The Acid-Promoted Opening of the Three-Membered Ring in *endo*-6-Methylbicyclo[3.1.0]hexane[1]

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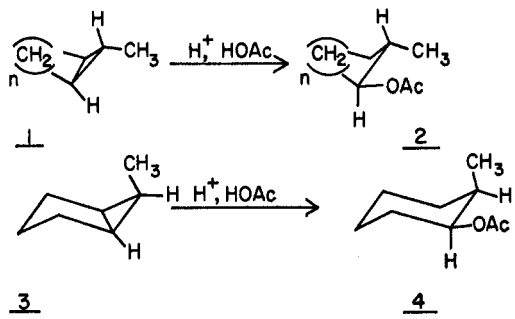
Received November 19, 1969

Addition of acetic acid to *endo*-6-methylbicyclo[3.1.0]hexane gives nearly equal amounts of methylcyclopentyl acetate and *cis*-2-methylcyclohexyl acetate. Addition of acetic acid-O-*d* gave methylcyclopentyl acetate containing 1% d_2 labeled species as determined by mass spectral analysis. The d_2 content of the *cis*-2-methylcyclohexyl acetate produced in the same reaction was assumed to be the same. The stereoselectivity of acetate formation in the cleavage of the bond common to both rings is reflected in the 47:2 ratio of *cis*-/*trans*-2-methylcyclohexyl acetate. These results are compared with earlier studies of the acid-promoted opening of *exo*-6-methylbicyclo[3.1.0]hexane. The mechanistic rationale for these results is discussed in terms of bond-protonated or carbon-bridged intermediates.

Stereoselectivity in the acid-promoted addition of acetic acid across the internal strained bond of bicyclo[*n*.1.0] alkanes has been observed for *exo*-7-methylbicyclo[4.1.0]heptane (**1**, $n = 4$) and *exo*-6-methylbicyclo[3.1.0]hexane (**1**, $n = 3$).[2] Respectively, *trans*-2-methylcycloheptyl (**2**, $n = 4$) and *trans*-2-methylcyclohexyl (**2**, $n = 3$) acetates were by far the predominant acetates produced in the internal mode of cleavage.



In order to learn whether internal cleavage is truly stereoselective or not, the acid-promoted addition of acetic acid to *endo*-6-methylbicyclo[3.1.0]hexane (**3**), has been studied. Should cleavage of the internal bond of **3** and resulting acetate formation again occur with inversion, *cis*-2-methylcyclohexyl acetate (**4**) would be expected.

Results

The treatment of *endo*-6-methylbicyclo[3.1.0]hexane with 0.09 *N* sulfuric acid in glacial acetic acid at 47° for 26 hr gave a product mixture containing 11% olefins and 89% acetates as determined by gas–liquid partition chromatography (glpc). Further glpc analysis of the olefin mixture demonstrated the presence of 1-methylcyclohexene, 1-ethylcyclopentene, and 3-methylcyclohexene in the relative percentages given in Table I. These olefins were identified by gas chromatographic retention times using two different columns. In addition 1-methylcyclohexene, the predominant olefin, was isolated by preparative glpc and identified by comparative infrared (ir) and nuclear magnetic resonance (nmr) spectra. No detectable peaks corresponding to the retention times of ethylidenecyclopentane, 3-ethylcyclopentene, vinylcyclopentane, or unconverted 6-*endo*-methylbicyclo[3.1.0]hexane could be found in the chromatograms.

The mixture of acetates was not analyzed directly but was converted, by lithium aluminum hydride hydrogenolysis, to a mixture of alcohols which was more readily separated by glpc than the mixture of acetates. The alcohol mixture consisted of methylcyclopentylcarbinol, *cis*-2-methylcyclohexanol, *trans*-2-methylcyclohexanol, *cis*-2-ethylcyclopentanol, and *trans*-2-ethylcyclopentanol in the relative percentages given in Table I. Methylcyclopentylcarbinol and *cis*-2-methylcyclohexanol, the two major alcohols, were separated by preparative glpc and identified by comparative ir.

The ring-opening solvolysis of *endo*-6-methylbicyclo[3.1.0]hexane was repeated using 0.09 *N* deuteriosulfuric acid in acetic acid-O-*d* solution. The deuterated acids were used primarily to ascertain the degree of reversible protonation prior to cyclopropyl bond cleavage and the extent of olefin to acetate conversion. Glpc analyses showed the distribution of acetates (alcohols) and olefins as given in the second row of Table I. The mixture of alcohols was oxidized to a mixture of ketones which consisted of two major components as revealed by glpc. These were separated and identified as methylcyclopentyl ketone and 2-methylcyclohexanone by comparative glpc and mass spectra. 1-Methylcyclohexanol, clearly distinguishable from the ketones by gas chromatography, could not be detected in the chromatogram of the mixture of ketones.

The isotopic distribution of the labeled methycyclopentylcarbinol was 17% d_0, 82% d_1, and 1% d_2 and was assumed to be the same for labeled *cis*-2-methycyclohexanol. The latter was not isolated for mass spectral isotopic analysis because of anticipated difficulty in obtaining a meaningful isotopic analysis when $M^+ - 1$ becomes significantly large relative to a low intensity M^+ peak, as is frequently the case for cyclohexanols. The isotopic distribution of methylcyclopentyl ketone was 16% d_0, 83% d_1, and 1% d_2 before, and 17% d_0, 83% d_1, and 0% d_2 after sodium methoxide–methanol exchange. For 2-methylcyclohexanone, the distribution was 19% d_0, 80% d_1, and 1% d_2 before, and 20% d_0, 80% d_1, and 0% d_2 after exchange.

A further test of the kinetic control of acetate formation was the observation that neither methylcyclo-

(1) (a) Paper VIII in a series dealing with carbon–carbon bond fission in cyclopropanes. (b) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for support of this work. Acknowledgment is also made to the National Science Foundation for assistance in the purchase of the mass spectrometer used in this study.

(2) R. T. LaLonde and M. A. Tobias, *J. Amer. Chem. Soc.*, **86**, 4068 (1964).

Table I

Product Distribution from *endo*- and *exo*-6-Methylbicyclo[3.1.0]hexane on Acid-Promoted Acetolysis[a]

	Acetates (alcohols), 100%						Olefins, 100%				
Reactant	Acetate, %	AcO	OAc *cis*	OAc *trans*	OAc *cis*	OAc *trans*	Olefin, %				
3[b]	89	48	2	1	47	2	11	0	14	80	7
3[c]	86	49	2	1	46	2	14	0	17	77	7
1 (n = 3)[d]	80	52	2	7	2	37	20	1	27	55	18

[a] The accuracy of the distributions is qualified by the lack of control experiments to determine the degree of fractionation of olefins and acetates occurring in work-up. [b] Glacial acetic acid, 0.09 N sulfuric acid, 47°, 26 hr. [c] Acetic acid-O-*d*, 0.09 N deuteriosulfuric acid, 47°, 26 hr. [d] Reference 2.

pentylcarbinyl acetate nor *cis*-2-methylcyclohexyl acetate is isomerized on treatment with 0.09 N sulfuric acid in glacial acetic acid at 47°.

The reactivities of two of the olefins produced from **3** were assessed. Treatment of 1-methylcyclohexene with 0.09 N sulfuric acid in acetic acid at 47° for 26 hr resulted in a 6% conversion to 1-methylcyclohexyl acetate. Similar treatment of 3-methylcyclohexene for 52 hr resulted in less than 5% conversion to acetates which consisted of 1% methylcyclopentylcarbinyl acetate, 17% 2-methylcyclohexyl acetate, and 82% 3-methylcyclohexyl acetate. The relative amounts of these acetates and their identities is based on mass spectral analysis of the mixture of alcohols, obtained on lithium aluminum hydride hydrogenolysis of the acetates, and mass and infrared spectral and gas chromatographic analysis of the corresponding mixture of ketones.

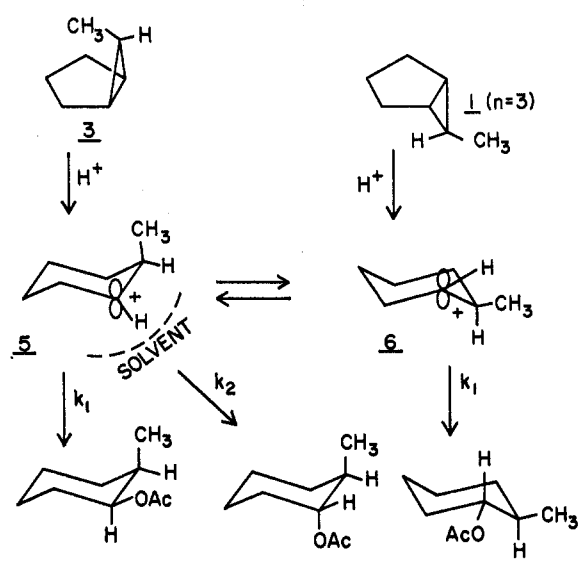
Discussion

The product analyses as summarized in Table I reveal that internal bond rupture in **3** gives *cis*- and *trans*-2-methylcyclohexyl acetate in a ratio of 47:2. The results of earlier work with the isomeric 6-*exo*-methylbicyclo[3.1.0]hexane (**1**, n = 3) are also summarized in Table I and show a somewhat lower degree of stereospecificity, the ratio of *trans* to *cis* acetate being 37:2.

The results of the ancillary experiments indicate that acetates are formed directly by addition of acetic acid across the internal bond of **3**. Thus the absence of 1-methylcyclohexyl acetate formation as well as multiple deuterium labeling show that acetates are not formed competitively by addition to the olefins produced. The low level of olefin reactivity, relative to the bicycloalkane **3**, is also demonstrated. Less than 10% of 1- and 3-methylcyclohexene are converted to acetates under conditions which completely transform **3** to acetate. Finally, the demonstrated stability of the two major acetates, *cis*-2-methylcyclohexyl acetate and methylcyclopentylcarbinyl acetate, shows that the acetate distribution represents largely the products generated directly in the ring cleavage step. Relevant confirmatory evidence comes from an earlier observation. When ring cleavage of bicyclo[3.1.0]hexane was carried out in 0.07 N sulfuric acid at 47°, the distribution of acetates remained constant for reaction periods of 0.5, 1.0, 41, and 61 hr.[3] When cleavage of bicyclo[4.1.0]heptane was carried out under the same conditions, the acetate distribution remained constant for reaction periods of 0.5, 1.0, 24 and 86 hr.[3]

The observed stereospecificity of acetate formation in internal bond cleavage clearly is inconsistent with a mechanism involving equilibrating 2-methylcyclohexyl carbonium ions (Scheme I). If equilibrating 2-methylcyclohexyl carbonium ions, **5** and **6** had been involved, both 6-methylbicycloalkanes would have furnished the same mixture of acetates.

Scheme I



Other variations of a secondary carbonium ion rationale would also be inconsistent with results. An unsymmetrically solvated carbonium ion (**5**), one in which the solvent is associated with the side of the ring opposite the methyl group, could possibly account for stereoselectivity, but such a carbonium ion would lead on collapse (k_2) to the *trans*, not the *cis* isomer. Assuming symmetrical solvation of the carbonium ion **5**, a slight predominance of the *cis* acetate could be expected on the basis of the nearly fourfold preference[4,5] for equatorial (k_1) over axial (k_2) attack of a chair cyclohexyl carbonium ion. Reasonably, the estimated preference for equatorial solvolysis would be even less than fourfold in the case of **5** because of the obstruction to equatorial attack by the adjacent axial methyl group. The observed preference for *cis* over *trans* acetate formation from **3** is 47:2, a ratio much in excess of what could be expected from equatorial solvent attack of **5**. Moreover should the principal pathway to 2-methylcyclohexyl acetates involve a carbonium ion

(3) R. T. LaLonde and L. S. Forney, *J. Amer. Chem. Soc.*, **85**, 3767 (1963).

(4) J. A. Berson and P. Reynolds-Warnhoff, *ibid.*, **86**, 595 (1964).

(5) A. Streitweiser and C. E. Coverdale, *ibid.*, **81**, 4275 (1959).

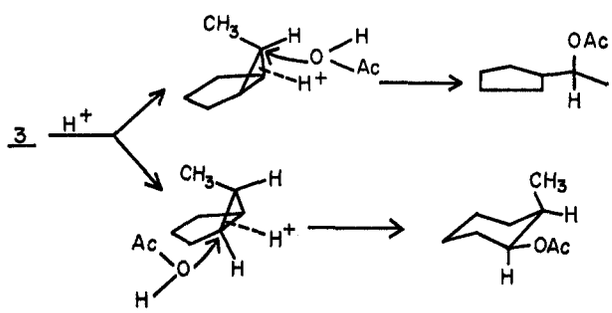
intermediate, then solvolysis of **1** (n = 3) occurring with preferential equatorial attack of carbonium ion **6** would be expected to give a *trans* to *cis* ratio of nearly four, but the observed ratio is 37:2. Nevertheless, while a carbonium ion pathway does not appear to be the major one, it cannot be dismissed altogether. The formation of some *trans*-2-methylcyclohexyl acetate from **3** and *cis*-2-methylcyclohexyl acetate from **1** (n = 3) suggests the involvement of a carbonium ion process competing to a minor degree with a more stereospecific one.

Besides stereospecificity, there are two other features of the ring opening of **3** which should be considered in attempting to formulate a mechanistic rationale. One of these is the distribution of acetates resulting from internal and external modes of bond rupture. In the case of **3**, 50% of the acetates arise from external bond cleavage and 50% arise from internal cleavage. By comparison, the *exo*-methyl isomer **1** (n = 3) produces 39% of the acetates by internal bond rupture and 61% by external rupture.

The other feature of the acetate distribution to be considered is the disparity of acetates arising from two possible modes of external cleavage. As the data in Table I illustrates, methylcyclopentylcarbinyl acetate formation far exceeds the formation of 2-ethylcyclopentyl acetate. Possibly the predominance of methylcyclopentylcarbinyl acetate formation might be attributed to a relatively larger number of low energy pathways leading to this type of product. Conceivably one such additional pathway could involve a carbonium ion–ring contraction route. However, this route to cyclopentylcarbinyl acetate does not seem likely on the basis of known structural requirements for ring contraction. Goering[6] has pointed out that ring contraction is involved in the dehydration of equatorial cyclohexanols if C_2 is substituted with (1) two alkyl groups, (2) an alkyl group and a hydroxyl group, (3) a hydroxyl group, or (4) a phenyl group. Evidently a single alkyl substituent is insufficient for contraction. There are numerous other examples which illustrate that the potential leaving group must be *trans* coplanar to the migrating carbon atom. Acetolysis of *trans*-2-phenylcyclohexyl tosylate produces 40% ring-contracted product but less than 2% of this type of product results from the acetolysis of *cis*-2-phenylcyclohexyl acetate.[7] No ring contractions have been observed in the acetolysis of either *cis*- or *trans*-2-alkylcyclohexyl tosylates,[8,9] although deamination of *trans*-2-methylcyclohexyl amine in aqueous acetic acid gives about 7% ring-contracted olefin[10] and 10% ring-contracted alcohol. The bicyclo[n.1.0]alkanes possess neither the substituent nor stereochemical requirement for contraction,[11] and therefore the ring contraction route to methylcyclopentylcarbinyl acetate seems remote. In connection with the consideration of rearrangement routes to products, it should be mentioned that the stereospecificity in 2-methylcyclohexyl acetate formation could not be accounted for by the reverse rearrangement, *i.e.*, a ring expansion–carbonium ion route.

The three features of the acetate distribution which must be accounted for are stereospecificity, the disproportionately large extent of internal bond rupture, and the preference for the formation of methylcyclopentylcarbinyl acetate resulting from the external mode of rupture. Possibly one way to account for these reactivity characteristics is by nucleophilic solvent attack of bond-protonated intermediates as postulated earlier[2,3,12,13] and depicted in Scheme II. According to this interpretation, the ratio of the two predominating

SCHEME II



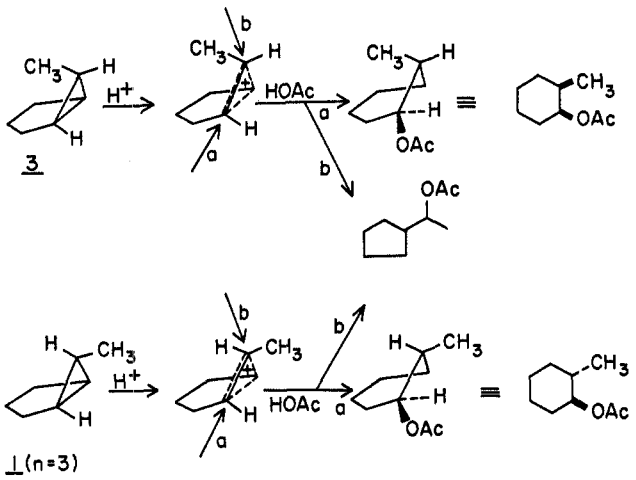
acetates would, for the most part, reflect the populations of externally and internally protonated intermediates. In terms of the bond-protonated species, the greater degree of internal rupture in **3** can be attributed to the greater strain of the internal bond in **3**, relative to that of **1** (n = 3), which results from the crowding of methyl and trimethylene ring hydrogens. The direct relationship between the extent of internal cleavage and strain has already been noted in connection with earlier work.[14] For example, bicyclo[2.1.0]pentane, which possesses a severely strained internal bond,[15] undergoes only internal bond cleavage.[3] In contrast the ratio of total acetates produced by internal and external bond rupture in *exo*-methylbicyclo[4.1.0]heptane, **1** (n = 4), is 32:68,[2] a value close to the statistical ratio of 33:67.

An explanation to account for the preference for methylcyclopentylcarbinyl acetate formation in the external mode of cleavage may lie in the greater accessibility of C_6 than C_1 to an approaching nucleophile. An examination of a model of **3** and **1** (n = 3) shows that hydrogens lying beneath the trimethylene ring (C_2, C_3, and C_4) make backside approach at the bridgehead positions more difficult than the same mode of approach to C_6.

Alternatively, carbon-bridged intermediates, as depicted in Scheme III, possibly might be used to explain the formation of methylcyclopentylcarbinyl and *cis*-2-methylcyclohexyl acetates, although the role of such intermediates has been discounted in the deamination of propyl amines and in the addition of sulfuric acid to cyclopropane.[16] To the extent that such intermediates are generated from **1** (n = 3) and **3** (Scheme III) in the

(6) H. L. Goering, R. L. Reeves, and H. H. Espy, *J. Amer. Chem. Soc.*, **78**, 4926 (1956).
(7) S. A. Roman and W. D. Closson, *ibid.*, **91**, 1701 (1968).
(8) H. L. Goering and R. L. Reeves, *ibid.*, **78**, 4831 (1956).
(9) W. Hückel and C. M. Jennewien, *Justus Liebigs Ann. Chem.*, **683**, 100 (1965).
(10) W. Hückel and M. Hanack, *Angew. Chem., Int. Ed. Engl.*, **6**, 534 (1967).
(11) In the bicyclo[n.1.0]alkanes, the potential leaving group, a strained carbon–carbon bond, is *cis* to the migrating carbon atom.
(12) R. T. LaLonde and M. A. Tobias, *J. Amer. Chem. Soc.*, **85**, 3771 (1963).
(13) For other references, see C. J. Collins, *Chem. Rev.*, **69**, 541 (1969).
(14) R. T. LaLonde and L. S. Forney, *J. Org. Chem.*, **29**, 2911 (1964).
(15) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Amer. Chem. Soc.*, **90**, 4315 (1968).
(16) For a review, see the source given in ref 13.

Scheme III



slow step of a two-step sequence, equal amounts of methylcyclopentylcarbinyl and 2-methylcyclohexyl acetates should be formed, but actual amounts of the two acetate types produced from **1** ($n = 3$) and **3** could also reflect the factors of relative strain relief and selective obstruction to nucleophilic solvent attack, even though the second step be the faster of the two. Since the importance of the relief of strain and the selective obstruction to nucleophilic attack cannot be assessed, the influence of these two factors in altering the product distribution from carbon-bridged ions cannot be known. Consequently, a distinction between carbon-bridged and bond-protonated mechanisms cannot be made on the basis of the product analysis reported here.

Experimental Section

Spectra were obtained as follows: nmr, in CCl_4, 2% TMS (τ 10) using a Varian A-60A spectrometer; ir, in CCl_4 using a Perkin-Elmer 137 spectrometer; mass using a Hitachi Perkin-Elmer RMU6 spectrometer with all glass heated inlet, chamber temperature 165°, 70eV.

Elemental analyses were determined by Galbraith Laboratories, Knoxville, Tenn. Melting points are uncorrected and were determined on a Mel-Temp apparatus. Glpc analyses were obtained on a Varian Aerograph Model 200 using helium as the carrier gas and the columns indicated.

Materials.—Acetic acid-O-*d* was prepared from acetic anhydride and D_2O. The D_2SO_4 was purchased from Merck and Co. Ltd. 1-Methylcyclohexene, methylcyclopentylcarbinol, 2-methylcyclohexanone, and methylcyclopentyl ketone were purchased from the Aldrich Chemical Company and purified. *cis*- and *trans*-2-methylcyclohexanol were prepared by the method of Eliel and Lukach.[17] All other olefins and cycloalkanols used as authentic comparison samples were prepared earlier[18] by well-known procedures.

***endo*-6-Methylbicyclo[3.1.0]hexane (3). A. From Bicyclo[3.1.0]hexane-*endo*-6-carboxylic Acid.**—The title acid was prepared by the method of Meinwald, Labana, and Chada,[19] mp 83–84°. A 15.5-g sample of the acid (0.12 mol) in 100 ml of anhydrous ether was added dropwise to 5.6 g (0.15 mol) of $LiAlH_4$ in 250 ml of ether. After heating to reflux for 5 hr, the mixture was cooled, water was added cautiously, and 100 ml of 4 *N* H_2SO_4 was added to dissolve the salts. The aqueous layer was extracted with ether. The combined extracts were washed successively with water, 5% aqueous $NaHCO_3$, and saturated brine, and then dried ($MgSO_4$). The ethereal extract was concentrated and distilled giving 12.5 g (83.5%) of *endo*-6-hydroxymethylbicyclo[3.1.0]hexane: mp 86–87° (12 mm), reported[20] 79–85° (9 mm); ir 3300 (OH), 2950 (CH), 1025 cm^{-1} (CO); nmr 6.41 (s, 1, D_2O exchangeable and concentration dependent, OH), 6.55 (d, 2, J = 1.8 Hz, CH_2OH), 7.8–9.3 (m, 9 H); 3,5-dinitrobenzoate mp 103–104° (from EtOH), reported[20] 102.5–103.8°.

endo-6-Hydroxymethylbicyclo[3.1.0]hexane, 11 g (0.10 mol), was added to 7 g (0.085 mol) of aluminum isopropoxide. The stirred mixture was heated at 95° until all the isopropyl alcohol had distilled. Twenty grams of freshly distilled anisaldehyde was added and the mixture was maintained at 120° and 10 mm for 1 hr in a distillation apparatus. The 7 g of colorless liquid which distilled was then redistilled giving 5 g (47%) of bicyclo[3.1.0]hexane-6-carboxaldehyde: bp 63–65° (10 mm); ir 3130, 3090, 2990 (CH), 1700 (CH=O), 1210, 1100, 935 cm^{-1}; nmr τ 0.55 (d, 1, J = 5.2 Hz, CH=O), 7.7–8.7 (m, 9 H). The aldehyde was stored at Dry Ice temperature since it was unstable at room temperature.

Bicyclo[3.1.0]hexane-6-carboxaldehyde, 5.5 g (0.05 mol), 6.5 g of 85% hydrazine hydrate, and 0.2 ml of glacial acetic acid were heated at 120° in a distillation apparatus until water no longer distilled. To the distillation residue was added 0.5 g of powdered sodium hydroxide in 2 ml of triethylene glycol. The resulting mixture was maintained at 160° for 1 hr. During this time 3.5 ml of hydrocarbon distilled. Glpc (8 ft × 0.25 in., 4% squalane on Celite, 80°) showed *exo*- and *endo*-6-methylbicyclo[3.1.0]hexane present in the ratio of 1:7. Preparative-scale glpc gave *exo*-6-methylbicyclo[3.1.0]hexane (1, n = 3)[2] and *endo*-6-methylbicyclo[3.1.0]hexane (**3**): ir 3000, 2930, 2860, 1450, 1390, 1330 cm^{-1}; nmr τ 7.9–8.9 (m, 8 H), 9.0–9.2 (m, 4 H).

Anal. Calcd for C_7H_{12}: C, 87.42; H, 12.58. Found: C, 87.65; H, 12.70.

B. From Cyclopentene, Ethylidene Iodide, and Diethyl Zinc.—According to the procedure of Nishimura, Kawabate, and Furukawa,[21] 9.4 ml of ethylidene iodide (0.1 mol) was added dropwise over a period of 1 hr to a mixture of 3.4 g (0.05 mol) of cyclopentene, 6.0 ml (0.006 mol) of diethylzinc, and 25 ml of hexane under nitrogen. The resulting mixture was heated to reflux for 2 hr, cooled, and poured cautiously into a stirred mixture of 25 ml of 1% aqueous HCl and 20 ml of ether. The aqueous layer was extracted several times with ether. The combined extracts were washed successively with water, 5% aqueous $NaHCO_3$, and saturated brine, and dried ($MgSO_4$). The ethereal extract was concentrated and then distilled giving 1.6 g of hydrocarbon, bp 120–132° (1 atm). Glpc analysis (5 ft × 0.25 in., 20% Se-30, 75°) showed the presence of two components in the ratio of 2:3. The two hydrocarbons were separated by preparative scale gas chromatography. The minor component was identified by comparative ir as the *exo*-6-methyl isomer; the major component displayed the same ir and nmr characteristics as the sample of the *endo*-6-methyl isomer described in part A.

Opening of *endo*-6-Methylbicyclo[3.1.0]hexane. A. With H_2SO_4 and Acetic Acid.—A sealed glass tube containing 0.80 g (8.3 mmol) of *endo*-6-methylbicyclo[3.1.0]hexane, 50 mg of 96% H_2SO_4, and 11.0 ml of glacial acetic acid was maintained at 47° for 26 hr. The reaction mixture was processed as described earlier.[3] In this manner was obtained 1.54 g of yellow oil: ir 1710, 1370, 1240, and 1130 cm^{-1}. This oil contained 11% hydrocarbon, 89% acetate, and some residual ether as determined by glpc (8 ft × 0.25 in., 20% Se-30, 75°).

A 1.50-g sample of the above-described product mixture in 20 ml of anhydrous ether was added to 0.5 g of $LiAlH_4$ in 20 ml of ether, and the resulting mixture was heated to reflux for 2 hr and cooled. Cold water and then 25 ml of 5 *N* H_2SO_4 were added and the aqueous layer was immediately extracted with ether. The combined ether solutions were washed successively with H_2O, 5% aqueous $NaHCO_3$, and saturated brine, and dried ($MgSO_4$). The bulk of the ether was removed by careful distillation through a 12-in. Vigreux column to give 1.35 g of yellow oil which was added to a column containing 20 g of alumina. Elution of the column with pentane and subsequent careful removal of the solvent by distillation left 150 mg of a colorless mixture of olefins. Continued elution with ether and then methanol and removal of the solvent gave 1.1 g of a colorless mixture of alcohols.

The first glpc analysis of olefins (10 ft × 0.25 in., 30% silver

(17) E. L. Eliel and C. A. Lukach, *J. Amer. Chem. Soc.*, **79**, 5986 (1957).
(18) M. Tobias, Ph.D. Thesis, State University College of Forestry, Syracuse, N. Y., 1965.
(19) J. Meinwald, S. S. Labana, and M. S. Chadha, *J. Amer. Chem. Soc.*, **85**, 583 (1963).
(20) K. B. Wiberg and A. J. Ashe, III, *ibid.*, **90**, 63 (1968).
(21) J. Nishimura, N. Kawabata, and J. Furukawa, *Tetrahedron*, **25**, 2647 (1969).

nitrate–triethylene glycol on firebrick, 45°) showed the presence of peaks at 6.9 (80%), 7.6 (7%), and 10.8 min (14%). The retention time of these three peaks in the order given corresponded to 1-methylcyclohexene, 1-ethylcyclopentene, and 3-methylcyclopentene. There was no detectable amounts of ethylidenecyclopentane (7.3 min), 3-ethylcyclopentene (13.4 min), and vinylcyclopentane (14.2 min). The second glpc analysis (10 ft × 0.25 in., 4% squalane on Celite, 65°) showed peaks which corresponded to 3-methylcyclohexene (7.1 min), 1-ethylcyclopentene (8.1 min), and 1-methylcyclohexene (9.6 min). The major peak (80%) at 9.6 min was separated by preparative glpc (10 ft × 0.25 in., 4% squalane on Celite), and its ir and nmr spectra were identical with those of a purified sample of 1-methylcyclohexene. There was no detectable *endo*-6-methylbicyclo[3.1.0]hexane (11 min).

Glpc (11 ft × 0.25 in., 17% triethylene glycol on Celite, 75°) analysis of the mixture of alcohols obtained from the $LiAlH_4$ reduction showed the presence of at least five components: 17.9 (2%), 25.4 (47%), 28.3 (48%), 30.0 (2%), and 31.6 min (1%). These retention times in the order listed correspond to *cis*-2-ethylcyclopentanol, *cis*-2-methylcyclohexanol, methylcyclopentylcarbinol, *trans*-2-methylcyclohexanol, and *trans*-2-ethylcyclopentanol. The two major components were separated by preparative glpc. The ir of the material whose retention time was 25.4 min (47%) was identical with the ir of *cis*-2-methylcyclohexanol. The ir of the material with the retention time of 28.3 min (48%) was identical with an ir of cyclopentylmethylcarbinol.

B. With D_2SO_4 and Deuterioacetic Acid.—A sealed glass tube containing 0.41 g (4.2 mmol) of *endo*-6-methylbicyclo[3.1.0]-hexane, 25 mg of concentrated D_2SO_4, and 6.5 ml of acetic acid-*d* was kept at 47° for 26 hr and then processed as described earlier.[3] Glpc analysis (8 ft × 0.25 in., Se-30, 75°) showed 86% acetate and 14% hydrocarbons.

The mixture of acetate and olefins in ether was converted by $LiAlH_4$ in the manner described in part A to a mixture of alcohols and olefins (0.68 g) containing some ether. Glpc analysis of the olefins (10 ft × 0.25 in., 4% squalane on Celite, 45%) showed three peaks: 9.0 (77%), 7.7 (17%), and 7.0 min (7%). These peaks in the order listed correspond to 1-methylcyclohexene, 1-ethylcyclopentene, and 3-methylcyclohexene.

The glpc analysis of alcohols showed the presence of five components: 17.5 (2%), 24.8 (46%), 28.1 (49%), 29.8 (2%), and 31.3 min (71%). The retention times in the order given correspond to *cis*-2-ethylcyclopentanol, *cis*-2-methylcyclohexanol, methylcyclopentylcarbinol, *trans*-2-methylcyclohexanol, and *trans*-2-ethylcyclopentanol. Methyl cyclopentylcarbinol was separated by glpc: mass spectrum *m/e* 115 (17% d_0, 82% d_1, and 1% d_2).[22]

A cooled solution containing 420 mg of chromic anhydride 620 mg of 96% sulfuric acid in 5 ml of water was added dropwise to 0.65 g of the mixture of alcohols in acetone. The mixture was stirred 30 min and immediately thereafter mixed with 25 ml of ice water and 25 ml of ether. The aqueous layer was extracted with ether. The combined ethereal extract was washed with H_2O, 5% $NaHCO_3$, and saturated brine, and dried ($MgSO_4$). Concentration of the extract gave 0.52 g of yellow liquid which consisted of equal amounts of methylcyclopentyl ketone (4.3 min) and 2-methylcyclohexanone (5.5 min) as determined by glpc (10 ft × 0.25 in., triethylene glycol, 125°). Peaks could not be found at 6.1 and 9.8 min, the retention times of 3-methylcyclohexanone and 1-methylcyclohexanol, respectively. Separation of a small quantity of the ketone mixture by preparative glpc gave methylcyclopentyl ketone, mass spectrum *m/e* 113 (16% d_0, 83% d_1, and 1% d_2), and 2-methylcyclohexanone, mass spectrum *m/e* 113 (19% d_0, 80% d_1, and 1% d_2).

The remaining mixture of ketones, 0.41 g, 2 ml of MeOH, and 0.35 g of NaOMe in a sealed glass tube was kept at 25° for 8 days. Under these conditions 80–90% of any α-deuterium would have been exchanged.[23] The contents of the tube were poured into 25 ml of ice water and 25 ml of ether. The aqueous layer was extracted with ether. The combined ethereal extracts were washed with water, 5% aqueous $NaHCO_3$, and saturated brine, and dried ($MgSO_4$). Concentration of the extract gave 0.33 g of yellow liquid which consisted of only the original two ketones as determined by glpc. Separation of the mixture by glpc (conditions as above) gave methylcyclopentyl ketone [mass spectrum *m/e* (% relative intensity) 113 (67) (17% d_0, 83% d_1, and 0% d_2), 98 (20), 72 (48), 71 (71), 70 (100), 43 (80)] and 2-methylcyclohexanone [mass spectrum *m/e* 113 (83) (20% d_0, 80% d_1, and 0% d_2), 98 (15), 85 (38), 70 (72), 69 (97), 68 (100), 57 (43), 56 (46), 55 (46), 44 (30), 43 (32)].

Treatment of Methylcyclopentylcarbinyl and *cis*-2-Methylcyclohexyl Acetate with Acetic Acid and H_2SO_4.—Methylcyclopentylcarbinyl acetate, 428 mg, 66 mg of concentrated H_2SO_4, and 12 ml of glacial acetic acid were heated at 46° in a sealed glass tube for 26 hr. Thereafter the mixture was processed in the same manner as described for the acetolysis of **3** above. Analysis of the crude acetate by glpc (8 ft × 0.25 in., 20% Se-30, 80°) showed the presence of a trace (<1%) of olefin in addition to acetate. Separation of the ester fraction by glpc gave material whose ir was the same as methylcyclopentylcarbinyl acetate and showed no bands in the regions 10.0–10.3 or 11.0 μ as shown by *cis*- and *trans*-2-methylcyclohexyl acetates. The nmr was identical with that of starting acetate.

cis-2-Methylcyclohexyl acetate, 400 mg, 25 mg of H_2SO_4, and 5.5 ml of glacial acetic acid were kept in a sealed glass tube at 47° for 26 hr. The reaction mixture was processed in the customary manner[3] to give 620 mg of clear liquid containing some ether. This liquid was treated with $LiAlH_4$ in the customary manner to give 580 mg of alcohol showing only one peak on glpc analysis (triethylene glycol) and whose ir was identical with that of *cis*-2-methylcyclohexanol.

Treatment of 1- and 3-Methylcyclohexene with H_2SO_4–Acetic Acid.—1-Methylcyclohexene, 420 mg, 25 mg of concentrated H_2SO_4, and 5.5 ml of glacial acetic acid were heated at 47° in a sealed glass tube for 26 hr. Processing the reaction mixture in the customary manner[3] gave 550 mg of a light yellow liquid which consisted of 94% olefin and 6% acetate as determined by glpc (Se-30). Olefin and acetate (ir, 5.74 μ) components were separated by preparative glpc. The nmr and ir of the olefin and the ir of the alcohol were identical with the corresponding spectra of starting 1-methylcyclohexene and 1-methylcyclohexyl acetate, respectively.

3-Methylcyclohexene, 1 g, 50 mg of concentrated H_2SO_4, and 11 ml of acetic acid were heated at 48° for 52 hr in a sealed glass tube. The reaction mixture was processed in the customary manner[3] to give 1.5 g of a mixture containing 5% acetate, 95% olefin, and some residual ether. This mixture was treated with $LiAlH_4$ in ether in the customary manner to afford, after glpc separation (5 ft × 0.25 in., 15% Carbowax 20M, 130°), 25.2 mg of a mixture of alcohols: mass spectrum *m/e* (% relative intensity) 114 (4), 96 (65), 81 (60), 71 (100), 68 (28), 57 (50), 55 (38), 45 (20). To a cooled solution of 24.2 mg of the mixture of alcohols in 2.5 ml of acetone was added dropwise a solution of 15.4 mg of chromic anhydride and 30.2 mg of concentrated H_2SO_4 in four micro drops of water. The reaction mixture was stirred for 20 min, concentrated at the rotary evaporator, and mixed with 5 ml of ether and 25 ml of water. The aqueous layer was extracted with ether, the combined ether extract was washed with water, 5% aqueous $NaHCO_3$, dried, and concentrated giving 19.6 mg of a mixture of 1% methylcyclopentyl ketone, 17% 2-methylcyclohexanone, and 82% 3-methylcyclohexanone as determined by glpc (5 ft × 0.25 in., 15% Carbowax 20M, 103°): ir 5.84 μ; mass spectrum *m/e* (% relative intensity) 112 (31), 97 (12), 94 (7), 84 (8), 71 (11), 69 (100), 68 (19), 56 (50), 55 (35), 43 (14). Mass spectrum of individual components [*m/e* (relative intensity)]: 3-methylcyclohexanone 112 (28), 97 (12), 94 (7), 84 (5), 69 (100), 68 (10), 56 (48), 55 (29), 43 (8); 2-methylcyclohexanone 112 (44), 97 (29), 84 (29), 69 (48), 68 (100), 56 (58), 55 (49), 43 (13); methylcyclopentyl ketone 112 (25), 97 (10), 84 (3), 71 (54), 69 (78), 56 (1), 55 (5), 43 (100).

Registry No.—3, 24903-99-9.

(22) Isotopic distributions were calculated by the method of K. Biemann, "Mass Spectrometry," McGraw-Hill, New York, N. Y., 1962, pp 224–225.

(23) Unpublished results, J-y Ding.