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Acid-Catalyzed Rearrangements in the Bicyclo[3.2.0]heptenyl System[1]

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Acid-catalyzed rearrangement of *exo*- and *endo*-1,2,4,4-tetramethylbicyclo[3.2.0]hept-6-en-2-ol (**3a** and **3b**, respectively) resulted in the formation of 2,2,4-trimethyl-7-methylenebicyclo[2.2.1]hept-5-ene (**5**), 1,3,3,5-tetramethyl-2-oxabicyclo[3.3.0]oct-7-ene (**9**), *anti*-2,2,4,7-tetramethylbicyclo[2.2.1]hept-5-en-7-ol (**6a**), and an unidentified material **10**. The formation of **9** was shown to proceed *via* rearrangement of **6a**. Analogous rearrangements of *exo*- and *endo*-2,4,4,6-tetramethylbicyclo[3.2.0]hept-6-en-2-ol (**4a** and **4b**, respectively) resulted in the formation of 1,3,5,5-tetramethyl-1-formylcyclohex-4-ene (**14**). The intermediacy of *anti*-2,2,4,6-tetramethylbicyclo[2.2.1]hept-5-en-7-ol (**11a**) in the latter rearrangement was demonstrated. The mechanism and possible significance of these rearrangements are discussed.

Part A

The bicyclo[3.2.0]hept-6-en-2-ol system is of interest as a precursor of the bicyclo[3.2.0]hept-6-en-2-yl cation which by Wagner–Meerwein rearrangement can be transformed to the well-studied norborn-2-en-7-yl cation. Both cations possess a carbonium ion center which is homoallylic and therefore are good subjects for investigation of homoallylic participation. The *anti*-norborn-2-en-7-yl system[3] has received extensive study. The bicyclo[3.2.0]hept-6-en-2-yl system has been investigated by Lewis and Whitham[4] who studied the acetolysis of the *p*-toluenesulfonates of *exo*- and *endo*-1,4,4-trimethyl- (**1a**, **1b**) and 4,4,6-trimethylbicyclo-[3.2.0]hept-6-en-2-ol (**2a**, **2b**) in buffered acetic acid. Rearranged materials having the norbornyl skeleton were found to predominate in the solvolysis products. Qualitative rate comparisons and detailed product studies led the authors to conclude that the exo isomers reacted *via* homoallylic participation in the initial ionization step while the endo derivatives reacted without participation in the rate-determining transition state.

Winstein, *et al.*,[5] observed a corresponding rearrangement of *exo*- and *endo*-bicyclo[3.2.0]heptadienols in fluorosulfonic acid to form 7-norbornadienyl salts.

In contrast to the results of Whitham[4] and Winstein,[5] Story and Cooke[6] on the basis of their study of the *p*-nitrobenzoates of *exo*- and *endo*-bicyclo[3.2.0]heptadienols have concluded that assistance by the homoallylic double bond is not a factor in the solvolyses of these compounds and that only the allylic double bond stabilizes the carbonium ion center.

We have investigated the acid-catalyzed rearrangement of the bicyclo[3.2.0]hept-6-en-2-ol system. The objects of our study were *exo*- and *endo*-1,2,4,4-tetramethylbicyclo[3.2.0]hept-6-en-2-ol (**3a**, **3b**) and *exo*- and *endo*-2,4,4,6-tetramethylbicyclo[3.2.0]hept-6-en-2-ol (**4a**, **4b**), methyl homologs of the systems investigated by Lewis and Whitham[4] in which the incipient carbonium ion center acquires further stabilization from the additional methyl group. Since tertiary alkyl halides solvolyze more rapidly than 3-halo-1-butenyl systems, it was of interest to determine whether the 2-methyl substituent was able to effectively quench homoallylic participation.

Alcohols **3a** and **3b** were found to rearrange smoothly in the presence of a catalytic amount of sulfuric acid to give 2,2,4-trimethyl-7-methylenebicyclo[2.2.1]hept-5-ene (**5**) as the major product with 1,3,3,5-tetramethyl-2-oxabicyclo[3.3.0]oct-7-ene (**9**) and *anti*-2,2,4,7-tetramethylbicyclo[2.2.1]hept-5-en-7-ol (**6a**) as minor products. Compound **9** became the major product when the rearrangement was carried out in aqueous acetic acid containing a catalytic amount of sulfuric acid. The appearance of a new product (**10**) was observed, to which a structure has not been assigned. The structures of **5** and **6a** follow unambiguously from spectral data (see Experimental Section). Compound **6a** was also obtained upon carrying out the acid-catalyzed rearrangement of **3a** and **3b** in aqueous methanol, in addition to the methyl ether **6b**. Solvolysis of the *p*-nitrobenzoate of **3b** in buffered and unbuffered acetic acid yielded **5** and the rearranged acetate **6c**. Alcohol **3a** did not form a *p*-nitrobenzoate. Reduction of **6c** with lithium aluminum hydride gave **6a**. Acid-catalyzed rearrangement of **6a** in aqueous acetic acid resulted in the

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[1] A portion of this work has appeared in preliminary form: V. K. Jones and L. B. Jones, *Tetrahedron Lett.*, 3171 (1970).

[2] Author to whom inquires should be addressed.

[3] A. Diaz, M. Brookhart, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 3133 (1966), and references cited therein.

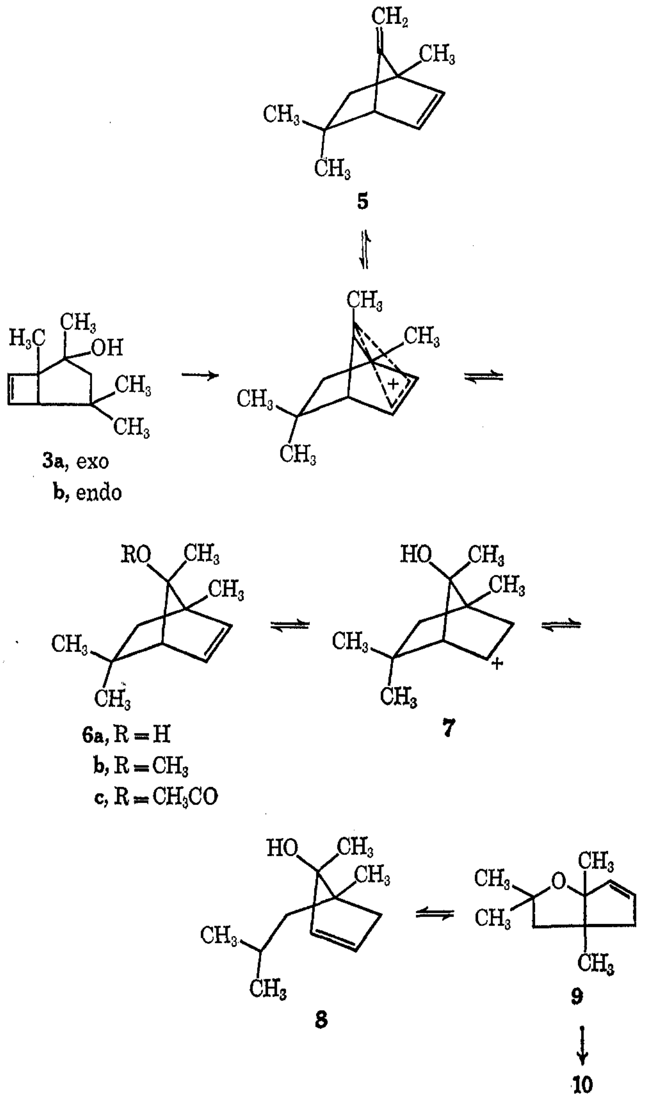
[4] S. C. Lewis and G. H. Whitham, *J. Chem. Soc. C*, 274 (1967).

[5] R. K. Lustgarten, M. Brookhart, and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 6350 (1967).

[6] P. R. Story and B. J. A. Cooke, *Chem. Commun.*, 1080 (1968).

formation of **5** and **9**. Acid-catalyzed rearrangement of **5** in aqueous acetic acid resulted in the formation of **6a** and **9** as the major products. Acid-catalyzed rearrangement of **9** led to the formation of **10**. A scheme consistent with these observations is presented (Scheme I).

SCHEME I

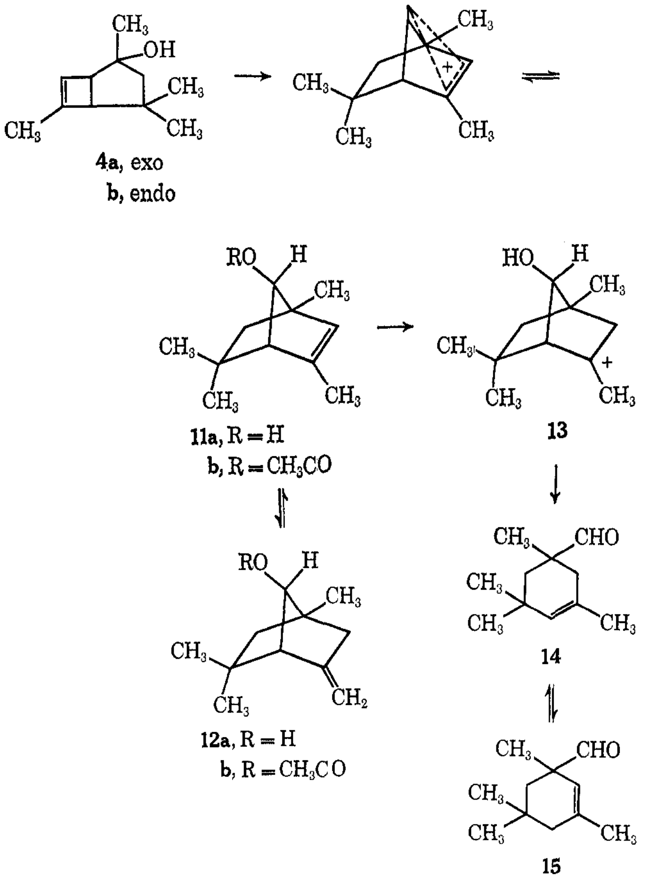


The structure assigned to **9** is based on mechanistic considerations and is consistent with spectral data and results of deuterium-labeling experiments (see Part B).

Alcohols **4a** and **4b** were found to undergo rearrangements formally similar to those of **3a** and **3b**. Treatment of **4a** and **4b** with a catalytic amount of sulfuric acid in aqueous acetic acid solution and without solvent yielded 1,3,3,5-tetramethyl-1-formylcyclohex-4-ene (**14**) as the primary reaction product, which under equilibrating conditions isomerized to 1,3,3,5-tetramethyl-1-formylcyclohex-5-ene (**15**). Compounds **14** and **15** could not be separated gas chromatographically but could clearly be distinguished in the nmr spectrum from the shifts of the aldehydic and vinyl protons (see Experimental Section). Lithium aluminum hydride reduction of a mixture of **14** and **15** gave 1,3,3,5-tetramethyl-1-(hydroxymethyl)cyclohex-4-ene (**16**) and 1,3,3,5-tetramethyl-1-(hydroxymethyl)cyclohex-5-ene (**17**) which were nicely separable with gas chromatography. Catalytic hydrogenation of **14** at atmospheric pressure yielded **16**, demonstrating the inaccessibility of the double bond. The assigned structures are consistent with spectral data.

Acetolysis of the *p*-nitrobenzoate of **4a** (the exo derivative) yielded two acetates, *anti*-2,2,4,6-tetramethyl-7-acetoxybicyclo[2.2.1]hept-5-ene (**11b**) and *anti*-2,2,4-trimethyl-6-methylene-7-acetoxybicyclo[2.2.1]heptane (**12b**), whose structures were clearly indicated by spectral data. Compound **12b** is formed by isomerization of **11b**. Lithium aluminum hydride reduction of **11b** and **12b** yielded *anti*-2,2,4,6-tetramethylbicyclo[2.2.1]-hept-5-en-7-ol (**11a**) and *anti*-2,2,4-trimethyl-6-methylenebicyclo[2.2.1]heptan-7-ol (**12a**), respectively. Acid-catalyzed rearrangement of **11a** resulted in aldehyde formation, demonstrating the intermediacy of **11a** in the formation of **14** from **4a** and **4b**. Neither **11a** nor **12a** was detected in the products from **4a** and **4b**, indicating their high reactivity. Catalytic hydrogenation of **11b** and **12b** resulted in reduction of the double bonds with formation of the saturated acetate. Acid-catalyzed rearrangement of **4a** and **4b** in deuterium oxide–deuterioacetic acid solution resulted in deuterium incorporation into position 6 of **14**. A scheme consistent with these observations is presented (Scheme II).

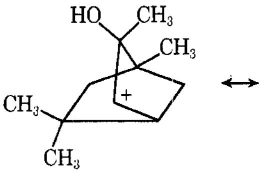
SCHEME II



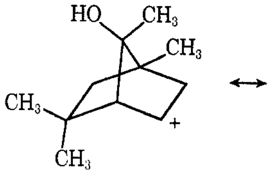
We had initially hoped to investigate the solvolysis reactions of the *p*-nitrobenzoates of **3a**, **3b**, **4a**, and **4b**. However, the preparatively unfavorable ratio of **4a** and **4b** upon their lengthy preparation and the inability to generate the *p*-nitrobenzoate of **3a** presented major obstacles. In addition, preliminary solvolysis of **3b** in 60% aqueous acetone at 100° showed the rate to be too slow to conveniently monitor. Qualitatively, our results are consistent with those of Lewis and Whitham[4] indicating homoallylic interaction. The exo alcohols **3a** and **4a** upon acid-catalyzed rearrangement in aqueous solvents (see Experimental Section) qualitatively appear to rearrange at a faster rate than the corresponding endo alcohols and only rearranged products can be isolated. For the compounds studied by Story and Cooke[6] in which homoallylic participation was quenched, neither rearranged products nor significant rate differences for reaction of the exo and endo derivatives could be detected. The magnitude of homoallylic participation in the bicyclo[3.2.0]hept-6-en-2-ol system cannot be further evaluated in the absence of more quantitative data.

Of particular interest is the observation that rearrangements of **6a** and **11a** proceed with fragmentation of the C_1–C_6 bond in the case of **6a** and of the C_1–C_7 bond in the case of **11a**. These two modes of fragmentation must in some way be related to the presence or absence of the C_2 and/or C_7 methyl group, although there is no apparent explanation in simple electronic terms.

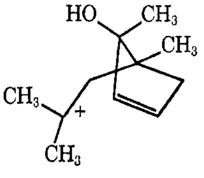
The particular mode of cleavage may possibly be a reflection of the fact that the tertiary ion **13** produced by reaction of **11a** possesses a classical structure, while the secondary ion **7** produced from **6a** is nonclassical.[7] If **7** is nonclassical, resonance structures **7a**, **7b**, and **7c** should make variable contributions. Schleyer, *et al.*,[8] demonstrated on the basis of their study of 6,6-dimethyl-2-norbornyl tosylates that the possibility of tertiary carbonium ion formation is not sufficient to promote C_1–C_6 fragmentation. The results of Gassman, *et al.*,[9] suggest that inductively electron-withdrawing groups located at C_7 are insufficient to dramatically enhance the importance of resonance structures such as **7c** in the absence of C_6 alkyl groups. It is possible that the presence of both factors, inductively electron-withdrawing substituents at C_7 and electron-donating alkyl groups at C_6, is sufficient to increase the contribution of structure **7c** and hence lead to C_1–C_6 fragmentation. The tertiary carbonium ion **13** in this formulation would be considered classical (or at least resonance structures analogous to **7b** would be of major importance) and presumably would open to the more stable ion **18** rather than the less stable cyclopentenyl derivative **19**. As a result C_1–C_7 cleavage would be observed. This type of cleavage has recently been detected by Gassman, *et al.*[9c]



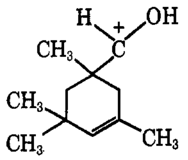
7a



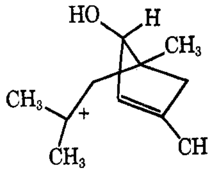
7b



7c



18



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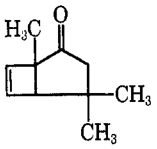
A less likely explanation for the different modes of fragmentation would involve a concerted protonation–fragmentation process. If protonation of **6a** occurs from the endo direction (as a result of steric factors) while protonation of **11a** takes place exo, it is conceivable that fragmentation, if concerted, could proceed in a different manner for the two compounds. Deuteration results outlined in Part B would appear to exclude this possibility.

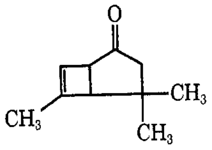
Further studies are in progress to more fully delineate the factors responsible for the different behavior of compounds **6a** and **11a**.

Part B

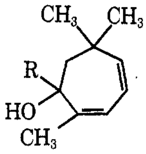
Synthesis and Structural Assignments of Starting Materials.—The exo and endo alcohols **3a**, **3b**, **4a**, and **4b** could be prepared by addition of methylmagnesium bromide to 1,4,4-trimethylbicyclo[3.2.0]hept-6-en-2-one (**20**) and 4,4,6-trimethylbicyclo[3.2.0]hept-6-en-2-one (**21**), which are available by photoisomerization of eucarvone.[10] We have found that a more convenient way of preparing **3a** and **3b** is photocyclization of methyleucarvol (**22a**). For preparation of **4a** and **4b** we utilized the suggestion of Chapman[11] that **20** could be prepared more conveniently by photocyclization of eucarvol (**22b**) with subsequent oxidation of the bicyclic alcohols.



20



21



22a, R = CH_3
b, R = H

With respect to **1a**, **1b**, **2a**, and **2b**, Lewis and Whitham[4] based their configurational assignments on (a) intramolecular hydrogen bonding between the double bond and the hydroxyl group and (b) consideration of the spin–spin coupling pattern of the C_2 proton in the nmr spectrum. We base our configurational assignments on the following considerations. Lewis and Whitman[4] observed that reduction of **20** and **21** with reagents more susceptible to the steric environment of the carbonyl group led to predominant attack from the concave side of the molecule to give the exo alcohols. We have assumed that addition of methylmagnesium bromide is also subject to the steric environment of the

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[7] S. Winstein and D. S. Trifan, *J. Amer. Chem. Soc.*, **74**, 1147, 1154 (1952).

[8] P. v. R. Schleyer, M. M. Donaldson, and W. E. Watts, *ibid.*, **87**, 375 (1965).

[9] (a) P. G. Gassman and J. L. Marshall, *ibid.*, **88**, 2822 (1966); (b) P. G. Gassman and J. L. Marshall, *Tetrahedron Lett.*, 2429, 2433 (1968); (c) P. G. Gassman and J. G. Macmillan, *J. Amer. Chem. Soc.*, **91**, 5527 (1969).

[10] G. Büchi and E. M. Burgess, *ibid.*, **82**, 4333 (1960).

[11] O. L. Chapman, "Advances in Photochemistry," Vol. 1, W. A. Noyes, G. S. Hammond, and J. N. Pitts, Ed., Interscience, New York, N. Y., 1963, p 389.

carbonyl group and will attack from the concave side to give exo alcohol. Therefore, we have assigned the exo configuration to the major products obtained upon addition of methylmagnesium bromide to **20** and **21**. The assignments are supported by the following observations. First, **3a** was found qualitatively to be more reactive with respect to acid-catalyzed rearrangement in aqueous methanol than **3b** (see Experimental Section). This is in agreement with the observed[4] greater reactivity of the exo derivatives **1a** and **2a**. Second, the ir spectrum of **4b** shows doublet absorption at 3610 and 3595 cm^{-1} attributable to free and bonded hydroxyl. Third, the nmr spectrum of **3a** shows the vinyl protons as a singlet at δ 6.01 ppm. In **3b** they appear as two doublets at δ 6.14 and 6.21 ppm (J = 3 Hz). Intramolecular hydrogen bonding should result in deshielding of the vinyl protons with a corresponding shift to lower field. This is in agreement with the nmr spectra of **1a** and **1b**[4] in which the vinyl protons appear at δ 5.80 and 5.90 ppm, respectively; *i.e.*, the vinyl protons in the exo epimer appear at higher field. Analogously, the nmr spectrum of **4a**, assigned the exo configuration, shows the vinyl proton as a broadened singlet at δ 5.69 ppm. In the nmr spectrum of **4b**, assigned the endo configuration, it appears as a broadened singlet at δ 5.86 ppm. In addition, the vinyl methyl in **4b** would be expected to be shifted to lower field due to deshielding by the hydroxyl group, which is what is observed (δ 1.82 ppm in **4b** and 1.70 ppm in **4a**).

Structural Assignment of 9.—The structure assigned to **9** is based on mechanistic considerations and is consistent with spectral data and results of deuterium-labeling experiments. The nmr of **9** shows the methyl groups at δ 1.03, 1.10, and 1.16 (12 H), the C_4 hydrogens as an AB quartet with δ_B 1.73 and δ_A 1.82 (J_{AB} = 12 Hz), the C_6 hydrogens as an AB quartet with δ_B 2.08 and δ_A 2.34 (J_{AB} = 16 Hz) containing further splitting (J = 2 Hz), a one-hydrogen doublet at 5.44 (J = 6 Hz) containing fine splitting (J = 2 Hz), and a one-hydrogen doublet at 5.61 ppm (J = 6 Hz) containing fine splitting (J = *ca.* 1.54 Hz). The ir spectrum of **9** shows a sharp band at 3050 cm^{-1} (olefinic CH), strong absorption at 1050–1200 cm^{-1} (CO), and a strong band at 735 cm^{-1} (cis-disubstituted double bond). The uv spectrum shows no maximum (ϵ_{210} 690) and is consistent with a disubstituted double bond.

Acid-catalyzed rearrangement of **3a** and **3b** in deuterium oxide–deuterioacetic acid solution yielded **9** which showed increasing amounts of deuterium incorporation depending on the length of reaction. The amount of deuterium incorporation was estimated from the nmr spectrum using the C_4-methylene protons as an internal standard. The nmr spectrum showed increasing deuterium incorporation into one methyl group (assigned to the C_1 methyl) and at C_6 (see Experimental Section), which is compatible with Scheme I and the proposed structure. Catalytic hydrogenation of **9** resulted in reduction of the double bond. Hydrogenolysis was not observed.

Compound **10** is isomeric with **9** and contains no unsaturation as determined by nmr and uv spectra and chemical tests for unsaturation. Upon isolation under deuteration conditions, the material was found to contain up to 18 deuterium atoms, *i.e.*, exchange of every proton in the molecule. Due to the obvious complexity of the rearrangement leading to **10** and lack of functional group "handles," compound **10** was not investigated further and any structures which we could suggest at this point would be completely speculative.

Experimental Section[12]

exo- **and** *endo-***1,2,4,4-Tetramethylbicyclo[3.2.0]hept-6-en-2-ol (3a, 3b). A.**—Eucarvone[13] was allowed to react with excess methylmagnesium bromide. After normal work-up with aqueous ammonium chloride, drying, and concentration, the crude methyleucarvol[14] was irradiated with an equal volume of cyclohexane in a Vycor tube over *ca.* 0.5 g of barium carbonate with a Hanovia medium-pressure mercury arc lamp for 6 days. Glc of the crude mixture showed no starting material. The mixture was concentrated and distilled to give 12.15 g (0.073 mol, 66%) of material, bp 63–66° (0.75–0.95 mm), which glc showed to consist of two peaks in the amounts of 55% **3a** and 45% **3b**, in order of retention.

A glc-purified sample of **3a** gave the following spectral and analytical data: nmr δ 0.90, 1.10, 1.14, 1.20 (s, 12 H, CCH_3), 1.49 (d, 1 H, J = 14 Hz, HCH), 1.98 (d, 1 H, J = 14 Hz, HCH), 2.40 (s, 1 H, C_5 bridgehead proton), and 6.01 ppm (s, 2 H, vinyl protons); ir (10% in CCl_4) 3640, 3520 (OH), 3145, 3050 (olefinic CH); ir (neat) 730 cm^{-1} (cis-1,2-disubstituted double bond).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.45; H, 10.91. Found: C, 79.44; H, 10.86

A glc-purified sample of **3b** gave the following spectral and analytical data: nmr δ 0.91, 0.99, 1.17, 1.23 (s, 12 H, CCH_3), 1.58 (d, 1 H, J = 14 Hz, HCH), 2.12 (d, 1 H, J = 14 Hz, HCH), 2.29 (s, 1 H, C_5 bridgehead proton), 6.14 (d, 1 H, J = 3 Hz, CH=CH), and 6.21 ppm (d, 1 H, J = 3 Hz, CH=CH); ir (10% in CCl_4) 3580, 3450 (OH), 3130, 3040 (olefinic CH); ir (neat) 730 cm^{-1} (cis-1,2-disubstituted double bond).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.45; H, 10.91. Found: C, 79.47; H, 10.84.

B.—An ether solution of 170 mg of **20** (prepared as described below and purified by glc) was allowed to react with excess methylmagnesium bromide. After normal work-up with aqueous ammonium chloride, drying, and concentration, glc of the crude reaction mixture showed 92% **3a** and 8% **3b**, in order of retention.

exo- **and** *endo-***2,4,4,6-Tetramethylbicyclo[3.2.0]hept-6-en-2-ol (4a, 4b).**—A solution of crude eucarvol[13] prepared by reduction of 40 g of eucarvone with lithium aluminum hydride was irradiated with an equal volume of cyclohexane in a Vycor tube over *ca.* 0.5 g of barium carbonate for 6 days. The mixture was concentrated and distilled to give 15.5 g of material, bp 110–120° (30 mm), which was shown by glc to consist of *ca.* 90% two partially resolved peaks in the relative amounts of *ca.* 44% and 56%. Treatment of an ether solution of this material with an oxidizing mixture prepared from 10 g of sodium dichromate dihydrate, 7.5 ml of concentrated sulfuric acid, and 50 ml of water by the procedure of Brown and Garg[15] yielded after work-up and distillation 9.0 g of material, bp 94–98° (30 mm), which was 60% **20** as determined by glc, and ir of a collected sample compared with a sample of **20** prepared earlier.[16] This material was isomerized[10] without further purification by refluxing with 1.5 g of *p*-toluenesulfonic acid in 250 ml of benzene for 7 hr to give after work-up and fractionation 4.8 g of **21**, bp 101–103° (30 mm), identified by

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(12) All boiling points are uncorrected. Magnesium sulfate was employed as a drying agent. Ultraviolet spectra of solutions in 95% ethanol were determined with a Cary Model 14 recording spectrophotometer. Nuclear magnetic resonance spectra of carbon tetrachloride solutions with tetramethylsilane as internal reference were determined at 100 Mc with a Varian Model HA-100 spectrometer unless otherwise noted. Infrared spectra were determined with a Perkin-Elmer Model 337 ir recording spectrophotometer as a film unless otherwise noted. Vapor phase chromatography was carried out on an Aerograph Model A-90-P3 gas chromatograph employing a column packed with Carbowax 20M suspended on base-washed Chromosorb P. Product composition was estimated from the relative areas of the corresponding peaks on the gas chromatograms. Mass spectra were determined with a Hitachi Perkin-Elmer RMV-6E mass spectrometer. Microanalyses were performed by Huffman Laboratories, Inc., Wheatridge, Colo. Methylmagnesium bromide was supplied by Alfa Inorganics, Beverly, Mass., as a 3 *M* solution in diethyl ether.

(13) E. J. Corey and H. J. Burke, *J. Amer. Chem. Soc.*, **78**, 174 (1956).

(14) E. J. Corey, H. J. Burke, and W. A. Remers, *ibid.*, **78**, 180 (1956).

(15) H. C. Brown and C. P. Garg, *ibid.*, **83**, 2952 (1961).

(16) L. B. Jones and V. K. Jones, *ibid.*, **89**, 1880 (1967).

comparison of ir with a sample prepared earlier.[16] This material was allowed to react with excess methylmagnesium bromide. Glc of the crude reaction mixture after work-up with aqueous ammonium chloride showed the two alcohols in the relative amounts of 75% **4a** and 25% **4b**, in order of retention. Distillation yielded 2.7 g of material, bp 69–71° (1.1–1.3 mm), which consisted of 80% **4a** and 20% **4b**. Fractionation yielded samples containing varying amounts of **4a** and **4b**.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.45; H, 10.91. Found (for a mixture of 80% **4a** and 20% **4b**): C, 79.54; H, 10.92.

A glc-purified sample of **4a** gave the following spectral data: nmr δ 1.00, 1.13, 1.18 (s, 9 H, CCH_3), 1.70 (br s, 3 H, vinyl CH_3), 1.48 (d, 1 H, J = 14 Hz, HCH), 1.91 (d, 1 H, J = 14 Hz, HCH), 2.72 (br s, 2 H, C_1 and C_5 bridgehead protons), and 5.69 ppm (s, 1 H, C=CH); ir (10% in CCl_4) 3600, 3450, (OH), 3030 (olefinic CH), and 1640 cm^{-1} (C=C). A collected sample of **4a** crystallized upon standing to give a material having mp 44–51°.

A glc-purified sample of **4b** gave the following spectral data: nmr δ 0.95, 1.02, 1.29 (9 H, CCH_3), 1.72 (br s, 3 H, $C{=}CCH_3$), 1.55 (d, 1 H, J = 14 Hz, HCH), 2.04 (d, 1 H, J = 14 Hz, HCH), 2.55 and 2.74 (br s, 2 H, C_1 and C_5 bridgehead protons), and 5.86 ppm (s, 1 H, C=CH); ir (10% in CCl_4) 3604 (sh), 3590, 3450 (OH), 3030 (olefinic CH), and 1640 cm^{-1} (C=C).

Acid-Catalyzed Rearrangement of 3a and 3b. A. Without Solvent.—To a two-necked flask containing 1 drop (*ca.* 0.02 ml) of concentrated sulfuric acid maintained in a bath at 150–155° and 30 mm and connected to a short-path stillhead was added dropwise 4.0 g of a mixture consisting of 60% **3a** and 40% **3b**. The volatile products which distilled were collected. The distillate was taken up in ether, washed with aqueous sodium carbonate, dried, and concentrated to give 2.1 g of material. Glc showed a trace of solvent and *ca.* 78% **5**, 4% **9**, 2% an unknown (probably **10**), 9% **3a**, 3% **6a**, and 4% **3b**, in order of retention (identification by ir and retention time). Redistillation through a short-path stillhead yielded 1.0 g of **5**, bp 68–70° (28 mm).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found for **5**: C, 88.84; H, 10.83.

A glc-purified sample of **5** gave the following spectral data: nmr δ 0.88, 1.08, 1.22 (s, 9 H, CCH_3), 2.42 (d, 1 H, J = 3 Hz, C_1 bridgehead proton), 4.15 (s, 2 H, $C{=}CH_2$), 5.94 (d, 1 H, J = 6 Hz, C_5 vinyl proton), and 6.18 ppm (d, 1 H, J = 6 Hz, further split into a doublet, J = 3 Hz, C_6 vinyl proton); ir 3060 (olefinic CH), 1680 (strained C=C), 870 (terminal=CH_2), 770, and 735 cm^{-1}; uv $\epsilon_{210\,\mathrm{nm}}$ 3200; mass spectrum (80 eV) *m/e* (rel intensity) 148 (1.5), 133 (7), 117 (4), 115 (5), 105 (30), 93 (34), 92 (100), 91 (91), etc.

B. In Aqueous Acetic Acid.—A mixture consisting of 3.0 g of alcohols (55% **3a**, 45% **3b**), 1 ml of concentrated sulfuric acid, 30 ml of water, and 60 ml of glacial acetic acid was refluxed for 0.5 hr, cooled, diluted with ether, and washed with aqueous sodium carbonate until evolution of carbon dioxide ceased. The organic layer was dried and concentrated. Glc of the crude mixture showed the product to consist of *ca.* 1% **5**, 74% **9**, 12% **10**, and 15% three components (probably **3a**, **6a**, **3b**) in order of retention. The mixture was distilled through a short-path stillhead to give 2.0 g of material, bp up to 60° (0.6 mm). Glc showed virtually the same product composition as in the crude material.

A glc-purified sample of **9** gave the following analytical and spectral data in addition to what was presented earlier: mass spectrum (80 eV) *m/e* (rel intensity) 166 (3), 152 (11), 151 (100), 123 (21), 110 (9), 109 (60), 108 (20), 107 (17), 105 (9), 95 (24), 94 (6), 93 (90), etc.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.45; H, 10.91. Found: C, 79.58; H, 11.10.

A glc-purified sample of **10** gave the following spectral data: nmr no absorption below δ 2.5 ppm; ir no absorption above 3000 cm^{-1}; uv $\epsilon_{210\,\mathrm{nm}}$ 53; mass spectrum (80 eV) *m/e* (rel intensity) 166 (18), 151 (3), 147 (11), 133 (50), 123 (43), 119 (11), 110 (49), 109 (67), 108 (100), 107 (4), 95 (42), 94 (15), 93 (88), etc.

Compound **10** did not decolorize either a carbon tetrachloride solution of bromine or an acidic aqueous solution of potassium permanganate.

C. In Aqueous Methanol. 1.—A mixture of 0.5 ml of alcohols (55% **3a**, 45% **3b**), 10 drops of concentrated sulfuric acid, 10 ml of methanol, and 5 ml of water was refluxed for 2 hr, then poured into ether, and neutralized with aqueous sodium carbonate. The organic layer was dried and concentrated. Glc showed the products to consist of *ca.* 41% **6b**, 31% **6a**, and 26% **3b**, in order of retention.

A glc-purified sample of **6b** gave the following spectral data: nmr[17] δ 0.78, 0.96, 1.10, 1.23 (s, 12 H, CCH_3), 1.82 (d, 1 H, J = 11 Hz, C_3 exo proton), 2.12 (d, 1 H, J = 4 Hz, C_1 bridgehead proton), 3.11 (s, 3 H, CCH_3), 5.65 (br d, 1 H, J = 6.5 Hz, C_5 vinyl proton), and 6.08 ppm (d, 1 H, J = 6.5 Hz, further split into a doublet with J = 4 Hz, C_6 vinyl proton).

A glc-purified sample of **6a** gave the following spectral and analytical data: nmr δ 0.78, 0.96, 1.14, 1.31 (s, 12 H, CCH_3), 1.72 (d, 1 H, J = 11 Hz, C_3 exo proton), 1.90 (d, 1 H, J = 4 Hz, C_1 bridgehead proton), 5.68 (d, 1 H, J = 6 Hz, C_5 vinyl proton), and 6.06 ppm (d, 1 H, J = 6 Hz, further split into a doublet with J = 4 Hz, C_6 vinyl proton); ir 3400 (OH), 740, 710 cm^{-1}.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.45; H, 10.91. Found: C, 79.13; H, 11.04.

2.—A mixture of 100 μl of **3a**, 2 drops of concentrated sulfuric acid, 3 ml of methanol, and 1 ml of water was refluxed for 1 hr, cooled, poured into water, and extracted with ether. The ether layer was neutralized with aqueous sodium carbonate, dried, and concentrated. Glc showed no starting alcohol, 5% an unknown, 38% **6b**, and 57% **6a**, in order of retention (identification by ir and retention time).

3.—A 100-μl sample of **3b** was treated simultaneously and identically with the preceding. Glc showed 2% an unknown, 12% **6b**, and 86% **3b**, in order of retention (identification by ir and retention time).

Acid-Catalyzed Rearrangement of 5.—A solution of 300 μl of **5**, 5 drops of concentrated sulfuric acid, 2.5 ml of water, and 5 ml of glacial acetic acid was refluxed for 15 min. The mixture was cooled and poured into ether. The ether layer was neutralized with aqueous sodium carbonate, dried, and concentrated. Glc showed 13% **5**, 60% **9**, 6% an unknown (probably **10**), 1% an unknown, 19% **6a**, and 2% an unknown, in order of retention (identification by retention time and ir).

Acid-Catalyzed Rearrangement of 6a. A. Without Solvent.—A 130-mg sample of **6a** was distilled from 1 drop of concentrated sulfuric acid at a bath temperature of 130–140° and 30 mm through a short-path stillhead. The stillhead was rinsed with ether into the receiver. The ether solution was dried and concentrated to give 72 mg of material. Glc showed 56% **5**, 4% an unknown, 38% **9**, 1% an unknown, and 11% **6a**, in order of retention time (identification by retention time and ir).

B. In Aqueous Acetic Acid.—A 50-mg sample of **6a** was refluxed with 1 ml of glacial acetic acid, 0.5 ml of water, and 1 drop of concentrated sulfuric acid for 10 min. The mixture was diluted with ether and neutralized with aqueous sodium carbonate. The ether layer was dried and concentrated. Glc showed the products to consist of 12% **5**, 63% **9**, 8% an unknown (probably **10**), 3% an unknown, and 15% **6a** (**5** and **6a** identified by retention time and **9** identified by retention time and ir.

Acid-Catalyzed Rearrangement of 9.—A mixture of 100 μl of **9**, 5 drops of concentrated sulfuric acid, 1 ml of water, and 2 ml of glacial acetic acid was refluxed for 3 hr, cooled, diluted with ether, and neutralized with aqueous sodium carbonate. Glc showed the products to consist of *ca.* 75% **9** and 25% **10**, in order of retention (identification by retention time and ir).

Acid-Catalyzed Rearrangment of 3a and 3b in Deuterium Oxide–Deuterioacetic Acid Solution. A.—A mixture of 0.25 ml of alcohols (55% **3a**, 45% **3b**), 5 ml of deuterioacetic acid (prepared from acetic anhydride and deuterium oxide), 2.5 ml of deuterium oxide, and 5 drops of concentrated sulfuric acid was refluxed for 30 min. The mixture was cooled and diluted with pentane, and solid sodium carbonate was added until evolution of carbon dioxide ceased. The mixture was filtered, dried, and concentrated. Glc of the product showed 23% deuterio-**5**, 66% deuterio-**9**, 3% deuterio-**10**, and 8% other material.

A glc-purified sample of deuterio-**5** gave the following spectral data: mass spectrum (80 eV) *m/e* (rel intensity) 94 (27), 93 (80), 92 (100), 91 (80), 77 (6), 65 (22), etc. Increased intensity of 93 and 94 support deuterium incorporation into the C_7 methylene.

A glc-purified sample of deuterio-**9** gave the following spectral data: nmr δ 1.03 (s, 1 H, partially deuterated CH_3), 1.10, 1.16 (s, 9 H, CCH_3), 1.73 (d, 1 H, J = 12 Hz, HC**H**), 1.82 (d, 1 H, J = 12 Hz, **H**CH), 2.08 (br t, 0.85 H, J = 2 Hz, C_6 proton coupled with C_6 deuterium), 5.48 (d, 1 H, J = 6 Hz, vinyl proton), and 5.64 ppm (d, 1 H, J = 6 Hz, further split into a doublet, J = 2 Hz, vinyl proton).

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[17] Determined at 60 Mc with a Varian Model A-60 spectrometer.

B.—A mixture of 0.3 g of alcohols (55% **3a**, 45% **3b**), 5 ml of deuterioacetic acid, 2.5 ml of deuterium oxide, and 5 drops of concentrated sulfuric acid was refluxed for 6 hr and then treated as in the preceding experiment. Glc showed 1% deuterio-**5**, 60% deuterio-**9**, 26% deuterio-**10**, and 12% other material.

The nmr spectrum of a glc-purified sample of deuterio-**9** showed virtually no absorption at δ 1.03 (CCD_3), a triplet at 2.08 (0.5 H, J = 2 Hz, C_6 proton coupled with C_6 deuterium), a one-hydrogen doublet at 5.52 (J = 6 Hz), and a broadened one-hydrogen doublet at 5.68 ppm (J = 6 Hz). The remainder of the spectrum was unchanged from that presented in the preceding experiment.

The mass spectrum of a glc-purified sample of deuterio-**10** showed highest *m/e* at 184.

Catalytic Hydrogenation of 9.—A solution of 369 mg (2.2 mmol) of **9** in 12 ml of ethyl acetate was hydrogenated at atmospheric pressure over the catalyst prepared from 64 mg of platinum oxide. The hydrogen uptake (76 ml or 1.25 equiv) ceased after 1.25 hr. The reaction mixture was filtered and concentrated. Glc showed one product peak which was collected. The nmr spectrum of this material showed no absorption below δ 2.0 ppm. The ir spectrum showed no absorption above 3000 and below 900 cm^{-1}. The mass spectrum (80 eV) showed *m/e* (rel intensity) 168 (0.2), 153 (10), 126 (65), 125 (10), 111 (12), 110 (11), 95 (100), 83 (45), 69 (21), 55 (31), etc.

Preparation of the *p*-Nitrobenzoate of 3b.—A mixture of 2.0 g (0.912 mol) of alcohols (55% **3a**, 45% **3b**), 3.0 g (0.016 mol) of *p*-nitrobenzoyl chloride, and 20 ml of anhydrous pyridine was stirred at room temperature for 3 days. The pyridine was removed at room temperature and reduced pressure, and the moist residue was suspended in pentane and filtered. The pentane filtrate was concentrated and crystallized in Dry Ice to give 0.94 g (0.003 mol) of material, mp 102–106°. A 100-mg sample of this material was reduced with lithium aluminum hydride. After aqueous work-up, glc of the concentrated product showed 5% **3a** and 95% **3b** (identification by ir and retention time). Recrystallization of the *p*-nitrobenzoate derivative from pentane yielded material having mp 105–108° which gave the following spectral data: nmr δ 1.00, 1.10, 1.44, 1.68 (s, 12 H, CCH_3), 2.28 (d, 1 H, J = 14 Hz, HCH), 2.46 (d, 1 H, J = 14 Hz, HCH), 2.42 (s, 1 H, C_5 bridgehead proton), 6.12 (d, 1 H, J = 3 Hz, vinyl proton), 6.18 (d, 1 H, J = 3 Hz, vinyl proton), and 8.0–8.3 ppm (4 H, aromatic protons).

The pentane filtrate was concentrated at reduced pressure to give 1.48 g of a liquid residue which consisted of *ca.* 40% pyridine and 60% **3a**. Distillation through a short-path stillhead gave 0.40 g of material which was 95% **3a** as determined by glc (identification by ir and retention time).

Acetolysis of the *p*-Nitrobenzoate of 3b. A.—A solution of 0.9198 g (0.003 mol) of the *p*-nitrobenzoate of **3b**, 0.5030 g (0.0062 mol) of anhydrous sodium acetate, and 25 ml of glacial acetic acid was refluxed for 24 hr (a reflux period of 4 hr was insufficient for complete acetolysis). The mixture was cooled, diluted with ether, and neutralized with aqueous sodium carbonate. The organic layer was dried and concentrated to give 350 mg of residue. Glc showed the product to consist of *ca.* 58% **5**, 2% other material, and 40% **6c**, in order of retention (**5** identified by ir and retention time).

A glc-purified sample of **6c** gave the following spectral data: nmr δ 0.80, 1.02, 1.10, 1.23 (s, 12 H, CCH_3), 1.68 (d, 1 H, J = 12 Hz, C_3 exo proton), 1.90 (2, 3 H, $COCH_3$), 2.78 (d, 1 H, J = 4 Hz, C_1 bridgehead proton), 5.62 (d, 1 H, J = 6 Hz, C_5 vinyl proton), and 6.06 ppm (d, 1 H, J = 6 Hz, further split into a doublet with J = 4 Hz, C_6 vinyl proton); ir 3040 (olefinic CH) and 1720 cm^{-1} (ester C=O).

B.—A solution of 0.3426 g of the *p*-nitrobenzoate of **3b** in 20 ml of glacial acetic acid was refluxed for 24 hr. The mixture was worked up as in the preceding experiment. Glc showed the product to consist of 65% **5** and 35% **6c**.

Reduction of 6c with Lithium Aluminum Hydride.—A 130-mg sample of **6c** was reduced with lithium aluminum hydride. After aqueous work-up glc of the product showed one peak corresponding to **6a** in ir and retention time.

Acid-Catalyzed Rearrangement of 4a and 4b. A. Without Solvent.—A mixture of 0.54 g of alcohols (75% **4a**, 25% **4b**) and one drop of concentrated sulfuric acid was distilled from a bath maintained at 150–160° and 40 mm to give 0.46 g of material, bp 100–105° (40 mm). Glc showed *ca.* 80% **14**. A glc-purified sample of **14** gave the following spectral and analytical data: nmr δ 0.85, 0.96, 0.98 (s, 9 H, CCH_3), 1.32 (d, 1 H, J = 14 Hz, HCH), 1.82 (d, 1 H, J = 14 Hz, HCH), 1.63 (d, 1 H, J = 18 Hz, allylic HCH), 2.17 (d, 1 H, J = 18 Hz, allylic HCH), 1.63 (br s, superimposed on preceding AB spectrum, 3 H, vinyl CH_3), 5.04 (br s, 1 H, vinyl proton), and 9.36 ppm (s, 1 H, CHO); ir 2680 (aldehydic CH), 1715 (aldehydic C=O), and very weak absorption below 1300 cm^{-1}; mass spectrum (80 eV) *m/e* (rel intensity) 166 (1.6), 151 (6.6), 149 (10), 148 (42), 138 (12), 137 (100), 135 (7), 133 (21), 124 (6), 123 (32), 121 (12), 110 (6), 109 (12), 108 (9), 107 (79), 105 (11), 97 (13), 96 (9), 95 (39), 93 (10), 91 (22), etc.; uv λ_{max} 274 (ϵ 56) and 266 nm (ϵ 56) with $\epsilon_{210\,nm}$ 4330 (trisubstituted double bond).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.45; H, 10.91. Found: C, 79.37; H, 10.91.

B. In Aqueous Acetic Acid.—A mixture of 295 mg of alcohols (74% **4a**, 21% **4b**, 5% impurity), 2 ml of water, 5 ml of glacial acetic acid, and 4 drops of concentrated sulfuric acid was refluxed for 30 min. The mixture was cooled, poured into ether, and neutralized with aqueous sodium carbonate. Glc showed the product to consist of 93% one peak which was collected to give 170 mg (57%) of material. The nmr spectrum of this material showed the appearance of new absorption at δ 0.75 with a corresponding decrease in absorption at 0.98 and new absorptions at 1.60 (vinyl CH_3), 5.24 (C=CH), and 9.32 ppm (CHO), as compared to the spectrum of **14** obtained in the preceding experiment. From the relative intensities of the absorptions of the vinyl proton and aldehydic proton peaks the material was estimated to be 60% **14** and 40% **15**.

C. In Deuterium Oxide–Deuterioacetic Acid Solution.—A mixture of 0.25 ml of alcohols (80% **4a**, 20% **4b**), 5 ml of deuterioacetic acid, 2.5 ml of deuterium oxide, and 5 drops of concentrated sulfuric acid was refluxed for 30 min. The mixture was cooled, diluted with pentane, and neutralized with solid sodium carbonate. The residue was filtered and concentrated. Glc showed 75% one peak which was collected. The deuterium content was estimated from the mass spectrum to be 5% d_0, 78% d_1, and 17% d_2. The nmr spectrum[16] of this material showed that isomerization to deuterio-**15** had not occurred and showed the methyl groups at δ 0.85, 0.96, 0.98, the vinyl methyl group at 1.64, and the C_2-AB spectrum at 1.32 (d, J = 14 Hz) and 1.80 ppm (d, J = 14 Hz). The C_6-AB spectrum exhibited by **14**-d_0 had collapsed to a *ca.* one-proton absorption at δ 1.60 ppm, confirming deuterium incorporation at C_6. The remainder of the spectrum showed absorption at δ 5.12 (br s, 1 H, C=CH) and 9.36 ppm (s, 1 H, CHO).

Acid-Catalyzed Isomerization of 14. A.—A mixture of 60 mg of **14** (containing 10% **15** from the nmr spectrum), 1 ml of water, 2 ml of glacial acetic acid, and 2 drops of concentrated sulfuric acid was refluxed for 2.5 hr, cooled, diluted with ether, and neutralized with aqueous sodium carbonate. Glc showed one product peak which was collected. The nmr spectrum showed this material to consist of 40% **14** and 60% **15**.

B.—A mixture of 300 mg of **14**, 5 ml of water, 10 ml of glacial acetic acid, and 10 drops of concentrated sulfuric acid was refluxed for 2 hr, cooled, diluted with ether, neutralized with aqueous sodium carbonate, dried, and reduced with lithium aluminum hydride. Glc of the reduced material showed 10% an unknown material which showed no functional groups in the ir spectrum, 57% **17**, and 33% **16**, in order of retention.

A glc-purified sample of **17** gave the following spectral data: nmr δ 0.93 (s, 9 H, CCH_3), 1.66 (br s, 3 H, $C{=}CCH_3$), 3.12 (s, 2 H, CH_2), and 5.04 ppm (br s, 1 H, C=CH); the remaining protons absorbed at δ 1–2 ppm and did not give clearly resolved patterns; ir 3350 (OH), 1040, 835 cm^{-1}; mass spectrum (80 eV) *m/e* (rel intensity) 168 (2.8), 138 (30), 137 (100), 135 (35), 121 (7), 109 (7), 108 (6), 107 (27), 105 (10), 96 (10), 95 (91), etc.

A glc-purified sample of **16** gave the following spectral data: nmr δ 0.80–1.05 (9 H, CCH_3), 1.18 (d, 1 H, J = 14 Hz, HCH), 1.38 (d, 1 H, J = 14 Hz, HCH), 1.47 (d, 1 H, J = 16 Hz, allylic HCH), 1.78 (d, 1 H, J = 16 Hz, allylic HCH), 1.58 (singlet superimposed on preceding AB spectrum, $C{=}CCH_3$), 3.24 (s, 2 H, OCH_2), and 5.05 ppm (s, 1 H, C=CH); ir 3350 (OH), 1040, 840 cm^{-1}; mass spectrum (80 eV) *m/e* (rel intensity) 168 (4.8), 153 (8), 138 (17), 137 (100), 136 (8), 122 (13), 121 (19), 109 (14), 108 (11), 107 (85), 105 (13), 97 (21), 96 (15), 95 (52), etc.

Catalytic Hydrogenation of 14.—A 53-mg sample of **14** in 5 ml of ethyl acetate was hydrogenated at room temperature and atmospheric pressure over the catalyst from 53 mg of platinum oxide. The hydrogen uptake (11 ml or 1 equiv) ceased after 1 hr. The mixture was filtered and concentrated. Glc showed only one product peak which was collected. The nmr and ir spectra were identical with those of **16** obtained upon reduction of **14** with lithium aluminum hydride.

Preparation of the *p*-Nitrobenzoate of 4a.—A mixture of 2.3 g (0.0138 mol) of alcohols (88% **4a**, 12% **4b**), 10 ml of anhydrous pyridine, and 4.5 g (0.024 mol) of *p*-nitrobenzyl chloride was stirred overnight at room temperature and then poured into a ligroin-water mixture and filtered. The ligroin layer was separated and the aqueous layer was extracted with ligroin. The combined organic layers were dried, concentrated, and crystallized in Dry Ice to give 3.2 g (0.014 mol, 75%) of material, mp 72–92°. Recrystallization from pentane gave 2.0 g of material, mp 83–87°, which gave the following nmr spectral data: δ 0.99, 1.07 (s, 6 H, CCH_3), 1.73 (br s, 3 H, $C{=}CCH_3$), 1.58 (s, 3 H, $OCCH_3$), 2.00 (d, 1 H, J = 14 Hz, HCH), 2.39 (d, 1 H, J = 14 Hz, HCH), 2.72 (br s, 1 H, C_1 bridgehead proton), 3.46 (br s, 1 H, C_5 bridgehead proton), 5.80 (br s, 1 H, $C{=}CH$), and 8.0–8.3 ppm (4 H, aromatic protons).

Acetolysis of the *p*-Nitrobenzoate of 4a.—A mixture of 0.3336 (10.8 mmol) of the *p*-nitrobenzoate of **4a**, 0.2036 g (25 mmol) of anhydrous sodium acetate, and 10 ml of glacial acetic acid was refluxed for 26 hr, cooled, diluted with ether, and neutralized with aqueous sodium carbonate. The organic layer was dried and concentrated to give 400 mg of material. Glc showed the product to consist of 73% **11b** and 27% **12b** in order of retention. When a similar acetolysis mixture was refluxed for 6 hr, glc showed 87% **11b** and 13% **12b**. A reflux period of 52 hr resulted in 37% **11b** and 63% **12b**.

A glc-purified sample of **11b** gave the following spectral data: nmr[18] 1.00, 1.16, 1.31 (s, 9 H, CCH_3), 1.91 (d, 3 H, J = 1.5 Hz, $CH{=}CCH_3$), 2.10 (s, 3 H, $COCH_3$), 2.20 (br s, 1 H, C_1 bridgehead proton), 4.25 (br s, 1 H, OCH), and 5.55 ppm (br s, 1 H, $C{=}CH$), remainder of spectrum not clearly enough resolved for assignment; ir 3030 (olefinic CH), 1735 (ester $C{=}O$), 1200–1280, 1035, 795 cm^{-1}.

A glc-purified sample of **12b** gave the following spectral data: nmr[17] δ 1.00, 1.09, 1.29 (s, 9 H, CCH_3), 2.12 (br s, 5 H, $COCH_3$ plus other protons), 2.40 (br s, 1 H, C_1 bridgehead proton), 4.55 (br s, 1 H, OCH), and 4.80 and 4.94 ppm (br s, 2 H, $={CH_2}$); ir 3050 (olefinic CH), 1735 (ester $C{=}O$), 1200–1280, 1050, 855–900 cm^{-1}.

Isomerization of 11b to 12b under Acetolysis Conditions.—A 200-μl sample of acetates consisting of 85% **11b** and 15% **12b** was refluxed with 99 mg of anhydrous sodium acetate in 5 ml of glacial acetic acid for 24 hr. The mixture was worked up as above. Glc showed the product to consist of 55% **11b** and 45% **12b**.

Preparation of 11a and 12a.—A 1.08-g sample of the *p*-nitrobenzoate of **4a** was subjected to acetolysis for 24 hr as described above to give 0.6 g of crude acetates (45% **11b**, 55% **12b**). The crude mixture was reduced with lithium aluminum hydride. Glc of the reduction product showed 50% **11a** and 50% **12a**, in order of retention.

A glc-purified sample of **11a** gave the following analytical and spectral data: nmr[17] δ 0.90, 1.08, 1.34 (s, 9 H, CCH_3), 1.58 (d, 1 H, J = 11 Hz, C_3 exo proton), 1.74 (d, 3 H, J = 1.5 Hz, $CH{=}CCH_3$), 1.88 (br s, 1 H, C_1 bridgehead proton), 3.30 (br s, 1 H, OCH), and 5.43 ppm (q, 1 H, J = 1.5 Hz, $CCH_3{=}CH$); ir 3400 (OH), 3040 (olefinic CH), 1060, 795 cm^{-1}.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.45; H, 10.91. Found: C, 79.46; H, 10.92.

A glc-purified sample of **12a** gave the following analytical data: nmr[17] δ 0.92, 1.04, 1.28 (s, 9 H, CCH_3), 1.82–2.05 (m, 2 H, CH_2), 2.12 (br s, 1 H, C_1 bridgehead proton), 3.62 (br s, 1 H, OCH), and 4.60 and 4.74 ppm (br s, 2 H, $={CH_2}$); ir 3400 (OH), 3050 (olefinic CH), 1640 ($C{=}C$), 1070, 875 cm^{-1}.

Acid-Catalyzed Rearrangement of 11a and 12a. A.—A mixture of 100 μl of **11a**, 2 ml of glacial acetic acid, 1 ml of water, and 2 drops of concentrated sulfuric acid was refluxed for 30 min. The mixture was cooled, diluted with ether, and neutralized with aqueous sodium carbonate. Glc of the concentrated mixture showed one product peak which was collected and gave the following spectral data: ir 2680 (aldehydic CH) and 1715 cm^{-1} (aldehydic $C{=}O$); nmr correspond to *ca.* 60% **14** and 40% **15**.

B.—A mixture of 100 μl of **12a** was treated as in the preceding experiment. Glc showed one product peak which was collected and gave the following spectral data: ir 2680 (aldehydic CH) and 1715 cm^{-1} (aldehydic $C{=}O$); nmr corresponded to *ca.* 50% **14** and 50% **15**.

Catalytic Hydrogenation of 11a and 12a. A.—A 49.3-mg sample of **11a** (containing 10% **12a**) in 10 ml of ethyl acetate was hydrogenated at room temperature and atmospheric pressure over the catalyst from 35 mg of platinum oxide. The hydrogen uptake (6 ml or 0.93 equiv) ceased after 5 min. The reaction mixture was filtered and concentrated. Glc showed the product to consist of 95% one peak which was collected. The ir spectrum of this material showed a band at 1735 cm^{-1} (ester $C{=}O$).

B.—A 59.4-mg sample consisting of 55% **11a** and 45% **12a** in 10 ml of ethyl acetate was hydrogenated at room temperature and atmospheric pressure over the catalyst from 35 mg of platinum oxide. The hydrogen uptake (9.0 ml or 1.1 equiv) ceased after 10 min. Glc of the product showed two peaks in the relative amounts of 10 and 90% which were collected. The ir spectrum of the minor component showed absorption at 1735 cm^{-1} (ester $C{=}O$) and was identical with that of the product obtained in the preceding experiment. The glc-purified sample of reduced acetate gave the following additional spectral data: nmr[17] δ 3.69 (s, 1 H, OCH), 1.66 (s, $COCH_3$), and 0.70–2.0 ppm (remaining protons); mass spectrum (80 eV) m/e (rel intensity) 135 (65), 107 (74), 97 (42), 95 (64), 94 (78), 85 (50), 83 (80), 71 (43), 69 (37), 67 (35), 55 (100), etc.

Registry No.—**3a**, 27730-24-1; **3b**, 27730-25-2; *p*-nitrobenzoate of **3b**, 27730-26-3; **4a**, 27730-27-4; *p*-nitrobenzoate of **4a**, 27730-28-5; **4b**, 27730-29-6; **5**, 27669-94-9; **6a**, 27730-30-9; **6b**, 27730-31-0; **6c**, 27730-32-1; **9**, 27723-23-5; **11a**, 27730-33-2; **11b**, 27730-34-3; **12a**, 27730-35-4; **12b**, 27723-24-6; **14**, 27669-95-0; **16**, 27723-25-7; **17**, 27723-26-8.