very vigorous stirring provided adequate, rapid equilibration in most cases.

The system proved to be satisfactorily gas tight in operation. Periodic tests with 100–200-mm positive or negative pressure applied in the gas-measuring buret revealed no pressure loss during the time required for a typical kinetic run. This test is severe, since the pressure differential during a run was never more than a few millimeters. The infinity point was checked for drift in every case in which an infinity volume was measured. In a few instances, drift indicating a leak was observed, and those runs were discarded. Replacing the inner O-ring seal always corrected the trouble.

The temperature of the gas collected was controlled by pumping thermostated water from the constant-temperature bath through a jacket enclosing the gas-measuring buret. The connecting lines, which were not thermostated, were mostly made of capillary tubing and had a total volume of less than 5 ml. Laboratory temperature varied no more than a few degrees during a run.

Technique. Reagents were always purified soon before use. Phenyl azide, for example, seemed to be stable for at least 2 months when stored at 10° in the dark, but it was always freshly redistilled within 1 month of use.

The reagents were weighed into small volumetric flasks, solutions were made up to volume, and aliquots were measured and transferred to the reaction flask by syringe. All but one of the reagents were placed in the reaction flask, and the mixture was stirred for 5 or 10 min to establish thermal and gas–liquid equilibria. After the mercury levels in the gas buret had been adjusted to zero, the stirrer was stopped momentarily, and the reaction was initiated by injecting the final reaction component (either azide or trivalent phosphorus compound) into the flask through an ampoule stopper. A three-way stopcock between the reaction flask and gas buret was quickly closed to the atmosphere, the timer was started, and the stirrer was restarted. This start-up operation required about 5 sec. Volume readings were begun at once and could be made very conveniently and accurately to the nearest 0.1 ml with a 50-ml gas buret. Values were measured dynamically, by moving the leveling bulb until the mercury levels in the parallel open and closed buret tubes coincided. Paralax and capillarity effects were completely eliminated by this technique.

Infinity volumes were determined by two methods. In most runs, the gas volume was observed until it became constant, at least until 12 reaction half-lives. Observed infinity volumes agreed with calculated values; lack of agreement was taken as evidence for leakage or weighing errors, and the run was discarded. With very slowly reacting compounds runs were planned to give very large infinity volumes, and the calculated values alone were used.

Acknowledgments. The authors wish to express their gratitude to the National Science Foundation for support of this project and to Professors D. F. DeTar and P. D. Bartlett for their helpful discussions.

Mechanistic Aspects of the Anomalous Hydride Reduction of Cyclobutene Epoxides[1]

Leo A. Paquette,[2a] A. A. Youssef,[2b] and Mary Lee Wise

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received May 5, 1967*

Abstract: The lithium aluminum hydride reduction of *exo*-bicyclo[3.2.0]hept-6-ene oxide and *exo*-2-oxabicyclo-[3.2.0]hept-6-ene oxide has been shown to afford ring-cleaved primary alcohols in addition to the derived cyclobutanols. The structures of the products have been assigned on the basis of comparison with authentic samples and further chemical transformations. Evidence was obtained by means of deuterium labeling, solvent basicity, and related experiments to suggest that the formation of the abnormal ring-opened products probably results from initial C–O bond cleavage followed by Lewis acid catalyzed opening of the strained cyclobutanoxide system.

In general, the lithium aluminum hydride (LAH) reduction of epoxides proceeds by nucleophilic attack of hydride ion from the less hindered back-side position to give rise to the more highly substituted alkoxide ion *via* carbon–oxygen bond cleavage.[3] A striking exception to this customary mode of reaction has been noted, however, in the case of certain cyclobutene epoxides.[4,5] For example, exposure of cyclobutene epoxide to the LAH reagent affords cyclobutanol and 1-butanol in approximately equal amounts.[5] Thus, a substantial degree of carbon–carbon bond cleavage, presumably caused by excessive compression of bond angles in the starting material, is found in such highly strained systems.

To ascertain whether *exo*-bicyclo[3.2.0]hept-6-ene oxide derivatives would be appropriate mechanistic probes, initial experiments were performed in which epoxide **1** was treated with LAH. When an ethereal solution of **1** and suspended hydride was heated at reflux for 4 hr, less than 5% reduction occurred as judged by vpc analysis. This surprising result was at variance with earlier reports, in particular that dealing with the rapid reduction of the closely related bicyclo[4.2.0]-oct-7-ene oxide under the same conditions,[4] and may be a reflection of greater steric hindrance to back-side attack in **1**. Accordingly, **1** was reduced in refluxing tetrahydrofuran; vpc analysis of aliquots removed at various time intervals indicated the reduction to be approximately 90–95% complete after 48 hr. The two-component product mixture was readily separated by preparative gas chromatography. The major component (64%) was assigned structure **2** on the basis of the identity of its infrared spectrum with that of an authentic sample of *exo*-bicyclo[3.2.0]heptan-2-ol.[6]

---

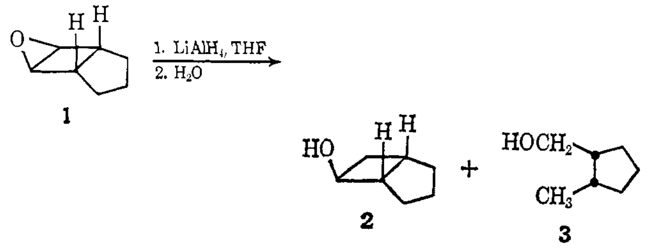
[1] Paper XXX of the series entitled "Unsaturated Heterocyclic Systems." For previous paper in this series, see L. A. Paquette and W. C. Farley, *J. Org. Chem.*, 32, 2725 (1967).

[2] (a) Alfred P. Sloan Foundation Fellow, 1965–1967. (b) Visiting Research Associate on leave of absence from Alexandria University, Egypt, UAR.

[3] L. A. Paquette, "Principles of Heterocyclic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1967, Chapter 1.

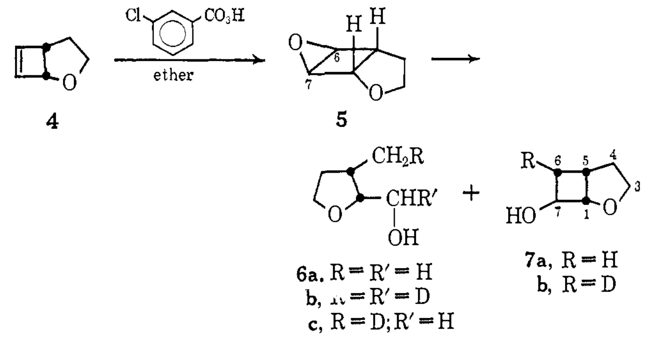
[4] A. C. Cope and R. W. Gleason, *J. Am. Chem. Soc.*, 84, 1928 (1962).

[5] W. R. Moore and C. H. Beede, Abstracts, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., 1963, p 11M.

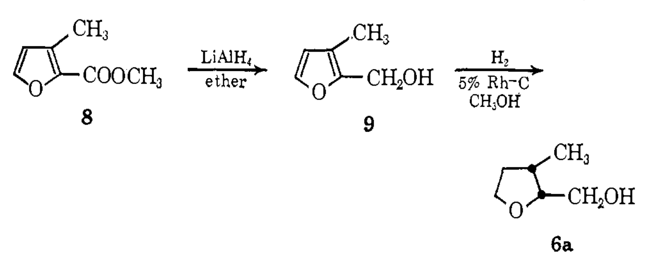


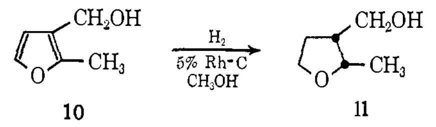
The structure of the alcohol obtained in lesser yield (36%) was easily delineated on the basis of its nmr spectrum and comparison of the melting point of its 3,5-dinitrobenzoate with that derived from pure *cis*-2-methylcyclopentanemethanol (**3**).[7]

We then examined epoxide **5**. The synthesis of **5** was accomplished in good yield by *m*-chloroperbenzoic acid oxidation of the known 2-oxabicyclo[3.2.0]hept-6-ene (**4**).[8] When **5** was treated with lithium aluminum hydride in refluxing ether, the rate of disappearance of **5** was found to be significantly more rapid than that of **1**. After 24 hr in this solvent, reduction has proceeded to the extent of 80–85%; furthermore, the reduction of **5** in refluxing tetrahydrofuran was complete in less than 8 hr (compare incomplete reduction of **1** after 2 days). Of utmost significance were the facts that only two alcohols (**6a** and **7a**) were formed (*a priori*, the formation of four alcohols is possible) and that the ratio of **6a**:**7a** varied reproducibly with the medium employed. Progression from ether (ratio 60:40) to tetrahydrofuran (ratio 46:54) revealed an increase in the proportion of "normal" product in the more basic solvent (THF) or, in other words, an increase in carbon–carbon bond cleavage in ether.

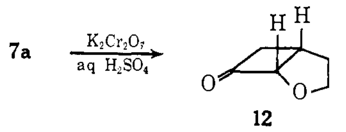


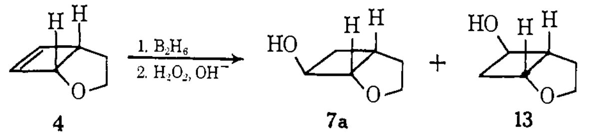
An authentic sample of **6a** was obtained by submitting methyl 3-methyl-2-furoate (**8**) to consecutive lithium aluminum hydride and catalytic reductions. The isomeric alcohol **11**, prepared by catalytic hydrogenation of 2-methyl-3-furfuryl alcohol (**10**), possessed physical properties which were at variance with those of either alcohol obtained in the LAH reduction of **5**.



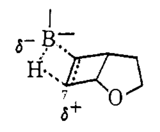


Oxidation of **7a** with potassium dichromate in sulfuric acid afforded in fair yield the cyclobutanone **12**, which was characterized as its semicarbazone. The presence of a one-proton broadened doublet (J = *ca.* 2.5 cps) at δ 4.05 in the nmr spectrum of **12** was considered confirmatory for this structure,[9,10] and effectively removed from consideration the remaining possible cyclobutanone formulation. In addition, hydroboration of **4** resulted in the predominant (80%) formation of **7a** in combination with a lesser quantity (20%) of a second alcohol, presumably **13**, although the structure of this material was not investigated further.

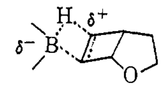




A substantial directive influence in the addition of diborane to **4** was not entirely unexpected. Thus, in the two possible transition states for hydroboration of the *exo* face of **4**, namely **14** and **15**, the development of partial positive charge at C-7 in **14** can be expected to be disfavored by the inductive effect of the proximate ether oxygen atom. Such an interaction, which is greatly diminished in transition state **15**, is apparently sufficient to raise the energy of activation leading to **13** to an extent which permits predominant formation of **7a** *via* **15**.[11]



14



15

As a means of exploring the details of the bond-forming and bond-breaking steps at two distinct stages of the reduction process, *i.e.*, hydride attack and aqueous hydrolysis, deuterium labeling was used.[12]

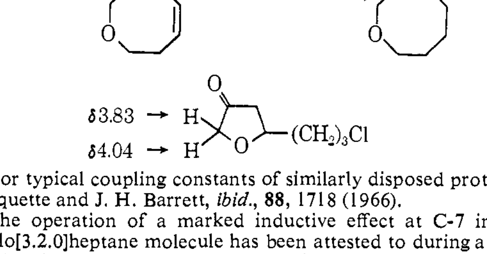
---

[6] F. F. Nelson, Ph.D. Thesis, University of Wisconsin, 1960.

[7] L. N. Owen and A. G. Peto, *J. Chem. Soc.*, 2383 (1955).

[8] L. A. Paquette, J. H. Barrett, R. P. Spitz, and R. Pitcher, *J. Am. Chem. Soc.*, 87, 3417 (1965).

[9] The chemical shift of a proton of the type —O—(H)C—C(=O)— generally falls in the region δ 3.7–4.1. The following molecules may be considered exemplary [L. A. Paquette and R. W. Begland, *ibid.*, 87, 3784 (1965)].



[10] For typical coupling constants of similarly disposed protons, see L. A. Paquette and J. H. Barrett, *ibid.*, 88, 1718 (1966).

[11] The operation of a marked inductive effect at C-7 in the 2-oxabicyclo[3.2.0]heptane molecule has been attested to during a preliminary study of the kinetics of solvolysis of the 3,5-dinitrobenzoates of **2** and **7a** [A. A. Youssef, unpublished observations].

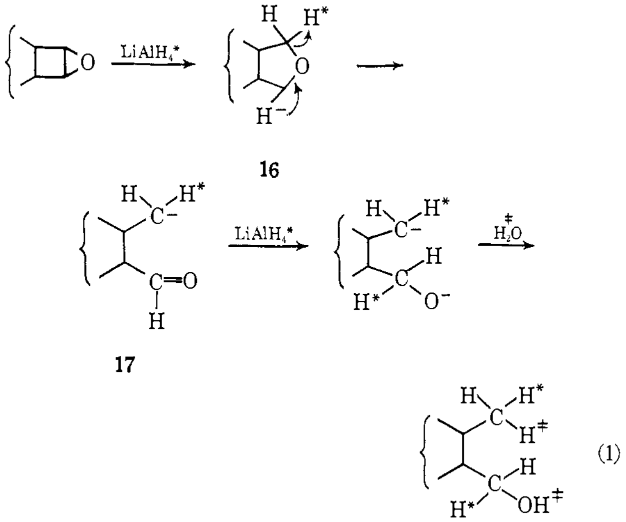
[12] A similar study has also been carried out by Moore and Beede.[5]

In parallel experiments, **5** was treated with lithium aluminum deuteride (H_2O work-up) and LAH (D_2O work-up) to give **6b–7b** and **6c–7a**, respectively. The position of isotopic labeling in the two alcohols was conveniently determined by nmr spectroscopy; the details of the spectral analyses are presented in the Experimental Section.

Finally, it was shown that cyclobutanols **2** and **7** can be recovered quantitatively when resubmitted to the original conditions of the LAH reduction.

Discussion

On the basis of the deuterium-labeling studies, two mechanistic rationalizations can be advanced in explanation of the anomalous hydride reduction of cyclobutene epoxides.[13] In the first of these, the ring-cleaved alcohol finds its origin in initial carbon–carbon bond cleavage of the epoxide ring to form an anion such as **16** which subsequently is transformed into **17** by a route reminiscent of the Wittig rearrangement;[14] this latter species is reduced in turn to produce the observed primary alcohol.

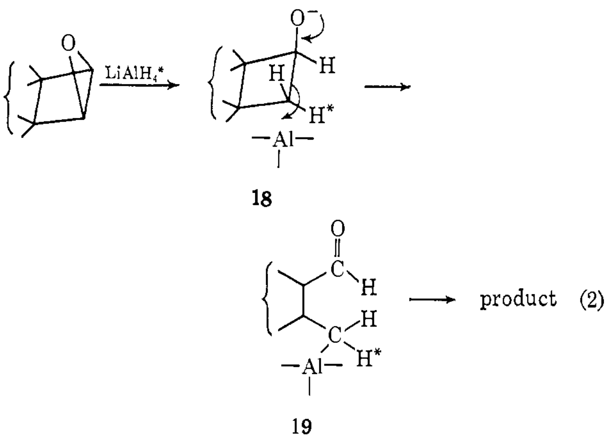


16

17

(1)

Alternatively, the abnormal cleavage of cyclobutene epoxides could arise by means of initial C–O bond cleavage to give, *at the instant of hydride or deuteride ion transfer*, a species such as **18** in which the proximity of the aluminum atom and the strain inherent in the cyclobutene ring combine to induce ring opening as shown.



18

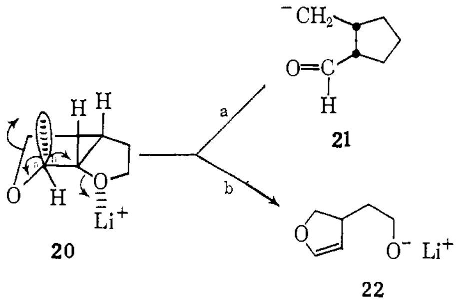
19

(2)

Because cyclobutanols such as **2** and **7a** can be recovered nearly quantitatively when resubmitted to the original conditions of hydride reduction, earlier workers had concluded[4] that the first step in the formation of the ring-cleaved alcohols cannot be carbon–oxygen bond cleavage, but must proceed by way of a species such as **16**. However, this argument was advanced on the basis of the supposed similarity of the cyclobutanoxide anions under both sets of conditions, and did not consider the possibly influential role that the relative position of the aluminum-containing moiety could play. Thus, the discrete difference between **18** and cyclobutanoxide anions under more normal circumstances lies in the proximity of the aluminum atom to the back side of the α-carbon atom demanded by the transition state for C–O rupture.

The results obtained in the case of epoxide **5** provide evidence for two highly relevant points. First, the structural specificity of the reduction in this instance suggests that the tetrahydrofuranyl type oxygen atom in **5** is sufficiently well complexed with lithium cations[15,16] that approach of the relatively bulky aluminohydride anion to the back side of C-7 is sterically prevented; thus, attack at C-6 occurs exclusively.

Secondly, should the reaction by which **5** is converted to **6** be proceeding by means of the sequence outlined in eq 1, then anion **20** becomes a requisite intermediate along the reaction pathway. The unique nature of anion **20** becomes especially clear when its two most plausible modes of further reaction are considered. It then becomes apparent that the rate of reaction b leading to alkoxide ion **22** should be competitive with (if not more rapid than) the rate of path a cleavage. Especially significant in this assumption is not only the disposition in path b of the leaving group in a *trans* orientation to the carbanion sphere and the fact that lithium-complexed ether oxygen can be displaced with relative ease,[17] but also the fact that exposure of 2-tetrahydrofurfuryl bromide to magnesium in ether for short periods of time results in the exclusive formation of 4-penten-1-ol.[18] Since none of the alcohol derived



20

21

22

---

[13] Rearrangement of cyclobutene epoxides prior to reduction need not be considered, since cyclopropyl ketones and aldehydes are known to result exclusively in such cases [J.-L. Ripoll and J.-M. Conia, *Bull. Soc. Chim. France*, 2755 (1965)], and such substances are subject to normal LAH reduction.

[14] See, for example, A. J. Weinheimer, S. W. Kantor, and C. R. Hauser, *J. Org. Chem.*, **18**, 901 (1953). Although P. T. Lansbury, *et al.* [*J. Am. Chem. Soc.*, **88**, 78 (1966)], have demonstrated that the Wittig rearrangement of *sec*-alkyl and *t*-alkyl ethers involves free-radical pairs, these conclusions do not necessarily apply in all cases and the carbanion pathway is likely operative in a significant number of examples.

[15] The efficient solvation of lithium ions by tetrahydrofuran has recently been demonstrated: R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *Tetrahedron Letters*, 199 (1967).

[16] For the sake of simplicity, complexation of lithium ions by the epoxide oxygen atom is not depicted; however, we do not imply that no electrophilic assistance is provided by this means in the cleavage of the epoxide ring.

[17] R. L. Letsinger and E. Bobko, *J. Am. Chem. Soc.*, **75**, 2649 (1953).

from **22** was formed in the reduction of **5**, it appears most logical to conclude that the anomalous reduction of cyclobutene epoxides proceeds by means of initial C–O bond cleavage (eq 2).

In further agreement with this view is the finding that α-metallation of 2-phenyltetrahydrofuran results in the formation of acetophenone (85–92%) and ethylene rather than a butyrophenone derivative (which could react further) as suggested by eq 1.[19]

Implicit in the above conclusion is the fact that the ratio of cyclobutanol to "abnormal" product should depend on the rate of diffusion of aluminum atom away from the back-side environment of alkoxide **18**. In other words, cyclobutanol production should be less prevalent when tetrahydrofuran is replaced by a less basic solvent such as ether. The latter can be expected to compete less favorably for the AlH_3 species and allow this Lewis acid greater opportunity to induce rupture of the strained ring as in **18**. This concept was tested in the case of **5**; as described above, a 14% increase in the proportion of cyclobutanol **7a** was consistently observed when the solvent was changed from ether to tetrahydrofuran. It appears, therefore, that cyclobutanols probably are formed in these hydride reductions because of rapid diffusion of the aluminum-containing species away from a relatively crowded, or at least compressed, environment. In the absence of such an effect, cyclobutanoxide anions appear to be quite stable.

The unusual reactivity of these anions under conditions of epoxide reduction with hydride parallels in general terms earlier observations made with cyclopropanols,[20] and with cyclobutylcarbinyl[21] and cyclopropylcarbinyl organometallics.[22]

Experimental Section[23]

exo-**Bicyclo[3.2.0]hept-6-ene Oxide (1).** To a stirred solution of 4.2 g (0.045 mole) of bicyclo[3.2.0]hept-2-ene[24] in 25 ml of chloroform was added dropwise a solution of 9.1 g of *m*-chloroperbenzoic acid (85% assay) in 100 ml of the same solvent. After the exothermic reaction had subsided, the reaction mixture was stirred and heated (60°) for 2 hr. The flask was cooled in an ice-salt mixture, and the precipitated *m*-chlorobenzoic acid was filtered and washed with cold chloroform. The chloroform solution was washed twice with 25-ml portions of 20% sodium sulfite solution and once each with equivalent portions of saturated aqueous sodium bicarbonate and sodium chloride solutions. The chloroform solution was dried, evaporated, and distilled to give 3.53 g (70%) of pure colorless liquid, bp 84–85° (73 mm), $n^{24}\mathrm{D}$ 1.4673. Vpc analysis indicated the presence of only one component; $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 3.40 (multiplet, 2 H, epoxide protons), 2.48 (broad peak, 2 H, tertiary cyclobutyl protons), and 1.70 (multiplet, 6 H, methylene groups).

Anal. Calcd for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 76.41; H, 9.09.

LAH Reduction of 1. To a slurry of 1.0 g (0.026 mole) of lithium aluminum hydride in 50 ml of dry tetrahydrofuran was added a solution of 2.8 g (0.025 mole) of **1** in 25 ml of the same solvent. The mixture was refluxed with stirring for 48 hr, cooled, and decomposed by the slow addition of 1 ml of water, 1 ml of 33% sodium hydroxide solution, and 2 g of anhydrous magnesium sulfate. The organic layer was separated from the solids, and the latter was washed thoroughly with ether and dried. Evaporation of the ether and distillation of the residue afforded 0.92 g of colorless liquid, bp 64° (2.8 mm), $n^{24}\mathrm{D}$ 1.4734. Vpc analysis (1% Carbowax 20M) indicated the sample to be a mixture of two components in the ratio of 64:36. Preparative vpc was employed in the separation of the two components.

The major product (**2**) displayed $n^{23}\mathrm{D}$ 1.4806 (lit.[6] $n^{25}\mathrm{D}$ 1.4803); infrared spectrum identical in all respects with a published curve;[6] $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 5.01 (singlet, 1 H, O*H*), 3.69 (multiplet, 1 H, >C*H*OH), 2.55 (multiplet, 2 H, tertiary cyclobutyl protons), and 1.35–2.30 (multiplet, 8 H, methylene groups).

The minor product (**3**) displayed the following nmr spectrum: $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 4.04 (singlet, 1 H, O*H*), 3.47 (multiplet, 2 H, CH_2OH), 1.20–2.25 (multiplet, 8 H, cyclopentyl protons), and 1.36 (doublet, 3 H, J = 7.5 cps, >C(H)CH_3). Conversion to a 3,5-dinitrobenzoate afforded shiny white plates (from hexane), mp 68–69° (lit.[7] mp 66–67°).

exo-**2-Oxabicyclo[3.2.0]hept-6-ene Oxide (5).** A solution of 6.0 g (0.063 mole) of **4**[8] in 20 ml of chloroform was oxidized with 13 g (0.064 mole) of *m*-chloroperbenzoic acid (85% assay) in 100 ml of chloroform in a manner paralleling that utilized for **1**. Distillation of the residue afforded 4.66 g (77%) of colorless liquid, bp 90–92° (55 mm). Vpc analysis indicated the presence of only one component; $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 3.88–4.30 (multiplet, 3 H, protons at C-1, C-6, and C-7), *ca.* 3.55 (multiplet, 2 H, CH_2O), *ca.* 2.78 (multiplet, 1 H, C-5 proton), and *ca.* 1.80 (multiplet, 2 H, C-4 methylene group).

Anal. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 64.45; H, 7.23.

LAH Reductions of 5. A. H_2O Work-up. To a slurry of 1.5 g (0.04 mole) of lithium aluminum hydride in 50 ml of dry tetrahydrofuran was added a solution of 4.4 g (0.04 mole) of **5** in 20 ml of the same solvent. The reaction mixture was refluxed with stirring for 8 hr, cooled, and worked up as described above. Vpc analysis of the crude residue indicated a mixture of two components in a ratio of 46:54. Preparative vpc (1% Carbowax 20M) was employed in the separation of the two components.

The lesser product (**6a**) displayed the following physical data: bp 57–59° (0.75 mm); $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ *ca.* 3.78 (multiplet, 3 H, CH_2OC*H*<), 3.50 (multiplet, 2 H, CH_2OH), 3.15 (singlet, 1 H, O*H*), 1.30–2.54 (multiplet, 3 H, remaining ring protons), and 1.00 (doublet, 3 H, J = 7 cps, >CHCH_3).

Conversion to a 3,5-dinitrobenzoate afforded colorless plates which rapidly yellowed on exposure to air, mp 69–70° [from petroleum ether (bp 30–60°)].

Anal. Calcd for $C_{13}H_{14}N_2O_7$: C, 50.32; H, 4.55; N, 9.03. Found: C, 50.26; H, 4.60; N, 9.02.

The *p*-nitrobenzoate derivative was obtained as yellow plates from pentane–benzene, mp 114–116°.

Anal. Calcd for $C_{13}H_{13}NO_5$: C, 59.31; H, 4.98; N, 5.32. Found: C, 59.61; H, 5.22; N, 5.31.

The major product (**7a**) displayed the following physical data: bp 79–81° (0.75 mm); $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 4.41 (singlet, 1 H, O*H*), *ca.* 4.00 (multiplet, 4 H, protons at C-1, C-3, and C-7), *ca.* 2.85 (multiplet, 1 H, C-5 proton), *ca.* 1.80 (multiplet, 4 H, protons at C-4 and C-6).

Conversion to a 3,5-dinitrobenzoate afforded yellowish-white plates, mp 119–120° (from petroleum ether–benzene or ethanol).

Anal. Calcd for $C_{13}H_{12}N_2O_7$: C, 50.65; H, 3.92; N, 9.09. Found: C, 50.54; H, 4.13; N, 9.12.

When the reduction was performed in refluxing ether as solvent for 24 hr, the ratio of **6a**:**7a** was found to be 60:40.

B. D_2O Work-up. Reduction of 2.2 g (0.02 mole) of **5** with 0.80 g of lithium aluminum hydride as above, except that D_2O was employed exclusively in the work-up, led to the formation of two al-

---

[18] N. D. Zelinskii and N. V. Elagina, *Dokl. Akad. Nauk SSSR*, **87**, 755 (1952); *Chem. Abstr.*, **48**, 542 (1954).

[19] R. L. Letsinger and D. F. Pollart, *J. Am. Chem. Soc.*, **78**, 6079 (1956).

[20] The cleavage shown in **18** is pictured as involving electrophilic substitution (assuming AlH_3 to play a dominant role as acid) with retention at the "leaving" carbon; strictly speaking, therefore, comparison should be made only with acid-catalyzed cyclopropanol openings which occur with retention of configuration (base-catalyzed cleavages in this instance proceed with inversion): C. H. DePuy, F. W. Breitbeil, and K. R. DeBruin, *ibid.*, 88, 3347 (1966); C. H. DePuy and L. R. Mahoney, *ibid.*, **86**, 2653 (1964); P. S. Wharton and T. I. Bair, *J. Org. Chem.*, **31**, 2480 (1966).

[21] E. A. Hill and J. A. Davidson, *J. Am. Chem. Soc.*, **86**, 4663 (1964); E. A. Hill, H. G. Richey, Jr., and T. C. Rees, *J. Org. Chem.*, **28**, 2161 (1963).

[22] H. G. Richey, Jr., and E. A. Hill, *ibid.*, **29**, 421 (1964); P. T. Lansbury and V. A. Pattison, *J. Am. Chem. Soc.*, **85**, 1886 (1963).

[23] Melting points are corrected and boiling points are uncorrected. The infrared spectra were determined with a Perkin-Elmer Infracord spectrophotometer fitted with sodium chloride prisms. The vpc analyses were obtained with an Aerograph A-90P gas chromatograph; helium was used as the carrier gas and percentage compositions refer to the relative areas observed for the different components. The nmr spectra were obtained with a Varian A-60 spectrometer purchased with funds made available from the National Science Foundation. Deuterium analyses (falling-drop method) were determined by Josef Nemeth, Urbana, Ill.

[24] O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Am. Chem. Soc.*, **84**, 1220 (1962).

cohols in the ratio of 45:55. The major component was found to be identical with **7a** with the exception that no O*H* signal was observable in the nmr spectrum.

The minor component possessed the same vpc retention time as **6a**, but the nmr spectrum indicated it to be **6c**; $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ multiplets centered at 3.78, 3.50, and 1.30–2.54 were unchanged from those in **6a**; 1.00 (doublet of triplets, 2 H, J = 7 and 1.5 cps, >C(H)C*H*$_2$D).

Anal. Calcd for $C_6DH_{11}O_2$: D, 8.33. Found: D, 8.24.

Lithium Aluminum Deuteride Reduction of 5. Reduction of 3.0 g of **5** with 1.0 g of lithium aluminum deuteride in tetrahydrofuran as above, followed by the usual aqueous work-up and preparative vpc, led to the isolation of **6b** and **7b** (ratio 48:52): **6b**: $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 3.90 (singlet, 1 H, O*H*), *ca.* 3.78 (multiplet, 3 H, C*H*$_2$OC*H*<), 3.47 (multiplet, 1 H, DC*H*OH), 1.30–2.50 (multiplet, 3 H, remaining ring protons), and 0.98 (doublet of triplets, 2 H, J = 7 and 1.5 cps, >C(H)C*H*$_2$D) (*Anal.* Calcd for $C_6D_2H_{10}O_2$: D, 16.67. Found: D, 16.50); **7b**: $\delta_{\mathrm{TMS}}^{\mathrm{CCl_3}}$ 4.71 (singlet, 1 H, O*H*), *ca.* 3.95 (multiplet, 4 H, protons at C-1, C-3, and C-7), *ca.* 2.82 (multiplet, 1 H, C-5 proton), *ca.* 1.77 (multiplet, 3 H, protons at C-4 and C-6) (*Anal.* Calcd for $C_6DH_9O_2$: D, 10.00. Found: D, 9.90).

Hydroboration of 4. A solution of 3.0 g (0.032 mole) of **4** in 60 ml of anhydrous tetrahydrofuran was treated at 20° with externally generated diborane[25] produced by adding dropwise 60 ml of 0.25 *M* sodium borohydride in diglyme to a stirred solution of 4.26 g (0.03 mole) of boron trifluoride etherate in 20 ml of the same solvent. The organoboron derivative(s) was oxidized at 30–50° by the addition of 5 ml of 3 *N* sodium hydroxide solution followed by careful dropwise addition of 4 ml of 30% hydrogen peroxide. The reaction mixture was stirred for an additional hour; 60 ml of ether was added, and the organic phase was separated. The aqueous layer was saturated with sodium chloride and extracted twice with 50-ml portions of ether. The combined extracts were washed twice with 10-ml portions of saturated sodium chloride solution, dried, and evaporated. Distillation of the residue afforded 1.7 g (46.5%) of a colorless liquid, bp 93–96° (1.1 mm), n^{23}D 1.4774. Vpc analysis of this material indicated a mixture of two products in a ratio of 80:20. Preparative vpc (1% Carbowax 20M) of the major product gave pure **7a**; infrared and nmr spectra superimposable upon those of an earlier sample; 3,5-dinitrobenzoate mp 119–120° (from methanol); melting point undepressed when admixed with an authentic sample.

Action of LAH on 2 and 7a. In separate experiments, 200-mg samples of **2** and **7a** and 100 mg of lithium aluminum hydride in 10 ml of anhydrous tetrahydrofuran were refluxed with stirring for 48 hr. Work-up as above led to the recovery of the appropriate alcohol with no observable contamination by a second component.

3-Methyl-2-furfuryl Alcohol (9). To a magnetically stirred slurry of 1.52 g (0.04 mole) of lithium aluminum hydride in 50 ml of ether was added dropwise 5.0 g (0.0356 mole) of methyl 3-methyl-2-furoate (**8**)[26] in 50 ml of ether. The resulting slurry was stirred overnight at reflux temperature and cooled. After the dropwise addition of 1.5 ml of water, 1.5 ml of 30% potassium hydroxide solution, and 4.5 ml of water, the mixture was filtered, and the solids were washed with several portions of ether. The combined organic layers were dried, filtered, and evaporated. The residue was distilled to give 3.6 g (90%) of a clear colorless liquid, bp 44–46° (0.3 mm), n^{20}D 1.4881 [lit.[27] bp 79–81° (3 mm), n^{20}D 1.4880].

***cis*-2-Hydroxymethyl-3-methyltetrahydrofuran (6a).** A solution of 2.4 g (0.0212 mole) of **9** in 50 ml of anhydrous methanol was hydrogenated over 500 mg of 5% rhodium on carbon for 45 hr at *ca.* 40 psig. The catalyst was removed by filtration, and the filtrate was evaporated *in vacuo*. Distillation of the residue yielded 1.2 g (48.4%) of colorless liquid, bp 55–58° (0.7 mm). Vpc analysis indicated the sample to be 95% pure.

Conversion of this liquid to its 3,5-dinitrobenzoate gave colorless plates which rapidly yellowed on exposure to air, mp 68–69° (from petroleum ether–ether); this sample was identical in all respects with the material prepared earlier.

***cis*-3-Hydroxymethyl-2-methyltetrahydrofuran (11).** A solution of 800 mg (7.1 mmoles) of **10**[28] in 35 ml of methanol was hydrogenated as above. The residue was purified by molecular distillation and was converted to its 3,5-dinitrobenzoate, white crystals from hexane–ether, mp 53–55°.

Oxidation of 7a. A solution of 500 mg of **7a** in 1.5 ml of water was cooled in ice and stirred while a solution of 640 mg of potassium dichromate in 2.4 ml of concentrated sulfuric acid and 5 ml of water was added dropwise over a 10-min period. After the addition was completed, the mixture was stirred at room temperature for 30 min and was extracted exhaustively with ether. The green aqueous layer was saturated with sodium chloride and reextracted with ether. The combined organic layers were dried, filtered, and evaporated.

The remaining oil displayed the following physical properties: $\nu_{\mathrm{max}}^{\mathrm{CCl_4}}$ 1785 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 4.05 (doublet, J = *ca.* 2.5 cps, 1 H, proton at C-1); the remainder of the absorption was upfield from these peaks, but was not amenable to ready analysis due to complex spin–spin splitting and overlapping of bands.

Treatment of the oil with semicarbazide in the usual manner afforded a crystalline semicarbazone, mp 177–179° (from ethanol).

Anal. Calcd for $C_7H_{11}N_3O_2$: C, 49.69; H, 6.55. Found: C, 49.81; H, 6.79.

Acknowledgment. The authors are grateful to the Alfred P. Sloan Foundation and the Army Research Office (Durham) for grants which contributed to the financial support of this research.

---

(25) G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 31 (1963).

(26) D. M. Burness, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 649.

(27) E. Sherman and E. D. Amstutz, *J. Am. Chem. Soc.*, **72**, 2195 (1950).

(28) The authors are indebted to Professor John Dyer for a sample of this alcohol.