Table II. Comparison of Rates[a] of Initiation and Autoxidation in Benzene at 50 °C and 1.0 Atm of O_2

compd	rate of autoxidation	[AIBN], M	rate of initiation	ratio of rates
$P(OEt)_3$	2.07×10^{-6}	0.010 5	2.9×10^{-8}	7.1×10
$P(OEt)_3$	5.44×10^{-6}	0.029 13	8.1×10^{-8}	6.7×10
$EtP(OEt)_2$	1.50×10^{-4} [b]	0.020 0	5.6×10^{-8}	2.7×10^{3}
Et_2POEt	4.74×10^{-5} [b]	0.017 83	5.0×10^{-8}	9.5×10^{2}
Et_2POEt	4.74×10^{-5} [b]	0.020 22	5.6×10^{-8}	8.5×10^{2}

[a] Units of mol L^{-1} s^{-1}. [b] Initial rates.

centration but first order in the concentration of the other two esters. Phosphite autoxidation is found to be first order in oxygen pressure, and this is presumed to be true for the other two esters as well.

Triethyl phosphite autoxidation is first order in AIBN concentration, and there is no reaction in the absence of added initiator. In contrast, both of the other two esters do undergo autoxidation in solution in the absence of added AIBN, the phosphinite very slowly (5 days at 60 °C and 1 atm of oxygen) and the phosphonite more rapidly.[5] Since this result might depend on adventitous traces of impurities, the kinetic studies of their autoxidations were conducted with added AIBN to provide much more rapid and equal initiation.

From the data given by Huyser,[17] one may calculate for AIBN a half-life of 85.6 h at 50 °C and a rate of formation of initiating radicals as in eq V, where k_1 is 2.25×10^{-6} s^{-1}

$$d[(CH_3)_2(CN)C\cdot]/dt = 2ak_1[AIBN] \qquad (V)$$

and a, the efficiency of radical generation,[18] is 0.62. Under the conditions of each of the present experiments, the AIBN concentration changes by 2% or less, i.e., is effectively constant. It is of interest to compare the (initial) rates of autoxidation of the organophosphorus substrates with the rate of formation of initiating radicals; this is done in Table II. Assuming comparable efficiencies of initiation, the ratio of these rates should be an approximate relative measure of the chain length. The result is 1–2 orders of magnitude smaller for the phosphite than for the phosphonite or phosphinite. Presumably this is the reason for the diffferent dependence of the rate of phosphite autoxidation on substrate concentration. The zero-order dependence is not in agreement with the previous report of Floyd and Boozer[4] but agrees with previous more qualitative observations.[6,9]

The autoxidation of the phosphonite and the phosphinite to mixtures of products, e.g., in the latter case to phosphinate, phosphonite, phosphonate, phosphite, and phosphate, is in complete agreement with and provides experimental proof of the postulate of Buckler[10] for the mechanism of autoxidation of tertiary phosphines (Scheme I). Under conditions of comparable initiation, the phosphonite reacts more rapidly than the phosphinite, showing that the reactivity order $R_3P > R_2POR > RP(OR)_2 > P(OR)_3$ postulated by Razumov et al.[19] is incorrect.

Registry No. $P(OEt)_3$, 122-52-1; $EtP(OEt)_2$, 2651-85-6; Et_2POEt, 2303-77-7.

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[17] E. S. Huyser, "Free Radical Chain Reactions", Wiley-Interscience, New York, 1970.

[18] G. S. Hammond, J. N. Sen, and C. E. Boozer, *J. Am. Chem. Soc.*, 77, 3244 (1955).

[19] A. I. Razumov, O. A. Mukhacheva, and Sim Do Khen, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 894 (1952).

Photorearrangements of Epoxy Ketones. Epoxides of Hexamethylbicyclo[3.2.0]hepta-2,5-dienone, a Valence Tautomer of Hexamethyltropone

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The double bond in the four-membered ring of hexamethylbicyclo[3.2.0]hepta-3,6-dien-2-one (**1**) is selectively oxidized by *m*-chloroperbenzoic acid, whereas the enone double bond is selectively epoxidized by alkaline hydrogen peroxide to give **2** and **3**, respectively. In each case, a single stereoisomer is formed. The exo stereochemistry of the epoxides was deduced from X-ray structures on diepoxides **4** and **5** obtained by further epoxidation of **2** and **3**. Irradiation of **2** gives pentamethylphenol (**6**) and ketene; if **2** is labeled at the C_4 methyl with deuterium, the resulting **6** is labeled para to the hydroxyl group. A novel rearrangement of the four-membered ring to give a 7-norbornenyl-type intermediate is suggested to rationalize the labeling result. Irradiation of **3** gives, in addition to minor amounts of pentamethylphenol and its acetate, a tetracyclic product formulated as **10**, which rearranges thermally to 1-acetylpentamethylcyclopentadiene (**12**). A mechanism involving photochemical C–C bond cleavage of the epoxide ring in **3** is suggested to account for the results.

Although the photochemistry of ketones, alkenes, and epoxides has been extensively studied,[1] it is still not easy to predict with a high degree of accuracy what will happen when a particular molecule containing these three functions is irradiated. This is because the arrangement of these groups with respect to one another and the substituents which they carry affect the reaction outcome. Although some generalizations can be made,[2] empiricism is still a very prevalent feature of this area of photochemistry. The extent to which this is so is apparent in the

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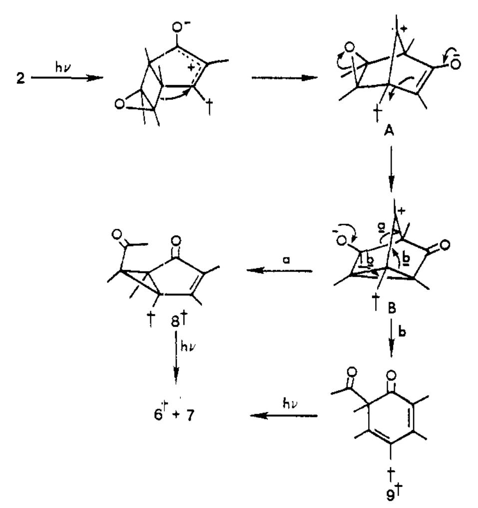
[1] The extent to which this is so each year is evident by the large fraction of each volume of *Photochemistry* (published annually by the Chemical Society) that is devoted to these three functional groups.

[2] Hart, H.; Peng, C.-T.; Shih, E.-M. *J. Org. Chem.* **1977**, *42*, 3635.

0022-3263/80/1945-2091$01.00/0

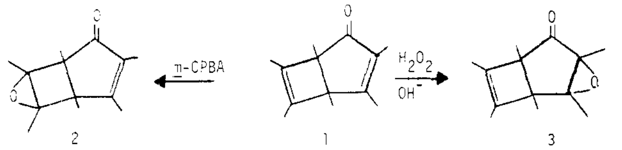
Scheme I

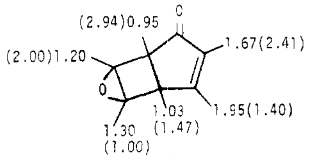


present study. We report here on the photoisomerization of epoxy enones 2 and 3.[3]

Results and Discussion

Synthesis and Stereochemistry of Epoxy Ketones 2 and 3. In an attempt to prepare hexamethyltropone, its valence tautomer 1 was synthesized in two steps, from hexamethyl(Dewar benzene).[4] By oxidation with *m*-chloroperbenzoic acid or with alkaline hydrogen peroxide, either double bond in 1 could be selectively epoxidized; a single stereoisomer was formed in each case.[5] The chemical shift of each methyl group in each epoxide could be uniquely assigned from the Eu(fod)$_3$ shift data and from deuterium labeling (vide infra), as shown on the structures of 2 and 3 [Eu(fod)$_3$ slopes are in parentheses]. Unfortunately, these data did not permit a stereochemical assignment, and crystals were not satisfactory for X-ray analysis. Consequently, each monoepoxide was oxidized further, with the hope that the resulting diepoxides would be suitable for X-ray structure determination.

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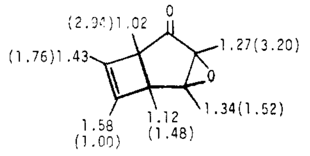
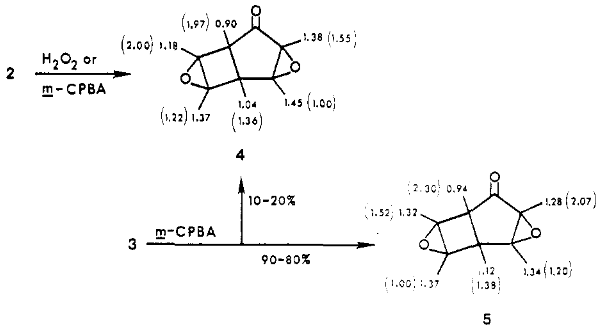
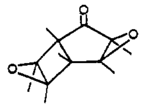

3

Epoxidation of 2 with either *m*-CPBA or alkaline hydrogen peroxide gave diepoxide 4.[5] In contrast, further epoxidation of 3 with *m*-CPBA gave two diepoxides, 4 (10–20%) and 5 (90–80%). Deuterium labeling permitted the unequivocal assignment of the C_4 methyl group in each diepoxide, and the remaining assignments, necessarily tentative, are made from Eu(fod)$_3$ shift data and by comparison with the monoepoxide spectra, giving groups with similar chemical shifts and slopes with similar environments.



The structures of 4 (D.L.W.) and 5 (W.-J.K.) were determined by X-ray diffraction (for details, vide infra), and the stereochemistry is as shown. We conclude that the epoxide ring in 2 and 3 is exo in each case. Predominant attack of oxidant on the exo face of either double bond in 1 is consistent with what one would intuitively expect, and the only assumption in this assignment is that no rearrangement occurs during the second epoxidations. The only surprise in these results is that the predominant epoxidation product of 3 is 5, not 4.[6]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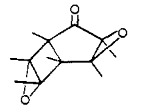
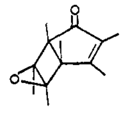
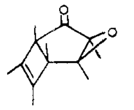
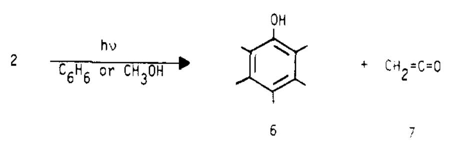

5

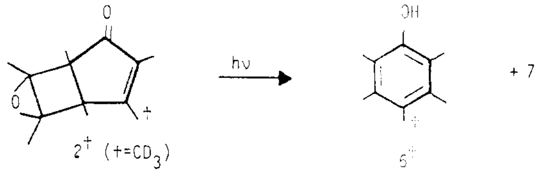

2


3

Irradiation of 2. A benzene solution of 2 irradiated through Pyrex gave one major product, pentamethylphenol. When the solvent was changed to methanol, an equivalent amount of methyl acetate was also isolated. Consequently, the other photoproduct must be ketene.

Since a variety of plausible mechanisms can be envisioned to explain the formation of these photoproducts, a labeling experiment was done to narrow the possibilities. Epoxide 2 was labeled with a CD_3 group at C_3, either by treatment of 2 with excess $NaOCH_3/CH_3OD$ overnight at room temperature or by carrying out a similar exchange with 1, followed by epoxidation. Irradiation of 2† gave pentamethylphenol labeled exclusively in the para position! The label in 6† was located by NMR. All five methyl





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[3] For a parallel study of the rearrangements which occur when these compounds are treated with acid, see: Hart, H.; Chen, S.-M.; Lee, S. *J. Org. Chem.*, following paper in this issue.

[4] Hart, H.; Nitta, M. *Tetrahedron Lett.* **1974**, 2109.

[5] No other isomer was detected by NMR or VPC. Further epoxidation of 2, however, gave diepoxide containing 98% of 4 and 2% of 5. We suspect that 5 comes from a trace of endo monoperoxide present in 2.

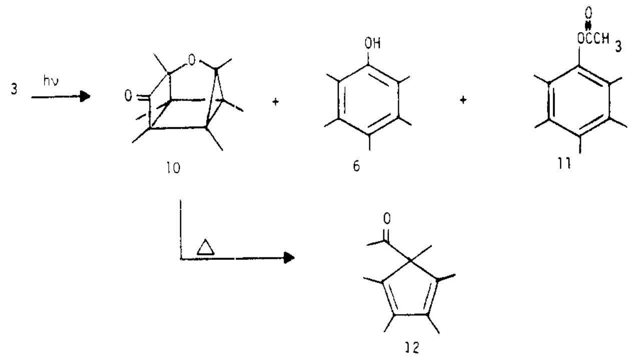
[6] We have no good explanation for this preference. Perhaps the oxidant complexes with the carbonyl oxygen prior to delivery of oxygen to the double bond. It might do so preferentially from the "underneath" face of 3, which is blocked only by two methyl groups, whereas the "top" face is blocked by two methyl groups and the epoxide ring.

groups in **6** ordinarily appear as a broad singlet at 60 MHz. Eu(fod)$_3$ shift reagent, however, resolves this peak into three singlets with relative areas of 2:2:1, the ortho methyl groups being most shifted. When the NMR spectrum of **6**† was taken in the presence of shift reagent, only two singlets with equal areas were observed. Consequently, all of the label must be in the para methyl group.

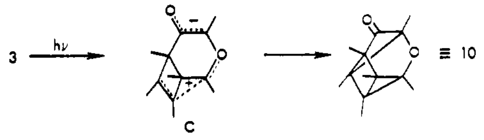
This was a surprising result, because reasonable mechanisms require the phenolic hydroxyl group in **6** to come from the carbonyl oxygen, and in **2**† the labeled methyl and carbonyl carbon have a 1,3 relationship. Scheme I shows two mechanisms whereby the label could end up in the observed position. We have arbitrarily written the rearranging species as dipolar, although no mechanistic information on the nature of the excited state or other intermediates is known. The first step following excitation involves a 1,2-shift to expand the cyclobutane ring. Intermediate A would be a stabilized 7-norbornenyl intermediate. The exo geometry of the epoxide ring should allow facile conversion to B. B is a key intermediate since it enables the necessary 1,4 relationship between the original carbonyl carbon and C_3 methyl to be attained. Two paths are then open to B. Collapse according to path a would give the bicyclo[3.1.0]hexenone **8** with the acetyl group at C_6 in the endo configuration necessary for subsequent photoisomerization to **6** and **7**. Separate irradiation of **8**[7] under the same conditions used with **2** gave a quantitative yield of **6** and **7**, showing that **8** is a plausible reaction intermediate.

Alternatively, B could collapse to the acetylcyclohexadienone **9** which could also photoisomerize to **6** and **7**. Thus either alternative in Scheme I is plausible, and we cannot distinguish between them.

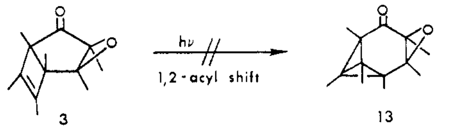
Irradiation of 3. Compound **3** is simultaneously an α,β-epoxy ketone and a β,γ-unsaturated ketone. Although the photochemistry of both of these classes of compounds has been studied extensively,[8,9] our results with **3** do not fit the commonly anticipated reactions of either type of chromophore. Compound **3** has an n,π^* absorption at 315 nm (ϵ 320) and was irradiated through Pyrex. When the reaction was followed by vapor-phase chromatography, peaks due to one major and two minor products appeared. These were identified as 1-acetylpentamethylcyclopentadiene (**12**), pentamethylphenol (**6**), and acetate **11**, respectively. However, examination of the crude photolysis product by NMR showed no peaks due to **12** but instead a group of methyl singlets all of which were in the aliphatic region ($\delta \leq 1.26$), as well as weak peaks due to the minor products **6** and **11**. Consequently, **12** is not a primary photolysis product but is formed from a precursor which thermally rearranges on VPC. Attempts to isolate this precursor in pure form by TLC failed, but from its spectra, method of formation, and rearrangement to **12**, we suggest that its structure is **10**.



Scheme II



The NMR spectrum of the crude photolyzate contained four singlets ascribable to **10** at δ 1.00 (6 H), 1.03 (3 H), 1.08 (3 H), and 1.26 (6 H). Addition of Eu(fod)$_3$ resolved the spectrum into six singlets corresponding to 3 H each; thus all six methyl groups are unique and aliphatic. The molecule cannot contain any symmetry feature and must be tetracyclic. The IR spectrum had a carbonyl band at 1760 cm^{-1}, consistent with a cyclobutanone moiety. These spectral data severely limit the plausible structures for this photoproduct. Aside from **10**, the only other likely structure is **13**, which could arise from the oxa-di-π-methane rearrangement of **3**.[9] Although **13** would have six unique aliphatic methyl groups, its infrared spectrum would not be expected to have a carbonyl band at 1760 cm^{-1}. Consequently, we rule out structure **13**.



Structure **10** is made reasonable by plausible mechanisms for its formation and for its rearrangement to **12**. Scheme II describes a straightforward mechanism for obtaining **10** from **3**. Following excitation, the C–C bond of the epoxide ring is broken instead of the more common[8] C–O bond cleavage. C–C bond cleavage is particularly favorable in **3** because of the possibilities for electron delocalization. We have written the proposed intermediate as a carbonyl ylide, C, for which there is ample precedent in epoxide photochemistry.[10,11]

One can envision several mechanisms by which **10** can isomerize thermally to **12**. A labeling experiment limits

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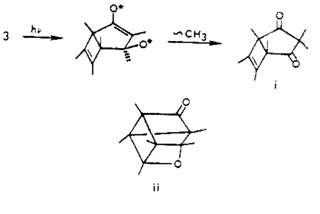
(7) For preparation, see: Chen, S.-M. Thesis, Michigan State University, 1975, p 136–7.

(8) For reviews, see: (a) Padwa, A. *Org. Photochem.* **1967**, *1*, 91; (b) Padwa, A. *Acc. Chem. Res.* **1971**, *4*, 48; (c) Bertoniere, N. R.; Griffin, G. W. *Org. Photochem.* **1973**, *3*, 138.

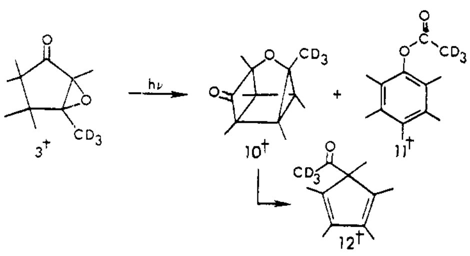
(9) For reviews, see: (a) Houk, K. N. *Chem. Rev.* **1976**, *76*, 1. (b) Dauben, W. G.; Lodder, G.; Ipaktchi, J. *Fortschr. Chem. Forsch.* **1975**, *54*, 73.

(10) C–C cleavage of appropriately substituted epoxides to give carbonyl ylides has been extensively studied; for a recent example and leading references, see: Griffin, G. W.; Ishikawa, K.; Lev, I. J. *J. Am. Chem. Soc.* **1976**, *98*, 5697. For examples of C–C bond cleavage during photolysis of epoxy ketones, see: Ehrenfreund, J.; Gaoni, Y.; Jeger, O. *Helv. Chim. Acta* **1974**, *57*, 2704; Frei, B.; Wolf, H. R. *Ibid.* **1976**, *59*, 82; Eichenberger, E.; Wolf, H. R.; Jeger, O. *Ibid.* **1976**, *59*, 1253; also see ref 8c, particularly pp 139–42.

(11) The alternative reaction path (C–O bond cleavage) would be expected to give i; this product was not detected. The exo geometry of the epoxide ring in **3** rules out yet another otherwise mechanistically plausible structure for **10**, i.e. structure ii, which fits both the IR and NMR data; also, there is no simple plausible mechanism to **12** from ii.



some of the possibilities. A sample of **3**† was prepared by epoxidizing **1** which had been exchanged at the C_4 methyl group. Irradiation of **3**† gave **10**† in which the peak at δ



1.26 was diminished in area from 6 H to 3 H; addition of $Eu(fod)_3$ showed that of the two methyls with that chemical shift, the one with the larger slope was absent. The peak at δ 2.20 in the pentamethylphenyl acetate was also absent, showing that the product is **11**†. Thermal rearrangement of **10**† gave **12**† in which the acetyl methyl was labeled.[12]

Two mechanisms for the thermal isomerization of **10** to **12** that are consistent with the label result are shown in Scheme III. Each involves cleavage of the C–O bond α to the carbonyl group and cleavage of one of the cyclopropane bonds. The ether oxygen in **10** becomes the acetyl oxygen in **12**, and the carbonyl group is lost as carbon monoxide, via either a cyclopropanone or a ketene intermediate.

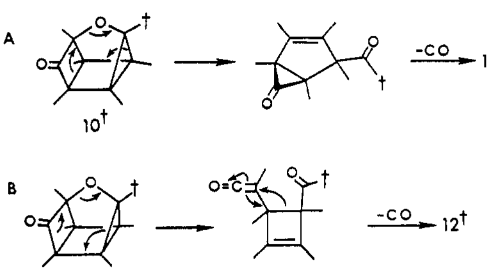
The minor products **6** and **11** could arise from **3** in many ways. The most plausible schemes involve acetylpentamethylcyclohexadienones (either 2,4 or 2,6) as intermediates, and all predict that the acetyl methyl in **11** comes from the C_4 methyl of **3**, consistent with the labeling results. Further speculation regarding the formation of these minor products is unwarranted at present.

In summary, photoisomerization of **2** is best explained through a mechanism (Scheme I) involving a novel 1,2-shift of the cyclobutane ring, whereas **3** provides another example of an α,β-epoxy ketone which photolyzes via carbon–carbon rather than carbon–oxygen cleavage of the epoxide ring.

Crystallographic Data and X-ray Structure Analysis of Diepoxides 4 and 5. Crystals of **4**, $C_{13}H_{18}O_3$, are orthorhombic: space group $P2_12_12_1$; a = 13.111 (6), b = 11.738 (3), c = 8.110 (4) Å; Z = 4; M_r = 222.29; ρ_{calcd} = 1.183 g cm^{-3}. Crystals of **5**, $C_{13}H_{18}O_3$, are orthorhombic: space group $P2_12_12_1$; a = 13.125 (6), b = 11.571 (9), c = 8.206 (4) Å; Z = 4; M_r = 222.29; ρ_{calcd} = 1.185 g cm^{-3}. Lattice dimensions were determined by using a Picker FACS-I diffractometer and Mo Kα_1 (λ = 0.709 26 Å) radiation.

Intensity data were measured by using Mo Kα radiation ($2\theta_{max}$ = 45°), yielding 2062 (**4**) and 2087 (**5**) total unique data and, based on $I > 2\sigma(I)$, 1283 (**4**) and 1092 (**5**) observed data, respectively. The data were reduced,[13] the structures were solved by direct methods,[14] and the refinement was by full-matrix least-squares techniques.[15] The final R values were 0.044 (**4**) and 0.051 (**5**). The final difference Fourier maps showed densities ranging from +0.18 to −0.27 (**4**) and from +0.31 to −0.33 (**5**) with no indication of misplaced or missing atoms. ORTEP[16] drawings of **4** and **5** are shown in Figure 1.

Scheme III



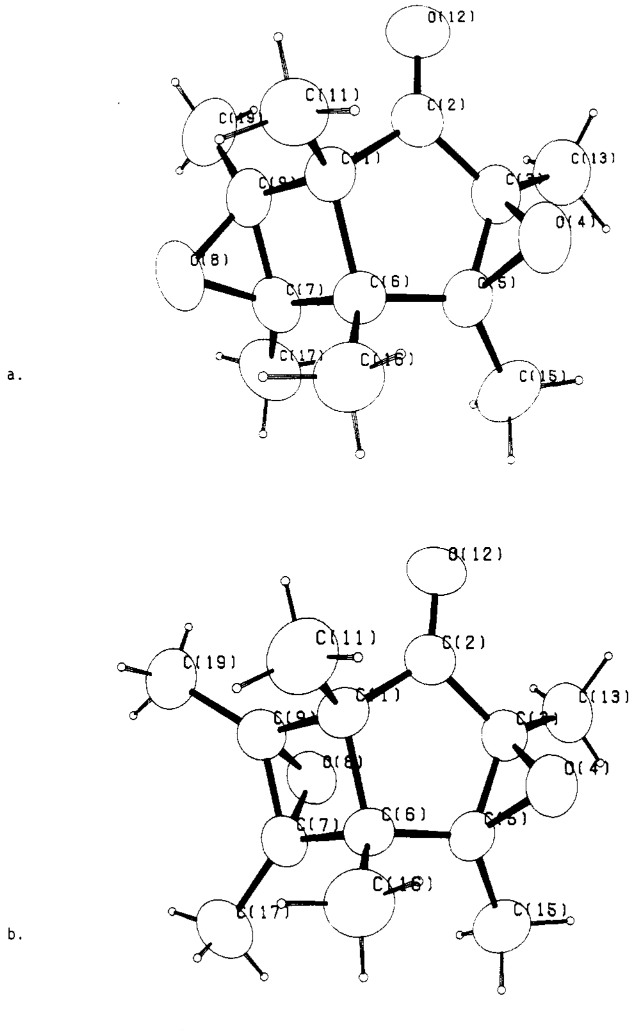


Figure 1. ORTEP[16] drawings of the molecular structures of **4** (a) and **5** (b) with the thermal ellipsoids scaled to enclose 50% probability; hydrogen atoms have been assigned arbitrary temperature factors of 0.1 Å^2 for B_{iso}.

Experimental Section

General Procedures. All NMR spectra were measured at 60 MHz with $(CH_3)_4Si$ as an internal standard. Shift data were obtained by adding small increments of $Eu(fod)_3$ to the sample and noting the extent to which each absorption was shifted. Normalized slopes were then obtained by dividing each by the shift of the least shifted signal. IR spectra, obtained on a Unicam SP-200 or a Perkin-Elmer 237 spectrometer, were calibrated

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[12] The acetyl methyl appears at δ 1.45, apparently shielded by the diene moiety. This peak was not absent in **11**† but was reduced about 50% in area; all other methyl signals were full intensity. It is possible that some back-exchange occurred during VPC collection of **11**†.

[13] Wei, K.-T.; Ward, D. L. *Acta Crystallogr., Sect. B* **1976**, *32*, 2768.

[14] Main, P. "MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data"; University of York: England, 1978.

[15] Zalkin, A. 1974, private communication.

[16] Johnson, C. K. Report ORNL-3794 (Revised); Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

against a polystyrene film. UV spectra were obtained with a Unicam SP-800 spectrometer, and mass spectra were obtained at 70 eV on a Hitachi Perkin-Elmer RMU-6 instrument. Melting points, determined with a Thomas-Hoover melting point apparatus, are uncorrected. All VPC separations were performed on Varian Aerograph instruments. Analyses were performed by Spang Microanalytical Laboratories.

Irradiations were performed with a Hanovia 450-W lamp placed in a water-cooled quartz jacket equipped with different filters. The solution to be irradiated was placed in a quartz or Pyrex test tube which was sealed with a serum cap after being deoxygenated with a stream of N_2 or Ar. The tube was then taped to the immersion well, and the irradiation was monitored by chromatographic or spectroscopic methods.

1,3,4,5,6,8-Hexamethyl-7-oxatricyclo[3.3.0.0^{6,8}]oct-3-en-2-one (2). To a solution of 1[4] (2.0 g, 10.5 mmol) in 20 mL of methylene chloride was added at 0 °C a solution of *m*-chloroperbenzoic acid (2.5 g, 12.6 mmol) in 30 mL of the same solvent. The mixture was stirred at 0 °C for 5 h. After the solvent was evaporated under reduced pressure, petroleum ether (bp 30–60 °C) was added to the residue, and the *m*-chlorobenzoic acid was removed by filtration. The filtrate was cooled at 0 °C for 30 min and filtered again. Evaporation of the solvent from the filtrate left 2.15 g of a colorless oil, shown by NMR to be 95% pure 2. The crude product was chromatographed on Florisil (CH_2Cl_2 eluent) to give 1.98 g (90%) of 2: mp 59–60 °C; IR (KBr) 2990 (m), 1680 (s), 1340 (m), 1260 (w), 1175 (m), 1080 (m), 1030 (m), 930 (w), 835 (m) cm^{-1}; UV (EtOH) λ_{max} 245 nm (ϵ 5970), 215 (6390); NMR (CCl_4), see structure; the peaks at δ 1.67 and 1.95 were homoallylically coupled, J = 1 Hz; mass spectrum,[17] *m/e* (relative intensity) 206 (25), 191 (2.5), 178 (2.5), 165 (12), 164 (100), 163 (16), 150 (10), 149 (75), 124 (11), 121 (10), 93 (10), 91 (10), 43 (23).

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.68; H, 8.79.

Epoxidation of 1 with a CD_3 group at C_4[4] gave $2^{\dagger}$ in which the peak at δ 1.95 was absent, and that at δ 1.67 was sharpened to a singlet. Allowing a solution of 2 (206 mg, 2 mmol) to stand overnight at room temperature in 5 mL of CH_3OD containing 20 mg of $NaOCH_3$ followed by the usual workup also gave a quantitative yield of $2^{\dagger}$.

1,3,5,6,7,8-Hexamethyl-4-oxatricyclo[4.2.0.0^{3,5}]oct-7-en-2-one (3). To a solution of 1 (2.0 g, 10.5 mmol) and 30% hydrogen peroxide (3.6 g, 31.5 mmol) in 10 mL of methanol was added at 0 °C 1 mL (6 mmol) of 6 N aqueous sodium hydroxide. The mixture was stirred overnight, diluted with water, and extracted with ether. The combined ether extracts were washed with saturated sodium chloride solution, dried ($MgSO_4$), and evaporated to give 2.01 g (93%) of 3 as a colorless oil which crystallized on standing for 1 h at room temperature: mp 40–41 °C; IR (neat) 3000 (s), 2900 (m), 1720 (s), 1455 (s), 1380 (s), 1315 (w), 1280 (w), 1250 (w), 1175 (m), 1110 (m), 1070 (m), 1060 (m), 1050 (m), 1020 (s), 860 (s), 740 (w) cm^{-1}; UV (MeOH) λ_{max} 315 nm (ϵ 320), 237 (1340), 215 (1950); NMR (CCl_4) see structure; the peaks at δ 1.43 and 1.58 were homoallylically coupled, J = 1 Hz; mass spectrum,[17] *m/e* (relative intensity) 206 (33), 178 (8), 164 (9), 163 (8), 149 (15), 136 (53), 135 (100), 121 (32), 119 (35), 107 (20), 105 (26), 93 (16), 91 (23), 79 (12).

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.49; H, 8.82.

Epoxidation of 1 with a CD_3 group at C_4[4] gave $3^{\dagger}$ lacking the singlet at δ 1.34.

Irradiation of 2 and $2^{\dagger}$. A deoxygenated solution of 2 (100 mg) in 20 mL of methanol was irradiated through Pyrex, and the reaction was monitored by NMR. After 10 h 2 was essentially absent, and a singlet at δ 2.10 had built in area to maximum intensity. The product, isolated in 56% yield by preparative TLC (silica gel, CH_2Cl_2 eluent), was identified as pentamethylphenol by comparison of its melting point (127.5–128 °C) and spectra with those of an authentic sample.[18]

Irradiation of 2 (20 mg) in 0.2 mL of CD_3OD in a similar manner gave two sharp singlets, one at δ 2.10 due to pentamethylphenol and another at δ 2.07 due to $CH_3CO_2CD_3$ (identified by comparison with an authentic sample).

Irradiation of $2^{\dagger}$ (80 mg) in 20 mL of benzene for 15 h followed by evaporation of the solvent and TLC purification gave 4-methyl-d_3-2,3,5,6-tetramethylphenol ($6^{\dagger}$) as the only major product. Eu(fod)$_3$ separates the singlet ordinarily observed for pentamethylphenol into three singlets with relative intensities of 2:2:1 and relative shift slopes of 5.5:2.0:1.0 for the ortho, meta, and para methyls, respectively. The product from this photolysis showed only the first two of these peaks.

Irradiation of *endo*-6-Acetyl-1,3,4,5,6-pentamethylbicyclo[3.1.0]hex-3-en-2-one (8). A 1% methanol solution of 8[7] was irradiated through a Corex filter. The reaction, followed by VPC, was complete in 2 h. Removal of the solvent and workup gave a quantitative yield of pentamethylphenol.

Irradiation of 3 and $3^{\dagger}$. An oxygen-free solution of 3 (75 mg, 0.36 mmol) in 25 mL of anhydrous ether was irradiated through Pyrex. The photolysis was followed by VPC (5 ft × 0.125 in. column, 5% FFAP on Chromosorb W, AW-DMCS, 80/100 mesh, 145 °C, 60 mL/min of He). As the reaction proceeded, the peak due to 3 (retention time 3.9 min) decreased in area, and new peaks appeared at 3.7 min (12), 20.6 min (6), and 27 min (11), along with several very minor peaks. The reaction was complete in 18 h. An NMR spectrum (CCl_4) of the crude reaction mixture showed four peaks at δ 1.00 (s, 6 H), 1.03 (s, 3 H), 1.08 (s, 3 H), and 1.26 (s, 6 H) due to 10 (70% from integration) as well as minor peaks in the δ 1.97–2.12 region corresponding to 6 (8%) and 11 (5%). Addition of Eu(fod)$_3$ resolved the peaks due to 10 into six three-proton singlets with relative slopes as follows: δ 1.00 (1.74, 2.11), 1.03 (1.06), 1.08 (2.15), 1.26 (1.00, 1.34). An IR spectrum of the crude product mixture showed a strong $\nu_{C=O}$ at 1760 cm^{-1} and other bands as follows: 3500 (w), 3000 (s), 2960 (s), 2900 (m), 1640 (w), 1450 (s), 1380 (s), 1170 (s), 1080 (m), 1065 (m), 865 (w), 835 (w), 780 (m) cm^{-1}. The mixture was subjected to preparative VPC (5 ft × 0.25 in. column, 10% FFAP on Chromosorb W, 80/100 mesh) to give 1-acetylpentamethylcyclopentadiene (12): 60%; NMR (CCl_4) δ 1.10 (s, 3 H), 1.45 (s, 3 H), 1.65 (q, 6 H, J = 1 Hz), 1.80 (q, 6 H, J = 1 Hz); IR (neat) 2950 (w), 1695 (s), 1650 (w), 1450 (s), 1355 (s), 1200 (s), 1090 (s), 1070 (m), 970 (m), 875 (w), 765 (w) cm^{-1}; UV (MeOH) λ_{max} 255 nm (ϵ 6400), 217 (4800); mass spectrum, *m/e* (relative intensity) 178 (51), 163 (7), 136 (100), 135 (63), 121 (72), 120 (20), 119 (42), 107 (21), 105 (32), 93 (17), 91 (27). Compound 6 was identified as pentamethylphenol by its melting point (127–128 °C) and NMR spectrum, δ 2.12 (s). Compound 11 was identified as pentamethylphenyl acetate: NMR (CCl_4) δ 1.97 (s, 6 H), 2.12 (s, 9 H), 2.20 (s, 3 H); IR (KBr) 2950 (m), 1740 (s), 1460 (m), 1380 (m), 1230 (s), 1090 (m) cm^{-1}; UV (MeOH) λ_{max} 227 nm (ϵ 3000); mass spectrum, *m/e* (relative intensity) 206 (17), 165 (13), 164 (100), 163 (11), 149 (63), 105 (12), 91 (13).

Irradiation of $3^{\dagger}$ in similar fashion gave a crude product in which the singlet at δ 1.26 (10) was reduced in area to 3 H, and europium shift reagent showed that it was the peak with a slope of 1.34 that was absent. Also, the signal at δ 2.20 (11) was absent. Workup by VPC gave $12^{\dagger}$, whose NMR spectrum was identical with that of 12 except that the peak at δ 1.45 was reduced 50% in area.

Epoxidation of 2 with Alkaline Peroxide. To a solution of 2 (103 mg, 0.5 mmol) and 30% hydrogen peroxide (170 mg, 1.5 mmol) in 0.5 mL of methanol was added at 0 °C 0.1 mL (0.6 mmol) of 6 N aqueous NaOH. The mixture was stirred at room temperature overnight, diluted with water, and extracted with ether. The combined ether extracts were washed with saturated salt solution, dried ($MgSO_4$), and evaporated to give 108 mg (98%) of 4, mp 86–87 °C. Beautiful rhombic single crystals suitable for X-ray analysis were obtained by recrystallization from cyclohexane and pentane (1:1) at 0 °C: IR (neat) 2970 (m), 2940 (m), 2880 (w), 1740 (s), 1450 (m), 1375 (m), 1265 (w), 1175 (w), 1160 (m), 1110 (w), 1085 (w), 1065 (w), 1050 (m), 850 (w), 820 (w), 760 (w) cm^{-1}; UV (MeOH) λ_{max} 310 nm (ϵ 60), 215 (1110); NMR (CCl_4), see structure; mass spectrum,[19] *m/e* (relative intensity) 222 (1),

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(17) The difference between the mass spectra of 2 and 3 is striking. The base peak at *m/e* 164 in the spectrum of 2 corresponds to pentamethylphenol (loss of ketene), consistent with the photolysis. This peak is very weak in the spectrum of 3 which has a base peak at *m/e* 135. This latter peak corresponds to the pentamethylcyclopentadienyl moiety, consistent with the formation of 12 as the major isolated product from the successive photolysis and thermolysis of 3.

(18) Kolka, A. J.; Vogt, R. R. *J. Am. Chem. Soc.* **1939**, *61*, 1463.

164 (8), 151 (36), 149 (8), 137 (22), 136 (9), 125 (11), 124 (100), 123 (30), 109 (41), 91 (10), 81 (11).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.22; H, 8.16.

Examination of the crude epoxidation product by VPC (SE-30, 140 °C) indicated a 49:1 mixture of 4 and 5.

Epoxidation of 2 with *m*-Chloroperbenzoic Acid. To a solution of 2 (103 mg, 0.5 mmol) in 1 mL of CH_2Cl_2 was added at 0 °C a solution of *m*-chloroperbenzoic acid (500 mg, 2.5 mmol) in 3 mL of CH_2Cl_2, and the mixture was stirred at room temperature for 72 h. The solvent was evaporated, petroleum ether (bp 30–60 °C) was added, and the *m*-chlorobenzoic acid was removed by filtration. Evaporation of the solvent gave a quantitative yield of 4, with properties identical with those from the alkaline peroxide oxidation.

Epoxidation of 3. To a solution of 3 (206 mg, 1 mmol) in 2 mL of CH_2Cl_2 was added at 0 °C a solution of *m*-chloroperbenzoic acid (250 mg, 1.23 mmol) in 3 mL of the same solvent. The mixture was stirred at 0 °C for 5 h and evaporated under reduced pressure, and petroleum ether (30–60 °C) was added to the residue. The *m*-chlorobenzoic acid was removed by filtration. The filtrate was washed successively with aqueous sodium bicarbonate and saturated salt solution, dried ($MgSO_4$), and evaporated to give 200 mg of a colorless oil. The crude material was a mixture of two stereoisomers, 4 and 5, in the ratio of approximately 1:9 (NMR integration). In other preparations, VPC analysis (SE-30, 140 °C) indicated a ratio of about 1:4. The isomers were separated by preparative VPC (6 ft × 0.25 in. column, 15% SE-30 on Chromosorb W, AW-DMCS, 60/80 mesh, 165 °C, 60 mL/min of He) to give 4 (retention time 4 min), identical with that obtained from the epoxidation of 2 (vide supra), and 5 (retention time 4.5 min): IR (neat) 2975 (m), 2940 (m), 2880 (w), 1740 (s), 1470 (m), 1450 (m), 1385 (m), 1375 (m), 1310 (w), 1255 (w), 1215 (m), 1185 (w), 1105 (m), 1080 (m), 1010 (m), 890 (w), 845 (m), 720 (w) cm^{-1}; UV (MeOH) λ_{max} 308 nm (ϵ 50), 218 (830); NMR (CCl_4), see structure; mass spectrum,[19] *m/e* (relative intensity) 222 (2), 164 (10), 151 (39), 149 (10), 137 (23), 136 (10), 125 (11), 124 (100), 123 (33), 109 (42), 91 (11), 81 (12).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.21; H, 8.14.

Similar epoxidation of $3^\dagger$ gave $4^\dagger$, whose spectrum was identical with that of 4 but lacked the singlet at δ 1.45, and $5^\dagger$, whose spectrum was identical with that of 5 but lacked the singlet at δ 1.34. Beautiful rhombic single crystals of 5 suitable for X-ray analysis were obtained by recrystallization from cyclohexane and pentane (1:1); mp 72.5–73.5 °C.

Acknowledgment. We are indebted to the National Institutes of Health Grant No. GM 15997 for the financial support of this research. We also thank Dr. Katsuhiko Takagi for preparing crystals of 4 and 5 suitable for X-ray structure determination and for discussions.

Registry No. 1, 54283-35-1; 2, 73396-38-0; 3, 73396-39-1; 4, 73396-40-4; 5, 73465-13-1; 6, 2819-86-5; 8, 73396-41-5; 10, 73396-42-6; 11, 73396-43-7; 12, 15971-76-3.

Supplementary Material Available: Table I, positional and thermal parameters for 4; Table II, anisotropic thermal parameters for 4; Table III, bond lengths for 4; Table IV, bond angles for 4; Table V, positional and thermal parameters for 5; Tables VI, anisotropic thermal parameters for 5; Table VII, bond lengths for 5; Table VIII, bond angles for 5 (8 pages). Ordering information is given on any current masthead page.

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[19] The mass spectra of 4 and 5 are nearly identical. The base peak at *m/e* 124 corresponds to the tetramethylfuran moiety, for which plausible fragmentation routes are readily apparent. A minor peak is evident at this *m/e* value in the mass spectrum of 2 but not in that of 3.

Acid-Catalyzed Rearrangements of the Epoxides of Hexamethylbicyclo[3.2.0]hepta-2,5-dienone

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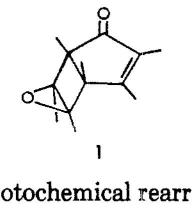
Epoxy enone 1 rearranges in trifluoroacetic acid (TFA) at 0 °C to hexamethyl-8-oxabicyclo[3.2.1]octa-3,6-dien-2-one (3). A mechanism involving initial protonation of the carbonyl oxygen of 1, cleavage of the C–C bond of the epoxide ring, and the intermediacy of a dicyclopropylcarbinyl-type carbocation intermediate is suggested and supported by deuterium labeling. Epoxy enone 2 rearranges in TFA at 0 °C to give products containing the TFA moiety in a form not easily hydrolyzed by base. The products have a structure with a plane of symmetry and are thought to be stereoisomers containing a 7-norbornenone skeleton and an ortho ester type of moiety (5). A mechanism involving intramolecular trapping of a carbocation by neighboring trifluoroacetate is suggested to explain the results. Pyrolysis of 3 (500 °C) gives pentamethylphenol.

Epoxy ketones rearrange in acid in a variety of ways.[1] Our interest in these rearrangements[2] prompted us to study the title compounds 1 and 2, whose synthesis and novel photochemical rearrangements were described in the preceding paper.[3] Isomer 1 afforded a new synthesis of the 8-oxabicyclo[3.2.1]octane ring system, whereas isomer 2 resulted in a novel type of product which included in its structure the trifluoroacetic acid (TFA) moiety used to bring about the rearrangement.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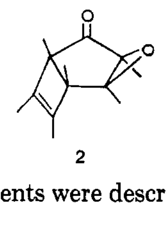
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Results and Discussion

Rearrangement of 1. Treatment of 1 with TFA at 0 °C for a few minutes caused its nearly quantitative rearrangement to an isomer. Longer reaction times gave no further rearrangement. The product was a colorless liquid with a $\nu_{C=O}$ at 1700 cm^{-1} and an NMR spectrum that showed two aliphatic methyl singlets and four vinyl me-

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[1] For leading references, see: House, H. "Modern Synthetic Methods", 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972; p 320.

[2] Hart, H.; Huang, I.; Lavrik, P., *J. Org. Chem.*, 1974, *39*, 999. Hart, H.; Huang, I., *Ibid.* 1974, *39*, 1005. Hart, H.; Shih, E.-M., *Ibid.* 1975, *40*, 1128.

[3] Hart, H.; Chen, S.-M.; Lee, S.; Ward, D. L.; Kung, W.-J., *J. Org. Chem.*, preceding paper in this issue.

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