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ON THE PHOTOISOMERIZATION OF BICYCLO[3.2.n]DIENONES

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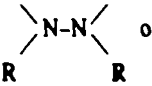
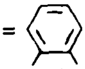
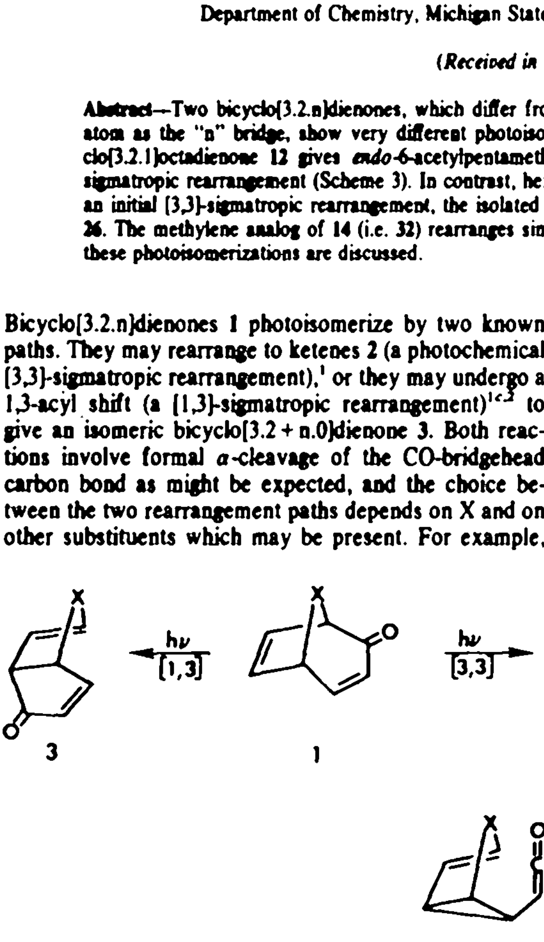
Abstract—Two bicyclo[3.2.n]dienones, which differ from one another only by the presence or absence of an O atom as the "n" bridge, show very different photoisomerization behavior. Irradiation of hexamethyl-8-oxabicyclo[3.2.1]octadienone **12** gives *endo*-6-acetylpentamethylbicyclo[3.1.0]hexenone **16**, probably via an initial [1,3] sigmatropic rearrangement (Scheme 3). In contrast, hexamethylbicyclo[3.2.0]heptadienone **14** photoisomerizes via an initial [3,3]-sigmatropic rearrangement, the isolated product being the relatively stable cyclopentadiene-ketene **26**. The methylene analog of **14** (i.e. **32**) rearranges similarly, giving allene **33** and alkyne **34**. The mechanisms of these photoisomerizations are discussed.

Bicyclo[3.2.n]dienones **1** photoisomerize by two known paths. They may rearrange to ketenes **2** (a photochemical [3,3]-sigmatropic rearrangement),[1] or they may undergo a 1,3-acyl shift (a [1,3]-sigmatropic rearrangement)[1c,2] to give an isomeric bicyclo[3.2 + n.0]dienone **3**. Both reactions involve formal α-cleavage of the CO-bridgehead carbon bond as might be expected, and the choice between the two rearrangement paths depends on X and on other substituents which may be present. For example, when X was a zero-atom bridge[1a] or when X = $-CH_2-$,  $\underset{R}{>}N{-}N\underset{R}{<}$ or $-CH{=}CH-$,[1b] the [3,3] path was followed, but when X =  both types of products were formed[1b,c] and in examples with a hydroxyl substituent on the bridgehead carbon α to the CO, only the [1,3] path was observed.[2] In the case of **4**, it has been proposed that the [3,3]-rearrangement occurs via the ^{1}S state and the [1,3]-rearrangement via the ^{3}T state and a diradical intermediate (Scheme 1).[3]



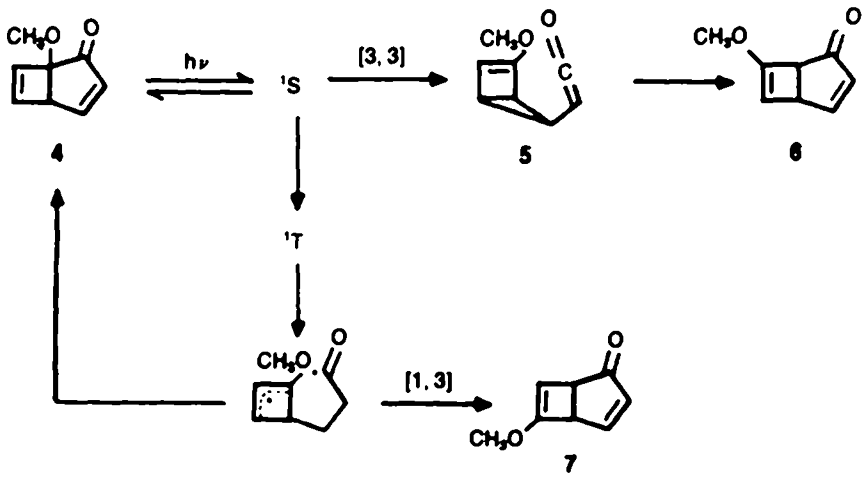
3

1

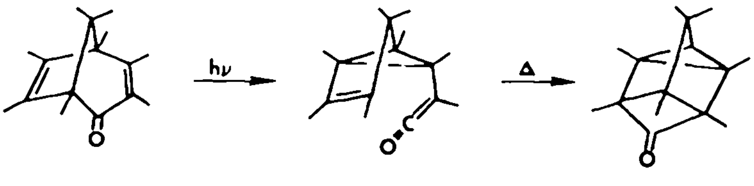
2

On several occasions the ketenes formed by the [3,3]-path have been observed spectroscopically[1a,b] and have been trapped by nucleophiles.[1b,c] In the absence of nucleophiles, the ketenes usually recyclize thermally. Since in ketene **5** the termini of the cyclobutene double bond are differentiated by the OMe substituent, recyclization gives either **4** or **6**.

In some instances, the ketene **2** may cyclize in quite a different way. For example, if X is a one-carbon bridge and the ketene is either highly substituted[4] or specially activated,[5] a thermal [2+2]-cycloaddition of the two C=C double bonds in **2** may occur to give a tetracyclic product. An example is the facile, high yield conversion of **8** to **10** via the ketene intermediate **9**.[4]

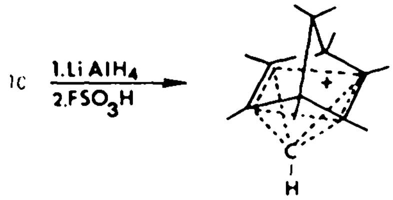


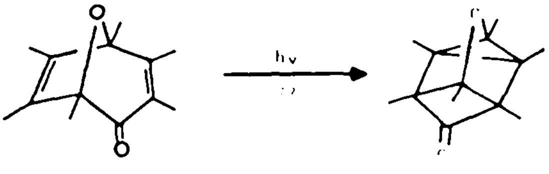
Scheme 1.



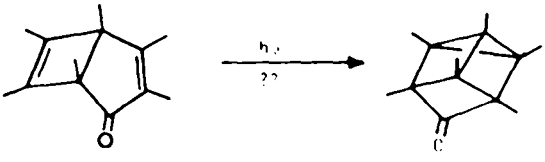
8 9 10

Tetracyclic ketone **10** was the precursor of the fascinating pyramidal carbocation **11**[6] and of several related carbocations which undergo a variety of novel rearrangements.[7] We were prompted to irradiate the highly substituted bicyclic dienones **12** and **14** with the hope that they would behave similarly to **8** and furnish **13** and **15** respectively. Although strained, the ring system in **15** is known.[8] Ketones **13** and **15**, in turn might give pyramidal carbocations analogous to **11** but with the gem-dimethyl-bearing carbon replaced by an O atom or a bond. In the event, the photochemistry of **12** and **14** did not follow the desired paths, but the results have intrinsic interest, and we describe them here.





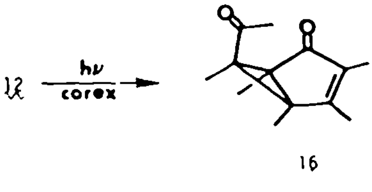
12 13



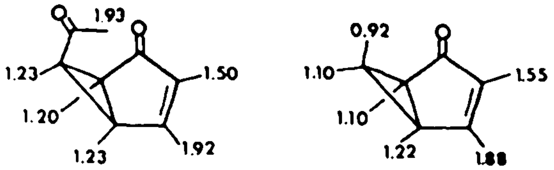
14 15

RESULTS AND DISCUSSION

Photoisomerization of oxabicyclodienone **12**. Irradiation of a 10 mM methanol solution of **12**[9] through Corex gave **16** as the major product, together with some pentamethylphenol. The lack of symmetry in the NMR spectrum immediately ruled out the desired structure **13**, as did the IR spectrum, which showed two CO frequencies (1710, 1690 cm^{-1}). Structure **16** was assigned in part by comparison of the IR, UV and NMR spectra with those of the known **17**[10] (which differ only by replacement of the acetyl with a Me group). The acetyl Me signal appears about 0.2 ppm upfield from its normal position, suggesting that the group has the *endo* configuration. This surmise is supported by the quantitative photochemical conversion of **16** to pentamethylphenol and ketene (Scheme 2). Only if the acetyl group in **16** is endo can the necessary H-abstraction occur.

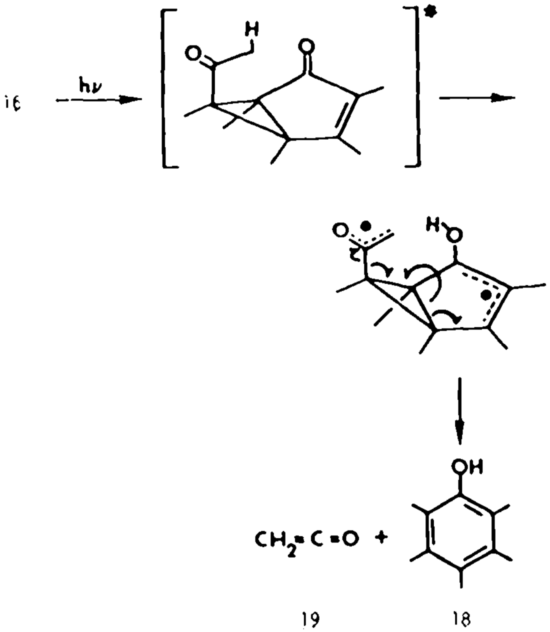


16



16 17

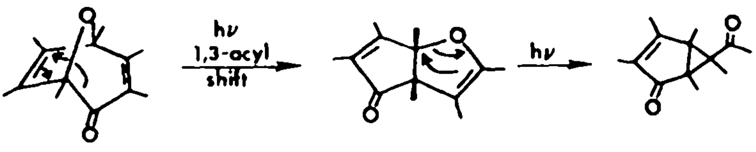
	16	17
IR(CCl$_4$)	1710, 1690, 1645 cm^{-1}	1690, 1640 cm^{-1}
UV	232 nm (ε 5970)	235 nm (ε 6270)
	272 (3780)	274 (3240)
	325 (340)	320 (605)



19 18

Scheme 2.

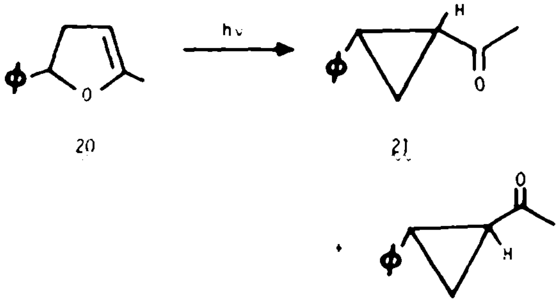
A likely mechanism by which **16** might be formed from **12** is shown in Scheme 3. A 1,3-acyl shift would give the dihydrofuran intermediate **A** which, since its chromo-



12 A 16

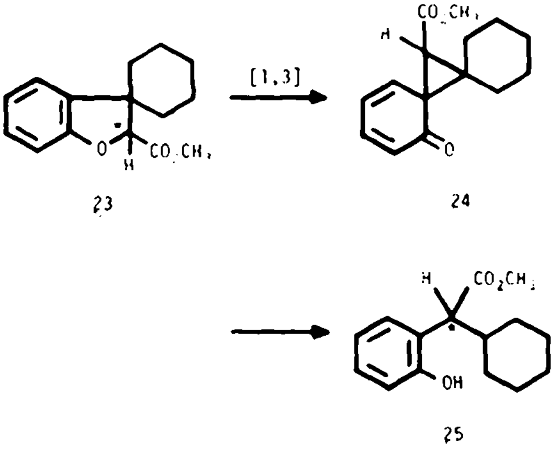
Scheme 3.

phore would be very similar to that of **12**, could absorb further light and undergo the "bond-switching" or [1,3]-rearrangement to **16**. Regarding the first step, we note that **12** has a C–O bond at the bridgehead carbon α to the CO and may be analogous to the bridgehead OH compounds which Sasaki[2] observed to only undergo the [1,3]-shift. As for the second step, there is ample precedent for the photoisomerization of dihydrofurans to cyclopropylcarbonyl compounds.[11] There is, however, a possible difficulty with Scheme 3 and it lies in the second step. We observed that only one of the two possible epimers of **16** was formed, with the acetyl group *endo*. Most dihydrofuran isomerizations reported in the literature[11] are non-stereospecific. For example, **20** gives a mixture of **21** and **22**.[11d] Diradical intermediates have been proposed to rationalize this non-stereospecificity. Also, the product acylcyclopropanes may undergo *cis–trans* photoisomerization.[12]



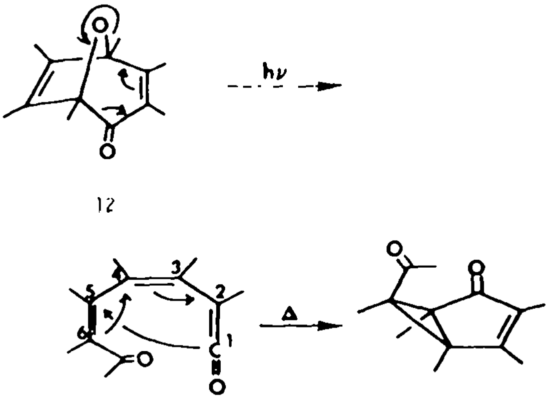
20 21 22

On the other hand, Schultz[13] has presented evidence that the rearrangement may sometimes be orbital symmetry controlled. He found that chiral dihydrofuran **23** rearranges to chiral **25**, presumably via the acylcyclopropane **24**. There are similar examples in a related photoisomerization.[14] Although the Schultz example is not fully analogous to the rearrangement of **A** to **16** because it deals with the stereochemistry at a different cyclopropane carbon in the product (β rather than α to the CO), it tends to leave Scheme 3 as a possible viable mechanism.



23 24 25

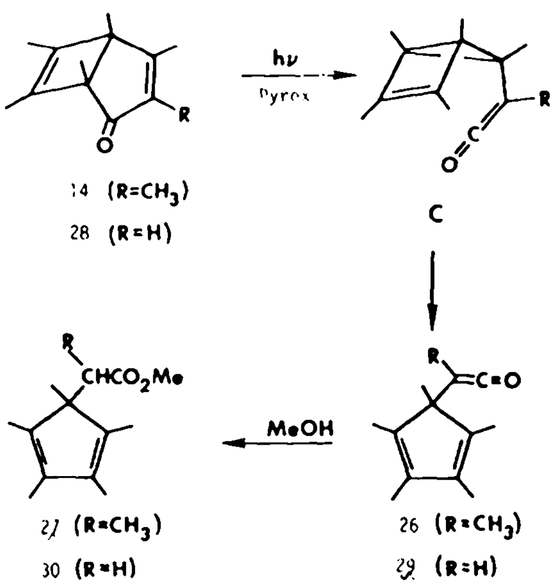
Because of the stereochemical question, we considered alternative mechanisms. One is shown in Scheme 4. Because of the initial bicyclic geometry in **12**, the 5,6-double bond in ketene **B** would necessarily have the *Z*-configuration. Cyclization of highly substituted diene-ketenes to bicyclo[3.1.0]hexenones has ample precedent.[10,15] Unfortunately this route also suffers from the problem that **B** might give either **16** or its *exo* epimer, and the reason why only one epimer would be formed is not clear. Furthermore, attempts to trap **B** with amine nucleophiles under conditions where such trapping is usually successful[15] have failed.[16] Consequently we tend to favor Scheme 3 despite the stereochemical problem.



12 B 16

Scheme 4.

Photoisomerization of bicyclodienone **14**. Dienone **14**[17] differs from **12** only in that the oxygen bridge is replaced by a zero-atom bridge. Nevertheless, the photochemistry takes an entirely different path. Irradiation of a 10 mM hexane solution of **14** through Pyrex gave an essentially quantitative yield of ketene **26** (Scheme 5). The product had a sharp, intense ketene CO band at 2120 cm^{-1}. Its NMR spectrum was somewhat simpler than might be expected; both aliphatic Me's accidentally had the same chemical shift, and appeared as a singlet at δ 1.00. The high field position of the Me attached to the ketene function is accounted for by a preferred conformation in which the Me is "over" and deshielded by the double bonds in the cyclopentadiene ring. The remainder of the spectrum consisted of quartets at δ 1.73 and 1.79 (J = 0.5 Hz) for the two sets of homoallylically coupled vinyl

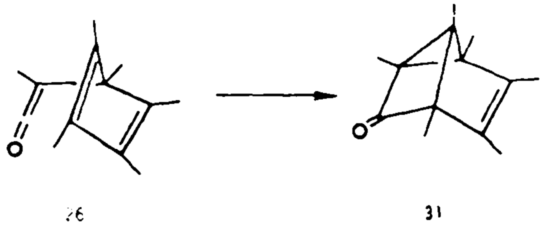


Scheme 5.

Me's. These chemical shifts rule out the alternative ketene structure C (R = Me) for the product.

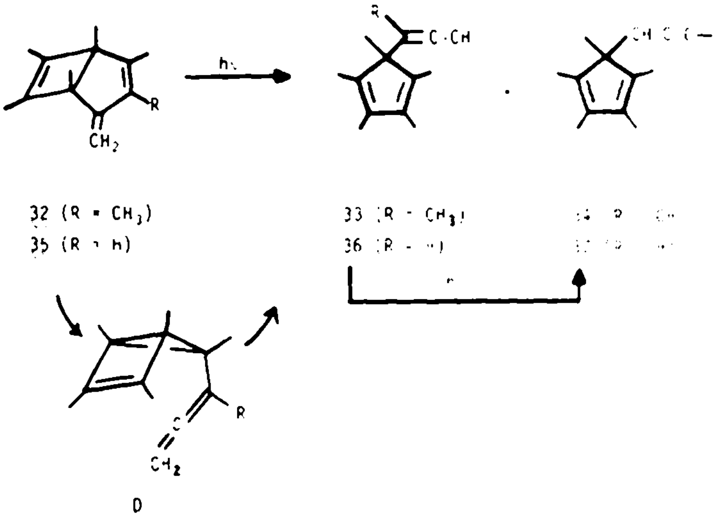
The structure of **26** was further established by treatment with methanol at room temperature, which gave methyl ester **27** in excellent yield. The same ester was obtained by irradiating **14** in methanol. The ester structure was clear from its spectral properties ($\nu_{C=O}$ 1730 cm^{-1}; ^{1}H NMR peaks at δ 0.92 (quaternary Me singlet), 0.65 and 2.43 (doublet and quartet, respectively, J = 7 Hz, for the MeCH$\langle$ moiety), 1.72 (four vinyl Me's) and 3.58 (OMe). Compound **28**,[18] lacking the C-3 Me substituent, photoisomerized in an entirely analogous manner to give **29**.

Ketene **26** is moderately stable, and can even withstand VPC at temperatures below 120°. The neat liquid, however, decomposes after several hours at 0°. Hexane or carbon tetrachloride solutions of **16** gradually show transformation to a new product with a $\nu_{C=O}$ at 1745 cm^{-1} and an NMR spectrum with singlets at δ 1.10, 1.17, 1.27 and 1.43 and two quartets centered at δ 1.63 (J = 0.5 Hz), all with equal intensity. We tentatively assign this product structure **31**, which could form from via [2 + 2]-cycloaddition to one of the two equivalent C=C double bonds.



The formation of **26** from **14** can be rationalized via the bicyclic ketene intermediate C (Scheme 5). The reaction is entirely analogous to the formation of **5** from **4** (*vide supra*). Ketene **5** rearranged so rapidly by a Cope [3,3]-sigmatropic process to **4** or **6** that it could only be observed at low temperatures and could not be trapped by methanol. With C, however, the Me substituents probably facilitate electrocyclic opening of the cyclobutene ring to give the less strained and relatively stable ketene **26**. Apparently this process is much more rapid than the reaction we originally sought, the cyclization of C to **15**.

Photoisomerization of the methylene analog of **14**. It seemed of some interest to photolyze the methylene analog of **14**, to determine whether or not analogous rearrangements would occur via $\pi\pi^*$ excitation. Irradiation of **32** in pentane at 254 nm gave the allene **33** and alkyne **34**. The cyclopentadiene-allene **33** is presumably the initial photoproduct formed via D (Scheme 6), analogous to the formation of **26** from **14** via C. The acetylenic cyclopentadiene **34** presumably arises from further photolysis of **33**, either via radical-pair dis-



Scheme 6.

sociation and recombination, or via an electrocyclic 8π electron process. The structures of **33** and **34** were assigned from their spectra, and received further support when it was observed that **35** photoisomerizes analogously to **36** and **37** (Scheme 6).

SUMMARY

Bicyclo[3.2.n]dienones photoisomerize by either a [3,3]- or a [1,3]-sigmatropic rearrangement. The particular path apparently depends on details of structure and substitution. Dienones **12** and **14**, which differ in structure only by the oxygen bridge, rearrange by entirely different paths. The observed products, **16** and **26** respectively, are formed by further rearrangement of initial photoproducts, which are believed to arise by [1,3] and [3,3] processes, respectively. It seems as if an oxygen function at Cl in these systems favors the [1,3] path. Triene **32**, the methylene analog of **14**, rearranges similarly.

EXPERIMENTAL

General procedures. All NMR spectra were measured at 60 MHz using Me_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 peak was shifted. Normalized slopes were obtained by dividing each slope by the slope of the least shifted signal. IR spectra, obtained on a Unicam SP-200 spectrometer, were calibrated against a polystyrene film. UV spectra were obtained with a Unicam SP-800 spectrometer. Mass spectra were obtained at 70 eV with a Hitachi–Perkin Elmer RMU-6 instrument. M.Ps are uncorrected. Vpc separations were performed on Varian Aerograph instruments and analyses were performed by Spang Microanalytical Laboratories, Eagle Harbor, Michigan.

Irradiations were carried out using a Hanovia 450 W lamp placed in a water-cooled jacket equipped with different filters, or a Rayonet RPR-100 reactor. The solution to be irradiated was placed in a quartz test tube and, after deoxygenation with a stream of Ar was sealed with a serum cap. The tube was taped to the immersion well or placed in the Rayonet reactor and the irradiation was monitored chromatographically or spectroscopically.

Irradiation of hexamethyl - 8 - oxabicyclo[3.2.1]*octa - 3,6 - dien - 2 - one* (**12**). A soln of **12**[9] (100 mg, 0.48 mmol) in 50 mL MeOH was irradiated through a Corex filter. The reaction was monitored by VPC (5 ft × 0.125 in. column, 3% SE-30 on Chromosorb W 60/80 mesh, 125°, 30 mL/min He). After 2 hr, analytical vpc showed the presence of 40% unchanged **12** (ret. time 6.5 min), 50% of **16** (ret. time 8.5 min) and 10% of **18** (ret. time 16 min). These products were separated by preparative vpc (5 ft × 0.25 in. column, 5% SE-30 on Chromosorb W, AW-DMCS 60/80 mesh, 130°, 60 mL/min He). The first product (ret. time 3.2 min) was recovered **12**. The second product (ret. time 4.0 min) was identified as 6-*endo*- **16**: IR (neat) 2960 (m), 2900 (w), 1710 (s), 1690 (s), 1645 (m), 1465 (w), 1450 (m), 1390 (m), 1360 (w), 1340 (w), 1255 (m), 1215 (m), 1110 (w), 1020 (w) cm^{-1}; UV (EtOH) λ_{max} 325 nm (ϵ 340), 272 (3780), 232 (5970); NMR ($CDCl_3$), see text; mass spectrum, *m/e* (relative intensity) 206 (25), 191 (2), 178 (3), 164 (85), 163 (15), 150 (10), 149 (100), 135 (10), 121 (15), 91 (15), 77 (15), 43 (65). (Found: C, 75.69; H, 8.71. Calc. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80%).

Treatment of **16** (30 mg) with 5 mL of MeOD containing 20 mg of NaOMe overnight at room temp, followed by dilution with water and extraction with ether gave, after the usual workup, a quantitative yield of labeled **16** whose NMR spectrum lacked the signals at δ 1.92 and 1.93.

The third product (ret. time 8 min) was identified as pentamethylphenol, m.p. 127.5–128° (lit.[19] 128°), with IR and NMR spectra identical with those of authentic material.

Irradiation of 12^* (C_6–CD_3). A soln of **12** (206 mg, 1 mmol) in 5 ml of MeOD containing 20 mg of NaOMe was stirred overnight at room temp. The solvent was removed *in vacuo* and the solid residue was treated with water (5 mL) and extracted with ether. Combined organic layers were washed with water, dried ($MgSO_4$) and evaporated to give 12^* whose NMR spectrum differed from that of **12** by lacking the signal at δ 1.92 due to the C_6–Me group; the peak at δ 1.63 (C_7–Me) sharpened to a singlet. Irradiation of 12^* using the same procedure described for **12** gave labeled 16^* whose NMR spectrum differed from that of **16** by lacking the quartet at δ 1.92; also, the peak at δ 1.50 sharpened to a singlet. The pentamethylphenol obtained from this reaction was labeled in the *m*-Me group, as shown by use of $Eu(fod)_3$, which split the singlet originally at δ 2.16 into three peaks with (from low to high field) relative areas 2 : 1 : 1.[20]

Irradiation of **16**. Irradiation of a 1% MeOH soln of **16** through Corex for several hr (as described for **12**), followed by evaporation of the solvent gave a residue which was essentially pure pentamethylphenol in quantitative yield. The other product was methyl acetate.

Irradiation of **14**. A soln of **14**[17] (190 mg, 1 mmol) in 100 mL hexane was irradiated through Pyrex. The reaction was followed by vpc (5 ft × 0.125 in. column, 5% SE-30 on Chromosorb G, 60/80 mesh, DMCS, 100°C). After 20 hr starting material had disappeared and a single product with a shorter retention time was present. Removal of the solvent under reduced pressure gave 188 mg of a colorless oil identified as **26**: IR (CCl_4) 2950 (m), 2120 (s), 1450 (m), 1385 (m), 1290 (w), 1185 (m), 1090 (w), 1060 (w), 910 (w) cm^{-1}; UV (hexane) λ_{max} 228 nm (ϵ 2500); NMR (CCl_4) see text; mass spectrum, *m/e* (relative intensity) 190 (28), 162 (26), 161 (13), 148 (42), 147 (100), 119 (20), 105 (15), 91 (18), 77 (10), 53 (10). (Found: C, 81.96; H, 9.51. Calc. for $C_{13}H_{18}O$: C, 82.06; H, 9.54%).

Reaction of **26** *with methanol.* A soln of **26** (200 mg) in 10 mL abs MeOH was stirred at room temp for 5 min, then evaporated to give 233 mg (100%) of a colorless liquid identified as **27**: IR (neat) 2980 (s), 1730 (s), 1460 (m), 1390 (w), 1360 (w), 1200 (w), 1180 (w), 1080 (w) cm^{-1}; UV (MeOH) λ_{max} 262 nm (ϵ 3410); NMR (CCl_4) δ 0.65 (*d*, 3 H, $J = 7$ Hz), 0.92 (s, 3 H), 1.72 (m, 12 H), 2.42 (q, 1 H, $J = 7$ Hz), 3.58 (s, 3 H); mass spectrum, *m/e* (relative intensity) 222 (50), 164 (18), 163 (100), 160 (10), 149 (20), 148 (28), 147 (20), 136 (34), 135 (100), 134 (85), 133 (40), 121 (24), 119 (62), 107 (20), 105 (26), 91 (22), 88 (18), 76 (18), 65 (10), 43 (40). (Found: C, 75.69; H, 9.99. Calc. for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97%).

Irradiation of **28**. A degassed soln of **28**[18] (352 mg, 2 mmol) in 15 mL abs MeOH was irradiated through Pyrex for 33 hr. Evaporation of the solvent and separation by tlc (silica gel, benzene) gave 72 mg (20%) of recovered **28** and 90 mg (32%) of **30** as a colorless oil: IR (neat) 2930, 1730, 1445, 1330, 1260, 1175 cm^{-1}; UV (MeOH) λ_{max} 245 nm (ϵ 4760); NMR (CCl_4) δ 0.92 (s, 3 H), 1.71 (br s, 12 H), 2.25 (s, 2 H), 3.38 (s, 3 H). (Found: C, 74.81; H, 9.61. Calc. for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68%).

When the irradiation of **28** (50 mg) was carried out in pentane (7 mL) for 18 hr and the solvent then evaporated *in vacuo* at room temp the residue showed a ketene band at 2120 cm^{-1} due to **29**; addition of MeOH and workup gave 85% recovered **28** and 5% of **30**. An identical photolysis but in MeOH gave 51% recovered **28** and 26% of **30**, the photoisomerization being faster in methanol than in pentane.

2 - *Methylenehexamethylbicyclo*[3.3.0]*hepta - 3,6 - diene* (**32**). To a soln of **14** (170 mg, 0.9 mmol) in 10 ml anhyd ether was added 2 mL 2 M MeLi in ether. The mixture was stirred for 2 hr, then quenched with water (5 mL) and 1 mL 6 NHCl. Ether extraction, washing successively with water, $NaHCO_3$ aq, water, and drying ($MgSO_4$) gave, on evaporation of the solvent, 162 mg (96%) of **32** as an oil which was purified by vpc (10% SE-30 on Chromosorb W, 5 ft × 0.25 in. column, 120°): IR (neat) 2950 (m), 1620 (s), 1445 (w), 1380 (w), 1080 (s), 1060 (s), 870 (s); UV (MeOH) λ_{max} 238 nm (ϵ 13, 790); NMR (CCl_4) δ 1.10 (s, 3 H), 1.15 (s, 3 H), 1.57 (m, 3 H), 1.73 (m, 3 H), 4.53 (br s, 1 H), 4.67 (br s, 1 H); mass spectrum, *m/e* (relative intensity) 188 (83), 174 (100), 158 (40), 134 (84), 119 (100), 105 (22), 91 (35), 77 (24). (Found: C, 89.36; H, 10.80. Calc. for $C_{14}H_{20}$: C, 89.29; H, 10.71%).

Irradiation of **32**. A degassed soln of **32** (715 mg, 3.8 mmol) in 50 mL pentane was irradiated in a quartz test tube in the Rayonet using 254 nm lamps for 30 hr. Evaporation of the solvent and removal from insoluble polymer gave 630 mg of an oil which was purified by vpc (10 ft × 0.625 in. column, 20% FFAP on Chromosorb W, 120°) to give in sequence 164 mg (49%) of **33**, 57 mg (17%) of **34** and 379 mg (53%) of recovered **32**. For **33**: colorless oil, IR (neat) 3000, 2940, 2900, 1960, 1660, 1600, 1460, 1378, 1090, 860 cm^{-1}; UV (MeOH) λ_{max} 264 nm (ϵ 4,475); NMR (CCl_4) δ 0.93 (s, 3 H), 1.03 (t, 3 H, J = 3.0 Hz), 1.30 (s, 6 H), 1.77 (s, 6 H), 4.70 (q, 2 H, J = 3.0 Hz); mass spectrum, *m/e* (relative intensity) 188 (82), 143 (100). (Found: C, 89.27; 10.79. Calc. for $C_{14}H_{20}$: C, 89.29; H, 10.71%). For **34**: colorless oil, IR (neat) 2990, 2950, 2880, 1660, 1620, 1450, 1388, 1070, 870 cm^{-1}; UV (MeOH) λ_{max} 252 nm (ϵ 4880); NMR (CCl_4) δ 0.90 (s, 3 H), 1.67 (t, 3 H, J = 2.2 Hz), 1.75 (s, 12 H), 2.03 (q, 2 H, J = 2.2 Hz); mass spectrum, *m/e* (relative intensity) 188 (6), 163 (15), 162 (56), 149 (55), 148 (16), 147 (100), 135 (11), 134 (22), 133 (50). (Found: C, 89.28; H, 10.72. Calc. for $C_{14}H_{20}$: C, 89.29; H, 10.71%).

2 - *Methylene* - 1,4,5,6,7 - *pentamethylbicyclo*[3.2.0]*hepta* - 3,6 - *diene* (**35**). This triene was prepared in 93% yield from **28** and MeLi using the same procedure and workup as for **32**; colorless oil; IR (neat) 2920, 1625, 1440, 1365, 1260, 860 cm^{-1}; UV (MeOH) λ_{max} 240 nm (ϵ 11,930); NMR (CCl_4) δ 1.04 (s, 3 H), 1.08 (s, 3 H), 1.53 (m, 6 H), 1.76 (br s, 3 H), 4.48 (br s, 1 H), 4.65 (br s, 1 H), 5.58 (br s, 1 H); mass spectrum, *m/e* (relative intensity) 174 (80), 159 (100), 144 (41), 120 (62), 105 (95). (Found: C, 89.51, H, 10.50. Calc. for $C_{13}H_{18}$: C, 89.59; H, 10.41%).

Irradiation of **35**. A degassed soln of **35** (1.56 g, 9.0 mmol) in 100 mL pentane was irradiated in the Rayonet at 254 nm for 30 h. Evaporation of the solvent and removal of the insoluble polymer gave 1.397 g of an oil which was subjected to vpc separation (10 ft × 0.625 in. column, 20% FFAP on Chromosorb W, 120°) to give in sequence 329 mg (21%) of recovered **35**, 376 mg (30%) of **36** and 297 mg (24%) of **37**. For **36**: colorless oil; IR (neat) 2980 (s), 2913 (s), 2890 (s), 1953 (s), 1660 (m), 1452 (w), 1385 (s), 1072 (m), 885 (s), 860 (s) cm^{-1}; UV (MeOH) λ_{max} 274 nm (ϵ 5120); NMR (CCl_4) δ 0.97 (s, 3 H), 1.73 (s, 6 H), 1.76 (s, 6 H), 4.3–4.85 (m, 3 H); mass spectrum, *m/e* (relative intensity) 174 (68), 159 (100), 144 (40), 135 (26), 129 (26), 120 (54), 119 (42), 105 (68), 91 (31), 77 (22), 41 (17), 39 (17). (Found: C, 89.59; H, 10.55. Calc. for $C_{13}H_{18}$: C, 89.59; H, 10.41%). For **37**: colorless oil; IR (neat) 3340 (s), 2980 (s), 2940 (s), 2880 (s), 2150 (s), 1660 (w), 1450 (w), 1390 (s), 1070 (m) cm^{-1}; UV (MeOH) λ_{max} 252 nm (ϵ 4350); NMR (CCl_4) δ 0.92 (s, 3 H) 1.60 (t, 1 H, J = 2.5 Hz), 1.75 (s, 12 H), 2.25 (d, 2 H, J = 2.5 Hz); mass spectrum, *m/e* (relative intensity) 174 (56), 159 (100), 144 (29), 135 (40), 120 (56), 119 (48), 117 (23), 105 (47), 93 (19), 91 (31), 77 (19), 41 (18), 39 (16). (Found: C, 89.61; H, 10.62. Calc. for $C_{13}H_{18}$: C, 89.59; H, 10.41%).

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