Cyclic Ether Formation in Superacid Media

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The formation of ethers in superacids by interaction of a primary hydroxy group with a carbocation centre has been investigated by a study of cyclisation of suitable substrates, mainly 1-(2-hydroxyethyl)cyclohexanols to give hydrobenzo[*b*]furans. Cyclisation traps thermodynamically stable ionic species, with rates of reaction dependent upon the size of the ether ring formed. Three- and four-membered ether rings were not formed, five-membered ether rings formed readily, the reaction being comparable in rate with a 1,2-methyl shift. Six-membered rings formed a little less readily and seven-membered rings less readily still, though a yield of 34% from a suitable substrate has been recorded. An unexpected feature of the reactions was their stereospecificity; in one case, this is believed to result from a methyl shift concerted with attack of the primary hydroxy group, the reaction proceeding through hindered transition state, in which methyl loss, probably as CH_3^+, competes with a 1,2-methyl shift.

Fluorosulphuric acid has long been used as a reagent for[1] cyclisation reactions; its high acidity and low nucleophilicity suppress elimination reactions and reactions with external nucleophiles, favouring intramolecular nucleophilic reactions.[2] The reagent has been used to make extensively rearranged cyclic ethers from geraniol,[3,4] and we have recently[5] shown that a number of simple terpenoid diols and unsaturated alcohols can be converted into cyclic ethers with limited rearrangement in substrates of suitable structure. We have, therefore, carried out a systematic investigation of ether formation from diols in superacid media. Since we are in all cases studying the stable product of reaction, we cannot control which product is formed, but we can readily predict it.

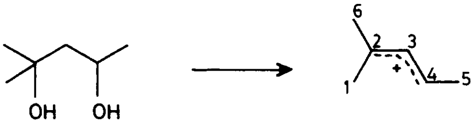
The reactions of diols in superacid media have already been studied by Olah and his co-workers,[6] who found that they give rise to dications[7] under suitable conditions. In most cases, the di-tertiary alcohol was used. In our work,[5] we were able to obtain ethers only from diols which had a primary, or in some cases secondary, hydroxy group. Ditertiary alcohols gave the allylic carbocation, under conditions much more vigorous than those used in dication formation.

In this work, we have studied the reaction of a primary hydroxy group with a carbocation centre, usually generated by ionisation of a tertiary hydroxy group in fluorosulphuric acid–sulphur dioxide.

Results and Discussion

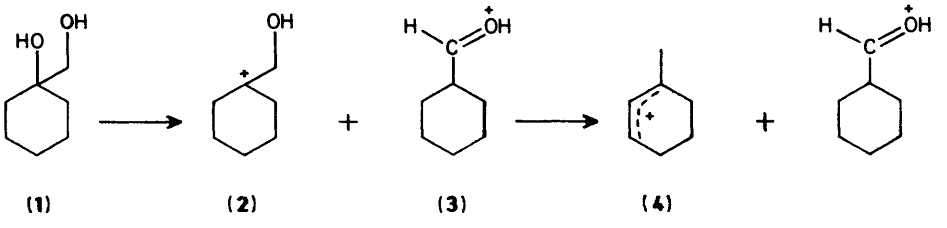
(a) *Oxirane Formation.*—Although oxiranes would not be expected to be stable in superacid conditions, we prepared 1-hydroxycyclohexylmethanol (**1**) to see if there was any evidence of ether formation at low temperature. In FSO_3H–SO_2 at −78 °C, (**1**) gave a mixture the spectrum of which could not be fully assigned, but is consistent with the formation of (**2**) by ionisation of the tertiary hydroxy group of (**1**), together with peaks at δ_C 238 and 52 p.p.m., indicating the presence of protonated cyclohexylformaldehyde (**3**). The hydroxy carbocation (**2**) showed no signs of cyclisation to the oxirane. On being warmed to −30 °C, the ion (**2**) decomposed, yielding the alkenyl cation (**4**), the structure of this ion being confirmed by its generation from 3-methylcyclohex-2-enol in FSO_3H–SO_2 at −78 °C. The experiment offers no evidence for oxirane formation, though it does not exclude its presence as a reactive intermediate.

(b) *Oxetane Formation.*—We were similarly unable to obtain any evidence for the formation of ethers having a four-membered ring. Both 3-methylbutane-1,3-diol and 3-methylbut-2-enol gave only polymer when added to FSO_3H–SO_2 at −78 °C, even when extracted into the acid from CS_2 solution. Reaction of 2-methylpentane-2,4-diol (**5**) gave the allylic ion (**6**).

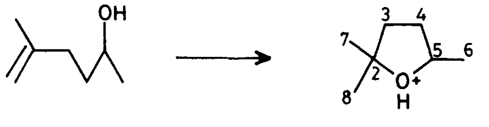


(5) **(6)**

(c) *Tetrahydrofuran Formation.*—Formation of tetra hydrofurans in superacid was expected to proceed very readily from 1,4-diols, since they are normally synthesised by dehydration of these substrates,[8] and this proved to be so. For example, addition of 5-methylhex-5-en-2-ol to FSO_3H–SO_2 solution at −78 °C, gave a product the ^{13}C n.m.r. spectrum of which showed only the protonated tetrahydrofuran. We therefore investigated in some detail the formation of bicyclic ethers, which are more difficult to prepare.

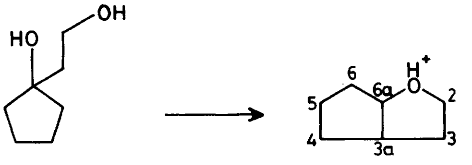


(1) **(2)** **(3)** **(4)**



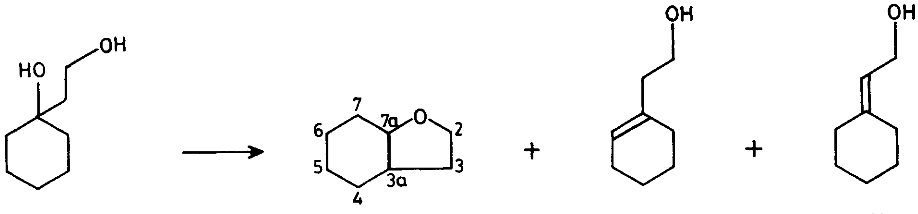
(7)

The first attempt to prepare a bicyclic ether was by cyclisation of 1-(2-hydroxyethyl)cyclopentanol (**8**) in FSO_3H–SO_2 at −50 °C. The ^{13}C n.m.r. spectrum of the reaction mixture was complex; only a spectrum subsequently identified as that of the protonated hydrocyclopenta[*b*]furan (**9**) was distinguished. On quenching the reaction mixture, (**9**) was isolated in 36% yield. Although (**9**) has been prepared previously,[9] its ^{1}H n.m.r. spectrum has not been discussed. In fact, few ^{1}H n.m.r. spectra of bicyclic ethers are recorded in the literature,[10,11] but the partial assignments of the ^{1}H n.m.r. spectra in Table 2 present few problems. The ^{1}H n.m.r. spectrum of (**9**) was considered on the assumption that the ring junction is *cis*, as a *trans* junction appears to be too strained to exist. The coupling of 6 Hz between 6a- and 6ax-H gives a dihedral angle of 30° by application of the Karplus equation, consistent with the cyclopentane ring in an envelope configuration. The coupling of 8 Hz between 2eq- and 3ax-H, together with the lack of coupling between 2ax- and 3eq-H is consistent with a similar shape for the ether ring.

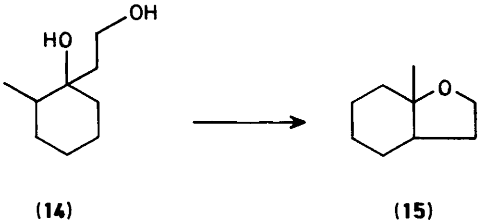


(8) (9)

We then treated 1-(2-hydroxyethyl)cyclohexanol (**10**) in FSO_3H–SO_2, this time at −70 °C. On quenching, the bicyclic ether perhydrobenzo[*b*]furan (**11**) was obtained, but in only 7% yield; 85% of the reaction mixture consisted of the unsaturated alcohols (**12**) and (**13**). On repeating the experiment at −40 °C, the yield of (**11**) rose to 37%. Preparative g.l.c. gave the pure ether, the identity of which was confirmed by comparison of its ^{1}H n.m.r. spectrum with published data.[9] This further confirmed that it was the *cis* ether. Models suggest that the energy difference between conformations with chair and twist-boat cyclohexanol rings may well be small. We found that 7a-H has equal couplings (*J* 4.25 Hz) to 7-H_2, and a further coupling to 3a-H with *J* 3.9 Hz. A boat cyclohexane ring requires 3a- and 7a-H to be eclipsed, a chair ring and a dihedral angle of *ca.* 30°. The coupling constant of 3.9 Hz, probably reduced by the axial C–O group, favours the latter.



(10) (11) (12) (13)



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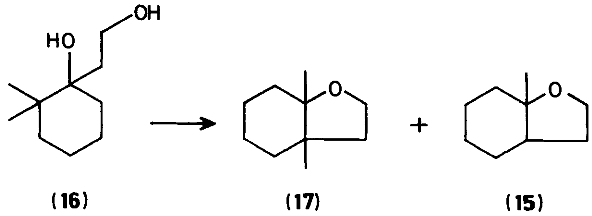


(16) (17) (15)

The low ether yields probably result from the rearrangement which must precede cyclisation being an unfavoured migration of the carbocation centre from the tertiary C-1 to the secondary C-2. In an attempt to increase the ether yield, we prepared the 2-methyl version of (**10**), 2-methyl-1-(2-hydroxyethyl)cyclohexanol (**14**). Reaction of (**14**) in FSO_3H–SO_2 at −70 °C gave 7a-methylhydrobenzo[*b*]furan (**15**) as the sole volatile product with the yield increased to 64%.

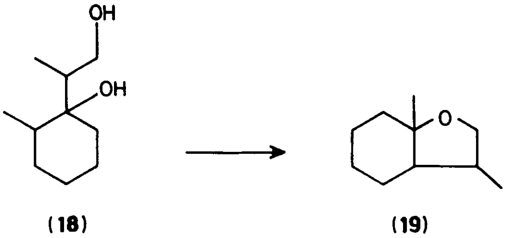
The ^{1}H n.m.r. spectrum of (**15**) shows that the peaks for 2-H_2 overlap at δ 3.84 giving a multiplet. If the conformation of the ether ring was the same as in (**11**), the equatorial proton would be further deshielded by the methyl group, suggesting that the ether ring has 'flipped', interchanging the axial and equatorial protons. Consistent with this, 2ax-H is now shielded by oxygen but deshielded by the methyl group, while 2eq-H is in the deshielding area of oxygen. Models suggest that such a process would only result from the cyclohexane ring flipping into the boat conformation.

In connection with another investigation,[12] we were interested in steric effects on ether cyclisation. We therefore, prepared 2,2-dimethyl-1-(2-hydroxyethyl)cyclohexanol (**16**) which was dissolved in FSO_3H–SO_2 at −60 °C. The ^{13}C n.m.r. spectrum of the solution showed peaks at δ_C 113 and 76 p.p.m., consistent with a protonated ether, but did not show peaks characteristic of a carbocation. On quenching the solution, the volatile component, comprising 68% of the product, was shown to consist of two ethers in the ratio 12:1. The major product was purified by g.l.c. and identified spectroscopically as 3a,7a-dimethylperhydrobenzo[*b*]furan (**17**); the minor component was found by g.l.c.–m.s. to be 7a-methylperhydrobenzo[*b*]furan (**15**).

Loss of a methyl group during a carbocation rearrangement is an unexpected reaction, with only one previous example having been reported.[4] We have already discussed the phenomenon elsewhere,[13] and suggest that it is a unimolecular expulsion of CH_3^+ from the carbocation, leaving an alkene which is rapidly protonated. The CH_3^+ is subsequently trapped by fluorosulphonate ion, yielding methyl fluorosulphonate which has been detected,[4] though we did not look for it.

The ^{1}H n.m.r. spectrum of (**17**) reveals that 2-H_2 form a triplet at δ_H 3.87. On expansion, this is revealed to be a doublet of doublets (*J* 8.0, 7.1 Hz). Decoupling the triplet at δ_H 1.82 resulting from 3-H_2 resolved 2-H_2 into a single peak. These couplings suggest that either 2-H_2 eclipse 3-H_2 exactly, which is unlikely as J_{trans} 2.4 Hz, or that the ring is 'flipping' rapidly on the n.m.r. time scale. This is more likely if repulsion between the methyl groups is minimised by the cyclohexane ring adopting a twisted boat conformation rather than the alternative chair form.

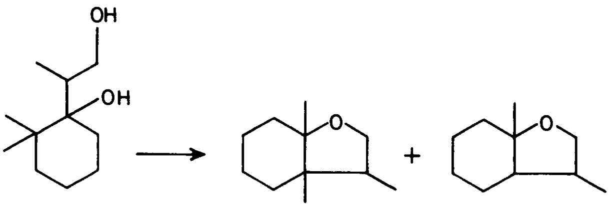
We next tried increasing steric hindrance by putting a methyl substituent on the side chain. We prepared 2-methyl-1-(1-methyl-2-hydroxyethyl)cyclohexanol (**18**) and treated it with FSO_3H–SO_2 at −50 °C. It gave the ether, 3,7a-dimethylhydrobenzo[*b*]furan (**19**) as the sole volatile product.



(18) **(19)**

The ^1H n.m.r. spectrum of (**19**) showed the *cis* and *trans*-coupling constants for 2-H_2 to be approximately equal, producing two triplets. The equatorial proton is furthest downfield at δ_H 3.98 (J 8.3 Hz) whereas the axial proton appears at δ_H 3.3 (J 8.4 Hz). 3-H occurs as a septet, suggesting similar couplings with 3a-H, 2-H_2, and the methyl protons. This implies a flat ether ring, which is again best accommodated by a boat cyclohexane ring. The ether (**19**) can, in theory, exist in two isomeric forms, depending on whether 3-Me is *cis* or *trans* to 7a-Me. Our spectra clearly showed only one isomer, though we could not decide which it was.

Rearrangement of (**18**) proceeded without methyl loss, so we next tried a more hindered version of (**16**) in which a methyl shift was necessary if cyclisation to a hydrobenzo[*b*]furan were to take place but in an environment constricted by a methyl group on the side chain. We prepared 2,2-dimethyl-1-(1-methyl-2-hydroxyethyl)cyclohexanol (**20**) and treated it with FSO_3H–SO_2 at −50 °C. The reaction gave an 80% yield of volatile products, which consisted of two ethers in the ratio 4:1. The major component was identified as 3,3a,7a-trimethylperhydrobenzo[*b*]furan (**21**); the minor product was identical with 3,7a-dimethylhydrobenzo[*b*]furan (**19**) obtained previously.



(20) **(21)** **(19)**

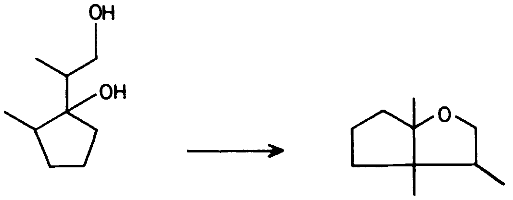
Clearly, the methyl loss reaction increased from 6 to 20% of the overall reaction as steric hindrance increased.

The ^1H n.m.r. spectrum shows that (**21**), like (**19**), is a single isomer. The 2-H_2 signals occur at δ_H 3.95 (t, J 8.5 Hz) and 3.44 (dd, J 9.3, 8.5 Hz). Assuming the axial geminal proton is shielded by the ethereal oxygen,[11] this places 3-Me *trans* to the two bridgehead methyl groups. It also indicates that the ether ring is less flattened than that in (**21**), probably to reduce strain between the bridgehead methyl groups. 3-H appears as a sextet at δ_H 2.26.

In a related investigation, we prepared the cyclopentyl-substrate, 2-methyl-1-(1-methyl-2-hydroxyethyl)cyclopentanol (**22**), and treated it with FSO_3H–SO_2 at −50 °C. The product contained two ethers, in yields of 60 and 12%, both of which were shown by mass spectrometry to have masses of 154, thus ruling out methyl loss. The major peak was identified as 3β,3aα,6aα-trimethyl-*cis*-perhydrocyclopenta[*b*]furan (**23**); the minor component has not been identified.

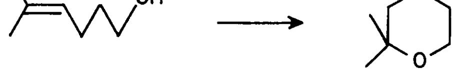
Table 1. ^{13}C N.m.r. chemical shifts (p.p.m. from Me_4Si) in FSO_3H–SO_2

Compound	C-1	C-2	C-3	C-4	C-5	C-6	Methyl
(4)	254	144	211	42	30	34	36
(6)	31	258	148	211	29	39	
(7)		112	39	34	94		20, 28, 28
(27)		105	36	30	33	89	23, 21, 19



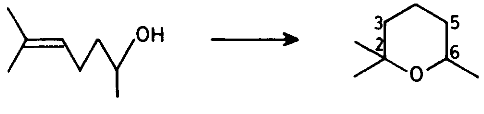
(22) **(23)**

(d) *Tetrahydropyran Formation.*—Since five-membered ring ethers were formed readily, our first experiments on the formation of six-membered ring ethers used substrates designed to favour this reaction strongly. First, we treated 5-methylhex-4-enol (**24**) with FSO_3H–SO_2 at −70 °C, and obtained 2,2-dimethyltetrahydropyran (**25**) in 70% yield.



(24) **(25)**

Similarly, we treated 6-methylhept-5-en-2-ol (**26**), and obtained only the 2,2,6-trimethyltetrahydropyran (**27**). The n.m.r. spectrum of the reaction mixture, recorded as soon as possible (1 h required) after adding the alcohol to the acid, was that of the protonated tetrahydropyran (Table 1).

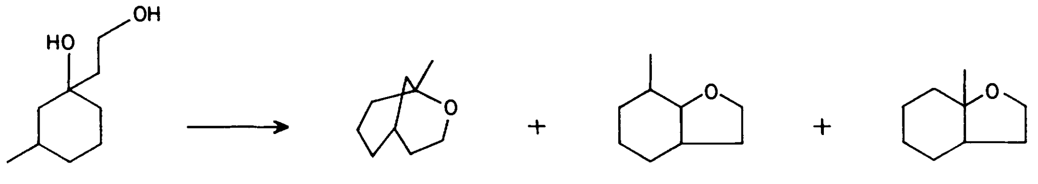


(26) **(27)**

The results contrast the report of Olah[14] that cyclisation of unsaturated ketones strongly favours the formation of five-membered heterocyclic rings, but this would be expected, as ethers should be formed more readily and be more stable than the oxonium ions derived from ketones.

Since we can prepare tetrahydropyrans from selected substrates, we next tried a substrate where formation of alternative products would be competitive. We prepared the substrate 3-methyl-1-(2-hydroxyethyl)cyclohexanol (**28**) and treated it with FSO_3H–SO_2 at −50 °C. The product was mainly polymeric, but contained three ethers in yields of 0.8, 4.3, and 4% of the total. We therefore repeated the reaction at −30 °C, and found ether yields of 9.9, 12.4, and 6.6%. The ethers were subsequently identified by g.l.c.–m.s. as 1-methyl-2-oxabicyclo[3.3.1]nonane (**29**) (9.9%), 7-methylperhydrobenzo[*b*]furan (**30**) (6.6%), and 7a-methylperhydrobenzo[*b*]furan (**15**) (12.4%).

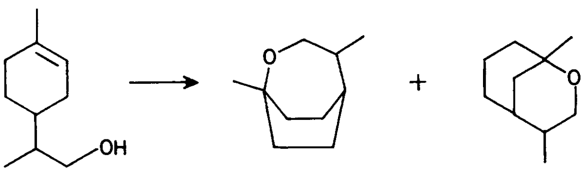
Clearly, the carbocation centre, migrating from C-1, can be trapped at C-2, giving (**30**); there is then competition between hydride shift to give the ion centre at C-3 [capture of which gives



(28) **(29)** **(30)** **(15)**

(**29**)] or methyl shift to give the ion centre at C-3, followed by a further hydride shift to give the ion centre at C-2, capture of which gives (**15**). Formation of the bridged tetrahydropyran is thus a difficult process, and subject to competition from alternative reactions and from polymerisation, but even so, a 9.9% yield of bridged tetrahydropyran is obtained.

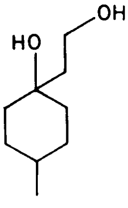
(e) *Seven-membered Ring and Larger Cyclic Ether Formation.*—We have already reported[5] reactions whereby *p*-menth-1-en-9-ol (**31**) can be cyclised to give 1,4-dimethyl-2-oxabicyclo[3.2.2]nonane (**32**) in 34% yield, together with 1,4-dimethyl-2-oxabicyclo[3.3.1]nonane (**33**) (21%). 4-Methyl-1-(2-hydroxyethyl)cyclohexanol (**34**) can be cyclised to give 1-methyl-2-oxabicyclo[3.2.2]nonane (**35**) in 8% yield, together with 6-methylperhydrobenzo[*b*]furan (**36**) (12%) and 1-(2-hydroxyethyl)-4-methylcyclohex-1-ene (**37**) (65%).



(31) **(32)** **(33)**

It may be possible to increase yields of these products by further raising of reaction temperatures.

Other examples of formation of seven-membered ring ethers have been reported[4] in the cyclisation of citronellol (2,6-dimethyloct-2-en-8-ol).



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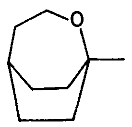

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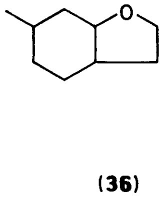

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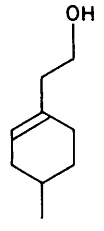


(37)

Attempts to make even larger cyclic ethers were unsuccessful. Reaction of dec-9-en-1-ol with FSO_3H-SO_2 gave a product containing 12% of volatile material, which was found to consist of three components. However, attempts to identify these by g.l.c.–m.s. were inconclusive.

Our results indicate that ethers are formed, as expected, by attack of the primary hydroxy group on a carbocation. This process is sufficiently rapid to prevent observation of the carbocation in most cases. When cyclisation is preceded by a shift of the positive centre, we are still unable to detect the ions involved, so we suggest that the carbocation rearrangements are comparable in rate to the cyclisation reactions. Formation of a five-membered ring from (**28**) shows that the rate is comparable to that of a 1,2-methyl shift; formation of larger rings is probably less favourable. The reactions appear to consist of a series of ionic rearrangements, which compete with the cyclisations, products depending on ring size and the stability of the ion which is trapped. When a suitable combination of ion stability and position does not exist, reactions give complex mixtures of products or polymers. This occurs for reactions potentially forming large and small rings. We may have more success with 8–10-membered rings if we start from more rigid substrates.

An unexpected feature of the reactions is the loss of a methyl group in up to 20% of reaction in those cases in which cyclisation is preceded by a methyl shift towards the hydroxylic side-chain. We have already[13] pointed out that methyl loss is favoured by steric hindrance near the reaction centre, favouring a unimolecular dissociation of the parent carbocation.

The second unexpected feature of these reactions is the stereospecificity of formation of the hydrobenzopenta[*b*]furans. In all cases, a single isomer was obtained. Formation of a *cis* fused ring system is to be expected on stability grounds, and in the cases of products substituted on the carbocyclic ring other than at the bridgehead, the stereochemistry of the starting material should be unchanged. However, substituents on the heterocyclic ring can be either α or β; both (**19**) and (**21**) are single isomers.

The substrate for formation of (**19**), the cyclohexane derivative (**18**), has chiral C-1, C-2, and C-1′. Its n.m.r. spectra are consistent with a single isomer being formed, though we cannot say which. On ionisation, C-1 loses chirality. However, the reaction requires a hydride shift from C-2 to C-1; assuming this to be concerted, the direction of ring fusion must be controlled by the stereochemistry at C-2 in the starting material and hence the stereochemistry of the product is controlled entirely by that of the starting material.

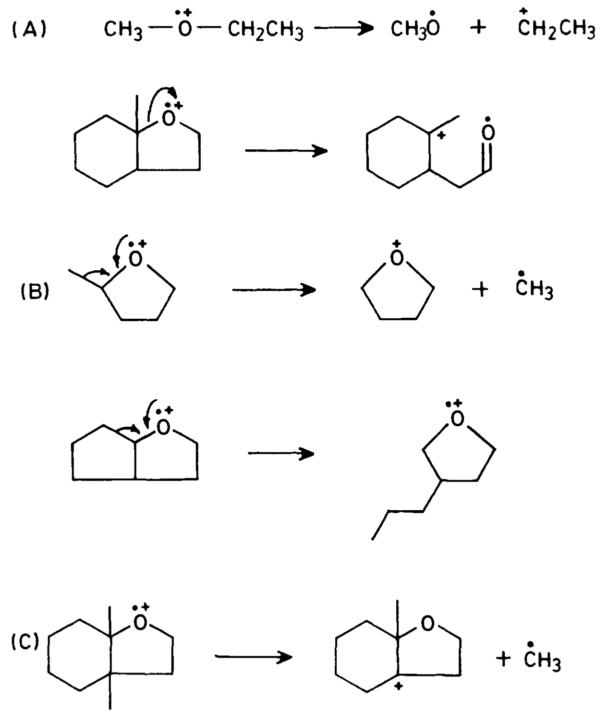
This simple argument cannot be applied to the formation of (**21**) from (**20**). The n.m.r. spectra of (**20**) show it to be a single isomer, of unassigned stereochemistry, while (**21**) is a single isomer with 3-Me *trans* to the other two methyl groups. However, (**20**) has only two chiral carbon atoms, C-1 and -1′, since C-2 carries two methyl groups. Ionisation of 1-OH thus leads to an ion in which the only chiral carbon atom is on C-1′, and to produce a single product, this must control the whole of the cyclisation process. The first step of this process, methyl migration from C-2 to C-1, can be controlled only if it is part of a

Table 2. ^1H N.m.r. chemical shifts (from Me_4Si) of cyclic ethers

Compound	2ax-H	2eq-H	3-H	3a-H	4-H	5-H	6-H	7-H	Methyl groups
(9)	3.83	3.55	2.05(ax) 1.5(eq)	2.62	← 1.4–1.5 →		1.78[a] 1.5[e]		(6a-H 4.37)
(11)	3.81	3.96	← 1.2–2.0 →						(7a-H 3.8)
(15)	3.84	3.84	1.98(ax) 1.77(eq)	← 1.3–1.6 →					1.14
(19)	3.3	3.98	2.29	1.43	← 1.25–1.17 →				1.21, 0.92
(17)	3.87	3.87	1.82	—	← 1.3–1.8 →				1.05, 0.99
(21)	3.44	3.95	2.31	—	← 1.1–1.7 →				1.02, 0.92, 0.85

Table 3. ^{13}C N.m.r. chemical shifts (p.p.m. from Me_4Si) of perhydrobenzo[*b*]furans

Compound	C-2	C-3	C-3a	C-4	C-5	C-6	C-7	C-7a	Methyl groups
(11)	66.5	32.7	38.1	24.7	21.3	28.0	28.8	77.7	
(19)	73.1	52.1	35.9	24.4	21.2	24.1	35.2	82.1	25.5, 17.1
(17)	63.0	42.1	39.0	22.4	22.2	34.2	35.6	82.4	22.7, 15.4
(21)	71.3	31.5	43.2	25.0	22.6	30.7	34.9	82.0	22.5, 10.8, 19.6



Scheme.

concerted process, in which 2′-OH approaches C-2, and simultaneously the methyl group is assisted in its migration. Assistance of migration of a leaving group by approach of a nucleophile is well-documented, so need not be discussed. The least hindered transition state for this concerted process will then be that which leads to the methyl group on C-3 being *trans* to the bridgehead methyl groups in the product. In this way, the stereochemistry of C-2′ in the starting material (**20**) would control the whole reaction, and lead to a single product.

Methyl migration in a crowded transition state, driven by anchimeric assistance from the hydroxy group, may well be the reason why methyl loss is observed during the reaction. A similar explanation for methyl loss may be applied to the cyclisation of (**16**); in that case, the reaction is modified by the absence of a chiral centre in the carbocation, but the concerted mechanism suggested above may well apply. In this case, the transition state is less hindered, so that methyl loss is reduced. It is not possible to say if the concerted reaction is general without a more detailed stereochemical study.

Identification of Ethers.—The most useful tool for ether identification was mass spectrometry. It was found that mass spectrometry of ethers involved three cleavage patterns: (A) *ipso*-cleavage, the normal pattern; (B) α-cleavage, when C-2 carries a single substituent; (C) β-cleavage, when C-3a carries a methyl group (Scheme).

These criteria were used for interpretation of mass spectra given in the Experimental section.

When samples were isolated by preparative g.l.c., ^1H and ^{13}C n.m.r. spectra were also recorded. The spectra are listed in Tables 2 and 3; ^1H spectra have already been discussed.

Experimental

^1H N.m.r. spectra were recorded on a Perkin-Elmer R34 (220 MHz) spectrometer, using $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. Decoupling experiments were carried out on a Bruker WM250 (250 MHz) spectrometer operating in the Fourier transform mode. ^{13}C N.m.r. spectra were recorded on a Varian XL 100 (25.2 MHz) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as an internal standard for neutral solution and sulphur dioxide as solvent for superacid solutions with an external deuterium lock of $[^2H_6]$acetone or $[^2H_4]$methanol and an external standard of tetramethylsilane enclosed within a 5 mm tube.

I.r. spectra were recorded on a Perkin-Elmer 1320 spectrometer using either liquid films or Nujol mulls. Mass spectra were recorded on an AEI MS 12 spectrometer. Accurate mass and g.l.c.–m.s. analyses were recorded on a VG 7070E mass spectrometer.

Reaction mixtures were analysed by Perkin-Elmer F17 and Dani 3800 gas–liquid chromatographs with flame ionisation detectors using nitrogen as the carrier gas. The F17 instrument employed a 5 ft stainless steel column of 2 mm internal diameter using 10% OV351 on Celite as support material. The 3800 instrument employed a 25 m capillary column with 0.3 mm internal diameter, coated with OV351.

Preparative g.l.c. separations were carried out on a Perkin-Elmer F21 column of 3 mm internal diameter containing Celite 60–80 mesh coated with 20% Reoplex 100.

1-*Hydroxycyclohexanecarboxylic Acid.*—Sodium metabisulphite (48.4 g, 0.25 mol) in distilled water (200 ml) was added over 30 min to a stirred mixture of cyclohexanone (40 g, 0.41 mol), potassium cyanide (33 g, 0.51 mol) and water (200 ml). The mixture was kept at 25 °C for 2 h; then ether extraction, drying, and solvent removal gave cyclohexanone cyanohydrin. The cyanohydrin (20 g, 0.18 mol) was refluxed with glacial acetic acid (300 ml) and concentrated HCl (300 ml) for 3 h. The solution was then concentrated *in vacuo*, the residue dissolved in chloroform, washed with water, and purified by means of the sodium salt, leaving a solid (19 g, 32%). After recrystallisation from n-hexane, it had m.p. 105 °C (lit.,[15] 106–107 °C); *m/z* 99 (CO_2H); $\nu_{max.}$ 3 500–2 500, 1 700, 1 430, and 1 300 cm^{-1}.

Ethyl 1-*Hydroxycyclohexanecarboxylate*.—To a stirred solution of hydroxycyclohexanecarboxylic acid (18 g, 0.125 mol) and ethanol (12 g, 0.26 mol) in dry benzene (50 ml) was added concentrated H_2SO_4 (0.5 ml), and the mixture was refluxed overnight. The solvent was removed *in vacuo*, and the residue dissolved in ether, then unchanged acid was filtered off, the solution washed with sodium hydrogencarbonate solution, dried, and concentrated. The residue was distilled to give the ester (9 g, 42%), b.p. 67 °C at 0.6 Torr; *m/z* 172; δ 1.29 (3H, t, Me), 1.6–1.8 (10H, m, CH_2), 3.3 (1H, br s, OH), and 4.23 (2H, q, CH_2); $\nu_{max.}$ 3 450, 2 900, 2 840, 1 700, 1 430, 1 140, and 980 cm^{-1}.

1-*Hydroxycyclohexylmethanol* (**1**).—Ethyl 1-hydroxycyclohexanecarboxylate (8 g, 0.46 mol) in dry ether (30 ml) was reduced with $LiAlH_4$ (1.1 g, 0.026 mol) for 30 min, then refluxed for 1 h. After quenching with ammonium sulphate solution, and the usual work-up, the diol was obtained and crystallised from ether–hexane (3.4 g, 56%), m.p. 72–74 °C (lit.,[16] 73 °C); *m/z* 130; δ 1.3–1.7 (10H, br m, CH_2), 3.2 (2H, br s, OH), and 3.43 (2H, s, CH_2OH); $\nu_{max.}$ 3 300, 2 900, 1 450, 1 380, and 1 050 cm^{-1}.

3-*Methylbutane*-1,3-*diol*.—Tetrahydrofuran (100 ml) was run into a stirred solution of mercury(II) acetate (31.9 g, 0.1 mol) in water (100 ml), giving an orange-yellow suspension. After stirring for 15 min, 3-methylbut-3-en-1-ol (8.6 g, 0.1 mol) was added, and stirring was continued for 1 h. Sodium hydroxide (100 ml, 3M aqueous solution) was then added, followed by a solution of sodium borohydride (1.9 g, 0.05 mol) in 3M aqueous sodium hydroxide solution (100 ml). The solution was cooled to below 25 °C. After stirring for 3 h, the mixture was left in a stoppered separating funnel overnight. The mercury layer was removed, the aqueous phase saturated with NaCl, and extracted with ether (3 × 50 ml). The extracts were combined, dried, the ether removed and distilled at 70 °C and 0.35 Torr (lit.,[17] 70 °C at 0.35 Torr) yielding the diol (6.7 g, 65%); *m/z* 108; δ 1.02 (6H, s, Me), 1.5 (2H, t, CH_2), 3.63 (2H, t, CH_2OH), and 4.02 (1H, br s, OH); $\nu_{max.}$ 3 400, 3 000, 1 390, 1 370, 1 150, 1 070, and 1 030 cm^{-1}.

5-*Methylhex*-5-*en*-2-*ol*.—5-Methylhex-5-en-2-one (7.6 g, 0.067 mol), prepared by the literature method,[18] was reduced with $LiAlH_4$ (1.5 g, 0.038 mol). After work-up, the oil was distilled to give the alcohol (6.3 g, 85%), b.p. 90 °C at 25 Torr (lit.,[19] 73–74 °C at 27 Torr), *m/z* 114; δ 1.18 (3H, d, Me), 1.55 (2H, m, CH_2–C–OH), 1.7 (3H, s, Me–C=), 2.1 (2H, m, CH_2–C=), 2.4 (1H, br s, OH), 3.77 (1H, m, CH), and 4.7 (2H, s, =CH_2); $\nu_{max.}$ 3 400, 3 100, 2 950, 1 650, 1 380, 1 150, and 880 cm^{-1}.

Ethyl 1-*Hydroxycyclopentylacetate*.—This preparation was carried out using a modified Reformatsky reaction.[20] Part (50 ml) of a mixture of cyclopentanone (12.6 g, 0.15 mol), benzene (120 ml), toluene (100 ml), and ethyl bromoacetate (26.5 g, 0.158 mol) was added to zinc powder (10.3 g, 0.157 mol), in a 500 ml three-necked round bottomed flask, equipped with condenser, stirrer, and dropping funnel. The contents were heated to 100 °C, whereupon a vigorous reaction set in. The rest of the solution was run in to maintain reflux. When addition was complete the mixture was refluxed for a further 2 h. After cooling, the solution was acidified with dilute H_2SO_4 and the organic layer separated, dried, and concentrated. Distillation of the oil obtained gave the acetate (18 g, 72%), b.p. 82–89 °C at 2 Torr (lit.,[21] 77–79 °C at 11 Torr); *m/z* 172; δ 1.27 (3H, t, CH_3), 1.6–1.9 (8H, m, ring CH_2), 2.6 (2H, s, CH_2CO_2Et), 3.4 (1H, br s, OH), and 4.2 (2H, q, CH_2CH_3); $\nu_{max.}$ 3 500, 2 940, 1 700, 1 360, 1 200, and 1 000 cm^{-1}.

1-(2-*Hydroxyethyl*)*cyclopentanol* (**8**).—Reduction of ethyl 1-hydroxycyclopentylacetate (9 g, 0.052 mol) with $LiAlH_4$ (4.5 g, 0.12 mol) in ether, followed by conventional work-up and continuous flow extraction from the aqueous layer with chloroform, gave a viscous oil (5 g, 85%) which was purified by short-path distillation, b.p. 100 °C at 0.4 Torr; *m/z* 130; δ 1.62 (4H, m, CH_2 ring), 1.8 (4H, m, CH_2 ring), 1.85 (2H, t, CH_2COH), 2.5 (1H, br s, OH), 3.85 (1H, br s, OH), and 3.9 (2H, t, CH_2OH); $\nu_{max.}$ 3 340, 2 920, 1 450, and 1 000 cm^{-1}.

Quenching of 1-(2-*Hydroxyethyl*)*cyclopentanol*.—A solution of 1-(2-hydroxyethyl)cyclopentanol (3 g, 0.026 mol) and FSO_3H (12 g) in SO_2 (12 ml) was prepared at −50 °C. After stirring for 2 h at −50 °C it was quenched in a slurry of potassium carbonate in methanol cooled to −78 °C, and stirred vigorously. Water was added to the solution, then the product was extracted with ether. Removal of the ether by fractional distillation gave an orange oil (1.6 g), which g.l.c. showed to be 57% of the main product, subsequently identified as perhydrocyclopenta[*b*]furan (**9**) in 36% yield. This was purified by distillation, b.p. 45 °C at 15 Torr (lit.,[9] 49–50 °C at 28 Torr), followed by preparative g.l.c. which gave a 99% pure sample (Found: C, 74.4; H, 10.8. Calc. for $C_7H_{12}O$: C, 74.9; H, 10.8%); *m/z* (α-fission), 112 (M^+, 16%), 83 (100), 67 (17), 55 (17), and 41 (18); $\nu_{max.}$ 2 920, 2 840, 1 435, 1 200, 1 050, and 910 cm^{-1}. The ^1H n.m.r. spectrum discussed earlier is in Table 2.

1-(2-*Hydroxyethyl*)*cyclohexanol* (**10**).—Cyclohexanone (15.5 g, 0.15 mol) was treated with ethyl bromoacetate as described above. Work-up gave ethyl 1-hydroxycyclohexylacetate (17 g, 57%), b.p. 85–90 °C at 2 Torr; *m/z* 186; δ 1.25 (3H, t, Me), 1.4–1.7 (10H, m, ring CH_2), 2.45 (2H, s, CH_2CO_2Et), 3.4 (1H, s, OH), and 4.2 (2H, q, CH_2CH_3); $\nu_{max.}$ 3 450, 2 960, 1 760, 1 360, 1 100, 1 000, and 950 cm^{-1}.

Reduction of the ester with $LiAlH_4$, followed by work-up as described above gave 1-(2-hydroxyethyl)cyclohexanol (11.9 g, 48% overall), which was used without distillation. The product had *m/z* 114; δ 1.4–1.7 (10H, m, CH_2 ring), 1.74 (2H, t, CH_2–C–OH), 3.4 (1H, br s, CH_2OH), 3.7 (1H, s, OH), and 3.88 (2H, t, CH_2OH); $\nu_{max.}$ 3 350, 2 920, 2 820, 1 440, 1 040, and 850 cm^{-1}.

Quenching of 1-(2-*Hydroxyethyl*)*cyclohexanol*.—The quenching procedure described above was followed using 1-(2-hydroxyethyl)cyclohexanol (3 g, 0.023 mol), the reaction being carried out at −40 °C. Extraction after quenching gave an oil (1.8 g), which contained 40% of a substance subsequently identified as perhydrobenzo[*b*]furan (**11**) in 25% yield. It was distilled at 50 °C and 15 Torr (lit.,[9] 66 °C at 15 Torr), and further purified by preparative g.l.c. (Found: C, 76.2; H, 11.4. Calc. for $C_8H_{14}O$ requires C, 76.2; H, 11.2%), *m/z* (α-fission) 126 (M^+, 25%), 83 (100), 55 (25), 41 (20), and 32 (35); $\nu_{max.}$ 2 900, 2 810, 1 435, 1 110, 1 000, 1 010, 980, and 920 cm^{-1}. The ^1H n.m.r. spectrum in Table 2 has been discussed earlier; the ^{13}C n.m.r. spectrum is in Table 3.

1-(2-*Hydroxyethyl*)-2-*methylcyclohexanol* (**14**).—2-Methylcyclohexanone (17.7 g, 0.15 mol) was treated with ethyl bromacetate as described above. Work-up yielded ethyl 2-methyl-1-hydroxycyclohexylacetate (19.5 g, 62%), which was distilled at 75–82 °C and 0.5 Torr; *m/z* 200; δ (3H, d, Me), 1.25 (3H, t, CH_3), 1.3–1.7 (9H, m, ring CH_2 and CH), 2.26 (1H, d, C*H*COOEt), 3.25 (1H, br s, OH), and 4.15 (2H, q, CH_2O); $\nu_{max.}$ 3 500, 2 900, 2 840, 1 700, 1 450, 1 360, 1 300, 1 270, 1 020, and 980 cm^{-1}.

Reduction with $LiAlH_4$ gave 1-(2-*hydroxyethyl*)-2-*methylcyclohexanol* (14.2 g, 58% overall) as an oil which solidified on standing and was recrystallised from hexane, m.p. 46–50 °C (Found: C, 68.3; H, 11.7. $C_9H_{18}O_2$ requires C, 68.3; H, 11.5%); *m/z* 158; δ 0.9 (3H, d, Me), 1.3–1.7 (8H, m, ring CH_2), 1.65 (2H, m, CH_2COH), 2.0 (1H, d, CH), 3.2 (1H, br s, OH), 3.75 (1H, m, C*H*–COH), and 3.85 (1H, m, CH_2OH), and 4.1 (1H, br s, OH); $\nu_{max.}$ 3 300, 2 900, 1 450, 1 360, 1 050, and 950 cm^{-1}.

Quenching of 1-(2-*Hydroxyethyl*)-2-*methylcyclohexanol*.—The quenching procedure described above was followed using 1-(2-hydroxyethyl)-2-methylcyclohexanol (4 g, 0.028 mol), the reaction being carried out at −40 °C. Work-up yielded an oil containing 7a-*methylperhydrobenzo*[b]*furan* (**15**) (2.5g, 64%), b.p. 70 °C at 15 Torr (Found: C, 77.1; H, 11.7. $C_9H_{16}O$ requires C, 77.1; H, 11.5%); *m/z* (*ipso* fission), 140 (M^+, 10%), 125 (46), 97 (100), 81 (10), 55 (35), and 43 (58); $\nu_{max.}$ 2 900, 1 440, 1 360, 1 110, 1 040, 1 020, and 945 cm^{-1}. The ^1H n.m.r. spectrum is given in Table 2, and has been discussed earlier.

1-(2-*Hydroxyethyl*)-2,2-*dimethylcyclohexanol* (**16**).—2,2-Dimethylcyclohexanone (12 g, 0.095 ml) prepared by the method of Boatman *et al.*[22] was reacted with ethyl bromacetate, as described above. Work-up yielded ethyl 1-hydroxy-2,2-dimethylcyclohexylacetate (6 g, 29%), b.p. 95–98 °C at 0.6 Torr; *m/z* 214; δ 0.96 (3H, s, Me), 1.0 (3H, s, Me), 1.2–1.7 (8H, m, CH_2 ring), 1.3 (3H, t, CH_2CH_3), 2.46 (1H, d, C*H*COOEt), 2.65 (1H, d, C*H*COOEt), 3.6 (1H, br s, OH), and 4.22 (2H, q, CH_2CH_3); $\nu_{max.}$ 3 500, 2 900, 2 840, 1 700, 1 450, 1 360, 1 310, 1 170, and 1 015 cm^{-1}. The ester was then reduced with $LiAlH_4$. Work-up as described above gave 1-(2-*hydroxyethyl*)-2,2-*dimethylcyclohexanol* (**16**) (4 g, 24%) m.p. 95 °C (from hexane) (Found: C, 69.7; H, 11.7. $C_{10}H_{20}O_2$ requires C, 69.7; H, 11.7%); *m/z* 172; δ 0.95 (3H, s, Me), 1.0 (3H, s, Me), 1.2–1.7 (8H, m, ring CH_2), 2.0 (2H, m, CH_2COH), 2.75 (1H, br s, OH), 3.5 (1H, br s, OH), 3.8 (1H, m, C*H*OH), and 4.0 (1H, t d, C*H*OH); $\nu_{max.}$ 3 300, 2 900, 1 450, 1 380, 1 170, 1 040, and 950 cm^{-1}.

Quenching of 1-(2-*Hydroxyethyl*)-2,2-*dimethylcyclohexanol*.—1-(2-Hydroxyethyl)-2,2-dimethylcyclohexanol (2 g, 0.013 mol) was dissolved in FSO_3H (10 ml) and SO_2 (10 ml) at −60 °C, then quenched, yielding an oil (1.5 g) which was shown by g.l.c. to be 92% volatile (68% yield), the volatile fraction consisting of two ethers in the ratio 92:8. The major component was purified by preparative g.l.c. to yield an oil consisting of 3a,7a-*dimethylperhydrobenzo*[b]*furan* (**17**) which solidified on standing, m.p. 32–34 °C (Found: C, 77.7; H, 11.9. $C_{10}H_{18}O$ requires C, 77.9; H, 11.8%); *m/z* (mainly β-fission, some *ipso* fission); 154 (M^+, 0.1%), 140 (9.7), 139 (100), 97 (85), and 43 (71); $\nu_{max.}$ 2 900, 2 850, 1 440, 1 370, 1 160, 1 100, 1 020, and 940 cm^{-1}. The ^1H and ^{13}C n.m.r. spectra are given in Tables 2 and 3; the ^1H spectrum has been discussed earlier. The minor component was shown by g.l.c.–m.s. to be 7a-methylperhydrobenzo[*b*]furan (**15**).

1-(2-*Hydroxy*-1-*methylethyl*)-2-*methylcyclohexanol* (**18**).—2-Methylcyclohexanone (17.7 g, 0.158 mol) was esterified using ethyl 2-bromopropionate (28.6 g, 0.158 mol) following the method used for esterification with ethyl bromoacetate. Work-up gave an oil which was distilled at 92–97 °C and 0.8 Torr to give the ester (23.0 g, 72%), which was reduced with $LiAlH_4$ to give (**18**) as an oil (16.3 g, 65% overall) which solidified on standing. After recrystallisation from hexane, (**18**) had m.p. 45–50 °C; *m/z* 172; δ 0.7 (3H, d, Me), 0.82 (3H, d, Me), 1.2–1.75 (9H, m, CH_2 ring and CH ring), 2.06 [1H, m, –C*H*(Me)CH_2OH], 3.5 (1H, m, C*H*OH), 3,55 (1H, br s, OH), and 3.74 (1H, t, C*H*OH); $\nu_{max.}$ 3 350, 2 940, 1 450, 1 020, 960, and 890 cm^{-1}.

Quenching of 1-(2-*Hydroxy*-1-*methylethyl*)-2-*methylcyclohexanol*.—Compound (**18**) was quenched by a solution in FSO_3H–SO_2 at −50 °C in the usual manner, giving an oil which was shown by g.l.c. to consist of a single component, 3,7a-*dimethylperhydrobenzo*[b]*furan* (**19**), b.p. 65 °C at 15 Torr (Found: C, 77.7; H, 11.8. $C_{10}H_{18}O$ requires C, 77.9; H, 11.8%); *m/z* (α-fission) 154 (M^+, 15.7%), 139 (40), and 111 (100); $\nu_{max.}$ 2 900, 1 430, 1 360, 1 190, 1 110, 1 010, and 850 cm^{-1}. The ^1H and ^{13}C n.m.r. spectra are given in Tables 2 and 3; the ^1H spectrum has been discussed earlier.

1-(2-*Hydroxy*-1-*methylethyl*)-2,2-*dimethylcyclohexanol* (**20**).—2,2-Dimethylcyclohexanone (3.25 g, 0.025 mol) was esterified using ethyl 2-bromopropionate (5.06 g, 0.028 mol) and zinc powder (1.83 g), as described earlier, yielding ethyl 2-(1-hydroxy-2,2-dimethylcyclohexyl)propionate (2 g, 34%), an oil b.p. 99–103 °C at 0.8 Torr. The oil (1.6 g) was reduced with $LiAlH_4$ to give (**20**) (1.1 g, overall 29%) as an extremely viscous oil which was not further purified; *m/z* 184; δ 0.81 (3H, d, Me), 0.96 (3H, s, Me), 1.18 (3H, s, Me), 1.2–1.8 (8H, m, ring CH_2), 2.0 (1H, q, CH), 3.45 (1H, dd, C*H*OH), and 3.71 (1H, t d, C*H*OH); $\nu_{max.}$ 3 300, 2 950, 1 460, 1 380, 1 200, and 1 030 cm^{-1}.

Quenching of 1-(2-*Hydroxy*-1-*methylethyl*)-2,2-*dimethylcyclohexanol*.—1-(2-Hydroxy-1-methylethyl)-2,2-dimethylcyclohexanol (1 g, 0.0053 mol) was dissolved in FSO_3H–SO_2 at −50 °C, and quenched as described above. Analysis of the oil produced by g.l.c. showed it to contain two volatile materials, present in the ratio 4:1. The major component, 3,3a,7a-*trimethylperhydrobenzo*[b]*furan* (**21**), was purified by preparative g.l.c. (Found: C, 78.4; H, 12.1. $C_{11}H_{20}O$ requires C, 78.5; H, 12.0%); *m/z* (β-fission), 168 (M^+, 0.1%), 153 (100), 112 (33), 111 (19), 109 (10), 97 (35), 95 (60), 69 (29), 55 (77), and 43 (86); $\nu_{max.}$ 2 900, 2 840, 1 450, 1 370, 1 020, 940, and 900 cm^{-1}. The ^1H and ^{13}C n.m.r. spectra are given in Tables 2 and 3; the ^1H spectrum has been discussed earlier.

5-*Methylhex*-4-*enol* (**24**).—5-Methylhex-4-enal (2.3 g, 0.02 mol), prepared by the method of Marbet and Savoy,[23] was reduced with $LiAlH_4$ to give the alcohol (1.6 g, 66%), b.p. 70 °C at 16 Torr (lit.,[24] 90 °C at 25 Torr); $\nu_{max.}$ 3 350, 2 900, 2 830, 1 430, 1 370, and 1 050 cm^{-1}.

Quenching of 5-*Methylhex*-4-*enol*.—Compound (**24**) (1.5 g, 0.013 mol) was extracted from CS_2 solution into a solution of FSO_3H (5 ml) in SO_2 (5 ml) at −70 °C. Quenching as described above gave an oil which was distilled to give 2,2-dimethyltetrahydropyran (1 g, 67%), 99% pure by g.l.c, b.p. 116–117 °C (lit.,[25] 119–120 °C); *m/z* 114 (M^+, 1%) and 99 (100); δ 1.2 (6H, s, Me), 1.5–1.65 (6H, m, CH_2), and 3.7 (2H, t, CH_2OH); $\nu_{max.}$ 2 900, 2 830, 1 440, 1 350, 1 210, 1 070, 1 030, 950, 830, and 800 cm^{-1}.

6-*Methylhept*-5-*en*-2-*ol* (**26**).—Reduction of 6-methylhept-5-en-2-one with $LiAlH_4$ gave the alcohol (**26**), b.p. 78–79 °C at 15 Torr (lit.,[26] 90–91 °C at 30 Torr); $\nu_{max.}$ 3 400, 2 900, 1 460, 1 380, 1 150, 1 080, 970, 950, and 830 cm^{-1}.

Quenching of 6-*Methylhept*-5-*en*-2-*ol*.—Compound (**26**) (3 g, 0.023 mol) was extracted from CS_2 solution into a solution of FSO_3H (10 ml) in SO_2 (10 ml) at −70 °C. Quenching as described above gave an oil which was distilled to give 2,2,6-

trimethyltetrahydropyran (**27**) (1.5 g, 50%), b.p. 125 °C (lit.,[27] 126–127 °C); *m*/*z* 128; δ 1.3 (3H, d, Me), 1.45–1.7 (6H, m, CH_2), 1.23 (6H, s, Me), and 3.72 (1H, m, -CH–O–); $\nu_{max.}$ 1 430, 1 100, and 1 050 cm^{-1}.

1-(2-*Hydroxymethyl*)-3-*methylcyclohexanol* (**28**).—3-Methylcyclohexanone (17.7 g, 0.15 mol) was esterified with ethyl bromoacetate and zinc as described above, yielding ethyl 1-hydroxy-3-methylcyclohexylacetate (18.5 g, 59%), b.p. 93–100 °C at 1.7 Torr; *m*/*z* 200; δ (3H, d, CH_3 *cis*). 1.85 (3H, d, CH_3 *trans*), 1.25 (3H, t, CH_2CH_3), 1.2–1.8 (9H, m, CH_2), 2.37 (2H, s, CH_2COOEt *cis*), 2.52 (2H, s, CH_2COOEt *trans*), 3.36 (1H, br s, OH), and 4.14 (2H, q, CH_2CH_3); $\nu_{max.}$ 3 500, 2 900, 1 700, 1 350, 1 320, 1 170, 1 015, 945, and 840 cm^{-1}. Reduction with $LiAlH_4$ gave 1-(2-*hydroxymethyl*)-3-*methylcyclohexanol* (**28**) (12.2 g, 54%) which solidified on standing, m.p. 56–60 °C (from hexane); (Found: C, 68.4; H, 11.3. $C_9H_{18}O_2$ requires C, 68.4; H, 11.4%); *m*/*z* 158; δ 0.88 (3H, d, Me *cis*), 1.1 (3H, d, Me *trans*), 1.65 (2H, t, CH_2COH), 1.3–1.75 (9H, m, CH_2 ring and CH), 3.32 (2H, s, OH), and 3.86 (2H, t, CH_2OH); $\nu_{max.}$ 3 300, 2 900, 1 450, 1 060, 1 030, 940, and 900 cm^{-1}.

Quenching of 1-(2-*Hydroxymethyl*)-3-*methylcyclohexanol*.—1-(2-Hydroxyethyl)-3-methylcyclohexanol was quenched in the usual manner. G.l.c. examination of the product showed the presence of three ethers in total 28% yield. These were identified by g.l.c.–m.s. as 1-methyl-2-oxabicyclo[3.3.1]nonane (**29**) (9.9%) *m*/*z* (*ipso* fission), 140 (M^+, 7%), 125 (1), 97 (100), 43 (25), and 55 (10); 7-methylperhydrobenzo[*b*]furan (**30**) (6.6%), *m*/*z* (α-fission, minor amount of *ipso* fission) 140 (M^+, 20%), 139 (15), 125 (4), 97 (15), 83 (100), 55 (20), and 43 (8); and 7a-methylperhydrobenzo[*b*]furan (**15**) (12.4%), details given earlier.

Generation and Study of Carbocations.—Sulphur dioxide (1 ml) was condensed in a 10 ml round-bottomed flask and FSO_3H (2 ml) added. The solution was cooled to −78 °C, and the substrate (250–500 mg) in SO_2 (1 ml) at −78 °C was added dropwise with stirring. This was placed in a 12 mm bore n.m.r. tube cooled to −78 °C. An external lock of [$^2H_6$]acetone or [$^2H_4$]methanol in a sealed 5 mm tube held in place by two guides was added, and the 12 mm tube stoppered and placed in the Varian X-L 100 spectrometer. The tube was cooled in a stream of nitrogen passed through a cooling coil immersed in liquid nitrogen. The temperature of the probe was controlled using a heating coil in the nitrogen stream. The tube was spun at 14 r.p.s. A sweep width of 10 000 Hz was used in conjunction with an acquisition time of 4 s.

For substrates which polymerised rapidly the substrate was dissolved in carbon disulphide (2 ml) before being cooled to −70 °C and adding to the acid–SO_2 solution.

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