2, 1929 (1972). These workers stressed the importance of the valency angle defined by the C(3)–C(5)–C(6) bonds in cyclosteroids as an additional factor to be considered.

(22) (a) M. B. Hursthouse and S. Neidle, *J. Chem. Soc., Perkin Trans. 2,* 781 (1973); (b) F. H. Allen, O. Kennard, and J. Trotter, *Acta Crystallogr., Sect. B,* **29,** 1451 (1973); (c) W. J. Seifert, T. Debaerdemaeker, and U. Müller, *ibid.,* **31,** 537 (1975); (d) for a vinylcyclopropane, see S. F. Nelsen and J. C. Calabrese, *J. Am. Chem. Soc.,* **95,** 8385 (1973); (e) J. C. Gilbert, T. Luo, and R. E. Davis, *Tetrahedron Lett.,* 2545 (1975).

(23) (a) C. S. Foote, *Tetrahedron Lett.,* 579 (1963); (b) for a summary and references, see F. J. Weigert and J. D. Roberts, *J. Am. Chem. Soc.,* **89,** 5962 (1967).

(24) J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *J. Am. Chem. Soc.,* **92,** 7107 (1970).

(25) The unusually short C(6)–CH_3 distance, 1.49 Å, supports this contention.

(26) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron,* **5,** 166 (1959).

(27) P. G. Gassman, J. L. Marshall, and J. G. Macmillan, *J. Am. Chem. Soc.,* **95,** 6319 (1973). An alternative process involving protonation of the ketal followed by concerted loss of methanol and ring cleavage also is feasible. This mechanism appeared less likely in later stages, and we omit detailed discussion in the interest of brevity.

(28) W. von E. Doering, E. T. Fossel, and R. L. Kaye, *Tetrahedron,* **21,** 25 (1965).

(29) R. C. Cookson, *J. Chem. Soc.,* 282 (1954).

(30) H. K. Hall, Jr., *J. Am. Chem. Soc.,* **82,** 1209 (1960).

(31) W. G. Dauben, J. L. Chitwood, and K. V. Scherer, Jr., *J. Am. Chem. Soc.,* **90,** 1014 (1968); K. V. Scherer, Jr., *Tetrahedron Lett.,* 5685 (1966).

(32) C. S. Foote, *J. Am. Chem. Soc.,* **86,** 1853 (1964).

(33) M. O'Sullivan and A. C. Testa, *J. Am. Chem. Soc.,* **92,** 5842 (1970).

(34) J. C. Dalton and N. J. Turro, *J. Am. Chem. Soc.,* **93,** 3569 (1971).

(35) This estimate is based on the assumption of a "normal" fluorescence rate (5×10^5 s^{-1}) and a maximum Φ_f of 10^{-5}.[29,30]

(36) P. S. Engel and M. A. Schexnayder, *J. Am. Chem. Soc.,* **97,** 145 (1975); M. A. Schexnayder and P. S. Engel, *ibid.,* **97,** 4825 (1975).

(37) In addition to local programs for the IBM 370/158 computer, local modifications of the following programs were employed: Germain, Main, and Woolfson's MULTAN tangent formula program, Zalkin's FORDAP Fourier program, Busing, Martin and Levy's ORFLS least-squares function programs, and Johnson's ORTEP II thermal ellipsoid plotting program.

(38) (a) G. Germain and M. M. Woolfson, *Acta Crystallogr., Sect. B,* **24,** 91 (1968); (b) G. Germain, P. Main, and M. M. Woolfson, *ibid.,* **26,** 274 (1970).

(39) D. T. Cromer and J. T. Waber, *Acta Crystallogr.,* **18,** 104 (1965).

(40) (a) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962, pp 213–216; (b) Hydrogen scattering factors were obtained from ref 40a, pp 201–209.

(41) The analysis of variance was performed using program NANOVA obtained from Dr. I. Bernal; see J. S. Ricci, Jr., C. A. Eggers, and I. Bernal, *Inorg. Chim. Acta,* **6,** 97 (1972).

Photochemical Cyclization of 4-Methallyl-4-methylcyclopentenone. 220-MHz Nuclear Magnetic Resonance Spectra of Tricyclo[3.3.0.0^{2,7}]octanes

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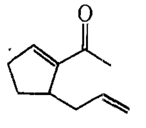
Received February 24, 1976

Preparation of 4-methallyl-4-methylcyclopentenone (**4**) from hydroxy ketone **5** is described. Irradiation of **4** leads to [2 + 2] cycloaddition and formation of tricyclic ketone **10** in high yield. NMR spectra (220 MHz) of ketones **10–13** are recorded and interpreted in a consistent fashion.

Irradiation of 1-acetyl-5-allylcyclopentene (**1**) leads to [2 + 2] cycloaddition between the two olefinic double bonds with formation of tricyclic ketone **2**.[1] Other representatives of this tricyclo[3.3.0.0^{2,7}]octane ring system have been long known through intramolecular photocycloaddition of vinylcyclohexenes.[2-5] However, the cyclization of **1** was the first example of formation of this skeleton from an allylcyclopentene, and this result suggests that similar cyclization might occur photochemically in suitable 4-allylcyclopentenones (**3**), as illustrated in eq 1. The position of the carbonyl group on the ring double bond is reversed on passing from **1** to **3**, but the available evidence indicates that this change should not influence the mode of cyclization.[3,5] As others have noted before,[5] regiospecificity in intramolecular photocycloaddition of 1,5-hexadienes to yield bicyclo[2.1.1]hexanes (and not bicyclo[2.2.0]hexanes) is quite general, and apparently it is insensitive to the nature and position of substituents on the reacting double bonds. The only aberrant example of which we are aware has been described as being "structurally inhibited" from reaction in the usual fashion.[6] In this report we describe the intramolecular cycloaddition of an allylcyclopentenone according to eq 1, along with the 220-MHz ^1H NMR spectra of several tricyclo[3.3.0.0^{2,7}]octanes that were determined in the course of securing the structure of the photoproduct.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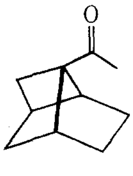
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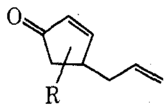

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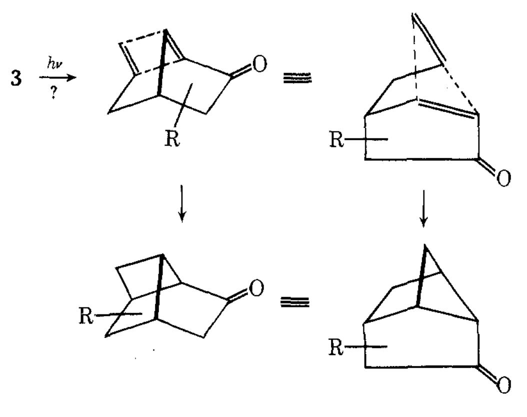
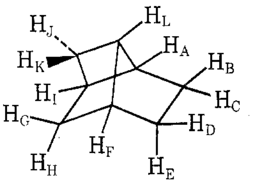
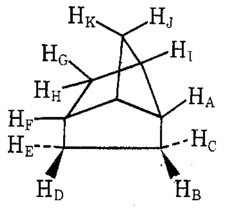


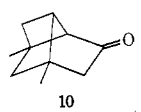
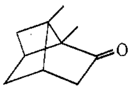
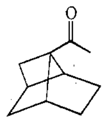
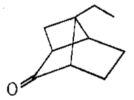
(1)

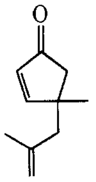
A convenient substrate for this work was 4-methallyl-4-methylcyclopent-2-enone (**4**), since it could be prepared from the related hydroxy ketone **5**, which was already on hand for another investigation.[7] The hydroxyl group of **5** was converted to the corresponding tosylate **6**, which yielded bromide **7** on reaction with sodium bromide in acetone. Treatment of **7** with bromine in ethylene glycol, according to the procedure of Garbisch,[8] then gave the dibromo ketal **8**. A double dehydrohalogenation took place when **8** was exposed to potassium *tert*-butoxide in dimethyl sulfoxide, furnishing the diene ketal **9**. Use of the primary bromide **7** rather than the corresponding tosylate **6** was desirable in this sequence in order to minimize competing ether formation during treatment with alkoxide;[9] for the same reason we employed *tert*-butoxide as base rather than methoxide, which was originally suggested.[8] In the event

Table I. NMR Spectra of Tricyclo[3.3.0.0^{2,7}]octanes 10–13





	 10 (59463-13-7)	 11 (39196-52-6)	 12 (52358-84-6)	 13 (52358-99-3)
H$_A$	2.21 dd J_{AL} ~2, J_{AH} ~0.5		2.25–2.35 m	2.46 m $W_{1/2}$ = 8
H$_D$	2.05 dd J_{DE} = 16.5, J_{DG} = 1.5	2.15 ddd J_{DE} = 17, J_{DF} = J_{DG} = 2		
H$_E$	1.96 d J_{ED} = 16.5	2.04 d J_{ED} = 17		
H$_F$		2.28 br s $W_{1/2} \geq 6$	2.25–2.35 m	2.25 br s $W_{1/2}$ = 7
H$_G$	1.19 dd J_{GH} = 11, J_{GD} = 1.5	1.24 ddd J_{GH} = 11, J_{GD} = J_{GF} = 2	1.26 ddd J_{GH} = 10, J_{GD} = J_{GF} = 2	
H$_H$	1.46 dd J_{HG} = 11, J_{HA} = 0.5	1.90 dd J_{HG} = 11, J_{HI} = 7		
H$_I$		2.33 m $W_{1/2}$ ~14	2.25–2.35 m	2.73 dd J_{IA} = J_{IJ} = 3
H$_J$	1.79 $W_{1/2}$ ~8	2.05 m $W_{1/2} \leq 14$	1.93 ddd J_{JK} = 7, J_{JF} = J_{JI} = 3	
H$_K$	1.52 d J_{KJ} = 7	1.41 d J_{KJ} = 7	1.58 d J_{KJ} = 7	1.67 d J_{KJ} = 8
H$_L$	2.31 dd J_{LA} = 2, J_{LJ} = 1.5			
Me	1.28 s 1.22 s	1.05 s 1.00 s	2.02 s	0.93 t J = 7.5



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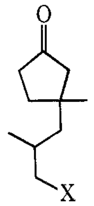
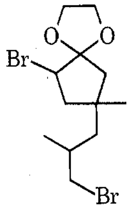


5, X = OH
6, X = OTs
7, X = Br



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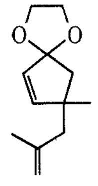

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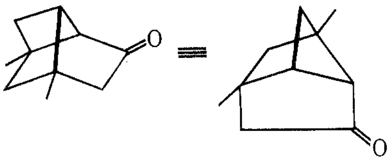

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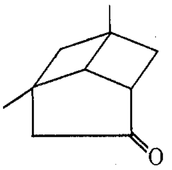
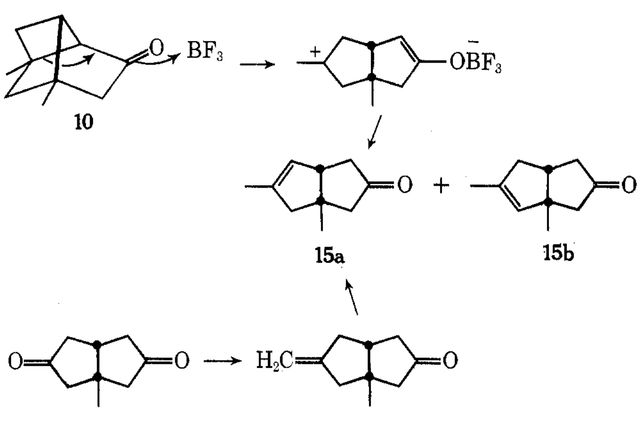


14

dehydrohalogenation of 8 was clean, and no *tert*-butyl ether was found. Brief treatment of ketal 9 with 3% aqueous sulfuric acid then gave the desired cyclopentenone **4**.

Irradiation of this ketone in benzene solution (~0.0067 M, λ >3400 Å) led to rapid isomerization to a single photoproduct in 87% yield. The assignment of structure **10** to this product rests on the NMR data in Table I and on chemical evidence discussed below. In Table I are presented the interpretable portions of spectra of **10** and three tricyclo[3.3.0.0^{2,7}]octane derivatives of known structure.[10] For **12** (≡ **2**) and **13** only partial analyses are possible, but **10** and **11** give 220-MHz spectra which can be completely interpreted. The recorded assignments are internally consistent and also agree well with earlier data[11] for bicyclo[2.2.1]heptanes and bicyclo[2.1.1]hexanes. Both of these simpler rigid ring systems are incorporated in the tricyclo[3.3.0.0^{2,7}]octane skeleton. The alternative mode of photocyclization of **4** would lead to structure **14**, a tricyclo[4.1.1.0^{3,7}]octan-4-one that incorporates a bicyclo[2.2.0]hexane in its skeleton. No members of the tricyclic series are available for comparison, but it is well known that representative bicyclo[2.2.0]hexanes have NMR spectra quite different from those of bicyclo[2.1.1]hexanes.[12] The data in Table I therefore strongly support **10** as the correct structure for the photoproduct.

Treatment of the photoproduct with boron trifluoride in ether led to rupture of the cyclobutane ring and generation of a mixture of the bicyclo[3.3.0]octenones **15a,b.** An authentic sample of these olefins was prepared starting with the readily



10

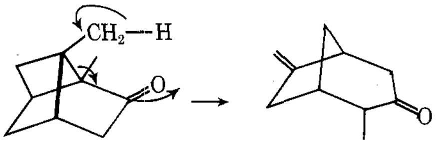
15a

15b

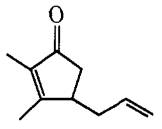
16

17

available diketone **16**.[13] A Wittig reaction yielded methylene ketone **17**, which was fully characterized, and which on exposure to the acid conditions used with **10** gave the bicyclooctenones **15a,b**. The path depicted for rearrangement of **10** to **15a,b** is straightforward, but such a rearrangement starting with **14** is unlikely; thus, this transformation provides further evidence favoring structure **10**. The ring opening of **10** may be contrasted with the cleavage which occurs on prolonged exposure of carvonecamphor (**11**) to basic alumina. In the latter case, presumably because of the different location of the methyl substituents, it is the alternative cyclobutane bond that breaks with formation of the bicyclo[3.2.1]octanone **18**.[3]



11 **18**



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Pyrolysis of carvonecamphor (**11**) results in cleavage of two cyclobutane bonds and formation of the allylcyclopentenone **19**.[3] For this reason we anticipated that pyrolysis of **10** would furnish starting dienone **4**. This proved correct; in the event **4** was accompanied by the mixture of bicyclooctenones **15a,b**, which possibly arises from thermal cleavage of a single cyclobutane bond of **10** and subsequent hydrogen transfer.

These results then provide a new example of regiospecificity in the intramolecular photocyclization of 1,5-hexadienes as well as a route to tricyclo[3.3.0.0^{2,7}]octan-3-ones alternative to the irradiation of vinylcyclohexenes.

Experimental Section

Materials and Equipment. In general these were as previously described.[12] VPC columns used in the present work were A, 25% DEGS, 25 ft × 0.375 in.; B, 10% Carbowax 20M, 5 ft × 0.25 in.; C, 25% DEGS, 15 ft × 0.25 in.; D, 25% DEGS, 25 ft × 0.25 in. All were prepared using 40/60 Chromosorb W and aluminum tubing.

3-Methyl-3-(3-bromo-2-methylpropyl)cyclopentanone (7). The ketol 5[7] (6.107 g, 35.9 mmol) was treated with *p*-toluenesulfonyl chloride (10.25 g, 53.8 mmol) in pyridine (75 ml) at 0 °C overnight. Standard workup with ether yielded the tosylate as an oil (9.654 g, 83%): ir 3050 (w), 2945 (s), 2860 (m), 1745 (s), 1595 (m), 1462 (m), 1402 (m), 1370 (s), 1185 (s), 1175 (s), 1098 (m), 945 (s), 660 cm^{-1} (m). A mixture of this crude tosylate (9.654 g, 29.8 mmol) and lithium bromide (5.16 g, 59.6 mmol) was heated to reflux in anhydrous acetone (215 ml) for 24 h with protection from atmospheric moisture. The reaction mixture was cooled and some of the acetone was removed in vacuo; water (200 ml) was added and the mixture was extracted twice with ether. The combined ethereal extracts were washed with sodium bisulfite, water, and brine and were dried over $MgSO_4$. Distillation afforded the bromo ketone (6.120 g, 89%, mixture of diastereomers): bp 95–100 °C (0.75 mm); ir 2950 (s), 2925 (m), 2880 (m), 1747 (s), 1458 (m), 1405 (m), 1380 (m), 1227 (m), 1155 cm^{-1} (m); NMR (220 MHz) δ 3.29 (m, 2 H), 2.23–1.60 (m, 8 H), 1.33 (m, 1 H), 1.11 and 1.08 (d, J = 6 Hz, 3 H), 1.08 (s, 3 H); mass spectrum *m/e* 232.0461 (M^+, calcd for $C_{10}H_{17}BrO$, 232.0462).

4-Methyl-4-(2-methylprop-2-enyl)cyclopentenone (4). The bromo ketone 7 (6.120 g, 26.4 mmol) was brominated in ethylene glycol–tetrahydrofuran (50:2 ml) at 40 °C according to the procedure of Garbisch.[8] The crude dibromo ketal (9.165 g) was taken up in dimethyl sulfoxide (125 ml), and potassium *tert*-butoxide (18 g) was added with external cooling. The mixture was heated at 80 °C for 3.5 h under a nitrogen atmosphere. After cooling and addition of water, the reaction mixture was extracted thrice with pentane. The combined pentane extracts were washed with water and brine and dried over $MgSO_4$. After solvent removal, deketalization was effected with 3% H_2SO_4.[8] Bulb-to-bulb distillation afforded 1.89 g, bp 130–140 °C (8 mm). VPC analysis on column A indicated a multicomponent mixture. The major peak (~35%) was collected and identified as **4**: ir 3060 (w), 2950 (m), 2910 (m), 2855 (w), 1718 (s), 1640 (w), 1585 (w), 1450 (m), 1410 (m), 1370 (m), 1340)w), 1188 (m), 895 cm^{-1} (s); NMR (220 MHz) δ 7.44 (d, J = 6 Hz, 1 H), 6.02 (d, J = 6 Hz, 1 H), 4.96 (br t, J = 0.5 Hz, 1 H), 4.78 (br s, 1 H), 2.34 (d, J = 18 Hz, 1 H), 2.22 (d, J = 0.5 Hz, 2 H), 2.00 (d, J = 18 Hz, 1 H), 1.76 (d, J = 0.5 Hz, 3 H), 1.22 (s, 3 H); mass spectrum *m/e* 150.1052 (M^+, calcd for $C_{10}H_{14}O$, 150.1044).

5,7-Dimethyltricyclo[3.3.0.0^{2,7}]octan-3-one (10). A benzene solution (70 ml) of dienone 4 (98.5 mg) was irradiated through an uranium glass filter as previously described.[12] The photolysis was terminated when ir spectroscopy indicated no remaining starting material. VPC analysis of the residue remaining after solvent removal indicated one major component. Bulb-to-bulb distillation gave **10** in 87% yield: ir 2950 (s), 2910 (m), 2860 (s), 1742 (s), 1450 (m), 1405 (w), 1375 (m), 1318 (m), 1230 (w), 1185 (w), 1157 (w), 1130 (m), 1090 (w), 1040 (w), 1015 cm^{-1} (w); for NMR see Table I; mass spectrum *m/e* 150.1043 (M^+, calcd for $C_{10}H_{14}O$, 150.1044).

1-Methyl-7-methylenebicyclo[3.3.0]octan-3-one (17). Dione 16[13] (912 mg, 6 mmol) was treated with ethylene glycol (0.34 ml, 6 mmol) and *p*-toluenesulfonic acid (10 mg) in refluxing benzene for 1.5 h with separation of water. The resulting solution was washed with 5% aqueous $NaHCO_3$, then water and dried. The solvent was removed in vacuo to give a yellow oil (988 mg, 84%). Ir and NMR of the crude oil confirmed that ketalization had occurred: ir 1150–1050 cm^{-1} (4 bands, br); NMR (60 MHz) δ 3.80 ($-OCH_2CH_2O-$). VPC on column B revealed the presence of unreacted dione, some diketal, and the desired monoketal (>50%). A solution of the crude ketal mixture (0.59 g, ~3 mequiv of carbonyl functionality) in dimethyl sulfoxide (0.5 ml, freshly distilled from CaH_2) was added to a solution of methylenetriphenylphosphorane reagent (9 mmol, freshly prepared[14] from 0.45 g of 50% NaH dispersion in oil and 3.24 g of $(C_6H_5)_3PCH_3Br$ in 13.5 ml of dry Me_2SO). The mixture was stirred overnight at room temperature, under nitrogen atmosphere. The resulting mixture was poured over ice (ca. 20 ml), and the water layer was saturated with NaCl and extracted with pentane. The combined pentane layer was dried and the solvent removed in vacuo to give a yellowish oil (0.514 g, 88%). NMR of the crude product confirmed the formation of the desired product **17**: (60 MHz) δ 3.80 ($-OCH_2CH_2O-$), 4.74 ($=CH_2$). This crude oil (330 mg, 1.7 mmol) was deketalized using 3.5 ml of 5% HCl for 1 h at room temperature, and the reaction mixture was worked up in the usual fashion to give a yellowish oil (140 mg, 55%). The major component of the mixture was isolated by VPC on column C and identified as enone **17**: ir 3065 (w), 2950 (m), 2920 (w), 2860 (w), 2825 (w), 1745 (s), 1650 (w), 1455 (w), 1432 (w), 1405 (m), 1378 (w), 1265 (w), 1245 (w), 1167 (w), 1130 (w), 880 cm^{-1} (m); NMR (60 MHz) δ 1.18 (s, 3 H), 1.88–2.97 (m, 9 H), 4.83 (m, 2 H); mass spectrum *m/e* 150.1047 (M^+, calcd for $C_{10}H_{14}O$, 150.1044).

1,7-Dimethylbicyclo[3.3.0]oct-6- (and 7-) en-3-one (15a,b). A. From 17. A solution of ketone 17 (10 mg) in CH_2Cl_2 (2.5 ml) was treated with boron trifluoride etherate (22 μl of a 1:1 solution in CH_2Cl_2) at 0 °C for 1 h. The mixture was washed with 5% aqueous $NaHCO_3$ and dried over $MgSO_4$. Removal of solvent and VPC on column D gave one peak (>90%). This material was isolated and identified as a mixture of **15a,b** by the characterization data given below.

B. From 10. The procedure described in A above was applied to **10** (20 mg) and yielded >90% of the same mixture of **15a,b**, having ir and NMR spectra and retention time virtually identical with those of the authentic material.

C. From the Ketal of 17. For preparative purposes it was convenient to prepare **15a,b** from the crude ketal of **17** described above. This mixture of olefins was not separable under any conditions tried. In all cases material which was an ~65:35 mixture with the following properties was obtained: ir 3020 (w), 2945 (m), 2905 (m), 2850 (m), 2825 (w), 1740 (s), 1650 (w), 1442 (m), 1400 (m), 1375 (w), 1323 (w), 1245 (m), 1160 (m), 860 cm^{-1} (s); NMR (60 MHz) δ 1.20 and 1.25 (both s, total 3 H, 1.20 major), 1.68 (br s, 3 H), 1.93–2.93 (m, 7 H), 5.13 (m, 1 H).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.07; H, 9.38.

Cyclopentenone 4 from Pyrolysis of 10. Ketone **10** (20 mg, 0.13 mmol) was placed in a glass tube, and the tube sealed under vacuum and held in a Wood's metal bath at 280 °C for 15 min. VPC of the resulting mixture on column D revealed several products and starting material (50%). Two of these were identified as **15a,b** and **4** by ir and NMR spectral comparisons with authentic materials.

Acknowledgments. We thank Mrs. Vivian S. Montalban for technical assistance, Mr. S. T. Bella for the microanalysis, and The Rockefeller University Mass Spectrometry Laboratory, supported by NIH Grant RR-00862, for mass spectra. The 220-MHz NMR spectra were obtained on an instrument at The Rockefeller University and operated by a consortium supported in part by NSF Grant BMS74-12247. This research was supported by NSF Grant MPS74-21436.

Registry No.—**4,** 59463-14-8; **5,** 59463-15-9; **6,** 59473-88-0; **7** isomer a, 59463-16-0; **7** isomer b, 59463-17-1; **15a,** 59463-18-2; **15b,** 59463-19-3; **16,** 21170-08-1; **16** ethylene acetal, 59463-20-6; **17,** 59463-21-7.

References and Notes

(1) R. A. Cormier and W. C. Agosta, *J. Am. Chem. Soc.,* **96,** 1867 (1974).
(2) G. Ciamician and P. Silber, *Ber.,* **41,** 1928 (1908); G. L. Hodgson, D. F. MacSweeney, and T. Money, *J. Chem. Soc., Chem. Commun.,* 236 (1973).
(3(G. Büchi and I. M. Goldman, *J. Am. Chem. Soc.,* **79,** 4741 (1957).
(4) J. Meinwald and R. A. Schneider, *J. Am. Chem. Soc.,* **87,** 5218 (1965).
(5) W. F. Erman and T. W. Gibson, *Tetrahedron,* **25,** 2493 (1969); J. J. Bloomfield and D. C. Owsley, *Tetrahedron Lett.,* 1795 (1973); (c) J. R. Scheffer and R. A. Wostradowski, *J. Org. Chem.,* **37,** 4317 (1972); Y. Tamura, H. Ishibushi, M. Hirai, Y. Kita, and M. Ikeda, *ibid.,* **40,** 2702 (1975); W. L. Dilling, *Chem. Rev.,* **66,** 373 (1966).
(6) H. Yoshioka, T. J. Mabry, and A. Higo, *J. Am. Chem. Soc.,* **92,** 923 (1970).
(7) Ketol **5** was prepared by conjugate addition of the lithium organocuprate from 1-bromo-2-methyl-3-(1-ethoxyethoxy)propane to 3-methyl-2-cyclopentenone, followed by hydrolysis. The procedure was based on that of P. E. Eaton, G. F. Cooper, R. C. Johnson, and R. H. Mueller, *J. Org. Chem.,* **37,** 1947 (1972). Full details will be given in a future publication.
(8) E. W. Garbisch, Jr., *J. Org. Chem.,* **30,** 2109 (1965).
(9) For studies of differences between bromides and tosylates in competitive elimination–substitution reactions, see P. Veeravagu, R. T. Arnold, and E. W. Eigenmann, *J. Am. Chem. Soc.,* **86,** 3072 (1964), and N. F. Wood and F. C. Chang, *J. Org. Chem.,* **30,** 2054 (1965).
(10) For **11** (carvonecamphor) see ref 3, 4; we thank Professor Jerrold Meinwald, Cornell University, for a generous gift of **11.** For **12** and **13** see ref 1.
(11) For references and discussion see (a) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2d ed, Pergamon Press, Oxford, 1969; (b) J. L. Marshall and S. R. Walter, *J. Am. Chem. Soc.,* **96,** 6358 (1974).
(12) References for spectra of both types of bicyclohexanes are given by R. A. Cormier, W. L. Schreiber, and W. C. Agosta, *J. Am. Chem. Soc.,* **95,** 4873 (1973).
(13) U. Weiss and J. M. Edwards, *Tetrahedron Lett.,* 4885 (1968). See also P. Yates, E. S. Hand, and G. B. French, *J. Am. Chem. Soc.,* **82,** 6347 (1960), and references cited therein.
(14) R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.,* **28,** 1128 (1963).

Photochemistry of 3-Cyano-4,4-dimethyl-2,5-cyclohexadienone. Evidence for Selectivity during the Photorearrangement of Unsymmetric Cyclohexadienones[1]

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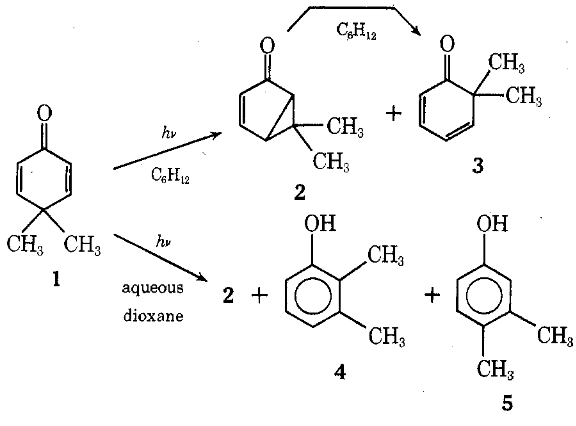
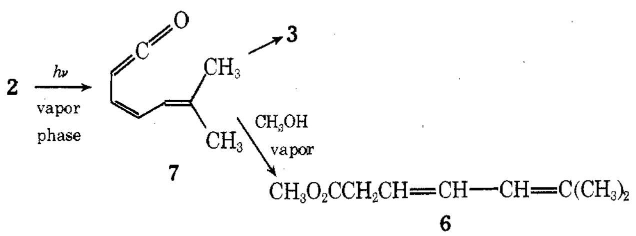
Received July 28, 1975

The irradiation of 3-cyano-4,4-dimethyl-2,5-cyclohexadienone (**13**) in *tert*-butyl alcohol gave *tert*-butyl 3-cyano-6-methylhepta-3,5-dienoate (**19**). Irradiation of **13** in moist *tert*-butyl alcohol yielded, in addition to **19**, (3-methyl-2-butenylidene)succinimide (**14**) and 3-carbamoyl-6-methylhepta-3,5-dienoic acid (**16**). Although no isomers resulting from photorearrangement of **13** were observed, the structures of the isolated products indicated that this process had occurred. Consistent with studies of similar systems, the results may be explained in terms of dienone rearrangement to one of two possible bicyclo[3.1.0]hexenones, which affords the observed products via a common ketene intermediate. The exclusive intermediacy of only one bicyclic ketone suggests that the photorearrangement of **13** involves excited-state diradical species.

The intramolecular photorearrangements of 2,5-cyclohexadienones in general give rise to three product types: bicyclo[3.1.0]hex-3-en-2-ones, phenols, and 2,4-cyclohexadienones, the latter resulting from recyclization of an intermediate ketene. In nucleophilic media, solvent addition to the ketene affords unsaturated acids or esters. All of these processes are well documented[2] and are typified by the photochemistry of 4,4-dimethyl-2,5-cyclohexadienone (**1**).[3] Irradiation of **1** in cyclohexane yields 6,6-dimethylbicyclo[3.1.0]hex-3-en-2-one (**2**) and 6,6-dimethyl-2,4-cyclohexadienone (**3**). Irradiation of **2** in cyclohexane affords **3**, while photolysis of **1** in aqueous dioxane gives **2** plus phenols **4** and **5**. The gas-phase irradiation of **2** likewise affords **3**, whereas addition of methanol vapor effects the formation of ester **6**. The intermediacy of a ketene (**7**) was postulated[3] to account for this behavior.





Extensive investigations of the photorearrangements of 2,5-cyclohexadienones have shown that the bicyclic ketone (e.g., **2**) is the only primary photoproduct.[2c,3] Further transformations of this intermediate are responsible for production of the other species isolated from cyclohexadienone photolysates. To some extent the stepwise nature of these photoconversions has facilitated elucidation of mechanistic details. For example, compelling evidence is available for the intermediacy of a zwitterionic species (e.g., **2a**,[3] **8**[4]) in the photoformation of phenols from bicyclic ketones, and spectroscopic