(10 H). *Anal.* Calcd for $C_{19}H_{16}OS$: C, 78.05; H, 5.52; O, 5.47; S, 10.96. Found: C, 77.97; H, 5.69; S, 11.07.

A mixture of 0.1 g of Vc and 0.1 g of P_2S_5 in 10 ml of benzene was refluxed for 24 hr and worked up as before. An orange solid, 0.065 g (63%), was obtained and identified as 3,4,5,6-tetraphenyl-2*H*-pyran-2-thione, mp 195–197°. The infrared spectrum was characterized by bands at 1605, 1590, 1440, 1290, and 1270 cm^{-1} and the nmr spectrum showed a multiplet at δ 6.6–7.3. *Anal.* Calcd for $C_{29}H_{20}OS$: C, 83.62; H, 4.84; O, 3.84; S, 7.70. Found: C, 83.44; H, 4.69; S, 7.57.

Diels–Alder Reaction of 3,6-Diphenyl-4,5-dimethyl-2*H*-pyran-2-one (Vd) with Benzyne. A mixture of 0.138 g of Vd and 0.225 g of diphenyliodonium-2-carboxylate[20] in 3 ml of diethylbenzene was heated with a microburner until the reaction turned to an amber solution. After diethylbenzene was carefully distilled off, 10 ml of 95% ethanol was added to the residual oil and refluxed for 1 hr. Upon standing the solution at 0°, a colorless solid was separated, which on recrystallization from ethanol afforded 0.1 g (65%) of pure 1,4-diphenyl-2,3-dimethylnaphthalene (VIII), mp 160–161°. The ultraviolet spectrum in cyclohexane exhibited maxima at 234 (log ϵ 4.78) and 292 nm (4.06). The nmr spectrum in carbon tetrachloride showed a singlet at δ 2.14 (6 H) and a multiplet at δ 7.1–7.5 (14 H). *Anal.* Calcd for $C_{24}H_{22}$: C, 93.48; H, 6.52. Found: C, 93.48; H, 6.77.

Oxidative Photocyclization of 2,3,5,6-Tetraphenyl-4*H*-pyran-4-one to 5,6,7,8-Dibenzo-2,3-diphenyl-4-chromen-4-one (IX). The olution containing 0.4 g of Ie and 0.126 g of iodine in 350 ml of methylene chloride was irradiated under nitrogen with a Ushio 500-W medium-pressure mercury lamp with a Pyrex filter for 5 hr. After removal of the solvent under vacuum, the residue was chromatographed over silica gel using chloroform as the eluant. The first fraction gave 0.2 g (50%) of IX and the second 0.19 g of the starting material.

Photolysis of 0.4 g of Ie in 350 ml of methylene chloride was carried out in the presence of air for 5 hr using a Ushio 500-W medium-pressure mercury lamp with a Pyrex filter. By removal of the solvent *in vacuo* and working up in the usual way, 0.14 g (35%) of IX, 0.05 g of an unidentified product, and 0.16 g of the starting material were obtained.

Measurement of Quantum Yields. The quantum yields for the formation of Vd were measured by irradiating 10 ml of 1–3 × 10^{-3} *M* Id in appropriate solvents in quartz test tubes using four RPR 253.7 nm lamps (New England Ultraviolet Co.) in a merry-go-round apparatus. The samples in the photolysis tubes were degassed using three freeze–thaw cycles using a pump, 10^{-2} mm, before being sealed off. Potassium ferrioxalate actinometry[30] provided light intensities in the order of 6.0 × 10^{-3} mEinstein/min (10 cm^3). After irradiation, the concentration of the photoproduct was determined by quantitative ultraviolet spectroscopy at 325 nm for Vd. The absorption due to the starting material was corrected to determine the degree of reaction.

Acknowledgment. We thank Dr. R. Mukherjee for his help in preparation of this paper.

Photoisomerization of Bicyclo[3.1.0]hexan-2-ones[1,2]

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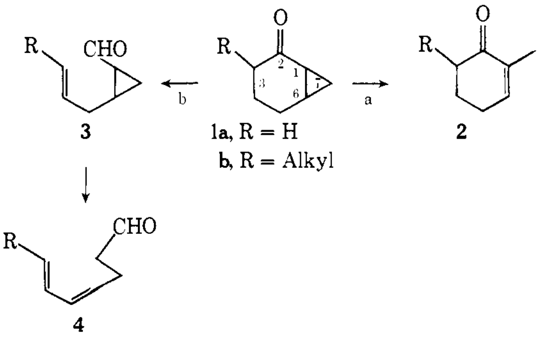
Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. *Received June 26, 1972*

Abstract: The photoisomerization of alkyl-substituted bicyclo[3.1.0]hexan-2-ones has been studied. Using the n → π^* excitation, two different isomerizations have been found: one route involves opening of the cyclopropane ring with hydrogen migration to give an unsaturated ketone, the other route a type I α cleavage independent of the cyclopropane ring. Opening of the cyclopropane ring as a primary photochemical reaction only occurred when the 3 position was unsubstituted. The product resulted from the opening of the internal C-1:C-5 bond to yield a cyclohexenone in all but one case, compound **5**. The opening of this bond was in contrast with the previous findings in the photoisomerization of bicyclo[4.1.0]heptan-2-ones. Type I α cleavage to yield unsaturated aldehydes was favored by increased substitution on C-3. The aldehydes, in turn, were found to undergo further photoisomerization to yield acyclic ketenes. The mechanisms for all photoisomerizations reported are discussed.

The photoisomerization of conjugated cyclopropyl ketones to unsaturated carbonyl compounds (aldehydes, ketones, or ketenes) has been shown to proceed *via* a direct rearrangement of the chromophore, itself (see path a),[5] or to proceed stepwise such that the opening occurred *via* a Norrish type I cleavage reaction (see path b).[5,6] When this chromophoric grouping is part of a bicyclo[4.1.0]heptan-2-one ring system, the reaction pathway followed is controlled by the substitution pattern of the ring system. If there is no substituent on C-3 (**1a**), the primary photoreaction is the opening of the cyclopropane ring involving that cyclopropane bond which has the optimum overlap with the carbonyl group with the least movement of atoms during the reaction of **1a** to **2** (path a). The efficiency of the rearrangement process has been found to be dependent upon the substitution pattern at C-6 and C-7.[2] If there is a substituent on C-3 (**1b**), the preferred, but not necessarily exclusive, primary photoreaction is a type I α cleavage to yield first the cyclopropane alde-



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(1) This work was supported by Public Health Service Grant No. 00709, National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service, and the Hoffmann-La Roche Foundation.

(2) For the previous paper in this series, see W. G. Dauben and W. M. Welch, *Tetrahedron Lett.*, 4531 (1971).

(3) National Institutes of Health Predoctoral Fellow.

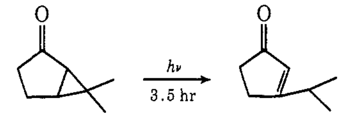
(4) National Institutes of Health Postdoctoral Fellow.

(5) For a general discussion, see W. G. Dauben, G. W. Shaffer, and E. J. Deviny, *J. Amer. Chem. Soc.*, **92**, 6273 (1970).

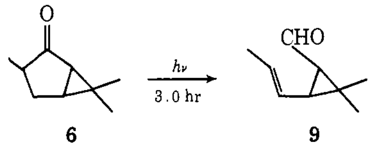
(6) W. G. Dauben, L. Schutte, and R. E. Wolf, *J. Org. Chem.*, **34**, 1849 (1969).

hyde **3**; the subsequent isomerization of the cyclopropane ring *via* the Norrish type II cleavage process yields the acyclic diene aldehyde **4**.

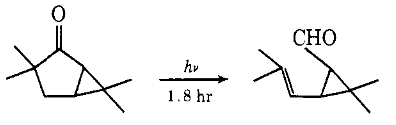
Such a sensitivity of the course of the photoreaction of this chromophoric group to alkyl substitution indicated that the various possible reaction pathways were competitive. Since it is well known that in smaller ring systems the type I α cleavage process becomes a more efficient process,[7] a series of substituted bicyclo[3.1.0]hexan-2-ones has been studied in order to obtain a better qualitative understanding of the substituent effect. The effect of the α substitution on C-3 was first evaluated using compounds **5–7** and the results are summarized in eq 1–3. All irradiations were performed in *tert*-butyl alcohol and excitation was limited to the n,π^* band by use of a filter (cutoff at 250 nm).



5 (32%)[9] **8** (64%)[9] (1)



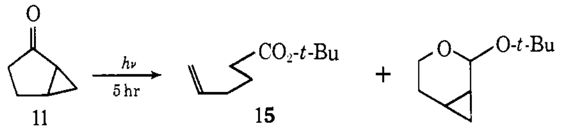
6 (30%)[9] **9** (31%)[9] (2)



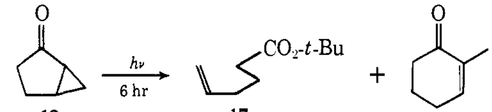
7 (30%)[9] **10** (10%)[9] (3)

The irradiation of 6,6-dimethylbicyclo[3.1.0]hexan-2-one (**5**) has been reported to induce cleavage of the cyclopropane ring to yield the conjugated enone **8**;[8] under the conditions used in the present study the same result was obtained (eq 1).[9] Since the type I cleavage reaction of the five-ring ketone did not compete with the cyclopropane ring isomerization, it showed that the generation of a tertiary reaction center by cyclopropane ring opening still was the controlling factor in the reaction. The delicate balance between the two possible modes of reaction was indicated, however, by the exclusive type I α cleavage for the 3-methyl and 3,3-dimethyl derivatives **6** and **7**, respectively (eq 2 and 3). The higher efficiency of the α-cleavage reaction in the five-ring ketone system was clearly evident since the homologous 3,7,7-trimethylbicyclo[4.1.0]heptan-2-one gave photoproducts resulting from each reaction pathway.[5]

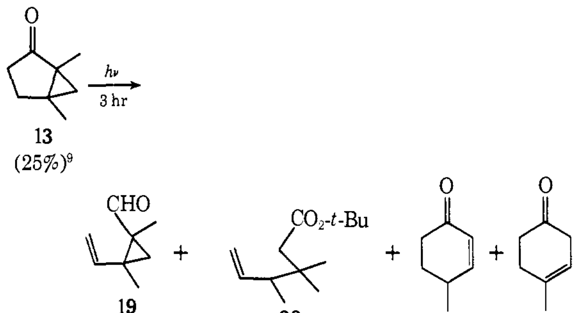
The primary photoproducts from **6** and **7** were the unsaturated aldehydes **9** and **10**; no ketene products were formed. Such a selective second step hydrogen abstraction is often found in cyclopentanones and appears to be related to the unfavorable geometry in the five membered transition state required for the hydrogen transfer to form the ketene.[7b,10] It is of interest to note that in the more flexible *trans*-bicyclo[6.1.0]nonan-2-one, ketene formation was the exclusive product of the photoreaction.[11] The primary photoproducts **9** and **10** are photolabile and the detailed photochemistry of **10** has been reported in an earlier publication.[12]



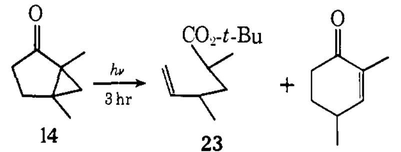
11 (70%)[9] **15** (6%)[9] **16** (22%)[9] (4)



12 (80%)[9] **17** (6%)[9] **18** (5%)[9] (5)



19 (7%)[9] **20** (5%)[9] **21** (10%)[9] **22** (4%)[9] (6)



14 (23%)[9] **23** (5%)[9] **24** (72%)[9] (7)

The importance of the substituents on the cyclopropyl ring was next evaluated by study of the compounds **11–14**. The results obtained by n,π^* excitation of these ketones in *tert*-butyl alcohol are listed in eq 4–7. These results show, in contrast to the related substituted bicyclo[4.1.0]heptan-2-ones, type I cleavage does occur to some extent in all cases regardless of the substitution pattern. However, as the degree of substitution of the cyclopropane ring increased, the cleavage of the ring became the more preferred reaction pathway.[13] The increase in amount of cyclopropane ring

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(7) (a) P. S. Wagner and R. W. Spoerke, *J. Amer. Chem. Soc.*, **91**, 4437 (1969); (b) J. C. Dalton, K. Dawes, N. J. Turro, D. S. Weiss, J. A. Barltrop, and J. D. Coyle, *ibid.*, **93**, 7213 (1971).

(8) O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *Tetrahedron Lett.*, 2049 (1963).

(9) In this equation and all subsequent equations the percentage given under the compound represents the amount present at the end of the listed irradiation period. The varying lengths of time of the irradiation period depended upon the rates of reaction of the primary photoproducts. The reactions were run for the length of time necessary to maximize the per cent of product(s) of interest in this present study. When the photochemistry of the primary product is known, the further reaction products are not listed and thus yields represent the actual amount of compound present.

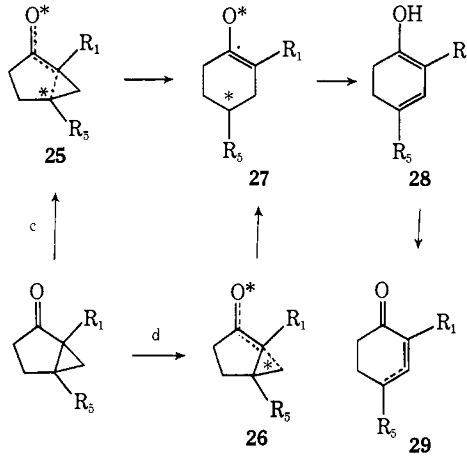
(10) G. Quinkert, *Angew. Chem., Int. Ed. Engl.*, **4**, 211 (1965).

(11) L. A. Paquette and R. F. Eizember, *J. Amer. Chem. Soc.*, **91**, 7108 (1969).

(12) W. G. Dauben and G. W. Shaffer, *J. Org. Chem.*, **34**, 2301 (1969).

(13) It has been reported (L. D. Hess and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **89**, 1973 (1967)) that upon irradiation in the vapor phase, bicyclo[3.1.0]hexan-2-one yielded mainly 3-methyl-2-cyclopenten-1-one. The relationship of this result to those reported in the present work is

opening displayed by compounds **12–14** did not follow the same substitution pattern as the bathochromic shifts of the π,π^* absorption band.[14] The most striking feature of the cyclopropane ring opening was the formation of a cyclohexenone resulting from the formal breaking of the internal C-1 : C-5 bond.

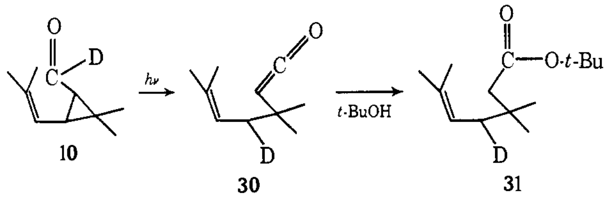


(8)

In earlier studies of the direct photoisomerization of the cyclopropane ring in a bicyclo[*n*.1.0]alkan-2-one system the bond which opened had the optimum conjugative overlap with the carbonyl group with the least motion of atoms. The present results call attention to the importance of strain relief in the isomerization reaction, an energy consideration which must be evaluated along with conjugative overlap stabilization. With the 6,6-dimethyl derivative **5** (see eq 1) the presence of the tertiary substitution on C-6 made the opening of the C-1 : C-6 external bond still preferred. With the unsubstituted parent compound **11** (see eq 4), only type I cleavage of the ketone occurred. The placement of substituents on C-1 and/or C-5 (see eq 5–7) now again made the isomerization reaction competitive with the α-cleavage process and the position of placement of the substituent along with the strain released in going to a six-membered ring brought about C-1 : C-5 cleavage. The efficiency of the reaction increased in the expected manner, **14** > **13** > **12**, since the substituent at C-5 would be expected to give greater stabilization of the developing charge separation. The overall pathway for rearrangement, as shown in eq 8, most likely proceeds *via* species **27** which upon hydrogen rearrangement (or abstraction) gives the dienol **28** and ultimately the cyclohexenone product **29**. The formation of species **27** can be in a concerted process *via* excited species **25** as shown in path c, or the process may proceed in a stepwise fashion *via* the excited species **26** followed by bond migration to **27**. This latter process which can be viewed as a reverse "lumi" rearrangement of an enone would also fit well the dependence upon substitution.

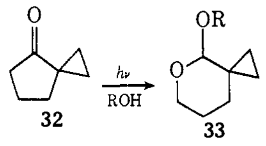
The photochemical interconversion of *cis*- and *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones has been studied in great detail.[15] It was found that the stereochemistry of the substituent at C-6 had an effect upon the efficiency of the breaking of the internal bond of the cyclopropane ring but at best did not bring the efficiency within 10% of that found for the opening of the outside bond. The final product of the reaction in each case was 3,4-diphenylcyclohex-2-en-1-one, suggesting strain and thermodynamic factors are also important factors in the overall photoisomerization reaction.

The formation of *tert*-butyl esters was found in all compounds studied in this present research except **5**. As reported earlier for the aldehyde **10**,[12] study of the deuterium labeled aldehyde showed the isomerization proceeded by intramolecular transfer of the aldehydic deuterium to yield the ketene **30**, characterized as the ester **31** (eq 9). In all cases when the photoisomerization was monitered at an early stage of the reaction, the aldehyde was observed (see eq 2, 3, and 6). The structures of the various irradiation products were based upon comparison of spectral properties with authentic samples or by comparison with related materials.



(9)

In many of the irradiations there were indications (vpc retention times) that ethers were formed in low yield. In the case of bicyclo[3.1.0]hexan-2-one, however, the cyclic acetal was one of the two major products of the photochemical reaction. In many highly strained cyclic ketones the formation of a cyclic acetal has also been found to be a major irradiation product[16] and it is of interest to note that the irradiation of the related cyclopropyl conjugated ketone **32** also yielded a cyclic acetal (**33**) when the reaction was conducted in an alcoholic solvent.[16b,c]



With this study of the irradiation of substituted bicyclo[3.1.0]hexan-2-ones, it is possible to make qualitative comparisons with the related bicyclo[4.1.0]heptan-2-ones. The ring size and the substituent effects for the various isomerizations are summarized in Table I and the results clearly indicate the importance of ring size in the photoisomerization of cyclopropyl-conjugated ketones. In addition to the present study, very few bicyclo[3.1.0]hexan-2-ones have been studied. The compounds **34**,[17] **35**,[18] and **36**[16a] have been reported to photoisomerize upon irradiation and the bond broken (marked on the structure) would indicate that a geminal substituted cyclopropane prefers cleavage of bond Y, as suggested in Table I.

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difficult to evaluate since the characterization and actual yield of the product were not listed. The work does call attention to the risk in extrapolation of vapor-phase results to those expected to be obtained in the liquid phase.

[14] W. G. Dauben and G. H. Berezin, *J. Amer. Chem. Soc.*, **89**, 3449 (1967).

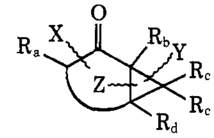
[15] H. E. Zimmerman, K. G. Hancock, and G. C. Licke, *ibid.*, **90**, 4892 (1968).

[16] (a) P. Yates, *Pure Appl. Chem.*, **16**, 93 (1968); (b) J. K. Crandall and R. J. Seidewald, *J. Org. Chem.*, **35**, 697 (1970); (c) D. R. Morton, E. Lee-Ruff, R. M. Southam, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 4349 (1970).

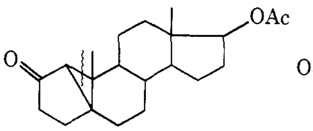
[17] B. Naun, D. Gravel, R. Schorta, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **46**, 2473 (1963).

[18] O. L. Chapman, J. B. Siega, and W. J. Welstead, Jr., *J. Amer. Chem. Soc.*, **88**, 161 (1966).

Table I. Summary of Photoisomerizations of Bicyclo[*n*.1.0]alkan-2-ones



Substitution	Bonds cleaved Bicyclo[3.1.0]-hexan-2-one	 Bicyclo[4.1.0]-heptan-2-one
R_a, R_b, R_c, R_d = H	X	Y
R_b = alkyl; R_a, R_c, R_d = H	X, Z	X
R_c = alkyl; R_a, R_b, R_d = H	Y	Y
R_d = alkyl; R_a, R_b, R_c = H	X, Z	Polymer
R_a, R_c = alkyl; R_b, R_d = H	X	X, Y
R_b, R_d = alkyl; R_a, R_c = H	X, Z	Polymer



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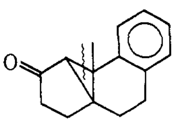

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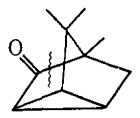

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Experimental Section

All infrared spectra were obtained in carbon tetrachloride solution with Perkin-Elmer spectrometers, Models 137 and 237; the ultraviolet spectra were obtained with a Perkin-Elmer spectrometer Model 202 above 215 nm and with a Beckman spectrometer Model DK2-A below 215 nm. All nmr spectra were obtained with Varian spectrometers, Models A-60, T-60, and HA-100, using tetramethylsilane as an internal standard. Mass spectra using Consolidated Electrodynamics spectrometers, Models 21-103C and 21-110B, or a Varian spectrometer, Model M-66, and combustion analyses were obtained from the Analytical Laboratory, College of Chemistry, University of California, Berkeley, Calif.

Starting Materials. 6,6-Dimethylbicyclo[3.1.0]hexan-2-one (5). This material was prepared in 16% yield by irradiation of 4,4-dimethyl-2-cyclohex-2-en-1-one in *tert*-butyl alcohol following the procedure of Chapman, *et al.*[8] The spectral properties of the material were as follow: ir 3040, 1721 cm^{-1}; nmr δ 2.20–1.40 (m, 6), 1.14 (s, 6).

3,6,6-Trimethylbicyclo[3.1.0]hexan-2-one (6). This material was kindly supplied by Professor M. Julia and Dr. S. Julia; the spectral properties of the material were as follow: ir 1724 cm^{-1}; uv (95% EtOH) 208 (ϵ 3,700), 278 nm (shoulder, ϵ 38); nmr δ 2.70–1.47 (m, 6), 1.45–0.90 (8 H, strong singlet at 1.16).

3,3,6,6-Tetramethylbicyclo[3.1.0]hexan-2-one (7).[19] This material was kindly supplied by Professor M. Julia and Dr. S. Julia; the spectral properties of the material were as follow: ir 1730 cm^{-1}; uv (95% EtOH) 205 (ϵ 4,500), 287 nm (shoulder, ϵ 48); nmr δ 2.20–1.40 (m, 4), 1.12, 1.02, 0.97, 0.90 (s, 12).

Bicyclo[3.1.0]hexan-2-one (11). This compound was prepared as previously described.[14]

1-Methylbicyclo[3.1.0]hexan-2-one (12). The compound was prepared in 60% yield from 2-methyl-2-cyclopenten-1-one[20] and dimethylsulfoxonium methylide[21] and purified by vpc: ir 1748 cm^{-1}; uv (95% EtOH) 200 nm (ϵ 4,400); nmr δ 1.96 (s, 4), 1.96–1.50 (m, 1), 1.16 (s, 3), 1.00–0.83 (m, 2); mol wt, 110 (mass spectrum). *Anal.* Calcd for $C_7H_{10}O$: C, 76.33; H, 9.15. Found: C, 76.45; H, 9.11.

5-Methylbicyclo[3.1.0]hexan-2-one (13). The compound was prepared in 82% yield from 3-methyl-2-cyclopenten-1-one[22,23] and dimethylsulfoxonium methylide;[21] bp 64–65° (13 mm). The vpc purified material had the following spectral properties: ir 1727 cm^{-1}; uv (95% EtOH) 194 (ϵ 3,700), 280 nm (ϵ 56); nmr δ 2.23–1.72 (m, 4, strong singlet at 1.95), 1.70–1.20 (m, 4, strong singlet at 1.35), 1.12–0.81 (m, 2); mol wt, 110 (mass spectrum). *Anal.* Calcd for $C_7H_{10}O$: C, 76.33; H, 9.15. Found: C, 76.14; H, 8.92.

1,5-Dimethylbicyclo[3.1.0]hexan-2-one (14). The starting material, 2,3-dimethyl-2-cyclopenten-1-one, was prepared from 2-methyl-3-isobutoxy-2-cyclopentenone and methylmagnesium iodide, yield 25%, bp 68–69° (8 mm); ir 1709, 1664 cm^{-1}; uv (95% EtOH) 206 nm (ϵ 13,000); nmr δ 2.62–1.79 (m, 7, strong singlet at 1.99), 1.56 (br s, 3). *Anal.* Calcd for $C_7H_{10}O$: C, 76.33; H, 9.15. Found: C, 76.11; H, 9.32.

The enone was allowed to react with dimethylsulfoxonium methylide[21] to yield the cyclopropyl ketone **14** (40%). The product was purified by vpc:[24] ir 1724 cm^{-1}; uv (95% EtOH) 204 (ϵ 5,100), 280 nm (ϵ 68); nmr δ 2.22–1.68 (m, 4), 1.28 (s, 3), 1.10 (s, 3), 1.05 (m, 0.5) and 0.68 (d, 1, J = 4.5 Hz). *Anal.* Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.32; H, 9.69.

Irradiation Procedure. All irradiations were conducted using outgassed 0.2–0.5% solutions in 125 ml of spectral grade *tert*-butyl alcohol. The irradiation solution was stirred and degassed with argon during the irradiation with a Hanovia 450-W mercury arc lamp equipped with a filter ($\lambda > 250$ nm). The reactions were monitored by vpc (10% Carbowax) and the products isolated following previously described procedures.[5]

Identification of Reaction Products. *cis–trans*-**2,2-Dimethyl-3-propenylcyclopropanecarboxaldehyde (9):** ir 2725, 1706, 966, 847 cm^{-1}; uv (95% EtOH) ϵ_{200} 9250 (end absorption); nmr δ 9.30, 9.21 (two doublets superimposed to give triplet, 1), 5.8–5.19 (m, 2), 2.33–1.50 (m, 4, broad doublet at 1.70, J = 4 Hz), 1.49–0.68 (m, 7); mass spectrum, *m/e* 138, 123 (M − 15), 109 (M − 29, base peak). *Anal.* Calcd for $C_9H_{14}O$: 138.1044585. Found: 138.1037528.

cis-**2,2-Dimethyl-3-[1′-(2-methylpropenyl]cyclopropylcarboxaldehyde (10).** Spectral properties and vpc retention times compared with those of an authentic sample.[12]

tert-**Butyl 5-Hexenoate (15):** ir 1730, 1650, 1150 cm^{-1}; mass spectrum *m/e* 114 (M − 54, loss of isobutylene).

2-*tert*-Butoxy-3,4-methanotetrahydropyran (16): ir 1250, 1175, 1075, and 1020 cm^{-1}; nmr δ 5.10 (s, 1), 4.00–3.10 (m, 2), 3.00–1.35 (m, 3), 1.27 (s, 9), 1.00–0.40 (m, 3); mass spectrum *m/e* 170, 155, 114, 113 and 97.

tert-**Butyl 2-Methyl-5-hexenoate (17):** ir 1730, 1635, 1150 cm^{-1}; mass spectrum *m/e* 128 (M − 54, loss of isobutylene).

2-Methyl-2-cyclohexen-1-one (18). Spectral properties and vpc retention times compared with those of an authentic sample.[25]

3-Methyl-3-vinylcyclopropanecarboxaldehyde (19): nmr δ 9.30 (d, 1, J = 5 Hz).

tert-**Butyl 4-Methyl-5-hexenoate (20).** Spectral properties and vpc retention times compared with those of an authentic sample:[26] ir 1730 cm^{-1}; nmr δ 5.96–5.35 (m, 1), 5.02–4.80 (d of d, 2), 2.42–1.86 (m, 3), 1.75–1.29 (M, 10, strong singlet at 1.40), 1.00 (d, 3, J = 6.5 Hz); mass spectrum m/e 128 (M − 54).

4-Methyl-2-cyclohexen-1-one (21). Spectral properties and vpc retention times compared with authentic sample.[27]

4-Methyl-3-cyclohexen-1-one (22). Spectral properties and vpc retention times compared with authentic sample.[28]

tert-**Butyl 2,4-Dimethyl-5-hexenoate (23):** ir 1730 cm^{-1}; mass spectrum *m/e* 140 (M − 54, loss of isobutylene).

2,4-Dimethyl-2-cyclohexen-1-one (24): ir 1678, 887 cm^{-1}; uv (95% EtOH) 236 nm (ϵ 9,700); nmr δ 6.60–6.42 (m, 1), 1.68 (d of d, 3, J = 2 Hz, J' = 1.5 Hz), 2.75–1.50 (m, 5), 1.10 (d, 3, J = 6.5 Hz); mass spectrum *m/e* 124. *Anal.* Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.51; H, 9.66.

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