THE JOURNAL OF Organic Chemistry®

VOLUME 37, NUMBER 4

FEBRUARY 25, 1972

Acid-Catalyzed Rearrangement of Tricyclo[4.4.0.0^{2,7}]decan-3-ols

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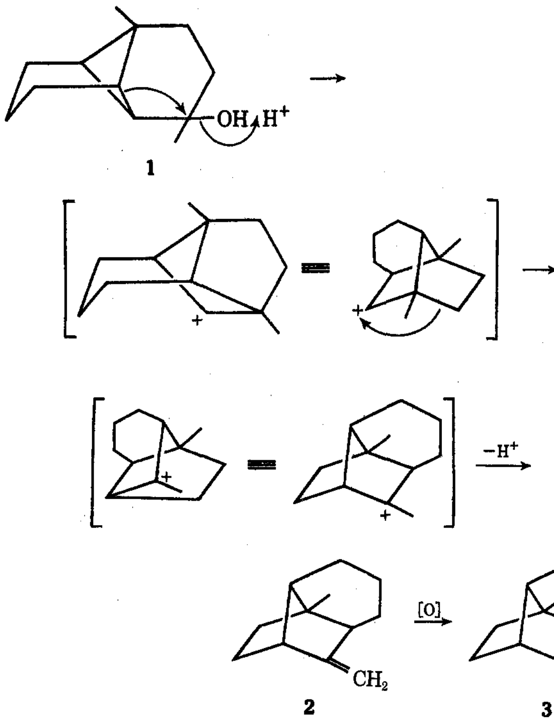
Received September 8, 1971

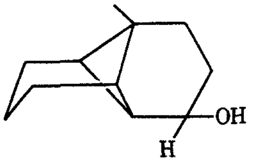
Tertiary alcohol 1 and its secondary counterpart 4 undergo acid-catalyzed rearrangement to olefin 5 and alcohol 8, respectively. Both 5 and 8 may be oxidized to tricyclic ketone 7, the structure of which has been rigorously defined by degradation to the known bicyclic ketone 19. Tricyclic alcohols 34 and 35 also yield, respectively, alcohol 8 and olefin 5 when treated with acid.

We previously reported that 3,6-dimethyltricyclo[4.4.0.0^{2,7}]decan-3-ol (**1**) undergoes acid-catalyzed rearrangement in the heterogeneous medium, ether–50% aqueous sulfuric acid, giving a single olefinic product in good yield.[1] Structure **2** was assigned to this olefin on the basis of spectral data obtained from it and the derived nor ketone (assigned structure **3**) and the reasonable mechanistic scheme outlined in Scheme I.[1]

SCHEME I



These assignments were called into question when we discovered a different tricyclic ketone with a better mechanistic claim on structure **3** in a related rearrangement.[2] In this paper we report a reexamination of the acid-catalyzed rearrangement of tertiary alcohol **1** and its secondary counterpart **4** and a rigorous identification of the products of these reactions.



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As reported in our earlier communication,[1] alcohol **1** was found to undergo acid-catalyzed rearrangement to a single bicyclic olefin **5**, having the empirical formula $C_{12}H_{18}$. When the reaction is carried out in the heterogeneous medium, pentane–50% aqueous sulfuric acid, the olefinic product, which has a highly camphoraceous odor, is obtained in 76% yield. The presence of an exocyclic methylene group is apparent from the ir (ν_{max} 881 cm^{-1}) and pmr spectra (one-proton multiplets at δ 4.50 and 4.78) of the product. Hydrocarbon **5** reacts with osmium tetroxide to give a crystalline diol **6**, which is cleaved by periodic acid to give the tricyclic ketone **7**, $C_{11}H_{16}O$. Ketone **7** is also obtained by ozonolysis of hydrocarbon **5**. The tricyclic ketone shows typical norbornanone absorption in its ir spectrum (ν_{max} 1750 cm^{-1}),[3] possesses a bridgehead methyl group (pmr singlet at δ 1.17), and exchanges no hydrogens when passed through a deuterium exchange column.[4]

Secondary alcohol **4**, when treated under the same conditions, gives an isomeric secondary alcohol **8** in 66% yield. Oxidation of alcohol **8** affords ketone **7**,

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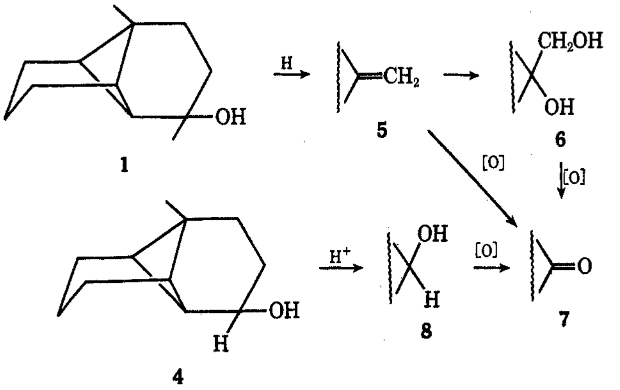
(1) C. H. Heathcock, R. A. Badger, and J. W. Patterson, Jr., *J. Amer. Chem. Soc.*, **89**, 4133 (1967).

(2) C. H. Heathcock and B. E. Ratcliffe, *J. Org. Chem.*, in press.

(3) 2-Norbornanone has ν_{max} 1751 cm^{-1}, Sadtler Standard Spectrum No. 20280.

(4) (a) M. Senn, W. J. Richter, and A. L. Burlingame, *J. Amer. Chem. Soc.*, **87**, 680 (1965); (b) G. J. Kallos and L. B. Westover, *Tetrahedron Lett.*, 1223 (1967).

demonstrating that the two rearrangement products, hydrocarbon **5** and alcohol **8**, have the same carbon skeleton.

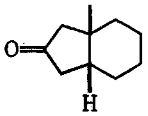


Baeyer–Villiger oxidation of tricyclic ketone **7** gives a crystalline lactone **9** in 87% yield. Saponification of **9** affords a crystalline hydroxy acid **10**, which is oxidized by chromic acid to an oily keto acid **11**. The ir spectrum of **11** contains carbonyl bands at 1755 and 1716 cm^{-1}, showing that the ketonic carbonyl is in a six-membered ring. Keto acid **11** incorporates but two deuterons per molecule when treated with sodium deuterioxide in refluxing deuterium oxide. The ir spectrum of **11** also contains a sharp band at 1422 cm^{-1}, affirming the presence of a methylene group adjacent to the cyclohexanone carbonyl.

The derived keto methyl ester **12** has corresponding spectral properties (ν_{CH_2CO} 1429 cm^{-1}). Keto ester **12** incorporates three deuterons per molecule when allowed to exchange with sodium methoxide in deuteriomethanol.[5] The evidence to this point establishes that one terminus of the carbonyl-containing bridge in tricyclic ketone **7** is a cyclohexyl position flanked by a methylene group and a quaternary carbon. The exchange data on keto ester **12** show that the other terminus (the carbon α to the new carboxyl group) bears one hydrogen.

Clemmensen reduction of keto acid **11** gives a mixture of epimeric acids **13**, which react with diazomethane to give the corresponding methyl esters **14**, obtained in a ratio of 4:1 (stereochemistry undefined). The ir spectrum of this mixture ($\nu_{C=O}$ 1735 cm^{-1}) confirms the loss of the cyclohexanone carbonyl. Epimeric acids **13** are converted, by treatment of the derived acid chlorides **15** with dimethylcadmium, into methyl ketones **16**. Analysis of this mixture by glpc showed that two epimers (stereochemistry undefined) were produced in a ratio of 3:2. Baeyer–Villiger oxidation of mixture **16** gives a corresponding mixture of acetates **17**, obtained in the ratio of 7:3, which is reduced by lithium aluminum hydride to the corresponding alcohols **18**. Oxidation of this mixture by chromic acid gives a single ketone **19**, $C_{10}H_{16}O$, whose ir spectrum ($\nu_{C=O}$ 1745 cm^{-1}) reveals that the carbonyl group is in a five-membered ring. Ketone **19** also has a bridgehead methyl group (δ 1.13) and has four enolizable hydrogens adjacent to its carbonyl.

On the basis of the foregoing evidence, ketone **19** may be assigned the unambiguous structure shown below. The correctness of this assignment was confirmed by comparison of its ir spectrum with that of an authentic sample of **19**.[6] The structure of tricyclic ketone **7**, and hence olefin **5** and alcohol **8**, is thus revealed. The complete degradative scheme is outlined in Scheme II.



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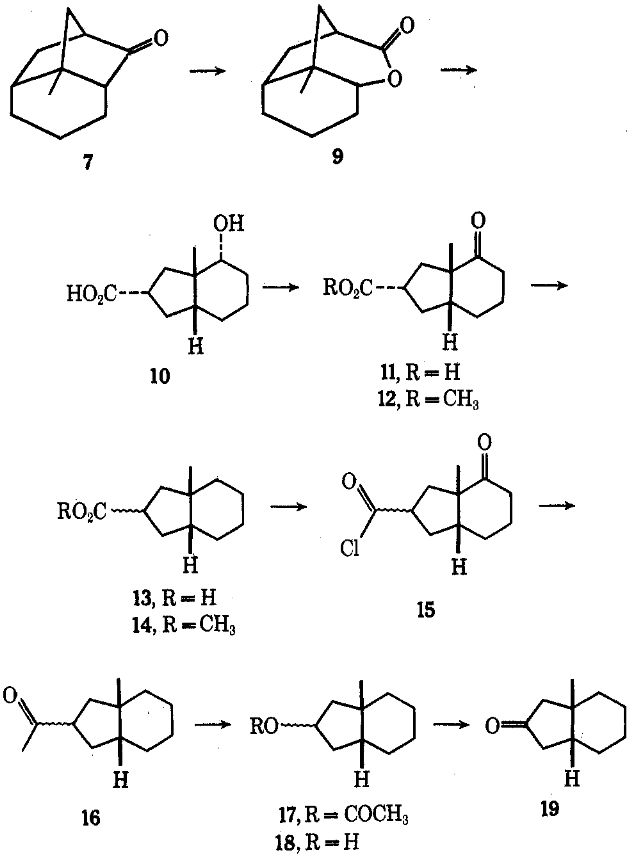
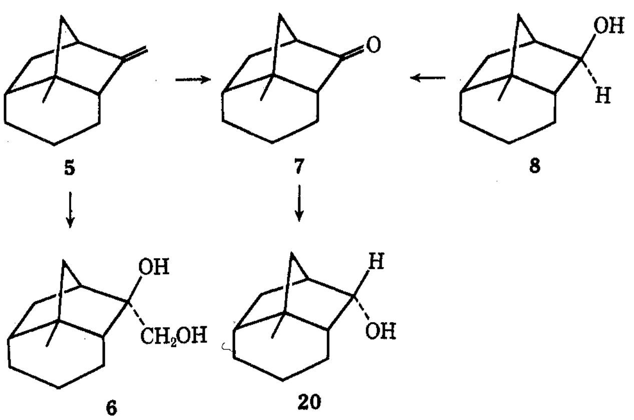
SCHEME II



With the complete structure of olefin **5** and the gross structure of alcohol **8** established, it remained only to ascertain the stereochemistry of the latter substance. As reported earlier, oxidation of alcohol **8** yields tricyclic ketone **7**. Lithium aluminum hydride reduction of **7** affords a new secondary alcohol **20**, which must



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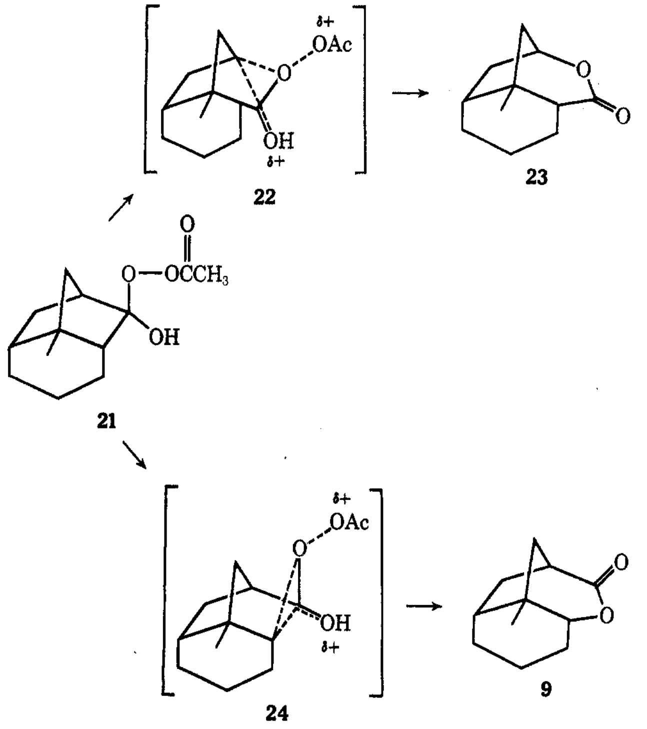
[5] We thank Professor Andrew Strietweiser, Jr., for a generous gift of CH_3OD.

[6] F. T. Bond, Ph.D. Dissertation, University of California, Berkeley, Calif., 1962. We thank Professor W. G. Dauben for providing an infrared spectrum of compound **19**.

be epimeric with **8**. The well-known propensity of hindered ketones to undergo hydride reduction from the less encumbered face enables assignment of the endo configuration to the hydroxyl group in **20**, and thus the exo configuration to **8**. Confirmatory evidence for these assignments was obtained from the pmr spectra of the two alcohols. The C-2 proton of **20** (exo) should be moderately coupled to both the C-1 and C-3 protons (dihedral angles of 20 and 0°). In accord with this expectation, this resonance is found as a doublet of doublets centered at δ 4.16 with $J_{1,2} = 5$ and $J_{2,3} = 9$ Hz. The corresponding resonance in epimer **8** occurs at δ 3.58 as a broadened singlet. One expects only weak coupling in the exo alcohol (endo proton) since the dihedral angles are 85 and 120°. Diol **6**, obtained by osmium tetroxide hydroxylation of olefin **5**, may likewise be assigned the *exo*-OH configuration on steric grounds.

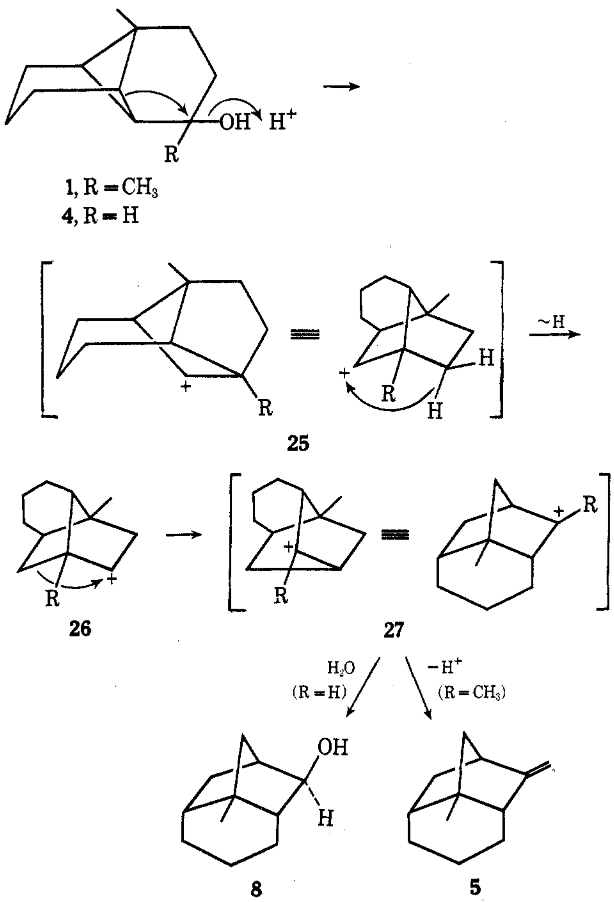
At this point, it is interesting to note that but one lactone is obtained in the peracid oxidation of ketone **7** (Scheme II). Assuming peracid attack from the less hindered exo face of **7**, intermediate **21** would be formed. Migration of C-1 would lead, *via* the chair-like transition state **22**, to lactone **23**. Migration of C-3 would lead, *via* the boat-like transition state **24**, to lactone **9**, the observed product. Examination of Dreiding stereomodels suggests that transition state **22** is more sterically encumbered than **24**.



22 **23** **21** **24** **9**

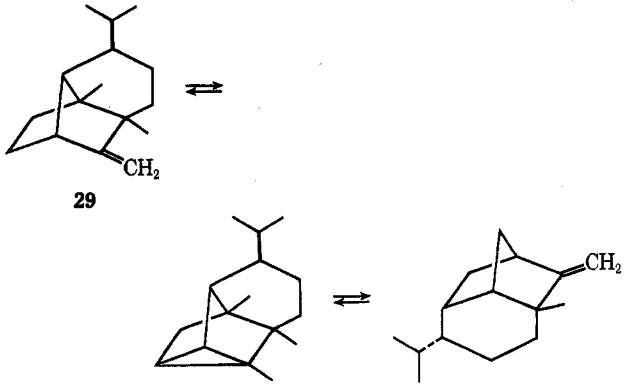
With the structures of olefin **5** and alcohol **8** rigorously defined, we may now reinterpret the rearrangement reactions. A reasonable mechanistic scheme is outlined in Scheme III. Initial expansion of the cyclobutane ring probably yields ion **25**, which suffers a 1,3-hydride shift to ion **26**, rather than a second Wagner–Meerwein shift, as we had originally proposed (Scheme I). Subsequent Wagner–Meerwein rearrangement of **26** gives the endo-bridged norbornyl cation **27**, which either ejects a proton (when R = CH$_3$) or becomes hydrated (when R = H).

SCHEME III



25 **26** **27** **8** **5**

It is tempting to implicate cyclopropane **28** as an intermediate in the rearrangement of ion **25** to ion **27** (see Scheme IV). McMurry has shown that the rearrangement of (±)-sativene (**29**) to (±)-isosativene (**31**), catalyzed by cupric acetate in refluxing acetic acid, certainly involves the intermediacy of (±)-cyclosativene (**30**).[7,7a]



29 **30** **31**

One interesting observation which we have made may be relevant to this point. Olefins **32** and **33**, obtained by dehydration of tertiary alcohol **1** with phosphoryl chloride in pyridine, *are recovered unchanged* when submitted to the pentane–50% aqueous sulfuric acid treatment. Apparently these olefins are not

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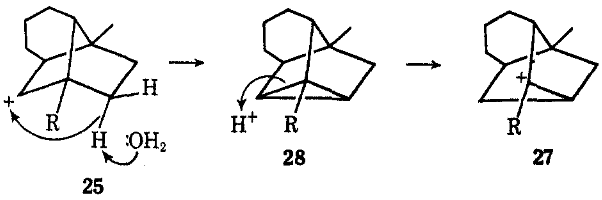
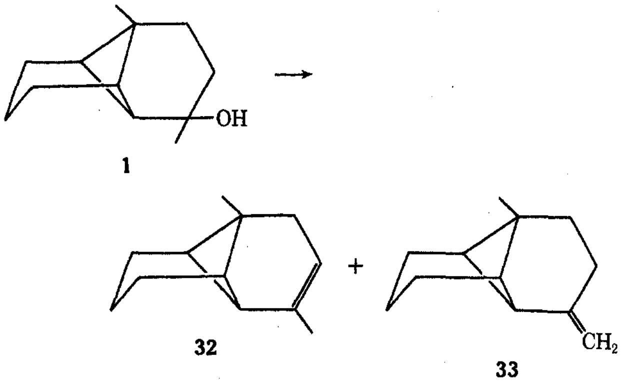
[7] J. E. McMurry, *Tetrahedron Lett.*, 55 (1969).

[7a] NOTE ADDED IN PROOF.—McMurry has now shown that hydrocarbon **30** is not an intermediate in the rearrangement of **29** to **31** when the reaction is carried out in the hexane–50% aqueous sulfuric acid system: J. E. McMurry, *J. Org. Chem.*, **36**, 2826 (1971).

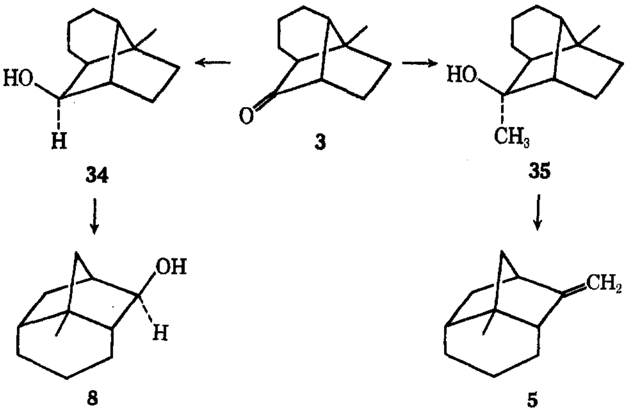
SCHEME IV



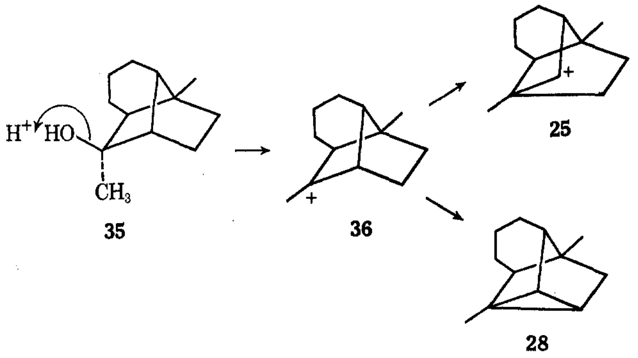
sufficiently protonated by sulfuric acid at this concentration to be drawn into the aqueous phase where rearrangement must occur.[8] Cyclopropane **28** should be even less soluble in the aqueous phase than olefins **32** and **33**. If this substance is an intermediate in the rearrangement of alcohols **1** and **4**, it must undergo protolysis before it can be extracted into the organic phase, which seems unlikely. On the basis of this argument, we favor the mechanistic scheme outlined in Scheme III. A final decision on this point must await the results of experiments with deuterium-labeled compounds.



Alcohols **34** and **35**, produced by treatment of tricyclic ketones **3**[2] with sodium borohydride or methyllithium, respectively, were also submitted to the pentane–50% aqueous sulfuric conditions. Secondary alcohol **34** gives alcohol **8** as the sole product in an isolated yield of 54%. Tertiary alcohol **35** gives olefin **5** in 75% yield.



In the case of secondary alcohol **34**, ionization of the protonated species leads to cation **25**, which can further react as in Scheme III. In the case of tertiary alcohol **35**, ionization leads to tertiary cation **36**, which must either undergo Wagner–Meerwein rearrangement to secondary cation **25** (Scheme III, R = CH_3) or suffer deprotonation to yield cyclopropane **28** (Scheme IV, R = CH_3). For the reasons advanced above, we favor the former pathway.



Experimental Section

Melting points (Pyrex capillary) and boiling points are uncorrected. Infared spectra (ir) were recorded on Perkin-Elmer 137 and 237 spectrophotometers. Proton magnetic resonance spectra (pmr) were recorded on Varian A-60 and T-60 spectrometers. Line positions are given in the δ scale, with internal tetramethylsilane as standard. The multiplicity, peak areas, coupling constants, and proton assignments are given in parentheses. Ultraviolet spectra (uv) were measured on a Perkin-Elmer 202 spectrophotometer. Consolidated 21-103C and Varian M-66 mass spectrometers provided the mass spectra. High-resolution molecular weight determinations were obtained on a Consolidated 21-110 spectrometer.

Gas–liquid partition chromatography (glpc) analyses were performed on Aerograph Models 204B, A90-P, and A90-P3 instruments. Silica gel G was used for thin layer chromatography (tlc) and silica gel PF_{254} for preparative tlc. Unless otherwise stated, the supports for column chromatography were Mallinckrodt 100–200 mesh SilicAR CC-7 and Woelm neutral alumina. Elemental analyses were performed by the Microanalytical Laboratory, operated by the Department of Chemistry, University of California, Berkeley, Calif.

2-Methylene-8-methyltricyclo[5.2.1.0^{3,8}]decane (5).—To a solution of 13.6 g of alcohol **1**[1] in 660 ml of olefin-free pentane was added 330 ml of 50% sulfuric acid. The flask was stoppered and stirred at room temperature for 18.5 hr. The pentane layer was separated, washed with water, and dried over magnesium sulfate. The solvent was removed by rotary evaporation to afford 11.43 g of a pale yellow liquid with a highly camphoraceous odor. The crude material was distilled at reduced pressure to yield 9.27 g (76%) of a water-white liquid, bp 42–43° (1.0 mm). The analytical sample was obtained by preparative glpc (5 ft × 0.25 in. Carbowax 20M at 120°, He flow = 50 cc/min): ir (CCl_4) 3067, 2933, 1664, 1460, 1372, 881 cm^{-1}; pmr (CCl_4) δ 1.08 (s, 3, angular Me), 4.50 (d, 1, J = 2.5 Hz, olefinic H), 4.78 (d, 1, J = 2.5 Hz, olefinic H).

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.28. Found: C, 88.99; H, 11.09.

***exo*-2-Hydroxy-*endo*-2-hydroxymethyl-8-methyltricyclo[5.2.1.0^{3,8}]decane (6).**—To a solution of 3.0 g of osmium tetroxide in 70 ml of benzene containing 3 ml of pyridine was added 1.94 g of olefin **5**. The black solution was stirred at room temperature for 43 hr and concentrated to a viscous oil on a rotary evaporator. The oil was dissolved in 250 ml of water containing 6.0 g of potassium hydroxide and 6.0 g of mannitol. The resulting solution was stirred at room temperature for 5 hr and extracted with methylene chloride (two 100-ml portions). The extracts were washed with 50 ml of water and 200 ml of 5% hydrochloric acid and dried over anhydrous magnesium sulfate. The dried solution was evaporated to afford a dirty-white semisolid which crystallized upon addition of pentane. The crystals were filtered, washed with pentane, and air-dried. There was obtained 1.121 g of diol **6**, mp 148.5–149.5°. The analytical sample, mp 163.5–164.0°, was obtained by recrystallization from acetone–pentane: ir (KBr) 3400, 1145, 1060, 1050, 1025, 1000, 980, 960, 890 cm^{-1}; pmr ($CHCl_3$ containing 10% pyridine) δ 0.83

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[8] More vigorous treatment of this mixture (pentane–70% aqueous sulfuric acid) leads to a complex mixture consisting mostly of polymeric products.

(s, 3, bridgehead Me), 3.82 (d, 1, J = 10 Hz), 3.45 (d, 1, J = 10 Hz).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.50; H, 10.17.

8-Methyltricyclo[5.2.1.0^{3,8}]decan-2-one (7). A. From Diol 6.—To a solution of 1.121 g of diol 6 in 25 ml of methanol was added a solution of 3.2 g of periodic acid in 50 ml of water. The reaction mixture was stirred for 21.5 hr at room temperature and extracted with ether (100 ml, two 50-ml portions). The ether extracts were washed with water, dried over magnesium sulfate, and evaporated at reduced pressure to yield 0.930 g (99%) of ketone 7 as a waxy solid. Sublimation of 109 mg of the crude ketone at 40° (2.0 mm) gave 100 mg of the ketone as waxy prisms, mp 151–152°. The analytical sample obtained by preparative glpc (5 ft × 0.25 in. NPGS at 180°) melts at 161.0–162.5°: ir (CCl_4) 1750, 1458, 992, 974 cm^{-1}; pmr (CCl_4) δ 1.17 (s, 3, bridgehead Me), 2.40 (broad s, 1, bridgehead H).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.24; H, 9.78.

The 2,4-dinitrophenylhydrazone melts at 165–167° after three recrystallizations from 95% ethanol.[9]

Anal. Calcd for $C_{17}H_{20}N_4O_4$: C, 59.27; H, 5.86; N, 16.28. Found: C, 59.44; H, 5.81; N, 16.40.

B. From Olefin 5.—A solution of 5.472 g of olefin 5 in 55 ml of methylene chloride containing 1.65 ml of pyridine[10] was ozonized (Welsbach Ozonator, air pressure = 8 psi, flow rate = 0.01, voltage = 82 V) for 7.5 hr at −78°. The reaction mixture was warmed to room temperature, washed with 10% hydrochloric acid (55 ml) and water (50 ml), and dried over magnesium sulfate. The solvent was removed by rotary evaporation to yield 6.229 g of viscous liquid. Glpc analysis of the crude product (6 ft × 0.25 in. 10% FFAP at 180°, He flow = 40 cc/min) showed the product to consist of a 90:10 mixture of ketone 7 and olefin 5.

C. From Alcohol 8.—To a solution 181.6 mg of tricyclic alcohol 8 in 3 ml of ether was added, dropwise over a period of 15 min, 0.8 ml of chromic acid solution.[11] The reaction mixture was stirred at room temperature for 0.5 hr and the ether layer separated. The aqueous layer was extracted with ether (two 5-ml portions). The combined ether layers were washed with saturated sodium bicarbonate and water and dried over magnesium sulfate. The ether was removed at reduced pressure to yield 156.2 mg (87%) of tricyclic ketone 7, whose spectral properties were identical with a sample prepared from olefin 5.

8-Methyltricyclo[5.2.1.0^{3,8}]decan-*exo*-2-ol (8).—To a solution of 960 mg of tricyclic alcohol 4[1] in 50 ml of olefin-free pentane was added 25 ml of 50% sulfuric acid. The flask was stoppered and stirred at room temperature for 20 hr. The pentane layer was separated, washed with water, and dried over magnesium sulfate. The solvent was removed at reduced pressure to afford 633.2 mg (66%) of crude alcohol 8 as a yellow solid. The crude alcohol was sublimed at 40° (0.2 mm) to afford 450.8 mg of a clear crystalline solid, mp 135–138°, having a camphorous odor: ir (CCl_4) 3610, 1456, 1376, 1053, 1026, 1001 cm^{-1}; pmr ($CDCl_3$) δ 1.06 (s, 3, bridgehead Me), 3.06 (s, 1, hydroxyl H, chemical shift concentration dependent), 3.58 (broad s, 1, $W_{h/2}$ = 4.5 Hz, C-2 H).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.21; H, 10.98.

4α-Hydroxy-3aβ-methyl-7aβ-octahydroinden-2α-oic Acid Lactone (9).—To a solution containing 930 mg of ketone 7, 5 ml of glacial acetic acid, and 333 mg of sodium acetate was added 1.85 ml of 40% peracetic acid.[12] The reaction mixture was stirred at room temperature for 5 days, diluted with water, and extracted with ether. The ether extracts were dried over magnesium sulfate and the solvent was removed on a rotary evaporator leaving 889 mg (87%) of lactone 9 as a white crystalline mass. The analytical sample was obtained by recrystallization from pentane as white needles: mp 135–136°; ir (CCl_4) 1745, 1724, 1370, 1239, 1050, 1022 cm^{-1}; pmr (CCl_4) δ 1.12 (s, 3, angular Me), 2.68 (broad m, 1, C-2 H).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 72.97; H, 9.10.

4α-Hydroxy-3aβ-methyl-7aβ-octahydroinden-2α-oic Acid (10).—A solution of 350 mg (8.70 mmol) of sodium hydroxide in 15 ml of water was added with stirring to 783.7 mg (4.35 mmol) of lactone 9. The stirred mixture was gently heated overnight, during which time the lactone dissolved. The reaction mixture was cooled on an ice bath and acidified until all the hydroxy acid 10 had precipitated. The mixture was extracted with ether (three 20-ml portions) and the ether extracts were dried over magnesium sulfate. The solvent was removed by rotary evaporation to yield 721.5 mg (84%) of white crystalline hydroxy acid 10. The analytical sample was obtained after recrystallization from benzene: mp 115.0–115.5°; ir (KBr) 3472, 1712, 1447, 1394, 1370, 1237, 1208, 1183, 1031, 1010, 950 cm^{-1}; pmr (CS_2) δ 1.30 (s, 3, angular Me), 2.58 (broad m, 1, C-2 H), 4.06 (m, 1, C-4 H).

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.39; H, 9.03.

3aβ-Methyl-4-oxo-7aβ-octahydroinden-2α-oic Acid (11).—A solution of 608.5 mg of hydroxy acid 10 in 15 ml of acetone was cooled to 0° in an ice bath. Jones reagent[13] was added dropwise, with stirring, until the solution turned brown. The solution was stirred an additional 15 min, diluted to twice its volume with water, and extracted with ether (four 25-ml portions). The combined ether extracts were washed with 25 ml of water and dried over magnesium sulfate. The ether was removed by rotary evaporation to yield 560.2 mg (93%) of keto acid 11 as an oil. Crystallization was attempted in a number of solvent systems, but to no avail: ir (CCl_4) 1755, 1716, 1463, 1422, 1379, 1241, 1052, 1029 cm^{-1}; pmr (CCl_4) δ 1.18 (s, 3, angular Me), 9.44 (s, 1, acidic H).

A solution of 38.2 mg of keto acid 11, 15.7 mg of sodium metal, and 4 ml of deuterium oxide (Bio-Rad Laboratories, 99.88 mol %) was stirred overnight under gentle reflux. The solution was cooled in an ice bath and acidified to pH 3 with concentrated sulfuric acid. The solution was extracted with ether and the ether extracts were washed with water. The ether extracts were dried over magnesium sulfate and evaporated at reduced pressure to yield 29.3 mg of the deuterated keto acid. The deuterated keto acid was subjected to low-resolution mass spectral analysis for deuterium incorporation. The parent peak was measured at m/e 198 as compared to m/e 196 for the undeuterated keto acid 11, indicating the incorporation of two deuterium atoms per molecule.

Methyl 3aβ-Methyl-4-oxo-7aβ-octahydroinden-2α-oate (12).—To a cooled solution of 356.7 mg of keto acid 11 in ether was slowly added an ethereal solution of diazomethane prepared from nitrisomethylurea.[14] The diazomethane solution was added until the yellow color of diazomethane persisted for at least 15 min. The yellow solution was gently heated on a steam bath until the solution turned colorless. The ether was removed by rotary evaporation to afford 363 mg (95%) of crude keto ester 12. The analytical sample was obtained by preparative glpc (6 ft × 0.25 in. SE-30 at 190°, He flow = 40 cc/min): ir (CCl_4) 1739, 1709, 1429, 1370, 1183, 1172, 1119, 1020 cm^{-1}; pmr (CCl_4) δ 1.12 (s, 3, angular Me), 3.62 (s, 3, ester Me).

Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.82; H, 8.85.

A solution of 44.6 mg of keto ester 12, 10 mg of sodium metal, and 4 ml of deuteriomethanol (Stohler Isotope Chemicals, 99% D) was refluxed overnight with stirring. Excess deuteriomethanol was removed by rotary evaporation. The residue was dissolved in ether, washed with 10% hydrochloric acid and water, and dried over magnesium sulfate. The ether was removed by rotary evaporation to yield 36.5 mg of deuterated keto ester. The deuterated material was subjected to low-resolution mass spectral analysis for deuterium content, which showed the presence of 10.6% $C_{12}H_{17}DO$, 34.6% $C_{12}H_{16}D_2O$, and 54.8% $C_{12}H_{15}D_3O$.

3aβ-Methyl-7aβ-octahydroinden-2ξ-oic Acid (13).—A mixture of 4.0 g of mossy zinc, 0.4 g of mercuric chloride, 0.2 ml of concentrated hydrochloric acid, and 6 ml of water was stirred for 5 min. The aqueous solution was decanted and the zinc amalgam added to 950 mg of keto acid 11. The mixture was covered with 3 ml of water and 4 ml of concentrated hydrochloric acid and refluxed for 28 hr. After refluxing had proceeded for 20 hr,

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[9] R. I. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," Wiley, New York, N. Y., 1956.

[10] See J. Krepinsky, Z. Samek, and F. Sorm, *Tetrahedron, Suppl.*, **8**, 53 (1966).

[11] H. C. Brown and C. Garg, *J. Amer. Chem. Soc.*, **83**, 2952 (1961).

[12] R. R. Sauers and G. P. Ahearn, *ibid.*, **83**, 2759 (1961).

[13] A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

[14] F. Arndt, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 165.

an additional 2 ml of concentrated hydrochloric acid was added to the reaction mixture.[15] At the completion of the reflux period, the mixture was diluted with water and extracted with ether. The ether extracts were dried over magnesium sulfate and evaporated at reduced pressure to yield 819 mg of crude carboxylic acid **13** as an oil: ir (CCl_4) series of weak bands from 3636 to 2481, 1701, 1456, 1446, 1410, 1370, 1287, 1232, 1224 cm^{-1}; pmr (CCl_4) δ 1.01 (s, 3, angular Me), 11.00 (broad s, 1, acidic H).

Methyl 3aβ-Methyl-7aβ-octahydroinden-2ξ-oate (14).—An ethereal solution of diazomethane[14] was carefully added to a solution of 819 mg of crude carboxylic acid **13** in 25 ml of ether until the yellow color of diazomethane persisted for 15 min. The ether was removed by rotary evaporation to afford 852 mg of crude methyl ester **14** as a mixture of epimers. The two epimers could be separated by glpc (6 ft × 0.25 in. 10% FFAP at 125°, He flow = 40 cc/min) showing an 80:20 mixture. An analytical sample of the major epimer was obtained by preparative glpc: ir (CCl_4) 1735, 1456, 1429, 1373, 1353, 1200, 1170 cm^{-1}; pmr (CCl_4) δ 0.98 (s, 3, angular Me), 3.57 (s, 3, ester Me). The ir of the minor epimer was almost identical with that of the major epimer.

Anal. Calcd for $C_{12}H_{20}O_2$: mol wt, 196.1462. Found: mol wt, 196.1457 (by high-resolution mass spectroscopy).

2ξ-Acetyl-3aβ-methyl-7aβ-octahydroindene (16).—To a solution of 420 mg of 85% potassium hydroxide in 5 ml of water was added 658 mg of methyl ester **14**. The mixture was refluxed for 1 hr, cooled to room temperature, acidified with 10% hydrochloric acid, and extracted with ether (two 20-ml portions). The ether extracts were dried over magnesium sulfate and evaporated at reduced pressure to yield 565.2 mg of crude carboxylic acid **13**. Thionyl chloride (0.45 ml) was added to the crude acid in one portion. The mixture was refluxed for 2 hr and cooled to room temperature, and excess thionyl chloride was removed at reduced pressure.

A dimethylcadmium solution was prepared[16] by adding 0.6 g of anhydrous cadmium chloride to a solution containing 2.1 ml of methylmagnesium bromide (3 *M* ethereal solution) and 10 ml of ether at 0°. The solution was stirred and refluxed for 1 hr. The crude acid chloride **15**, dissolved in 20 ml of benzene, was added to the dimethylcadmium solution and the reaction mixture was refluxed for 2 hr with stirring. The reaction mixture was cooled to room temperature, acidified with excess cold dilute hydrochloric acid, and extracted with two portions of ether. The ether extracts were washed with 5% sodium bicarbonate, dried over magnesium sulfate, and evaporated at reduced pressure to afford 473.3 mg of crude ketone **16** as a dark oil. The crude ketone was chromatographed on 15 g of silica gel (20:1 petroleum ether–ether) to give 297 mg (77%) of pure ketone **16** as a clear oil. Glpc (6 ft × 0.25 in. 10% FFAP at 150°) showed the product to be a mixture of epimers in a ratio of 60:40. An analytical sample of the major epimer was obtained by preparative glpc: ir (CCl_4) 1715, 1463, 1445, 1372, 1355, 1174 cm^{-1}; pmr (CCl_4) δ 0.98 (s, 3, angular methyl), 2.03 (s, 3, acetyl Me).

Anal. Calcd for $C_{12}H_{20}O$: mol wt, 180.1513. Found: mol wt, 180.1519.

3aβ-Methyl-7aβ-octahydroinden-2ξ-ol Acetate (17).—A solution of 357 mg (1.75 mmol) of 85% *m*-chloroperbenzoic acid in 4 ml of anhydrous cloroform was added to 283.2 mg (1.57 mmol) of methyl ketone **16**. The reaction mixture was stirred in the dark at room temperature for 11 days and washed with saturated sodium bicarbonate (two 5-ml portions) and 10 ml of water. The combined aqueous washings were extracted with 20 ml of ether, and the combined organic layers were dried over magnesium sulfate. The solvents were removed by rotary evaporation to give 265.4 mg (89%) of crude acetate **17**. The pmr spectrum (CCl_4) of the crude acetate indicates it to be a 70:30 mixture of epimers.

3aβ-Methyl-7aβ-octahydroinden-2ξ-ol (18).—A solution of 265 mg of crude acetate **17** in 30 ml of anhydrous ether was added to a solution of 517 mg of lithium aluminum hydride in 20 ml of anhydrous ether. The mixture was stirred at room temperature for 22.5 hr and quenched by the dropwise addition of 3 ml of 10% potassium hydroxide. After stirring for 5 min, the solid was filtered and washed with ether. The combined ethereal solutions were dried over magnesium sulfate and evaporated at reduced pressure to yield 189.4 mg (91%) of the crude alcohol **18** as a yellowish oil. The pmr spectrum ($CDCl_3$) of the crude product indicates it to be a 70:30 mixture of epimeric alcohols.

3aβ-Methyl-7aβ-hexahydroinden-2(1*H*)-one (19).—To a solution of 180 mg of the crude alcohol **18** in 3 ml of ether was added 0.75 ml of chromic acid solution[11] over a period of 15 min. The reaction flask was fitted with a condenser and stirred at room temperature for 2.25 hr. The ether layer was separated and the aqueous layer extracted with ether (two 5-ml portions). The combined ether layers were washed with saturated sodium bicarbonate and water and dried over magnesium sulfate. Evaporation of the ether afforded 131.3 mg of crude ketone **19** as a yellowish oil. An analytical sample was obtained by preparative glpc (6 ft × 0.25 in. 10% FFAP at 150°, He flow = 40 cc/min): ir (CCl_4) 1745, 1443, 1401, 1373, 1252, 1202 cm^{-1}; pmr (CCl_4) δ 1.13 (s, 3, angular Me), 1.47 (broad s, 8, cyclohexyl methylenes). Ir (CS_2) was identical that of with a sample prepared by catalytic reduction of 7a-methyl-4,5,6,7-tetrahydroinden-2-(1*H*)-one.[6]

Anal. Calcd for $C_{10}H_{16}O$: mol wt, 152.1201. Found: mol wt, 152.1201 (by high-resolution mass spectroscopy).

The 2,4-dinitrophenylhydrazone melts at 143–144° (corrected) after two recrystallizations from methanol.

The deuterated hydrindanone was obtained by preparative glpc (6 ft × 0.25 in. 10% KOD, 20% Carbowax 20M on Chromosorb W 60–80 at 150°).[4] The procedure consisted of injecting 10 μl of ketone **19** on the column which had been equilibrated with 100 μl of deuterium oxide and collecting the effluent. The collected sample was subjected to mass spectral analysis which showed the presence of 6.1% $C_{10}H_{15}DO$, 20.4% $C_{10}H_{14}D_2O$, 40.6% $C_{10}H_{13}D_3O$, and 32.9% $C_{10}H_{12}D_4O$.

8-Methyltricyclo[5.2.1.0^{3,8}]decan-*endo*-2-ol (20).—A solution of 168.2 mg of tricyclic ketone **7** in 5 ml of anhydrous ether was added, dropwise, to a stirred refluxing suspension of 116 mg of lithium aluminum hydride in 10 ml of anhydrous ether. The reaction mixture was refluxed for 13 hr and excess lithium aluminum hydride decomposed with 10% hydrochloric acid. The ethereal solution was separated, dried over magnesium sulfate, and evaporated at reduced pressure to afford 147.1 mg (86.5%) of crude tricyclic alcohol **20** as a crystalline white solid having a highly camphorous odor. The crude alcohol was sublimed at 40° (0.4 mm) to afford 103 mg of white crystalline solid: mp 146° (sublimes); ir (CCl_4) 3665, 1456, 1376, 1140 1055 cm^{-1}; pmr (CCl_4) δ 1.00 (s, 3, bridgehead Me), 4.16 (d of d, 1, $J_{2,3}$ = 9, $J_{1,2}$ = 5 Hz, C-2 H).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.53; H, 10.89.

1-Methyltricyclo[4.4.0.0^{2,8}]decan-*exo*-7-ol (34).—A solution of 239.4 mg of tricyclic ketone **3**[2] in 10 ml of anhydrous ether was added, dropwise, to a refluxing mixture of 175 mg of lithium aluminum hydride and 20 ml of anhydrous ether. The mixture was gently refluxed for 17 hr and cooled to room temperature, and excess lithium aluminum hydride decomposed with 5% aqueous potassium hydroxide. The resulting white precipitate was filtered and washed with ether. The filtrate was dried over magnesium sulfate and evaporated at reduced pressure to yield 194.6 mg (80%) of crude alcohol **34** as a white solid. A portion of the crude product was sublimed at 40° (1.0 mm) to afford white crystals: mp 106–110° (sublimes); ir (CCl_4) 3660, 1471, 1445, 1377, 1130, 1041 cm^{-1}; pmr ($CDCl_3$) δ 1.07 (s, 3, bridgehead Me), 3.86 (d, 1, J = 6 Hz, C-7 H).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.48; H, 11.19.

1,7-Dimethyltricyclo[4.4.0.0^{2,8}]decan-*exo*-7-ol (35).—A solution of 82 mg of tricyclic ketone **3** in 5 ml of anhydrous ether was added to 20 ml of a 5.07% solution of methyllithium in ether. The reaction mixture was refluxed for 2 days under nitrogen and stirred an additional day at room temperature. The mixture was quenched with water and the ether layer separated. The aqueous layer was extracted with ether, and the combined ether layers were washed with brine and dried over magnesium sulfate. The solvent was removed by evaporation to afford 92.6 mg (100%) of methyl carbinol **35** as a crystalline solid. The analytical sample was prepared by sublimation at reduced pressure: mp 57–58°; ir (CCl_4) 3660, 1449, 1376, 1140, 1087, 1047, 924 cm^{-1}; pmr (CCl_4) δ 1.07 (s, 3, bridgehead Me), 1.23 (s, 3, C-7 Me).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.32; H, 11.25.

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Acid-Catalyzed Rearrangement of Tricyclic Alcohol 34.—To a solution of 194 mg of tricyclic alcohol **34** in 10 ml of spectro-quality pentane was added 5 ml of a 50% aqueous sulfuric acid solution. The two phase system was stirred for 14 hr at room temperature. The pentane layer was separated from the aqueous layer, washed with water, and dried over magnesium sulfate. The pentane was removed by evaporation to afford 113.8 mg of tricyclic alcohol **8** as a white solid (53.6% yield). The spectral properties were identical with those of alcohol **8** prepared by rearrangement of alcohol **4**.

Acid-Catalyzed Rearrangement of Tricyclic Carbinol 35.—To a solution of 72.6 mg of tricyclic carbinol **35** in 3 ml of spectro-quality pentane was added 1.5 ml of 50% aqueous sulfuric acid. The two-phase system was stirred at room temperature for 18 hr. The pentane layer was separated and washed with water. The combined aqueous layers were extracted with ether, and ether extracts were washed with water. The combined organic extracts were dried over magnesium sulfate and evaporated at reduced pressure to give 48.9 mg (75%) of a clear liquid having a camphorous odor. The spectral properties of this material were identical with those of tricyclic hydrocarbon **5** prepared from compound **1**.

3,6-Dimethyltricyclo[4.4.0.$0^{2,7}$]dec-3-ene (32) and 3-Methylene-6-methyltricyclo[4.4.0.$0^{2,7}$]decane (33).—To a solution of 180 mg of alcohol **1** in 1 ml of pyridine was added 0.25 ml of phosphorus oxychloride. The solution was slowly warmed to 90° and then allowed to cool to room temperature. The partially crystalline mixture was mixed with 25 ml of ice water and extracted with ether (three 30-ml portions). The combined ether extracts were washed with 5% HCl (50 ml), 10% K_2CO_3 (10 ml), and saturated NaCl (50 ml). After drying over $MgSO_4$, the ether was evaporated under reduced pressure to yield 135.5 mg of colorless liquid. Glpc analysis (10% NPGS, 135°) showed the product to be a mixture of **32** and **33** in a ratio of 80:20. The major product (endocyclic double bond isomer **32**) had the following spectral properties: ir (CCl_4) 3050, 3025, 2930, 2830, 1480, 1450, 1385, 1370, 1270, 1225, 1190, 1040, 982, 960, 940, 880, 860 cm^{-1}; pmr (CCl_4) δ 0.92 (s, 3, angular Me), 5.17 (m, 1, vinyl H). The minor product (exocyclic double bond isomer) had the following spectral properties: ir (CCl_4) 3030, 1680, 1500, 1480, 1470, 1465, 1400, 883 cm^{-1}; pmr (CCl_4) δ 0.87 (s, 3, angular Me), 2.60 (s, 1, C-2 H), 2.45 (broad t, 2, C-4 H's), 4.52 (q, 2, vinyl H's).

A solution of 199 mg of the olefin mixture, prepared as above, in 10 ml of pentane was layered over 5 ml of 50% aqueous sulfuric acid. After stirring vigorously for 16 hr, the pentane layer was decanted, dried, and evaporated to yield 181 mg of clear oil. Analysis by glpc and pmr showed that no reaction had occurred.

Registry No.—**5**, 32980-12-4 **6**, 32970-82-4; **7**, 32980-13-5; **7** 2,4-DNP, 32980-14-6; **8**, 32970-83-5; **9**, 32970-84-6; **10**, 32970-85-7; **11**, 32970-86-8; **12**, 32970-87-9; **13**, 32970-81-3; **13** epimer, 32970-88-0; **14**, 32970-89-1; **14** epimer, 32970-90-4; **16**, 32970-91-5; **16** epimer, 33020-76-7; **19**, 13351-29-6; **19** 2,4-DNP, 32970-93-7; **20**, 32970-94-8; **32**, 33015-39-3; **33**, 33015-40-6; **34**, 33020-77-8; **35**, 33020-78-9.

Acknowledgment.—We thank the National Science Foundation and the Alfred P. Sloan Foundation for financial support.

Synthesis and Chemistry of Some 2-Substituted Tricyclo[3.3.0.$0^{3,7}$]octane Derivatives[1]

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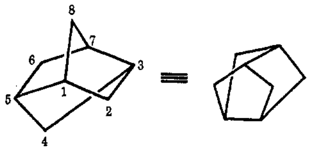
Received July 22, 1971

A survey of the chemistry of 2-substituted tricyclo[3.3.0.$0^{3,7}$]octyl derivatives was initiated. Experiments were conducted which produced the following reactive intermediates at the 2 position: free radicals, carbanions, and carbonium ions. It was found that those reactions which involved formation of cationic intermediates yielded rearranged products *via* a formal ring contraction of a five- to a four-membered ring. Analysis of solvolysis data of the 2-brosylate suggests that this rearrangement proceeds with a rate enhancement of the order of *ca.* 10^8.

Exploitation of the unique properties of strained molecules has provided physical organic chemists with significant insights into the mechanistic details of organic transformations. In addition, there has been a special fascination with the synthesis and behavior of molecules which possess a high degree of symmetry: *e.g.*, tetrahedrane, cubane, adamantane. These three molecules are notable in that the smallest rings in each system are all of the same size, three-, four-, and six-membered, respectively. We have for some time been interested in the most symmetrical all five-membered ring homolog: tricyclo[3.3.0.$0^{3,7}$]octane (1).[2-4] In this report we wish to detail the synthesis of several derivatives of **1** and to report the results of a survey of some of the chemistry of this system.



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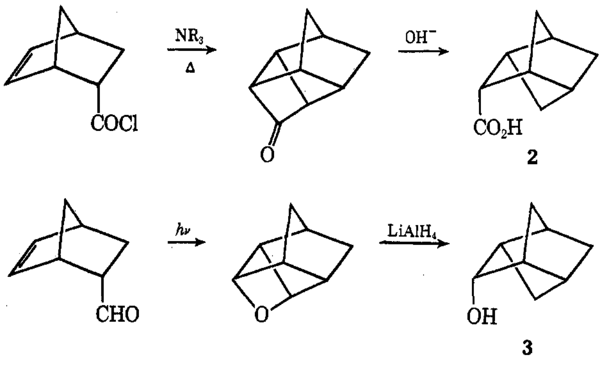
The key intermediates used in this study were the acid **2** and the alcohol **3**. The detailed procedure for



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[1] Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstracts, ORGN 74; see also R. R. Sauers and B. R. Sickles, *Tetrahedron Lett.*, 1067 (1970).

[2] (a) R. R. Sauers, W. Schinski, and M. M. Mason, *ibid.*, 79 (1969); (b) R. R. Sauers and K. W. Kelly, *J. Org. Chem.*, **35**, 3286 (1970).

[3] For other syntheses of this ring system see (a) O. W. Webster and L. H. Sommer, *ibid.*, **29**, 3103 (1964); (b) P. K. Freeman, V. N. M. Rao, and G. E. Bigam, *Chem. Commun.*, 511 (1965); (c) B. R. Vogt, S. R. Suter, and J. R. E. Hoover, *Tetrahedron Lett.*, 1609 (1968).

[4] This molecule may be regarded as a bis nor homo log of adamantane or twistane depending on whether the methylenes are inserted at the zero-carbon bridges or at the appropriate methylene sites, respectively. The symmetry of this molecule (D_{2d}) precludes both structural isomerism and optical activity in monosubstituted derivatives.