INTRAMOLECULAR PHOTOCHEMICAL CYCLOADDITION REACTIONS OF NONCONJUGATED OLEFINS

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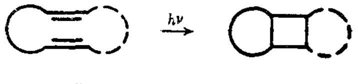
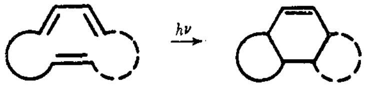
CONTENTS

I. INTRODUCTION AND SCOPE OF THE REVIEW

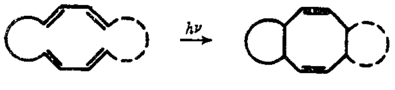
This review is intended to cover all work, except as noted below, published through 1964 and most of 1965 on photochemical cycloaddition reactions which occur intramolecularly with nonconjugated olefins, *i.e.*, molecules in which the two addend groups are not conjugated in the classical sense (Eq 1–3). These reactions may be 1,2 or 1,4 additions or a combination of the two. So far as is known no 1,6 or higher intramolecular photochemical addition types have been reported.



(Eq 1)

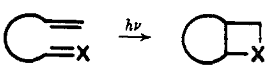


(Eq 2)

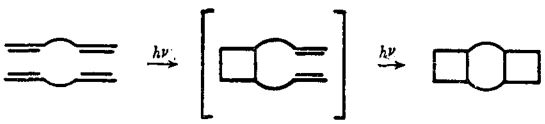


(Eq 3)

This review also includes intramolecular cycloadditions involving atoms other than carbon, such as oxygen in carbonyl groups (Eq 4). A number of intermolecular photochemical cycloaddition reactions involving two such additions have been reported (Eq 5). The second reaction probably involves an intramolecular addition of an intermediate formed from the initial cycloaddition (57). These reactions are included.



(Eq 4)



(Eq 5)

The photochemical cycloaddition of adjacent pyrimidine rings in polynucleotide chains, such as DNA, to give substituted cyclobutanes is an intramolecular addition which would fall under the scope of this review. However, these reactions have been reviewed recently (65, 103) and therefore will not be discussed in this review.

The review does not include cyclobutene formation from conjugated olefins, a process which could be considered an intramolecular cycloaddition (Eq 6).

(Eq 6)

Several very limited reviews of the intramolecular photochemical cycloaddition of nonconjugated olefins have appeared recently in conjunction with their more common intermolecular counterparts (12, 52, 57, 62, 63, 69, 79, 81, 87, 104).

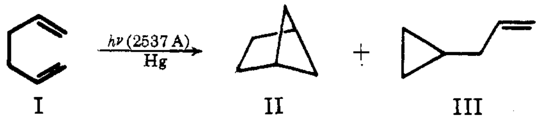
A discussion of the proposed mechanisms and excited states involved in these reactions is included where possible. The reactions are grouped according to structural types rather than mechanistic types since in a majority of the cases the mechanism is unknown or only partially known. The terms acyclic, monocyclic, bicyclic, etc., refer to that portion of the molecule containing the two reacting unsaturated linkages, not the molecule as a whole. The sources of radiation were generally medium- or high-pressure mercury arc lamps unless otherwise specified.

II. CYCLOADDITIONS INVOLVING CARBON 1,2 ADDITION

A. ACYCLIC COMPOUNDS

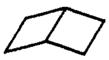
1. Olefins

The mercury-sensitized isomerization of 1,5-hexadiene (I) in the vapor phase gave a mixture of the bicyclohexane (II), allylcyclopropane (III), and other free-radical-derived products (93) (Eq 7). The yield



(Eq 7)

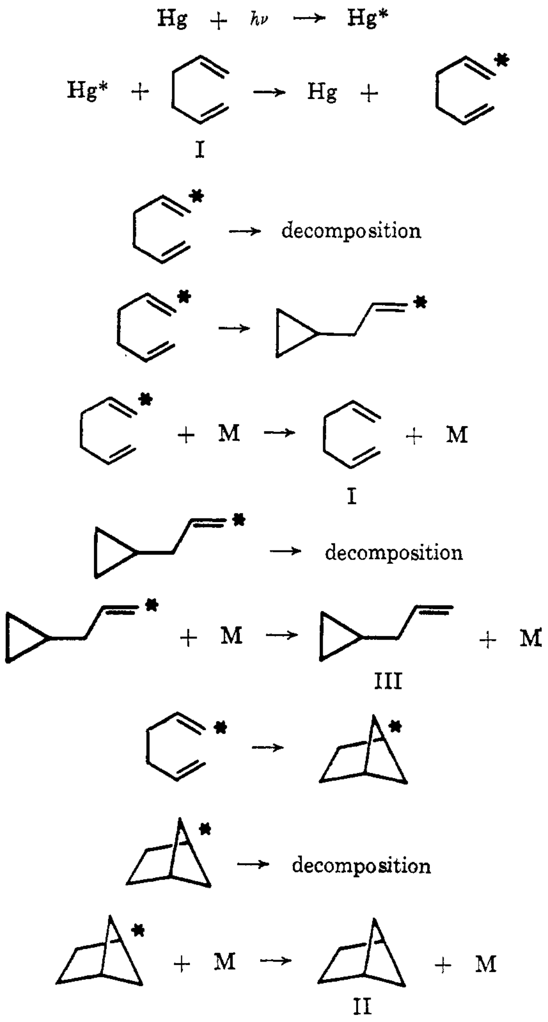
of II increased gradually with increasing pressure in the range 0–200 mm, while the yield of III reached a maximum at a pressure of 28 mm of I and then decreased with increasing pressure. The yields of the other free-radical-derived products continuously decreased with increasing pressure. The quantum yield (Φ) for III at 28 mm was *ca.* 0.10, while that of II was *ca.* 0.012 at 200 mm. Two mechanisms were proposed for this reaction on the basis of the quantum yield dependence on the pressure (93). The first is shown in Scheme I. The second proposed mechanism involved three vibrational levels (or sets of levels), 2, 1, and 0, of the excited electronic state of I (see Scheme II). Both mechanisms predict maximum quantum yields for II and III at some pressure. That II did not show a maximum was attributed to the experimental difficulties of determining the maximum due to a combination of a relatively high value of $M_{\max}$ and a low value of $\Phi_{\max}$ (93). The process Hg* → Hg at 2537 A involves a triplet → singlet transition ($6^3P_1 \rightarrow 6^1S_0$), and therefore the excited state of I was probably a triplet. The formation of II rather than the isomeric bicyclo[2.2.0]hexane (IV), which



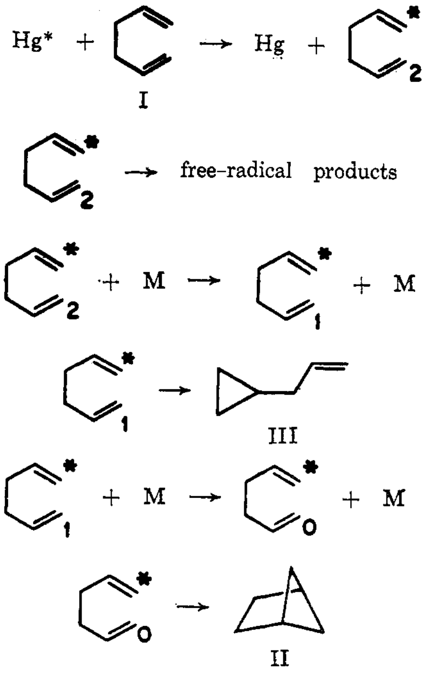
IV

would have arisen from the alternate mode of addition

SCHEME I

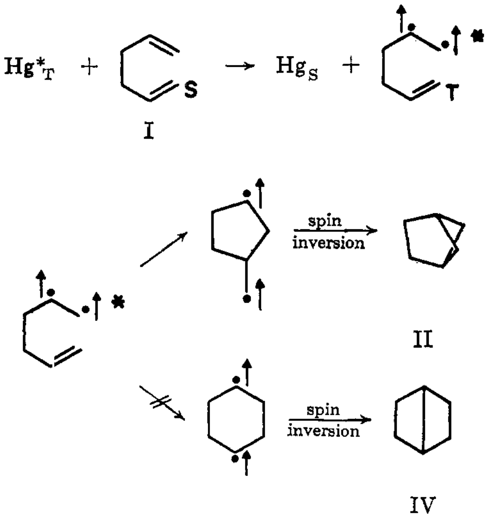


SCHEME II

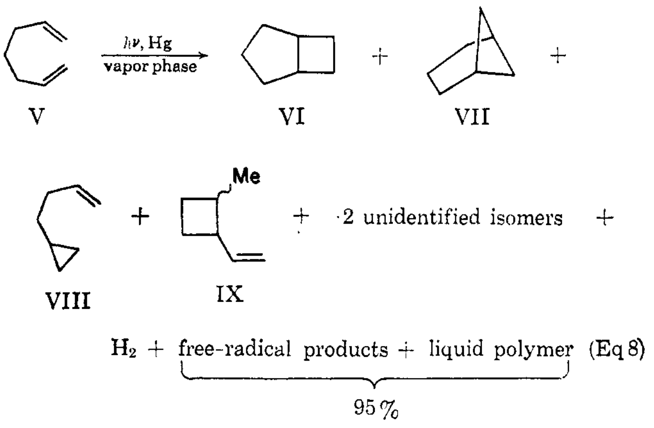


of the double bonds of I, may reflect the instability of IV with respect to II (Scheme III). The excited IV, if formed, may have decomposed to I or other products.

Scheme III

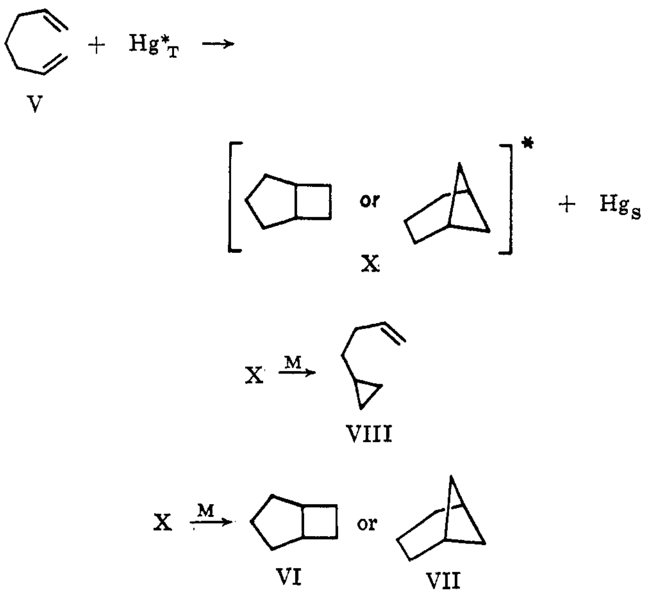


Mercury-sensitized photoisomerization of 1,6-heptadiene (V) at 3–65 mm pressure gave both of the possible intramolecular cycloaddition products, VI and VII, in addition to other products resulting from hydrogen migration, VIII and IX, and free-radical processes (96) (Eq 8). The quantum yield for the disappearance of V was 0.6 at 15 mm and 0.3 at 46 mm. The quantum yield for the formation of all isomers was 0.015 at 21–65 mm. At lower pressures the latter quantum yield decreased. The amount of VI increased with increasing pressure while that of VII appeared to reach a maximum at *ca.* 15 mm. More of VI was formed than VII, the ratio being *ca.* 4:1 at the higher pressures. The mechanism for the formation of VI and VII is believed to be similar to that of II above, the relative amounts of VI or VII and VIII depending on the pressure (96). A "hot" cyclobutane derivative (X) was proposed as the precursor to these isomers (96) (Scheme IV).

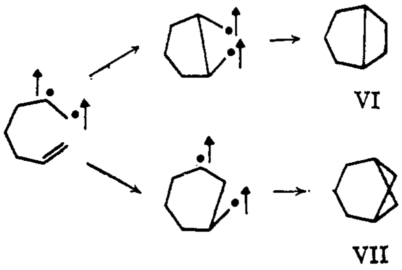


In this case (Scheme V) the excited triplet of V closed in both directions.

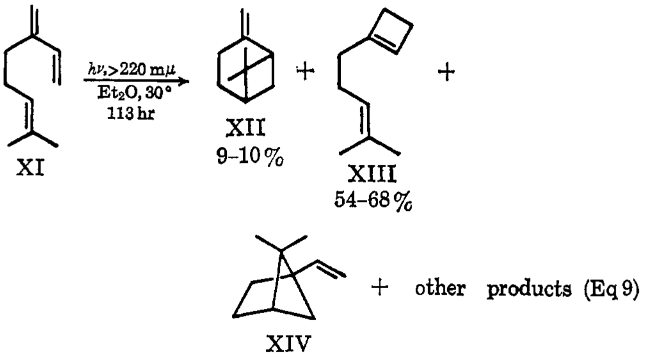
Scheme IV

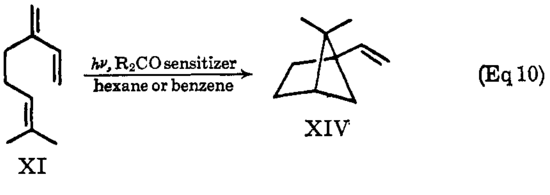


Scheme V



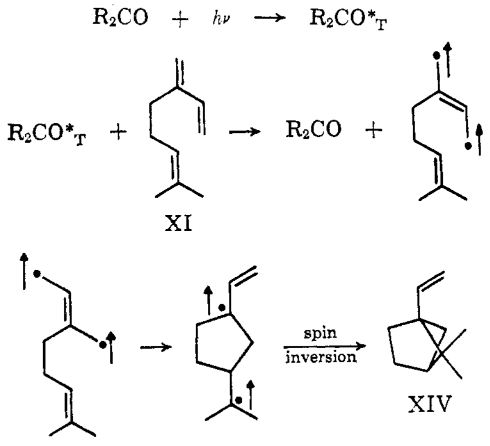
Irradiation or myrcene (XI) at λ >220 mμ gave a mixture of products (Eq 9), the major ones being β-pinene (XII) and the cyclobutene XIII (32–35). A small amount of XIV has also been observed in this reaction (35, 37). In contrast, irradiation of XI in the presence of a sensitizer (Eq 10) gave the isomeric bicyclo[2.1.1]hexane XIV as the only product (61). Ben-



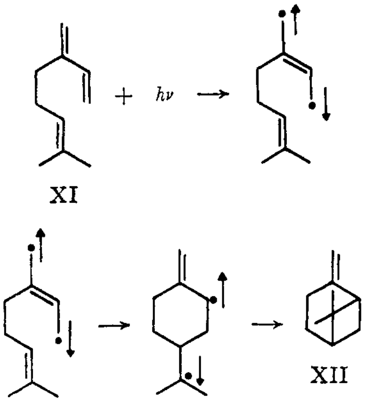


zophenone, β-acetonaphthone, and fluorenone all act as sensitizers for this reaction; the quantum yield in the case of benzophenone was 0.05. The mechanism in the presence of a sensitizer (Scheme VI) is believed to involve the transfer of triplet energy to the olefin XI and subsequent ring closure (61). It appears that the nonsensitized reaction (Scheme VII) (32–35) may proceed *via* the excited singlet π,π* state of XI (61).

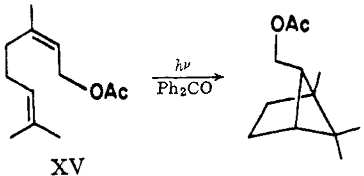
SCHEME VI



SCHEME VII



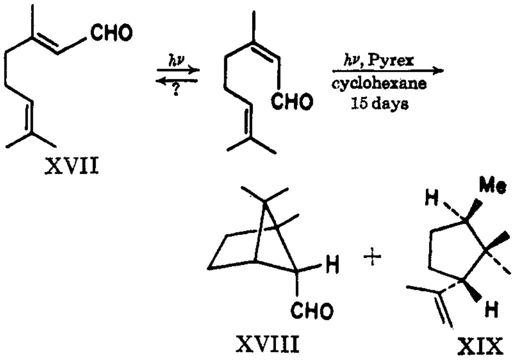
Irradiation of neryl acetate (XV) in the presence of benzophenone gave the isomeric acetate XVI as 90% of the volatile product (16) (Eq 11).



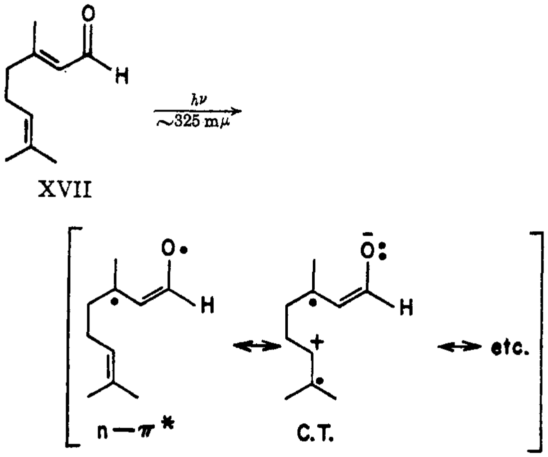
XV XVI (Eq 11)

2. α,β-Unsaturated Carbonyl Compounds

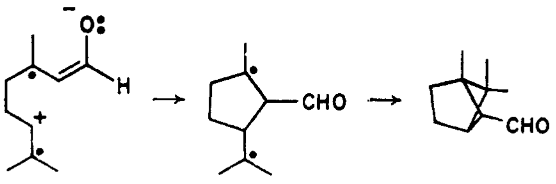
A mixture of *cis*- and *trans*-citral (XVII) gave the cycloaddition product XVIII and a hydrogen migration product (XIX) on irradiation at the wavelength of the n → π* transition of XVII in either cyclohexane (25, 26) or ethanol (11) (Eq 12). The interconversion of the *cis* and *trans* forms of XVII is probably rapid compared with the cyclization (26). One mechanism proposed for the formation of XVIII involved the n → π* excited state of XVII mixed with some charge-transfer character (26). The high extinction coefficient (ε 72) of the n → π* transition (λ_{max} 325 mμ) of XVII was attributed to the mixing of the pure localized n → π* transition with a charge-transfer (CT) transition from the isolated double bond to the same antibonding π* orbital (Eq 13). This excited state may be either a singlet (26) or a triplet (11,26). Ring closure could then give XX or a zwitterionic form, followed by the second ring closure (15, 16, 26) (Eq 14).



(Eq 12)

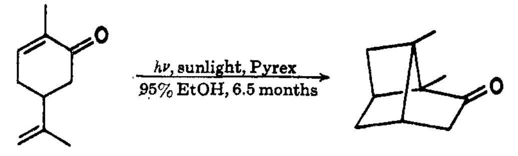


(Eq 13)



XX XVIII (Eq 14)

The α,β-unsaturated ketone, carvone (XXI), was converted to carvonecamphor XXII on irradiation through Pyrex (10, 14, 88, 89) (Eq 15). A more detailed study of this reaction using artificial light sources has shown that the product XXII was photolyzed to the ester XXIII (or XXIV) during the reaction (66).

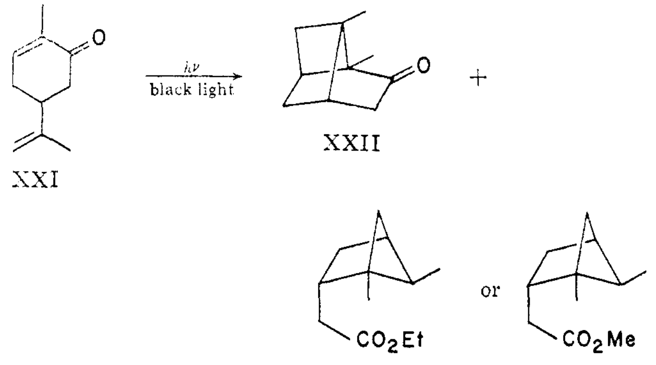


(Eq 15)

XXI

XXII, 9.4%

Use of a black-light fluorescent lamp (maximum intensity at *ca.* 355 mμ) gave larger amounts of the isomer XXII than did a high-pressure mercury arc lamp with a Pyrex filter. These results indicated that higher energy radiation was required for the destruction of the saturated ketone XXII than for its formation. Irradiation of 0.5% solutions of carvone (XXI) with the black-light source gave increasing amounts of the ester XXIII after longer exposure times; larger amounts of the isomer XXII were formed with solvents of greater polarity (66) (see Table I). On a preparative scale, the ketone XXII could be isolated in 35% yield by irradiation of XXI in 95% ethanol for 23 days (66). The formation of XXII presumably involves the n,π* state of the α,β-unsaturated carbonyl system (10) and may involve the triplet state based on other work with cyclic α,β-unsaturated ketones (41) (Scheme VIII).



XXI

XXII

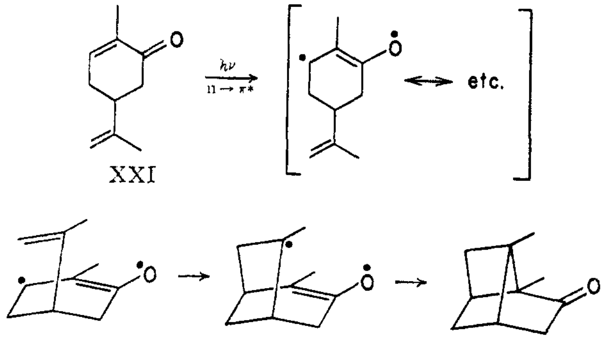
XXIII

XXIV

Table I

Solvent	Time, days	% conversion		
		XXII	XXIII	XXIV
EtOH	1	13	. .	
	2	32	6	
	3	44	24	
	4	44	56	
	5	27	73	
	6	12	88	
	7	3	97	
95% EtOH	3	46	35	
MeOH	3	46		29
$HCONMe_2$	3	13 + 13% unknown		
MeCN	3	12		
C_6H_6	3	5		
Et_2O	3	4		
Cyclohexane	3	2		

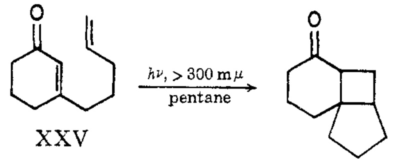
Scheme VIII



XXI

XXII

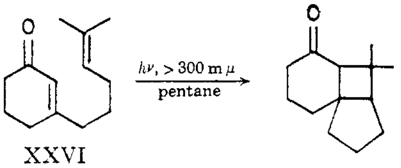
Two other alkenylcyclohexenones, XXV and XXVI (1% solutions), have been intramolecularly cyclized to XXVII and XXVIII, respectively, as the only distillable products (28) (Eq 16 and 17, respectively).



(Eq 16)

XXV

XXVII, 52%

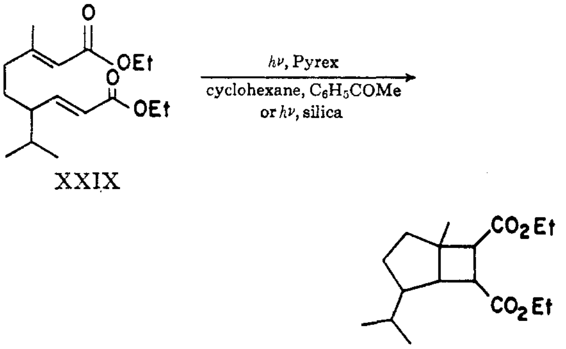


(Eq 17)

XXVI

XXVIII, 38%

The α,β-unsaturated ester XXIX was converted to the same mixture of isomeric cyclopentane derivatives XXX by either photosensitization with acetophenone or direct irradiation (8) (Eq 18). This reaction probably occurs *via* the triplet state of XXIX (8). In a similar manner the diacid XXXI and the diketone XXXII were cyclized to the isomers XXXIII and XXXIV, respectively (8) (Eq 19 and 20, respectively).

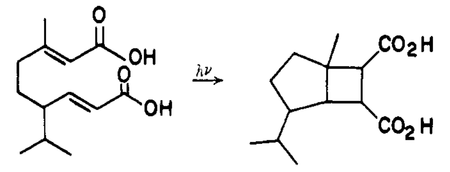


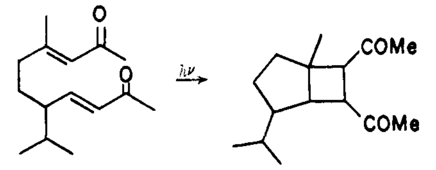
XXIX

(Eq 18)

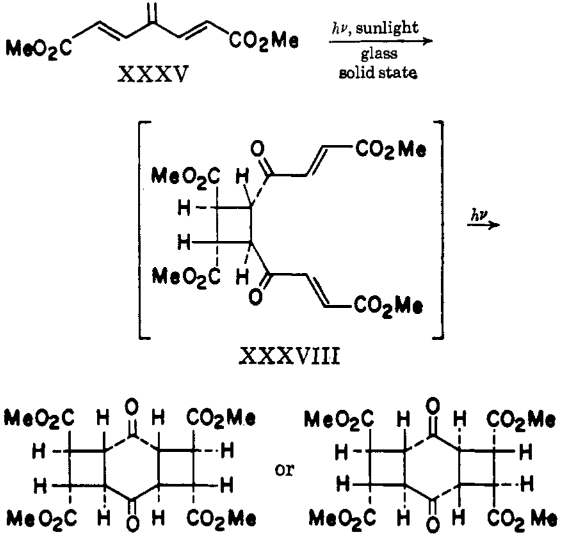
XXX, 55%

The dimethyl ester XXXV gave an all-*trans* dimer on irradiation with sunlight through glass (18, 29, 67, 97, 100). The dimer could have either structure XXXVI (57) or XXXVII. The half-closed dimer XXXVIII


XXXI XXXIII (Eq 19)


XXXII XXXIV (Eq 20)

(57) was probably an intermediate in the formation of XXXVI or XXXVII (Eq 21).

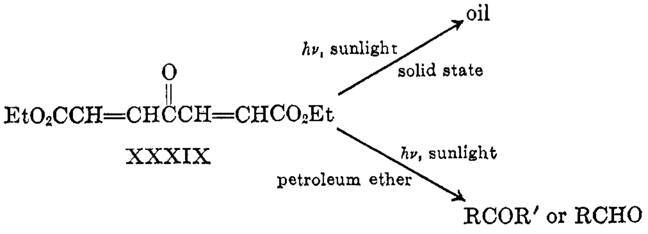


XXXV

XXXVIII

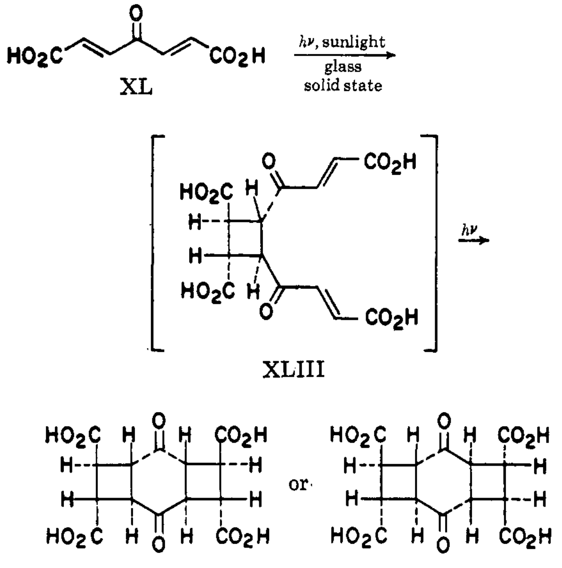
XXXVI or XXXVII (Eq 21)

The diethyl ester XXXIX was rather inert to irradiation compared with the dimethyl ester XXXV (100). An unidentified oil was formed on irradiation in the solid state and a ketone or aldehyde in solution (97).


$$\mathrm{EtO_2CCH{=}CH\overset{\overset{O}{\|}}{C}CH{=}CHCO_2Et} \xrightarrow[\text{solid state}]{h\nu,\ \text{sunlight}} \text{oil}$$
$$\xrightarrow[\text{petroleum ether}]{h\nu,\ \text{sunlight}} \mathrm{RCOR'}\ \text{or}\ \mathrm{RCHO}$$
XXXIX

The diacid XL was converted to the same carbon skeleton XLI or XLII as formed from XXV (67), presumably *via* XLIII (Eq 22).

Duroquinone (XLIV) added twice to the olefins XLV and XLVI to give XLVII and XLVIII, probably *via* the open dimers XLIX and L (59). A 2:1 adduct



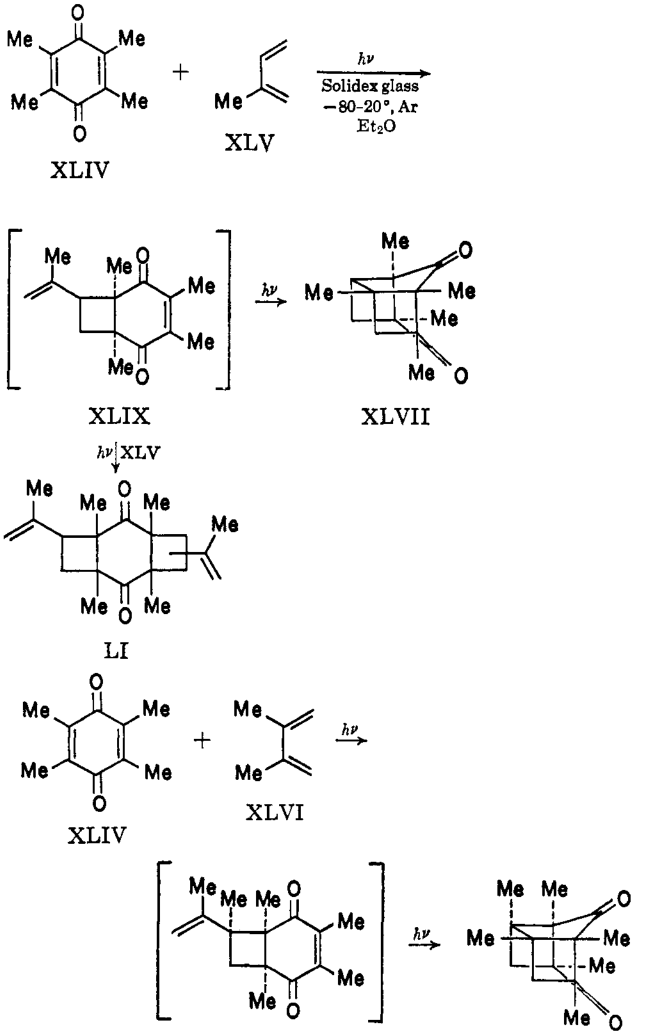
XL

XLIII

XLI XLII (Eq 22)

LI was also isolated from XLIV and XLV (Scheme IX).

SCHEME IX



XLIV XLV

XLIX XLVII

LI

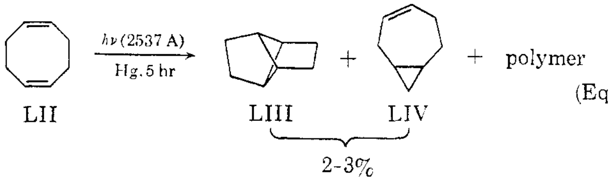
XLIV XLVI

L XLVIII

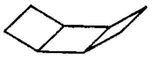
B. MONOCYCLIC COMPOUNDS

1. *Olefins*

The mercury-sensitized intramolecular photocycloaddition of *cis,cis*-1,5-cyclooctadiene (LII) in the gas phase gave a low yield of the tricyclooctane LIII in addition to other products (91, 94) (Eq 23). The crossed olefin addition is again the preferred mode of ring closure; none of the isomeric tricyclooctane LV, which would result from *cis* addition, was detected (91).

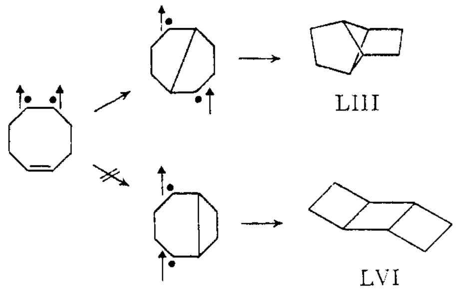


(Eq 23)


LV

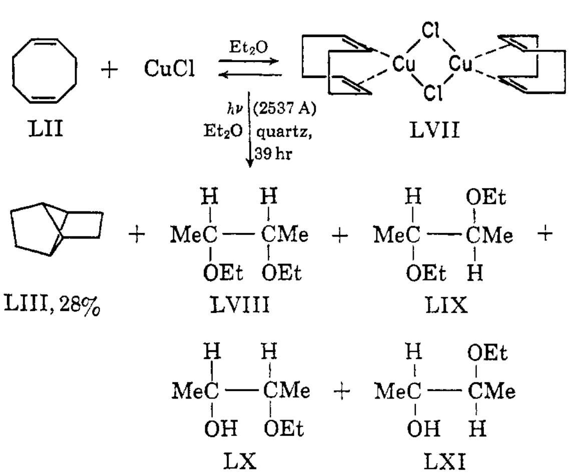
Since the product LIII was derived from the *trans,-trans* isomer of LII, either both double bonds of LII had to twist in the excited state or the product LIII was derived from the small portion of the *cis,trans* isomer of LII present as an impurity in the LII (91). In either case it appears that the *trans* isomer of LV, LVI, could arise by formation of a 4,6 ring system, whereas formation of LIII requires a 5,5 ring system. Again a triplet excited state was probably involved (Scheme X). It was pointed out that LV or LVI, once formed in an excited state, may not have been stable and may have decomposed before deactivation to their ground states could occur (91).

SCHEME X

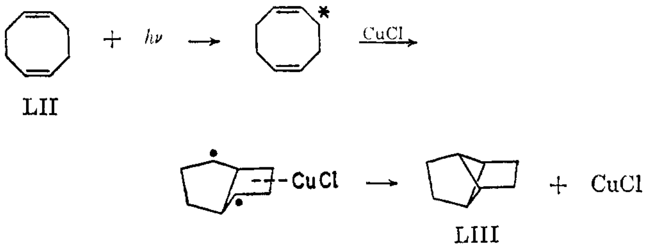


In contrast to the gas phase photochemistry of LII, in solution in the presence of cuprous chloride reasonable yields of LIII were formed (92, 94) (Scheme XI). The quantum yield for the formation of LIII was *ca.* 0.1 based on the amount of LII. The quantum yield was too high (*ca.* 10) based on the amount of complex LVII which could be present. Therefore the diene LII must absorb most of the radiation. The solvent-derived products, LVIII–LXI, were also formed in the absence of LII. A mechanism proposed for the catalytic action of cuprous chloride involved complexing with the excited state of LII (94) and is shown in Scheme XII.

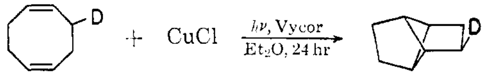
SCHEME XI



SCHEME XII



An alternate mechanism has been proposed for the cuprous chloride promoted ring closure of LII to LIII (4). Under conditions similar to those noted above (using a high-pressure mercury arc source) the deuterated diene LXII gave the isomer LXIII containing less deuterium than the starting material (4) (see Eq 24). The undeuterated diene LII gave LIII in 39.5% yield under these conditions. The calculated deuterium content of LXIII for the free-radical mechanism shown in Scheme XIII was 13.4% d_0, 86.1% d_1, and 0.5% d_2 (4).

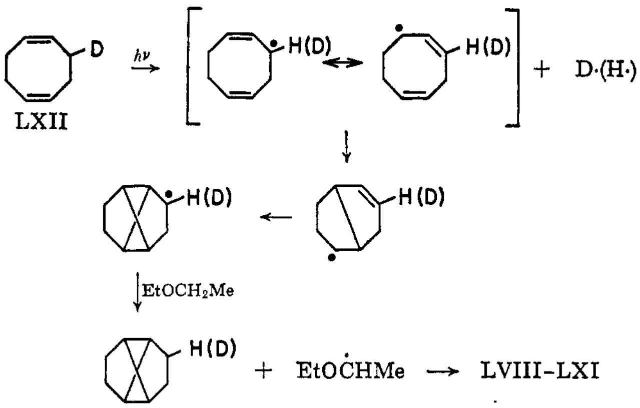


(Eq 24)

LXII	LXIII, 24%
2.3% d_0	14.4% d_0
96.7% d_1	84.7% d_1
1.0% d_2	0.9% d_2

Irradiation of the tetraphenylcyclooctadiene (LXIV) was originally thought to give a compound analogous to LIII (106). However, a recent report (106a) showed that the products were diphenylacetylene and probably a 1:1 adduct of LXIV and isooctane (Eq 25). A dihydrophenanthrene of partial structure LXV was also a possible product.

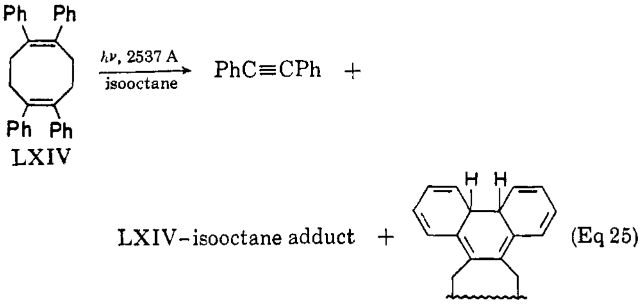
SCHEME XIII



LXII

LXIII

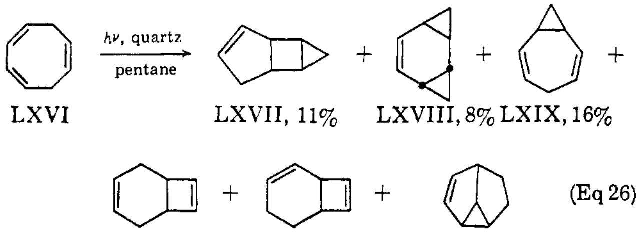
Irradiation of 1,3,6-cyclooctatriene (LXVI) in pentane through quartz with a high-pressure mercury arc gave quantitatively a mixture of products, among which were the products of 1,2 addition, LXVII, and a combined 1,2–1,4 addition, LXVIII (116) (Eq 26).



LXIV

LXV

(Eq 25)

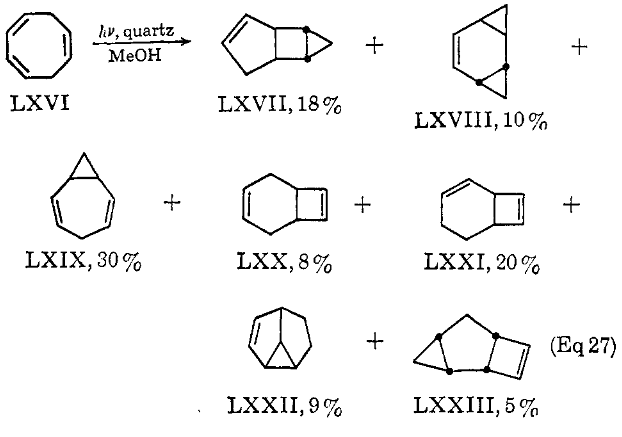


LXVI LXVII, 11% LXVIII, 8% LXIX, 16%

LXX, 31% LXXI, 20% LXXII, 13%

(Eq 26)

Another report indicated that similar irradiation of LXVI in either methanol solution (1%) (77, 78) or the gas phase (77) gave the same products plus another isomer, LXXIII (Eq 27). A reasonable primary process for this reaction is $\pi \rightarrow \pi^*$ excitation of the conjugated diene system since photons of this energy would be available under the reaction conditions. Scheme XIV was proposed to explain the products LXVII and LXVIII (116). The question of whether a singlet or triplet excited state is involved is not yet settled (116).



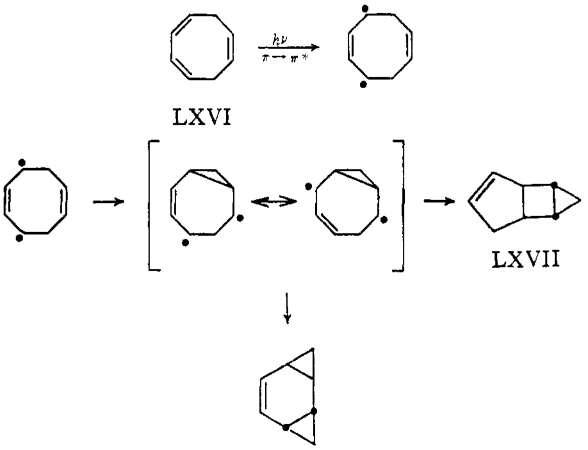
LXVI LXVII, 18% LXVIII, 10%

LXIX, 30% LXX, 8% LXXI, 20%

LXXII, 9% LXXIII, 5%

(Eq 27)

SCHEME XIV



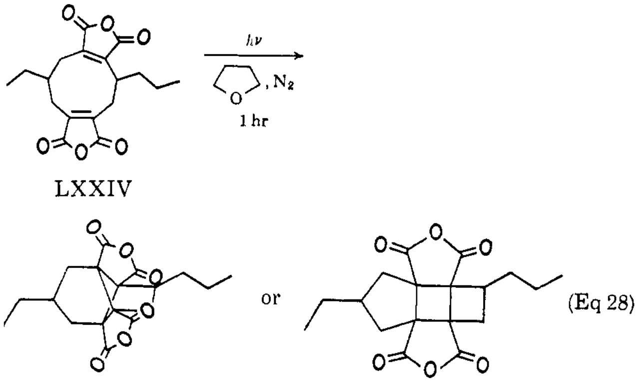
LXVI

LXVII

LXVIII

2. *α,β-Unsaturated Carbonyl Compounds*

The dianhydride, byssochlamic acid (LXXIV), was converted to photobyssochlamic acid having either structure LXXV or LXXVI (3, 5) (Eq 28). Structure LXXV was favored based on the thermal stability exhibited by the photoproduct (3).



LXXIV

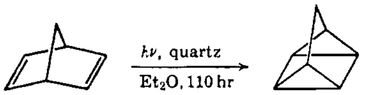
LXXV 70% LXXVI

(Eq 28)

C. BICYCLIC COMPOUNDS

1. *Bicyclo[2.2.1]heptadienes*

Bicyclo[2.2.1]heptadiene (LXXVII) was converted to quadricyclene (LXXVIII) by direct irradiation in ether solution (36) (Eq 29). The ultraviolet absorption spectrum of LXXVII in the vapor state showed a series of 17 bands at 1985–2258 A with maximum intensity at 2113 A (55, 107). A maximum was also ob-

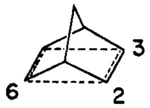


(Eq 29)

LXXVII LXXVIII, 67%

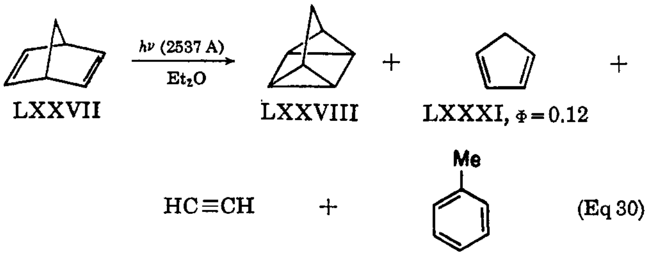
served at 188 mμ (55). In ethanol solution LXXVII had absorption maxima at 205 mμ (ε 2100), 214 (1480), and 220 (870) and a shoulder at 230 (200) (107). Since nonconjugated olefins do not absorb radiation at energies this low, there apparently is interaction between the two double bonds of LXXVII (36). Bicyclo[2.2.1]hept-2-ene (LXXIX) had an absorption maximum at 195 mμ in ethanol (107), and significant maxima at 1956 A (ε 5410), 2064 (3210), and 2077 (2940) in the vapor state (98). Molecular orbital calculations indicated a bond order of 0.12 or 0.50 for the C-2–C-6 bond depending on the model used and 1.50 for the C-2–C-3 bond in the lowest excited state of LXXVII, as shown in LXXX (107).

LXXIX



LXXX

Irradiation of LXXVII in the vapor phase at 4–31 mm and 25–50° with the 2537-A line of a low-pressure mercury arc failed to give any LXXVIII, the products being cyclopentadiene (LXXXI) ($\Phi = 0.50$), acetylene (LXXXII) ($\Phi = 0.49$), and toluene (LXXXIII) ($\Phi = 0.056$) (75). 1,3,5-Cycloheptatriene was also formed at higher conversions (76). Addition of small amounts of oxygen (up to 36 mm with 10 mm of LXXVII) or hydrogen had no effect on the quantum yields. The lack of effect of oxygen indicated that only excited singlet states were involved (75). Addition of 650 mm of hydrogen or helium decreased the quantum yield slightly for LXXXI and LXXXII but had no effect on the quantum yield for LXXXIII. In ether solution, in which the reaction is equivalent to that in the vapor phase at extremely high pressure, LXXVIII was formed along with LXXXI, LXXXII, and LXXXIII (75)(Eq 30). Based on these data the mechanism



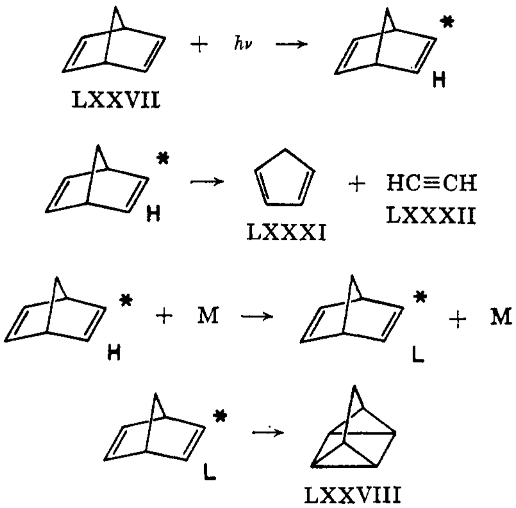
LXXVII LXXVIII LXXXI, $\Phi = 0.12$

(Eq 30)

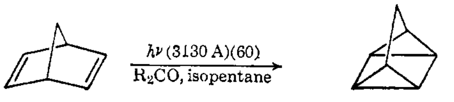
LXXXII, $\Phi = 0.14$ LXXXIII, $\Phi = 0.042$

shown in Scheme XV was proposed where H designates a higher vibrational level of an excited state, and L a lower vibrational level (75). The origin of LXXXIII may be a different vibrational level of the electronic state giving LXXXI, LXXXII, and LXXVIII, or a different electronic state entirely (75).

SCHEME XV



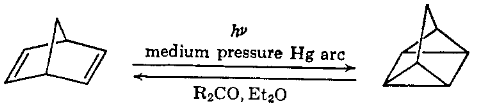
The same transformation, LXXVII → LXXVIII, has also been achieved in high yield by photosensitization using acetone, acetophenone, or benzophenone (53) (Eq 31). A more detailed examination of this reaction



(Eq 31)

LXXVII LXXVIII, ~ 95%

has shown that the process is reversible (54) (Eq 32). The relative amounts of LXXVII and LXXVIII depended on the triplet energies of the sensitizer. The sensitizers, R_2CO, used are shown in Table II (54).



(Eq 32)

LXXVII LXXVIII

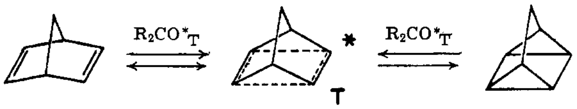
TABLE II

PHOTOSENSITIZED CYCLOADDITION OF BICYCLO[2.2.1]HEPTADIENE (LXXVII)

R_2CO	E_T, kcal/mole	% LXXVIII from LXXVII after 6 hr	% LXXVII from LXXVIII after 6 hr
C_6H_5COMe	73.6	100	0
$(C_6H_5)_2CO$	68.5	86	16
2-Naphthaldehyde	59.5	53	10
$(C_6H_5CO)_2$	53.9	50	2

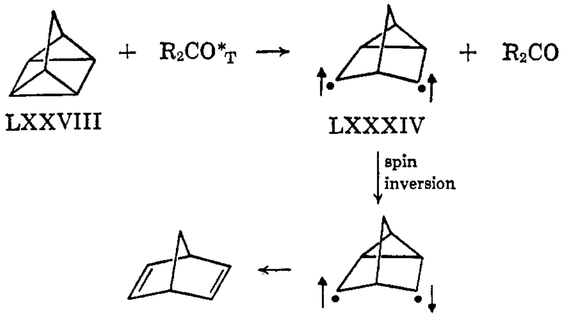
With fluorenone (E_T = 54 kcal/mole) as a sensitizer it appeared that the photostationary-state concentration of LXXVII would be >80% in mixtures with LXXVIII (54). Side reactions were a serious complication in the study of these reactions. Side products acting as sensitizers apparently accounted for the large amount of LXXVIII at the end of the reactions. Two mechanisms have been proposed for the LXXVII–LXXVIII interconversion (54). One involved excitation of either LXXVII or LXXVIII to triplets having approximately the same nuclear configuration in accordance with the Franck–Condon principle (Scheme XVI). An alternate mechanism involved the breaking of single bonds of LXXVIII to give a biradical (54) (Scheme XVII).

SCHEME XVI



LXXVII LXXVIII

SCHEME XVII

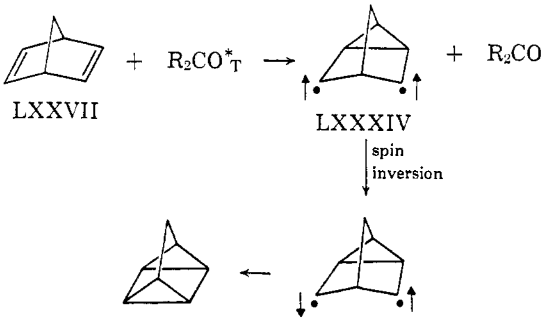


LXXVIII LXXXIV

LXXVII

Presumably the reverse of this process could account for the LXXVII → LXXVIII conversion if LXXVII were converted to LXXXIV by energy transfer from $R_2CO^*_T$ (Scheme XVIII).

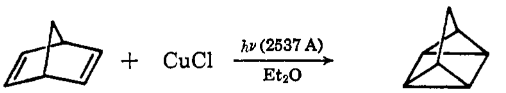
SCHEME XVIII



LXXVII LXXXIV

LXXVIII

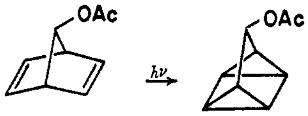
The formation of LXXVIII could also be catalyzed or sensitized by cuprous chloride (95) (Eq 33). The exact function of the metal ion is not clear.



(Eq 33)

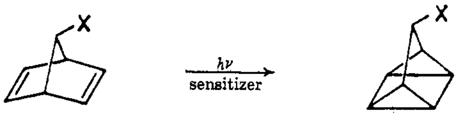
LXXVII LXXVIII, ~70%

Several 7-substituted bicycloheptadienes have been converted to the corresponding 7-substituted quadricyclenes by irradiation. The 7-acetoxy derivative LXXXV gave LXXXVI on direct irradiation (74) (Eq 34). Several other derivatives, LXXXVII–XC, of LXXVII gave the ring-closed isomers, XCI–XCIV, on irradiation in the presence of a sensitizer (not specified but probably acetone, acetophenone, or benzophenone) (99) (Eq 35).



(Eq 34)

LXXXV LXXXVI

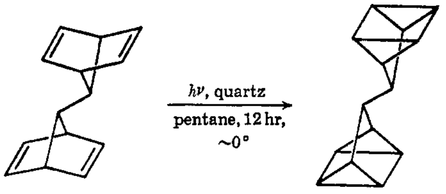


(Eq 35)

LXXXVII, X = Cl
LXXXVIII, X = OH
LXXXIX, X = OEt
XC, X = p-$BrC_6H_4SO_3$–

XCI, X = Cl
XCII, X = OH
XCIII, X = OEt
XCIV, X = p-$BrC_6H_4SO_3$–

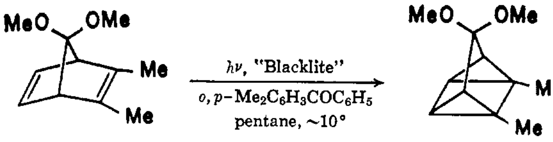
The bisbicycloheptadiene (XCV) gave the saturated isomer XCVI on direct irradiation (101) (Eq 36). The ultraviolet absorption spectrum of XCV was similar to that of LXXVII (101).



(Eq 36)

XCV XCVI, 36%

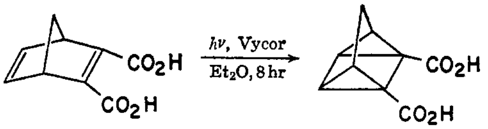
The dimethyldimethoxy derivative XCVII gave XCVIII in good conversion on irradiation in the presence of 2,4-dimethylbenzophenone as a sensitizer (46) (Eq 37).



(Eq 37)

XCVII XCVIII

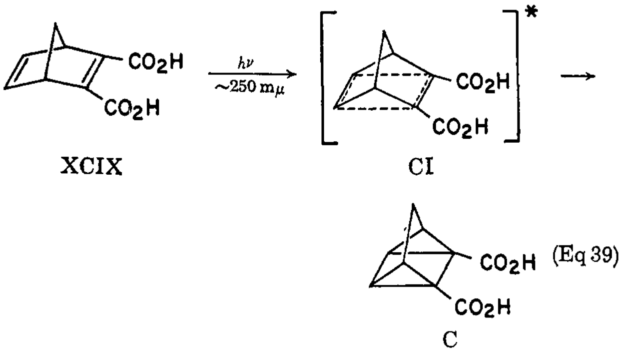
The bicycloheptadienedicarboxylic acid (XCIX) has also been converted to the quadricyclene isomer C (30, 31) (Eq 38). The ultraviolet absorption spectrum of XCIX had a maximum at 243 mμ (ϵ 5400) (31) [247 mμ (ϵ 5150) (58)] and end absorption, ϵ 13,000 at200 mμ in 95% ethanol (58). The low-energy absorption XCIX probably involves excitation to an electronic state in which the electrons of the nonconjugated double bond are involved. Once this excited state CI of XCIX



(Eq 38)

XCIX C, >47%

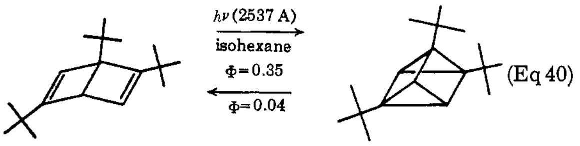
is reached it could easily pass to the closed form C (58) (Eq 39).



XCIX CI C (Eq 39)

2. *Other Bicyclic Compounds*

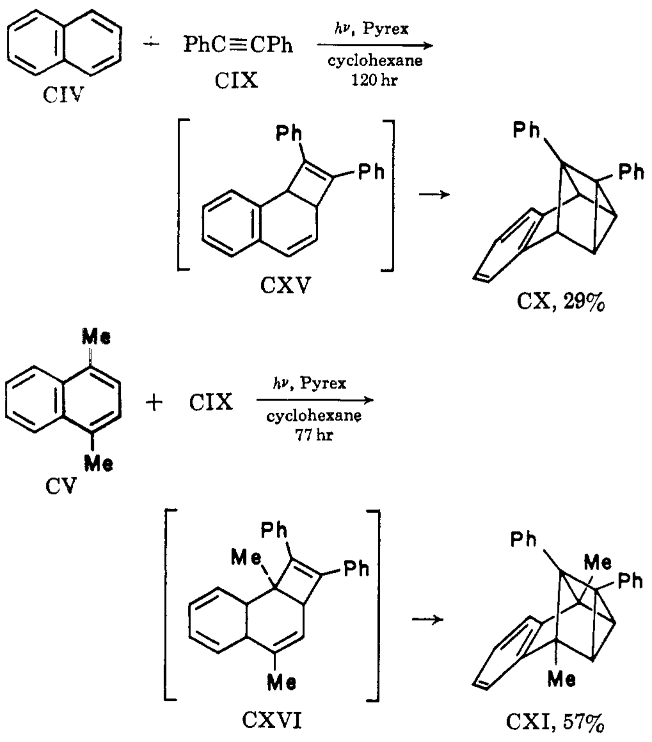
The Dewar benzene CII was closed to the prismane CIII by irradiation at 2537 A (108). The reverse reaction also occurred, being part of the over-all photochemical isomerization of the tri-*t*-butylbenzenes (108) (Eq 40). At the photostationary state CIII constituted 64.8% of the total reaction mixture and CII, 7.1%.



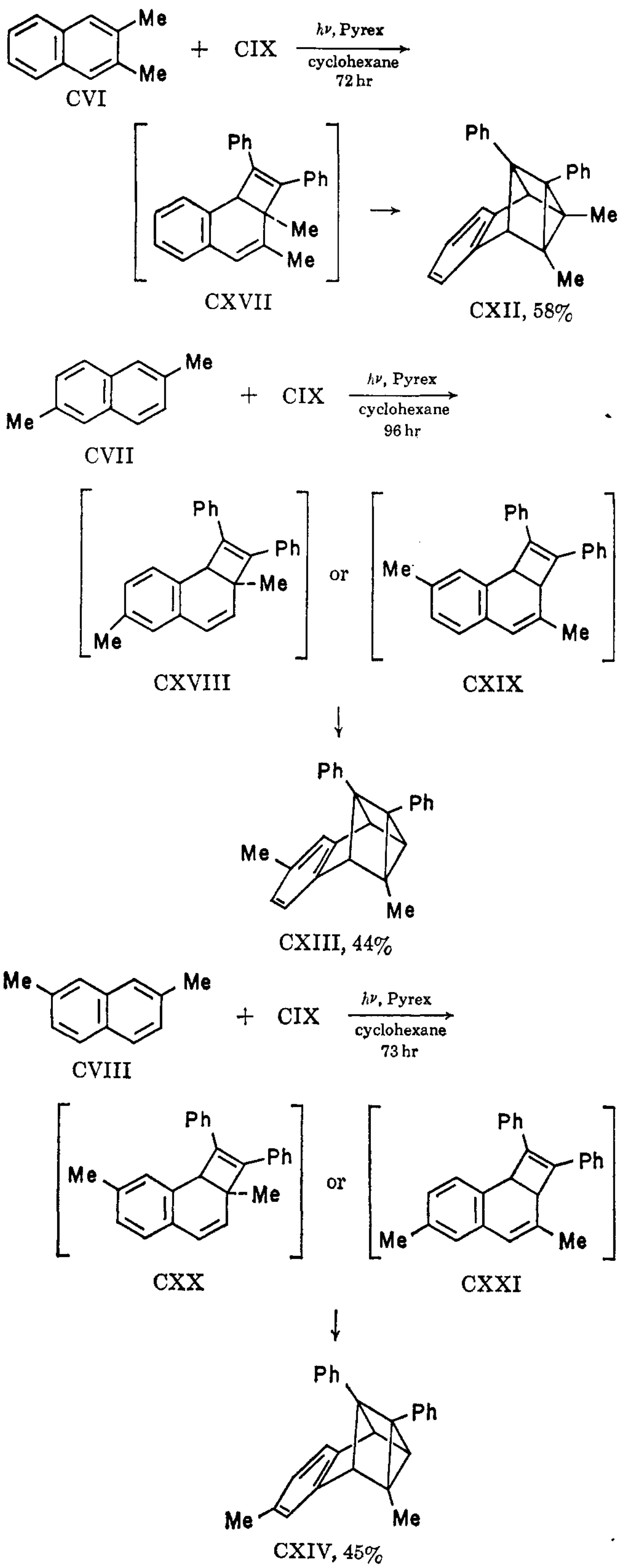
CII CIII (Eq 40)

A series of methylated naphthalenes CIV–CVIII in 3–4 molar excess were irradiated with diphenylacetylene (CIX) to give caged adducts CX–CXIV containing two cyclobutane rings (80) (Scheme XIX). These products were probably formed *via* the cyclobutenes CXV–CXVII, CXVIII or CXIX, and CXX or CXXI, respectively (80).

Scheme XIX

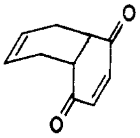


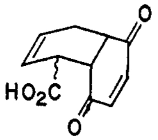
CIV CXV CX, 29%
CV CXVI CXI, 57%



CVI CXVII CXII, 58%
CVII CXVIII CXIX CXIII, 44%
CVIII CXX CXXI CXIV, 45%

Attempted intramolecular cycloaddition of CXXII and CXXIII by irradiation in the solid state or in ethyl acetate solution gave only tars or dimers (20).

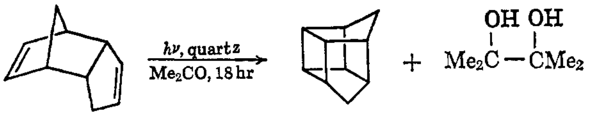

CXXII


CXXIII

D. TRICYCLIC COMPOUNDS

1. *endo-Dicyclopentadienes*

A number of *endo*-dicyclopentadiene derivatives have been converted photochemically to the closed cage isomers, pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{5,8}]decanes. The parent hydrocarbon CXXIV was converted to CXXV by employing acetone as a sensitizer (84, 85) (Eq 41). Pinacol (CXXVI), biacetonyl (CXXVII), a 1:1 adduct CXXVIII of the diene CXXIV and acetone, and numerous other products were also formed (39). Under the same conditions using cyclohexane as a solvent without acetone only a small amount of an unidentified brown oil formed (85). It has been postulated that this ring closure involves nonvertical excitation energy transfer to CXXIV (79). The same type of process has been proposed for the sensitized ring closure, LXXVII to LXXVIII (79). The ultraviolet absorption spectrum of CXXIV indicated that some type of interaction does occur between the double bonds in the excited state since CXXIV absorbed at longer wavelengths than either bicycloheptane (LXXIX) or cyclopentene (CXXIX). Dicyclopentadiene (CXXIV) absorbed weakly in the range 220–300 mμ with increasing intensity toward shorter wavelengths; $\epsilon_{225} \approx 40$ in hexane (72). Cyclopentene (CXXIX) absorption in the gas phase dropped to $\epsilon \approx 30$ at 211 mμ and fell sharply in intensity above 210 mμ (71). Bicycloheptene (LXXIX) absorption dropped sharply above 208 mμ as noted above (98). In the absence of interaction of the two double bonds, CXXIV should absorb at wavelengths no longer than those observed for LXXIX or CXXIX.

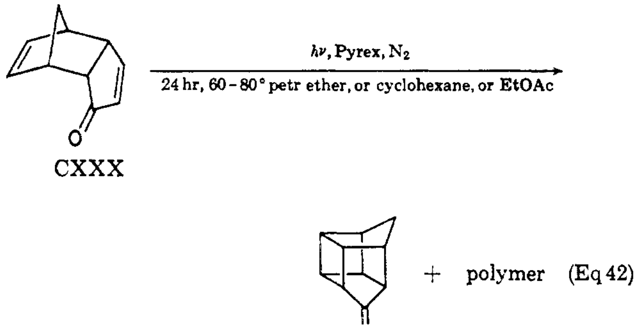


$$\overset{\text{OH}}{\text{Me}_2\text{C}}-\overset{\text{OH}}{\text{CMe}_2}$$

CXXIV CXXV, 62% CXXVI

$+ (\text{MeCOCH}_2 \text{-})_2 + C_{13}H_{18}O$ (Eq 41)

CXXVII CXXVIII



CXXX

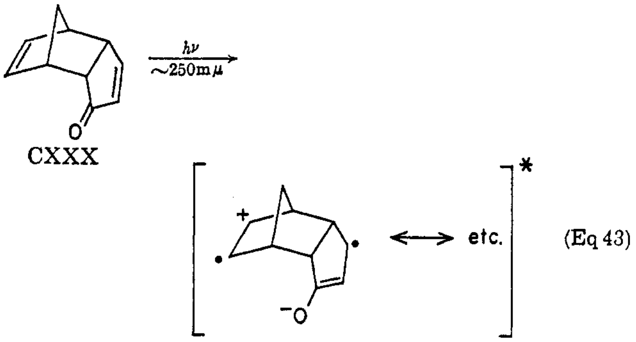
CXXXI, 89%

TABLE III

ULTRAVIOLET ABSORPTION MAXIMA OF DICYCLOPENTADIENONE (CXXX)

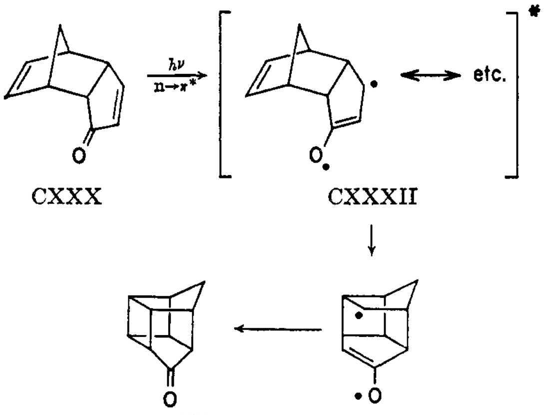
	λmax, mμ (ε)		
Solvent	π → π*	CT	n → π*
Cyclohexane	220.3 (7810)	245 sh (900)	342.8 (37)
EtOH	227.0 (7730)	257 sh (720)	323.0 (38)

Dicyclopentadienone (CXXX) was smoothly converted to the cage isomer CXXXI on irradiation through Pyrex (17, 23, 27, 51) (Eq 42). Irradiation of CXXX in the crystalline state gave only a polymer (17). The ultraviolet absorption spectrum of CXXX is given in Table III (23). The charge-transfer (CT) absorption was attributed to charge transfer from the olefinic double bond to the α,β-unsaturated ketone chromophore (23) (Eq 43). However, since the reaction proceeded readily through a Pyrex filter which effectively cuts off radiation at wavelengths less than 280 mμ, this transition was probably not involved in the production of CXXXI. More likely the n → π* transition was the initiating process (Scheme XX). This



CXXX

SCHEME XX

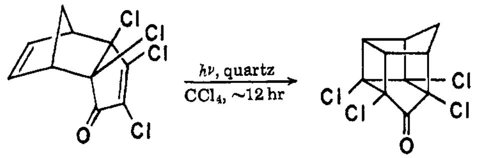


CXXX CXXXII

CXXXI

transition could account for the formation of CXXXI. Intermolecular attack of the excited state CXXXII would account for the formation of polymer. The above reaction, CXXX → CXXXI, also occurred on irradiation through quartz (38).

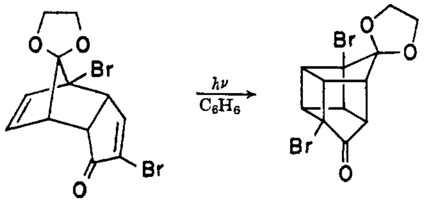
The tetrachloro analog of CXXX, CXXXIII, gave an analogous product CXXXIV on irradiation (111, 112) (Eq 44).



(Eq 44)

CXXXIII CXXXIV, 24%

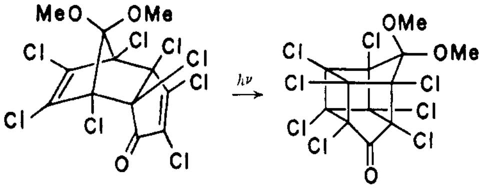
The dibromoketone ketal CXXXV gave CXXXVI in high yield (43) (Eq 45).



(Eq 45)

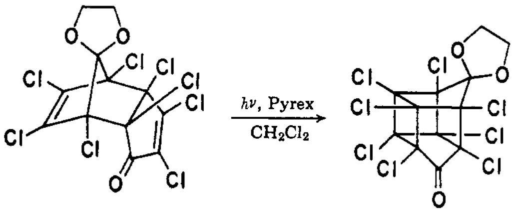
CXXXV CXXXVI, 95%

In an analogous manner the octachloro ketone ketal CXXXVII gave the caged isomer CXXXVIII (45), while the ethylene ketal CXXXIX gave CXL (86) (Eq 46 and 47, respectively).



(Eq 46)

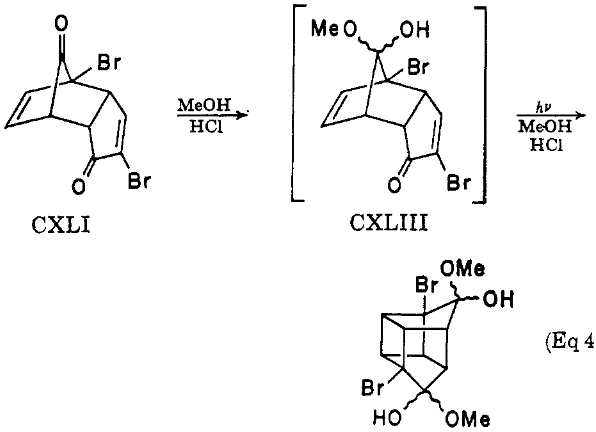
CXXXVII CXXXVIII



(Eq 47)

CXXXIX CXL, 100%

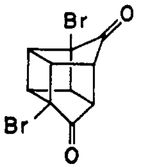
Attempted ring closure of the dibromodione CXLI in benzene or methylene chloride gave polymer (42). In methanol containing hydrogen chloride the caged isomer CXLII was readily formed (42) (Eq 48). It was reasoned that the failure to obtain the caged diketone CXLIV in the nonprotic solvents was due to the sp² character of the one-carbon bridge in CXLI while in CXLIII this bridge is sp³ (42).



CXLI CXLIII

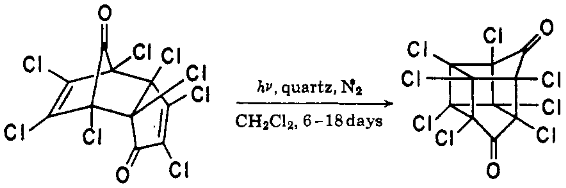
CXLII

(Eq 48)



CXLIV

On the other hand, the perchloro diketone CXLV gave good yields of CXLVI on irradiation through quartz (40, 51) (Eq 49). The ultraviolet absorption spectrum of CXLV showed an n → π* transition above 300 mμ (Table IV) (39, 64, 105). Irradiation of CXLV through Pyrex (λ >~280 mμ) in methylene chloride solution gave CXLVI efficiently, ~90% (39). Therefore the n,π* state (singlet or triplet) of CXLV is probably the reactive state.



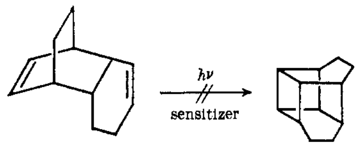
(Eq 49)

CXLV CXLVI, 73–84%

TABLE IV
ULTRAVIOLET ABSORPTION MAXIMA OF OCTACHLORODICYCLOPENTADIENEDIONE (CXLV) (39)

Solvent	λmax, mμ (ε) π → π*	n → π*
Hexane	254.5 (8800)	316 (83)
		329 (101)
		343.5 (104)
		359.5 (77)
		378 (32)
MeCN	258 (9400)	~310 sh (110)
		323 (107)
		336 (108)
		351 (82)
		367 sh (36)

A compound closely related to dicyclopentadiene (CXXIV), dicyclohexadiene (CXLVII), was not closed to the caged isomer CXLVIII on irradiation in acetone or benzene solution with sensitizers such as benzophenone, β-acetonaphthone, benz[a]anthracene, eosin, or 9,10-dibromoanthracene (102) (Eq 50).



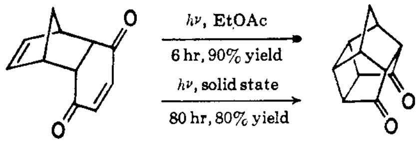
(Eq 50)

CXLVII CXLVIII

The *exo* isomer of CXLVII was also unaffected under the same conditions (102).

2. *Quinone Adducts*

A number of Diels–Alder adducts of cyclic dienes and quinones which have the *endo* configuration have been converted to the caged isomers by irradiation. The adduct CXLIX of cyclopentadiene and quinone gave CL on irradiation either in solution or the solid state (20, 21, 23) (Eq 51). The ultraviolet spectrum of CXLIX is given in Table V (23). Irradiation of CXLIX through a filter which cut out all wavelengths shorter than 415 mμ gave a small amount of CL (20). Therefore the initial excitation of CXLIX in the photochemical reaction was probably n → π* (20). The mechanism may be pictured as shown in Scheme XXI.



(Eq 51)

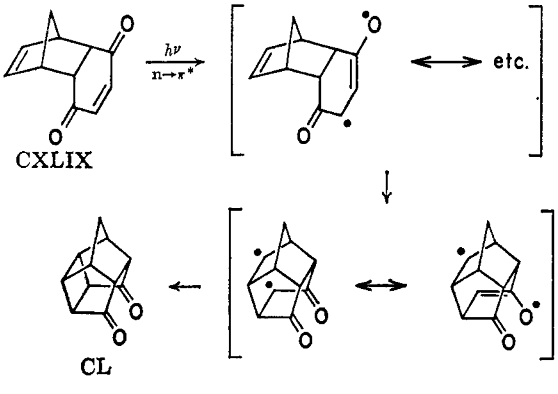
CXLIX CL

TABLE V
ULTRAVIOLET ABSORPTION MAXIMA OF *endo*-TRICYCLO[6.2.1.0^{2,7}]UNDECA-4,9-DIENE-3,6-DIONE (CXLIX)

Solvent	λ$_{max}$, mμ (ε)		
	π → π*	CT	n → π*
Cyclohexane	226 (12,900) 238 sh (6,800)	278 (248)	385 f[a] (58)
EtOH	226 (13,000) 239 sh (8400)	284 (254)	374 f (63)

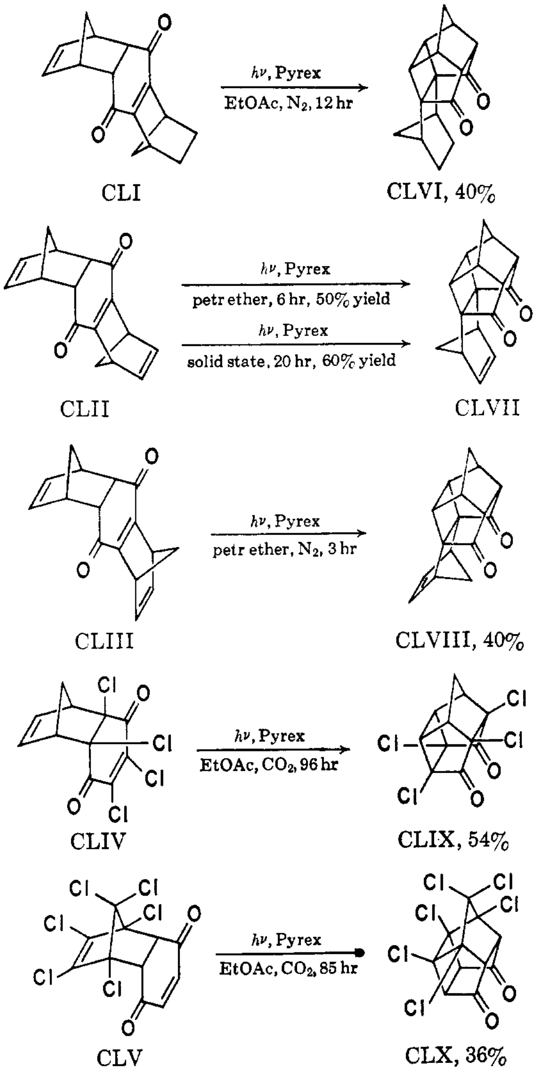
[a] Fine structure.

SCHEME XXI



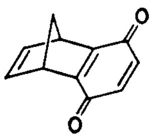
Several closely related compounds CLI–CLV were also converted to the cage isomers CLVI–CLX on irradiation, probably *via* similar mechanisms (20, 21, 23) (Scheme XXII).

SCHEME XXII

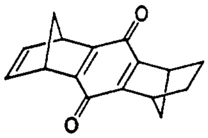


Several quinone adducts of formal cyclohexadienes CLXI–CLXIII have been cyclized photochemically (20, 21, 102) (Scheme XXIII). The quantum yield for the formation of CLXIV was reported to be high (102).

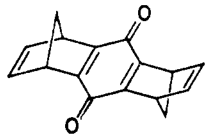
Under conditions similar to those shown above, compounds CLXVII–CLXIX failed to give intramolecularly cyclized products, giving instead dimers or tar (23).



CLXVII



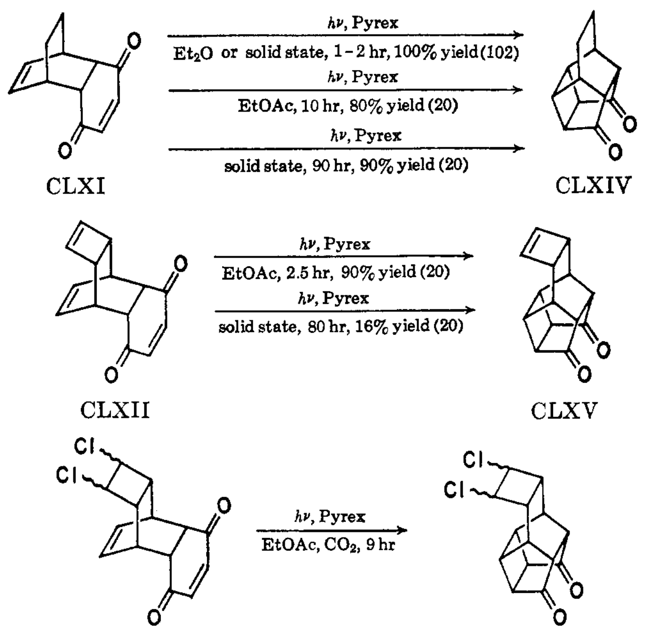
CLXVIII



CLXIX

The caged adducts of duroquinone (XLIV), CLXX and CLXXI, were formed on irradiation of XLIV in

SCHEME XXIII



CLXI CLXIV

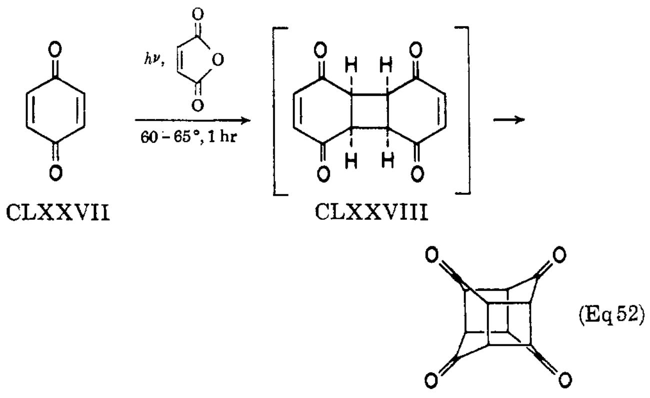
CLXII CLXV

CLXIII CLXVI, 35% (20)

the presence of the olefins LXXXI and CLXXII (59, 82). The half-closed adducts CLXXIII and CLXXIV would be likely intermediates (Scheme XXIV). From LXXXI the 1,4-addition product CLXXV was also isolated.

3. *Quinone Dimers*

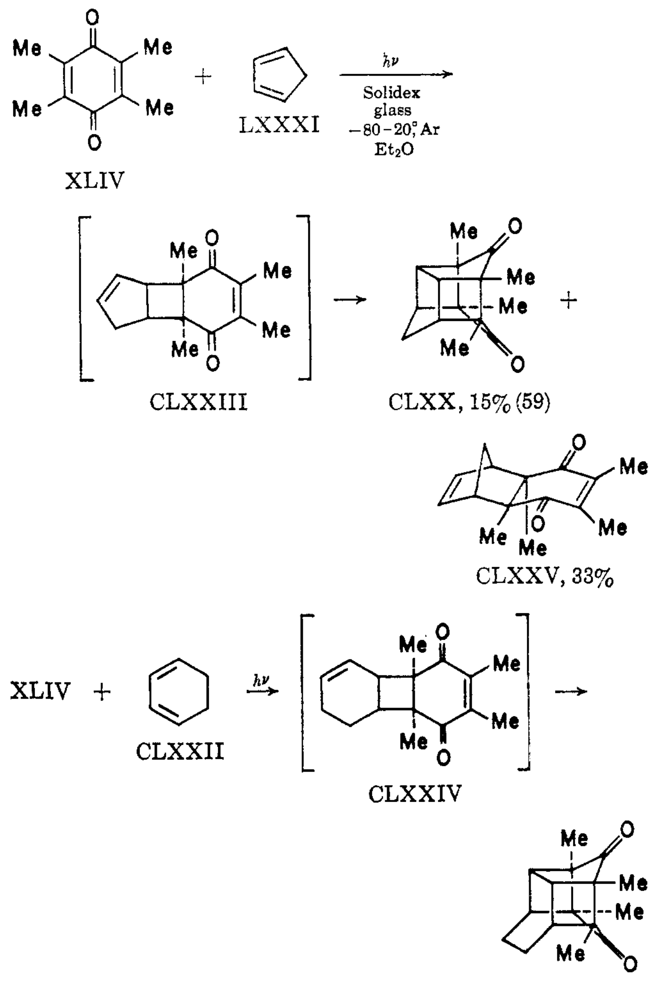
In this series of reactions some of the half-closed dimers have been isolated while others have not. The *cis* half-closed dimers gave the caged compounds readily on further irradiation. A caged dimer CLXXVI of *p*-benzoquinone (CLXXVII) was obtained in low yield in a number of attempts to add CLXXVII to other unsaturated centers (9). The half-closed dimer CLXXVIII of CLXXVII may be an intermediate in the formation of CLXXVI (Eq 52). Another report indicated that CLXXVII gave only polymer and hydroquinone on irradiation (18).



CLXXVII CLXXVIII

CLXXVI, 0.2% (Eq 52)

SCHEME XXIV



XLIV LXXXI

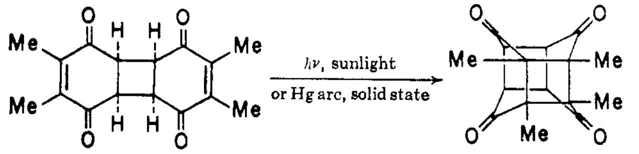
CLXXIII CLXX, 15% (59)

CLXXV, 33%

CLXXII CLXXIV

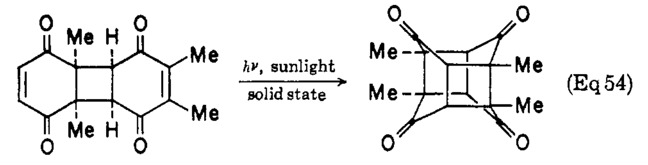
CLXXI, 37%

Two different open dimers, CLXXIX and CLXXX, of 2,3-dimethyl-*p*-benzoquinone have been reported, each of which gave a caged isomer, CLXXXI and CLXXXII, on further irradiation (6, 18, 44) (Eq 53 and 54, respectively). The question whether CLXXIX and CLXXX (and CLXXXI and CLXXXII) are really different has not been resolved (18).



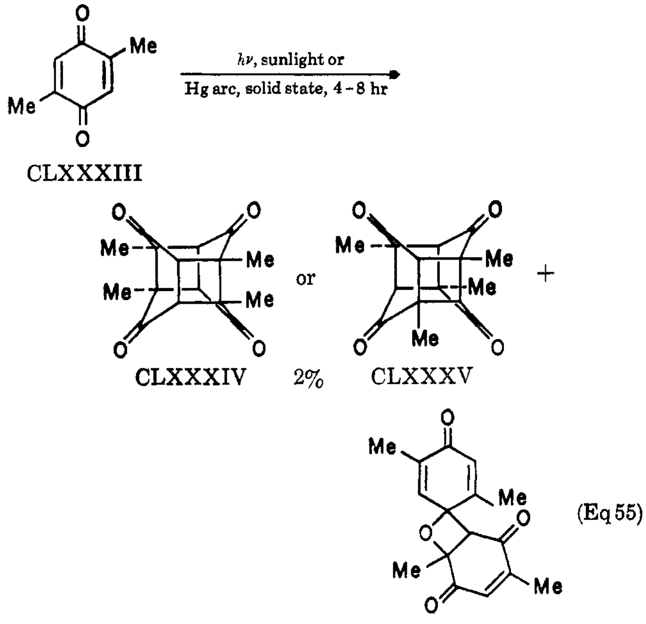
CLXXIX CLXXXI, 100% (18)

(Eq 53)



CLXXX CLXXXII (44)

2,5-Dimethylquinone CLXXXIII also gave a cage dimer of uncertain structure, CLXXXIV or CLXXXV, in addition to the oxetane CLXXXVI (6, 18, 22, 24) (Eq 55). The half-cage dimers CLXXXVII and CLXXXVIII are possible precursors to CLXXXIV and CLXXXV, rexpectively (57). A crystal structure analysis of the quinone CLXXXIII indicated that CLXXXIV was the probable structure of the dimer assuming that the crystal lattice controlled the orientation in the photoaddition (73).

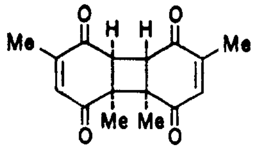


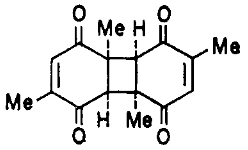
CLXXXIII

CLXXXIV 2% CLXXXV

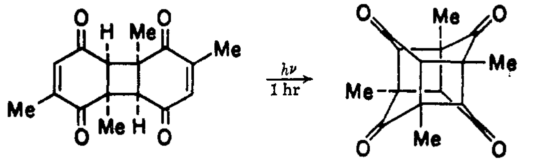
CLXXXVI, 40%

(Eq 55)


CLXXXVII


CLXXXVIII

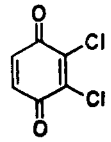
The open dimer of 2,6-dimethylquinone CLXXXIX gave CXC (18) (Eq 56).

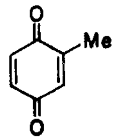


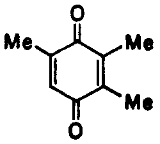
CLXXXIX CXC, 100%

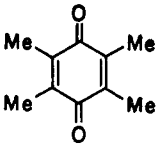
(Eq 56)

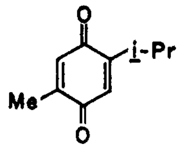
The dichloroquinone CXCI gave a nearly colorless dimer (3%) of undetermined structure on irradiation (6). Quinones CXCII–CXCIV failed to give any dimer on irradiation through Pyrex either in solution or as crystals, while CXCV gave only an open *trans* dimer (18).


CXCI


CXCII


CXCIII

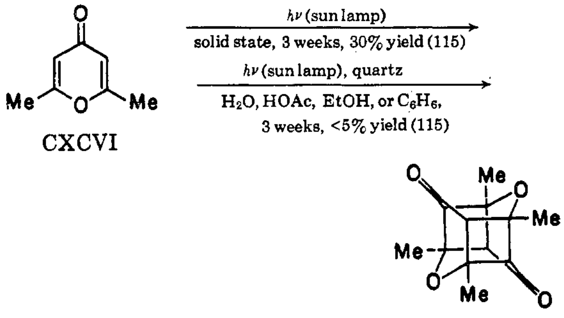

CXCIV


CXCV

The products and their stereochemistry of irradiations carried out in the solid state appear to be highly dependent on the crystal structure in the solid.

4. Pyrone Dimers

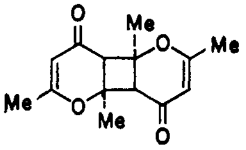
Dimethylpyrone (CXCVI) gave a caged dimer CXCVII on irradiation in solution or the solid state (47, 70, 114, 115) (Eq 57). The half-closed dimer CXCVIII could be an intermediate in this reaction (57).



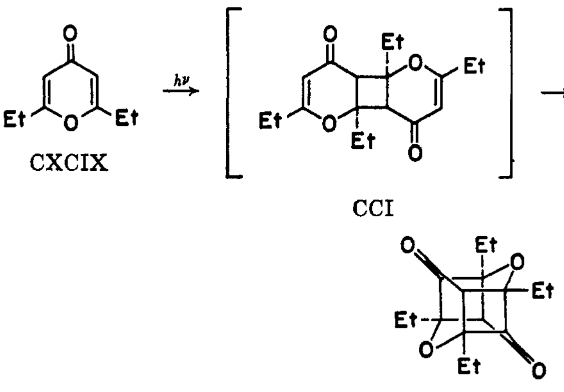
CXCVI

CXCVII

(Eq 57)


CXCVIII

In an analogous manner the diethylpyrone CXCIX gave the dimer CC (113) on irradiation of CXCIX, either as the neat liquid or in solution (110), possibly *via* the half-closed dimer CCI (Eq 58).



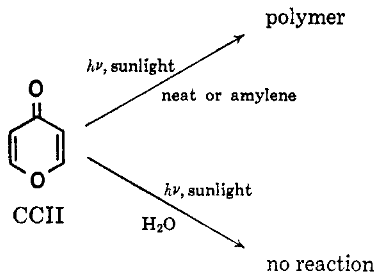
CXCIX

CCI

CC

(Eq 58)

The unsubstituted pyrone CCII gave a polymer or no reaction on attempted dimerization (70) (Eq 59).

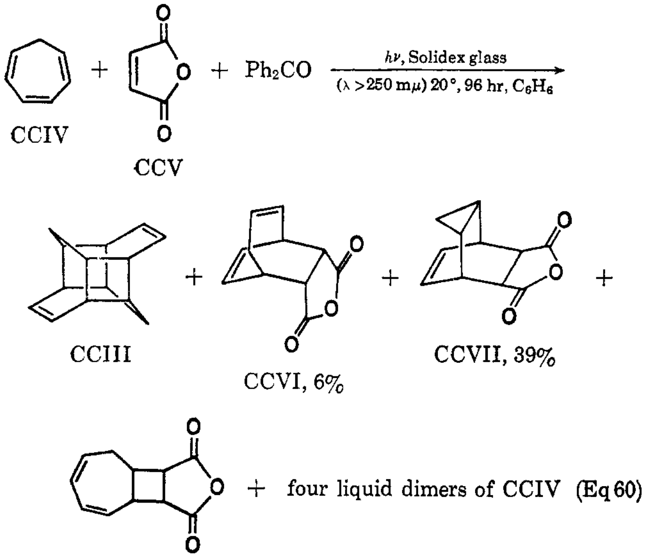


CCII

(Eq 59)

5. *Other Tricyclic Compounds*

An intramolecularly cyclized dimer CCIII of cycloheptatriene (CCIV) was obtained on sensitized cycloaddition of maleic anhydride (CCV) to CCIV in addition to several other products, CCVI–CCVIII (83) (Eq 60). The open tetraene CCIX was the probable intermediate in the formation of CCIII.

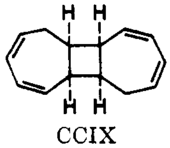


CCIV CCV

CCIII CCVI, 6% CCVII, 39%

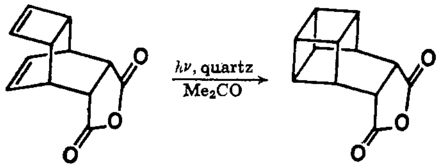
CCVIII, 2%

(Eq 60)



CCIX

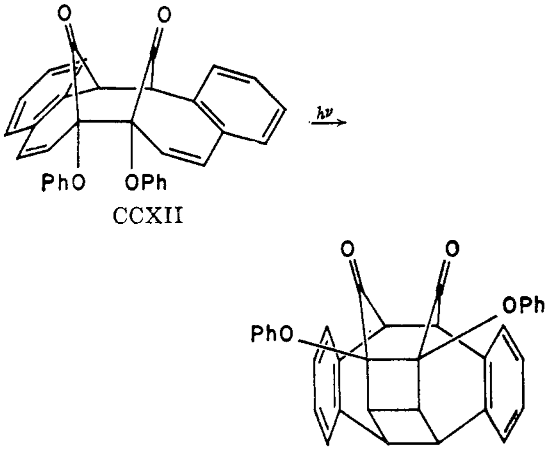
Irradiation of the photoadduct CCX of cyclooctatetraene and maleic anhydride in acetone solution gave the caged anhydride CCXI (83) (Eq 61).



CCX CCXI

(Eq 61)

The cyclododecatetraene CCXII was intramolecularly cyclized in low yield to CCXIII by irradiation without a Pyrex filter (13) (Eq 62).



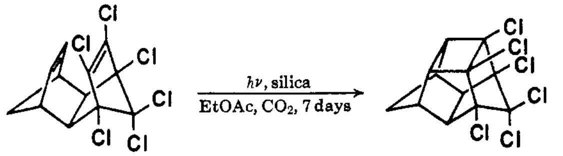
CCXII

CCXIII

(Eq 62)

E. TETRACYCLIC COMPOUNDS

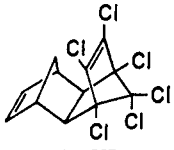
Three examples of this type of photochemical cycloaddition reaction have appeared. Isodrin (CCXIV) was converted to the isomer CCXV (7, 19) (Eq 63).



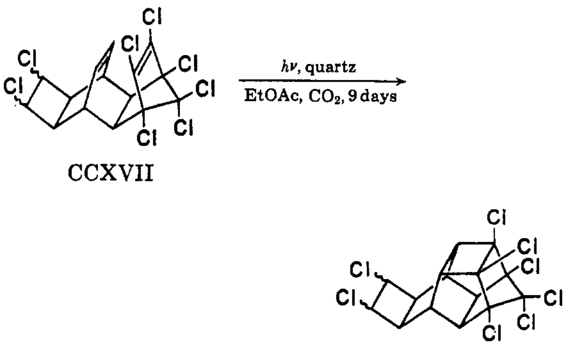
CCXIV CCXV

(Eq 63)

The stereoisomer of isodrin, aldrin (CCXVI), was not changed on irradiation. The related compounds CCXVII and CCXVIII were intramolecularly photocyclized to CCXIX and CCXX, respectively (20, 21) (Eq 64 and 65, respectively).



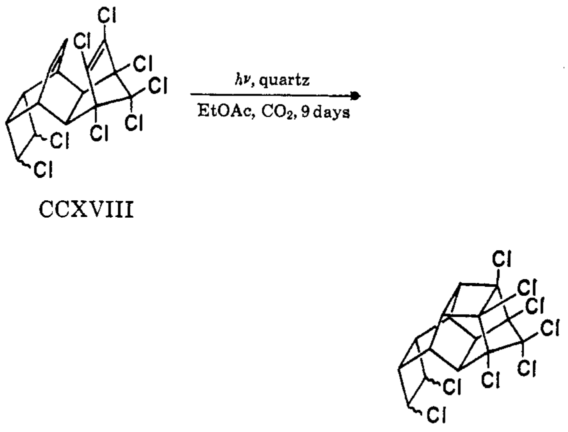
CCXVI



CCXVII

CCXIX, 28%

(Eq 64)



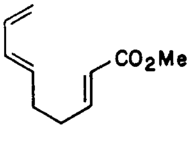
CCXVIII

CCXX, 25%

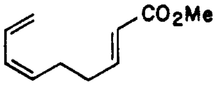
(Eq 65)

III. CYCLOADDITIONS INVOLVING BOTH CARBON 1,2 AND 1,4 ADDITIONS

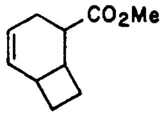
Attempts to photochemically cyclize the isomeric trienes CCXXI and CCXXII gave at least four new unidentified compounds, none of which were the expected cyclohexene CCXXIII (56). The only other reported reaction of this type is the formation of LXVIII from 1,3,6-cyclooctatriene (LXVI) (Eq 66) which has been discussed in a previous section in connection with 1,2 additions (77, 78, 116).



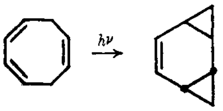
CCXXI



CCXXII



CCXXIII

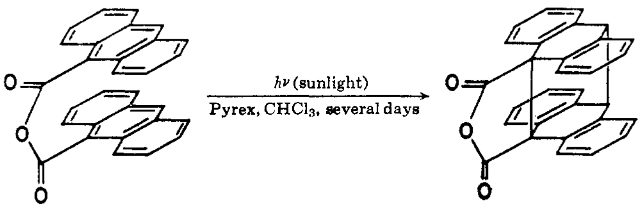


LXVI LXVIII

(Eq 66)

IV. CYCLOADDITIONS INVOLVING CARBON 1,4 ADDITION

The anhydride of anthracene-9-carboxylic acid (CCXXIV) gave the 1,4 addition product CCXXV on irradiation (50) (Eq 67). It is thought that an anthracene 9,10-diradical (CCXXVI) best represents the excited state of CCXXIV involved in the isomerization (50), but there is some question on this point (1, 2).



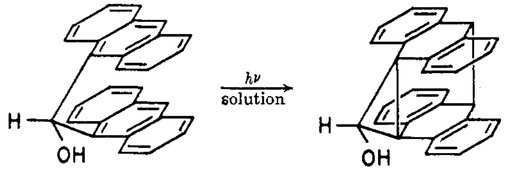
CCXXIV

CCXXV, 68%

(Eq 67)

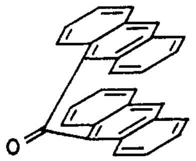
CCXXVI

In a similar manner the carbinol CCXXVII gave the cyclopropane CCXXVIII on irradiation (49) (Eq 68). On the other hand the related anthracene derivative CCXXIX failed to react on irradiation while CCXXX gave a head-to-tail polymer (49).

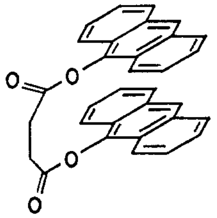


CCXXVII CCXXVIII

(Eq 68)

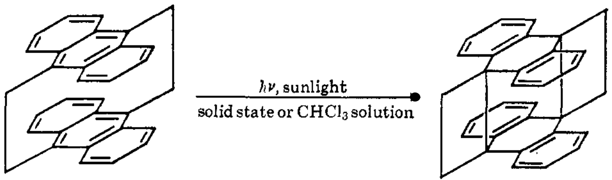


CCXXIX



CCXXX

The paracyclophane CCXXXI gave the isomer CCXXXII (48) (Eq 69).

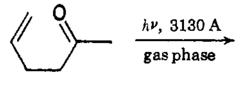


CCXXXI CCXXXII

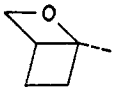
(Eq 69)

V. CYCLOADDITIONS INVOLVING CARBON AND OXYGEN 1,2 ADDITION

Irradiation of 5-hexen-2-one (CCXXXIII) in the gas phase with the mercury arc lines at 3130 A gave the oxetane CCXXXIV in addition to other free-radical-derived products (90) (Eq 70). The quantum yield for



CCXXXIII



$+ CO + CH_4 + CH_2{=}CH_2 +$

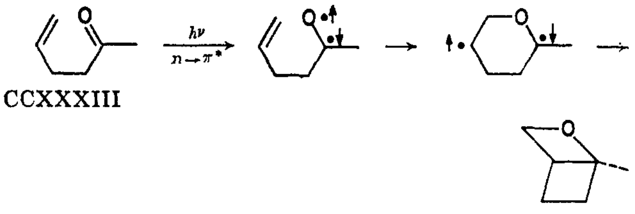
CCXXXIV

$CH_3CH_3 + CH_3CH_2CH_3 + CH_3CH{=}CH_2 +$

$CH_2{=}C{=}CH_2$ (?) (Eq 70)

the formation of the oxetane CCXXXIV was 0.006, while that of carbon monoxide was 0.005 at 139°. The ratio of the oxetane CCXXXIV to that of carbon monoxide was 8.0 at 27° and 1.2 at 139°, due mainly to an increase in the yield of carbon monoxide at the higher temperature. The efficiency of formation of CCXXXIV was not a function of temperature or of added oxygen pressure. Therefore, it appeared that CCXXXIV was formed intramolecularly and did not involve separated free-radical fragments. It also appeared that the triplet state was not involved since oxygen had no effect on the isomerization (90). The ketone CCXXXIII had an n → π* absorption maximum at 2815 A (ε 22) in cyclohexane solution (90). A possible mechanism would involve the n → π* excited singlet (Scheme XXV).

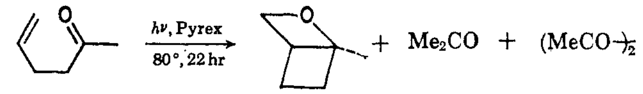
Scheme XXV



CCXXXIII

CCXXXIV

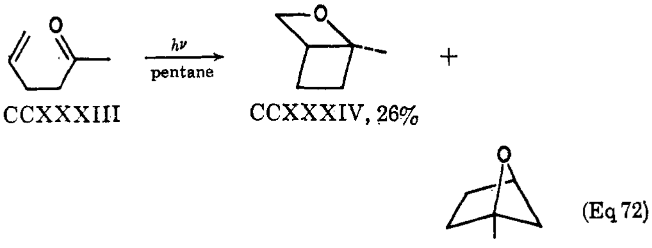
Irradiation of the ketone CCXXXIII in the liquid phase gave the oxetane CCXXXIV in addition to other products (90) (Eq 71).



CCXXXIII CCXXXIV

+ higher boiling material (Eq 71)

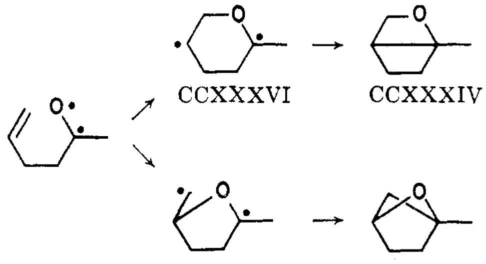
In pentane solution CCXXXIII gave both possible intramolecular cycloaddition products CCXXXIV and CCXXXV (109) (Eq 72). A two-step diradical process would account for the relative amounts of CCXXXIV and CCXXXV formed based on the predicted relative stabilities of intermediates CCXXXVI and CCXXXVII (Scheme XXVI).



CCXXXIII CCXXXIV, 26%

CCXXXV, 18% (Eq 72)

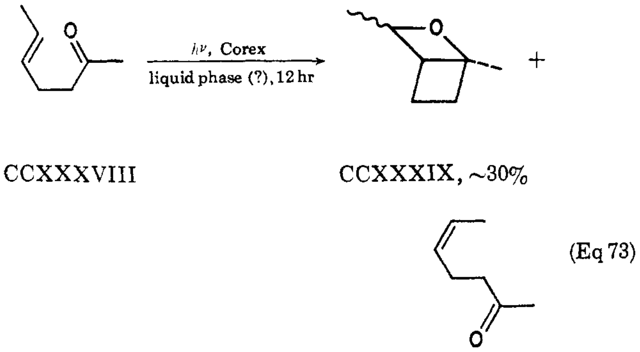
Scheme XXVI



CCXXXVI CCXXXIV

CCXXXVII CCXXXV

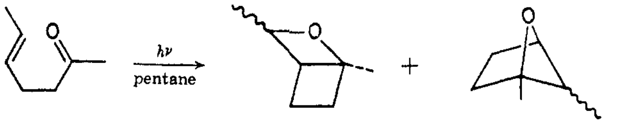
Irradiation of *trans*-5-hepten-2-one (CCXXXVIII) at the wavelength of the n → π* transition gave the oxetane CCXXXIX and the *cis*-olefin CCXL (68) (Eq 73).



CCXXXVIII CCXXXIX, ~30%

CCXL, ~30% (Eq 73)

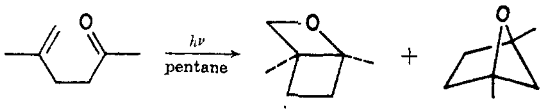
In pentane solution again both isomers CCXXXIX and CCXLI were reported as products (109) (Eq 74).



CCXXXVIII CCXXXIX CCXLI

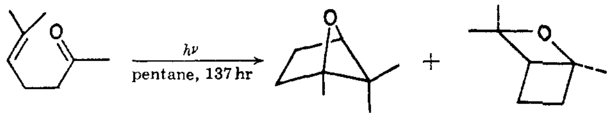
(Eq 74)

The unsaturated ketone CCXLII gave the photoisomers CCXLIII and CCXLIV (109) (Eq 75).



CCXLII CCXLIII CCXLIV (Eq 75)

The γ,δ-unsaturated ketone CCXLV disappeared with a quantum yield of *ca.* 0.003 when irradiated in pentane solution (109). The products were the isomeric oxetanes, CCXLVI and CCXLVII (Eq 76).

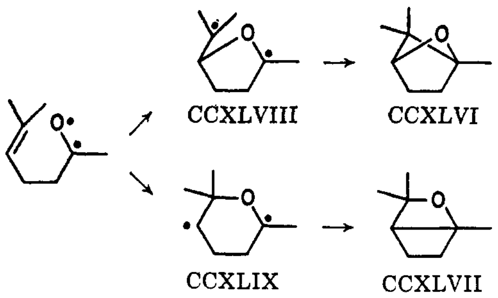


CCXLV CCXLVI, 40% CCXLVII, 16%

+ nonvolatile material, 24% (Eq 76)

Here again the major isomer CCXLVI is formed from the more stable intermediate CCXLVIII (Scheme XXVII).

SCHEME XXVII



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