The hexane was dried over magnesium sulfate, filtered, and added dropwise to an ice-cooled mixture of iodine pentafluoride (4.7 ml, 0.061 mol) and pyridine (24.1 g, 0.305 mol). After work-up, chromatography on 200 g of base-washed alumina, and distillation, there was obtained 2.23 g (44%) of 1,1′-dicyclopropyl-2,2′-azopropane: bp 43–45° (1.0 mm); uv max (cyclohexane) 372 mμ (ϵ 22); nmr ($CDCl_3$) δ 1.03 (s, CH_3), superposed on 0.77–1.38 (m, total 14.10, cyclopropyl methine), 0.25–0.32 (m, 7.90, cyclopropyl methylene).

Anal. Calcd for $C_{12}H_{22}N_2$: C, 74.17; H, 11.41; N, 14.42. Found: C, 74.14; H, 11.44; N, 14.63.

Cyclopropylmethylcarbinylazine (34).—To cyclopropyl methyl ketone (8.4 g, 0.1 mol) in 30 ml of pentane was added anhydrous hydrazine (1.7 ml, 0.053 mol). The solution was refluxed for 24 hr and dried over calcium chloride, and the pentane was removed *in vacuo*. Distillation gave 4.44 g (54%) of cyclopropylmethylcarbinylazine: bp 76° (1.5 mm); nmr ($CDCl_3$) δ 1.76 (s, 5.6, $-CH_3$) 1.18–1.70 (m, 2.4, cyclopropyl methine), 0.50–0.90 (m, 8.0, cyclopropyl methylene).

Anal. Calcd for $C_{10}H_{16}N_2$: C, 73.12; H, 9.82; N, 17.06. Found: C, 73.01; H, 9.84; N, 17.20.

1,1′-Dichloro-1,1′-dicyclopropyl-1,1′-azoethane (35).—The azo compound was prepared by the method of Goldschmidt and Acksteiner.[11,12] After three recrystallizations from pentane at −30° there was obtained a 57% yield of the azo compound, mp 43–50°, presumably as a mixture of isomers: nmr ($CDCl_3$) δ 1.82 (s, 6.05, $-CH_3$), 1.30–1.75 (m, 1.95, cyclopropyl methine), 0.40–0.80 (m, 8.00, cyclopropyl methylene).

Anal. Calcd for $C_{10}H_{16}N_2Cl_2$: C, 51.07; H, 6.86; N, 11.91. Found: C, 50.91; H, 6.73; N, 11.83.

Dicyclopropylcarbinylazine (32).—The azine was prepared according to the method of Hart and Curtis in 78% yield, mp 91–91.5° (lit.[20] mp 92–93°).

1,1′-Dichloro-1,1,1′,1′-tetracyclopropylazomethane (33).—The azo compound was prepared in 72% yield by the procedure described for 1,1′-dichloro-1,1′-dicyclopropyl-1,1′-azoethane: mp 48–52°; nmr ($CDCl_3$) δ 1.32–1.90 (m, 4.09, cyclopropyl methines), 0.35–0.85 (m, 15.91, cyclopropyl methylenes).

Anal. Calcd for $C_{14}H_{20}N_2Cl_2$: C, 58.54; H, 7.02; N, 9.75. Found: C, 58.52; H, 7.14; N, 9.72.

Reaction of 1,1′-Dichloro-1,1,1′,1′-tetracyclopropylazomethane with Methylmagnesium Bromide.—To 1,1′-dichloro-1,1,1′,1′-tetracyclopropylazomethane (250 mg, 0.871 mmol) in 20 ml of sodium-dried ether was added methylmagnesium bromide (2 ml of approximately 3 *M* solution, 6 mmol). The solution was stirred at room temperature for 30 min and treated with water. The ether layer was dried, and the ether was removed *in vacuo*. The resulting liquid was chromatographed on 20 g of base-washed alumina to give 110 mg (51%) of a compound whose nmr and ir spectra were identical with those of 1,1,1′,1′-tetracyclopropyl-1,1′-azoethane.

It was found that addition of the chloroazo compound to a Grignard reagent generated from methylmagnesium iodide gave only dicyclopropylcarbinylazine in 85% yield.

Reaction of 1,1′-Dichloro-1,1′-dicyclopropyl-1,1′-azoethane with Methylmagnesium Bromide.—To 1,1′-dichloro-1,1′-dicyclopropyl-1,1′-azoethane (1.17 g, 5 mmol) in 35 ml of sodium-dried ether was added excess methylmagnesium bromide (5 ml of approximately 3 *M* solution, 15 mmol). After a slight induction period the reaction refluxed gently for several minutes. The solution was stirred for 2 hr at room temperature and hydrolyzed with water. The ether layer was dried over magnesium sulfate, concentrated, and chromatographed on 100 g of base-washed alumina to give 710 mg (73%) of a compound whose nmr and ir spectra were identical with those of 1,1′-dicyclopropyl-2,2′-azopropane.

Registry No.—**1a,** 17396-98-4; **1b,** 17396-99-5; **1c,** 17397-00-1; **1e,** 17397-01-2; **4,** 17397-02-3; **5,** 17397-03-4; **6,** 17397-04-5; **7,** 17397-05-6; **9,** 17397-06-7; **10,** 17397-07-8; **11,** 17397-08-9; **12,** 17397-09-0; **15,** 17414-37-8; **16,** 17397-21-6; **17,** 17397-10-3; **18,** 17397-11-4; **21,** 17396-20-2; **25,** 17396-19-9; **30,** 17397-12-5; **31** HCl, 17397-13-6; **33,** 17397-14-7; **34,** 17397-15-8; **35,** 17397-16-9; **10** HCl, 17397-17-0; **16** HCl, 17397-18-1; 6-amino-2-methyl-3-isopropyl-3-hexene, 17397-19-2; diisopropylcyclopropylcarbinylamine, 17397-20-5.

Acknowledgments.—This work was supported in part by a grant from the U. S. Public Health Service, GM-12296. Predoctoral fellowship support for J. W. T. was provided by the Rohm and Haas Co. and the National Institutes of Health. Fellowship support for J. C. M. was provided by the Alfred P. Sloan Foundation and the John Simon Guggenheim Memorial Foundation.

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[20] H. Hart and O. E. Curtis, *ibid.*, **78**, 112 (1956).

Alkyl-Substitution Effects in the Photochemistry of 2-Cyclohexenones[1]

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The scope of photochemical lumirearrangement in alkyl-substituted 2-cyclohexenones has been investigated. The rearrangement occurs only if the fourth carbon atom of the 2-cyclohexenone ring is fully alkyl substituted. If this requirement is not met, photodimers are the major products. The substituent requirement is necessary but not sufficient to ensure rearrangement as the presence of other substituents either retard or inhibit the reaction.

Photochemical Reactions of Conjugated Ketones.—In recent years the scope and mechanistic aspects of conjugated ketone photochemistry has received a great deal of attention. Photoreactions involving *cis–trans* isomerization,[3,4] molecular rearrangement,[5] dimerization,[6,7] solvent addition,[8] cycloaddition,[9] and reduction[10] have been reported.

The most widely investigated group of compounds possessing this chromophore has been the substituted cyclohexenone type, and in this series the characteristic rearrangements are the lumirearrangement[5] and cyclo-

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[1] This work was supported in part by Public Health Service Grant No. G 0709, National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service.

[2] National Institutes of Health Predoctoral Fellow, 1965–1967.

[3] P. E. Eaton and K. Lin, *J. Amer. Chem. Soc.*, **86**, 2087 (1964); **87**, 2052 (1965).

[4] E. J. Corey, M. Tada, R. LaMahieu, and L. Libit, *ibid.*, **87**, 2051 (1965).

[5] O. L. Chapman, *Advan. Photochem.*, **1**, 323 (1963).

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

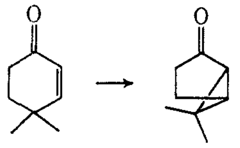
[7] P. E. Eaton, *Accounts Chem. Res.*, **1**, 50 (1968), and references therein.

[8] B. J. Ramey and P. D. Gardner, *J. Amer. Chem. Soc.*, **89**, 3949 (1967).

[9] E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *ibid.*, **86**, 5570 (1964).

[10] H. Koller, G. P. Rabold, K. Weiss, and T. K. Muhkerjee, *Proc. Chem. Soc.*, 332 (1964).

butanone formation.[11-13] The lumirearrangement is an example of a bond-switching reaction in which a cyclohexenone is transformed into a bicyclo[3.1.0]hexan-2-one as shown below. The rearrangement has been found to proceed in a stereospecific manner[14] and in low quantum yield,[15] but the scope and generality of the process has not been evaluated. The present study was undertaken to evaluate these qualities of the photoreaction.

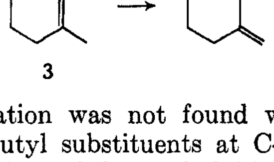


In Table I, the series of 2-cyclohexenones studied are categorized in groups having the same pattern of alkyl substitution, *e.g.*, C-2 substitution, C-3 substitution, etc. The products from the irradiations of each member of a group were found to be similar, and the types of reactions found are readily classifiable into the groups. From this Table I, a striking correlation between alkyl substitution and photoproduct type can be seen.

Group A.—The photochemistry of cyclohexenone has been studied in detail, and recent results[6] show that no monomeric products are formed under the usual "lumirearrangement condition." The dimeric products found have been suggested to arise from triplets, and the ground-state enones apparently exist as aggregates and possibly excimer formation leads directly to the dimers. The ratio between the two cyclobutane-type dimers that are formed is effected by solvent polarity.

Group B.—The irradiation of **2**, using Vycor-filtered light, yielded 44% of dimer plus polymer with a total of only 6% of several volatile photoproducts being formed. Ketone **2** reacted very slowly when Corex-filtered light was used. This slow rate of reaction is consistent with the reported slow rate for the cycloaddition reaction of **2** with isobutylene.[9]

Group C.—With a single substituent at C-3, dimerization is the principal reaction. When the group is methyl (as in **3** and **4**), a 1,3-hydrogen rearrangement from the methyl group to C-2 of the ring occurs[16,17] to yield the exocyclic β,γ isomer in 10% yield. Similar hydrogen migration was not found with ethyl, isopropyl, and *t*-butyl substituents at C-3. Irradiation of benzene solutions of the 3-ethyl (**5**) and 3-isopropyl derivations (**6**) yielded dimers, but under the same conditions 3-isopropyl-6-methyl (**7**) and 3-*t*-butyl (**8**) derivations were stable to the light. More forcing conditions, however, using Vycor-filtered light in *t*-butyl alcohol yielded nonmonomeric materials from **7** and **8**. Apparently, excessive steric hindrance can slow the reaction to the point where demotion from the triplet to ground state is the only efficient process open to the molecule, or less likely, decrease the efficiency of $S_1 \rightarrow T_1$ intersystem crossing.

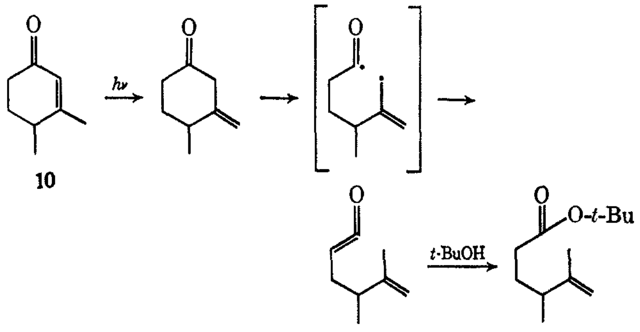


3

Group D.—Monoalkyl sulbstitution at C-4 does not confer any special facility for photorearrangement of a 2-cyclohexenone. Dimeric products and traces of monomeric products were obtained on uv irradiation of **9**.

Group E.—Monosubstitution at both C-3 and C-4 does not induce the lumirearrangement in 2-cyclohexenones. Hydrogen migration, followed by further photorearrangement, was found in **10** which has the C-3 methyl group, shown in group C to be important for photochemical deconjugation.[17] None of the bicyclic compounds **11–14** showed any tendency toward hydrogen migration, a feature that is consistent with the results from **5–8**, the side-chain homologs of the 3-methyl-2-cyclohexenones.

The actual photoproduct isolated from the irradiation of **10** was the *t*-butyl ester **29**, identical with a synthetic sample (see Experimental Section), and the mechanism of its formation is thought to be as shown below.

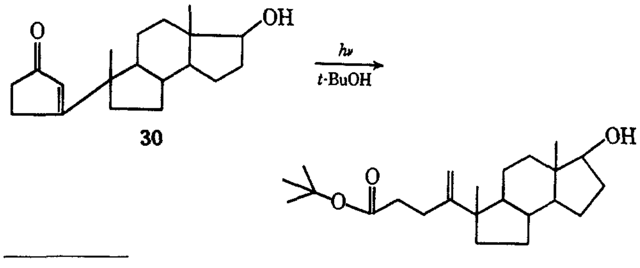


10

29 (26%)

Chemical deconjugation[18] of **10** yielded the $\Delta^{3,4}$ isomer which did not yield **29** upon irradiation. Thus, the $\Delta^{3,4}$ isomer does not appear to be involved in the photochemical reactions of **10**. The α cleavage of β,γ-unsaturated ketones and the formation of ketenes, as proposed here, have ample precedent in the literature.[19,20] Irradiation of **10** in slightly acidic *t*-butyl alcohol did not increase the yield of **29**.

The photochemical formation of **29** from **10** is the first example of such a reaction from a 2-cyclohexenone; an analogous formation of a *t*-butyl ester from the 3-substituted 2-cyclopentenone **30** has been reported.[21]



30

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(11) H. E. Zimmerman and D. J. Sam, *J Amer. Chem. Soc.*, **88**, 4114, 4905 (1966).

(12) J. J. Hurst and G. H. Whitham, *J. Chem. Soc.*, 2864 (1960).

(13) V. H. Kapadia, B. A. Nagasampagi, V. G. Naik, and S. Dev, *Tetrahedron*, **21**, 607 (1965).

(14) O. L. Chapman, J. B. Sieja, and W. J. Welstead, *J. Amer. Chem. Soc.*, **88**, 161 (1966).

(15) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *ibid.*, **88**, 1965 (1966).

(16) See footnote *b*, Table I.

(17) See reference in footnote *c*, Table I.

(18) H. J. Ringold and S. K. Malhotra, *Tetrahedron Lett.*, 669 (1962).

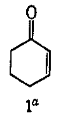
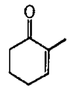
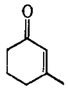
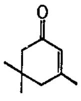
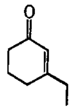
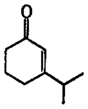
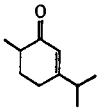
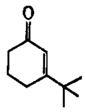
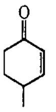
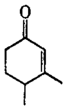
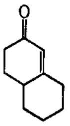
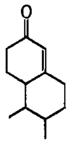
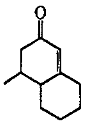
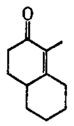
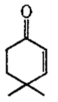
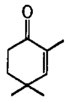
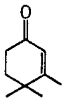
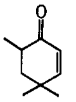
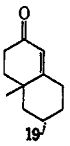
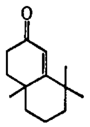
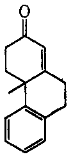
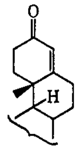
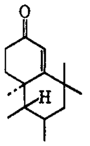
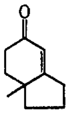
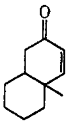
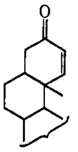
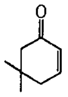
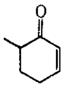
(19) J. R. Williams and H. Ziffer, *Chem. Commun.*, 194 (1967).

(20) J. R. Williams and H. Ziffer, *ibid.*, 469 (1967).

(21) See reference in footnote *l*, Table I.

TABLE I

COMPOUNDS IRRADIATED GROUPED BY SUBSTITUTION PATTERN

Group	Compounds	Photoreaction
A	 1[a]	Dimerize
B	 2	Dimerize
C	 3[b]  4[c]  5  6  7  8	Dimerize,[d] deconjugate[e]
D	 9[f]	Dimerize
E	 10  11  12a[g] 12b[h]  13  14	Dimerize, hydrogen abstraction
F	 15[i]  16[f]  17  18  19[j]  20  21[k]  22a[l] 22b[n] 22c[o]  23[m]  24	Lumirearrange, deconjugate, or unreactive
G	 25  26a[p] 26b[q]	Dimerize
H	 27	Dimerize
I	 28	Dimerize

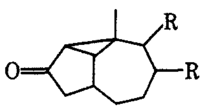
[a] See ref 6. [b] Y. Yamada, H. Uda, and K. Nakanishi, *Chem. Commun.*, 423 (1966). [c] Irradiation reported by P. W. Jennings, Ph.D. Dissertation, University of Utah, 1965; *Dissertation Abstr.*, **26**, 698 (1965). [d] Irradiation of 3-methyl-, 3,5-dimethyl-, and 3-methyl-6-isopropyl-2-cyclohexenone in concentrated solutions (20–50% by volume) has been reported to yield dimeric materials. W. Treibs, *Chem. Ber.*, **63**, 2738 (1930); *J. Prakt. Chem.*, **138**, 299 (1933). [e] Deconjugation only found in the 3-methyl-2-cyclohexenones **3** and **4**. [f] T. A. Rettig, Ph.D. Dissertation, Iowa State, 1966; *Dissertation Abstr.*, **B27**, 114 (1966). [g] **12a** = 3,17-diketo-Δ^4-androstane. [h] **12b** = 19-nortestosterone. [i] Also reported by O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *Tetrahedron Lett.*, 2049 (1963). [j] Also reported by Zimmerman in ref 15. [k] See ref 14 and 15. [l] **22a** = testosterone; reported also by B. Nann, D. Gravel, R. Schorta, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **46**, 2473 (1963). [m] **23** = 10-α-testosterone; reported by H. Wehrli, R. Wenger, K. Schaffner, and O. Jeger, *ibid.*, **46**, 678 (1963). [n] **22b** = testosterone; reported also by Nann, *et al.*, in footnote *l* above. [o] **22c** = cholestenone; reported by B. A. Shoulders, W. W. Kwie, W. Klyne, and P. D. Gardner, *Tetrahedron Lett.*, **21**, 2973 (1965), and by Chapman in footnote *i*. [p] **26a** = 3-keto-Δ^1-cholestene. [q] **26b** = 3-keto-Δ^1-17β-hydroxyandrostene; reported by P. J. Kropp as a private communication from O. L. Chapman in "Organic Photochemistry," O. L. Chapman, Ed., M. Dekker, Inc., New York, N. Y., 1967, p 74.

With the bicyclic members of group E, in addition to dimerization, an important photochemical reaction is hydrogen abstraction to yield saturated ketones. Solvent "dimers" resulting from the abstraction could be isolated. Irradiation of **11** in glyme, dioxane, cyclohexane, acetone, and *t*-butyl alcohol yielded only varying amounts of decalones (2:1, *trans/cis* ratio) and dimers (see Experimental Section). No rearranged products were found.

Group F.—This is the only group of 2-cyclohexenones in which lumirearrangement has been found. Compounds **15**, **18**, **19**, **21**, **22a**, **22b**, **22c**, and **24** all form bicyclo[3.1.0]hexanones *via* the lumiproduct pathway. In each case, it is an inefficient process, a quantum yield of 4×10^{-3} and 8×10^{-3} has been reported for **19** and **21**.[15] From the bicyclic examples **19** and **24**, it can be seen that the size of the B ring (five or six members) is not critical for lumirearrangement, though the lumiproduct yield in **24** is considerably higher than that in **19**. This result is thought to be due to the photochemical stability of the lumiproduct from **24** and not due to an intrinsic difference in the lumirearrangements of each enone. Small amounts of dimer (2%) were found in the case of **19**.

Hydrogen migration within the cyclohexenone ring is blocked by the two C-4 substituents in this class of substituted cyclohexenones, and double-bond migration into the B ring of polycyclic members of the group has been found only in 10α-testosterone (**23**).[22] Compound **20** contains all the requirements for rearrangement, but **20** also has the geminal-methyl substituents in the B ring, a position which is not expected to effect rearrangement by any mechanism proposed to date. This compound, however, would not undergo lumirearrangement even under vigorous conditions (Vycor filter), and the material was completely stable to the reaction conditions. Irradiation of 3,4,4-trimethyl-2-cyclohexenone (**17**) also did not undergo molecular rearrangement, instead a slow dimerization or polymerization were the only reactions found. Similar results have been reported[23] for compound **16**, and it would appear that excessive alkyl substitution beyond the 4,4-dimethyl requirement sometimes causes the molecule to be photochemically less reactive.

Group G.—Compounds **25**, **26a**, and **26b** all contain the 4,4-dialkyl substitution of group F but did not undergo skeletal rearrangement. These constitute further exceptions to the apparent substitution requirement of group F. The cause of this lack of reactivity is unknown but may be related to the strain of the lumiproduct **31** which would be formed. The products from the irradiation of **25** and **26a** were extremely complex mixtures of ketonic material which failed to resolve into any recognizable spot on tlc. The products from **25** were shown to be dimeric by mass spectrometry.



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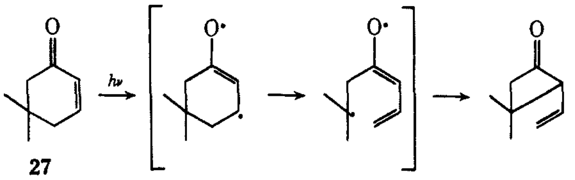
Group H.—The absence of a lumirearrangement in **4** and **27** shows that the ability of the migrating group to stabilize an intermediate carbonium ion or radical is insufficient to cause rearrangement. Furthermore, this type of substitution by stabilization of electron deficiency of C-5 did not enhance a skeletal rearrangement of the type shown for **27** and found for verbenone[12] and 4,5-diphenyl-2-cyclohexenone.[11] The enone **27** yielded one major crystalline dimer of the cyclobutane type, and the only volatile photoproduct produced (4%) was 3-*t*-butoxy-5,5-dimethylcyclohexanone (**32**). This probably arises formally by a similar reaction to the methanol addition to Pummerer's ketone (**33**).[24]



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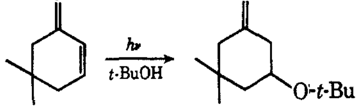

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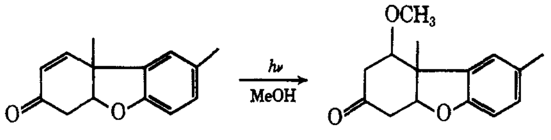

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Group I.—Irradiation of compound **28** did not differ from that of the parent compound 2-cyclohexenone. Only nonmonomeric material was formed.

Lumirearrangement.—As can be seen from Table I, the results from this series of cyclohexenones conclusively points to a striking substitution requirement. Only compounds belonging to group F show any tendency toward skeletal rearrangement of any kind. Lumiproducts are formed only in 2-cyclohexenones which have bis alkyl substitution at the fourth carbon atom of the enone ring. That this substitution requirement is not sufficient to ensure lumirearrangement can be seen from the enones in group G as well as enones **16**, **17**, and **20** in group F, all of which have more alkyl substitution than required and all of which fail to rearrange. Lumirearrangement is thus a very specific reaction, highly dependent on substituents peripheral to the 2-cyclohexenone ring. In the absence of quantum yield information we cannot determine if the specificity is due to a more efficient lumirearrangement or a less efficient side reaction. The hydrogen migration found in **23**, when compared with the rearrangment of the epimeric series **22a–c**, shows that lumirearrangement also has a geometrical requirement, but further work is needed to define the scope of this.

Lumiproduct yields based on total amount of starting enone vary from 5 to 30% (except for **24**) (Table II). Often the low yield of the lumiproduct is due to the formation of a 2-cyclopentenone product, as in ketones **15**, **18**, and **22b**, which arises either directly from

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[22] H. Wehrli, R. Wenger, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **46**, 678 (1963).

[23] See footnote *f*, Table I.

[24] T. Matsuura and K. Ogura, *J. Amer. Chem. Soc.*, **88**, 2602 (1966); *Bull. Chem. Soc. Jap.*, **40**, 945 (1967).

starting material or from the lumiproduct itself. In these latter cases, there is no difficulty in detecting the occurrence of both processes, and thus it seems unlikely that the absence of lumiproduct in the majority of enones can be ascribed to an extreme photolability of the lumiproducts themselves.

TABLE II
YIELDS OF LUMIPRODUCTS

Compound	% yield
15	16
18	5
19	33
22a	24
22b	9
22c	25
24	60

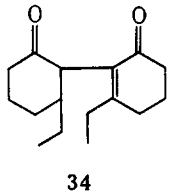
In the case of **15**, the rearrangement was found to be markedly dependent on solvent polarity and proceeded well in *t*-butyl alcohol. Irradiations in benzene and cyclohexane failed to yield the rearranged product. This result has been also noted by Chapman.[25] In the case of **21**, however, rearrangement is promoted with equal facility by irradiation in the nonpolar solvent benzene.[15]

No wavelength effect was noted in **15**, **19**, **20**, and **22a**, and the course of the reactions was unchanged by irradiation at shorter wavelengths than the n → π absorption band of each. This result is consistent with the concept of facile intersystem crossing in the excited-state manifold of ketones so as to yield the state of greatest stability.

Deconjugation.—This reaction appears to have a specific substitution requirement. Except for 10α-testosterone (**23**), those 2-cyclohexenones which undergo photochemical deconjugation (**3**, **4**, and **10**) all have a C-3 methyl group. Enones with C-3 ethyl or isopropyl groups fail in this reaction. A temperature effect has been noted by previous workers (high temperature induces reversal of the reactions).[17] The migration is apparently always into the peripheral substituent and not by deconjugation within the ring.

Hydrogen Abstraction.—Only a few of the cyclohexenones (**11**, **12a**, and **19**) underwent photoreduction to cyclohexanones. The reaction was studied in detail only in the case of **11** and was found to be solvent dependent. The order of ease of reduction found was cyclohexane > glyme = dioxane > *t*-butyl alcohol. No evidence for this reaction was found in **10** and **17**, the monocyclic analogs of **11** and **19**. The cause of this specificity is unknown at this time.

Dimerization.—Dimeric materials have been found from 2-cyclohexenones in each of the groups in Table I. Of all the enones studied, only those of group F do not give high yields of dimeric materials. Although dimers could be analyzed, quantitative yield data are not available from our results because of nonlinear glpc detector response to the dimer mixtures. Dilution of the irradiation solutions to $1 \times 10^{-3}\ M$ did not stop dimerization/polymerization in the case of **11** and did not induce other reactions. No wavelength effect on the dimerization yield was found in **6**, **8**, **11**, and **25**. No solvent effect on this yield was found in **6**, **11**, **12a**, and **12b**. The dimers from the enones are thought to have the normal cyclobutane structure based on their cyclohexanone-type ir absorptions and lack of uv absorption. Only in the case of 3-ethyl-2-cyclohexenone (**5**) was there exception to this finding. Irradiation of this enone yielded a major dimer which possessed characteristic uv and ir absorptions of a cyclohexenone, as well as ir absorption for a saturated cyclohexanone ring; the structure is thought to be **34** or **35**. Dimers were found as mixtures in all groups, except H, where one crystalline cyclobutane-type compound was formed in high yield during the irradiation of **27**. The cause of this unique specificity for **27** is unknown.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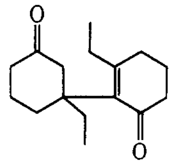
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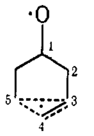
From these results there is no doubt that dimerization is the most universal photoreaction of alkyl-substituted 2-cyclohexenones and that molecular rearrangement occurs only in a few compounds with very specific substitution patterns.

Mechanism.—In evaluating the mechanistic pathway of the lumirearrangement, Zimmerman[15] has invoked the intermediacy of bridged intermediates of the type **26**. In a similar manner, Chapman[5] has suggested a discrete dipolar form (**37**) for the intermediate. Such electron-deficient intermediates suggest that the substitution on the centers involved in the rearrangement of C-5 to C-3, *i.e.*, groups on C-3, C-4, C-5, should lower the energy of the intermediate and thus enhance the rearrangement. This expected result was not found since the substitution patterns of 4-alkyl-, 3,4-dialkyl-, and 5,5-dialkyl-2-cyclohexenones did not enhance the rearrangement. In view of the substitution effects found in the present work it appears likely that a highly developed positively charged intermediate does not occur in the reaction coordinate leading to the lumirearrangement.



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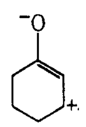

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It has recently been reported[26] that the dipole moment of the n → π* excited carbonyl system is decreased over that of the ground state, but, nonetheless, the charge displacement is still toward oxygen as it is in the ground state. Such charge displacement is the origin of the electron-deficient carbon centers, the deficiency of which should increase on going from the excited state to the ground state. Thus, a possible process for the lumirearrangement is that, as the molecule demotes from the excited state, positive charge on C-3 increases. This partial positive center at C-3 can

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[25] See reference in footnote *i*, Table I.

[26] (a) D. E. Freeman and W. Klemperer, *J. Chem. Phys.*, **45**, 52 (1966); D. E. Freeman, J. R. Lombardi, and W. Klemperer, *ibid.*, **45**, 58 (1966); (b) For calculated π-electron densities which are in agreement with the dipole moment, see H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman, *J. Amer. Chem. Soc.*, **89**, 6589 (1967).

induce the rearrangement of the C-4–C-5 bond only if the resulting charge at C-4 can be stabilized on a tertiary center and if this center in turn can be bridged with the resulting enolic center at C-2. This concept is in general agreement with the previously postulated mechanism but differs in that a role is indicated for C-4 in the process.

In line with the need for an interaction between C-3 and C-5 and C-2 and C-4 in the lumirearrangement the well-known tendency of enone triplet states to undergo twisting motion about the double bond[3] is an important feature. Such a twisting motion brings the lobes of charge at C-3 into close proximity with C-5, the atom to which C-3 is ultimately bonded during lumirearrangement. Such incorporation of twist provides a direct correlation between *cis–trans* isomerization reactions[3] and lumirearrangement. It also correlates ring-size effects and the variance between the photoreactions of cyclic and acyclic conjugated ketones.

The occurrence of an apparent steric effect in the nonreactivity of **16**, **17**, and **20** is unusual in a unimolecular process but can be rationalized by consideration of the steric environment of intermediates along the reaction coordinate. For example, this effect could be important if the lifetime of such intermediates were dependent on solvation. The solvent effect noted in irradiation of 4,4-dimethyl-2-cyclohexenone (**15**) where nonpolar solvents failed to yield lumiproducts (in contrast to polar solvents) is also indicative that solvation of intermediates may be important to lumirearrangement.

It is to be realized that, although partial positively charged intermediates have been suggested for the lumirearrangement, the photoreactions of dimerization, hydrogen abstraction, and *cis–trans* isomerization are distinctly radical processes. In both types of reaction, the intermediate triplets have long been considered to be of n,π^* type. However, the recent suggestion of π,π^* triplet in cyclohexenone dimerization[6] and solvent additions to acetylcyclohexene[8] makes the earlier generalization less secure.

Experimental Section

All irradiations were carried out using dilute solutions in purified solvents (see Table III). Except where noted, see Table III, a 450-W Hanovia lamp (Model 79-A36) in the standard Hanovia quartz probe was used. Glass tubing filters were cut to size and fitted around the lamp. The few experiments (see Experimental Section) using Nester–Faust low-pressure mercury lamp (Model NFUV-300) utilized a standard three-necked irradiation vessel and a quartz insert for lamp housing. Irradiation solutions were outgassed with argon for 30 min prior to irradiation. Progress of the reaction was followed by uv spectroscopy (except when benzene was used as solvent) and by gas–liquid partition chromatography (glpc) (except for the steroidal enones). The crude photomixtures were isolated by removal of solvent under vacuum on a warm water bath. Separation of monomeric materials was carried out by distillation under high vacuum. Monomeric photoproducts were isolated by standard glpc techniques (Carbowax 20M). Dimeric materials were isolated from the distillation residue by glpc on short (2 ft) columns having only 5% of the stationary phase. The products were characterized mainly by mass spectrometry. The results of the irradiations are summarized in Table III. Spectral data are described for those photoproducts not previously reported in the literature. Those irradiations which gave only a few per cent of several minor volatile photoproducts or complex mixtures of nonmonomeric material are not described in detail.

Combustion analyses were performed by the Microanalytical Laboratory, College of Chemistry, University of California. Mass spectral analyses were performed by Miss Sherri Firth, Mass Spectral Laboratory, University of California.

2-Methyl-2-cyclohexenone (**2**).—From 10.0 g (0.089 mol) of 2-methylcyclohexanone,[27] following the method of Warnhoff and Johnson,[28] there was obtained 4.86 g (49.5%) of **2**: bp 77–78° (23–24 mm) [lit.[28] bp 98–101° (27 mm)]; ν_{max} 1675 (s), 1357 (m), 1105 (m), 903 (m), and 882 (m) cm^{-1}; $\lambda_{max}^{95\%\ EtOH}$ 235 mμ (ϵ 9400); nmr spectrum, τ 3.18–3.46 (1.0 H, broad singlet, vinylic H), 7.44–8.22 (6.0 H, multiplet) and 8.31 (2.8 H, doublet with further fine splitting, J = 1.5 cps, vinylic methyl H).

3-Ethyl-2-cyclohexenone (**5**).—From 10.0 g (0.071 mol) of 3-ethoxy-2-cyclohexenone,[29] following the method of Woods, *et al.*,[30] there was obtained 5.67 g (64.5%) of **5**: bp 75–76° (4 mm) [lit.[30] bp 56–57° (0.8 mm)]; ν_{max} 1672 (s), 1631 (m), and 893 (s) cm^{-1}; $\lambda_{max}^{95\%\ EtOH}$ 236 mμ (ϵ 14,100); $\lambda_{max}^{cyclohexane}$ 226 mμ (ϵ 14,700) and 340.5 (30); nmr spectrum, τ 4.32 (0.8 H, triplet, J = 1 cps, vinylic H), 7.52–8.30 (8.0 H, multiplet), and 8.92 ppm (3.2 H, triplet, J = 8 cps, methyl H).

3-Isopropyl-2-cyclohexenone (**6**).—From 12.7 g (0.102 mol) of a mixture of 1- and 3-isopropylcyclohexenes (obtained by dehydration of 2-isopropylcyclohexanol), following the method of Rao and Dev,[31] there was obtained 3.66 g (32%) of **6**: bp 66–69° (2.5 mm) [lit.[30] bp 83–84° (1–1.5 mm)]; 98% pure by glpc on a 20% DEGS column; mol wt, 138 (mass spectrum); ν_{max} 1669 (s), 1623 (m), and 893 (m) cm^{-1}; $\lambda_{max}^{95\%\ EtOH}$ 236.5 mμ (ϵ 14,600); $\lambda_{max}^{cyclohexane}$ 227 mμ (ϵ 14,300); nmr spectrum, τ 4.30 (0.9 H, doublet, J = 1 cps, vinylic H), 7.35–8.30 (6.8 H, multiplet), and 8.92 ppm (6.3 H, doublet, J = 7 cps, *gem*-dimethyl H).

2-Carvenone (**7**).—From 16.7 g (0.110 mol) of dihydrocarvone, following the method of Büchi and Erickson,[32] there was obtained 11.6 g (69.5%) of **7**: bp 80–81° (3.5 mm) [lit.[32] bp 95–96° (8 mm)]; mol wt, 152 (mass spectrum); ν_{max} 1672 (s), 1631 (m), 1211 (s), and 885 (m) cm^{-1}; $\lambda_{max}^{95\%\ EtOH}$ 235.5 mμ (ϵ 13,100); nmr spectrum, τ 4.30 (1.0 H, doublet, J = 1 cps, vinylic H), 7.33–8.73 (5.8 H, multilpet), 8.89 (strong doublet, J = 7 cps, *gem*-dimethyl H), 8.95 ppm (weaker doublet, J = 6.5 cps, methyl H), and combined methyl doublets integrated to 9.2 H.

3-*t*-Butyl-2-cyclohexenone (**8**).—From 14.1 g (0.102 mol) of 1-*t*-butylcyclohexene, using the above procedure for the synthesis of **6**, there was obtained 2.90 g (19%) of **8**: bp 80–81° (4 mm) [lit.[30] bp 70° (0.3 mm)]; ν_{max} 1666 (s), 1613 (m), and 893 (s) cm^{-1}; $\lambda_{max}^{95\%\ EtOH}$ 237 mμ (ϵ 13,750); nmr spectrum, τ 4.25 (1.1 H, triplet, J = 1 cps, vinylic H), 7.52–8.27 (6.2 H, multiplet), and 8.88 ppm (8.7 H, singlet, *t*-butyl H).

4-Methyl-2-cyclohexenone (**9**).—From 34.0 g (0.278 mol) of 4-methylanisole, following the reduction procedure of Wilds and Nelson,[33] there was obtained 13.8 g (45%) of **9**: bp 45.0–45.5° (4.5 mm) [lit.[23] bp 76° (24 mm)]; ν_{max} 1678 (s), 1626 (w), and 1248 (m) cm^{-1}; $\lambda_{max}^{95\%\ EtOH}$ 225 mμ (ϵ 9100); nmr spectrum, τ 3.26 (0.9 H, two doublets of doublets, J = 10 cps, J' = 3 cps, J'' = 1 cps, vinylic H β to the carbonyl), 4.20 (0.9 H, doublet of doublets, J = 10 cps, J' = 2.5 cps, vinylic H α to the carbonyl), 7.22–8.61 (5.4 H, multiplet), and 8.85 ppm (2.8 H, doublet, J = 7 cps, methyl H).

3,4-Dimethyl-2-cyclohexenone (**10**).—From 38.0 g (0.279 mol) of 3,4-dimethylanisole, using the above procedure for the synthesis of **9**, there was obtained 17.8 g (52%) of **10**: bp 60–62° (4.5–5.0 mm); mol wt, 124 (mass spectrum); ν_{max} 1672 (s), 1629 (m), and 861 (m) cm^{-1}; $\lambda_{max}^{95\%\ EtOH}$ 238 mμ (ϵ 13,230); nmr spectrum, τ 4.34 (0.8 H, quartet, J = 1 cps, vinylic H), 7.25–8.50 (8.3 H, multiplet with a strong doublet at 8.08 (vinylic methyl H), J = 1 cps), and 8.82 ppm (2.9 H, doublet, J = 6.5 cps, methyl H).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.58; H, 9.72.

3-Keto-Δ^4-octalin (**11**).—From 134 g (0.80 mol) of 1-morpholino-1-cyclohexene in 750 ml of acetone and 59 g (0.84 mmol) of methyl vinyl ketone, there was obtained 75.2 g (65%) of **11**

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(27) Aldrich Chemical Co., Milwaukee, Wis.

(28) E. W. Warnhoff and W. S. Johnson, *J. Amer. Chem. Soc.*, **75**, 494 (1953).

(29) R. L. Frank and H. K. Hall, Jr., *ibid.*, **72**, 1645 (1950).

(30) G. R. Woods, P. H. Griswold, Jr., B. H. Armbrecht, D. I. Blumenthal, and R. Plapinger, *ibid.*, **71**, 2028 (1949).

(31) G. S. K. Rao and S. Dev, *J. Indian Chem. Soc.*, **33**, 539 (1956).

(32) G. Büchi and R. E. Erickson, *J. Amer. Chem. Soc.*, **76**, 3493 (1954).

(33) A. L. Wilds and N. A. Nelson, *ibid.*, **75**, 5360 (1953).

TABLE III
REACTION CONDITIONS AND YIELD DATA FOR IRRADIATIONS

Group	Compound	Concn × 10^3	Solvent	Filter	Irradn time, hr	% conversion	% monomeric products
B	**2**	51	*t*-BuOH	Vy[a]	25	50	6
C	**5**	34	C_6H_6	Py[b]	15	80	
	6	28	C_6H_6	Py	29	55	
	7	33	*t*-BuOH	Vy	4.5	78	8
			t-BuOH	Co[c]	10		
			C_6H_6	Co	17		
		30	Cyclohexane	Co	25	57	8
	8		Cyclohexane	Co	36		
			t-BuOH	Co	5		
		26	*t*-BuOH	Vy	23	58	8
D	**9**	31	*t*-BuOH	Co	7	63	
E	**10**	35	*t*-BuOH	Co	84	87	36
	11	24	*t*-BuOH	Py	7	37	2
		4	*t*-BuOH	*d*		98	5
		1	*t*-BuOH	Py		20	4
		10	*t*-BuOH	*d*		87	5
		12	Dioxane	Py		80	5
		15	Dioxane	Py		50	6
		8	Glyme	Py		66	6
		12	Cyclohexane	Py		56	42
	12a	5	Cyclohexane	*d*			
			t-BuOH	*d*			
	12b	48	*t*-BuOH	*d*	3.5	91	
		5	Dioxane	Quartz			
	13		*t*-BuOH	*d*	9.5	97	
	14		*t*-BuOH	Co	20	60	
F	**15**	28	*t*-BuOH	Co	5.5	74	38
		37	C_6H_6	Co	36	*e*	
		30	C_6H_6	Co	11.5	*e*	3
	17	28	*t*-BuOH	Co	22	80	
		26	*t*-BuOH	Co	4	85	
		28	*t*-BuOH	Py	24	5	
	18	53	*t*-BuOH	Co	11	55	13
		53	*t*-BuOH	Co	3	26	12
	19	85	*t*-BuOH	Co	60	40	28
	20	42	*t*-BuOH	Co	21		
		42	*t*-BuOH	Vy	6		
	22a		*t*-BuOH	Py	19	58	51
	24	39	*t*-BuOH	Co		60	60
G	**25**	8	*t*-BuOH	Co	19.5		
		8	*t*-BuOH	Vy	4	74	
	26a	1.3	*t*-BuOH	Vy	20	89	
H	**27**	35	*t*-BuOH	Co	8	49	4
I	**28**	30	C_6H_6	Co	7	68	

[a] Vy = Vycor filter. [b] Py = Pyrex filter. [c] Co = Corex filter. [d] Irradiation carried out with low-pressure mercury resonance lamp. [e] Amount of starting material converted not determined.

by the method of Augustine and Caputo:[34] bp 74° (0.1 mm)–103° (0.5 mm) [lit.[34] bp 143–145 (15 mm)]; $\nu_{\max}^{CCl_4}$ 1675 (s) and 1621 (w) cm^{-1}; $\lambda_{\max}^{EtOH}$ 236 mμ (ϵ 17,000).

3,17-Diketo-Δ^4-19-norandrostane (12a).—From 6.8 g (0.02 mol) of 3,17-diketo-19-aldehydo-Δ^4-androstene in 300 ml of methanol and a solution of sodium methoxide (18 g of sodium in 150 ml of methanol), there was obtained[35] 5.86 g (95%) of **12a**: mp 166–169° (lit.[35] mp 172°); $\nu_{\max}^{CS_2}$ 1745 (s), 1678 (s), and 1618 (w) cm^{-1}; $\lambda_{\max}^{95\%\ EtOH}$ 234 mμ (ϵ 16,000).

19-Nortestosterone (12b).—Commercial material[36] was used, mp 120–124°.

Synthesis of 3-keto-1-methyl-Δ^4-octalin (13).—From 1100 g (19 mol) of acetone, an ethanol solution of potassium hydroxide (4.25 g in 75 ml), and 182 g (3.0 mol) of acetaldehyde, there was obtained,[37] after dehydration with 0.3 g (0.024 mol) of iodine, 76.7 g (31%) of 3-penten-2-one: bp 118–124° (lit.[37] bp 122°); $\nu_{\max}^{CCl_4}$ 1675 and 1631 cm^{-1}.

From 57 g of 3-penten-2-one, a solution of 16.5 g (0.42 g-atom) of potassium in 200 ml of anhydrous ethanol, and 150 g (0.88 mol) of 2-carbethoxycyclohexanone, there was obtained[38] 69 g (43%) of 3-keto-10-carbethoxy-1-methyl-Δ^4-octalin (**38**): bp 160–170° (2 mm); mp 70.5–72° [petroleum ether (bp 30–60°)]; $\nu_{\max}^{CCl_4}$ 1730 (s), 1276 (m), 1026 (m), 1672 (s), and 1629 (m) cm^{-1}; nmr, τ 10.03 (3 H, methyl doublet, J = 7 cps), 873 (3 H, methyl triplet J = 7.5 cps), 5.83 (2 H, methylene quartet, J = 7.5 cps), and 4.27 ppm (1 H, vinyl singlet); mol wt, 236 (mass spectrum).

Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.24; H, 8.64.

To a 2-l. flask fitted with stirrer was added 84 g of potassium hydroxide (1.5 mol), 1000 ml of 95% ethanol, and 69 g of **38** (0.29 mol). The mixture was refluxed for 24 hr, neutralized with glacial acetic acid, and concentrated at reduced pressure. Water was added, and the solution was extracted with ether. The combined ethereal extracts were washed with water, dried over magnesium sulfate, evaporated, and distilled through a Claisen head. The material distilling at 90–125° (2 mm) was fractionated to yield 11.6 g (24%) of **13**: $\nu_{\max}^{CCl_4}$ 3040 (w), 1670 (s), and 1630

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(m) cm^{-1}; $\lambda_{\max}^{t\text{-BuOH}}$ 237 mμ (ϵ 12,600); nmr, τ 8.95 (3 H, methyl doublet, J = 5 cps) and 4.40 ppm (1 H, vinyl singlet); mol wt, 164 (mass spectrum).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.62; H, 9.81.

3-Keto-4-methyl-Δ^4-octalin (14).—To a 250-ml three-necked flask fitted with stirrer, reflux condenser, and addition funnel, and with provision for maintaining a dry nitrogen atmosphere, was added 150 ml of anhydrous ethanol and 5.4 g (0.14 g-atom) of potassium. To this solution was slowly introduced a mixture of freshly distilled ethyl vinyl ketone[39] (16 g, 0.19 mol) and 100 g (0.6 mol) of 2-carbethoxycyclohexanone. The addition was carried out during 2 hr with vigorous stirring and in the dry nitrogen atmosphere. When the addition was complete, the mixture was allowed to stir for 15 hr. To the thick, red reaction product was added 100 ml of water containing 8 ml of glacial acetic acid, and the neutral solution was extracted with three 150-ml portions of ether. The combined ethereal extracts were washed with two 100-ml portions of water, dried over magnesium sulfate, and evaporated. The crude product resisted attempts at recrystallization and was distilled to remove starting materials. The crude distillation residue (20 g, 0.079 mol) was dissolved in 100 ml of ethanol in a 250-ml flask fitted with stirrer and with provision for maintaining a nitrogen atmosphere. To the solution was added 100 ml of 10% hydrochloric acid. The acidic solution was refluxed for 24 hr, neutralized with sodium bicarbonate solution, and dried over magnesium sulfate; the solvent was evaporated. The product was distilled in a short-path still to remove high-boiling material and gave 16.5 g of 10-carbethoxy-3-keto-4-methyl-Δ^4-octalin (**39**) (89% yield from the acid dehydration, 36% over-all yield from ethyl vinyl ketone). The keto ester **39** exhibited $\nu_{\max}^{CCl_4}$ 1729 (s), 1670 (s), and 1180 (s, broad) cm^{-1}; mol wt, 236 (mass spectrum).

Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.34; H, 8.40.

To a 100-ml flask fitted with magnetic stirrer and reflux condenser, and with provision for maintaining a dry nitrogen atmosphere, was added 5 g (0.02 mol) of the keto ester **39** and 50 ml of 10% ethanolic sodium hydroxide. The reaction mixture was refluxed for 24 hr, neutralized with dilute hydrochloric acid, concentrated at reduced pressure, diluted with 100 ml of water, and extracted with three 100-ml portions of ether. The combined ethereal extracts were dried over magnesium sulfate and evaporated. The product was distilled to remove high-boiling material and gave 1.6 g (30% yield) of **14**: $\nu_{\max}^{CCl_4}$ 1670 (s) and 1625 (w) cm^{-1}; $\lambda_{\max}^{EtOH}$ 244 mμ (ϵ 15,500); nmr, τ 8.29 ppm (3 H, vinyl methyl doublet, J = 1 cps) and no vinyl hydrogens were visible; mol wt, 164 (mass spectrum).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.17; H, 9.67.

4,4-Dimethyl-2-cyclohexenone (15).—A solution of 46.7 g (0.667 mol) of freshly distilled methyl vinyl ketone, 48.0 g (0.667 mol) of freshly distilled isobutyraldehyde, 70 ml of water, and sufficient methanol to ensure homogeneity was slowly added to a stirred solution of 2.5 g of potassium hydroxide in 15 ml of methanol. Heating with an oil bath was started at the same time as addition. After about one-fifth of the solution had been added, the reaction mixture changed immediately from clear yellow to light orange, and two layers began to separate. The addition was completed in 70 min, at which time the oil-bath temperature was 75–80°. The mixture was allowed to cool, diluted with 100 ml of water, and extracted with ether (seven 75-ml portions). The ethereal extract was washed with water, dried over magnesium sulfate, filtered, and concentrated. Spinning-band distillation of the crude oil (78.6 g) gave a colorless distillate (52.0 g), the major fraction of which was 4,4-dimethyl-2-cyclohexenone (**15**): 39.3 g (47.5% yield); bp 42–43° (3 mm) [lit.[23] bp 76° (21 mm)]; mol wt, 124 (mass spectrum); $\nu_{\max}$ 1678 (s), 1626 (w), and 1116 (m) cm^{-1}; $\lambda_{\max}^{95\%\ EtOH}$ 226 mμ (ϵ 11,130); $\lambda_{\max}^{cyclohexane}$ 340 mμ (ϵ 24); $\lambda_{\max}^{benzene}$ 339 mμ; nmr spectrum, τ 3.38 (1.0 H, doublet of doublets, J = 10 cps, J = 0.5 cps, vinylic H β to the carbonyl), 4.32 (0.9 H, doublet, J = 10 cps, vinylic H α to the carbonyl), 7.49–7.81 (2.1 H, multiplet, methylene H α to the carbonyl), 7.99–8.33 (2.0 H, multiplet, methylene H), and 8.85 ppm (6.2 H, singlet, *gem*-dimethyl H).

3,4,4-Trimethyl-2-cyclohexenone (17).—From 46.7 g (0.667 mol) of methyl vinyl ketone and 57.3 g (0.667 mol) of methyl isopropyl ketone, following the procedure of Eliel and Lukach,[40] there was obtained 9.2 g (10%) of **17**: bp 42–43° (1.0–2.0 mm); mol wt, 138 (mass spectrum); $\nu_{\max}$ 1678 (s) and 1626 (w) cm^{-1}; $\lambda_{\max}^{95\%\ EtOH}$ 234 mμ (ϵ 13,700); nmr spectum, τ 4.4 (1.0 H, multiplet, vinylic H α to the carbonyl), 7.7 (2.3 H, triplet, methylene H α to the carbonyl), 8.1 (3.8 H, singlet, methyl H), 8.3 (1.3 H, multiplet, methylene H), and 9.0 ppm (6.2 H, singlet, *gem*-dimethyl H).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.42; H, 10.29.

4,4,6-Trimethyl-2-cyclohexenone (18).—From 25.9 g (0.308 mol) of isopropenyl methyl ketone[41] and 27.5 g (0.382 mol) of isobutyraldehyde, following the procedure of Eliel and Lukach,[40] there was obtained 18.1 g (42.5%) of **18**: bp 44.5–45.5° (2.5–3.0 mm); mol wt, 138 (mass spectrum); $\nu_{\max}$ 1678 (s), 1621 (w), and 1370 (m) cm^{-1}; $\lambda_{\max}^{95\%\ EtOH}$ 227 mμ (ϵ 9500); nmr spectrum, τ 3.46 (0.9 H, doublet of doublets, J = 10 cps, J' = 1.5 cps, vinylic H β to the carbonyl), 4.32 (0.9 H, doublet, J = 10 cps, vinylic H α to the carbonyl), 7.25–7.85 (1.2 H, multiplet, H α to the carbonyl), 8.01–8.52 (2.5 H, multiplet, methylene H), 8.80 and 8.86 ppm (two singlets, *gem*-dimethyl H), 8.96 (doublet, J = 6.5 cps, methyl H), and integration from 8.80–9.01 ppm totaled 8.5 H.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.51; H, 10.06.

3-Keto-10-methyl-Δ^4-octalin (19).—The material used had been synthesized by a previously described method:[42] bp 97–98° (2 mm) [lit.[32] bp 97–98° (2 mm)]; $\nu_{\max}^{CCl_4}$ 1672 (s) and 1616 (m) cm^{-1}; $\lambda_{\max}^{95\%\ EtOH}$ 238 mμ (ϵ 16,400).

3-Keto-6,6,10-trimethyl-Δ^4-octalin (20).—From 38.3 g (0.22 mol) of 6,6,10-trimethyl-Δ^4-octalin,[42] 225 ml of acetic anhydride, and 38 g (0.23 mol) of anhydrous potassium chromate, there was obtained 21 g (52%) of **20**: bp 85–86° (0.4 mm) [lit.[42] bp 129–130° (10 mm)]; $\nu_{\max}^{CCl_4}$ 1669 (s) and 1600 (m) cm^{-1}; $\lambda_{\max}^{t\text{-BuOH}}$ 242 mμ (ϵ 13,700).

Testosterone Acetate (22a).—From 1.20 g (4.17 mmol) of testosterone, 10 ml of acetic anhydride, and 5 ml of anhydrous pyridine, following recrystallization from aqueous ethanol, there was obtained 1.16 (84.5%) of testosterone acetate (**22a**): mp 139.5–141.0 (lit.[43] mp 140–141°); mol wt, 330 (mass spectrum); $\nu_{\max}^{CHCl_3}$ 1727 (s), 1667 (s), and 1613 (m) cm^{-1}; $\lambda_{\max}^{95\%\ EtOH}$ 241 mμ (ϵ 16,350); nmr spectrum, τ 4.30 (0.9 H, singlet, vinylic H), 5.40 (0.9 H, triplet, J = 7.0–7.5 cps, H geminal to acetyl group), 7.45–9.32 (28.2 H, multiplet with sharp singlet at 7.99, acetyl methyl H), 8.80 (C-19 methyl H), and 9.16 ppm (C-18 methyl H).

5-Keto-8-methyl-Δ$^{4(9)}$-tetrahydroindan (24).—From 71.52 g (0.73 mol) of 2-methylcyclopentanone, 4.55 ml of 3 *N* sodium ethoxide, and 49.2 g (0.73 mol) of methyl vinyl ketone,[27] there was obtained[44] 35.05 g (32% yield) of **24**: bp 65° (0.3 mm); $n^{20}D$ 1.5155; $\lambda_{\max}^{EtOH}$ 239.3 mμ (ϵ 13,850); $\nu_{\max}$ 3230, 1669, 887, and 861 cm^{-1}; nmr, τ 8.83 (3 H, singlet; angular CH_3), 7.68–7.88 (2 H, multiplet; allylic), 7.2–7.6 (2 H, multiplet; H α to carbonyl), and 4.38 ppm (1 H, triplet, J = 2.0 cps; vinyl H split by C-3 H); 2,4-dinitrophenylhydrazone, red platelets from ethanol, mp 151.5–153°.

3-Keto-Δ^1-10-methyloctalone (25).—Synthesis of the sample of **25** used in this study was previously described.[45]

3-Keto-Δ^1-cholestene (26a).—From 48.8 g (0.105 mol) of 3-keto-2α-bromocholestane, 40 g of calcium carbonate, and 500 ml of N,N-dimethylformamide, there was obtained 21.7 g (54%) of **26a**: mp 97.5–99.5° (hexene) (lit.[46] mp 98°); $\lambda_{\max}^{hexane}$ 225 mμ (ϵ 9800).

5,5-Dimethyl-2-cyclohexenone (27).—Lithium aluminum hydride reduction of 84.3 g (0.479 mol) of 3-ethoxy-5,5-dimethyl-2-cyclohexenone (monoethyl ether of dimedone), followed by stirring over 3 *N* sulfuric acid, yielded 52.5 g (89%) of 5,5-dimethyl-2-cyclohexenone (**27**): bp 77–78° (18 mm) [lit.[29] bp 75° (15 mm)]; mol wt, 124 (mass spectrum); $\nu_{\max}$ 1681 (s), 1631 (w), 1385 (m), 1366 (m), and 905 (m) cm^{-1}; $\lambda_{\max}^{95\%\ EtOH}$ 226 mμ (ϵ 9100); nmr spectrum, τ 3.03–3.38 (1.0 H, doublet

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of triplets, $J_d = 10$ cps, $J_t = 4$ cps, vinylic H β to the carbonyl), 4.10 (0.8 H, doublet of triplets, $J_d = 10$ cps, $J_t = 2$ cps, vinylic H α to the carbonyl), 7.66–7.83 (4.1 H, 4-peak multiplet), and 8.95 ppm (6.2 H, singlet, *gem*-dimethyl H).

6-Methyl-2-cyclohexenone (28).—From 40.0 g (0.374 mol) of *o*-toluidine, following the reduction procedure of Stork and White,[47] there was obtained 12.2 g (30%) of **28**: ν_{max} 1684 (s), 1626 (m), 1215 (s), and 890 (m) cm^{-1}; $\lambda_{max}^{95\%\ EtOH}$ 224.5 mμ (ϵ 9400); nmr spectrum, τ 2.92–3.28 (1.0 H, multiplet, vinylic H β to the carbonyl), 4.15 (1.0 H, doulet of triplets, $J_d = 10$ cps, $J_t = 1.5$ cps, vinylic H α to the carbonyl), 7.41–8.71 (5.0 H, multiplet), and 8.93 ppm (2.9 H, doublet, $J = 6.5$ cps, methyl H).

Data Obtained for Isolated Photoproducts. 3-Ethyl-3- (or -2-) [1′-(6-keto-2-ethyl-Δ'-cyclohexenyl)]cyclohexanone from Irradiation of 5.—The solvent was removed from the irradiation mixture of **5**. Glpc of the yellow oil (577 mg) on a 20% DEGS column (5 ft × 0.25 in.) gave no peaks other than starting material. Glpc on a 10% Carbowax 6000 column (2.5 ft × 0.25 in.) showed four major photoproducts, all of which had mass spectral molecular ions at *m/e* 248 (*i.e.*, dimers). The major dimer had $\lambda_{max}^{cyclohexane}$ 239 mμ (ϵ 11,500) and ν_{max} 1715 (s), 1667 (s), and 1629 (m) cm^{-1}, and on the basis of this spectral evidence it was identified as 3-ethyl-3- (or -2-) [1′-(6-keto-2-ethyl-Δ^1-cyclohexenyl)]cyclohexanone.

***t*-Butyl 4,5-Dimethyl-Δ^5-hexenoate from Irradiation of 10.**—The solvent was removed from the irradiation mixture of **10**; the residue was distilled to obtain volatile products; and the photoproduct (26%) was isolated by glpc. This product was identified as *t*-butyl 3,4-dimethyl-Δ^5-hexenoate (**29**) by comparison with authentic *t*-butyl 3,4-dimethyl-Δ^5-hexenoate (see below).

***t*-Butyl 4,5-Dimethyl-Δ^5-hexenoate (29).**[48]—Hydrogen peroxide (9.90 g of 30%, 0.0874 mol) was added rapidly, but dropwise, to 22.6 g (0.179 mol) of 3,4-dimethylcyclohexanone (prepared by Jones oxidation[49] of 3,4-dimethylcyclohexanol)[27] in a 300-ml, three-necked flask, equipped with mechanical stirrer, dropping funnel, and thermometer. The mixture was rapidly stirred for 45 min; 0.5 ml of 6 *N* sulfuric acid was added; and stirring was continued for 15 min. The suspension, cooled in an ice bath to 20°, was swept with nitrogen, and a cupric–ferrous sulfate solution (45 g of $CuSO_4 \cdot 5H_2O$, 50 g of $FeSO_4 \cdot 7H_2O$, 10 ml of concentrated H_2SO_4, and 180 ml of H_2O) was added as rapidly as temperature control (30°) would permit. Rapid stirring was continued at room temperature for 2 hr, and the mixture was then diluted with 100 ml of 10% sulfuric acid. The mixture was extracted with chloroform (three 100-ml portions), and the combined chloroform extract was washed with saturated salt solution (one 25-ml portion) and extracted with 5% sodium hydroxide solution (two 50-ml portions). The basic extract was acidified with 10% sulfuric acid and extracted with ether (three 75-ml portions). The combined ethereal extract was dried and concentrated.

Oxalyl chloride (4.0 g) was added dropwise to the unpurified acid (1.33 g), and the brown solution was stirred for 24 hr at room temperature. Most of the excess oxalyl chloride was removed under reduced pressure, and then a solution of 5.0 g of *t*-butyl alcohol and 5.0 g of pyridine was added dropwise. The mixture was stirred for several minutes and diluted with 75 ml of water and 75 ml of ether, and the layers were separated. The aqueous layer was washed with ether (two 25-ml portions), and the combined ethereal extract was washed with 10% sulfuric acid (one 25-ml portion), washed with saturated sodium bicarbonate solution (one 25-ml portion), dried, and concentrated. The residual oil (2.34 g), which contained crystalline di-*t*-butyloxalate, was analyzed on a 20% Carbowax 20M column (5 ft × 0.25 in.). The glpc trace showed one minor product and two major products, as well as a large peak for di-*t*-butyl oxalate. Two major products (61 and 39%) were found.

The 61% compound was collected from glpc and was identified as *t*-butyl 3,4-dimethyl-Δ^5-hexenoate on the basis of the following data: mass spectrum, last peak at 142 (M − 56); ν_{max} 1727 (s), 1642 (w), 1151 (s, broad), 1000 (m), 958 (m), 917 (s), and 848 (m) cm^{-1}; nmr, τ 4.01–4.66 (0.9 H, multiplet, vinylic H), 4.90–5.30 (1.7 H, multiplet, terminal vinylic H), 7.50–8.71 [13.9 H, multiplet with a very strong singlet at 8.59 (*t*-butyl H)], and 9.03 and 9.13 ppm (5.5 H, two overlying doublets that appeared as a broad triplet, $J_1 = 7$ cps, $J_2 = 5$ cps).

The 39% compound was collected from glpc and was identified as *t*-butyl 4,5-dimethyl-Δ^5-hexenoate (**29**) on the basis of the following data: mass spectrum, last peak at 142 (M − 56); ν_{max} 1730 (s), 1642 (w), 1149 (s, broad), 896 (m), and 852 (m) cm^{-1}; nmr, τ 5.36 (1.4 H, broad singlet, vinylic H), 7.74–8.68 [17.0 H, multiplet with a broad singlet at 8.36 (vinylic methyl H) and a very strong singlet at 8.60 (*t*-butyl H)], and 8.98 ppm (3.6 H, doublet, $J = 6.5$ cps, methyl H).

An analysis was obtained on a sample of both esters, collected together from glpc.

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.65; H, 11.24.

Irradiation of 3-Keto-Δ^4-octalin (11).—In every irradiation of **11** the disappearance of the starting material could be followed by examination of the vpc tracings and the uv spectrum. No equal increase in photoproducts was observed. The starting material gave rise mainly to products of higher molecular weight which were not detectable under the vpc conditions nor by uv spectroscopy. The photoproduct mixtures were isolated by evaporating the solvent, and the thick oily product was analyzed, by utilizing vpc conditions with low stationary-phase concentrations, short columns, and high temperatures. Three peaks were collected separately and subjected to mass spectral analysis. In each case they demonstrated molecular ions for dimers of **11** at 300 mass units. Analysis of the dimers using high-efficiency analytical vpc columns showed the presence of at least 13 dimeric products; none occurred in greater proportion than 10% of the mixture. The close similarity in retention times of these left little doubt that all of them were dimeric in nature. Attempts at recrystallization failed to resolve this dimer mixture as did alumina chromatography and analytical thin layer chromatography. The formation of dimeric photoproducts was unchanged between irradiation of the n → π^* or π → π^* absorption bands (high-pressure arc lamp or low-pressure resonance lamp), but in the second case the reaction was more rapid because of the higher uv absorption of the π → π^* band. During irradiation in *t*-butyl alcohol two monomers could be seen forming slowly, but after 90% of the octalone (**11**) had been converted into photoproducts the two monomers were only present in 2 and 3% of the amount of starting material, respectively. These photoproducts were collected, and their ir spectra were identical with those of *cis*- and *trans*-3-decalones. *trans*-3-Decalone was the major (3%) monomeric photoproduct.

A summary of the irradiations with different solvents appears in Table IV. The only solvent that gave a respectable yield of monomeric photoproducts was cyclohexane where 75% of the 3-keto-Δ^4-octalin which had been converted into photoproduct appeared as *cis*- and *trans*-3-decalone. All of the solvents gave hydrogen abstraction to some extent. Enone dimers were isolated from irradiation in each solvent. Unfiltered photolyses in benzene, acetone, and glacial acetic acid yielded thick, dark, immobile irradiation mixtures which were not further investigated.

The photomixtures from all the irradiations demonstrated a weight increase over the amount of enone used, and, in each ir-

TABLE IV

SUMMARY OF RESULTS FROM IRRADIATION OF 11

Solvent	Procedure[a]	Filter	Concn × 10^{-3} *M*	% conversion	% decalones[b]
t-Butyl alcohol	A	Pyrex	24	37	2
t-Butyl alcohol	B		4	98	5
t-Butyl alcohol	A	Pyrex	1	20	4
t-Butyl alcohol	B		10	87	5
Dioxane	A	Pyrex	12	80	5
Dioxane	A	Pyrex	15	50	6
Glyme	A	Pyrex	8	66	6
Cyclohexane	A	Pyrex	12	56	42

[a] Procedure A, 450-W mercury arc lamp; procedure B, low-pressure mercury resonance lamp. [b] Based on total amount of starting material and not on amount of starting material converted.

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radiation, products that are attributed to reaction of the solvent could be isolated. When glyme was used as solvent, higher molecular weight ethers were isolated from the photomixture (by vpc), and from *t*-butyl alcohol the "dimer" 2,5-dihydroxy-2,5-dimethylhexane (**40**) was isolated and compared with an authentic[50] sample.

The length of time needed for reaction varied among the solvents. Concise comparisons are not possible, as the age of lamp and transmission properties of the probes were not identical in all cases; however, irradiations in cyclohexane which caused mainly reduction to the decalones proceeded approximately three times more rapidly than did irradiation in the other solvents which caused dimerization to predominate. It was found that a tenfold dilution reduced the reaction time even more and yet no new monomeric photoproducts formed.

3,6,6-Trimethylbicyclo[3.1.0]hexan-2-one and 3-Isopropyl-5-methyl-2-cyclopentenone from Irradiation of 18.—The solvent was removed from the irradiation mixture which was distilled, and two photoproducts were isolated by glpc. The first eluted product (5% yield) was identified as 3,6,6-trimethylbicyclo[3.1.0]hexane-2-one on the basis of the following data: mol wt, 138 (mass spectrum); ν_{max} 1724 (s), 1374 (m), 1192 (m), 1117 (m), 996 (m), 893 (w), and 868 (m) cm^{-1}; $\lambda_{max}^{95\%\cdot EtOH}$ 208 mμ (ϵ 3690); nmr, τ 7.3–8.53 (5.6 H, multiplet) and 8.54–9.10 (8.4 H, multiplet with a strong singlet at 8.84 ppm (*gem*-dimethyl H)). The structural assignment was verified by comparison with authentic 3,6,6-trimethylbicyclo[3.1.0]hexan-2-one. Both samples had identical ir spectra and glpc retention times and almost identical nmr spectra.

The second product (8%) was identified as 3-isopropyl-5-methyl-2-cyclopentenone on the basis of the following data: mol wt, 138 (mass spectrum); ν_{max} 1706 (s), 1616 (m), and 867 (m) cm^{-1}; $\lambda_{max}^{95\%\ EtOH}$ 227 mμ (ϵ 14,000); nmr, τ 4.21 (0.9 H, broad singlet, vinylic H), 6.84–8.09 (4.1 H, multiplet), 8.82 (doublet, J = 7 cps, *gem*-dimethyl H), 8.91 ppm (doublet, J = 6.5 cps, methyl H), and both doublets combined integrated to 9.0 H.

Anal. Calcd for $C_9H_{14}O$: mol wt, 138.10446. Found: mol wt, 138.10623 (high-resolution mass spectrum).

The low absolute yields of the photoproducts are probably due to secondary photochemical reactions as 3,6,6-trimethylbicyclo[3.1.0]hexan-2-one was shown to be unstable to the irradiation conditions.

Photoproducts from 19.—The crude photoproduct (11.5 g) was isolated by evaporation of the solvent and was chromatographed on neutral activity III alumina. Petroleum ether eluted 9.7 g (89% of total product) of a mobile yellow oil. Further elution with ether, ethyl acetate, and methanol yielded small amounts of material that were later characterized as dimers of **19** and as the solvent "dimer" **40**. The first chromatographic fraction was distilled [bp 53–55° (0.1 mm)] to give a clear oil which was shown to contain 60% **19** and 12% lumiproduct **41** (25% converted **19**) and 16% a saturated ketone (33% converted **19**). The photoproduct **41** possessed the following properties: λ_{max}^{EtOH} 208 mμ (ϵ 4200); $\nu_{max}^{CCl_4}$ 3020 and 1715 cm^{-1}; nmr, τ 8.80 ppm (3 H, methyl singlet, no absorption for vinyl or allyl protons). The material was identical with that previously described.[15] The saturated ketone was identical with *trans*-10-methyl-2-decalone when compared by infrared and vpc retention times on two different columns.

This reaction was reproducible, and smaller samples were irradiated to greater conversion and followed by analytical vpc. No new major photoproducts could be observed upon extended irradiation; the lumiproduct **41** could be gained in 33% yield after about 70% irradiation. Extended irradiation led to a decrease in the amount of **41**. Large vpc injections and high attenuations revealed the presence of five minor materials (11%) with retention times similar to those of **19**; these were not investigated.

Two major dimers exhibiting mass spectral molecular ions of twice the weight of **19** were detected by analysis of the chromatography fractions using the short (2 ft), low stationary-phase (5%) vpc column.

Photoproduct from 24.—Aliquots removed from the irradiation solution at regular intervals were analyzed by uv spectroscopy and vpc and demonstrated the formation of a photoproduct that possessed only weak uv end absorption and a vpc retention time approximately half that of the starting material. This photoproduct was formed exclusively and did not react further. The irradiation was ceased when 60% of the starting material had been converted and the solution contained 60% photoproduct which was shown to be the lumiproduct: $\nu_{max}^{CCl_4}$ 3021 (w) and 1721 (s) cm^{-1}; $\lambda_{max}^{95\%\ EtOH}$ 205 mμ (ϵ 5700); nmr spectrum, τ 9.13 (3 H, methyl singlet) and 8.5–8.8 ppm (11 H, methylene hump, no vinyl hydrogens).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39; mol wt, 152. Found: C, 80.11; H, 9.40; mol wt, 152 (mass spectrum).

3-*t*-Butoxy-5,5-dimethylcyclohexanone and Crystalline Dimer from Irradiation of 27.—The solvent was removed from the irradiation mixture of **27**, and the volatile photoproduct was isolated by glpc, after the mixture was distilled, on a 20% Carbowax 20M column (5 ft × 0.25 in.). This product (4% yield) was identified as 3-*t*-butoxy-5,5-dimethylcyclohexanone on the basis of the following data: mol wt, 198 (mass spectrum); ν_{max} 1718 (s), 1389 (m), 1362 (m), 1196 (m), and 1063 (s) cm^{-1}; $\lambda^{95\%\ EtOH}$ only end absorption; nmr, τ 6.09–6.50 (1.0 H, multiplet, H geminal to oxygen), 7.43–8.10 (4.0 H, multiplet, methylene H α to carbonyl), and 8.24–8.58 ppm (2.5 H, multiplet, methylene H).

The residual oily crystals (43%), remaining after distillation, were a mixture of dimers. The major dimer, which recrystallized as white plates from 95% ethanol, was identified as 5,5,10,-10- or 11,11-tetramethyltricyclo[6.4.0.0^{2,7}]-3,12- or 9-dodecadione on the basis of the following data: mp 114–115°; mol wt, 248 (mass spectrum); ν_{max} 1706 (s) cm^{-1}; $\lambda^{95\%\ EtOH}$ only end absorption; nmr, τ 6.63–7.21 and 7.32–7.69 (4.4 H, two multiplets, cyclobutyl H), 7.90 (4.0 H, singlet, methylene H α to carbonyl), 8.07–8.77 (4.1 H, multiplet, methylene H), and 8.94 and 9.04 ppm (11.5 H, two singlets, *gem*-dimethyl H).

Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.64; H, 9.80.

Registry No.—**2**, 1121-18-2; **5**, 17299-34-2; **6**, 6328-22-9; **7**, 499-74-1; **8**, 17299-35-3; **9**, 5515-76-4; **10**, 10463-42-0; **11**, 1196-55-0; **12a**, 734-32-7; **12b**, 434-22-0; **13**, 17299-39-7; **14**, 5164-37-4; **15**, 1073-13-8; **17**, 17299-41-1; **18**, 13395-73-8; **19**, 826-56-2; **20**, 17299-44-4; **22a**, 1425-10-1; **24**, 17299-55-7; **24** dinitrophenylhydrazone, 17299-45-5; **25**, 17299-46-6; **26a**, 601-55-8; **27**, 4694-17-1; **28**, 6610-21-5; **29**, 17299-49-9; 3,6,6-trimethylbicyclo[3.1.0]hexan-2-one, 2198-79-0; 5-methyl-3-isopropyl-2-cyclopentenone, 17299-51-3; 3-*t*-butoxy-5,5-dimethylcyclohexanone, 17299-52-4; **38**, 17299-53-5; **39**, 723-05-7; *t*-butyl 3,4-dimethyl-Δ^5-hexenoate, 17299-09-1.

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[50] H. A. Bruson and J. W. Kroeger, *J. Amer. Chem. Soc.*, **62**, 36 (1940).