PHOTOCHEMICAL CYCLOADDITION REACTIONS OF NONAROMATIC CONJUGATED HYDROCARBON DIENES AND POLYENES[1]

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Contents

I. Introduction and Scope of the Review

A large number of cycloaddition (ring-forming)[2] reactions of unsaturated molecules brought about by ultraviolet or visible radiation have been reported, the great majority in the last 10 years. These reactions have found considerable synthetic utility and have been the subjects of numerous mechanistic studies. This review deals with these reactions of one class of important compounds, namely nonaromatic conjugated hydrocarbon dienes and higher polyenes. The term nonaromatic means that an aromatic ring is not a part of the polyene system, but could be present as a substituent. For example, the reactions of anthracene or styrene are not included, but those of phenylbutadiene are.

A number of reviews and research summaries have dealt noncomprehensively with these reactions in connection with other photochemical reactions.[2-37] The present review is intended to cover all reactions falling under the above scope and which have been published through 1968. Both the synthetic and mechanistic aspects of these reactions are discussed.

These reactions include both sensitized and nonsensitized reactions, and both dimerizations and cross-additions. Sensitized reactions generally occur *via* the triplet state by energy transfer from the sensitizer (S) to the acceptor (A) (eq 2). Compounds which act as sensitizers usually are materials

$$S \xrightarrow{h\nu} S^{*1} \xrightarrow[\text{crossing}]{\text{intersystem}} S^{*3} \qquad (1)$$

$$S^{*3} + A \longrightarrow S + A^{*3} \qquad (2)$$

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(23) W. G. Dauben, "Reactivity of the Photoexcited Organic Molecule," Interscience Publishers, New York, N. Y., 1967, pp 177–180.

(24) G. J. Fonken, *Org. Photochem.*, 1, 197 (1967).

(25) G. S. Hammond, "Reactivity of the Photoexcited Organic Molecule," Interscience Publishers, New York, N. Y., 1967, pp 129–136.

(26) D. C. Neckers, "Mechanistic Organic Photochemistry," Reinhold Publishing Corp., New York, N. Y., 1967, pp 110–112, 124, 127, 134.

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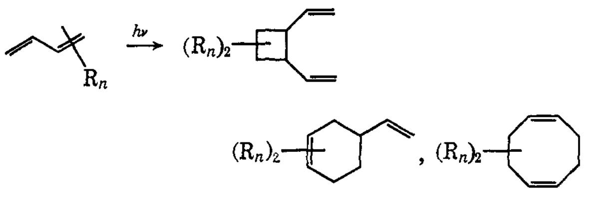
$$A^{*3} + A \longrightarrow (A\text{–}A)^{*3} \xrightarrow[\text{crossing}]{\text{intersystem}} A_2 \text{ (dimer)} \qquad (3)$$

which have a high efficiency for the ($S^{*1} \rightarrow S^{*3}$) process (eq 1). Nonsensitized reactions occur by direct absorption of the photon by the reacting molecule (eq 4). In the latter case A*

$$A + h\nu \longrightarrow A^{*} \qquad (4)$$

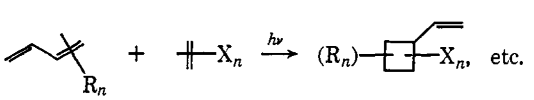
$$A^{*} + A \longrightarrow A_2 \text{ (dimer)} \qquad (5)$$

may be either a singlet or a triplet depending on the nature of A. For hydrocarbon dienes A* is generally a singlet. Dimerization of dienes can give at least three types of simple cycloaddition products (eq 6). Cross-addition gives the adduct of a diene



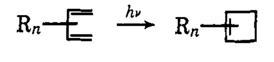
(6)

and another olefin (eq 7).



(7)

The intramolecular analogs of these reactions, *i.e.*, internal cycloadditions where both the diene or polyene and other olefinic moiety are contained in the same molecule, are included in this review. Only those cases where the two unsaturated moieties are not conjugated with each other are considered. The cyclization (valence isomerization) of polyene systems such as butadienes (eq 8) and hexatrienes (eq 9) have been reviewed elsewhere[18,38,39] and will not be considered here.



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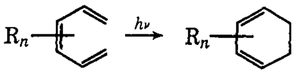
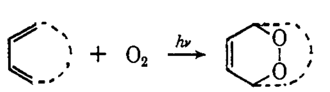


(9)

Only reactions in which both reacting partners are organic compounds are included. The most common reaction of this type involving inorganic compounds is the cycloaddition of oxygen to dienes (eq 10); these reactions have been reviewed recently.[40]



(10)

A number of theoretical treatments of these reactions have been reported in the last few years.[41–46] No attempt will be made here to summarize all the conclusions derived from these studies. Probably the most significant result for this review is that the excited-state concerted cycloaddition of an m π-electron system with an n π-electron system is an allowed process only for the following geometrical modes of addition.

Table I

$m + n$	*Allowed excited state process*
$4q$	*cis–cis; trans–trans*
$4q + 2$	*cis–trans; trans–cis*

$q = 1, 2, 3, \ldots$

Any reaction not following these restrictions is predicted to proceed *via* a stepwise process. These restrictions apply only to excited-singlet-state reactions. Triplet-state reactions presumably must occur in a stepwise manner to allow for a spin inversion.

The reactions discussed below are grouped according to type: dimerization or cross-addition and sensitized or nonsensitized. Within each section the dienes and polyenes are discussed in order of structural complexity, starting with the simplest. The radiation sources were usually medium- or high-pressure mercury arc lamps unless otherwise noted.

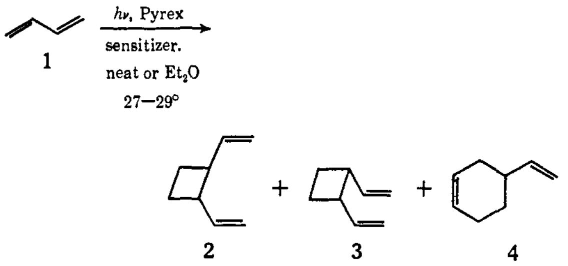
II. Dimerization

A. SENSITIZED

1. Acyclic Dienes and Trienes

a. 1,3-Butadiene

The sensitized dimerization of the simplest conjugated diene, butadiene (**1**), has been studied extensively (eq 11).[47–53] A typical isolated yield of dimers **2**, **3**, and **4** was 73% using 2,3-pentanedione as the sensitizer.[48] This dimerization using *p,p′*-bis(dimethylamino)benzophenone as the sensitizer has been developed into a standard synthetic procedure for the preparation of *trans*-1,2-divinylcyclobutane (**2**, 60–65% yield).[52]



(11)

The composition of the dimers as a function of the energy of the lowest triplet level (E_{T_1})[54] of the sensitizer is given in

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(38) W. G. Dauben, *Chem. Weekblad*, 60, 381 (1964).

(39) Reference 23, p 171.

(40) K. Gollnick and G. O. Schenck, "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York, N. Y., 1967, pp 255–344.

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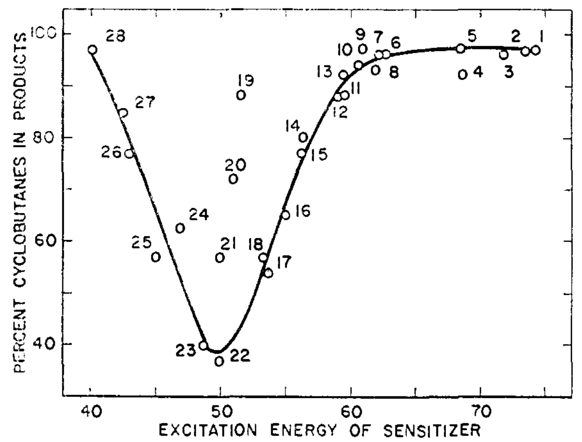


Figure 1. Butadiene dimer composition *vs.* triplet energy of sensitizers. Reprinted from the *Journal of the American Chemical Society* by permission of the authors and the copyright owners, The American Chemical Society.

Table II and shown graphically in Figure 1.[61] For these studies conversions of butadiene were carried to 5–10%.

Table II

Composition of Products from Photosensitized Dimerization of Butadiene

Sensitizer[a]	E_{T_1}, *kcal/mole*	*Distribution of dimers, %* 2	3	4
1 Xanthone[b]	74.2	78	19	3
2 Acetophenone[b]	73.6	78	19	3
3 Benzaldehyde	71.9	80	16	4
4 *o*-Dibenzoylbenzene	68.7	76	16	7
5 Benzophenone[b]	68.5	80	18	2
6 2-Acetylfluorenone	62.5	78	18	4
7 Anthraquinone	62.4	77	19	4
8 Flavone	62.0	75	18	7
9 Michler's ketone	61.0	80	17	3
10 4-Acetylbiphenyl	60.6	77	17	6
11 β-Naphthyl phenyl ketone	59.6	71	17	12
12 β-Naphthaldehyde	59.5	71	17	12
13 β-Acetonaphthone[b]	59.3	76	16	8
14 α-Acetonaphthone	56.4	63	17	20
15 α-Naphthaldehyde	56.3	62	15	23
16 Biacetyl	54.9	52	13	35
17 Benzil	53.7	44	10	45
18 Fluorenone	53.3	44	13	43
19 Duroquinone[c]	51.0	72	16	12
20 β-Naphthil	51.0	57	15	28
21 Benzoquinone[c]	50	~51	~6	~43
22 Camphorquinone	50	30	7	63
23 Pyrene	48.7	~30	~10	~60
24 Benzanthrone	47	55	10	35
25 3-Acetylpyrene	45	43	12	45
26 Eosin	43.0	60	17	23
27 Anthracene	42.5	75	10	15
28 9,10-Dibromoanthracene	40.2	78	19	3

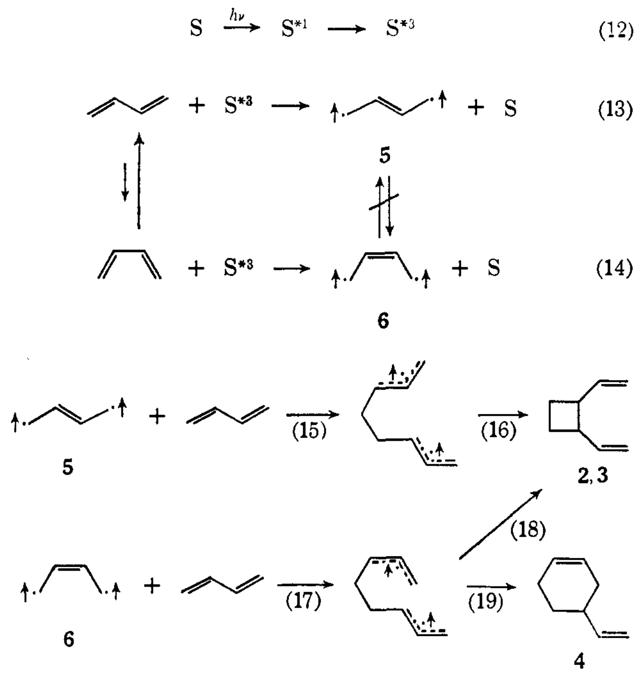
[a] Sensitizer was 0.1 *M* in ether unless otherwise specified. [b] Sensitizer 0.1 *M* in benzene. [c] By-products formed may have influenced the course of the reaction.

A slightly different product distribution was obtained by another group of workers.[60] With a 10:1 mixture of diene **1** to acetophenone (irradiation through quartz for 16 hr) the distribution was 70% **2**, 20% **3**, and 10% **4** (compare 3% **4** in Table II).[60] A saturated solution of benzil in **1** (irradiation time 80 hr) gave 45% **2**, 4% **3**, and 49% **4**.[60] (Note that the terms *cis* and *trans* have been interchanged for the divinylcyclobutanes in Table II of ref 50.)

Benzene, E_T = 84.0 kcal/mole, has also been used as a sensitizer for the dimerization of **1** (two parts of **1**, one part of benzene, irradiation through quartz, 100 hr).[50] The product distribution was 47% **2**, 17% **3**, 18% **4**, and 18% of an unknown compound.[50]

The explanation offered for the dependence of the cyclobutane **2** and **3**:cyclohexene **4** ratio on the triplet energy of the sensitizer was based on an energy transfer from the triplet sensitizer, S^{*3}, to either the *s-trans* (eq 13) or *s-cis* (eq 14) conformer of diene **1** (Scheme I).[51] The resulting *trans*-**5** and *cis*-butadiene triplets **6** are not expected to be easily interconvertible since the electron being excited is promoted from a molecular orbital which is antibonding in the ground state between carbon atoms 2 and 3 to one which is bonding in the excited state.[55] The triplet energy level of butadiene has been determined to be 59.8 kcal/mole above the ground state[56,57] and is assumed to be the energy level of the *trans* triplet **5**.[51] The energy of the *cis* triplet **6** is not known, but is assumed to be *ca.* 53 kcal/mole[51] based on the triplet energy of a model *s-cis* diene, 1,3-cyclohexadiene, E_T = 52.5 kcal/mole.[56,57]

Scheme I



However, it should be noted that another *s-cis* diene, cyclopentadiene, has a triplet energy, 58.1 kcal/mole,[56] much closer to that of butadiene. The relative proportion of *s-trans*- and *s-cis*-butadiene is believed to be *ca.* 96:4 at room temperature.[51,58] If it is assumed that the energy-transfer process (eq

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(55) J. D. Roberts, "Notes on Molecular Orbital Calculations," W. A. Benjamin, Inc., New York, N. Y., 1961, p 51.

(56) R. E. Kellogg and W. T. Simpson, *J. Am. Chem. Soc.*, 87, 4230 (1965).

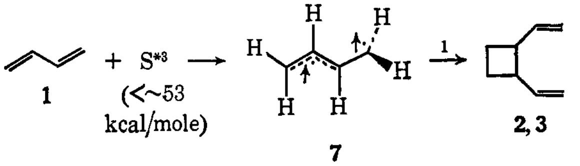
(57) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

(58) W. B. Smith and J. L. Massingill, *J. Am. Chem. Soc.*, 83, 4301 (1961).

13 and 14) is diffusion controlled when the energy of the donor is above that of the acceptor, one would predict that sensitizers with $E_{T_1} >$ *ca.* 60 kcal/mole would produce mainly *trans* triplets **5** and therefore give predominantly cyclobutanes. Sensitizers with $E_{T_1} =$ *ca.* 50–60 kcal/mole would give proportionately more *cis* triplets **6** since the energy transfer to *s-trans*-butadiene would become more inefficient as the energy of the sensitizer drops below 60 kcal/mole. The *cis* triplet **6** is the only intermediate which can lead to the formation of the cyclohexene **4** assuming configurational stability of the intermediate diallyic radicals and neglecting reactions of diene triplets with ground-state *s-cis* diene **1**. The 1,4 closure (eq 18) is believed to be a minor reaction course compared with the 1,6 closure (eq 19),[4] but no evidence has been presented concerning this point.

In the benzene-sensitized dimerization of diene **1**,[60] it is surprising that the amount of cyclohexene **4** is so high when one considers that the triplet energy of benzene is 84.0 kcal/mole.[59] Based on the data presented above it appears that the amount of **4** should be no higher than 3–4% if this is truly a triplet-sensitized reaction. The temperature of this experiment was not reported. The unknown product was thought to be either 1,5-cyclooctadiene or a benzene–butadiene adduct[50] (see below). A 0.2 *M* solution of diene **1** in benzene gave the same products but in concentrations too low to analyze quantitatively.[50]

The reason for the form of the curve in the 40–50 kcal/mole region of Figure 1 is not well established. It has been proposed that this increase in the relative amounts of cyclobutanes **2** and **3** is due to "nonvertical" excitation of the planar ground-state butadiene to a nonplanar excited state **7** (non-Franck–Condon transition), which is lower in energy than either planar triplet, and which gives predominantly cyclobutanes (eq 20).[11,51] An alternate explanation for the large proportion of cyclobutane derivatives **2** and **3** formed with the low-energy triplet (T_1) sensitizers, particularly the anthracene derivatives, is that energy transfer occurs from the second triplet state (T_2) rather than the first.[53] Experiments using a large number of anthracene derivatives as sensitizers gave product distributions characteristic of "high-energy," *i.e.*, >60 kcal/mole, sensitizers (Table III).[53]



1 **7** **2,3** (20)

The rate constants for the addition of diene triplets **5** and **6** to ground-state diene **1** (eq 15 and 17) have been estimated to be $\leqslant 10^6$ l./(mole sec).[60] The quantum yield for the dimerization of concentrated solutions of **1** was *ca.* 0.001 for sensitizers with $E_{T_1} >$ *ca.* 50–54 kcal/mole.[61,62] The quantum yield decreased markedly for sensitizers with lower triplet (T_1) energies.[51,61] An increase in temperature produced a large relative increase in the amount of 4-vinylcyclohexene,[4,61] presumably due to an increase in the concentration of the *s-cis* diene conformer.

Table III

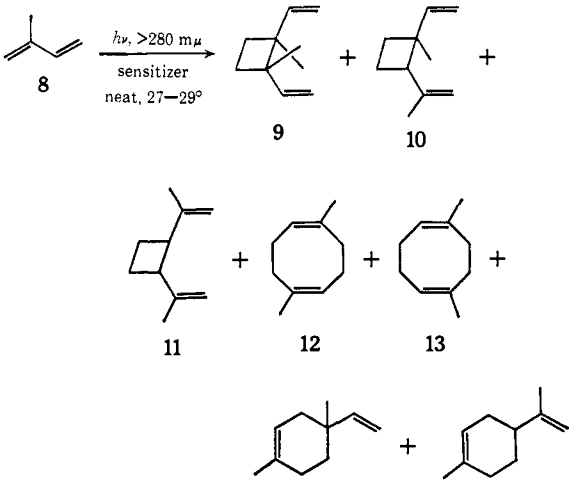
Composition of Dimers from Butadiene Photosensitized by Anthracene Derivatives

Sensitizer[a]	E_{T_2}, *kcal/mole*	E_{T_1}, *kcal/mole*	*Distribution of dimers, %* **2 + 3**	**4**
9,9′-Bianthryl	...	...	96	4
Anthracene	74.4	42.5	95	5
2-Methylanthracene	73.5	40.6	95	5
9-Methylanthracene	...	40.6	95	5
9,10-Dichloroanthracene	...	40.2	95	5
9-Methyl-10-chloro-methylanthracene	...	...	95	5
1,5-Dichloroanthracene	72.6	40.7	94	6
9,10-Dibromoanthracene	...	40.2	94	6
9-Methyl-10-chloro-anthracene	...	...	92	8

[a] Sensitizer in neat butadiene.

b. Isoprene

Isoprene (**8**), in a manner similar to butadiene, gave seven dimers, **9–15** (eq 21).[48,49,51,63] In a typical preparative experiment using benzophenone as the sensitizer, a 65% conversion to dimers **9–15** was realized after irradiation for 5 days.[48] Another large-scale preparative run using acetophenone as the sensitizer and 4-butylcatechol as a polymerization inhibitor gave the dimethyldivinylcyclobutane **9** in 30% isolated yield after 3 days.[64]



8 **9** **10** **11** **12** **13** **14** **15** (21)

The variation in the distribution of products 9–15 as a function of the sensitizer energy (Table IV, Figure 2[61]) roughly parallels that of butadiene.[51,63] Another report on the dimerization of isoprene (Pyrex filter, 72 hr, 20°) using benzil as a sensitizer indicated a slightly different set of dimers: **9**, 19.9%; **10**, 17.9%; **12** and **13**, 11.9%; **14**, 37.7%; **15** and **16**, 13.5%.[64,65] However, it may be that the diene **16** is not a

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(59) D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).

(60) R. S. H. Liu and G. S. Hammond, *J. Am. Chem. Soc.*, **89**, 4936 (1967).

(61) Reference 13, p 212.

(62) M. Herberhold and G. S. Hammond, *Ber. Bunsenges. Physik. Chem.*, **72**, 309 (1968).

(63) G. S. Hammond and R. S. H. Liu, *J. Am. Chem. Soc.*, **85**, 477 (1963).

(64) D. J. Trecker and J. P. Henry, *ibid.*, **86**, 902 (1964).

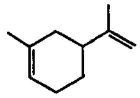
(65) D. J. Trecker, R. L. Brandon, and J. P. Henry, *Chem. Ind.* (London), 652 (1963).

Table IV

Composition of Products from Photosensitized Dimerization of Isoprene

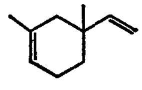
Sensitizer[a]	E_{T_1}, *kcal/mole*	Distribution of dimers, % 9	10	11	12 + 13	14	15
1 Propiophenone	74.6	29.7	30.7	9.7	23.2	4.4	2.2
2 Cyclopropyl phenyl ketone	74.4	28.0	30.5	8.0	25.2	5.4	2.9
3 Acetophenone	73.6	29.0	29.7	8.2	25.4	4.8	3.0
4 1,3,5-Triacetylbenzene	73.3	29.5	29.6	6.7	25.8	4.6	3.7
5 Benzaldehyde	71.9	28.4	26.1	7.5	28.2	6.3	3.4
6 *o*-Dibenzoylbenzene	68.7	29.6	31.2	7.7	23.9	4.9	2.8
7 Benzophenone	68.5	29.0	30.1	9.0	25.2	4.7	2.1
8 Thioxanthone[b]	65.5	28.6	26.0	8.0	28.9	5.2	3.2
9 2-Acetylfluorene[b]	62.5	29.2	30.0	8.0	23.8	6.1	3.0
10 Anthraquinone[b]	62.4	28.6	29.5	7.5	25.1	6.2	3.2
11 Flavone[b]	62.0	26.2	28.3	5.8	28.1	7.8	3.9
12 Michler's ketone[b]	61.0	27.8	29.5	7.7	25.8	5.8	3.3
13 Acetylbiphenyl	60.6	28.6	29.1	8.3	24.2	6.8	3.1
14 *β*-Naphthyl phenyl ketone	59.6	24.4	26.9	8.7	21.1	13.7	5.9
15 *β*-Naphthaldehyde	59.5	22.1	21.7	6.3	26.5	15.9	7.5
16 *β*-Acetonaphthone	59.3	26.3	27.2	9.3	18.2	14.5	4.5
17 *α*-Naphthyl phenyl ketone	57.5	23.2	25.0	5.4	20.9	18.7	6.9
18 *α*-Acetonaphthone	56.4	19.6	19.5	8.7	17.4	27.0	7.7
19 *α*-Naphthaldehyde	56.3	18.3	19.3	5.2	16.8	29.2	11.0
20 Biacetyl	54.9	18.8	19.8	4.1	10.0	34.6	12.7
21 2,3-Pentanedione	54.7	14.5	14.6	4.9	15.0	38.6	12.4
22 Benzil	53.7	13.5	12.4	3.5	15.3	38.5	16.9
23 Fluorenone	53.3	12.7	11.7	4.6	14.1	42.5	14.6
24 1,2,5,6-Dibenzanthracene	52.3	11.9	10.0	2.6	13.6	43.3	18.6
25 Pyrene[b]	48.7	12.1	12.4	2.1	9.5	45.4	18.4
26 Benzanthrone[b]	47	11.9	11.8	2.2	8.7	46.6	18.7
27 3- Acetylpyrene	45	13.5	15.5	6.4	15.7	36.6	12.3
28 9,10-Dimethyl-1,2-dibenzanthracene[b]	44.4	17.5	19.0	5.0	16.1	30.3	12.1
29 Anthracene[b]	42.5	27.3	29.8	8.2	21.4	8.5	4.9
30 9,10-Dibromoanthracene[b]	40.2	30.8	33.8	7.9	21.8	3.6	2.1

[a] Sensitizer (0.1 *M*) in neat isoprene unless otherwise stated. [b] Saturated solution of sensitizer in isoprene.



16

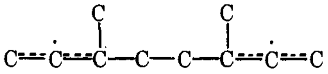
photoproduct but instead arises from the isomerization of **11**.[49] It is likely that the two cyclooctadienes **12** and **13** are not photoproducts, but rather are formed *via* thermal rearrangements of *cis*-1,2-dialkenylcyclobutanes.[48,66] Thus the cyclooctadienes are grouped with the cyclobutanes in Figure 2. Conspicuous by their absence from the dimeric products are the two "*meta*" cyclohexenes **16** and **17**. Since all of the other possible ring-closure products resulting from the intermediate



17

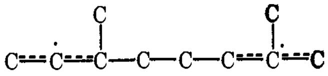
diallylic radicals **18–20** were observed in this reaction (disregarding the *cis*-dialkenylcyclobutanes), one would also expect cyclohexenes **16** and **17** to be formed. It is not obvious why these latter dimers were not formed. Analogous "*meta*" cyclohexenes were formed in a cross-addition reaction involving isoprene (see section III.A.1.b below).

An explanation analogous to that used for the butadiene dimerization has been applied to the variation in the isoprene dimer distributions with different sensitizers.[51,63] The triplet energy of isoprene, 60.1 kcal/mole,[56] is nearly the same as that of butadiene. The quantum yield for the formation of all dimers in neat (10 *M*) isoprene was 0.40 with benzophenone, 0.25 with *β*-acetonaphthone, and 0.29 with fluorenone.[51,62]



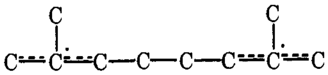
$C\cdots\dot{C}\cdots\overset{\overset{C}{|}}{C}-C-C-\overset{\overset{C}{|}}{C}\cdots\dot{C}\cdots C$

18



$C\cdots\dot{C}\cdots\overset{\overset{C}{|}}{C}-C-C-C\cdots\overset{\overset{C}{|}}{\dot{C}}\cdots C$

19



$C\cdots\overset{\overset{C}{|}}{\dot{C}}\cdots C-C-C-C\cdots\overset{\overset{C}{|}}{\dot{C}}\cdots C$

20

Stern–Volmer plots for these three sensitizers were all linear with approximately the same slopes, indicating that the ratio of the rate constant for unimolecular decay of the diene triplets to the rate constant for reaction of the diene triplets with ground-state diene was nearly the same for all three sensitizers. Apparently the ratios of these rate constants are similar for both the *cis* and *trans* isoprene triplets.[67] Quenching experiments with azulene (E_T = 31–38 kcal/mole) were consistent with the above mechanism,[61] indicating that this quenching was more important with the *cis* triplets than with the *trans* triplets.[67]

Ferrocene (0.05 *M*) has also been used as a sensitizer for the dimerization of neat isoprene (**8**).[68] The rate was faster when the irradiation was carried out through quartz than through Pyrex. The product distribution was 92% cyclobutanes **9–11** and cyclooctadienes **12** and **13** and 8% cyclo-

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(66) Reference 25, p 144.

(67) Reference 25, p 136.

(68) J. J. Dannenberg and J. H. Richards, *J. Am. Chem. Soc.*, **87**, 1626 (1965).

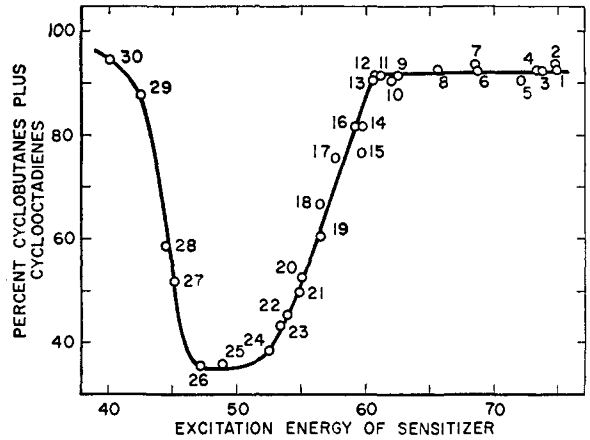


Figure 2. Isoprene dimer composition *vs.* triplet energy of sensitizers. Reprinted from the *Journal of the American Chemical Society* by permission of the authors and the copyright owners, The American Chemical Society.

hexenes **14** and **15**[68] even though the triplet energy of ferrocene is 40.5 kcal/mole.[69] This is the same product distribution obtained with "high-energy" sensitizers (E_T > 60 kcal/mole).[51] To account for this product distribution with a "low-energy" sensitizer, the mechanism shown in Scheme II was proposed.[68]

Scheme II

$$\text{ferrocene} + \mathbf{8} \rightleftharpoons \text{complex} \quad (22)$$

$$\text{complex} \xrightarrow{h\nu} \text{complex}^{S_n} \quad (23)$$

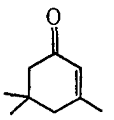
$$\text{complex}^{S_n} \longrightarrow \mathbf{8}^{T_n} + \text{ferrocene}^{T_n} \quad (24)$$

$$\mathbf{8}^{T_n} \longrightarrow \mathbf{8}^{T_1} \quad (25)$$

$$\mathbf{8}^{T_1} + \mathbf{8} \longrightarrow \text{dimers} \quad (26)$$

Some evidence supporting the first three steps (eq 22–24) was obtained.[68] The fourth step (eq 25) may not be necessary.[68] It was proposed that both *cis*- and *trans*-diene triplets were formed in reaction 24 in the same ratio as formed with a "high-energy" sensitizer.[51,68] Thus it was implied that both *s-cis*- and *s-trans*-diene **8** complexes with ferrocene were formed.[68] A slight variation to Scheme II may be proposed by analogy with the ferrocene–piperylene reaction.[69] The "complex^{S_n}" may undergo intersystem crossing to "complex^{T_n}" which then dissociates to ground-state ferrocene and triplet isoprene.[69] However, other interpretations of these data are possible since the 92:8 product distribution is just what is predicted for a sensitizer with a triplet energy of 40.5 kcal/mole which undergoes "nonvertical" energy transfer to diene **8**.[51]

Isoprene (**8**) has been used as a quencher in a study of the photodimerization of isophorone (**21**).[70] The same seven dimers **9–15** described above were formed.[70]

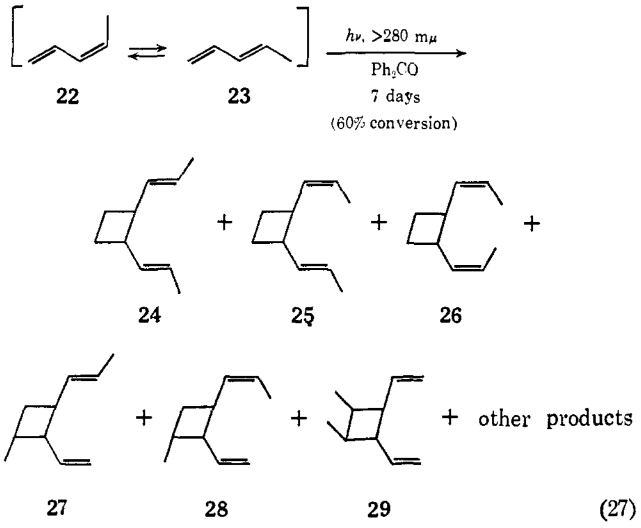


21

The slightly larger amounts of cyclohexenes produced from isoprene compared with those produced from butadiene for any given sensitizer probably reflects the slightly greater concentration of *s-cis*-isoprene in equilibrium with the *s-trans* form compared with the concentration of *s-cis*-butadiene in equilibrium with its *s-trans* form.

c. Piperylene

Photosensitized (benzophenone, benzil, β-acetonaphthone) dimerization of a mixture of *cis*- (**22**) and *trans*-piperylene (**23**) gave at least 15 products, the major of which were tentatively identified as cyclobutanes **24–29** (eq 27).[48] The isomeric piperylenes **22** and **23** are interconverted under the reaction conditions.

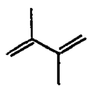


Ferrocene was also used as a sensitizer for the dimerization of a neat mixture of *cis*- and *trans*-piperylene.[68] The structures of the dimers were not specified.

A solid film of polymeric benzaldehyde, $E_T = 55 \pm 5$ kcal/mole, has been used as a sensitizer for the vapor-phase *cis–trans* isomerization and dimerization of the piperylenes **22** and **23**.[71]

d. Other Dienes and Trienes

2,3-Dimethylbutadiene (**30**) gave seven unidentified dimers on irradiation in the presence of six different ketonic sensitizers.[48]



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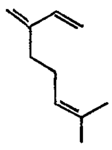

31

A dimer of undetermined structure was obtained from irradiation of myrcene (**31**) with an unspecified sensitizer.[8,29,72] Other reports indicated that only intramolecular cyclization

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[69] J. P. Guillory, C. F. Cook, and D. R. Scott, *J. Am. Chem. Soc.*, **89**, 6776 (1967).

[70] O. L. Chapman, P. J. Nelson, R. W. King, D. J. Trecker, and A. A. Griswold, *Record Chem. Progr.*, **28**, 167 (1967).

[71] G. R. DeMaré, M.-C. Fontaine, and P. Goldfinger, *J. Org. Chem.*, **33**, 2528 (1968).

[72] G.-O. Schenck, W. Hartmann, S. P. Mannsfeld, W. Metzner, R. Steinmetz, I. v. Wilucki, R. Wolgast, and C. H. Krauch, *Angew. Chem.*, **73**, 764 (1961).

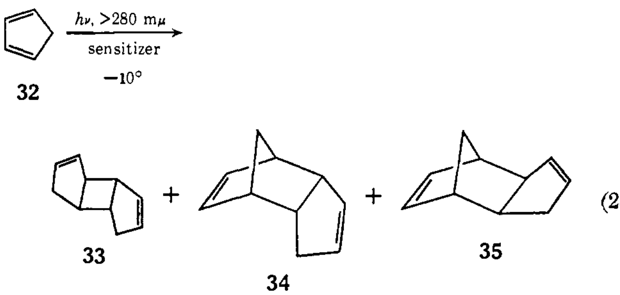
occurred on irradiation of the triene **31** with sensitizers (see below).[60,73,74]

Unspecified dienes have been converted to their dimers by using either 2-cyclopentenone or 2-cyclohexenone as a sensitizer, implying that the triplet states of these enones are formed on irradiation.[75]

2. *Cyclic Dienes and Trienes*

a. 1,3-Cyclopentadiene

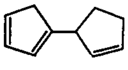
Cyclopentadiene (**32**) when photosensitized by acetophenone, benzophenone, fluorenone, mesityl oxide, acetone (see also under Cross-Addition section below), benzil, or 2,3-pentanedione gave approximately equal amounts of three dimers, **33**–**35** (eq 28).[48,76] The product distribution for an unspecified sensitizer at 1° was 32.5% **33**, 39.7% **34**, and 28.6% **35**.[77] There was some indication that a part of the *endo* dimer **34** may have been a thermal product.[77] The quantum yield for the dimerization was approximately unity.[61,78] The product distribution was insensitive to the sensitizer as expected for a cyclic diene where only a *cis* triplet can be formed. 9-Anthraldehyde (E_{T_1} = *ca.* 42 kcal/mole)[79] was incapable of sensitizing the dimerization of diene **32** presumably because of the lower triplet energy of the aldehyde. However, some of the above sensitizers also have lower triplet energies than does cyclopentadiene, E_T = 58.1 kcal/mole (see Table II).



32

33 + **34** + **35** (28)

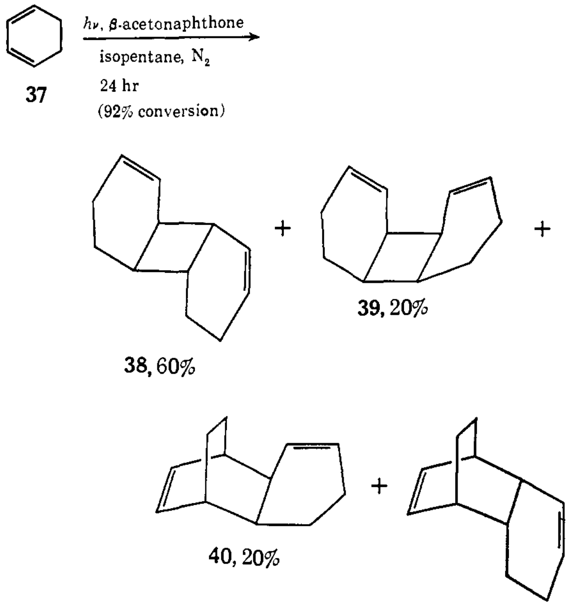
Other workers have reported that with benzophenone as the sensitizer (Corex filter) another dimer, **36**, is also formed in addition to the three cyclo dimers **33**–**35**.[80] At −10° the ratio of **33**–**35**:**36** was 92:8 while at −78° the ratio was 67:33 (13% yield).[80] These authors did not report the distribution among dimers **33**–**35**. Hydrocarbon **36** very likely arises *via* abstraction of an allylic hydrogen atom from diene **32** by the n,π* excited ketone, followed by addition of the allylic radical to **32** and subsequent hydrogen-atom abstraction.



36

b. 1,3-Cyclohexadiene

Irradiation of 1,3-cyclohexadiene (**37**) with a sensitizer[3,72,81] gave three major dimers, **38**–**40**, plus trace amounts of a fourth dimer, **41** (eq 29).[81] Dimer **41** was not formed *via* a thermal side reaction. The relative amounts of products **38**–**40** were relatively insensitive to the sensitizer as shown in Table V.[78,82]



37

38, 60% + **39**, 20% +

40, 20% + **41**, trace (29)

Table V

Product Distribution from Photosensitized Dimerization of 1,3-Cyclohexadiene

Sensitizer	E_{T_1}, *kcal/mole*	*Distribution of dimers, %* 38	39	40	*Quantum yield for* 38–40 *formation*
Benzophenone	68.5	62	16	22	0.30[a]
β-Acetonaphthone	59.3	58	19	23	0.30
Biacetyl	54.9	60	19	21	
Fluorenone	53.3	58	19	23	0.20

[a] 0.037 *M* diene. Quantum yields were 0.31 and 0.40 at diene concentrations of 0.080 and 0.157 *M*, respectively.

The same dimers have been obtained by using a number of other compounds as triplet sensitizers, **42**–**50**, for the liquid-phase dimerization of diene **37**; the distribution was not specified.[83–86] Most of these studies were directed toward gaining an understanding of the photochemistry of the sensitizer rather than of the diene **37**. A solid film of polymeric benzal-

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(73) R. S. H. Liu and G. S. Hammond, *J. Am. Chem. Soc.*, 86, 1892 (1964).

(74) R. S. H. Liu and G. S. Hammond, U. S. Patent 3,380,903 (1968); *Chem. Abstr.*, 69, 44062 (1968).

(75) Reference 13, p 207.

(76) N. J. Turro and G. S. Hammond, *J. Am. Chem. Soc.*, 84, 2841 (1962).

(77) (a) P. D. Bartlett, R. Helgeson, and O. A. Wersel, *Pure Appl. Chem.*, 16, 187 (1968); (b) "Organic Photochemistry," Vol. 2, Plenum Press, New York, N. Y., 1968, pp 187–200.

(78) Reference 13, p 213.

(79) N. C. Yang, M. Nussim, M. J. Jorgenson, and S. Murov, *Tetrahedron Letters*, 3657 (1964).

(80) E. H. Gold and D. Ginsburg, *Angew. Chem.*, 78, 207 (1966); *Angew. Chem. Intern. Ed. Engl.*, 5, 246 (1966).

(81) D. Valentine, N. J. Turro, Jr., and G. S. Hammond, *J. Am. Chem. Soc.*, 86, 5202 (1964).

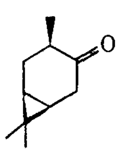
(82) N. J. Turro and P. D. Bartlett, *J. Org. Chem.*, 30, 1849, 4396 (1965).

(83) D. C. Heckert and P. J. Kropp, *J. Am. Chem. Soc.*, 90, 4911 (1968).

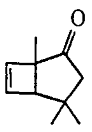
(84) G. S. Hammond, "Twentieth National Organic Chemistry Symposium of the American Chemical Society," 1967, p 141.

(85) D. I. Schuster and D. J. Patel, *J. Am. Chem. Soc.*, 90, 5145 (1968).

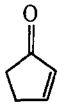
(86) D. I. Schuster, A. C. Fabian, N. P. Kong, W. C. Barringer, W. V. Curran, and D. H. Sussman, *ibid.*, 90, 5027 (1968).



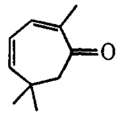
42[83]



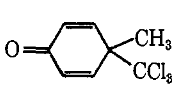
43[86]



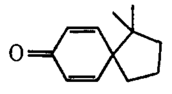
44[86]



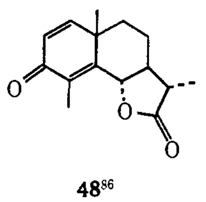
45[86]



46[85,86]



47[86]



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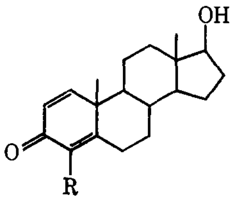
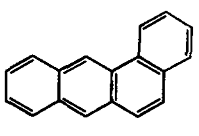


49[86]



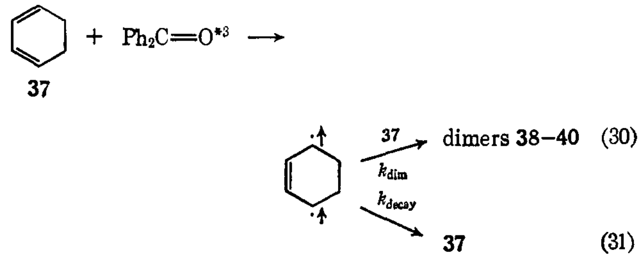
50[64]

R = H, Me, Et, *n*-Bu, *i*-Bu, isoamyl

dehyde has been used as a sensitizer for the vapor-phase dimerization of diene **37**.[71]

The quantum yield for the formation of dimers of diene **37** was reported to be 0.88 for 0.2 *M* benzophenone in neat diene **37**[62,87] or approximately unity.[61] When benzophenone was used as the sensitizer with a 0.21 *M* solution of diene **37**, 88% of the diene triplets underwent dimerization.[88] The ratio of k_{dim} (eq 30) : k_{decay} (eq 31) (Scheme III) is thus 35 : 1.[88] The quantum yield was 0.028 for the formation of the dimers using a 0.21 *M* solution of diene **37** and α-methylnaphthalene as the sensitizer.[87,88] The fluorescence of the sensitizer was largely quenched by diene **37** (ϕ_f/ϕ_{f_0} = 0.054), indicating singlet energy transfer. Naphthalene behaved similarly to α-methylnaphthalene.[87] Naphthalene was also observed to be a very inefficient sensitizer for various diene dimerizations.[87]

Scheme III

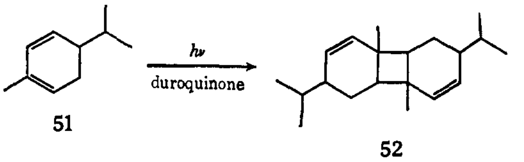


The sensitized dimerization of diene **37** has been used as a means of determining intersystem-crossing efficiencies for sensitizers.[85] This was done by comparing the amount of dimers using a given sensitizer with the amount obtained using a sensitizer for which the quantum yield of intersystem crossing was known, such as benzophenone ($\Phi_{S\to T}$ 1.00).[85]

One report showed a considerable temperature effect on the dimer distribution (Table VI).[89] Another report indicated that the same temperature increase, which had a large relative effect on the dimer distribution from butadiene, had no effect on the distribution from cyclohexadiene (**37**).[78]

c. α-Phellandrene

α-Phellandrene (**51**) gave dimer **52** on irradiation with duroquinone (eq 32)[8,72,90] (however, see section III.B.2.d below concerning this reaction). In contrast to this result, irradiation of (−)-α-phellandrene (**53**) with naphthalene as the sensitizer gave three products, **54**–**56**, all different from **52** (eq 33).[91] Dimer **52** appears to be anomalous compared with the other diene dimers in that it would appear to be formed from a non-di(allylic radical) intermediate.



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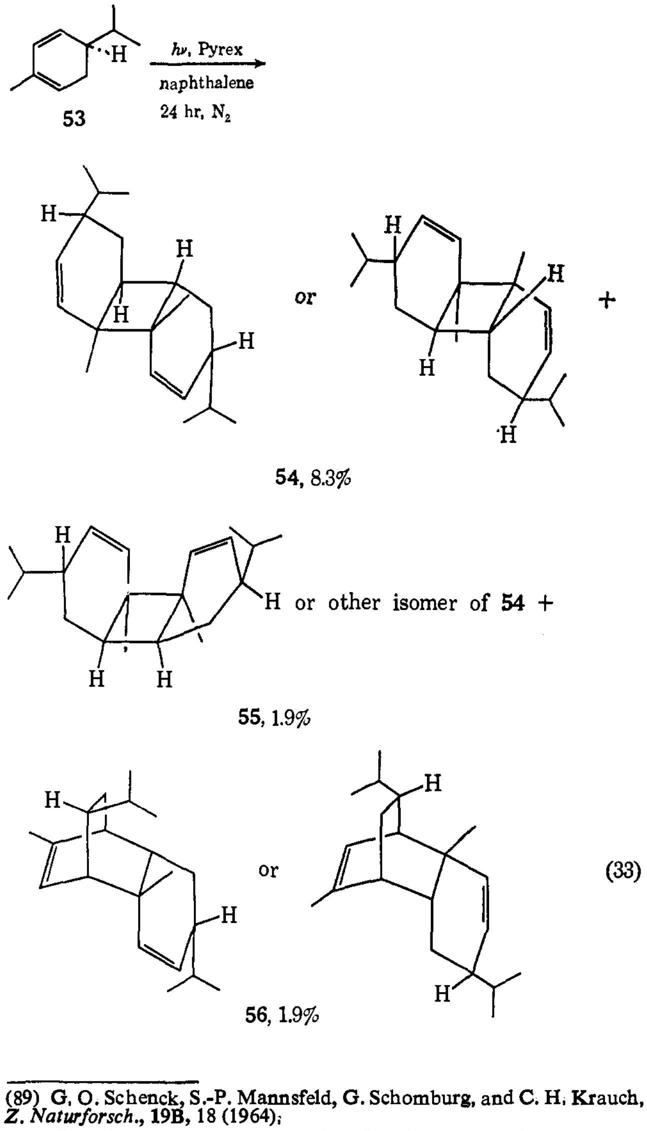

(33)

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(87) L. M. Stevenson and G. S. Hammond, *Pure Appl. Chem.*, 16, 125 (1968); ref 77b, pp 130–131.

(88) L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Am. Chem. Soc.*, 88, 3665, 3893 (1966).

(89) G. O. Schenck, S.-P. Mannsfeld, G. Schomburg, and C. H. Krauch, *Z. Naturforsch.*, 19B, 18 (1964).

(90) G. Koltzenburg, K. Kraft, and G. O. Schenck, *Tetrahedron Letters*, 353 (1965).

(91) J. E. Baldwin and J. P. Nelson, *J. Org. Chem.*, 31, 336 (1966).

Table VI

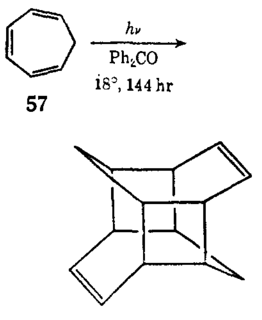
Temperature Effect on Distribution of Dimers from 1,3-Cyclohexadiene[a]

Temp, °C	*Distribution of dimers, %* 38	39	40
−80	83	5	12
20	60	15	25

[a] Benzophenone used as the sensitizer with radiation >330 mμ.

d. Cycloheptatriene

Benzophenone-sensitized dimerization of cycloheptatriene (**57**) gave five dimers, only one of which, **52**, was identified.[92] Another report of the same reaction indicated that only four dimers were formed, one of which was the caged compound **58**.[29] Of the other three, one was a cyclobutane derivative while the other two were 4 + 2 Diels–Alder-type adducts, *endo* and *exo*.[29]



57

58, 2.6%

+ four dimers (34)
52.6%, 23.9%, 14.4%, 5.8%

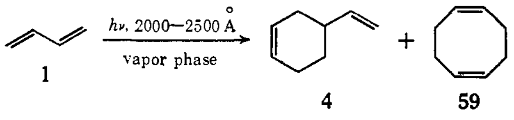
Some sensitized dimerizations are discussed below in the sections on sensitized (III.A) and nonsensitized (III.B) cross-additions where the dimerization of the diene was a side reaction.

B. NONSENSITIZED

1. *Acyclic Dienes*

a. 1,3-Butadiene

Butadiene (**1**) in the gas phase at 4 mm pressure gave two dimers, **4** and **59**, in addition to a large number of other products on irradiation with a medium-pressure mercury arc lamp (eq 35).[93]

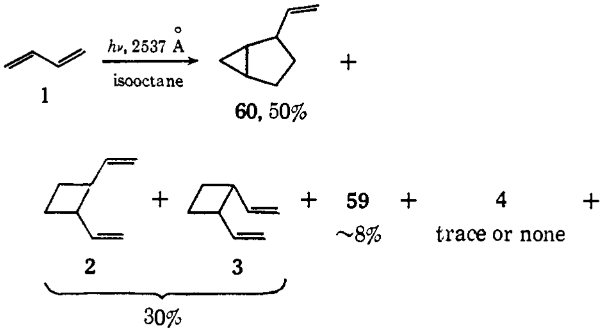


1 4 59

$$+ \underset{6\%}{H_2} + \underset{14\%}{C_2H_2} + \underset{14\%}{C_2H_4} + \underset{8\%}{C_2H_6} + \underset{5\%}{HC{\equiv}CEt} + \underset{5\%}{CH_2{=}C{=}CHMe} +$$

$$\underbrace{CH_4 + MeC{\equiv}CMe + \text{pentene} + C_6H_{12}(\text{two isomers}) + C_6H_6(\text{two isomers}) + C_7H_{10} + \text{polymer}}_{\text{minor products}} \quad (35)$$

The nonsensitized liquid-phase dimerization of butadiene (**1**) has been studied by several groups of workers. In isooctane solution at an intermediate (not specified) concentration, **1** gave at least five dimers, **2–4**, **59**, and **60**, and an unidentified dimer (eq 36).[94] These dimeric products amounted to 10% of the butadiene consumed, the remainder probably being isomers of **1** and polymer.[94] Irradiation of a 6% (volume) solution of diene **1** in cyclohexane with the unfiltered radiation from a 1000-W high-pressure mercury arc lamp (λ ≳200 mμ) gave the isomers **61** and **62** in addition to unidentified dimers and polymer.[95] The quantum yield for the formation of olefin **61** was *ca.* 0.01.[95] Another report indicated **2** (24%), **3** (20%), and **63** (3%) to be some of the products of the direct irradiation of **1**.[45] Both stereoisomers **63** and **64** have been suggested as products of the direct irradiation of **1** among a large number of other dimeric products, all formed almost exclusively *via* an excited singlet state and with a very low quantum yield.[96] Still other reports list **2–4**, **59**, and **60**,[8] and **60**, **63**, and/or **64**, and other dimers[97] as the products of direct irradiation. Apparently the products which one obtains from this reaction are highly sensitive to the reaction conditions.



1

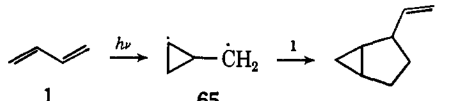
60, 50% +

2 + 3 (30%) + 59 (~8%) + 4 (trace or none) +

unidentified dimer (36)
~10%

61 62 63 64

The formation of the bicyclic dimer **60** has been postulated to involve the addition of **1** to bicyclobutane **62**[97] or alternatively to the 1,3 biradical **65** (eq 37).[98]



1 65 60 (37)

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[92] G. O. Schenck, J. Kuhls, and C. H. Krauch, *Ann.*, **693**, 20 (1966).

[93] R. Srinivasan, *J. Am. Chem. Soc.*, **82**, 5063 (1960).

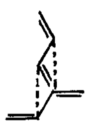
[94] R. Srinivasan and F. I. Sonntag, *ibid.*, **87**, 3778 (1965).

[95] I. Haller and R. Srinivasan, *J. Chem. Phys.*, **40**, 1992 (1964).

[96] Reference 25, p 132.

[97] Reference 13, p 216.

[98] R. Srinivasan, *J. Am. Chem. Soc.*, **90**, 4498 (1968).

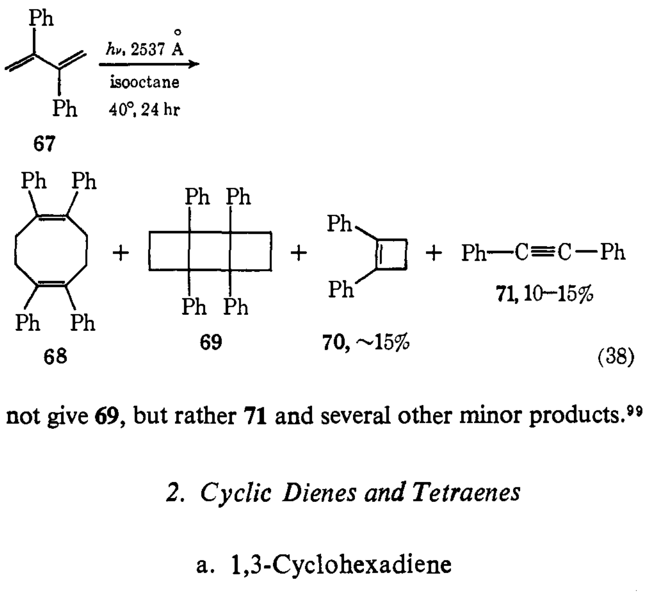


66

The existence of a butadiene eximer, **66**, in which the two central bonds interact, has been predicted from theoretical considerations.[45]

b. 2,3-Diphenyl-1,3-butadiene

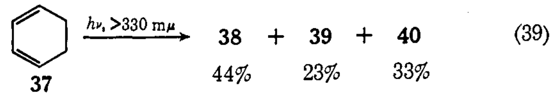
Direct irradiation of 2,3-diphenyl-1,3-butadiene (**67**) gave four products, **68–71**, one of which, **68**, could have been a product of two 1,4 additions, and one, **69**, which could have resulted from two 1,2 additions (eq 38).[99] Further irradiation of **68** did not give **69**, but rather **71** and several other minor products.[99]

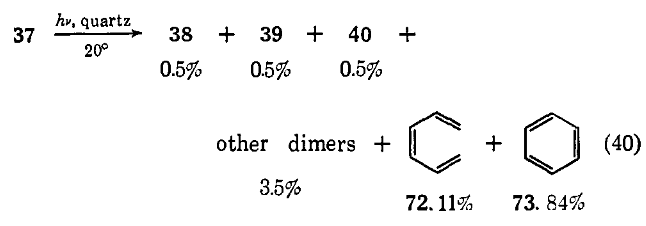


2. Cyclic Dienes and Tetraenes

a. 1,3-Cyclohexadiene

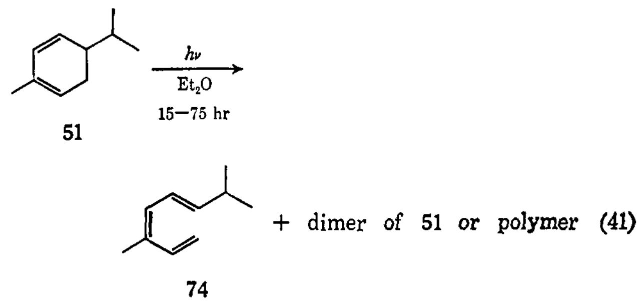
Direct irradiation of diene **37** with light of wavelengths greater than 330 mμ gave the same products as in the sensitized irradiation described above, with the product distribution being more nearly statistical (eq 39).[89] Irradiation through quartz produced primarily ring opening and fragmentation, to give **72** and **73**, respectively (eq 40).[89] Irradiation of **37** through quartz in ether solution at 20° gave only the triene **72**[89] or possibly some dimer or polymer.[100]



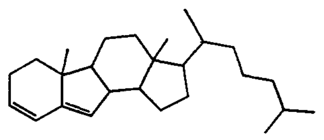


b. Other Dienes and Tetraenes

On direct irradiation α-phellandrene (**51**) gave an unidentified dimer or polymer in addition to a ring-opened product, **74** (eq 41).[100]

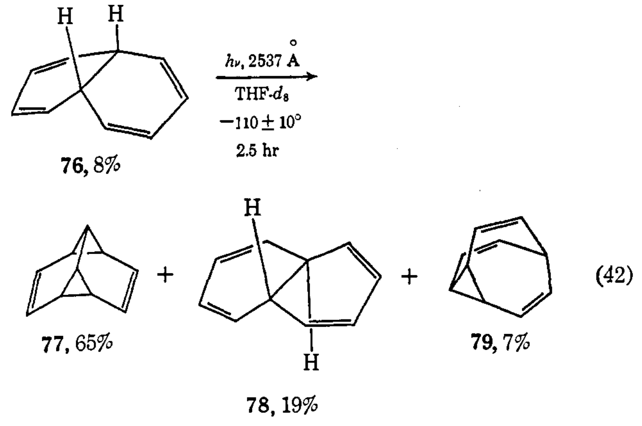


The B-norcholestadiene **75** gave an unidentified dimer (80%) and an alcohol (5%) on direct irradiation in a protic solvent.[38]



75

Although strictly not a dimerization, the valence isomerization of *cis*-9,10-dihydronaphthalene (**76**) is analogous to a dimerization where two identical dienes are contained in the same molecule. Irradiation of a 0.25–0.5 M solution of **76** in tetrahydrofuran-d_8 at low temperature gave one product, **77**, resulting from two 1,4 additions, the *trans*-tetraene **78**, and bullvalene (**79**) (eq 42).[101] The percentages shown in eq 42 represent the composition at the photostationary state. Irradiation of **76** through a Corex filter with a high-pressure mercury arc lamp under the same conditions produced none of the *trans* isomer **78**.[101] Irradiation of the same tetraene **76** in a degassed pentane solution at 0° for 15 hr with the 2537-Å mercury arc line gave bullvalene (**79**), naphthalene, and two unidentified products.[102] It was suggested that these products may have arisen *via* the intermediate formation of the isomer **77**.[102]



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[99] E. H. White and J. P. Anhalt, *Tetrahedron Letters*, 3937 (1965).

[100] R. J. de Kock, N. G. Minnaard, and E. Havinga, *Rec. Trav. Chim.*, 79, 922 (1960).

[101] S. Masamune, R. T. Seidner, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *J. Am. Chem. Soc.*, 90, 5286 (1968).

[102] W. von E. Doering and J. W. Rosenthal, *ibid.*, 88, 2078 (1966).

III. Cross-Addition

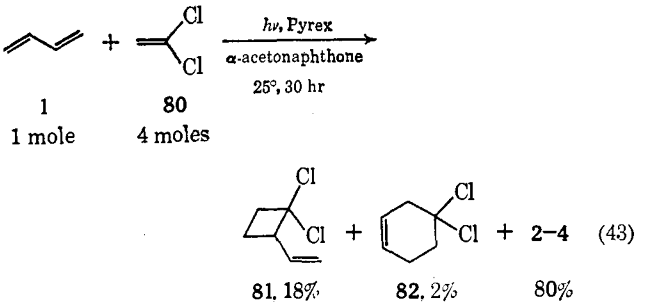
A. SENSITIZED

1. Acyclic Dienes and Trienes

a. 1,3-Butadiene

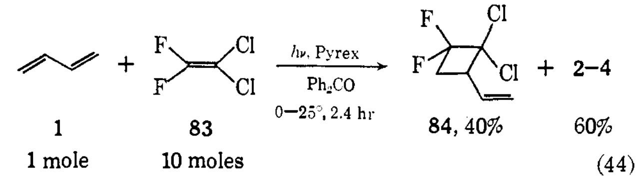
In most of the photosensitized cross-addition reactions described in this section, the diene was probably the species which was the acceptor in the energy-transfer process. In the additions to anhydrides, energy transfer probably occurred to both of the reactants, or possibly in some cases to ground-state complexes of the two reactants.

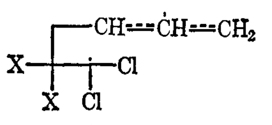
The cross-addition of butadiene (1) to 1,1-dichloroethylene (80) gave small amounts of the cross adducts 81 and 82 in addition to the dimers 2–4 (eq 43).[82] Irradiation of olefins 1 and 80



at −18° for 5 days with β-acetonaphthone as the sensitizer gave the vinylcyclobutane 81 in 11% isolated yield.[103]

With 1,1-difluoro-2,2-dichloroethylene (83), 1 gave only the cyclobutane 84 in addition to dimers when a higher energy sensitizer was used (eq 44).[82] The quantum yield for the formation of 84 was *ca.* 0.001.[82] In both of these reactions the cyclobutanes 81 and 84 were formed *via* the most stable diradical intermediate 85.[82]





85

Table VII

Composition of Products from Photosensitized Cross-Addition of Butadiene and α-Acetoxyacrylonitrile

	Sensitizer^a	E_{T_1}, kcal/mole	*Distribution of cross-adducts and dimers, %* 87 + 88	89	2	3	4
1	Acetophenone	73.6	34	0.7	56	7	2
2	Benzophenone	68.5	33	0.9	54	10	3
3	Triphenylene^b	66.6	30	0.9	69	*c*	*d*
4	Anthraquinone^b	62.4	60	3	31	6	*d*
5	Flavone	62.0	32	1.6	52	12	3
6	β-Naphthyl phenyl ketone	59.6	41	7	47	4	2
7	Biacetyl	54.9	38	12	28	7	14
8	Benzil	53.7	34	12	30	5	18
9	Camphorquinone	50	28	12	23	7	29
10	Pyrene^b	48.7	38	17	34	11	*d*
11	Anthracene^b	42.5	41	6	45	8	*d*
12	9,10-Dibromoanthracene^b	40.2	45	1	44	10	*d*

^a Sensitizer (1.0 mmole) in 5.0 mmoles of 1 and 5.0 mmoles of 86. ^b Saturated solution of sensitizer in equimolar mixture of 1 and 86. ^c Not determined due to low over-all conversion. ^d Not determined due to interference by a large excess of 86 and the presence of a small amount of 4 in the starting diene 1.

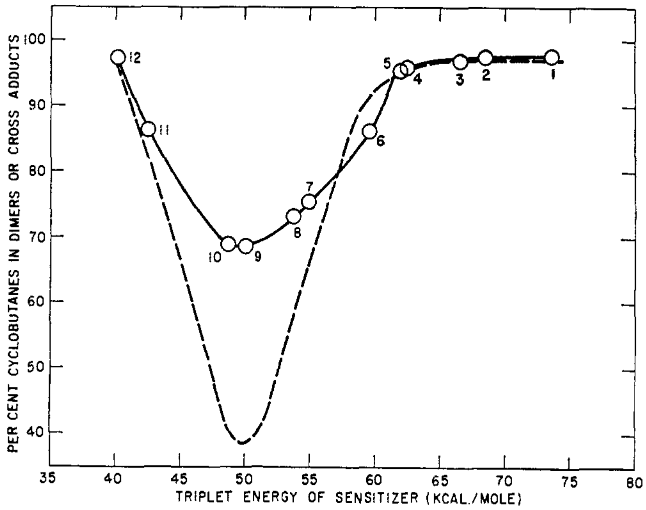
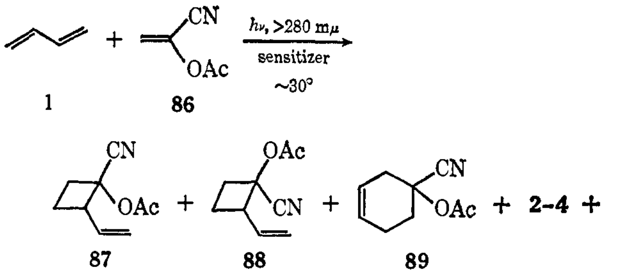


Figure 3. Butadiene–α-acetoxyacrylonitrile cross-adduct composition *vs.* triplet energy of sensitizer (solid line); butadiene dimer composition (dashed line, data from ref 51). Reprinted from the *Journal of the American Chemical Society* by permission of the copyright owners, The American Chemical Society.

Irradiation of equimolar quantities of butadiene (1) and α-acetoxyacrylonitrile (86) with 0.2 mole of a sensitizer gave three cross-adducts 87–89 and the three dimers 2–4 (eq 45).[104] The distribution of the six products, 87–89 and 2–4, as a function of the sensitizer triplet energy is given in Table VII.[105] The ratio of cyclobutanes to cyclohexenes is shown in Figure 3.[105] The explanation[105] for the general shape of the curve was the same as that given for the butadiene (1) dimerization.[51] The greater amount of cyclobutanes 87 and 88 which were found in the cross-addition than were found in the dimerization of 2 and 3 with sensitizers of *ca.* 50 kcal/mole triplet energy was attributed to a ring closure of the cross-adduct diradical 90 which was faster than that of the dimer diradical



copolymer of 1 and 86 (45)

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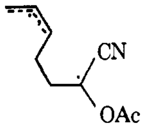
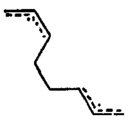
(103) P. D. Bartlett and K. E. Schueller, *J. Am. Chem. Soc.*, 90, 6071 (1968).

(104) W. L. Dilling and J. C. Little, *ibid.*, 89, 2741 (1967).

(105) W. L. Dilling, *ibid.*, 89, 2742 (1967).



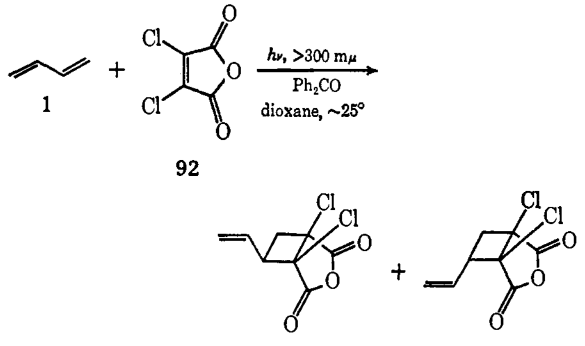
90



91

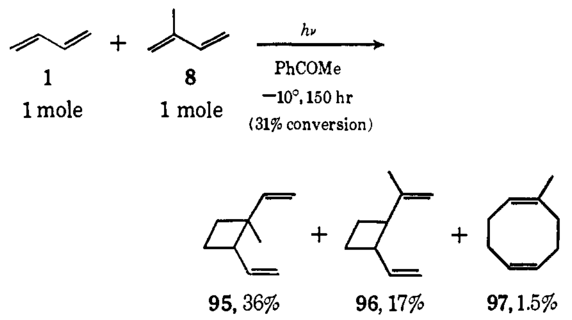
91.[105] This greater rate was attributed to a polar contribution in the transition state for coupling of the two unlike radicals.[105] However, it should be pointed out that other factors, such as rates of intersystem crossing, may play a part in determining these product distributions.

Dichloromaleic anhydride (**92**) could be added to diene **1** in the presence of benzophenone (eq 46).[106] This reaction could be achieved in the absence of a sensitizer but with lower efficiency.[106]

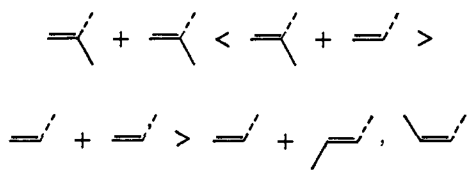


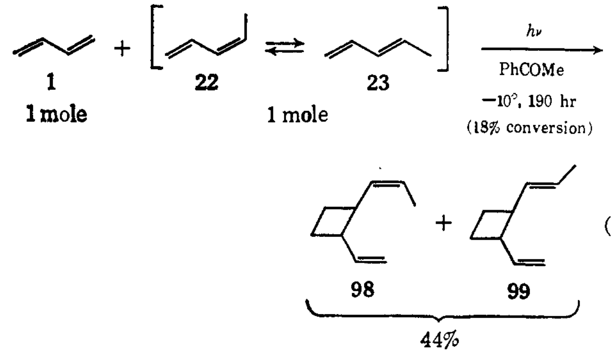
(46)

Diene **1** has been added to several other acyclic conjugated dienes, **8** (eq 47), **22** and **23** (eq 48), and **30** (eq 49), to give cross-addition products **95–101** in addition to other unidentified products.[107] It is not clear which diene in the above reactions is being excited since the triplet energies of all of them are similar.[56] Probably both of the reacting pairs of dienes were excited in these reactions. A part of the cyclooctadiene **101** was formed *via* a thermal reaction from another photoproduct.[107] Based on the relative amounts of products from the cross-additions of the dienes **1**, **8**, **22**, **23**, and **30**, the following relative reactivities toward addition of the different types of olefinic groups were determined.[107]

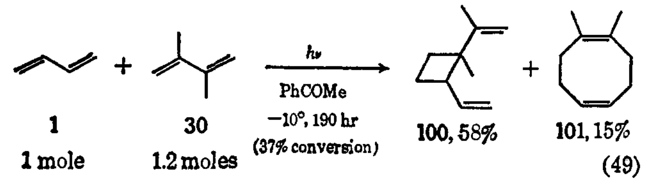


(47)



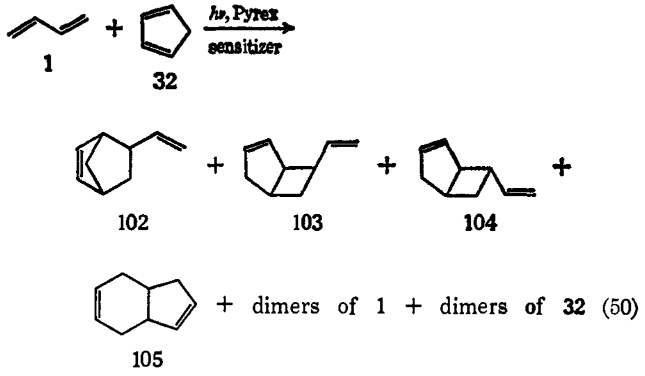


(48)



(49)

Cross-addition of the two dienes **1** and **32** to give **102–105** was achieved by irradiation with either acetophenone[108] or benzophenone (eq 50).[109] The product distribution and yield varied slightly with the sensitizer (Table VIII).[108, 109] It may be noted that butadiene (**1**) reacted mainly *via* 1,2 addition, while cyclopentadiene (**32**) reacted about equally *via* 1,2 and 1,4 addition.[109] Also it may be noted that the distribution between cross-adducts and dimers was nearly statistical.



(50)

Irradiation of a mixture of dienes **1** and **37** with a sensitizer gave a cross-adduct of unreported structure.[110]

b. Isoprene

Benzophenone-sensitized addition of isoprene (**8**) to the olefin **83** gave two cyclobutane derivatives, **106** and **107**, in addition to dimers of **8** (eq 51).[82]

Cross-addition of **8** to α-acetoxyacrylonitrile (**86**) (eq 52) gave the six cycloadducts **108–113** and the same seven diene dimers **9–15**, which were obtained in the photosensitized dimerization of **8**.[111] Less than 1%, with respect to the cross-adducts **108–113**, of the nitrile dimers **114** and **115** were formed in this reaction, indicating that the major portion of the reaction proceeded *via* the diene triplets rather than the nitrile triplet.[111] Small amounts of unidentified adducts of diene **8**

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(106) H.-D. Scharf and F. Korte, *Chem. Ber.*, **99**, 1299 (1966).

(107) G. Sartori, V. Turba, A. Valvassori, and M. Riva, *Tetrahedron Letters*, 211 (1966).

(108) G. Sartori and V. Turba, French Patent 1,479,949 (1967); *Chem. Abstr.*, **68**, 12562 (1968).

(109) G. Sartori, V. Turba, A. Valvassori, and M. Riva, *Tetrahedron Letters*, 4777 (1966).

(110) R. S.-H. Liu, *Dissertation Abstr.*, **26**, 2478 (1965).

(111) W. L. Dilling and R. D. Kroening, *Tetrahedron Letters*, 5101 (1968).

Table VIII

Yields of Products from Photosensitized Cross-Addition of Butadiene and Cyclopentadiene

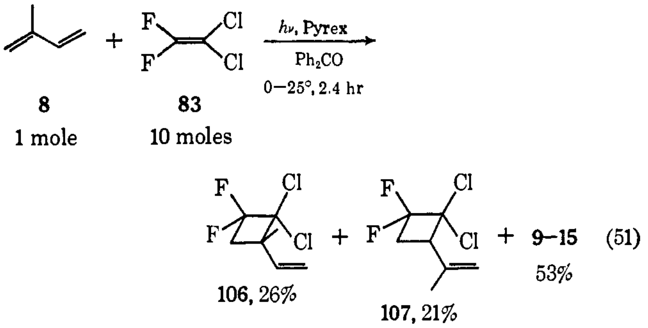
Sensitizer	*Molar ratio* 1/32	*Temp, °C*	*Time, hr*	*Product yields, %* 102	103	104	105	*Dimers of* 1	*Dimers of* 32
Acetophenone	1.04	−20°	170	25	30	9	3	...[b]	...[b]
Benzophenone	1.00	−15°	200[a]	20	19.5	6.5	1.5	26.5	26

[a] 32% conversion. [b] Not reported.

Table IX

Product Distribution from Photosensitized Cycloaddition of Isoprene to α-Acetoxyacrylonitrile

Sensitizer	E_{T_1}, *kcal/mole*	*Product distribution, %* 108	109	110 + 111	112	113	9	10	11	12 + 13	14	15
Acetophenone	73.6	8.1	8.4	10.7	(1.5)		19.9	22.0	6.4	20.6	2.1	0.5
Benzil	53.7	7.6	5.6	10.0	~11.2	~5.6	7.2	7.2	1.8	12.6	22.8	8.4



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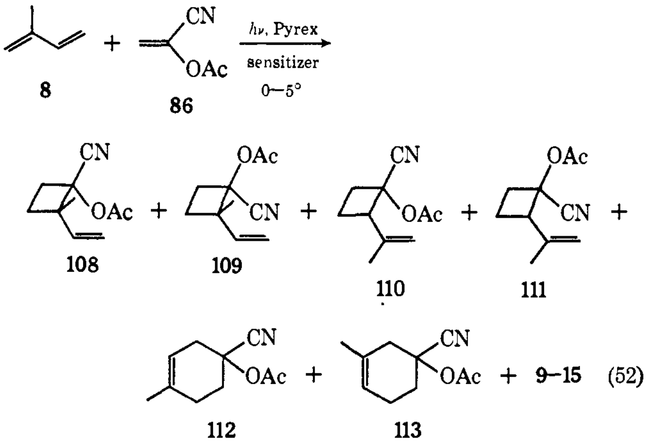

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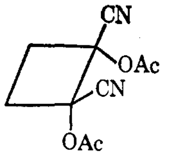

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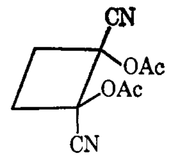
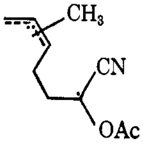


115

with benzil were formed when the latter was used as the sensitizer.[111] At diene 8 conversions above 30–40% extensive polymerization of the monomers 8 and 86 occurred, thus limiting the usefulness of this reaction for synthetic purposes.[111] The product distribution at low conversions starting with equimolar amounts of the olefins 8 and 86 (Table IX) again demonstrates the dependence of the product ratios on the sensitizer triplet energy.[111] The cyclobutane:cyclohexene ratios for cross-addition and dimerization are consistent with the cross-adduct diradical, **116**, undergoing a faster ring closure then the dimer diradical, **117**.[111]



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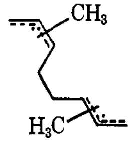
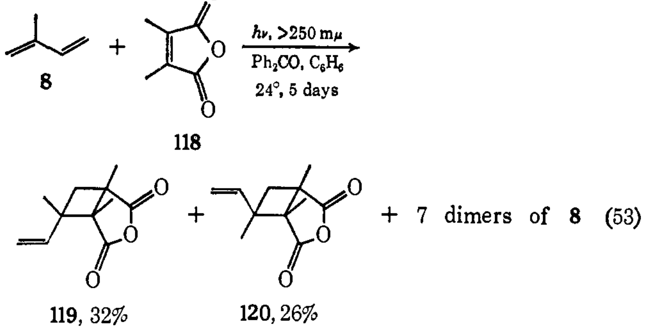


117

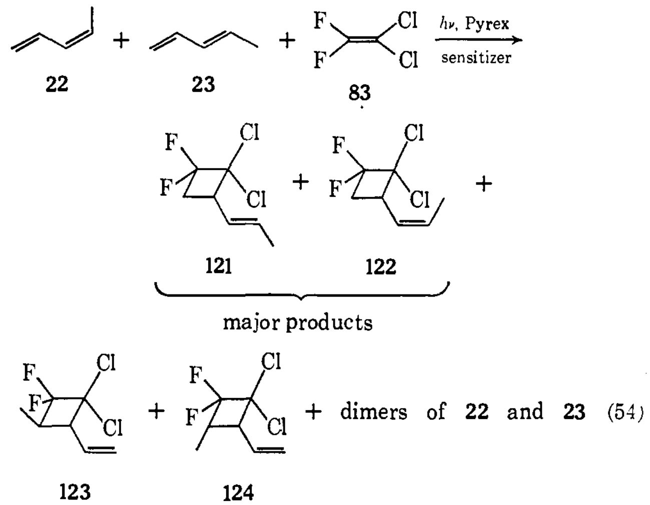
Isoprene (**8**) has also been added to dimethylmaleic anhydride (**118**) (eq 53).[92,112]



(53)

c. Piperylene

A mixture of *cis*- and *trans*-piperylene (**22** and **23**) gave cross-adducts **121–124** with olefin **83** in addition to other products (eq 54).[82]



(54)

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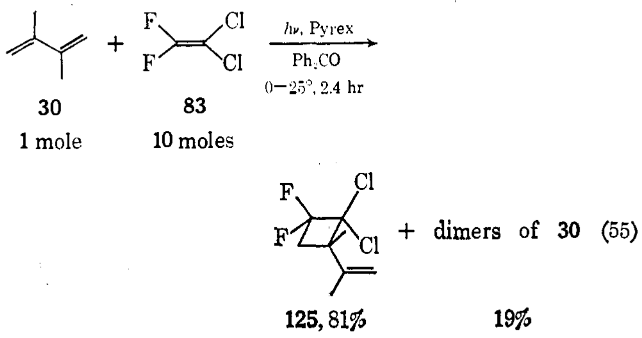
(112) G. O. Schenck, J. Kuhls, and C. H. Krauch, *Z. Naturforsch.*, 20B, 635 (1965).

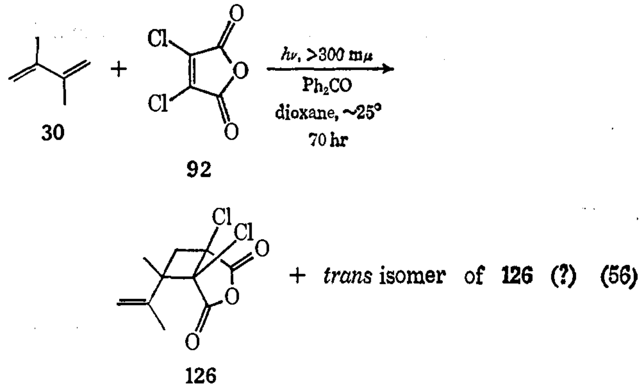
d. 2,3-Dimethyl-1,3-butadiene

2,3-Dimethylbutadiene (**30**) was added to the haloethylene **83** (eq 55).[82]



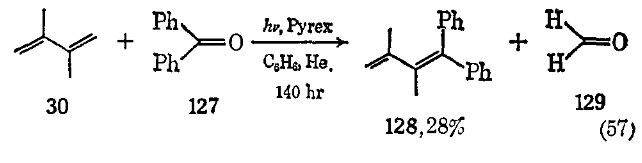
30 1 mole + **83** 10 moles → **125**, 81% + dimers of **30** 19% (55)

As with butadiene (**1**) above, the dimethyl derivative **30** could be added to the anhydride **92** in the presence of benzophenone, although the addition also was observed in lower yield without the sensitizer (eq 56).[106,113]



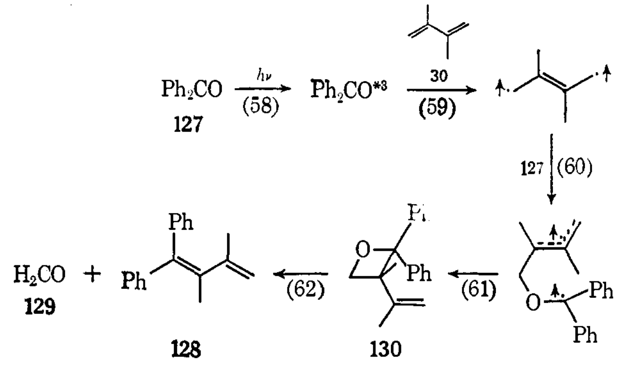
30 + **92** → **126** + *trans* isomer of **126** (?) (56)

A reaction which probably involves a photosensitized cycloaddition of **30** is that with benzophenone (**127**) (eq 57).[114] A high concentration of ketone **127** (0.5–2.0 equiv) was required for this reaction. The products **128** and **129** were rationalized as arising from decomposition of the oxetane **130** formed *via* addition of the diene triplet to ketone **127** (eq 60).[114] The proposed mechanism is outlined in Scheme IV.[114] Evidence for the quenching of benzophenone triplets by **30** was obtained by comparing the rate of photoreduction of **127** by benzhydrol in the presence and absence of the diene.[114] The only difference between this reaction and the photosensitized dimerization of **30** described above apparently is the much lower concentration of ketone **127** in the dimerization.[114]



30 + **127** → **128**, 28% + **129** (57)

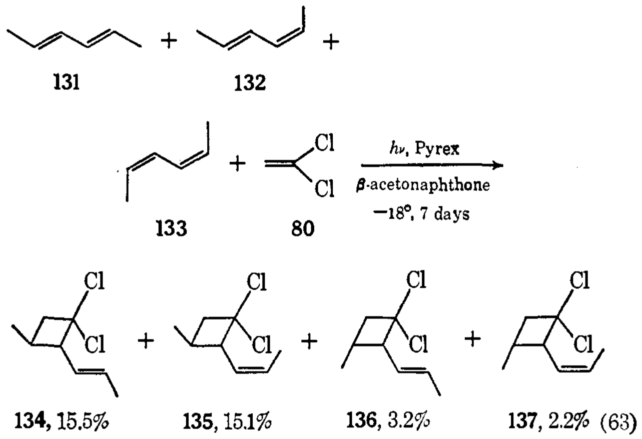
Scheme IV



127 **129** **128** **130**

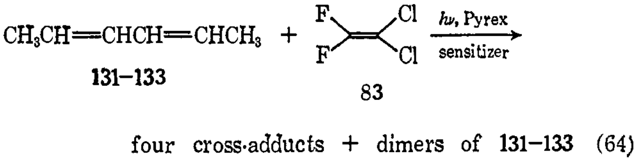
e. 2,4-Hexadiene

Irradiation of a mixture of hexadiene isomers **131–133** in 1,1-dichloroethylene (**80**) containing β-acetonaphthone gave four stereoisomeric cyclobutane derivatives **134–137** (eq 63).[104] The stereochemistry about the cyclobutane ring was uncertain.[104]



131 + **132** + **133** + **80** → **134**, 15.5% + **135**, 15.1% + **136**, 3.2% + **137**, 2.2% (63)

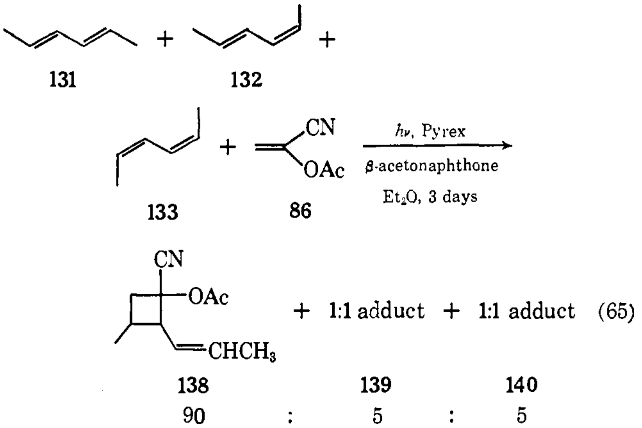
The hexadienes **131–133** were also added to the haloolefin **83** (eq 64).[82] The dienes **131–133** underwent *cis–trans* isomerization under the reaction conditions. In general all of the above additions to olefin **83** required sensitizers with triplet



$CH_3CH{=}CHCH{=}CHCH_3 + F_2C{=}CCl_2 \xrightarrow[\text{sensitizer}]{h\nu,\ \text{Pyrex}}$

131–133 **83**

four cross-adducts + dimers of 131–133 (64)



131 + **132** + **133** + **86** → **138** + 1:1 adduct **139** + 1:1 adduct **140** (65)

90 : 5 : 5

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(113) H. D. Scharf and F. Korte, *Angew. Chem.*, 77, 1037 (1965); *Angew. Chem. Intern. Ed. Engl.*, 4, 989 (1965).

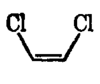
(114) J. Saltiel, R. M. Coates, and W. G. Dauben, *J. Am. Chem. Soc.*, 88, 2745 (1966).

energies above 53 kcal/mole.[82] No appreciable effect on the reaction was observed by a variation in the solvent: acetonitrile, ether, cyclohexane, or methanol.[82]

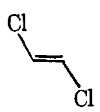
Similarly, dienes **131–133** were added to olefin **86** (eq 65).[115] The cyclobutyl adducts **138** consisted of at least two isomers in a 83:17 ratio.[115] The 1:1 adduct **139** may be a cyclohexene derivative.[115]

f. Other Dienes and Trienes

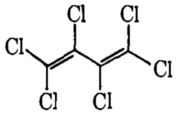
Dienes (unspecified) were also successfully added to the *cis*- and *trans*-dichloroethylenes **141** and **142**, but not to the diene **143**.[82]



141

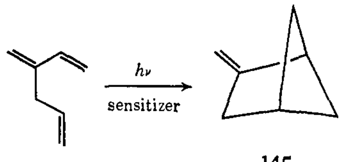


142

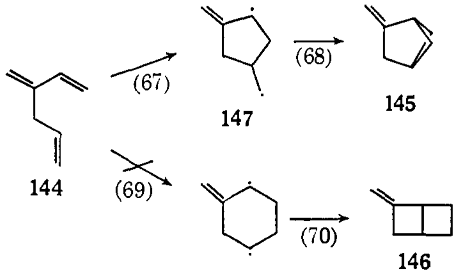


143

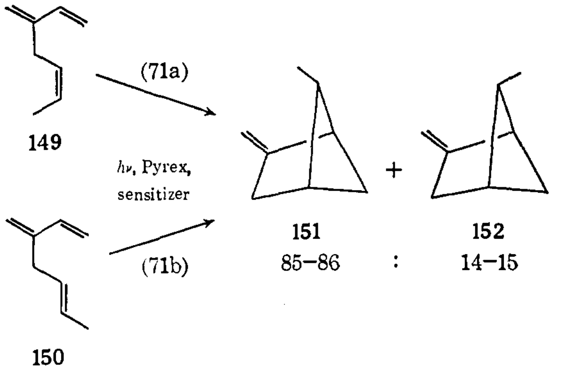
Several intramolecular analogs of sensitized cross-addition reactions have been reported. 3-Methylene-1,5-hexadiene (**144**) gave the methylenebicyclohexane **145** quantitatively on photosensitization with acetophenone, benzophenone, triphenylene, β-acetonaphthone, or fluorenone in hexane, benzene, or ether solution (eq 66).[60,116] From a 1.7% solution of the triene **144** in ether with β-acetonaphthone as the sensitizer was isolated the bicyclohexane **145** in 68% yield;[60] a 0.3% solution of **144** in *n*-pentane or cyclopentane with benzophenone as the sensitizer gave **145** in 85% yield.[117] Photosensitization of solutions of **144** more concentrated than 2% led to side products such as dimers. Direct irradiation of triene **144** in *n*-pentane or cyclopentane through a Corex filter led to valence isomerization of the conjugated diene to a cyclobutene as the only product.[117] The formation of the bicyclo[2.1.1]hexane **145** instead of a bicyclo[2.2.0]hexane, **146**, is probably due to a selectivity for the formation of a five-membered ring, **147** (eq 67), rather than a six-membered ring, **148** (eq 69).[60] This selectivity may be due to kinetic control in the first addition step. Triplet states of conjugated dienes have large amounts, *ca.* 60 kcal/mole, of excitation energy, and therefore the course of the reaction may be determined by the probability of the various available pathways.[60] The formation of a five-membered ring as in **147** is more probable than the formation of a six-membered ring as in **148** owing to the radicals being closer together in the 1,5 positions than in the 1,6 positions.[60] Apparently the stability of the two diradicals **147** and **148** has little effect on the course of the ring closure. It was pointed out that the failure to form the bicyclo[2.2.0]hexane **146** was not due to the reversibility of the first step (eq 69) and the failure of the second step (eq 70), since no isomerization of a methyl group on C-5 occurred in a related triene (see below).



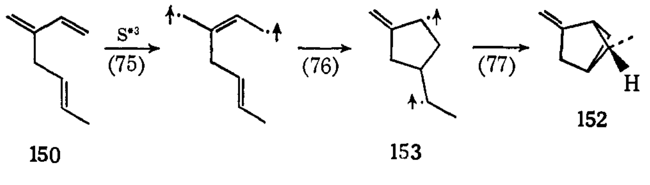
(66)



The isomeric trienes **149** and **150** gave the same mixture of bicyclohexanes **151** and **152** on irradiation either as 1% solutions in ether with β-acetonaphthone as the sensitizer or as 2% solutions in methanol with 0.01 *M* triphenylene as the sensitizer (eq 71a and b).[60,116] The trienes **149** and **150** were not interconverted under the reaction conditions.[60,116] There was no variation in the initial rates of reaction of **149** and **150**, implying that there was no selectivity in energy transfer to the two trienes (eq 72 and 75) nor any difference in the efficiencies of cyclization of the triplets derived from them (eq 73 and 76).[60] The formation of the same product mixture from either triene **149** and **150** indicates a common intermediate **153** which is rotationally equilibrated before ring closure occurs (Scheme V).[60] The slow rate of ring closure of the triplet diradical **153** (eq 74 and 77) relative to rotation (eq 78) may be due either to the relatively slow rate of spin inversion, which must occur before the final ring closure, or to the strain, compared with acyclic 1,4 diradicals, involved in bringing the two radical sites of **153** within bonding distance.[60]



Scheme V



The dimethyl triene **154** (2% solution) underwent an analogous ring closure (eq 79).[60,116]

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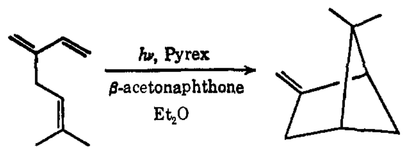
(115) P. D. Bartlett and K. E. Schueller, *J. Am. Chem. Soc.*, 90, 6077 (1968).

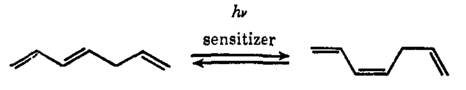
(116) R. S. H. Liu, *Tetrahedron Letters*, 2159 (1966).

(117) J. L. Charlton, P. deMayo, and L. Skattebøl, *ibid.*, 4679 (1965).

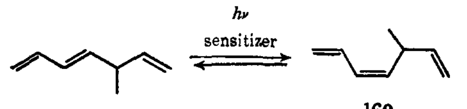


154 **155**, 100% (79)

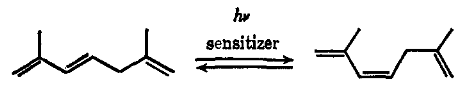
Three related trienes **156–158**, with the allylic moiety on the terminus of the diene, led only to *cis–trans* isomerization on photosensitization (eq 80–82).[60] Two minor unidentified products were also formed from triene **157** (eq 81).[60] After irradiation of triene **158** for 2 days as a 2% solution in ether with β-acetonaphthone as the sensitizer, a photostationary state consisting of approximately equal amounts of isomers **158** and **161** was reached (eq 82).[60]



156 **159** (80)

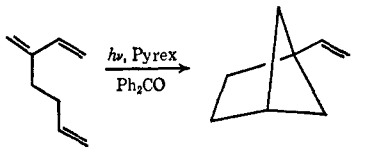


157 **160** (81)



158 **161** (82)

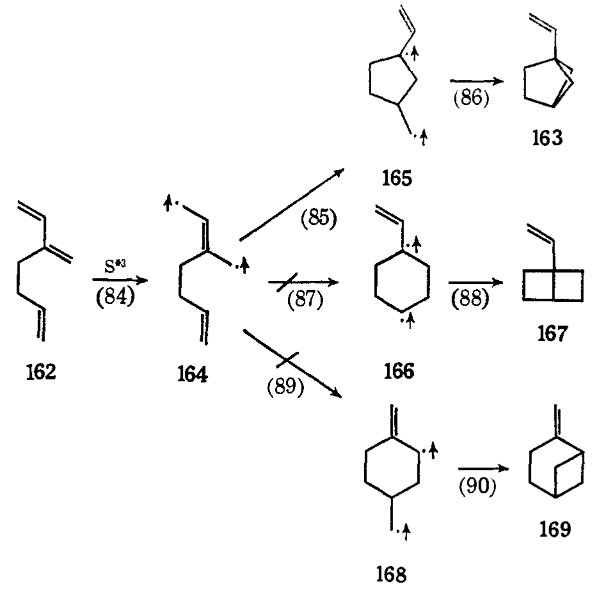
A bicyclo[2.1.1]hexane, **163**, is also formed on the photosensitized ring closure of 3-methylene-1,6-heptadiene (**162**) (eq 83).[60] The quantum yield for the formation of the bicyclohexane **163** was 0.021 with 0.100 *M* triene **162** and 0.011 *M* benzophenone in *n*-hexane solution using 3500-Å radiation.[60] This ring closure was also achieved using β-acetonaphthone as the sensitizer in a 1% solution of triene **162**.[60] In this reaction one again sees the preference for the formation of a five-membered ring intermediate, **166** (eq 85), probably for the same reasons outlined above for compound **144**.[60]

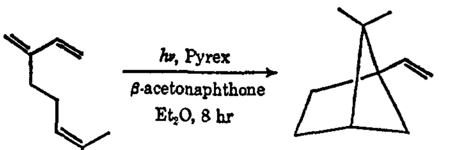


162 **163**, 100% (83)

Myrcene (**31**) gave the bicyclohexane **170** on irradiation with acetophenone, benzophenone, triphenylene, β-acetonaphthone, benzil, or fluorenone as the sensitizer in ether, benzene, or hexane solutions (eq 91).[60,73,74] With benzophenone in a 5% solution of triene **31** the quantum yield for the formation of the bicyclohexane **170** was 0.05.[73] The quantum yield was 0.023 ± 0.01 using 0.1 *M* benzophenone and a 1% solution of myrcene (**31**) in benzene solution.[60] At a concentration of 10% **31** side reactions occurred.[60] Naphthalene has also been used as a sensitizer for this ring closure.[87] Less product **170** was formed at 1.0 *M* triene **31** than at 0.5 *M*, and none was formed at 5.0 *M* (half-quenching of naphthalene occurred at 0.29 *M* **31**).[87] No other cyclization products were detected.[87]

The same transformation (eq 91) also has been achieved using a heterogeneous sensitizing system.[118] Irradiation of a suspension of polyvinyl phenyl ketone, E_T = 72.4 kcal/mole, in myrcene (**31**) for 17 hr gave the bicyclohexane **170** in 20% yield.[118]



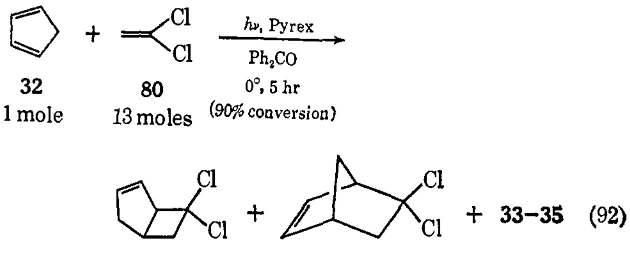


31 **170**, 75% (91)

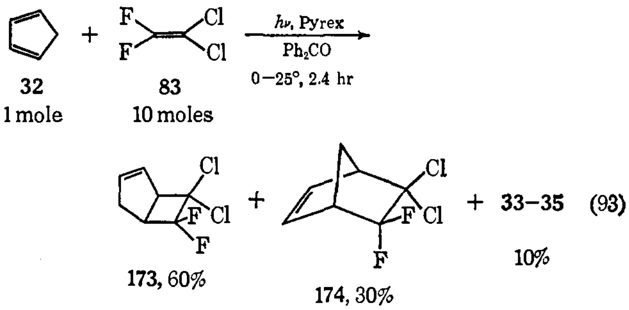
2. *Cyclic Dienes and Trienes*

a. 1,3-Cyclopentadiene

Cyclopentadiene (**32**) was successfully added to olefins **80**, **83**, and **175** (eq 92–94).[82]



171, 48% 172, 32% 20% (92)



173, 60% 174, 30% 10% (93)

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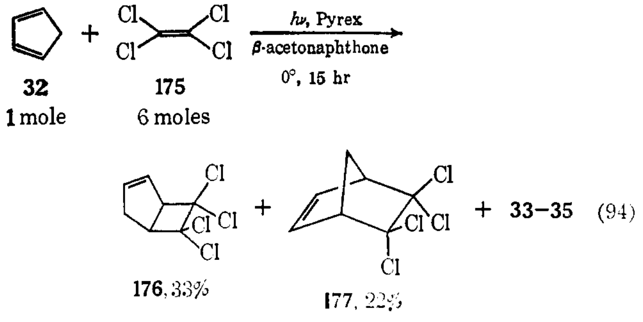
(118) P. A. Leermakers and F. C. James, *J. Org. Chem.*, **32**, 2898 (1967);

Table X

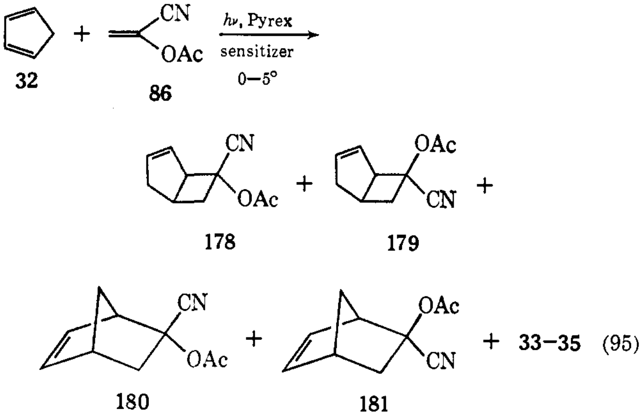
Product Distribution from the Photosensitized Cycloaddition of Cyclopentadiene to *cis*- and *trans*-Dichloroethylene. Effect of Sensitizer[a]

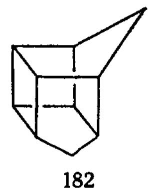
Olefin	*Sensitizer*	E_T, *kcal/mole*	*Olefin isomerization, %* *With* **32**	*Without* **32**	*Distribution, %* **184–189**	**33–35**	*Distribution of cross-adducts, %* **184**	**185**	**186** *or* **187**	**187** *or* **186**	**188**	**189**
141	β-Acetonaphthone	59.3	1	2.8	30.6	69.4	2.8	21.7	53.0	8.8	1.0	12.7[b]
	α-Acetonaphthone	56.4	1	0.9	31.6	68.4	2.8	21.6	52.6	9.3	1.0	12.6
	Biacetyl	54.9	<1	...	35.5	64.5	2.9	22.4	52.6	8.2	0.9	13.0
142	β-Acetonaphthone	59.3	2.1	1.7	68.0	32.0	4.1	10.0	18.9	11.1	2.4	53.5[c]
	α-Acetonaphthone	56.4	1.7	1.1	68.4	31.6	4.2	10.0	18.5	10.8	2.5	54.0
	Biacetyl	54.9	<3	...	73.0	27.0	3.8	9.4	18.5	11.7	2.4	54.2

[a] Molar ratio of **32**:**141** or **142**:sensitizer was 1:10:*ca.* 0.2. Irradiated with a 450-W high-pressure mercury arc lamp through a Pyrex filter at 1 ± 0.5° for 15 hr. [b] Less than 0.3% of *exo,cis*-4,5-dichlorobicyclo[2.2.1]-2-heptene formed. [c] Less than 0.2% of *exo,cis*-4,5-dichlorobicyclo[2.2.1]-2-heptene formed.



Diene **32** has also been added to α-acetoxyacrylonitrile (**86**) using either acetophenone or benzil as the sensitizer (eq 95).[1] Approximately equal amounts of the four cross-adducts **178**–**181** were formed using either sensitizer.[1] At high conversions using acetophenone as the sensitizer the caged dimer **182** was also formed, probably by a secondary reaction of the *endo* dimer **34**.[1] The intermediate in the cross-addition was postulated to be the diradical **183**.[1]





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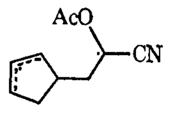

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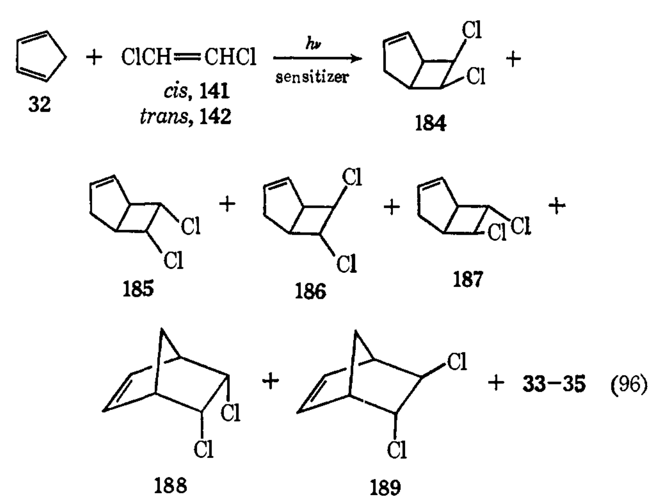

Irradiation of diene **32** with either *cis*- or *trans*-dichloroethylene (**141** or **142**) and a sensitizer gave four 1,2 adducts, **184**–**187**, and two 1,4 adducts, **188** and **189** (eq 96).[77,119] The data in Table X show that there is no significant effect of the sensitizer on the product distribution, nor is there a significant amount of isomerization of the dichloroethylenes **141** and **142**.[77,119] The triplet energy of *trans*-dichloroethylene (**142**) is *ca.* 60–62 kcal/mole, and therefore should not be excited by the sensitizers used. However, the two lower energy sensitizers in Table X also have lower triplet energies than does cyclopentadiene (**32**), E_T = 58.1 kcal/mole. Nonvertical energy transfer may be occurring in these cases. The relative reactivity of cyclopentadiene (**32**) and *cis*-dichloroethylene (**141**) toward triplet cyclopentadiene is >20:1 while that for **32** and the *trans* isomer **142** is <5:1, making the *trans* isomer **142** about four times as reactive as the *cis* isomer **141**.[77] No complexes between diene **32** and the dichloroethylenes **141** and **142** were detected; the data in Table XI for solutions of different concentrations also are in accord with this conclusion.[77] The effect of temperature on the product distribution is shown in Table XII.[77] The relative amounts of products containing *cis*- and *trans*-chlorine atoms and the relative amounts of products resulting from 1,2 and 1,4 cycloaddition to the diene at −25 and 25° are shown in Table XIII.[77] It is obvious that some rotation about the CHCl–CHCl bond occurs in the intermediate diradicals **190** and **191**. However, the diradicals have not reached rotational equilibrium at the moment of ring closure as evidenced by the fact that the cyclobutyl product ratios from

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(119) P. D. Bartlett, *Science*, **159**, 833 (1968).

Table XI

Product Distribution from the α-Acetonaphthone-Sensitized Cycloaddition of Cyclopentadiene to *cis*- and *trans*-Dichloroethylene. Effect of Concentration[a]

		Distribution, %		*Distribution of cross-adducts, %*					
Olefin	*Diluent,*[b] *moles*	184–189	33–35	184	185	186 *or* 187	187 *or* 186	188	189
141	7.2	17.0	83.0	2.7	21.2	53.4	8.9	1.1	12.7
	0	19.5	80.5	3.0	21.2	52.6	9.5	1.2	12.6
142	7.2	46.7	53.3	5.5	10.1	16.4	10.9	3.0	54.1
	0	48.8	51.2	4.6	10.5	18.3	10.7	2.5	53.3

[a] 1.0 mole of **32**, 2.0 moles of **141** or **142**, and 0.26 mole of sensitizer. Irradiated at 1 ± 0.5° through Pyrex filter. [b] 1,2-Dichloroethane.

Table XII

Product Distribution from the α-Acetonaphthone-Sensitized Cycloaddition of Cyclopentadiene to *cis*- and *trans*-Dichloroethylene. Effect of Temperature[a]

			Distribution, %		*Distribution of cross-adducts, %*					
Olefin	*Temp, °C*	**141** *or* **142** *isomerization, %*	184–189	33–35	184	185	186 *or* 187	187 *or* 186	188	189
141	−24.8 ± 0.2	~0.5	30.4	69.6	2.7	22.3	56.8	5.2	1.2	11.8
	1 ± 0.5	1.0	31.6	68.4	2.8	21.6	52.6	9.3	1.0	12.6
	25.0 ± 0.02	1	40.5	59.5	3.1	20.3	49.4	13.6	0.9	12.7
142	−24.8 ± 0.2	~1	69.1	30.9	4.1	7.6	17.3	6.8	2.2	62.0
	1 ± 0.5	1.7	68.4	31.6	4.2	10.0	18.5	10.8	2.5	54.0
	25.0 ± 0.02	3	72.0	28.0	3.8	14.1	20.9	17.4	2.9	40.8

[a] Molar ratio of **32**:**141** or **142**:sensitizer was 1:10:*ca.* 0.2. Irradiated through a Pyrex filter.

Table XIII

***cis–trans* Chlorine Atom Ratio and 1,2–1,4 Addition Ratio from α-Acetonaphthone-Sensitized Cycloaddition of Cyclopentadiene to *cis*- and *trans*-Dichloroethylene**

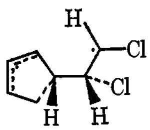
	From **141** (*cis*)		*From* **142** (*trans*)	
Ratio	−25°	+25°	−25°	+25°
trans:*cis* Cl's	73.8:26.2	75.7:24.3	86.1:13.9	79.1:20.8
1,2:1,4 addition	87.0:13.0	86.4:13.6	35.8:64.2	56.2:43.7

Table XIV

Product Distribution from the Photosensitized Cycloaddition of Cyclopentadiene to Trichloroethylene

	Distribution of cross-adducts, %			
Sensitizer	193	194	195	196
β-Acetonaphthone	27	17	10	46
Biacetyl	29	17	10	44

190 and from **191** are not the same starting from the isomeric



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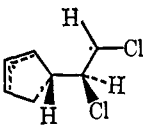
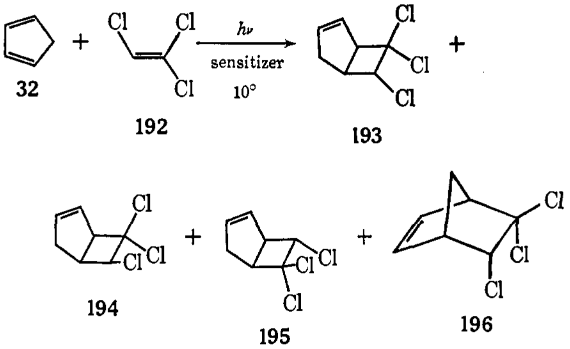


191

olefins **141** and **142**. The structures of the *trans*-dichloro products **186** and **187** will have to be determined before a more complete picture of these reactions can be achieved. The ratio of 1,2 to 1,4 cycloaddition from the isomeric olefins is quite different, even at 25° where the *cis–trans* chlorine atom ratio is nearly the same. It has been pointed out[77] that there are three stereochemical characteristics at the moment of the first addition step in the addition of triplet cyclopentadiene to *cis*- and *trans*-dichloroethylene which can have an effect on the product distribution: (1) the phase of rotation about the CHCl–CHCl bond, initially *cis* or *trans*; (2) one of two permanent diastereomeric configurations with respect to the initially formed new bond (**190** or **191**); (3) the conformation about the new bond formed in (2).

Trichloroethylene (**192**) also has been added to cyclopentadiene (**32**) with a sensitizer to give three 1,2- and one 1,4-addition products **193–196** (eq 97).[77] The product distributions for two sensitizers are given in Table XIV.[77] The distribution of cyclobutyl adducts **193–195** from the β-acetonaphthone-sensitized reaction indicates that the head-to-head **197** and **198** and head-to-tail **199** intermediates (Scheme VI) are formed in a ratio of 81.5:18.5 (eq 98 and 99) assuming that the formation of these intermediates is irreversible. If the 1,4-addition product **196** also is formed from the head-to-head and head-to-tail intermediates in an 81.5:18.5 ratio (eq 102 and 103), the over-all process for the addition of the diene triplet to the olefin **192** can be visualized as in Scheme **VI**. However, it is



(97)

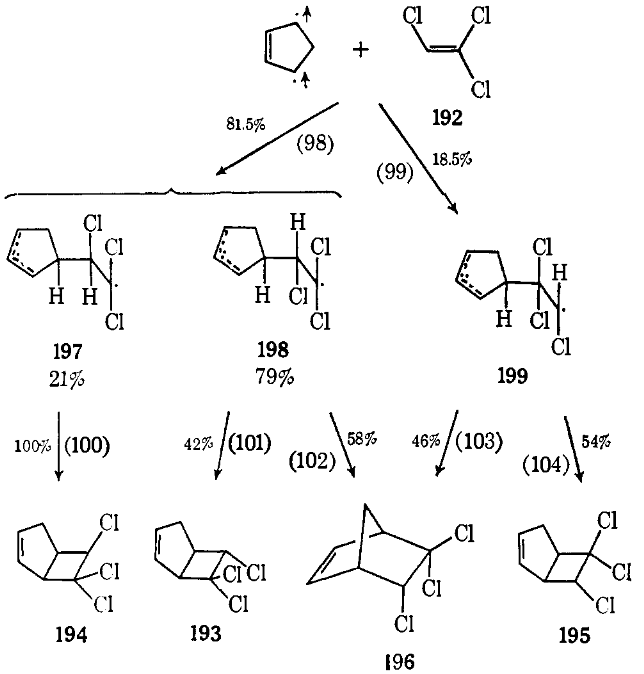
Table XV

Product Distribution from the Photosensitized Cycloaddition of Cyclopentadiene to Dimethylmaleic Anhydride[a]

		Product distribution, %			
Solvent	*Sensitizer*	200	201	202	*1:1 copolymer*
Dioxane	. . .	35	6	3	50
	Ph_2CO[b]	60	10	. . .	. . .
	Naphthalene[c]	11.2	4.2	2.5	80
	$(PhCO)_2$[d]	60	16.2	6	. . .
MeCN	Ph_2CO[b]	86	7	. . .	. . .
Me_2CO	. . .	30	7	3	60
	Ph_2CO[b,e]	88	5	. . .	. . .

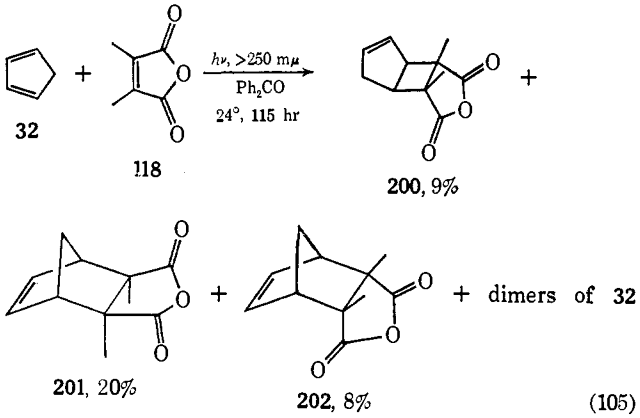
[a] Reaction conditions: 20 ml of **32**, 2 g of **118**, 30 ml of solvent, 20°, 4 days of irradiation. [b] 2 g. [c] 0.5 g. [d] 2.5 g. [e] Dimers of **32** were also formed in this reaction.[92,112]

Scheme VI



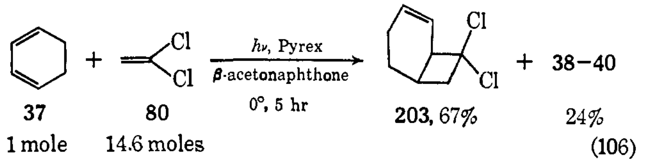
not clear that this ratio of precursors for the 1,4-adduct **196** is a good assumption. The low orientational selectivity in the addition of triplet cyclopentadiene to trichloroethylene is presumably due to the exothermic nature of the reaction.[77]

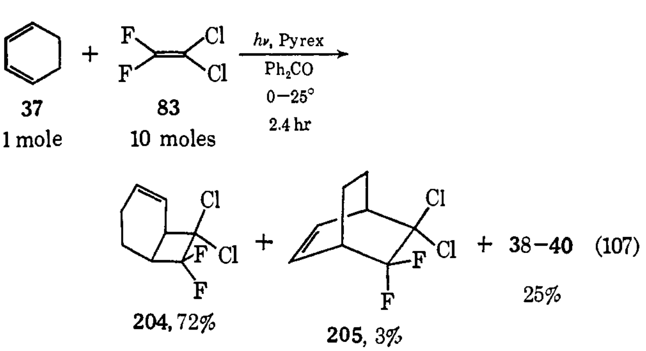
The photoaddition of the diene **32** to dimethylmaleic anhydride **(118)** has been carried out under a variety of conditions (eq 105) (Table XV).[92,112] Apparently the entire *endo* adduct **201** results from a thermal reaction and is not a photoproduct.[92]

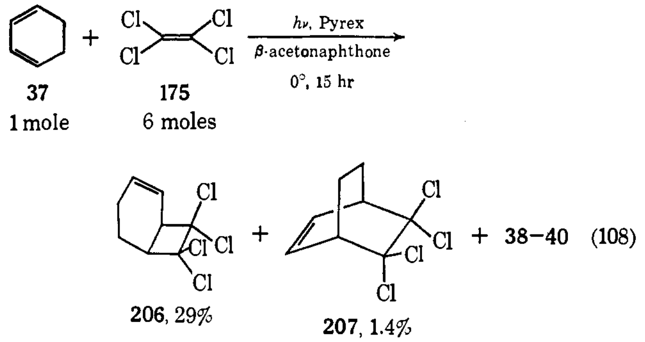


b. 1,3-Cyclohexadiene

The three olefins **80**, **83**, and **175** also have been added to cyclohexadiene **37** (eq 106–108).[82] Irradiation of a 12:1 molar ratio of **80**:**37** at 25° through Pyrex using β-acetonaphthone as the sensitizer gave the 1,2-addition product **203** in 70% yield in addition to the dimers **38–40**.[82] The quantum yields, Φ, have been determined for the addition of the diene **37** to the haloolefin **83** as a function of the triplet energy of the sensitizer (Table XVI) and the relative concentrations of **37** and **83** using benzophenone as the sensitizer (Table XVII).[84] Since the quantum yield for cross-addition, Φ(**204**, **205**), dropped off only slightly as the concentration of the diene **37** decreased, while the quantum yield for dimerization, Φ(**38–40**), dropped







sharply, it was concluded that the attacking species in these reactions was the diene triplet.[84]

Cyclopentene (**208**) has been added to the diene **37** to give three new products in addition to diene dimers (eq 109).[73]

Maleic anhydride (**211**) gave both the *exo*-**212** and *endo*-**213** adducts with **37** (eq 110).[92,112] A portion (13%) of the *endo* adduct **213** resulted from the competing thermal reaction of olefins **37** and **211**.[92]

Table XVI

Quantum Yields for Cross-Addition and Dimerization of 1,3-Cyclohexadiene and 1,1-Difluoro-2,2-Dichloroethylene (Sensitizer Energy Dependence)[a]

Sensitizer	E_{T_1}, *kcal/mole*	Φ(**204**, **205**)	Φ(**38–40**)
Benzophenone	68.5	0.50	0.16
β-Acetonaphthone	59.3	0.49	0.17
Fluorenone	53.3	0.04	0.01

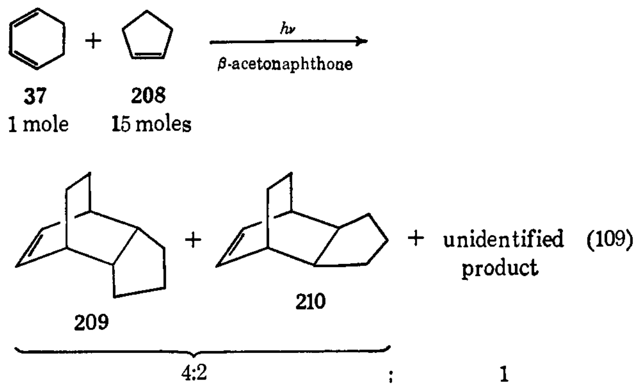
[a] Molar ratio of olefin **83**:diene **37** was 10:1; irradiated through Pyrex filter.

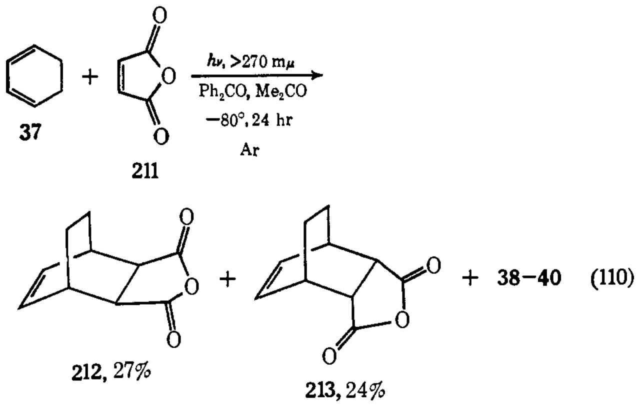
Table XVII

Quantum Yields for Cross-Addition and Dimerization of 1,3-Cyclohexadiene and 1,1-Difluoro-2,2-Dichloroethylene (Concentration Dependence)[a]

Molarity of **37** *in* **83**	Φ(**204**, **205**)	Φ(**38–40**)
0.157	0.41	0.23
0.080	...	0.16
0.063	0.41	0.085
0.037	0.36	0.025

[a] Benzophenone sensitization.





Dimethylmaleic anhydride (**118**), on the other hand, gave no *endo*-1,4 addition product (eq 111).[92,112] Different product distributions were found under varying reaction conditions as shown in Table XVIII.[92] There was no competing thermal reaction in this case. No rationalization was offered for these results.

Attempts to obtain cross-adducts between dienes **32** or **37** and the olefins, cyclohexene, norbornene, or 1,5-hexadiene, with β-acetonaphthone as a sensitizer were unsuccessful.[73]

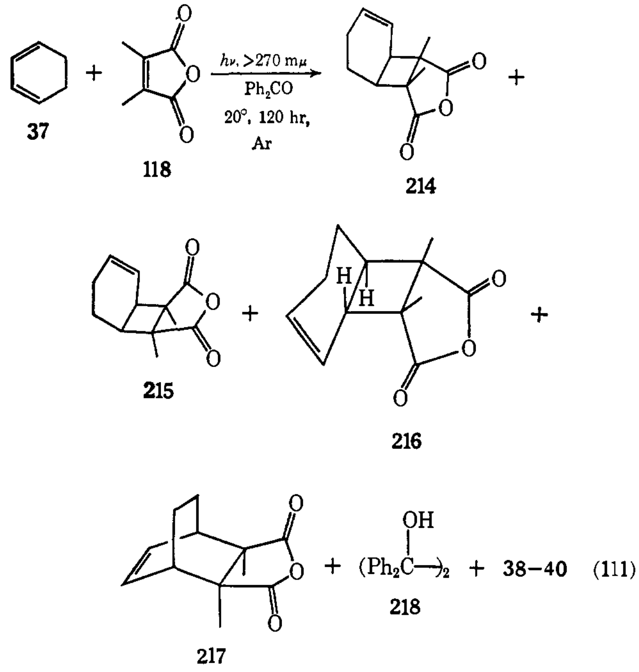


Table XVIII

Photoaddition of Cyclohexadiene to Dimethylmaleic Anhydride

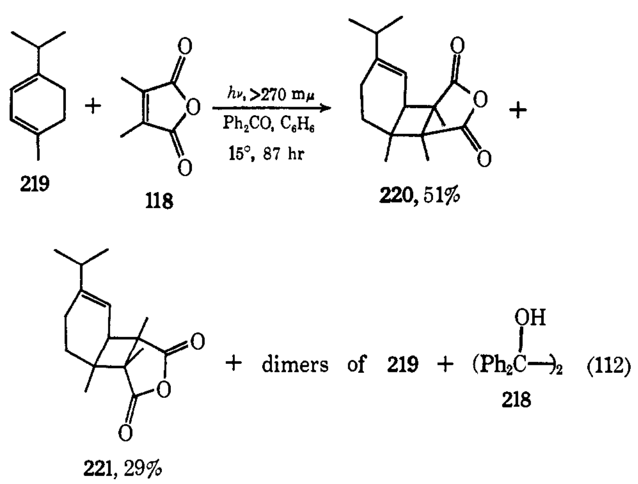
Solvent	*Sensitizer*	*Yield of products, %* 214	215	216	217	218
Benzene	...	14	18	11	..	..
Benzene	Ph₂CO	30	26	34	6	Some
Benzene	Ph₂CO[a]	18	22	15	..	..
Me₂CO	Ph₂CO	44	9	27	..	..

[a] Irradiated through quartz.

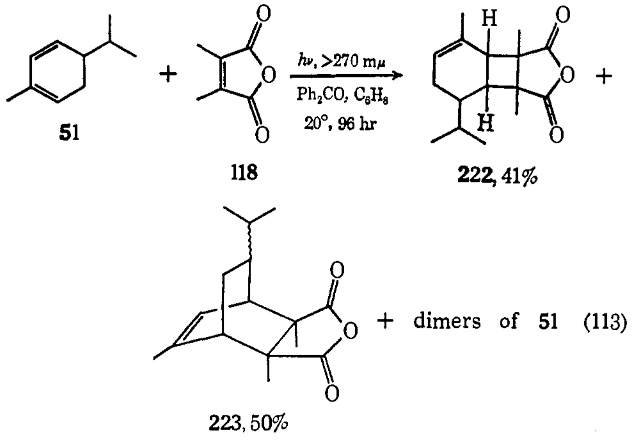
These results are surprising in view of the successful addition of diene **37** to cyclopentene (**208**) (eq 109).

c. Other Dienes and Trienes

α-Terpinene (**219**) gave two 1,2-cross-addition products **220** and **221** with the anhydride **118** (eq 112).[87,107]

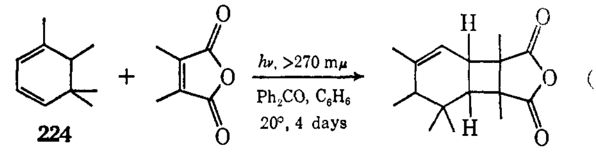


By way of contrast, when the alkyl groups are not in the 1,4 positions as in **219** but rather in the 2,5 positions as in α-phellandrene (**51**), both 1,2- and 1,4-cross-addition products **222** and **223** were formed (eq 113).[87,107]

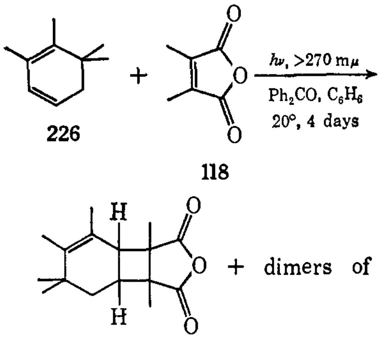


α-Pyronene (**224**) and β-pyronene (**226**) both gave 1,2-cross-addition products **225** and **227**, respectively, with the anhydride **118** (eq 114 and 115).[92,112]

The triene **228** on sensitized photoaddition to maleic anhydride (**211**) gave products of 1,2 addition, **229**, and two products arising from 1,4-addition, **230** and **231** (eq 116).[72,92,112]

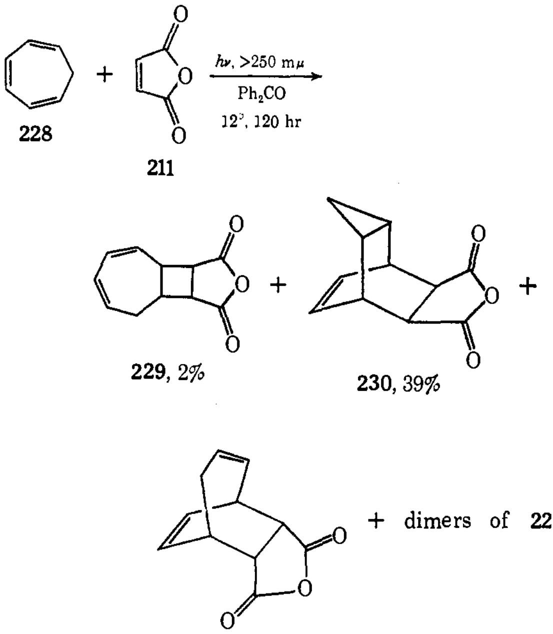


224 + **118** → **225**, 97% (114)



226 + **118** →

227, 66% + dimers of **226** + $(\mathrm{Ph_2}\overset{\mathrm{OH}}{\mathrm{C}}\text{—})_2$ (115)



228 + **211** →

229, 2% + **230**, 39% +

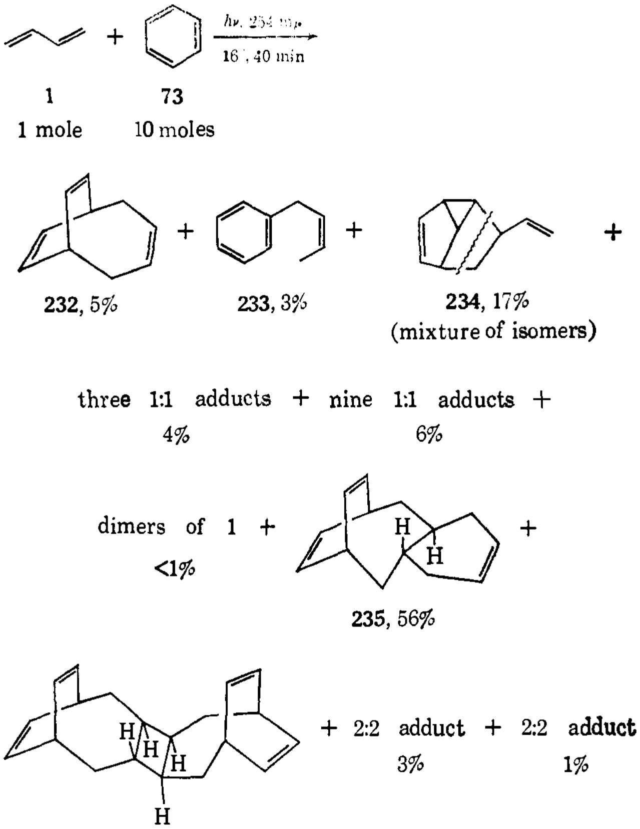
231, 6% + dimers of **228** (116)

B. NONSENSITIZED

1. Acyclic Dienes and Trienes

a. 1,3-Butadiene

In most of the reactions in this section on nonsensitized reactions the nondiene reacting partner probably was the species which initially was excited by the ultraviolet radiation. Several nonsensitized cross-additions have been discussed above in the section on the sensitized reactions for comparison purposes.



1 + **73** →
1 mole 10 moles

232, 5% + **233**, 3% + **234**, 17% (mixture of isomers) +

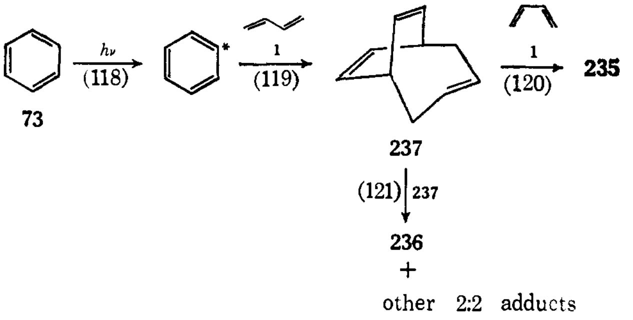
three 1:1 adducts + nine 1:1 adducts +
4% 6%

dimers of **1** + **235**, 56% +
<1%

236, 6% + 2:2 adduct + 2:2 adduct
3% 1%

(117)

Irradiation of a solution of butadiene (**1**) in benzene (**73**) gave a mixture of 1:1 adducts, **232–234**, a 2:1 adduct, **235**, a 2:2 adduct, **236**, and several unidentified adducts (eq 117).[120–122] The over-all quantum yield was *ca.* 0.4. The mechanism for the formation of the 2:1 and 2:2 adducts is believed to involve the concerted 4 + 4 addition of excited benzene to the *s-trans* diene **1** (eq 119) to give the highly reactive triene **237** which then either dimerizes (eq 121) or reacts with ground-state diene **1** (eq 120).[122] Irradiation of a 1:1 molar ratio of **1** and benzene at −80° in pentane followed by removal of excess diene and warming gave mainly the 2:2 adduct **236** while treatment of the cold irradiated mixture with cyclopentadiene (**32**) gave a C_{15} adduct; no 2:1 adduct **235** or 2:2 adducts were formed.[122] Irradiation of a 10:1:1 molar ratio of benzene:diene **1**:nitric oxide gave mainly the all-*cis* diene **232** and the other 1:1 adducts; little **235** or **236** was formed.[122] It is proposed that the *cis,cis,trans*-triene **237** may be isomerized to the all-*cis* triene **232** by nitric oxide.[122] The stereochemistry of the 2:2 adduct **236** is consistent with a concerted ground-state *cis–trans* 1,2–1,2 cycloaddition.[46]



73 → **237** → **235**

236 + other 2:2 adducts

In a similar manner the deuterio analogs of the above products were prepared from various combinations of hexadeuteriobenzene (**238**), hexadeuteriobutadiene (**239**), and tetradeuteriobutadiene (**240**) (**1** + **238**, **239** + **73**, **240** + **238**) to aid in the structure elucidation.[121,122] Benzene has also been used

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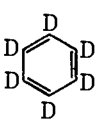
(120) G. Koltzenburg and K. Kraft, *Angew. Chem.*, 77, 1029 (1965); *Angew. Chem. Intern. Ed. Engl.*, 4, 981 (1965).

(121) G. Koltzenburg and K. Kraft, *Tetrahedron Letters*, 389 (1966).

(122) K. Kraft and G. Koltzenburg, *ibid.*, 4357 (1967).



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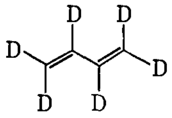

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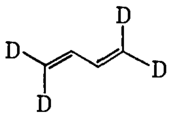
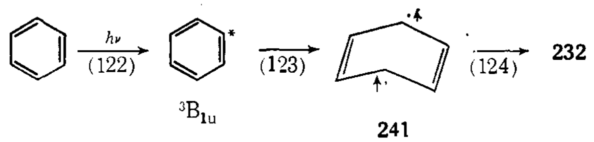


240

as a sensitizer for dimerization of diene **1** (see above).[50]

It has been pointed out that the molecular orbital symmetry of the benzene B_{1u} or E_{1u} states is such that the 1,4–1,4 cycloaddition to butadiene to give triene **232** is an allowed concerted process.[46] It has also been postulated that triene **232** may be formed *via* the lowest triplet state of benzene ($^3B_{1u}$) (eq 123 and 124) since this state has the correct molecular orbital symmetry correlation with the triplet diradical **241**.[123]



241

Alkyl-substituted derivatives of benzene gave similar, but unidentified, cycloadducts with diene **1** (Table XIX).[122]

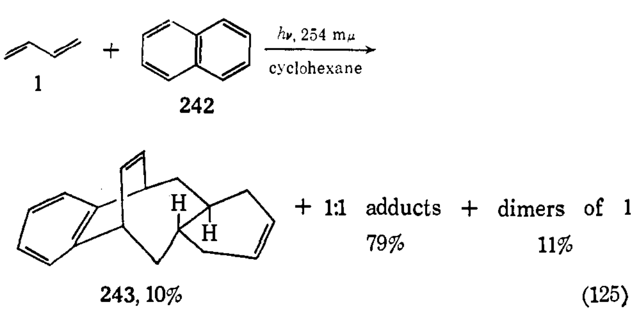
Table XIX

Photocycloadducts of Butadiene with Alkyl Derivatives of Benzene[a]

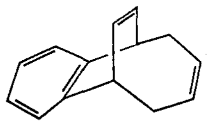
Benzene deriv	*Total quantum yield*	*Yield, %*[b] *1:1 adducts*	*2:1 adducts*[c]	*2:2 adducts*
Toluene	~0.6	30	36, 12, 11	10
o-Xylene	~0.7	36	27, 21, 7	8
m-Xylene	~0.8	21	37, 28, 3	11
p-Xylene	~0.9	20	54, 9, 3	14
t-Butylbenzene	~0.7	42	39, 6	12

[a] One mole of diene **1** in 10 moles of benzene derivative irradiated with 254-mμ light at 12 or 13° for 40 min. [b] Based on unrecovered benzene derivative. [c] Two molecules of diene **1** per benzene derivative. Three isomers formed.

Irradiation of an equimolar mixture of butadiene (**1**) and naphthalene (**242**) gave a 2:1 adduct **243** in addition to several unidentified 1:1 adducts (eq 125).[124] It has been pointed out that the concerted cycloaddition of naphthalene in the excited B_{2u} state to diene **1** to give a 1:1 adduct **244** is an orbital symmetry allowed process.[46]



The nitro olefin **245** gave a mixture of 1,2 adducts **246** and **247** on irradiation in presence of butadiene (**1**) (eq 126).[22]



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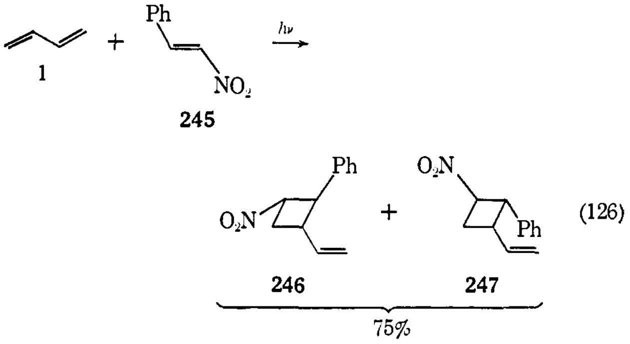
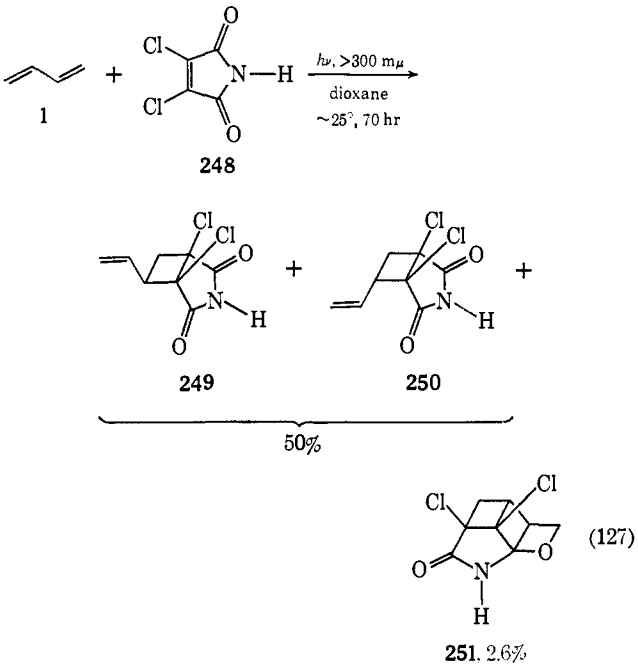


Dichloromaleimide (**248**) gave three adducts, **249–251**, on irradiation in butadiene (eq 127).[106,113,125] No 1,4 adducts of **1** with **248** could be detected.[113] The oxetane **251** did not arise from further irradiation of the *cis* isomer **250**.[125]



A 1,4-addition product, **253**, of **1** and *p*-benzoquinone (**252**) was obtained in addition to other products on direct irradiation (eq 128).[126] The geometry about the double bonds of **254** has not been firmly established.[126] These products are believed to result from reaction of the n,π* state of the quinone **252**.[126,127] It should be noted that quinone **252** was used as a sensitizer for the dimerization of **1** (Table II). The reaction of **252** with **1** to give the 1:2 adduct[126] **256** (eq 129) has been classified as a 14-center reaction.[20] It is not clear whether these reviewers[20] mean to imply any mechanistic significance to eq 129, or whether they are merely classifying the over-all transformation. It seems highly unlikely that this reaction would be a termolecular process.

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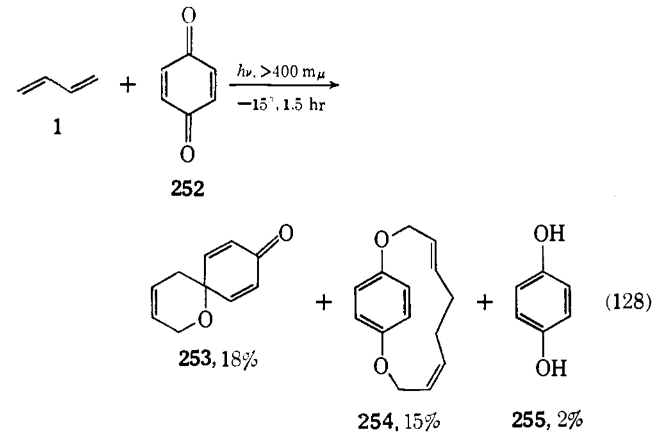
[123] D. Bryce-Smith and H. C. Longuet-Higgins, *Chem. Commun.*, 593 (1966).

[124] K. Kraft and G. Koltzenburg, *Tetrahedron Letters*, 4723 (1967).

[125] H.-D. Scharf and F. Korte, *ibid.*, 2033 (1966).

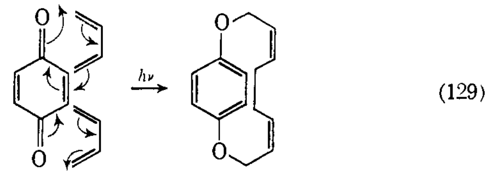
[126] J. A. Barltrop and B. Hesp, *J. Chem. Soc.*, 5182 (1965).

[127] J. A. Barltrop and B. Hesp, *Proc. Chem. Soc.*, 195 (1964).



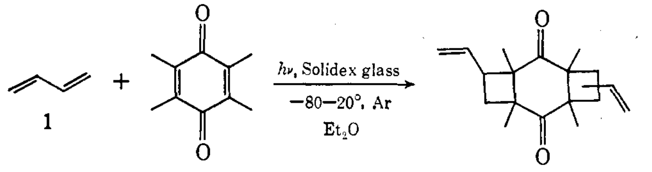
1 252

253, 18% 254, 15% 255, 2% (128)



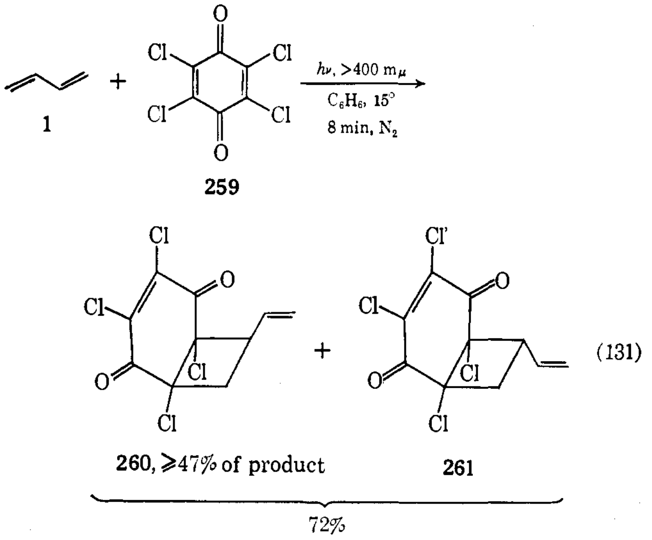
252 1 256 (129)

Butadiene (1) gave a 2:1 adduct, **258**, with the quinone **257** (eq 130).[90]



1 257 258 (130)

Irradiation of chloranil (**259**) with an excess of diene **1** gave a mixture of 1,2 cycloadducts, whose structures are probably **260** and **261** (eq 131).[128]

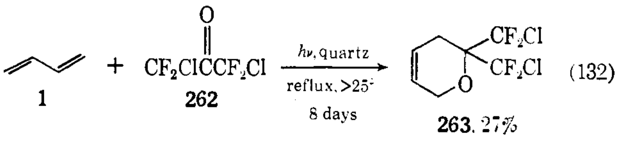


1 259

260, ≥47% of product 261 (131)

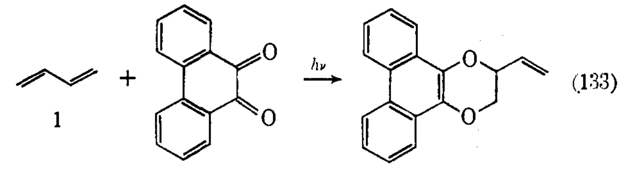
72%

Irradiation of **1** with an excess of the perhalo ketone **262** gave the dihydropyran **263** (eq 132).[129] The same reaction also occurs thermally at 200°.



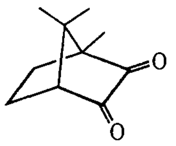
1 262 263, 27% (132)

Diene **1** gave a 1,2–1,4 cycloadduct, **265**, with phenanthraquinone (**264**) (eq 133).[40, 130] This reaction proceeds only when the quinone **264** is irradiated at its long-wavelength band.[40]



1 264 265 (133)

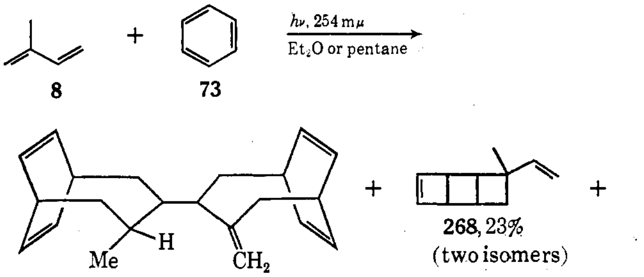
Use of camphorquinone (**266**) as a photosensitizer for the cross-addition of diene **1** and olefin **86** gave a mixture of vinyloxetanes (from **1** and **266**) of unspecified structure in addition to other cycloadducts (see above).[104]



266

b. Isoprene

Irradiation of isoprene (**8**) and benzene (**73**) in solution gave the 2:2 adduct **267** and a mixture of two stereoisomeric 1:1 adducts, **268**, in addition to isoprene dimers and an unidentified product (eq 134).[120, 121] Use of benzophenone or benzil as sensitizers gave no products,[120] although it is known that these sensitizers do lead to dimerization of diene **8**.[61] Direct irradiation of isoprene (**8**) with hexadeuteriobenzene (**238**) (2537 Å, 18°) gave the hexadeuterio analog of **268** in 47% yield in addition to the dodecadeuterio analog of **267** and dimers of diene **8**.[121]



8 73

267, 46% 268, 23% (two isomers) + dimers of 8 20% (134)

Irradiation of diene **8** in an excess of benzene (**73**) gave a different set of adducts (eq 135).[124] At *ca.* 0.1% conversion of benzene the quantum yield for the formation of all adducts was *ca.* 0.4.[124] The yields of this reaction determined by gas chromatography were *ca.* 65% of 1:1 adducts, 33% of the 2:2 adduct(s) (**272**), and 1–2% of isoprene dimers. The mechanism of these additions was proposed to involve at least two different excited states of benzene, **273** and **274**.[124] The second

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[128] J. A. Barltrop and B. Hesp, *J. Chem. Soc., C*, 1625 (1967).

[129] J. F. Harris, Jr., U. S. Patent 3,136,786 (1964); *Chem. Abstr.*, **61**, 4321 (1964).

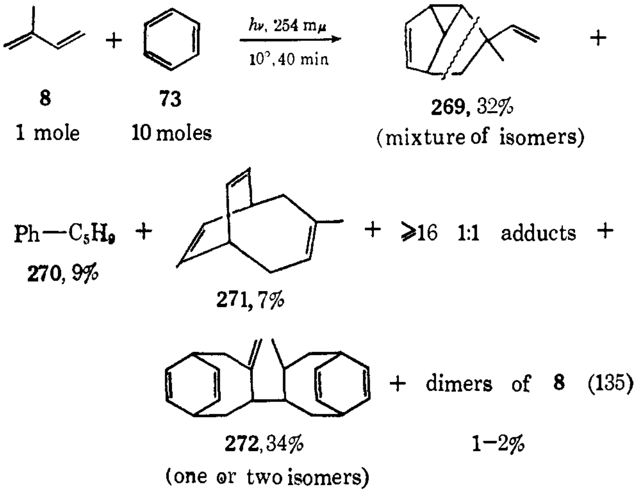
[130] G. O. Schenck, *Z. Electrochem.*, **64**, 997 (1960).

Table XX

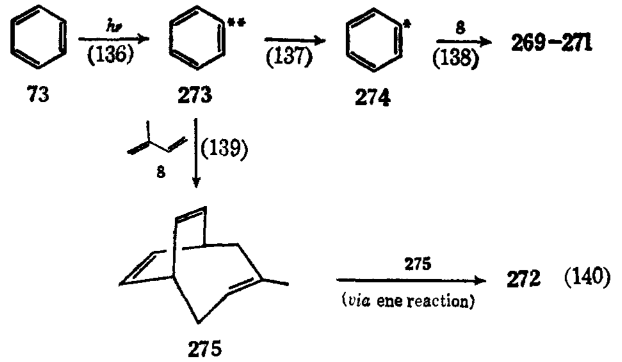
Product and Quantum Yield (Φ) Dependence on Molar Ratio of Isoprene and Benzene

Moles		% of light absorbed by benzene	Temp, °C	Φ^a	Product distribution, %		
8	73				1:1 adducts	2:2 adduct 272	Dimers of 8
1	100	99.8	16	~0.2	~78	22	~1
1	9	98.6	16	~0.4	~55	44	1-2
1	1	86	10	~0.4	~19	76	~5

^{a} Based on benzene.



8 1 mole + 73 10 moles → 269, 32% (mixture of isomers) + 270, 9% + 271, 7% + 272, 34% (one or two isomers) + dimers of 8 1–2% (135)

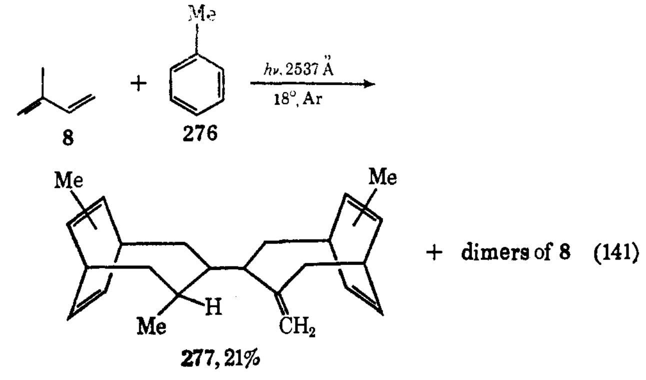


73 (136) → 273 (137) → 274 (138) → 269–271

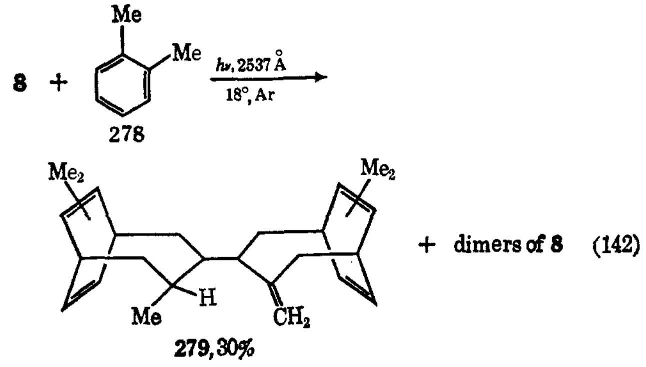
273 + 8 (139) → 275 (140) → 272

excited state of benzene, **274**, may actually consist of more than one state.[124] Irradiation of a mixture of benzene (10 moles), isoprene (1 mole), and nitric oxide (0.14 mole) gave no 2:2 adduct **272**, but did give more of the 1:1 adduct **271**.[124] It was proposed that the *cis,cis,trans* adduct **275** was isomerized to the all-*cis* adduct **271** by the nitric oxide.[124] Irradiation of a mixture of benzene (**73**), isoprene (**8**), and cyclopentadiene (**32**) in pentane at −80° gave a mixture of C_{16} adducts different from those formed from the all-*cis* adduct **271** and the cyclic diene **32** at room temperature.[124] It was proposed that the C_{16} adducts arose from formation of the *trans* adduct **275** followed by its addition to the cyclic diene **32**.[125] Changing the molar ratio of diene **8** to benzene had a pronounced effect on the product distribution and quantum yield (Table XX).[124] Addition of 0.1 mole of naphthalene to 100 moles of benzene and 10 moles of isoprene reduced the quantum yield for the formation of all adducts by one-fifth; it was therefore reasoned that benzene was reacting in its excited singlet state.[124]

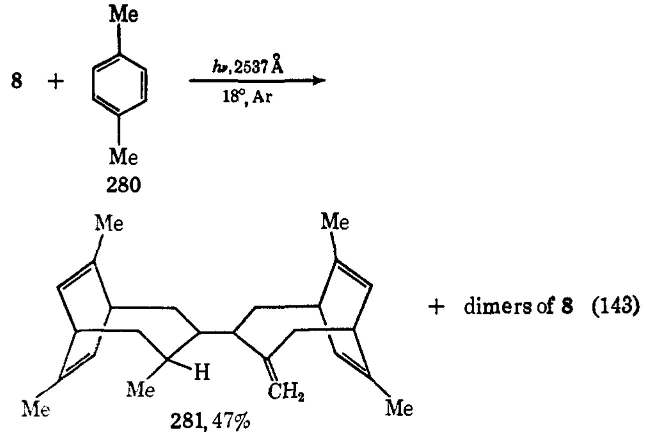
With toluene (**276**) and the xylenes **278** and **280**, analogous 2:2 adducts were obtained with isoprene (**8**) (eq 141–143).[121] Both unspecified methyl groups of adduct **277** are on double bonds, while three of the four methyl groups of adduct **279** are



8 + 276 → 277, 21% (141)



8 + 278 → 279, 30% (142)



8 + 280 → 281, 47% (143)

on double bonds, one being on a bridgehead carbon atom.[121]

Somewhat different results were obtained on irradiation of diene **8** (1 mole) in an excess of the aromatic compound (10 moles) at slightly lower temperature (Table XXI).[120,124] The results for several other aromatic compounds are also given in Table XXI.[120,121,124] The structures of the adducts have not been reported.

The mechanism of the addition of these aromatic compounds with diene **8** is presumed to occur *via* excitation of the aromatic partner and subsequent reaction with the ground-

Table XXI

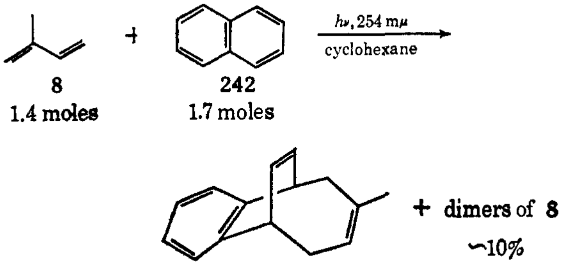
Photocycloaddition of Isoprene to Aromatic Compounds

Aromatic compound	*Temp, °C*	*Total quantum yield*	*Product distribution, %*		
			1:1 adducts	*2:2 adducts*	*Dimers of* **8**
Toluene[a]	10	~0.3	~55	44	1–2
o-Xylene[a]	13	~0.5	~56	43	1–2
m-Xylene[a]	13	~0.3	~53	46	1–2
p-Xylene[a]	13	~0.4	~38	61	1–2
Durene[a]	24	~0.4	~55	43	1–2
Hexafluorobenzene[b]				30[c]	
1,2,4,5-Tetrafluorobenzene[b]				10[c]	50[c]

[a] Irradiated with 254-mμ light for 40 min. [b] Irradiated with 254-mμ light. [c] Yield.

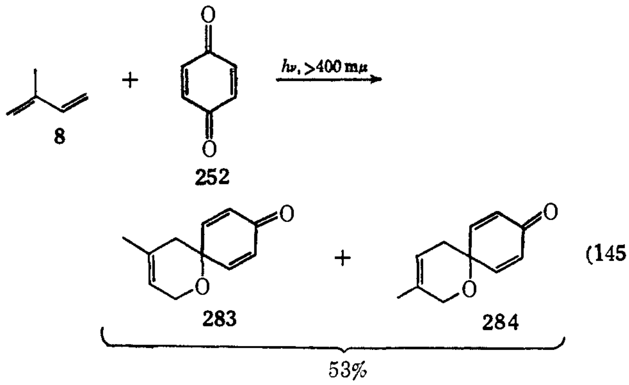
state diene.[121] A number of other reactions of isoprene (**8**) with benzene derivatives (C_6H_5R) have been studied (R = *t*-Bu, NH_2, NMe_2, Cl, CF_3, and C_6H_5).[121] Also studied were furan, and phenanthrene additions to **8**.[121]

Naphthalene (**242**) gave a 1:1 adduct, **282**, on irradiation with isoprene (**8**) (eq 144).[121,124]



8 1.4 moles; **242** 1.7 moles; **282**, 80% (144)

Isoprene (**8**) gave a mixture of two isomeric dihydropyran derivatives, **283** and **284**, on irradiation with quinone (**252**) (eq 145).[126]



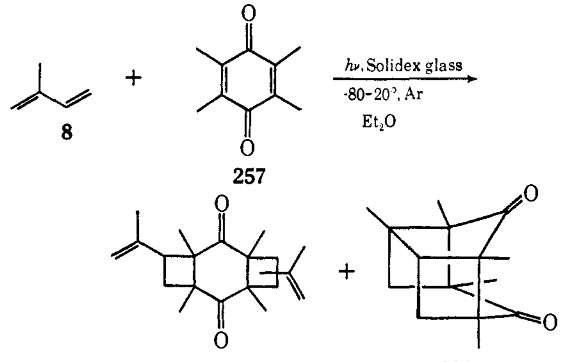
8; **252**; **283**; **284** (145)

53%

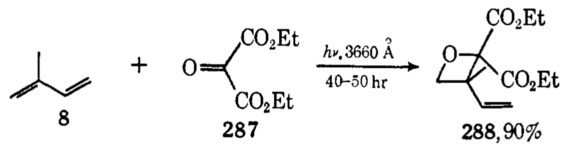
Isoprene (**8**) gave a 2:1 adduct, **285**, with the quinone **257** in addition to an intramolecularly cyclized 1:1 product, **286** (eq 146).[90]

Irradiation of a mixture of **8** and the keto ester **287** gave only one of the possible cycloadducts **288** (eq 147).[131]

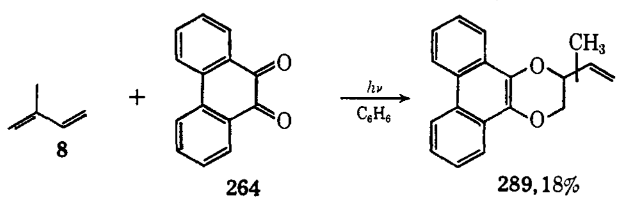
Reaction of **8** with the *o*-quinone **264** gave only the product(s), **289**, of 1,2 addition to the diene (eq 148).[40,130]



8; **257**; **285**; **286** (146)

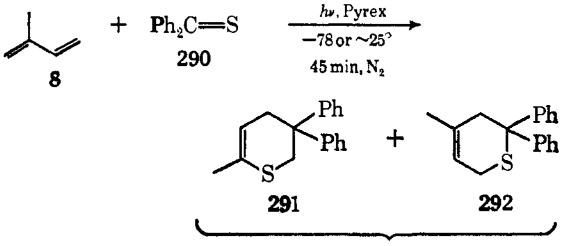


8; **287**; **288**, 90% (147)



8; **264**; **289**, 18% (148)

In contrast to the above results, irradiation of **8** with thiobenzophenone (**290**) at low temperature gave only 1,4-addition products **291** and **292** (eq 149).[132] The initial formation of a vinylthiacyclobutane followed by a thermal rearrangement to the thiacyclohexenes **291** and **292** was considered unlikely.[132]

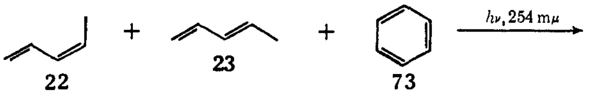


8; $Ph_2C{=}S$ **290**; **291**; **292** (149)

94%

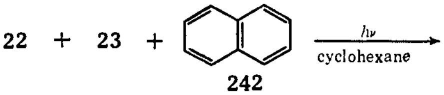
c. Piperylene

Benzene (**73**)[88,121,122] and naphthalene (**242**)[124] gave unidentified cycloadducts with a mixture of *cis*- (**22**) and *trans*-piperylene (**23**) (eq 150 and 151). In the case of benzene the quantum



22; **23**; **73**

1:1 adducts + 2:1 adducts + 2:2 adducts (150)
(> three isomers) (seven isomers)



22 + **23** + **242**

1:1 adducts + 2:1 adducts + dimers of 22 and 23 (151)
77% 13% 10%

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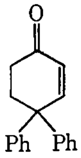
(131) M. Hara, Y. Odaira, and S. Tsutsumi, *Tetrahedron Letters*, 2981 (1967).

(132) K. Yamada, M. Yoshioka, and N. Sugiyama, *J. Org. Chem.*, **33**, 1240 (1968).

yield was about the same as for the reaction with butadiene (see above). The addition to benzene is believed to involve the excited singlet state of the latter.[88]

Attempted use of *trans*-piperylene (**23**) as a quenching agent for the triplet state of the enone **293** gave a mixture of 1:1 cyclobutyl cross-adducts.[22]

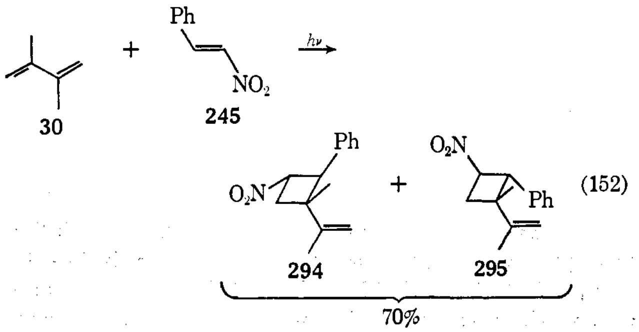


293

d. 2,3-Dimethyl-1,3-butadiene

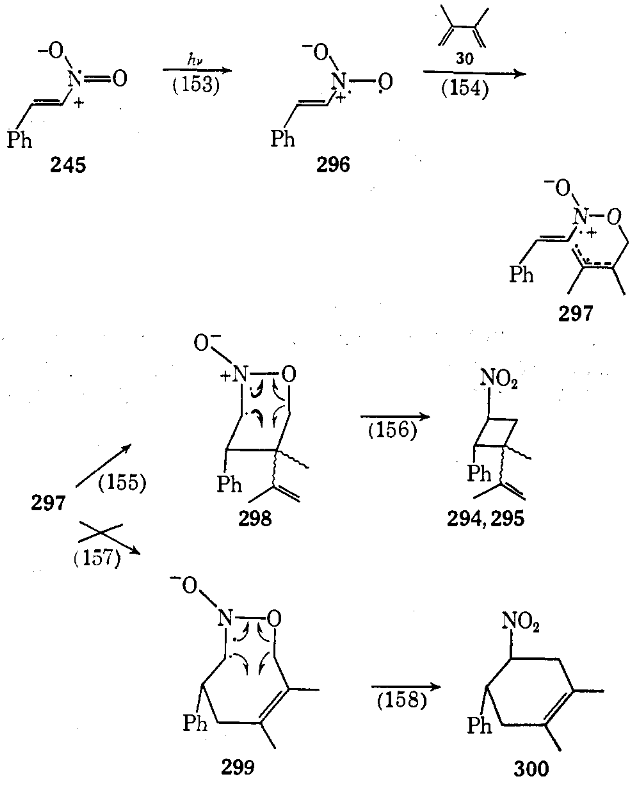
2,3-Dimethylbutadiene (**30**) gave two unidentified isomeric 1:1 adducts on irradiation with benzene (**73**) at 254 mμ.[121,124]

Irradiation of a mixture of the nitroolefin **245** with **30** gave the cyclobutyl cross-adducts **294** and **295** (eq 152).[22] No 1,4-addition products were formed. A possible explanation for formation of 1,2-addition products and the absence of 1,4 products is shown in Scheme VII.[133] The formation of the cyclohexene **300** would require the less likely eight-membered ring transition state (or intermediate) **299**.[133] Another factor involved may be the conformational preference of diene **30**. The formation of **299** and **300** requires the *s-cis* diene while the *s-trans* diene would suffice for the formation of **298** and **294** or **295**.

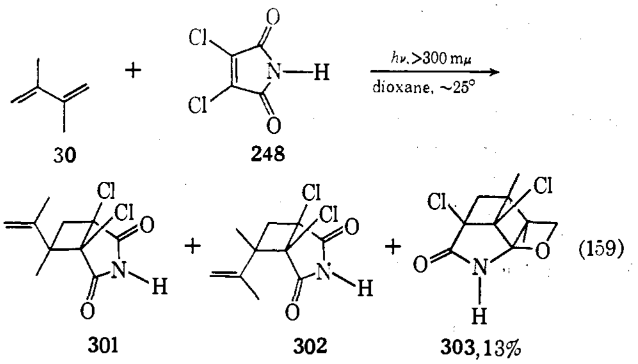


(152)

Scheme VII

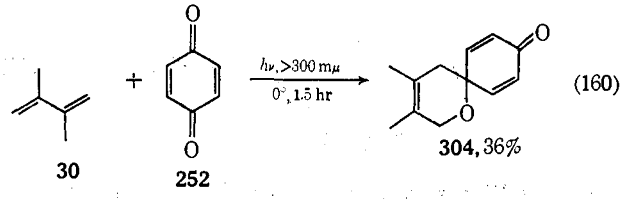


As with butadiene (**1**) the 2,3-dimethyl derivative **30** also reacted with dichloromaleimide (**248**) to give both 1,2-addition products **301** and **302** and the oxetane **303** (eq 159).[106,113,125] Again no 1,4-addition product of **30** could be found.[113]



(159)

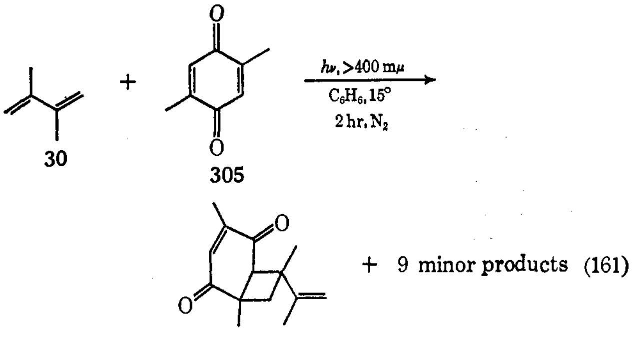
p-Benzoquinone (**252**) was added to **30** to give the spirodihydropyran **304** (eq 160).[126,127] This reaction is also believed to occur *via* the n,π* state of the quinone **252** in a manner analogous to that outlined for the reaction of **1** and **252** above.[126,127] Irradiation under the same conditions, except that the wavelength region was restricted to that above 400 mμ, gave the spiro compound **304** in 33% yield.[126,127]



(160)

In contrast to this result irradiation of 2,5-dimethylquinone (**305**) with an excess of **30** at the wavelength of the n → π* band of the quinone gave a cyclobutyl adduct believed to have structure **306** and other unidentified products (eq 161).[128] The quinone **305** and diene **30** form a charge-transfer complex.

When **30** was added to tetramethylquinone **257**, the product **307** resulted from a double addition of the four carbon–carbon double bonds of **30** and **257**.[90]



(161)

306, 6% yield,
45% of total product

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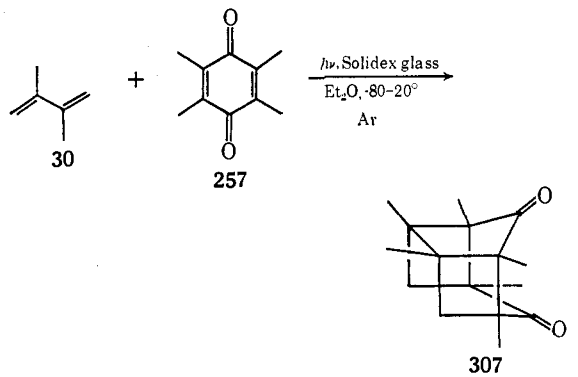
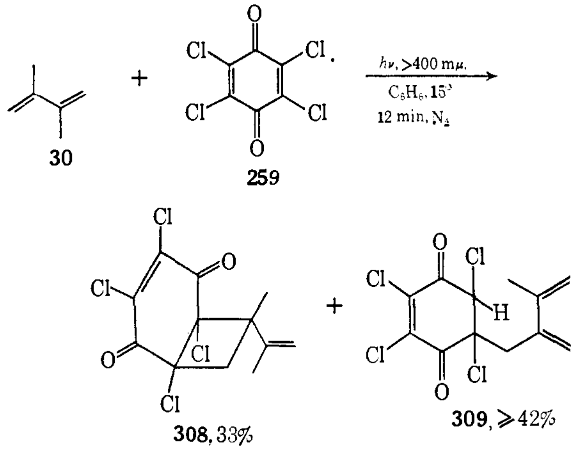
(133) Reference 16, p 191.



(162)

Chloranil (**259**) and **30** gave products of both cycloaddition, believed to be **308**, and hydrogen-atom transfer, **309**; the latter was isolated as the dehydrochlorinated product (eq 163).[128] The quinone **259** forms charge-transfer complexes with both **30** and benzene (**73**).[128] The mechanism is believed to involve formation of the diradical **310** (probably triplet) (eq 164) which either undergoes ring closure to give **308** (eq 165) or hydrogen-atom transfer to give **309** (eq 166).[128] An alternate mode of formation of triene **309** would involve hydrogen-atom abstraction from **30** by quinone **259** to give radicals **311** and **312** (eq 167) followed by coupling (eq 168).[128]



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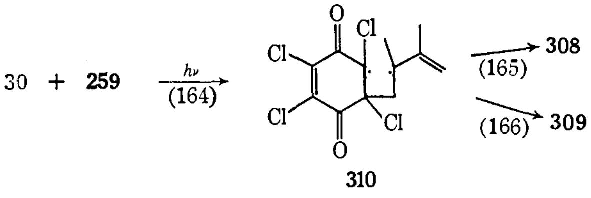
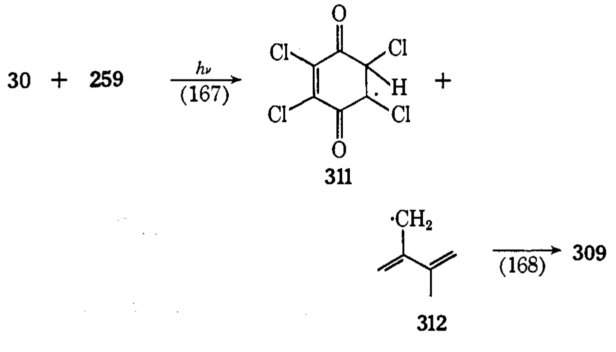
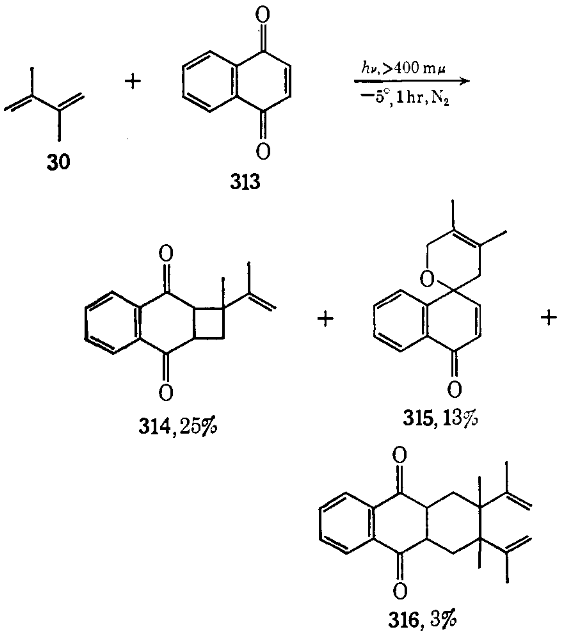




Irradiation of 1,4-naphthoquinone (**313**) at the $n \rightarrow \pi^*$ transition in an excess of diene **30** gave three different types of products.[128] Double addition to give the fused ring system **316** occurred as well as dihydropyran **315** and cyclobutane **314** formation (eq 169).[128] The two reactants form a charge-transfer complex.[128] The 2:1 adduct **316** is probably formed *via* the diradical intermediates **317** and **318** (eq 170, 172, and 173).[128] It is interesting to note that the addition of **30** to the diradical **317** (eq 172) can compete with ring closure of **317** (eq 171), indicating some finite lifetime of diradical **317**. **317** is thus likely to be a triplet. It was suggested that the cycloadditions of quinones at the carbon–carbon double bond involve the π,π^* excited state while additions at the carbonyl bond involve the n,π^* excited state.[128]



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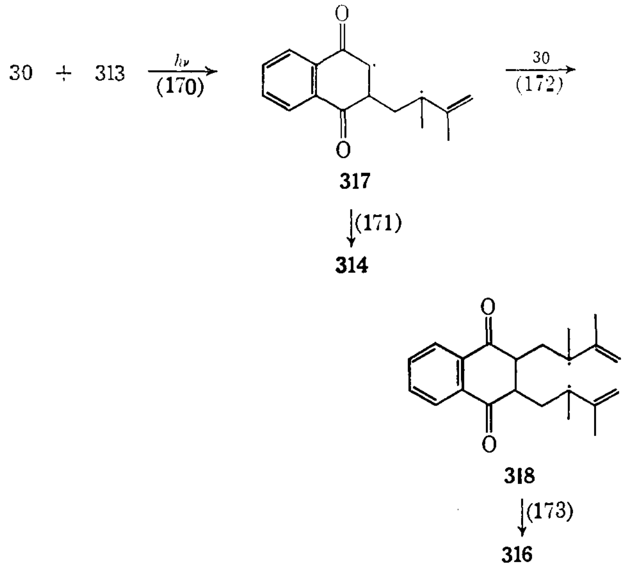
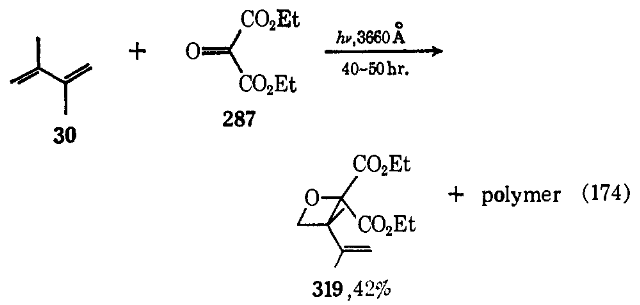
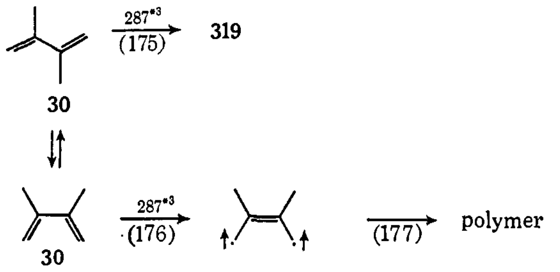


Photoaddition of **30** to the keto ester **287** gave the oxetane **319** and polymer (eq 174).[131] The quantum yield for the formation of **319** was 0.30.[131] It was suggested that **319** was formed *via* addition of the n,π^* triplet ketone **287** to *s-trans* ground-state diene ($E_T \approx 60$ kcal/mole; eq 175) while the polymer



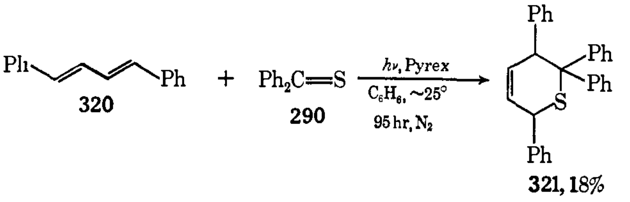
(174)

was formed by an energy-transfer process from triplet ketone to *s-cis* diene ($E_T \approx 54$ kcal/mole; eq 176).[131]



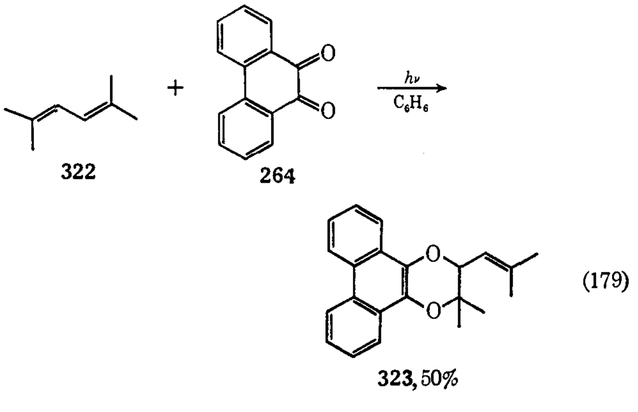
e. Other Dienes and Trienes

1,4-Diphenylbutadiene (**320**) gave only a 1,4-addition product, **321**, on irradiation with thiobenzophenone (**290**) (eq 178).[132]



(178)

The two tetramethylbutadienes **322** and **324** gave the dioxene derivatives **323** and **325** on irradiation with phenanthraquinone (**264**) (eq 179 and 180).[40,130] Nopadiene (**326**), homoverbenene (**327**), and alloocimene (**328**) also gave 1,4-dioxene derivatives on irradiation with the quinone **264**.[40,130] The structures of these latter products have not been reported.



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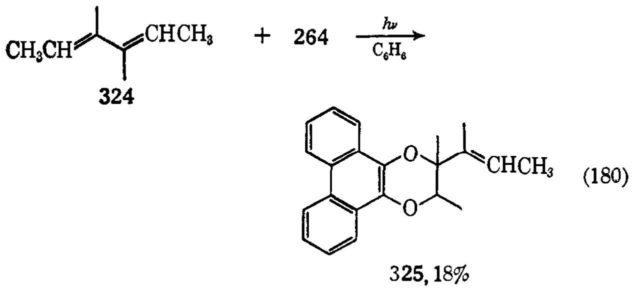

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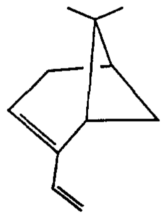

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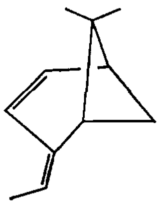

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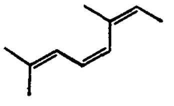

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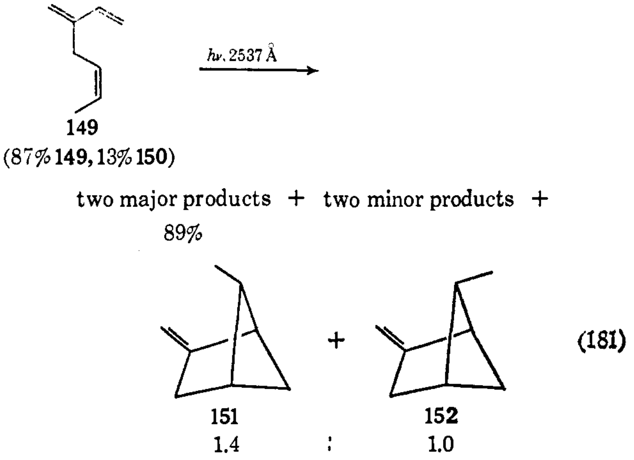
In contrast to the sensitized irradiation described above, *direct irradiation of the isomeric trienes* **149** *and* **150** *as 1%* solutions gave only small amounts of the bicyclohexane derivatives **151** and **152** (eq 181 and 182).[60,116] The major products may be cyclobutene derivatives.[116] If the formation of the bicyclohexanes **151** and **152** in the nonsensitized reaction is a stepwise process, then the intermediate, or at least one of the intermediates if more than one is involved, must be different from that involved in the sensitized reaction.[116] A singlet diradical is a possibility.[116]



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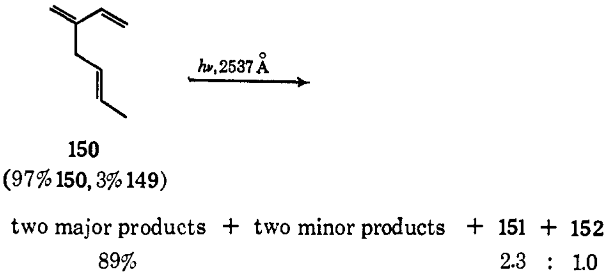

(182)

Similarly direct irradiation of myrcene (**31**) gave only a small amount of the bicyclohexane **170**, and gave larger quantities of the cyclobutene **329** and β-pinene (**330**) (eq 183).[60] Another report was substantially in agreement with these results indicating that the yield of the bicyclohexane **170** was less than 5%.[6,134] Irradiation of myrcene (**31**) as a 1–4% solution in ether with radiation of wavelengths longer than 220 mμ at 30° gave mainly the cyclobutene **329** (54–68%) along with

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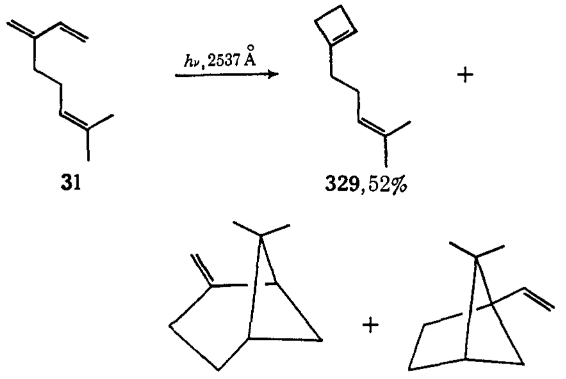
(134) W. G. Dauben, R. L. Cargill, R. M. Coates, and J. Saltiel, *J. Am. Chem. Soc.*, 88, 2742 (1966).

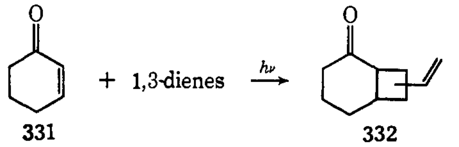


31 → 329, 52% + 330, 22% + 170, 12% (183)

β-pinene (330) (9–10%) and at least four other products totaling 3% or less.[135–138]

Direct irradiation of solutions of various dienes **1**, **37**, etc., and the haloolefins **80**, **83**, or **175** gave low yields of the same adducts as obtained from the sensitized reactions described above in addition to many other products.[82]

Cyclohexenone (**331**) underwent cycloaddition with 1,3-dienes (unspecified) to give vinylbicyclooctanones **332** (eq 184) as well as sensitizing the dimerization of the dienes (see above).[22]

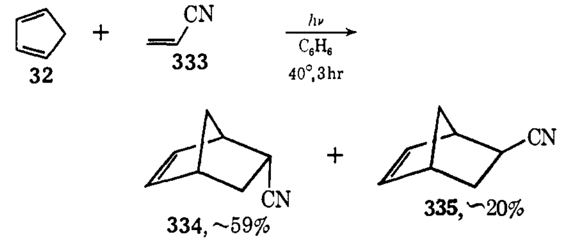


331 332 (184)

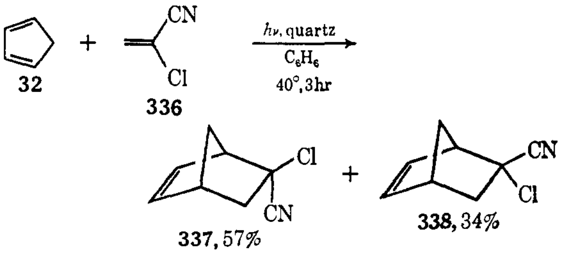
2. *Cyclic Dienes, Trienes, and Tetraenes*

a. 1,3-Cyclopentadiene

The cycloadditions of acrylonitrile (**333**)[139] and α-chloroacrylonitrile (**336**)[140] to cyclopentadiene (**32**) have been carried out with simultaneous ultraviolet irradiation (eq 185 and 186). However, exactly the same results were obtained when the ultraviolet radiation was omitted.[139,140] Thus either the irradiation had no effect on the reactants, or under the reaction conditions reported[139,140] no excitation energy reached diene **32** or olefins **333** or **336**; it is possible that the solvent benzene absorbed all of the radiation and did not undergo energy transfer to the olefins. It would be of interest to carry out these reactions under conditions where it is assured that the reactants are excited either directly or *via* sensitization.

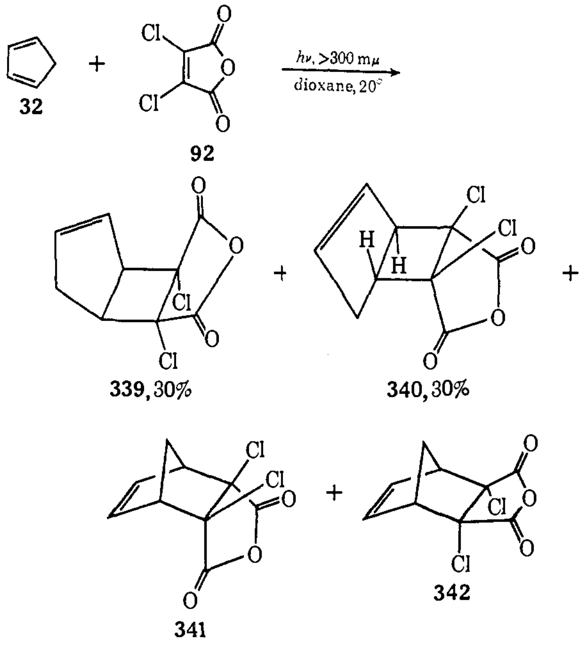


32 + 333 → 334, ~59% + 335, ~20% (185)



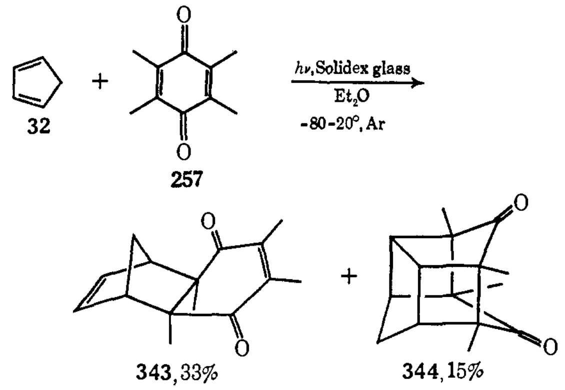
32 + 336 → 337, 57% + 338, 34% (186)

Irradiation of an equimolar mixture of cyclopentadiene with the anhydride **92** gave both 1,2- and 1,4-cycloaddition products (eq 187).[141] The reactants **32** and **92** form a charge-transfer complex, λ_{max} 350 mμ.[141] Benzophenone will sensitize this reaction.[141] The small amount of 1,4-addition products **341** and **342** observed may arise *via* a thermal reaction.[141] The *trans*-fused 5,4-ring system **340** is interesting in that this is the first example of the formation of such a system in a photocycloaddition although the photoformation of the *trans*-fused 6,4-ring system is well known (see below).



32 + 92 → 339, 30% + 340, 30% + 341 + 342 (187)

Duroquinone (**257**) was added to cyclopentadiene to give products of both 1,4-addition, **343**, and 1,2-addition, **344** (eq 188).[3,90,130]



32 + 257 → 343, 33% + 344, 15% (188)

Irradiation of solutions of **32** and acetone (**345**) gave appreciable amounts of the oxetane **346** in addition to dimers **33–35** and the tetrahydrofulvalene **36** (eq 189).[80] The product

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(135) K. J. Crowley, *Proc. Chem. Soc.*, 245 (1962).

(136) K. J. Crowley, *ibid.*, 334 (1962).

(137) K. J. Crowley, *Acta Cient. Venezolana Suppl.*, No. 1, 194 (1959–1963); *Chem. Abstr.*, **62**, 1691 (1965).

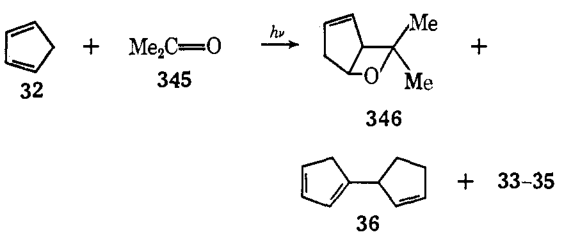
(138) K. J. Crowley, *Tetrahedron*, **21**, 1001 (1965).

(139) H. Krieger, *Suomen Kemistilehti*, **B35**, 4 (1962).

(140) H. Krieger, *ibid.*, **B36**, 68 (1963).

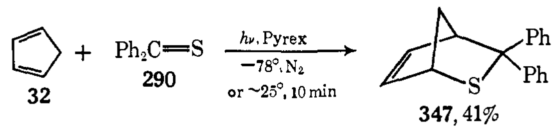
(141) H.-D. Scharf, *Tetrahedron Letters*, 4231 (1967).

distribution as a function of several variables is given in Table XXII.[80] Decreasing the temperature appears to lower the rate of energy transfer more than the rate of acetone addition to the diene **32**. It is somewhat surprising that increasing the concentration of acetone fivefold should decrease the amount of adduct **346** compared with the dimers **33–35**.



(189)

As in the other photoadditions of thiobenzophenone (**290**) described above, the reaction with cyclopentadiene (**32**, 2 moles per mole of **290**) led only to the 1,4-addition product **347** (eq 190).[132] Irradiation of a 0.03% solution of the thioketone **290** with an excess of **32** in *n*-hexane at −78° for 52 hr gave the adduct **347** in 22% yield.[132]



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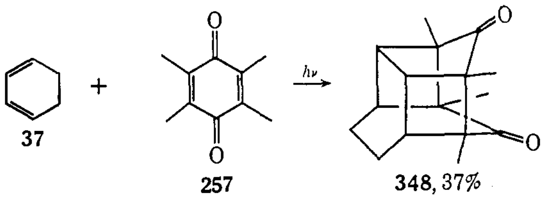
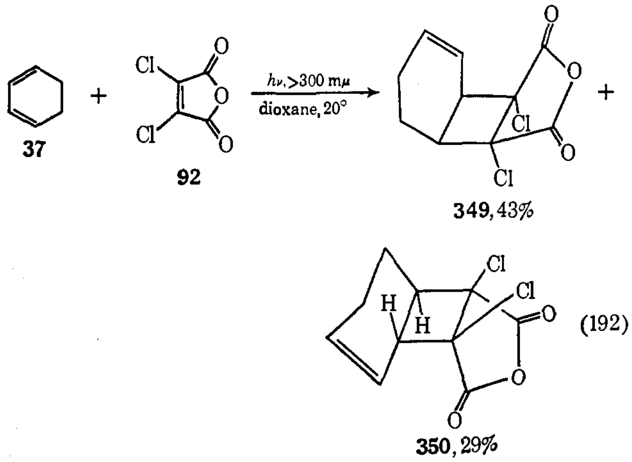
b. 1,3-Cyclohexadiene

In contrast to cyclopentadiene (see above), cyclohexadiene (**37**) gave only a 1,2-addition product, **348**, on irradiation with duroquinone (**257**) (eq 191).[3,90,130]



(191)

37 gave only 1,2-cycloaddition products **349** and **350** on irradiation with the anhydride **92** (eq 192), again in contrast with the reaction of cyclopentadiene.[141] The reactants form a charge-transfer complex, λ_{max} 360 mμ.[141] Addition of benzophenone accelerated the reaction, but gave the same products.[141]



(192)

Table XXII

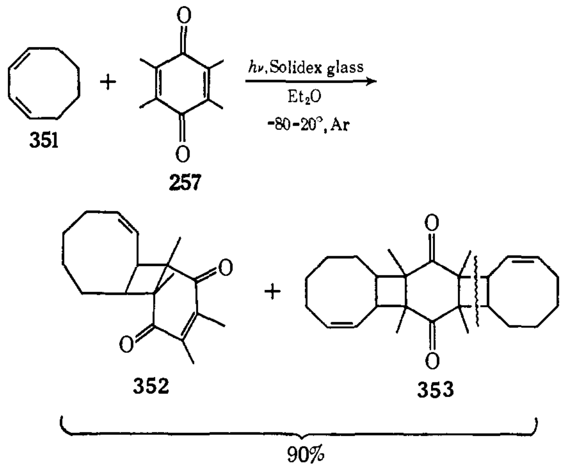
Photoaddition of Cyclopentadiene to Acetone

Weight ratio, %		Temp, °C	Product distribution, %		
32	345		346	33–35	36
90	10	−10[a]	49	46	4
90	10	−78[b]	79	16	5
50	50	−78[b]	73	19	8

[a] Irradiated through a Pyrex filter for 2 hr. A polymer of cyclopentadiene (**32**) was also formed. [b] Either a Pyrex or Corex filter was used.

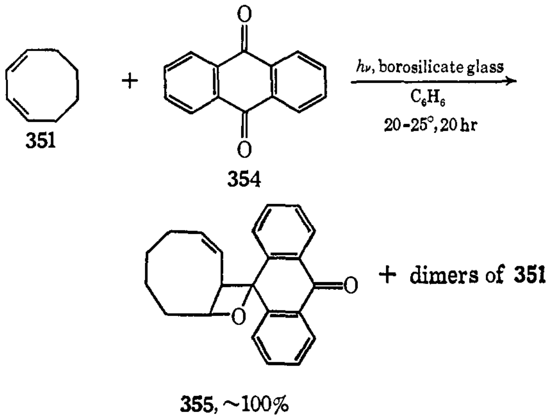
c. 1,3-Cyclooctadiene

1,3-Cyclooctadiene (**351**) gave both 1:1 **352** and 2:1 **353** adducts with the quinone **257** (eq 193).[90] Irradiation of the 1:1 adduct **352** with the diene **351** gave the 2:1 adduct **353**.[90]



(193)

Irradiation of **351** with 9,10-anthraquinone (**354**) gave the oxetane **355** in nearly quantitative yield (eq 194).[142] Small amounts of cyclobutyl dimers of **351** were also formed.[142] No 2:1 adduct (**351**:**354**) was detected.[142] By way of contrast, the two acyclic dienes **1** and **30** gave no cross-adducts,[142] only diene dimers in the case of **1** (Table II).[51] The rationalization offered to account for these differences was based on the triplet excitation energies of the dienes. The octadiene **351**, having the diene moiety in a nonplanar skew conformation, has a vertical triplet energy of 70–72 kcal/mole, too high to undergo energy transfer from the excited quinone **354**, E_T = 62.4 kcal/mole.[137] The acyclic dienes **1** and **30**, which have vertical



(194)

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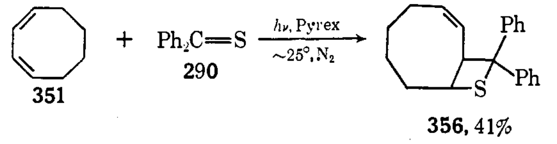
[142] D. Bryce-Smith, A. Gilbert, and M. G. Johnson, *Tetrahedron Letters*, 2863 (1968).

triplet energies of *ca.* 60 kcal/mole, undergo energy transfer from the excited quinone **354** at near the diffusion-controlled rate.[51,142] These triplet dienes then lead to dimers as described above. The triplet quinone **354**, unable to transfer energy to the cyclic diene **351**, adds to it to give the oxetane **355**.[142] The small amount of diene dimers which are formed from **351** probably result from energy transfer from the excited product ketone **355** to the diene **351**.[142] The triplet energy of **355** is expected to be *ca.* 70 kcal/mole by analogy with benzophenone. This triplet energy also explains the lack of a 2:1 adduct of **351** and **354** since the energy-transfer process is now more favorable than addition.[142]

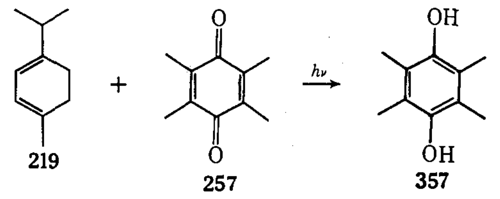
Cyclooctadiene (**351**) is the only diene, except for α-phellandrene (**51**) (see below), which has been reported to give a 1,2-addition product with thiobenzophenone (**290**) (eq 195).[132] The lack of formation of a 1,4-addition product has been attributed to the nonplanarity of the diene moiety of **351**.[132]



(195)

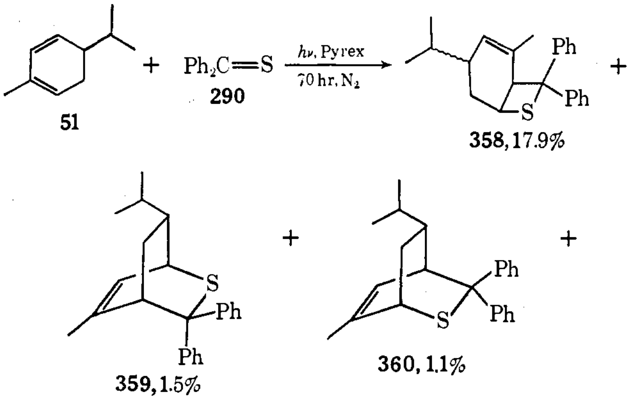
d. Other Dienes, Trienes, and Tetraenes

Attempted addition of α-terpinene (**219**) to the quinone **257** gave the hydroquinone **357** (eq 196) instead of an adduct,[3] possibly indicating a hindrance to addition by the alkyl groups attached to the 1,4 positions of **219** and the 1,2 positions of **257**.



(196)

α-Phellandrene (**51**) gave an unidentified adduct with duroquinone (**257**) when irradiated under conditions such that only the quinone absorbed the radiation (>416 mμ).[90] However, under similar conditions with other sensitizers the dimer **52** was formed[90] (see section II.A.2.c above).



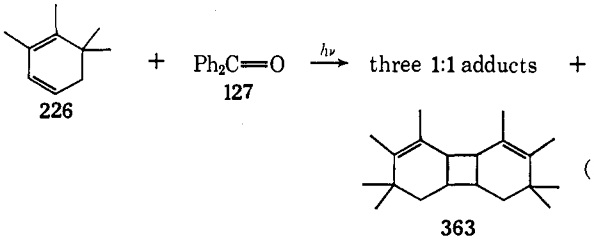
$(Ph_2CHS\!\!-\!\!)_2$ + $Ph_2C{=}CPh_2$ (197)

361, 6.0% 362, 1.9%

Irradiation of a mixture of α-phellandrene (**51**) and thiobenzophenone (**290**) gave a mixture of a 1,2 adduct, **358**, two 1,4 adducts, **359** and **360**, and other products (eq 197).[143]

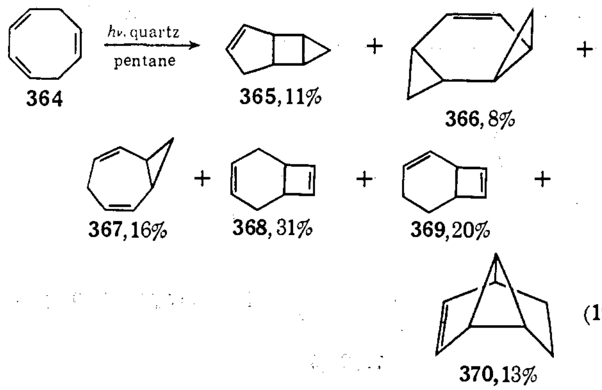
α-Pyronene (**224**) gave only a 1:1 adduct of undetermined structure on irradiation with benzophenone.[29]

β-Pyronene (**226**) on irradiation with benzophenone (**127**) gave both 1:1 adducts (unidentified) and a dimer, **363** (eq 198).[29]



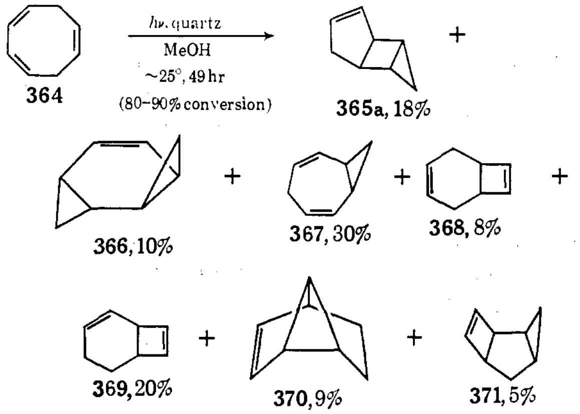
(198)

An intramolecular analog of these cross-addition reactions involving 1,3,6-cyclooctatriene (**364**) has been reported under several different conditions. Irradiation of **364** in pentane solution gave quantitatively a mixture of products, among which were the products of 1,2 addition, **365**, and a combined 1,2–1,4 addition, **366** (eq 199).[144]



(199)

Another report indicated that similar irradiation of **364** either as a 1% solution in methanol[145,146] or in the gas phase[145] gave the same products in addition to another isomer, **371** (eq 200). Excitation of the diene moiety of **364** (eq 201) followed by sequential ring closures (eq 202–204) would account for the cycloaddition products **365** and **366**.[144] The singlet or



(200)

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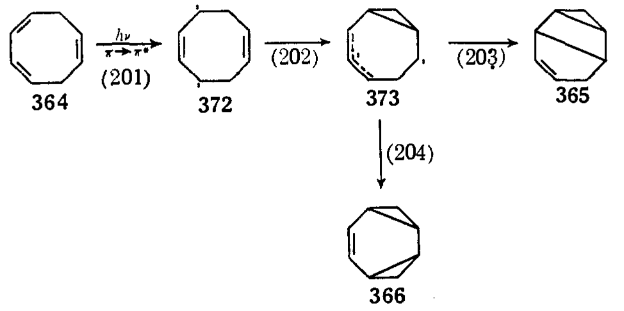
(143) Y. Omote, M. Yoshioka, K. Yamada, and N. Sugiyama, *J. Org. Chem.*, **32**, 3676 (1967).

(144) J. Zirner and S. Winstein, *Proc. Chem. Soc.*, 235 (1964).

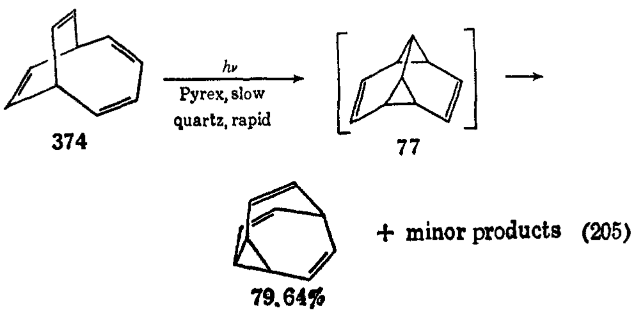
(145) W. R. Roth and B. Peltzer, *Angew. Chem.*, **76**, 378 (1964); *Angew. Chem. Intern. Ed. Engl.*, **3**, 440 (1964).

(146) W. R. Roth and B. Peltzer, *Ann.*, **685**, 56 (1965).

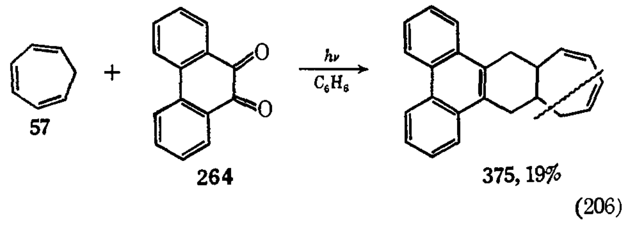
triplet character of the excited triene **372** has not been determined. If the diradical **372** is a singlet, as is likely the case, the formation of the cyclobutane derivative **365** could be a concerted process[41] which bypasses the diradical intermediate **373**; however, the stereochemistry of **365a** would require either a *trans–trans* addition[46] for the all-*cis* precursor **372** or a *cis,trans,trans* stereochemistry of the precursor **372** for a *cis–cis* addition. The formation of the cyclohexene derivative **366** would require a stepwise process.[41,46]



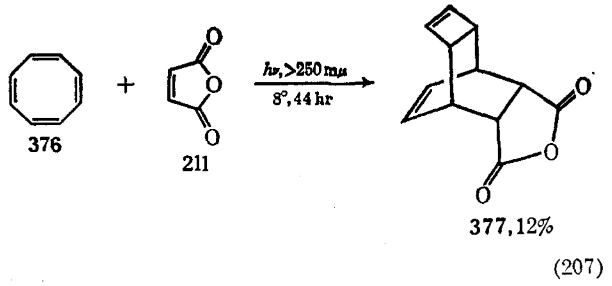
The photochemical conversion of the tetraene **374** to bullvalene (**79**) has been suggested to involve the intramolecularly cyclized isomer **77** as an intermediate (eq 205).[147]

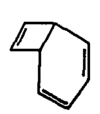


Cycloheptatriene (**57**) on irradiation with phenanthraquinone (**264**) gave a 1,4-dioxene derivative, **375**, resulting from 1,2 cycloaddition of one of the triene double bonds and 1,4 cycloaddition of the 9,10-dione system (eq 206).[40,130]



Cyclooctatetraene (**376**) with maleic anhydride (**211**) gave the 1,4-addition product **377** (eq 207).[72,92,112] No dimers of **376** were formed.[92] In a control dark (thermal) reaction the adduct **377** was formed in 3% yield.[92] It was suggested that the adduct was formed *via* the triene **378** which arose *via* excitation of the tetraene **376**.[92]





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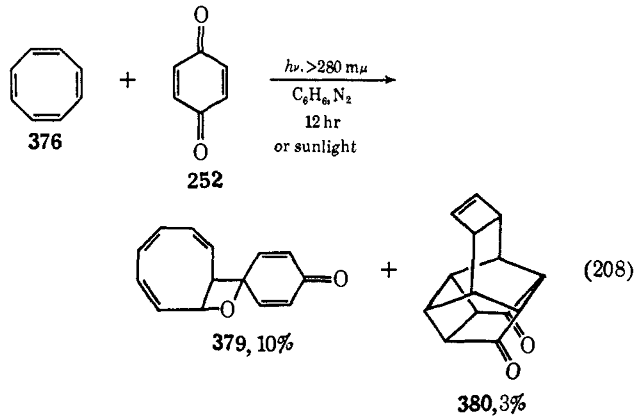
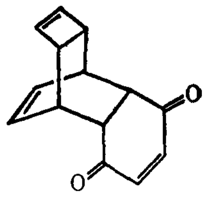
In contrast, cyclooctatetraene (**376**) with *p*-benzoquinone (**252**) gave the 1,2-addition product **379** (eq 208).[148,149] The caged product, **380**, presumably arises from the intramolecular photocycloaddition of the 1,4 adduct, **381**, which is formed *via* a thermal side reaction.[149]





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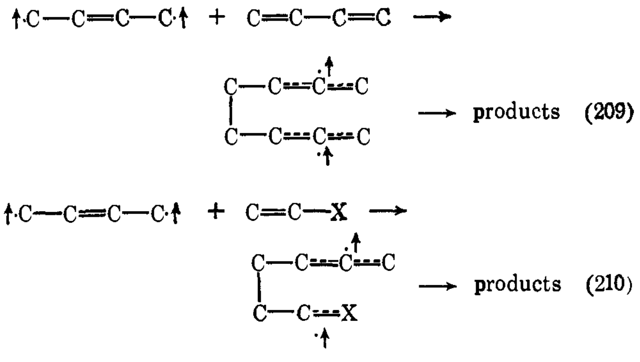
IV. Summary

A few of the generalizations which emerge from this review will be outlined in this section.

Nearly all of the cycloaddition reactions of triplet dienes lead to products which can be rationalized as arising *via* the formation of the most stable diradical intermediates (eq 209 and 210). On the other hand, reactions of singlet dienes are in



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[147] M. Jones, Jr., and L. T. Scott, *J. Am. Chem. Soc.*, **89**, 150 (1967).

[148] D. Bryce-Smith and A. Gilbert, *Proc. Chem. Soc.*, **87** (1964).

[149] D. Bryce-Smith, A. Gilbert, and M. G. Johnson, *J. Chem. Soc.*, *C*, 383 (1967).

general much less selective, although this type of reaction has not been studied in as much detail.

The product distribution in photosensitized dimerizations of acyclic dienes is a function of the sensitizer triplet energy, while the sensitizer energy has little or no effect in the dimerization of cyclic dienes.

Many compounds which act as sensitizers at low concentration will react with dienes at higher concentration, *i.e.*, when their concentration approaches that of the diene. In this connection it may be noted that slight changes in the experimental conditions often have a profound effect on the course of photocycloadditions. These changes may be responsible for some of the seemingly contradictory results from different laboratories.

In general, photocycloadditions of conjugated dienes produce mainly cyclobutane derivatives, while the products of the thermal reactions of the same reactants are usually cyclohexene derivatives. The photosensitized cycloaddition of conjugated dienes has become one of the most important synthetic methods for the preparation of cyclobutane derivatives.

Acknowledgment. The author wishes to thank Professor G. S. Hammond for permission to reproduce Figures 1 and 2.