used for the kinetic measurements were established in all cases by means of ir, nmr, and glpc criteria.

4-Carboxycyclohexanone was prepared by oxidation of the precursor alcohol with Jones reagent[9] at 15°. The product recrystallized from benzene–hexane melted at 67–68°.[10]

4-Carbomethoxycyclohexanone was prepared in analogous fashion starting from 4-carbomethoxycyclohexanol. The product was distilled under reduced pressure and the fraction used for kinetic study had bp 74–75° (0.3 mm).

4-Benzoxycyclohexanone was prepared by the method of Jones and Sondheimer:[11] after recrystallization from ether–hexane, mp 58–59°; dinitrophenyl hydrazone mp 159–160°.

4-Methoxycyclohexanone was prepared according to directions of Helfer[12] by chromate oxidation of 4-methoxycyclohexanol. The latter was obtained by reduction of hydroquinone monomethyl ether with Raney nickel and hydrogen following familiar procedures.[13]

Cyclohexanone was purified *via* the Girard T reagent.[14]

4-Phenylcyclohexanone was synthesized by a two-step procedure starting from *p*-phenylphenol reduction[15] to a cis–trans mixture of 4-phenylcyclohexanol. The mixture was oxidized to the ketone using the Jones reagent.[9] The product[15] used for kinetic studies had mp 73–74°.

4-Methylcyclohexanone was purified (as a commercial sample) by distillation, $n^{20}{}_{\mathrm{D}}$ 1.4448.[16]

4-Cyclohexylcyclohexanone was obtained in a two-step procedure[15] beginning with reduction of *p*-phenylphenol with palladium/charcoal and hydrogen at 1500 psi and 150°. The reduction product mixture was oxidized with Jones reagent[9] in the usual way to ketone product which was isolated and purified by means of the Girard T reagent according to the method described by Büchi and Pappas,[17] mp 27–28°.

4-*tert*-Butylcyclohexanone was prepared according to directions of Winstein and Holness,[18] mp 45–46°.

4-Cyanocyclohexanone and 4-trimethylsilylcyclohexanone were provided by Dr. A. A. Khan[19] who prepared them according to methods in the literature. Their structures and purities were confirmed in the usual ways before use in kinetic procedures.

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[9] E. R. H. Jones and K. Bowden, *J. Chem. Soc.*, 39 (1946).

[10] W. H. Perkin, Jr., *J. Amer. Chem. Soc.*, **85**, 416 (1904).

[11] E. R. H. Jones and F. Sondheimer, *J. Chem. Soc.*, 616 (1949).

[12] L. Helfer, *Helv. Chim. Acta*, **7**, 950 (1924).

[13] R. B. Thompson, "Organic Syntheses,' Collect. Vol. III, Wiley, New York, N. Y., 1955, p. 278.

[14] A. E. Osterberg and E. C. Kendall, *J. Amer. Chem. Soc.*, **42**, 2612 (1920).

[15] H. E. Ungnade, *J. Org. Chem.*, **13**, 361 (1948).

[16] H. E. Ungnade and A. D. MacLaren, *ibid.*, **10**, 29 (1945).

[17] G. Büchi and J. J. Pappas, *J. Amer. Chem. Soc.*, **76**, 2963 (1954).

[18] S. Winstein and J. J. Holness, *ibid.*, **77**, 5562 (1955).

[19] Detailed directions for the preparation of these compounds will appear in a forthcoming publication by A. A. Khan.

Structural Constraints on Electrocyclic Reactions of Unsaturated Ketenes. Synthesis and Irradiation of 2,4,4,5-Tetramethylbicyclo[4.2.0]octa-1,5-dien-3-one

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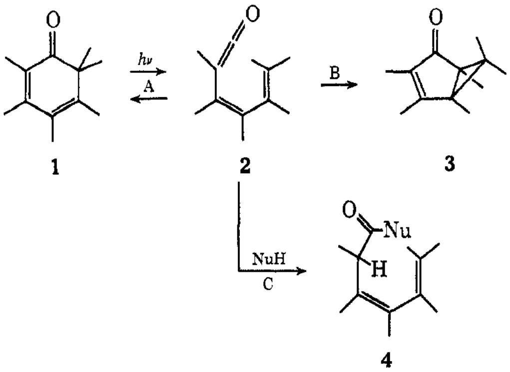
Oxidation of tetramethylbenzocyclobutene (**7**) with peroxytrifluoracetic acid–boron fluoride gave as the sole volatile cyclohexadienone (34% yield) 2,4,4,5-tetramethylbicyclo[4.2.0]octa-1,5-dien-3-one (**5**). The oxidation provides a striking illustration of the preference for β- (over α-) benzenonium ions in reactions of electrophiles with benzocyclobutenes, since both steps (electrophilic attack and methyl migration) are regiospecific. Irradiation of **5** in methanol (Pyrex) gave five methyl esters, **13** (55%) and the four stereoisomers of **14** (nearly equal amounts of each). This result contrasts with the irradiation of hexamethyl-2,4-cyclohexadienone (**1**), which under identical conditions gave no methyl esters. Reasons for the difference are discussed.

The unsaturated ketene **2**, produced by irradiation of the hexamethyldienone **1**, may react thermally in three different ways (A–C).[1,2] The particular reaction path depends on the nucleophile strength and on the solvent polarity. Methanol is not sufficiently nucleophilic to compete with the electrocyclic paths, but secondary amines divert the reaction completely along path C.[2] Of the two electrocyclic paths, B is favored by polar solvents and A by nonpolar solvents. For example, in ethanol virtually every ketene molecule produced by irradiation of **1** goes on to **3**, whereas in hexane approximately two-thirds of the ketene produced recyclizes to **1**.[2]



The reaction scheme shown for **1** is general, except that path B is only observed for heavily substituted ketenes.[1-5] This reaction path requires overlap of the ketene π-orbital lobes at C-4 with C-6, and C-1 with C-5, which can only be affected if the ketene twists appreciably from planarity and approaches the geometry of the bicyclo[3.1.0]hexenone product (*i.e.*, **3**).[4] To examine structural constraints on the electrocyclic reaction (B), we have studied the effect of incorporating two adjacent substituents into a ring. This would be expected to limit the conformations accessible to the ketene, and therefore affect the cyclization reaction. We report here on the synthesis and irradiation of the

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[1] H. Hart, P. M. Collins, and A. J. Waring, *J. Amer. Chem. Soc.*, **88**, 1005 (1966).

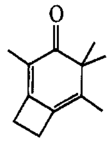
[2] J. Griffiths and H. Hart, *ibid.*, **90**, 3297 (1968).

[3] P. M. Collins and H. Hart, *J. Chem. Soc. C*, 895 (1967); H. Hart and R. K. Murray, Jr., *J. Org. Chem.*, **32**, 2448 (1967); H. Hart and D. C. Lankin, *ibid.*, **33**, 4398 (1968); J. Griffiths and H. Hart, *J. Amer. Chem. Soc.*, **90**, 5296 (1968); H. Perst and K. Dimroth, *Tetrahedron*, **24**, 5385 (1968); M. R. Morris and A. J. Waring, *Chem. Commun.*, 526 (1969); H. Hart and R. K. Murray, Jr., *J. Org. Chem.*, **35**, 1535 (1970); H. Perst and I. Weisemeier, *Tetrahedron Lett.*, 4189 (1970).

[4] M. R. Morris and A. J. Waring, *J. Chem. Soc. C*, 3266, 3269 (1971); A. J. Waring, M. R. Morris, and M. M. Islam, *ibid.*, 3274 (1971).

[5] However, not all heavily substituted cyclohexadienones react by path B; some, with electron-withdrawing substituents, react with nucleophiles (path C) in preference to cyclizing [*cf.* P. Vogel, B. Willhelm, and H. Prinzbach, *Helv. Chim. Acta*, **52**, 584 (1969)].

title dienone **5**,[6] which differs from **1** only in that the C-3 and C-4 substituents are joined in a small ring. If the ketene derived from **5** were to cyclize according to path B, it would lead to the highly strained bicyclo[3.1.0]hexenone **6**.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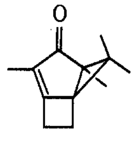
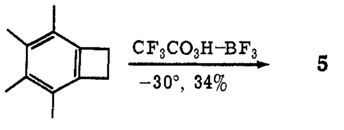
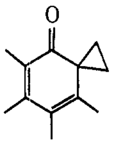

6

Synthesis of 5.—Oxidation of tetramethylbenzocyclobutene (**7**)[7] with peroxytrifluoracetic acid–boron fluoride[8] was not clean, even at −30°, possibly due to the fact that benzocyclobutenes can suffer ring opening and polymerization under electrophilic substitution conditions.[9] Nevertheless, a 34% yield of a single volatile product was obtained, to which we assign structure **5**. The ir and uv spectra were consistent with the conjugated cyclohexadienone structure.



7

Three other cyclohexadienones which could conceivably arise from the electrophilic oxidation of **7** are **8–10**. The nmr spectrum showed a singlet at τ 8.90 (6 H) for the aliphatic *gem*-dimethyl group, ruling out structure **8**. To distinguish **10** from **5** and **9**, advantage was taken of the fact[1] that base-catalyzed hydrogen–deuterium exchange in alkyl 2,4-cyclohexadienones occurs much more rapidly at C-3 than at C-5. The oxidation product was treated with NaOCH$_3$–CH$_3$OD at room temperature; mass spectral and nmr analysis showed that only two deuterium atoms were introduced, thus eliminating structure **10**, which should readily exchange three hydrogen atoms.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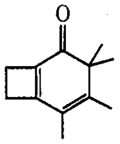
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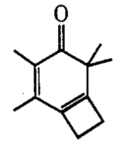
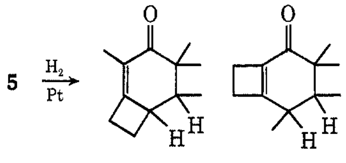
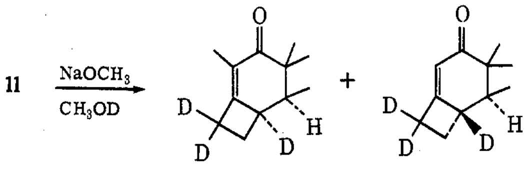

10

The distinction between structures **5** and **9** was made by partial hydrogenation of the dienone over platinum. A conjugated enone ($\nu_{C=O}$ 1655 cm^{-1}, λ_{max}^{MeOH} 247 nm) with two additional mass units was obtained. The nmr spectrum of this enone still showed one allylic methyl group (τ 8.45), as well as an aliphatic methyl doublet (τ 9.14, J = 7 Hz). This compound must have structure **11**, since structure **12**, which would have been obtained if the original dienone were **9**, is inconsistent with the nmr results. The hydrogenation product **11** is thought to have the hydrogens cis. When **11** was treated with NaOCH$_3$–CH$_3$OD, two enones were obtained, each of which contained three deuterium atoms. One had an nmr spectrum with bands for the four distinctive methyl groups at identical shifts as in **11**, whereas the other had the same overall band pattern, but with different chemical shifts. Presumably base caused epimerization as well as exchange; the products are formulated as shown.



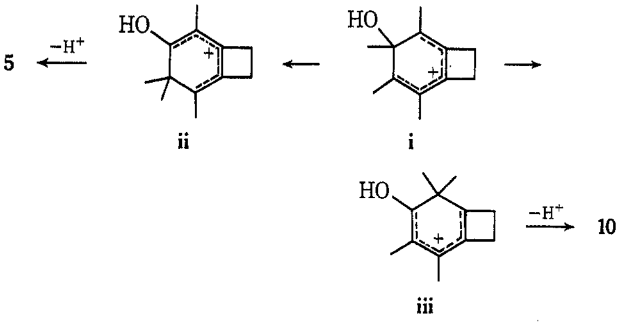
11 **12**



cis-**11**-d_3 *trans*-**11**-d_3

These data are consistent only with structure **5** for the oxidation product of **7**.

The Oxidation Mechanism.—Electrophilic attack on benzocyclobutenes generally occurs at the β aromatic position.[10] The two expected oxidation products of **7** are therefore **5** and **10**, which could arise from the intermediate benzenonium ion i by methyl migration in either of the two possible directions. Rearrangement to ii (and, after proton loss, **5**) gives another β-type benzenonium ion, whereas rearrangement to iii gives an α-type benzenonium ion. Since **5** was the only observed product, it is clear that whatever factors direct the initial electrophilic attack to the β position also control the direction of methyl migration. Several plausible explanations for the greater reactivity of the β position toward electrophiles have been offered.[11] The present case provides a rather striking example of the preference for β- (over α-) benzenonium ions in reactions of electrophiles with benzocyclobutenes, since both steps are regiospecific.



Irradiation of Dienone 5.—Irradiation of a methanol solution of **5** through Pyrex, or in a Rayonet reactor with a 300-nm light source, rapidly gave a mixture of methyl esters. The major product (55%) was the

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[6] For a preliminary account, see R. J. Bastiani, D. J. Hart, and H. Hart, *Tetrahedron Lett.*, 4841 (1969).

[7] This hydrocarbon is readily available in three steps (overall yield 70%) from pentamethylbenzene: H. Hart, J. A. Hartlage, R. W. Fish, and R. R. Rafos, *J. Org. Chem.*, **31**, 2244 (1966); D. J. Hart and H. Hart, *Org. Prep. Proced.*, **2**, 89 (1970).

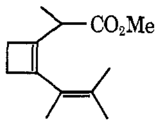
[8] For a review, see H. Hart, *Accounts Chem. Res.*, **4**, 337 (1971).

[9] J. B. F. Lloyd and P. A. Ongley, *Tetrahedron*, **20**, 2185 (1964); **21**, 245 (1965).

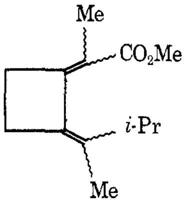
[10] I. L. Klundt, *Chem. Rev.*, **70**, 471 (1970).

[11] A. Streitwieser, Jr., G. R. Ziegler, P. C. Mowery, A. Lewis, and R. G. Lawler, *J. Amer. Chem. Soc.*, **90**, 1357 (1968); R. Taylor, G. J. Wright, and A. J. Homes, *J. Chem. Soc. B*, 780 (1967).

nonconjugated ester **13**; the remainder (45%) consisted of nearly equal amounts of the four geometric isomers of the completely conjugated ester **14**.



13

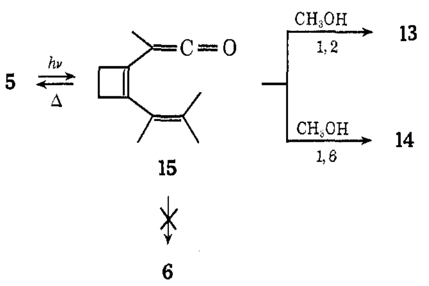


14

The structures were assigned on the basis of spectral properties. Whereas **13** had a $\lambda_{\max}^{\mathrm{MeOH}}$ at 239 nm and a $\nu_{\mathrm{C=O}}$ at 1715 cm^{-1}, all isomers of **14** had a $\lambda_{\max}^{\mathrm{MeOH}}$ at 288–290 nm and a $\nu_{\mathrm{C=O}}$ at 1700 cm^{-1}. These data show that in **13** the carbon–carbon double bonds are not conjugated with the ester function, whereas in **14** they are fully conjugated.[12]

The nmr spectrum of **13** showed a doublet at τ 8.80 (3 H) and a quartet at τ 6.73 (1 H), J = 7.0 Hz, for the α-methyl group and hydrogen atom, clearly eliminating any alternative structure. In contrast with the spectrum of **13**, which had a peak corresponding to three allylic methyl groups, the spectrum of each isomer of **14** had two singlets in the expected region for the two allylic methyl groups as well as peaks due to the isopropyl group.[13]

The photolysis of **5** therefore follows the path shown.

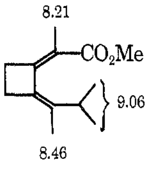


Irradiation of a methylene chloride solution of **5** containing no added nucleophile resulted only in recovered, unchanged starting material. Since the ketene **15** was almost certainly formed under these conditions (irradiation was carried out for a much longer time than is needed to convert **5** completely to esters on irradiation in methanol), it must recyclize entirely to **5**, since no product corresponding to **6** was detected. Presumably steric strain prevents the C-1–C-5 and C-4–C-6 overlap essential to the formation of **6**.

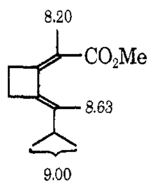
In contrast with ketene **2**, **15** reacts rapidly with methanol. Possibly the constraints of the cyclobutene ring enlarge the C-2,3,4 and C-3,4,5 angles over what they would be in the acyclic ketene. This has the effect of decreasing steric hindrance, and makes the ketene more susceptible to nucleophilic attack than it would otherwise be. The formation of **14** represents, we believe, the first authentic example of 1,6 addition to dieneketenes.[13a]

In a subsequent paper, the effect of incorporating the C-3 and C-4 dienone substituents in a ring larger than cyclobutyl will be described.

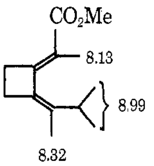
Assignment of Geometry to Esters 14.—The four stereoisomers of **14** were readily separated from **13** and from one another by preparative vpc. Though a definitive assignment of the geometry of each ester was not attempted, careful analysis of the uv and nmr spectrum of each isomer permits a reasonable assignment to be made. The structures are believed to be as shown.



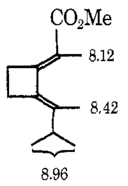
Z,Z-**14**
6700^a



Z,E-**14**
8100^a



E,Z-**14**
14,000^a



E,E-**14**
17,000^a

$^a\epsilon_{\max}^{280-290}$

Although the $\lambda_{\max}$ values were nearly identical for all four isomers, the extinction coefficients varied considerably and fell into two distinct groups. The two isomers with the lower extinction coefficients are thought to have the carbomethoxy group in the most hindered position (*Z,Z* and *Z,E* isomers), whereas those with the larger extinction coefficients have the carbomethoxy group in a position where the carbon–oxygen and carbon–carbon double bonds can interact more strongly (*E,Z* and *E,E* isomers). Within each of these pairs, the isomer with the lower extinction coefficient is assigned the structure in which the isopropyl group (attached to the γ,δ double bond) is in the most obstructive position to coplanarity of the chromophore (*Z,Z* and *E,Z* isomers).

The nmr spectra provide several lines of support for certain of these assignments. For example, the cyclobutyl protons in the *Z,Z* and *Z,E* isomers appear as a fairly sharp peak at τ 7.50–7.55, whereas in the *E,Z* and *E,E* isomers, where two of these protons are close to the carbomethoxy group, a broad and complex pattern is seen between τ 6.9–7.8. The α-methyls appear at τ 8.20–8.21 in the *Z,Z* and *Z,E* isomers, where they are located "away" from the remainder of the molecule, but at somewhat lower field (τ 8.12–8.13) when directed toward the γ,δ double bond. Finally, in one isomer the allylic methyl on the γ carbon appears at unusually high field (τ 8.63); this is clearly the *Z,E* isomer, in which that methyl must be shielded by the nearby carbomethoxy group. Thus the assignments of the *Z,Z* and *Z,E* structures seem fairly certain; since the nmr and uv spectra of the *E,Z* and *E,E* isomers

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(12) The calculated values of $\lambda_{\max}$ for **13** and **14** are 247 and 316 nm, respectively; if only one double bond were conjugated with the ester function, the calculated value would be 234 nm (R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed, Wiley, New York, N. Y., 1967, pp 157 and 161). Some expected twisting due to steric crowding apparently lowers the observed values from those calculated.

(13) The nmr data clearly rule out the alternative conjugated structure

(13a) NOTE ADDED IN PROOF.—Professor G. Quinkert reported, at the 4th IUPAC International Symposium on Photochemistry, Baden-Baden, Germany, July 1972, that 6-acetoxy-2,4,6-trimethyl-2,4-cyclohexadienone gave 5% of a 1,6-ketene adduct.

are very similar, it is possible that these two assignments may be reversed.[14]

Experimental Section

Melting points are uncorrected. Ir spectra were calibrated against polystyrene film, and tetramethylsilane was an internal reference for all nmr spectra. The ir and nmr solvent was carbon tetrachloride; the uv solvent was methanol. All elemental analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.

Oxidation of Tetramethylbenzocyclobutene (7).—A solution of peroxytrifluoroacetic acid was prepared from 2.28 ml (83 mmol) of 90% hydrogen peroxide and 17.7 g (83 mmol) of trifluoroacetic anhydride in 24 ml of methylene chloride. The solution was maintained at 0° as it was added with stirring (45 min) to a solution of 9.0 g (57 mmol) of 7[7] in 400 ml of methylene chloride which had previously been cooled to $-30°$. Boron fluoride etherate (27 ml of 48% $BF_3 \cdot Et_2O$) was added concurrently with the peracid. The temperature was maintained at $-30°$ during the addition and for 2 hr of stirring thereafter. The mixture was hydrolyzed (100 ml of water), and the organic layer was washed with water (2 × 100 ml), saturated sodium bicarbonate (3 × 100 ml), 5% aqueous sodium hydroxide (3 × 100 ml), and again with water (3 × 100 ml). The dried ($MgSO_4$) organic layer was concentrated to a deep red, viscous oil which on distillation gave 3.41 g (34%) of 2,4,4,5-tetramethylbicyclo[4.2.0]octa-1,5-dien-3-one (**5**): bp 80–90° (0.2 Torr); λ_{max} 320 nm (ϵ 4800); $\nu_{C=O}$ 1685 cm^{-1}, $\nu_{C=C}$ 1630 cm^{-1}; nmr τ 8.90 (s, 6 H, *gem*-dimethyl), 8.31, 8.36 (br s, 6 H, allylic methyls), 7.14 (br s, 4 H, cyclobutyl); mass spectrum *m/e* 176.

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.89; H, 9.26.

A solution containing 100 mg of **5** in 0.5 ml of 1 *M* sodium methoxide in methanol-*d*, after standing for 1.5 hr at room temperature, was diluted with 2 ml of carbon tetrachloride, then washed with water (3 × 5 ml). The dried organic layer ($MgSO_4$) gave, on concentration, a quantitative yield of **5**-d_2: ν_{CD} 2200 cm^{-1}; nmr identical with that of **5**, except for the cyclobutyl protons, τ 7.18 (br s, 2 H); mass spectrum *m/e* 178.

Hydrogenation of 5.—To 50 mg of prereduced platinum oxide suspended in 13 ml of absolute ethanol was added 100 mg (0.57 mmol) of **5** in 1 ml of absolute ethanol. The mixture was stirred under 1 atm of hydrogen. After 13 min, when 1 equiv of hydrogen had been absorbed, there was a sharp decrease in the rate of hydrogen absorption. After removal of the catalyst and solvent, a yellow oil remained which constituted a 95% yield of 2,4,4,5-tetramethylbicyclo[4.2.0]octa-1-en-3-one (**11**). The product, when purified by preparative vpc (10 ft × 0.25 in. SE-30 column, 180°, 80 ml/min He) was a colorless oil: λ_{max} 247 nm (ϵ 4800); $\nu_{C=O}$ 1655 cm^{-1}; nmr τ 9.14 (d, 3 H, J = 7 Hz, C-5 methyl), 9.0, 8.83 (s, 6 H, *gem*-dimethyls), 8.45 (br s, 3 H, allylic methyl), 7.8–8.3 (m, 3 H, C-7 and C-6 protons), 7.1–7.5 (m, 2 H, C-8 protons), 6.34 (q, 1 H, C-5 proton); mass spectrum *m/e* 178.

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.91; H, 10.23.

A solution containing 100 mg of **11** in 0.5 ml of 1 *M* sodium methoxide in methanol-*d*, after standing for 1.5 hr at room temperature, was diluted with 2 ml of carbon tetrachloride, then washed with water (3 × 5 ml). The dried ($MgSO_4$) organic layer, after concentration, showed (vpc) the presence of two components, which were separated by preparative vpc (10 ft × 0.25 in. SE-30 column, 180°, 80 ml/min of He). One product, with an identical retention time with that of **11**, was *cis*-**11**-d_3, nmr identical with that of **11** except that the band at τ 8.45 became a sharp singlet, the area of the τ 7.8–8.3 multiplet decreased to 2 H, and the multiplet at τ 7.1–7.5 was absent. The second product, *trans*-**11**-d_3, had ir and uv spectra similar to those of **11**, but the following nmr: τ 9.10 (d, 3 H, J = 6.5 Hz, C-5 methyl), 9.11, 8.98 (s, 6 H, *gem*-dimethyls), 8.45 (s, 3 H, allylic methyl), 8.0–8.6 (m, 3 H, C-5 and C-7 protons); mass spectrum *m/e* 181.

Irradiation of 5 in Methanol.—A solution of 200 mg of **5** in 18 ml of methanol was irradiated using a Rayonet photochemical reactor equipped with 3000-Å lamps. The photolysis, which was monitored by vpc, was complete in 22 hr. Using a 450-W Hanovia lamp with a Pyrex filter, reaction was complete in 2 hr. The five photoproducts were separated by preparative vpc (10 ft × 0.25 in. SE-30 column, 200°, 80 ml/min of He). Product ratios varied slightly with irradiation conditions and are given here for the Rayonet conditions.

The product with retention time of 10.5 min (55%) is methyl 2-(1,2-dimethylpropenyl)-α-methyl-1-cyclobutene-1-acetate (**13**): λ_{max} 239 nm (ϵ 8100); $\nu_{C=O}$ 1715 cm^{-1}, $\nu_{C=C}$ 1630 cm^{-1}; nmr τ 8.80 (d, 3 H, J = 7 Hz, α-methyl), 8.30 (br s, 9 H, allylic methyls), 7.61 (br d, 4 H, cyclobutyl), 6.73 (q, 1 H, J = 7 Hz, α proton), 6.40 (s, 3 H, OCH_3); mass spectrum *m/e* 208.

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.79; H, 9.67.

The product with retention time of 14.7 min (12%) is considered to be (*Z,Z*)-methyl 2-(1,2-dimethylpropylidene)-α-methyl-$\Delta^{1,\alpha}$-cyclobutaneacetate (*Z,Z*-**14**): λ_{max} 289 nm (ϵ 6700); $\nu_{C=O}$ 1700 cm^{-1}, $\nu_{C=C}$ 1650 cm^{-1}; nmr τ 9.07 (d, 6 H, J = 7.0 Hz, isopropyl methyls), 8.46 (br s, 3 H, allylic methyl), 8.22 (s, 3 H, allylic methyl), 7.57 (br s, 4 H, cyclobutyl), 6.36 (s, 3 H, OCH_3); mass spectrum *m/e* 208.

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.04; H, 9.78.

The product with retention time of 17.7 min (12%) is considered to be *Z,E*-**14**: λ_{max} 289 nm (ϵ 8100) $\nu_{C=O}$ 1702 cm^{-1}, $\nu_{C=C}$ 1650 cm^{-1}; nmr τ 8.99 (d, 6 H, J = 7.0 Hz, isopropyl methyls), 8.63 (s, 3 H, allylic methyl), 8.20 (s, 3 H, allylic methyl), 7.50 (br s, 4 H, cyclobutyl), 6.36 (s, 3 H, OCH_3); mass spectrum *m/e* 208.

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.92; H, 9.63.

The product with retention time of 20.5 min (9%) is either *E,E*-**14** or *E,Z*-**14**: λ_{max} 288 nm (ϵ 17,000); $\nu_{C=O}$ 1700 cm^{-1}, $\nu_{C=C}$ 1640 cm^{-1}; nmr τ 8.96 (d, 6 H, J = 7.0 Hz, isopropyl methyls), 8.42 (s, 3 H, allylic methyl), 8.15 (s, 3 H, allylic methyl), 6.95–7.95 (br m, 5 H, cyclobutyl and isopropyl protons), 6.35 (s, 3 H, OCH_3); mass spectrum *m/e* 208.

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.90; H, 9.65.

The product with retention time of 22.5 min (12%) is either *E,Z*-**14** or *E,E*-**14**: λ_{max} 290 nm (ϵ 14,000); $\nu_{C=O}$ 1700 cm^{-1}, $\nu_{C=C}$ 1640 cm^{-1}; nmr τ 8.99 (d, 6 H, J = 7.0 Hz, isopropyl methyls), 8.32 (s, 3 H, allylic methyl), 8.13 (s, 3 H, allylic methyl), 6.93–7.65 (br m, 5 H, cyclobutyl and isopropyl protons), 6.36 (s, 3 H, OCH_3); mass spectrum *m/e* 208.

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.80; H, 9.65.

Irradiation of 5 in Methylene Chloride.—A solution of 200 mg of **5** in 18 ml of methylene chloride was irradiated for 8 hr using a 450-W Hanovia lamp with a Pyrex filter. The starting material was recovered unchanged.

Registry No.—**5**, 28124-15-4; **11**, 34922-01-5; **13**, 34922-02-6; *Z,Z*-**14**, 34922-03-7; *Z,E*-**14**, 34922-04-8; *E,Z*-**14**, 34922-05-9; *E,E*-**14**, 34922-06-0.

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[14] If the assignment were reversed, the chemical shift of the δ-methyl (τ 8.42) would agree better with that of the similar methyl in the *Z,Z* isomer (τ 8.46).