Stereoselectivity in the Nonconcerted Reductive Rearrangement of Some Bicyclic Spiro Oxides[1]

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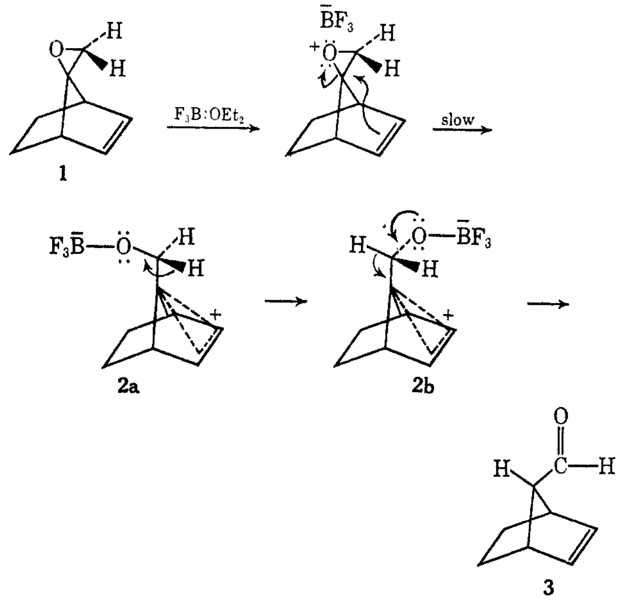
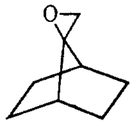
The reductive rearrangement of the series of bicyclic spiro oxides **1** and **4–8** has been examined using mixtures of lithium aluminum deuteride (or hydride) and aluminum trichloride. Three types of monodeuterated products are found: primary-deuterated tertiary alcohol in the case of **4** and **6**, tertiary-deuterated primary alcohol in the case of **1**, and α-deuterated primary alcohol in the case of **5–8**. The stereochemistry of the products has been determined in each case and the mechanisms of the reductions are discussed. Evidence is presented in the cases of **1**, **6**, and **8** that the reductive rearrangement occurs exclusively or predominately in a nonconcerted fashion by way of a zwitterionic intermediate. It is suggested that the tendency of a terminal spiro oxide to be reduced in a nonconcerted fashion, in addition to being dependent upon the nature of the reducing species in solution, is governed by the stability of the cationic portion of the intermediate. Further, it is suggested that the tendency of such an intermediate to react by hydride migration (internal nucleophilic attack) rather than deuteride (or hydride) transfer from the coordinated alane (external nucleophilic attack) is governed by the extent of charge delocalization in the cationic portion of the intermediate. Finally, the ratio of *exo*/*endo* attack by the internal nucleophile, hydride, in the intermediates formed during the reduction of **6** and **8** is shown to be unusually low for a carbonium ion type of process, 3.3–7.1 and ~5.2, respectively. It is suggested that these ratios are consistent with the idea of steric hindrance to *endo* attack on the norbornyl ion or with the operation of a torsional effect.

During the course of an investigation directed toward the synthesis of 7-functionally substituted norbornenes we observed that spiro[2-norbornen-*anti*-7,2′-oxacyclopropane] (**1**) is converted stereoselectively into 2-norbornen-*syn*-7-carboxaldehyde (**3**) by heat and/or Lewis acids.[2] Because epoxides normally rearrange in a concerted fashion with inversion of configuration at the migration terminus[3] we suggested that the reaction in this case is nonconcerted and probably involves the charge-delocalized intermediate **2**[2] (Scheme I).

Scheme I



With the expectation that their rearrangements may also occur *via* cationic intermediates similar to those which had previously been investigated under solvolytic conditions,[4] we attempted to extend our studies to include the spiro oxides **4–8**.[5] We found that the results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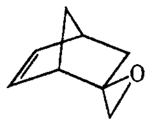
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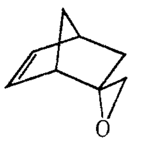
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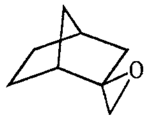
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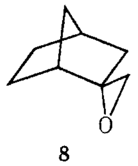
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were stereochemically meaningless in these cases because the aldehydic products were epimerized and/or polymerized under the reaction conditions.[6] Since the extensive investigations of Eliel and coworkers had demonstrated that terminal oxides could be converted into mixtures of primary and secondary or tertiary alcohols by treatment with lithium aluminum hydride and aluminum trichloride,[7] it appeared that the epoxides **1** and **4–8** should react with lithium aluminum deuteride–aluminum trichloride mixtures to yield stable products of three types: primary alcohols having a tertiary deuterium, primary alcohols with a primary (α) deuterium label, and tertiary alcohols containing a primary deuterium (*viz.*, Scheme II). Thus an examination of the product distribution and stereochemistry in each case might allow us (1) to distinguish those products that were formed in a nonconcerted manner,

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[1] Portions of this work have been presented before the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, Abstract K8; the 39th Meeting of the South Carolina Academy of Science, Clinton, S. C., April 1966 [*Bull. S. Carolina Acad. Sci.*, **28**, 46 (1966)]; and the 19th Southeastern Regional Meeting of the American Chemical Society, Atlanta, Ga., Nov 1967, Abstract 26.

[2] R. K. Bly and R. S. Bly, *J. Org. Chem.*, **28**, 3165 (1963).

[3] *Cf.* ref 2, footnotes 26–29.

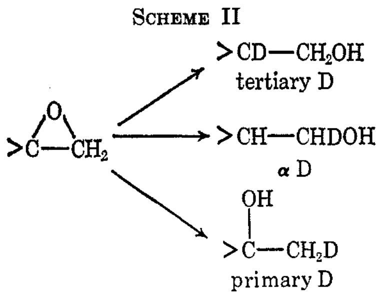
[4] For recent reviews, see (a) J. A. Berson in "Molecular Rearrangements," P. De Mayo, Ed., John Wiley & Sons, Inc., New York, N. Y., 1963, p 111 ff; (b) B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms—1965," Interscience Publishers, New York, N. Y., 1966, p 1 ff; (c) B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms—1966," Interscience Publishers, New York, N. Y., 1967, p 1 ff.

[5] (a) R. S. Bly, C. M. DuBose, Jr., and G. B. Konizer, *J. Org. Chem.*, **33**, 2188 (1968); (b) R. K. Bly and R. S. Bly, *ibid.*, **34**, 304 (1969).

[6] G. B. Konizer, Ph.D. Dissertation, Department of Chemistry, University of South Carolina, 1968.

[7] (a) E. L. Eliel and D. W. Delmonte, *J. Amer. Chem. Soc.*, **80**, 1744 (1958); (b) E. L. Eliel and M. N. Rerick, *ibid.*, **82**, 1362 (1960); (c) M. N. Rerick and E. L. Eliel, *ibid.*, **84**, 2356 (1962).

SCHEME II

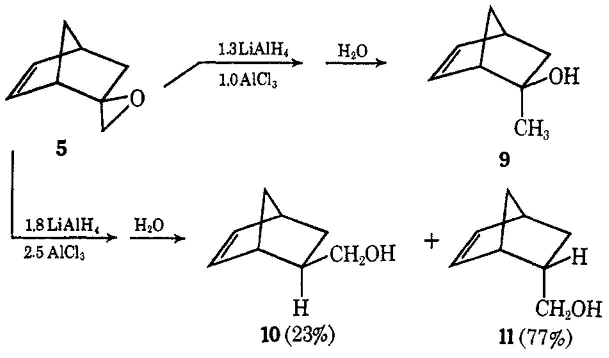


(2) to compare the relative stabilities of the intermediates, and (3) to assess the relative tendency of each intermediate to undergo attack by an external (deuteride) or internal (hydride) nucleophile with retention or inversion of configuration. The results of our investigations are reported here.

Methods and Results

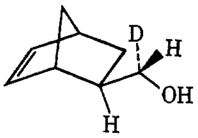
Each of the terminal oxides **1**[2] and **4–8**[5] is reduced and/or rearranged and reduced to a mixture of known tertiary and/or primary alcohols when treated with an ethereal solution of lithium aluminum hydride and aluminum chloride. As in previously reported cases,[7] the relative amount of primary alcohol(s) formed is proportional to the relative amount of halide used. For example, at −10–0° the reaction of 30 mol % spiro[2-norbornen-*exo*-5,2′-oxacyclopropane] (**5**), with 40 mol % lithium aluminum hydride and 30 mol % anhydrous aluminum chloride produces only the tertiary alcohol, *endo*-5-methyl-2-norbornen-*exo*-5-ol (**9**),[5a] but a mixture of 19 mol % **5**, 34 mol % hydride, and 47 mol % aluminum trichloride yields only the two primary alcohols, 2-norbornene-*exo*- and -*endo*-5-methanol (**10** and **11**, respectively)[8] (Scheme III).

SCHEME III

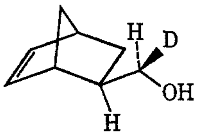


Although more than one oxide/reducing agent/halide mixture was used with most of the oxides, the approximate ratio of 19:34:47 was adopted as a "standard" and each oxide was reduced in this manner. This particular mixture was chosen because it provides appreciable amounts of the primary alcohol(s) in most cases, yet differentiates the various oxides according to their tendency to undergo electrophilic rearrangement (*cf.* Experimental Section).

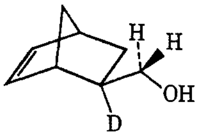
When lithium aluminum deuteride is substituted for hydride in the "standard" mixture the proportions of tertiary to primary alcohols remain essentially unchanged. Under these conditions the *endo*-methanol **11** produced from the unsaturated *exo* oxide **5** appears to be monodeuterated (>95% D_1) exclusively at the α position and is composed of approximately equal amounts of the two diastereomers **11a** and **11b**. The *exo*-methanol **10** produced in this reaction consists of approximately equal amounts of the α-deuterated diastereomers **10a** and **10b**, but may also contain as much as 5% (1–2% over-all) tertiary-deuterated isomer **10c**. We can detect none of the tertiary-deuterated *endo*-methanol **11c** in the mixture.



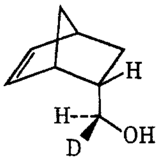
10a



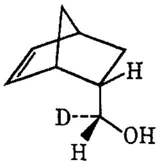
10b



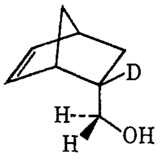
10c



11a



11b



11c

The position and extent of the deuterium label was deduced from mass spectral and/or nmr data. For example, the 100-MHz spectrum[9] of the collected *endo*-methanol **11** exhibits doublets of similar magnitude at δ 3.24 ($J \approx 5$ Hz) and 3.06 ($J \approx 8$ Hz) which together integrate for one hydrogen, as well as a one-hydrogen multiplet at δ 2.36–2.04 due apparently to the *exo*-5 hydrogen.[10] In the spectrum of the undeuterated material these two hydrogens are found as part of a complex, ABX-type, three-proton multiplet. The α-hydrogen resonances of the deuterated *exo*-methanol **10** also appear as doublets, δ 3.63 ($J \approx 5$ Hz) and 3.45 ($J \approx 8$ Hz) in the 100-MHz nmr spectrum,[9] and together integrate for one hydrogen. In the spectrum of the *exo*-methanol, the *endo*-5-hydrogen signal ($\delta \approx 1.6$) is no longer sufficiently resolved from those of the C-6 and C-7 hydrogens ($\delta \approx 1.0$–1.5) for accurate individual integration, but it is evident from the mass spectrum of the deuterated material that this *exo* alcohol consists of 97.95% D_1 and 2.05% D_0 species.[11] Since the relative integrals of the α (area, 1) and C-5 plus C-6 plus C-7 hydrogens (area, 5) indicate that the deuterium label must be present predominately at the α position, it follows that the tertiary-deuterated species **10c** comprises less than 5% of the total product.[12]

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[8] (a) K. Alder and E. Windemuth, *Chem. Ber.*, **71**, 2409 (1938); (b) P. Resnick and J. G. Pucknat, 136th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1959, Abstracts, p 95P; (c) J. A. Berson, J. S. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff, and D. Willner, *J. Amer. Chem. Soc.*, **83**, 3986 (1961).

[9] We are indebted to Dr. M. R. Wilcott, III, Department of Chemistry, University of Houston, for determining the 100-MHz spectra.

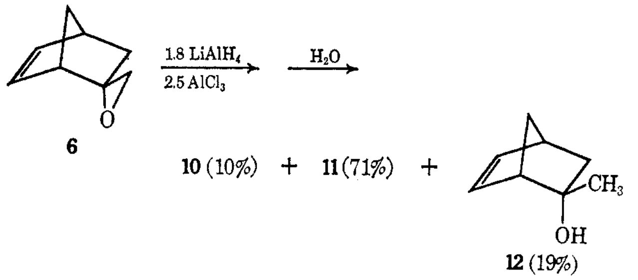
[10] *Cf.* (a) P. Laszlo and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **85**, 2709 (1963); (b) *ibid.*, **86**, 1171 (1964); (c) S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Org. Chem.*, **31**, 2726 (1966).

[11] The mass spectrum was determined and interpreted by the Morgan Schaffer Corp., 5110 Courtrai Ave., Montreal 26, Quebec, Canada.

[12] An indication of the position of the deuterium label was also obtained by analysis of the mass spectrum.[11] A comparison of the relative intensities of the m/e 93 (P − CHDOH?) and 94 (P − CH$_2$OH?) fragments in the monodeuterated species with those in the mass spectrum of the nondeuterated material indicates that approximately 5% of the deuterium label is located somewhere other than at C-8 and may therefore be at C-5. However, the quantitative analysis is complicated since ions are present corresponding to P − 29, P − 30, P − 32, and P − 33. Under the circumstances we believe that the results obtained by nmr analysis are probably more reliable.

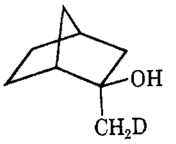
The unsaturated *endo* oxide, spiro[2-norbornen-*endo*-5,2′-oxacyclopropane] (**6**) reacts with the "standard" hydride mixture at −10–0° to produce 10% **10**, 71% **11**, and 19% tertiary alcohol *exo*-5-methyl-2-norbornen-*endo*-5-ol (**12**)[5a,13] (*e.g.*, see Scheme IV).

Scheme IV



When the reductive rearrangement is repeated with "standard" lithium aluminum deuteride–aluminum trichloride, the 100-MHz nmr spectra[9] of the collected primary alcohols **10** and **11** again show no evidence of either of the tertiary-deuterated species **10c** and **11c**, although the mass spectrum[11] of the *endo*-methanol **11** indicates that it consists of 3.0% D_0, 94.5% D_1, and 2.5% D_2 species and *may* contain as much as 10% of the deuterium at C-5.[12]

When the two saturated oxides, spiro[norbornane-*exo*- and -*endo*-2,2′-oxacyclopropanes] (**7** and **8**), respectively, are reduced with the "standard" lithium aluminum deuteride–aluminum trichloride mixture they yield essentially identical mixtures of the α-deuterated norbornane-*exo*- and -*endo*-2-methanols,[14] **13** and **14** (Scheme V). Neither of the deuterated tertiary alcohols **15** or **16** could be detected by gas–liquid partition



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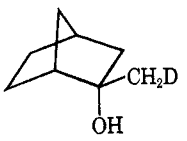

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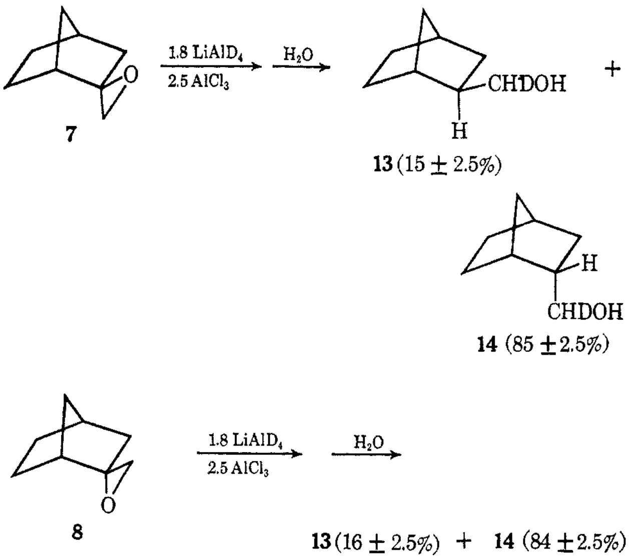
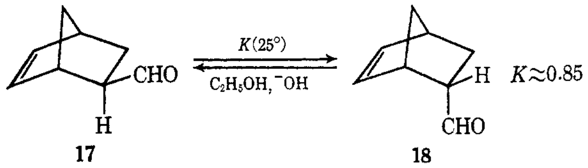
chromatographic (glpc) analysis of these mixtures, but we were able to demonstrate by control experiments using their known[13] nondeuterated counterparts that either would have been readily apparent had it been present. Although the primary alcohols were partially separated by glpc on a 300-ft Ucon-coated capillary, their relative abundance could be determined with greater precision by analysis of the 60- and 100-MHz[9] nmr spectra of the collected mixtures. The *endo*-C-3-hydrogen resonance of **14**, though split by those of the *exo*-C-2 ($J \approx$ 3–4.5 Hz)[10] and *exo*-C-3 hydrogens ($J \approx$ 11 Hz)[10] into a perturbed quartet centered at δ ~0.6, is well resolved from all the other methylene hydrogen resonances of **13** and **14**. Therefore estimates of the relative proportion of these two alcohols in the mixtures were made by comparing the integral of this *endo*-C-3-hydrogen resonance in **14** with that of the combined hydroxyl–hydrogen resonances of **13** and **14**. Mass spectral analyses of the reaction mixtures[11] indicate that the methanols from **7** consist of <6.6% D_0 and >93.4% D_1 species, while those from **8** contain <4.9% D_0 and >95.1% D_1. The 60-MHz nmr spectrum of each mixture reveals that the areas of the carbonyl- and hydroxyl-hydrogen resonances differ by less than 5%. Thus it follows that in each case both isomers are deuterated predominately at the carbinol carbon.

Scheme V

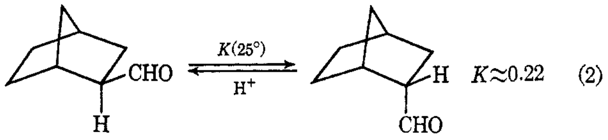


It is evident that aldehydes are not formed as intermediates during the reductive rearrangements of any of the 5,2′- or 2,2′-spiro oxides **4**–**8**. Treatment of either 2-norbornene-*exo*- or -*endo*-5-carboxaldehyde (**17** or **18**)[14] with the "standard" hydride mixture yields only the corresponding *exo*- or *endo*-methanol, **10** or **11**, respectively. Under similar conditions, a 56:44 mixture of norbornane-*exo*- and -*endo*-2-carboxaldehydes (**19** and **20**)[14] is reduced to the same ratio of the corresponding carbinols **13** and **14**. Furthermore, the epimerization of either of the unsaturated aldehydes **17** or **18** with dilute ethanolic sodium hydroxide at 25° produces an identical 54:46 mixture of *exo*/*endo*, *viz*.



17 **18**

while the acid-catalyzed equilibration at 25° of the two saturated aldehydes **19** and **20** yields a mixture consisting of 82% **19** and 18% **20**, *e.g.*



19 **20**

The *exo*/*endo* ratio in each of these two mixtures differs significantly from either of those observed for the carbinols formed in the reductive rearrangements of the unsaturated or saturated epoxides **5** and **6** or **7** and **8**, respectively.

In sharp contrast to the 5,2′- and 2,2′-spiro oxides **5**–**8**, which yield exclusively or predominantly α-

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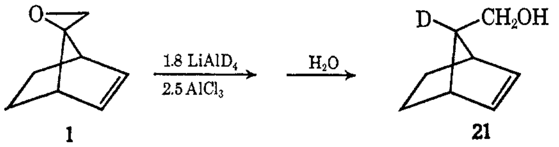
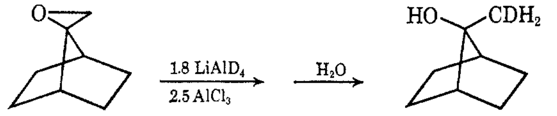
[13] (a) N. J. Toivonen and P. J. Mälkönen, *Suomen Kemistilehti*, *B*, **32**, 277 (1959); (b) P. Hirsjarvi and K. Salo, *ibid.*, **32**, 280 (1959); (c) P. J. Mälkönen and N. J. Toivonen, *ibid.*, **33**, 53 (1960).

[14] For the nondeuterated compound(s), see K. Alder, G. Stein, and E. Rolland, *Ann. Chem.*, **525**, 247 (1936).

deuterated products, the 7,2′-spiro oxides 1 and 4, react with the "standard" deuteride mixture to produce alcohols deuterated solely at the β position. Spiro[2-norbornen-*syn*-7,2′-oxacyclopropane] (1)[2] yields only *anti*-7-deuterio-2-norbornene-*syn*-7-methanol (21) as attested by the presence of a two-hydrogen singlet (due to the unsplit methylol hydrogens) at δ 3.38 in the 60-MHz spectrum of the collected product. (The spectrum of the nondeuterated alcohol exhibits a two-hydrogen doublet, $J = 7$ Hz, at this position.[2]) Under these same conditions the saturated epoxide spiro[norbornan-7,2′-oxacyclopropane] (4)[5b] yields a single alcohol whose glpc retention time on an 8-ft Carbowax 20M column is identical with that of authentic 7-methylnorbornan-7-ol.[2] Since the 60-MHz spectrum of the product shows no signals which can be assigned to a hydrogen α to the hydroxyl group while the mass spectrum indicates that each molecule contains a single deuterium (M$^+$ = 172), we conclude that this product is the primary-deuterated tertiary alcohol 22.



1 21



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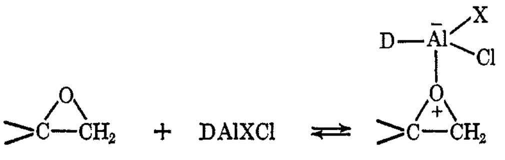
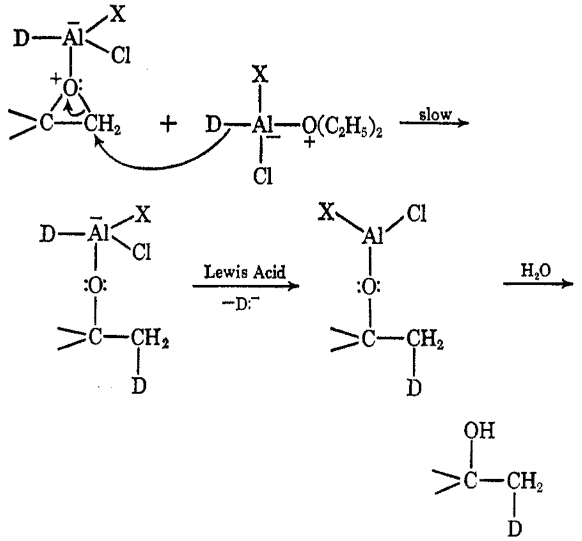
Discussion

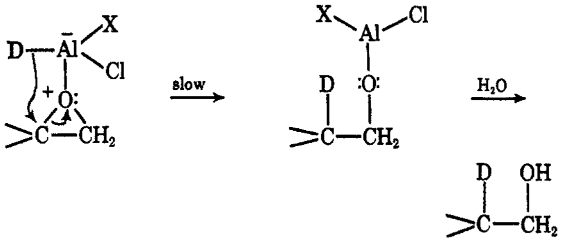
The extensive and detailed investigations originally of Eliel, Delmonte, and Rerick[7] and recently of Ashby, Prather, Cooke, and Lott[15] have done much to define the scope and mechanistic detail of the reactions between epoxides and mixtures of lithium aluminum hydride (or deuteride) and aluminum halides. Since the reductions are invariably less facile in the absence of halide, it is likely that the initial step involves the formation of a complex between the epoxide and some electrophilic species.[15b] Ashby and Prather[15a] have demonstrated that this species in 1:1 hydride/halide mixtures is chloroalane, H$_2$AlCl; in 1:3 mixtures, dichloroalane, HAlCl$_2$. The reductions reported here normally utilized 1.8:2.5 mol ratios of deuteride/halide; hence the effective Lewis acid is actually a mixture of dideuteriochloroalane and deuteriodichloroalane, represented as DAlXCl where X is deuterium or chlorine. The initial step in the reaction may thus be formulated as shown below.



Ashby and Cooke[15b] have argued that reduction occurs directly on the undissociated complex itself when the coordinating electrophile is a relatively weak Lewis acid such as alane (AlH$_3$).[16] In the case of an isobutylene-type oxide, direct *inter*molecular reduction (path A) should yield a primary-deuterated tertiary alcohol predominantly. A concerted *intra*molecular process (path B) should give a tertiary-deuterated, primary alcohol as the major product. The direct reduction paths A and B predict that the initial configuration at the tertiary center should be retained in the products.

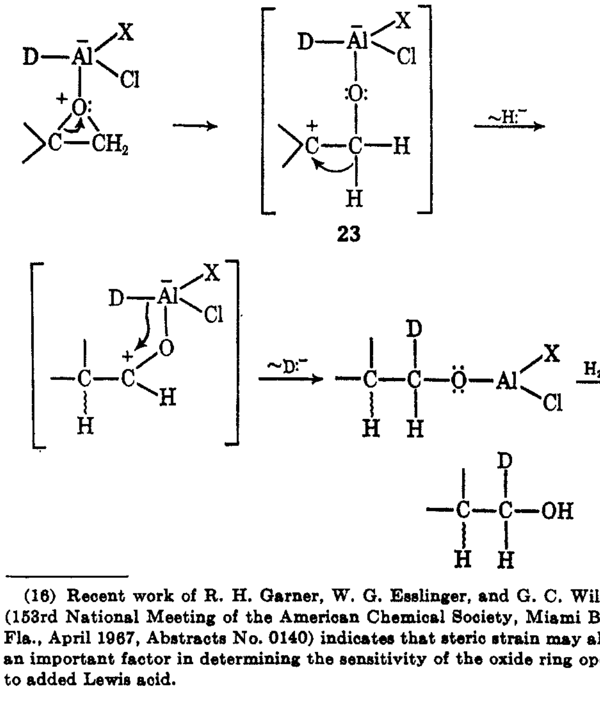


(A)



(B)

When a stronger Lewis acid such as dichloroalane (HAlCl$_2$) is employed, Ashby and Cooke[15b] suggest that the complex undergoes ring opening with hydrogen (or alkyl) migration prior to reduction. An isobutylene-type oxide reacting in this manner (path C) should



(C)

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(15) (a) E. C. Ashby and J. Prather, *J. Amer. Chem. Soc.*, **88**, 729 (1966); (b) E. C. Ashby and B. Cooke, ibid., **90**, 1625 (1968); (c) B. Cooke, E. C. Ashby, and J. Lott, *J. Org. Chem.*, **33**, 1132 (1968).

(16) Recent work of R. H. Garner, W. G. Esslinger, and G. C. Williams (153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Abstracts No. 0140) indicates that steric strain may also be an important factor in determining the sensitivity of the oxide ring opening to added Lewis acid.

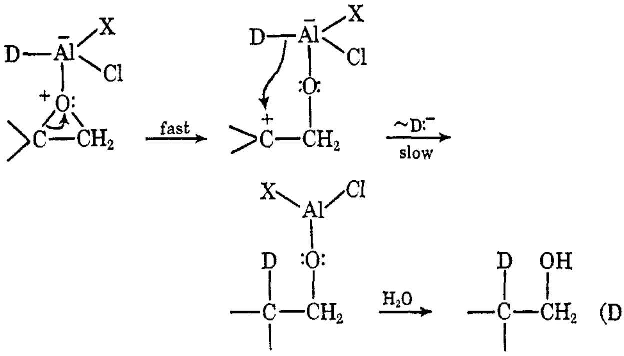
yield a primary-deuterated primary alcohol[13] predominantly or exclusively. If hydride migration is concerted with the ring opening, then the configuration at the tertiary center should be inverted in the product, but, if the free cation **23** is an intermediate, the product could be of either retained or inverted configuration.[3]

Inherent in the suggestions of Ashby and Cooke is the expectation that those epoxides which can form the most stable cations upon heterolysis will show the greatest tendency to react by the indirect route (path C). If the relative unimolecular acetolysis rates of the corresponding secondary brosylates,[17] *i.e.*

$$>\mathrm{CHOBs} \xrightarrow[25°]{\mathrm{AcOH-AcO^-}} >\overset{+}{\mathrm{C}}\mathrm{-H} + \overset{-}{\mathrm{O}}\mathrm{Bs}$$

can be taken as a measure of the relative stabilities of the tertiary cations (**23**), then the tendency of the spiro oxides to react by the indirect route should increase in the following order: **4** ≪ **6** < **8** < **5**, **7** < **1**.

Our data appear to confirm this prediction. Spiro[norbornan-7,2′-oxacyclopropane] (**4**) does not rearrange when treated with the "standard" hydride mixture but yields only the direct intermolecular reduction product, 7-deuteriomethyl-7-norbornanol (**22**), *via* path A. As expected, spiro[2-norbornen-*endo*-5,2′-oxacyclopropane] (**6**) exhibits a greater tendency to react in the indirect fashion and gives but 19% tertiary alcohol *exo*-5-methyl-2-norbornen-*endo*-5-ol (**12**) under these conditions. None of the other spiro oxides yields detectable amounts of such direct intermolecular reduction products. Although it is predicted to exhibit the greatest tendency for indirect reduction, spiro[2-norbornen-*anti*-7,2′-oxacyclopropane] (**1**) reacts with the lithium aluminum deuteride–aluminum trichloride mixture to produce the reduction product anticipated from the direct intramolecular path B, *viz.*, *anti*-7-deuterio-2-norbornene-*syn*-7-methanol (**21**). Since this oxide is known to rearrange in a nonconcerted fashion with retention of configuration when treated with boron trifluoride etherate[2] or when subjected to glpc on a diethylene glycol succinate or Carbowax column, it is likely that this tertiary-deuterated primary alcohol **21** actually arises *via* the nonconcerted direct intramolecular path D, shown below. Cations of the 7-norbornenyl type normally react with nucleophiles at C-7 to yield products of retained configuration so that the stereochemistry of **21** is correctly predicted by either B or D.[18] The four remaining spiro oxides, **5**–**8**, react with the "standard" deuteride mixture exclusively or predominantly in the "indirect" manner, path C. Except for the relatively small amount of tertiary alcohol (**12**) produced in the case of **6**, each of these oxides yields only α-deuterated, primary alcohols.

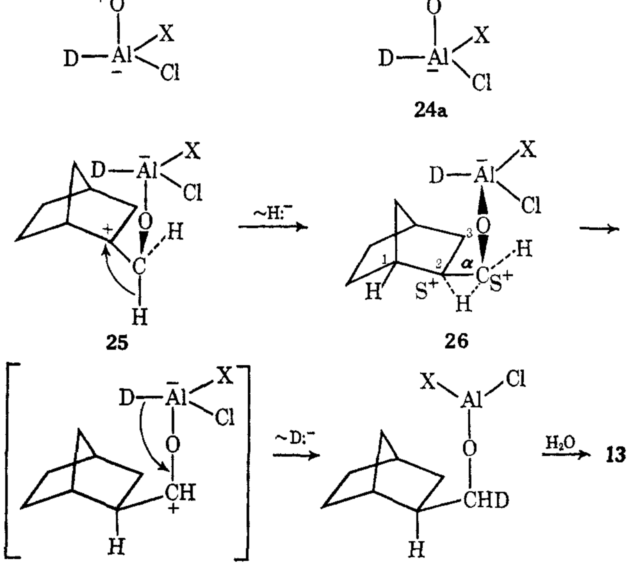


(D)

It is not possible in most cases to specify exactly that fraction of the carbinols which is formed in a nonconcerted process by way of a cationic intermediate such as **23** (nonconcerted C), but certain limits can be placed on this possibility. For example, spiro[norbornan-*exo*-2,2′-oxacyclopropane] (**7**) yields 15% inverted product, α-deuterionorbornane-*exo*-2-methanol (**13**), and 85% **14**, which has the retained configuration at C-2. Since a concerted path would require that the product have an inverted configuration,[3] it is clear that *at least* 85% of **7** is reacting by nonconcerted C. Alternatively, since nonconcerted C could occur with retention or inversion, this path *may* constitute the exclusive mode of reduction.

In the case of the saturated *endo* oxide, **8**, we can be more precise. When treated with the "standard" lithium aluminum deuteride–aluminum chloride mixture this epoxide yields 16% **13** and 84% **14**; *i.e.*, it reacts with 16% retention and 84% inversion. A nonconcerted path is the only rational route by which the α-deuterated methanol of retained configuration, **13**, can be formed from **8**, but for this to occur it is necessary that the initial carbonium ion, **24a**, rotate ~120° about the C-2–C-α bond to give **25**, before the migrating hydride can attack the *endo* side of the ring (*e.g.*, see Scheme VI). Because this rotation is about twice as great as that required to produce **25** from **24b** (*e.g.*, see Scheme VII), it is clear that the relative

Scheme VI



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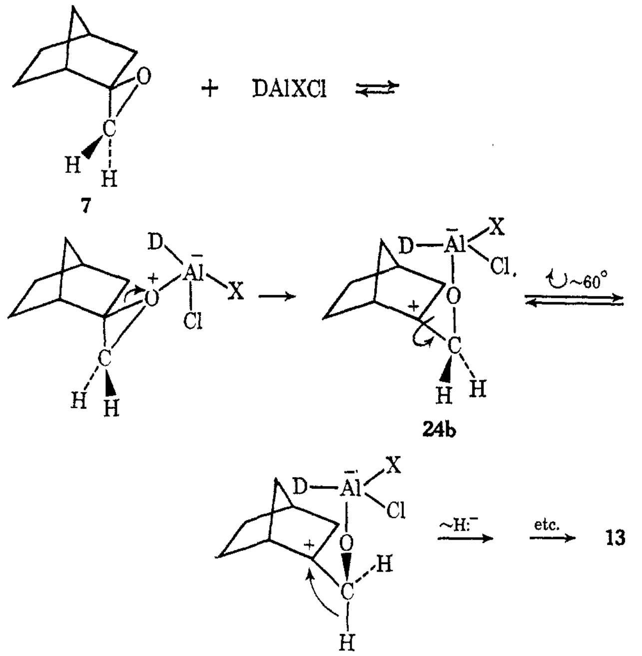
[17] *Cf.* ref 4a, p 193, and references cited therein.

[18] (a) A. Diaz, M. Brookhart, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 3133 (1966); (b) M. Brookhart, A. Diaz, and S. Winstein, *ibid.*, **88**, 3135 (1966); (c) H. Tanida, T. Tsuji, and T. Irie, *ibid.*, **88**, 864 (1966).

Scheme VII



amount of 13/14 produced in a nonconcerted process from **8** cannot exceed the relative amount produced in a similar manner from **7**, but, even if the *exo* oxide **7** reacts *exclusively via* the nonconcerted path (C) the ratio of **13**/**14**, *i.e.*, of *endo*/*exo* hydride migration, cannot be greater than ~15:85 or 0.18. Hence, in the case of **8**, the nonconcerted path can produce no more than 15 parts of *exo*-methanol **13** for every 85 parts of *endo*-methanol **14** that are formed in this manner. Since the observed ratio of **13**/**14** is actually 14:86 in this case, it follows that within experimental error **8** *is reduced exclusively via the indirect, nonconcerted path C under these conditions.*

In a similar manner it may be concluded that *at least* 77% of the α-deuterated primary alcohols **10** and **11** from reduction of the unsaturated *exo* oxide **5** and 10% (*i.e.*, 12% of the total methanols) of those from the *endo* isomer **6** are formed in a nonconcerted manner *via* an intermediate cation such as **23** (path C). Again the possibility that **5** and **6** react exclusively by way of the nonconcerted indirect route (C) cannot be ruled out.

We have suggested that those oxides which can form stable cations by C–O cleavage ought to show a greater tendency to react in a nonconcerted fashion. Why then does **1**, which should form the most stable cation of all, not yield any hydride-migrated product, *i.e.*, the α-deuterated primary alcohol **26**? We believe that the tendency of an oxide to undergo hydride migration (C) rather than deuteride transfer (D) when reduced in a nonconcerted fashion is governed by the extent of charge delocalization at the migration terminus in the intermediate cation. In the case of **1** the intermediate cation owes much of its stability to the fact that the positive charge is extensively delocalized to the C-2 and C-3 positions.[19] Hence there is little driving force for the migration of the weakly basic carbon-bonded internal nucleophile, hydride, from C-8 to C-7, and the more strongly basic aluminum-bonded external nucleophile, deuteride, is transferred from the coordinated deuterioalane instead. Attack is exclusively at C-7 rather than at C-2 or C-3 as in the case of the free carbonium ion[19] because the coordinated alane, $^{+}$RO–Al^{-}DXCl, is a much stronger reducing agent (nucleophile) than is the deuterioalane–diethyl ether complex, $R_2O \rightarrow AlDXCl$.[7c] Internal nucleophilic attack (hydride migration) is the exclusive reaction when **1** is rearranged to aldehyde by treatment with boron trifluoride etherate[2] because no stronger external nucleophile is present. In the reduction of the oxides **6**–**8**, the intermediate cations are not so highly delocalized and internal neucleophilic attack (hydride migration) occurs before the external nucleophile (deuteride) can be transferred.

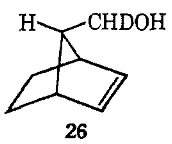


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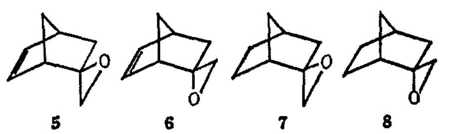
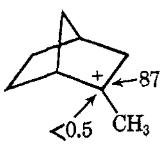
Table I

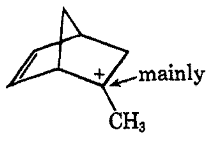


	Starting oxide			
	5	6	7	8
Ratio of *exo*/*endo* primary-deuterated methanol	0.30	0.14	0.18	0.19
Fraction of primary-deuterated methanols produced in a nonconcerted process (C)	0.77–1.0	0.12–1.0	0.85–1.0	$\sim$1.0
Ratio of *exo*/*endo* hydride attack in the nonconcerted reaction	$\geqslant$3.3	3.3–7.1	$\geqslant$5.7	$\sim$5.2

Of particular interest are the ratios of *exo*/*endo* hydride attack which are observed when the spiro oxides **5**–**8** are reduced in an indirect nonconcerted manner (C). These ratios may be derived in each case from the product composition and the estimated extent of nonconcerted reaction. The results are summarized in Table I.

Where a firm upper limit can be placed on the ratio of *exo*/*endo* attack in the nonconcerted process, *e.g.*, in **6** and **8**, the observed values of 3.3–7.1 and ~5.2, respectively, are much smaller than those usually found for reactions which proceed *via* tertiary norbornyl or tertiary norbornenyl cations.[20] For example, the hydrolysis of 2-methyl-*exo*-norbornyl chloride in 65% aqueous dioxane yields 170 times more 2-methyl-*exo*-2-norborneol than 2-methyl-*endo*-2-norborneol,[21] while the mild alkaline hydrolysis of 5-methyl-2-norbornen-*exo*-5-yl chloride gives "mainly" 5-methyl-2-norbornen-





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[19] (a) H. C. Brown and H. M. Bell, *J. Amer. Chem Soc.*, **85**, 2324 (1963) (b) S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963).

[20] P. von R. Schleyer, *ibid.*, **89**, 699, 701 (1967), and references cited therein.

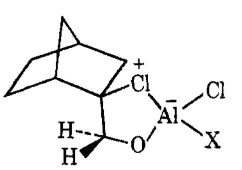
[21] H. C. Brown and H. M. Bell, *ibid.*, **86**, 5006 (1964).

exo-5-ol.[22] Even larger *exo/endo* ratios are observed when such cations react with "internal" nucleophiles: *exo,exo*-3,2-hydride or methyl shifts in these systems occur at least 300 times more rapidly than do their corresponding *endo,endo* counterparts.[23]

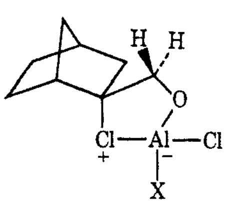
These large preferences for *exo* attack in norbornyl cations where charge delocalization is probably not an important factor[20,24] have been variously attributed to steric hindrance[25] or to a torsional effect between the asymmetrically placed hydrogen at C-1 and the C-2 substituent (methyl) which leads to more severe nonbonded interactions when attack is from the *endo* direction.[20] Schleyer has suggested that a torsional effect may also account for the relatively low *exo/endo* ratios that are observed in reactions which involve the formation or dissociation of exocyclic double bonds in norbornane derivatives,[20] *viz.*, reduction of dehydronorcamphor with sodium borohydride (6.2)[26] or lithium aluminum hydride (10),[27] exchange reactions of dehydronorcamphor dimethyl ketal (16),[28] and chromic acid oxidations of *exo*- and *endo*-norborneols (2.5).[29]

The relatively small preferences for *exo*-hydride attack which are observed in the nonconcerted reductions of the spiro oxides **6** and **8** could be due to either steric or torsional effects. The steric bias for *exo* attack by migrating hydride should be less here than in those cases where the nucleophile must approach the ring from a more remote position. Similarly, even though these nonconcerted reductive rearrangements clearly do not involve exocyclic double bonds, the torsional bias against *endo* attack by the internal nucleophile would also be less than for attack by an external nucleophile. The transition state for *endo* hydride migration (**26**) can be reached from the intermediate **25** with relatively little deflection (<15?) of the C-2–C-α bond from the plane of carbons 1, 2, and 3, and thus entails but a small increase in the nonbonding interaction between C-α and the bridgehead hydrogen at C-1.

If chlorine-bridged charge-transfer complexes rather than free cations are the actual product-forming intermediates, *e.g.*



or



then relatively low ratios of *exo/endo* attack might also be observed. Even though hydride migration should invert the configuration at C-2, there would probably be little difference in stability between the *exo* and *endo* isomers of such complexes. We doubt that chlorine bridging can be important here though for no products are observed that might be expected to result from chlorine migration, *e.g.*, chlorohydrins,[7c] tertiary-deuterated primary alcohols, or glycols.

Experimental Section[30]

2-Norbornene-*exo*- and -*endo*-5-carboxaldehydes (17 and 18).—A mixture of the isomeric aldehydes **17** (26%) and **18** (74%) was prepared by the addition of cyclopentadiene to acrolein according to the procedure for Alder and coworkers:[14] bp 61–63° (9 mm) [lit.[14] 70–72° (20 mm)]. The isomers were separated by glpc on the 8-ft Carbowax column (column temperature 150°, helium flow 60 ml/min).

The first component had retention time of 9.4 min; relative abundance 26%; ir (CCl_4) 3140, 3067, 714 (CH=CH), 2809, 2710, 1723 cm^{-1} (CHO); nmr (CCl_4) δ 9.72 [doublet, *J* = 2.6 Hz (1 >CHC**H**O)], 6.12 [asymmetric triplet (2 C**H**=C**H**)], 3.20–2.82 [two broad overlapping singlets (2 ⩾C**H**, bridgehead)], 2.44–1.72 [complex multiplet (1 >CH**H** + 1 >C**H**CHO)], 1.57–0.90 [complex multiplet (3 >CH**H** + >C**H**H)]; uv (isooctane) 301 mμ (ε 430); **semicarbazone**, mp 163.5–164°, uv (95% ethanol) 234 mμ (ε 16,000).

Anal. Calcd for $C_9H_{13}N_3O$: C, 60.31; H, 7.31; N, 23.45. Found. C, 60.13 H, 7.38; N, 23.23.

The reduction of a 57-mg (0.47 mmol) sample of the aldehyde with excess lithium aluminum hydride yielded, after collection from the 8-ft Carbowax column (column temperature 150°, helium flow 100 ml/min), 32 mg (0.26 mmol, 55%) of 2-norbornene-*exo*-5-methanol (**10**):[8] ir (CCl_4) 3629, 3339, 1028 (CH_2OH), 3060, 708 cm^{-1} (CH=CH); nmr (CCl_4) δ 5.91 [asymmetric triplet (2 C**H**=C**H**)], 4.3 [concentration-dependent singlet (1 O**H**)], 3.50 [octet (2 $>CH^XCH^AH^BOH$)], 2.73 [broad multiplet (2 ⩾C**H**, bridgehead)], 1.86–0.90 [complex multiplet (1 $>CH^XCH^AH^BOH$ + 4 >C**HH**)].

The **second component** had a retention time of 11.7 min; relative abundance 74%; ir (CCl_4) 3140, 3067, 723 (CH=CH), 2811, 2715, 1729 cm^{-1} (CHO); nmr (CCl_4) δ 9.31 [doublet, *J* = 2.5 Hz (1 >CHC**H**O)], 6.02 [octet (2 C**H**=C**H**)], 3.21 [broad singlet (1 ⩾C**H**, bridgehead)], 3.08–2.63 [complex multiplet (1 >C**H**CHO + 1 ⩾C**H**, bridgehead)], 2.15–1.13 [complex multiplet (4 >CH**H** + >C**H**H)]; uv (isooctane) 298 mμ (ε 260); **semicarbazone**, mp 160–161°, uv (95% ethanol) 233 mμ (ε 22,000).

Anal. Calcd for $C_9H_{13}N_3O$: C, 60.31; H, 7.31; N, 23.45. Found: C, 60.06; H, 7.28; N, 23.17.

Reduction of a 67-mg (0.55 mmol) sample of the second aldehyde with excess lithium aluminum hydride gave 42 mg (0.34 mmol, 62%) of 2-norbornene-*endo*-5-methanol (**11**):[8] ir (CCl_4) 3627, 3333, 1031 (CH_2OH), 3055, 721 cm^{-1} (CH=CH); nmr (CCl_4) δ 5.96 [septet (2 C**H**=C**H**), 4.43 [concentration-dependent singlet (1 O**H**)], 3.19 [octet (2 $>CH^XCH^AH^BOH$)], 3.0–2.6 [two broad overlapping singlets (2 ⩾C**H**, bridgehead)], 2.22 [multiplet (1 $>CH^XCH^AH^BOH$)], 2.0–1.1 [complex multiplet (2 >C**HH** + 1 >CH**H**, *exo*)], 0.47 [octet (1 >C**H**H, *endo*)].

The Epimerization of 2-Norbornene-*exo*- and -*endo*-5-carboxaldehydes (17 and 18).—To a 0.5-g sample of the mixture of **17** (26%) and **18** (74%) (*vide supra*) was added 35 ml of a 5% aqueous sodium hydroxide solution and enough 95% ethanol to render the mixture homogeneous. The solution was stirred at

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[22] P. von R. Schleyer and R. E. O'Connor, 134th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1958, Abstracts, p 39P.

[23] J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick, and D. Houston, *J. Amer. Chem. Soc.*, **87**, 3248 (1965); A. M. T. Finch, Jr., and W. R. Vaughn, *ibid.*, **87**, 5520 (1965).

[24] (a) H. C. Brown, *Chem. Brit.*, 199 (1966); (b) H. C. Brown and K. Takeuchi, *J. Amer. Chem. Soc.*, **88**, 5336 (1966).

[25] (a) H. C. Brown, "The Transition State," Special Publications of the Chemical Society, No. 16, The Chemical Society, London, 1962, p 140 ff; (b) H. C. Brown, I. Rothberg, P. von R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Natl. Acad. Sci., U. S.*, **56**, 1653 (1966).

[26] H. C. Brown and J. Muzzio, *J. Amer. Chem. Soc.*, **88**, 2811 (1966).

[27] R. Howe, E. C. Friedrich, and S. Winstein, *ibid.*, **87**, 379 (1965).

[28] T. G. Traylor and C. L. Perrin, *ibid.*, **88**, 4934 (1966).

[29] H. Kwart and P. S. Francis, *ibid.*, **81**, 2116 (1959).

[30] Melting and boiling points are uncorrected. Microanalyses were performed by Bernhardt Mikroanalitisches Laboratorium, 5251 Elbach über Engelskirchen, Germany. The ir spectra were determined on a Perkin-Elmer grating spectrophotometer, Model 337, the 60-MHz nmr spectra on a Varian A-60 spectrometer using tetramethylsilane (δ 0.00) and/or chloroform (δ 7.31) as internal standards, and the uv spectra on a Perkin-Elmer Model 202 spectrophotometer. The gas chromatographic analyses, uncorrected for differences in thermal conductivity of the components, were carried out in an F & M Model 500 chromatograph equipped with a hot-wire detector using either an 8 ft × 0.25 in. column packed with 20% Carbowax 20M on 60/80 mesh nonacid-washed Chromosorb W or a 12 ft × 0.25 in. column packed with 20% TCEP on 60/80 mesh nonacid-washed Chromosorb P or in an F & M Model 500 equipped with a Model 1609 flame ionization detector using a 300 ft × 0.02 in. capillary coated with water-insoluble Ucon. Preparative gas chromatography was performed on an Aerograph Autoprep Model 700-A using a 20 ft × 0.375 in. column packed with 20% Carbowax 20M on 60/80 mesh Chromosorb W. The mass spectra were determined either by the Morgan Schaffer Corp.[11,12] or on a Hitachi Model RMU-6E mass spectrometer.

room temperature and at intervals samples were withdrawn. The samples were extracted with pentane and the extracts were analyzed by glpc on the 8-ft Carbowax column (column temperature 150°, helium flow 75 ml/min). The pure aldehydes are stable to glpc under these conditions. Approximate equilibrium is apparently reached after 15–20 min at which point the mixture contains 54% unsaturated *exo* aldehyde **17** and 46% *endo* aldehyde **18**.

Norbornane-*exo*- and -*endo*-2-carboxaldehydes (19 and 20).[14]—A 7.0-g (0.057 mol) sample of mixed (26% *exo* and 74% *endo*) 2-norbornene-5-carboxaldehydes (**17** and **18**) was hydrogenated in a Parr apparatus at about 3-atm pressure using 100 mg of 5% palladium-on-carbon catalyst in an ethyl acetate solvent. The initial rapid uptake of hydrogen ceased after about 30 min. The catalyst was removed by filtration and the solvent was distilled under nitrogen at 760 mm. The residue was distilled to yield 6.0 g (0.048 mol, 85%) of product, bp 69–70° 13 mm). The *exo* and *endo* isomers were partially separated by glpc on the TCEP column at 115° using a helium flow of 100 ml/min; retention times 21.4 (minor component, **19**) and 23.4 min (major component, **20**). The nmr spectrum (CCl$_4$) of the mixture shows a perturbed singlet at δ 9.67 and a doublet ($J \approx 1.5$ Hz) at 9.54 due to the aldehyde hydrogens of **19** and **20**, respectively. Addition of 1 drop of 6 N hydrochloric acid to the sample tube results, after an induction period of ~15 min, in a simultaneous increase of the upfield and decrease of the downfield signal.

Because of the extreme ease with which they are oxidized or epimerized, no further attempt was made to isolate or characterize the individual saturated aldehydes. The mixed 2,4-dinitrophenylhydrazones melted at 147–148° (lit.[14] mp 141–142°).

The Epimerization of Norbornane-*exo*- and -*endo*-2-carboxaldehydes (19 and 20).—To a 0.5-g sample of the hydrogenated Diels–Alder mixture in 6 ml of ether was added 1 ml of 6 N hydrochloric acid. The reaction mixture was stirred at room temperature and at various times samples of the ethereal layer were withdrawn, dried over anhydrous sodium sulfate, and analyzed by glpc on the TCEP column (column temperature 130°, helium flow 95 ml/min). An equilibrium mixture of 82% *exo* and 18% *endo* was reached in about 25–30 hr.

An attempt to equilibrate these saturated aldehydes in the manner described for **17** and **18**, *i.e.*, using sodium hydroxide catalyst, resulted in the formation of an apparently polymeric, high-boiling material.

Norbornan-*exo*- and -*endo*-2-methanols (13 and 14).[14]—A 20:80 mixture of the unsaturated alcohols **10** and **11** (Interchemical Corp.[31]) was separated by preparative glpc on the 20-ft Carbowax column. Each of the components was hydrogenated in ethyl acetate solution using 5% palladium on carbon as catalyst. The solvent was removed by distillation at atmospheric pressure.

The *exo* isomer (**13**)[8,14] was distilled in a short-path still at 100° (3 mm): ir (CCl$_4$) 3624, 3323, 1038 cm^{-1} (CH$_2$OH); nmr δ 3.26 [perturbed doublet, $J = 7$ Hz (2 >CH^{X}CH^{A}H^{B}OH)], 3.0 [concentration-dependent singlet (1 OH)], 2.17 [broad singlet (2 ⩾CH, bridgehead)], 1.8–0.8 [complex multiplet (8 >CHH + 1 >CH–)].

The *endo* isomer (**14**)[8,14] was distilled at 85° (10 mm): ir (CCl$_4$) 3627, 3340, 1051 cm^{-1} (CH$_2$OH); nmr (CCl$_4$) δ 3.47 [perturbed doublet, $J = 7$ Hz (2 >CH^{X}CH^{A}H^{B}OH)], 3.2 [concentration-dependent singlet (1 OH)], 2.40–0.84 [complex multiplet (2 ⩾CH, bridgehead + 6 >CHH + 1 >CHH (*exo*) + 1 >CH–)], 0.60 [broad quartet (1 >CHH *endo*)].

***endo*-2-Methylnorbornan-*exo*-2-ol (15).**[13]—An 87-mg (0.70 mmol) sample of spiro[norbornan-*exo*-2,2′-oxacyclopropane][4a] (**7**) in 5 ml of anhydrous ether was added in small portions to a stirred slurry of 61 mg (1.6 mmol) of lithium aluminum hydride in 2 ml of ether. The mixture was stirred for 30 min after the addition had been completed and was then decomposed by the addition of a few drops of 15% aqueous sodium hydroxide. The precipitated salts were washed with ether and the combined ethereal extract was dried over anhydrous magnesium sulfate. The solvent was distilled at atmospheric pressure and the residue was sublimed at 65° (65 mm) to yield 23 mg (0.18 mmol, 26%) of white needles. A glpc analysis on the 8-ft Carbowax column (column temperature 150°, helium flow 125 ml/min) showed only one peak. The ir spectrum of the product was identical with that of authentic **15**.[13]

***exo*-2-Methylnorbornan-*endo*-2-ol (16)** was prepared by the reduction of spiro[norbornan-*endo*-2,2′-oxacyclopropane] (**8**)[4a] in the manner described for **15** (*vide supra*) or by the addition of methylmagnesium iodide to norcamphor.[13]

The Reduction of Epoxides with Lithium Aluminum Deuteride (or Hydride) and Aluminum Trichloride. A. Spiro[2-norbornen-*exo*- and -*endo*-5,2′-oxacyclopropanes] (5 and 6).—A slurry of 30 mg (0.79 mmol, 34 mol %) of lithium aluminum hydride and 142 mg (1.07 mmol, 47 mol %) of anhydrous aluminum chloride in 5 ml of anhydrous ether was prepared in a drybox and stirred in an ice–salt bath for 30 min. A solution of 53 mg (0.43 mmol, 19 mol %) of epoxide **5** in 3 ml of anhydrous ether was dropped slowly into the cold, stirred slurry. The reaction mixture was stirred for an additional 30 min in the ice–salt bath and then for 60 min at room temperature. Sufficient 15% aqueous sodium hydroxide was added to decompose the complex. The ethereal solution was decanted from the precipitated salts which were washed thoroughly with ether. The combined ethereal solution was dried over anhydrous magnesium sulfate, filtered, and concentrated to about 0.5 ml by distillation of the solvent at atmospheric pressure. Analysis by glpc on the 8-ft Carbowax column (column temperature 150°, helium flow 70 ml/min) showed two components which were identified as 2-norbornene-*exo*-5-methanol (**10**, 23%) and 2-norbornene-*endo*-5-methanol (**11**, 77%) by glpc collection (over-all yield 30 mg, 0.24 mmol, 56%) and comparison with authentic samples. No unreacted starting material, aldehyde, or tertiary alcohol **9** could be detected in the reaction mixture.

When the composition of the reactants was changed to 97 mg (0.79 mmol, 30 mol %) of epoxide **5**, 146 mg (1.09 mmol, 40 mol %) of aluminum chloride, and 30 mg (0.79 mmol, 30 mol %) of lithium aluminum hydride, only one product, identical in all respects with authentic *endo*-5-methyl-2-norbornen-*exo*-5-ol (**9**),[4a] was obtained.

The reaction was also carried out using 81 mg (0.66 mmol, 19 mol %) of **5**, 219 mg (1.64 mmol, 45 mol %) of aluminum chloride, and 55 mg (1.31 mmol, 36 mol %) of lithium aluminum deuteride. Glpc analysis on the 8-ft Carbowax column at 150° and a helium flow of 67 ml/min showed two products with retention times of 17.0 and 20.7 min, identical with those of authentic **11** and **10**, respectively. The products were separated by glpc and the position of the deuterium label was determined by analysis of their 100-MHz nmr spectra. The nmr spectrum of the *endo* isomer had signals at δ 5.96 [octet (2 CH=CH)], 3.4 [concentration-dependent singlet (1 OH)], 3.24 [doublet, $J \approx 5$ Hz (~$^1/_2$ >CHCHDO)], 3.06 [doublet, $J \approx 8$ Hz (~$^1/_2$ >CHCDHO)], 2.88 [broad singlet (1 ⩾CH, bridgehead)], 2.72 [broad singlet (1 ⩾CH, bridgehead)], ~2.20 {broad multiplet [1 >CH(CHD)O]}, 2.0–1.1 [complex multiplet (2 >CHH + 1 >CHH, *exo*)], 0.46 [octet (?) (1 >CHH, *endo*)]; the mass spectrum[11] showed M$^+$ = 125. We conclude that this product is a mixture of the α-deuterated alcohols **11a** and **11b**. The nmr spectrum of the *exo* isomer has signals at δ 6.04 [multiplet (2 CH=CH)], 3.63 [perturbed doublet, $J \sim 5$ Hz (~$^1/_2$ >CHCHDO)], 3.45 [perturbed doublet, $J \sim 8$ Hz (~$^1/_2$ >CHCDHO)], 2.78 [broad singlet (2 ⩾CH, bridgehead)], 2.6 [concentration-dependent singlet (1 OH)], 1.8–1.0 [complex multiplet (4 >CHH + 1 >CH–)]; the mass spectrum[11] showed M$^+$ (relative abundance) = 124 (2.05%), 125 (97.95%). We conclude that this product is a mixture of the α-deuterated alcohols **10a** and **10b**.

A sample of 54 mg (0.44 mmol, 18 mol %) of the epoxide **6** was reduced in ether solution with a mixture of 155 mg (1.17 mmol, 49 mol %) of aluminum chloride and 30 mg (0.79 mmol, 33 mol %) of lithium aluminum hydride in the manner described for the isomeric oxide **5**. Glpc analysis on the 8-ft Carbowax column showed three components. The products were collected (combined yield 38 mg, 70%) and identified by comparison with authentic samples as the tertiary alcohol **12** (19%) and the primary alcohols **10** (10%) and **11** (71%). The reduction of **6** was repeated using 90 mg (0.74 mmol, 19 mol %) of the epoxide, 243 mg (1.87 mmol, 46 mol %) of aluminum chloride, and 60 mg (1.42 mmol, 35 mol %) of lithium aluminum deuteride. The primary alcohols were separated on the 8-ft Carbowax column. The 100-MHz nmr spectra of the *exo* and *endo* isomers were identical with those of **10a** plus **10b** and **11a** plus **11b**, respectively, obtained in the reduction of epoxide **5**. From the mass spectrum of the *endo* isomer it was calculated[11] that M$^+$ (relative abundance) = 124 (3.0%), 125 (94.5%), 126 (2.5%).

B. Spiro[norbornan-*exo*- and -*endo*-2,2′-oxacyclopropanes] (7 and 8).—The reaction of 103 mg (0.82 mmol, 19 mol %) of the

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(31) We thank the Interchemical Corp. for a generous sample of this material.

oxide **7** with 271 mg (2.04 mmol, 47 mol %) of aluminum chloride and 62 mg (1.47 mmol, 34 mol %) of lithium aluminum deuteride as described for **5** gave, after collection from the 8-ft Carbowax column (column temperature 150°, helium flow 125 ml/min), 63 mg (0.50 mmol, 60%) of product which appeared as a single peak, retention time 16.8 min. On a capillary Ucon column at 95° (N_2 at 18 psi) two broad poorly resolved peaks are evident whose retention times, 53 and 55 min, are identical with those of the authetic primary alcohols **14** and **13**, respectively. No tertiary alcohols (**15** and **16**) were found even though mixed glpc with authentic samples indicates that they would have been separated under our analysis conditions. The proportion of *exo/endo* isomers and the position of the deuterium label was estimated from the 100-MHz and 60-MHz nmr spectra of the collected mixture: δ ~3.4 [broad poorly resolved multiplet (1 >CHCHDO)], 2.8 [concentration-dependent singlet (1 OH)], 2.23–1.98 [broad multiplet (2 ⩾CH, bridgehead?)], 1.98–0.80 [complex multiplet (6 >CHH + 1 >CHH, *exo*, + 1 >CH– + <1 >CHH, *endo*], 0.60 [octet (<1 >CHH, *endo*)]. The ratio of the areas of the signals at δ 3.4, 2.8, and 0.6 is estimated to be 1.0:1.0:0.85 (accurate to ~5%). The mass spectrum[11] showed $M^+ - 18$[32] (relative abundance) = 108 ($\leqslant$4.9%), 109 ($\geqslant$95.1%). From these measurements we conclude that essentially all of the deuterium is in the α position and that the isomeric primary alcohols **14** and **13** are present in the proportion of 15:85.

The oxide **8** was reduced in a similar manner using 54 mg (0.44 mmol, 19 mol %) of the epoxide, 152 mg (1.14 mmol, 47 mol %) of aluminum chloride, and 33 mg (0.76 mmol, 34 mol %) of lithium aluminum deuteride. Collection from the 8-ft Carbowax column gave 38 mg (68%) of primary alcohol(s). No tertiary alcohol could be detected by glpc. Analysis of the nmr spectrum indicates that virtually all of the product is α deuterated and that it consists of ~84% **14** and ~16% **13**. The mass spectrum[11] showed $M^+ - 18$[32] (relative abundance) = 108 ($\leqslant$6.6%), 109 ($\geqslant$93.4%).

C. **Spiro[2-norbornen-*anti*-7,2′-oxacyclopropane] (1).**—The reaction of 230 mg (1.89 mmol, 19 mol %) of **1** with 617 mg (4.63 mmol, 47 mol %) of aluminum chloride and 140 mg (3.34 mmol, 34 mol %) of lithium aluminum deuteride in the manner described in part A yielded 207 mg (72%) of distilled product.[2] Glpc analysis on the 8-ft Carbowax column showed the presence of a single component: nmr (CCl_4) δ 5.83 [triplet (2 CH=CH)], 3.38 [singlet (2 $>CDCH_2O$)], 3.1 [broad concentration-dependent singlet (1 OH)], 2.73 [multiplet (2 ⩾CH, bridgehead)], 1.9–0.8 [complex multiplet (4 >CHH)]. We conclude that the product is the tertiary-deuterated primary alcohol **21**. When the experiment was repeated using 946 mg (7.75 mmol, 47 mol %) of epoxide **1**, 530 mg (4.01 mmol, 24 mol %) of aluminum chloride, and 200 mg (4.76 mmol, 29 mol %) of lithium aluminum deuteride, alcohol **21** was again the only product obtained.

D. **Spiro[norbornan-7,2′-oxacyclopropane] (4).**—The reaction of 348 mg (2.80 mmol, 19 mol %) of epoxide **4** with 215 mg (5.13 mmol, 34 mol %) of lithium aluminum deuteride and 919 mg (6.88 mmol, 47 mol %) of aluminum chloride gave, after sublimation [80° (50 mm)], 286 mg (80%) of a single alcohol. The retention time of the product on the 8-ft Carbowax column at 100° was identical with that of authentic 7-methylnorbornan-7-ol.[2] The nmr spectrum was too complex and insufficiently resolved for detailed analysis but showed no signals which could be attributed to a methylol-type hydrogen. The mass spectrum showed M^+ (relative abundance) = 126 ($\leqslant$2.0%), 127 ($\geqslant$98.0%). Although our data do not permit an unambiguous assignment of the position of the deuterium label, we believe that the product is the primary-deuterated tertiary alcohol **22**.

The Reduction of Aldehydes with Lithium Aluminum Hydride–Aluminum Chloride. A. **2-Norbornen-*exo*- and -*endo*-5-carboxaldehydes (17 and 18).**—Samples of 53 mg (0.43 mmol) of aldehydes **17** and **18** were each reduced in ether solution with mixtures of 30 mg (0.79 mmol) of lithium aluminum hydride and 150 mg (1.13 mmol) of aluminum chloride as described for the epoxides (*cf.* epoxide **5**). The products were identified by comparison of their glpc retention times and ir spectra with those of authentic samples. Each of the aldehydes was found to give only one product, the corresponding primary alcohol **10** or **11**, respectively.

B. **Norbornane-*exo*- and -*endo*-5-carboxaldehydes (19 and 20).**—A mixture of **19** (56%) and **20** (44%) was reduced in the usual manner using 1.28 g (10.3 mmol) of the aldehydes, 0.76 g (19 mmol) of lithium aluminum hydride, and 3.25 g (25.6 mmol) of aluminum chloride. After work-up and distillation in a modified Hickmann still [90° (3 mm)], 1.08 g (8.25 mmol, 83%) of a product mixture was obtained whose composition was determined by analysis of the 60-MHz nmr spectrum. A comparison of the integrated areas of the methylol doublets at δ 3.26 and 3.47 showed the distillate to consist of 56% *exo* alcohol **13** and 44% *endo* alcohol **14**.

Registry No.—**10a**, 19926-82-0; **10b**, 19926-83-1; **11a**, 19926-84-2; **11b**, 19926-85-3; **13**, 19926-86-4; **14**, 19926-87-5; **17**, 19926-88-6; **17** (semicarbazone), 19926-89-7; **18**, 19926-90-0; **18** (semicarbazone), 19926-91-1; **21**, 19926-92-2.

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[32] The parent ion was too weak to calculate the isotopic distribution. The calculation was therefore performed on the ion corresponding to $P - H_2O$ making the assumption that no 1,1 elimination of water had taken place.