phenyl-2,3-*cis,exo*-norbornanediol 3-*p*-toluenesulfonate.[19] Gas chromatographic analysis of the crude product showed the presence of mesityl oxide, diacetone alcohol, and a mixture of glycols, of long retention time, which was not investigated further. No peaks due to **14**, **16**, or **19** were detectable.

Registry No.—**2**, 35623-80-4; **3**, 35623-81-5; **4**, 35623-82-6; **5**, 35623-83-7; **6**, 35623-84-8; **7**, 35623-85-9; **8**, 35623-86-0; **9**, 35623-87-1; **10**, 35623-88-2; **11**, 35623-89-3; **12**, 35623-90-6; **17**, 35623-91-7; **20**, 35623-92-8; **22**, 35623-93-9; **24**, 35623-94-0; bismethanesulfonate of 3-*exo*-hydroxynorbornane-2-*exo*-methanol, 35623-95-1; 2-*exo*-methyl-2,3-*cis,endo*-norbornanediol cyclic carbonate, 35623-96-2.

Structural Constraints on Electrocyclic Reactions of Unsaturated Ketenes. Synthesis and Irradiation of 2,4,4,5-Tetramethylbicyclo[4.4.0]deca-1,5-dien-3-one

HAROLD HART* AND RICHARD J. BASTIANI

Department of Chemistry, Michigan State University, East Lansing, Michigan 48823

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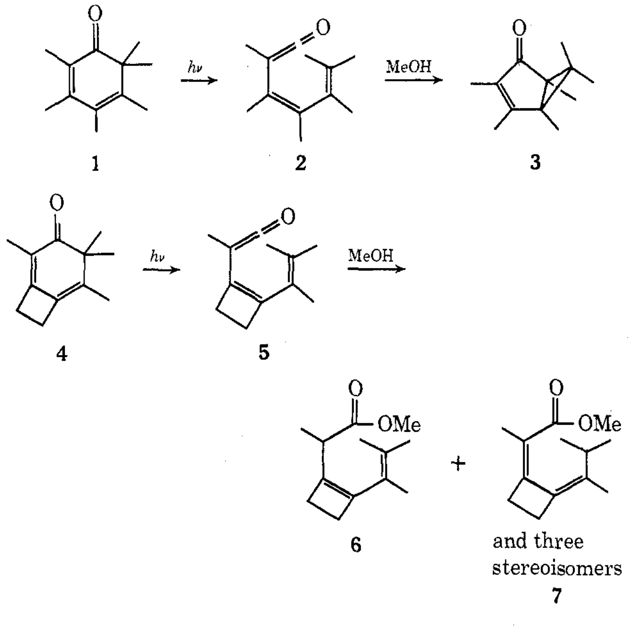
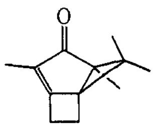
Oxidation of 5,6,7,8-tetramethyltetralin (**9**) with peroxytrifluoracetic acid–boron fluoride gave a mixture of three 2,4-cyclohexadienones (**10**, **11**, and **12**) and the 2,5-cyclohexadienone **13**, as a result of electrophilic attack at all possible ring positions. Irradiation of **13** at 2537 Å gave the expected lumiproducts **14** and **15**; similarly, irradiation of **11** and **12** at 3000 Å gave **14** and **15**, respectively. Irradiation of **10** at 3000 Å in methylene chloride or methanol gave the tetracyclic enone **26**; no methyl esters were formed. Thus the ketene **25** derived from **10** undergoes the electrocyclic reaction faster than it reacts with the nucleophile methanol; its behavior is analogous to that of **2**, not **5**.

The two ketenes formed on irradiation of the 2,4-cyclohexadienones **1** and **4**, respectively, react very differently in methanol. Ketene **2** does not react with the nucleophile to form methyl esters but cyclizes quantitatively to **3**.[1] Ketene **5**, on the other hand, reacts with methanol to produce a mixture of esters **6** and **7**, and does not cyclize to **8**, the highly strained analog of **3**.[2] In the present paper we explore the consequence of enlarging the four-membered ring in **5** to a six-membered ring on the behavior of the ketene toward methanol.





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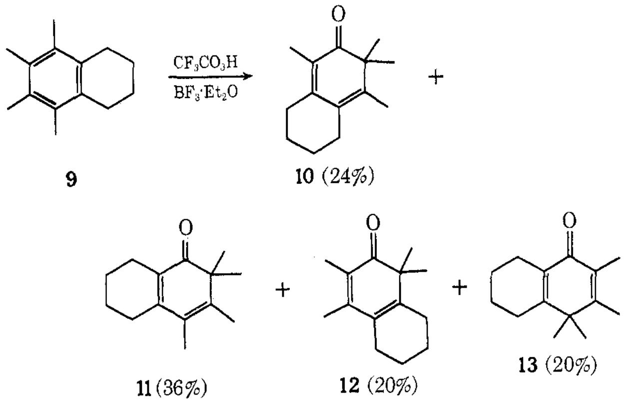
Oxidation of 5,6,7,8-Tetramethyltetralin.—The oxidation of highly substituted aromatic compounds with peroxytrifluoracetic acid–boron fluoride affords a useful general route to 2,4-cyclohexadienones.[3] It was anticipated that the oxidation of 5,6,7,8-tetramethyltetralin (**9**)[4] would give the desired cyclohexadienone **10**, together with other isomeric dienones. Oxidation of **9** with peroxytrifluoracetic acid–boron fluoride etherate at −10° gave an 84% yield of a mixture of isomeric dienones **10–13**. Unfortunately it was not possible to obtain **10** free of contamination with **11** and **12**. However it was possible to obtain **11**, **12**, and **13** pure (by column and gas-liquid chromatography), to identify each, and to identify the photoisomerization product(s) of each. Irradiation of a mixture of **10–12** then permitted us to establish the photochemical behavior of **10** and to isolate its photoproduct on irradiation in methanol.



The oxidation product with the longest vpc retention time was a crystalline solid, mp 87–89°, identified as **13**. Its uv and ir spectra were characteristic of a 2,5-

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

(2) R. J. Bastiani and H. Hart, *J. Org. Chem.*, **37**, 2830 (1972).

(3) H. Hart, *Accounts Chem. Res.*, **4**, 337 (1971).

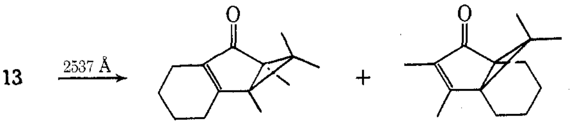
(4) B. V. Gregorovitch, C. S. Liang, D. M. Auguston, and S. F. MacDonald, *Can. J. Chem.*, **46**, 3291 (1968).

cyclohexadienone.[5] The nmr spectrum showed a *gem*-dimethyl singlet at τ 8.82, two homoallylically coupled methyl groups (τ 8.20, 8.07, J = 0.9 Hz), and two sets of four-proton multiplets at τ 7.57–7.88 and 8.25–8.55 for the methylene groups.

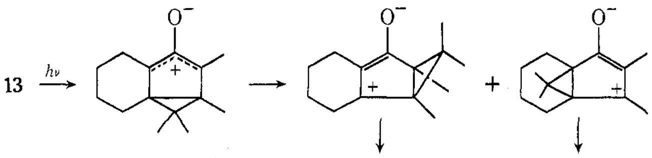
The remaining three dienones were fully conjugated, with λ_{max} at 329 nm characteristic of a hexaalkyl-2,4-cyclohexadienone.[5] The compound with the shortest retention time was identified as **12**. The nmr spectrum, with a singlet at τ 8.90 for the *gem*-dimethyl group, two broadened singlets at τ 8.18 and 8.03 for the allylic methyls, and two broad four-proton methylene multiplets at τ 8.12–8.53 and 7.60–7.95, was consistent with the structure but insufficient to distinguish **12** from **10** or **11**. However, when the compound was treated briefly at room temperature with CH_3OD–$NaOCH_3$, the peak for the allylic methyl at τ 8.03 disappeared. Since C-3 methyls in 2,4-cyclohexadienones exchange rapidly under these conditions whereas C-5 methyls do not,[1] the only plausible structure is **12**. Photoisomerization experiments (*vide infra*) support this assignment.

The remaining two conjugated dienones had vpc retention times which were so close that only the one with the slightly shorter retention time could be obtained pure. This turned out to have structure **11**, though its spectral properties (see Experimental Section) and the fact that it only exchanged two protons with CH_3OD–$NaOCH_3$ could not distinguish it from **10**. The structures were assigned by the following photochemical methods.

Irradiation of Dienones 11–13.—The cross-conjugated dienone **13**, on irradiation at 2537 Å in methylene chloride solution, gave complete conversion in a short time into two photoisomers, which were separated by vpc and identified as the expected[6] **14** and **15**. Both products had ir and uv spectra characteristic of cyclopentenones. The nmr spectrum of **14** had three-proton singlets at τ 9.03, 8.90, 8.87, and 8.80, whereas the product assigned structure **15** had two sharp singlets at τ 9.07 and 8.83, and homoallylically coupled quartets at τ 8.45 and 8.10 (J = 1.0 Hz) for the allylic methyl groups. Both compounds had complex multiplets in the region τ 7.55–8.7 for the eight methylene protons. The two photoproducts presumably arise through the common intermediate **13***, which undergoes a cyclopropylcarbinyl rearrangement in either of the two possible directions.

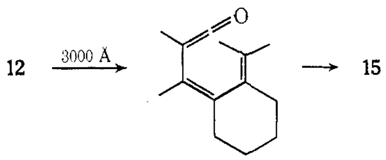


14 **15**



13* **14** **15**

Consistent with the assignment based on the base-catalyzed deuterium exchange experiment (*vide supra*), dienone **12** gave, on irradiation in methylene chloride at 3000 Å, a single photoproduct identical in all respects with **15**. It presumably arises from the cyclization of ketene **16**. In an analogous fashion, irradiation of the dienone with the shorter retention time (either structure **10** or **11**) gave a single photoproduct identical in all respects with **14**; it must therefore have structure **11**. By the process of elimination, the remaining conjugated dienone must be the desired **10**.



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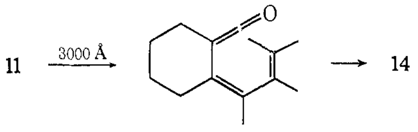
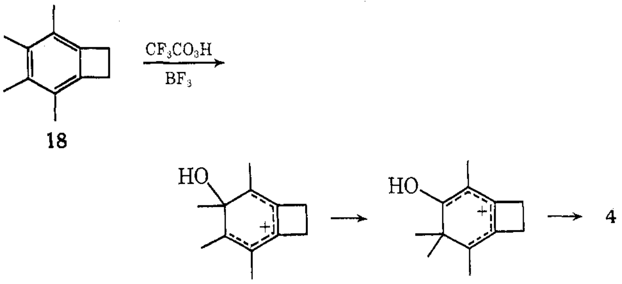
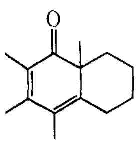


17

Comments on the Oxidation Mechanism.—Electrophilic oxidation of tetramethylbenzocyclobutene **18** involves only β-type benzenonium ion intermediates, the sole monomeric product being the dienone **4**.[2] In contrast, tetramethyltetralin appears to react with the electrophile at all three positions. The products can be rationalized according to Scheme I.



Ion **9a** leads directly to **11**; apparently methyl migration occurs mainly to the adjacent methyl, rather than methylene-bearing carbon atom, since products such as **20–22** which could arise through the latter path were not observed. It is possible that traces of these products escaped detection. The observed product **13** could conceivably arise from **11** through two additional methyl shifts; this route to **13** can be ruled out, since **11** was stable to the oxidizing conditions.



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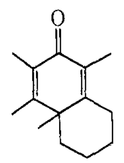

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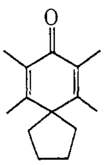

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Ion **9b** leads to products **10** and **12** in nearly equal amounts; apparently there is no regiospecificity to the methyl migration. Product **13** is thought to arise from ion **9c**, through a sequence of three Wagner-Meerwein rearrangements. This result is exactly analogous to

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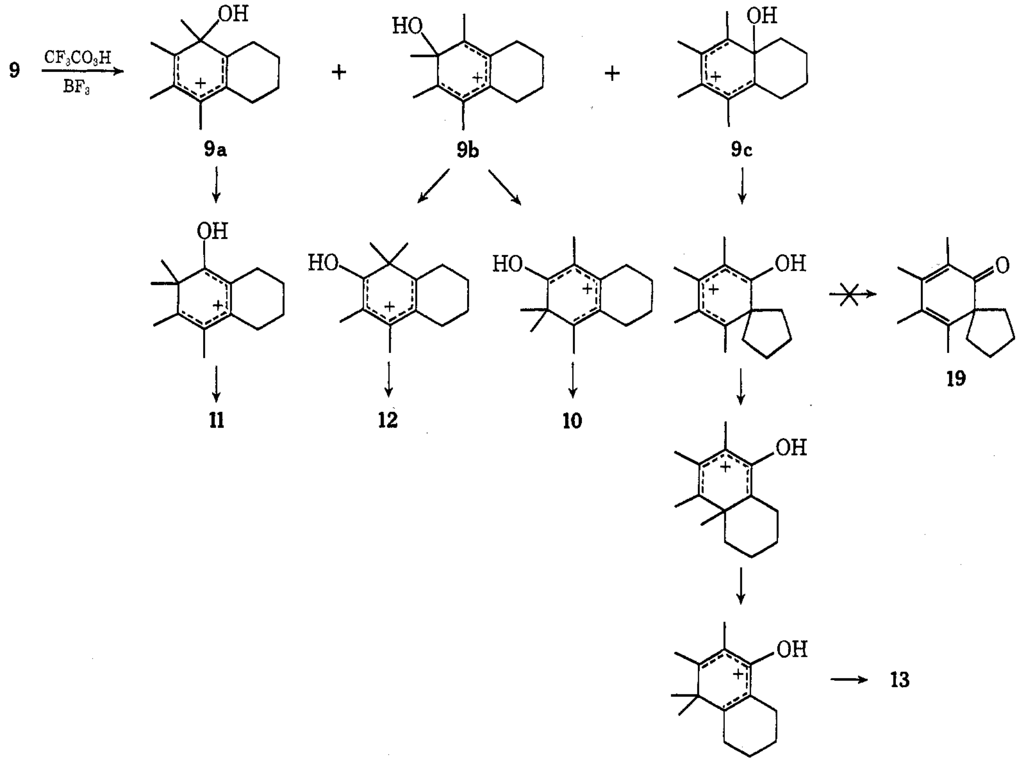
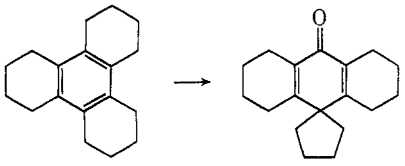
[5] A. J. Waring, *Advan. Alicycl. Chem.*, **1**, 184 (1966).

[6] H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **84**, 4527 (1962); H. E. Zimmerman and J. S. Swenton, *ibid.*, **89**, 906 (1967).

Scheme I

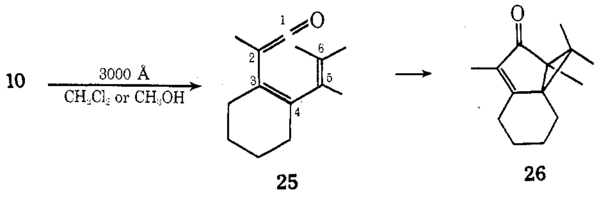


what was previously observed in the oxidation of dodecahydrotriphenylene (**23**) to **24**.[7] Spirodienones



such as **19** rearrange rapidly to 2,5-cyclohexadienones under the oxidation conditions.

Irradiation of Dienone 10.—A mixture of dienones **10**–**12** was irradiated with 3000-Å light in either methanol or methylene chloride. The same three photoproducts were observed in both solvents. Two of them were **14** and **15**, identical with the photoisomerization products of pure **11** and **12**, respectively. The third photoproduct was a colorless oil, isomeric with the starting material, to which we assign structure **26**. The ir and uv spectra were consistent with the



conjugated enone structure. The nmr methyl signals were particularly distinctive, with only one allylic methyl at τ 8.23 (br) and three sharp aliphatic singlets at τ 9.10, 9.05, and 8.92.

No esters were present in the photolysate of **10** in methanol. Thus the ketene **25** (the presumed photoproduct of **10**) reacts like **2**, not **5**, in preferring to cyclize rather than react with the nucleophile methanol. Apparently the six-membered ring in **25** does not prevent it from attaining the conformation necessary to permit overlap of the π-orbital lobes at C-4 with C-6 and C-1 with C-5 that is essential to the formation of **26**. As with **2**, the electrocyclic reaction of **25** proceeds more rapidly than attack by methanol.

Experimental Section[8]

Oxidation of 5,6,7,8-Tetramethyltetralin (9).—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, over 45 min, to a solution of 10.7 g (57 mmol) of 9[4] in 400 ml of methylene chloride which had previously been cooled to −10°. Boron fluoride etherate (25 ml of 48% $BF_3 \cdot Et_2O$) was added concurrently with the peracid. The temperature was maintained at −10° 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, and the residue was distilled to give a yellow oil, bp 108–114° (0.2 Torr), 9.80 g (84%). The oil was analyzed by vpc (10 ft × $^1/_4$ in., OV-25, 200°, 60 ml/min of He), which showed the presence of four major products with retention times of 20, 22.8, 24, and 28 min.

The product with a retention time of 28 min (20% of the mixture) is **3,4,5,5-tetramethylbicyclo[4.4.0]deca-1(6),3-dien-2-one** (**13**): mp 87–89°; ir 1655 (s), 1625 (vs), 1600 (sh), 1475 (s), 1460 (m), 1440 (m), 1400 (s), 1380 (m), 1365 (m), 1330 (s), 1280 (s), 1220 (s), 1180 (w), 1140 (w), 1100 (m), 1000 (w), 930 (w), 890 (w) cm^{-1}; uv λ_{max} 250 nm (ϵ 12,000), 275 sh, (4500); nmr τ 8.82 (6, s, *gem*-dimethyls), 8.25–8.55 (4, m, C-8 and C-9

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[7] H. Hart and D. C. Lankin, *J. Org. Chem.*, **33**, 4398 (1968).

[8] 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. Elemental analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.

methylenes), 8.20 (3, q, J = 0.9 Hz, C-3 methyl), 8.07 (3, q, J = 0.9 Hz, C-4 methyl), 7.57–7.88 (4, m, C-7 and C-10 methylenes); m/e 204.

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.08; H, 9.96.

A solution of **13** (50 mg) in 0.5 ml of 1 M sodium methoxide in methanol-d, after standing for 30 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 **13**-d: m/e 209; nmr τ 8.82 (6, s), 8.37 (4, m), 8.20 (3, s), 7.72 (2, m).

The product with a retention time of 20 min (20% of the mixture) is **2,2,4,5-tetramethylbicyclo[4.4.0]deca-1(6),4-dien-3-one (12)**: ir 1650 (br, vs), 1580 (s), 1470 (m), 1460 (s), 1440 (m), 1385 (s), 1360 (w), 1338 (s), 1270 (m), 1220 (m), 1060 (m), 1040 (s) cm^{-1}; uv λ_{max} 329 nm (ϵ 4600); nmr τ 8.90 (6, s, *gem*-dimethyls), 8.12–8.53 (4, m, C-8 and C-9 methylenes), 8.18 (3, br s, C-4 methyl), 8.03 (3, br s, C-5 methyl, 7.60-7.95 (4 m, C-7 and C-10 methylenes); m/e 204.

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 81.78; H, 10.12.

A sample of **12** was treated at room temperature with sodium methoxide–methanol-d as **13** above, but exchange was complete in 1.5 hr to give **12**-d_3: m/e 207; nmr τ 8.90 (6, s), 8.37 (4, m), 8.18 (3, sharp s), 7.47–7.93 (4, m).

The product with a retention time of 22.8 min (36% of the mixture) is **3,3,4,5-tetramethylbicyclo[4.4.0]deca-1(6),4-dien-2-one (11)**: ir 1645 (br, vs), 1580 (s), 1460 (br, s), 1400 (s), 1360 (m), 1320 (m), 1290 (m), 1280 (m), 1000 (m), 955 (m), 890 (m) cm^{-1}; uv λ_{max} 329 nm (ϵ 3000); nmr τ 8.89 (6, s, *gem*-dimethyls), 8.18 (6, s, C-4 and C-5 methyls), 8.07–8.53 (4, m, C-8 and C-9 methylenes), 7.48–7.88 (4, m, C-7 and C-10 methylenes); m/e 204.

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.42; H, 9.83.

A sample of **11**, treated with sodium methoxide–methanol-d as **12** above, gave **11**-d_2: m/e 206; nmr τ 8.90 (6, s), 8.18 (6, s), 8.37 (4, m), 7.47–7.93 (2, m).

A sample of **11**, subjected to the procedure used to oxidize **9**, was recovered unchanged; in particular, no **13** was formed.

The product with a retention time of 24 min (*ca.* 24% of the mixture) is **2,4,4,5-tetramethylbicyclo[4.4.0]deca-1,5-dien-3-one (10)**. This product could not be obtained pure, but was identified as a consequence of its method of synthesis and its photoisomerization to **26** (*vide infra*).

Irradiation of 13.—A solution of 100 mg of **13** in 9 ml of methylene chloride was irradiated at 2537 Å in a Rayonet reactor. The photolysis, which was monitored by vpc (5 ft × $^1/_4$ in., SE-30, 190°, 60 ml/min He) was complete in 1.25 hr. One of the products, isolated by vpc under the above conditions, is identified as **3,4,4,5-tetramethyltricyclo[4.4.0.0^{3,5}]deca-1(6)-en-2-one (14)**: ir 1690 (br, vs), 1640 (s), 1460 (br, s), 1430 (m), 1405–1390 (s), 1355 (w), 1310 (m), 1280 (m), 1260 (w), 1225 (m), 1190 (m), 1150 (m), 990 (m), 940 (s) cm^{-1}; uv λ_{max} 320 nm (ϵ 600), 275 (2400), 237 (7500); nmr τ 9.03, 8.90, 8.87, 8.80 (3 each, s), 7.55–8.55 (8, br m); m/e 204.

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.07; H, 9.66.

The second product was thermally labile under the above vpc conditions. It was isolated by column chromatography on alumina (J. T. Baker activity 1, 80–200 mesh) and elution with hexane, then purified by vpc (2 ft × $^1/_4$ in., 14% OV-25, 90°, 80 ml/min of He). It is assigned the structure **8,9,10,10-tetramethyltricyclo[4.3.1.0]deca-8-en-7-one (15)**: ir 1680 (vs), 1635 (s), 1450 (s), 1385 (s), 1345 (w), 1320 (m), 1260 (m), 1190 (w), 1170 (w), 1150 (w), 1130 (w), 1100 (m), 1055 (m), 970 (m), 895 (m) cm^{-1}; uv λ_{max} 320 nm (ϵ 500), 275 (2500), 239 (4800); nmr τ 9.07, 8.83 (3 each, s, cyclopropyl methyls), 8.45 (3, q, J = 1.0 Hz, C-8 methyl), 8.10 (3, q, J = 1.0 Hz, C-9 methyl), 7.7–8.7 (8, br m); m/e 204.

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.24; H, 9.89.

Irradiation of 12.—A solution of **12** (100 mg) in 9 ml of methylene chloride was irradiated at 3000 Å in a Rayonet reactor. The photolysis, which was monitored by uv, was complete in 28 hr. The sole photoproduct was **15**, identical (ir, nmr) with the same material isolated from the photolysis of **13**.

Irradiation of 11.—A solution of **11** (100 mg) in 9 ml of methylene chloride was irradiated at 3000 Å in a Rayonet reactor. The photolysis, monitored by vpc (2 ft × $^1/_4$ in., 15% OV-25, 145°, 120 ml/min of He), was complete in 24 hr. The sole photoproduct was **14**, identical (ir, nmr) with the same material isolated from the photolysis of **13**.

Irradiation of 10.—A solution containing 300 mg of **10**, **11**, and **12** in the approximate ratio 1:1:2 in 20 ml of methylene chloride was irradiated at 3000 Å in a Rayonet reactor. The reaction, monitored by ir, was complete in 24 hr. Analysis of the photolyzate by vpc (2 ft × $^1/_4$ in., 15% OV-25, 140°, 100 ml/min of He) showed the presence of three photoproducts. Two were identified (retention time, ir, nmr) as **14** and **15**. The third (*ca.* 25–30% of the mixture) was purified by vpc (above conditions) and identified as **2,2,3,5-tetramethyltricyclo[4.4.0.0^{1,3}]deca-5-en-4-one (26)**: ir 1690 (s), 1625 (m), 1600 (s), 1460 (m), 1430 (m), 1380 (m), 1340 (m), 1280 (m), 1255 (s), 1200 (m), 1080 (w), 965 (m), 890 (vs) cm^{-1}; uv λ_{max} 300 nm (ϵ 1850), 231 (6250); nmr τ 9.10, 9.05, 8.92 (3 each, s, aliphatic methyls), 8.23 (3, br s, allylic methyl), 7.47–7.90 (8, br m); m/e 204.

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.20; H, 9.90.

Repetition of the photolysis in methanol gave the same three products.

Registry No.—**10**, 36707-33-2; **11**, 36707-34-3; **12**, 36707-35-4; **13**, 36707-36-5; **14**, 36707-37-6; **15**, 36763-73-2; **26**, 36707-38-7.

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