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The photochemistry of some 2-cyclohexenones

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THE PHOTOCHEMISTRY OF SOME 2-CYCLOHEXENONES

by

Thomas Albert Rettig

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1966

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VITA

The author was born on December 24, 1939 to Mr. and Mrs. Henry A. Rettig. After attending twelve schools in eleven years he was graduated in June, 1957, from Flint Central High School at Flint, Michigan. In June, 1957, he enrolled at Flint Junior College and received the degree of Associate in Science in February, 1959. He then enrolled in the University of Michigan, receiving the degree of Bachelor of Arts, with distinction, in February, 1961.

He then began his graduate study at Iowa State University of Science and Technology in March, 1961. Initially, his major was analytical chemistry with Dr. J. S. Fritz as major professor. This association resulted in the publication of a paper on nonaqueous cation exchange chromatography. In June, 1962, the author changed his major to organic chemistry with Dr. O. L. Chapman as major professor. He was married on May 31, 1963, to Kathryn K. Dalbey.

The author received a National Science Foundation Cooperative Graduate Fellowship for the period September 1963-June 1965. He was a Procter and Gamble fellow for the period June-September, 1965. In February, 1966, he was granted the degree, Doctor of Philosophy from Iowa State University of Science and Technology. He then continued his academic career at the University of Illinois as a National Science Foundation Postdoctoral Fellow.

And God said, "Let there be light"; and there
was light. And God saw that the light was good;
and God separated the light from the darkness.

Genesis 1.3.

INTRODUCTION

The subject of this thesis is the photochemistry of α, β unsaturated ketones, specifically 2-cyclohexenones. The photochemistry of α, β unsaturated ketones has been the subject of several recent reviews (1-9).

α, β Unsaturated ketones generally exhibit two characteristic absorption maxima in the ultraviolet spectrum. An intense absorption ($\epsilon \cong 10,000$) in the region of 225 millimicrons (~ 125 kcal/mole) is conventionally labelled the $\pi \rightarrow \pi^*$ transition. A weak absorption ($\epsilon \cong 100$) in the region of 325 millimicrons (~ 88 kcal/mole) is assigned to the $n \rightarrow \pi^*$ transition. Excitation employing the $n \rightarrow \pi^*$ wavelengths are most frequently used in synthetic photochemistry of ketones and were the wavelengths used in this investigation.

Following $n \rightarrow \pi^*$ excitation, several paths of chemical reaction of the excited ketone are available. The most important photochemical reactions of α, β unsaturated ketones which have been observed are:

1. *Cis-trans* isomerization about the carbon-carbon double bond.
2. Intermolecular cycloaddition either at the carbonyl group or the double bond to yield 1:1 adducts.
3. Addition of solvent molecules to the excited ketone molecule.

4. Skeletal rearrangement to an isomer.
5. Cleavage of the molecule with concomitant elimination of a neutral fragment.

The purpose of this investigation was to determine whether the course of photochemical skeletal rearrangement of ketones is dependent upon the ketone structure. The 2-cyclohexenone system was chosen because cis-trans isomerization is apparently not an effective path for deactivation of the excited state, whereas the excited states of acyclic α, β-unsaturated ketones are deactivated by cis-trans isomerization with a quantum yield of near unity. Excessive dimerization was precluded in this study by irradiation in dilute solution. The solvent generally used was tertiary butyl alcohol which is inert with respect to addition of photochemically excited α, β-unsaturated ketones (10). In addition, hydrogen abstraction by excited ketone is minimized since tertiary butyl alcohol has no hydrogens α- to the hydroxyl group. Thus, the experimental conditions were selected to ensure photochemical rearrangement as the major mode of fruitful chemical deactivation of the excited state. This study has shown that radiationless decay of the excited state to the starting material ground state is generally the major deactivation mode, resulting in low quantum yields for rearrangements of 2-cyclohexenones.

The structures of the starting materials and products in this work are known. With this knowledge an attempt has been made to interpret some of the mechanistic details of the reactions. This interpretation, as with any proposed reaction mechanism, is certainly subject to change.

Until a camera capable of recording short lived excited state molecular events is available, the photosensitive emulsion will continue to be the observer's imagination which is all too often underexposed and overdeveloped.

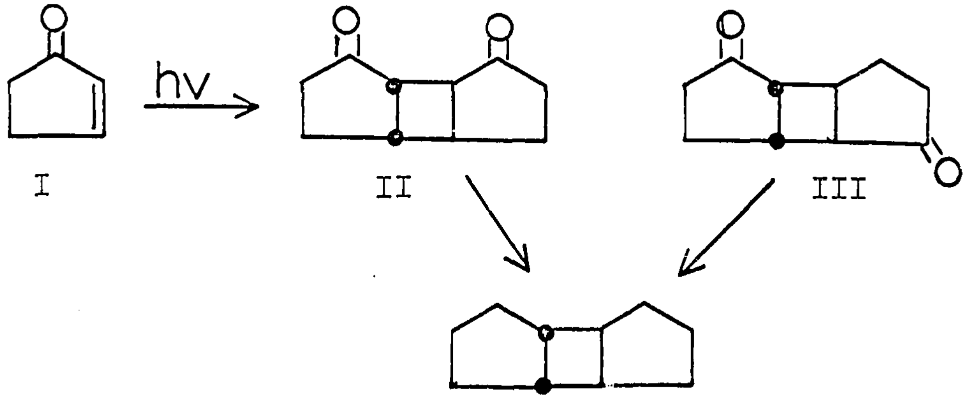
HISTORICAL

Photochemical Reactions of α, β Unsaturated Ketones

Dimerization reactions

The first report of a photochemical reaction of a 2-cyclohexenone was a photodimerization. Treibs (11) found that 2-cyclohexenone, 3-methyl-2-cyclohexenone and 3,5-dimethyl-2-cyclohexenone formed photodimers. None of the dimer structures were rigorously proven, and only 2-cyclohexenone gave a crystalline product. In 1933, Treibs (12) reported the photodimerization of piperitone. Three crystalline isomers were isolated, but no definite structures were assigned. The difficulty in proving structures of this type was not surmounted until nuclear magnetic resonance (n.m.r.) spectroscopy became available to the organic chemist.

Eaton (13) isolated two dimers from the irradiation of neat cyclopentenone (I).

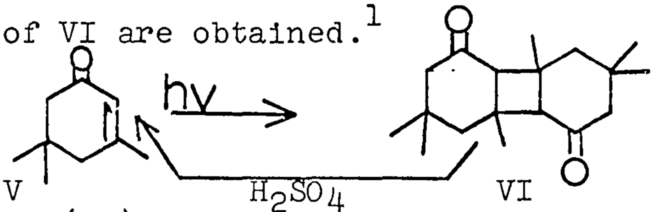


I II III

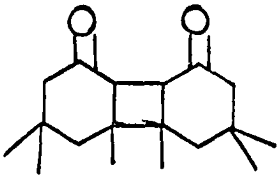
IV

II and III were shown to be isomeric by Wolff-Kishner reduction to IV. An elegant n.m.r. study determined the trans-stereochemistry of the cyclobutane ring.

Griswold (14) investigated the photodimerization of isophorone (V). Two dimers were isolated. One of the dimers is cleaved readily by sulfuric acid to yield isophorone, thus the structure VI was assigned. The other dimer has been tentatively assigned structure VII on the basis of chemical and spectral evidence. Later work has shown that two stereo isomers of VI are obtained.[1]



V VI



VII

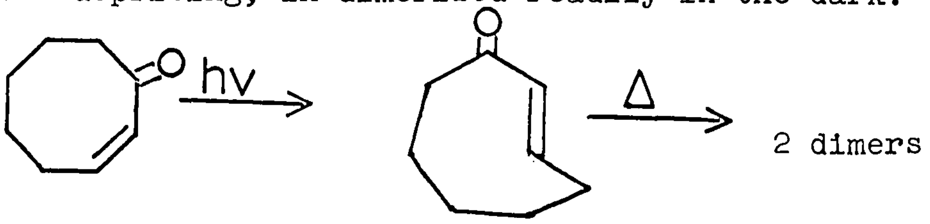
Eaton (15) has postulated that when cycloalkenones are irradiated and undergo intersystem crossing to the triplet state, a rotation about the α, β double bond is induced. The rotation is due to the lower energy of a triplet system with electrons in orthogonal orbitals (16). The maximum twist angle of the α, β-bond in the triplet excited state was estimated as a function of ring size (15).

Ketone	Maximum Twist Angle of α, β dehedral Angle
Cyclopentenone	20°
Cyclohexenone	60°
Cyclooctenone	~180°

---

[1] O. L. Chapman, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information regarding new studies by A. A. Griswold. Private communication. 1965.

Thus Eaton predicts that *trans*-cyclooctenone (IX) should be attainable by irradiation of the *cis*-isomer (VIII). In fact, IX was isolated after irradiation of VIII in cyclohexane. Even more surprising, IX dimerized readily in the dark.



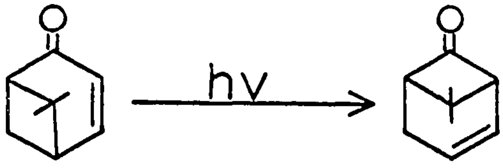
VIII IX

This has led Eaton to postulate that cycloalkenone dimerization may generally be preceeded by this photo-induced trans isomerization. This conclusion was strengthened by the independent observation of Corey (17) and Eaton (18) that irradiation of *cis*-cycloheptenone in a hydrocarbon glass at -190°C yields an unstable intermediate which has an infra-red spectrum in accord with *trans*-cycloheptenone. When the irradiated glass is warmed, only cycloheptenone dimer and a small amount of *cis*-cycloheptenone was isolated. Cyclohexenone did not appear to isomerize under the same conditions.

Rearrangement reactions

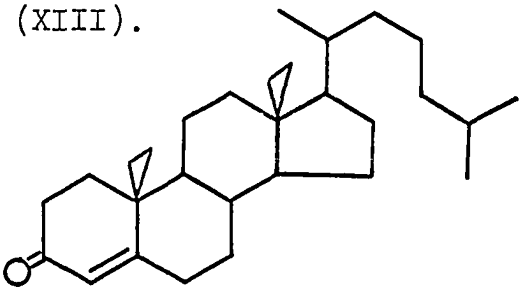
Photochemical rearrangements of 2-cyclohexenone or its analogs lay dormant for nearly thirty years after Treibs (10, 11) initially reported photodimerization.

Hurst and Whitham (19) reported the first intramolecular rearrangement of a 2-cyclohexenone. Verbenone (X) was found to give XI upon irradiation.

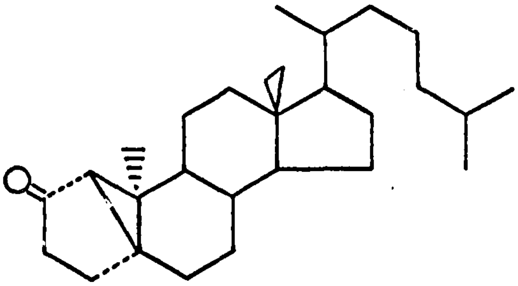


X XI

Kwie et al. (10) irradiated Δ^4-cholesten-3-one (XII) in tertiary butyl alcohol and obtained only one photoproduct (XIII).

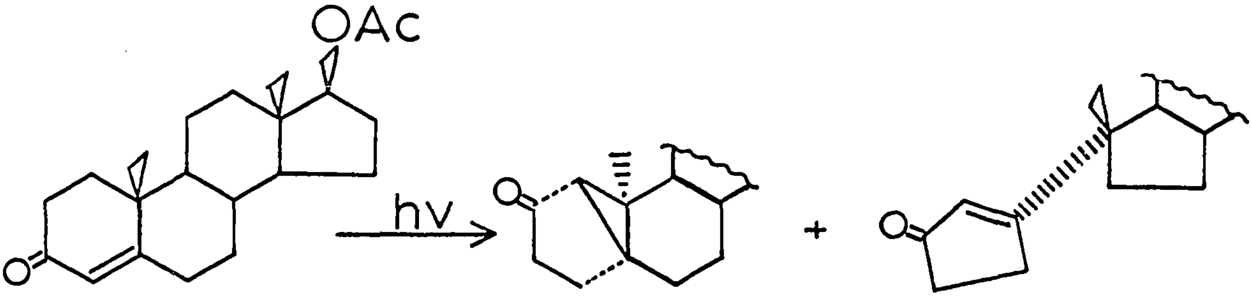


XII



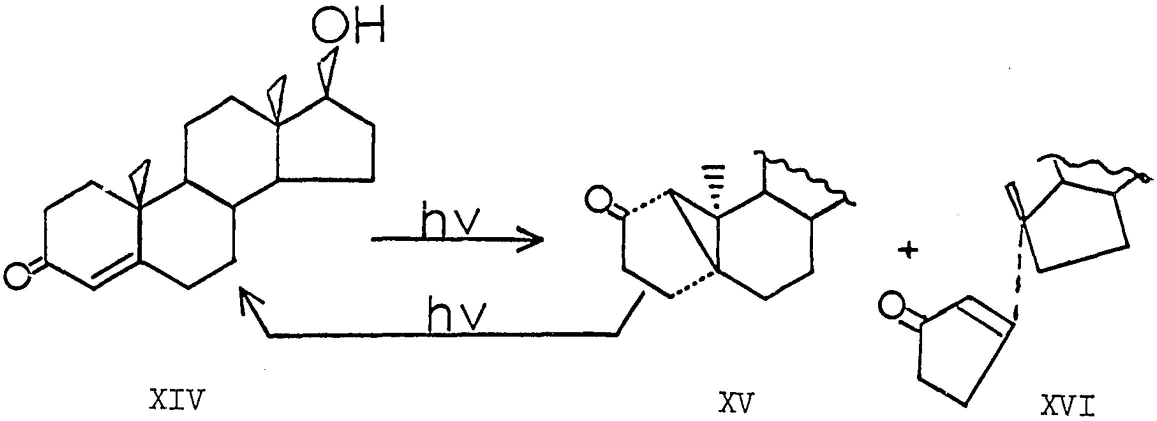
XIII

Griswold (20) studied the photochemistry of testosterone acetate (LXIV), isolating two compounds, LXV and LXVI.



LXIV LXV LXVI

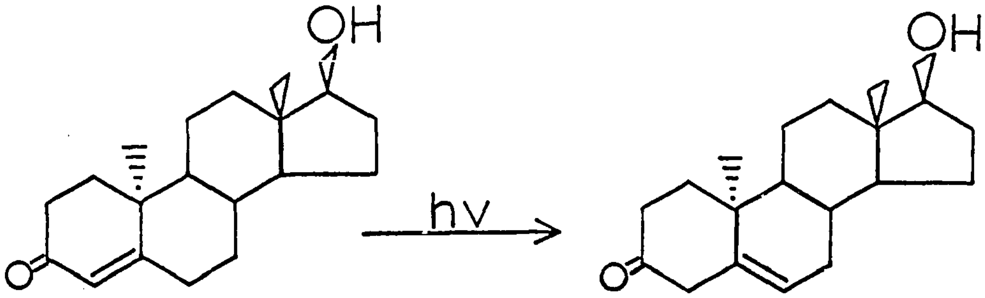
Shortly thereafter, Jeger et al. (21) irradiated testosterone (XIV) in tertiary butyl alcohol and isolated two major photoproducts, XV and XVI.



XIV XV XVI

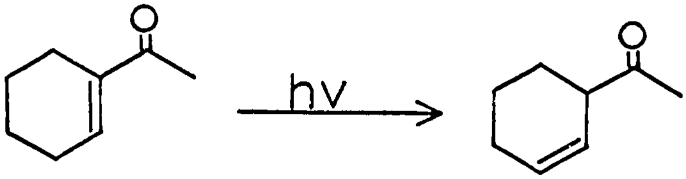
XV has been postulated to be photochemically unstable, yielding XIV (7).

An unusual exception to this type of reaction was observed by Jeger (22). 10-α-methyltestosterone (XVII) yielded only the β, γ isomer XVIII upon irradiation.



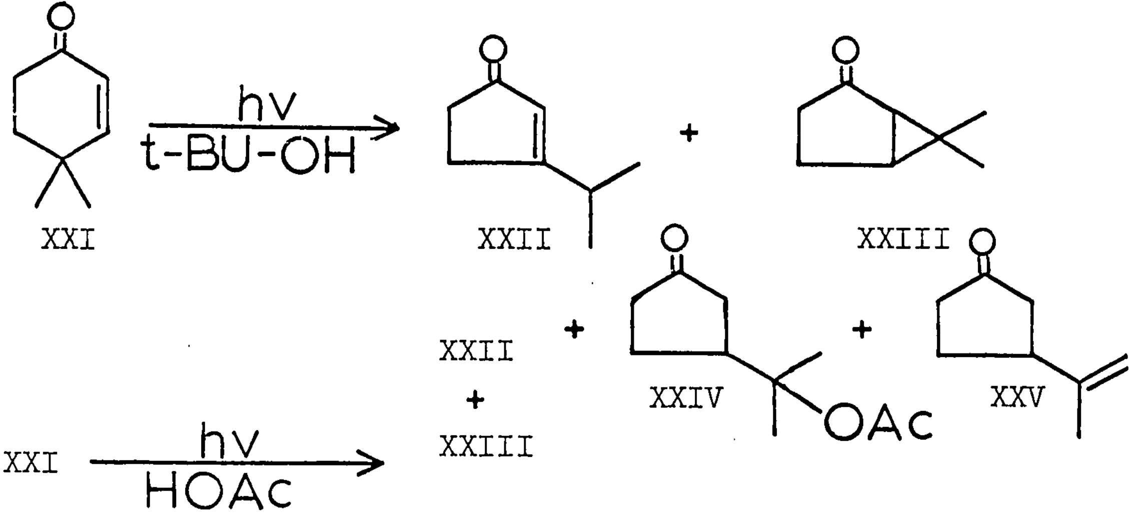
XVII XVIII

Similarly, XIX was reported to yield the β, γ isomer (XX) upon irradiation (23). This result has been shown to be in error (24).



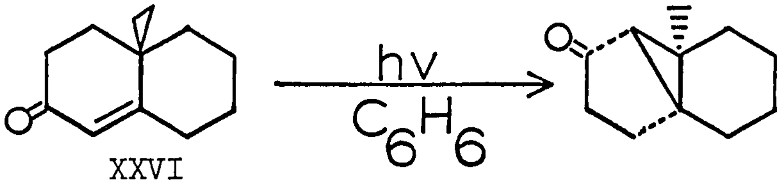
XIX XX

In a preliminary communication, Chapman <u>et</u> <u>al</u>. (20) isolated several photoproducts from the irradiation of 4,4-dimethylcyclohexenone (XXI). The product structures were found to be solvent dependent.

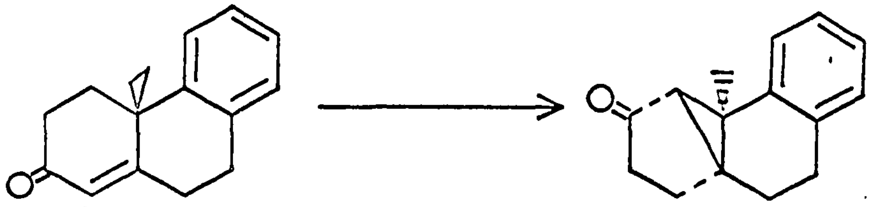


This study continued an investigation initiated by A. Dutton and P. Fitton. The continuation of this work provides the starting point for this thesis.

Zimmerman (25) has reported the photorearrangement of XXVI. The reaction has a quantum yield of 6×10^{-3}.



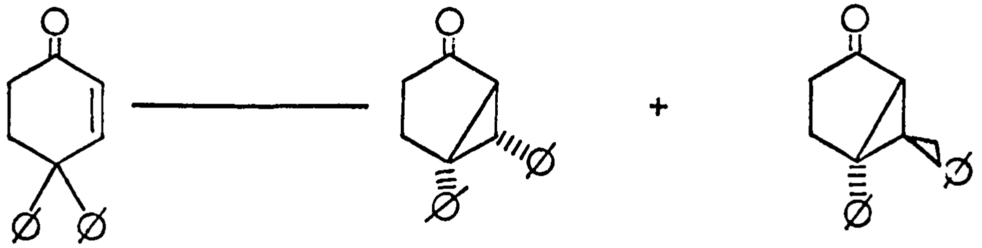
A related compound, XXVII, rearranges with a quantum yield of 8 x 10^{-3}.



XXVII XXVIII

Sieja (26) has completely resolved XXVII and found that upon irradiation XXVIII of greater than 95% optical purity is obtained. These results imply that the rearrangement must be concerted and does not proceed through a "free" carbonium ion or radical intermediate.

Zimmerman (27) has irradiated 4,4 diphenylcyclohexenone (XXIX) and obtained two stereoisomeric products.



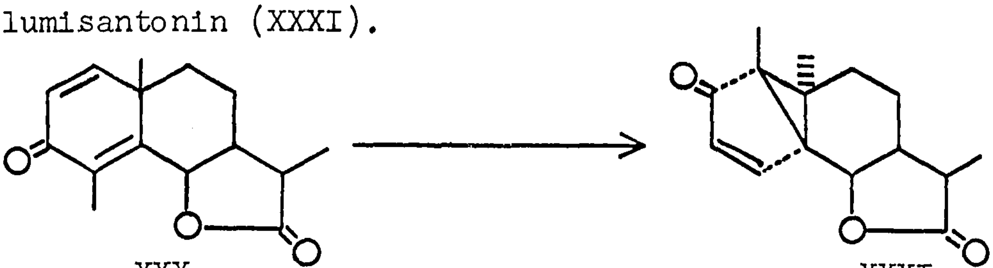
XXIX

The mechanism presented for this rearrangement will be given in a later portion of this section.

The most complete mechanistic discussion offered to date for α, β unsaturated ketones was an out growth of Zimmerman's interpretation of cross-conjugated cyclohexadienone photorearrangements. Consequently, a historical development of dienone photochemistry will be given to put these ideas in perspective.

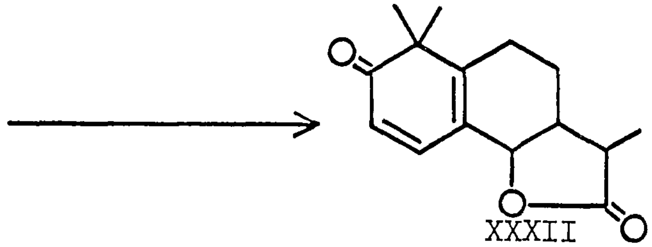
Photochemical rearrangements of cyclohexadienones

Santonin (XXX) was the first cross-conjugated dienone to be irradiated (28). In ethanol the primary photoproduct is lumisantonin (XXXI).



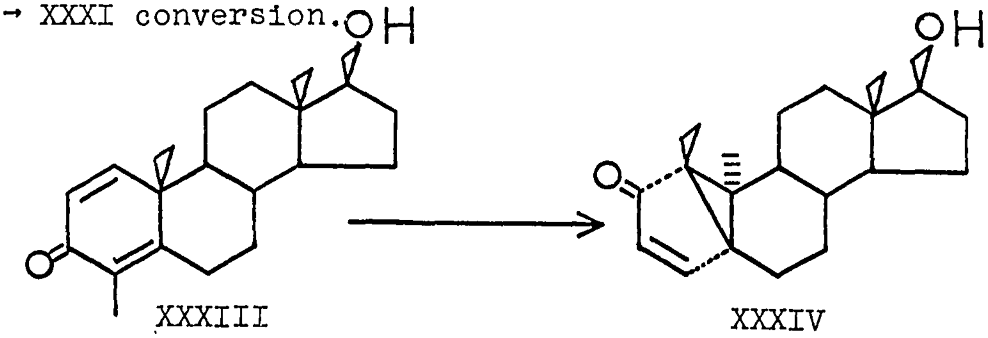
XXX XXXI

Chapman and Englert (29) have shown that continued irradiation of XXXI in ethanol yields a new dienone (XXXII).



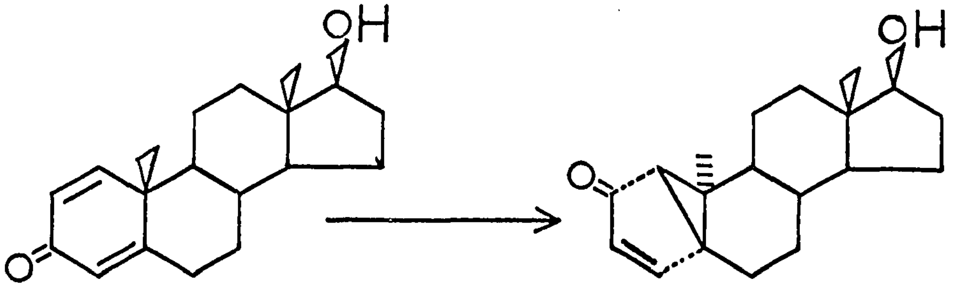
XXX XXXII

Jeger et al. (30) have observed that the steroidal analog to santonin, 4-methyl-1-dehydrotestosterone (XXXIII), cleanly undergoes photochemical rearrangement in either acidic or neutral media to XXXIV. This is exactly analogous to the XXX → XXXI conversion.



XXXIII XXXIV

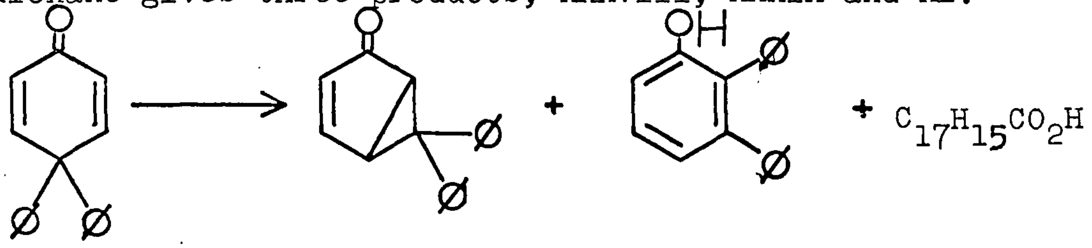
In contrast, Jeger et al.(31,32) have found that irradiation of 1-dehydrotestosterone (XXXV) in acetic acid yields a multitude of products. The "lumi" product (XXXVI) was isolated in fair yields when dioxane was used as solvent. XXVI was found to be an intermediate in the production of many photoproducts in acetic acid irradiations.



XXXV XXXVI

The reason for the greatly increased photostability of XXXIII relative to XXXV is not known.

In a structurally simple dienone, 4,4-diphenylcyclohexadienone (XXXVII), Zimmerman and Schuster (33) have reported a "lumi" type photorearrangement. Irradiation in dioxane gives three products, XXXVIII, XXXIX and XL.



XXXVII XXXVIII XXXIX

XXXVIII was found to be an intermediate in the production of XXXIX and XL.

Fisch and Richards (34) reported that the santonin → lumisantonin rearrangement (XXX → XXXI) was sensitized by benzophenone and suggested that it was probably the result of excitation to the π, π* triplet state. This implied that the rearrangement was due to an electron deficient carbon skeleton.

In contrast, Zimmerman and Swenton (35) reported that the conversion of XXXVII to XXXVIII is a triplet reaction since it was sensitized by benzophenone but that the triplet state of XXXVII is actually an n → π* triplet. Evidence supporting this is that the phosphorescence spectrum of XXXVII is nearly identical to that of benzophenone which is known to be an n → π* triplet. Zimmerman concludes that the β carbon must therefore be electron rich in the excited state. Whether the "electron rich" β carbon is odd electron bearing or a full carbanion has not been distinguished.

A complete mechanistic scheme as given by Zimmerman et al. (33, 35) for dienone photorearrangements is given in Figures 1 and 2. Figure 1 depicts the n → π* excitation process in stepwise fashion. The n → π* excitation corresponds to promotion of one of the 2 py electrons (n electron) to the π* orbital. The pair of 2s electrons are not involved in the excitation.

Figure 2 illustrates the n → π* excitation and subsequent photorearrangement of XXVII to XXVIII. Step 1 is the initial

Figure 1. Orbital diagram representing n → π* excitation in α, β unsaturated ketones according to Zimmerman (33).

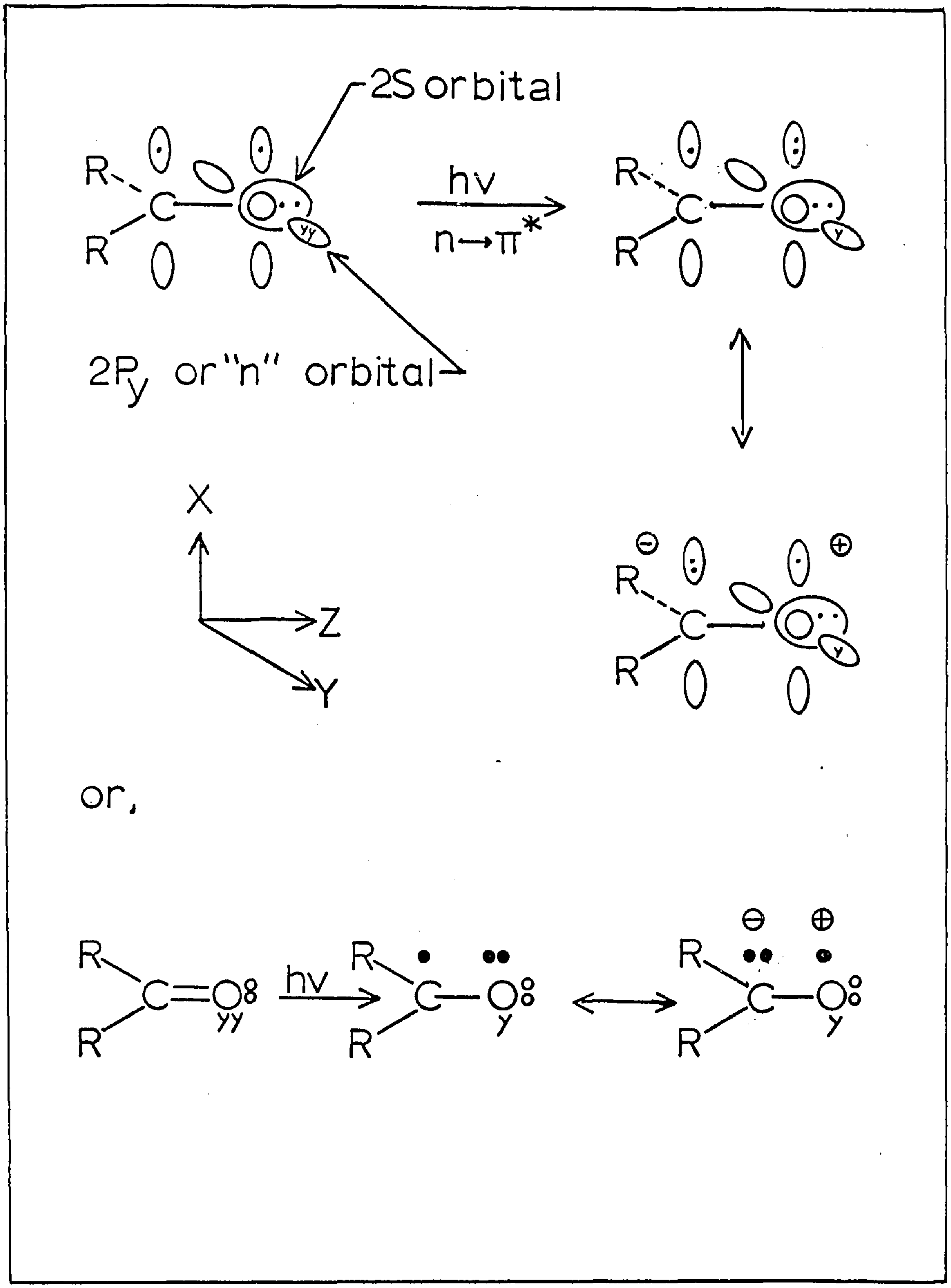
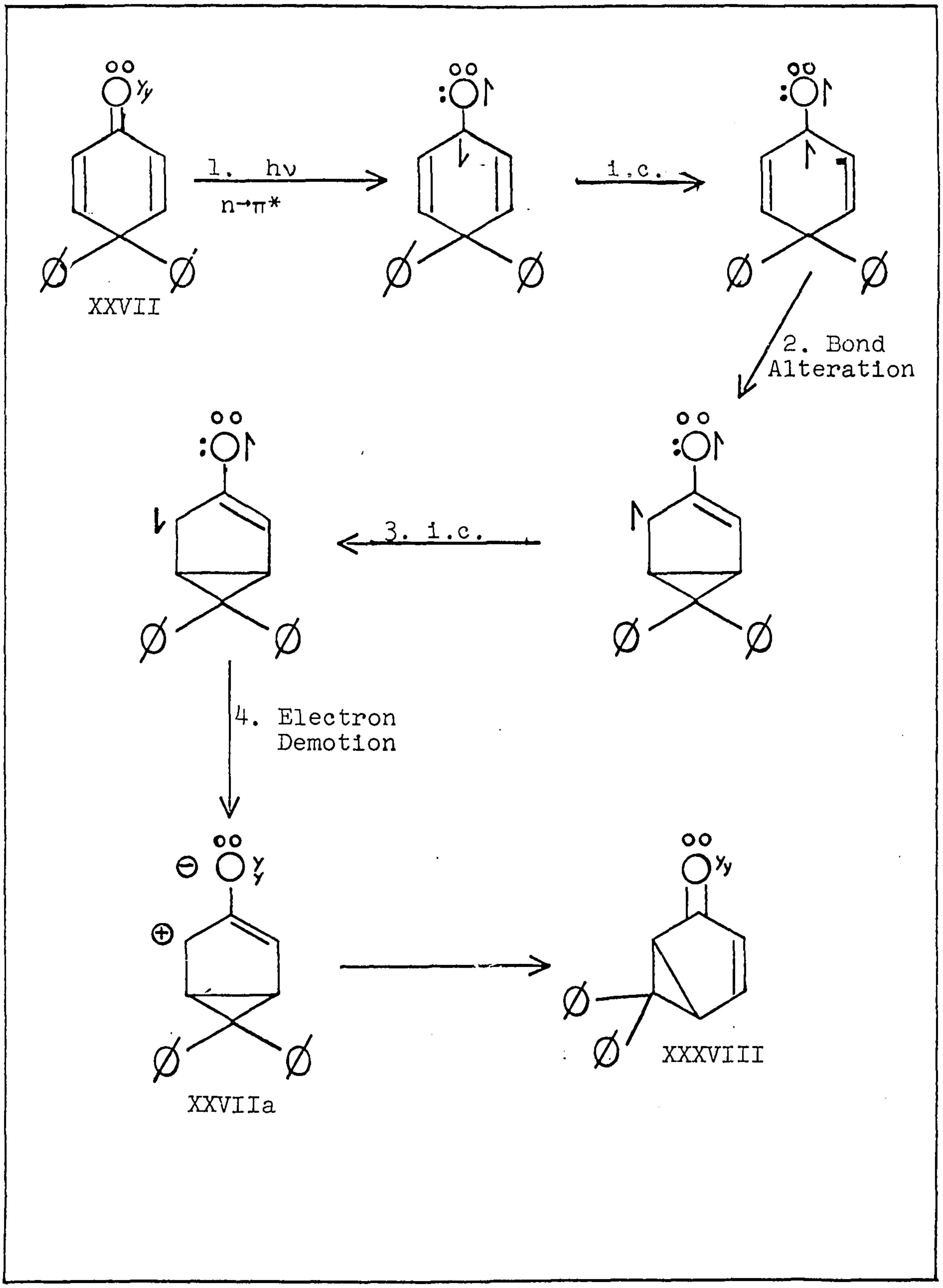

2S orbital
R
R
C
O
yy
hv
n→π*
2Py or "n" orbital
X
Z
Y
or,
R
R
C
O
y
hv
R
R
C
O
yy
R
R
C
O
y
⊖
⊕
R
R
C
O
y

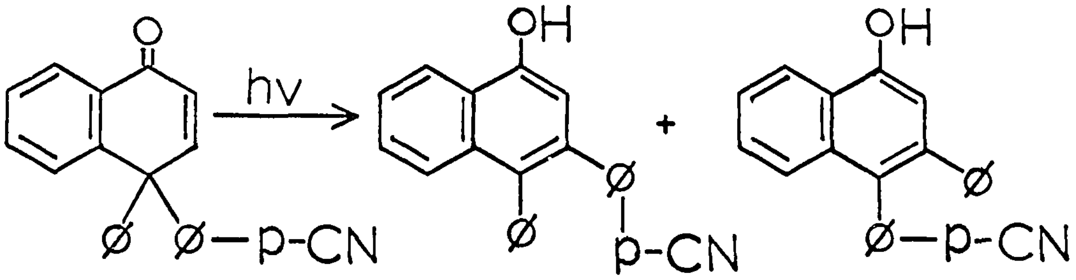
Figure 2. Stepwise representation of n → π* excitation followed by photochemical rearrangement of 4,4-diphenylcyclohexadienone (33, 35).


XXVII
1. hν
n→π*
i.c.
2. Bond Alteration
3. i.c.
4. Electron Demotion
XXVIIa
XXXVIII

excitation, followed by intersystem crossing (i.c.) to the excited n → π* triplet. Step 2 is the "bond alteration" step, involving participation of the second π bond. A molecular orbital calculation by Zimmerman (35) supports this step. Step 3 involves intersystem crossing to a singlet followed by electron demotion to a dipolar state XXVIIa. Step 4 is a rebonding step through XXVIIa to give the ground state product XXXVIII.

An interesting footnote (No. 39) appears with the publication of Zimmerman's mechanism (33). "Although the four steps are formulated as discrete processes, some of these steps could be concerted". In the text of the publication (33) the following qualification is given: "The π* → n demotion step is inevitable; however, whether this occurs in the sequence as suggested is subject to argument". With these remarks at hand, the mechanism is given a fantastic breadth of interpretation, to the point that discussion of any single point becomes hazy.

Zimmerman et al. (36) have recently offered more definite proof that the excited triplet state carbon skeleton of α, β-unsaturated ketones is electron rich in character. Irradiation of XLIin methanol yields both XLII and XLIII in the product ratios shown. In benzene, slightly more migratory specificity is found.



XLI XLII XLIII

$$\begin{array}{lcccc} \text{XLI} \xrightarrow[C_6H_6]{h\nu} & \text{XLII} & + & \text{XLIII} \\ & 2 & : & 1 \end{array}$$

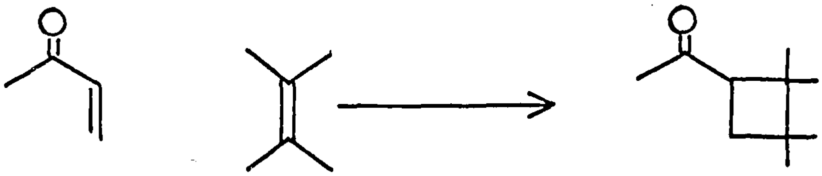
This reaction is sensitized by benzophenone, suggesting a triplet intermediate. Reaction of XLI with acid yields <u>only</u> XLIII. The acid catalyzed rearrangement surely proceeds through an electron deficient carbonium ion type carbon skeleton, leading to phenyl migration as the only product controlling step. In contrast, the photorearrangement leads to slightly preferred *para*-cyanophenyl migration, indicating that the migration terminus is electron rich since the *para*-cyanophenyl group can delocalize the electron(s) more than the unsubstituted phenyl group.

Zimmerman has utilized the mechanistic principles from the dienone rearrangements (33, 35) and aryl migrations (36) to interpret the cyclohexenone rearrangements of XXIX and

XXI. The scheme is given in Figure 3.

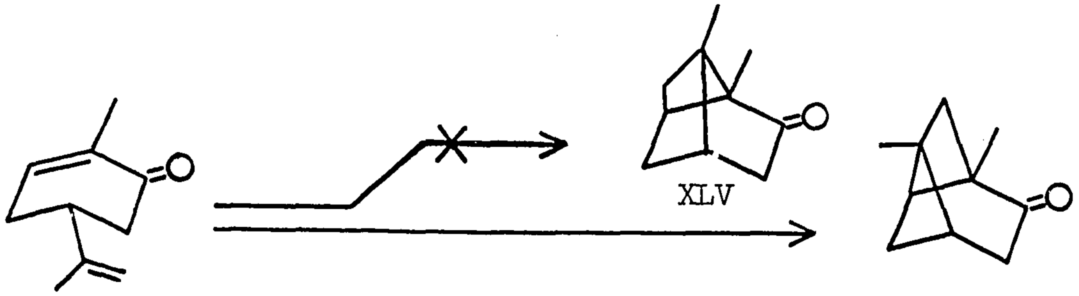
Cycloaddition reactions of 2-cyclohexenones

α, β-Unsaturated ketones may undergo photocycloaddition with olefins either at the carbonyl group or at the double bond. A special case, photodimerization, arises when another unsaturated ketone molecule provides the olefin moiety. These examples have been discussed earlier in this section. Intermolecular photocycloadditions between ketones and olefins generally yield cyclobutanes.



The exact path of reactions, the kinetics and the stereochemistry of the products should yield some information about the nature of the ketone excited state.

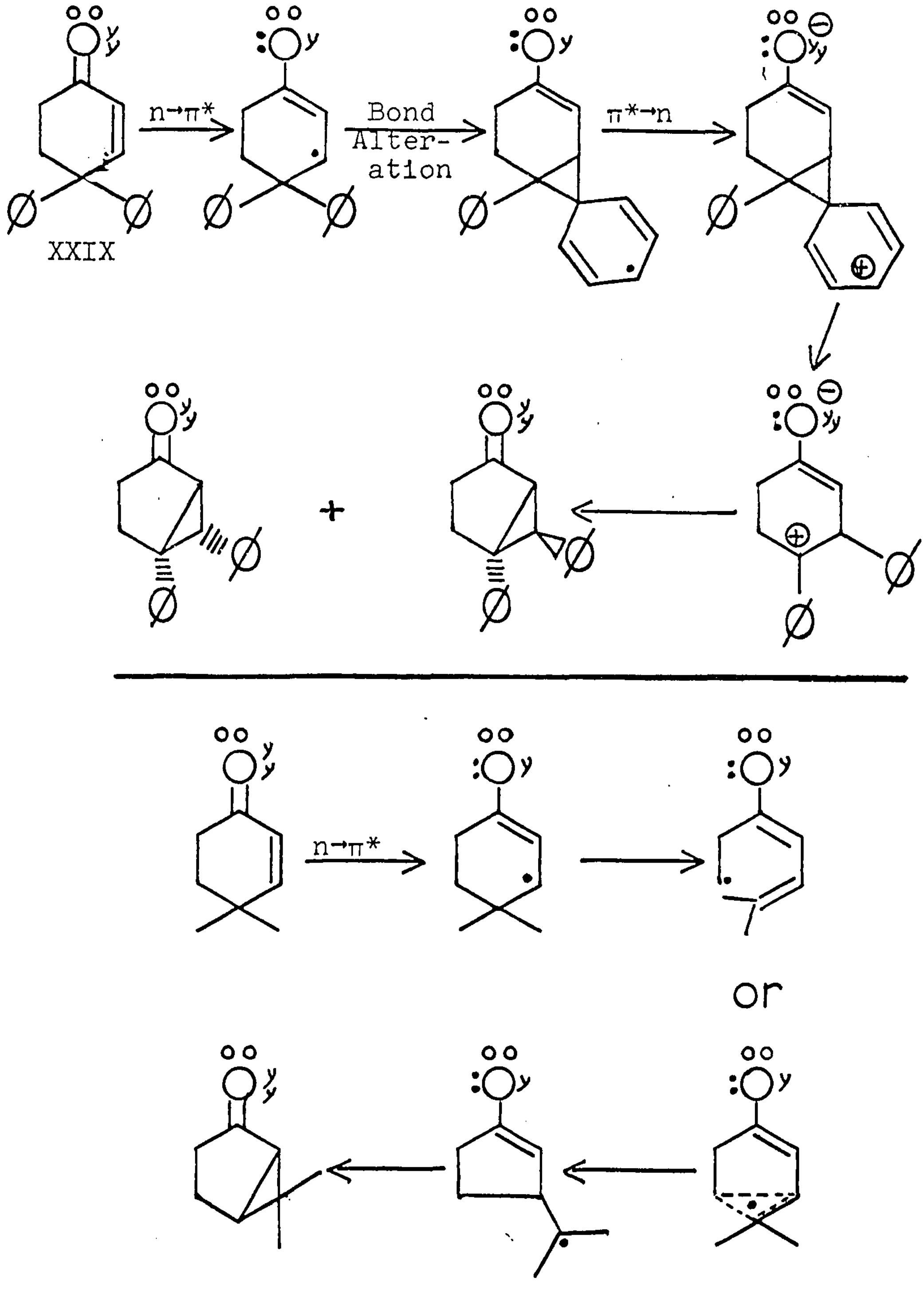
Ciamician and Silber (37) reported an interesting intramolecular photocycloaddition of carvone (XLIV). The product was assigned structure XLV. The structure was later corrected to XLVI by Buchi *et al.* (38).



XLIV

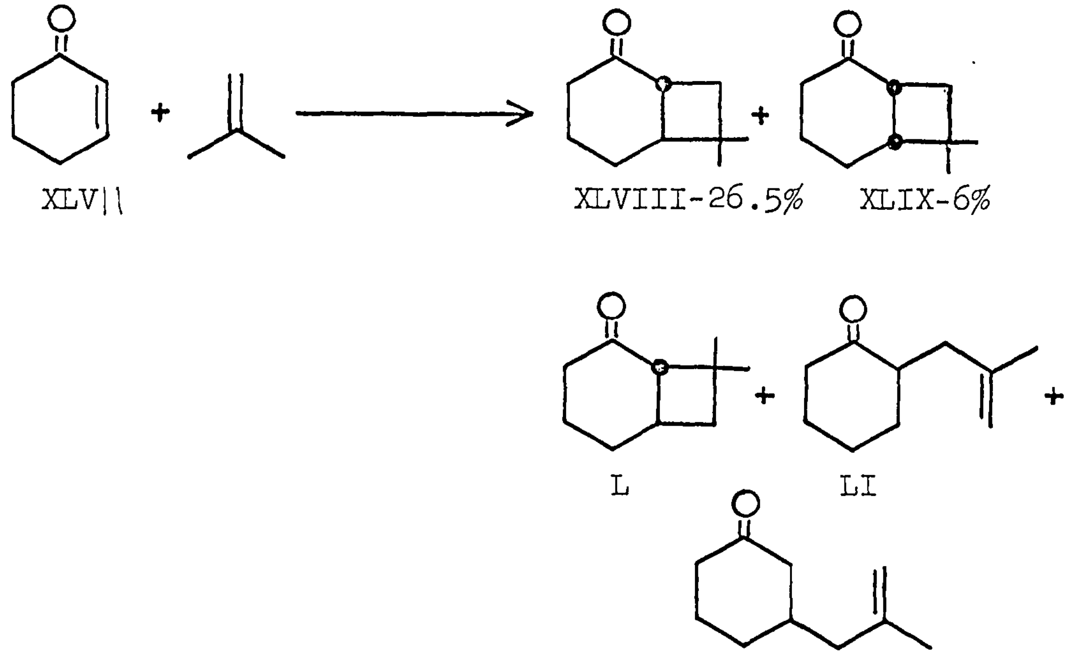
XLVI

Figure 3. Zimmerman's interpretation of the mechanism of photorearrangement of 4,4-diphenylcyclohexenone and 4,4-dimethylcyclohexenone (27).



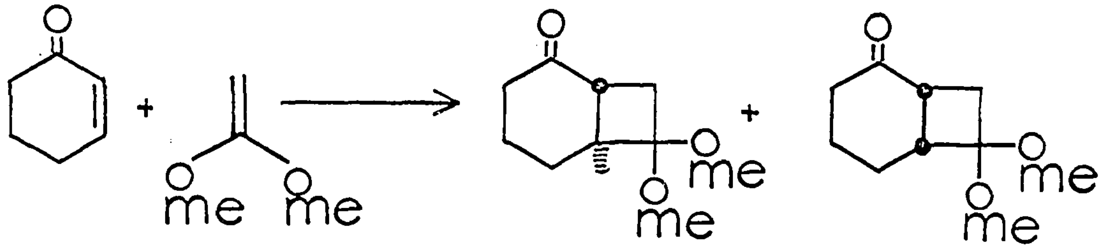
XXIX

Corey et al. (39) have studied the photocycloaddition of 2-cyclohexenone (XLVII) to various olefins. Irradiation of XLVII in the presence of isobutylene yielded the products XLVIII through LII.



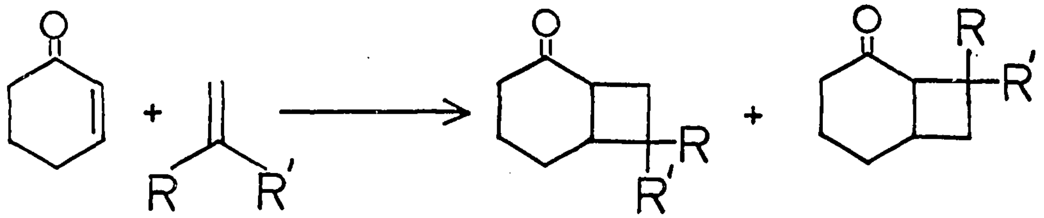
XLVII XLVIII-26.5% XLIX-6% L LI LII

Cycloaddition of XLVII with 1,1-dimethoxyethylene was much more stereospecific, giving two major products, LIII and LIV.



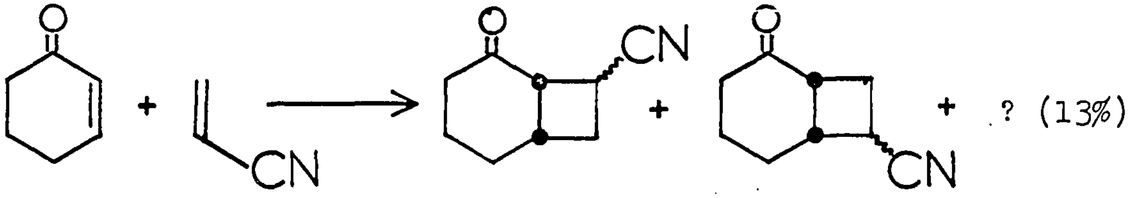
XLVII LIII-49% LIV-21%

Isobutylene, 1,1 dimethoxyethylene and methoxyethylene all gave predominantly the 7-substituted isomer (LV) rather than the 8-substituted isomer LVI.



XLVII LV LVI

The trans-6,4 ring juncture also predominated over the cis-juncture with isobutylene, 1,1 dimethoxyethylene and methoxyethylene. In contrast, photocycloaddition of acrylonitrile to XLVII yields the 8 substituted isomer (LVII) as the major product. In addition, no trans-isomers were found.



XLVII LVII-73% 12%

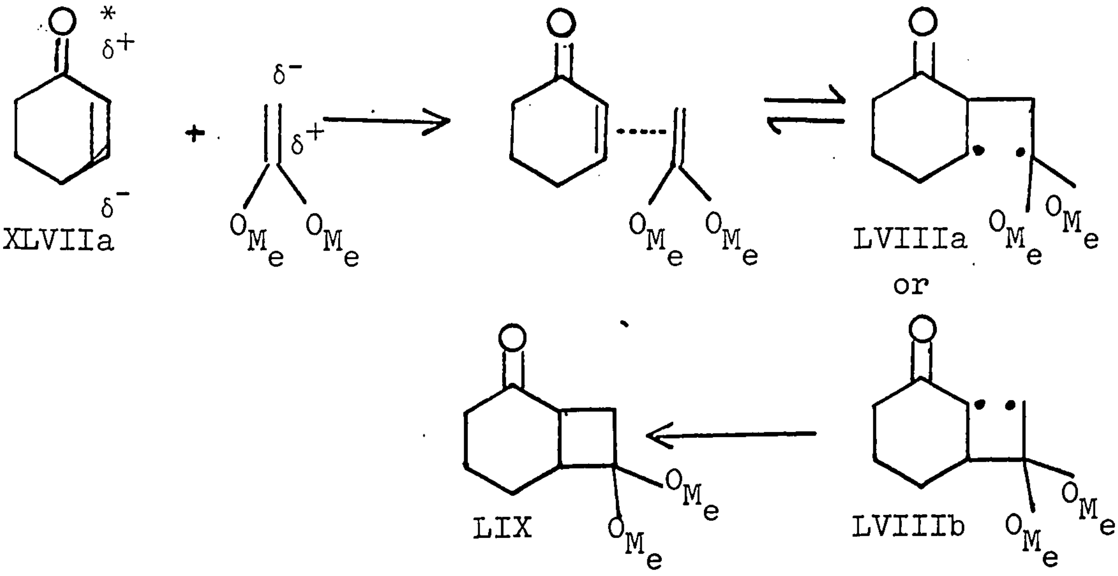
The rate of acrylonitrile addition was much slower than the isobutylene and 1,1 dimethoxyethylene additions. A relative reactivity study showed in decreasing order of reactivity 1,1 dimethoxyethylene > methoxyethylene > cyclopentene > isobutylene > allene >> acrylonitrile. The most reactive olefin, 1,1 dimethoxyethylene, shows a high degree of orientational preference for the 7-substituted products (LV) and a fairly low degree of stereochemical preference for a trans-ring juncture. The least reactive olefin, acrylonitrile, shows a high degree of sterochemical preference for a cis ring juncture and a rather high degree of orientational preference for the 8 substituted products (LVI). Nearly the same reaction mixture was produced from the photocycloaddition reaction with either cis- or trans-2-butene and XLVII. These observations have led to a postulated mechanism for cycloaddition of enones to olefins.

Corey (39) states that the orientational specificity arises from an initially formed π complex involving excited state ketone and ground state olefin. The π complex is in equilibrium with a diradical species which then yields cycloaddition product. An example can be described

$$\text{K(ketone)} + h\nu \rightarrow \text{K*}$$

$$\text{K*} + \text{O (olefin)} \rightarrow \underset{\text{Oriented } \pi \text{ Complex}}{[\text{K*....O}]} \rightleftarrows \text{Diradical}$$

or,



Whether the diradical is LVIIIa or LVIIIb is not known. Also, the multiplicity of the excited state was not determined. Neither fluorescence nor phosphorescence could be observed from XLVII under any circumstances. Corey does assume the n → π* excited state is involved, and that it is probably the triplet state. The orientational specificity is due to the oriented π-complex. The geometry of the complex is determined by the dipole of the olefin and by the excited enone dipole. Corey uses XLVIIa to represent the enone dipole. Justification for this charge distribution arises from an "extended Huckel method" calculation by R. Hoffman (39), Footnote 16). The olefin reactivity sequence supports this mechanism since the most electron "rich" olefins are the most reactive, which would be expected if an electron rich olefin is attacked by an electron poor excited enone. Evidence for the two step diradical intermediate lies in the fact that <u>cis</u> and <u>trans</u>-2-butene give the same photoadduct mixture with XLVII.

Corey has thus offered a neat mechanism which lies within the bounds of his data. Curiously, 2-methyl-2-cyclohexenone does not cycloadd to isobutylene whereas 3-methyl-2-cyclohexenonecycloadds in good yield. This phenomenon is reminiscent of the effect of the 4-methyl group on the dehydrotestosterone photorearrangement (30).

RESULTS AND DISCUSSION

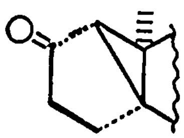
The Photochemistry of 17α-Methyltestosterone

This study was complementary and concurrent to the work initiated by Griswold (14), who investigated the photochemistry of testosterone acetate (LXIV). A preliminary communication of this work has appeared (20). Shortly thereafter, Jeger _et_ _al_. independently reported the photochemistry of testosterone (21).

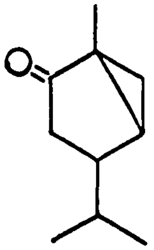
17α-methyltestosterone (LX) is essentially a trisubstituted 2-cyclohexenone. Since the purpose of this thesis is to investigate photochemical rearrangement as a function of structure, LX offers a good model for a 3,4,4-trisubstituted 2-cyclohexenone.

Irradiation of LX in tertiary butyl alcohol yields two products. The photoproducts were named photo-17α-methyltestosterone (LXI), m.p. 241.5-243°C, and lumi-17α-methyltestosterone (LXII), m.p. 140.5-143°C. The photoproducts were isolated in 46 and 28% yield, respectively, based on recovered LX.

The infrared spectrum of LXI, Figure 5, shows a 5.93μ carbonyl group. No double bond absorption is evident in the infrared spectrum. The n.m.r. spectrum, Figure 7, shows no olefinic protons. The entire spectrum shows no absorption below 2.15δ. The methyls appear at 0.83, 1.17 and 12.0 δ. Thus, a ring must have been formed to account for the site of unsaturation. The general structure LXIa fits this data.



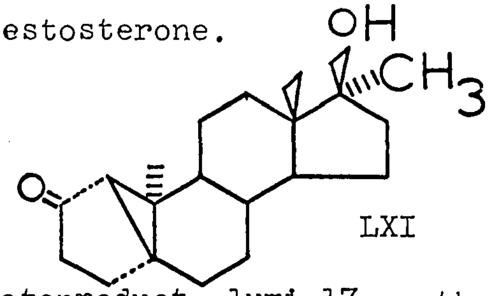
LXIa



LXII

The ultraviolet spectrum of LXI [$\lambda_{max}^{95\%\ \text{ethanol}}$ 210 mμ (5,923)] is in excellent agreement with that of dihydroumbellulone (40) (LXII) which shows $\lambda_{max}^{95\%\ \text{ethanol}}$ 210 mμ (2,470).

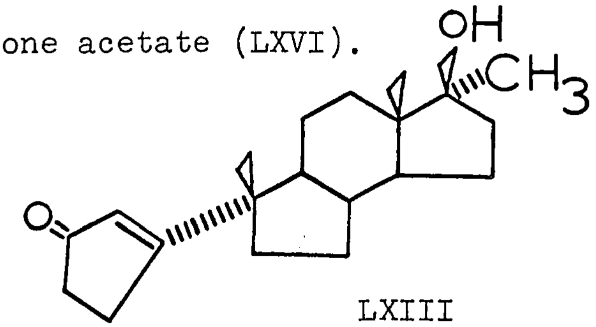
Further support of LXI as being the correct structure is derived from the fact that only a mono-benzal derivative is obtained. This proves that the carbonyl group has only one α-methylene group free for condensation. The mono-benzal derivative (LXVII), m.p. 237.5-239°, shows infrared absorption at 2.90 (O-H), 3.42 (C-H), 5.93 (unsaturated C=O) and 6.18 μ (C=C), and $\lambda_{max}^{95\%\ \text{ethanol}}$ 224 mμ (8,764), 229 mμ (9,319(and 299.5 mμ (24,911). The near identity of these physical constants with Griswold's (14) data for photo-testosterone acetate (LXV) firmly support structure LXI for photo 17α-methyltestosterone.



LXI

The second photoproduct, lumi-17α-methyltestosterone (LXIII) shows infrared carbonyl absorption of 5.86 and 5.96 μ, Figure 6. This phenomenon, presumably due to Fermi resonance, has been observed in 3-phenyl-2-cyclopentenone (41). LXIII shows a 6.26 μ double bond absorption. Combination of the infrared and ultraviolet data [$\lambda_{max}^{95\%\ ethanol}$ 232 mμ (18,737)] strongly suggested the presence of an α, β-unsaturated ketone moiety, most likely a cyclopentenone.

The n.m.r. spectrum of LXIII, Figure 8, shows a single olefinic proton at 5.93 δ, which is split. A rather characteristic ABCDX pattern (ABCD portion) appears centered at 2.50 δ. This data strongly suggests that a cyclopentenone moiety is present. The methyl groups appear at 0.87, 1.13 and 1.23 δ. Figure 8 shows that two methyl groups appear at 1.20 and one at 0.89 δ in the starting material LX. Non-equivalence of all three methyls in LXIII would be expected although exact assignment of each peak is not possible. On the basis of this spectral evidence, the structure LXIII is suggested for lumi-17α-methyltestosterone. The stereochemistry is inferred by analogy from Griswold's (14) proof of structure of lumi-testosterone acetate (LXVI).



LXIII

Jeger et al. (7) reported that XV could be converted to XIV. Irradiation of LXI in tertiary butyl alcohol in a pyrex well for twenty hours did not yield amounts of LX that were detectable on the v.p.c. In fact, LXI appears to be photostable. The reason for this anomaly is not understood.

Figure 4 summarizes the data of Jeger (7), Griswold (14,20), Gardner (10) and this investigation (20). The reason for the absence of product analogous to LXIII in Gardner's (10) work is not clear. It is by no means a minor product in any of the other investigations.

Irradiation of 2-Cyclohexenone, 4-Methyl-2-Cyclohexenone and 2,4,4-Trimethyl-2-Cyclohexenone

The photochemistry of 2-cyclohexenone (XLVII) and 4-methyl-2-cyclohexenone (LXXVI) was studied in order to determine whether there is any structural requirement in the ketone which is requisite to or precludes skeletal rearrangement. 2,4,4-Trimethyl-2-cyclohexenone (LXXVII) was studied because it was of interest to know whether a 2-substituted cyclohexenone would exhibit any anomalous behavior as in the case of the steroidal 2-substituted cyclohexadienone XXXIII (30).

Irradiation of a .025 M solution of 2-cyclohexenone (XLVII) for 29.5 hours in tertiary butyl alcohol (50% destruction)

Figure 4. Comparison of androstenone and cholestenone photochemistry in tertiary butyl alcohol (14, 20, 21, 22, 10).

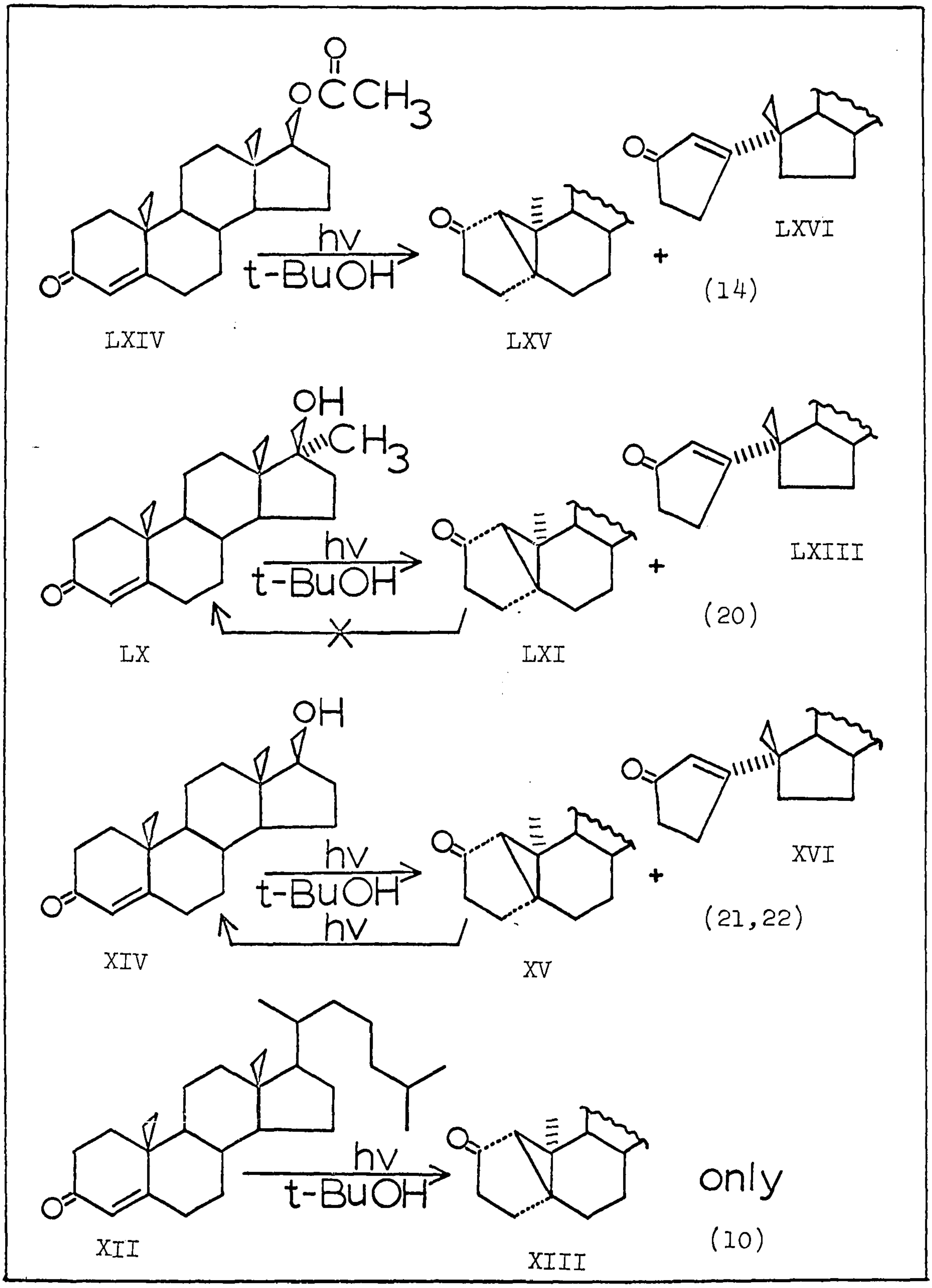

OCCH3
LXIV
hv
t-BuOH
LXV
+
LXVI
(14)
OH
CH3
LX
hv
t-BuOH
LXI
+
LXIII
(20)
OH
XIV
hv
t-BuOH
hv
XV
+
XVI
(21,22)
XII
hv
t-BuOH
XIII
only
(10)

Figure 5. Immersion well irradiation apparatus.

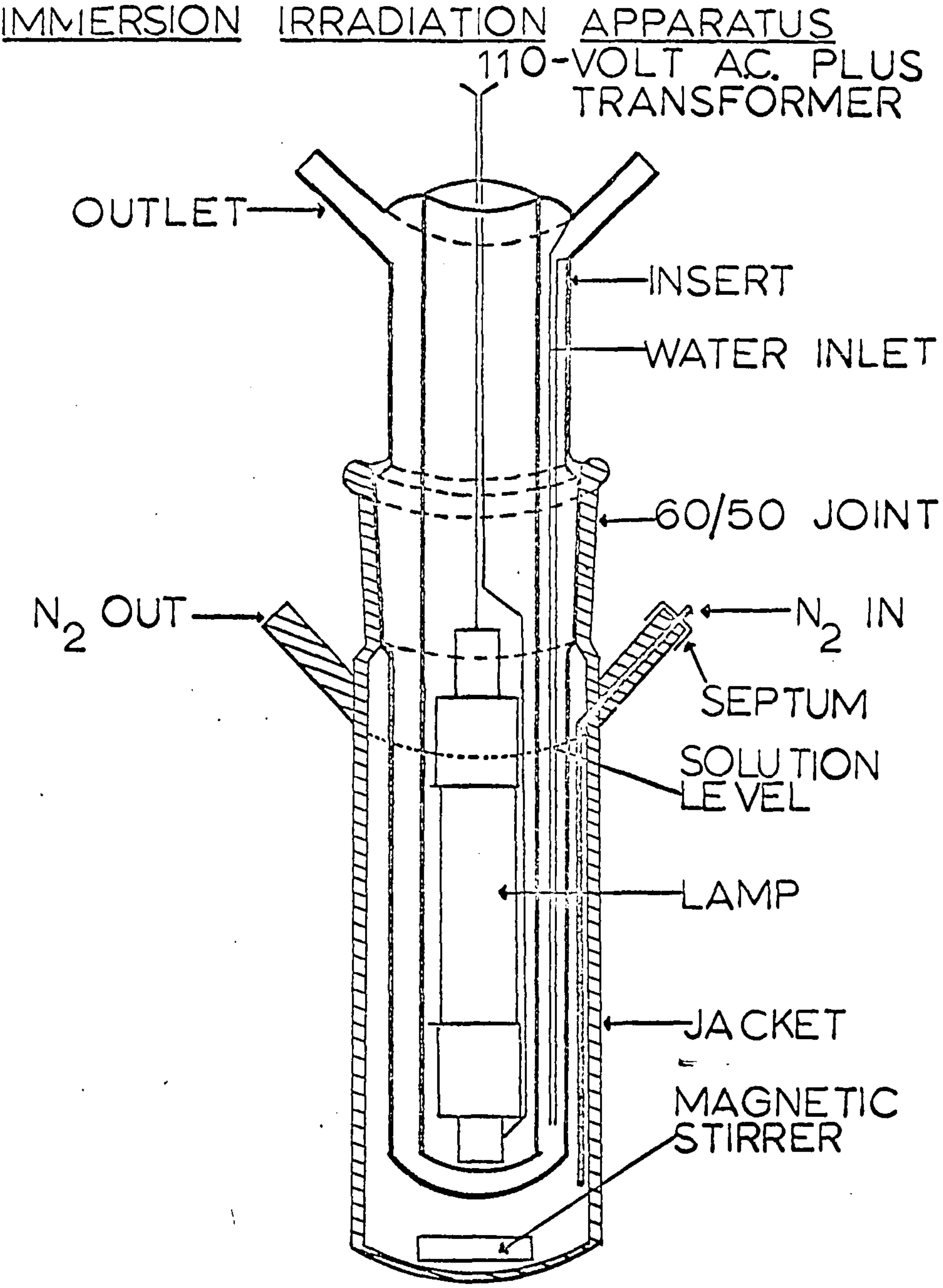
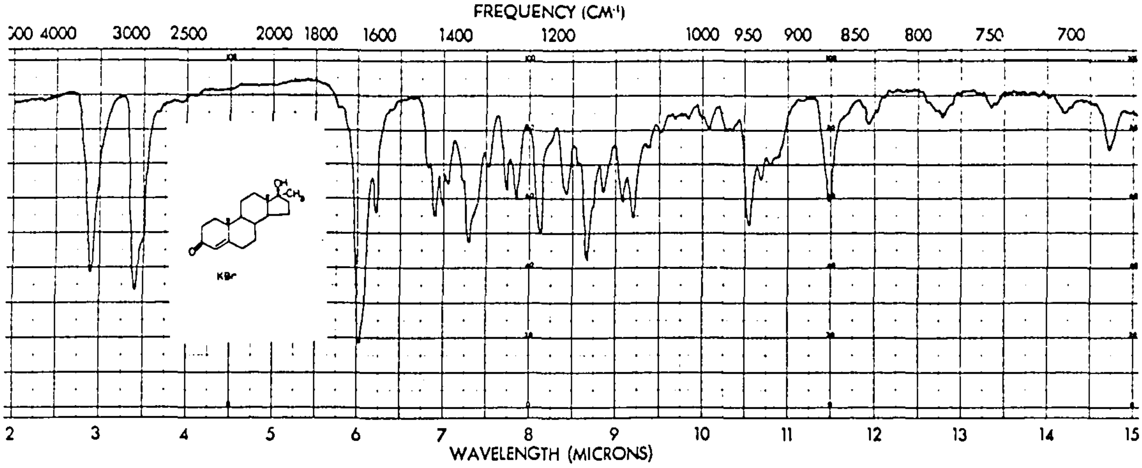

IMMERSION IRRADIATION APPARATUS
110-VOLT A.C. PLUS TRANSFORMER
OUTLET
INSERT
WATER INLET
60/50 JOINT
N_2 OUT
N_2 IN
SEPTUM
SOLUTION LEVEL
LAMP
JACKET
MAGNETIC STIRRER

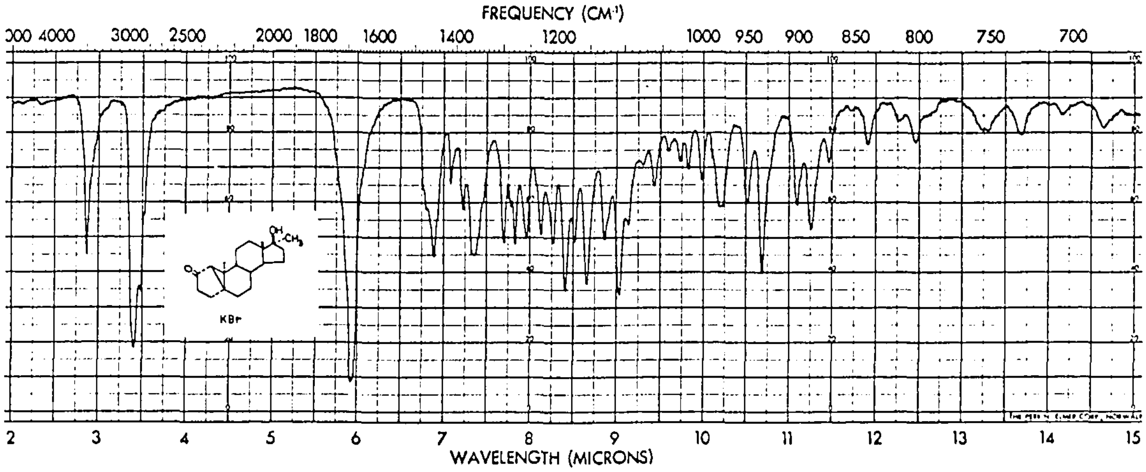
Figure 6. Infrared spectra.

Top - 17α-methyltestosterone (LX) (KBr Pellet)

Middle - Photo-17α-methyltestosterone (LXI) (KBr Pellet)

Bottom - Lumi-17α-methyltestosterone (LXIII) ($CHCl_3$)


FREQUENCY (CM⁻¹)
4000
3000
2500
2000
1800
1600
1400
1200
1000
950
900
850
800
750
700
OH
CH₃
KBr
2
3
4
5
6
7
8
9
10
11
12
13
14
15
WAVELENGTH (MICRONS)


FREQUENCY (CM⁻¹)
4000
3000
2500
2000
1800
1600
1400
1200
1000
950
900
850
800
750
700
OH
CH₃
KBr
2
3
4
5
6
7
8
9
10
11
12
13
14
15
WAVELENGTH (MICRONS)

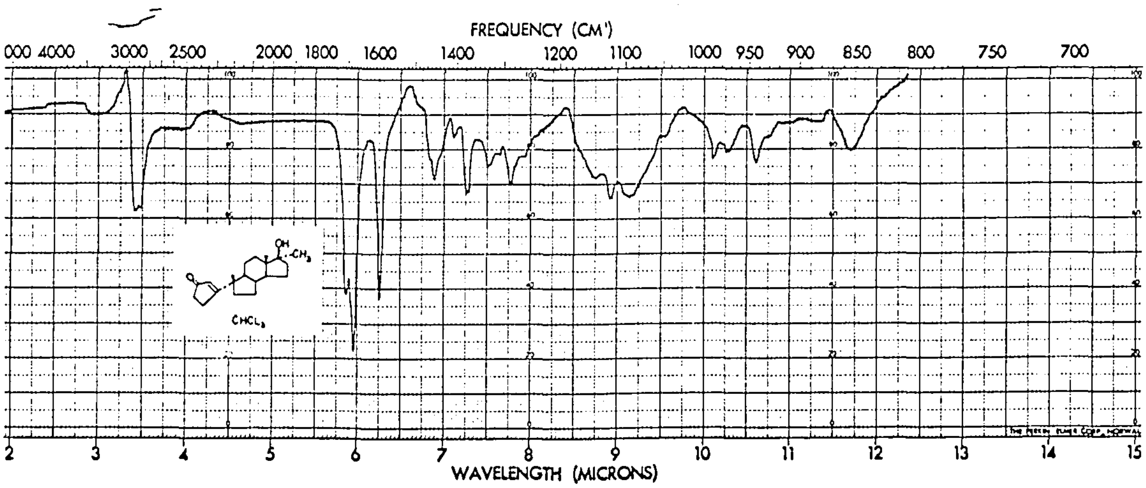
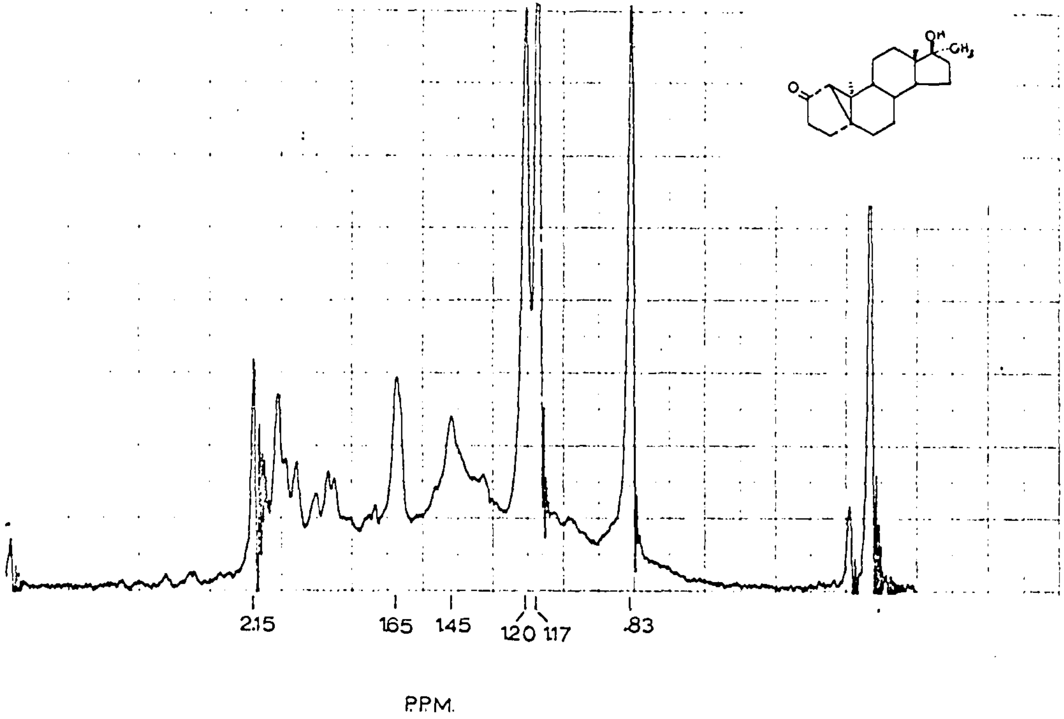

FREQUENCY (CM⁻¹)
4000
3000
2500
2000
1800
1600
1400
1200
1100
1000
950
900
850
800
750
700
OH
CH₃
CHCl₃
2
3
4
5
6
7
8
9
10
11
12
13
14
15
WAVELENGTH (MICRONS)

Figure 7. Nuclear magnetic resonance spectra (CCl_4).

Top - Photo-17α-methyltestosterone (LXI)

Bottom - 1-Benzoylcyclohexene (LXXI)


2.15
1.65
1.45
1.20
1.17
.83
P.P.M.
OH
CH3
O

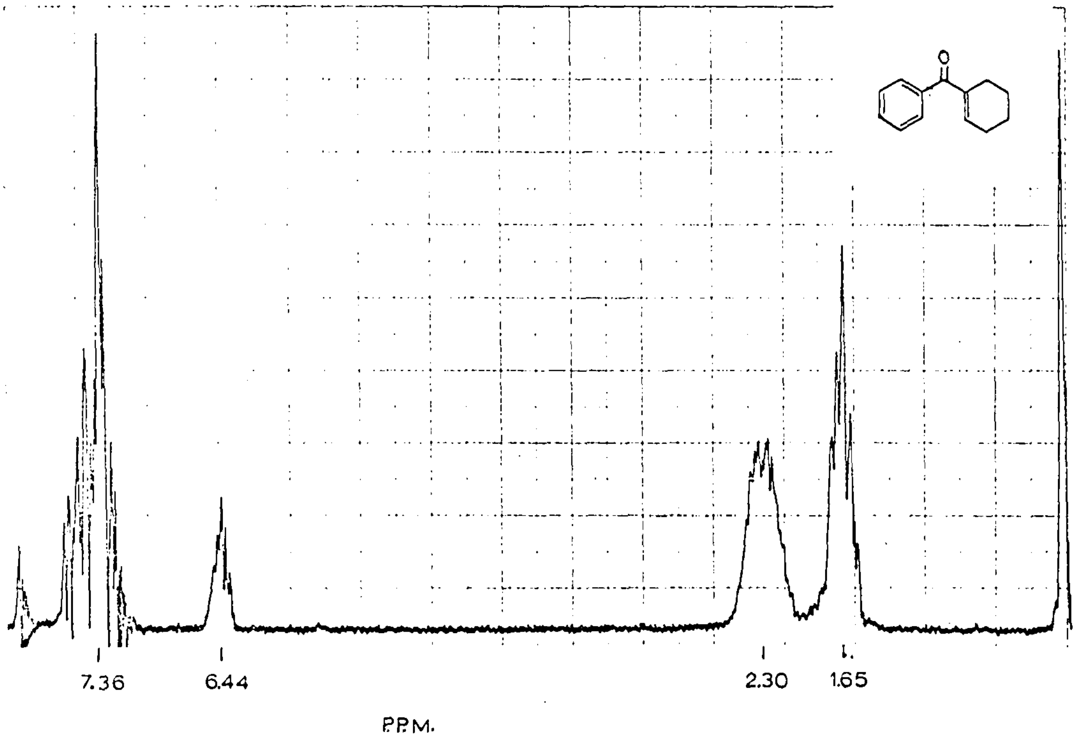
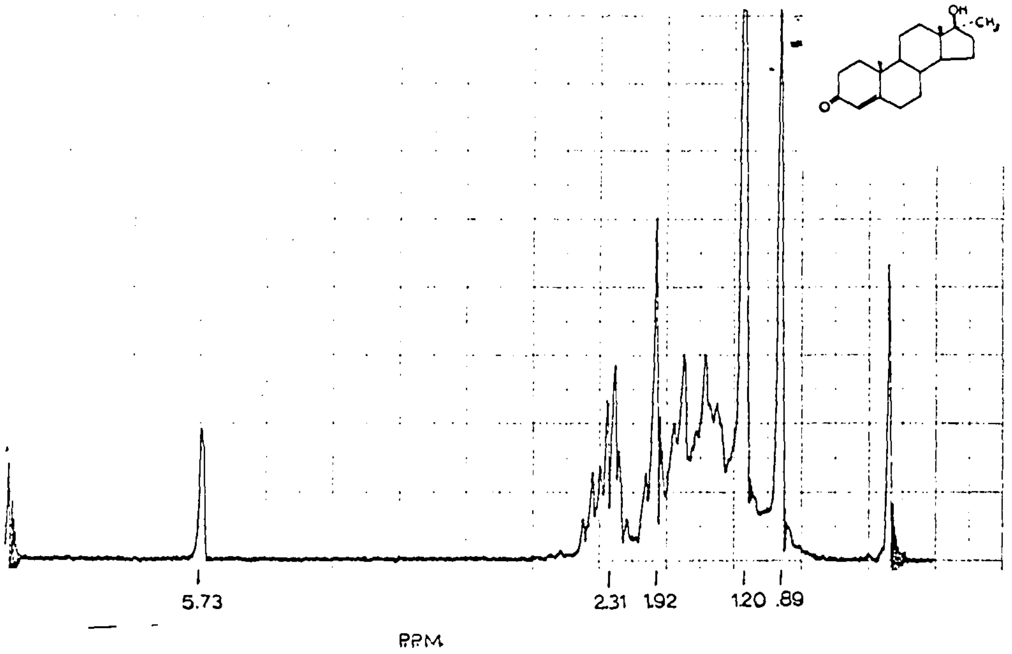
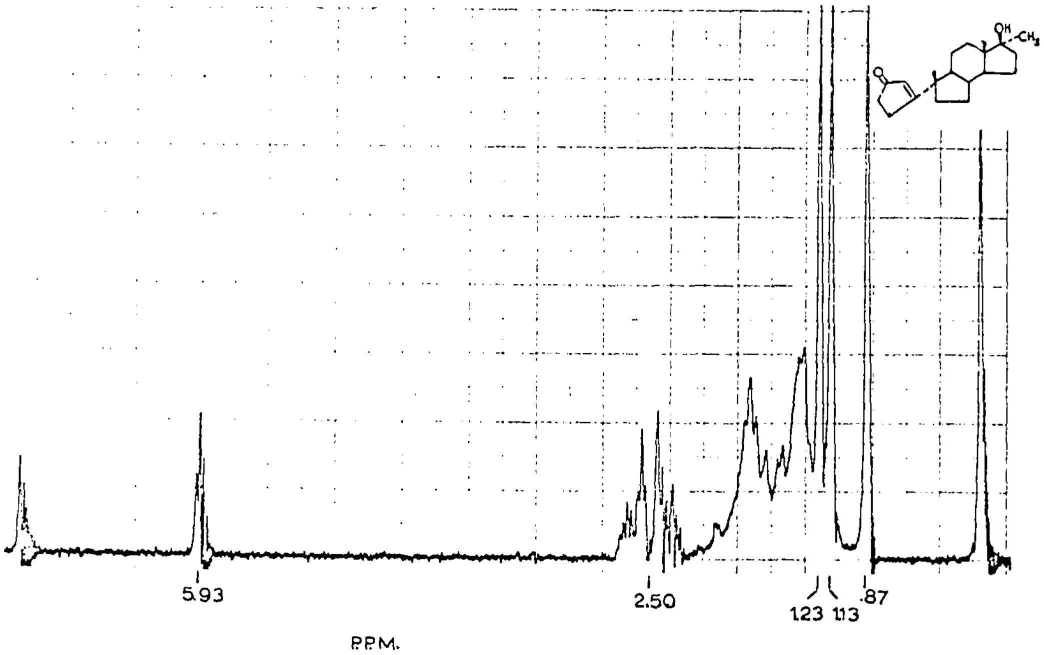

7.36
6.44
2.30
1.65
P.P.M.
O

Figure 8. Nuclear magnetic resonance spectra (CCl_4).

Top - 17α-methyltestosterone (LX)

Bottom - Lumi-17α-methyltestosterone (LXIII)


OH
CH3
O
5.73
2.31
1.92
1.20
.89
P.P.M.


OH
CH3
O
5.93
2.50
1.23
1.13
.87
P.P.M.

yields no photoproducts resulting from skeletal rearrangement. Only a gummy intractable residue could be obtained upon steam distillation of the crude irradiation mixture. This residue was not steam volatile and did not come through the v.p.c., indicating that it was high molecular weight material, probably dimer and higher polymers. The steam volatile portion of the crude irradiation material was found to be unreacted XLVII by i.r., n.m.r. and v.p.c. analysis. No other volatile, low molecular weight products due to skeletal rearrangement were detected.

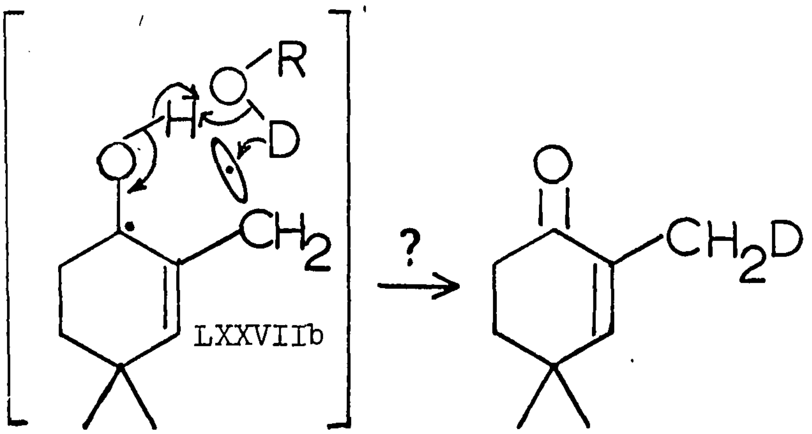
Exactly analogous results were obtained in the irradiation of a .02 M solution of 4-methyl-2-cyclohexenone (LXXVI) in tertiary butyl alcohol. Irradiation of LXXVI for 24.5 hours (54% destruction) yielded only starting material and a gummy dark red non-steam volatile residue upon workup by steam distillation. Thus, polymerization is an important mode of reaction of excited XLVII and LXXVI, even in dilute solution.

XLVII and LXXVI apparently do not have the correct structural features requisite to skeletal rearrangement. Since XXI rearranges to XXII and XXIII under identical irradiation conditions, it may be concluded that 4,4-disubstitution is a necessary condition for rearrangement.

The fact that a 4,4 disubstituted cyclohexenone is a necessary but not sufficient condition was discovered from the study of the photochemistry, or in reality the absence thereof, of 2,4,4-trimethyl-2-cyclohexenone (LXXVII). Irradiation of .019 M LXXVII in tertiary butyl alcohol for twenty-four hours and subsequent workup gave 96% of unreacted starting material. No higher molecular weight products were obtained. Thus, the rearrangement of type XXI → XXII + XXIII has been completely precluded by the 2-methyl group.

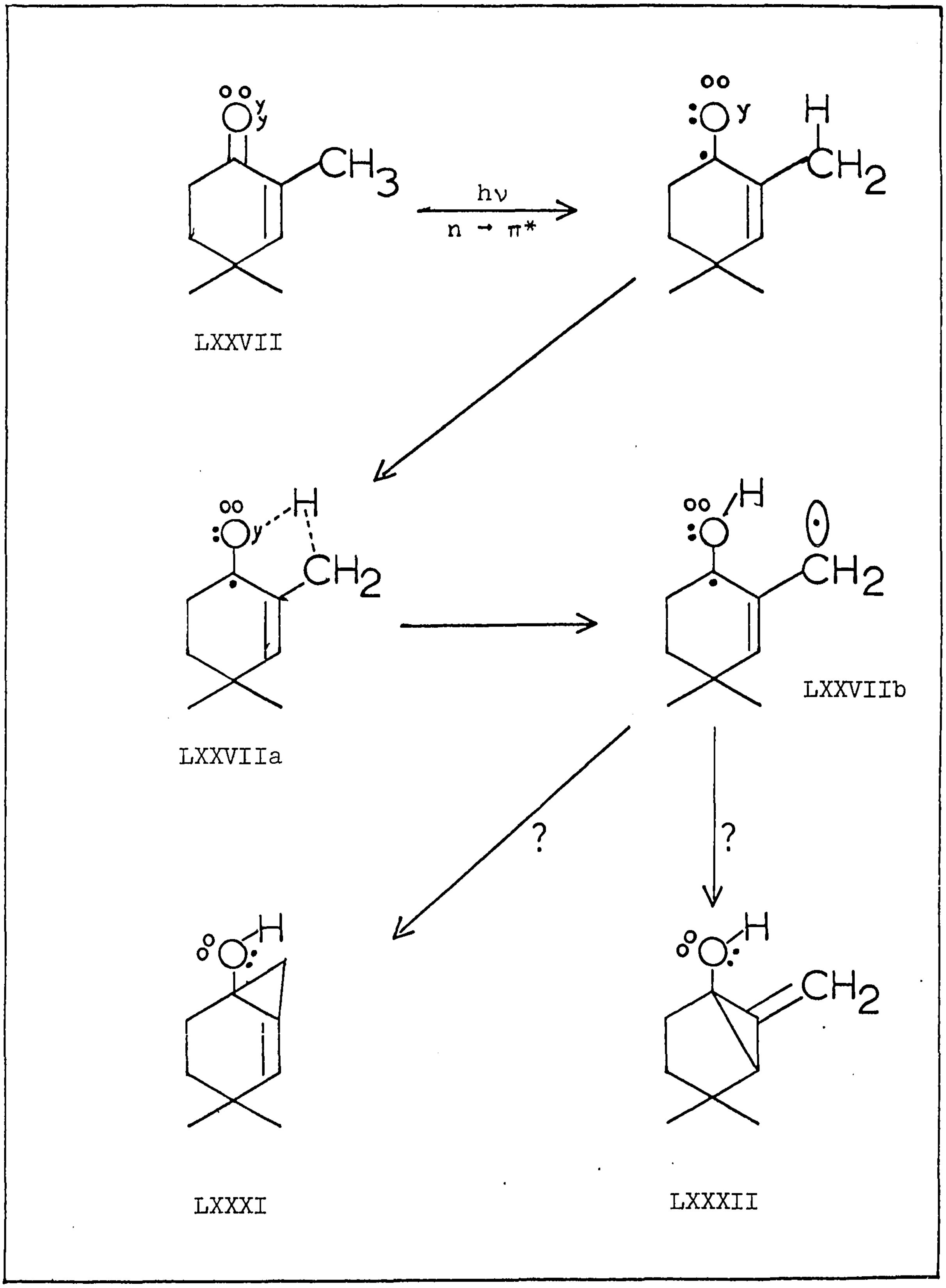
It was thought that the extreme light stability of LXXVII might be due to quenching of the excited state carbonyl group by a process analogous to γ-hydrogen abstraction which is observed frequently in saturated ketones (42). This "quenching effect" is depicted in Figure 9.

Following n → π* excitation, the remaining n electron ("y" electron in Figure 9) is available for hydrogen abstraction. If abstraction did occur, either the bridged structure LXXVIIa or the completely abstracted LXXVIIb could result. Further, if LXXVIIb is involved it should be possible to exchange protons or deuterons with the solvent, perhaps via a "cage" mechanism such as shown below.



LXXVIIb

Figure 9. Postulated self quenching scheme for 2,4,4-trimethyl-2-cyclohexenone (LXXVII).



LXXVII

LXXVIIa

LXXVIIb

LXXXI

LXXXII

In order to test this hypothesis, LXXVII was dideuterated to 94% isotopic purity at the 6-position. This material (LXXX) was then irradiated in deuterio-tertiary butyl alcohol (> 0.97 atom D/mole) for a period of forty-eight hours with the medium pressure mercury lamp. Non-deuterated LXXVII was also irradiated simultaneously under identical experimental conditions. The extent of exchange was determined by measuring the molecular ion (M) and molecular ion + 1 (M+1) peak ratio (M+1/M). This ratio was corrected for C^{13} isotope contribution to measure the fraction of exchanged material. The following results were obtained:[1]

Compound	M+1/M before irrad.	M+1/M after irrad.
LXXX	0.094	0.0975
LXXVII	0.094	0.0985

The extent of exchange ϵ was calculated by the following formula:

$$\frac{M+1}{M}\text{ after irrad.} = \frac{\frac{M+1}{M}\text{ before irrad. }(1-\epsilon)+\epsilon}{1-\epsilon}$$

where ϵ = the fraction of material which has exchanged 1 hydrogen for deuterium.

Using the above data, ϵ was found to be 0.35% for LXXX and 0.44% for LXXVII. This very slight amount of incorporation is

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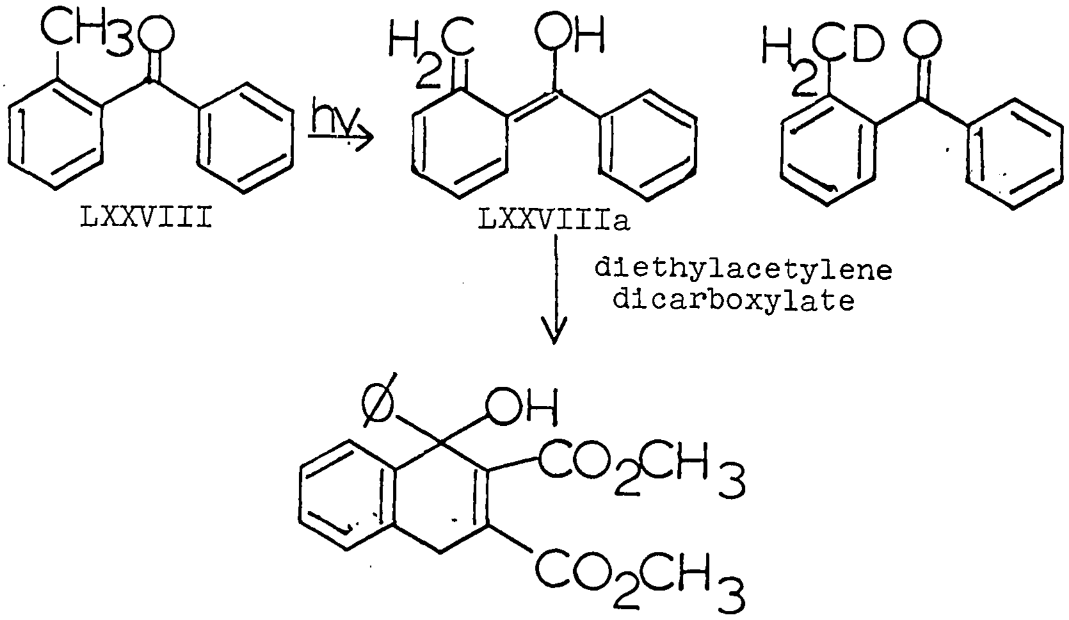
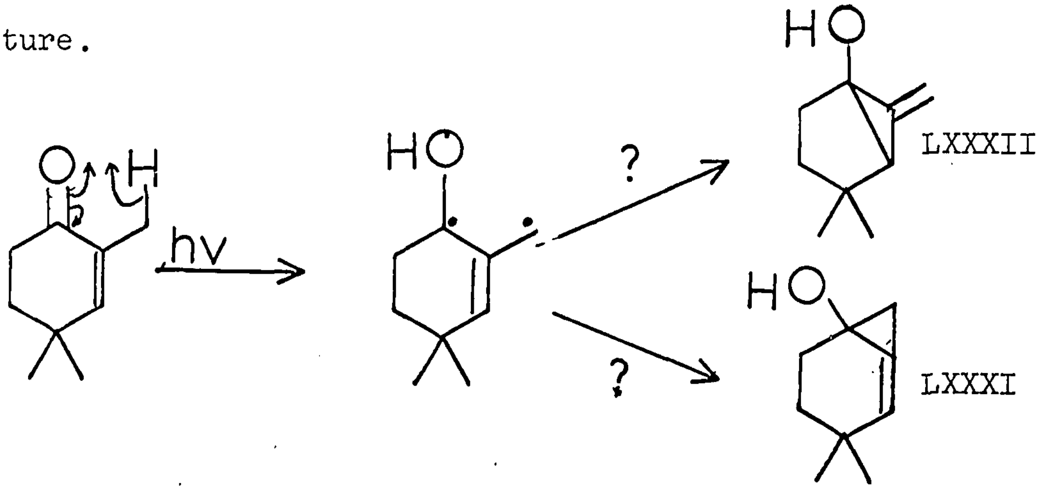
[1] The author wishes to thank Dr. T. H. Kinstle for measuring the mass ratios.

not significant enough to be real, since it lies within the range of instrumental error. The author interprets the result as one of no incorporation of deuterium. If the deactivation process occurs as depicted in Figure 9, the 2-methyl protons are never labile to solvent exchange, and simply "jump" back and forth between the excited carbonyl oxygen and the methyl group. This may well be described as a degenerate deactivation. The energy requirements of this partial or complete proton transfer are postulated to be sufficient to "cool" the molecule and preclude skeletal rearrangement.

An interesting analogy for this type of deactivation has been observed in the photoreduction of benzophenones. The quantum yield for the photoreduction of benzophenone in isopropyl alcohol is 2.0 (43). In contrast, the quantum yield for the photoreduction of 2-methyl benzophenone is .05 (44). Yang and Rivas (45) have shown that if 2-methyl benzophenone (LXXVIII) is irradiated in deuteriomethanol no photoreduction occurs and deuterium is incorporated into the 2-methyl group. Yang (45) postulates an intermediate photo-enol which is labile to deuterium exchange. Evidence for the photoenol (LXXVIIIa) is provided by the trapping experiment with acetylene dicarboxylate to give LXXIX.


LXXVIII LXXVIIIa

Thus a close analogy to the unreactivity of LXXVII is presented by 2-methyl benzophenone. In view of Yang's (45) postulation of deuterium exchange occurring in the intermediate photo-enol, the highly imaginative structures LXXXI and LXXXII could be postulated as "photoenols" of LXXVII, although an important difference in the analogy is that these two photoenols are not labile to intermolecular exchange of deuterium with solvent upon tautomerization to the ketone structure.


LXXXII
LXXXI

Whatever the reason for the photostability of LXXVII, no other experiment to study the mechanism of this self deactivation could be imagined by the author due to the photochemical unreactivity of the molecule.

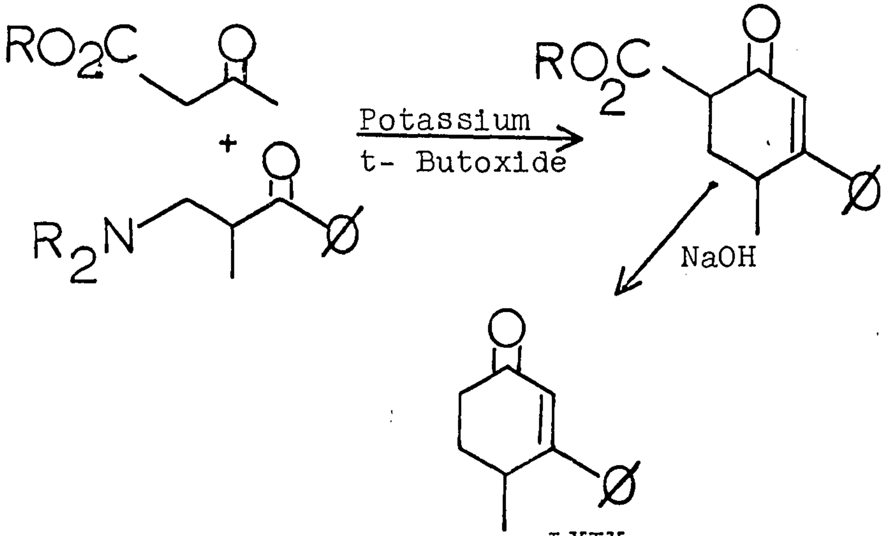
It is possible that the reason lies in a subtle geometric or stereoelectronic effect in the excited state, phenomena which are as yet uninferrable by our present "mix and watch" approach. The fact remains that the 2-methyl group precludes photochemical rearrangement and demonstrates that the presence of a 4,4-disubstituted cyclohexenone is a necessary but not sufficient condition for rearrangement.

The Photochemistry of 4-Methyl-4-Phenyl-2-Cyclohexenone

The photochemistry (see Historical) of 4,4-diphenyl-2-cyclohexenone and 4,4-diphenylcyclohexadienone has been reported by Zimmerman _et al_. (27, 33). In view of the photochemistry of 4,4-dimethylcyclohexenone reported in this study (20), it became of interest to investigate the photochemistry of 4-methyl-4-phenyl-2-cyclohexenone (LXVIII).

Irradiation of LXVIII in tertiary butyl alcohol led to the formation of three photo products in 12, 10 and 43% yields, respectively. The crude irradiation mixture contained 35% unreacted starting material. This analysis was by v.p.c. peak area measurement.

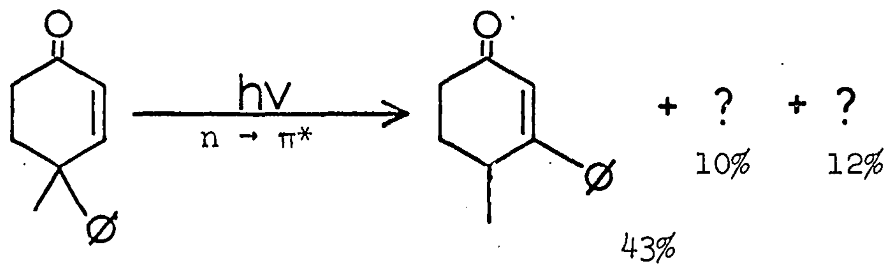
The major product (43%, 75% on the basis of unreacted starting material) was isolated by preparative scale vapor phase chromatography. The n.m.r. spectrum is shown in Figure 10, and the infrared spectrum is shown in Figure 11. The course of the irradiation was followed by periodically measuring the ultraviolet spectrum of the solution. It was observed that a new peak appeared at 280 $m\mu$ which increased in intensity during the irradiation and then came to a constant value. The irradiation was terminated when the rate of decay at λ_{max} for starting material (222 $m\mu$) approached zero. This time also coincided with the time when the 280 $m\mu$ peak did not increase significantly (see Experimental Section). The growth of the peak at 280 $m\mu$ suggested the production of an α, β-unsaturated ketone chromophore which was substituted with a phenyl group and prompted the synthesis of 4-methyl-3-phenyl-2-cyclohexenone (LXIX). The synthesis was that of Novello *et al*. (46).



LXIX

The authentic LXIX which was synthesized was in fact identical to the major photoproduct from the irradiation of LXVIII. Identical n.m.r. and i.r. spectra and identical v.p.c. retention times as well as lack of mixed melting point depression of the 2,4-dinitrophenylhydrazone derivatives (m.p. 187-188.5°) concretely proves the major photoproduct to be LXIX.

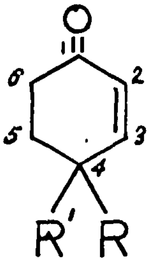
The other two photoproducts could not be obtained in sufficient yield to identify their structures. Both photoproducts were collected from the v.p.c. in small amounts. Both photoproducts showed a 5.81 μ carbonyl frequency (CCl_4), suggesting a basic bicyclo-[3.1.0]-hexan-2-one structure. This conclusion is supported by the 5.81 μ absorption (CCl_4) for XXIII and by the lack of olefinic protons in the n.m.r. spectra. The n.m.r. spectra of both photoproducts could not be rigorously interpreted due to the poor quality of the spectra which was caused by lack of material. The nature of these products was not investigated further. The photochemistry of LXVIII is thus summarized as:



LXVIII LXIX

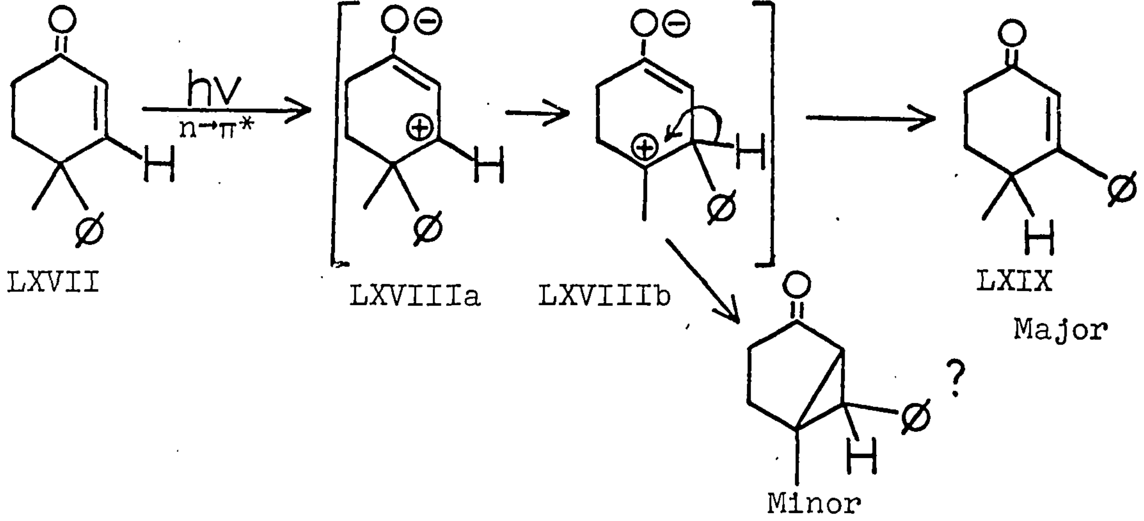
In the conversion of LXVIII to LXIX, the β olefinic proton is replaced by a phenyl group and vice versa. It became of interest to know whether this proton shift is intra- or inter-molecular. This point was answered by irradiation of LXVIII in deuterio-tertiary butyl alcohol. Analysis of the integral of the n.m.r. spectrum of the crude irradiation mixture showed that the area of the α-olefinic proton (sharp singlet at 6.12 δ) of LXIX was equal to the area of the C-4 proton (multiplet centered at 3.22 δ) of LXIX. This analysis was done on the crude reaction mixture since the peaks of the protons involved could be integrated accurately. Thus, the shift of the hydrogen atom from C-3 to LXVIII to C-4 of LXIX is intramolecular.

The photochemical rearrangement of LXVIII to LXIX represents a third type of reaction which 4,4-disubstituted cyclohexenones (LXX) may undergo.



LXX

XXIX (R=R'=Ø) when irradiated yields products resulting from 4 → 3 migration followed by 2,4 bonding (27). XXI (R=R'=CH$_3$) yields products from 4,5 cleavage and no 4 → 3 migration products. In contrast, (R=CH$_3$,R'=Ø) yields as the major product the 4 → 3 migration product which has undergone an intramolecular back transfer of the C-3 hydrogen to C-4. This process is summarized as:



LXVII LXVIIIa LXVIIIb LXIX

It is possible that the two unidentified products from this irradiation are isomers which resulted from 2,4 bonding. The driving force for the intramolecular hydrogen back-transfer is postulated to be due to the conversion of a tertiary alkyl carbonium ion (LXVIIIa) to a tertiary and benzylic carbonium ion (LXVIIIb). These "carbonium ions" are excited state electron deficient carbon skeletons.[1] A post facto extension of this postulate would predict that back transfer in the rearrangement of XXIX would not be important since both species (XXIXa and XXIXb) are tertiary and benzylic, with no resultant driving force for the back transfer.

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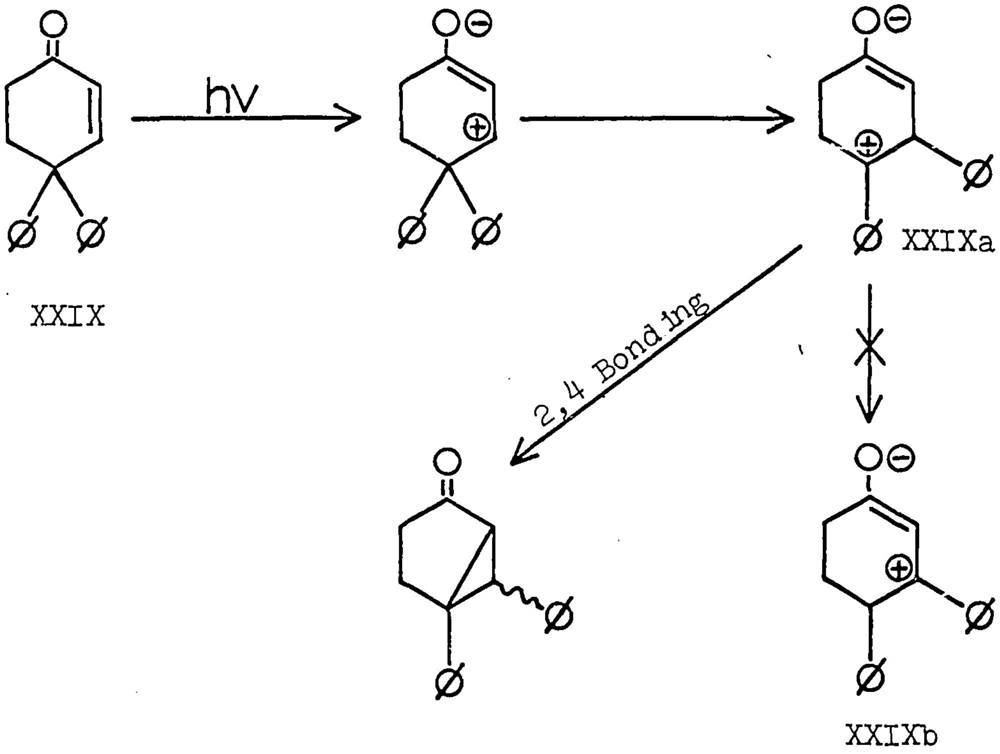
[1] The use of a dipolar excited state is merely for convenience. If the excited state is diradical, the same argument should still apply.



In view of the paucity of 1,2 hydrogen free radical shifts (47), and the plenitude of 1,2 hydrogen carbonium ion shifts the production of LXIX can most easily be interpreted as due to a carbonium ion like excited state rather than a diradical excited state. Thus, the photochemical rearrangement of LXVIII to LXIX seems to support a dipolar excited state as being responsible for product producing migrations. The exact nature of this state is as yet unknown.

Figure 10. Nuclear magnetic resonance spectrum (CCl_4) of 4-methyl-3-phenyl-2-cyclohexenone (LXIX).

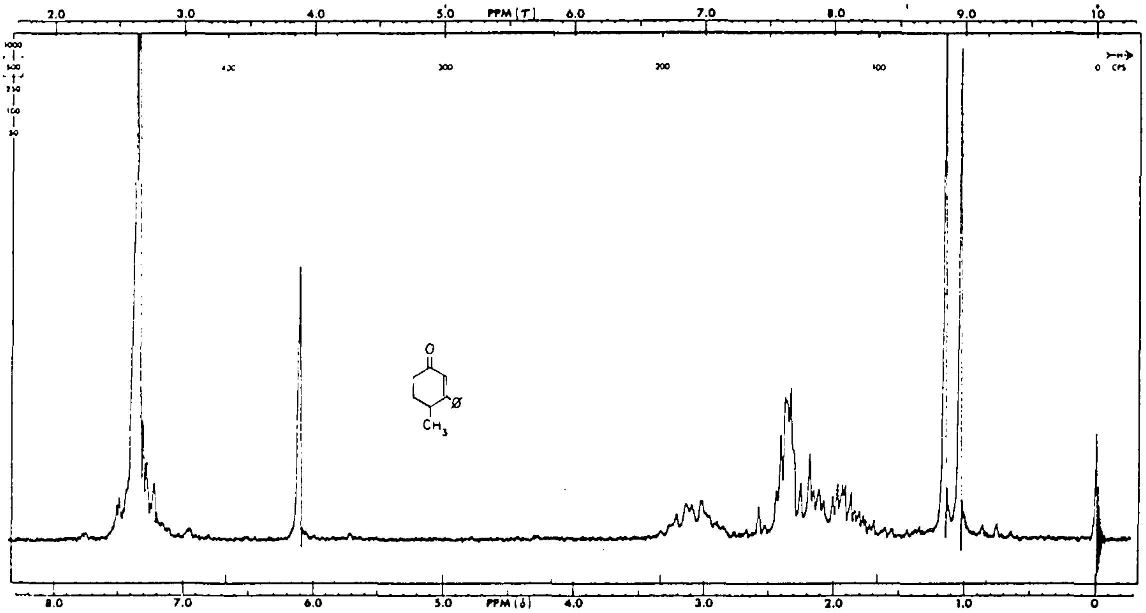
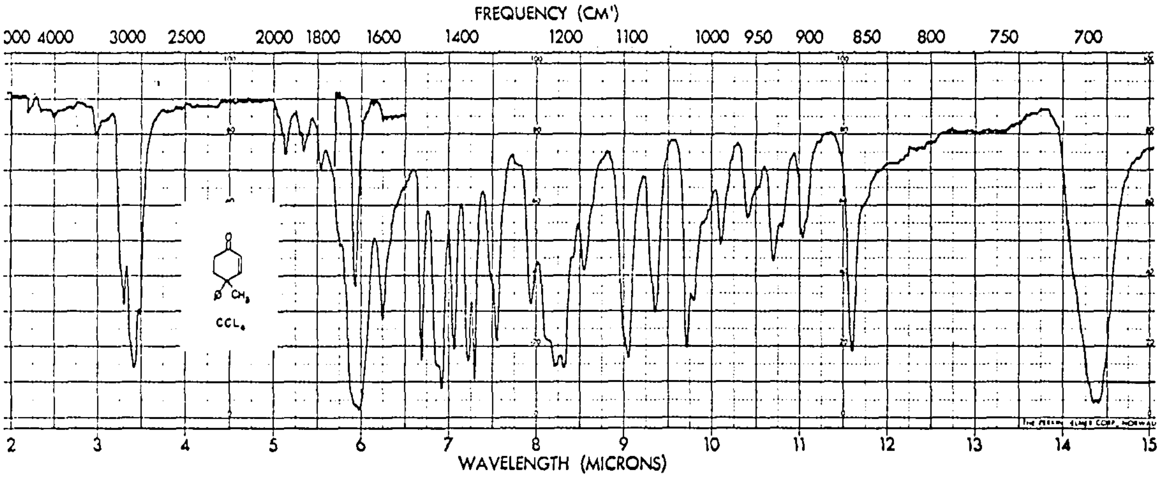

2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
1000
500
250
100
50
400
300
200
100
0 CPS
O
Ø
CH3
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0

Figure 11. Infrared spectra (CCl_4).

Top - 4-methyl-4-phenyl-2-cyclohexenone (LXVIII)

Bottom - 4-methyl-3-phenyl-2-cyclohexenone (LXIX)


FREQUENCY (CM⁻¹)
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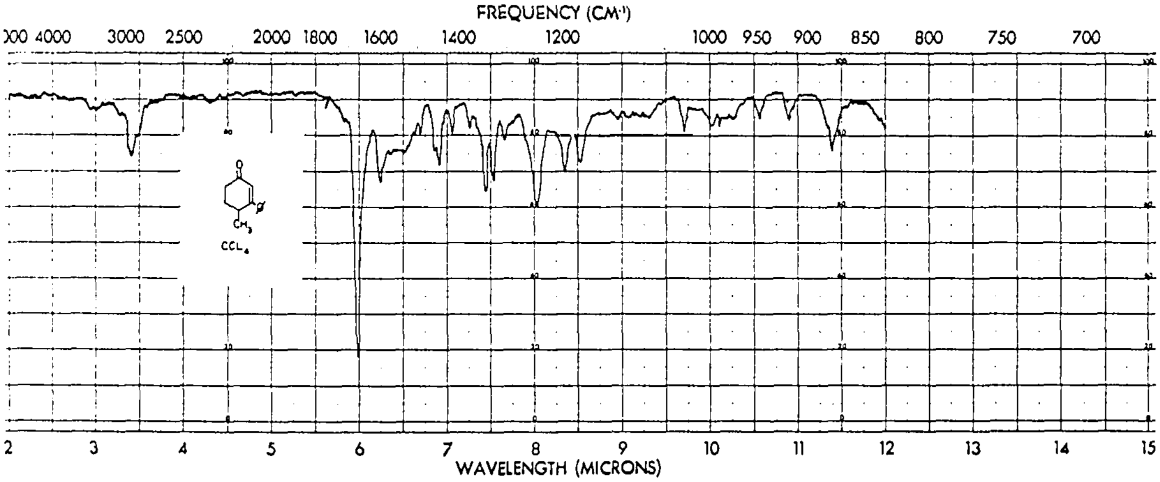
O
CH₃
CCL₄
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)


FREQUENCY (CM⁻¹)
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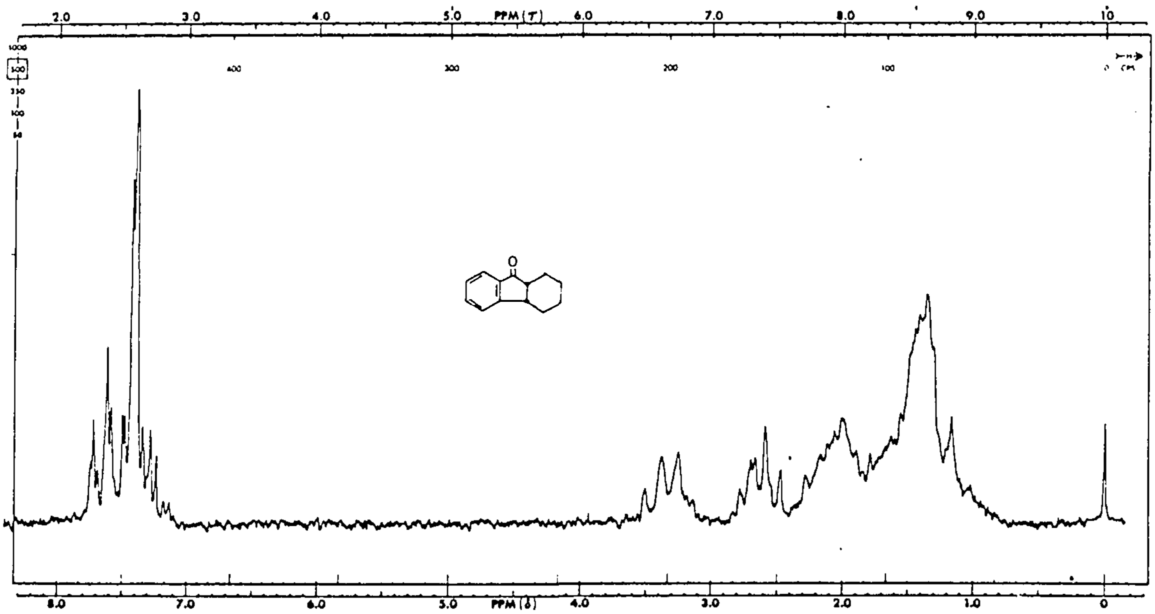
O
CH₃
CCL₄
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

Figure 12. Nuclear magnetic resonance spectra (CCl_4).

Top - Photoproduct from irradiation of 1-Benzoylcyclohexene (LXXI)

Bottom - 4-methyl-4-phenyl-2-cyclohexenone (LXVIII)


2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
500
400
300
200
100
0 CPS
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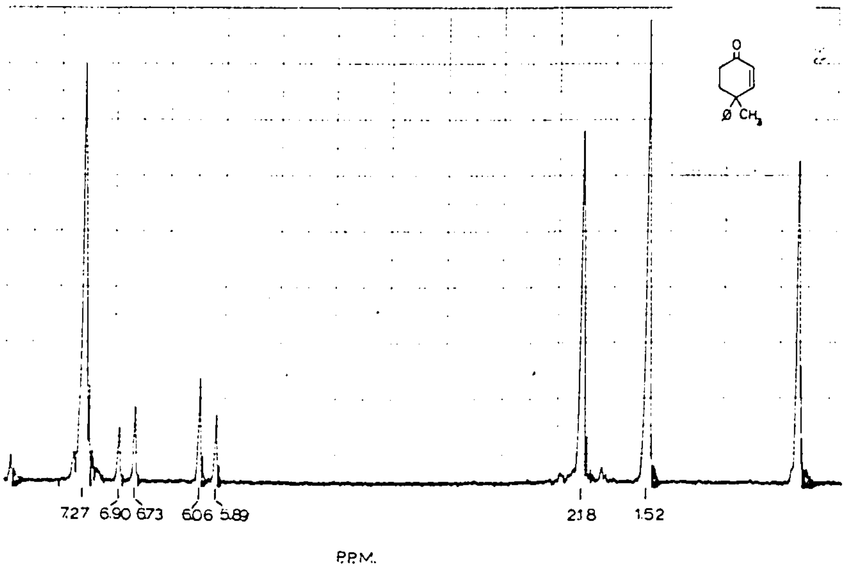
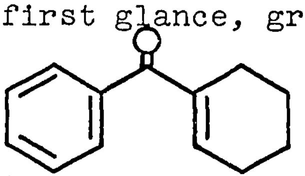
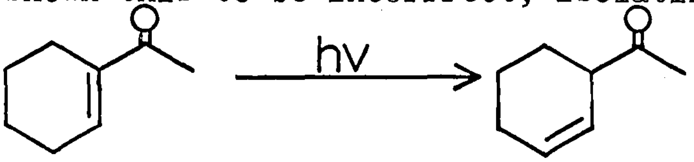
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0


O
Ø CH$_3$
7.27
6.90
6.73
6.06
5.89
2.18
1.52
P.P.M.

The Photochemistry of 1-Benzoylcyclohexene

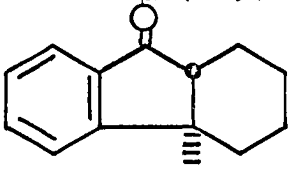
1-Benzoylcyclohexene (LXXI) is an interesting α, β unsaturated ketone. At first glance, granting the extension of analogy that it is a 2-cyclohexenone, it offers no apparent skeletal features which will make it labile to rearrangement since it is not 4,4-disubstituted. It was of interest to study the effect of the exocyclic carbonyl group. XIX has been reported to undergo isomerization to the β, γ isomer (23). Yang (24) has shown this to be incorrrect, isolating no β, γ isomer or other rearrangement products. Thus, on the basis of precedent, exocyclic carbonyl substitution did not seem to offer much of interest. In fact, LXXI rearranges upon irradiation with a quantum yield which is much higher than for homocyclic 2-cyclohexenone rearrangements of molecules such as XXI, XXVI and XXVII.

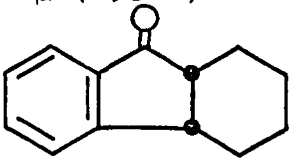

LXXI

XIX


XX

Irradiation of a .027 M solution of LXXI in tertiary butyl alcohol for eleven hours leads to complete destruction of starting material. The course of the irradiation was followed by measurement of the ultraviolet spectrum. A new peak appeared at 287 $m\mu$ upon irradiation. Interestingly enough, the ultraviolet spectrum of the solution came to a steady value after six hours with insignificant change thereafter, indicating completion of the reaction. The ratio of the absorbances at 243 mμ and 287 mμ was 4.75 after six hours irradiation. This offered the first clue to the nature of the rearrangement, since House (48) reported $\lambda_{max}^{95\% \text{ ethanol}}$ 245 mμ (12,000), 291 mμ (2,500) for LXXII and $\lambda_{max}^{95\% \text{ ethanol}}$ 246 mμ (11,700), 291 mμ (2,360) for LXXIII.


LXXI, m.p. 91-92°


LXXIII, m.p. 40-41°

The isolated crude product showed a broad carbonyl absorption at 5.86 μ with no carbonyl absorption at 6.06 μ indicating a nearly complete destruction of LXXI. This crude product could not be crystallized by any attempted procedure, including seeding with a dead fly.[1]

Molecular distillation of the crude oil gave a 45% yield of a bright yellow oil which would not solidify. The n.m.r. spectrum of this oil is shown in Figure 12. This oil showed a 5.85 μ carbonyl absorption (see Figure 13) and the ultraviolet spectrum showed $\lambda_{max}^{95\% \text{ ethanol}}$ 244.5 mμ (10,737) and 290.5 mμ (2,163). The spectral properties suggested that the photoproduct is indeed the cis-isomer LXXIII but the breadth of the carbonyl group absorption and the failure of the oil to crystallize still suggested that the product was a mixture.

---

[1] The author is deeply indebted to Dr. Hans Dieter-Becker for teaching him this occasionally successful technique.

An authentic sample of LXXIII was synthesized by the acid catalyzed ring closure of LXXI by the procedure of House (48). The authentic material showed i.r. and n.m.r. spectra which were identical to those of the distilled photoproduct. The authentic material could be crystallized from Skelly B and was used to seed the photoproduct oil. The photoproduct did not solidify.

Comparison of the infrared spectrum (Figure 13) of the photoproduct with infrared spectra of authentic LXXIII and LXXII indicated that the oil was in fact the cis-isomer.[1] The failure to solidify was probably due to traces of starting material or the trans-isomer.

The photoproduct oil gave a 2,4-dinitrophenylhydrazone (m.p. 189.5-190.5°) which was identical as shown by spectral and mixed melting point methods to the 2,4-dinitrophenylhydrazone of LXXIII which was prepared by the acid catalyzed ring closure. This does not mean that the photoproduct itself is pure LXXIII, since House (48) has observed that both LXXII and LXXIII give the same 2,4-dinitrophenylhydrazone (m.p. 190°), which has the cis-ring juncture (LXXIV).

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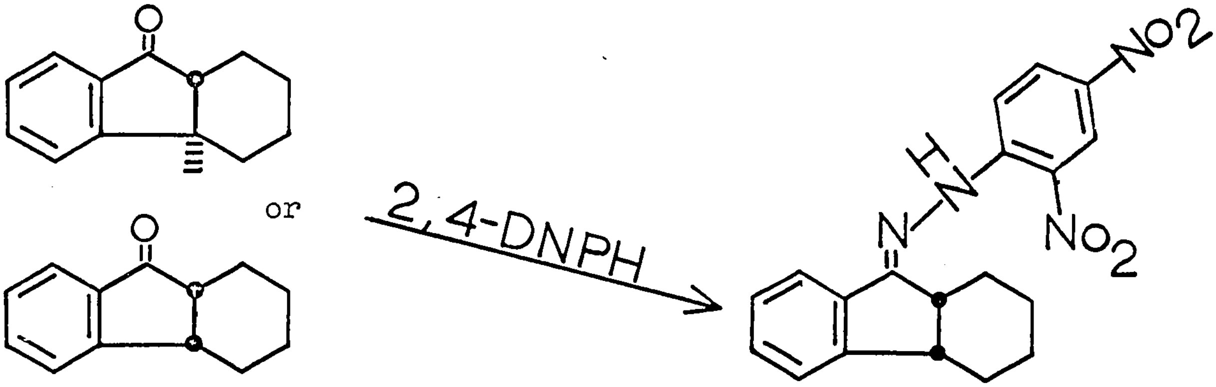
[1] The author is indebted to Professor H. O. House for sending him these spectra.



LXXIV

The yield of the photochemical reaction of LXXI to LXXIII was found to be at least 75% if a chromatographic workup was employed. Thus, the photochemical conversion of LXXI to LXXIII can be brought about in good yield in neutral media. This is in contrast to the synthesis of LXXIII from LXXII by ring closure in neat sulfuric acid.

The quantum yield for the photodecomposition of LXXI was measured. This quantum yield is relative to that of the photoreduction of .10 M benzophenone by .10 M benzhydrol in benzene, which has a quantum yield of .68 at 366 mμ and .69 at 313 mμ.[1] This measurement was made at 366 mμ by jacketing the lamp in Figure 14 with a saturated copper sulfate solution which absorbs greater than 95% of the 313 mμ wavelength (49). The per cent reduction of benzophenone was measured by a standard u.v. analysis (see Experimental) to be 14.7. The

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[1] The author wishes to thank Dr. N. J. Woolsey for the measurement of the benzophenone-benzhydrol quantum yields.

per cent destruction of LXXI was calculated by an analysis of the n.m.r. integral of the olefinic (O) to aromatic (A) proton area ratio. Before irradiation, the O/A ratio of LXXI was 1.24/6.85 or .182. After simultaneous irradiation leading to 14.7% photoreduction of benzophenone, the average O/A ratio of the reaction mixture was .167. The calculation of per cent destruction is as follows, correction being made for the fact that the O/A ratio for pure LXXI was 1.24/6.85 or .182 instead of .20.

Let x = fraction of LXXI reacted, and thus the fraction of LXXIII produced,

and 1-x = fraction of LXXI remaining.

The O/A ratio may be expressed as

$$O/A = \frac{\text{Olefinic Area of LXXI}}{\text{Aromatic Area of LXXI} + \text{Aromatic Area of LXXIII}}$$

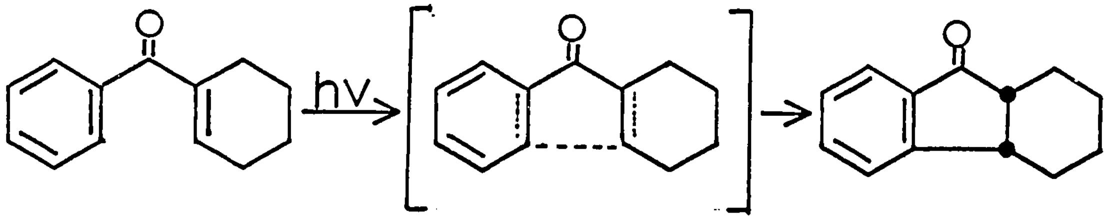
$$\text{Thus } O/A \doteq \frac{1.24\,(1-x)}{6.85(1-x) + 4(x)} = .167 \qquad (1)$$

This expression allows for the .182 O/A ratio of the starting material. The factor 4(x) represents the contribution to the aromatic area by the four protons of LXXIII. Solution of (1) for x gives a value of .132. Thus, LXXI has been converted to LXXIII to the extent of 13.2%. The relative quantum yield is $\frac{13.2}{14.7}$ (.68) or .62.

It should be emphasized that this quantum yield is based on the assumption that the only reaction occurring is the conversion of LXXI to LXXIII. This assumption is strengthened by allowing the reaction to proceed to only a fraction of completion, ensuring that the majority of the light is absorbed by LXXI. The ideal way to measure the quantum yield would be to measure the amount of LXXIII formed. This was not possible by ultraviolet analysis at these low conversions, since the 287 mμ maximum of LXXIII is only a small contribution to the intense $\pi \rightarrow \pi^*$ maximum of LXXI. The reason for the ratio of 1.24/6.85 for the olefinic to aromatic area of LXXI is not understood. The material was pure. Even if this correction is neglected, Equation 1 simplifies to

$\frac{1(1-x)}{5(1-x)+4x}$ or $\frac{1-x}{5-x}$ which when set equal to .167 and solved, gives $x = .137$. This is a very small error.

This quantum yield is rather high when compared to that of the photorearrangement of XXI ($\Phi = 1.7 \times 10^{-2}$). The reason for such a high efficiency may be due to π-bonds of the molecule being nearly co-planar in the ground state. The carbonyl and cyclohexene system would presumably have a favored co-planar conformation due to the stability derived from the greater π overlap. Excitation to the excited state should obey the Franck-Condon principle, yielding an excited species with very favorable geometry for ring closure.



LXXI LXXIII

An alternate explanation for the high quantum yield may be the inherently greater polarizability of the π system and thus more facile participation in bonding than in the case of XXI where σ breakage is requisite to rearrangement.

The Photochemistry of 4,4-Dimethyl-2-Cyclohexenone

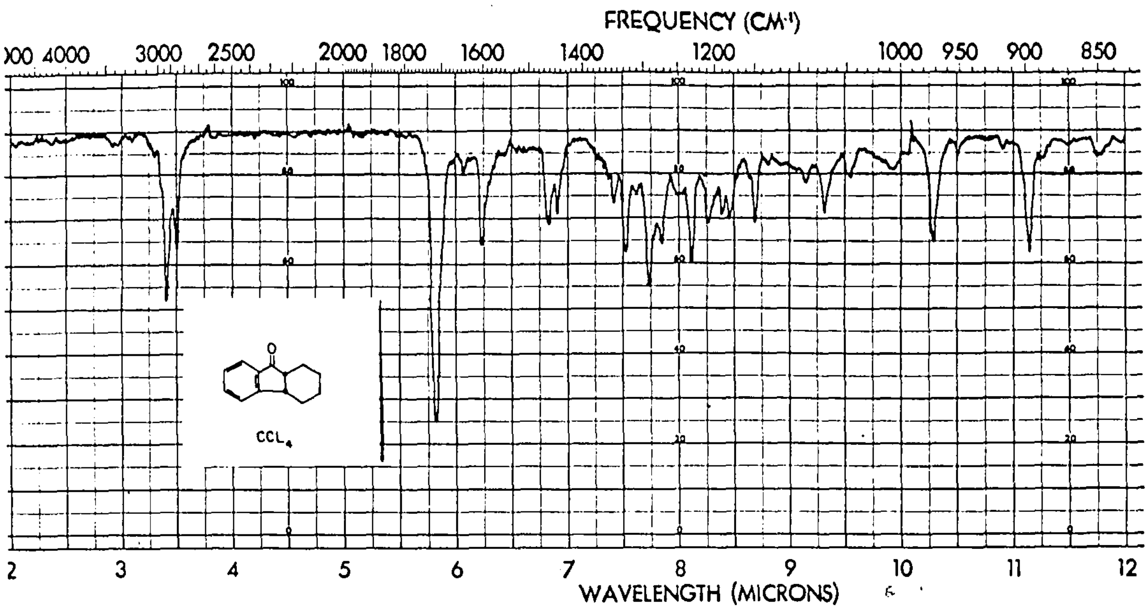
The study of the photochemistry of 4,4-dimethyl-2-cyclohexenone (XXI) was initiated by A. Dutton and Dr. P. Fitton. At the time the author continued the study, the photoproducts from the irradiation of XXI in tertiary butyl alcohol and acetic acid had been isolated. Structures were proposed for each of the photoproducts on the basis of spectral properties and elemental analyses. The data given in this section is the description of the author's contribution to the study of this reaction.

The synthesis of 4,4-dimethyl-2-cyclohexenone (XXI) was an adaptation of the enamine synthesis described by Stork (50). For the nuclear magnetic resonance spectrum of XXI see

Figure 13. Infrared spectra (CCl_4).

Top - Photoproduct from irradiation of 1-Benzoylcyclohexene (LXXI)

Bottom - 1-Benzoylcyclohexene (LXXI)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00 4000
3000
2500
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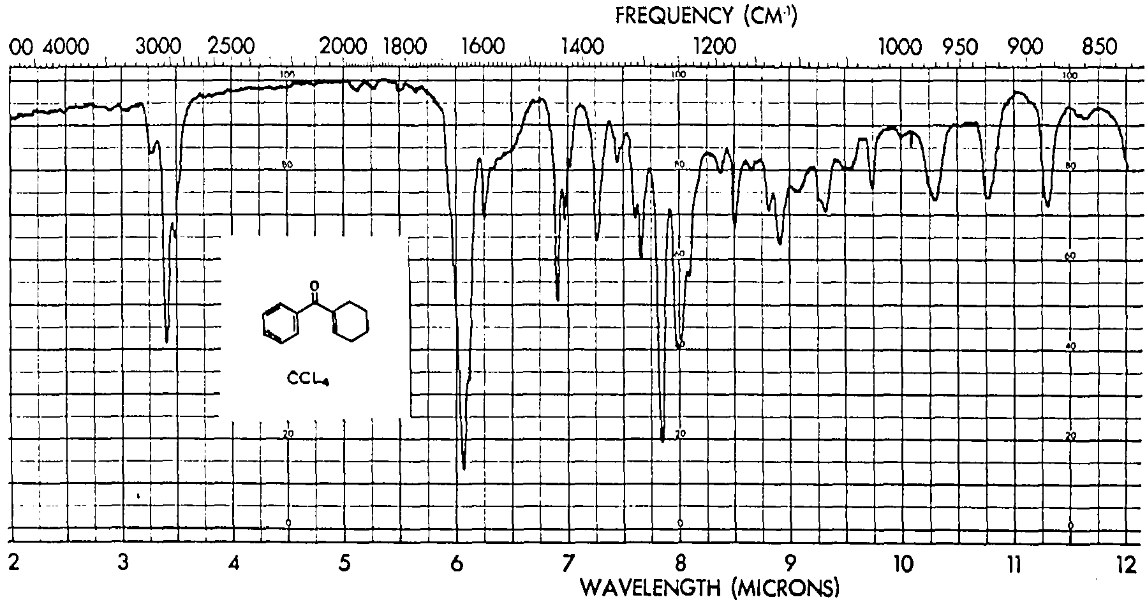
1800
1600
1400
1200
1000
950
900
850
100
80
60
40
20
0
O
CCL4
2
3
4
5
6
7
8
9
10
11
12
WAVELENGTH (MICRONS)


FREQUENCY (CM-1)
00 4000
3000
2500
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1800
1600
1400
1200
1000
950
900
850
100
80
60
40
20
0
O
CCL4
2
3
4
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6
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11
12
WAVELENGTH (MICRONS)

Figure 14. "Wheel" apparatus used for simultaneous irradiation of several samples under identical conditions.

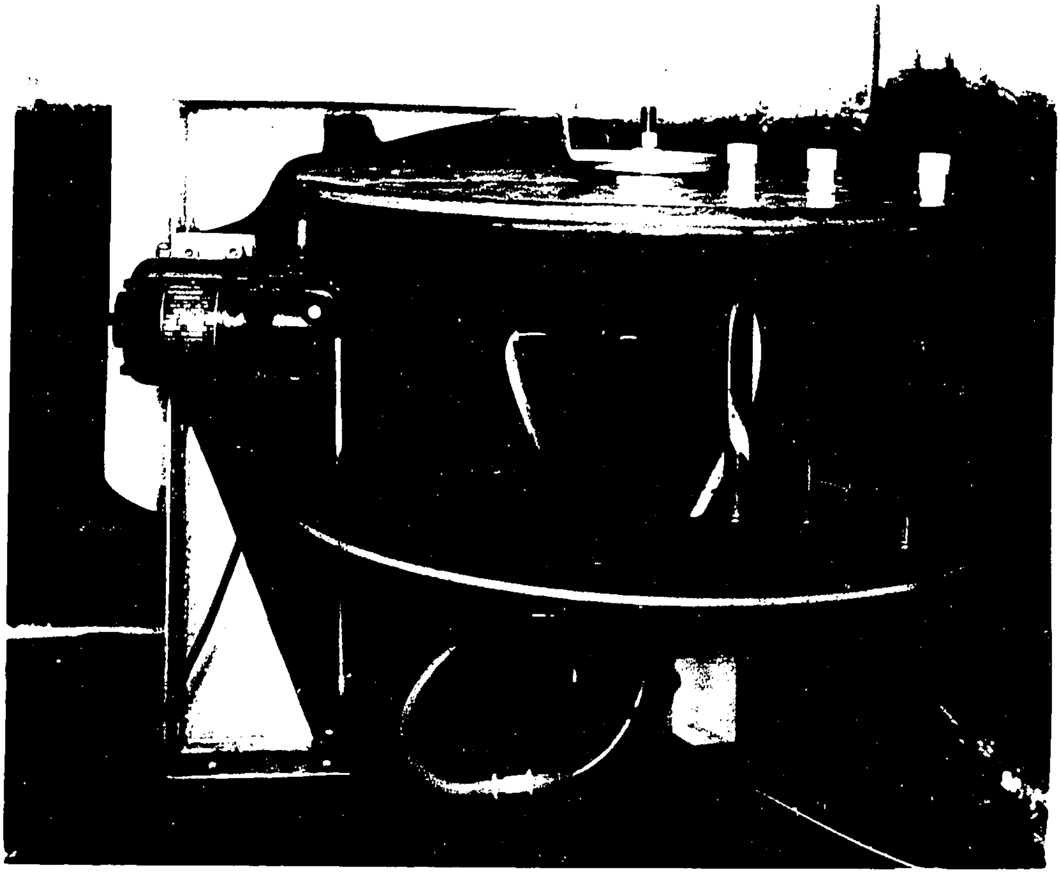
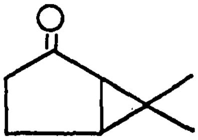


Figure 15 and for the infrared spectrum (CCl_4) see Figure 18.

Irradiation of XXI in tertiary butyl alcohol for 82 hours gives a crude product mixture which by v.p.c. analysis contains unreacted XXI (40%) and two new photoproducts in 26 and 34% yields, respectively.

4,4-Dimethyl-2-cyclohexenone (XXI) and both photoproducts were found to be stable under the v.p.c. conditions, precluding the possibility that the new products arise thermally from XXI or are thermally interconvertible.

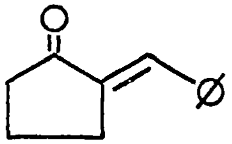
The product present in 26% yield was postulated (20) to be 6,6-dimethyl bicyclo [3.1.0.]-hexan-2-one (XXII). For the nuclear magnetic resonance spectrum of XXII see Figure 17



XXII

and for the infrared spectrum see Figure 18. The ultraviolet spectrum ($\lambda_{max}^{95\% \text{ ethanol}}$ 207 mμ, ε = 5,122) is in good agreement with that of LXI ($\lambda_{max}^{95\% \text{ ethanol}}$ 210 mμ, ε = 5,923). The n.m.r. spectrum of XXII shows no olefinic protons, suggesting that an additional ring must have been formed in order to account for the site of unsaturation in XXI. The methyl absorption of XXII in the n.m.r. spectrum appears at 1.09 and 1.11 δ, suggesting that the methyls are geminally substituted at a saturated carbon, with each methyl in a slightly different magnetic environment. The near infrared spectrum of XXII showed a 1.673 μ absorption which is characteristic of a cyclopropyl methine (C-H) absorption (51).

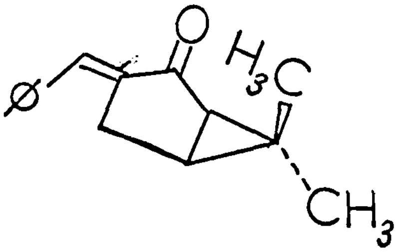
Confirmation of structure XXII is given by the isolation of only a mono-benzylidene derivative (LXXIII) after reaction of XXII with benzaldehyde. Since XXII gives only a mono-benzylidene, there is only one methylenic carbon atom α to the carbonyl group. The other α carbon atom must be tri-substituted. The u.v. spectrum of the mono-benzylidene ($\lambda_{max}^{95\%\ ethanol}$ 300.5 mμ, ϵ = 11,800 and 230.5 mμ, ϵ = 12,300) is in good agreement with that of LXVII ($\lambda_{max}^{95\%\ ethanol}$ 299.5 mμ, ϵ = 24,911 and 229 mμ, ϵ = 9,319). The u.v. spectrum of 2-benzylidene cyclopentanone (LXXXIV) shows $\lambda_{max}^{95\%\ ethanol}$ 298 mμ, ϵ = 20,000 and 227 mμ, ϵ = 8,500 (52).



LXXIV

The n.m.r. spectrum of the benzylidene derivative (LXXXIII) (Figure 17) shows methyl absorption at 0.985 and 1.13 δ, indicating greater differences in magnetic environment for the methyl groups in LXXIII than for the methyl groups in

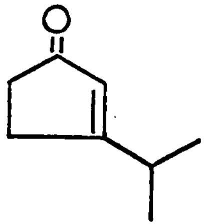
XXII. This data, coupled with the u.v. absorption of LXXIII and the fact that XXII must have at least one tertiary C-H moiety leave no other possibility than 3-benzylidene-6,6-dimethyl bicyclo [3.1.0.] hexan-2-one as the structure for LXXXIII. The difference in chemical shift of the gem-



LXXXIII

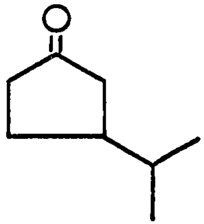
dimethyls in LXXXIII arises from the syn-anti relationship to the magnetic anisotropy of the conjugated carbonyl group. This anisotropy was first observed by Chapman et al. (53). Thus, structure XXII is firmly secured.

The photoproduct present in 34% yield was postulated to be 3-isopropyl-2-cyclopentenone (XXIII). The n.m.r. spectrum is shown in Figure 15 and the i.r. spectrum in Figure 18. The ultraviolet spectrum showed $\lambda_{\max}^{95\%\ \text{ethanol}}$ 227.5 mμ, ϵ = 12,730 and 303 mμ, ϵ = 50.82. Structure XXIII was proven by catalytic hydrogenation to 3-isopropylcyclopentanone (LXXXV). 3-isopropyl cyclopentanone was then synthesized



XXIII

from cyclopentadiene (see Experimental Section) by the path shown in Figure 21. The infrared spectrum (CCl_4) of this material was identical to that reported by Smith and Gonzalez (54). The hydrogenation product of XXIII showed nuclear magnetic resonance (see Figure 22) and infrared (see Figure 20) spectra which were identical to that of the idependently synthesized LXXXV. Thus, structure XXIII is firmly supported



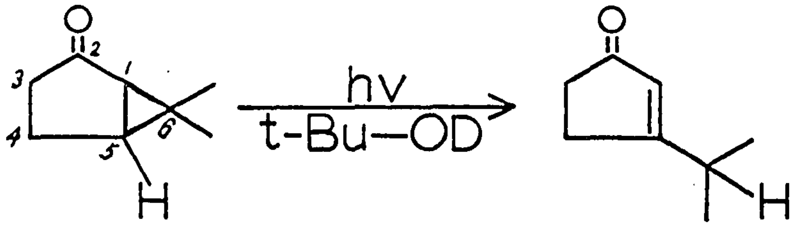
LXXXV

as 3-isopropyl-2-cyclopentenone.

The independent synthesis of LXXXV also yielded 2-isopropyl cyclopentanone (LXXXVI). The infrared spectrum (CCl_4) showed a 5.75 μ carbonyl absorption. The n.m.r. spectrum of LXXXVI is shown in Figure 22. This spectrum shows the methyl groups of the isopropyl moiety to be non-equivalent, giving rise to two doublets (J = 6.6 cps), the methyl groups appearing at 0.825 and 0.995 δ. The spectrum is included for the sake of pedantic comparison with that of LXXXVI.

In another experiment, the crude photoproduct mixtures from several irradiations were combined. This material was steam distilled to yield the volatile low molecular weight materials. The steam volatile fraction was then carefully distilled through a one meter spinning band column to give XXII in 7.6% yield and XXIII in 9% yield. The isolated yield of XXIII was low due to extensive polymerization of the heat-sensitive XXIII in the distillation pot. The isolated yield of XXII was low due to the difficulty of the distillation separation from XXI. XXIII was isolated in low yield due to extensive polymerization in the distillation pot as the distillation proceeded.

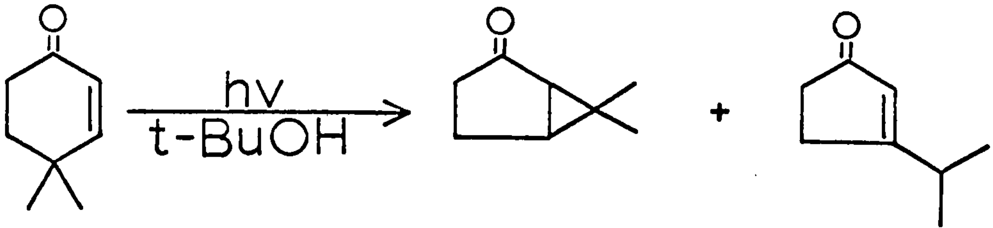
During the course of this study, it became of interest to know if XXII and XXIII were photochemically interconvertible. In order to glean the most information from the experiment, XXII was irradiated in deuterio-tertiary butyl alcohol. The reaction was followed by vapor phase chromatography. XXIII was found to result from the irradiation of XXII. The XXIII was isolated from the crude irradiation mixture. The n.m.r. spectrum was identical to that of Figure 15, the methyl groups appearing as a doublet (J = 6.6 cps). Thus, upon conversion of XXII to XXIII, deuterium from solvent is not incorporated, and the rearrangement may be represented by an intramolecular shift of the C-5 hydrogen of XXII to the isopropyl group of XXIII. This rearrangement is analogous



XXII XXIII

to the conversion of methyl cyclopropyl ketone to 3-penten-2-one (55). Under the same conditions, XXIII yielded no XXII or any other volatile product. The v.p.c. showed loss of XXIII and no other product buildup. This is apparently due to dimerization, a facile photochemical reaction of cyclopentenones (13). It will be shown in a later portion of this section that XXIII does not arise solely from XXII, but is in fact a primary photoproduct of XXI.

The quantum yield for the production of XXII and XXIII from XXI in tertiary butyl alcohol at 26°C was measured (see Experimental section). The quantum yield for the production of XXIII was found to be 0.65×10^{-3}. The quantum yield for the production of XXIII was 1.06×10^{-2}.



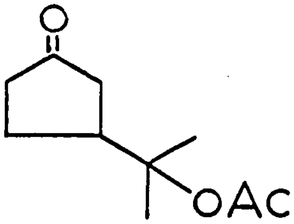
XXI XXII XXIII

$\Phi = 0.65\text{x}10^{-3}$ $\Phi = 1.06\text{x}10^{-2}$

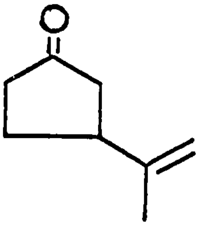
The product analysis in this measurement was done after approximately 6% conversion of XXI in order to ensure total light absorption by XXI. The quantum yield was measured at 313 mμ.

This quantum yield indicates that approximately two percent of excited XXI molecules are converted to rearranged product, whereas ninety-eight percent of the excited state molecules are deactivated by a chemically fruitless path to the ground state of XXI. This is in contrast to the rather high quantum yields for cross-conjugated dienone rearrangements. Fisch and Richards (34) report a quantum yield of one for the santonin to lumi-santonin conversion (see Historical). Similarly, Zimmerman (35) reports a quantum yield of 0.12 for the rearrangement of XXXVII to XXXVIII. The possible reasons for the low quantum yield of XXI will be discussed later.

Irradiation of XXI in glacial acetic acid for 24 hours yields a crude irradiation mixture showing the following v.p.c. analysis (XXI, 43%; XXII, 3%; XXIII, 9%; XXIV, 30% and XXV, 15%). XXIV and XXV were postulated (20) to have the following structures.



XXIV



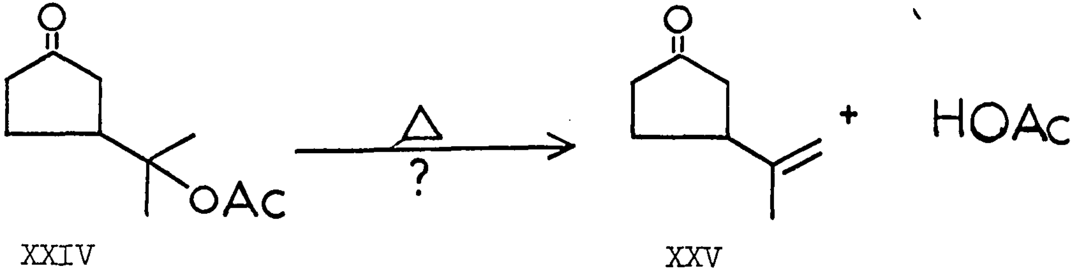
XXV

For the nuclear magnetic resonance spectrum of XXIV see Figure 16, and for the infrared spectrum (CCl_4) see Figure 19. The structure XXIV stands on the basis of spectral data and elemental analysis. Further structure proof was not attempted by this author. The structure, 3-(2-acetoxy propyl) cyclopentanone rests on the basis of the evidence reported by Chapman <u>et</u> <u>al</u>. (20).

The nuclear magnetic resonance spectrum of XXV shows a slightly split three proton resonance at 1.93 δ (allylic methyl), a complex four proton methylene absorption at 2.15 δ, a single methine at 2.65 δ and two olefinic protons as a slightly split signal at 4.76 δ. The infrared spectrum (Figure 19) shows 5.73 μ carbonyl absorption and terminal methylene absorption at 11.19 μ. The structure of XXV was proven by hydrogenation to 3-isopropylcyclopentanone. This product showed identical infrared and nuclear magnetic resonance spectra to the 3-isopropyl cyclopentanone (LXXXV) which was synthesized from cyclopentadiene.

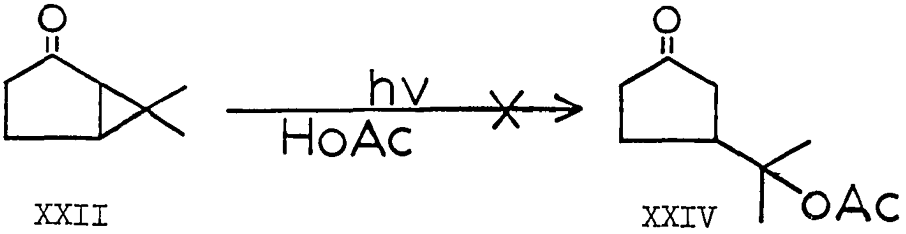
A summary of the structure proof for XXII, XXIII and XXV is shown in Figure 21.

During the course of this investigation, the question arose whether XXV arose from XXIV by a thermal reaction in

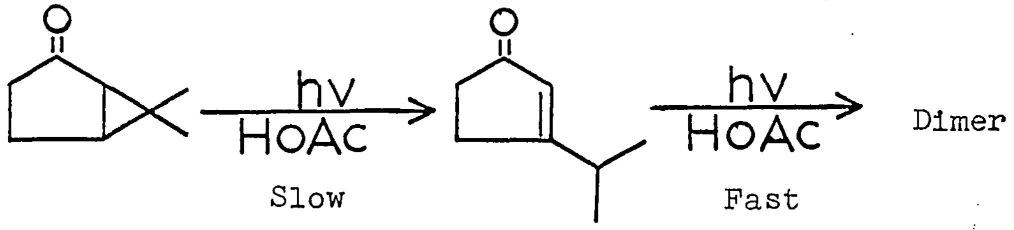


the gas chromatograph. Injection of XXIV showed no XXV in the gas chromatograph recording chart and isolation of the material corresponding to the XXIV peak followed by i.r. analysis showed only XXIV to be present. Thus, XXV is a genuine photoproduct from the irradiation of XXI.

The question also arose whether XXIV arose from XXII during the acetic acid irradiation of XXI. XXII was



irradiated in acetic acid. The course of the reaction was followed by gas chromatography. No XXIV was observed upon destruction of XXII. In fact, as XXII was destroyed, only a small amount of XXIII was formed, which then apparently dimerized nearly as fast as it was formed. These results are in agreement with the irradiation of XXII in tertiary butyl alcohol.



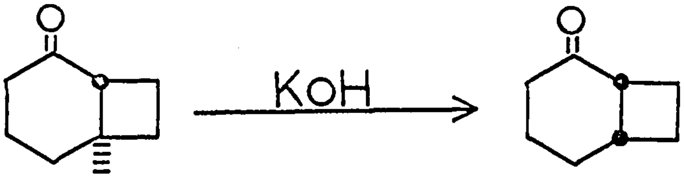
XXII XXIII

Thus XXII gives rise to XXIII but not to XXIV upon irradiation in acetic acid. A simultaneous companion irradiation of XXI in acetic acid under identical conditions showed the production of XXII, XXIII, XXIV and XXV. The rapid dimerization of XXIII in acetic acid undoubtedly accounts for its low yield (9%) in the product mixture.

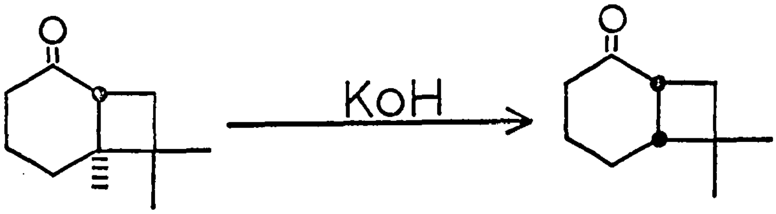
The Cycloaddition of 4,4-Dimethyl-2-Cyclohexenone with 1,1-Diphenylethylene and Piperylene

Irradiation of a tertiary butyl alcohol solution of 4,4-dimethyl-2-cyclohexenone (XXI, 0.012 M) and 1,1-diphenylethylene (LXXXVII, 0.055 M) for seven hours gave a 75% isolated yield of a 1:1 adduct (LXXXVIII, m.p. 164.5-165.5°).

The nuclear magnetic resonance spectrum is shown in Figure 17. The gem-dimethyl groups appear as three proton singlets at 0.31 and 1.24 δ respectively. The infrared spectrum (Figure 20) of LXXXVIII shows a 5.81 μ carbonyl absorption. Treatment of LXXXVIII with dilute methanolic potassium hydroxide yielded a new compound, LXXXIX (m.p. 115-116°). The nuclear magnetic resonance spectrum of LXXXIX (Figure 23) shows methyl absorption at 1.03 and 1.11 δ which is superimposed on a two proton absorption. The infrared spectrum (Figure 20) shows a 5.88 μ carbonyl absorption. The change in carbonyl absorption upon epimerization conditions suggest that LXXXVIII was trans-fused and that LXXXIX was cis-fused.



This result is analogous to Corey's (39) observations in the epimerization of XLVIII to XLIX.



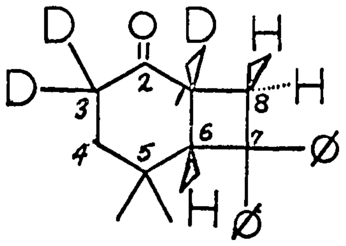
5.81 μ

XLVIII

5.87 μ

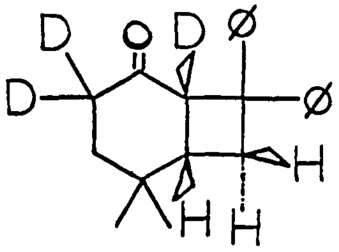
XLIX

The question remained whether LXXXVIII and LXXXIX are 7- or 8-diphenyl substituted. Deuteration of LXXXVIII with deuterio-methanol-deuterium oxide-sodium hydroxide gave a tridueterio compound XC which showed a 5.88 μ carbonyl absorption, indicating that the exchange conditions have also caused epimerization. The nuclear magnetic resonance spectrum (Figure 23) of XC showed methyl absorption at 1.01 and 1.12 δ in agreement with epimerization to the <u>cis</u>-fuxed isomer. In addition, a two proton absorption lies under the methyl absorption. The balance of the alkyl absorption is an AB pattern (JAB = 12.6 cps) at 2.50 and 3.29 δ and a singlet at 3.47 δ. The singlet and AB portion support XC as being the 7,7-disubstituted isomer.



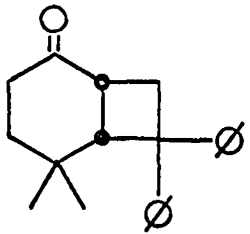
XC

The AB portion arises from the methylene protons at C-8 and is probably due to the <u>syn</u>-<u>anti</u>-relationship of these protons relative to the carbonyl group. The singlet at 3.47 δ is due to the C-6 proton. If the product were the 8,8-disubstituted isomer XCI the proton at C-6 would not be a singlet and the protons at C_7 would not be an AB because



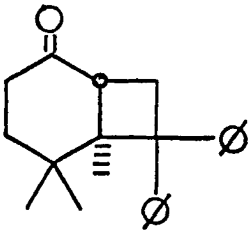
XCI

of the vicinal coupling. The cis-stereochemistry of XC is assigned on the basis of infrared absorption and epimerization. Thus, the structure of LXXXIX is



LXXXIX

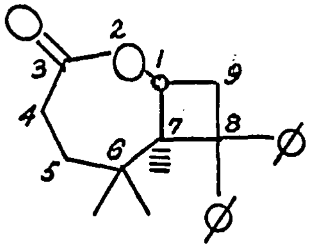
and therefore the structure of LXXXVIII is



LXXXVIII

Further proof that LXXXVIII (trans-5,5-dimethyl-7,7-diphenyl bicyclo [4.2.0.] octan-2-one) is 7,7 disubstituted was obtained by the Baeyer-Villiger oxidation of LXXXVIII.

The lactone, trans-6,6-dimethyl-8,8-diphenyl-2-oxabicyclo [5.2.0.] nonan-3-one (XCII, m.p. 225-227°) showed a 5.71 μ carbonyl absorption. The nuclear magnetic resonance spectrum of XCII showed the methyl groups as three proton singlets at 0.124 and 1.15 δ, a two proton multiplet at 1.57 δ, a five proton absorption spread from 2.3 to 3.6 δ, the C_1 proton as a four line multiplet (4.79, 4.94, 5.09, 5.23 δ) and ten aromatic protons at 7.28 δ. If in fact the lactone were derived from the 9,9-diphenyl-disubstituted isomer, the C_1 proton would be a doublet due to vicinal coupling with the C_7 proton. Since the C_1 proton is a four line absorption due to coupling with the C_7 and C_9 protons, unequivocal proof is offered that LXXXVIII is in fact the 8,8-diphenyl-disubstituted isomer.



XCII

The n.m.r. spectra of LXXXVIII (Figure 17), LXXXIX (Figure 23), XC (Figure 23) and XCII offer a subtle yet definite support to the assignment of the ring fusion stereochemistry in each of the above molecules. Examination of a Dreiding model of LXXXVIII shows that regardless of molecular conformation one of the methyl groups must lie in the magnetic shielding region of a phenyl group (56) when the molecule is trans-fused. This is in accord with the unusually high methyl at 0.31 δ in LXXXVIII and 0.12 δ in XCII. The retention of configuration at C_1 during the Baeyer-Villiger oxidation of LXXXVIII to XCII is in accord with Berson's (57) observation of retention of configuration during Baeyer-Villiger oxidation. Further, examination of the Dreiding model of the cis-fused isomer shows that no gross non-equivalence of the methyls is to be expected. In fact, the methyls are nearly equivalent in LXXXIX and XC (Figure 23). The Dreiding model of LXXXIX shows that the protons at C_4 are shielded slightly by the phenyl groups at C_7, thus accounting for the two proton absorption in LXXXIX and XC which is shifted upfield under the methyl absorption. Although the n.m.r. inference of stereochemistry of the ring fusion was post facto, it is valuable and interesting because of the validity of its predictions.

The effect of oxygen on the cycloaddition of XXI and LXXXVII was studied by continuously bubbling oxygen through the irradiation solution (XXI, 0.05 M; LXXXVII, 0.10 M). The nuclear magnetic resonance spectrum of the crude product showed only XXI, LXXXVII and the trans-adduct LXXXVIII. The solution yellowed considerably during the irradiation, but the reaction to yield LXXXVIII was not quenched by the oxygen.

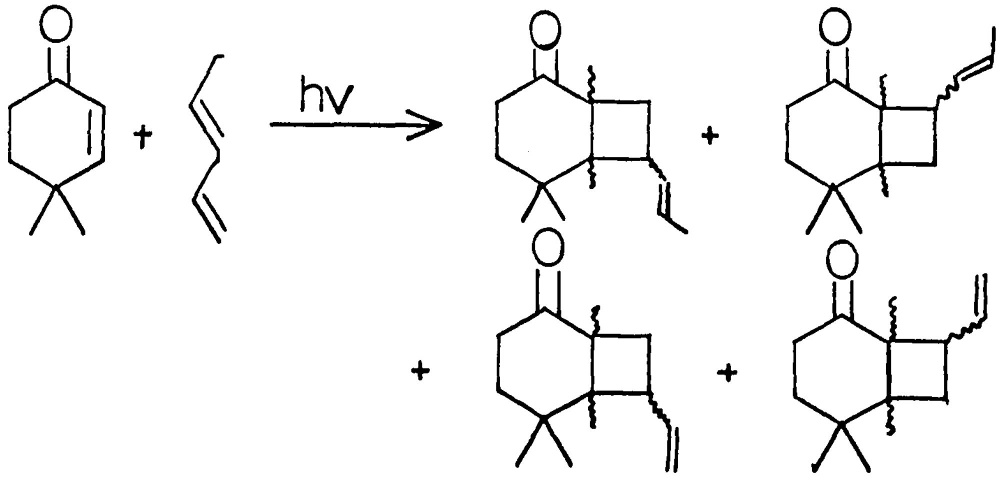
The effect of solvent upon cycloaddition of XXI to LXXXVII was studied. Irradiation in either benzene or acetic acid (see Experimental) gave a crude reaction mixture which by n.m.r. analysis (Figure 25) contained only XXI, LXXXVII and the *trans*-adduct LXXXVIII. Interpretation of these crude spectra is with the following absorptions: LXXXVII - 5.40 and 7.2 δ, XXI - methyls at 1.15 δ and the typical methyl absorptions of LXXXVIII and LXXXIX. Slight changes in chemical shift in Figure 25 apparently are due to the large amount of diphenylethylene present. Thus, the range of solvents acetic acid-tertiary butyl alcohol-benzene seems to have no effect upon the course of cycloaddition.

The possibility of quenching the cycloaddition with piperylene was studied. A tertiary butyl alcohol solution (XXI, 0.05 M; LXXXVII, 0.10 M and piperylene 0.05 M) was irradiated. The nuclear magnetic resonance spectrum (Figure 25) of the crude product mixture showed XXI, LXXVII and the *trans*-adduct LXXXVIII, indicating that the cycloaddition between XXI and LXXXVII cannot be completely quenched by piperylene.

Additional mechanistic details of the cycloaddition of XXI to LXXXVII will be discussed in the next section. The synthetic features of the cycloaddition have been given here in order to separate fact from hypothesis. The most striking feature of the addition of 4,4-dimethyl-2-cyclohexenone (XXI) to 1,1-diphenylethylene LXXXVII is the fact that a single product is obtained, which is in contrast to the complex mixtures obtained by Corey (39) in the cycloaddition of 2-cyclohexenone to various alleyl-substituted olefins.

The possibility of cycloaddition of XXI to a diene was also investigated. Irradiation of a tertiary butyl alcohol solution of XXI (0.2 M) and trans-piperylene (XCII, 1.8 M) gave a 91% yield of a 1:1 adduct. XXI was completely destroyed at the end of the ten hour irradiation. The infrared spectrum of the crude adduct mixture is shown in Figure 26. Analysis of the crude material by v.p.c. showed 2 compounds to be present in the ratio of 1:20. The major product was isolated by preparative scale vapor phase chromatography. The infrared spectrum of the major product is shown in Figure 26 and is quite similar to that of the crude material (Figure 26), exhibiting a 5.86 μ carbonyl absorption. The n.m.r. spectrum of the major product is shown in Figure 26. The integral of 1:10 for the olefinic to aliphatic region and the complexity of the methyl region (0.8-1.3 δ) indicates that the "major product" is actually a mixture of isomers. The mass spectrum of this material showed a parent peak at m/3 192, clearly indicating a 1:1

adduct. The isomer mixture would surely result from attack at either double bond, yielding a complex mixture of molecules which are structurally very similar. The possibilities for cycloaddition (ignoring stereochemistry) are shown below.

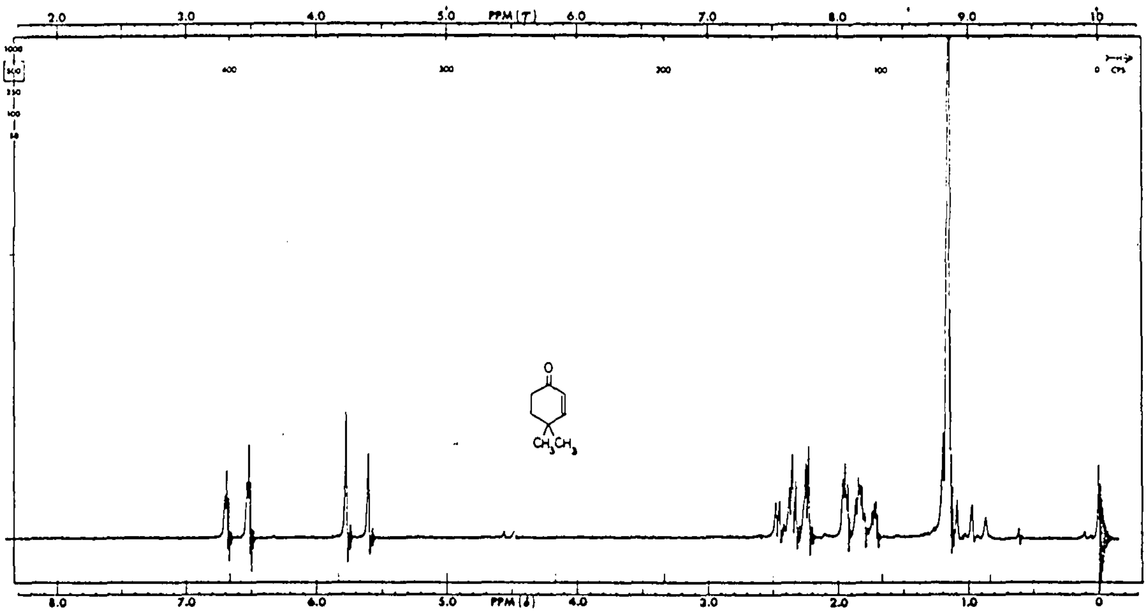


The number of isomers possible is frightening. The significance of this experiment lies in the fact that α, β-unsaturated ketones are reported not to add to dienes (58). To the contrary, these results show that a 1:1 adduct mixture may be isolated in 91% yield.

Figure 15. Nuclear magnetic resonance spectra (CCl_4).

Top - 4,4-Dimethyl-2-cyclohexenone (XXI)

Bottom - 3-Isopropylcyclopentenone (XXIII)


2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
CPS
O
CH3 CH3
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0

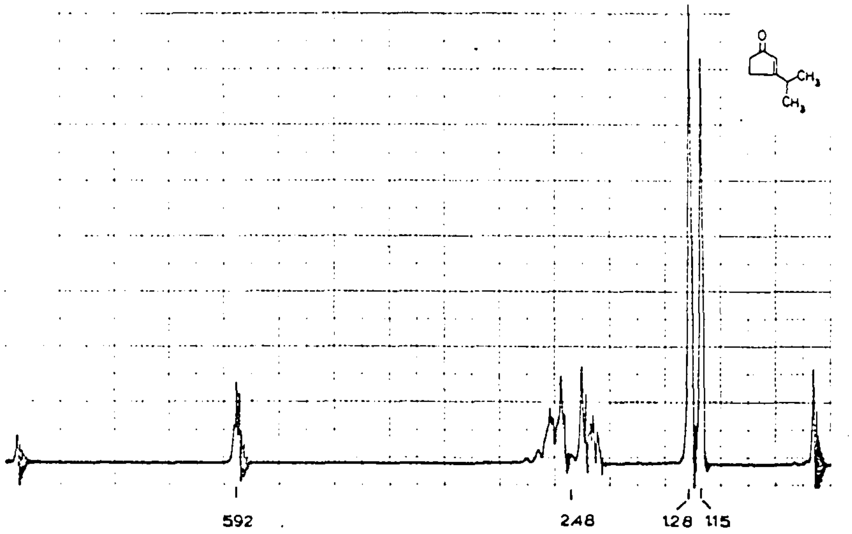
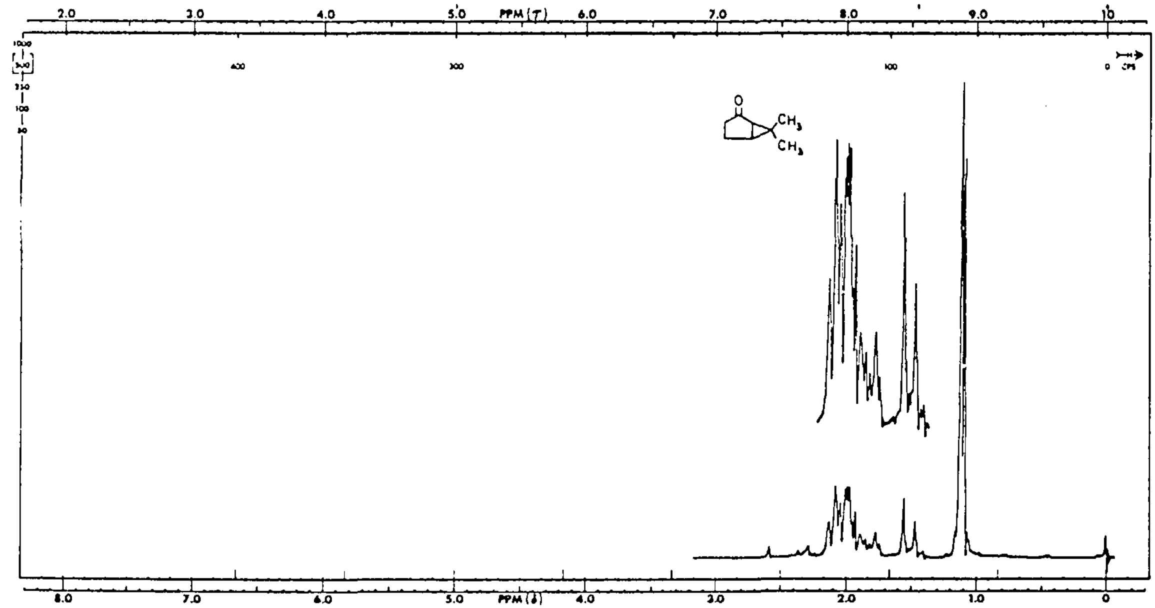

O
CH3
CH3
5.92
2.48
1.28
1.15
P.P.M.

Figure 16. Nuclear magnetic resonance spectra (CCl_4).

Top - 6,6-Dimethylbicyclo [3.1.0.] hexan-2-one (XXII)

Bottom - 3-(2-acetoxypropyl)-cyclopentanone (XXIV)


2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
400
300
100
0 CPS
O
CH₃
CH₃
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0

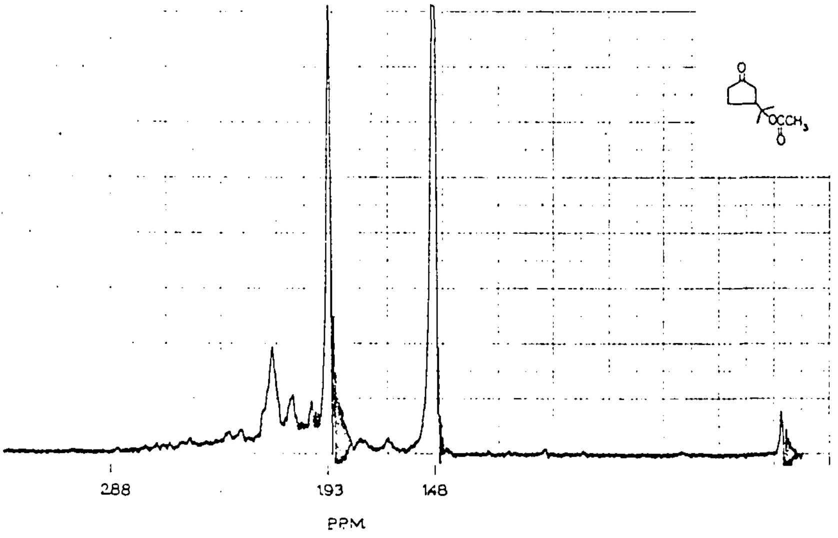
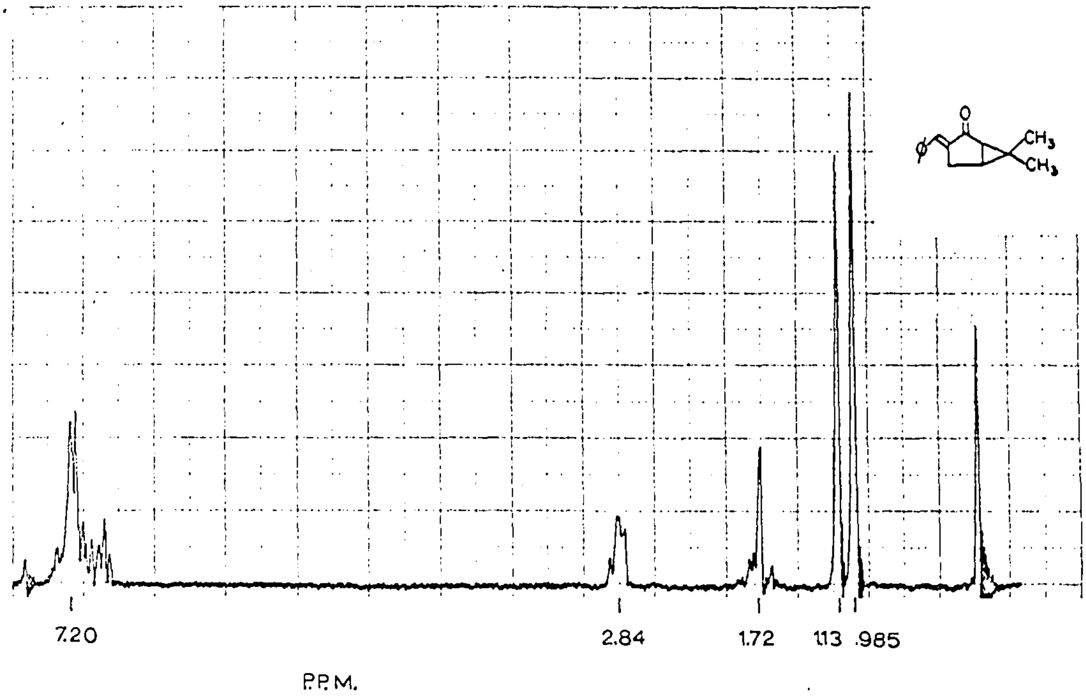

O
OCCH₃
O
288
193
148
PPM

Figure 17. Nuclear magnetic resonance spectra (CCl_4).

Top - 3-Benzylidene-6,6-dimethylbicyclo [3.1.0.]hexan-2-one (LXXXIII)

Bottom - trans-5,5-dimethyl-7,7-diphenyl bicyclo [4.2.0.] octan-2-one (LXXXVIII)


O
ø
CH₃
CH₃
7.20
2.84
1.72
1.13
.985
P.P.M.

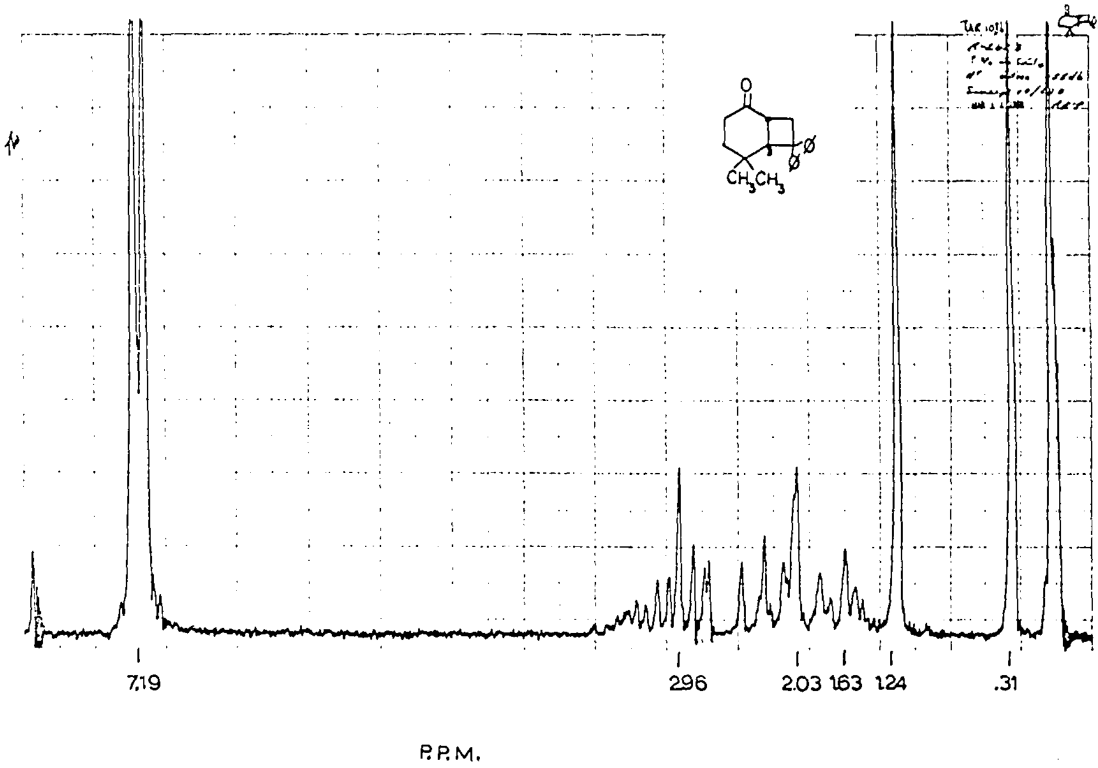
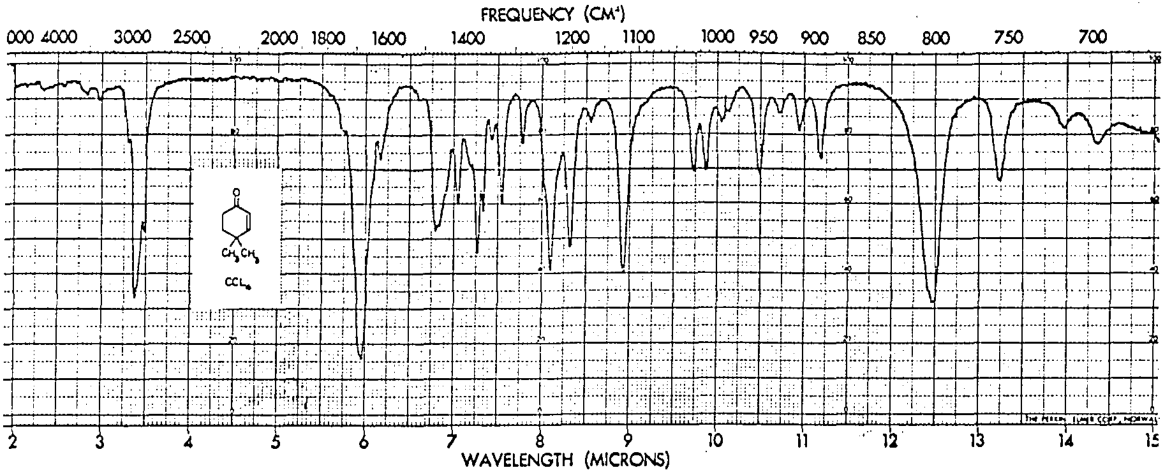

O
ø
ø
CH₃CH₃
7.19
2.96
2.03
1.63
1.24
.31
P.P.M.

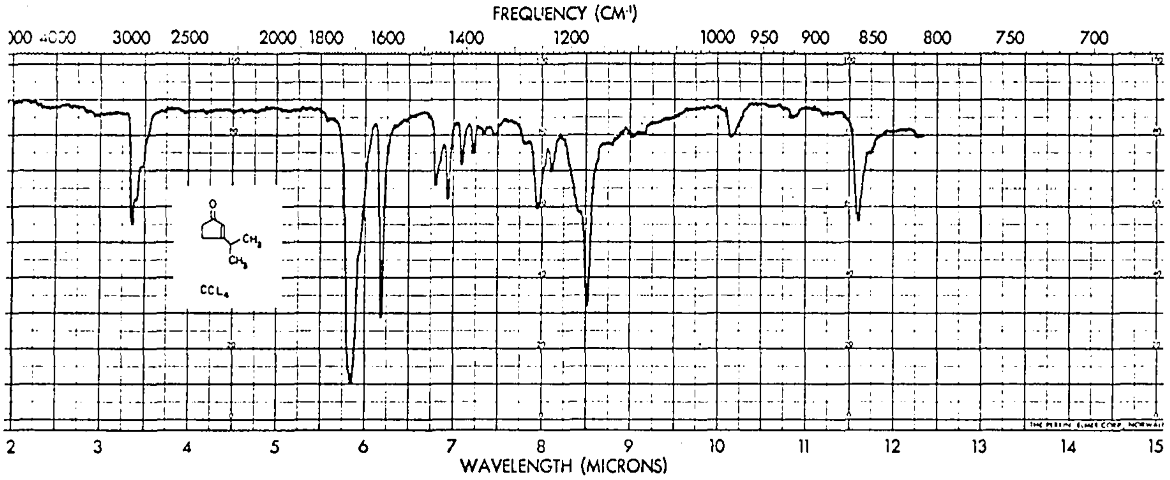
Figure 18. Infrared spectra (CCl_4).

Top - 4,4-Dimethyl-2-cyclohexenone (XXI)

Middle - 3-isopropylcyclopentenone (XXIII)

Bottom - 6,6-dimethylbicyclo [3.1.0.] hexan-2-one (XXII)


FREQUENCY (CM⁻¹)
000 4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700
CH₃ CH₃
CCl₄
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)


FREQUENCY (CM⁻¹)
000 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700
CH₃
CH₃
CCl₄
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

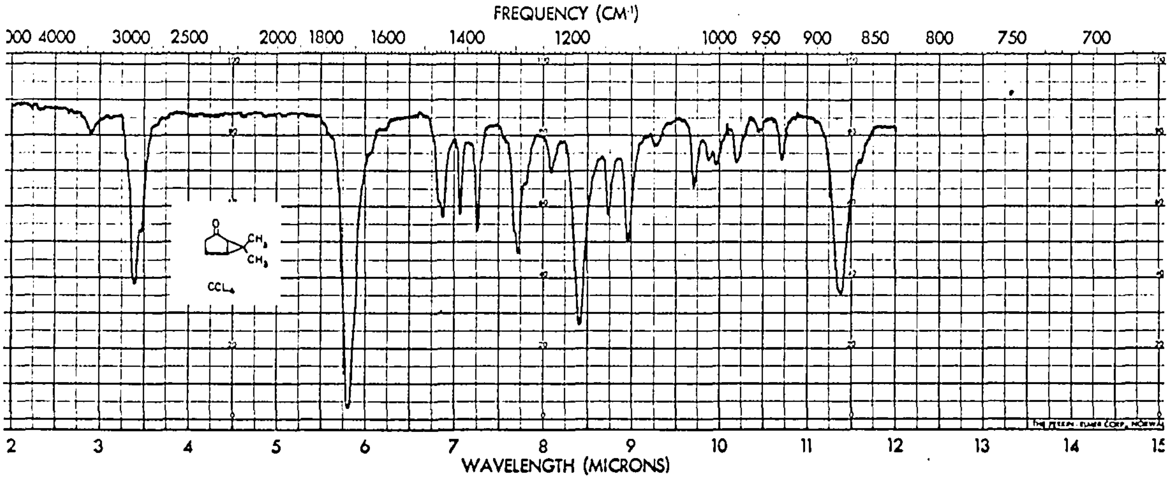
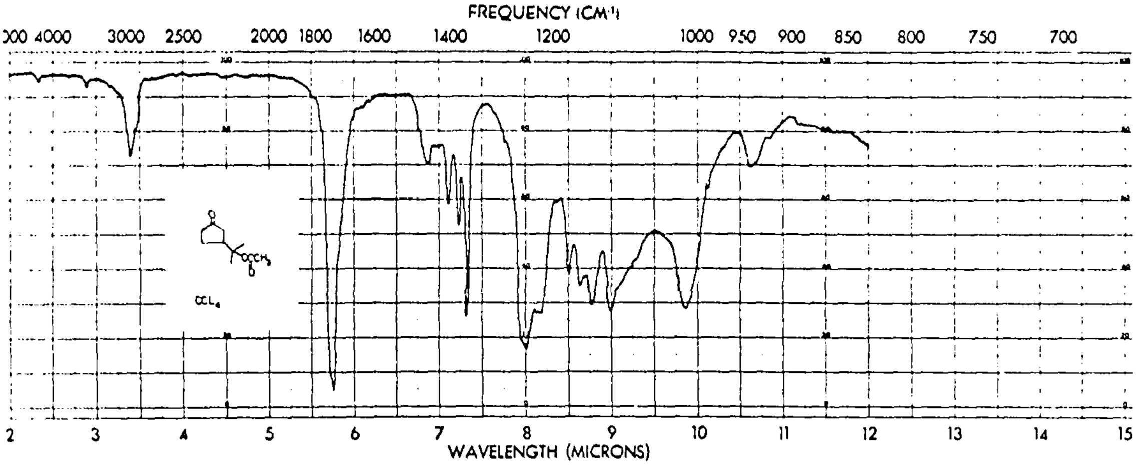

FREQUENCY (CM⁻¹)
000 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700
CH₃
CH₃
CCl₄
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

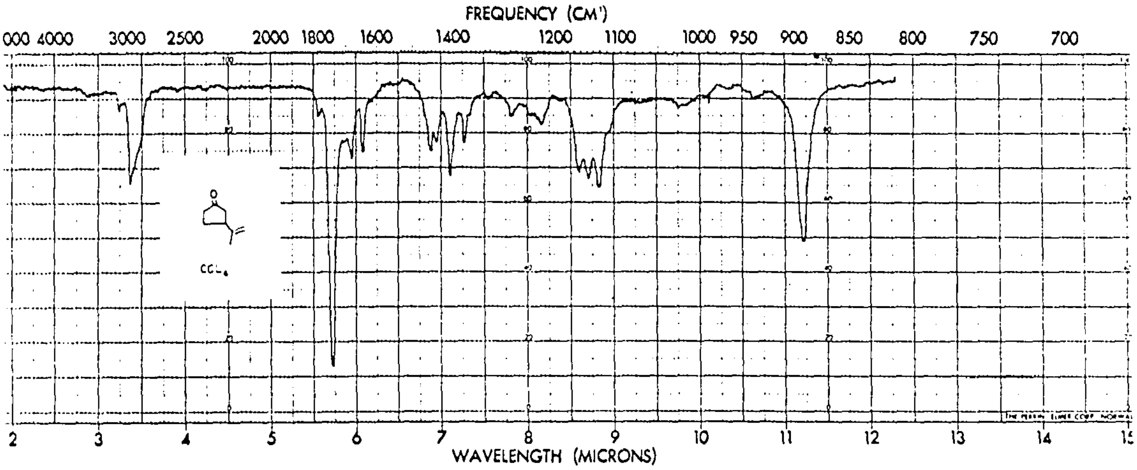
Figure 19. Infrared spectra (CCl_4).

Top - 3-(2-acetoxypropyl) cyclopentanone (XXIV)

Middle - 3-isopropenylcyclopentanone (XXV)

Bottom - 3-benzylidene-6,6-dimethylbicyclo [3.1.0.] hexan-2-one (LXXXIII) (KBr Pellet)


FREQUENCY (CM⁻¹)
4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700
OCCH₃
O
CCL₄
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)


FREQUENCY (CM')
4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700
CCL₄
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

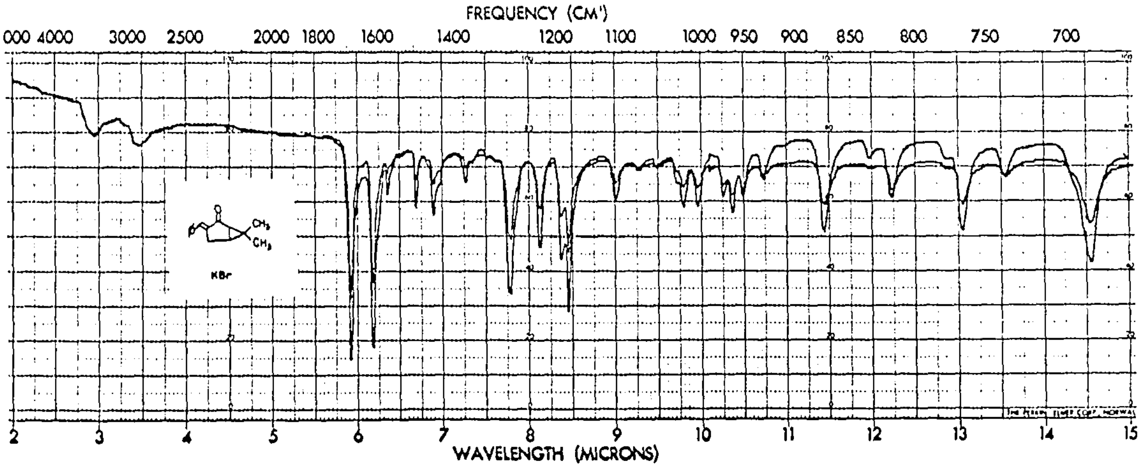
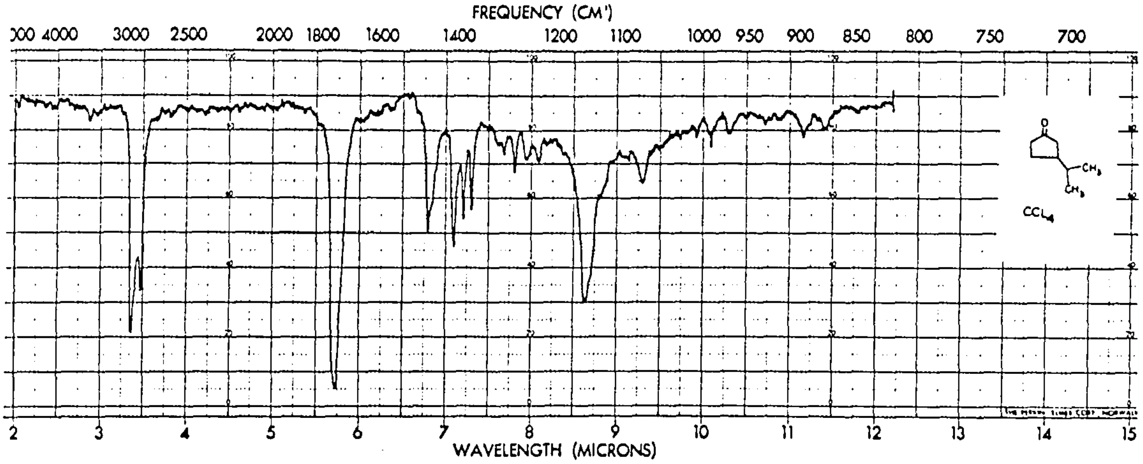

FREQUENCY (CM')
4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700
CH₃
CH₃
KBr
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

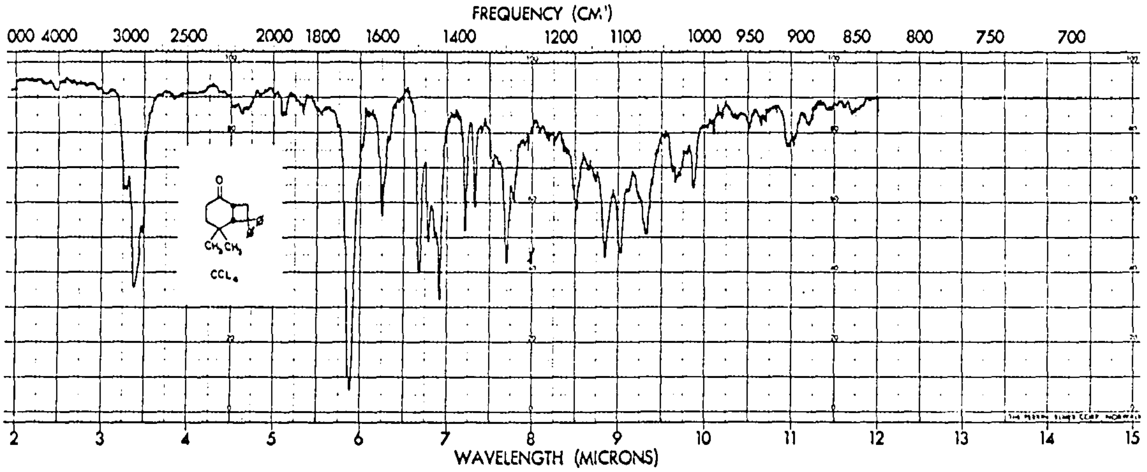
Figure 20. Infrared spectra (CCl_4).

Top - 3-isopropylcyclpentanone (LXXXV)

Middle - *cis*-5,5-dimethyl-7,7-diphenylbicyclo [4.2.0.] octan-2-one (LXXXIX)

Bottom - *trans*-5,5-dimethyl-7,7-diphenylbicyclo [4.2.0.] octan-2-one (LXXXVIII)


FREQUENCY (CM⁻¹)
000 4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700
CH₃
CH₃
CCl₄
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)


FREQUENCY (CM⁻¹)
000 4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700
CH₃ CH₃
CCl₄
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

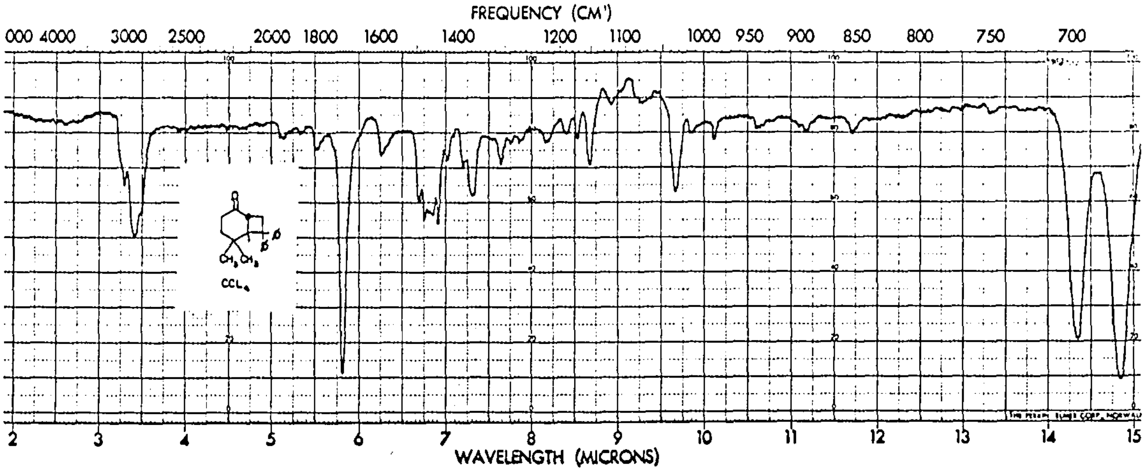

FREQUENCY (CM⁻¹)
000 4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700
CH₃ CH₃
CCl₄
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

Figure 21. Summary of structure proofs for XXII, XXIII and XXV.

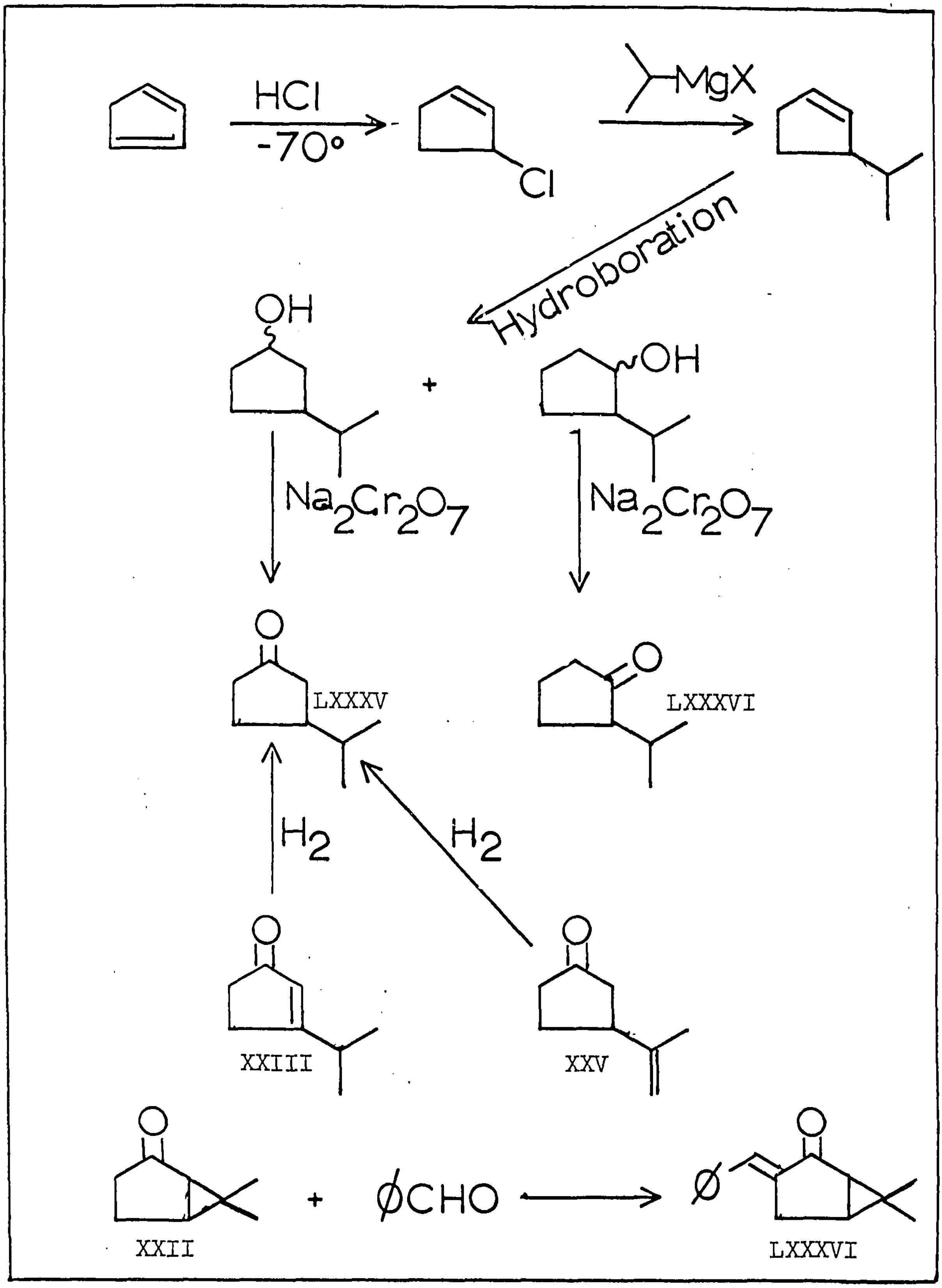
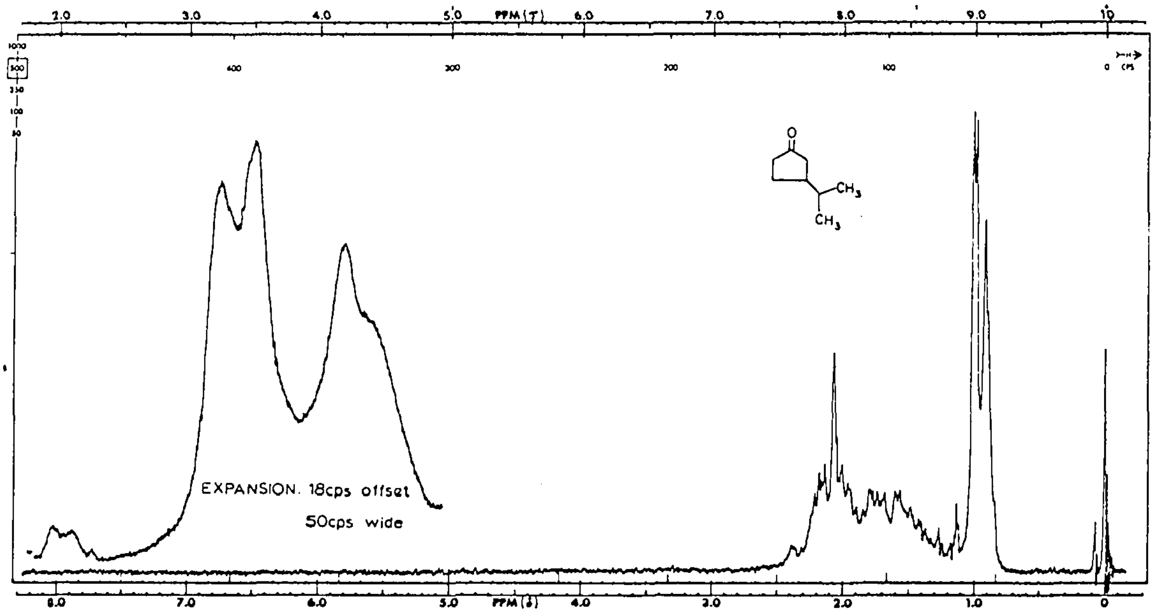

HCl
-70°
Cl
MgX
Hydroboration
OH
+
OH
Na$_2$Cr$_2$O$_7$
Na$_2$Cr$_2$O$_7$
LXXXV
LXXXVI
H$_2$
H$_2$
XXIII
XXV
XXII
+
ØCHO
Ø
LXXXVI

Figure 22. Nuclear magnetic resonance spectra (CCl_4).

Top - 3-isopropylcyclpentanone (LXXXV)

Bottom - 2-isopropylcyclopentanone (LXXXVI)


2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
1000
500
250
100
50
400
300
200
100
0 CPS
O
CH3
CH3
EXPANSION. 18cps offset
50cps wide
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0

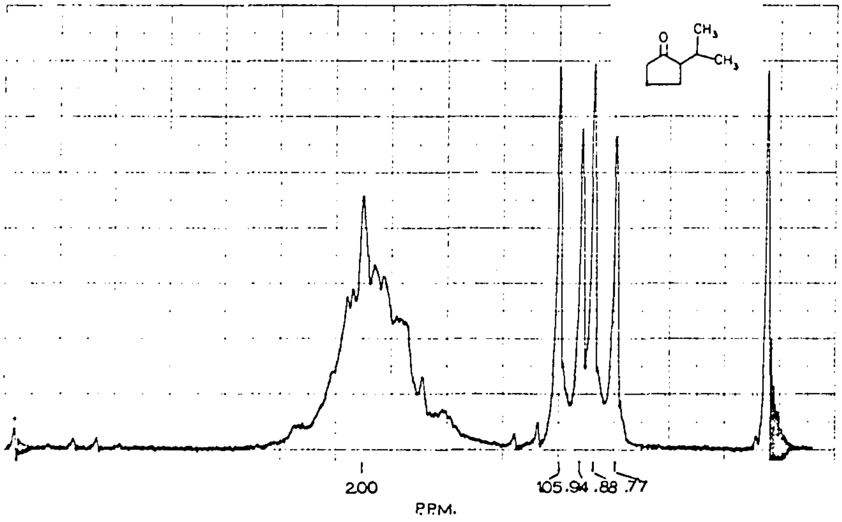
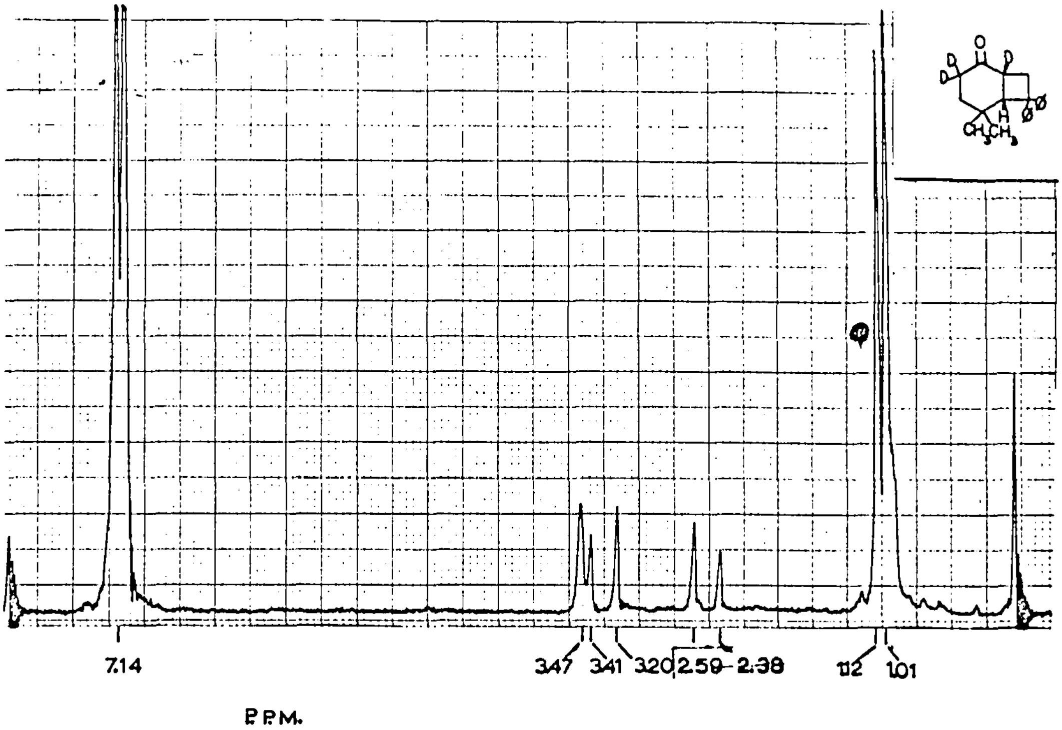

O
CH3
CH3
2.00
105.94 .88 .77
P.P.M.

Figure 23. Nuclear magnetic resonance spectra (CCl_4).

Top - *cis*-1,3,3-tridueterio-5,5-dimethyl-7,7-diphenylbicyclo [4.2.0.] octan-2-one (XC)

Bottom - *cis*-5,5-dimethyl-7,7-diphenylbicyclo [4.2.0.] octan-2-one (LXXXIX)


O
D
D
D
D
H
Ø
CH3CH3
Ø
7.14
3.47
3.41
3.20
2.59
2.38
1.12
1.01
P.P.M.

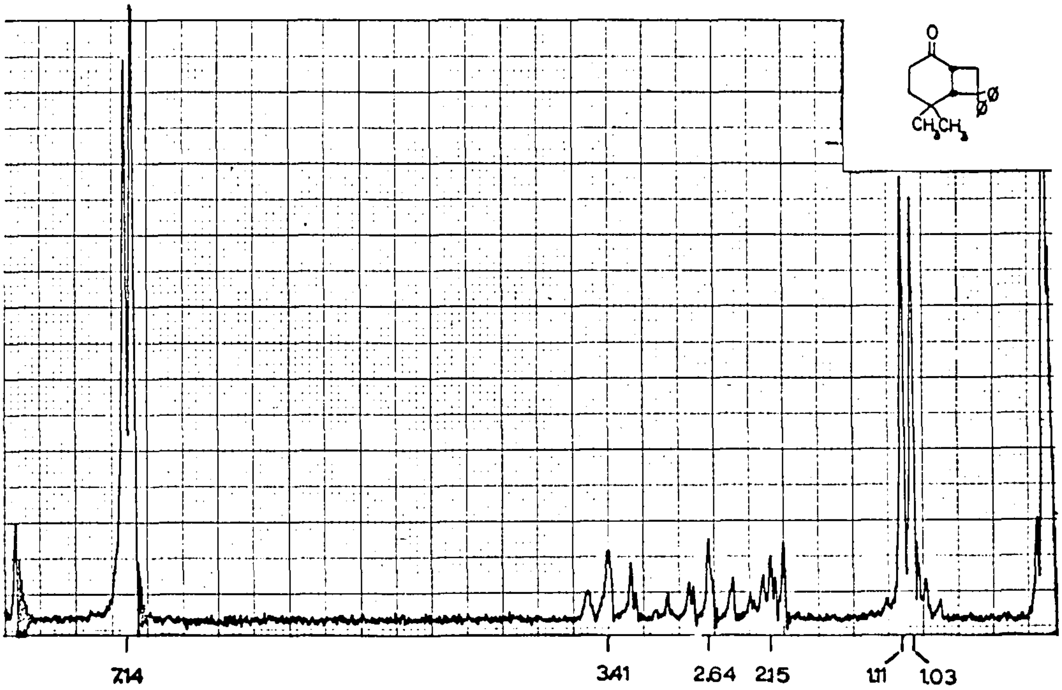

O
Ø
CH3CH3
7.14
3.41
2.64
2.15
1.11
1.03

Figure 24. Linear quantum yield apparatus.

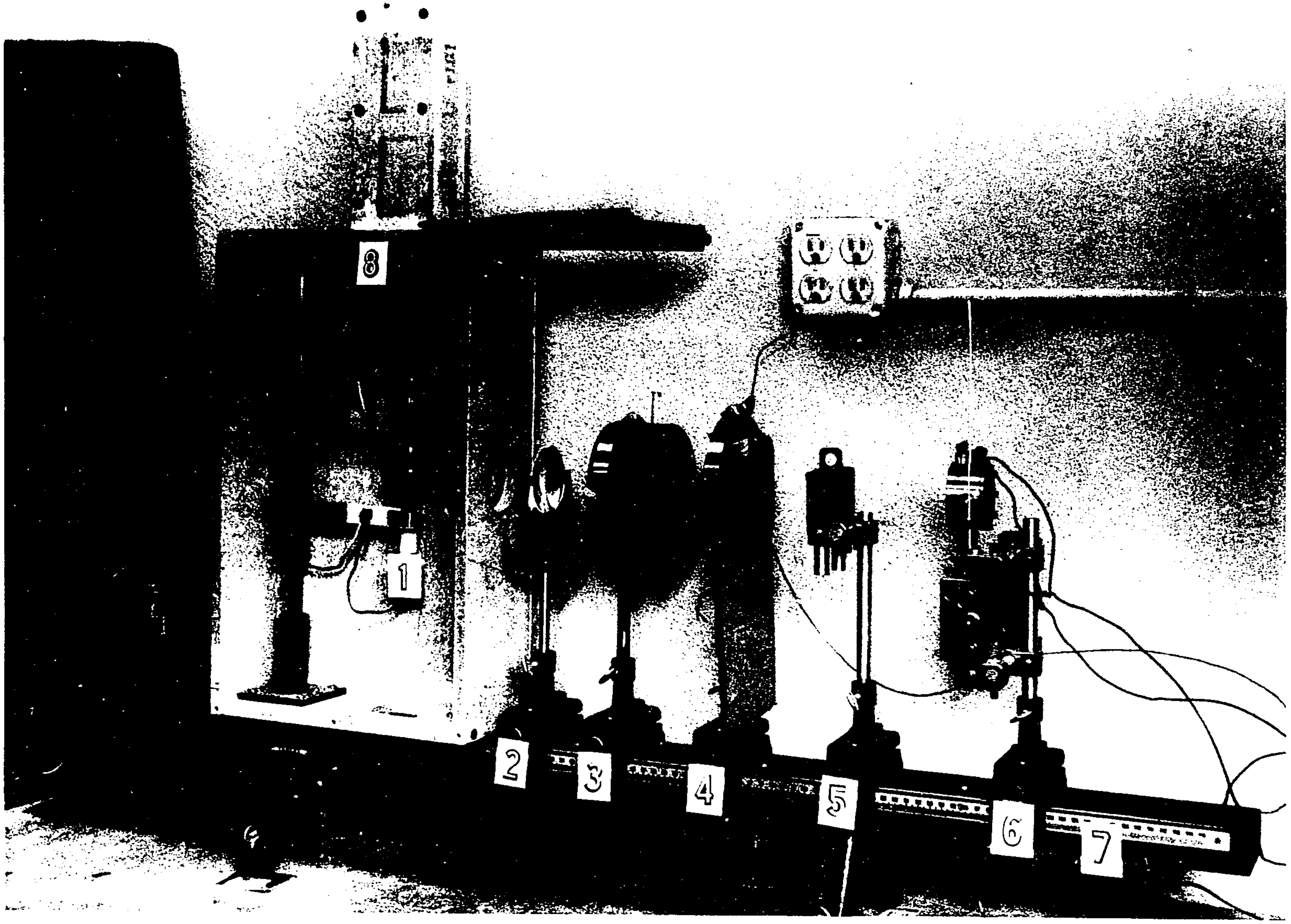
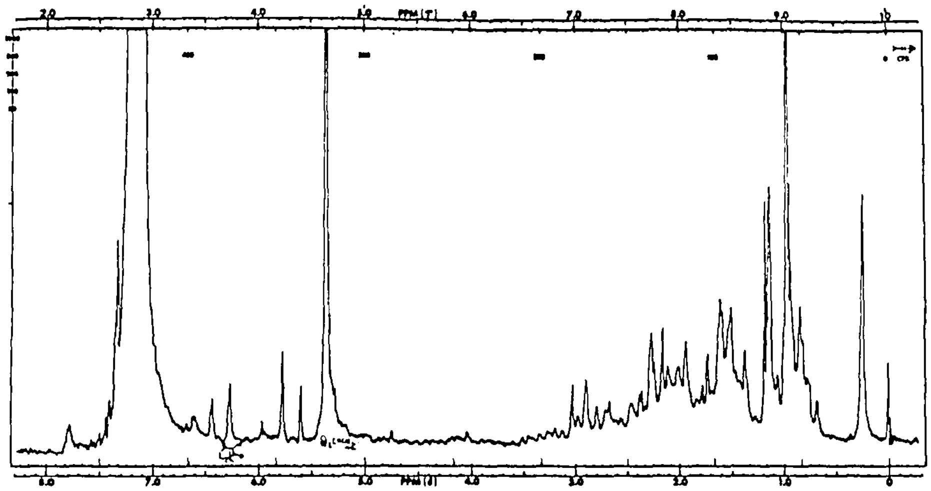

8
1
2
3
4
5
6
7

Figure 25. Nuclear magnetic resonance spectra (CCl_4).

Top - Crude irradiation mixture from attempted piperylene (LXXXXII) quenching of cycloaddition between 4,4-dimethyl-2-cyclohexenone (XXI) and 1,1-diphenylethylene (LXXXVII)

Middle - Crude irradiation mixture from acetic acid irradiation of 4,4-dimethyl-2-cyclohexenone (XXI) and 1,1-diphenylethylene (LXXXVII)

Bottom - Crude irradiation mixture from benzene irradiation of 4,4-dimethyl-2-cyclohexenone (XXI) and 1,1-diphenylethylene (LXXXVII)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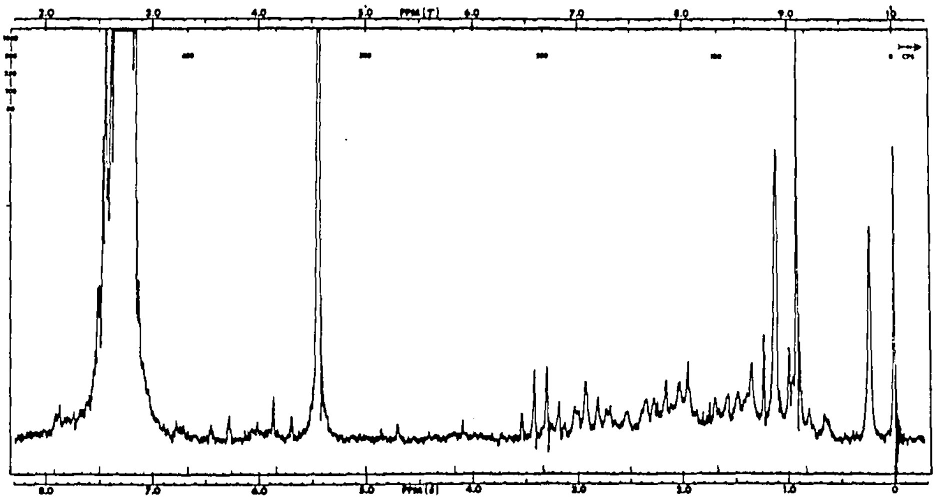
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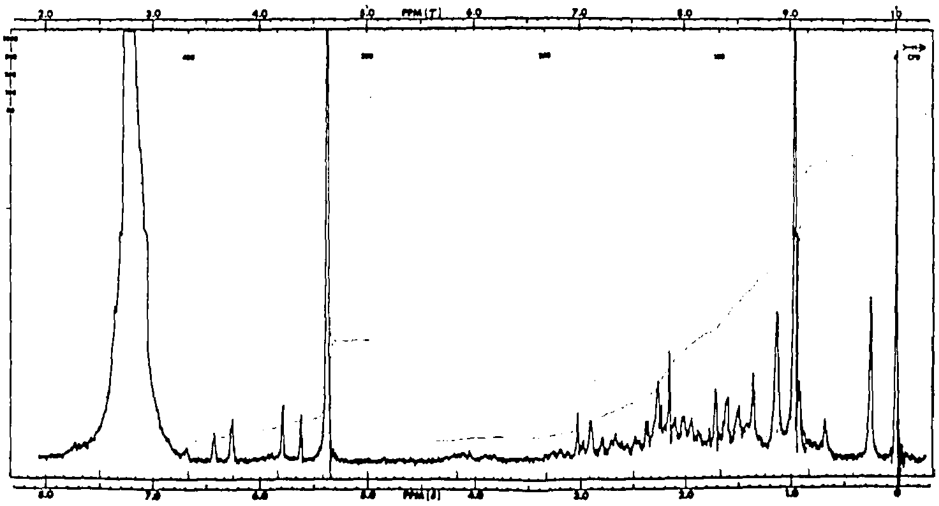
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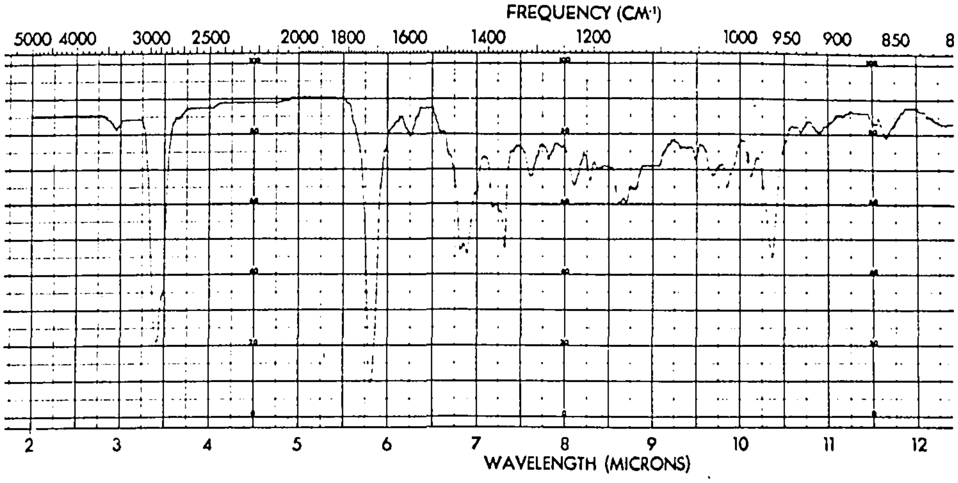
Figure 26. Infrared spectra (CCl_4).

Top - Crude irradiation product from cycloaddition of 4,4-dimethyl-2-cyclohexenone (XXI) and piperylene (LXXXXII)

Bottom - Major "product" from cycloaddition of 4,4-dimethyl-2-cyclohexenone (XXI) and piperylene (LXXXXII)

Middle - Nuclear magnetic resonance spectrum (CCl_4) of major "product" from cycloaddition of 4,4-dimethyl-2-cyclohexenone (XXI) and piperylene (LXXXXII)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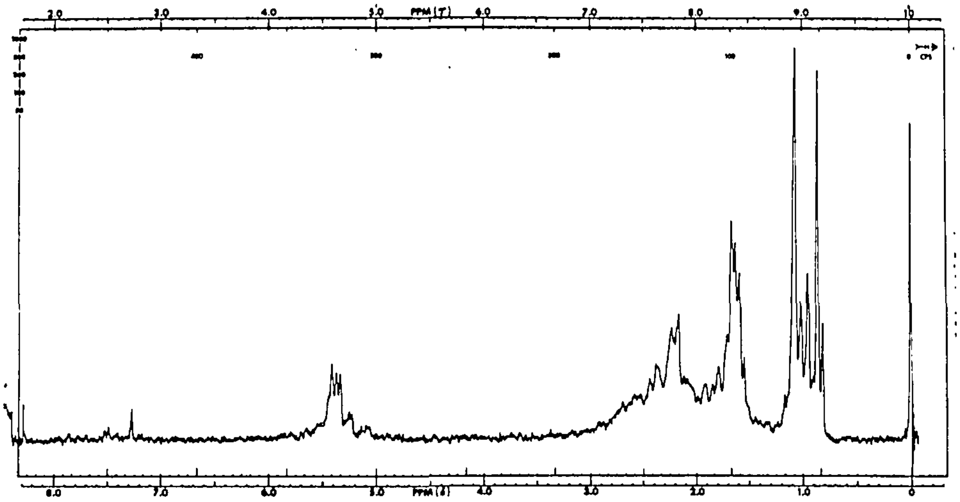
WAVELENGTH (MICRONS)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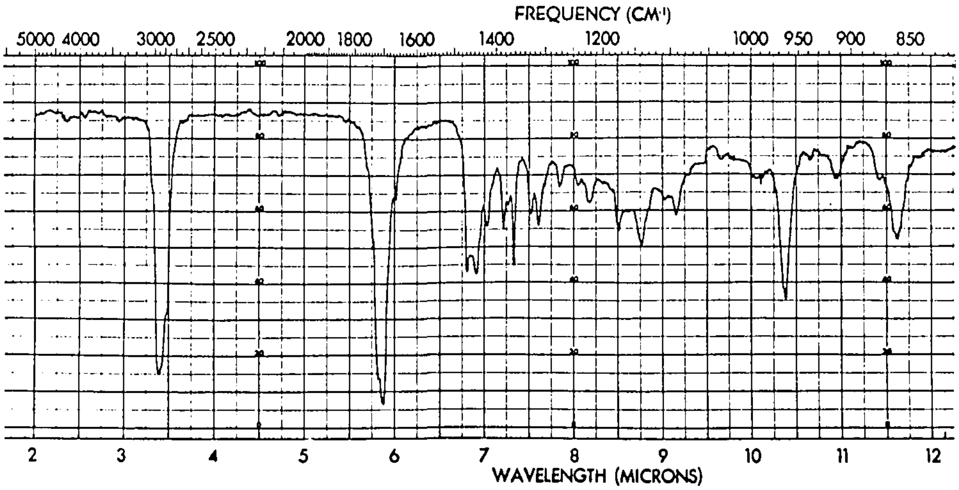
8.0 7.0 6.0 5.0 PPM (δ) 4.0 3.0 2.0 1.0 0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WAVELENGTH (MICRONS)

The Measurement of Some Photochemical Kinetics

"Where there is much light, the shadows are deepest".
-Goethe-

The study of a reaction mechanism usually involves the measurement of the kinetic features of the reaction. In the case of photochemical reactions, kinetic measurements are often very laborious. Perhaps the largest source of error is comparison of rates which were measured at different times which leads to erroneous interpretation due to variations in spectral output and intensity of most sources of irradiation. This error was largely circumvented in this study by construction of the apparatus illustrated in Figure 14 which allows simultaneous irradiation of several samples. An important consideration is that all samples being compared simultaneously absorb the same amount of light, since photons are essentially a reagent. In theory, the easiest way to assure identical absorption is to have the solution concentrations high enough so that greater than 99.5% of the light is absorbed. In actual practice this is difficult to do, for two reasons. First, the ultraviolet source emits a polychromatic spectrum of radiation, and the absorption spectrum of most compounds is broad, making calculation of total percent absorption a first-order approximation. Second, if the concentration of the compound is made high enough to ensure > 99% absorption at all wavelengths the time required for a significant molar conversion will be increased prohibitively. Consequently, a compromise was made in this study. A ketone concentration of 0.05 M concentration was generally used. Since the irradiations were done in circular (1.8 cm. i.d.) tubes, calculation of the path length is an approximation. In the specific example of 4,4-dimethyl-2-cyclohexenone (XXI) (XXI, $\epsilon_{318\ m\mu} = 38$, $\epsilon_{366\ m\mu} = 7$, ethanol) the average path length was assumed to be 1.0 cm. This gives values of 1.25% transmittance at 318 mμ and 44.5% transmittance at 366 mμ. The basis for valid comparison of the kinetics of these non-totally absorptive solutions arises from simultaneous irradiation of samples having the same initial reactant concentrations and following the reaction kinetically to no more than thirty percent completion. The kinetic data was obtained with these factors in mind.

Unimolecular photochemical reactions are generally zero order. Thus, the slope of a reactant concentration-irradiation time plot is equal to the zero order rate constant. The zero order rate constant is the basis for comparison of relative rates in the experiments discussed herein. The zero order rate constants were determined by measurement of at least four points during the first thirty percent reaction. For details on analyzing the crude concentration-time data, see the Experimental Section. The zero order rate constants are the average of two simultaneous measurements in different tubes. The average of the two results was generally within ± ten percent of the individual measurement. Consequently, although three figures are given, only two are considered to be significant.

The relative rates of photochemical reaction of 2-cyclohexenone (XLVII), 4-methyl-2-cyclohexenone (LXXVI) and 4,4-dimethyl-2-cyclohexenone (XXI) were found to be nearly equal. The data is shown below.

Compound	Relative Zero Order Rate of Disappearance
2-Cyclohexenone (XLVII)	0.850
4-Methyl-2-cyclohexenone (LXXVI)	0.865
4,4-Dimethyl-2-cyclohexenone (XXI)	1.0

Since XXI rearranges with a quantum yield of 1.7×10^{-2}, the above data suggests that the quantum yield for dimerization of XLVII and LXXVI is nearly equal to that for the rearrangement of XXI and that XLVII and LXXVI also have efficient paths for deactivation of the excited state to the ground state starting material. 2,4,4-Trimethyl-2-cyclohexenone was found to be totally unreactive toward $n \rightarrow \pi^*$ excitation in agreement with a larger scale experiment (see Experimental).

In the above experiment, 4,4-dimethyl-2-cyclohexenone (XXI) was consumed with a zero order rate constant of -0.0939. The rearrangement products XXII and XXIII were formed with a zero order rate constant of 0.0465 and 0.0459 respectively, indicating that XXIII results directly from 4,4-dimethyl-2-cyclohexenone. In an earlier experiment, (see Experimental) irradiation of XXII gave XXIII under conditions where XXII absorbed > 95% of the incident light. In the synthetic irradiation of 4,4-dimethyl-2-cyclohexenone (XXI), the fact that both XXII and XXIII are formed at the same rate means that XXIII results directly from XXI and that the amount of XXIII resulting from XXII under these conditions (major portion of light absorbed by 4,4-dimethyl-2-cyclohexenone) is very small.

Photosensitization by means of excitation transfer has recently become of extreme value in studying the nature of photochemical excited states. Hammond (59-62) and coworkers have published a large amount of information regarding photosensitization and triplet energy levels of various sensitizers as derived from the study of the photochemical *cis*-*trans*-isomerization of olefins. A recent report of Lamola and Hammond (63) gives an elegant method of determination of intersystem crossing efficiencies of triplet sensitizers. This data, when combined with the rather complete compilation of triplet energy levels of various organic molecules also reported by Hammond (64) allows facile choice of experimental conditions and firm interpretation of photosensitization experiments.

The photochemical rearrangement of 4,4-dimethyl-2-cyclohexenone (XXI) in the presence of benzophenone, 9-fluorenone and flavone was studied. The experimental conditions were such that greater than 95% of the incident light was absorbed by the sensitizer. The rate of rearrangement was measured relative to that in the absence of sensitizer. The relative rates of disappearance of XXI and appearance of the photoproducts XXII and XXIII are given below. The measurements were made with the 300-366 mμ wavelength emission from the mercury lamp.

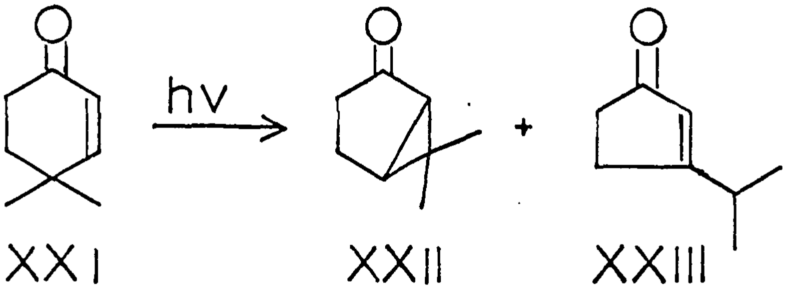


Table 1. Dependence of rate of rearrangement of XXI upon sensitizer triplet energy (E_T)

Sensitizer	Triplet Energy (E_T)	Relative Rate of Rearrangement		
		XXI Loss	XXII Appearance	XXIII Appearance
None	-	1.00	1.00	1.00
Benzophenone	69 kcal/mol.	1.43	1.26	1.16
Flavone	62	0.24	0.32	0.35
9-Fluorenone	53	0.036	0.014	0.008

In an unsensitized synthetic irradiation of XXI (see Experimental), the major product is 3-isopropyl-2-cyclopentenone (XXIII). The apparent lower rate of appearance of XXIII in the above sensitized irradiations may be due to triplet sensitized photodimerization of XXIII. The intersystem crossing efficiency of benzophenone is 100%, and that of 9-fluorenone is 93% (63). The intersystem crossing efficiency of flavone, although not reported to date, should be near that of acetophenone (100%,63).

The fact that the rearrangement of XXI to XXII and XXIII proceeds when benzophenone is absorbing > 95% of the light means that the benzophenone triplet state is transferring triplet energy to XXII, yielding the excited triplet state of XXII which then rearranges to XXII and XXIII. This process is summarized below.

$$\emptyset_2C = O(S_0) \longrightarrow \emptyset_2C = O(S_1) \qquad (2)$$

$$\emptyset_2C = O(S_1) \longrightarrow \emptyset_2C = O(T_1)\Phi = 1.0 \qquad (3)$$

$$\emptyset_2C{=}O(T_1) + XXI(S_0) \longrightarrow XXI(T_1) + \emptyset_2C{=}O(S_0) \qquad (4)$$

$$XXI(T_1) \xrightarrow[\text{steps}]{\text{several}} XXII + XXIII \qquad \Phi = 1.7\text{x}10^{-2} \qquad (5)$$

Details of the steps in Equation 5 will be considered later. The fact that the rate of disappearance of XXI is faster in the presence of benzophenone is probably due to the much lower percent transmittance of the benzophenone solution. It is seen from Table 1 that flavone is less efficient than benzophenone and that 9-fluorenone nearly precludes photochemical rearrangement. Bäckstrom and Sandros (65) have shown that triplet energy transfer as shown in Equation 4 only occurs when the triplet energy of the donor (sensitizer) is greater than that of the triplet energy of the acceptor (XXI). Thus, the data of Table 1 suggests that the triplet energy of XXI lies below benzophenone (69 kcal./mol.) and probably slightly above that of flavone (62 kcal./mol.). Transfer of triplet energy from 9-fluorenone (53 kcal./mol.) would thus be endothermic and less probable, giving rise to the nearly complete "quenching" of the rearrangement. Thus, the rearrangement of XXI to XXII and XXIII is secured as arising from an excited triplet state. The low quantum yield of the unsensitized rearrangement (1.7×10^{-2}) is probably due to effective radiationless deactivation of the triplet state of XXI back to the ground state and not to a low intersystem crossing efficiency since the rate of rearrangement when benzophenone is a triplet donor is very nearly the same as the unsensitized reaction.

A duplication of the benzophenone sensitization experiment using 340-360 mμ wavelengths gave exactly analogous results (see Experimental). Thus, there is little doubt that the rearrangement of XXI is due to a triplet intermediate.

Since the benzophenone sensitization experiments strongly suggested the intermediacy of triplet XXI, the effect of various triplet quenchers on the rearrangement was studied. Ferric dipivaloyl methane (66), trans-piperylene (67) and oxygen (65) have been observed to quench triplets. The effect of each of these quenchers on the rate of rearrangement of XXI was studied. The results are summarized in Table 2.

Table 2. Dependence of relative rate of rearrangement upon quenchers

Quencher	Concentration	Relative Rate of Rearrangement XXI Loss	 XXII Appearance	 XXIII Appearance
None	-	1.00	1.00	1.00
Ferric Dipivaloyl Methane	10^{-5} M	0.71	0.87	0.75
Oxygen	Saturated solution	0.79	0.76	0.75
Piperylene	0.001 M	1.03	1.05	0.92

These results clearly show that ferric dipivaloyl methane and oxygen quench the rearrangement, in agreement with triplet XXI as being intermediate in the rearrangement. The effect of piperylene is a slight increase in rate. The reason for this result is not understood, but piperylene is a poor choice for a quencher of XXI since it reacts chemically to form an adduct (see Experimental) and is probably consumed early (requiring 2% of XXI), thus giving a normal rate of reaction.

Thus, the sensitization and quenching results are in agreement with the rearrangement of XXI to XXII and XXIII as being due to a triplet intermediate. This is the first example of a proven triplet intermediate in a 2-cyclohexenone skeletal rearrangement.

Some kinetic aspects of the cycloaddition of 4,4-dimethyl-2-cyclohexenone (XXI) with 1,1-diphenylethylene (LXXXVII) were then studied. The rate of cycloaddition (see Experimental) was found to be dependent upon the concentration of LXXXVII at constant ketone concentration. This result is in accord with a reaction which is zero order in excited ketone and first order in the olefin moiety, as would be expected for a bimolecular cycloaddition. The concentration dependence was not studied further.

A study of the multiplicity of the cycloaddition reaction of XXI with LXXXVII was undertaken. The quenching effect of ferric dipivaloyl methane, oxygen and piperylene was measured. The data is summarized in Table 3.

Table 3. Dependence of rate of cycloaddition of XXI upon quenchers

Quencher	Concentration	Relative Rate of Cycloaddition
None	-	1.00
Ferric dipivaloyl Methane	10^{-5} M	0.94
Oxygen	Saturated solution	0.975
Piperylene	0.05 M	1.27

In contrast with the quenching effect on the rearrangement, neither ferric dipivaloyl methane nor oxygen significantly quench the cycloaddition of XXI to LXXXVII, suggesting that the reaction may be due to excited singlet ketone. The effect of piperylene is probably due to reaction of piperylene with XXI thus increasing the apparent rate of cycloaddition.

The effect of sensitizers upon the cycloaddition of 4,4-dimethyl-2-cyclohexenone (XXI) with 1,1-diphenylethylene (LXXXVII) was then studied. Surprisingly, tertiary butyl alcohol solutions of XXI (0.05 M), LXXXVII (0.10 M) and either benzophenone (0.10 M) or acetophenone (0.60 M) were completely photostable (see Experimental). Since it was established that benzophenone transfers triplet energy to 4,4-dimethyl-2-cyclohexenone in the absence of 1,1-diphenylethylene, it was apparent that 1,1-diphenylethylene acted as a triplet quencher, quenching benzophenone triplets and 4,4-dimethyl-2-cyclohexenone triplets. The mechanism of this quenching was deduced as follows by several control experiments.

It is well known that benzophenone undergoes photoreduction to benzpinacol in isopropanol with a quantum yield of near unity (68). A casual observation during the course of this work showed that benzophenone was also reduced in tertiary butyl alcohol upon prolonged irradiation. A quantitative measurement (see Experimental) of the relative rates of photoreduction of benzophenone in isopropyl alcohol and tertiary butyl alcohol gave the following results.

Solution	Percent Photoreduction of Benzophenone (320-360 mμ)
0.10 M benzophenone in isopropyl alcohol	33
0.10 M benzophenone in tertiary butyl alcohol	3.3

The percent photoreduction of benzophenone in the presence of 1,1-diphenylethylene in each solvent was then measured.

Solution	Percent Photoreduction of Benzophenone
0.10 M benzophenone, 0.05 M diphenylethylene in isopropyl alcohol	2.3
0.10 M benzophenone, 0.05 M diphenylethylene in tertiary butyl alcohol	1.8

This experiment conclusively shows that 1,1-diphenylethylene (LXXXVII) is capable of quenching benzophenone triplets, even in the presence of isopropanol where photoreduction has a quantum yield of 1.0. When this data is combined with that of the preceeding experiment, it can be seen that in isopropanol, 33-2.3/33 or 96% of the photoreduction and hence the benzophenone triplet state is quenched by 1,1-diphenylethylene. The 1,1-diphenylethylene triplets apparently have an efficient path other than chemical reaction for deactivation to the ground state since no 1,1-diphenylethylene is consumed during the irradiation. The photostability of the 1,1-diphenylethylene-benzophenone-4,4-dimethyl-2-cyclohexenone system will be discussed later.

Attention will now be turned to the mechanistic study of the XXI-LXXXVII cycloaddition since this has also yielded information about the mechanism of the rearrangement of XXI.

Four possibilities for the multiplicities of the cycloaddition present themselves:

A. Excited singlet ketone (XXI) reacting with 1,1-diphenylethylene LXXXVII to form adduct.

B. Excited singlet olefin (LXXXVII) reacting with ketone (XXI) to form adduct.

C. Excited triplet ketone (XXI) reacting with olefin (LXXXVII) to form adduct.

D. Excited triplet olefin (LXXXVII) reacting with ketone (XXI) to form adduct.

The photostability of the 4,4-dimethyl-2-cyclohexenone-1,1-diphenylethylene-benzophenone system allows C and D to be ruled out as possible mechanisms for cycloaddition. Irradiation of this solution yields benzophenone triplets with a quantum yield of one. Assuming that the benzophenone triplets then transfer to <u>both</u> olefin and ketone. Assuming diffusion controlled transfer, twice as many of the diphenylethylene molecules as 4,4-dimethyl-2-cyclohexenone molecules accept the triplet energy since the ratio of the concentrations is two to one. Rearrangement of 4,4-dimethyl-2-cyclohexenone (XXI) is not observed in this solution, therefore the triplet state of XXI must be quenched by

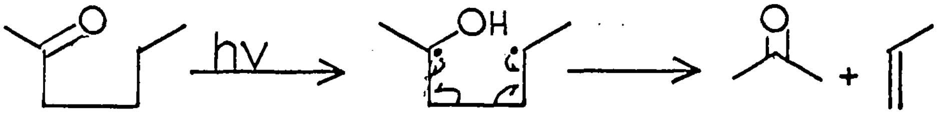
1,1-diphenylethylene via energy transfer since XXI triplets produced by energy transfer from benzophenone in the absence of 1,1-diphenylethylene yield the rearrangement products XXII and XXIII. Since ketone triplets are formed, and no cycloaddition occurs, one may conclude that C is not the path for cycloaddition.

The photostability of the benzophenone - 4,4-dimethyl-2-cyclohexenone (XXI) - 1,1-diphenylethylene (LXXXVII) solution with respect to lack of photoreduction of benzophenone, complete absence of rearrangement of XXI and lack of cycloaddition of XXI with LXXXVII was explained above in terms of energy transfer with 1,1-diphenylethylene as the eventual recipient of <u>all</u> of the triplet energy due to quenching of XXI triplets which resulted from energy transfer from benzophenone. It was found upon closer analysis that during the cycloaddition of XXI with LXXXVII in the absence of benzophenone the rearrangement of XXI was not quenched 100 percent. The data is as follows.

Solution	Rate of Rearrangement	
	XXII Appearance	XXIII Appearance
0.05 M XXI	0.012	0.018
0.05 M XXI, 0.25 M LXXXVII	0.004	0.003

Since XXI still rearranges to XXII and XXIII in the presence of 1,1-diphenylethylene and 1,1-diphenylethylene is quenching XXI triplets the rearrangement of XXI in the presence 1,1-diphenyl ethylene must be due to excited <u>singlet</u> XXI. It is not impossible for the same rearrangement products to arise both from excited singlet and excited triplet XXI.

Hammond (69) and Dougherty (70) have recently reported independently that the photolysis of 2-pentanone and 2-hexanone may yield cleavage products



(6)

from either the excited singlet singlet or the excited triplet state. These conclusions were derived from a study of the dependence of quantum yield of Reaction 6 on the concentration of triplet quenchers. The quencher used by Hammond (69) was trans-piperylene. Dougherty (70) used trans-piperylene and cis-dichloroethylene to quench the triplet reaction. Hammond (69) reports the following data for the photolysis of 2-cyclohexenone.

Quantum Yields for the Disappearance of 2-Hexanone

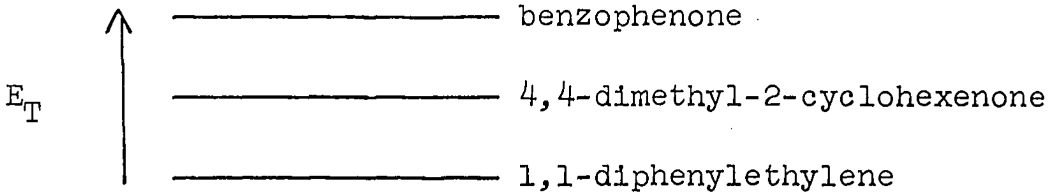
Experiment	Quantum Yield
No piperylene	0.50
8 M piperylene	0.21

In 8 M piperylene, Hammond assumes from a Stern-Volmer plot that all triplets are quenched, thus the intrinsic singlet quantum yield is 0.21 and the triplet quantum yield is equal to 0.50-0.21 or 0.29. Thus, in the absence of quencher,

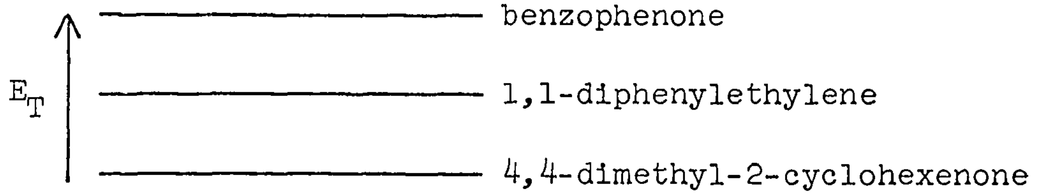
0.21/0.50 or 42% of the disappearance of 2-hexanone is due to excited singlet reacting directly and 58% is due to excited triplet reacting directly.

Thus, analogy is offered for the possibility of the rearrangement of XXI to XXII and XXIII as being due to excited singlet and triplet states. This conclusion is in agreement with the partial quenching of the 4,4-dimethyl-2-cyclohexenone (XXI) rearrangement by ferric dipivaloyl methane and oxygen.

An alternative explanation to the lack of rearrangement or cycloaddition of 4,4-dimethyl-2-cyclohexenone (XXI) in the presence of benzophenone and 1,1-diphenylethylene is that the excited triplet benzophenone may selectively transfer energy to 1,1-diphenylethylene which is then deactivated to the ground state. In view of the principles postulated by Arnold (71), this would require the following order of triplet energies (E_T) of benzophenone, 4,4-dimethyl-2-cyclohexenone and 1,1-diphenylethylene.



The alternate order,



is not probable, since transfer to 1,1-diphenylethylene should yield 4,4-dimethyl-2-cyclohexenone triplets by a second energy transfer which would yield both cycloaddition and rearrangement products, neither of which are observed. If the alternative mechanism of selective triplet transfer from benzophenone to 1,1-diphenylethylene is in fact occurring, path D can still be ruled out since triplet olefin yields no cycloaddition products. Path C can be ruled out since the ordering of triplet energies E_T benzophenone > E_T 4,4-dimethyl-2-cyclohexenone > E_T 1,1-diphenylethylene predicts only energy transfer from ketone to olefin (71).

Thus, regardless of which of the above two alternatives for photostability of the benzophenone-4,4-dimethyl-2-cyclohexenone-1,1-diphenylethylene system is chosen, evidence against paths C and C is offered. The alternative singlet mechanisms (A and B) are not as easily differentiated.

The absence of quenching by oxygen or ferric dipivaloyl methane is in agreement with either A (singlet ketone + olefin) or B (singlet olefin + ketone) as the adduct producing route. Consideration of the light absorption by olefin (16% in 0.05 M XXI, 0.05 M LXXXVII) suggests that the light absorbed by LXXXVII may just as well be responsible for cycloaddition, supporting path B. Srinivasan (72) has reported recently that the singlet-singlet 0 → 0 bond transition for butadiene may lie at 320 mμ, even though the π → π* maximum for butadiene is at 210 mμ. Thus, the 16% of incident light absorbed by 1,1-diphenylethylene (LXXXVII) may well be due to population of excited singlet LXXXVII followed by cycloaddition.

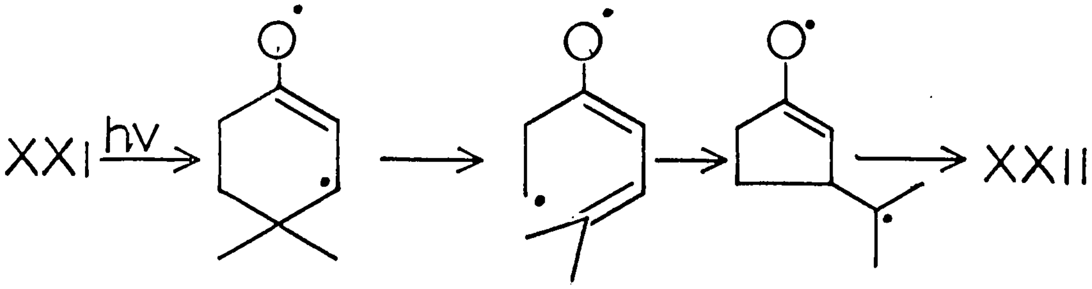
Similarly, the fact that cycloaddition occurs in a 1, 2 manner between piperylene (XCII) and 4,4-dimethyl-2-cyclohexenone (XXI) under conditions (see Experimental) where piperylene was absorbing a portion of the light may also be due to excited olefin reacting with ketone. In contrast, Corey's (39) cycloadditions with alkyl olefins are not subject to this uncertainty since the alkyl substituted olefins did not absorb light at the wavelengths used.

None of the data in this study can clearly rule out either mechanism A or B. The author would prefer to consider mechanism A as the cycloaddition route since this thesis is concerned with ketone photochemistry, and since the course of cycloaddition with LXXXVII gives the same stereochemistry and product orientation as the cycloadditions of 2-cyclohexenone with completely transparent olefins as reported by Corey (39).

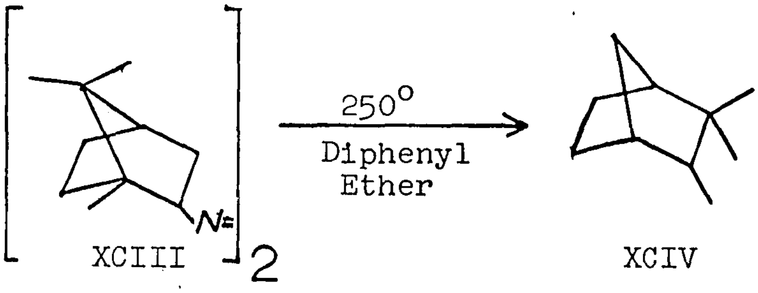
The Question of Mechanism in the Photochemical Rearrangement and Cycloaddition of 4,4-Dimethyl-2-Cyclohexenone

> "All truly wise thoughts have been thought already thousands of times; but to make them really ours we must think them over again honestly, until they take firm root in our personal experience."
>
> -Goethe-

A detailed mechanism for the rearrangement of 4,4-dimethyl-2-cyclohexenone (XXI) has been offered by Zimmerman (27, see Historical Figure 3). Perhaps the most controversial step in this mechanism is the requirement that the primary step of the photorearrangement be a 1,2-alkyl shift in a free radical process. This portion of the mechanism is shown below.

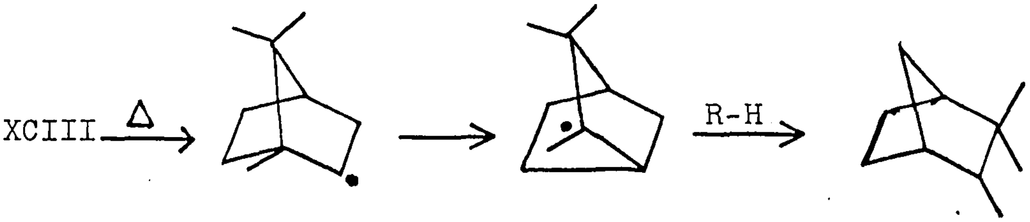


The net effect of the above steps as proposed by Zimmerman is the conversion of a secondary free radical to a tertiary free radical via a 1,2 shift. There is only one known example of such a 1,2 alkyl free radical shift in the chemical literature to date. Berson (47) has observed the only documented 1,2 free radical alkyl group rearrangement in the thermal decomposition of 2-azobornane (XCIII).



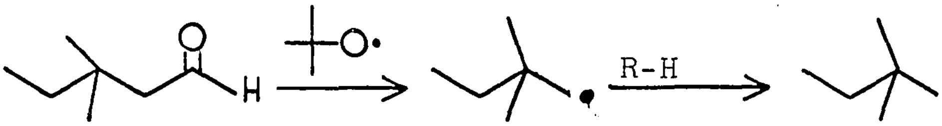
XCIII XCIV

The product XCIV is postulated to result from a 1,2 alkyl shift. Perhaps the closest analogy to Zimmerman's (27) scheme is the photochemical



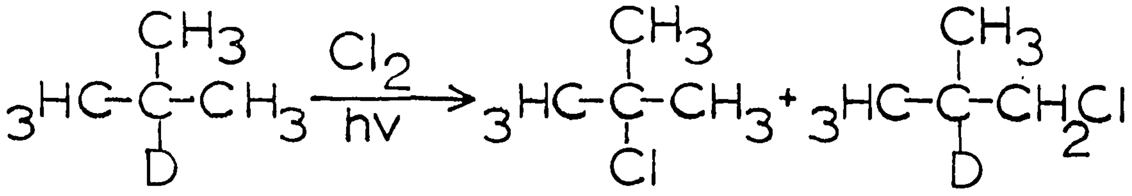
XCIV

decarbonylation of XCV (73). The free radical initiator was tertiary butoxyl radical. Only the product (XCVI) resulting from hydrogen abstraction was observed, illustrating



XCV XCVI

that conversion of a primary to a tertiary radical does not occur in this system. Similarly, Brown and Russell (74) showed earlier that the isobutyl radical produced by chlorination of XCVII does not rearrange to the tertiary butyl radical by either a 1,2-deuterium or methyl migration.



$$H_3C-\overset{CH_3}{\underset{D}{C}}-CH_3 \xrightarrow[h\nu]{Cl_2} H_3C-\overset{CH_3}{\underset{Cl}{C}}-CH_3 + H_3C-\overset{CH_3}{\underset{D}{C}}-CH_2Cl$$

XCVII

This author believes that the mechanism(s) of photochemical rearrangement of α, β unsaturated ketones must follow pathways which are energetic minima which are exactly analogous to accepted chemical principles. Therefore, an essential feature of the mechanism of rearrangement of XXI to XXII and XXIII is that the rearrangement be due to an excited state electron deficient species which rearranges as if the carbon skeleton were a carbonium ion and not a free radical as proposed by Zimmerman (27). The number of 1,2 alkyl shifts in carbonium ion chemistry is too high to be documented here, suggesting that the carbonium ion rearrangement is a path of lower energy than a free radical rearrangement regardless of the electronic state of the molecule.

The mechanism to be given below represents the author's interpretation and is not intended to be indicative of his research supervisor's interpretation of the mechanism. In fact, substantial objection to the mechanism has been raised by Professor Chapman.[1]

In recent studies on the photoproduction of _trans_-cycloheptenone and _trans_-cyclooctenone, Eaton has suggested (see Historical) that one may regard the isomerization of the carbon-carbon double bond as due to an energy transfer from the initially excited carbonyl group to the double bond (15). This author believes that it is not possible to speak of the double bond as an isolated reacting system when it is conjugated with the carbonyl group. Figure 27 shows the energy level diagram for the carbon-carbon double bond and the carbonyl group as separate structures and the resultant molecular orbital energy levels which arise from bonding to give an α, β unsaturated ketone system. This diagram is an adaptation of that given by Jaffe and Orchin (75). The $n \rightarrow \pi^*$ transition is shown in Figure 27. The mechanism for photorearrangement of 4,4-dimethyl-2-cyclohexenone (XXI) following $n \rightarrow \pi^*$ excitation is proposed to be as follows.

Excitation of XXI is certainly due to an $n \rightarrow \pi^*$ transition at the wavelengths employed in this work (> 300 mμ). This process is illustrated below depicting only the highest

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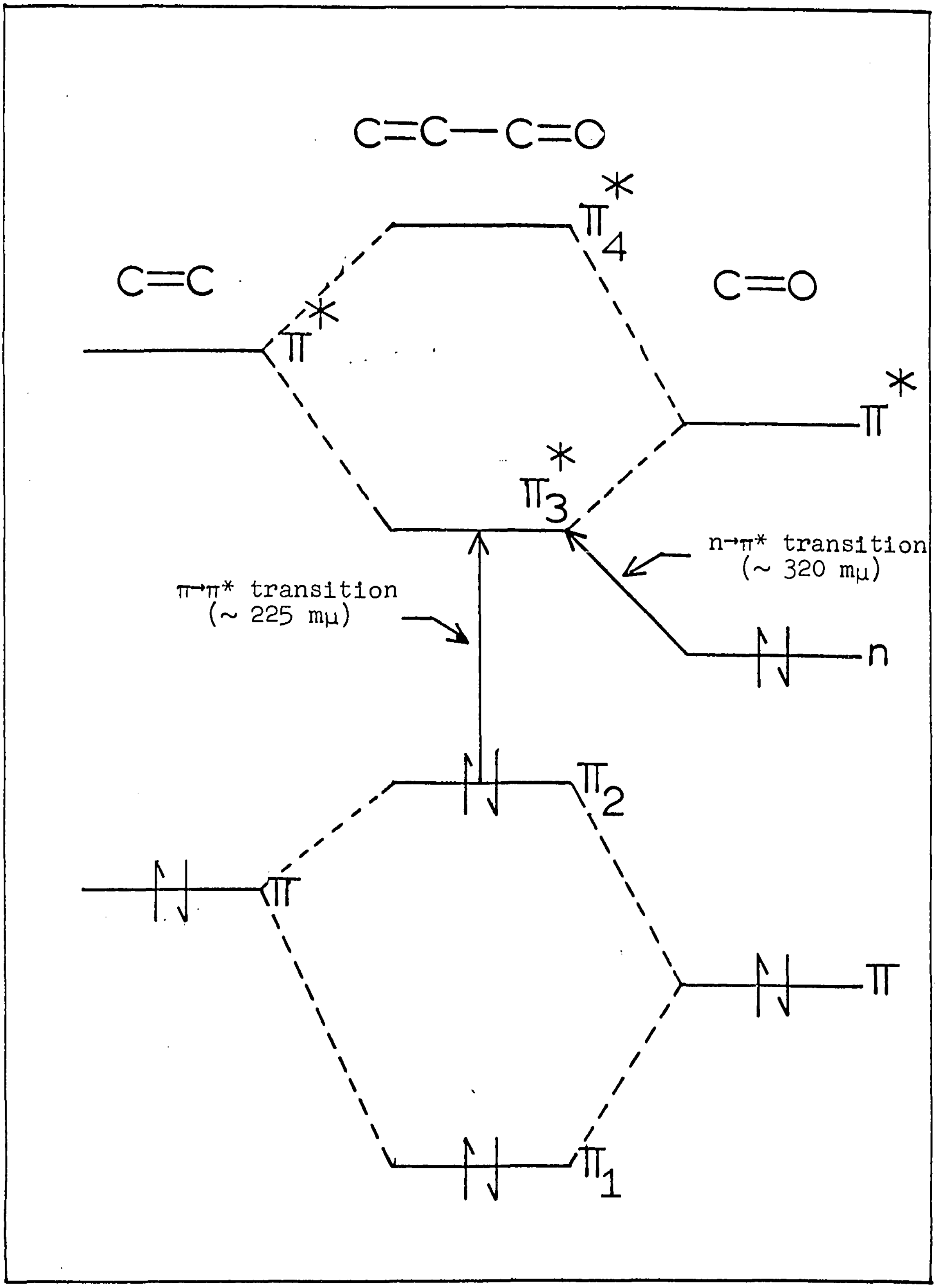
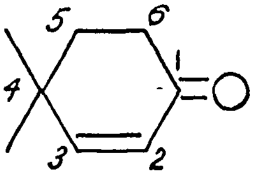
[1] Chapman, O. L., Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Recent views on the mechanism of rearrangement of α, β unsaturated ketones. Private communication. 1965.

Figure 27. Energy level diagram of α, β unsaturated carbonyl compounds (75).

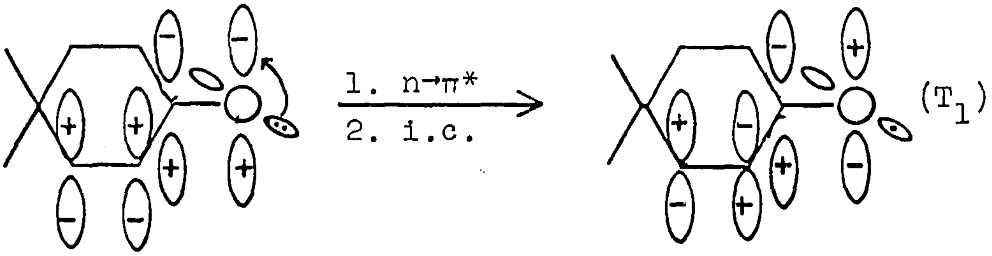

C=C—C=O
C=C
C=O
π*
π_4^*
π*
π_3^*
π→π* transition
(~ 225 mμ)
n→π* transition
(~ 320 mμ)
n
π_2
π
π
π_1

occupied π orbitals. The orbital symmetries are assumed to be exactly analogous to those of butadiene. The explanation of the mechanism in this discussion is from the viewpoint of the highest occupied orbitals in each of the excited state structures. A diagram showing all of the π levels and their respective electron population and multiplicity is shown in Figure 28 and a diagram of the orbital symmetry of the π levels of each of the excited state structures is given in Figure 29. The mechanism is considered with triplet multiplicity during a portion of the excited state rearrangement; since this work (see Experimental) has concretely shown that the rearrangement can proceed via a triplet state.

The following number system is used in this discussion.

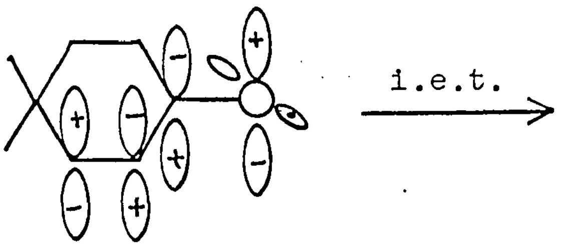


Following n → π* excitation, XXI is assumed to undergo intersystem crossing (i.c.) to the triplet state (T_1) to give XXIa.



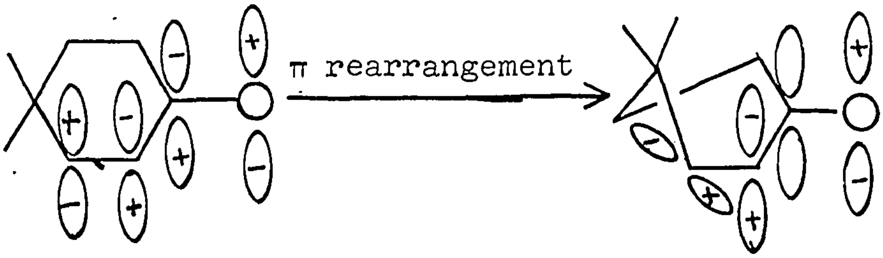
XXI XXIa

XXIa has one electron in the antibonding π orbital. This process is shown diagrammatically in Figure 29. Since the exact orbital energies are not known, and the diagram is only a general illustration. XXIa then undergoes an intramolecular energy transfer (i.e.t.). This process involves return of the n electron to oxygen and simultaneous promotion of a π_2 electron to π_3^*. (See Figure 29)



XXIa XXIb

The structure XXIb is considered to have the majority of the antibonding character at C_2-C_3 and the majority of the bonding character at the carbonyl group and is thus a result of "energy transfer" from the excited state antibonding carbonyl group of XXIa to an antibonding double bond in XXIb. The repulsion of these unpaired electrons in non-orthogonal orbitals provides the driving force for rotation in the following step. XXIb then undergoes a simultaneous rearrangement of the π system and 90° rotation about the C_2-C_3 bond to give XXIc.



XXIb XXIc

As shown in Figure 28, this π rearrangement involves rotation such that the orbitals of the unpaired electrons are orthogonal. The rotation is entirely at C_3, since the orbital at C_2 has hybridized with π_1 of XXIb to form ψ_1 and ψ_2. This orbital rearrangement results in a node at C_1 for ψ_2, precluding delocalization over all three atoms (O, C_1 and C_2). The energy of ψ_2 is shown to be equal to that of ψ_3 (the orbital bearing the electron at C_3) although the hetero atom may affect the energy slightly. It should be emphasized that this step has not isolated the double bond from the rest of the molecule, and only represents a π rearrangement to a new non bonding orbital system, one electron of which is described by the orthogonal orbital at C_3, the other electron being described by the molecular orbital at C_1, C_2 and O.[1] Following π rearrangement to XXIc, electron transfer from ψ_3 to ψ_2 occurs to give XXId. This process may be nearly degenerate due to the fact that the orbitals are orthogonal, although the electronegativity of the oxygen should favor this transfer. Intersystem crossing (i.c.) to the singlet must also occur at this stage since the three atom molecular orbital ψ_2 now has both electrons. This process is depicted as

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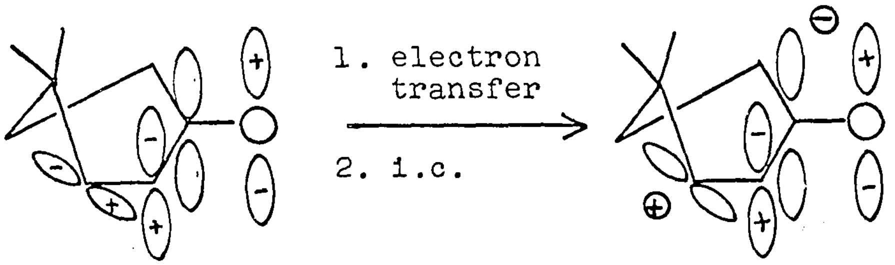
[1] The author is indebted to Dr. W. S. Trahanovsky for several interesting discussions regarding this point.

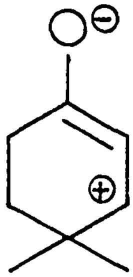


XXIc XXId

This demotion results in a positively charged β carbon atom (C_3) with the vacant orbital at C_3 orthogonal to the ψ_1 and ψ_2 molecular orbitals. The ψ_1 and ψ_2 molecular orbitals have four electrons spread over the three atom system. The orbital symmetries are as shown in Figure 29.

In the above and subsequent discussion, the orbital structure of XXIc and XXId is considered to be orthogonal. This approximation is made for the sake of clarity in illustration and explanation. It is probable that a full 90° rotation is not possible in the 2-cyclohexenone system due to the increased ring strain which would be introduced (15). The mechanistic discussion given here still holds, even if the induced rotation is slightly less than 90°. In addition, the fact that XXIc may not be orthogonal allows a firmer basis for retaining the symmetry signs in the C_3 orbital after rotation. The fact that XXIc and XXId are probably near-orthogonal and not orthogonal should be kept in mind in this discussion.

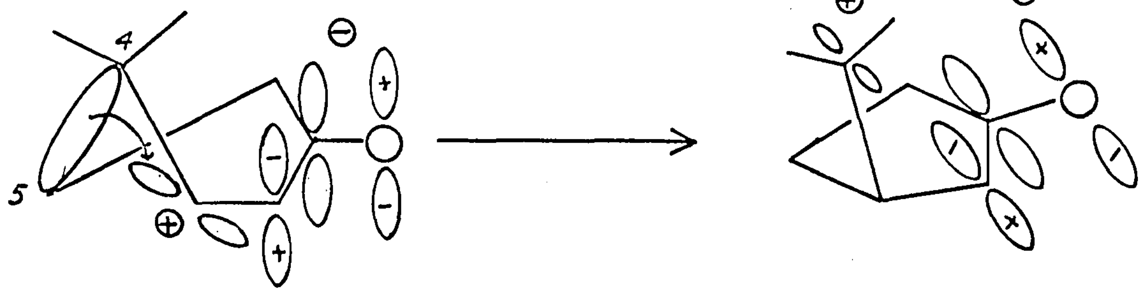
Thus, without regard to conformation XXIa could be represented as



XCVIII

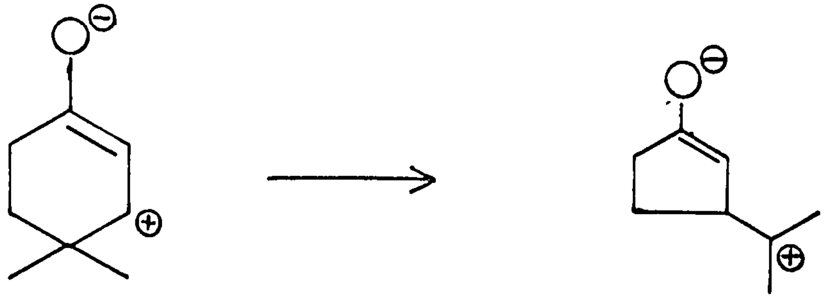
which has been used as a predictive structure for rationalizing α, β unsaturated ketone photochemistry (5). The conformational arrangement at C_3 is an important difference between XCVIII and XXId. It should be kept in mind that XXId is an <u>excited state</u> electronic structure due to the orbital structure depicted above.

The selective reactivity of XXId in forming a C_3-C_5 bond is explained on the basis of co-planar orbital alignment of the C_4-C_5 σ bond with the empty orbital at C_3. This process is shown below.



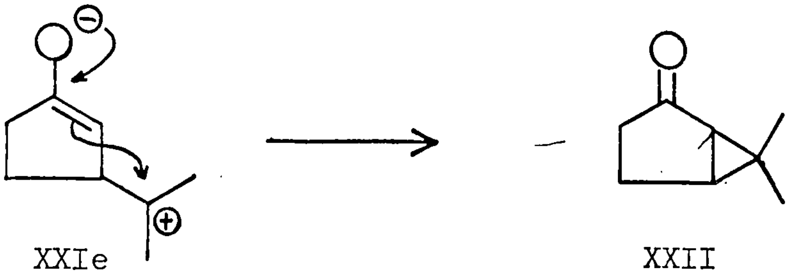
XXId XXIe

In terms of a dipolar rearrangement (keeping the conformation of XXId in mind), the process is written more simply as



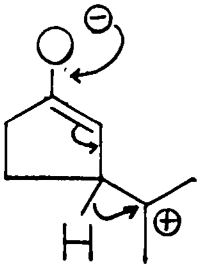
XXId XXIe

XXIe may then yield XXII

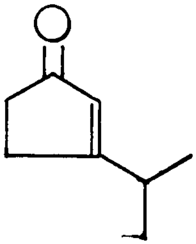


XXIe XXII

by direct rebonding or XXIII after a 1,2 hydride shift.



XXIe



XXIII

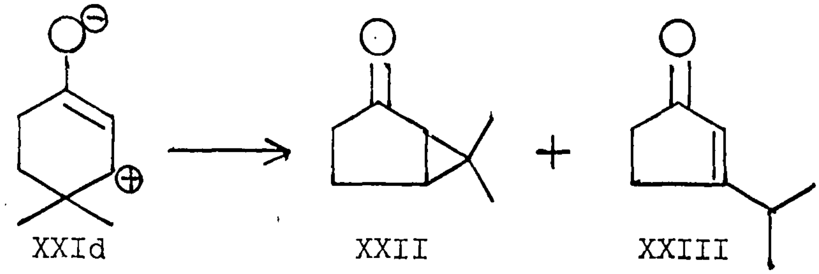
The rebonding stages to XXII and XXIII must proceed with rearrangement of the XXIe π framework.

The above scheme should be independent of multiplicity. Singlet XXIb would still hybridize with rotation to orthogonality at C_3 due to the electron repulsion of vicinal non-orthogonal orbitals. Thus, the mechanism is qualitatively the same, regardless of spin.

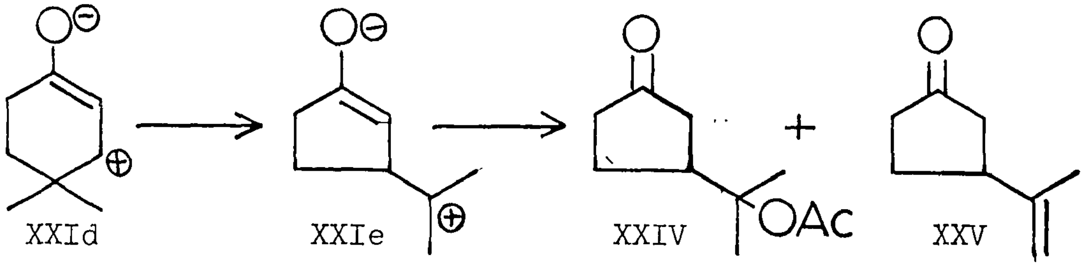
The objection may be raised that the intramolecular energy transfer step XXIa → XXIb essentially yields a high energy π, π^* state from an n, π^* state. This objection would be quite valid if this were the only step in the reaction. The sequence XXIa → XXIb → XXIc may be nearly concerted and exothermic, making inclusion of structure XXIb perhaps unnecessary except for the sake of showing a stepwise mechanism. Since the actual energy of the π, π^* triplet of XXI or similar molecules is not known, the sequence XXIa → XXIb → XXIc cannot be rejected solely on the basis of energetics.

Thus, the above mechanism can account for reaction through the triplet state to give a species which has carbonium ion character at the β carbon atom. Evidence was given that a portion of the rearrangement of XXI to XXII and XXIII may be due to a singlet reaction. As shown above, the same mechanistic scheme with only singlet character yields the same electron deficient species XXId.

The solvent dependence of the irradiation of XXI may be most simply explained on the basis of difference in solvent nucleophilicity. Thus, in tertiary butyl alcohol, XXId rearranges intramoleculary to give XXII and XXIII.

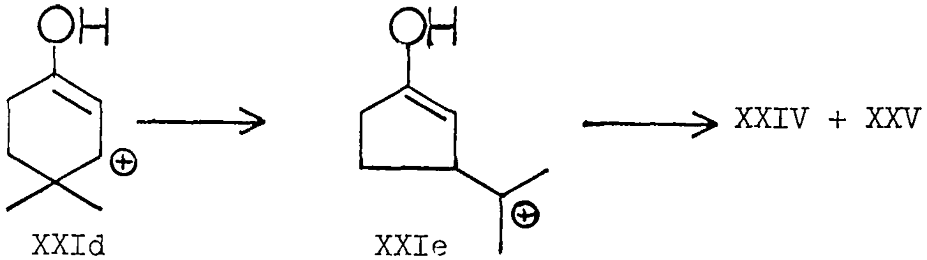

XXId XXII XXIII

In acetic acid, the nucleophilic solvent participates to give XXIV as the major product.



XXId XXIe XXIV XXV

The fact that XXV is formed may mean that XXId or XXIe is protonated and is essentially a carbonium ion, giving the olefin which would result from a β elimination of a proton, i.e.,



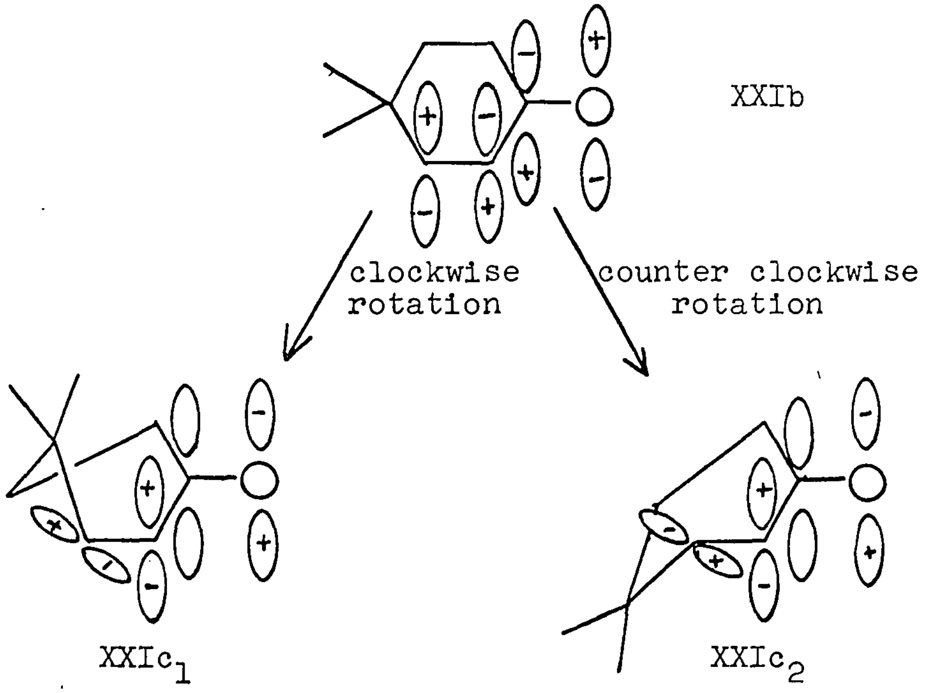
XXId XXIe

The "neutral solvent" products XXII and XXIII are thus understandably minor products in acetic acid.

An interesting point is that production of structures analogous to XXIc in 2-cycloheptenone or 2-cyclooctenone would probably lead in these less strained rings to a full 180° rotation followed by demotion to the trans-ground state.

Consideration of the cycloaddition reaction of XXI in view of the above mechanism leads to correct prediction of the *stereochemistry* *and* *orientation* of the cycloaddition product. The cycloaddition was shown definitely not to be a triplet reaction and is probably due to singlet XXI reacting with olefin.

Excitation of XXI by the above mechanism yields XXIc, a singlet with orthogonal molecular orbitals ψ_3 at C_3 and ψ_2 at C_2-C_1-O, each orbital containing one electron. The orbital symmetry of XXIc is determined by the direction of rotation from XXIb as shown below. Depending upon direction of rotation to give the more stable orthogonal state a doubly degenerate state is obtained. For the sake of illustration, the states are labeled $XXIc_1$ and $XXIc_2$.



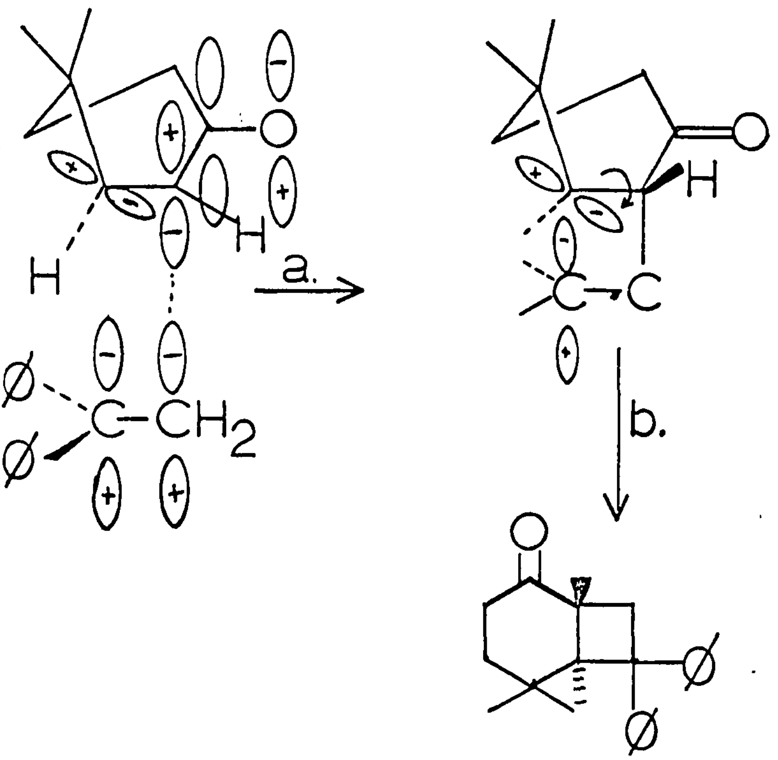
XXIb

$XXIc_1$

$XXIc_2$

Attack by 1,1-diphenylethylene on XXIc$_1$ must be from below the molecule due to steric interaction with the alkyl chain. The orbital symmetry approach developed by Hoffmann and Woodward (76) for cycloadditions is used as the framework for depicting the σ bond formation of the adduct. Thus, if diphenylethylene approaches XXIc$_1$ the following diagram shows the symmetry requirements.

XXIc$_1$



LXXXVIII

(7)

Similarly, approach of diphenylethylene to XXIc$_2$ must come from above the molecule in XXIc$_2$, leading to trans-adduct. Thus, the prediction of trans-stereochemistry in the cycloaddition is logically based on a consideration of orbital symmetries in the mechanism given for photo excitation of

XXI. The preferential orientation to give the 7,7-disubstituted product (LXXXVIII) is interpreted on the basis of α bond formation occurring prior to β bond formation due to the stereoelectronic factors in XXIc which preclude initial β bond formation. This imparts a partial radical character to the olefin which should be sensitive to the olefin substituents making α bond formation proceed to yield the most stable olefin radical prior to formation of the second double bond. Thus, the above scheme would predict <u>trans</u>-stereochemistry and 7,7-disubstitution as the major product path for photochemical cycloaddition to 2-cyclohexenones. This is in agreement with Corey's (39) investigations for most of the olefins which he studied. In contrast to Corey's hypothesis that triplet ketone is involved in cycloaddition, evidence that singlet XXI is responsible for cycloaddition has been presented in this work. Whether the cycloaddition is completely concerted or a two step 7a → 7b reaction cannot be determined at this time although this author feels that the preferential orientation of the product implies a prior formation of the α bond. Although there is a difference of opinion regarding multiplicity, the mechanism presented here is in agreement with Corey's (39) two step diradical mechanism and is an attempt to understand the cycloaddition from the viewpoint of the orbitals involved and not from the usage of dotted lines or induced bond polarizations.

The reason for absence of photochemical rearrangement of 2-cyclohexenone and 4-methyl-2-cyclohexenone may be understood in terms of the above mechanism. Production of an excited dipolar state analogous to XXId should occur with either 2-cyclohexenone or 4-methyl-2-cyclohexenone. However, the exothermic driving force for C_4-C_5 σ breakage in XXId (conversion of a secondary orthogonal carbonium ion to a tertiary carbonium ion) is absent in both 2-cyclohexenone (which would require conversion of a secondary orthogonal carbonium ion to a primary carbonium ion and is therefore endothermic) and 4-methyl-2-cyclohexenone (which would require conversion of a secondary orthogonal carbonium ion to another secondary carbonium ion and therefore be approximately isothermic). In considering the above energy relationships within the framework of the mechanism, the carbonium ion at C_3 is considered to be unconjugated, due to the orthogonality condition.

The above mechanism has been used to interpret the results of this work. It is consistent with either singlet or triplet intermediacy in the rearrangement, preferential breakage of the C_4-C_5 bond in XXI and rearrangement to give carbonium ion products and prediction of stereochemistry and orientation of the products of cycloaddition of XXI with 1,1-diphenylethylene.

Figure 28. Orbital energy and population diagram for intermediates in photoexcitation of XXI.

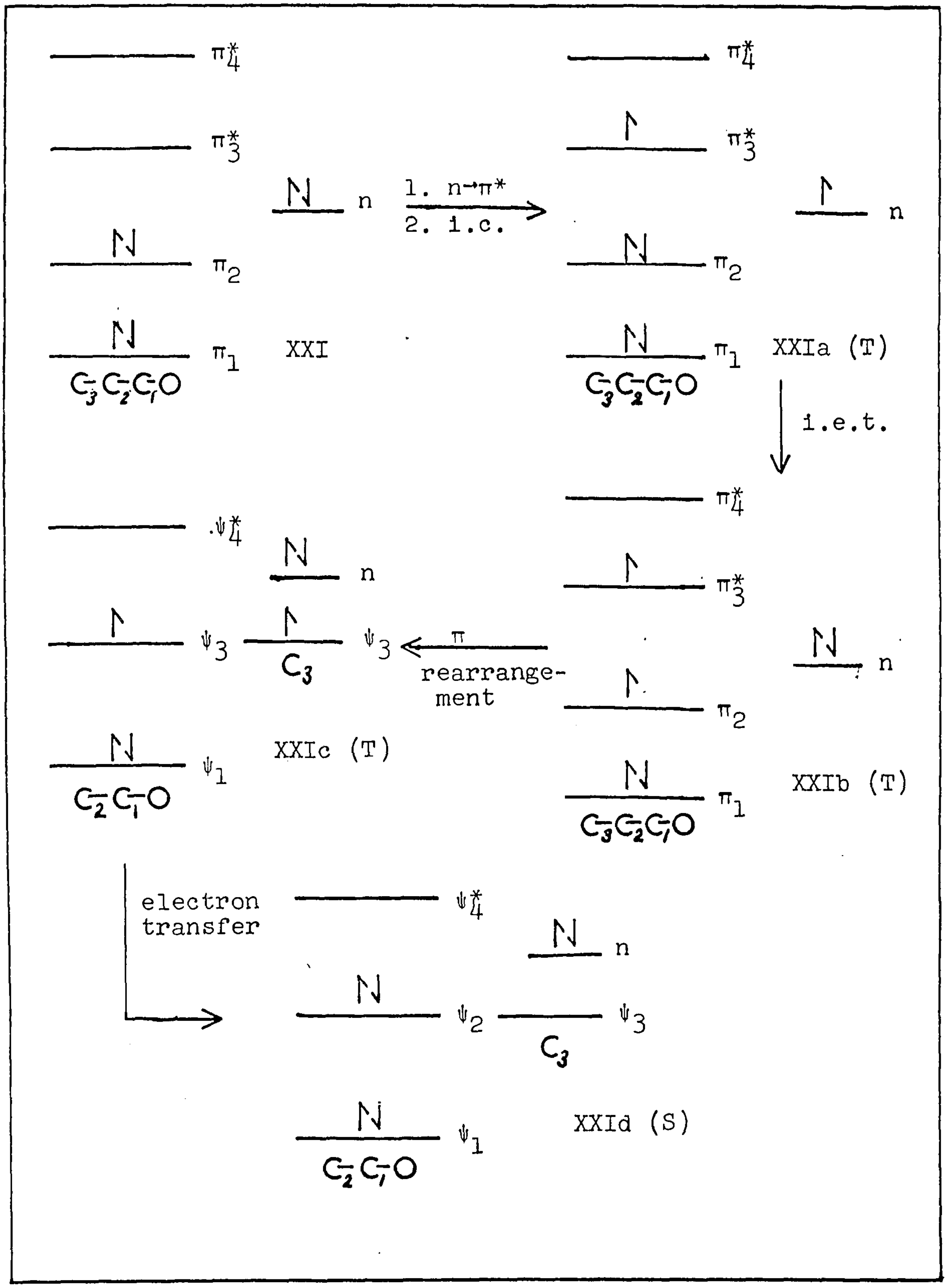
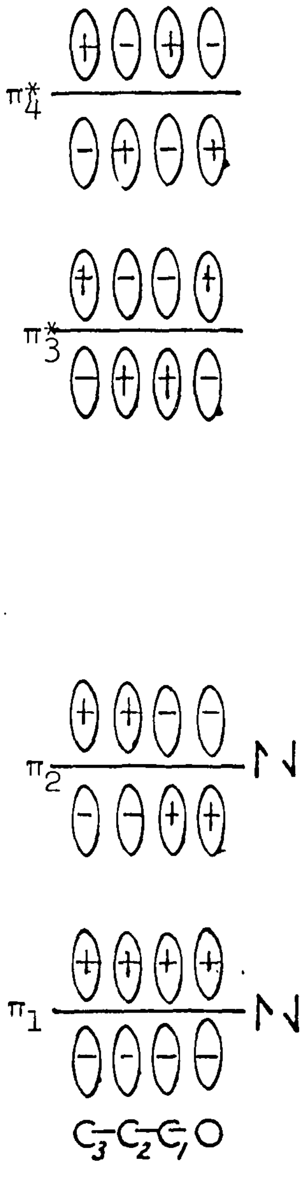
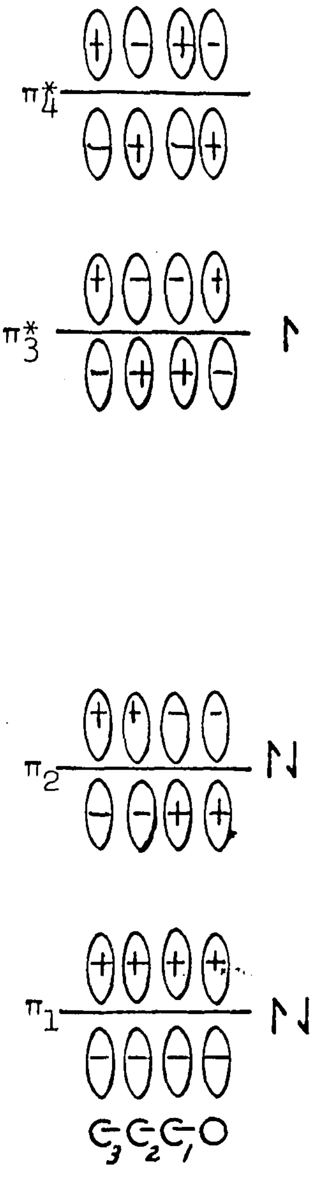

π*4
π*3
n
π2
π1
C3 C2 C1 O
XXI
1. n→π*
2. i.c.
XXIa (T)
i.e.t.
XXIb (T)
π
rearrange-ment
ψ*4
ψ3
C3
ψ1
C2 C1 O
XXIc (T)
electron transfer
ψ2
XXId (S)

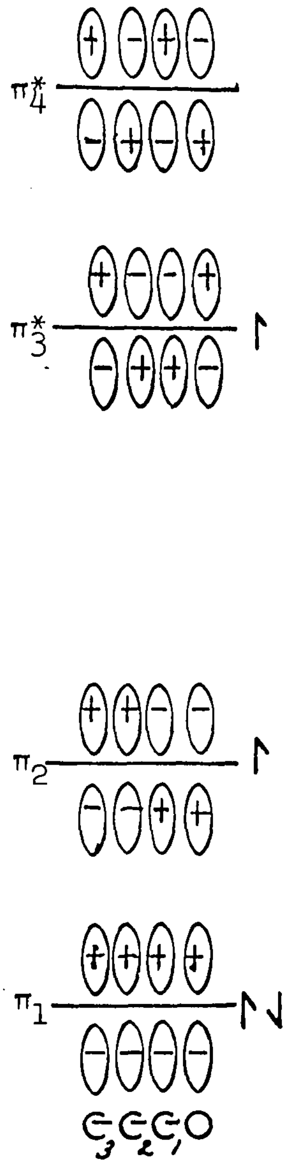
Figure 29. Orbital symmetry diagram for the excited states resulting from the excitation of XXI.



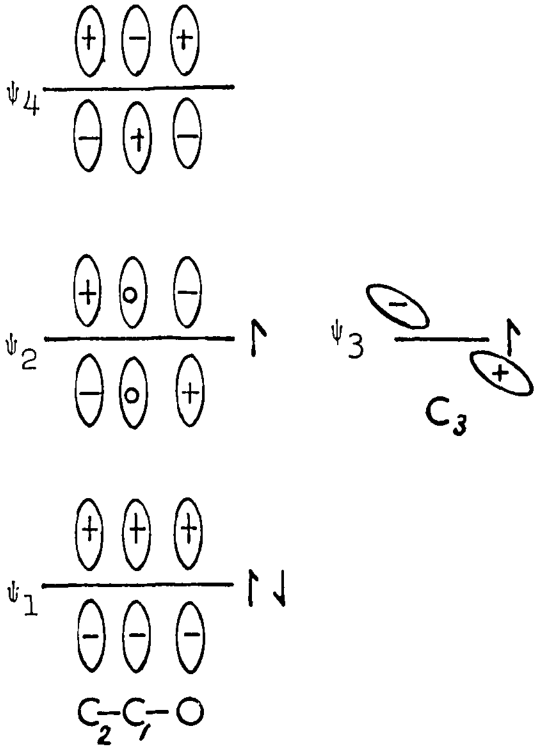
XXI



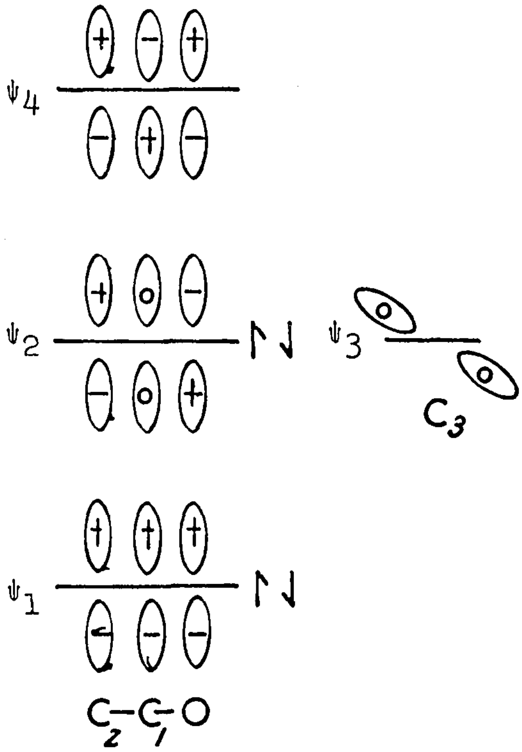
XXIa (T)



XXIb (T)



XXIc (T)



XXId

Figure 29 (Continued)

EXPERIMENTAL

Instruments and Methods

All melting points are uncorrected and were measured on a Kofler microscope hot stage equipped with a polarizer.

The ultraviolet spectra were obtained in 95% ethanol solution unless otherwise noted. The spectra were recorded on a Beckman Model DK-2A spectrophotometer made available by a grant (NSF-G14916) from the National Science Foundation.

All infrared spectra were recorded on a Perkin-Elmer Model 21 spectrometer.

The nuclear magnetic resonance spectra were measured on a Varian associates Model HR-60 or A-60 spectrometer operating at 60 Mc. Spectra obtained with the HR-60 spectrometer were calibrated by the side band technique using tetramethyl silane as internal standard. Chemical shifts are reported as δ-values in p.p.m.

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

The source of ultraviolet irradiation for all of the synthetic experiments was the 550 watt Hanovia Type A lamp. According to the manufacturer's specifications, the spectral output of this lamp is as follows(77).

Wavelength - mμ.	% of Total Emission
404.5-578	43
366.0	15
344.0	1
313.0	7
302.5	4
296.7	2
222.4-289.4	28

Experimental for the Photochemistry of 17α-Methyltestosterone

Irradiation of 17α-methyltestosterone (LX)

17α-methyltestosterone (LX, 4g., 0.013 m) was dissolved in tertiary butyl alcohol (2l.). The solution was irradiated in the apparatus shown in Figure 5. A pyrex well was used to filter out wavelengths below 300 mμ. A Hanovia Type A (550 watt) medium pressure mercury arc lamp was used. The water flow was maintained at a rate to prevent freezing of the solvent. The course of the irradiation was followed by vapor phase chromatography (v.p.c.) using a twelve foot, $\frac{3}{16}$in. column which was packed with 1% General Electric 5E-30 on acid washed chromosorb P (80-100 mesh). The irradiation was continued until approximately 75% of the starting material had been converted to photoproducts. Upon termination of the irradiation, the solvent was removed under reduced pressure with a rotary film evaporator. The light yellow gum was then pumped free of residual solvent with a vacuum pump.

Analysis by v.p.c. showed two major photoproducts to be present. All attempts to separate the crude mixture by adsorption chromatography (alumina, silica gel or silicic acid) were unsuccessful. It was found that one photoproduct could be separated by fractional crystallization. It was then possible to separate the other photoproduct from starting material by adsorption chromatography. The following is an example of the separation procedure.

The crude photoproduct mixture was dissolved in boiling benzene. The benzene was then evaporated until a fine white precipitate formed. The solution was allowed to stand at room temperature until crystallization was complete. The solution was filtered. The mother liquors were then evaporated again to half-volume and allowed to stand at room temperature. A second crop of crystals formed and was filtered off. The two crops were combined and recrystallized from pentane-benzene to give 1.4 g. (46%), m.p. 241.5-243°C. For the infrared spectrum see Figure 6, and for the n.m.r. spectrum see Figure 7. The optical rotation was $[\alpha]_D^{23} = 44.2^\circ$ ($CHCl_3$). This material showed $\lambda_{max}^{95\%\ ethanol}$ 210 mμ (5,923). The spectral data indicated that the compound, LXI, (10α-methyl-1β, 5β-cycloandrostan-17β-ol-2-one-17α-methyl) is exactly analogous to Griswold's (14) photo-testosterone acetate.

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.42 H, 10.00. Found: C, 79.60 H, 10.00.

The mother liquors from the above procedure were then evaporated under reduced pressure to dryness, yielding 2.4 g of a light yellow gum. This material was chromatographed on a 1.5 x 30 cm. column of Woelm grade III alumina which was prepared by the addition of 8 ml. of water to each 100 g. of Woelm grade I neutral alumina. The gum was dissolved in 1:1

Skelly B-benzene and pipetted onto the column. The elution was begun with 1 liter of 1:1 Skelly B-benzene. 1 liter of 70% benzene in Skelly B and then 1 liter of 90% benzene in Skelly B were eluted through the column. Continuation of the elution with 2 liters of neat benzene removed starting material and a slight amount of LXI. The weight of these combined fractions was 1.2 g. The elution was then continued with 10% ether in benzene. 1.1 g. (27.5%) of a crystalline substance was eluted. This material was recrystallized from ether-benzene to give a melting point of 140.5-142°C. Measurement of the optical rotation gave $[\alpha]_D^{23} = 52.3^\circ (CHCl_3)$. The infrared spectrum is shown in Figure 6 and the n.m.r. spectrum is shown in Figure 8. The ultraviolet spectrum showed $\lambda_{max}^{95\%\ ethanol}$ 232 mμ (18,737). The spectral data indicate this material to be analogous to Griswold's (14) lumi-testosterone acetate. Structure LXIII (3 α-3-keto-1-cyclopenten-1-yl)-3β, 5aβ-dimethyl-6α-hydroxy-6β-methyl-as-hydrindacene) was assigned to this compound.

Anal. Calcd. for $C_{20}H_{30}O_2$ C, 79.42 H, 10.00 Found: C, 79.28 H, 10.25.

3-Benzylidene-10α-methyl-1β, 5β-cycloandrostan-17β-01-2-one (LXVII)

LXVII (200 mg.) was dissolved in methanolic potassium hydroxide (20 ml., 1N). Freshly distilled benzaldehyde (1 ml.) was then added. The solution was refluxed under nitrogen for

12 hours. Water (50 ml.) was then added. The solution was cooled and extracted with three 50 ml. portions of ether. The combined ether extracts were then dried over magnesium sulfate. The ether was evaporated, leaving a solid which was recrystallized from absolute ethanol. A second recrystallization from absolute ethanol gave large prisms, m.p. 237.5-239°. The ultraviolet spectrum showed $\lambda_{max}^{95\% \text{ ethanol}}$ 224 mμ (8,764), 229 mμ (9,319), 299.5 mμ (24,911). The infrared spectrum (KBr) showed 5.96 μ (C=O) and 6.18 μ (C=C), in agreement with a benzylidene structure.

Anal. Calcd. for $C_{27}H_{34}O_2$ C, 83.00 H, 8.78. Found: C, 83.05 H, 8.80.

Irradiation of LXI in tertiary butyl alcohol

LXI (700 mg.) was dissolved in tertiary butyl alcohol (100 ml.) and irradiated with a medium pressure Hanovia type A lamp which was encased in a pyrex well. The course of the reaction was followed by g.p.c. analysis. During the irradiation, no peaks other than that of LXI were observed. After twenty hours, the irradiation was terminated. The solvent was evaporated under reduced pressure. An infrared spectrum ($CHCl_3$) of the residue was virtually identical to that of LXI, indicating no appreciable photochemical reaction.

Experimental for the Irradiation of 2-Cyclohexenone

Irradiation of 2-cyclohexenone (XLVII)

Freshly distilled 2-cyclohexenone (XLVII, 5 g., .052 m) was dissolved in two liters of tertiary butyl alcohol. The solution was then irradiated in the apparatus of Figure 5 using a pyrex well insert. The course of the irradiation was followed by periodic measurement of the ultraviolet spectrum of the solution. A 1 ml. aliquot was taken and diluted to 250 ml with 95% ethanol. The following data was obtained.

Time	Absorbance 226 mμ (λ_{max} of XLVII)
Initial	.96
18 hours	.57
29.5 hours	.49

The irradiation was terminated at 29.5 hours. The tertiary butyl alcohol was removed by distillation under reduced pressure. An n.m.r. spectrum of this oil showed the ratio of olefinic to alkyl protons to be approximately 1:17. The oil was then steam distilled in a semi-micro apparatus. Analysis of the steam volatile portion (1.8 g.) by i.r., n.m.r. and v.p.c. (6' 5% LAC-446 on 80-100 mesh Chromosorb P) showed only 2-cyclohexenone. An infrared spectrum (CCl_4) of the non-steam volatile fraction (2.3 g.) showed no definite peaks other than a 5.86 carbonyl band. All other absorption bands were broad and ill defined. Analysis by v.p.c. showed only a trace of 2-cyclohexenone and no other volatile compounds.

Experimental for the Irradiation of 4-Methyl-2-Cyclohexenone

Synthesis of 4-methyl-2-cyclohexenone (LXXVI)

1-Piperidinopropene was synthesized by the procedure of Mannich and Davidsen (78). The enamine (b.p. 52-55°/ 10 mm.) was distilled immediately before use. Methyl vinyl ketone was distilled immediately before use.

1-Piperidinopropene (203 g., 1.62 m) was placed in a 2 liter 3 neck round bottom flask which was equipped with a nitrogen inlet tube, a dropping funnel, a magnetic stirrer and a reflux condenser. A nitrogen atmosphere was maintained during the entire preparation. Methyl vinyl ketone (125 g., 1.78 m) was added dropwise with stirring. Upon completion of the addition, the ice bath was removed and the reaction mixture stirred for 48 hours at room temperature. Hydrochloric acid (1.5 l., 15% by volume) was then added, the solution was stirred for an additional 24 hours at room temperature. During this period an organic layer separated. The stirring was stopped, and the solution extracted with five 500 ml portions of ether. The combined ether fractions were washed successively with 5% sodium bicarbonate and water, then dried with magnesium sulfate.

The ether was removed under reduced pressure with a rotary film evaporator. V.p.c. analysis of the residual liquid (85 g.) showed a 75:25 mixture. An n.m.r. spectrum indicated that the mixture was an approximately 3:1 α,β to β,γ isomer mixture. The mixture was separated by careful distillation through a 1 meter spinning band column, taking fractions of about 2 g. each. 25 g. (14%) of pure 4-methyl cyclohexenone (LXXVI) (b.p. 76°/24mm) was obtained. Further separation of the intermediate fractions (total weight 53 g.) was not attempted. The infrared spectrum (CCl_4) of LXXVI showed a 5.94 μ carbonyl absorption. The n.m.r. spectrum shows a methyl appearing as a doublet (J = 7 cps) at 1.15 δ, a broad highly split alkyl absorption spread from 1.4 to 2.9 δ. The α olefinic proton appeared at 5.81 δ as a doublet ($J\alpha\beta$ = 10 c.p.s.), each line of which was split into a doublet ($J \cong 3$ c.p.s.). The β olefinic proton appeared at 6.78 δ as a doublet ($J\alpha\beta$ = 10 cps), each line of which was split into a doublet of doublets, making a total of eight lines for the β proton. The smaller coupling constants of the β proton could not be measured accurately from the spectrum.

Irradiation of 4-methyl-2-cyclohexenone (LXXVI)

LXXVI (4.0 g., .036 m) was dissolved in 1.8 liters of tertiary butyl alcohol. The solution was irradiated in the apparatus of Figure 5 using a pyrex well insert. The course of the reaction was followed by periodically measuring the ultraviolet absorption spectrum of the solution. The following data was obtained.

Time	Absorbance ($\lambda_{max}^{95\%\ ethanol}$ = 226 mμ)
Initial	.792
6.5 hours	.665
19.5 hours	.468
24.5 hours	.428

Analysis by v.p.c.(6 ft. 2.5% LAC-446 on 60-80 mesh chromosorb P) indicated that 50% of the starting material had been destroyed. No other peak appeared on the v.p.c., indicating that only non volatile dimeric or polymeric materials were formed. The tertiary butyl alcohol was stripped off under reduced pressure. The light orange oil was steam distilled to give 1.5 g. of a steam volatile fraction which was shown by i.r., n.m.r. and v.p.c. comparisons to be essentially pure LXXVI. After isolation with ether, the non-steam volatile fraction (2.2 g.) showed only a broad 5.86 μ carbonyl band. The rest of the spectrum had very little definition. The non-steam volatile fraction, a thick red gummy oil, did not come through the v.p.c., indicating the absence of low molecular weight compounds.

Experimental for the Irradiation of 2,4,4-Trimethyl-2-Cyclohexenone

Synthesis of 2,4,4-trimethyl-2-cyclohexenone (LXXVII)

1-Piperidino-2-methylpropene was prepared from isobutyraldehyde and piperidine by the Dean-Stark water removal method (50). The eneamine (b.p. 48-50°/18 mm) was redistilled immediately before use. Ethyl vinyl ketone (Aldrich Chemical Company E5130) was distilled immediately before use.

1-Piperidino-2-methylpropene (37.5 g., .270 m) was placed in a 500 ml. 3 neck round bottom flask which was fitted with a magnetic stirring bar, a nitrogen inlet tube, a dropping funnel and a reflux condenser. The flask was placed in an ice bath and maintained at 0-5°. A nitrogen atmosphere was maintained during the reaction. Ethyl vinyl ketone (25.0 g., .297 m.) was added dropwise with stirring. Upon completion of the addition, the reaction mixture was stirred for 36 hours of room temperature. Hydrochloric acid (400 ml., 15% by volume) was then added all at once, and the reaction was stirred at room temperature for 36 hours. At the end of this time, the reaction mixture was heated on the steam bath for fifteen minutes, cooled to room temperature and then extracted with three 250 ml portions of ether. The combined ether fractions were washed successively with 5% sodium bicarbonate and water and dried over sodium sulfate. The ether was removed by distillation. The light yellow residue was then distilled to give one fraction, b.p. 80-81°/10 mm. The yield was 21.4 g (54%). V.p.c. analysis (6 ft. 2.5% LAC-446 on 80-100 mesh chromosorb P) showed only one peak. The n.m.r. spectrum showed two methyl groups appearing as a singlet at 1.15 δ, a methyl group as a doublet

(J = 1.3 cps) at 1.65 δ, an A_2B_2 portion of an A_2B_2X system was centered at 2.1 δ, and the olefinic proton appeared as a complex multiplet at 6.33 δ. The olefinic proton is the X portion of the A_2B_2X system due to small cross ring coupling. The infrared spectrum (CCl_4) showed a 5.96 carbonyl absorption. The mass spectrum showed the molecular ion to be at mass 138, the ratio of $\frac{M}{M+1}$ was .9040.

Irradiation of 2,4,4-trimethyl-2-cyclohexenone (LXXVII)

LXXVII (2.0 g. .0145 m) was dissolved in tertiary butyl alcohol (750 ml.) and irradiated with a 550 watt mercury arc lamp in the apparatus of Figure 5. The course of the reaction was followed by v.p.c. (6 ft. 5% LAC-446 on 80-100 mesh chromosorb P). No change in concentration of LXXVII could be measured by v.p.c. during the irradiation. The v.p.c. showed no peaks other than LXXVII during the time of the irradiation. The reaction was stopped after twenty-four hours. The solvent was removed by distillation under reduced pressure. The light yellow residue (1.92 g.) was analyzed by n.m.r., v.p.c. and i.r. and was found to contain only pure unreacted starting material. The entire fraction was steam volatile.

Deuteration of LXXVII

LXXVII (5.0 g.,.036 m.) was dissolved in a solution of dueterium oxide (3 ml., > 99.5% D_2O) and deuterio-methanol (3 ml., > 97% CH_3OD). Potassium carbonate (100 mg.) was added to the solution. The solution was heated at reflux for 12 hours. The solution was then cooled. Deuterium oxide (10 ml.) was added, causing an emulsion to form. The mixture was extracted with three 10 ml portions of ether. The ether extracts were dried over magnesium sulfate. The ether was then evaporated by distillation under reduced pressure. The residue was subjected to two more exchanges by the above procedure and was distilled (b.p. 90°/14 mm.) to give 4 g (80%) of deuterated material. An n.m.r. spectrum showed the C-4 methyl absorption as a 6 proton singlet at 1.12 δ, the olefinic methyl as a doublet (J = 1.3 cps), the C-5 protons as a broad singlet at 1.81 δ and the olefinic proton as a multiplet at 6.48 δ. The n.m.r. indicated nearly complete exchange of the C-6 protons.

Analysis of the mass spectrum at 11 e.v. showed the following mass ratios:

$$\left(\frac{138}{140} = \frac{.0033}{.8540},\ \frac{139}{140} = \frac{.0453}{.8540},\ \frac{141}{140} = .0940\right)$$

corresponding to 0.39% nondeuterated material and 5.3% monodeuterated material after correcting for carbon-13 isotope contributions. Thus the above deuteration yields 6,6 dideutero-2,4,4-trimethyl-2-cyclohexenone (LXXX) in 94% isotopic purity.

Irradiation of 6,6-dideuterio-2,4,4-trimethyl-2-cyclohexenone (LXXX) in deuterio-tertiary butyl alcohol

A solution containing 8.4 mg/ml. of LXXX in deuterio-tertiary butyl alcohol was prepared. A solution containing

8.5 mg/ml of (LXXVII) in deutero-tertiary-butyl alcohol was prepared. The deuterio-tertiary-butyl alcohol was shown by n.m.r. to contain 0.97 atom of deuterium per mole of alcohol. The solutions were irradiated in duplicate in 1 cm. u.v. cells which were placed at a distance of 7.5 cm from the lamp housing in the apparatus shown in Figure 14. The cells were rotated around the lamp during the 48 hour irradiation. At the end of the irradiation, each solution was transferred to a 25 ml 14/20 pear shaped flask. The deuterio-tertiary butyl alcohol was removed by distillation under reduced pressure. The residue of each flask was then analyzed by mass spectrometry. The average $\frac{141}{140}$ peak ratio for the irradiated deuterated material was .0975. The average $\frac{139}{138}$ peak ratio for the irradiated undeuterated material was .0985. These ratios correspond to .35% deuterium incorporation for LXXX and .44% deuterium incorporation for LXXVII. The isotope ratios were measured at 11 e.v. to minimize M-1 fragmentation.

Experimental for the Photochemistry of 4-Methyl-4-Phenyl-2-Cyclohexenone

Synthesis of 4-methyl-4-phenyl-2-cyclohexenone (LXVIII)

An approximately 40% aqueous solution of triton B was prepared by the method of Zimmerman and Schuster (33).

Freshly distilled hydratropaldehyde (b.p. 45°/.3 mm, 134 g., 1.0 m.) and methyl vinyl ketone (77 g., 1.1 m.) were dissolved in 650 ml tertiary butyl alcohol. This solution was placed in a 2 liter 3 neck 24/40 round bottom flask which was cooled in an ice bath. The flask was equipped with a mechanical stirrer and a 250 ml dropping funnel. 165 ml of the aqueous Triton B was then added dropwise with rapid stirring. The temperature of the reaction mixture was not allowed to exceed 20°C during the addition. After all of the base was added (about 6 hours) the solution was stirred for ½ hour in the ice bath and then for ½ hour at room temperature. Ice (200 g.) was then added to the reaction mixture. When the ice had melted, the reaction mixture was extracted with three 100 ml portions of ether. The combined ether layers were washed with two 50 ml portions of water and then dried over sodium sulfate. The ether was removed by evaporation in a rotary film evaporator leaving a dark reddish orange oil. This oil was distilled at .25 mm pressure. After a slight forerun (b.p. 38-65°), 83.10 g. (45%, b.p. 125-128°) of 4-methyl-4-phenyl-2-cyclohexenone was obtained. The infrared spectrum is shown in Figure 11. The n.m.r. spectrum is shown in Figure 12.

Irradiation of 4-methyl-4-phenyl-2-cyclohexenone (LXVIII)

LXVIII (4.0 g.) was dissolved in tertiary butyl alcohol (1.7 l.) and irradiated in the apparatus shown in Figure 5. The irradiation was followed by periodic measurement of the ultraviolet spectrum of a series of aliquots which were taken from the reaction vessel. The following data was obtained:

Irradiation Time	A-222 mμ	A-215 mμ	A-280 mμ
0 hours	.557	.590	.02
23	.415	.450	.205
35	.390	.430	.259
47	.414	.410	.263

The irradiation was terminated after 47 hours, at which time the absorbance (A) came to a constant value. The solvent was removed by distillation under reduced pressure, leaving a bright yellow oil (3.96 g.). An n.m.r. spectrum of this oil showed a decrease in the AB quartet of the starting material relative to the phenyl absorption, and a new sharp singlet appearing at 6.12 δ. An infrared spectrum (CCl_4) of the crude product showed two new carbonyl peaks, an intense absorption at 5.99 μ and a lesser absorption at 5.81 μ.

The crude mixture was separated by gas chromatography (6 ft 15% LAC-446 on 80-12- mesh chromosorb P). 3 peaks besides starting material eluted from the column. The relative area and retention time of each peak is shown below

Peak	Area - %	Retention Time - 165°C
1	12	11.5 minutes
2	35	17 minutes
3	10	18 minutes (shoulder on peak 2)
4	43	22 minutes

Each peak was collected in a preparative scale separation. 50 ul injections were made at 160° (6 ft. 15% LAC-446 on 80-120 mesh chromosorb P). The effluent fractions were trapped in a U-tube which was immersed in an ice bath. Peak 2 was shown to be identical to starting material (LXVIII) by n.m.r., i.r. and g.p.c. retention time.

The n.m.r. spectrum of the fraction corresponding to peak 4 is shown in Figure 10. The infrared spectrum is shown in Figure 11. The 5.99 μ carbonyl absorption (CCl_4) accounts for one of the new peaks in the crude irradiation mixture. A 2,4-dinitrophenyl hydrazone was prepared in the usual way. The derivative was recrystallized from ethyl acetate to give plum red crystals, m.p. 187.5-188.5°C. The ultraviolet spectrum showed $\lambda_{max}^{95\%\text{ ethanol}}$ 392 mμ (30,452), 297.5 mμ (11,425), 257.5 mμ (14,093) and 233 mμ (17,415). The infrared spectrum of the 2,4 DNP derivative showed a 6.20 (C=N) and a 6.30 μ (C=C) absorption.

Anal. Calcd. for $C_{19}H_{17}N_4O_4$: C, 62.28; H, 4.95 Found: C, 62.06; H, 4.86.

Comparison of the physical constants of this material and its derivative with that of an authentic sample of 4-methyl-3-phenyl-2-cyclohexenone as synthesized below offers unequivocal proof of the identity of the two compounds.

Synthesis of 4-methyl-3-phenyl-2-cyclohexenone (LXIX)

LXIX was synthesized by the method of Novello *et al.* (46). The n.m.r. and i.r. spectra of this material were identical to those of peak 4, shown in Figures 10 and 11 respectively. A 2,4 dinitrophenylhydrazone was prepared in the usual manner to give dark plum purple crystals, m.p. 187-188.5°. The infrared and u.v. spectra of this derivative were identical to that of the 2,4 dinitrophenylhydrazone of peak 4. A mixed melting point of the two derivatives gave no depression.

Peak 1 was collected from the g.p.c. in very poor yield. The infrared spectrum (CCl_4) showed a 5.81 μ carbonyl absorption. The n.m.r. spectrum showed a singlet at 1.46 δ and lines at 1.86, 2.01, 2.52 and 2.67 δ. Diffuse absorption between 1.1 and 1.6 δ could hardly be distinguished from the baseline noise. A singlet appeared at 7.2 δ. The spectrum integrated poorly due to the small amount of material. An attempt was made to prepare a 2,4 dinitrophenylhydrazone of this material. After separation from unreacted 2,4 dinitrophenylhydrazine on a bentonite-kieselguhr column, only a very small amount of semi-solid material remained. This crude material showed $\lambda_{max}^{95\%\ ethanol}$ 366 mμ. The nature of this material was not examined further.

Peak 3 was isolated by careful v.p.c. chromatography. Since this peak was a shoulder on the starting material peak, less of the crude reaction mixture was injected to improve the separation. The amount of isolated material was very small. The infrared spectrum showed a 5.81 μ carbonyl absorption, and a 5.93 μ carbonyl absorption which was due to starting material. It was not possible to obtain peak 3 in pure form. The n.m.r. of this fraction showed sharp singlets at 1.13 and 1.38 δ. Other absorption was spread from 1.5 to 2.5 δ. The aromatic absorption appeared at 7.2 δ. This material was not investigated further.

Irradiation of 4-methyl-4-phenyl-2-cyclohexenone (LXVII) in deuterio-tertiary butyl alcohol

LXVII (300 mg.) was dissolved in deuterio-tertiary butyl alcohol (80 ml., >0.97 atom D/mole). The solution was irradiated for 12 hours in an apparatus shown in Figure 5. The apparatus was fitted with a drying tube to prevent entry of moisture. The solvent was removed by distillation at reduced pressure, leaving 295 mg of a light yellow oil. The n.m.r. of the crude product showed the area of the olefinic singlet at 6.12 δ (olefinic proton of LXIX) to be equal to the area of the tertiary hydrogen in the 4 position of LXIX which appears as a multiplet centered at 3.22 δ.

Experimental for the Photochemistry of 1-Benzoylcyclohexene

Synthesis of 1-benzoylcyclohexene (LXXI)

LXXI (b.p. 119°/.3 mm, m.p. 31-32°) was prepared from benzonitrile by the method of House *et al*. (48). For the n.m.r. spectrum, see Figure 7, and for the i.r. spectrum see Figure 13.

Irradiation of LXXI in tertiary butyl alcohol

LXXI (5.0 g., .027 m.) was dissolved in tertiary butyl alcohol (1.7 l.) and irradiated in the apparatus shown in Figure 5. The course of the reaction was followed by measuring the ultraviolet spectrum of the solution during the irradiation. The change in the ultraviolet spectrum at the λ_{max} of LXXI (244 mμ) was negligible after six hours. A new peak appeared at 285 mμ and did not grow appreciably after six hours. The irradiation was terminated after 11 hours. The following u.v. data was obtained.

Irradiation Time	A-243 mμ	A-287 mμ
0	.69	.05
3 hours	.59	.11
6 hours	.535	.109
11 hours	.505	.113

The solvent was removed by distillation at reduced pressure, leaving a dark yellow oil (4.9 g., 95%). An infrared spectrum (CCl_4) showed no carbonyl absorption at

6.06 μ, indicating nearly complete destruction of LXXI. A new, broad carbonyl absorption at 5.86 μ was observed in the crude material. 2.0 g. of this crude oil was then molecularly distilled. The first fraction (b.p. 118-127°/ .7 mm) showed a 5.85 μ carbonyl absorption (cap. cell) and a 6.21 μ aromatic double bond absorption. The second fraction (b.p. 133-165°C) showed an identical infrared spectrum. The combined weight of the two fractions was 0.9 g. (45%), the pot contained the balance as a dark brown polymer. An n.m.r. spectrum of the lower boiling molecular distillation fraction is shown in Figure 12. The ultraviolet spectrum of the lower boiling oil showed $\lambda_{max}^{95\%\ ethanol}$ 244.5 mμ (10,737) and 290.5 mμ (2,163).

A 2,4-dinitrophenylhydrazone was prepared as follows. 2,4-Dinitrophenylhydrazine (53 mg.) was dissolved in a hot solution of methanol (5 ml.) and hydrochloric acid (.1 ml., 6N). 80 mg. of the high boiling fraction was added. The solution was heated 5 minutes on the steam bath. Crystallization began during this time. The crystals were isolated and recrystallized twice from ethyl acetate to give m.p. 189.5-190.5°.

An n.m.r. of the dnp derivative showed a broad absorption (8H) from 1.0 to 2.2 δ, a broad absorption (2H) centered at 3.4 δ, a fairly sharp absorption (4H) at 7.3 δ, and the typical aromatic and N-H absorption of the 2,4 dinitrophenylhydrazine moiety (4H), all below 7.5 δ. An infrared spectrum (KBr) showed a 6.17 μ (C=N) absorption and 6.27 (C=C) absorption.

Anal. Calcd. for $C_{19}H_{18}N_4O_4$: C, 62.28 H, 4.95 Found: C, 62.17 H, 4.66.

In another experiment, LXXI (800 mg.) was irradiated in tertiary butyl alcohol (750 ml.). The reaction was terminated after one hour and twenty minutes and worked up in the usual manner. The yellow oil was then dissolved in carbon tetrachloride and towered through a 30 x 1cm Florisil column and collected in 50 ml fractions. The first two fractions, (603 mg, 75%) were found to be completely free of starting material since the 6.06 μ band was absent. The balance of the material (130 mg) was mainly starting material. A portion of the first two fractions was purified further by thin layer chromatography on a silica gel G plate. The elution system was a solution of 10% carbon tetrachloride in benzene. The portion of the layer containing the yellow spot after elution up the plate was removed with a razor blade and washed with ether. The ether was removed with the rota-vac to leave a bright yellow oil. The infrared spectrum (CCl_4) is shown in Figure 13, and is virtually identical to that of the photoproduct obtained above by molecular distillation.

Synthesis of cis-hexahydrofluorenone (LXXIII)

LXXIII (m.p. 40-42°) was prepared by the method of House et al. (48). An n.m.r. spectrum of this material was virtually identical to that of Figure 12. An i.r. spectrum (CCl_4) showed a 5.83 μ carbonyl absorption. The ultraviolet spectrum showed $\lambda_{max}^{95\%\ ethanol}$ 245 mμ (11,500) and 291 mμ (2,240). Each of the above physical constants is in good agreement with those of House et al. (48). A 2,4 dinitrophenylhydrazone (m.p. 189-190° from ethyl acetate) of the authentic LXXIII showed no depression of melting point when mixed with the 2,4 dinitrophenylhydrazone of the photoproduct of LXXI.

Deuterium exchange of authentic LXXIII

400 mg. of the crude ketone from the above synthesis was refluxed for $1\frac{1}{2}$ hours with deuterium oxide (5 ml.) and potassium carbonate (100 mg.). The cooled reaction mixture was poured into D_2O (5 ml.) and then extracted with three 5 ml portions of ether. The combined ether fractions were dried over sodium sulfate. The ether was removed with a rota-vac, leaving a yellow oil. An n.m.r. spectrum of the crude oil showed the multiplet (see Figure 12) centered at 2.6 δ to be absent, indicating that this multiplet is the proton α to the carbonyl group in LXXIII. The multiplet centered at 3.3 δ was simplified into a poorly resolved triplet, indicating that this proton is β to the carbonyl group and benzylic.

Measurement of the quantum yield for the conversion of LXXI to LXXIII

A benzene solution .10 M in benzophenone (m.p. 47-48°) and .10 M in benzhydrol (m.p. 68°) was prepared. A .10 M solution of LXXI in tertiary butyl alcohol was prepared. The solutions were irradiated in 30 x 1.8 mm pyrex tubes in the apparatus shown in Figure 14. The lamp was jacketed with a 2 cm layer of a saturated copper sulfate solution. The tubes were irradiated simultaneously in triplicate at a distance of 5½ inches from the lamp. The tubes were rotated around the lamp during the 60.02 minute irradiation. Each solution was degassed by bubbling nitrogen through the solution for five minutes.

The absorbance of the initial benzene-benzophenone solution and the three irradiated benzene-benzophenone solutions was measured by taking a 1 ml aliquot and diluting to 25 ml with benzene. The absorbance was measured at 332 mμ, the wavelength maximum of benzophenone. The following data was obtained.

Tube	Initial Absorbance (A_i)	Absorbance after Irradiation (A_f)
1	.723	.625
2	.723	.615
3	.723	.611

The average final absorbance was .617. The percent destruction of benzophenone was calculated as follows:

$$\% \text{ Destruction} = \frac{A_i - A_f}{A_i} = \frac{.106}{.723} = 14.7$$

The percent destruction of LXXI was measured by an n.m.r. integral analysis technique. The Varian HR-60 spectrometer was used for this measurement.[1] The n.m.r. spectrum of each solution was measured directly in the tertiary butyl alcohol solution. The ratio of the olefinic (O) to aromatic (A) peak areas was obtained by taking the average of four integrals which were taken by alternate up- and down-field sweeps over the olefinic and aromatic area. The following results were obtained.

Tube	O/A initial	O/A after irradiation
A	.182	.165
B	.182	.167
C	.182	.169

The average O/A ratio after irradiation was .167.

Experimental for the Photochemistry of 4,4-Dimethyl-2-Cyclohexenone

Synthesis of 4,4-dimethyl-2-cyclohexenone (XXI)

The piperidine enamine of isobutyraldehyde was prepared by the Dean-Stark water separation method (50). The enamine was redistilled (b.p. 60°/8 mm.) just before use.

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[1] The author is indebted to Mr. R. L. Thrift for his careful determination of the n.m.r. integrals.

Isobutyraldehyde piperidine enamine (250 g., 1.8 m.) was placed in a 3 l. 3 neck 24/40 round bottom flask which was equipped with a magnetic stirrer, a 250 ml. addition funnel and a nitrogen inlet tube. The flask was placed in an ice bath, and the contents maintained at 0-5° during the dropwise addition of freshly distilled methyl vinyl ketone (143 g., 1.98 m.). The solution was stirred rapidly during the addition, and a nitrogen atmosphere was maintained. At the end of the addition, the ice bath was removed, and the stirring was continued for 29 hours at room temperature. Hydrochloric acid (2.5 l., 15% by volume) was then added, and the reaction mixture was stirred for 48 hours at room temperature. The yellow solution was then heated for one hour on the steam bath and allowed to cool gradually to room temperature. A dark brown layer separated during the heating period. The solution was extracted with four 500 ml. portions of ether. The combined ether extracts were washed with three 100 ml. portions of 5% sodium bicarbonate and then with water. The ether layer was dried over sodium sulfate. The ether was distilled at reduced pressure. Distillation through a one meter spinning band column yielded 112 gm. (45%) XXI, b.p. 76°/21 mm. The n.m.r. spectrum is shown in Figure 15 and the i.r. spectrum in Figure 18. The ultraviolet spectrum showed $\lambda_{max}^{95\%\ ethanol}$ 224 mμ (ϵ = 15,600) and 318 mμ (ϵ = 34.5). The ultraviolet spectrum is in agreement with that reported by Bordwell (79) for XXI ($\lambda_{max}^{95\%}$ ethanol 224 mμ, ε = 16,000).

Irradiation of 4,4-dimethyl-2-cyclohexenone (XXI) in tertiary butyl alcohol

XXI (2.5 g., .02 m.) was dissolved in tertiary butyl alcohol (1.8 l.). The solution was irradiated in the apparatus shown in Figure 5. The course of the reaction was followed by periodically taking an aliquot, diluting it appropriately, and measuring the ultraviolet spectrum. The following data was obtained.

Irradiation time (hr.)	Absorbance (224 mμ)
0	0.73
24	0.63
49	0.49
68	0.38
82	0.32

The irradiation was terminated after 82 hours. The tertiary butyl alcohol was removed by distillation at reduced pressure, leaving 2.5 g. of a dark yellow oil. Analysis of this oil by v.p.c. (6 ft. LAC-446, $\frac{1}{4}$ in., 5% on 80-100 mesh chromosorb P) at 135° showed XXI and two new compounds to be present. The retention times at 122° are as follows: XXI - 5.2 minutes, compound 1 6.7 minutes and compound 2 11.6 minutes. The relative areas of each peak were measured by polar planimetry and found to be XXI - 22%, peak 1 - 32% and peak 2 - 46%.

Compound 1 was isolated by preparative scale gas chromatography. The spectral data indicated that this material was identical to that postulated (20) to be 6,6-dimethylbicyclo [3.1.0.] hexan-2-one (XXII). The n.m.r. spectrum is shown in Figure 16 and the i.r. spectrum is shown in Figure 18. The ultraviolet spectrum showed $\lambda_{max}^{95\%\ ethanol}$ 207 mμ (ε = 5,122) and 281.5 mμ (ε = 32.5). The near infrared spectrum (.5% solution in CCl_4, degassed with nitrogen) shows absorption at 1.673 μ (first overtone of the cyclopropane C-H stretching vibration).

Compound 2 was isolated by preparative scale gas chromatography. The spectral data indicated that this material was identical to that postulated (20) to be 3-isopropyl-2-cyclopentenone (XXII). The n.m.r. spectrum is shown in Figure 15 and the i.r. spectrum is shown in Figure 18. The ultraviolet spectrum showed $\lambda_{max}^{95\%\ ethanol}$ 227.5 mμ (ε = 12,730) and 303 mμ (ε = 50.82).

Test of stability of XXII and XXIII in the gas chromatograph

A pure sample of XXII was injected into the v.p.c. (6 ft. LAC-446, 10% on 80-100 mesh chromosorb P, 125°). Only XXII was eluted. This compound was collected and showed spectral properties (n.m.r. and i.r.) identical to those of the initial sample. Exactly analogous results were obtained with XXIII, demonstrating that the products are in fact not thermally interconvertible. 4,4-dimethyl-2-cyclohexenone (XXI) was also stable in the gas chromatograph under the same conditions as above.

Preparative scale irradiation of 4,4-dimethyl-2-cyclohexenone (XXI)

XXI (10 g., .08 m.) in tertiary butyl alcohol (1.7 l.) was irradiated for 60 hours in the apparatus shown in Figure 5. The solvent was removed by distillation at reduced pressure leaving a yellow oil. This procedure was repeated five times. The non-volatile yellow residues were combined (48 g.) and steam distilled to give 31 g. (62%) of a colorless liquid. The dark brown non-volatile fraction (16 g.) was isolated from the distillation pot liquor. An infrared spectrum (CCl_4) showed a broad carbonyl absorption from 5.75-5.90 μ and very little other detail. This material was not investigated further. Analysis of the steam volatile fraction showed XXI (40%), XXII (26%) and XXIII (34%) to be present. The areas were measured with an Ott planimeter.

The steam volatile fraction was distilled (21 mm.) through a 1 m. spinning band column. Fractions were cut when about 0.5 gm. had distilled. The fractions were analyzed by v.p.c. A forerun (14.5 g., b.p. 74-79°/21 mm.) was mainly XXI with some XXII. Several fractions (3.8 g., b.p. 79-81°/21 mm.) were found to be pure XXII. The next fractions (3 g., b.p. 81-86°/21 mm.) were a mixture of XXII and XXIII. Several succeeding fractions (4.5 g., b.p. 86-88°/21 mm.) were then obtained which were pure XXIII. The pot then became dark yellow and yielded no more volatile material.

Thus, the isolated yield of XXII is 7.6% and of XXIII is 9%.

Preparation of the mono-benzlidene derivative of 6,6-dimethylbicyclo [3.1.0.] hexan-2-one (XXII)

XXII (100 mg., 0.806 mm.) was dissolved in 95% ethanol (2 ml.). Freshly distilled benzaldehyde (205 mg., 1.95 mm.) was added. Sodium hydroxide (81 mg.) in water (1 ml.) was added. The mixture was stirred at room temperature for 2 hours. The mixture was then heated to 50° in a water bath and stirred for 6 hours. The water bath was removed, and the solution was allowed to stand overnight at room temperature. The solution was then neutralized to pH 7 with hydrochloric acid (1 N). A yellow precipitate formed after the neutralization. The precipitate was filtered. The crude light yellow solid was dissolved in Skelly B and towered through a neutral alumina column (5.0 x 1.2 cm.). A small amount of benzaldehyde was eluted with Skelly B (15 ml.). Elution with Skelly B-benzene (1:1) gave a light yellow oil which was taken up in methanol and allowed to crystallize. After two recrystallizations from methanol, fine yellow needles (m.p. $97\text{-}98^{\circ}\mathrm{C}$) were obtained. For the infrared spectrum see Figure 19 and for the n.m.r. spectrum see Figure 17. The ultraviolet spectrum showed $\lambda_{max}^{95\%\ \mathrm{ethanol}}$ 300.5 mμ ($\epsilon = 11{,}800$) and 230.5 mμ (4,090).

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.86 H, 7.60 Found: C, 84.82 H, 7.83.

Synthesis of 3-chlorocyclopentene

Cyclopentadiene monomer (60 g., .091 m.) was placed in a 2 l. 24/40 3 neck round bottom flask which was equipped with a drying tube and gas inlet tube. The inlet tube was adjusted to protrude below the surface of the solution. The flask was maintained at Dry Ice-acetone temperature by external cooling. Gaseous hydrogen chloride was bubbled into the flask at a rapid rate until a definite yellow color developed. The addition was then terminated and nitrogen gas was bubbled through the solution at a rapid rate for 15 minutes. The contents of the flask were then transferred to a 1 l. round bottom flask. The flask was connected to the rotary film evaporator at full aspirator vacuum until the solution turned purple (~ 1 hour). This material was then used immediately without further purification in the next step.

Synthesis of 3-isopropyl cyclopentene

A 1 l. 3 neck flask was equipped with a stirrer, dropping funnel, reflux condenser, drying tube and nitrogen inlet. The apparatus was flame-dried, maintaining a nitrogen atmosphere. Magnesium (18 g., 0.75 m.) was placed in the flask and covered with anhydrous ether.

2-Chloropropane (3 ml.) was added all at once to the stirred mixture. After 12 hours stirring, 2-chloropropane

(45 g., 0.575 m.) in anhydrous ether (400 ml.) was added at such a rate to maintain gentle reflux. The solution was stirred for one hour after the completion of the addition. The resultant Grignard reagent was then filtered through glass wool into a dry 1 l. 3 neck round bottom flask which was equipped with stirrer, addition funnel, reflux condenser, drying tube and nitrogen inlet. The flask was cooled to 0° with an external ice-salt bath. 3-chlorocyclopentene (59 g., 0.575 m.) in anhydrous ether (200 ml.) was then added dropwise to the cold, stirred solution. The solution was stirred for an hour at 0° after completion of the addition. The reaction mixture was then poured onto ice and acidified with hydrochloric acid (10%). The ether layer was separated and washed with sodium bicarbonate and water. After drying overnight with sodium sulfate, the ether was removed by distillation. Distillation of the yellow residue yielded 3-isopropyl cyclopentene (b.p. 73-76°/165 mm., 23.5 g., 37%). The n.m.r. showed nonequivalent methyl groups centered at 0.80 and 0.92 δ ($J = 6.1$ cps) a broad complex multiplet (8 H) spread from 1.2 to 2.7 δ and the olefinics (2 H) as a multiplet at 5.65 δ. The infrared spectrum (cap. film) shows a 6.33 double bond absorption.

Hydroboration of 3-isopropyl cyclopentene

A 500 ml. 3 neck flask was equipped with a condenser, dropping funnel, thermometer, stirrer, nitrogen inlet tube and drying tube. Diglyme (80 ml.) was placed in the flask. A nitrogen atmosphere was maintained during the reaction. 2-methyl-2-butene (23.1 g., 0.33 m.) and sodium borohydride (4.7 g., 0.125 m.) were added. The flask was immersed in an ice bath. Boron trifluoride-etherate (23.5 g., 0.165 m.) was added dropwise to the well stirred reaction misture over 30 minutes. The semi-solid mixture was stirred at 0-5° for 15 hours.

3-Isopropylcyclopentene (16.5 g., 0.15 m.) was then added over a period of twenty minutes. The reaction mixture was stirred at 0-5° for two hours and then 11 hours at room temperature. Aqueous sodium hydroxide (50 ml., 3 N) was added dropwise, followed by the dropwise addition of 30% hydrogen peroxide (50 ml.), maintaining the temperature at less than 50°C. The solution was stirred for one hour after the addition of the hydrogen peroxide. Water (200 ml.) was then added. The mixture was then heated on a steam bath for 1 hour. The reaction mixture was cooled and extracted with ether (4 x 50 ml.). The combined ether extracts were washed with water (3 x 15 ml.) and dried over sodium sulfate. The ether was then removed by distillation. Continued distillation gave a fraction (b.p. 90°/10 mm., 10 g., 50%) which was a mixture of alcohols as shown by v.p.c. analysis.

Synthesis of 3-isopropyl cyclopentanone

The above mixture of alcohols was oxidized by the procedure of Brown and Garg (80). The alcohol mixture (1.0 g., 0.008 m.) was dissolved in ether (5 ml.). The ethereal solution was placed in a 3 neck flask which was equipped with a magnetic stirring bar, condenser and addition funnel. The oxidizing agent was prepared by dissolving sodium dichromate dihydrate (0.83 g., 2.9 mm.) in concentrated sulfuric acid (96%, 0.7 ml.). This solution was then diluted with water (3.0 ml.). The dichromate solution was added dropwise to the stirred etheral solution. The reaction was stirred for 30 minutes after the completion of the addition. The ether layer was separated with a pipette. The aqueous layer was then extracted with ether (5 ml.). The combined ether fractions were washed with water (1 ml.) and dried over sodium sulfate. The ether was evaporated under reduced pressure, leaving 0.92 g. (14%) of a colorless liquid. Analysis by v.p.c. at 108° (6 ft. LAC-446, $\frac{1}{4}$ in., 10% on 80-100 mesh gaschrom P) showed the crude material to be a mixture of two ketones. Two compounds were isolated by preparative scale v.p.c. using the above column. Compound A had a retention time of 5.2 minutes. The infrared spectrum (CCl_4) of compound A shows a 5.75 μ carbonyl absorption. The n.m.r. spectrum of compound A is shown in Figure 22. Compound A was shown to be

2-isopropylcyclopentanone (LXXXVI) by virtue of its identity with an authentic sample which was synthesized from 1-pyrrolidinocyclopentene and 2-iodopropane by the method of Stork (50).

Compound B had a retention time of 7.3 minutes at 108°. Compound B was isolated by preparative scale v.p.c. The infrared spectrum of compound B is shown in Figure 20 (5.72 μ carbonyl absorption) and the n.m.r. spectrum is shown in Figure 22. The spectral data confirms the structure of compound B as 3-isopropyl cyclopentanone (LXXXV).

Catalytic hydrogenation of 3-isopropyl-2-cyclopentenone (XXIII)

Adams catalyst (PtO_2, 28 mg.) was suspended in absolute ethanol (2 ml.). The catalyst was pre-reduced with hydrogen gas (7.41 ml., 26°C, 734 mm. Hg) in a semi-micro hydrogenation apparatus. XXIII (104.4 mg., 0.844 mm.) in ethanol (4 ml.) was added. The hydrogenation was done at 1 cm. of Hg positive pressure. The reduction required 20.52 ml. hydrogen (94% of theory, 21.72 ml. at 26°C, 734 mm. Hg). At the end of the hydrogenation, the catalyst was filtered by gravity. The ethanol was removed by distillation at reduced pressure. The residue was then distilled through a micro-molecular still at atmospheric pressure to give 84.0 mg. of a colorless liquid (b.p 175-195°) which was homogeneous and pure as indicated by v.p.c. analysis. An infrared spectrum (CCl_4)

showed a 5.72 μ carbonyl absorption and was identical to the infrared spectrum of authentic LXXXV which is shown in Figure 20. Thus, the identity of XXIII as 3-isopropyl-2-cyclopentenone is established.

Irradiation of 6,6-dimethyl-bicyclo [3.1.0.] hexan-2-one (XXII) and 3-isopropylcyclopentenone (XXIII) in deuterio-tertiary butyl alcohol

XXII (45 mg., 0.36 mm.) was dissolved in deuterio-tertiary butyl alcohol (4.0 ml., > 0.96 atom D/mole). The solution was placed in a u.v. cell, degassed with nitrogen and sealed tightly. The cell was taped to the lower support platform in the apparatus shown in Figure 14. The cell was located at a distance of 7 cm. from the lamp and was oriented such that the transparent face was normal to the incident beam. The lamp was jacketed with a Pyrex cooling assembly. The cell was irradiated for ten hours, rotating the platform during the irradiation. At the end of the irradiation, the solvent was distilled at atmospheric pressure. The light yellow residue was analyzed and separated by preparative scale v.p.c. (6 ft. LAC-446, $\frac{1}{4}$ in., 5% on chromosorb P). Two compounds with retention times identical to authentic XXII and XXIII were observed. Analysis of the relative areas by polar planimetry showed XXII (20%) and XXIII (80%). Isolation of the XXIII fractions gave a colorless liquid. The infrared spectrum (CCl_4) was identical to that of authentic XXIII (Figure 18). The n.m.r. spectrum was identical to that of authentic XXIII

(Figure 15). The methyl groups appeared as a doublet (1.12 and 1.25 δ, J = 7.8 cps.) indicating that the 1,2-hydrogen shift is intramolecular. Simultaneous irradiation of XXIII (48 mg., .039 mm.) led to the destruction of XXIII and the formation of no other volatile products, indicating that irradiation of XXIII yields only dimer or polymer.

Measurement of the quantum yield of the photochemical rearrangement of 4,4-dimethyl-2-cyclohexenone (XXI) in tertiary butyl alcohol

The apparatus used is shown in Figure 24.[1] This apparatus is an adaptation of that described by Moore (81). The main features of this linear quantum yield apparatus are as follows. The description corresponds to the numbers in the illustration (Figure 24).

1. The lamp was a Westinghouse SAH 800c high pressure short arc mercury unit. The lamp was powered by a Northelfer 4031 E transformer which was regulated by a Stabiline constant voltage regulator.
2. The condensing lens (6.25 cm. diameter, 15 cm. focal length) was used to collimate the beam. The lens was made of quartz.
3. The beam then passed through a quartz faced filter solution cell (2 cm. deep, 6.25 cm. diameter). The cell was supported with two cork rings. The filter

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[1] The author wishes to thank Dr. Neil J. Woolsey for construction of the apparatus.

was a cobalt sulfate-nickel sulfate-potassium acid phthalate (49) solution which effectively isolates the 313 mμ line. This solution has less than 2% T at 366 mμ and less than 1% T below 300 mμ.

4. This unit held a Corning CS 054 glass filter which has less than 2% T below 300 mμ.(82).
5. The sample cell holder is a Beckman DU cuvette holder. The incident beam covered two adjacent cells.
6. The homogeneity of the beam across both solution cells was determined with an Eppley thirteen junction thermocouple. The thermocouple output was connected to a 1 mv. recorder. The components of the system were adjusted until the beam striking both sample cells was of equal intensity.
7. The apparatus was mounted on a Cenco Optical bench.
8. The lamp was encased in a 12 mm. transite box. The lamp housing was cooled by convection.

The reference quantum yield was the 0.10 M benzophenone-0.10M benzhydrol in benzene (66) system. The quantum yield for photoreduction at 313 mμ is 0.698.[1] The solution was flushed with pre-purified nitrogen before irradiation. The irradiation was done in 1 cm. diameter Pyrex tubes which were carefully matched with respect to equal light

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[1] The author wishes to thank Dr. N. J. Woolsey for this measurement.

transmittance. The destruction of benzophenone was measured by diluting the irradiated sample (1:25) with benzene and measuring the change in the ultraviolet spectrum at 341 mμ. The molar conversion was then calculated, and from this the number of protons incident upon the cells was then determined as follows:

$$\text{Total Quantum Output} = \frac{\text{Moles of Benzophenone Reduced} \times 6.02 \times 10^{23}}{.698}$$

The extent of conversion of XXI to XXII and XXIII was measured by vapor phase chromatography. A series of standard solutions of pure XXII and XXIII was prepared in the concentration range expected. The analysis was done on an Aerograph 1520 gas chromatograph, using an LAC-446 column (6 ft., 5% on 80-100 mesh chromosorb P). The peak areas at each concentration were measured with an Ott polar planimeter. The peak area was determined by taking the average of three readings. The peak areas are in arbitrary units. This crude concentration-area data was then analyzed by a least squares method to calculate the best fit. The equation of the line was determined. These calculations were done on the IBM 7074 computer.[1] The following data was obtained for the standard solutions.

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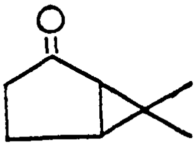
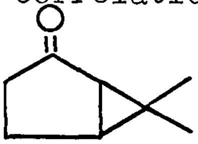
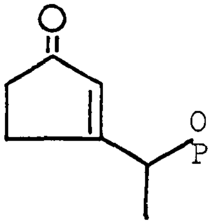
[1] The author wishes to thank Dr. G. F. Morris for writing this program and generously donating his time to make it work.



Observed Peak Area	Concentration Measured (mg./ml.)	Concentration Calculated (mg./ml.)
0	0	- .002
54	0.240	0.217
128	0.480	0.517
182	0.720	0.737
231	0.960	0.931

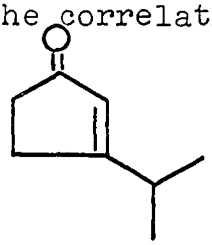
Using the measured concentration and the observed peak area, the computer program calculated the equation of the line in a y = mx + b format where y = calculated mg./ml., m = slope, x = observed peak area and b = intercept when peak area = zero. The equation for the correlation was:

Calculated mg./ml.  = Observed Peak Area(.00406) -.002



Observed Peak Area	Concentration Measured (mg./ml.)	Concentration Calculated (mg./ml.)
0	0.000	0.045
49	0.298	0.290
105	0.596	0.569
154	0.894	0.814
223	1.080	1.158
228	1.192	1.183

The equation for the correlation was:

Calculated mg./ml.  = Observed Peak Area (.00499) + .045.

A 1 cm. Pyrex tube was filled with 3.00 ml. of the 0.10 M solution of XXI. The level of the solution in the cell holder was such that the incident beam passed through the liquid only. A closely matched 1 cm. Pyrex tube was filled with 3.00 ml. of the 0.10 M benzophenone - 0.10 M benzhydrol solution. The tubes were placed in adjacent spaces in the cell holder and irradiated. Since the quantum yield of the reference system was near unity, it was necessary to irradiate a series of these tubes over spaced intervals while the tube containing XXI was irradiated for the entire time. The time interval of irradiation of each reference tube was measured, and the percent photoreduction was determined in each tube. An average value of quantum output was then calculated. Two determinations of the quantum yield of the rearrangement of XXI were made, one for 54.5 hours, the other for 61 hours. Analysis for percent conversion to XXII and XXIII was done by the v.p.c. and least squares procedure given above. The following data was obtained.

Irradiation Time-hours	mg. XXII produced	mg. XXIII produced	Quantum Output[1]
54.5	1.113	1.71	7.95×10^{20}
61	1.077	1.80	8.63×10^{20}

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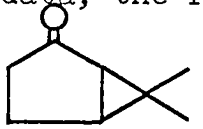
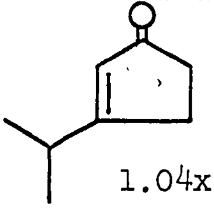
[1] The author wishes to thank Dr. N. J. Woolsey for measuring the quantum output.

The quantum yield was calculated from the following formula:

$$\text{Quantum yield} = \frac{\text{moles of product produced}}{\text{moles of quanta absorbed}}$$

Using the above data, the following values were obtained.

Irradiation Time-hours	 (XXII) quantum yield	 (XXIII) quantum yield
54.5	$6.8\text{x}10^{-3}$	$1.04\text{x}10^{-2}$
60	$6.1\text{x}10^{-3}$	$1.09\text{x}10^{-2}$

Thus, the average quantum yield for production of XXII was $6.5\text{x}10^{-3}$ and the average quantum yield for production of XXIII was 1.06×10^{-2}. The quantum yield for rearrangement is therefore

$$6.5 \times 10^{-3} + 1.06 \times 10^{-2} \text{ or } 1.71 \times 10^{-2}.$$

The measurement of this type of relative quantum yield is valid only when the solutions are absorbing > 99% of the light. The transmittance of 0.10 M benzophenone at 313 mμ was calculated to be < 0.0005% ($\epsilon_{313\ \text{m}\mu}^{\text{benzene}} = 137$). The transmittance of 0.10 M XXI at 313 mμ was calculated to be < 0.05% ($\epsilon_{313\ \text{m}\mu}^{t\text{-butanol}} = 32$). These calculations are on the basis of a 0.8 cm. path length which is an approximation to the 1.0 cm. circular cells used in this measurement. These values are low enough to permit valid comparison on the assumption of equal absorption of light.

Irradiation of 4,4-dimethyl-2-cyclohexenone (XXI) in glacial acetic acid

XXI (5.8 g., 0.467 m.) was dissolved in glacial acetic acid (1.8 l.). The solution was irradiated in the apparatus shown in Figure 5. The course of the reaction was followed by periodically taking an aliquot, diluting it appropriately, and measuring the ultraviolet spectrum. The following data was obtained.

Irradiation Time (hr.)	Absorbance (224 mm.)
0	1.36
13.5	0.45
21	0.23
23.5	0.20

The irradiation was terminated after 24 hours. The acetic acid was removed by distillation at reduced pressure leaving a dark red liquid residue. This residue was steam distilled, yielding a colorless liquid (4.1 g., 71%) which was analyzed by preparative scale vapor phase chromatography. Four compounds other than starting material were present in the crude mixture in significant amounts. The temperature of the column (8 ft. LAC-446, $\frac{1}{4}$ in., 15% on 80-100 mesh chromosorb P) was programmed to facilitate separation. At the time of injection, the column temperature was 80°. Peak 1 (21.3 min.) was isolated and found to be identical to unreacted XXI. Peak 2 (23.7 min.) was isolated and found to be identical to XXV. Peak 3 (25.4 min.) was found to be identical to XXII. After elution of XXII, the temperature was increased to 140°. A fourth compound was eluted 6.5 min. after this increase. This compound was shown to be identical to XXIII. After elution of XXIII, the temperature was raised to 160° giving a fifth peak 4 min. after the increase. This peak was shown to be identical to XXIV. The structural identity of these comparisons was established by comparison of infrared spectra.[1]

Analysis of the v.p.c. recording showed the following percentage composition for this mixture:

Compound	% of Mixture	% of Photoproducts
XXI	43	0
XXII	3	5
XXIII	9	16
XXIV	30	53
XXV	15	26

The n.m.r. spectrum of XXIV is shown in Figure 16 and the infrared spectrum is shown in Figure 19. The infrared spectrum of XXV is shown in Figure 19. The n.m.r. spectrum of XXV (CCl_4) showed a slightly split methyl at 1.93 δ (allylic methyl), a complex multiplet at 2.15 δ (methylene absorption), a single methine at 2.65 δ and a slightly split two proton olefinic absorption at 4.76 δ. A larger sample of XXV was isolated for the catalytic hydrogenation described below.

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[1] The spectra of authentic XXII, XXIII, XXIV and XXV were obtained from Dr. P. Fitton who performed the initial isolation of these compounds. Dr. Fitton obtained satisfactory elemental analyses for each of these compounds.

Catalytic hydrogenation of 3-isopropenylcyclopentenone (XXV)

Adams catalyst (PtO_2, 28 mg.) was suspended in absolute ethanol (2 ml.) and reduced with hydrogen (6.04 ml.) in a semi-micro hydrogenation apparatus. XXV (19.3 mg., 0.190 m.) in ethanol (4 ml.) was then added. The reduction was done at 1 cm. of Hg positive pressure, requiring 4.78 ml. of hydrogen (99%). The catalyst was filtered by gravity. Ether (15 ml.) was added. The ether layer was washed with water (4-4 ml. portions). The ether solution was then dried with sodium sulfate. The solvent was removed by distillation at reduced pressure leaving a colorless liquid (~ 10 mg.). The infrared spectrum (CCl_4) showed a 5.72 μ carbonyl absorption and was identical to the infrared spectrum of authentic 3-isopropylcyclopentanone (LXXXV) which is shown in Figure 20.

Test of stability of 3-(2-acetoxypropyl) cyclopentanone (XXIV) in the gas chromatograph

A sample of pure XXIV was injected onto a v.p.c. column (6 ft., 10% LAC-446, $\frac{1}{4}$ in., on 80-100 mesh chromosorb P) at 160°. The material was isolated in the usual manner. An infrared spectrum (CCl_4) of this material was identical with that of the initial sample. No peaks other than that due to XXIV was observed.

Irradiation of 6-6-dimethylbicyclo [3.1.0.]-hexan-2 one (XXII) in acetic acid

XXII (63 mg.) was dissolved in glacial acetic acid

(25 ml.). The solution was irradiated in a Pyrex tube (30x1.8 cm.) which was placed in front of a Pyrex jacketed mercury arc lamp (Hanovia Type A, 550 watt). The tube was placed 2.5 cm. from the lamp. The course of the reaction was followed by v.p.c. (6 ft. LAC 446, 2.5% on 80-100 mesh chromosorb P). A 1/8 inch diameter glass column was used. The gas chromatograph was an Aerograph Model 600 which was equipped with a flame ionization detector. Samples (0.1 ml.) were taken periodically during the irradiation. The samples were added carefully to a saturated sodium bicarbonate solution (2 ml.) and then extracted with ether (.3 ml.). This extraction was done in a test tube which was stoppered while shaking. The ether layer was analyzed directly by injection into the gas chromatograph. After 11 hours a faint trace of 3-isopropyl-2-cyclopentenone (XXIII) appeared. Continued irradiation (45 hours) led to nearly complete destruction of XXII. No other volatile compounds were present in the 45 hour sample and no peak due to XXIII was observed.

A simultaneous companion irradiation of 4,4-dimethyl-2-cyclohexenone (XXI, 65 mg./25 ml. glacial acetic acid) showed the presence of XXII, XXIV and XXV after 15 hours. Only a trace of 3-isopropyl-2-cyclopentenone (XXIII) was observed. After 45 hours, only XXI, XXII, XXIV and XXV were present and no peak corresponding to XXIII could be observed.

Experimental for the Cycloaddition of 4,4-Dimethylcyclohexenone to 1,1-Diphenylethylene and Piperylene

Cycloaddition of 4,4-dimethylcyclohexenone (XXI) with 1,1-diphenylethylene (LXXVII)

3.00 g. XXI (.024 m.) and 20.0 g. LXXVII (.11 m.) were dissolved in tertiary butyl alcohol (500 ml.) and irradiated in tertiary butyl alcohol in the apparatus shown in Figure 5. The course of the reaction was followed by v.p.c. (6 ft., $\frac{1}{4}$ in., 5% LAC-446 on 80-100 mesh chromosorb P). After seven hours, greater than 99.5% of XXI was destroyed. The irradiation was terminated at this point. The tertiary butyl alcohol was removed by distillation at reduced pressure, leaving a slightly yellow oil (22.9 g.). The oil was chromatographed on a 5x20 cm. silica gel column. The column was prepared in Skelly B. The oil was mixed with a small amount of Skelly B and loaded onto the column. Two liters of Skelly B were run through the column. Evaporation of the combined Skelly B fractions left 15.2 g. of a light yellow oil which was shown by n.m.r. to be pure LXXVII. The i.r. spectrum of the oil was also superimposable with that of LXXVII. The column was then stripped with 80% benzene to give 7.4 g. of a yellow oil which solidified upon addition of Skelly B followed by cooling in an ice bath. The crystals (6.8 g.) were filtered and recrystallized twice from ether to give 5.55 g. (75%) of colorless crystals, m.p. 164.5-165.5°. For the n.m.r. spectrum of the photoproduct (LXXXVIII), see Figure 17, and for the i.r. spectrum see Figure 20.

Anal. Calcd. for $C_{22}H_{24}O$: C, 86.80 H, 7.95 Found: C, 87.24 H, 8.35.

Base catalyzed isomerization of trans-5,5-dimethyl-7,7-diphenyl bicyclo [4.2.0.] octan-2-one (LXXXVIII)

LXXXVIII (600 mg.) was dissolved in 4% methanolic potassium hydroxide (10 ml.). Water (1 ml.) was added. The solution was refluxed for two hours in a nitrogen atmosphere. The solution was allowed to cool and then poured into 20 ml. of water. The milky solution was extracted with three 15 ml. portions of ether. The combined ether extracts were dried over magnesium sulfate. Evaporation of the ether gave 580 mg. (97%) of a white solid which was recrystallized twice from ether to give m.p. 115-116°. The infrared spectrum (CCl_4) is shown in Figure 20, and the n.m.r. spectrum is shown in Figure 23. This material was assigned structure LXXXIX.

Anal. Calcd. for $C_{22}H_{24}O$: C, 86.80 H, 7.95 Found: C, 87.17 H, 8.18.

Deuteration of trans-5,5-dimethyl-7,7-diphenyl bicyclo [4.2.0.] octan-2-one (LXXXVIII)

(300 mg., 1 mm.) was dissolved in deuteriomethanol (10 ml., > 0.92 atom D/mole). Deuterium oxide (2 ml., > 99.5% D_2O) and sodium methoxide (54 mg., 1 mm.) were then added. The solution was then refluxed for nine

hours. The solution was then cooled and the solvent removed at the rotary film evaporator. Carbon tetrachloride (10 ml.) was added to the crude residue. The carbon tetrachloride solution was then extracted with three 2 ml. portions of deuterium oxide. The organic layer was then dried with magnesium sulfate and concentrated. An infrared spectrum showed a 5.88 μ carbonyl absorption. For the n.m.r. spectrum, see Figure 23. Analysis of the AB portion of the spectrum (J_{AB} = 12.6 cps) showed the chemical shifts of the two protons to be 3.29 and 2.50 δ, respectively. This material (XC) was not examined further.

Baeyer-Villiger oxidation of trans-5,5-dimethyl-7,7-diphenyl bicyclo [4.2.0.] octan-2-one (LXXXVIII)

Trifluoroacetic anhydride (315 mg., 1.5 mm.) was dissolved in methylene chloride (1 ml.) in a 3 inch test tube. The test tube was then placed in an ice bath. Hydrogen peroxide (90%, 45.5 μl) was added dropwise with a microliter syringe to the ice cold anhydride. The addition required ten minutes. LXXXVIII (150 mg., 0.5 mm.) in methylene chloride (1 ml.) was placed in a 5 ml. 14/20 flask which was equipped with a magnetic stirrer. The flask was placed in an ice bath and sodium dihydrogen phosphate (395 mg.) was added. The hydrogen peroxide-trifluoroacetic anhydride solution was then added dropwise over a period of 30 minutes to the ketone solution. The solution was stirred vigorously during the addition.

After completion of the addition, the slurry was refluxed for one hour. After cooling, water (10 ml.) and methylene chloride (10 ml.) was added. The resultant mixture was shaken until the solid material dissolved. The aqueous layer was separated, and the organic layer extracted with two 5 ml. portions of 5% sodium bicarbonate. The organic layer was then washed with two 5 ml. portions of water. The organic layer was dried with sodium sulfate and evaporated to yield 120 mg. (80%) of a light yellow solid which was sublimed at 0.0005 mm. and 180° to give colorless crystals, m.p. 225-227° (Subl.). The i.r. spectrum (CCl_4) showed a 5.71 μ lactone carbonyl absorption. The n.m.r. spectrum showed a singlet methyl absorption at 0.124 δ, a singlet methyl at 1.15 δ, a two proton multiplet centered at 1.57 δ, a five proton multiplet spread from 2.3 to 3.6 δ, a single proton as a four line multiplet (4.79, 4.94, 5.09 and 5.23 δ) and ten aromatic protons at 7.28 δ.

The lactone, 6,6-dimethyl-8,8-diphenyl-2-oxabicyclo [5.2.0.] nonan-3-one (XCII) gave the following elemental analysis.

Anal. Calcd. for $C_{22}H_{24}O_2$: C, 82.46 H, 7.56 Found: C, 82.37, H, 7.56.

Irradiation of XXI and LXXXVII in the presence of oxygen

750 ml. of a tertiary butyl alcohol solution which was .05 M in XXI and .10 M in LXXXVII was irradiated in the

apparatus shown in Figure 5. An oxygen atmosphere was maintained by bubbling pure oxygen through the solution. The solution was irradiated for three hours. The solution was dark yellow at the end of this time. The solvent was removed by distillation at reduced pressure, leaving a yellow oil. An n.m.r. spectrum of this oil showed only XXI, LXXXVII and the _trans_-adduct LXXXVIII to be present. The characteristic methyl peaks of the _trans_-adduct were clearly present. The material was not worked up or examined further.

Irradiation of XXI and LXXXVII in benzene

A .05 M solution of XXI and .10 M LXXXVII in benzene was irradiated for 450 minutes in the apparatus of Figure 14. The tubes were placed on the 5½" radius. At the end of the irradiation, the benzene was stripped at the rota-vac, and the n.m.r. spectrum of the crude material was measured. The n.m.r. spectrum showed only XXI, LXXXVIII and the _trans_-cycloaddition product (LXXXVIII). There was no methyl absorption due to the _cis_-isomer (LXXXIX). For the n.m.r. spectrum see Figure 25.

Irradiation of XXI and LXXXVII in acetic acid

A .05 M solution of XXI and .10 M LXXXVII in acetic acid was irradiated in the apparatus shown in Figure 14 for 800 minutes. The tubes were placed on the 5½" radius. At the end of the irradiation, the acetic acid was distilled at reduced pressure. The residue was taken up in ether and washed with 5% sodium bicarbonate to remove the acetic acid. The ether layer was then washed with water and dried over sodium sulfate. The ether was evaporated and an n.m.r. spectrum was taken on the crude material. The n.m.r. spectrum showed only XXI, LXXXVII and the trans-cycloaddition product (LXXXVIII) to be present. For the n.m.r. spectrum see Figure 25.

Irradiation of XXI and LXXXVII in the presence of piperylene

.05 M XXI, .10 M LXXXVII and .05 M piperylene was irradiated for 450 minutes in tertiary butyl alcohol in the apparatus shown in Figure 14. The tubes were placed in the $5\frac{1}{2}''$ radius holes. At the termination of the irradiation, the solvent was removed by distillation at reduced pressure. The n.m.r. spectrum of the crude product showed only XXI, LXXXVII and trans-cycloaddition product (LXXXVIII). For the n.m.r. spectrum, see Figure 25.

Irradiation of 4,4-dimethyl cyclohexenone (XXI) in the presence of trans-piperylene (XCIII)

XXI (1 g., .008 m.) and trans-piperylene (6.2 g., .09 m.) were dissolved in tertiary butyl alcohol (40 ml.). This solution was irradiated in the apparatus shown in Figure 5. The course of the reaction was followed by measuring the disappearance of XXI using v.p.c. analysis (6 ft. LAC-446, $\frac{1}{4}$ in. 5% on 80-100 mesh chromosorb P). After ten hours irradiation, XXI was greater than 95% destroyed. No peaks corresponding to XXII or XXIII were observed. The irradiation was terminated after 10 hours. The solvent and excess piperylene were removed with the rotary film evaporator, leaving 1.38 g. (91%) of a light yellow liquid. The infrared spectrum (CCl_4) of the crude material is shown in Figure 26. Analysis by v.p.c. (6 ft. LAC-446, 5% on 80-120 mesh chromosorb P) showed two poorly resolved peaks in the approximate ratio of 1:20. The small peak (retention time 6.8 min. at 140°) could not be efficiently separated from the major component (retention time 7.2 min.). A small scale isolation of the major component by careful fractionation was done using the v.p.c. at 115°. The infrared spectrum of this material is shown in Figure 26. The n.m.r. spectrum of this component is shown in Figure 26. The material was sent for elemental analysis.

Anal. Calcd. for $C_{13}H_{20}O$: C, 81.20 H, 10.48 Found: C, 81.18 H, 10.60.

The mass spectrum showed a parent peak at m/3 192, indicating a 1:1 adduct. The minor product was not examined further.

The n.m.r. spectrum of the isolated major component (Figure 26) shows an integral of 1:10 for the olefinic to aliphatic region, indicating a mixture of double bond isomers resulting from attack at both double bond isomers. The complexity of the methyl region (0.8-1.3 δ) also indicates a mixture. This material was not investigated further. The ultraviolet spectrum of piperylene shows $\epsilon = 0.53$ at 318 mμ. The ultraviolet spectrum of XXI shows $\lambda_{max}^{95\% \text{ ethanol}}$ 318 mμ, $\epsilon = 38.0$. Thus, in this experiment the percent light absorption by piperylene is 0.09(0.53)/0.09(0.53)+0.008(38) = 12.5.

Experimental for Measurement of Photochemical Kinetics

An apparatus was constructed to facilitate the simultaneous measurement of several samples. This apparatus is illustrated in Figure 14.[1] The holes for the sample tubes were placed along a $3\frac{1}{2}$, $5\frac{1}{2}$ and $8\frac{1}{2}$ inch radius from the center. The lamp, a Hanovia 550 watt type A, was placed at the center of the wheel. The tubes were longer than the arc length, thus receiving a substantial portion of the emission. The wheel was rotated by a friction motor at a speed of fifteen revolutions per minute. All of the experiments in this section were done with this apparatus.

The lamp was housed in a combination cooling and filter jacket. Cold tap water was circulated through the inner jacket to provide cooling for the lamp. The outer jacket was filled with a saturated solution of copper sulfate. The path length of this filter solution in the jacket was 1.5 cm. This combination of three thicknesses of Pyrex and a copper sulfate filter has less than two percent transmittance below 305 mμ.

This filter system was used in all of the relative rate experiments (unless otherwise noted) to insure that only photochemistry due to n → π* excitation was being studied.

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[1] The author acknowledges the generous help given by Messrs. M. Needham, R. Seymour and L. Smith in the construction of this apparatus.

A graph of lamp output and transmittance of various filter solutions in this work is shown in Figure 30.

Calibration of sample tubes

Pyrex tubes, 30 cm. long x 1.8 cm. i.d., were made in the glass shop. The closed ends were squared off so that the tube would stand perpendicularly. The open end was fitted with a medium large septum cap which provided a vapor tight seal to prevent evaporation during the kinetic run. Each tube was labeled and numbered. In order to pair the tubes according to their light transmitting characteristics it was necessary to calibrate them with a photochemical system having a reproducible quantum yield and requiring $n \rightarrow \pi^*$ excitation.

The system chosen was the benozophenone-benzhydrol-benzene-system (66). The tubes were filled by pipeting 40 ml. of 0.1 M benzophenone, 0.1 M benzhydrol in benzene into each tube. The tubes were then degassed for five minutes with nitrogen and sealed with a septum cap. The tubes were irradiated at a distance of $5\frac{1}{2}$ inches from the lamp for a period of 50.0 minutes. The solutions were analyzed by pipeting one milliliter samples of each tube into a twenty-five milliliter volumetric flask, diluting exactly to volume with 95 percent ethanol and measuring the absorbance of the solution at the wave length maximum of benzophenone (332 mμ). The results are given as follows:

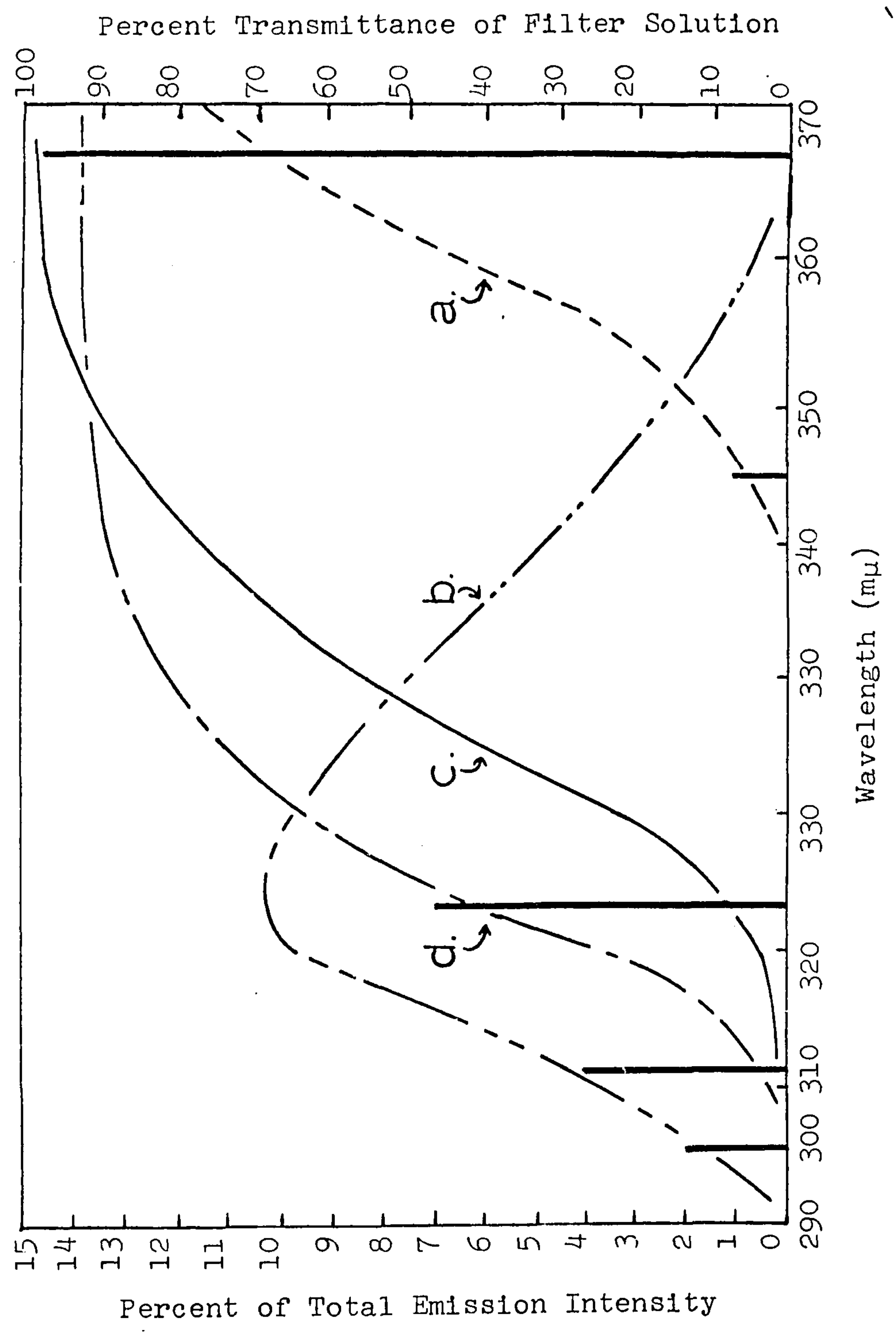
Figure 30. Wavelength-emission intensity from 290-370 $m\mu$ and wavelength-percent transmittance of filter solutions used in this work.

a. - - - - - - - - Corning 0-52 Filter (81)

b. ——— - - ——— Nickel sulfate-cobalt sulfate-potassium acid phthalate solution (49)

c. ———————— Aqueous saturated copper sulfate solution (49)

d. ——— – ——— Corning 0-54 filter (81)


Percent Transmittance of Filter Solution
100
90
80
70
60
50
40
30
20
10
0
Percent of Total Emission Intensity
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
Wavelength (mμ)
290
300
310
320
330
330
340
350
360
370
a.
b.
c.
d.

Type Number	Absorbance-332 mμ.
1	0.534
2	0.512
3	0.508
4	0.535
5	0.524
6	0.515
7	0.519
8	0.527
9	0.508
10	0.535
11	0.529
12	0.526
13	0.531
14	0.530
15	0.538

The average of these measurements is 0.525, the maximum deviation from the average being plus or minus 2 percent. Tubes with nearly identical absorbance readings in this experiment were paired for usage in the kinetic determinations.

General Technique Used in Kinetic Study

The solvent employed was tertiary butyl alcohol. It was necessary to distil the alcohol three times from sodium to remove impurities. The alcohol was protected from moisture. The tubes were cleaned with dichromate cleaning solution, washed with distilled water, rinsed with ethanol and dried in the drying oven before each usage.

The samples were degassed with nitrogen by bubbling the gas through a five inch syringe needle which was placed through the septum cap. The cap was allowed to fit loosely during the degassing stage. Each sample was degassed for at least five minutes before the start of the irradiation. A manifold with eight exits was constructed to permit simultaneous degassing of eight samples. Surgical tubing was used throughout.

Samples were periodically withdrawn by loosening the septum cap and pouring approximately one quarter of a milliliter into a 1 dram vial. The tube was then degassed with nitrogen for one minute. The tube was shaken thoroughly before taking a sample. The lamp was not turned off during the entire kinetic run.

The samples were analyzed by gas chromatography. The instrument used was an Aerograph Model 1520 with dual column thermal conductivity detectors. The column was a 6 ft., $\frac{1}{4}$ in., 5 percent LAC-446 on 60-80 mesh gaschrom P. The column was maintained at 115°, the injector at 250°, the detector at 220° C. A sample volume of twenty microliters was usually used for ketone concentrations in the range of 0.05 molar. The injection technique was standardized. A Hamilton 25 microliter syringe was used. It was filled and emptied four times with the solution to be analyzed. It was then filled the fifth time and carefully emptied to the 20 microliter graduation. The syringe needle was then pushed through the injection septum to the hilt of the syringe. The injection was made rapidly. The syringe was left in the septum until the recorder responded to the solvent peak.

The syringe was then removed and cleaned with acetone followed by drawing air through the barrel with the water aspirator.

The peak areas were then measured with an Ott polar planimeter. Each peak was scanned twice, the total area was then halved to give the proper area. It was found that a reproducibility of plus or minus 2 percent could be obtained with careful injection and planimetry technique. Time was measured with an electric stopwatch.

The peak area data was then used in a zero order rate constant calculation in which the concentration of the reacting ketone was plotted versus irradiation time. The calculation was done on the IBM 7074 computer. The program was written by Dr. G. F. Morris. The program calculated the slope, intercept and root mean square error term for the line of best fit. The root mean square error for the lines was generally less than ± 5 percent. The slope (zero order rate constant) is expressed in terms of concentration of ketone in arbitrary units per minute.

The zero order rate constants reported in the following experiments are the average of two simultaneous measurements on separate tubes. Although three figures are given, only two significant figures are used by the author for interpretation.

Unless otherwise noted, all of the irradiations described in this section were done with the tubes placed in the $5\frac{1}{2}$ in.

radius holes. The details of preparation of the solutions in the following kinetics experiments have been omitted for the sake of brevity. The concentrations were within ± 2% of those stated.

All of the following irradiations were done in the apparatus shown in Figure 14, using the Pyrex (30 x 1.8 cm.) tubes.

Measurement of relative zero order rates of decay for 2-cyclohexenone (XLVII), 4-methyl-2-cyclohexenone (LXXVI), 4,4-dimethyl-2-cyclohexenone (XXI) and 2,4,4-trimethyl-2-cyclohexenone (LXXVII) in tertiary butyl alcohol

The solutions of the above ketones were prepared in tertiary butyl alcohol. The concentration of each ketone was 0.05 M. The lamp was jacketed with the Pyrex cooling apparatus but no filter solution was used. The tubes were irradiated in the 3½ inch radius. The following data was obtained. Each solution was irradiated in duplicate.

Compound	Zero Order Rate of Decay
2-cyclohexenone	-0.0800
4-methyl-2-cyclohexenone	-0.0814
4,4-dimethyl-2-cyclohexenone	-0.0939
2,4,4-trimethyl-2-cyclohexenone	0.0000

In separate experiments a larger scale irradiation of 2-cyclohexenone and 4-methyl-2-cyclohexenone in t-butanol yielded only starting material and non volatile dark red tarry products. The slopes obtained above for these two compounds are thus assumed to be equal to the rate of dimerization or polymerization. In a separate experiment 2,4,4-trimethyl-2-cyclohexenone was found to be photostable.

Measurement of benzophenone sensitization of the rearrangement of 4,4-dimethyl-2-cyclohexenone (XXI) in tertiary butyl alcohol

A solution of 4,4-dimethyl-2-cyclohexenone (XXI, 0.05 M) in tertiary butyl alcohol was prepared. A solution of XXI (0.05 M) and benzophenone (0.25 M) in tertiary butyl alcohol was prepared. The lamp was jacketed with the Pyrex cooling apparatus but no filter solution was used. The tubes were irradiated in the $3\frac{1}{2}$ in. radius. The zero order rate of loss of XXI and the zero order rate of appearance of 6,6-dimethyl-bicyclo-[3.1.0.] hexan-2-one (XXII) and 3-isopropyl-2-cyclopentenone in each solution was measured. Each solution was irradiated in duplicate.

Solution	Zero Order Rate XXI Loss	 XXII Appearance	 XXIII Appearance
0.05 M XXI	-0.0939	+0.0465	+0.0397
0.05M XXI, 0.25 M Benzophenone	-0.1349	+0.0586	+0.0459

XXI shows $\lambda_{max}^{95\%\ ethanol}$ 318 mμ, $\epsilon = 38$ and benzophenone shows $\epsilon = 137$ at 318 mμ. Thus, the percent light absorption by benzophenone (0.25 M) in the above experiment (XXI, 0.05 M) is 0.25 (137)/0.05(38) + 0.25(137) or 95%.

Measurement of 9-fluorenone and flavone sensitization of the rearrangement of 4,4-dimethyl-2-cyclohexenone (XXI) in tertiary butyl alcohol

A solution of 4,4-dimethyl-2-cyclohexenone (XXI, 0.05 M) in tertiary butyl alcohol was prepared. A solution of XXI (0.05 M) and 9-fluorenone (0.05 M) was prepared. A solution of XXI and flavone (0.05 M) was prepared. The lamp was jacketed with the Pyrex cooling apparatus but no filter solution was used. The tubes were irradiated in the 3½ in. radius. The zero order rate of loss of XXI and the zero order rate of appearance of the rearrangement photoproducts XXII and XXIII were measured. Each solution was irradiated in duplicate.

Solution	Zero Order Rate		
	XXI Loss	XXII Appearance	XXIII Appearance
0.05 M XXI	-0.0822	+0.0352	+0.0380
0.05 M XXI, 0.05 M Flavone	-0.0194	+0.0116	+0.0108
0.05 M XXI, 0.05 M 9-Fluorenone	-0.00298	+0.0026	+0.0005

In the fluorenone solution, the zero order rate of appearance of XXII and XXIII could not be measured accurately due to the low conversion of XXI. The ultraviolet spectrum of 9-fluorenone at 318 mμ showed $\epsilon = 780$. The percent light absorbed by 9-fluorenone in the 0.05 M XXI, 0.05 M 9-fluorenone solution was therefore $0.05(780)/0.05(780) + 0.05(38) = 39/39+1.9 = 95.5\%$.

The ultraviolet spectrum of flavone at 318 mμ showed $\epsilon = 12{,}500$. The percent light absorbed by flavone in the 0.05 M XXI, 0.05 M flavone solution was therefore at least $0.05(12{,}500)/0.05(12{,}500) + 0.05(38) = 625/625 + 1.9 = > 99\%$.

<u>Measurement of benzophenone sensitization of rearrangement of 4,4-dimethyl-2-cyclohexenone (XXI) in tertiary butyl alcohol using 366 mμ irradiation</u>

The apparatus used was that illustrated in Figure 14. The tubes were irradiated on the 5½ in. radius. A Corning 052 glass filter was taped to the incident face of two adjacent 30 x 1.8 cm. i.d. Pyrex tubes. This filter has less than 0.5% transmittance below 334 mμ (82). The portions of the tubes above and below the filter were taped to prevent excitation by unfiltered light. The lamp was jacketed with the combination cooling water-saturated copper sulfate (1.5 cm. deep) filter solution apparatus. The saturated copper sulfate solution shows less than twelve percent transmission below 318 mμ and less than one percent transmission below 300 mμ. These conditions assured the 366 mμ line as being the main source of $n \rightarrow \pi^*$ excitation (see first page of Experimental for wavelength-percent energy distribution table). Since only one filter plate was available, the irradiation was not run in duplicate. The following data was obtained.

Solution	Zero Order Rate Constants XXI Loss	 XXII Growth	 XXIII Growth
0.05 M XXI	-0.0139	+0.0095	+0.0071
0.05 M XXI, 0.25 M benzophenone	-0.0229	+0.0092	+0.0088

The ultraviolet spectrum of XXI at 366 mμ shows ε = 7.0. The ultraviolet spectrum of benzophenone at 366 mμ shows ε = 51. The percent absorption by benzophenone at 366 mμ was therefore 0.25(51)/0.25(51) + 0.05(7) = 12.8/12.8 + 0.35 = 97.5%.

<u>Measurement of effect of ferric dipivaloyl methane on rate of rearrangement of 4,4-dimethyl-2-cyclohexenone (XXI) in tertiary butyl alcohol</u>

A solution of XXI (0.05 M) was prepared. A solution of XXI (0.05 M) and ferric dipivaloyl methane (10^{-5} M) was prepared. The solutions were degassed in the usual way and irradiated using the saturated copper sulfate filter system.

Solution	Zero Order Rate Constant XXI Loss	 XXII Appearance	 XXIII Appearance
0.05 M XXI	-0.02234	-0.00672	-0.0102
0.05 M XXI, 10^{-5} M Ferric-dipivaloyl methane	-0.01578	-0.00587	-0.00763

Ferric dipivaloyl methane (FeDPVM) shows an ε value of 2,500 at 366 mμ. Thus the percent light absorption due to 10^{-5} M FeDPVM is 10^{-5} M(2,500)/10^{-5} M(2,500) + 0.05(7) = 0.025/0.025 + 0.35 = 0.025/0.375 = 6.5%. This percent absorption is not enough to account for the 34% decrease in rate of disappearance of XXI in the presence of FeDPVM, indicating that the rearrangement of XXI is quenched by ferric dipivaloyl methane.

Measurement of effect of oxygen on rate of rearrangement of 4,4-dimethyl-2-cyclohexenone (XXI)

A solution of XXI (0.05 M) was prepared. The reference solution was degassed with nitrogen in the usual way. The other solution was degassed with oxygen for 15 minutes prior to irradiation. After the start of the irradiation, oxygen was bubbled through this solution for 5 minutes at each time that a sample was withdrawn for v.p.c. analysis. The following results were obtained.

Solution	Zero Order Rate Constant		
	XXI Loss	XXII Appearance	XXIII Appearance
0.05 M XXI	-0.01378	+0.00535	+0.00629
0.05 M XXI, Oxygen saturated	-0.01087	+0.00405	+0.00469

This data indicates that the rearrangement to XXII and XXIII is quenched by oxygen.

Measurement of effect of piperylene (XCII) on the rate of rearrangement of 4,4-dimethyl-2-cyclohexenone (XXI) in tertiary butyl alcohol

A solution of XXI (0.05 M) was prepared. A solution of XXI (0.05 M) and XCII (0.001 M) was prepared. The irradiation was done in the apparatus shown in Figure 14 using the saturated copper sulfate filter solution. The following results were obtained.

Solution	Zero Order Rate Constant XXI Loss	 XXII Appearance	 XXIII Appearance
0.05 M XXI	-0.0320	+0.0105	+0.0172
0.05 M XXI, 0.001 M XCII	-0.0329	+0.0108	+0.0158

Measurement of effect of concentration of 1,1-diphenylethylene (LXXXVIII) on the rate of cycloaddition with 4,4-dimethyl-2-cyclohexenone (XXI)

The apparatus was that illustrated in Figure 14. The saturated copper sulfate solution filter was used. The disappearance of XXI was measured and assumed to be equal to the rate of cycloaddition. No rearrangement products (XXII, XXIII) were observed on the v.p.c. during the kinetic run at 1,1-diphenylethylene concentrations greater than 0.50 M. At lower concentrations (0.01 M) of diphenylethylene, approximately 50% of the loss of XXI was due to rearrangement and not to cycloaddition. The following results were obtained.

Solution XXI Conc.	 LXXXVIII Conc.	Zero Order Rate Constant XXI Loss	Relative Rate
0.05 M	0.00 M	-0.0348	1
0.05	0.01	-0.062	1.78
0.05	0.05	-0.153	4.39
0.05	0.10	-0.229	6.60
0.05	0.25	-0.267	7.65
0.05	0.50	-0.278	8.00

1,1-Diphenylethylene LXXXVIII shows an ϵ value of 1.4 at 366 mμ (ethanol). 4,4-Dimethyl-2-cyclohexenone (XXI) shows an ε value of 7 at 366 mμ (ethanol). The percent absorption of light by XXI in each of the above solutions was calculated.

Solution XXI Conc.	LXXXVIII Conc.	% Light Absorbed by XXI
0.05 M	0.00 M	100
0.05	0.01	96
0.05	0.05	84
0.05	0.10	72
0.05	0.25	50
0.05	0.50	33

Measurement of effect of ferric dipivaloyl methane on rate of cycloaddition of 4,4-dimethyl-2-cyclohexenone (XXI) with 1,1-diphenylethylene (LXXXVII) in benzene

A solution of XXI (0.05 M) and LXXXVII (0.10 M) in benzene was prepared. A solution of XXI (0.05 M), LXXXVII (0.10 M) and ferric dipivaloyl methane (FeDPVM, 10^{-5} M) in benzene was prepared. The solutions were irradiated in the apparatus of Figure 14 using the saturated copper sulfate filter solution. The following results were obtained.

Solution	Zero Order Rate Constant XXI Loss
0.05 M XXI, 0.10 M LXXXVII	-0.102
0.05 M XXI, 0.10 M LXXXVII 10^{-5} M FeDPVM	-0.096

This data indicates negligible quenching by FeDPVM.

Measurement of effect of oxygen on rate of cycloaddition of 4,4-dimethyl-2-cyclohexenone (XXI) with 1,1-diphenylethylene (LXXXVII) in tertiary butyl alcohol

A solution of XXI (0.05 M) and LXXXVII (0.10 M) was prepared. The reference solution was degassed with nitrogen in the usual way. Oxygen was bubbled through the other solution for 15 minutes prior to irradiation. After the start of the irradiation, oxygen was bubbled through this solution for 5 minutes at each time that a sample was withdrawn for v.p.c. analysis. The following results were obtained.

Solution	Zero Order Rate Constant XXI Loss
0.05 M XXI, 0.10 M LXXXVII	-0.0901
0.05 M XXI, 0.10 M LXXXVII - Oxygen saturated	-0.0881

The results indicate a negligible quenching effect by oxygen.

Measurement of effect of trans-piperylene on rate of cycloaddition of 4,4-dimethyl-2-cyclohexenone (XXI) with 1,1-diphenylethylene (LXXXVII) in tertiary butyl alcohol

A solution of 4,4-dimethyl-2-cyclohexenone (0.05 M) and 1,1-diphenylethylene (0.10 M) was prepared. Another solution of XXI (0.05 M), LXXXVII (0.10 M) and *trans*-piperylene (0.05 M) was prepared. The irradiation was done using the saturated copper sulfate filter.

Solution	Zero Order Rate Constant XXI Loss
0.05 M XXI, 0.10 M LXXXVII	-0.112
0.05 M XXI, 0.10 M LXXXVII, 0.05 M *trans*-piperylene	-0.143

This unexpected result of a rate increase of cycloaddition in the presence of piperylene suggested that XXI was adding to piperylene. This was verified by the irradiation of XXI in the presence of piperylene (see previous section of Experimental). At 366 mμ, XXI shows an ε value of 7 and LXXXVII an ε value of 1.4. The percent light absorption by piperylene in the above experiment is negligible since piperylene shows ε = 0.017 at 366 mμ.

Measurement of effect of benzophenone and acetophenone on rate of cycloaddition of 4,4-dimethyl-2-cyclohexenone (XXI) with 1,1-diphenylethylene (LXXXVII) in tertiary butyl alcohol

The solutions listed in the data below were prepared. The irradiation was done in the apparatus illustrated in Figure 14 using the saturated copper sulfate filter solution. The following data was obtained.

Solution	Zero Order Rate Constant
0.05 M XXI, 0.10 M LXXXVII	-0.09507
0.05 M XXI, 0.10 M LXXXVII, 0.10 M benzophenone	0
0.05 M XXI, 0.10 M LXXXVII, 0.60 M acetophenone	0

Approximately 40% of XXI was consumed during this measurement in the solution containing no sensitizer. Analysis of both the benzophenone and acetophenone solutions by v.p.c. (6 ft., $\frac{1}{4}$ in. dia., 5% LAC-446 on 60-80 mesh gaschrom P) showed no detectable change in the concentration of 4,4-dimethyl-2-cyclohexenone. The n.m.r. spectra of the irradiated solutions containing the sensitizers were identical to those the non-irradiated solutions.

Measurement of the extent of rearrangement of 4,4-dimethyl-2-cyclohexenone in the presence of 1,1-diphenylethylene (LXXXVII)

A solution of 4,4-dimethyl-2-cyclohexenone XXI (0.05 M) in tertiary butyl alcohol was prepared. A solution of XXI (0.05 M) and 1,1-diphenylethylene (0.25 M) was prepared. The solutions were irradiated at a distance of $5\frac{1}{2}$ in. from the lamp, using the saturated copper sulfate solution filter. The following results were obtained.

Solution	Zero Order Rate Constant XXI Loss	 XXII Appearance	 XXIII Appearance
0.05 M XXI	-0.0283	+0.0117	+0.0178
0.05 M XXI, 0.25 M LXXXVII	-0.1640	+0.004	+0.0030

Measurement of relative rate of photoreduction of benzophenone in tertiary butyl alcohol and isopropanol

A 0.10 M solution of benzophenone in tertiary butyl alcohol was prepared. A 0.10 M solution of benzophenone in isopropyl alcohol (reagent grade) was prepared. The solutions were degassed with nitrogen and irradiated in the apparatus illustrated in Figure 14. No filter solution was used. The solutions were irradiated for a period of 79 minutes. At the end of the irradiation, a 1 ml. aliquot was taken and diluted with 95% ethanol. The absorbance (A) of 332 mμ (λ_{max} of benzophenone) was measured, and the percent reduction to benzhydrol was calculated by the following formula.

$$\%\ \text{Reduction} = \frac{A_{\text{initial}} - A_{\text{final}}}{A_{\text{initial}}}$$

The following data was obtained.

Solution	% Photoreduction of benzophenone
0.10 M benzophenone in isopropyl alcohol	32.8
0.10 M benzophenone in tertiary butyl alcohol	3.34

The quantum yield for photoreduction of 0.1 M benzophenone in isopropyl alcohol is 1.0 ( ). Thus the relative quantum yield for photoreduction in tertiary butyl alcohol is $\frac{3.34}{32.8} = 0.102$.

<u>Measurement of relative rate of photoreduction of benzophenone in tertiary butyl alcohol and isopropanol in the presence of 1,1-diphenylethylene (LXXXVII)</u>

A solution of benzophenone (0.10 M) and 1,1-diphenylethylene (0.05 M) in isopropyl alcohol (reagent grade) was prepared. A solution of benzophenone (0.10 M) and 1,1-diphenylethylene (0.05 M) in tertiary butyl alcohol was prepared. The solutions were degassed with nitrogen and irradiated in the apparatus illustrated in Figure 14. No filter solution was used. The solutions were irradiated for a period of 79 minutes. This experiment was simultaneous with the preceeding experiment. The analysis of percent photoreduction was as above. The following data was obtained.

Solution	% Photoreduction of benzophenone
0.10 M benzophenone, 0.50 M LXXXVII in isopropyl alcohol	2.3
0.10 M benzophenone, 0.50 M LXXXVII in tertiary butyl alcohol	1.8

Thus, the percent quenching of photoreduction in isopropyl alcohol is equal to 32.8-2.3/32.8 = 96%. The number 32.8 is the percent photoreduction under identical conditions in the absence of 1,1-diphenylethylene as measured in the preceeding experiment.

Measurement of relative rate of cycloaddition of 4,4-dimethyl-2-cyclohexenone (XXI) and 2,4,4-trimethyl-2-cyclohexenone (LXXVII) with 1,1-diphenylethylene (LXXXVII) in tertiary butyl alcohol

A solution of XXI (0.05 M) and LXXVII (0.10 M) in tertiary butyl alcohol was prepared. A solution of LXXVII (0.05 M) and LXXVII (0.10 M) in tertiary butyl alcohol was prepared. The solutions were irradiated in the apparatus shown in Figure 14. A saturated copper sulfate filter solution was used. The following results were obtained.

Solution	Zero Order Rate Constant
XXI (0.05 M), LXXXVII (0.10 M)	-0.0172
LXXVII (0.05 M), LXXXVII (0.10 M)	0.000 (no detectible change in concentration.)

The irradiation was continued until 69% of XXI was consumed.

Workup of the LXXVII-LXXXVII solution and measurement of the n.m.r. spectrum showed no peaks other than those of the two starting materials, indicating no reaction.

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