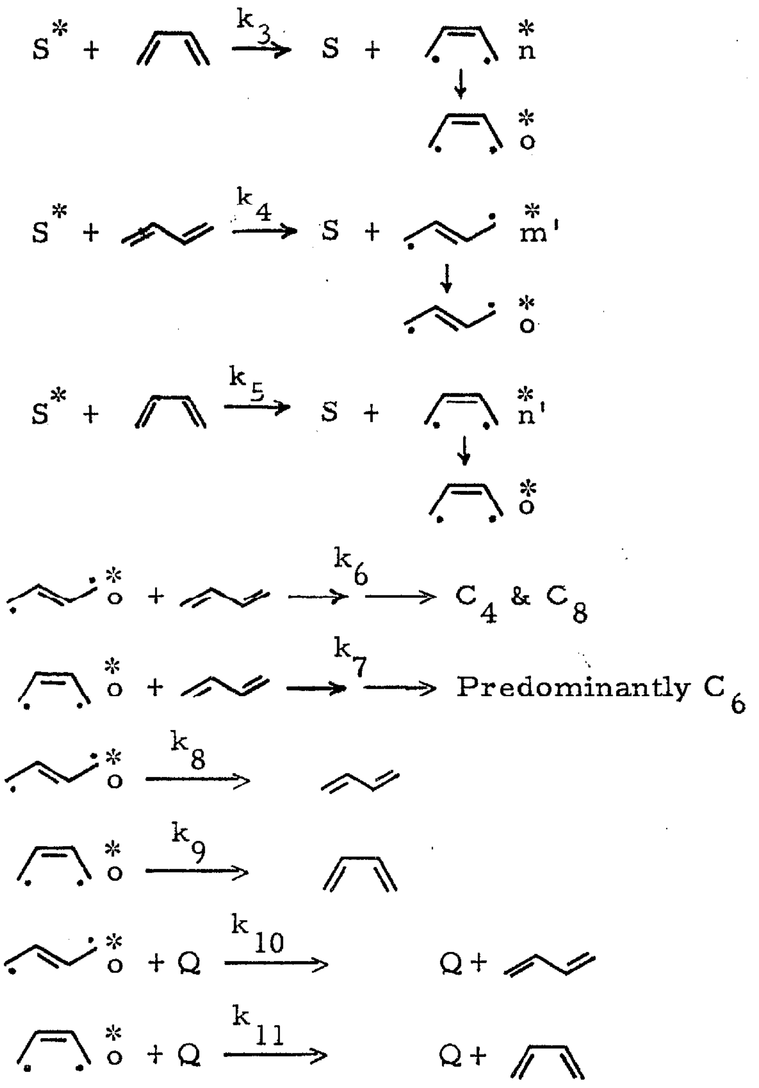
[*] A cyclic diene would be a special case in this scheme where sequences 2, 4, 6, 8, and 10 (or 3, 5, 7, 9, and 11 as the case may be) do not appear. In the case of dienes such as the piperylenes, the scheme will be more complex because of four possible transitions:

Such complication is reflected in the study of photosensitized isomerization of the dienes (3).



(3)

(4)

(5)

(6)

(7)

(8)

(9)

(10)

(11)

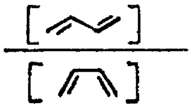
The same as the simple scheme postulated by Hammond and Turro, equation 1 is a short notation showing excitation of sensitizer by absorption followed by intersystem crossing to its triplet state, S^*. The energy transfer step is now represented by four equations, (2) - (5), with emphasis on the difference of excitation from the s-trans and s-cis forms of the diene. All excitations lead originally to vibrationally excited triplets (denoted by subscripts, m, n, etc.), but are accompanied by subsequent rapid loss of vibrational energy. Consequently, only triplets in the lowest vibrational levels (denoted by the subscript o) participate in the subsequent reactions. To avoid complication in the following derivation, steps (2) and (4), as well as (3) and (5) shall be distinguished in such a way that steps (2) and (3) only involve excitation of molecules in the zero vibrational level in accord with the Franck-Condon principle, whereas steps (4) and (5) include vertical excitation of vibrationally excited molecules as well as all "non-vertical" excitation processes. In this way, only one substrate is involved in each of the steps in (2) and (3), and the rate constant should be equal to the rate of collision regardless of the nature of the sensitizer.

Following this scheme, it can be shown that the ratio of the relative rates of formation of cyclobutane (C_4) and cyclooctadiene (C_8) dimers to cyclohexene dimers (C_6) can be expressed by equation 12 (see Appendix for the derivation).

$$\frac{\text{Rate } (C_4+C_8)}{\text{Rate } (C_6)} = K\,\frac{(k_2+k_4)}{(k_3+k_5)} \qquad (12)$$

K is the ratio of probabilities of forming cyclobutanes and cyclooctadienes to that of cyclohexenes in solutions of equal concentrations of the two isomeric triplets. It is essentially a constant in all cases (see below). Both k_2 and k_3 are equal to the rate of collision and by definition are independent of the nature of sensitizer. Rate constants k_4 and k_5 are dependent upon sensitizer. However, for a specific sensitizer under consideration, all quantities in (12) are constants; therefore, the ratio is independent of the concentration of the sensitizer and in agreement with the results of the biacetyl experiment. Clearly, the ratio also should not depend upon the concentration of diene. This is verified experimentally (Table IX).[*] Equation 12 also readily accounts for the variation of dimer composition when different sensitizers are used. For sensitizers having sufficiently high energy to allow vertical excitation (and $k_2 >> k_4$, $k_3 >> k_5$), expression 12 can be simplified to the form:

$$\frac{\text{Rate }(C_4+C_8)}{\text{Rate }(C_6)} \simeq K$$



At constant temperature, the relative amounts of transoid and

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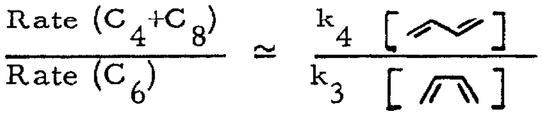
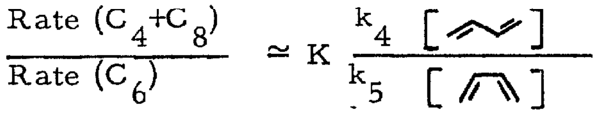
[*] This result also dismisses an alternative explanation for the variation of product mixture by assuming different sensitizers would produce diene triplets possessing varying vibrational energy, which on reaction with diene molecules would give corresponding dimer compositions. Lowering the concentration of diene, however, should allow the "hot" triplets to cool off before reaction.

cisoid isoprene are always the same; therefore, the dimer composition should be independent of the nature of the sensitizer as verified by experimental results (Fig. II). With sensitizers of energy between 50 and 60 kcal, process 2 becomes energetically impossible. Expression 12 becomes:



$$\frac{\text{Rate }(C_4+C_8)}{\text{Rate }(C_6)} \simeq \frac{k_4\,[\quad]}{k_3\,[\quad]}$$

Since k_4 is dependent upon sensitizer, the dimer composition is expected to vary accordingly. This is verified experimentally, and the good monotonic correlation of dimer composition versus triplet energy of sensitizer as shown in Figure II suggests that the dependence is such that k_4 is proportional to E_T of sensitizers. With sensitizers of energy less than 50 kcal, process 3 also becomes energetically impossible, and the ratio now becomes:



$$\frac{\text{Rate }(C_4+C_8)}{\text{Rate }(C_6)} \simeq K\,\frac{k_4\,[\quad]}{k_5\,[\quad]}$$

Since both k_4 and k_5 are dependent upon the energy of sensitizer, and since there is no way to estimate the dependence of the two constants upon the energy of a sensitizer, it is difficult to predict from the expression the direction of change of dimer composition in this energy region. However, the monotonic relation suggests that k_4 and k_5 are proportional to sensitizer triplet energy; the fact that low-energy sensitizers again give dimer mixtures rich in cyclobutanes and cyclooctadienes indicates that k_5 decreases more rapidly than k_4 upon decrease of sensitizer energy. With sensitizers of energy less than the 0-0 transitions of both isomeric triplets, one would expect the reaction not to be sensitized. Experimentally, this was tested with one compound, namely, azulene ($E_T \sim 30$-39 kcal).* Indeed, no dimers were formed even after long periods of irradiation. This result, unfortunately, cannot be interpreted without ambiguity because failure to sensitize the reaction can also be due to inefficiency of intersystem crossing of azulene.

The effect of quenchers (reactions 10 and 11) has not been considered and will be postponed until the next section because the importance of these processes is most clearly exhibited in quantum yield studies.

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* This value is determined from the fact that azulene quenches anthracene triplets ($E_T = 42.5$ kcal) at a diffusion-controlled rate but has no measurable effect upon those of naphthacene ($E_T = 29.3$ kcal) (56).

Quantum Yield and Mechanism of the Addition Step of the Dimerization Reaction

In the previous section, it was assumed that the addition step of the dimerization reaction involves a diene triplet adding to another diene molecule in the ground state. Although this assumption appears reasonable, experimental results are needed to exclude other possible mechanisms, in particular those involving two triplets. It has been observed that quantum yields of the reaction are dependent upon concentration of diene. Such dependence is not expected for a mechanism involving two triplets, but is consistent with the assumed mechanism.

In consideration of quantum yields of the reaction, only the total dimer yield is of interest. Therefore, in this section no effort will be made to distinguish the products of the two isomeric triplets and to simplify the scheme only one form of diene triplet will be considered.* The complete scheme of the reaction now takes the simple form:**

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* There is reason to believe that the reactivity of the two isomeric diene triplets is very much the same. That the dimer composition is independent of diene concentration demands a K with a similar independence. To be consistent with the definition of K (Appendix), $k_6=k_7$, and $k_8=k_9$; i.e., the reactivity and lifetimes of the isomeric triplets must be the same. Under such circumstances, $K=(2-p)/p$.

** The step $S^* \xrightarrow{k_{d'}} S$ is justifiably omitted here and also in the complete reaction scheme, because under experimental conditions $k_t[S^*][D]$ is always much greater than $k_{d'}[S^*]$.

$$S \xrightarrow{h\nu} \longrightarrow S^*$$

$$S^* + D \xrightarrow{k_t} S + D^*$$

$$D^* + D \longrightarrow \xrightarrow{k_r} D_2$$

$$D^* \xrightarrow{k_d} D$$

In the presence of a quencher, this step must be added:

$$D^* + Q \xrightarrow{k_q} D + Q$$

In the above steps, D represents diene and D_2 represents all the dimers.

The quantum yield of dimer formation in the absence of quencher is

$$\Phi = \frac{a\,k_r\,[D^*]\,[D]}{k_r[D^*]\,[D] + k_d[D^*]}$$

where a is the efficiency factor of intersystem crossing in the sensitizer. Alternately,

$$\frac{1}{\Phi} = \frac{1}{a} + \frac{1}{a}\,\frac{k_d}{k_r}\,\frac{1}{[D]} \qquad (13)$$

In the case of dimerization involving two triplets, the reaction step is replaced by:

$$D^* + D^* \xrightarrow{k_r} D_2$$

Following a similar procedure, one obtains:

$$\frac{1}{\Phi} = \frac{1}{a} + \frac{1}{a}\,\frac{k_d}{k_r}\,\frac{1}{[D^*]} \qquad (14)$$

Assumption of steady-state concentration of D^* gives

$$k_r[D^*]^2 + k_d\,[D^*] = I \times a$$

where I is the intensity of the light source. Solving for D^* explicitly, one obtains

$$[D^*] = \frac{-k_d + \sqrt{k_d^{\,2} + 4\,a\,I\,k_r}}{2\,k_r} \,.$$

Expression 14 can now be rewritten as

$$\frac{1}{\Phi} = \frac{1}{a} + \frac{1}{a}\,\frac{2}{\left(-1 + \sqrt{1 + 4\,a\,I\,k_r/k_d^{\,2}}\right)} \qquad (15)$$

A distinct difference between expressions 13 and 15 is that in expression 13, $\frac{1}{\Phi}$ is directly proportional to $\frac{1}{[D]}$, while in expression 15, $\frac{1}{\Phi}$ is not dependent upon the concentration of diene. This difference offers an easy experimental approach to ascertain the mechanism of the reaction.

As discussed previously, expression 13, and similarly expression 15, can be written as below:

$$\frac{1}{D_2} = \frac{1}{aT} + \frac{1}{aT}\,\frac{k_d}{k_r}\,\frac{1}{[D]} \qquad (16)$$

$$\frac{1}{D_2} = \frac{1}{aT} + \frac{1}{aT}\,\frac{2}{(-1 + \sqrt{1 + 4a\,I\,k_r/k_d^2})} \qquad (17)$$

The term D_2, to be consistent in units, is the total number of moles of dimers formed during irradiation, and T is the number of einsteins of light quanta absorbed by each sample. Results of the study with three sensitizers are plotted in Figure VIII. The dependence of dimer yield upon the concentration of isoprene is clearly shown; therefore, the mechanism involving two triplets can safely be discarded.

In the presence of a quencher, the quantum yield of dimerization is equal to:

$$\Phi = \frac{a\,k_r\,[D^*]\,[D]}{k_r[D^*][D] + k_d[D^*] + k_q[D^*][Q]} \qquad (18)$$

and, by inversion of terms,

$$\frac{1}{\Phi} = \frac{1}{a} + \frac{k_d}{a\,k_r}\,\frac{1}{[D]} + \frac{k_q}{a\,k_r}\,\frac{[Q]}{[D]}\ . \qquad (19)$$

Experimentally, this expression has been verified in two ways. First, with a constant concentration of quencher and varying concentration of isoprene, a plot of $\frac{1}{\Phi}$ versus $\frac{1}{[D]}$ gave a straight

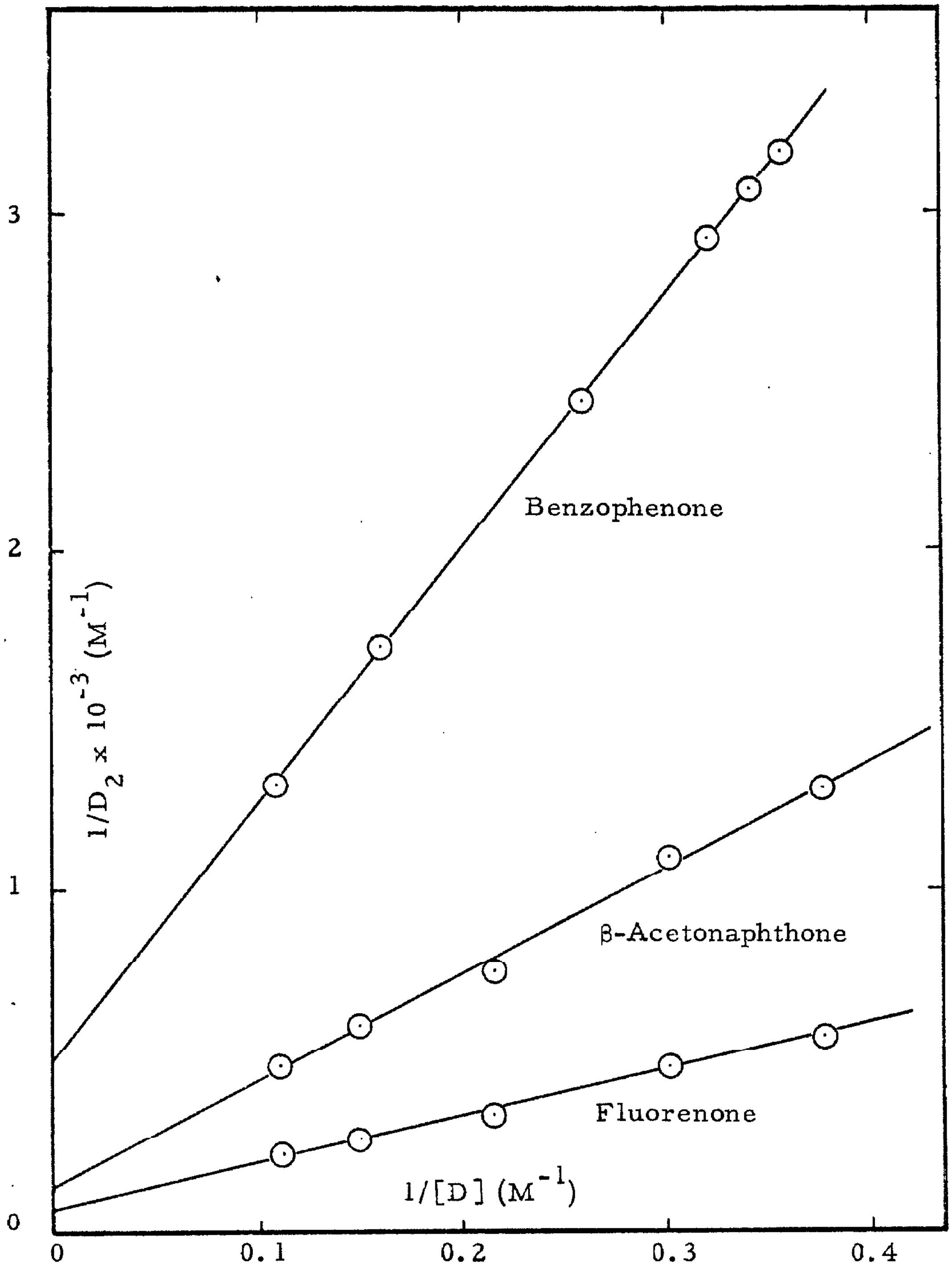

Figure VIII. Yield of dimers (D_2) with varying concentrations of isoprene line (Fig. IX); second, with a constant concentration of diene, and varying amounts of quencher, a plot of $\frac{1}{\Phi}$ versus $[Q]$ again gave a straight line (Fig. X). The quencher used in both experiments was azulene and the sensitizer was benzophenone.*

Values of k_d/k_r and k_q/k_r can be obtained from slopes and intercepts of the plots. If any one of the rate constants is known, absolute values of all the rate constants can be calculated. An attempt was made to estimate the magnitude of the quenching constant, k_q. The similarity of the values obtained with both isopentane ($\eta = 0.223$ cp) and hexadecane ($\eta = 3.34$ cp) as solvents suggests k_q is significantly smaller than diffusion controlled, but provides no information about the absolute value. Since ways of estimating either k_d or k_r are not presently available, absolute values for the remaining rate constants cannot be assigned.

An interesting aspect of the quenching experiments is the variation of dimer composition upon addition of quencher. Table VII shows that with benzophenone as sensitizer, Σ increases from $92.6 \pm 0.4\%$ of total yield of dimers to $95.6 \pm 0.7\%$ when the solution contains 5×10^{-3}M of azulene. Such variation becomes

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* An extremely fast process of quenching benzophenone singlets by azulene could also explain these results. However, such a process cannot account for the observed variation of dimer composition (vide infra).

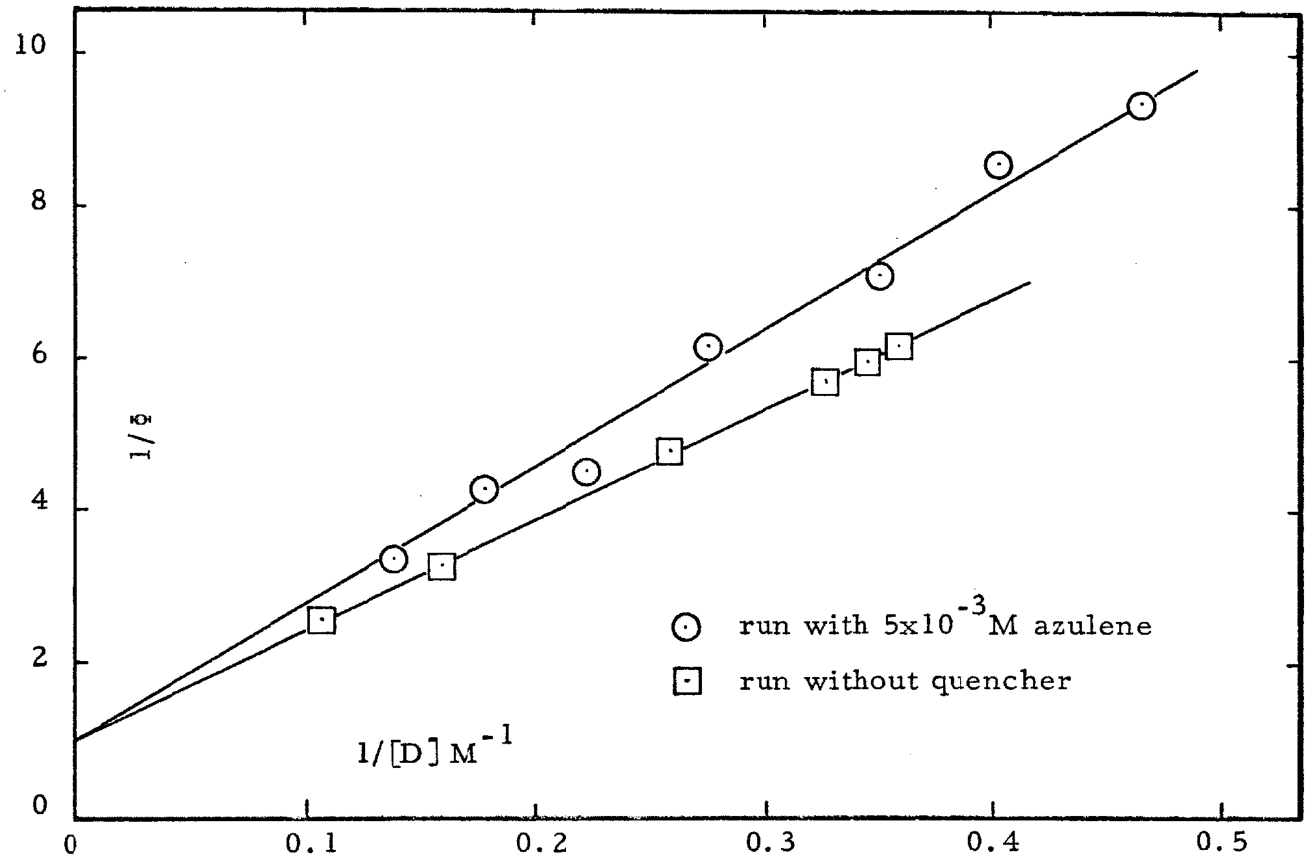

Figure IX. Quantum yield (Φ) of dimerization by varying concentrations of isoprene (D)

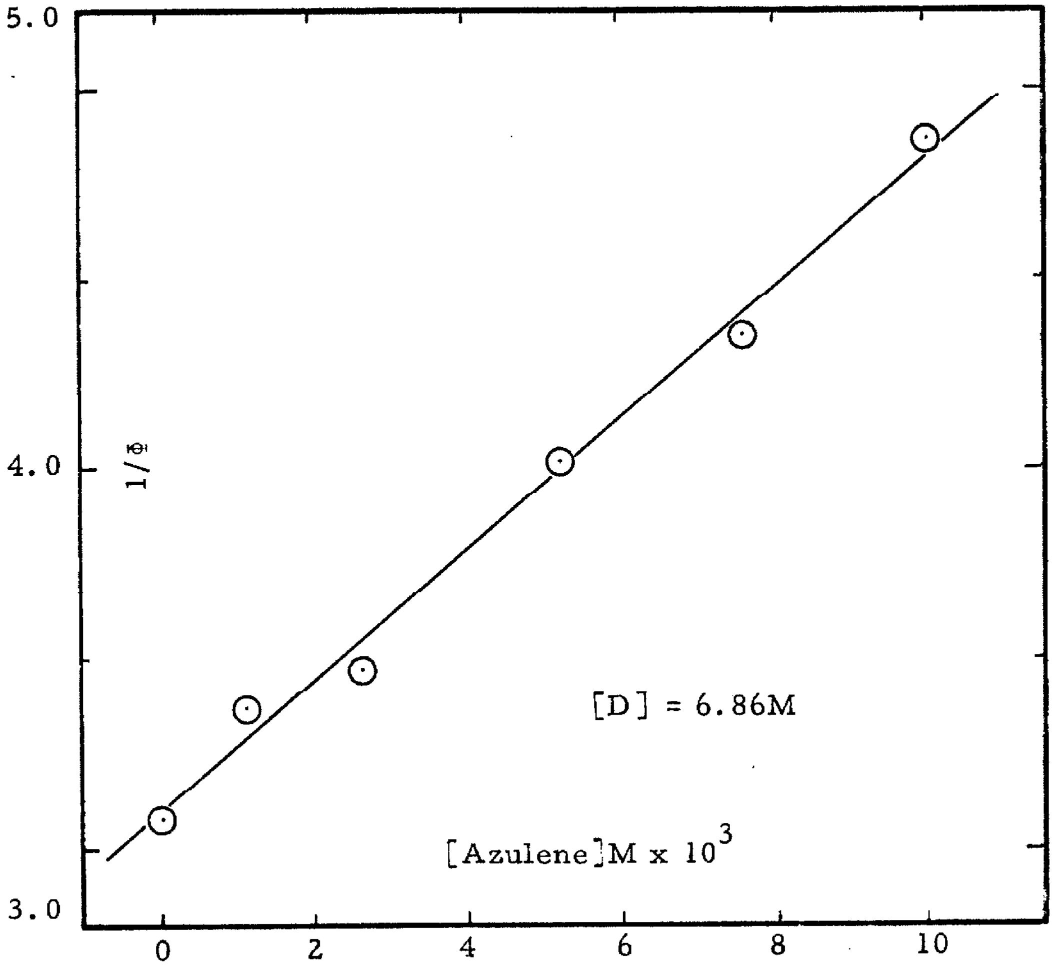

Figure X. Quantum yield of dimerization by varying concentrations of azulene more evident with sensitizers which give more cyclohexene dimers; for example, the corresponding numbers with biacetyl as sensitizer are 48.7 ± 1.6% and 54.5 ± 1.0%. Such variation indicates preferential quenching; i.e., the _cis_-triplets are quenched at a faster rate than the _trans_.*

The Diradical Intermediate

Since it has been firmly established that a triplet and a ground state diene molecule are involved in each addition step of the dimerization reaction, one can safely assume the existence of a diradical intermediate prior to formation of final products. Such a discrete intermediate is needed to provide for change of spin multiplicity prior to ring closure. In other words, the dimerization reaction is a two-step reaction.

Photochemical reactions _via_ direct irradiation are known not to be selective. The reason for such non-selectivity is obvious since reactive intermediates in photoreactions always have considerable excess energy. However, experience with the sensitized reactions indicates that this generalization cannot be applied

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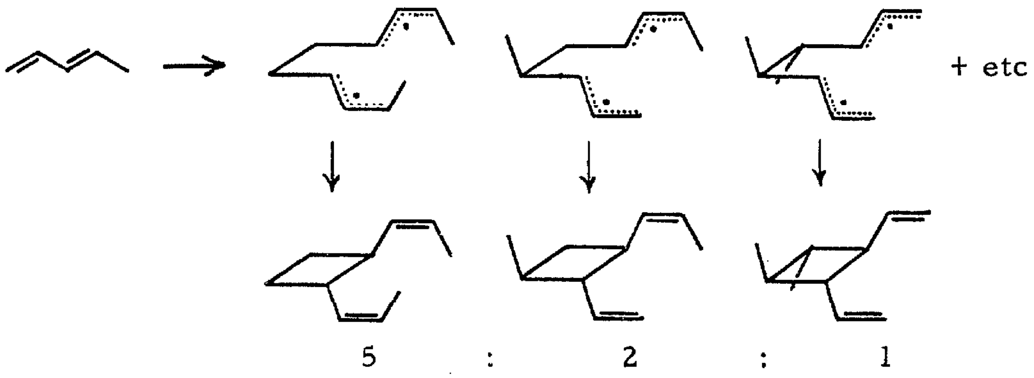
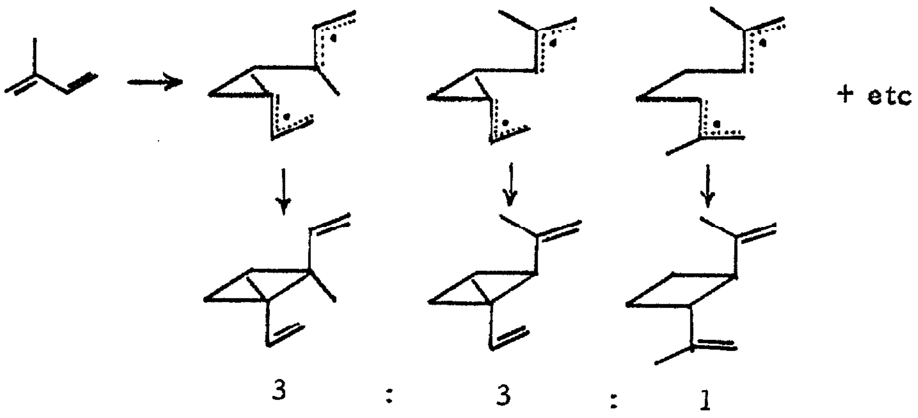
* Non-vertical deactivation of diene triplets is probably involved in these quenching processes.

to sensitized reactions and that, in general, triplet state reactions are more selective. Structures of all the photo-dimers of dienes are in accord with low-energy intermediates involving two allylic radicals. For instance, all the cyclobutanes formed are derivatives of 1, 2-divinylcyclobutane with no 1, 3-substituted cyclobutanes, products which would require higher energy intermediates with only one allylic radical. Selectivity in addition is also shown in the distribution of cyclobutane dimers of piperylenes. The major product corresponds to addition of the less hindered ends of the diene to give a diradical intermediate with the methyl groups situated at the loci of the odd electrons, the better position for methyl group contribution to stabilization of allylic radicals. Distribution of isoprene cyclobutane dimers shows selectivity due to



methyl stabilization in the diallylic intermediates; steric hindrance is unimportant in this case.

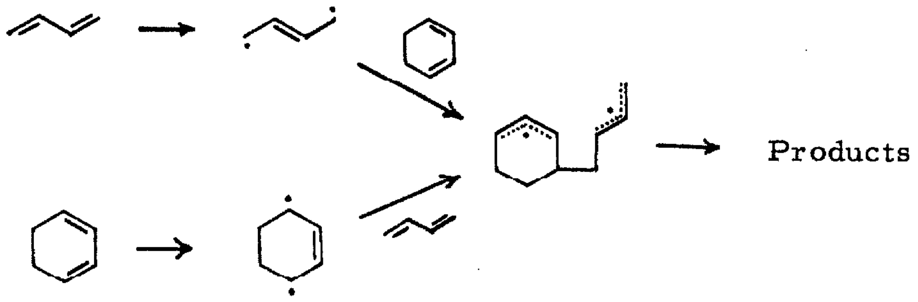


Cross Addition of Dienes

It has been shown that the ability of acyclic dienes to exist in the transoid and cisoid configurations brings about the interesting variation of dimer composition. It should be intriguing to investigate the cross addition reaction of dienes constrained in transoid and cisoid configurations. Relative amounts of the dienes can then be controlled at will. Such studies were started with mixtures of 1,3-cyclohexadiene and 3-methylenecyclohexene. The study was not successful and was discontinued mainly because pure products could not be isolated for identification. However, v.p.c. analysis showed the appearance of one new product whose formation is independent of the sensitizer.

The mixture of butadiene and 1,3-cyclohexadiene, except for the presence of a small amount of cisoid butadiene, is essentially as satisfactory a system as the one mentioned above. In this case the products formed have lower boiling points and are sufficiently stable for isolation and identification. This system was studied in more detail.

The mechanism of the cross addition reaction is believed similar to the dimerization reaction in that it involves excitation of a diene molecule by means of energy transfer from a sensitizer followed by addition of the triplets to a ground state molecule to produce either a dimer or a cross adduct. Low-energy sensitizers are expected to produce mostly cyclohexadiene triplets whereas high-energy sensitizers are expected to produce diene triplets in amounts proportional to concentrations of the two dienes in solution. The fact that invariant amounts of the cross adducts of butadiene and cyclohexadiene are formed is unexpected. Such invariance would normally suggest the presence of one common intermediate for all three products. Consideration of the nature of the intermediates indicates this is indeed the case. The relative amounts of the two diene triplets formed depend upon relative diene concentration and upon sensitizer employed, but the same intermediate is produced after reaction of the triplets with diene molecules. However, in a solution containing cyclohexadiene in low concentration, one would expect low-energy sensitizers to produce significant amounts of <u>cis</u>-triplets of butadiene, which on

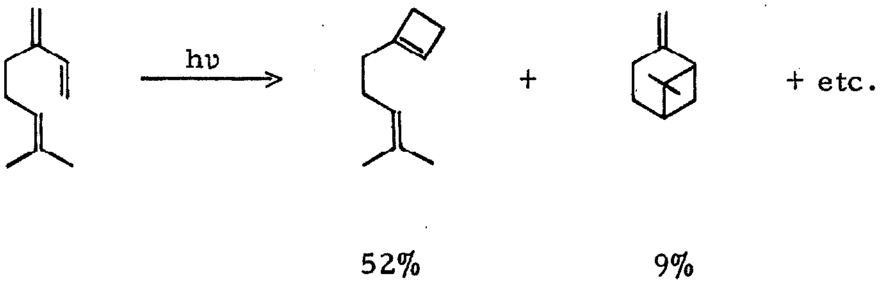


reaction with cyclohexadiene produce different intermediate and also different product(s). This has been verified experimentally. On irradiation of a solution containing butadiene and cyclohexadiene (99: 1 by volume) with fluorenone as sensitizer, in addition to the three cross products observed before, a new product was detected by analytical v.p.c. The retention time of this compound is slightly shorter than that of the minor product formed before. However, this new product is not formed in sufficient quantity for isolation.

Photosensitized Addition Reactions of Conjugated Dienes to Olefins

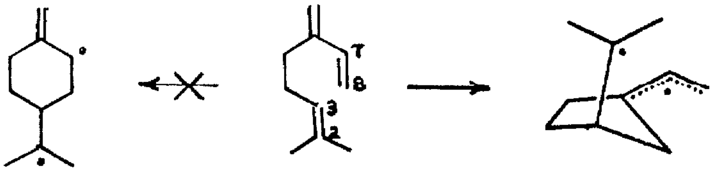
The purpose of studying the addition reactions of dienes to olefins is to generalize reactions of diene triplets. Results show that the reactivity of olefins as "triplet-dienophiles" is too inefficient to compete with the diene molecules. Substituted olefins (e.g. vinyl acetate and ketene acetal) were also tested as potential dienophiles in such reactions, but were found to be inefficient (57). Although isolation of cross-adducts was possible in one instance (1,3-cyclohexadiene-cyclopentene), the low yield of cross-adducts makes such reactions of little significance in synthetic applications.

The results from studies of myrcene, however, suggest that such reactions may be useful when addition takes place intramolecularly. The formation of 5,5-dimethyl-1-vinylbicyclo[2,1,1]-hexane as the only product in the sensitized reaction came as a surprise, since Crowley (9,58) reported that the direct irradiation yields at least nine products, two of which were identified. This

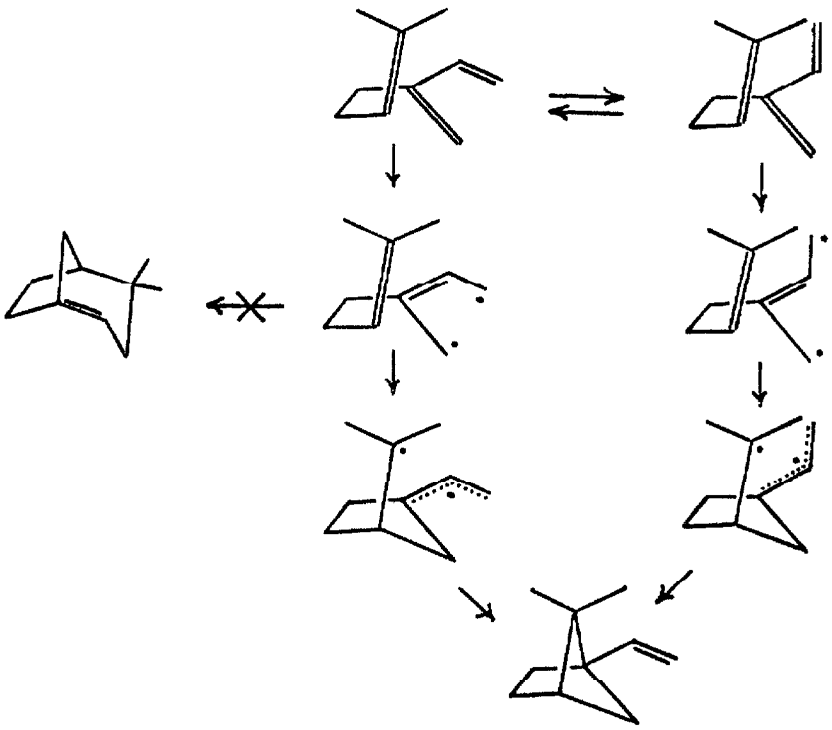


difference in results may be taken as a clear demonstration that, at best, diene singlets intersystem cross to the triplet state inefficiently. In the direct irradiation, the reaction proceeds either by way of the singlet state or higher vibrational levels of the ground state.

On the grounds that many other photochemical reactions involve six-membered transition states (e.g., the Barton reaction (59) and the ketone reduction reaction (60)), one would expect that the primary reaction of myrcene involves bond formation between C_3 and C_8 with β-pinene as a possible product. This was not observed experimentally. However, the structure of the bicyclic product is in accord with an intermediate which is the most stable diradical that can be formed from myrcene via internal addition.



Myrcene, containing an acyclic conjugated diene unit, should also exist as an equilibrium mixture of molecules with transoid and cisoid diene configuration. Energy transfer should again lead to stereoisomeric triplets which may react differently. However, results show that both high-energy (benzophenone) and low-energy (fluorenone) sensitizers give the same product. This invariance of product composition is not surprising in the case of myrcene since the normal <u>cis</u>-triplet product would have a double bond at the bridge head position and is probably too strained to form. On the other hand, the <u>cis</u>-triplet is geometrically as vulnerable as the <u>trans</u>-triplet to formation of diradical intermediates which lead to the product. It is suggested that with certain favorably constructed trienes, e.g., 1,3,7-octatriene, variation of product composition can again be observed as a function of sensitizer energy.



The Question of Possible Applicability of the Schenck Mechanism to Photosensitized Reactions of Conjugated Dienes

In the introductory section it was pointed out that the major differences between the Schenck mechanism (or more descriptively, the diradical addition-elimination mechanism) and the energy transfer mechanism are: (1) the former does not involve energy transfer as an essential step in a sensitized reaction; and (2) the former implies that the reactive intermediate is a diradical formed by addition of a sensitizer to a substrate molecule, rather than the triplet state of the substrate. Although the Schenck mechanism cannot be unequivocally excluded at present, there is evidence which suggests that this mechanism does not represent the major course of the sensitized reaction. Only those results pertaining to reactions of dienes will be used as evidence against the Schenck mechanism in the following paragraphs.

The rates of energy transfer from high-energy sensitizers (E_T = 60 kcal/mole) to quenchers have been measured both by chemical (61) and physical methods (62), and are of the same order of magnitude as the rate of diffusion. This process therefore involves an activation energy of no more than 2 kcal/mole. It is difficult to conceive that a process of bond formation, as required by the Schenck mechanism, could involve such a low activation energy when one realizes at the same time that excited molecules often were not efficiently quenched by substances reactive toward radicals and having high triplet energies.

It appears that the only reasonable way to account for the observed variation of dimer composition with choice of sensitizer in terms of the Schenck mechanism is to assume that the sensitizer structure is determinant in product formation of the diradical intermediate. However, such an explanation cannot account for the observed correlation between product composition and triplet energies of sensitizers, particularly in the high-energy region where sensitizers of vastly different structures gave the same product composition.

Another strong argument against the Schenck mechanism arises from the study of the photosensitized isomerization of the piperylenes. Excited sensitizers would be expected to add either at the 1 or 4 positions of piperylenes. Only addition at the 1 position could lead to isomerization, because addition at the 4 position, although less hindered, is expected to provide for retention of stereochemistry because of the stability of the resulting allyl radical. Such an effect should be evident in quantum yield studies. The fact that the sum of the quantum yields for the cis to trans and trans to cis quantum yields in the sensitized isomerization is unity(63) strongly argues against such a mechanism.

EXPERIMENTAL

Materials:

Benzene (B. & A., Reagent Grade) was used without further purification in most of the work. The benzene used in flash-photolysis experiments was supplied by Dr. A. Fry.

Butadiene (M. C. & B., Instrument Grade) was used without further purification.

1, 3-Cyclohexadiene was prepared by the method used by J. Warkentin (64). Distillation through spinning band column gave >99% purity.

Cyclohexene (M. C. & B., Reagent Grade) was used without further purification.

Cyclopentadiene was prepared by cracking endo-dicyclopentadiene (M. C. & B.) before each use.

Cyclopentene (Columbia Chemical) was used without further purification.

2, 3-Dimethylbutadiene (Columbia Chemical) was distilled and the fraction boiled at 68.5-70.0° was collected for use.

2,5-Dimethyl-2,4-hexadiene (M. C. & B., Practical Grade) was distilled once for preliminary work, Pure sample was obtained by v.p.c. method on Carbowax 20 M columns.

Ether (Mallinckrodt, anhydrous) was used without further purification.

Ethanol (absolute) was used without further purification.

Ethyl iodide (M. C. & B., Reagent Grade) was first passed through alumina column, then distilled for use.

Hexadecane was purified and supplied by Dr. H. Waits.

n-Hexane (Phillips, Pure Grade) was used without further purification.

1,5-Hexadiene (Columbia, Reagent Grade) was used without further purification.

Isopentane (Phillips, Pure Grade) was used without further purification.

Isoprene (Phillips, Pure Grade) was distilled before use, b.p. 33.0°.

3-Methylenecyclohexene was prepared by the method reported by Bailey et al. Product was distilled through spinning band column, b.p. 109-110°C.

Methylene iodide (M. C. & B., Reagent Grade) was passed through alumina column before use.

3-Methyl-1,4,6-heptatriene, an oligomer of butadiene, was kindly given by Dr. S. Otsuka (65). The sample consists only of the trans isomer, b.p. 117°.

Myrcene (Alderich, Technical Grade) was distilled under aspirator pressure through a 10'' Vigreux column (90% pure). The impurities do not interfere with the photochemical reaction; therefore, for preparative runs, such purity is satisfactory. For quantitative work, pure sample was obtained by preparative v.p.c. method using either Apiezon J or Carbowax 20 M column.

Norbornene (Alderich Chemical) was used without further purification.

2-Phenyl-1,4-pentadiene was prepared by reaction of vinyl magnesium bromide with 2-phenyl-allylbromide. The n.m.r. spectrum of the product shows correct proton ratios.

Piperylene (M. C. & B., Technical Grade) was distilled before use, b.p. 42.0°.

β-Acetonaphthone (Eastman Kodak, White Label) was recrystallized from ethanol, m.p. 50.5-50.8° (hot stage).

Acetophenone (M. C. & B., Reagent Grade) was distilled. The fraction boiled at 35-36°/1-2mm was collected for use.

Anthraquinone (Eastman Kodak, Sublimed) recrystallized from acetic acid.

Azulene (Calbiochem) was used from the bottle, m. p. 110°.

Benzil (M. C. & B., Reagent Grade) was recrystallized from ethanol, m. p. 96.5-96.8°C.

Benzophenone (M. C. & B., Reagent Grade) was recrystallized twice from ligroin (60-70), m. p. 48.2-48.5° C.

9-Fluorenone (M. C. & B., Reagent Grade) recrystallized from methanol, m. p. 85.4-86.0°C.

Michler's ketone (Eastman Kodak, Practical Grade) was recrystallized from methanol.

α-Acetonaphthone, 4-acetylbiphenyl, 2-acetylfluorene, cyclopropylphenyl ketone, o-dibenzoylbenzene, propiophenone, thioxanthrene, and 1,3,5-triacetylbenzene were purified and supplied by Dr. A. A. Lamola.

3-Acetylpyrene, benzanthrone, α-naphthaldehyde, α-naphthylphenyl ketone, β-naphthylphenyl ketone, α- and β-naphthils, and pyrene were purified and supplied by Dr. J. Saltiel.

Biacetyl and 2,3-pentadione were distilled by Dr. N. J. Turro.

Benzhydrol and 9,10-dibromoanthracene were purified by Mr. F. G. Moses.

Benzaldehyde was purified by Dr. W. Hardham.

Anthracene (M. C. & B., Reagent Grade), 1,2,5,6-dibenzanthracene (Aldrich Chemical), 9,10-dimethyl-1,2-dibenzanthracene (Eastman Kodak, Chemical), and flavone (Aldrich, Research Grade) were used without further purification.

General Procedure of Preparation of Dimers of Dienes

Solution of sensitizer (0.05M) in neat diene is distributed into previously constructed test tubes (Pyrex, 15x125mm). After at least two freeze-degas-thaw cycles, the tubes are sealed. They are placed around a pyrex immersion well, and irradiated with a 200-watt Hanovia lamp. No extra filter systems are needed, for the pyrex vessels are adequate to filter off all the light that can be absorbed by dienes. Length of irradiation period varies with dienes, but irradiation is generally continued sufficiently long to ensure at least 60% conversion. The contents of the tubes are then combined and vacuum distilled before being subjected to separation into components by vapor phase chromatography method.

This procedure was used to prepare dimers of isoprene, 2,3-dimethylbutadiene and piperylenes. Details on separation and properties of dimers of isoprene and piperylenes have been published. Dimers of 2,3-dimethylbutadiene were partially separated on 1,2,3-tris-(2-cyanoethoxy)propane columns. The four major products (12, 13, 15, 17) were collected. Structures of the n.m.r. spectra of the four compounds have been described in the Results section. Infrared spectrum of 12 shows absorptions at: 3.24 (w), 3.31 (w), 3.37 (s), 3.49 (s), 3.66 (w), 5.63 (w), 6.09 (s), 6.90 (s), 7.18 (s), 7.85 (w), 8.07 (m), 8.72 (w), 9.2 (w), 9.4 (w), 9.95 (m), 10.5 (s), 10.7 (s), 11.3 (s), 11.9 (w) μ; of 13: 3.24 (m), 3.37 (s), 3.48 (s), 3.66 (w), 5.59 (w), 6.11 (s), 6.90 (s), 7.30 (s), 8.03 (m), 8.67 (w), 8.77 (m), 9.4 (m), 9.6 (w), 10.0 (w), 10.5 (w), 11.4 (s), 11.9 (w) μ; of 15: 3.23 (m), 3.36 (s), 3.41 (s), 3.65 (w), 5.58 (w), 6.08 (m), 6.13 (m), 6.90 (s), 7.25 (s), 8.03 (w), 8.11 (w), 8.62 (w), 8.74 (w), 9.3 (w), 10.6 (m), 11.2 (s), 12.0 (w) μ; of 17: 3.37 (s), 3.45 (s), 3.66 (w), 5.98 (w), 6.10 (w), 6.70 (m), 6.91 (s), 7.24 (s), 8.32 (w), 8.81 (w), 9.45 (m), 10.41 (w), 11.2 (m) μ.

Anal. Calc. for $C_{12}H_{20}$: C, 87.73; H, 12.27.

Found for 12: C, 87.51; H, 12.24; for 13: C, 87.59; H, 12.35; for 15: C, 87.64; H, 12.31; for 17: C, 87.44; H, 12.12.

Determination of Isoprene Dimer Composition

Preparation of samples and analyses of composition of dimer composition were performed with the following general procedure. Solutions of 2-3 ml of isoprene containing 0.05M sensitizer (saturated solution, in cases where sensitizers were not very soluble in isoprene) were introduced into pyrex test tubes (13x100 mm) which had been constricted about 20 mm from the top. The samples were then degassed with three freeze-degas-thaw cycles. The tubes were then sealed. Irradiation of the samples was carried out in an apparatus known as the "merry-go-round," designed by F. G. Moses. Essential parts of the apparatus are: an immersion well with a 450-watt Hanovia medium pressure mercury lamp, a turntable surrounding the well and with holes for samples to be irradiated. All these are placed in a constant temperature water bath. For this study the bath temperature was maintained between 27-29° . No additional filter systems were used; the pyrex test tubes and immersion well were adequate to prevent transmission of light below 2900 Å. Irradiation period varied with the nature of sensitizer. In general, approximately 5-10% conversions were obtained before tubes were opened for analyses.

Analytical v.p.c. method was used for analyses of the irradiated samples. The seven dimers could be separated in parts on several columns, although not in one case were the dimers completely separated. Carbowax 10M column (6', 15% on firebrick, 70°) had the advantage of having short retention time; however, it could only separate the seven dimers into five components (1, 2, 3 & 4, 5, 6 & 7). Apiezon J column (6', 12% on firebrick, 80°) separated the seven dimers into six components, failing to separate compounds 6 and 7 only. β,β'-oxydipropionitrile or 1,2,3-tris-(2-ethoxypropion)-nitrile column separates compounds 6 and 7, but does not separate

3 and 4 completely. For determination of product composition, Apiezon J column was used, since the relative yields of compounds 6 and 7 were found to remain constant for all sensitizers. For quantum yield determinations, Carbowax column was used. Peak areas of the chromatographs were measured by the triangle approximation method.

Quantum Yield of Dimerization of Isoprene

Samples for quantum yield studies were prepared by introducing 0.3 ml stock solution (1.00M) of sensitizer in benzene and proper amounts of isoprene into pyrex test tubes (13x100mm) previously constricted near the top. Isopentane was added until all tubes contained solutions of 3 ml in volume. Concentration of sensitizer in all tubes was 0.1M. Degassing procedure was the same as described before. Irradiation was carried out in a modified "merry-go-round" apparatus, the turn-table of which contains windows of uniform dimensions of 3/4" x 1/4". These windows reduce reflection from the edges of the tubes and simultaneously promise equal amounts of quanta absorbed by all samples. Irradiation was continued to approximately 5% conversion. Vapor phase chromatography was used for analyses of the irradiated samples (Carbowax column, 6", 15%, 70°). Benzene in the solution served the purpose of an internal standard to calibrate absolute yield of dimers. It was noticed that relative peak areas of benzene to dimers cannot be used directly for calibration of concentration of dimers. The use of a correction factor of 1.41 was found necessary. Peak areas were again measured by the triangle approximation method. Three sensitizers were used for quantum yield measurements. They were benzophenone, β-acetonaphthone, and fluorenone.

During the run with benzophenone as sensitizer, tubes containing benzophenone and benzhydrol were irradiated simultaneously for independent calibration of light intensity. Details of using this actinometer system were already in the literature (66), and will not be elaborated on here. Samples were prepared by adding 0.60 ml benzene solution of benzophenone (0.5M), 1.20 ml benzene solution of benzhydrol (0.5M), and 1.20 ml of benzene into constricted pyrex test tubes (13x100mm). Volume measurements were made with the aid of automatic syringe attachments for reproducibility. The tubes were degassed and sealed. The tubes were irradiated one at a time (6 altogether) and sufficiently long to give 10% conversion in each tube. Since only approximately 1/20 of the irradiation time of isoprene was needed to irradiate these samples, average number of quanta per unit time absorbed by the samples was used to calculate total quanta by the isoprene tubes.

For runs when azulene was used, the samples were prepared by the same method except that proper amount of benzene solution of azulene was added with decrease of corresponding amount of isopentane, so that the contents remained 3 ml in volume. Irradiation was carried out in the modified "merry-go-round." In these runs, a combination of filter plate (Corning O-52 and 737) was used, which allowed transmission of light of wavelength centered at 3650 Å with width of half height of transmission peak of 50 Å.

Preparation of Cross Adducts of Butadiene and 1,3-Cyclohexadiene

1.3-Cyclohexadiene was found to dimerize more efficiently than butadiene; therefore, in order to achieve optimum yield of cross adducts, a mixture of 2:1 in favor of butadiene was used in preparative runs. The apparatus used for preparation of the cross adducts was a modified immersion apparatus with the jacket fused onto the well. A side arm leading to a pressure stop-cork was attached to the upper part of the jacket. The capacity of the apparatus was approximately 80 ml.

In a typical run, solution of 10 ml of benzene containing 0.2 g Michler's ketone was introduced into the apparatus through the stop-cork with the aid of a dropper. This was followed by addition of 19.1 g (0.24 moles) of 1,3-cyclohexadiene by the same method.

The stop-cork was closed and the apparatus immersed in a Dewar flask containing dry ice-acetone slurry. Approximately 40 ml (0.52 moles) of butadiene previously condensed in a round-bottomed flask with a side arm was then poured into the apparatus through a short vinyl tubing connecting the pressure stop-cork and the side arm of the flask. The partial vacuum in the apparatus resulting from cooling was found helpful for rapid flow of butadiene. The stop-cork was closed. Before the apparatus was allowed to warm up, it was shaken slowly to accelerate mixing of the contents. Then the apparatus was placed in a water bath containing ice water mixture at the beginning of reaction. Irradiation was carried out with a 200-watt Hanovia medium pressure mercury lamp for 24 hours. The dienes reacted nearly completely by the end of the irradiation period. The contents were transferred to a round-bottomed flask and vacuum distilled. The fraction boiled at 30-35°/3mm contained all the cross adducts (17 g, 54% yield).

Preparative v.p.c. method was used for separations of products. Satisfactory separation was achieved on 12' 1,2,3-tris-(2-cyanoethoxy)propane column (26%, 90°). The compound eluted first was the major product (86% of all cross adducts). The product was assigned the structure, trans-8-vinylbicyclo[4.2.0]-2-octene, 18. (See Results section.) The n.m.r. spectrum of it shows the following absorption: complex groups of signals between τ 3.9-4.7 with strong signal centered at τ 4.4 (relative area 3.0), complex signals between τ 5.0-5.4 (relative area 1.9), a broad band between τ 7.1-7.9 (area 3.1), and complex structure between τ 7.9-8.9 (area 5.8). It exhibits the following IR absorptions: 3.23 (m), 3.31 (s), 3.37 (s), 3.42 (s), 3.50 (s), 5.49 (w), 6.09 (s), 6.93 (m), 7.02 (w), 7.36 (w), 7.70 (w), 7.83 (w), 8.01 (w), 8.08 (w), 8.22 (w), 8.32 (w), 8.93 (m), 9.55 (m), 9.70 (w), 10.1 (s), 10.5 (m), 11.0 (s), 11.4 (m), 11.5 (m), 12.6 (w), 13.3 (w), 13.5 (m), 13.6 (m), 14.2 (s) μ. $n_D^{19.0} = 1.4961$.

The second component, which made up 12% of the total cross adducts, was assigned the structure <u>cis</u>-8-vinylbicyclo-[4.2.0]-2-octene, <u>19</u>. The general feature of its n.m.r. spectrum resembles that of <u>18</u> but shows more fine structure. The signals due to vinyl protons fall in the region τ3.9-5.3 (relative area 4.8), with no single strong absorption, and the remaining signals are in the range 6.6-8.9 (relative area 9.0). IR absorptions: 3.21 (w), 3.40 (s), 5.44 (w), 5.79 (w), 6.06 (m), 6.90 (s), 7.40 (w), 7.56 (w), 7.86 (w), 8.04 (w), 8.21 (w), 8.57 (w), 9.22 (w), 9.60 (w), 10.0 (s), 11.0 (s), 11.52 (m), 12.26 (w), 13.30 (s), 14.01 (m) μ.

The third cross adduct (2%) was not isolated.

<u>Anal. Calc.</u> for $C_{10}H_{14}$: C, 89.49; H, 10.51.

Found for <u>18</u>: C, 89.36; H, 10.58. Found for <u>19</u>:

C, 89.22; H, 10.53.

Thermal Rearrangement of the Photoproduct 18

Compound 18 (17 g) was refluxed in a round-bottomed flask equipped with a condenser for two days. Vapor phase chromatography analysis showed that the resulting solution contained three products in approximate ratio 1: 2: 2. They were separated on Carbowax column (6', 35%, 110°). The minor product, a colorless liquid, eluted first on this column. The n.m.r. spectrum consists of the following signals: a band of complicated structure between τ 2.48-4.05 (relative area 2.1), groups of multiplets between τ 4.05-5.04 (relative area 2.9), and overlapping groups of signals centered at τ 6.60, 7.14, and 8.70 of total area 7.0. Its infrared spectrum shows absorptions at: 3.22 (s), 3.36 (s), 3.41 (s), 5.46 (w), 6.06 (m), 6.80 (m), 6.87 (m), 7.03 (w), 7.28 (m), 7.75 (w), 8.52 (m), 8.76 (w), 9.58 (w), 10.02 (s), 10.30 (w), 10.51 (w), 10.99 (s), 11.63 (m), 11.77 (m), 12.13 (m), 12.31 (m), 12.70 (w) μ.

The compound is tentatively assigned the structure 5-vinylbicyclo-[2.2.2]-2-octene, 23. The second compound eluted from the column is also a colorless liquid, $n_D^{19.1} = 1.5099$. The n.m.r. spectrum consists of the following signals: a poorly resolved doublet centered at τ 4.4 with several side peaks (area 4.0) and two overlapping broad bands centered at τ 8.0 and 8.4 (total area 9.9). The infrared spectrum shows absorptions at: 3.34 (s), 3.47 (s), 6.05 (m), 6.88 (m), 7.00 (s), 7.23 (w), 7.53 (w), 7.70 (w), 7.88 (w), 8.14 (w), 8.36 (m), 8.52 (m), 8.76 (w), 9.20 (w), 8.46 (w), 9.97 (m), 10.60 (m), 11.2 (w), 11.65 (m), 12.23 (w) μ.

Together with the result from the hydrogenation experiment, this compound is assigned the structure cis-bicyclo[4.4.0]-2,8-decadiene, 22. The third product is a white solid of low melting point. The structure of the n.m.r. spectrum is rather simple, consisting of a quartet of nearly the same intensity and centered at τ 4.10 (relative area 0.9), a broad singlet centered at τ 6.59 (relative area 6.0), and a poorly resolved triplet centered at τ 7.28 (relative area 4.0). The infrared spectrum shows absorptions at: 3.31 (w), 3.46 (s), 6.05 (w), 6.86 (w), 6.93 (w), 7.03 (m), 8.12 (w), 8.30 (w), 9.04 (w), 10.27 (w), 11.31 (m) μ.

The compound is assigned the structure bicyclo[4.2.2]-2,6-decadiene, 21. This compound did not undergo photochemical reaction when irradiated in the presence of acetone.

Anal. Calc. for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found for 23: C, 89.57; H, 10.44. Found for 22: C, 88.30; H, 11.74. Compound 21 could not be obtained in sufficient pure form to give satisfactory analysis.

Thermal Rearrangement of Photoproduct 19

Compound 19 (0.5 g) was heated in a sealed tube at 150° for 1 hour. The contents of the tube solidified when allowed to cool. Vapor phase chromatography analysis showed that the product was homogeneous. The retention time was identical with the third thermal product, 21, from 18. The n.m.r. spectrum is also identical with that of 21.

Hydrogenation of Bicyclo[4.4.0]-2,8-decadiene, 22

Solution of the title diene (0.50 g) in ethanol with platinum oxide was stirred under hydrogen atmosphere until uptake of hydrogen was complete. Extraction of product from ether-water mixture followed by evaporation of the dried ether layer yielded colorless liquid. The crude product was distilled through molecular distillation giving 0.24 g of product (45% yield). Vapor phase chromatography analysis (Apiezon J column, 6' 14% 120°) showed that the product was homogeneous and the retention time was identical with that of an authentic sample [*] of cis-decalin. (Retention time of trans-decalin was considerably shorter on this column.) The infrared spectrum of the product was also identical with that of cis-decalin.

Photosensitized Addition of 1,3-Cyclohexadiene to Cyclopentene

To previously constricted test tubes (15x200mm) were added a solution of 30 ml cyclopentene, 2 ml 1,3-cyclohexadiene, and 0.1 g β-acetonaphthone. After being degassed and sealed, the tubes were irradiated for 24 hours. Another 2 ml of cyclohexadiene were added. After being sealed, the tubes were irradiated for the same period. All together, 10 ml of diene were added in this manner. Vapor phase chromatography analysis (Apiezon column 150°) showed that cross adducts and dimers were present in the irradiated solution in approximate ratio of 1:4. The solution was distilled. The fraction boiled at 30-35° /2-50mm contained all adducts together with some amount of diene dimers. The three cross adducts, formed in the ratio 4:2:1, were separated by v.p.c.

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[*] Authentic samples of cis- and trans-decalins were obtained by separation of commercial decalin on Apiezon J column. The infrared spectra of both isomers obtained in this way are identical with those reported in the literature (67).

Pure material of the major product was obtained. The signals of its n.m.r. spectrum consist of two groups (τ 4.1-4.3, 7.4-8.6) in the ratio 1.0:7.3. Its infrared absorption shows absorptions at 3.31 (m), 3.40 (sh), 3.41 (s), 3.52 (m), 6.40 (m), 5.58 (m), 6.94 (w), 8.00 (m), 8.30 (m), 9.95 (m), 10.21 (m) μ. A mixture of the major product and the second major one was also isolated. Structure of its n.m.r. spectrum was similar to that of the major product, but with proton ratio 1:6.3. Hydrogenation of the mixture gave one product which had the same retention time as that of the hydrogenated product from the major product. The minor product was not isolated in significant amount.

<u>5,5-Dimethyl-1-vinylbicyclo[2.1.1]hexane, 25</u>

Myrcene (2.80 g), purified by preparative v.p.c. method and β-acetonaphthone (0.4 g), were mixed with 100 ml anhydrous ether. The solution was added to a pyrex immersion apparatus and bubbled with nitrogen for 5 minutes. Irradiation was carried out with a 200-watt Hanovia medium pressure lamp. After eight hours, myrcene was found to have reacted completely. Ether was removed by distillation through a short Vigreux column at atmosphere pressure. Product was distilled under aspirator pressure, amount collected = 2.19 g (78%). The product was a colorless liquid, $n_D^{19.2} = 1.4641$. Its n.m.r. spectrum has been described in the Results section. Its infrared spectrum showed the following absorptions: 3.23 (w), 3.39 (s), 5.46 (w), 6.09 (m), 6.79 (s), 6.86 (s), 7.03 (m), 7.22 (m), 7.31 (s), 7.16 (w), 7.80 (m), 8.03 (w), 8.37 (w), 8.86 (w), 10.06 (s), 10.99 (s), 11.60 (w), 11.99 (w), 12.58 (w), 14.40 (m) μ.

Anal. Calc. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 87.96; H, 11.91.

For larger scale preparation, once distilled commercial myrcene (90-95% pure) was used. The impurities were found not to undergo photosensitized reactions. When the experiment was carried out with high concentration of myrcene (up to 10%), isomerization was accompanied by side reaction, possibly dimerization. Different solvents were used (benzene, n-hexane, and ether). All gave the photoproduct in good yield. The photoproduct was purified first by refluxing solvent in maleic anhydride to remove unreacted myrcene, then by fractional distillation through spinning band column under aspirator pressure (97-98% pure), or by preparative v.p.c. method on 6 ft. Apiezon J column (> 99% pure).

5,5-Dimethylbicyclo[2.1.1]hexane-1-carboxylic acid, 28

In a 300-ml round-bottomed flask was placed 11.0 g (0.081 moles) of the photoproduct, 25, and 200 ml methylene chloride. The flask was cooled to -78° . Ozonalysis procedure was similar to that used by Henne (68). At the end of reaction, the solution turned to purple in color. Methylene chloride was removed under reduced pressure and replaced by 60 ml ethyl acetate. To this solution 50 ml of water, 3 ml conc. sulfuric acid, and 22 ml of 30% hydrogen peroxide (0.2 moles) were then added. The solution was refluxed overnight. Another 50 ml of water were added and the solution was extracted with 4 portions of 100-ml ether. The combined ether solution was extracted with 5% sodium hydroxide solution. Acidification of the basic extract, followed by extraction with ether and evaporation of solvent, yielded colorless and viscous liquid. The crude product was sublimed, giving 2.4 g (19.3% yield) white, fluffy solid with melting point range 54-59° . The n.m.r. spectrum of the solid showed the following signals: a group of overlapping peaks between τ 7.5-8.6, two singlets at τ 8.70 and 9.07, and a doublet centered at τ 8.82 with splitting constant 8 c.p.c., and another low field singlet at τ -0.34.

5,5-Dimethylbicyclo[2.1.1]hexane-1-methanol, 29

Ether solution of the once sublimed acid, 28 (3.3 g, 0.0214 moles) was added dropwise to an ether suspension of lithium aluminum hydride (0.76 g, 0.02 moles) contained in a three-necked 100-ml round-bottomed flask. After completion of addition, the solution was refluxed for 2 hours, then allowed to cool to room temperature. Water was added slowly to remove unreacted metal hydride, followed by addition of 10% sulfuric acid. The ether layer was washed and dried. After evaporation of ether, a viscous, colorless liquid with strong camphor-like odor was obtained. From the crude product, white, fluffy solid (1.90 g, 68%) of low melting point was obtained by sublimation. The oily residue left in the sublimator weighed 0.20 g; its n.m.r. spectrum suggested that it contains a mixture of alcohols. The n.m.r. spectrum of the solid shows the following signals: singlets at τ 6.44, 8.83, and 9.23 of relative areas 1.8, 2.9, and 2.8, respectively; a doublet centered at τ 8.92 with splitting constant of 2.5 c.p.s. (relative area 1.0); and a group of multiplets between τ 7.85-8.60 (relative area 6.3); and another singlet of relative area 1.0, the chemical shift of which is dependent upon the concentration of the compound.

5,5-Dimethylbicyclo[2.1.1]hexane-1-methane tosylate, 30

The tosylate was prepared by reaction of the alcohol, 29, with tosyl chloride in pyridine. The tosylate is a viscous oil. Attempts to crystallize failed.

5,5-Dimethylbicyclo[2.1.1]hexane-1-methane brosylate, 31

The brosylate was supplied by A. Fry. It was prepared by reaction of the alcohol prepared before with brosyl chloride in pyridine. When given, the material had been recrystallized once from n-heptane, m.p. 67.2-67.7° . For analysis the brosylate was recrystallized once more from h-hexane.

Anal. Calc. for $C_{15}H_{19}OBrS$: C, 50.14%; H, 5.33%; Br, 22.24%; S, 8.93%. Found: C, 50.08%; H, 5.31%; Br, 22.29%; S, 8.88%.

1,5,5-Trimethylbicyclo[2.1.1]hexane, 26

The tosylate prepared before was refluxed in ether with excess amount of lithium aluminum hydride for 48 hours. After conventional work-up, a poor yield of crude product was obtained. It was a colorless liquid, and obviously was a mixture of the title hydrocarbon and the alcohol, 29, in approximate ratio of 3:1 (by n.m.r. spectroscopy). Positions of the three strong singlets

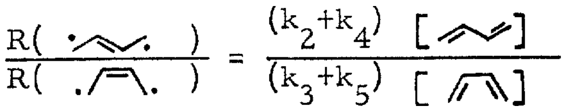
(τ 8.89, 9.04, and 9.30) in the n.m.r. spectrum are identical with the chemical shifts of protons of the three methyl groups in 1,5,5-trimethylbicyclo[2.1.1]hexane as reported by Srinivasan (38). The hydrocarbon had not been isolated.

Quantum Yield Determination of the Sensitized Reaction of Myrcene

Tubes (pyrex, 13x100mm) containing benzene solutions of myrcene (1%) and benzophenone (0.1M) were degassed and sealed. Irradiation was carried out simultaneously with benzophenone-benzhydrol actinometer tubes in the "merry-go-round" apparatus. The reaction was allowed to reach approximately 10% conversion before the tubes were opened for analysis. Vapor phase chromatography (Apiezon J column, 6', 14%, 90°) was used for analysis of samples. Since at this concentration the amount of dimers formed, if any, should be negligibly small, in calculation it was assumed that the bicyclic compound is the only product from myrcene. Quantum yield found is 0.049.

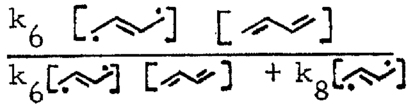
APPENDIX

Following the scheme on page 68, the ratio of relative rates of populating the isomeric diene triplets is:

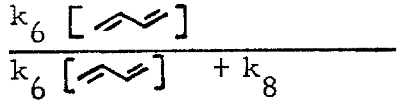


(12a)

Assuming no dimers of cyclohexene structure are formed, the probability of forming cyclobutane (C_4) and cyclooctadiene (C_8) dimers from trans-triplets is:



or after simplification,



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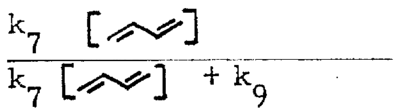
Similarly, the probability of forming dimers from cis-triplets is:



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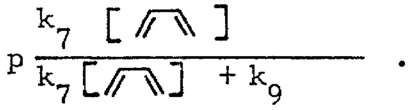
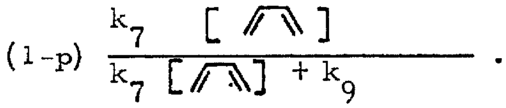
However, it is conceivable that C_4 and C_8 dimers, as well as cyclohexene (C_6) dimers, are found from cis-triplets. The probability of forming a C_6 dimer from a <u>cis</u>-triplet is:

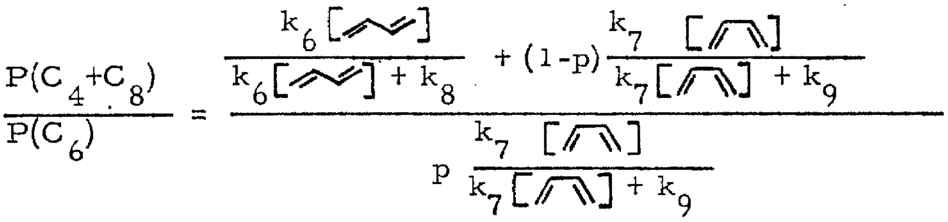


and the probability of forming a C_4 or C_8 dimer from a <u>cis</u>-triplet is



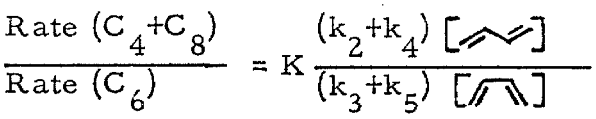
(p is a constant less than 1)

Therefore, the relative probability of forming different dimers with equal numbers of the two isomeric diene triplets is:



(12b)

This ratio is constant at constant concentration of diene. The product of 12a and 12b gives the relative rates of forming cyclobutanes plus cyclooctadienes versus that of cyclohexenes.



(12)

Here K represents the ratio in expression 12b.

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PROPOSITIONS

PROPOSITION I

The study of photosensitized isomerization of 3-methyl-2,4-hexadiene is proposed. Results of quantum yield study should provide direct information about the structure of the diene triplet.

Two possible structures* for diene triplets were suggested in the discussion of dimerization of conjugated diene (1). In one structure (structure I), the end methylene groups are in the perpendicular direction with respect to the C_2, C_3 atoms; the second (structure II) has only one methylene group oriented in the perpendicular direction while the other remaining one falls in phase with the central carbon atoms, thus forming an allyl radical. (The two structures are illustrated on page 65.) Obviously, both of these structures can readily account for the observed photosensitized cis-trans isomerization of 1-substituted, e.g., piperylenes (2) and 3-ethylidenecyclohexene (3), or 1,4-disubstituted, e.g., 2,4-hexadiene (4), dienes. It is believed that a detailed study of photosensitized isomerization of 1,4-disubstituted dienes should provide direct information as to the correct structure of diene triplets.

By invoking the criteria that the allyl radical retains its stereochemistry (5,6), it becomes obvious that each quantum can

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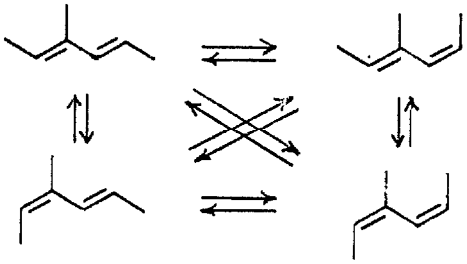
*For simplicity a linear model was used for both structures.

isomerize substituents at both ends of the diene unit if the triplet resembles structure I; while with structure II each quantum can enhance isomerization at one terminal only. This difference should reflect itself in total quantum yields of inter-conversion of isomers. It is believed that 3-methyl-2, 4-hexadiene is the simplest and an unambiguous system for such study. As shown in the drawing, this diene can exist as four distinct geometric isomers. In the diagram,



horizontal and vertical conversions involve isomerization of one terminal only, and diagonal conversions involve isomerization at both ends. Evidently only triplets with structure I can accommodate the latter processes. It is proposed that isomerization of the diene in the presence of high energy sensitizer ($E_T > 60$ kcal/mole) be studied, and the quantum yields of conversion of each isomer to others be determined. A value of two of the sum of quantum yields of all processes (quantum yields of the diagonal processes should be multiplied by two) would indicate that structure I correctly represents the diene triplet; on the other hand, a value of one would favor II as the correct structure.

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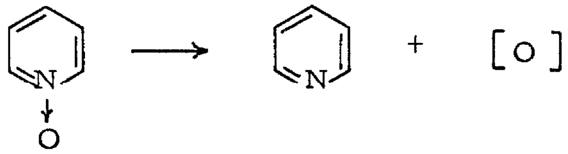
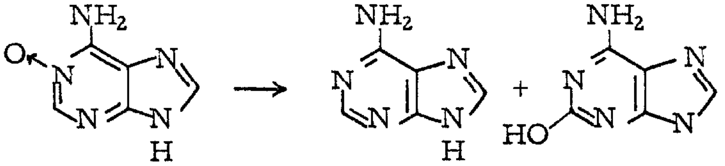
PROPOSITION II

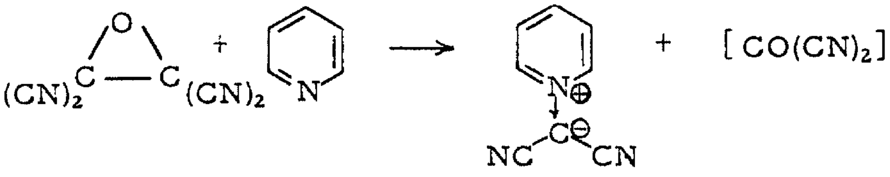
A convenient method for synthesis of dicyanocarbene is proposed.

Behavior of pyridine oxide (and 2-picoline N-oxide) toward light of different wavelengths has been studied in detail in the vapor phase by N. Hata and I. Tanaka (1). Although quantum efficiency of the reaction appears to vary with wavelength of incident light and temperature of reaction, in all conditions the primary process of the reaction appears to be decomposition of the N-oxide to pyridine and oxygen atom. Irradiation of adenine-N-oxide in aqueous solution gives several products. The two major ones are adenine and isoguanine (2). This reaction probably involves a primary process similar to that of the decomposition of pyridine oxide.





Recently the reaction of tetracyanoethylene oxide with pyridine was reported (3) with isolation of an excellent yield (80%) of the ylide I. Compound I contains an electronic structure similar to that of pyridine oxide. It is proposed that irradiation of the ylide should



I

generate the hitherto unknown dicyanocarbene.

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PROPOSITION III*

Tricyclo[2.1.1.$0^{5,6}$]-2-hexene, IV, is proposed as a possible intermediate in the photochemical interconversion of xylenes and related compounds. Labeling experiments should establish whether the said compound or prisbane (Ladenberg benzene) is the correct structure for the intermediate.

Photochemical interconversion of xylenes (in the vapor phase) (1), and di-t-butylbenzenes (in solution) (2) have been reported recently. Both reports show identical results in that starting with the ortho isomer, the meta isomer is first formed followed by subsequent conversion to the para compound (see Table).

Photochemical Isomerization of o-Di-t-butylbenzene (2)

Time, Hr.	ortho	meta	para
0	100%	--	--
6	80	20%	Traces
18	60	30	10%
41	15	55	30
64	5	50	45
76	--	50	50
146	--	20	80
158	--	20	80

No discussion on the mechanism of isomerization of xylenes was presented. However, in the case of di-t-butylbenzene, the authors suggested two mechanisms, "photoinitiated 1,2-migrations

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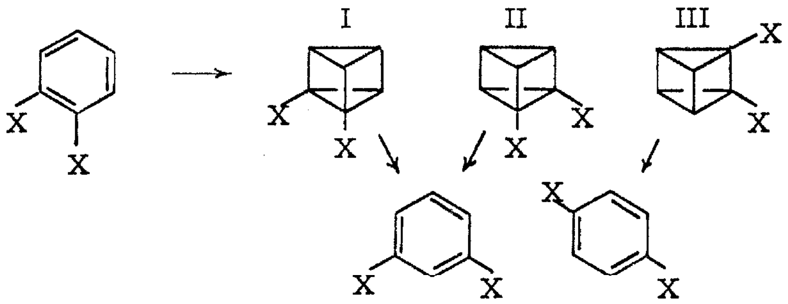
* Much of the material related to this proposition was brought to this proposer's attention through a discussion with Dr. A. A. Lamola and Professor G. S. Hammond.

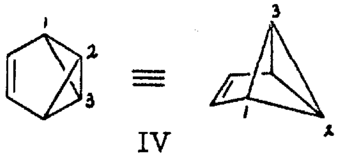
of a t-butyl group or excitation of the benzene ring to a Ladenberg-type structure with subsequent rearomatization to form the meta and then the para isomer," and they propose to distinguish the two mechanisms by appropriate labeling with C^{14}. Both of these mechanisms, although not being inconsistent with the results, are not able to account for all the observations satisfactorily. An alternative mechanism, which is more consistent with the results is proposed here.

It appears that a reasonable process of "photoinitiated 1,2-migration of a t-butyl group" is homolytic cleavage between one t-butyl group and the ring, followed by migration of hydrogen and recombination of radicals. In view of the fact that the xylene isomerization reactions were performed in the vapor phase with product mixture void of compounds like toluene and mesitylene, this process does not seem likely, but, of course, not vigorously excluded. As suggested, the C^{14} labeling experiment should easily establish the validity of such a mechanism.

Bond reorganization is a more attractive process. However, prisbane (Ladenberg benzene) does not seem to be able to account satisfactorily for the absence of direct conversion from the ortho to the para compound without imposing special properties on prisbane. Three prisbanes can be formulated from ortho di-substituted benzene, two of which (I and II) are equivalent and lead to the desired product; however, the third, III, should give the p-isomer as the only product. Prisbane, therefore, can be the intermediate only if (i) I and II are selectively formed, or, (ii), III, if formed, only reverts to

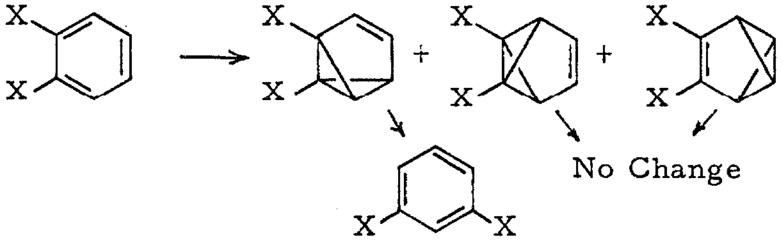


the starting material. On the other hand, an intermediate containing the tricyclo[2.1.1.$0^{5,6}$]-2-hexene (IV) structure (van Tamelen benzene*) can account for all the results without imposing any other special requirement. With IV as an intermediate, isomerization



IV

involves bond formation between C_1 and C_3, followed by bond breaking between C_1 and C_2. Thus, para isomer obviously cannot be formed directly from ortho. Isomerization can be represented by the following equation:



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*In a footnote of a communication, van Tamelen considered but discarded a compound of this structure as the possible photoisomer of 1,2,4-tri-t-butylbenzene (3).

The study of triplet-triplet energy transfer from benzene to biacetyl in solution seems to support the van Tamelen benzene as an unstable photoisomer of benzene.* Lipsky (5) showed that the sensitized emission of biacetyl decreases in intensity as the irradiation is prolonged. However, after the solution is allowed to stand in the dark for a short period, emission from biacetyl returns to the original intensity. Lipsky suggested that probably the decomposition products from biacetyl act as quenchers, thus diminishing biacetyl phosphorescence. However, the reported decomposition products from biacetyl are not potential quenchers (6). An alternative explanation is that an unstable compound from benzene is formed which competes with biacetyl to quench benzene triplets. Olefins have been shown to quench benzene triplets efficiently (7, 8). Therefore, in this respect, the van Tamelen benzene is a more reasonable intermediate than prisbane. On the other hand, identification of the photoisomer of 1, 2, 4-tri-_t_-butylbenzene with the Dewar benzene structure (3) (presumably the precursor to prisbane) appears to favor the prisbane.

In order to distinguish the two proposed intermediates, study of the photosensitized isomerization of 1, 2-substituted benzene labeled at the 3 and 4 positions is proposed. If the reaction proceeds through the prisbane intermediate, the _initially_ formed _m_-isomer

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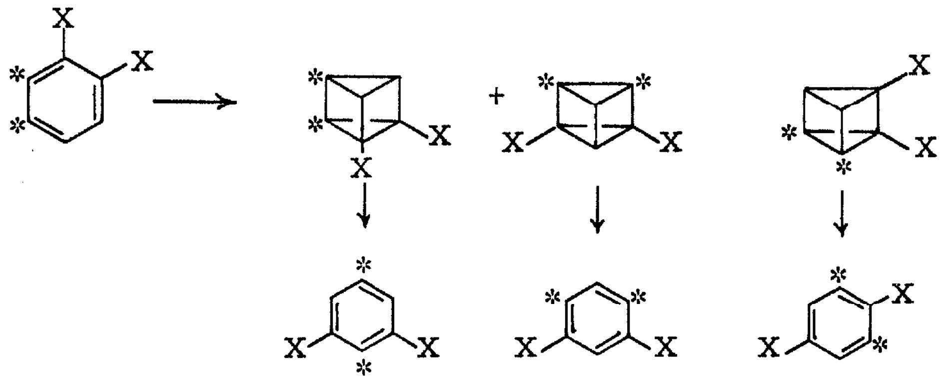
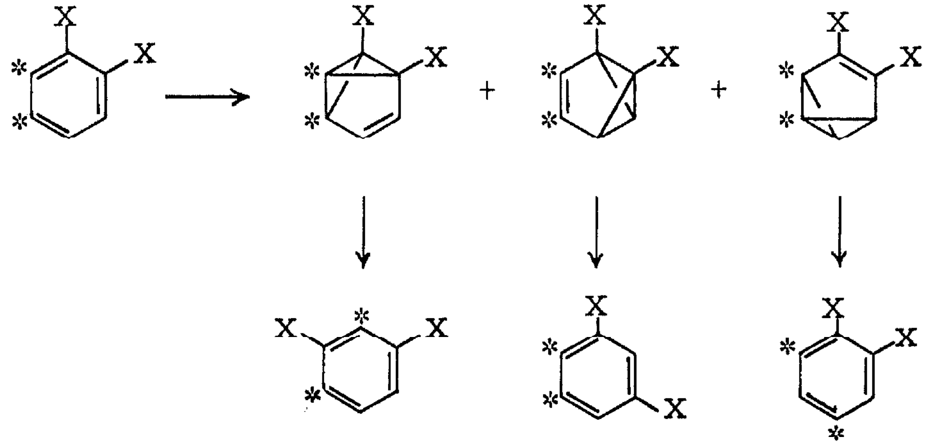
*Dr. A. A. Lamola recently summarized the confusing observations of photochemical behavior of benzene in solution (4). The probability of formation of transients from benzene instead of biacetyl was also discussed (see below).

should not contain labels at adjacent positions. On the other hand, if the reaction proceeds through the van Tamelen benzene, 50% of the m-isomer should contain the labels at juxtaposition.





Deuterium, carbon 13, or fluorine (if the reaction course is not altered in this case) can be used as labels for this study. In any case, n.m.r. spectroscopy can be applied for analysis.

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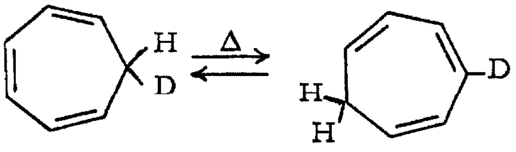
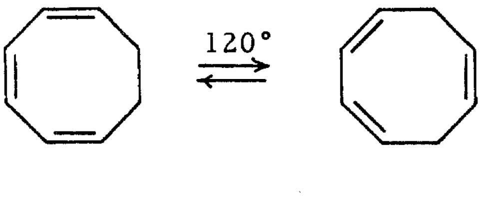
PROPOSITION IV

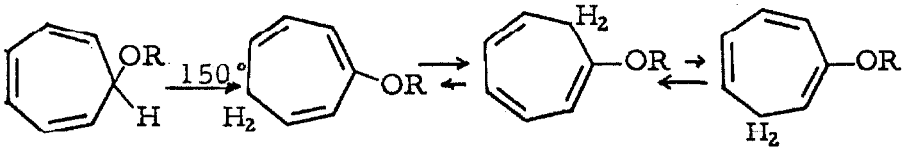
Study of 1, 5-transannular migration of hydrogen in tropilidene and related compounds by means of nuclear magnetic resonance spectroscopy is proposed.

Generality of uncatalyzed thermal 1, 5-hydrogen transfer in dienes was demonstrated by Wolinsky et al. (1) with four different systems. Recently numerous reports have appeared on hydrogen migration in cyclic dienes and trienes which are believed to involve similar 1, 5-hydrogen migration. 7-Monodeuterotropilidine isomerizes to 3-deuterotropilidene (2); 1, 3, 5-cyclooctatriene and 1, 3, 6-cyclooctatriene equilibrate readily at temperatures above 120° (3, 4); and 7-ethoxytropilidene isomerizes to its isomers at 150° (5). Other related examples are isomerization of cis-1-methyl-2-vinyl-

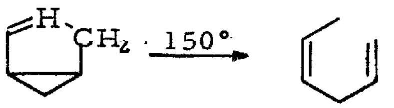


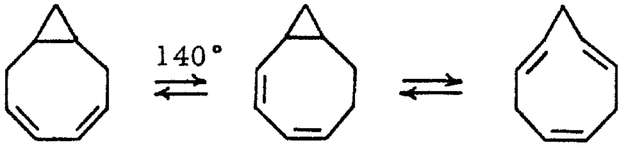
$\Delta H^{\ddagger} = 31$ kcal/mole
$\Delta S^{\ddagger} = -10$ e. u.





cyclopropane (6), and bicyclo[6, 1, 0]nonadienes (4).





The activation energies of these reactions are surprisingly low, generally around the vicinity of 30 kcal/mole. Such a low activation energy allows an unique experimental method, i.e., temperature dependent n.m.r. spectroscopy to be used for following the process of hydrogen migration in compounds constructed specially favored for such studies. Tropilidene is a satisfactory compound.

The low-temperature n.m.r. spectra of tropilidene have been reported (7, 8) and were shown to be temperature dependent. At room temperature, signals of the methylene protons (a triplet) correspond to two equivalent protons. However, at temperatures below −150°, the two protons become non-equivalent. High-temperature spectra of tropilidene have not been reported. It is believed that above 200°, the n.m.r. spectrum of tropilidene will again be temperature dependent, and at sufficiently high temperatures all protons will become equivalent. Tropilidene is known to isomerize to toluene at high temperature; but the activation energy of this reaction (51.1 kcal/mole) (9) is much higher than the hydrogen migration reaction so that it will not complicate the study.

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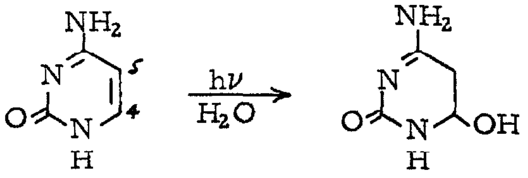
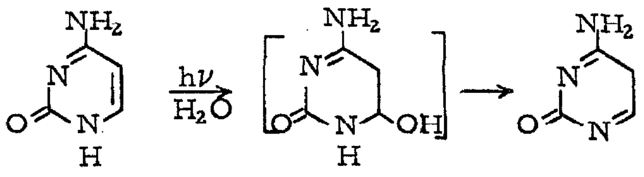
PROPOSITION V

Explanation is proposed for the 'inconsistent' photochemical behavior of cytosine, cytidine, and cytidilic acid. Experiments are suggested to test the validity of the explanation.

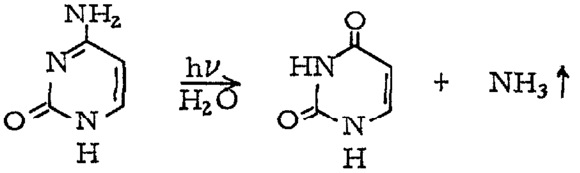
Aqueous solutions of cytosine, cytidine, and cytidylic acid undergo photochemical reaction with disappearance of the characteristic ~2700Å absorption maxima and appearance of new absorption at λ_{max} 2400Å (1, 2, 3, 4). The photoproduct is not stable, and reverts to the starting material (at least partially in some cases) on standing. Two structures have been suggested for the photoproduct. One is the compound resulting from addition of water at the 4 and 5 positions, which is analogous to the reaction product of addition of water to uracil (1,2, 3). The other is a tautomer of cytosine, which conceivably can be derived from the hydrated compound (5). The latter suggestion seems unlikely because it fails completely in cases of cytidine



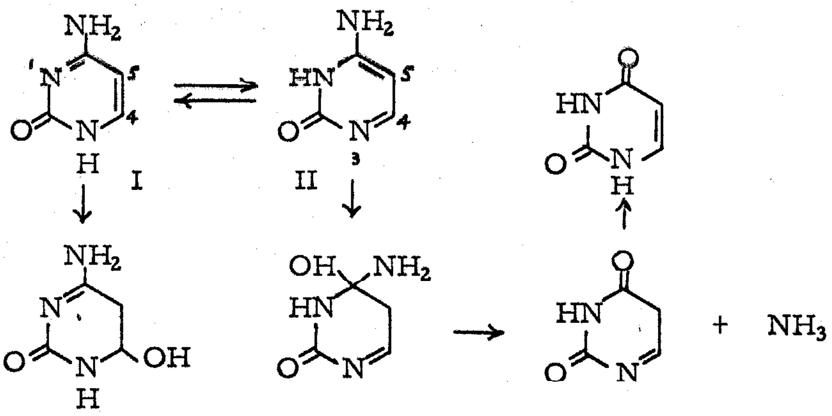


and cytidylic acid, in which the 3 position is connected to a sugar unit (3).

In the case of cytidine and cytidylic acid, the photochemical isomerization and the reverse dark reaction apparently proceed without side reactions because the ultra-violet absorption spectra of aliquots of reaction mixture taken at different times exhibit isosebestic points. On the other hand, cytosine does not give isosebestic points (4). Apparently, in the latter case, hydration is accompanied by side reaction(s). Recently, the identification of uracil in the product mixture obtained from irradiation of cytosine in water was reported (5). This reaction is accompanied by liberation of ammonia and formation of other unidentified products. The ratio of uracil and ammonia produced is approximately one. However, no mechanistic study of this reaction was presented.



It appears that these photochemical reactions of cytosine, and its nucleoside and nucleotide can be consistently accounted for by the following mechanistic scheme. Cytosine probably exists in two major tautomeric forms (<u>I</u> and <u>II</u>). Excitation of tautomer <u>I</u> leads to addition of water at the 4 and 5 positions; while excitation of tautomer <u>II</u> results in addition of water at the 5 and 6 positions, followed by dark reactions of liberation of ammonia and tautomerization,



Cytidine and cytidylic acid cannot exist in tautomeric form II, since in each case the 3 position is substituted; therefore, on irradiation hydration is not accompanied by deammination. To test this mechanistic scheme, among other possible experiments, irradiation of 1-alkylated cytosine (7) is proposed. The major reaction course of this compound should be deammination.

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