Hydrogenolysis by $LiAlH_4$–$AlCl_3$ of an ether solution of norcamphor isobutylene ketal[1]

P. C. Loewen, W. W. Zajac, Jr.,[2] and R. K. Brown
Department of Chemistry, University of Alberta, Edmonton, Alberta

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An approximately 1:1 mixture of the two isomers (**3** and **4**) of norcamphor isobutylene ketal was hydrogenolyzed by AlH_2Cl in ether at room temperature. The slow reaction (62% complete in 20 h; ~96% complete in 168 h) produced only 1-(2-*endo*-norbornyloxy)-2-methyl-2-propanol (**7**), 2-(2-*exo*-norbornyloxy)-2-methyl-1-propanol (**6**), 2-*exo*-norborneol (**10**), and unchanged **3** and **4** in the proportion 64.5:26.5:4.5:4.5. Recovery of materials was at least 95%.

Compound **10** is believed to arise from slow hydrogenolysis of the product **6**. Since the unreacted ketal was still an approximately 1:1 mixture of the isomers **3** and **4**, and because it is known that in the hydrogenolysis of acetals and ketals, the reduction by hydride donation is much faster than is the isomerization of the ketals, it is inferred that the two isomers (**3** and **4**) of norcamphor isobutylene ketal hydrogenolyze at approximately the same rate.

Arguments are presented to support the view that isomer **4** reacts with *two* molecules of AlH_2Cl, one as the Lewis acid and the other as the hydride donor, to provide product **7** and possibly some of product **6**, while isomer **3** reacts with *one* molecule of AlH_2Cl, which acts as the Lewis acid and the hydride donor, to provide most if not all of product **6** and some of product **7**.

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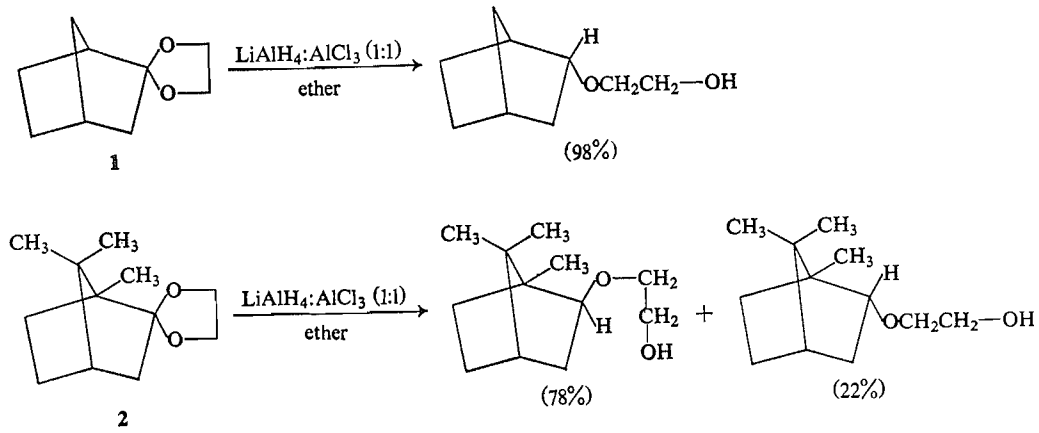
Introduction

Recent work from this laboratory (1) has shown that lithium aluminum hydride–aluminum chloride reductive cleavage of norcamphor ethylene ketal (**1**) gave 2-(2-*endo*-norbornyloxy)-ethanol in 98% yield whereas similar reduction of camphor ethylene ketal (**2**) gave both 2-(2-isobornyloxy)ethanol and 2-(2-bornyloxy)-ethanol in 78% and 22% yield respectively (Scheme 1). These products were considered to be the result of steric approach control.

The question concerning the detail of the reductive cleavage, as to whether it took place via route *a* (Scheme 2) involving *both* Lewis acid attack of the reactive reducing species AlH_2Cl (2,3) *and* hydride donation by the same molecule,

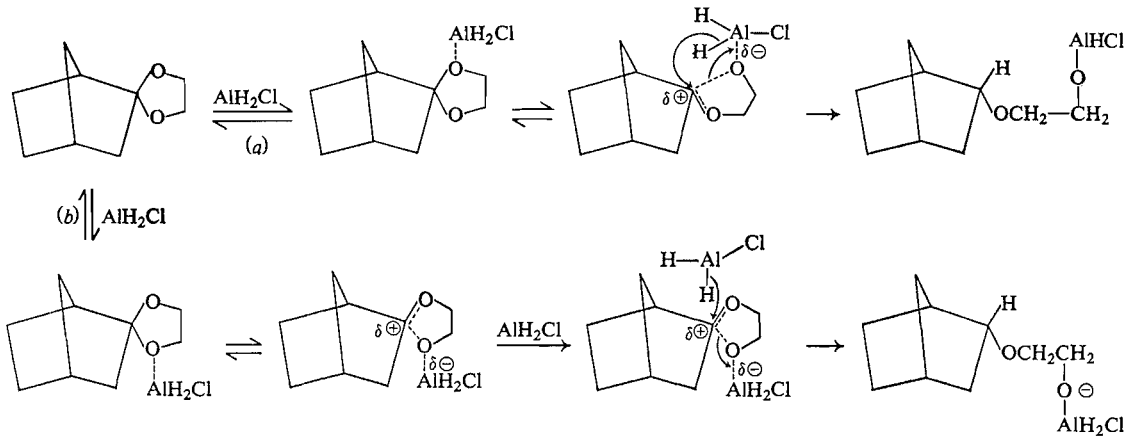


SCHEME 1

or via route *b* (Scheme 2) in which one molecule of AlH_2Cl played the part of the Lewis acid while a second molecule donated the hydride ion, could not be answered (1). However, considering the results of the hydrogenolysis of camphor

[1]Taken in part from the thesis of P. C. Loewen submitted to the Faculty of Graduate Studies, University of Alberta, Edmonton, Alberta, as part of the requirements for the degree of Doctor of Philosophy.

[2]On leave during 1965–1966 from Villanova University, Villanova, Pennsylvania, U.S.A.



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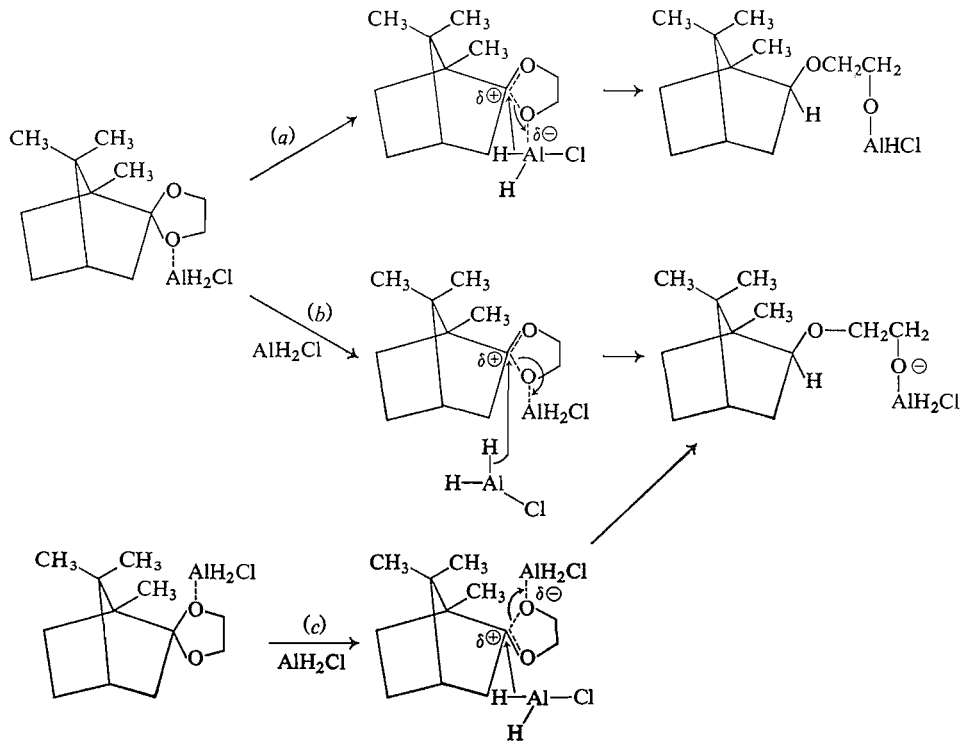
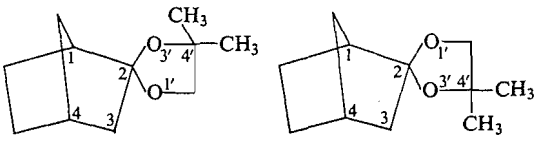


SCHEME 3

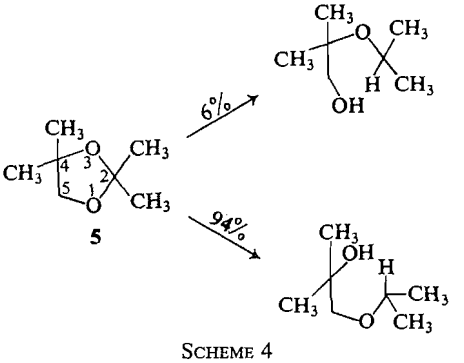
ethylene ketal, for the formation of the major product (78% yield), route *a* (Scheme 3) involving the dual function of the same molecule of AlH_2Cl would seem from a steric point of view to be more reasonable than routes *b* and/or *c* which involve two molecules of AlH_2Cl. As yet a suitable system for a kinetic study of this reaction has not been devised.

We have now examined the hydrogenolysis, by AlH_2Cl, of the isomeric norcamphor isobutylene ketals, **3** and **4**, in order to obtain more information concerning this question. The reason



3 4

for the choice of this particular ketal stemmed from some previous work (4) in this laboratory in which it was found that hydrogenolysis of 2,2,4,4-tetramethyl-1,3-dioxolane (**5**) did not cleave the O_1—C_2 bond as expected on the basis of the inductive effects of the C-4 methyl groups (5), but instead gave nearly total cleavage (94%) of the O_3—C_2 bond of the ketal (Scheme 4).[3] This anomalous cleavage was interpreted as being due to a steric repression in the intermediate oxocarbonium ion resulting from O_1—C_2 bond cleavage, such steric repression being minimal or absent in the oxocarbonium ion which arises due to O_3—C_2 cleavage.



SCHEME 4

It is seen that both **3** and **4** possess the same structural feature as is found in 2,2,4,4-tetramethyl-1,3-dioxolane (Scheme 4). One would then expect, on the basis of the results of the hydrogenolysis of the tetramethyl-1,3-dioxolane, that both **3** and **4** would hydrogenolyze preferentially by cleavage of the C_2—$O_{3'}$ bond. However, the work on the norcamphor ethylene ketal (1) shows that the favored approach of the reducing agent is to the *exo* side. This would result in preferential cleavage of the C_2—$O_{3'}$ bond in **3** and the C_2—$O_{1'}$ bond in **4**, thus forming the *endo*-norbornyloxy compound. It was thus of interest to find out how these two directive systems behaved in the hydrogenolysis of **3** and **4**.

Results and Discussion

Preparation of Compounds

The norcamphor isobutylene ketals were prepared by the acid catalyzed reaction of norcamphor with isobutylene glycol. The product of this reaction was no doubt an equilibrium mixture of the isomers **3** and **4**. The elemental analysis agreed well with that expected for these isomers. The 60 MHz nuclear magnetic resonance (n.m.r.) spectrum in $CDCl_3$ (Fig. 1) shows the presence of two isomers. It is expected that for each isomer the methylene protons of the 1,3-dioxolane portion of the ketal should provide a simple AB quartet and these signals should appear in the portion of the spectrum, between τ 6.0 and 7.0 where protons attached to carbon atoms which are in turn attached to an ether oxygen are known to absorb. Since the multiplet lying between τ 6.2 and 6.6 is not a simple quartet, it is clear that more than one isomer must be present. From the 100 MHz n.m.r. spectrum, expanded to show these signals more clearly (see inset, Fig. 1), it is seen that the multiplet between τ 6.2 and 6.6 is due to two overlapping quartets. The areas under the two sets of peaks are in the approximate ratio of 45:55 (i.e. nearly 1:1).

The gas liquid chromatogram (g.l.c.) of this mixture of isomers gave a single peak which showed no evidence whatsoever of the presence of two isomers. All attempts to separate these, either by careful fractional distillation with a spinning band column, or by using a variety of g.l.c. columns, among which were those containing butanediol succinate, carbowax, silicone rubber, or Apiezon L on Gas-Chrom W, were quite ineffective. This was a serious handicap, since the solution of this problem would have been greatly facilitated had the two pure isomers been individually available. Accordingly, there was no way of determining which of the two isomers was in the greater abundance.

Of the four possible reduction products of **3** and **4** (Scheme 5), only the tertiary alcohols **7** and **8** were successfully prepared. These were made by the reaction of 2-*exo*- and 2-*endo*-norborneol with ethyl bromoacetate by the method of Leffler and Calkins (6), followed by treatment of the product with methymagnesium bromide. That both of these compounds, **7** and **8**, were

[3]E. L. Eliel *et al.* (14) have also reported that the mixed hydride hydrogenolysis of cyclohexanone isobutylene ketal produces exclusively that product which is the tertiary alcohol.

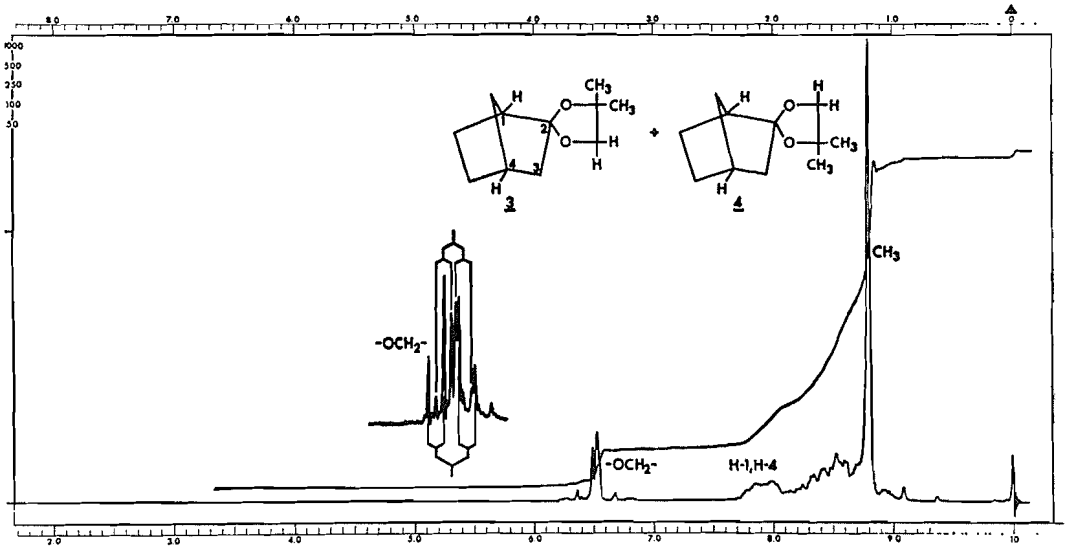


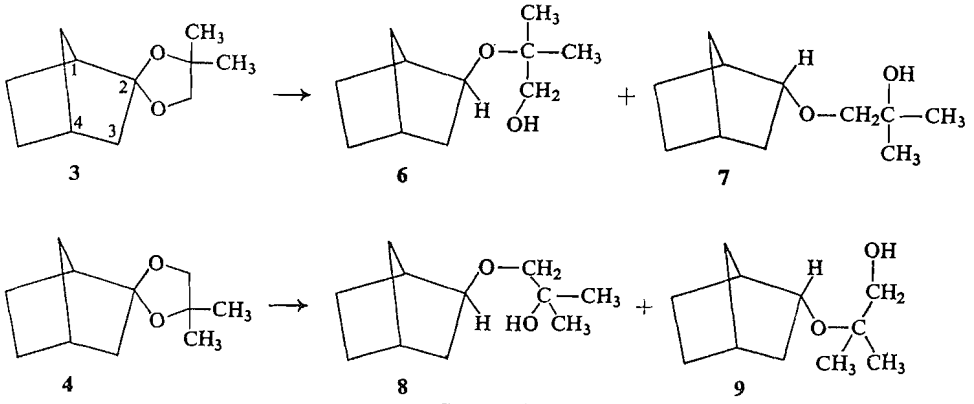
FIG. 1. The 60 MHz n.m.r. spectrum of the equilibrium mixture of the two isomeric norcamphor isobutylene ketals **3** and **4**; reference, tetramethylsilane. The inset is a partial 100 MHz n.m.r. spectrum, showing the two overlapping AB quartets of the two geminal protons of the methylene group in the dioxolane ring.

tertiary alcohols was verified by their infrared (i.r.) spectra, which showed a band for hydroxyl group absorption, and by their n.m.r. spectra in dimethyl sulfoxide-d_6 (DMSO-d_6) which showed the signal for the hydroxyl proton shifted downfield from τ 7.75 (in $CDCl_3$) to 5.85 as a sharp singlet (8). The *exo* and *endo* isomers could be distinguished by a characteristic feature indicated in our previous work (1). The signals for the bridgehead protons (C-1 and C-4) of the *endo* isomer, **7**, appear as *two* unresolved closely spaced multiplets ($W/2 \sim 10$ Hz and $W/2 \sim 12$ Hz) centred at τ 7.65 and 7.85 respectively in the spectrum in DMSO-d_6 (Fig. 2) whereas the spectrum of the *exo* isomer in the same solvent shows only *one* closely spaced unresolved multiplet at τ 7.8 ($W/2 \sim 10$ Hz)(Fig. 3).

All attempts to prepare the primary alcohols, **6** and **9**, met with failure. However, this did not interfere seriously with the identification of the products of hydrogenolysis of **3** and **4**.

Hydrogenolysis of 3 and 4

The hydrogenolysis of the mixture of the two isomers (**3** and **4**) of norcamphor isobutylene ketal was carried out according to published directions (7) using an equimolar mixture of $LiAlH_4$ and $AlCl_3$ in dry diethyl ether. The



SCHEME 5

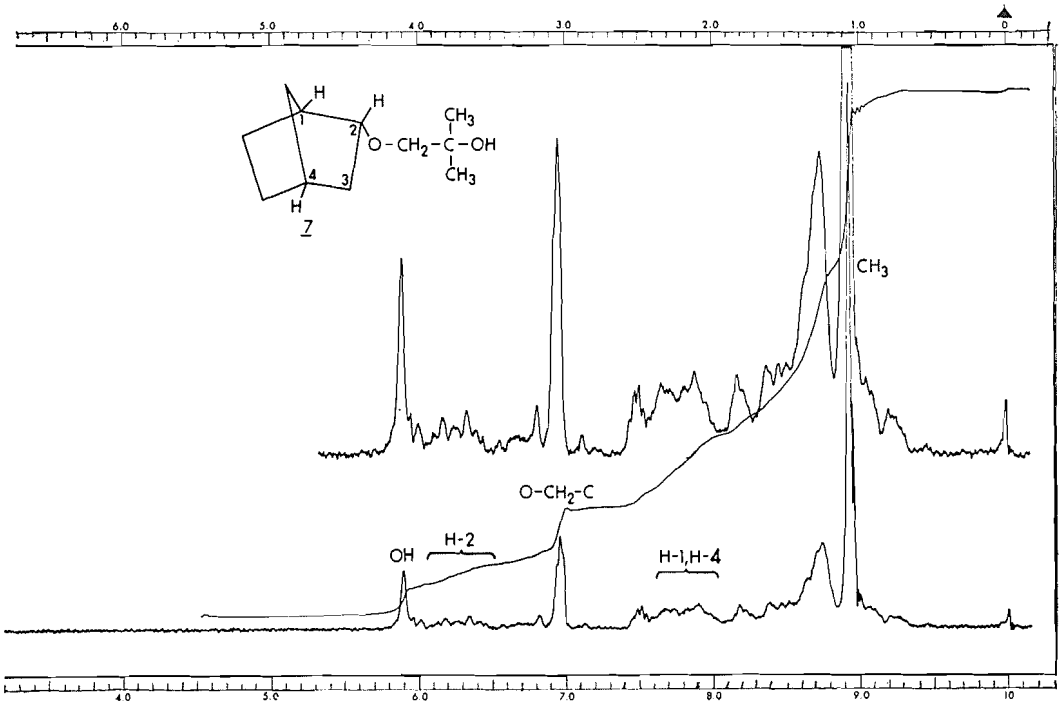
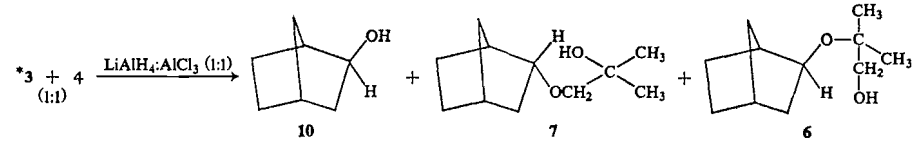


FIG. 2. The 60 MHz spectrum of synthetic 1-(2-*endo*-norbornyloxy)-2-methyl-2-propanol (7) in dimethylsulfoxide-d_6.

TABLE I

Hydrogenolysis of the mixture of the two isomers **3** and **4** of norcamphor isobutylene ketal by a 1:1 mixture of $LiAl_4$ and $AlCl_3$ in ether at room temperature*

Time of reaction (h)	Extent of reduction (%)	Products of the reaction, % of the total product				Total recovery of materials (%)
		10	**7**	**6**	**3**+**4**	
20	62	2.5	42.5	17.0	38	95
168	95.5	4.5	64.5	26.5	4.5	95



results of the hydrogenolysis are assembled in Table I.

Each of the products of hydrogenolysis was collected by preparative g.l.c. and identified with the aid of elemental analysis, a g.l.c. retention time and n.m.r. spectrum, and by comparison with these characteristics of authentic specimens of compounds **10** and **7**. The structure of the primary alcohol **6** obtained from the hydrogenolysis was determined by its elemental analysis, i.r. spectrum and particularly the n.m.r. spectrum in DMSO-d_6 (Fig. 4). The latter spectrum showed the hydroxyl proton signal shifted downfield from a broad singlet in $CDCl_3$ at τ 7.85 to a triplet (J = 6 Hz) centred at τ 5.6 which is indicative of a primary alcohol (8). The spectrum also showed one closely spaced unresolved multiplet ($W/2 \sim 12$ Hz) centred at

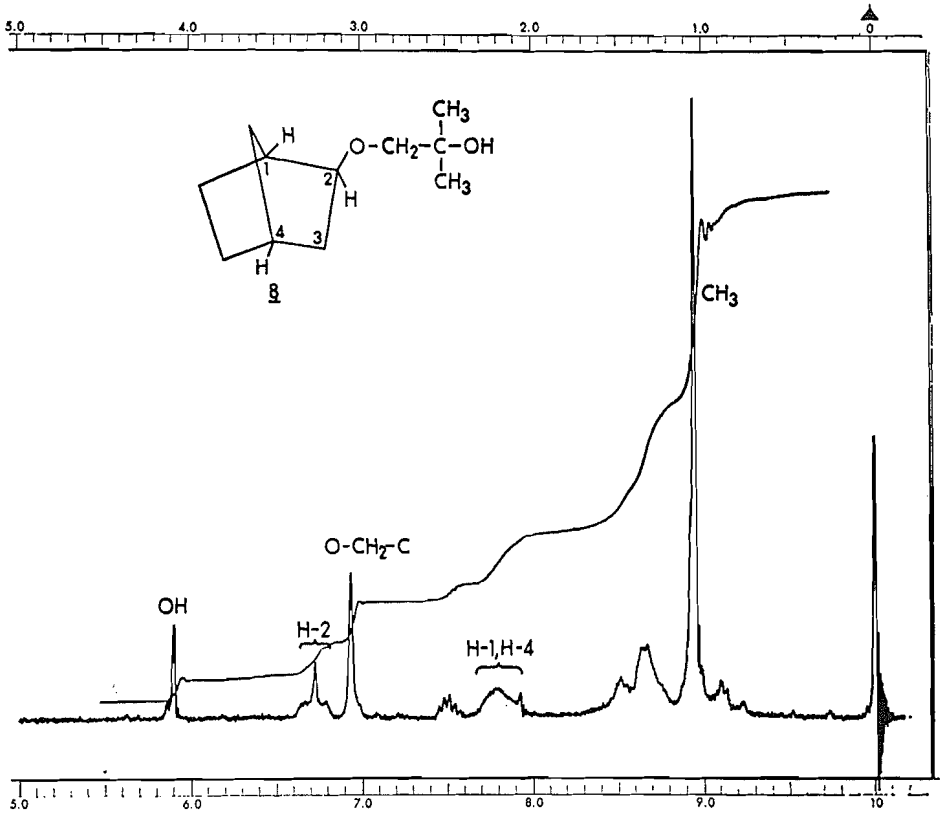


FIG. 3. The 60 MHz spectrum of synthetic 1-(2-*exo*-norbornyloxy)-2-methyl-2-propanol (8) in dimethylsulfoxide-d_6.

τ 7.92 indicative of the signals for the bridgehead protons when an *exo* substituent is present (1).

The n.m.r. spectrum of the recovered unreacted ketal mixture **3** and **4**, obtained after 20 h of reduction, was clearly identical to the n.m.r. spectrum of the starting isomeric mixture. This indicates that *either* the rate of hydrogenolysis of both isomers is practically the same, *or* that one isomer, **3** or **4**, might be reduced more rapidly, but the rate of isomerization of the unreduced material, under the reaction conditions, is sufficiently greater than the rate of reduction that maintenance of an equilibrium mixture of **3** and **4** is ensured. Work recently reported (9) has shown that when both *cis*- and *trans*-2,4-dimethyl-1,3-dioxolane were hydrogenolyzed separately and under identical conditions, but with sufficient $LiAlH_4$–$AlCl_3$ to reduce only half of the dioxolane, no significant isomerization of the unreacted *cis* or *trans* isomers had occurred. This supported the view that the slow, rate-determining step of the reaction was indeed the C_2—O bond breaking, leading to the formation (or incipient formation) of the intermediate oxocarbonium ion, and that subsequent (and nonreversible) reduction by hydride donation to this oxocarbonium ion was very much faster than was isomerization (Scheme 6).

Unfortunately, because we were unable to separate the isomers **3** and **4**, it was not possible to ascertain, by partial hydrogenolysis, whether isomerization of the starting isomer **3** or **4** did or did not occur. However it is not unreasonable to assume that, as in the case of the *cis*- and *trans*-2,4-dimethyl-1,3-dioxolanes, reduction by hydride donation here is also much faster than C—O bond cleavage to form the intermediate oxocarbonium ion. Accordingly, the following discussion is based on the acceptance of this view.

Several points are quite clear. (*i*) If indeed there is no significant isomerization of the unreacted isomers **3** or **4**, then from the knowledge

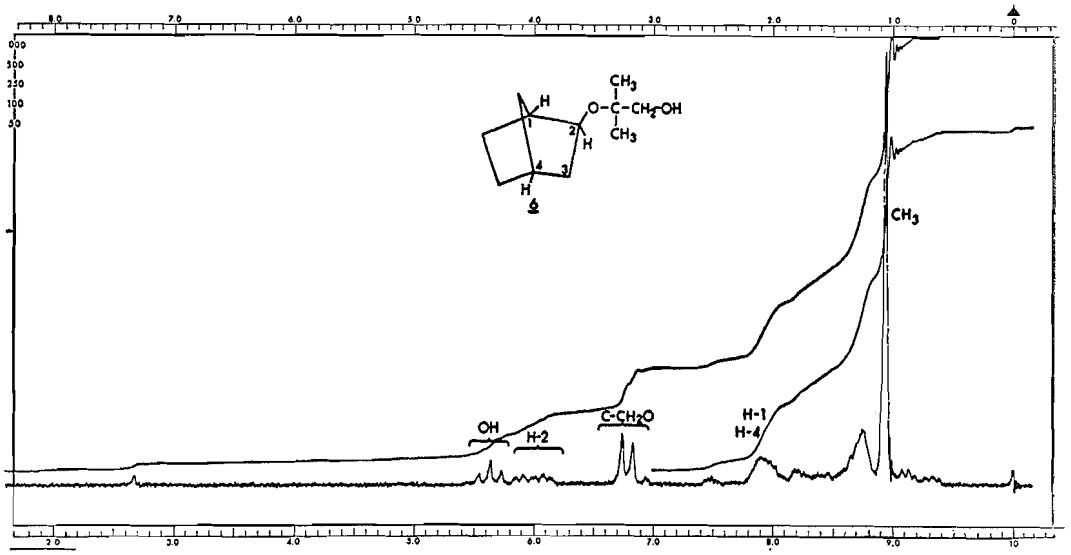
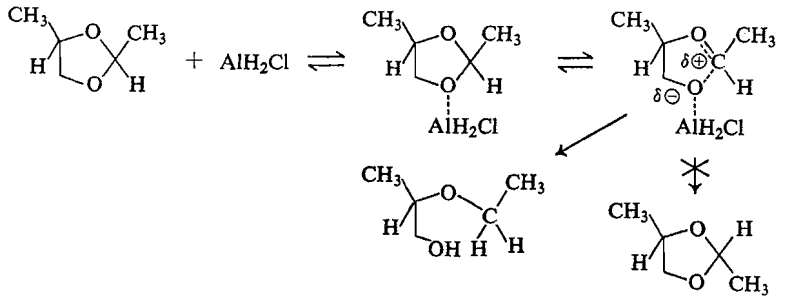
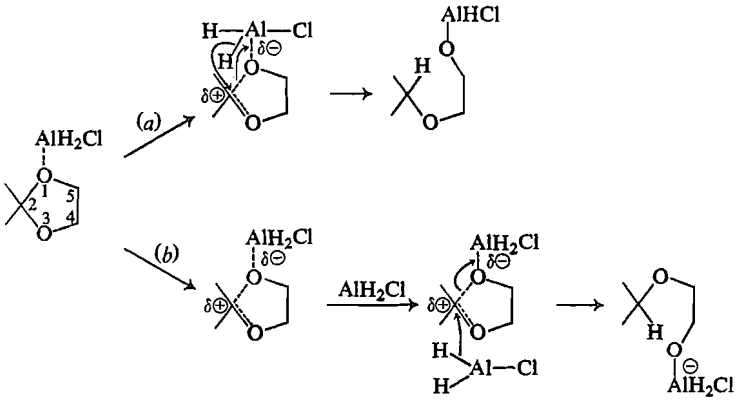


FIG. 4. The 60 MHz n.m.r. spectrum of one of the products from the AlH_2Cl hydrogenolysis of the equilibrium mixture of the two isomeric norcamphor isobutylene ketals **3** and **4**.



SCHEME 6

that the ratio of the products **7** to **6** is 64.5 to 26.5, it can be inferred that each of the two isomers **3** or **4** does not reduce specifically to one of the products. If this had been so, then the product ratio would also have been 55:45 (or 45:55), the same as that found for the original material. It is however quite possible that one isomer **3** (or **4**) could produce essentially the product **7**, while the other isomer **4** (or **3**) would then provide both **7** and **6**. (*ii*) Since a substantial amount (26.5%) of the product is the primary alcohol **6**, the steric restriction (4) which strongly retarded the C_2—O_1 bond breaking of **5** (Scheme 4) could not have been as important in retarding the C_2—O_1, bond cleavage in **3** and/or **4**. Some factor must then retard the alternate C_2—O_3, bond cleavage sufficiently to allow C_2—O_1, bond cleavage to become competitive to the extent of 26.5% (four times as much as was found for **5**). (*iii*) From the work on norcamphor ethylene ketal (1) it is also clear that approach of the reducing species to C-2 of structures **3** and **4**, from the *exo* side is preferred to approach from the *endo* side. However, if structural features are present which inhibit approach from the *exo* side, then *endo* attack by the reducing agent becomes competitive and important as shown by the hydrogenolysis of camphor ethylene ketal (1). (*iv*) It is also quite certain that for hydrogenolysis of the acetals or ketals to occur at all, the Lewis acid property of the reducing species, AlH_2Cl, must be involved, and the particular C—O bond which is broken is that in which the Lewis acid is associated with the oxygen atom.



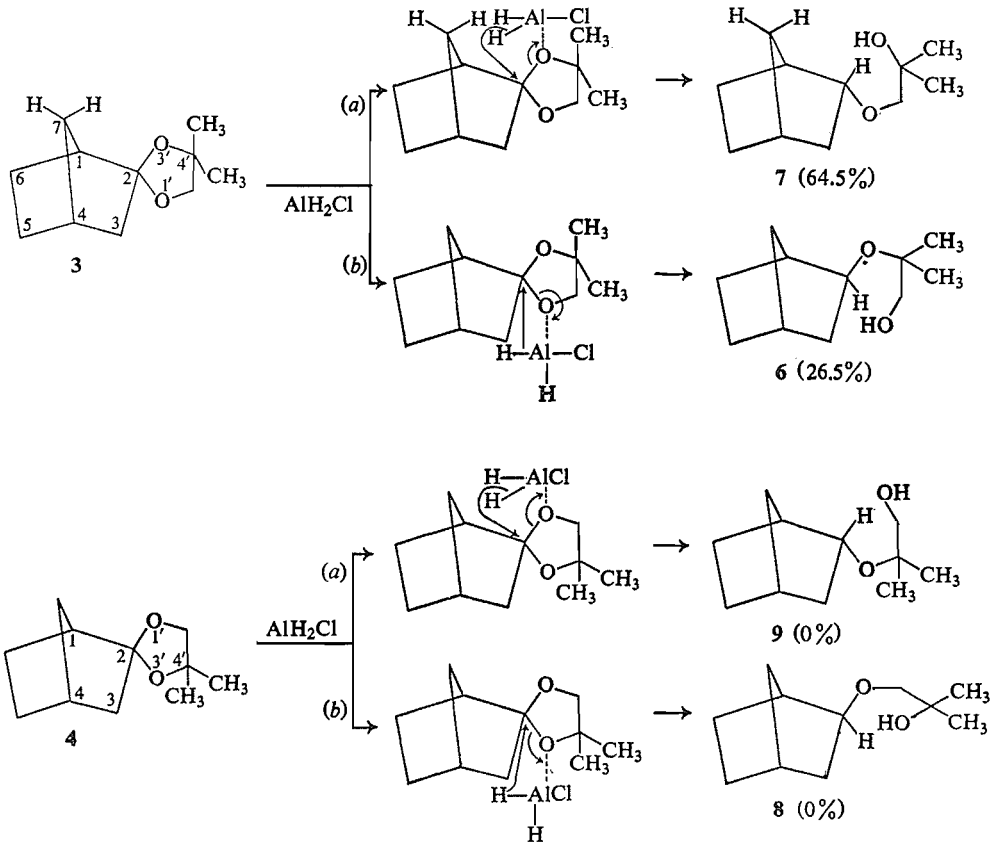
SCHEME 7

A point which has not been determined to date is whether the molecule which acts as the Lewis acid is also the one which donates the hydride ion (route *a*, Scheme 7). If this is so then the hydride ion will enter on the same side of the C-2 carbon atom of the 1,3-dioxolane as that from which the oxygen atom leaves, and thus the stereochemistry of the C-2 carbon is maintained. On the other hand, it is possible that one molecule of AlH_2Cl acts as the Lewis acid while a second molecule provides the hydride ion (route *b*, Scheme 7). If this is so, then the hydride ion will enter on the side of C-2 opposite to that from which the oxygen atom leaves, thus inverting the stereochemistry about the C-2 atom.

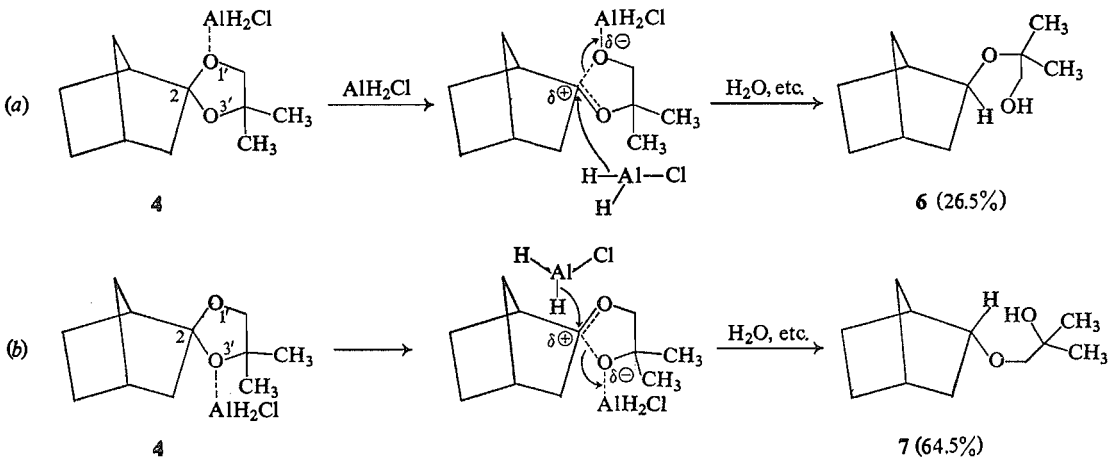
There are therefore, for each of the compounds **3** and **4**, two possible products if the stereochemistry about C-2 is maintained (Scheme 8). Compounds **7** and **6**, the products expected by hydrogenolysis of **3** by this route which maintains C-2 stereochemistry, are indeed those which are observed. Compounds **8** and **9**, the products expected from hydrogenolysis of **4** by the same route are *not* found among the products of hydrogenolysis. Hence, hydrogenolysis of **4** by such a route can be eliminated as a possibility.

Of the two courses of hydrogenolysis of compound **3** (Scheme 8), route *b* has two features militating against its easy accomplishment. The first is the cleavage of the C_2—$O_{1'}$ bond to produce an intermediate (or incipient) oxocarbonium ion which possesses the unfavorable steric factor (4) noted for the tetramethyl-1,3-dioxolane (**5**) (Scheme 4). As well, attack by the AlH_2Cl from the *endo* direction is also less favored (1). However, route *a* requires association of the AlH_2Cl with the oxygen atom in the *exo* position, an oxygen atom in a steric environment similar to that found for 2,2,5,5-tetramethyltetrahydrofuran. It is known that a bulky Lewis acid ($SnCl_4$) is associated to a lesser extent with 2,5-dimethyltetrahydrofuran than with 2-methyltetrahydrofuran or with tetrahydrofuran (10). This was considered to be due to steric factors rather than electronic factors. It is thus quite conceivable that such steric factors in compound **3** would retard association of the Lewis acid AlH_2Cl with the *exo* oxygen atom sufficiently so that the alternate route *b* becomes competitive.

Since isomer **4** does hydrogenolyze about as easily as does **3**, then it can do so by the route (route *b* in Scheme 7) involving *two* molecules of AlH_2Cl. This is shown in Scheme 9. It is seen that both of the compounds **6** and **7** actually found as hydrogenolysis products, can be obtained by this method. If one considers these two paths *a* and *b* (Scheme 9) in more detail, it is seen that the hydrogenolysis by route *a* which might provide compound **6** is less likely than the alternate route which provides **7** (route *b*). For route *a* to take place, there must be at least partial C_2—$O_{1'}$, bond breaking with a tendency for the remaining substituents at C-2 to become coplanar about C-2. Attack at C-2 by a second molecule of AlH_2Cl would require its approach via a path perpendicular to the plane in which C-2 lies. Models show that such an approach is strongly inhibited by the three *endo* hydrogen atoms of the norcamphor system. On the other hand, models show that the association of the Lewis acid with the *endo* oxygen atom (route *b*)



SCHEME 8



SCHEME 9

is possible. This would lead to incipient C_2—O_3, bond breaking. Subsequent attack at C-2 by the second molecule of AlH_2Cl is then quite easy (1). From these arguments, it is our view that compound **4** reacts practically completely via route *b* (Scheme 9) to provide the product **7**. We realize that this conclusion can be verified only by direct experimental evidence.

Reaction of compound **3** with two molecules of AlH_2Cl by the same sequence as is shown for compound **4** in Scheme 9, would provide the substances **8** and **9**. Since these were not observed as products of the hydrogenolysis, such a scheme of reaction for compound **3** can be dismissed.

If then practically all of **4** provides product **7**, then one must conclude that compound **3** provides all of the alternate product **6** along with some of **7**. The feasibility of such dual production from compound **3** has already been discussed above. Final proof as to whether this is in fact the case must await isolation or preparation of the individual isomers **3** and **4**. The necessity of this is quite apparent, but as yet this goal has not been realized.

Our view, based upon the above arguments, is that hydrogenolysis by AlH_2Cl can occur by two routes. One involves a single molecule of AlH_2Cl, and the other requires two molecules of AlH_2Cl. The proportion of hydrogenolysis taking place by these two methods depends upon the steric factors involved in the ketal under consideration.

A final point concerns the small amount of the third product, 2-*exo*-norborneol (**10**) isolated from the reduction. The source of this compound might be from Lewis acid catalyzed cleavage of the compound **6**, which is an ether containing an oxygen atom linked to a tertiary carbon. It is known that hydriodic acid cleaves ethers in such a way that the more stable carbonium ion is formed (11).

Experimental

All boiling points are uncorrected.

Infrared spectra were obtained with a Perkin–Elmer Model 337 grating spectrometer.

Nuclear magnetic resonance spectra were obtained with a Varian Associates A-60 instrument by Mr. Robert Swindlehurst, and an HR-100 spectrometer by Mr. Glen Bigham. All spectra were referred to tetramethylsilane.

Gas chromatographic analyses were carried out with either an F and M Model 700 instrument using 1/8″ × 12′ columns or an Aerograph Model A-700 equipped with 1/4″ × 12′ columns. The column packings employed were 20% butanediol succinate on Chromosorb W, 60–80 mesh (the most useful column packing); 25% Carbowax 6000 on Gas Chrom P, 60–80 mesh; 10% silicone rubber on Chromosorb W, 30–60 mesh and 10% Apiezon L on Chromosorb W. Helium was the carrier gas. The g.l.c. instruments were each equipped with an integrator and temperature programming unit. The temperature program was begun at ~50°.

2-Methyl-1,2-propanediol (Isobutylene Glycol)

This compound was prepared in 53% yield by $LiAlH_4$ reduction of methyl α-hydroxyisobutyrate(5).

Norcamphor Isobutylene Ketal (3 and 4)

This compound was prepared in 69% yield from norcamphor and isobutylene glycol according to the method of Salmi (12); b.p., 56–57° at 3.0 mm; η_D^{23}, 1.4603.

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.33; H, 9.82.

The i.r. spectrum (neat) showed no absorption attributable to hydroxyl or carbonyl groups. Significant features of the 60 MHz n.m.r. spectrum (Fig. 1) in $CDCl_3$ are described in the Discussion.

Ethyl(2-exo-norbornyloxy)acetate

This acetate was prepared in 30% yield by the reaction, in either benzene or 1,2-dimethoxyethane solution, of 2-*exo*-norborneol (Aldrich Chemical Co.) with ethyl bromoacetate in the presence of sodium hydride following the procedure of Leffler and Calkins (6); b.p., 83° at 2.5 mm; η_D^{23}, 1.4668 (lit. (1) b.p., 77° at 1 mm; η_D^{25}, 1.4162).

Ethyl(2-endo-norbornyloxy)acetate

This acetate was prepared in 25% yield by the reaction of 2-*endo*-norborneol (13) with ethyl bromoacetate in benzene or 1,2-dimethoxyethane, in the presence of sodium hydride (6); b.p., 77° at 0.8 mm; η_D^{22}, 1.4680 (lit. (1) b.p., 80° at 0.1 mm; η_D^{25}, 1.4160).

1-(2-exo-norbornyloxy)-2-methyl-2-propanol (8)

To a quantity (2.64 g, 0.11 mole) of magnesium turnings in 100 ml of dry ether kept at 0° to −5° by an ice bath, was added, with stirring, 15.4 g (0.11 mole) of methyl iodide dropwise. When all the methyl iodide had been added, the solution was stirred for 10 min at room temperature and then 10 g (0.05 mole) of ethyl (2-*exo*-norbornyloxy)acetate was added dropwise to the stirred solution at a rate which maintained the ether solution at gentle reflux. When the acetate had been added, the solution was stirred for 2 h at room temperature, whereupon 2 ml of water was cautiously added to decompose the complex. The ether layer was decanted and the residue diluted with sufficient 15% hydrochloric acid to dissolve the solids. An ether extract of this aqueous mixture, combined with the decanted ether, was dried ($MgSO_4$) and the drying agent then removed by filtration. Elimination of the solvent by rotary evaporator under vacuum gave an oil which was fractionally distilled to give 5 g (55%) of the alcohol **8**; b.p., 71° at 2.5 mm; η_D^{24}, 1.4640.

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.92; H, 10.91.

The n.m.r. spectrum in CCl_4 (reference, tetramethylsilane) was consistent with the structure of **8** and showed a multiplet between τ 6.6 and 6.8 (1H), a singlet at τ 6.9 (2H), *one* closely spaced unresolved multiplet centred at τ 7.72 (2H, bridgehead protons of the *exo* isomer), a singlet at τ 7.9 (1H), a multiplet between τ 8.1–9.3 overlapping a singlet at τ 8.91 (8H + 6H). In dimethylsulfoxide-d_6 (DMSO-d_6) the spectrum (Fig. 3) had essentially the same features except that the singlet at τ 7.9 (in CCl_4) moved downfield to τ 5.88 and remained a singlet, indicating that this signal was due to the proton of a tertiary hydroxyl group (8).

The i.r. spectrum (neat) showed a strong broad absorption band between 3100 and 3600 cm^{-1} and strong broad absorption in the region 1200 to 1050 cm^{-1} (C—O stretching).

The g.l.c. (butanediol succinate column) showed one sharp symmetrical peak.

1-(2-endo-norbornyloxy)-2-methyl-2-propanol (7)

This compound was prepared according to the method described immediately above for the preparation of the *exo* isomer, **8**. Because of the small quantity of material, it could not be satisfactorily purified by fractional distillation. The g.l.c. of each fraction still showed several small peaks of the contaminants. Final purification was carried out by preparative g.l.c. on a column using butanediol succinate; b.p. (micro), 79–80° at 3.0 mm; η_D^{25}, 1.4642.

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.44; H, 10.65.

The n.m.r. spectrum in CCl_4 agreed with the structure of **7**. The significant features were *two* narrowly spaced unresolved multiplets for the bridgehead protons centred at τ 7.65 and 7.86 indicative of the *endo* substitution (1) and a singlet at τ 7.57 in the n.m.r. spectrum in CCl_4 which shifted downfield to τ 5.93 and remained as a sharp singlet in the n.m.r. spectrum in DMSO-d_6 (Fig. 2), thus indicating that the proton was that of a tertiary hydroxyl group (8).

The i.r. spectrum (neat) showed strong broad absorption between 3600 and 3100 cm^{-1} (OH) and strong broad absorption between 1200 and 1050 cm^{-1} (C—O stretching).

2-(2-exo-norbornyloxy)-2-methyl-1-propanol (6)

This compound was isolated by g.l.c. on a column of 20% butanediol succinate on Chromosorb W, from the mixture of products obtained from the hydrogenolysis of the mixture of the two isomers of norcamphor isobutylene ketal, **3** and **4**; b.p. (micro), 77–79° at 1.5 mm; η_D^{23}, 1.4734.

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.35; H, 10.37.

The n.m.r. spectrum in DMSO-d_6 is shown in Fig. 4. The position of the signals and their integrated areas agree with a structure such as **6**. The significant details are described in the Discussion.

Hydrogenolysis of Norcamphor Isobutylene Ketal (3 and 4)

The hydrogenolysis was carried out either as described for the reduction of acetals and ketals (7) or preferably by adding the ketal to a previously prepared solution of equimolar amounts of $LiAlH_4$ and $AlCl_3$ in anhydrous ether. Both procedures gave the same results. The reduction was allowed to proceed at room temperature for the appropriate length of time (20 h or 168 h), whereupon sufficient 15% aqueous KOH was added dropwise to decompose the complex and form a colorless precipitate which was readily removed by filtration. The ether was then removed by rotary evaporator. Recovery of material was 95% (2.8 g from 3.0 g of ketal mixture). The oil was then subjected to g.l.c. and the products obtained were those indicated in Table I along with unreacted starting material.

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