

pentanol (3%), *cis*-2-methylcyclopentanol (7%), *trans*-2-methylcyclopentanol (68%), and cyclohexanol (22%).

A sealed tube containing 1.72 g. of bicyclo[3.1.0]hexane (21 mmoles) and 25 ml. of 0.07 *M* *p*-toluenesulfonic acid in acetic acid was kept at 48° for 1 hr. Analysis of the crude product mixture (1.56 g.) by gas chromatography showed the presence of 82% hydrocarbon and 18% acetate. The hydrocarbon fraction contained 80% bicyclo[3.1.0]hexane and cyclohexene, 16% 1-methylcyclopentene, and 4% 3-methylcyclopentene. The mixture of alcohols (0.76 g.) obtained from the lithium aluminum hydride treatment of the crude product mixture consisted of 2% 1-methylcyclopentanol, 6% *cis*-2-methylcyclopentanol, 68% *trans*-2-methylcyclopentanol, and 24% cyclohexanol.

A sealed tube containing 1.72 g. of bicyclo[3.1.0]hexane (21 mmoles) and 25 ml. of 0.07 *M* *p*-toluenesulfonic acid in acetic acid was kept at 48° for 0.5 hr. The mixture of alcohols obtained in the usual way from the crude product mixture consisted of 1% 1-methylcyclopentanol, 11% *cis*-2-methylcyclopentanol, 68% *trans*-2-methylcyclopentanol, and 20% cyclohexanol.

Reaction of Cyclohexene with Acetic Acid, 0.07 *M* in *p*-Toluenesulfonic Acid.—Treatment of 501 mg. of cyclohexene (6.1 mmoles) with 25 ml. of 0.07 *M* *p*-toluenesulfonic acid in acetic acid for 8 hr. in a sealed glass tube gave a product mixture consisting of cyclohexene and only a trace of cyclohexyl acetate. Similar treatment of 500 mg. of cyclohexene for 44.5 hr. gave a product mixture consisting of 78% unconverted cyclohexene and 22% acetate. Treatment of this mixture with lithium aluminum hydride gave only cyclohexanol in addition to olefin.

Reaction of Bicyclo[2.1.0]pentane with Acetic Acid, 0.07 *M* in *p*-Toluenesulfonic Acid.—Bicyclo[2.1.0]pentane was prepared according to the method of Criegee and Rimmelin.^{10a} A sealed glass tube containing 2.00 g. of bicyclopentane (25 mmoles) and 40 ml. of 0.07 *M* *p*-toluenesulfonic acid in glacial acetic acid was placed in a constant temperature bath at 47°. After 24 hr. the contents of the tube were subjected to the work-up procedure. Gas chromatographic analysis of the product (2.28 g.) employing

a 5% squalene on Celite column showed only the presence of residual ether in the short retention time region of the chromatogram. Distillation of 2.0 g. of the crude ring-opening product gave 962 mg. of material, b.p. 85° at 87 mm., whose infrared spectrum was identical with the spectrum of cyclopentyl acetate. Treatment of 921 mg. of the acetate with lithium aluminum hydride gave 609 mg. of material, b.p. 82–85° at 90 mm., whose infrared spectrum was identical with the spectrum of cyclopentanol. The gas chromatogram, obtained by employing a 17% glycerol on Celite column, showed only a single peak whose retention time was identical with the retention time of cyclopentanol.

Bicyclo[2.1.0]pentane, 544 mg., was treated with glacial acetic acid in a sealed glass tube at 47°. After 24 hr. the contents of the tube were subjected to the work-up procedure. Distillation of the ether from the ethereal solution of products using a 20-in. spinning band column gave an oil which by gas chromatographic analysis at 30° was shown to contain residual ether, unconverted bicyclopentane, but no cyclopentene. An infrared spectrum showed the presence of acetate ester bands at 5.78 and 8.08 μ and the bands (7.88, 9.55, 9.76, 10.30-doublet, 10.97 μ) characteristic of bicyclopentane.

Cyclopentene, 944 mg., was treated with glacial acetic acid in a glass tube at 47°. After 42 hr. the contents were subjected to the same work-up procedure as given immediately above. The material obtained was shown by gas chromatographic and infrared analyses to contain only residual ether and unconverted cyclopentene.

Infrared Spectra.—The infrared spectra of all the olefins were determined neat in microcavity cells using a Baird-Atomic infrared spectrophotometer. The spectra of the cycloalkenols were determined as solutions in carbon tetrachloride.

Acknowledgment.—The authors gratefully acknowledge the support of this research by the Research Corporation.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY, SYRACUSE 10, N. Y.]

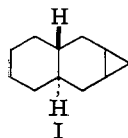
Carbon-Carbon Bond Fission in Cyclopropanes. II. The Acid-Promoted Opening of the Three-Membered Ring in 2,3-Methano-*trans*-decalin¹

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RECEIVED JUNE 13, 1963

2,3-Methano-*trans*-decalin was synthesized and subjected to treatment with sulfuric acid in glacial acetic acid in order to determine the steric course of carbon-carbon bond fission in a cyclopropane ring fused to a rigid ring system. The predominant acetate was found to be 2(a)-acetoxy-3(a)-methyl-*trans*-decalin, while the olefin fraction consisted of the isomeric 3-methyl-*trans*- Δ^1 -octalins, 2-methyl-*trans*- Δ^1 -octalin, and 2-methyl-*trans*- Δ^2 -octalin. The results are interpreted in terms of solvent attack on carbon or hydrogen.

The stereoselectivity in the formation of 2-methylcycloalkyl acetates by the acid-promoted addition of acetic acid to norcarane and bicyclo[3.1.0]hexane has been demonstrated.¹ The work reported herein is concerned with the acid-promoted opening of the three-membered ring in 2,3-methano-*trans*-decalin (I), a compound bearing a cyclopropane ring fused to a conformationally rigid ring system. Our primary purpose in



undertaking this work was to obtain additional information pertaining to the steric disposition of the fission of carbon-carbon bonds in cyclopropanes.

2,3-Methano-*trans*-decalin was prepared directly in 34% yield by the action of methylene iodide on *trans*- Δ^2 -octalin according to the method of Simmons and Smith.³ The preparation of I was also realized in 27% over-all yield by the two-step process involving the

treatment of *trans*- Δ^2 -octalin with bromoform and potassium *t*-butoxide and subsequent hydrogenolysis of the resulting 2,3-(dibromomethano)-*trans*-decalin with sodium in methanol. The infrared spectrum of I showed bands characteristic of cyclopropane derivatives⁴ and the n.m.r. spectrum displayed cyclopropyl proton resonance characteristics similar to those observed in the n.m.r. spectrum of norcarane.

The treatment of I with 0.09 *N* sulfuric acid in glacial acetic acid at 47° gave a product mixture containing acetates, alcohols, and olefins which were present in 40, 2, and 58%, respectively, of the total product mixture as shown by gas chromatography.

Product analysis of the acetates was not carried out directly; the acetates were converted by lithium aluminum hydride hydrogenolyses to a mixture of alcohols whose gas chromatograms indicated the presence of eight alcohols. The major alcohol was present in 59% as shown by gas chromatographic analysis and was the only pure alcohol which could be isolated by elution chromatography. This alcohol was found to be 3(a)-methyl-*trans*-2(a)-decalol⁵ (II, R = H). A second al-

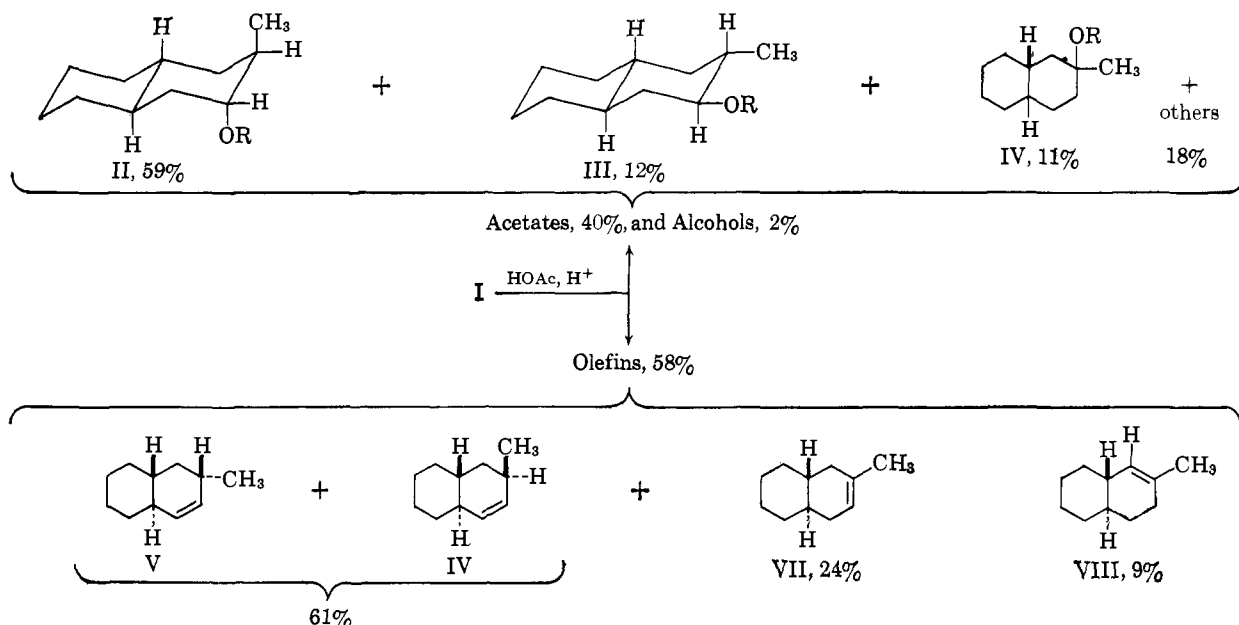
(1) Previous paper in this series: R. T. LaLonde and L. S. Forney, *J. Am. Chem. Soc.*, **85**, 3767 (1963).

(2) National Science Foundation Cooperative Fellow, 1963–1964.

(3) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).

(4) A. D. Cross, "Introduction to Practical Infrared Spectroscopy," Butterworths Publications Ltd., London, 1960, p. 57.

(5) The nomenclature employed here is: (a) for axial and (e) for equatorial substituents. This system of nomenclature has been used previously



cohol which represented 12% of the mixture of alcohols could not be isolated from the ring-opening mixture; however, the gas chromatographic retention time of this alcohol was identical with the retention time of 3(e)-methyl-*trans*-2(e)-decalol (III, R = H). Evidence for the structures of these decalols and the independent syntheses are presented in a later section of this paper.

Two decalols present in 3 and 8% of the mixture of alcohols were considered to be the isomeric 2-methyl-*trans*-2-decalols (IV, R = H) on the basis of the identity of their gas chromatographic retention times with the retention times of the two alcohols obtained on treating *trans*-2-decalone with methylmagnesium iodide. No attempt was made to identify the remaining four minor components of the alcohol mixture.

Analytical gas chromatographic analysis of the olefin fraction revealed the presence of what appeared to be four components, two of which were poorly resolved. These were present in 61, 33 (two unresolved olefins), and 6% of the total olefin fraction.

The olefins present in 61 and 33% of the olefin mixture were isolated by preparative scale gas chromatography. The olefin present in 61% was shown by its satisfactory analysis for C₁₁H₁₈ and infrared and n.m.r. spectra to be really a mixture of two olefins possessing structures V and VI. Thus, the infrared spectrum displayed bands characteristic of a *cis*-carbon-carbon

double bond and $-\text{C}-\text{CH}_3$. The n.m.r. spectrum con-

firmed the presence of a vinylene group by showing a vinyl proton band at 4.55 τ whose integrated band intensity was equivalent to two protons. That the material present in 61% was a mixture of olefins was based on the appearance of two doublets in the methyl region of the n.m.r. spectrum. The doublet centered at 8.96 τ was slightly more intense than the doublet at 9.17 τ and indicates a slight excess of one of the two olefins.

The infrared spectrum of the mixture of the two olefins comprising 33% of the olefin mixture showed bands characteristic of a trisubstituted double bond. The n.m.r. spectrum exhibited two vinyl proton multiplets at 4.64 and 4.85 τ whose half-height band widths were 10 and 5 c.p.s., respectively, and whose total integrated band intensity was equivalent to one proton. Individual integrated multiplet intensities revealed the

olefin giving the 4.64 τ resonance was present in two and one-half times the amount of the olefin giving the 4.85 τ resonance. On the basis of these spectral observations and that the broader of the two vinyl multiplets represented the greater number of first-order splittings, structure VII was assigned to the olefin giving a proton resonance at 4.64 τ and structure VIII was assigned to the olefin giving proton resonance at 4.85 τ .

It is reasonable to conclude that the product distribution represents for the most part products originating directly from the acid-promoted attack of acetic acid on I since the distribution of olefins and acetates closely resembles the product distribution from norcarane¹; the ring-opening reactions of both norcarane and I were carried out under nearly the same conditions and the products obtained from norcarane have been shown to be largely those originating directly from the opening of the three-membered ring. Interestingly, the addition of acetic acid to I proceeds predominantly in a stereoselective manner in giving the *trans*-diaxial decalol II. This result is similar to the acid-promoted *trans*-diaxial opening of epoxides.⁶ On the other hand, the formation of the 3-methyl-*trans*- Δ^1 -octalins is only slightly stereoselective as evidenced by the result that V and VI are afforded in nearly equal amounts. A consideration of bond orientations in a molecular model of I⁷ (Fig. 1) allows a rationalization of these results in terms of solvent attack on hydrogen or carbon in a protonated (or protonating) cyclopropane species. The pseudo-axial hydrogen attached to C₄ has nearly a *trans*-coplanar relationship to a protonated C₃-C₁₁ bond; the pseudo-equatorial hydrogen attached to C₁ has a similar relationship with respect to a protonated C₂-C₁₁. Thus the solvent should show little if any preference in abstracting either of the two protons because a preferred *trans*-coplanar transition state⁸ can be attained in both situations and consequently nearly equal amounts of the stereoisomeric olefins V and VI would result. Nucleophilic solvent attack with inversion at C₂ as shown in Fig. 1 would be accompanied by very

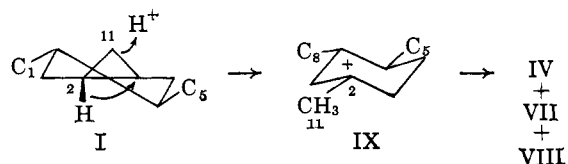
(6) H. B. Henbest, M. Smith, and A. Thomas, *J. Chem. Soc.*, 3293 (1958).

(7) We consider a six-membered ring fused to a three-membered ring to assume the same conformation as the six-membered ring of cyclohexene oxide which has been shown by X-ray diffraction data [B. Ottar, *Acta Chem. Scand.*, **1**, 283 (1947)] to resemble the half-chair conformation of cyclohexene.

(8) For a recent discussion of β -elimination reactions in which the stereochemical requirements are considered see C. K. Ingold, *Proc. Chem. Soc.*, 265 (1962).

little reorientation of ring carbon atoms and incipient axial substituents in an S_N2 -type transition state. Consequently, the formation of *trans*-diaxial product would result with relative ease compared to the formation of the diequatorial product where nucleophilic attack of C_3 with inversion must involve considerable reorientation of ring carbon atoms and incipient equatorial substituents.

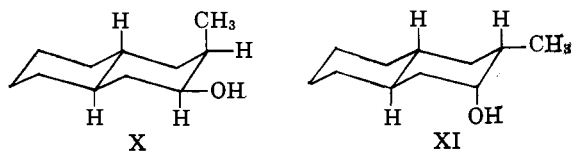
The two 2-methyl-*trans*-2-decalyl acetates and the two olefins VII and VIII might represent in part that fraction of the ring-opening reaction which proceeds by a carbonium ion mechanism. These products probably are formed through the intermediate carbonium ion IX produced by a hydride shift in a protonated I.



The major component of the mixture of alcohols from ring opening was assigned structure II on the basis of the following evidence. The alcohol was shown to be a secondary alcohol by its facile conversion with chromic acid to a ketone. Since an axial hydroxyl group is oxidized more rapidly than an equatorial hydroxyl group,⁹ the finding that decalol II was oxidized nearly twice as rapidly as 3(e)-methyl-*trans*-2(e)-decalol (III) (*vide infra*) suggested that II possessed an axial hydroxyl group while III possessed an equatorial hydroxyl group.

The infrared spectrum of both decalols II and III displayed three peaks in the region of 9.5–10.4 μ . On the basis that axial hydroxyl groups give rise to absorption in the specified region at longer wave lengths than do equatorial hydroxyl groups,¹⁰ the appearance of the three-band series of decalols II and III at long and short wave lengths, respectively, indicated that II possessed an axial hydroxyl group while III possessed an equatorial hydroxyl group.

The n.m.r. spectra of decalol II clearly demonstrated the stereochemistry of the hydroxyl group. Lemieux¹¹ found the axial-axial coupling constant (J_{aa}) in 1 α ,3 α -dimethoxy-2 β -acetoxycyclohexane to be 9.0 c.p.s. and the axial-equatorial coupling constant (J_{ae}) in 1 α ,3 β -dimethoxy-2 α -acetoxycyclohexane to be 2.6 c.p.s. Based on these coupling constants and assuming $J_{ae} = J_{ee}$, the calculated half-height band widths for the proton α to a hydroxyl group in II, III, X, and XI were 8.2, 20.6, 14.2, and 8.2 c.p.s., respectively. The n.m.r. spectrum of II displayed the α -proton resonance at



6.56 τ with a half-height band width of 6 c.p.s. Thus the agreement of the observed half-height band width with the calculated half-height band width of II indicated the presence of an equatorial α -proton (axial hydroxyl) in II.

Finally, 3(a)-methyl-*trans*-2(a)-decalol (II) was independently synthesized by treating 2,3-epoxy-*trans*-decalin with dimethylmagnesium. The assignment of diaxial configuration of methyl and hydroxyl groups in

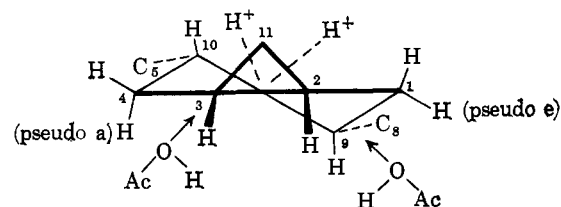
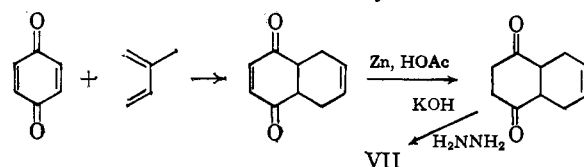


Figure 1.

the product was based on numerous findings of diaxial opening of epoxides by nucleophilic reagents.¹² Previous attempts to prepare II by heating 2,3-epoxy-*trans*-decalin in benzene with methylmagnesium iodide failed; only the tertiary alcohol, 2-methyl-*trans*-2-decalol, was produced.

3(e)-Methyl-*trans*-2(e)-decalol (III) was obtained through 2-methyl-*trans*- Δ^2 -octalin (VII) by the hydroboration procedure of Brown.¹³ The synthesis of the starting olefin was similar to the synthesis employed by Johnson and co-workers¹⁴ for the preparation of *trans*- Δ^2 -octalin and is summarized in the reaction equations below. Crude 2-methyl-*trans*- Δ^2 -octalin was purified by way of its crystalline bromohydrin. The predominant decalol afforded from the hydroboration of VII



was assigned the structure 3(e)-methyl-*trans*-2(e)-decalol on the basis of the known *cis*-anti-Markovnikov addition of diborane to unsymmetrical cycloalkenes,¹⁵ the experimental evidence, arguments presented above, and finally by the n.m.r. spectrum which displayed the resonance for the proton α to a hydroxyl group at 6.82 τ with a half-height band width of 20 c.p.s. The calculated half-height band width for the pertinent proton in III (*vide supra*) is uniquely the widest of all the 3-methyl-2-decalols. Consequently, the agreement of calculated and observed half-height band widths of decalol III not only indicates the equatorial configuration of the hydroxyl group but shows the presence of an equatorial methyl group as well. Confirmatory evidence for an axial hydroxyl group in II and an equatorial hydroxyl group in III comes from the observation that II shows the α -proton resonance downfield from the α -proton resonance in III. The observed relative positions of α -proton resonance is consistent with reports^{16,17} that an equatorial proton α to a hydroxyl group in a cyclohexane ring exhibits resonance at a lower field than the axial counterpart.

Gas chromatographic analysis of the mixture of decalols obtained by hydroboration of VII demonstrated that in addition to III (67%), 3(a)-methyl-*trans*-2(a)-decalol (II, 28%), and a mixture of the isomeric 2-methyl-*trans*-2-decalols (IV, 5%), were obtained as well. The stereochemical outcome of the hydroboration of 2-methyl-*trans*- Δ^2 -octalin is noteworthy. The hydroboration of Δ^2 -¹⁸ and Δ^5 -¹⁹ steroids and simpler com-

(12) See E. L. Eliel in M. Newman, Ed., "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 130-134.

(13) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(14) See reference given in footnote 5.

(15) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961).

(16) J. N. Shoolery and M. T. Rogers, *ibid.*, **80**, 5121 (1958).

(17) J. I. Musher, *ibid.*, **83**, 1146 (1961).

(18) F. Sondheimer and M. Nussim, *J. Org. Chem.*, **26**, 630 (1961); A. Hassner and C. Pillar, *ibid.*, **27**, 2914 (1962).

(19) W. J. Wechter, *Chem. Ind. (London)*, 294 (1959); S. Wolfe, M. Nussim, Y. Mazar, and F. Sondheimer, *J. Org. Chem.*, **24**, 1034 (1959).

(9) J. Schreiber and A. Eschenmoser, *Helv. Chim. Acta*, **38**, 1529 (1955).

(10) E. A. Braude and E. S. Wright in W. Klyne, "Progress in Stereochemistry," Vol. 1, Butterworth, London, 1954, p. 166.

(11) R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Am. Chem. Soc.*, **80**, 6098 (1958).

pounds studied by Brown and Zweifel¹⁵ is sterically controlled; the steric influence is exerted by a group which presumably hinders the attack by diborane from the same side. In the absence of steric influences, conformational control might be expected to determine the product. 2-Methyl-*trans*- Δ^2 -octalin possesses no group capable of exerting a large steric influence. The hydroboration of 2-methyl-*trans*- Δ^2 -octalin is largely conformationally controlled as is evidenced by the predominance of 3(e)-methyl-*trans*-2(e)-decalol formation. However, it appears that diborane is not completely discriminating in its attack of the double bond in a manner giving conformationally preferred product since a considerable amount of the *trans*-diaxial decalol II is produced as well.

Experimental

trans- Δ^2 -Octalin and 2,3-epoxy-*trans*-decalin were prepared by the method of Johnson.¹⁴

2,3-Methano-*trans*-decalin.—*trans*- Δ^2 -Octalin (40.8 g., 0.3 mole, b.p. 55–56° (6 mm.), n_D^{20} 1.4796), 100.5 g. (0.375 mole) of methylene iodide, 29.4 g. of Shank-Schechter zinc-copper couple,²⁰ and 0.2 g. of iodine were placed in 600 ml. of anhydrous ether and refluxed for 48 hr. The reaction mixture was filtered on a Celite pad and washed with 5% hydrochloric acid (5 × 50 ml.), 5% sodium bisulfite (2 × 25 ml.), and saturated sodium chloride (2 × 100 ml.) before drying over magnesium sulfate. The solvent was removed and the residual oil was distilled on a 20-in. spinning-band still, affording 15.2 g. (33.8% yield) of colorless liquid, b.p. 77° (9 mm.), n_D^{22} 1.4872. This material was shown to contain less than 1% of *trans*- Δ^2 -octalin by vapor phase chromatographic analysis.

2,3-(Dibromomethano)-*trans*-decalin.—After the method of Doering,²¹ 5 g. (0.125 g.-atom) of potassium was dissolved in 145 ml. of freshly distilled *t*-butyl alcohol to which 13.6 g. (0.1 mole) of *trans*- Δ^2 -octalin was added. Freshly distilled bromoform, b.p. 146–147°, was added dropwise with rapid stirring over a 40-min. interval, and the reaction allowed to continue an additional 15 min. before pouring into 250 ml. of water. This solution was extracted with hexane (3 × 100 ml.) and the combined extracts dried over magnesium sulfate. Removal of the solvent at reduced pressure left a light yellow oil which upon distillation yielded 9.9 g. (32.1% yield) of colorless liquid, b.p. 106–109° (0.7 mm.). This material was allowed to crystallize from absolute methanol giving clear, white prisms, m.p. 30–31°.

*Anal.*²² Calcd. for C₁₁H₁₈Br₂: C, 42.88; H, 5.24. Found: C, 43.01; H, 5.45.

2,3-Methano-*trans*-decalin from 2,3-(Dibromomethano)-*trans*-decalin.—After the method of Winstein,²³ 14.4 g. (0.046 mole) of 2,3-(dibromomethano)-*trans*-decalin, m.p. 30–31°, was dissolved in 50 ml. of ether to which 18.0 g. (0.81 g.-atom) of sodium and 78 ml. of wet methanol were added. After 2.5 hr., 5.7 g. of sodium and 100 ml. of wet methanol were added and the mixture stirred an additional 2 hr. The reaction was stopped by cautious addition of 90 ml. of water and an additional 50 ml. of ether. The solution was extracted with 100 ml. of hexane and 100 ml. of ether, and the combined extracts washed with water (6 × 50 ml.) and dried over magnesium sulfate-calcium chloride. The solvent was removed at reduced pressure and the residual oil distilled through a 20-in. spinning-band column, affording 4.2 g. (61% yield) of colorless oil, b.p. 73–73.5° (6.5 mm.), n_D^{20} 1.4878. This material was shown to be homogeneous by vapor phase chromatography.

*Anal.*²⁴ Calcd. for C₁₁H₁₈: C, 87.92; H, 12.08. Found: C, 88.05; H, 12.14.

The infrared spectrum showed bands at 3.26 (w) and 9.82 (m) μ . The n.m.r. spectrum showed a sextet centered at 10.11 τ (one proton) and an unresolved multiplet in the region of 9.2–9.7 τ . The n.m.r. spectrum of norcarane displayed a sextet centered at 10.04 τ ²⁵ (one proton) and an unresolved multiplet in the region of 9.1–9.7 τ .

Acid-Promoted Addition of Acetic Acid.—A sealed glass tube containing 4.97 g. (0.033 mole) of 2,3-methano-*trans*-decalin, 188 mg. of 96% sulfuric acid, and 43 ml. of glacial acetic acid was maintained at 47° for 85 hr. The tube was opened and the contents dissolved in 100 ml. of water and 100 ml. of ether. The water layer was separated, extracted with ether (3 × 30 ml.), and

the combined ether solutions washed with water (3 × 50 ml.), 5% sodium bicarbonate (200 ml.), and saturated sodium chloride (2 × 50 ml.). After drying over magnesium sulfate the solvent was removed through a 12-in. Vigreux column. The remaining 6.27 g. of bright yellow oil was analyzed on an 8-ft. Carbowax 20M column at 189°, flow rate 50 ml./min. The mixture was shown to be composed of 40% acetate, 58% hydrocarbon, 2% tertiary alcohols, and a small quantity of residual ether. The hydrocarbon fraction itself showed four peaks at 7.75 min. (61%), 9.25 min. (shoulder), 9.8 min. (33%), and 13.5 min. (6%). The infrared spectrum of the crude ring-opening mixture showed peaks at 5.81, 7.28, 7.35, 8.01 (broad), 9.73, 9.82, 10.28 μ ; shoulders at 5.86, 5.96, and 6.10 μ .

Hydrogenolysis of Acetates to Alcohols.—The ring-opening mixture (6.27 g.) was dissolved in 40 ml. of anhydrous ether and added dropwise to a solution of 1.0 g. (0.026 mole) of lithium aluminum hydride in 75 ml. of ether. The mixture was stirred vigorously for 5 hr. and hydrolyzed with 20 ml. of saturated sodium sulfate. The resulting salts were dissolved with dilute hydrochloric acid and the water layer separated and extracted with ether (2 × 30 ml.). The combined ether solutions were washed with 5% sodium bicarbonate (2 × 25 ml.), saturated sodium chloride solution (1 × 25 ml.), and dried over magnesium sulfate. Removal of the solvent at reduced pressure afforded 5.58 g. of light yellow oil which showed no carbonyl absorption in its infrared spectrum. When this material was analyzed, on a 10-ft. Castorwax capillary column at 171°, seven distinct alcohol peaks were found at 77 min. (8%), 89 min. (3%), 101 min. (3%), 118 min. (unsymmetrical) (71%), 128 min. (3%), 173 min. (8%), and 189 min. (4%) in addition to olefin peaks. The major unsymmetrical peak was further resolved on an 8-ft. Carbowax 20M column at 189°, flow rate 50 ml./min. and shown to be composed of two alcohols at 58 min. (12%) and 64 min. (59%).

Elution chromatography of 6.53 g. of the mixture obtained from lithium aluminum hydride hydrogenolysis using 60 g. of Fisher alumina and pentane as the eluting solvent gave four 25-ml. fractions of which the third afforded 2.53 g. of colorless oil which was subsequently found to be the olefin fraction. Continued elution with 1:1 ether-pentane gave fractions 5–24 (25 ml. each). The weights and melting points of the material recovered from specified fractions were: 5–6 (0.0 g.), 7–9 (418 mg., m.p. 35–65°), 10–11 (656 mg., m.p. 65–74°), 12–13 (430 mg., m.p. 30–64°), 14 (140 mg., semicrystalline material), 15–24 (321 mg., oil). Gas chromatographic analysis of fractions 15–24 showed five major peaks. Recrystallization of combined fractions 10–11 gave 3(a)-methyl-*trans*-2(a)-decalol, m.p. 75–76°. The gas chromatographic retention time of this material was identical with that material comprising 59% of the alcohol mixture.

*Anal.*²⁴ Calcd. for C₁₁H₂₀O: C, 78.51; H, 11.91. Found: C, 78.38; H, 12.03.

3(a)-Methyl-*trans*-2(a)-decalol was converted to its 3,5-dinitrobenzoate, m.p. 134.5–135.5°.

*Anal.*²⁴ Calcd. for C₁₈H₂₂O₆N₂: C, 59.66; H, 6.12; N, 7.73. Found: C, 59.56; H, 6.35; N, 7.71.

***cis*-5,8,9,10-Tetrahydro-6-methyl-1,4-naphthaquinone.**—Two hundred grams (1.84 moles) of quinone was suspended in 2 l. of benzene into which 250 g. (3.70 moles) of isoprene (Eastman) was distilled. The mixture was allowed to stand 6 days before the benzene was removed at reduced pressure, yielding 266 g. (82.1%) of yellow crystals, m.p. 78–83° (reported²⁶ 84–85°).

***cis*-2,3,5,8,9,10-Hexahydro-6-methyl-1,4-naphthaquinone**, m.p. 82–84°, was prepared in 94.5% yield from *cis*-5,8,9,10-tetrahydro-6-methyl-1,4-naphthaquinone by the method of Johnson.¹⁴

2-Methyl- Δ^2 -octalin.—Treatment of *cis*-2,3,5,8,9,10-hexahydro-6-methyl-1,4-naphthaquinone according to the method of Johnson¹⁴ gave a 76.8% yield of a 27% *cis* and 73% *trans* mixture of 2-methyl- Δ^2 -octalin, b.p. 91–92° (17 mm.).

2-Methyl-*trans*- Δ^2 -octalin Bromohydrin.—A 27% *cis*, 73% *trans* mixture of 2-methyl- Δ^2 -octalin was enriched to an 16%–84% mixture of isomers by two distillations through a 42-in. spinning-band still; 21.5 g. (0.143 mole) of this material was dissolved in 250 ml. of tetrahydrofuran containing 20 ml. of water and 25.5 g. (0.143 mole) of N-bromosuccinimide (recryst. from acetic acid) added over a 40-min. period. The temperature was maintained at 0° by an ice-salt mixture. The solution was diluted with 150 ml. of water and the resulting water layer extracted with ether (2 × 50 ml.). The organic layers were combined, washed with 5% sodium bisulfite (2 × 25 ml.), water (2 × 100 ml.), saturated sodium chloride solution (2 × 100 ml.), and dried over magnesium sulfate. Removal of the solvent at reduced pressure left 36 g. of orange oil which was allowed to crystallize from acetonitrile, affording 14 g. of colorless crystals, m.p. 72–78°. One recrystallization from acetonitrile gave 13 $\frac{1}{2}$ g. (37.4% yield) of crystals, m.p. 79–81°.

*Anal.*²² Calcd. for C₁₁H₁₈OBr: C, 53.46; H, 7.69; Br, 32.36. Found: C, 53.50; H, 7.70; Br, 32.52.

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2-Methyl-*trans*- Δ^2 -octalin.—Bromohydrin (25.7 g., 0.104 mole, m.p. 78–80°) was placed into a slurry of 150 ml. of 95% ethanol and 50 g. of Schank–Schechter catalyst. The mixture was refluxed for 20 hr., filtered on a Celite pad, and diluted with 200 ml. of water and 250 ml. of saturated sodium chloride solution. The solution was extracted with ether (3 \times 50 ml.) and the combined extracts washed with water (3 \times 50 ml.), saturated sodium chloride solution (50 ml.), and dried over calcium chloride. The solvent was removed at reduced pressure, and the residual oil distilled in a 20-in. spinning-band column giving 12.0 g. (77% yield) of homogeneous olefin, b.p. 91° (17.5 mm.), n_D^{20} 1.4818.

*Anal.*²⁴ Calcd. for C₁₁H₁₈: C, 87.92; H, 12.08. Found: C, 87.79; H, 11.97.

Hydroboration of 2-Methyl-*trans*- Δ^2 -octalin.—After the method of Brown,¹³ 15 g. (0.1 mole) of 2-methyl-*trans*- Δ^2 -octalin was dissolved in 50 ml. of tetrahydrofuran and allowed to react with the diborane generated from 1.58 g. of sodium borohydride and 11.3 g. of boron trifluoride etherate in, respectively, 42 and 10 ml. of diglyme. After 2 hr., 7 ml. of water, 11 ml. of 3 *N* sodium hydroxide, and 12 ml. of 30% hydrogen peroxide were added while keeping the exothermic reaction below 50°. The oxidation was allowed to continue 1 hr. after the addition of peroxide until room temperature had again been attained. The reaction mixture was extracted with ether (2 \times 50 ml.), the extracts washed with 50 ml. of saturated sodium chloride solution, and dried over magnesium sulfate. Removal of the solvent yielded 13.2 g. (78.6% yield) of opaque oil which solidified slowly on standing. Analysis of the alcohols on an 8-ft. Carbowax 20M column at 189° and a flow rate of 50 cc./min. showed peaks at 46 min. (5%), 58 min. (67%), and 64 min. (28%). When a sample of the alcohol mixture was submitted to elution chromatography on alumina two distinctly different alcohols were obtained. One of these was 3(e)-methyl-*trans*-2(e)-decalol (67% of the decalol mixture by gas chromatography), m.p. 84–85°.

*Anal.*²² Calcd. for C₁₁H₂₀O: C, 78.51; H, 11.91. Found: C, 78.77; H, 12.05.

3(e)-Methyl-*trans*-2(e)-decalol was converted to its 3,5-dinitrobenzoate, m.p. 142–143°.

*Anal.*²² Calcd. for C₁₈H₂₂O₆N₂: C, 59.66; H, 6.12; N, 7.73. Found: C, 59.43; H, 6.11; N, 7.76.

3(e)-Methyl-*trans*-2(e)-decalol displayed infrared bands at 2.75, 2.88, 7.30, 8.29, 9.67, 9.83, 9.88 (shoulder), 10.52, 10.65, and 10.79 μ , while the second alcohol obtained, m.p. 77–78°, showed bands at 2.81, 2.93, 7.29, 8.48, 8.77, 9.72, 10.00, 10.20, 10.46, and 11.06 μ (strong). The second alcohol proved to have the same gas chromatographic retention time as the material present in 28% of the hydroboration mixture, did not depress the melting point on admixture with either 3(a)-methyl-*trans*-2(a)-decalol (2,3-epoxy-*trans*-decalin plus dimethyl magnesium) or the major and only isolated alcohol (59%) from ring opening, and displayed identical infrared spectra with both the former and the latter compounds.

3(a)-Methyl-*trans*-2(a)-decalol from Epoxide.—Methylmagnesium iodide was prepared from 14.2 g. (0.1 mole) of methyl iodide and 2.43 g. (0.1 g.-atom) of magnesium in 100 ml. of anhydrous ether. The ether was displaced by 125 ml. of benzene²⁷ and the solution allowed to reflux 1 hr. Dioxane (35 g., 0.4 mole) was added dropwise in 25 ml. of anhydrous benzene, and the resulting milky solution stirred for 1.5 hr. under nitrogen. The gelatinous gray-white precipitate was removed by centrifugation, and the light yellow supernatant refluxed with 1.10 g. (0.0072 mole) of 2,3-epoxy-*trans*-decalin,¹⁴ b.p. 89° (9.5 mm.), n_D^{20} 1.4836, for 5 hr. under an atmosphere of nitrogen. The reaction mixture was hydrolyzed with 50 ml. of dilute hydrochloric acid, extracted with ether (3 \times 25 ml.), and the combined extracts washed with water (2 \times 25 ml.). After drying over magnesium sulfate, the solvent was removed to leave 1.66 g. of yellow oil. Chromatography on 20 g. of Fisher alumina yielded 294 mg. of unreacted epoxide; 272 mg. (22.8% yield) of 3(a)-methyl-*trans*-2(a)-decalol, m.p. 77–78° upon recrystallization from hexane; 423 mg. of *trans*-decalin-2 β ,3 α -diol, m.p. 163–164° upon recrystallization from hexane–benzene (reported⁶ m.p. 163–164°); and 40 mg. of unidentifiable alcohols.

2-Methyl-*trans*-2-decalol.—2,3-Epoxy-*trans*-decalin (4.6 g., 0.03 mole) was added dropwise to a solution of 4.5 g. (0.12 mole) of lithium aluminum hydride in 125 ml. of tetrahydrofuran and allowed to reflux for 3.5 hr. Work-up afforded 5.25 g. of light pink oil which was then oxidized by the Jones procedure²⁸ to yield 2.3 g. (50% yield for both steps) of *trans*- β -decalone, b.p. 50–51° (0.35 mm.), n_D^{20} 1.4811 (reported²⁹ n_D^{20} 1.4827).

Reaction of 1.90 g. (12.5 mmoles) of *trans*- β -decalone with methylmagnesium iodide produced 1.37 g. (65% yield) of alcohols which when analyzed on a 10-ft. Castorwax capillary column

at 181° showed two peaks at 77 (72%) and 89 min. (28%). Only one compound could be isolated by elution chromatography from alumina; m.p. 92–93° (reported³⁰ m.p. 92–93°). This same tertiary alcohol was produced when 2,3-epoxy-*trans*-decalin was allowed to react with methylmagnesium iodide in refluxing benzene for 5 hr.

Dehydration of 2-Methyl-*trans*-2-decalol.—2-Methyl-*trans*-2-decalol (450 mg., 2.7 mmoles) was dissolved in 3 ml. of 85% phosphoric acid and heated on a steam bath for 2 hr. The reaction mixture was diluted with water, extracted with ether, and the combined extracts dried over magnesium sulfate. The solvent was removed at reduced pressure and the residual yellow oil distilled, affording 85 mg. (21% yield) of colorless hydrocarbon, b.p. 65–67° (7 mm.), n_D^{20} 1.4838. Examination by v.p.c. on an 8-ft. Carbowax 20M column at 189° showed two peaks at 9.25 (shoulder) and 9.8 min. The infrared spectra of this material was almost superimposable on that of pure 2-methyl-*trans*- Δ^2 -octalin. Pertinent bands were to be found at 5.95, 6.05, 7.27, 8.52, 9.60 (s), 9.72 (m), 11.50, and 12.06 μ .

3(e)-Methyl-*trans*-2-decalone and 3(a)-Methyl-*trans*-2-decalone.—After the method of Brown,³¹ 1200 mg. (7.15 mmoles) of 3(e)-methyl-*trans*-2(e)-decalol, m.p. 84–85°, was dissolved in 2.5 ml. of ether to which 5.25 ml. of water containing 706 mg. (2.40 mmoles) of potassium dichromate and 999 mg. (9.61 mmoles) of 96% sulfuric acid was added. The mixture was stirred vigorously for 24 hr. at 28°, diluted with water, extracted with ether and the combined extracts dried over magnesium sulfate. Removal of the solvent at reduced pressure yielded a light yellow oil which showed considerable hydroxyl absorption in its infrared spectrum. Chromatography on 15 g. of Woelm, neutral, activity grade I, alumina afforded 940 mg. of ketone and 160 mg. of unoxidized alcohol. This material was further purified by distillation, b.p. 100–101° (7 mm.), n_D^{20} 1.4790, and its semicarbazone, m.p. 201–202°, prepared.

*Anal.*²² Calcd. for C₁₂H₂₁ON₃: C, 64.54; H, 9.48; N, 18.82. Found: C, 64.42; H, 9.60; N, 18.60.

Reported³² constants for a 3-methyl-*trans*-2-decalone are: b.p. 126–127° (18 mm.), n_D^{20} 1.4740, semicarbazone m.p. 207°.

3(a)-Methyl-*trans*-2(a)-decalol, m.p. 77–78°, was oxidized by the same procedure and the crude ketone converted directly into its semicarbazone, m.p. 184° (reported³² 183°).

Oxidation of Isomeric 3-Methyl-*trans*-2-decalols.—Fifty milligrams (0.294 mmole) of *trans*-diaxial and *trans*-diequatorial 3-methyl-2-decalol were dissolved in 10 ml. of acetone (distilled from potassium permanganate) and respectively oxidized with 3 ml. of a water solution of 25.5 mg. (0.25 mmole) of chromic anhydride and 36.4 mg. (0.35 mmole) of 96% sulfuric acid. The reaction was allowed to continue for 1 hr. and was then worked up by conventional means. Analysis by vapor phase chromatography showed only 40% oxidation of the equatorial hydroxyl function but 74% oxidation in the case of its axial counterpart.

Resolution of Hydrocarbons from Ring Opening.—The complex mixture of hydrocarbons and alcohols arising from ring opening and subsequent hydride reduction were separated by elution chromatography on alumina. The hydrocarbon fraction was then resolved by preparative scale gas chromatography. Hydrocarbon A (61%), b.p. 60–61° (6 mm.), n_D^{20} 1.4822, showed pertinent bands in its infrared spectrum at: 3.30, 5.95, 6.06, 7.32, 9.69, 10.94, 11.98, 14.04 (strong), and 14.55 μ . Hydrocarbons B (shoulder) and C (33%), b.p. 65–67° (7 mm.), n_D^{20} 1.4836, displayed the following bands in its spectra: 5.95, 6.05, 7.27, 8.52, 9.60, 9.72, 11.49, and 12.06 μ .

*Anal.*²² Calcd. for C₁₁H₁₈ (hydrocarbon A): C, 87.92; H, 12.08. Found: C, 87.91; H, 12.16. Calcd. for C₁₁H₁₈ (hydrocarbons B and C): C, 87.92; H, 12.08. Found: C, 87.72; H, 11.95.

Infrared and N.m.r. Spectra.—All infrared spectra were determined in carbon tetrachloride solution using a Baird infrared spectrophotometer. The n.m.r. spectra were obtained from a Varian Model A-60 employing carbon tetrachloride as a solvent and tetramethylsilane as an internal standard.

Acknowledgments.—The authors wish to express their gratitude to Dr. R. R. Fraser of Bristol Laboratories, Syracuse, N. Y., for his assistance in obtaining the n.m.r. spectra and for helpful comments concerning the interpretation of these spectra. We thank Dr. G. A. Wiley of Syracuse University for making his preparative scale gas chromatograph available to us. The authors gratefully acknowledge the support of this work by the Research Corporation.

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