Photoisomerization of Conjugated Cyclopropyl Ketones[1]

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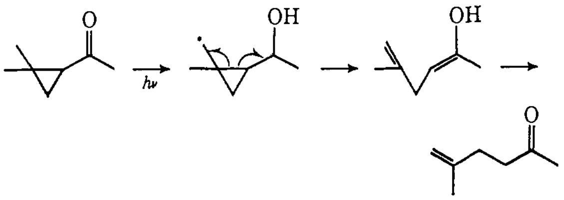
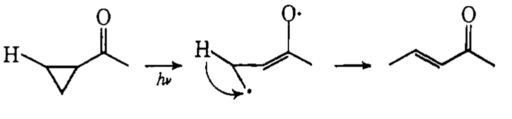
Abstract: The photoisomerization of alkyl-substituted bicyclo[4.1.0]heptan-2-ones has been studied. Using the $n \rightarrow \pi^*$ excitation, two different isomerizations have been found. The first involves opening of the geometrically preferred cyclopropane bond to yield 2-cyclohexenone products. The second, initiated by a type I α cleavage independent of the cyclopropane ring, leads to acyclic diene aldehydes, which is a new photoreaction of conjugated cyclopropyl ketones. Mechanisms for the formation of these products are discussed.

The photoisomerization of conjugated cyclopropyl ketones to unsaturated ketones is a well-known reaction which can occur *via* two different mechanistic sequences.[3,4] The first, observed when the cyclopropyl ring has alkyl substituents having γ-hydrogen atoms to the carbonyl oxygen atom, occurs[4] through the well-known type II reaction (eq 1).



(1)

The alternate sequence, found when γ-hydrogens are absent or their abstraction by the oxygen is sterically impossible, is cleavage of one of the cyclopropane bonds adjacent to the carbonyl group as the first step, with a subsequent 1,2-hydrogen migration and collapse to the enone (eq 2). In those fused bicyclic systems[3] where the cyclopropane ring is held in a rigid conformation with respect to the carbonyl π system, $n \rightarrow \pi^*$ excitation does not lead to equal cleavage of both of the cyclopropane bonds. The bond rupture is highly selective or specific, the bond that preferentially ruptures being the one with optimum geometry for overlap with the carbonyl group during the isomerization process. Using the bicyclo[4.1.0]heptan-2-one nucleus as a model, there are two possible conformations of the excited state which permit maximum electron delocalization. In the chairlike conformation C preferential overlap occurs with the C-1,C-7 bond while in the boatlike conformation B the overlap is with the C-1,C-6 bond. If the isomerization proceeds with *continuous* overlap, the reaction from the chairlike conformation C would be favored since there would be least movement of atoms.



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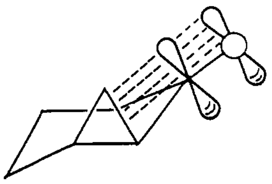

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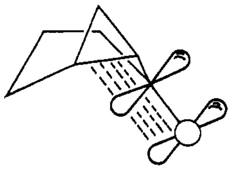
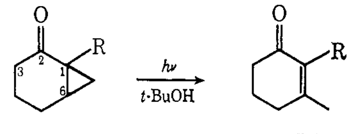


B

The photochemistry of bicyclo[4.1.0]heptan-2-ones has now been studied in detail in order to evaluate further the geometry features and substituent effects on the photoisomerization reaction and to obtain some measure of the efficiency of the process in regard to the well-known type I ketone cleavage reaction.[5] All irradiations were conducted in dilute *t*-butyl alcohol solution using a broad-spectrum mercury-vapor lamp. A Corex filter (>255 nm) was employed to assure that initial excitation was restricted to the $n \rightarrow \pi^*$ band (280–290 nm) of the chromophore.



(3)

1, R = H
3, R = CH_3

2, R = H (31%)[6]
4, R = CH_3 (40%)

The role of the substituent on the cyclopropane ring was first evaluated. Bicyclo[4.1.0]heptan-2-one (**1**) and the 1-methyl derivative (**3**) upon irradiation yielded 2-cyclohexenones **2** and **4**, respectively (eq 3), which were identified by their spectral properties. Photolytic cleavage of the cyclopropyl ring occurred with the rupture of the geometrically preferred C-1,C-7 bond even though opening of the C-1,C-6 bond would have yielded the more stable secondary radical. It must be pointed out that during the irradiation of **1** and **3**, other very minor products were evident from glpc monitoring of the reaction. It is possible that the C-1,C-6 bond underwent inefficient cleavage and the 2-cycloheptenone photoproducts dimerized.[7] The

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(2) National Institutes of Health Predoctoral Fellow, 1965–1967.

(3) J. N. Pitts, Jr., and I. Norman, *J. Amer. Chem. Soc.*, **76**, 4815 (1954); O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *Tetrahedron Lett.*, 2049 (1963); W. G. Brown, *U. S. Govt. Res. Rept.*, **38** (22), 25 (1963); *Chem. Abstr.*, **60**, 9159*e* (1964); R. M. Roberts and R. G. Landolt, *J. Amer. Chem. Soc.*, **87**, 2281 (1965); R. Beugelmans, *Bull. Chim. Soc. Fr.*, 3087 (1965); 244 (1967); C. H. Robinson, A. Gnoj, and F. E. Carlson, *Tetrahedron*, **21**, 2509 (1965); O. L. Chapman, J. B. Sieja, and W. J. Welstead, Jr., *J. Amer. Chem. Soc.*, **88**, 161 (1966); C. D. Hess and J. N. Pitts, Jr., *ibid.*, **89**, 1973 (1967); L. D. Hess, J. L. Jacobsen, K. Schaffner, and J. N. Pitts, Jr., *ibid.*, **89**, 3684 (1967); H. E. Zimmerman, K. G. Hancock, and C. C. Licke, *ibid.*, **90**, 4892 (1968).

(4) W. G. Dauben, L. Schutte, and R. E. Wolfe, *J. Org. Chem.*, **34**, 1849 (1969).

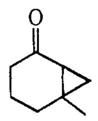
(5) For a preliminary communication of this work, see W. G. Dauben and G. W. Shaffer, *Tetrahedron Lett.*, 4415 (1967).

(6) Percentages are based on recovered starting material.

(7) P. E. Eaton and K. Liu, *J. Amer. Chem. Soc.*, **86**, 2087 (1964); E. J. Corey, M. Tada, R. LaMahieu, and L. Libit, *ibid.*, **87**, 2051 (1965).

small amounts of nonmonomeric material found when the irradiations were stopped after low conversion suggest that any dimerization is a secondary reaction of the 2-cyclohexenones formed in the reaction.[8]

The irradiation of ketones **5** and **6**, both of which have a methyl group in place of a hydrogen atom at C-6, resulted in the extremely slow disappearance of the starting material with the formation of only traces (<1%) of monomeric products. This extreme reluctance to photochemical rearrangement points to the importance of the geometric rather than the thermodynamic control of the rearrangement process. Opening of the lesser overlapped C-1,C-6 bond would give a tertiary center at C-6 to which the C-7 hydrogen atom could migrate to yield an enone.



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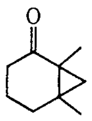
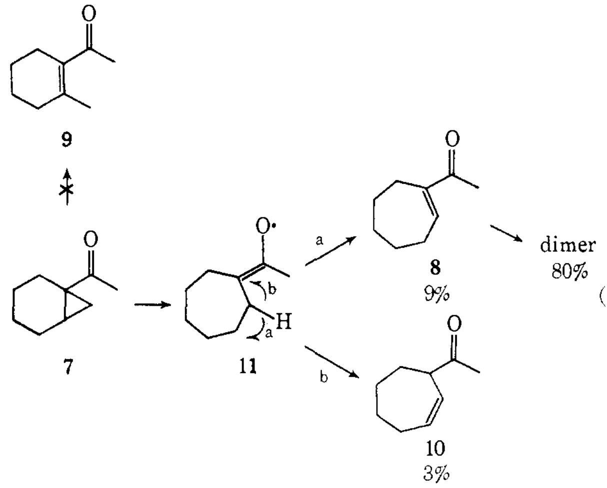


6

For a further evaluation of the steric control of the photoisomerization reaction in this bicyclic series, 1-acetylbicyclo[4.1.0]heptane (**7**) was studied. This ketone **7** with a freely rotating acetyl group allows the carbonyl function to overlap equally well with both conjugated bonds of the cyclopropane ring. Removal of the geometric overlap restriction should enhance the thermodynamic control of the ring opening of the C-1,C-6 bond rather than the C-1,C-7 bond (stability of a secondary *vs.* a primary radical) as was observed in the unconstrained acyclic cases.[4]

Irradiation of **7** in *t*-butyl alcohol gave two monomeric products (eq 4). The major one built up to 8–9% within 2 hr and then remained at this percentage as the starting material continued to decrease. This constant percentage suggested that the product was being formed in good yield from **7** but that it was undergoing an efficient secondary reaction leading to dimers.



(4)

This 9% product was isolated by glpc after the crude irradiation mixture was distilled (29% volatile) and was identified as 1-acetylcycloheptene (**8**).[9] Irradiation of **8** in *t*-butyl alcohol for less than half the irradiation time of ketone **7** gave no monomeric photoproducts and resulted in 80% dimerization. A small amount of the dimers could also be isolated directly from the irradiation of **7**. This result strongly suggests that **8** is formed in good yield from **7** but it is rapidly utilized in a secondary photochemical dimerization. When acetic acid was used as solvent, irradiation of **7** gave 16% of **8**.

The second photoproduct formed from **7** was quite difficult to identify because of the low yield (2–5% of the total mixture) and of the contamination with starting material in the glpc collected samples. A logical predicted structure would be 1-acetyl-2-methylcyclohexene (**9**), a compound resulting from the rupture of the alternate conjugated cyclopropyl bond. This possibility, however, was eliminated on the basis of spectral data. The compound possessed the characteristic ir band at 1715 cm^{-1} for a nonconjugated carbonyl group and nmr bands for two vinyl protons (τ 4.10–4.32). The absence of an absorption for a vinyl methyl group and the presence of a one-proton band at τ 6.8, characteristic for a proton flanked by a carbonyl group and a double bond,[10] permits a tentative structure assignment as 3-acetylcycloheptene (**10**). Mechanistically, **10** could arise from an alternate 1,2-hydrogen migration in an intermediate such as **11**.

During the study of the above irradiation, Winter and Lindauer[11] reported that irradiation of **7** gave a 4–5% yield of four unidentified volatile products. One of the materials was reported to possess an identical glpc retention time with that of **9**. In this present study, no evidence could be found for the formation of **9** during the irradiation. Furthermore, using 1-acetylcyclohexene as a model for **9**, it was found that upon irradiation under the same conditions used for **7**, the ketone disappeared much more slowly than had been found for **7**. Since the more substituted the double bond the slower the dimerization,[8] the results with 1-acetylcyclohexene imply that had **9** been formed under conditions used in this study, it would have been detected. Furthermore, the major photoproduct from 1-acetylcyclohexene was 1-acetyl-2-*t*-butoxycyclohexane[12] and if a similar addition product had been formed from **9**, it would also have been detected. Thus, it can be concluded that without preferential cyclopropyl bond overlap, the more substituted conjugated cyclopropane bond will open.

The photochemical behavior of the bicyclo[4.1.0]heptan-2-one system was markedly altered when C-3 was substituted. Irradiation of 3,7,7-trimethylbicyclo[4.1.0]heptan-2-one (**12**, 2-carone) gave two major photoproducts. Both materials were isomeric with starting material and one of them was readily identified as 3-isopropyl-6-methyl-2-cyclohexenone (**13**, 2-carvenone) by comparison with an authentic sample (eq 5). The second major photoproduct was assigned the structure of 3,3-dimethyl-$\Delta^{4,6}$-octadienal (**14**) from the following spectral data.

The presence of the aldehyde group was established by typical bands in the ir and nmr spectra. The uv

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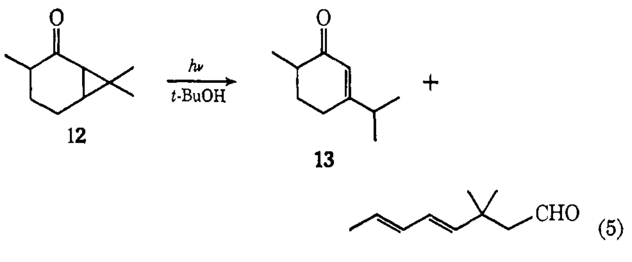
[8] W. G. Dauben, G. W. Shaffer, and N. D. Vietmeyer, *J. Org. Chem.*, 33, 4060 (1968).

[9] W. Taub and J. Szmuszkovicz, *J. Amer. Chem. Soc.*, 74, 2117 (1952); W. J. Rosenfelder and D. Ginsburg, *J. Chem. Soc.*, 2955 (1954).

[10] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Elmsford, N. Y., 1959, p 60.

[11] R. E. Winter and R. F. Lindauer, *Tetrahedron Lett.*, 2345 (1967).

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



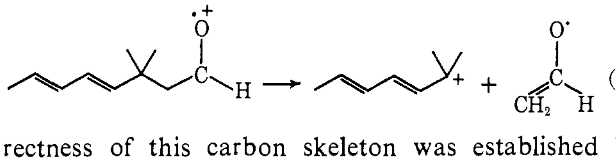
12

13

14

(5)

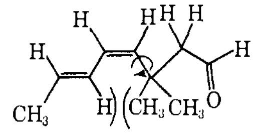
maximum at 228 mμ (ε 19,400) did not shift with solvent polarity, indicating a di- or trisubstituted diene chromophore which was not conjugated with the carbonyl group. The placement of the diene followed from the analysis of the nmr spectrum. The base peak in the mass spectrum at *m/e* 109 (M − 43) adds further confirmation to the overall structure (eq 6). The correctness of this carbon skeleton was established by reductions of **14** to an alcohol which, in turn, was tetrahydrogenated to yield 3,3-dimethyl-1-octanol.



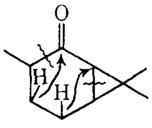
(6)

Based on the nmr spectrum of aldehyde **14**, the photoproduct is probably an equal mixture of the *cis* and *trans* isomers about the C-4,C-5 double bond. The aldehydic proton appears in the spectrum as two overlying triplets, the methylene protons as three doublets (two equal in intensity and one twice as intense), and the *gem*-dimethyl protons as three singlets (two equal in intensity and one twice as intense). The assignment of the methyl resonances as three singlets rather than one doublet and one singlet was confirmed by a 100-MHz spectrum of the alcohol formed by reduction of the aldehyde.

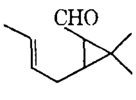
The difference in the spectrum of the C-4,C-5 *cis* and *trans* isomers must be due to a magnetic nonequivalence at C-2 and C-3 in the *cis* molecule due to restricted rotation of the C-3,C-4 single bond; this nonequivalence accounts for the two methyl singlets of equal intensity and the two methylene doublets of equal intensity. In the *trans* isomer, these centers are magnetically equivalent. The stereochemical purity of the C-6,C-7 double bond could not be ascertained.



Irradiation of 2-carvenone (**13**) did not produce the aldehyde **14**,[8] therefore, this aldehyde must arise from an independent photolytic reaction of the cyclopropyl ketone **12** that can compete favorably with the rupture of the C-1,C-7 bond of the cyclopropane ring. The formation of **14** from **12** requires an overall cleavage of the C-1,C-6 and the C-2,C-3 bonds with a hydrogen migration to C-1 and C-2. The rearrangement most likely occurs in two steps through either **15** or **16** as an intermediate. The glpc monitoring of the reaction did show a rapid buildup of a third photoproduct which was maximized after 1 hr and thereafter decreased as the dienaldehyde **14** increased; this intermediate could not be isolated. Ketone **16**, although its formation would involve the opening of the inner bond of the cyclopropane ring, could yield aldehyde **14** by the preferential α cleavage on the more substituted side of the carbonyl group. However, the absence of products resulting from a similar internal bond cleavage in the irradiation of ketone **1** and **3** tends to rule out **16**.



12



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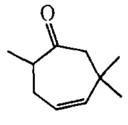
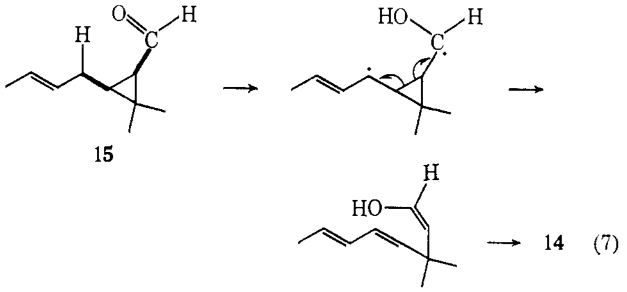


16

On the other hand, the aldehyde **15** is a very reasonable intermediate in the formation of **14**. The photoformation of acyclic unsaturated aldehydes from alicyclic ketones is well known[13] and might successfully compete with the cyclopropane ring opening as a primary process following excitation of **12**. This reaction pathway would also account for the absence of analogous dienaldehydes from the irradiation of ketones **1** and **3** which are unsubstituted at C-3. Increased substitution α to the carbonyl group greatly enhances the efficiency of α cleavage due to the increased stability of the radical character developed at C-3.[14]

The second step in the photoisomerization reaction leading from **15** to **14** would be a type II reaction (see eq 7), a process which has been shown to be highly efficient for 2-methylcyclopropyl methyl ketone when the carbonyl and methyl groups are *cis* to one another. In **15**, the two groupings must be *cis*, at least prior to any *cis–trans* isomerization,[15] because **15** was formed from the *cis*-fused cyclopropyl ketone **12**.



15

(7)

The hydrogen atoms of the *gem*-dimethyl group of aldehyde **15** are also located γ to the carbonyl group and as such **15** might be expected to yield a second type II product in a statistical ratio of 3:2 with respect to aldehyde **14**. However, such a product was not observed and probably reflects the difference in radical stabilities between the two γ positions. Ketones containing γ-hydrogen on both primary and secondary centers favor abstraction of a hydrogen from a secondary center in the ratio of 13:1.[16] Considering that the secondary radical leading to **14** is also allylic, it is not surprising that the alternate type II product was not formed.

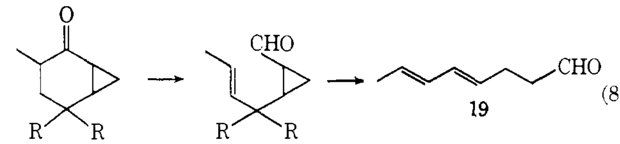
(13) O. L. Chapman, *Advan. Photochem.*, **1**, 323 (1963).

(14) P. J. Wagner and R. W. Spoerke, *J. Amer. Chem. Soc.*, **91**, 4437 (1969).

(15) G. W. Griffin, E. J. O'Connell, and H. A. Hammond, *ibid.*, **85**, 1001 (1963); R. C. Cookson, M. J. Nye, and G. Subrahmanyam, *Proc. Chem. Soc.*, 144 (1964); H. E. Zimmerman and J. W. Wilson, *J. Amer. Chem. Soc.*, **86**, 4036 (1964); R. M. Dodson and R. Klose, *ibid.*, **87**, 1410 (1965); W. G. Brown and J. F. Neumer, *Tetrahedron*, **22**, 473 (1966).

(16) P. Ausloos, *J. Phys. Chem.*, **65**, 1616 (1961).

To provide some experimental proof of the above proposal, ketones **17** and **20** were studied. The irradiation of **17** gave two photoproducts (eq 8) neither of which was the 2-cyclohexenone from the C-1,C-7 bond cleavage. The photoproduct which was first detected on the glpc monitor was maximized after 1 hr of irradiation (20% of the total mixture) and thereafter it steadily decreased. The second product appeared only after the first product had built up and thereafter steadily increased throughout the irradiation. The secondary photoproduct, which was the major component (44%) of the final irradiation mixture, was isolated by preparative glpc and was identified on the basis of its spectral properties as $\Delta^{4,6}$-octadienal (**19**), an aldehyde analogous to **14**. Lithium aluminum hydride reduction of **19** followed by catalytic hydrogenation yielded 1-octanol. The aldehyde is probably a mixture of C-4,C-5 double bond isomers, analogous to aldehyde **14**; however, the unhindered rotation about the C-3,C-4 bond would be expected to make the nmr spectra of the two isomers very similar and not readily analyzable.



(8)

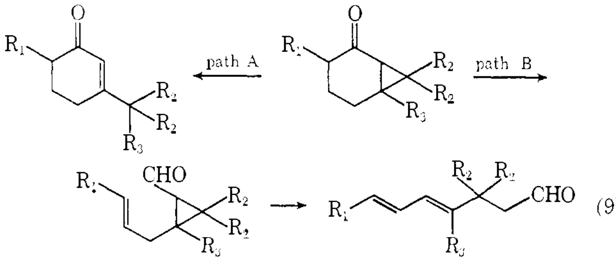
17, R = R = H　**18**, R = R = H

20, R = R = CH_3　**21**, R = R = CH_3

The primary photoproduct of **17** also was isolated and its spectral properties showed it to be 2,3-methano-Δ^5-heptenal (**18**). This aldehyde upon irradiation for a short time yielded dienaldehyde **19**. Thus it is established that **19** is formed from **17** in a two-quantum process and that the C-1,C-6 bond does not cleave as the first step of the reaction.

To establish that the cyclopropane ring opening was a type II process, the 3,5,5-trimethyl analog (**20**) having no γ-hydrogen atoms for abstraction was irradiated. The sole product formed was 2,3-methano-4,4-dimethyl-Δ^5-heptenal (**21**). This cyclopropyl aldehyde was quite stable to irradiation but slowly did give rise to several photoproducts, none of which was a dienaldehyde. All materials formed had very short glpc retention times, indicating that they were fragmentation products and they were not investigated. These results clearly show that the formation of the dienaldehydes **14** and **19** involves a two-step process.

Thus, depending upon the substitution pattern of a bicyclo[4.1.0]heptan-2-one, two different primary photoisomerizations can be followed. Except for special cases where photochemical stability was observed (**5** and **6**), either cyclopropane ring opening (eq 9, path A) or C-2,C-3 α cleavage (eq 9, path B) occurred as primary photochemical processes. When cyclopropane ring opening was a primary reaction, the only cyclopropane bond to open was the one with optimum overlap with the carbonyl group involving the least movement of atoms. When the geometry for optimal overlap in the continuous process was not fixed (see **7**) cyclopropane opening occurred only through that bond with the higher degree of terminal substitution. These substituent effects are summarized in Table I and clearly indicate that this series of cyclopropyl conjugated ketones can serve as starting materials for the preparation of a variety of unsaturated carbonyl compounds.

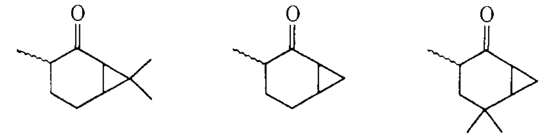


(9)

Table I. Summary of Photoisomerization

Substitution	Photoisomerization obsd
R_1, R_2, R_3 = H or R_1, R_3, H; R_2 = alkyl	Path A only
R_1, R_2 = alkyl; R_3 = H	Path A and path B
R_1 = alkyl; R_2 = H; R_3 = H or alkyl	Path B only
R_1 = H; R_2 = H; R_3 = alkyl	Neither path A nor path B

One other feature of this cyclopropyl carbonyl system is worthy of mention. The three cyclopropyl ketones containing a 3-methyl group exist as a mixture of *cis* and *trans* isomers which can be resolved by glpc. The isomer ratios for the synthetic mixtures of these three ketones are shown in eq 10. The *cis–trans* assignments were made from molecular models in conjunction with base-catalyzed epimerization of the ketones. Molecular models indicate that *trans*-**12** and *cis*-**20** are the thermodynamically favored isomers; therefore, the isomer that increased after injection on a Carbowax–potassium hydroxide column followed by reinjection on a neutral Carbowax column was assigned as *trans* and *cis*, respectively. From models no conclusion could be made as to which isomer of **17** should be the thermodynamically more stable. Base epimerization of **17** yielded approximately a 50–50 mixture. The stereochemical assignment for **17** was based on the observation that for both **12** and **20**, the *cis* isomer is eluted first from the Carbowax column and therefore the first eluted isomer of **17** was also assigned the *cis* configuration.



(10)

	12	17	20
cis	16%	64%	90%
trans	84%	36%	10%

Irradiation of **12**, **17**, and **20** caused epimerization prior to α cleavage, presumably through rupture and re-formation of the C-2,C-3 bond.[13,17] Irradiation of a 90–10 mixture of *cis*- and *trans*-**20** produced not only the aldehyde **21** but also more of the less stable *trans* isomer, the final mixture containing 20% *cis*- and 20% *trans*-ketone. It is not clear why the less stable *trans* isomer should accumulate during the irradiation of **20**. Spectrally, the two isomers are almost identical.

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(17) R. L. Alumbaugh, G. O. Pritchard, and B. Rickborn, *J. Phys. Chem.*, **69**, 3225 (1965).

Experimental Section

All infrared spectra were obtained in carbon tetrachloride solution with a Perkin-Elmer spectrometer either, 137 or 237, and ultraviolet spectra with a Perkin-Elmer spectrometer 202 above 215 nm and a Beckman spectrometer DK-2A below 215 nm. All nmr spectra were obtained with either a Varian A-60 or HA-100 using tetramethylsilane as internal standard. All melting points were taken with a Mel-Temp apparatus in open capillaries and are corrected; all boiling points are uncorrected. Mass spectra were obtained with either a Consolidated Electrodynamic 21-103C or a Varian M-66 mass spectrometer and elemental analyses were obtained from the Microanalytical Laboratory, College of Chemistry, University of California, Berkeley, Calif.

All irradiations were conducted using a Hanovia 450-W mercury arc lamp (679A-36) inserted into a water-cooled, quartz immersion probe. The filters employed were Corex (9700) and Vycor (7910) which were glass sleeves insertable between the lamp and the probe. All solutions were stirred and outgassed with argon for a minimum of 1 hr preceding irradiation. Argon was continuously bubbled through the solution during all irradiations. Irradiation benzene was prepared by stirring commercial benzene over concentrated sulfuric acid, washing with base, washing with water, drying over magnesium sulfate, and refluxing and distilling from phosphorus pentoxide. Irradiation *t*-butyl alcohol was prepared by refluxing and distilling commercial *t*-butyl alcohol from sodium.

All irradiations were monitored by gas-liquid chromatography (glpc) on a Wilkens Aerograph Hy-Fi 600 using an oven temperature range of 95–125°, a nitrogen pressure range of 10–18 psi, and, except where noted, a 5 ft × $^1/_8$ in. column packed with 10% Carbowax 20M on 100–120 mesh Gas Chrom Z. The percentage of nonmonomeric material formed in the irradiation was arrived at indirectly through integration of the starting material glpc trace before irradiation and the photoproducts plus starting material glpc trace after irradiation. The per cent decrease in the total peak areas after irradiation, using a constant volume injection, was used as an approximate percentage of nonmonomeric material and is probably accurate to 5–10%. All irradiations that produced a monomeric photoproduct were repeated at least once. The various product percentages, based on the integrations of constant volume glpc injections, were found to vary somewhat from run to run and the percentages reported in the experimental are for a typical irradiation.

All irradiations were worked up by rinsing the flask with distilled diethyl ether and removing the solvent with a water aspirator at water bath temperatures of 42–48°. The crude irradiation mixtures were then either microdistilled or analyzed directly on a Wilkens Aerograph A-90-P using an oven temperature range of 125–160° and a helium pressure range of 25–40 psi (30–60 cc/min).

Bicyclo[4.1.0]heptan-2-one (1).[18] The material used had the following properties: mol wt 110 (mass spectrum); ir (CCl$_4$) 3040 (w), 1689 (s), 1340 cm^{-1} (m); uv (EtOH) 191 (ϵ 5440), 275 (ϵ 30), $n \rightarrow \pi^*$ in cyclohexane 296 (ϵ 31), and in benzene 288 nm; nmr (τ, CCl$_4$) 7.59–8.66 (7.7 H, multiplet), 8.66–9.23 (2.3 H, multiplet, cyclopropyl H).

Anal. Calcd for $C_7H_{10}O$: C, 76.33; H, 9.15. Found: C, 76.51; H, 9.43.

The semicarbazone, white blunt needles from aqueous ethanol, had mp 185.5–187.0°.

Irradiation of Bicyclo[4.1.0]heptan-2-one (1). A solution of 400 mg of 1 in 125 ml of *t*-butyl alcohol (0.029 *M*) was irradiated for 6 hr using Corex-filtered light. Glpc monitoring of the irradiation on a 10% Carbowax 20M–10% KOH column (5 ft × $^1/_8$ in.) showed only one major photoproduct (retention time relative to starting material equaled 0.815) and one very minor photoproduct. The final percentages of the total mixture were 48% starting material, 16% major photoproduct, 34% nonmonomeric material, and 2% minor photoproduct. During the first part of the irradiation, the major photoproduct increased more rapidly than it did toward the end. After 2 hr 40 min this product was 16% of the total mixture with nonmonomeric material accounting for only 10%.

Solvent was removed and the major product isolated by glpc of the residual, almost colorless oil (325 mg) on a 20% PDEAS column (5 ft × $^1/_4$ in.). This compound was identified as 3-methyl-2-cyclohexenone (2) on the basis of the following data: mol wt 110 (mass spectrum); ir 1678 (s), 1639 (w), 1376 (m), 891 (m) cm^{-1}; uv (EtOH) 234 nm (ϵ 12,100); nmr (τ, CCl$_4$) 4.29 (1.0 H, quartet, J = 1.5 Hz, vinylic H), 7.53–8.40 (9.0 H, multiplet with a broad singlet at 8.08, methylene and vinylic methyl H). The structural assignment was verified by comparison to authentic 3-methyl-2-cyclohexenone (Aldrich). Both samples gave identical ir and nmr spectra, and identical retention times on a 10% Carbowax 20M–10% KOH column (5 ft × $^1/_8$ in.).

Irradiation in *t*-butyl alcohol, using a Vycor filter, yielded the same major photoproduct; however, there were four minor products, all with glpc retention times shorter than that of 1, instead of only one as found in the Corex irradiation. A collective ir spectrum of all the minor products had the strongest carbonyl-stretching frequency at 1727 cm^{-1} and a strong band at 1045 cm^{-1}. These compounds were not identified, but their ir absorption suggests the presence of a *t*-butyl ester.

Irradiation in benzene (421 mg, 125 ml of benzene, 0.031 *M*, Corex filter, 6 hr, 10% Carbowax 20M–10% KOH glpc monitor) yielded the same enone as the sole monomeric photoproduct, although its formation was slower than it was in *t*-butyl alcohol. The final percentages of the total mixture (357 mg) were 87% starting material, 6% enone **4**, and 7% nonmonomeric material.

Glpc of an irradiation mixture of 1 on a Carbowax column without KOH gave the same trace as that from the basic column.

1-Methylbicyclo[4.1.0]heptan-2-one (3).[19] The material used had the following characteristics: ir (CCl$_4$) 1681 (s), 1351 (m), 911 (s) cm^{-1}; uv (EtOH) 199 (ϵ 5230) and 277 nm (ϵ 35); nmr (τ, CCl$_4$) 7.71–8.91 (11.1 H, multiplet with a strong sharp singlet at 8.87, methyl H), 9.22 (0.9 H, doublet of doublets, J = 7.5 Hz, J' = 4.5 Hz, cyclopropyl H).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.10; H, 9.71.

Irradiation of 1-Methylbicyclo[4.1.0]heptan-2-one (3). A solution of 398 mg of 1-methylbicyclo[4.1.0]heptan-2-one (2) in 125 ml of *t*-butyl alcohol (0.026 *M*) was irradiated for 10 hr using Corex-filtered light. Glpc monitoring of the irradiation on either a 10% Carbowax 20M–10% KOH column (5 ft × $^1/_8$ in.) or a 5% Carbowax 20M column (5 ft × $^1/_8$ in.) showed one major photoproduct (retention time relative to starting material equaled 1.33), which appeared within 0.5 hr. Three very minor products were also found, all of which had very short retention times and none of which substantially increased during the irradiation. The final percentages of the total mixture were 38% starting material, 25% major photoproduct, 30% nonmonomeric material, and 7% of minor monomeric photoproducts. During the first hours of the irradiation, the major photoproduct increased more rapidly than it did toward the end. After 4 hr, this product was 22% of the total mixture with nonmonomeric material accounting for only 12–15%.

Solvent was removed and the major product isolated by glpc of the residual pale yellow oil (411 mg) on a 20% Carbowax 20M column (5 ft × $^1/_2$ in.). This compound was identified as 2,3-dimethyl-2-cyclohexenone (**4**) on the basis of the following data: mol wt 124 (mass spectrum); ir (CCl$_4$) 1667 (s), 1637 (m) cm^{-1}; uv (EtOH) 245 nm (ϵ 10,400); nmr (τ, CCl$_4$) 7.47–8.27 (8.9 H, multiplet with a singlet at 8.09, methyl H), 8.32 (3.1 H, singlet, methyl H).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.15; H, 9.90.

Irradiation of **2** in benzene (354 mg, 125 ml of benzene, 0.023 *M*, Corex filter, 21.75 hr, 5% Carbowax 20M glpc monitor) yielded the same enonic photoproduct, although its formation was slower than it was in *t*-butyl alcohol.

6-Methylbicyclo[4.1.0]heptan-2-one (5).[19] From 4.99 g (0.0454 mol) of 3-methyl-2-cyclohexenone (Aldrich), following the procedure of Corey,[20] there was obtained 3.23 g (57.5%) of **6**: bp 57–58° (3 mm); ir (CCl$_4$) 1686 (s), 1295 (m), 1242 (m), 934 (m), 867 (m) cm^{-1}; uv (EtOH) 197 (ϵ 7020) and 277 nm (ϵ 43); nmr (τ CCl$_4$), 7.63–8.72 (8.0 H, multiplet), 8.79 (3.0 H, singlet, methyl H), 9.00–9.37 (1.0 H, multiplet, cyclopropyl H).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.52; H, 9.74.

Irradiation of 6-Methylbicyclo[4.1.0]heptan-2-one (5). A solution of 481 mg of 6-methylbicyclo[4.1.0]heptan-2-one (**5**) in 125 ml of *t*-butyl alcohol (0.031 *M*) was irradiated for 7 hr using Vycor-filtered light. Glpc monitoring of the irradiation showed starting material disappearance with the formation of two or three photoproducts, all with retention time less than that of starting material, and none of which substantially increased during the irradiation.

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(18) W. G. Dauben and G. H. Berezin, *J. Amer. Chem. Soc.*, **85**, 468 (1963).

(19) W. G. Dauben and G. H. Berezin, *ibid.*, **89**, 3449 (1967).

(20) E. J. Corey and M. Chaykovsky, *ibid.*, **87**, 1353 (1965).

At the end of the irradiation there was 34% starting material remaining with 4% minor photoproducts.

Solvent was removed and the brown viscous oil (469 mg) was microdistilled. The distillate, by glpc, showed four or five products, all of which were too minor to be identified.

Irradiation in *t*-butyl alcohol for 7.25 hr, using Corex-filtered light, resulted in very slow disappearance of starting material. One irradiation, using Vycor, gave two products which were eluted very shortly after solvent on glpc. These photoproducts were formed in *ca.* 5–10% yield and had a 1730-cm^{-1} carbonyl stretching frequency, but their formation, in this acceptable percentage, could not be repeated.

Irradiation in benzene (372 mg, 125 ml of benzene, 0.024 *M*) showed little or no disappearance of starting material after 20.5 hr with Corex-filtered light. After 9.25 hr with Vycor-filtered light, 15–30% of the starting material had reacted, with the formation of no photoproducts detectable by the glpc monitor.

Irradiation of 1,6-Dimethylbicyclo[4.1.0]heptan-2-one (6). A solution of 300 mg of 1,6-dimethylbicyclo[4.1.0]heptan-2-one[19] (**6**) in 125 ml of *t*-butyl alcohol (0.017 *M*) was irradiated for 10 hr using Corex-filtered light. Glpc monitoring showed that no appreciable reaction took place; 95% of **6** still remained after 10 hr. The irradiation was continued with Vycor-filtered light and after 5 hr there was 20% starting material remaining, but no monomeric products were observed.

1-Acetylbicyclo[4.1.0]heptane (7). From 14.9 g (0.0675 mol) of trimethyloxosulfonium iodide and 8.00 g (0.0644 mol) of 1-acetylcyclohexene (Aldrich), following the procedure of Corey,[20] there was obtained 3.89 g (44%) of **7**: bp 60–61° (3 mm); ir (CCl_4) 1686 (s) and 1166 (m) cm^{-1}; uv (EtOH) 201 (ϵ 5960) and 273 nm (ϵ 38); nmr (τ, CCl_4) 7.26–8.12 (5.1 H, multiplet with a very strong singlet at 8.04, methyl H), 8.12–8.88 (8.0 H, multiplet), 9.36 (0.9 H, doublet of doublets, $J = 6$ Hz, $J' = 3.5$ Hz, cyclopropyl H).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.47; H, 10.03.

Irradiation of 1-Acetylbicyclo[4.1.0]heptane (7). A solution of 459 mg of 1-acetylbicyclo[4.1.0]heptane (**7**) in 125 ml of *t*-butyl alcohol (0.027 *M*) was irradiated 3.5 hr using Corex-filtered light. Glpc monitoring of the irradiation showed two photoproducts, both of which appeared within 0.5 hr (retention times relative to starting material equaled 0.79 and 1.12). The product eluted first accounted for 5% of the total mixture after 0.5 hr and then decreased to 2% by the end of the irradiation. The later eluted product accounted for 5% of the total mixture after 0.5 hr, increased to 8–9% within 2 hr, and then was maintained at this percentage until the end of the irradiation. After 3.5 hr, starting material was 21% of the total mixture and nonmonomeric material accounted for the other 69%.

Solvent was removed and the residual viscous oil (595 mg) was microdistilled. The 8% major photoproduct was isolated by glpc of the distillate (132 mg) on a 20% Carbowax 20M column (5 ft × 1/2 in.). This compound was identified as 1-acetylcycloheptene (**8**) on the basis of its spectra: mol wt 138 (mass spectrum); for other spectral data see below the synthesis of 1-acetylcycloheptene (**8**). The structural assignment was verified by comparison with authentic 1-acetylcycloheptene (**8**). Both samples gave identical ir and nmr spectra, and identical glpc retention times on a Carbowax 20M column.

The minor (2%) photoproduct was extremely difficult to isolate. It did not collect well on glpc and was always contaminated with starting material. Final isolation, in an impure state, was achieved by terminating an irradiation after 1.25 hr (607 mg of starting material, 125 ml of *t*-butyl alcohol, 0.035 *M*, Corex filter). The percentages of the total mixture were: 67% starting material, 8% 1-acetylcycloheptene (**8**), 5% of the minor product, and 20% nonmonomeric material. The minor product was tentatively identified as 3-acetylcycloheptene (**10**) on the basis of the following data: ir (CCl_4) 1715 (s), 1686 (m) (starting material), 1634 (w), 964 (w) cm^{-1}; nmr (τ, CCl_4) 4.10–4.32 (broad peak, vinylic H), 6.66–7.04 (very weak, broad peak, H α to acetyl and allylic), 7.25–9.49 (broad multiplet with sharper singlets at 7.92, methyl H, and 8.04, starting material); two integrations comparing the 4.1–4.3 to the 6.7–7.0 absorption gave the values 2.1–1.0 H and 1.6–1.0 H.

An ir spectrum taken of the crude irradiation mixture, before distillation, had a carbonyl band at 1709 cm^{-1} in addition to those for starting material (1684 cm^{-1}) and 1-acetylcycloheptene (1667 cm^{-1}). This absorption was too strong to be accounted for by the small amount of 3-acetylcycloheptene contained in the crude mixture. Glpc on a 10% SE 30 column (2 1/2 ft × 1/4 in.) showed peaks with retention times corresponding to dimers. Several irradiations of 1-acetylbicyclo[4.1.0]heptane (**7**) were conducted and these dimer peaks were not always seen. An ir spectrum of material corresponding to these peaks, always contaminated with starting material and 1-acetylcycloheptene, showed carbonyl absorption at *ca.* 1712 cm^{-1} and was very similar to the spectrum of the dimers collected from the irradiation of 1-acetylcycloheptene (see below).

Irradiation of **7** in benzene (278 mg, 125 ml of benzene, 0.016 *M*, Corex filter, 3.5 hr) gave essentially the same result as the *t*-butyl alcohol irradiation. The final percentages of the total mixture were: 44% starting material, 2% 3-acetylcycloheptene (**10**), 6% 1-acetylcycloheptene (**8**), 46% nonmonomeric material, and 2% of two or three other photoproducts (1718 cm^{-1}) that were not investigated further.

1-Acetylcycloheptane (8). This compound was synthesized following published procedures.[9] The following spectral properties were used for identification: ir (CCl_4) 1672, 1639 cm^{-1}; uv (EtOH) 236 (ϵ 10,850), 292 nm (ϵ 69); nmr (τ, CCl_4) 3.01 (1 H, triplet, $J = 6.5$ Hz, vinylic H), 7.39–7.91 (6.4 H, multiplet with strong singlet at 7.80, allylic and methyl H), 7.92–8.81 (6.6 H, multiplet, methylene H).

Irradiation of 1-Acetylcycloheptene (8). A solution of 455 mg of 93% pure 1-acetylcycloheptene (**8**) in 125 ml of *t*-butyl alcohol (0.026 *M*) was irradiated for 1.5 hr using Corex-filtered light. Glpc monitoring of the irradiation showed no monomeric photoproducts; 19% starting material remained after 1.5 hr.

An ir spectrum of the residual viscous oil (486 mg), after solvent removal, showed a new carbonyl stretching frequency band at 1706 (s) cm^{-1}, in addition to the carbonyl band for remaining starting material.

Glpc of the irradiation mixture on a 10% SE 30 column (2 1/2 ft × 1/4 in.) showed two photoproduct peaks with retention times greater than that of starting material. These peaks, glpc collected, had ir (CCl_4) 1706 (s) cm^{-1} and the last peak in their mass spectrum, although very small, at *m/e* 276 (dimeric mass). The structures of these dimers were not elucidated.

Dihydrocarvone.[21] There was added to a 1-l. three-necked flask, equipped with condenser and mechanical stirrer, 40.0 g (0.266 mol) of carvone, 100 g of zinc dust, 200 ml of water, 450 ml of methanol, and 100 ml of 1.35 *N* sodium hydroxide solution. The mixture was stirred under reflux for 5.5 hr and allowed to cool. The excess zinc dust was removed by filtration and the cloudy green solution was concentrated under reduced pressure. The solution was saturated with sodium chloride and the organic layer was extracted with ether (four 100-ml proportions). The brown ethereal extract was dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Spinning band distillation of the brown oil (34.0 g) yielded pure dihydrocarvone: 23.2 g (58%); bp 73° (3.5 mm); ir (CCl_4) 1715 (s), 1645 (m), 896 (s) cm^{-1}.

2-Carone (12).[21] Dry hydrogen chloride was bubbled through a solution of 21.0 g (0.138 mol) of dihydrocarvone in 130 ml of chloroform, containing a trace of anhydrous aluminum trichloride, until the 896-cm^{-1} ir band had disappeared. After 4.5 hr, the hydrogen chloride gas flow was stopped and the pink mixture was filtered. Solvent removal yielded crude 2-methyl-5-(2′-chloro-2′-propyl)cyclohexanone, which was neither purified nor characterized. To the oil (28.6 g) was added 9.6 g of potassium hydroxide in 45 ml of dry methanol and the cloudy mixture was heated on a steam bath for 2.5 hr. The mixture was allowed to cool, filtered, and diluted with ether. The ethereal solution was washed with saturated salt solution, dried over magnesium sulfate, filtered, and concentrated. Distillation of the residual, almost colorless oil (21.5 g) yielded 2-carone (**12**) in fractions ranging upward to 91% pure: 14.60 g (69.5%); bp 84–87° (7 mm); ir (CCl_4) 1686 (s), 1025 (m), 989 (m), 891 (m) cm^{-1}; uv (EtOH) 209 (ϵ 4810) and 287 nm (ϵ 75); nmr (τ, CCl_4) 7.70–8.68 (6.7 H, multiplet), 8.82 and 8.85 (6.1 H, two singlets, *gem*-dimethyl H), 9.04 (3.2 H, doublet, $J = 5.5$ Hz, α-methyl H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 79.14; H, 10.48.

The semicarbazone, white fluffy needles, had mp 170.5–172.5° (lit.[22] mp 170–172°).

The major impurity in the 2-carone synthesis was 2-carvenone (**13**) as determined by comparing its ir spectrum to that of an authentic sample.

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(21) O. Wallach, *Justus Liebigs Ann. Chem.*, 279, 378 (1894); I. M. Klotz, *J. Amer. Chem. Soc.*, **66**, 88 (1944).

(22) A. E. Gillam and T. F. West, *J. Chem. Soc.*, 95 (1945).

2-Carone on a 20% Carbowax 20M column (5 ft $\times$ $^1/_4$ in.) was resolved into two peaks, which were assigned as *cis* and *trans* isomers. The first eluted component was 16% of the 14.60 g of distilled 2-carone with the other accounting for 84%. The above spectral and analytical data were obtained on a sample containing almost entirely the later eluted isomer. Ir spectra of each isomer had essentially identical carbonyl stretching frequencies and were very similar; however, the fingerprint regions were definitely different. An nmr spectrum of the first eluted isomer was very similar to that reported above except that the two methyl singlets at τ 8.82 and 8.85 were each shifted upfield 5 Hz. Injection of a 70–30% (first eluted isomer was the 70% one) mixture on a 20% Carbowax 20M–10% KOH column (5 ft $\times$ $^1/_4$ in.) gave only one peak. Collection of this peak and reinjection on a 20% Carbowax 20M column again gave two peaks in the ratio 28–72%. Repetition of this procedure with a 32–68% mixture gave two peaks on the Carbowax column in the ratio 22–79%. Molecular models indicate the *trans* isomer to be sterically favored.

On the basis of these data, the first eluted isomer was assigned the *cis* configuration. A sample largely enriched in the *cis* isomer had the following uv absorption: uv (EtOH) 205 nm (ϵ 1340).

Irradiation of 2-Carone (12). A solution of 279 mg of a 95–5% mixture of *trans*- and *cis*-2-carone (**12**) in 125 ml of *t*-butyl alcohol (0.015 *M*) was irradiated for 3 hr using Corex-filtered light. Glpc monitoring of the irradiation showed two products within 0.25 hr (retention times relative to *trans* starting material equaled 0.55 and 1.45) with a third product developing within 0.5 hr (retention time relative to *trans* starting material equaled 0.64). The product with 0.55 relative retention time was maximized after 1 hr of irradiation (10% of the total mixture) and thereafter it decreased slightly. The other two products increased throughout the irradiation. The final percentages of the total mixture were 43% *trans* starting material, 2% *cis*, 6% first eluted photoproduct, 19% second eluted photoproduct, 26% latest eluted photoproduct, and 4% of two other minor products. Based on the integration of equal volume glpc injections, little or no polymer was formed.

Solvent was removed and the 19% secondary photoproduct isolated by glpc of the residual, strongly odorous, colorless oil (281 mg) on a 30% Carbowax 6000 Chromosorb W column (5 ft $\times$ $^3/_8$ in.). This compound was identified as 3,3-dimethyl-$\Delta^{4,6}$-octadienal (**14**) on the basis of the following data: no molecular ion in the mass spectrum, last large peak at 124 (M $-$ 28), and a very large peak at 109 (M $-$ 43); ir (CCl_4) 2849 (w), 2747 (w), 1724 (w), 1656 (w), 992 (s); uv (EtOH) 228 nm (ϵ 19,400), uv (cyclohexane) 231 nm; nmr (τ, CCl_4) 0.60 and 0.64 (0.8 H, two overlying triplets, both *J*'s = 3 Hz, aldehydic H), 3.70–4.92 (3.8 H, multiplet, vinylic H), 7.59, 7.70, and 7.73 (2.3 H, three doublets, the former two equal in the intensity and the latter twice as intense, all *J*'s = 3 Hz, methylene H), 8.26 (3.3 H, doublet with a broad base, *J* = 5.5 Hz, vinylic methyl H), 8.73, 8.82, and 8.86 (5.8 H, three singlets, the former two equal in intensity and the latter twice as intense, *gem*-dimethyl N).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.74; H, 10.41.

The 26% primary photoproduct was isolated by glpc on the same column and identified as 2-carvenone (**13**) on the basis of its spectra.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.68; H, 10.73.

The structural assignment was verified by comparison to authentic 2-carvenone (**13**).[8] Both samples had identical ir, uv, and nmr spectra, glpc retention times, and an undepressed mixture melting point of their semicarbazones.

The 6% primary photoproduct was difficult to resolve from aldehyde **14** on preparative glc columns and was unable to be isolated and identified.

Irradiation in benzene, using the same filter, essentially paralleled the *t*-butyl alcohol irradiation. Irradiation in hexane also gave similar results but more nonmonomeric material seemed to be produced.

Irradiation of a mixture consisting of 71% *cis*-carone, 23% *trans*, and 6% impurity (180 mg, 125 ml of *t*-butyl alcohol, 0.010 *M*, Corex filter, 2.5 hr) gave the following integrations: after 0.5 hr, the percentages of *cis*- and *trans*-carone were 30 and 32%, respectively; at the end of the irradiation the percentages were 4% *cis*-carone, 25% *trans*-, 33% of both early eluted photoproducts (unknown plus **15**), 13% 2-carvenone (**13**), and 25% nonmonomeric material.

Irradiation of a mixture consisting of 56% *cis*-carone and 44% *trans* (258 mg, 125 ml of benzene, 0.014 *M*, Corex filter, 1.5 hr) gave the following percentages at the end of the irradiation: 6% *cis*-carone, 48% *trans*-, 36% of both early eluted photoproducts, and 10% 2-carvenone. Other than glpc monitoring, neither of these two isomerization irradiations was investigated further.

Irradiation of synthetic 2-carvenone[8] did not yield any aldehyde.

Lithium Aluminum Hydride Reduction of a 2-Carone Photo-Mixture. A stirred mixture of 1.638 g (0.011 mol) of the crude oil from a 2-carone benzene irradiation, 100 ml of dry ether, and 2.0 g (0.053 mol) of lithium aluminum hydride was heated under reflux for 2.5 hr. The mixture was worked up using saturated ammonium chloride solution and the ethereal solution was dried over magnesium sulfate, filtered, and concentrated.

The residual colorless oil (1.702 g) was chromatographed on a 16.3 cm $\times$ 19 mm column packed with alumina (Woelm, neutral, activity II) and 40–50-ml fractions were taken. Benzene–ether mixtures eluted the diene alcohol, 3,3-dimethyl-$\Delta^{4,6}$-octadienol. None of the fractions (0.20 g, 12%), by glpc, consisted entirely of pure diene alcohol and the following ir and nmr spectral data were obtained on samples which were approximately 80% pure: mol wt 154 (mass spectrum), very large peak at 109 (M $-$ 45); ir (CCl_4) 3390 (m), 1661 (w), 1024 (s), 992 (s) cm^{-1}; uv (EtOH) 229 nm (ϵ 22,600); nmr (τ, CCl_4) 3.63–4.98 (3.5 H, multiplet, vinylic H), 6.33 and 6.39 (1.9 H, two triplets, both *J*'s = 7 Hz, H geminal to hydroxyl), 7.69 (1.4 H, broad singlet, hydroxyl H), 8.13–8.55 (4.8 H, multiplet, vinylic methyl and methylene H), 8.84, 8.95, and 8.97 (6.4 H, three singlets, the former two were equal in intensity and the latter was approximately twice as intense, *gem*-dimethyl H); the 100-MHz nmr confirmed the peaks at 8.84, 8.95, and 8.97 as three singlets rather than one doublet and one singlet. The three peaks were separated by 6.5 and 2 Hz in the 60-MHz nmr and were separated by 10 and 3 Hz in the 100-MHz nmr.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 78.04; H, 11.89.

The column chromatogram was not investigated further.

Reduction of 2-Carone Photoaldehyde (14) to 3,3-Dimethyloctanol. A mixture of 100 mg (0.658 mmol) of photoaldehyde (3,3-dimethyl-$\Delta^{4,6}$-octadienal (**14**)), glpc collected from a benzene irradiation of 2-carone, 10 ml of dry ether, and 0.15 g (4.0 mmol) of lithium aluminum hydride was stirred overnight at room temperature. Saturated ammonium chloride solution was added dropwise with stirring, until the dense lithium and aluminum salts settled. The ethereal solution, and ethereal washings, were decanted into a mixture of 50 mg of 30% palladium on charcoal and 5 ml of cold ether, and the mixture was hydrogenated for 3–4 hr, with stirring, under low hydrogen pressure.

The mixture was filtered, the catalyst washed with ether, and the solvent removed at reduced pressure. Glpc of the colorless oil (102 mg) on a 20% Carbowax 20M column (5 ft $\times$ $^1/_4$ in.) showed one major peak (67%) with two impurities, 13 and 20%, eluted, respectively, before and after the major product.

The major component, glpc collected, was identified as 3,3-dimethyloctanol by comparison to an authentic sample.

The two impurities can probably be explained as follows: the sample of 2-carone irradiated was rather impure and considerable material was found in the photomixture that was eluted before aldehyde **14**. Glpc collection of aldehyde **14** on a large scale undoubtedly contained some of these closely eluted impurities. Furthermore, an nmr spectrum of the crude reduction mixture still retained a small amount of olefinic hydrogen absorption (τ 4.50–4.72). This unidentified product of incomplete hydrogenation, calculated as 13% on the basis of the nmr integration assuming four vinyl hydrogens in unhydrogenated diene alcohol compared to the two hydrogens geminal to the hydroxyl group (τ 6.45), could account for the other impurity in the crude reduction mixture.

3,3-Dimethyloctanol. A Grignard reagent was prepared in the usual manner from 4.2 g (0.173 g-atom) of magnesium turnings and 20.2 g (0.164 mol) of propyl bromide was converted to the cadmium reagent with 23.9 g (0.130 mol) of anhydrous cadmium chloride. The ether was rapidly distilled on a steam bath and 65 ml of benzene was added when distillation became slow. A small amount of additional distillate was collected and a solution of the 3,3-dimethyl-4-carbomethoxybutyryl chloride[23] (15.8 g, 0.122 mol) in 70 ml of benzene was added in one portion. The mixture was stirred at room temperature for 80 min, cooling being necessary at first, and then 65° for 1 hr. The reaction was worked up as usual to yield 15.5 g (95%) of methyl 3,3-dimethyl-5-ketooctanoate; ir (CCl_4) 1739 (s) and 1718 (shoulder) cm^{-1}.

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(23) J. Cason, G. Summrell, and R. S. Mitchell, *J. Org. Chem.*, 15, 850 (1950).

The crude keto ester (15.5 g, 0.078 mol) was reduced according to the Huang–Minlon modification of the Wolff–Kishner reaction[24] with the final heating period being 5 hr at *ca.* 220°. The solution was diluted with water, acidified, and extracted to yield 10.0 g (75%) of 3,3-dimethyloctanoic acid; ir (CCl_4) 3300–2400 (broad absorption), 1715 (s), 1704 (shoulder) cm^{-1}; nmr (τ, CCl_4) 7.82 (1.9 H, singlet, H α to carboxyl), 8.54–8.89 (7.6 H, multiplet with a broad singlet at 8.71, methylene H), 8.90–9.32 (9.5 H, multiplet with a sharp singlet at 8.99, methyl H); the carboxyl hydrogen region of the nmr spectrum was not scanned.

A solution of the crude acid (10.0 g, 0.057 mol) in 15 ml of dry ether was added, dropwise, to a stirred mixture of 2.20 g (0.058 mol) of lithium aluminum hydride in 150 ml of dry ether, over a period of 15 min. The mixture was stirred under reflux for 2 hr, allowed to cool, and worked up with ammonium chloride. The combined ethereal extract was washed with water, dried, filtered, and concentrated to yield 3,3-dimethyloctanol: 8.1 g (88%); mass spectrum, last peak at 143 (M − 15); ir (CCl_4) 3322 (s), 1057 (s), 1024 (s) cm^{-1}; nmr (τ, CCl_4) 6.21 (1.1 H, singlet, hydroxyl H), 6.45 (1.9 H, triplet, J = 8 Hz, H geminal to hydroxyl), 8.39–8.98 (10.7 H, three small peaks and a broad singlet at 8.78, methylene H), 8.99–9.38 (8.3 H, sharp singlet at 9.13, methyl H). The singlet at 6.21 disappeared when the sample was shaken with D_2O.

Anal. Calcd for $C_{10}H_{22}O$: C, 75.83; H, 14.01. Found: C, 75.67; H, 14.12.

3-Methylbicyclo[4.1.0]heptan-2-one (17). From 10.5 g (0.048 mol) of trimethyloxosulfonium iodide and 5.00 g (0.045 mol) of 6-methyl-2-cyclohexenone[8] following the procedure of Corey,[20] there was obtained 3.53 g (63%) of 17: bp 68–70° (5 mm); mol wt 124 (mass spectrum); ir (CCl_4) 1686 (s) cm^{-1}; uv (EtOH) 191 nm (ϵ 5180), 279 nm (ϵ 35); nmr (τ, CCl_4) 7.52–8.66 (7.0 H, multiplet), 8.67–9.21 (5.0 H, multiplet with two doublets at 8.97 and 9.04, both J's = 6.5 Hz, methyl and cyclopropyl H). A 100-MHz nmr confirmed the two doublets (both J's = 6.5 Hz).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.12; H, 9.57.

Pure 17 on a 10% Carbowax 20M column (5 ft × $^1/_8$ in.) was resolved into two peaks. The first eluted component was 64% of the mixture with the other accounting for 36%. On a 20% Carbowax 20M–10% KOH column, the same sample was eluted as a single symmetrical peak. An ir spectrum of this symmetrical peak, glpc collected, was identical with a spectrum of a sample before injection. Glpc collection of this symmetrical peak from the Carbowax 20M–KOH column and reinjection on a 10% Carbowax 20M column (5 ft × $^1/_8$ in.) again gave two peaks, although the percentages had changed from 64–36 to 54–46. On the basis of this evidence, and the *cis–trans* assignments for the cyclopropyl ketones **12** and **20**, the component first eluted from glpc was assigned as *cis*-17 and the other component as *trans*-17.

Irradiation of 3-Methylbicyclo[4.1.0]heptan-2-one (17). A solution of 305 mg of a 64–36% mixture of *cis*- and *trans*-3-methylbicyclo[4.1.0]heptan-2-one (17) in 125 ml of *t*-butyl alcohol (0.020 *M*) was irradiated for 3 hr using Corex-filtered light. Glpc monitoring of the irradiation showed one photoproduct within 0.25 hr (retention time relative to *cis* starting material equaled 0.48) with a second product developing within 0.5 hr (retention time relative to *cis* starting material equaled 0.603). The first product was maximized after 1 hr of irradiation (28% of the total mixture) and thereafter it steadily decreased. The second product, which gave a rather unsymmetrical glpc peak, steadily increased throughout the irradiation. The final percentages of the total mixture were 19% starting material, 15 and 44% major photoproducts, 1% unidentified product, and 21% nonmonomeric material. The *cis* isomer of starting material decreased more rapidly than did the *trans*. After 0.5 hr the mixture contained 33% *cis* and 32% *trans*; at the end of the irradiation these percentages were 7 and 12%.

Solvent was removed and the 15% primary photoproduct isolated by glpc of the residual, almost colorless oil (353 mg) on a 20% Carbowax 20M–10% KOH column (5 ft × $^1/_4$ in.). This compound was identified as 2,3-methano-Δ^5-heptenal (18) on the basis of the following data: mol wt 124 (mass spectrum); ir (CCl_4) 2998 (w), 2817 (w), 2706 (w), 1708 (s) cm^{-1}; uv (EtOH) 220 (ϵ 2310) and 187.5 nm (ϵ 13,000); nmr (τ, CCl_4) 0.77 (0.8 H, doublet, J = 4 Hz, aldehydic H), 4.42–4.74 (1.7 H, multiplet, vinylic H), 7.43–8.52 (7.1 H, multiplet with a doublet of doublets at 8.35, methyl H, J = 3.5 Hz, J' = 1.5 Hz), 8.68 (1.2 H, misshapen doublet, J = 9 Hz, cyclopropyl H), 8.93 (1.2 H, misshapen doublet, J = 8.5 Hz, cyclopropyl H).

The 44% secondary photoproduct was isolated by glpc either on a 20% PDEAS (5 ft × $^1/_4$ in.) or a 30% Carbowax 6000 (5 ft × $^3/_8$ in.) column and was identified as $\Delta^{4,6}$-octadienal (**19**) on the basis of the following data: mol wt 124 (mass spectrum); ir (CCl_4) 3021 (m), 2817 (m), 2710 (m), 1730 (s) cm^{-1}; uv (CCl_4) 228 nm (ϵ 20,400); nmr (τ CCl_4) 0.53 (0.9 H, broad singlet, aldehydic H), 3.57–4.83 (4.0 H, multiplet, vinylic H), 7.53 and 7.58 (3.9 H, two overlapping singlets, methylene H), 8.28 (3.2 H; broad doublet, J = 6 Hz, methyl H). A 100-MHz nmr showed the 7.53 and 7.58 singlets to actually be more complex multiplets.

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.32; H, 9.86.

An ir spectrum of starting material, glpc recovered from the irradiation mixture, had an identical carbonyl stretching frequency (1689 cm^{-1}) with that of starting material before irradiation and identical peaks throughout the spectrum, although relative peak heights in the fingerprint region had definitely changed. The irradiation had altered the starting material mixture from a predominance of the *cis* isomer to a predominance of the *trans* isomer.

Irradiation of 17 in benzene (349 mg, 125 ml of benzene, 0.016 *M*, Corex filter, 3 hr) gave a crude mixture (258 mg), whose composition essentially paralleled that from the *t*-butyl alcohol irradiation. An estimate of the amount of nonmonomeric material produced was not made for the benzene irradiation. In benzene, both isomers of starting material decreased approximately equally, rather than the *cis* reacting more rapidly as it had in *t*-butyl alcohol.

Reduction of $\Delta^{4,6}$-Octadienal (19) to 1-Octanol. A stirred mixture of 148 mg (1.19 mmol) of the major photoaldehyde ($\Delta^{4,6}$-octadienal (**19**)), glpc collected from the irradiation of 3-methylbicyclo[4.1.0]heptan-2-one (**17**), 10 ml of dry ether, and 0.2 g (5.3 mmol) of lithium aluminum hydride, was heated under reflux for 2.25 hr. The mixture was processed as usual, solvent was removed, and the colorless oil (136 mg) was identified as $\Delta^{4,6}$-octadienol on the basis of the following data: ir (CCl_4) 3378 (s), 1631 (w), 990 (s), 949 (m) cm^{-1}; nmr (τ, CCl_4) 3.41–5.02 (3.8 H, multiplet, vinylic H), 5.96 (1.1 H, broad singlet, hydroxyl H), 6.47 (2.0 H, triplet, J = 6.5 Hz, H geminal to hydroxyl), 7.57–8.10 (2.1 H, five-peak multiplet, allylic methylene H), 8.13–8.68 (5.0 H, multiplet with a doublet at 8.28 (methyl H), J = 6 Hz).

A solution of 136 mg of the above diene alcohol in 95% ethanol was added to a mixture of prehydrogenated 10% palladium on charcoal (132 mg) in 20 ml of 95% ethanol. The mixture was rapidly stirred and exhaustively hydrogenated, under low pressure, overnight. The mixture was filtered and the catalyst was washed with ether. Solvent removal gave a colorless oil (59 mg) identified as 1-octanol on the basis of the following data: ir (CCl_4) 3333 (m), 1115 (s), 1045 (s) cm^{-1}; nmr (τ, CCl_4) 6.30–6.74 (1.6 H, broad multiplet, H geminal to hydroxyl), 6.91 (0.9 H, broad singlet, hydroxyl H), 8.70 (12.5 H, broad singlet, methylene H), 9.11 (2.9 H, misshapen triplet, J = 5 Hz, methyl H); the 6.91 peak shifted to higher field upon dilution. The structural assignment was verified by comparison to authentic 1-octanol.[25]

Irradiation of 2,3-Methano-Δ^5-heptenal (18). The minor photoproduct (2,3-methano-Δ^5-heptenal (**18**)) from the irradiation of 3-methylbicyclo[4.1.0]heptan-2-one (**17**) was glpc collected. A solution of 8 mg of this aldehyde in 1 ml of *t*-butyl alcohol in a Pyrex glpc collection tube was degassed with argon for 1 hr and the tube was then sealed with a septum cap. The tube was wired to the side of a quartz immersion probe and irradiated for 0.5 hr. After 0.25 hr, the irradiation consisted of 22% starting material, 60% of a photoproduct that had an identical glpc retention time with that of $\Delta^{4,6}$-octadienal (**19**) from the irradiation of 3-methylbicyclo[4.1.0]heptan-2-one (**17**), and *ca.* 18% of nonmonomeric material. Also there was a trace of another photoproduct. After 0.5 hr the percentages were: 6% starting material, 68% major photoproduct, 1–2% minor unidentified photoproduct, and 25% nonmonomeric material.

3,5,5-Trimethylbicyclo[4.1.0]heptan-2-one (20). From 6.26 g (0.0454 mol) of 4,4,6-trimethyl-2-cyclohexenone,[8] following the procedure of Corey,[20] there was obtained 3.86 g (56%) of **20**: bp 64–65° (3 mm); ir (CCl_4) 1692 (s), 960 (m) cm^{-1}; ir (CS_2) 888 (m), 840 (m), 823 (m) cm^{-1}; uv (EtOH) 198 (ϵ 2670) and 279 nm (ϵ 29); nmr (τ, CCl_4) 7.73–8.78 (5.2 H, multiplet), 8.79–9.32 (10.8 H, multiplet with two singlets at 8.84 and 8.91, and a doublet at 9.01, J = 7 Hz, *gem*-dimethyl, methyl, and cyclopropyl H).

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[24] Huang-Minlon, *J. Amer. Chem. Soc.*, **68**, 2487 (1946).

[25] S. M. McElvain, "The Characterization of Organic Compounds," Macmillan, New York, N. Y., 1953, p 202.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.90; H, 10.69.

Pure 3,5,5-trimethylbicyclo[4.1.0]heptan-2-one (**20**) on a 20% Carbowax 20M column (5 ft × $^1/_4$ in.) was resolved into two peaks, which were assigned as *cis* and *trans* isomers. The first eluted component was 90% of the 3.86 g of distillate with the other accounting for 10%. The above spectral and analytical data were obtained on a sample containing predominantly the first eluted isomer. Ir spectra of the pure isomers had identical carbonyl stretching frequencies (1692 cm^{-1}) and were very similar; however, the fingerprint regions were definitely different. Injection of a 78–22% (first eluted isomer was the 78% one) mixture on a 20% Carbowax 20M–10% KOH column (5 ft × $^1/_4$ in.) gave only one peak. Collection of this peak, and reinjection on a 20% Carbowax 20M column, again gave two peaks in the ratio 75–25%. Repetition of this procedure with a 91–9% mixture gave two peaks on the Carbowax column in the ratio 81–19%. Molecular models indicate the *cis* isomer to be sterically favored.

On the basis of these data, and the irradiation of **20** (see below), the first eluted isomer was assigned the *cis* configuration. A sample largely enriched in the *trans* isomer had the following uv absorption: uv (EtOH) 194 nm (ϵ 3160).

Irradiation of 3,5,5-Trimethylbicyclo[4.1.0]heptan-2-one (**20**). A solution of 373 mg of a 92–8% mixture of *cis*- and *trans*-3,5,5-trimethylbicyclo[4.1.0]heptan-2-one (**20**) in 125 ml of *t*-butyl alcohol (0.020 *M*) was irradiated for 1.75 hr using Corex-filtered light. Glpc monitoring of the irradiation showed the presence of one major photorearrangement product (retention time relative to *cis* starting material equaled 0.70) as well as an increase in the *trans* isomer of starting material (retention time relative to *cis* starting material equaled 1.20). The final percentages of the total mixture were 20% *cis* starting material, 26% *trans*, 38% major photoproduct, 4% minor photoproducts, and 12% of nonmonomeric material.

Solvent was removed and the major rearrangement product isolated by glpc of the residual, almost colorless oil (376 mg) on a 20% Carbowax 20M column (5 ft × $^1/_2$ in.). This compound was identified as 2,3-methano-4,4-dimethyl-Δ^5-heptenal (**21**) on the basis of the following data: mol wt 152 (mass spectrum); ir (CCl_4) 2857 (w), 2710 (w), 1709 (s), 983 (s), 971 (s) cm^{-1}; uv (EtOH) 220 (ϵ 1830) and 195 nm (ϵ 9610); nmr (τ, CCl_4) 1.18 (1.0 H, doublet, J = 6 Hz, aldehydic H), 4.52–4.75 (1.8 H, four-peak multiplet, vinylic H), 8.14–8.42 (3.8 H, multiplet with a doublet of doublets at 8.33, J = 3 Hz, J' = 2 Hz, one cyclopropyl H and vinylic methyl H), 8.43–9.04 (9.4 H, multiplet with a very strong singlet at 8.88, cyclopropyl H and *gem*-dimethyl H); 100-MHz nmr, the vinyl region was resolved into a multiplet of six peaks, the doublet of doublets at 8.33 was confirmed (J = 3 Hz, J' = 2 Hz), and the singlet at 8.88 was resolved into two singlets separated by 2 Hz.

A spin-decoupling experiment with the 100-MHz nmr gave the following result: irradiation of the 8.33 doublet of doublets collapsed the vinyl absorption to a singlet with two very small satellites at +12.5 and −10.5 Hz away from the singlet; irradiation of the vinyl region collapsed the 8.33 doublet of doublets to a singlet.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.66; H, 10.34.

The two geometrical isomers of starting material, after the irradiation, collected together from glpc, gave an nmr spectrum which was identical with that of a sample of starting material containing almost entirely the *cis* isomer. A crude irradiation mixture of **20** containing starting material in the ratio of 52% *cis* to 48% *trans* injected on a 20% Carbowax 20M–10% KOH column (5 ft × $^1/_4$ in.) gave only one peak. Collection of this peak gave an ir spectrum that was essentially identical with that of starting material before irradiation. Reinjection of this peak on a 20% Carbowax 20M column (5 ft × $^1/_4$ in.) again gave two peaks for starting material in the ratio of 74% *cis* to 26% *trans*.

Irradiation of cyclopropyl ketone **20** for 0.75 hr using no filter essentially paralleled the Corex irradiation except that almost everything polymerized. Glpc on a 10% SE-30 column ($2^1/_2$ ft × $^1/_4$ in.) gave no peaks that could be attributed to dimers. This irradiation was not investigated further.

Irradiation in benzene (336 mg, 89% *cis* and 11% *trans*, 125 ml of benzene, 0.018 *M*, Corex filter, 5 hr) essentially paralleled the *t*-butyl alcohol irradiation. The percentages at the end of the irradiation were 29% *cis* starting material, 24% *trans*, 25% 2,3-methano-4,4-dimethyl-Δ^5-heptenal (**21**), 16% of five minor products, and 6% of nonmonomeric material.

Reduction of 2,3-Methano-4,4-dimethyl-Δ^5-heptenal (**21**). A stirred mixture of 77 mg (0.506 mmol) of 2,3-methano-4,4-dimethyl-Δ^5-heptenal (**21**), glpc collected from the irradiation of 3,5,5-trimethylbicyclo[4.1.0]heptan-2-one (**20**), 10 ml of dry ether, and 0.1 g (2.6 mmol) of lithium aluminum hydride was heated under reflux for 2.5 hr. After the usual work-up, the residual colorless oil (76 mg), greater than 99% pure by glpc, was identified as 2,3-methano-4,4-dimethyl-Δ^5-heptenol (**24**) on the basis of the following data: mol wt 154 (mass spectrum); ir (CCl_4) 3436 (m), 1031 (s), 990 and 984 (both strong) cm^{-1}; ir (CS_2) 975 (m), 787 (s), 766 (s) cm^{-1}; nmr (τ, CCl_4) 4.50–4.77 (1.8 H, six-peak multiplet, vinylic H), 6.44 and 6.46 (1.9 H, two doublets, both J's = 7 Hz, H geminal to hydroxyl), 7.25 (1.0 H, very broad singlet, hydroxy H), 8.35 (3.1 H, doublet of doublets, J = 3.5 Hz, J' = 1.5 Hz, vinylic methyl H), 8.60–9.94 (10.2 H, multiplet with two strong singlets at 8.90 and 8.99, *gem*-dimethyl and cyclopropyl H). A 100-MHz nmr confirmed the above statements.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.65; H, 11.86.

The Photodimerization of Acenaphthylene. Heavy-Atom Solvent Effects[1]

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Abstract: The photodimerization of acenaphthylene has been studied in a number of solvents containing heavy atoms. These solvents have been found to promote the formation of triplet-derived products. Correlation of the relative yields of trans dimer with the square of the spin–orbit coupling parameters of these heavy atoms indicate that the heavy-atom solvent effect is a result of spin–orbit coupling.

Heavy atoms (atoms of high atomic number) have been extensively used in the experimental study of radiative and nonradiative molecular processes, either when substituted onto the framework of the molecule of interest or when present in the solvent. Some effects observed in the presence of heavy atoms are: (1)

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[1] Photochemical Reactions. Part V. Part IV: see D. O. Cowan and R. L. Drisko, submitted for publication.

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