Reactions of Some Cyclic Ethers in Superacids

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The reactions of some epoxides and tetrahydrofuran derivatives in superacidic media have been studied. The tetrahydrofurans decompose only at 0 °C or above, yielding, in some cases, unsaturated carbocations which react to give carbocyclic products, though many yield only tar. Cyclohexene oxides decompose more readily; unsubstituted, they slowly form an allylic ion; with one carbon at the epoxide link substituted they yield the ketone, and with both carbons substituted they give the ring-contracted aldehyde. Limonene 1,2-oxide behaves in a similar manner, though yielding small amounts of the ring-contracted protonated aldehyde (**10**). Reaction of geraniol 2,3-oxide is initially similar but the intermediate is intercepted intramolecularly to yield the hydroxy-iridoid ethers, 3,3,6β-trimethyl-*cis*-perhydrocyclopenta[*c*]furan and 3,3,6α-trimethyl-*cis*-perhydrocyclopenta[*c*]furan.

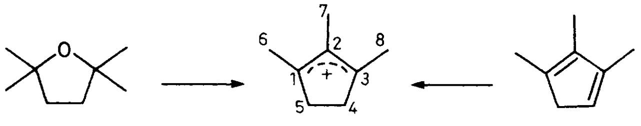
Protonation of cyclohexene oxide or norbornene oxide yields onium salts, stable at −70 °C, which show the addition to be either unsymmetrical (*i.e.* edge protonation) or to take place in two different positions.

In an earlier paper[1] we showed that diols and hydroxy alkenes can be cyclised in fluorosulphuric acid to form cyclic or bicyclic ethers from acyclic or cyclic substrates, respectively. Ethers are also known to form ions in superacidic media[2,3] and cleave by unimolecular fission of the conjugate acid to form a carbocation and an alcohol. Acyclic ethers having a tertiary alkyl group cleave at *ca.* −70 °C, those with a secondary alkyl group cleave at *ca.* −30 °C and those with primary alkyl groups at 40 °C, the only observed ion being a rearranged tertiary ion in the last two cases.

We have found[4] that the decomposition of 3β,4α,6aα-trimethyl-*cis*-perhydrocyclopenta[*b*]furan in superacid at room temperature yields the 1,3-dimethyl-2-isopropylcyclopentenium ion, and the decomposition[5] of 1,8-cineole (1,3,3-trimethyl-2-oxabicyclo[2.2.2]octane) yields the 1-methyl-4-isopropylcyclohexenium ion and 1,4-cineole (1-isopropyl-4-methyloxabicyclo-[2.2.2]heptane). Ethers, then, can behave as semi-stable intermediates in superacids, being formed from hydroxy carbocations and decomposing by rearrangement to more stable ethers or to other carbocations. We therefore examined the reactions of a number of cyclic ethers in superacids to see what conditions were required and what pathways were open to them. Cyclic ethers were chosen since they are more likely to yield rearranged products rather than to cleave into fragments as do their acyclic counterparts.

Results and Discussion

Since we have found tetrahydrofuran derivatives to be the most readily formed cyclic ethers in superacid systems, we chose these for the initial studies. They proved to be considerably more stable than acyclic ethers in fluorosulphuric acid, and all the ethers we studied were stable over the range −70 °C to −10 °C. The most reactive should be the tertiary alkyl ethers, so we studied the behaviour of 2,2,5,5-tetramethyltetrahydrofuran (**1**) in FSO_3H/SO_2. Up to −10 °C, the ^{13}C n.m.r. spectrum showed only three peaks, indicative of the protonated parent compound. However, after warming of the solution to 20 °C for 12 h, the ^{13}C n.m.r. spectrum revealed that the starting material had disappeared completely, leaving a product which was identified as the 1,2,3-trimethylcyclopentenyl cation (**2**). The identity of this species was confirmed by alternative generation from 1,2,3-trimethylcyclopenta-1,3-diene (**3**).



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

This same ion has been generated[6] from 1,2,3-trimethylcyclopentan-1-ol[3] in FSO_3H/SO_2 at −70 °C; this process involves the additional step of a hydride abstraction. Formation from (**1**) probably involves cleavage of the ether to a hydroxy carbocation, dehydration, and recyclisation.

In contrast, 2,2,5-trimethyltetrahydrofuran, generated *in situ* by cyclisation[1] of 2-methylhex-5-en-2-ol, in FSO_3H/SO_2 at −70 °C, decomposed by only 10% when allowed to stand at room temperature overnight, to yield a single ion which was present only in small amounts because of its subsequent decomposition. 2,5-Dimethyltetrahydrofuran proved even more intractable, being stable in FSO_3H/SO_2 at 10 °C and decomposing only slowly at 25 °C to an unidentifiable mixture of ions.

We decomposed a number of bicyclic tetrahydrofurans, prepared earlier,[1] but in all cases decomposition required temperatures >10 °C, and the ions obtained, if any, were unidentifiable.

We conclude that only in exceptional cases can tetrahydrofurans act as intermediates in rearrangements in superacids, since they are too stable and they decompose to yield mainly unidentifiable mixtures.

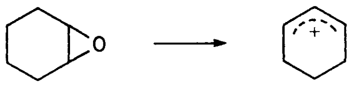
We then turned to the least stable ethers, epoxides, and studied their decomposition in superacid conditions. The first epoxide studied was cyclohexene oxide (**4**). At −70 °C the ^{13}C n.m.r. spectrum of a solution of cyclohexene oxide in FSO_3H/SO_2 showed two peaks characteristic of the α-carbon of ethers at 92 and 87 ppm, together with signals at 31, 30, and 24 ppm. The peak at 24 ppm was considerably larger than the other peaks, and could well be the result of superimposition. No change in the spectrum was observed on warming to −30 °C. The spectrum of (**4**) in $CDCl_3$ consisted of the expected three peaks.

The spectra of protonated tetrahydrofurans in FSO_3H/SO_2 showed no extra signals, so to check that this phenomenon was not specific to cyclohexene oxide, we studied the spectrum of *exo*-norbornene oxide (**5**) in FSO_3H/SO_2 at −70 °C. The same signal pattern was observed. The ^{13}C n.m.r. spectrum showed a single ether α-carbon peak at 51 ppm in $CDCl_3$, but in FSO_3H/SO_2 at −40 °C, the peak was replaced by two peaks, both showing slight further splitting (95.8, 95.5, 92.4 and 92.1 ppm). The remaining three peaks, at 43, 34, and 33 ppm are singlets.

Clearly the epoxides do not undergo protonation symmetrically in a single position. Three explanations of the observation may be put forward. Firstly, the epoxide may have undergone protonation on an edge of the ring, as has been suggested for cyclopropane rings, so that one of the ethereal carbon atoms is closer to the proton than the other. Secondly, protonation may take place on either the oxygen atom or the face of the epoxide ring. This would produce split peaks, provided that proton interchange between the two locations is slow on the ^{13}C n.m.r. timescale. Thirdly, protonation may take place on the oxygen atom with two different orientations. This would explain splitting in the norbornene oxide, where protonation could be *exo* or *endo*, but not in the cyclohexene oxide. Since the 'split' peaks are of approximately the same size, our evidence favours the edge-protonated explanation. Proof of this could be obtained by studying an unsymmetrical epoxide, but we have been unable to achieve sufficiently low temperatures to test this.

The sample of cyclohexene oxide was stored in FSO_3H/SO_2 at −30 °C for five days, after which time *ca.* half of the substrate had decomposed to form the cyclohexenium ion (**6**).

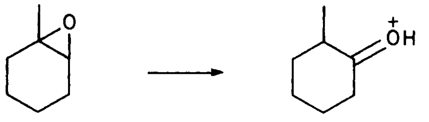
(5)



(4) **(6)**

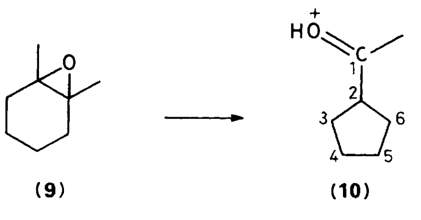
The conditions needed for fission of the epoxide ring are clearly sufficiently vigorous for dehydration of the hydroxy cation produced rather than a hydride shift to give cyclohexanone.

When the epoxide was substituted at one of the ethereal α-carbon atoms by a methyl group, the reaction proceeded readily, and 1-methylcyclohexene oxide (**7**) rearranged rapidly in FSO_3H/SO_2 at −70 °C to give protonated 2-methylcyclohexanone (**8**). Dehydration products were not observed in this case, suggesting that <10% of the reaction proceeded *via* this route.



(7) **(8)**

Substitution of the epoxide at both ethereal α-carbon atoms produced another complete change in the mechanism of the reaction. In FSO_3H/SO_2 at −70 °C, 1,2-dimethylcyclohexene oxide (**9**) rearranged rapidly to give the protonated ketone (**10**). In this case, the possible methyl shift to give 2,2-dimethylcyclohexanone is slow compared with the ring contraction reaction.



(9) **(10)**

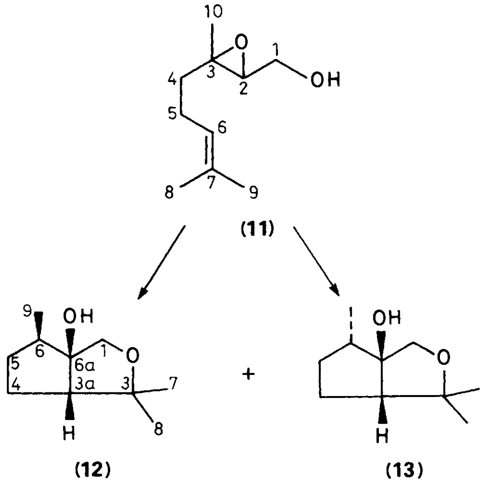
Since the reactions of simple epoxides in superacids were straightforward, we then attempted reactions with more complex terpenoid epoxides. The spectra of mixtures of ions are often impossible to assign, thus quenching of the ion solution, followed by chemical analysis of the products, is a valuable approach to a study of reaction mechanisms. The first to be studied was geraniol 2,3-oxide (**11**) (3,7-dimethyl-2,3-epoxyoct-6-en-1-ol) which was reacted with FSO_3H in SO_2 at −70 °C, to give a clear yellow solution which was then quenched to give a red oil. Distillation of the red oil gave a yellow oil (36%), the remainder of the product consisting of a high b.p. polymer. The volatile material was separated by preparative g.l.c. into two components (**12**) and (**13**) which comprised 26% and 10% of the product, respectively. Elemental analysis and mass spectrometry showed both (**12**) and (**13**) to be $C_{10}H_{18}O_2$, and i.r. spectroscopy showed the presence of a hydroxy group, in both products.

The ^1H n.m.r. spectra of these products were very similar, with 2 H peaks at δ 6.46 (12) and 6.44 (13), characteristic of a hydrogen atom on a carbon adjacent to an oxygen atom,[7] and a 1 H peak at δ 7.93 (12) and 7.96 (13), plus 3 H peaks at δ 8.73, 8.89, and 9.03 (12) and δ 8.73, 8.92, and 9.06 (13). The peaks at δ 9.03 and 9.06 were doublets (J = 6 Hz) while the other 3 H peaks were singlets.

The ^{13}C n.m.r. spectra (see Table) show peaks at 91 (singlet) (12) and 93 (singlet) (13). These data are consistent with a C–O–C unit, close to another electronegative group. Each compound has two further peaks, at 82 (singlet) and 72 (triplet) (12) and at 84 (singlet) and 72 (triplet) (13) which are consistent with carbon adjacent to oxygen. The compounds are saturated, so the data favours a trimethyl bicyclic hydroxy ether.

The mass spectral data further highlights the similarities. Each product has a parent ion at M 170, and each readily forms an $M-15$ fragment, probably by loss of a methyl group from the cyclic ether or by α-cleavage. Each has a peak at M 143 formed by loss of CH_2=CH– in an alternative α-cleavage.

Lanthanide shift data on the ^1H n.m.r. spectra suggest that the difference between (**12**) and (**13**) lies in the orientation of the methyl group on the carbon adjacent to the hydroxy group. We suggest that (**12**) is 3,3,6β-trimethyl-*cis*-perhydrocyclopenta[*c*]-furan, and that (**13**) is 3,3,6α-trimethyl-*cis*-perhydrocyclopenta[*c*]furan. The fragmentation patterns of both compounds under electron impact can be reasonably rationalised on the basis of these structural proposals. The proton and ^{13}C n.m.r. spectra are also consistent with these structures. [The latter was assigned with the aid of spectra of apposite model compounds with the structural units present in (**12**) and (**13**)].



(11)

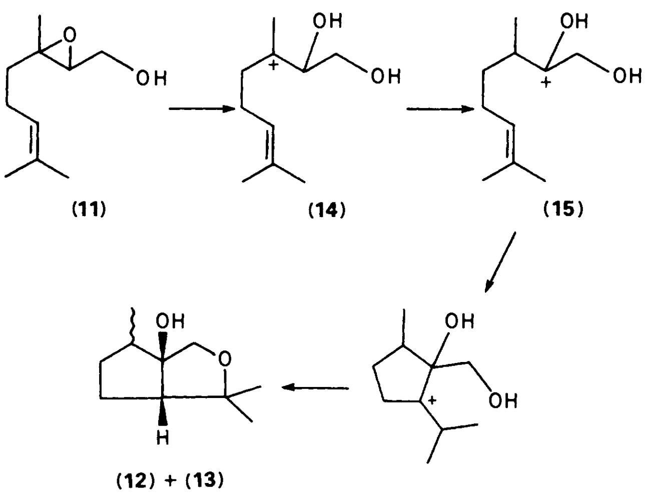
(12) **(13)**

Table. ^{13}C N.m.r. shifts (ppm from Me_4Si), measured in FSO_3H/SO_2 at −78 °C (A) or in $CDCl_3$ at room temperature (B).

Compound	Condition	C-1	C-2	C-3	C-3a	C-4	C-5	C-6	C-6a	C-7	C-8	C-9	C-10
(2)	A	249	159	159	—	49	49	26	—	11	26	—	—
(6)	A	229	152	229	—	53	48	53	—	—	—	—	—
(8)	A	255	48	39	—	24	32	42	—	14	—	—	—
(10)	A	255	60	42	—	28	28	42	—	28	—	—	—
(12)	B	76	—	82	66	26	35	44	91	28[a]	24[a]	13	—
(13)	B	72	—	84	60	25	33	44	93	29[a]	23[a]	13	—
(17)	B	41	202	123	—	171	27	31	—	15	21	36	21
(18)	B	47	212	45	—	47	31	35	—	14	20	148	110
(19)	B	205	54	39	—	123	29	34	—	21	20	132	20
(20)	B	154	40	38	—	52	26	40	—	107	80	144	111

[a] Assignments could be interchanged.

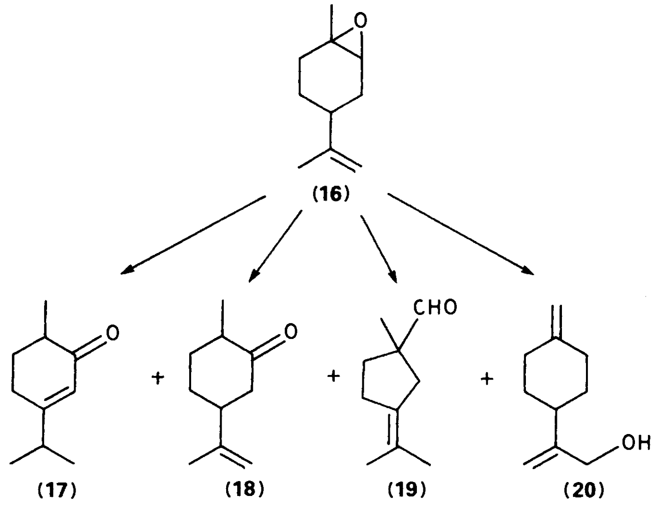
The mechanism of formation of (**12**) and (**13**) is consistent with the reaction of (**7**) to yield (**8**). The probable mechanism is shown in the scheme; opening of the epoxide ring yields the dihydroxy cation (**14**). This reaction may compete kinetically with ketone formation, or may result thermodynamically from reversible protonation of the ketone. The alternative route, cyclisation of (**14**)—by reaction of the double bond and the carbocation—would have to form a five-membered ring, which would involve steric strain in the transition state and would form a secondary carbocation; this presumably tips the balance in favour of the pathway shown.



Scheme 1.

We then studied the reaction of limonene 1,2-oxide (**16**) (a 1:1 mixture of the *cis*- and *trans*-epoxides was used) with FSO_3H in SO_2 at −78 °C. Quenching gave a brown oil (60%), which was analysed by g.l.c. and shown to consist of approximately 20 components with one major and three minor, the rest being in trace amounts only. The major component (70% of the oil) was identified as *p*-menth-3-en-2-one [carvenone, (**17**)], and one of the minor components (5% of the oil) *p*-menth-8-en-2-one [dihydrocarvone (**18**)]. Formation of the products closely parallels the conversion of (**7**) into (**8**); shift of the double bond into conjugation causes conversion of (**18**) into (**17**).

Another minor product (7% of the oil) was identified as the aldehyde (**19**), clearly formed by a bond shift of the type by which (**10**) is formed from (**9**). A further minor component (3% of the oil) is believed to have the structure (**20**), and will clearly involve a more extensive rearrangement than observed previously.



The results show similarities with the products of decomposition in acetic acid,[8] where the main products were dihydrocarvone (**18**) and carvenone (**19**); in base[9] the limonene oxides form the *cis*- and *trans*-isocarveols [*p*-mentha-1(7)8-dien-2-ols] together with the *cis*- and *trans*-carveols (*p*-mentha-1,8-dien-2-ols]. The product composition was not affected by the stereochemistry of the starting materials.

Our results show that tetrahydrofurans can behave as semi-stable species in superacids, though they are so stable that in many cases decomposition yields only tars. The more substituted tetrahydrofurans yield unsaturated carbocations, which react to form carbocyclic products. Epoxides, though not formed in superacids, decompose by relatively simple pathways, and the reactions show some promise for synthetic use.

Experimental

Analytical Methods.—^1H N.m.r. spectra were recorded using either a Perkin-Elmer R34 (220 MHz) spectrometer or a Varian HA 100 spectrometer with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal standard. Decoupling experiments were carried out on a Bruker WM250 (250 MHz) spectrometer operating in the FT 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 TMS as an internal standard for neutral solutions and sulphur dioxide or sulphuryl chloride fluoride as the solvent for superacidic solutions with an external deuterium lock of [$^2H_6$]acetone or [$^2H_4$]methanol and external standard of $SiMe_4$ enclosed within a 5 mm n.m.r. tube. Ether refers to diethyl ether throughout. Light petroleum refers to the fraction boiling 60–80 °C.

I.r. spectra were recorded on either a Perkin-Elmer 1320 i.r. spectrometer or a Pye-Unicam Sp 1000 spectrometer. Mass spectra were recorded on an AEI MS 12 spectrometer or an AEI-Kratos MS9 spectrometer. Accurate mass and g.l.c. mass spectral analyses were measured on either a VG 7070E mass spectrometer or a V.G. Micromass 12 F spectrometer.

Reaction mixtures were analysed using a Dani 3800 or a Perkin-Elmer F II or a Pye 104 gas/liquid chromatograph with flame-ionisation detectors using nitrogen (4 cm^3 min^{-1}) as the carrier gas. The columns used were capillary, 50 m × 0.25 mm, coated with either Carbowax 20M or OV351 or a column (4 m × 0.35 mm) coated with SE30, used with nitrogen at 18 cm^3 min^{-1} as carrier gas.

Preparative separations were carried out on a Varian Model 712 preparative gas chromatograph, using a 4 m × 1 cm column containing Supersorb 40/60 mesh as support, and 20% Carbowax 20M as coating on 40–60 Celite in a 4 m × 1 cm column with a nitrogen flow rate of 150 cm^3 min^{-1}. Preparative samples were condensed in a Volmann collector to eliminate aerosol formation.

Thin layer chromatography was also used for product analysis, using plates coated with silica gel H, silica ge HF$_{254}$ or silver nitrate/silica gel H. Plates were developed in EtOAc–CHCl$_3$ or EtOAc–hexane at 4 °C, and visualised with a phosphomolybdic acid spray, followed by heating in an oven to 110 °C for 3 min.

2,2,5,5-*Tetramethyltetrahydrofuran* (**4**).—2,5-Dimethylhexane-2,5-diol (18.4 g, 0.17 mol) and dimethyl sulphoxide (118 g, 1.5 mol) were heated to 170 °C for 17 h. The reaction mixture was cooled, distilled water (150 cm^3) was added, and the mixture was extracted with light petroleum. Work-up gave an oil which yielded the tetrahydrofuran (6.4 g, 40%) on distillation, b.p. 115–118 °C (lit.,[10] 115–117 °C).

2-*Methyl*-5-*acetylfuran.*—2-Methylfuran (50 g, 0.61 mol) and acetic anhydride (97.5 g, 0.95 mol) were cooled to −10 °C and $BF_3\cdot Et_2O$ (7.3 cm^3) was added. After 0.5 h of stirring, aqueous NaOH (2 mol dm^{-3}; 240 cm^3) was added, and the mixture was stirred for a further 2 h. Extraction with chloroform followed by concentration gave an oil which was distilled to give the furan (30 g, 40%), b.p. 72 °C at 10 Torr (lit.,[11] 100–101 °C at 25 Torr); m/z 124 (M^+); δ 2.43 (3 H, s, Me), 2.46 (3 H, s, Me), 6.25 (1 H, d, =CH), and 7.2 (1 H, d, =CH); ν_{max} 3 050, 1 670, 1 520, 1 380, 1 300, 1 100, 1 030, and 800 cm^{-1}.

2-*Methyl*-5-*ethylfuran.*—2-Methyl-5-acetylfuran (27 g, 0.217 mol), ethylene glycol (135 cm^3), potassium hydroxide (33.7 g), hydrazine hydrate (20.25 g), and water (9 cm^3) were refluxed for 2 h. Distillation gave the furan (18.1 g, 76%), b.p. 95 °C; m/z 110 (M^+).

Heptane-2,5-*dione.*—2-Methyl-5-ethylfuran (17.5 g, 0.16 mol) was added to a mixture of acetic acid (30 cm^3), water (12 cm^3) and conc. H_2SO_4 (2 cm^3) and refluxed for 5 h. Extraction (pentane) and distillation gave the diketone (13.9 g, 68%), b.p. 64–66 °C at 1.4 Torr (lit.,[12] 90 °C at 20 Torr); δ 1.05 (3 H, t, Me), 2.18 (3 H, s, Me), 2.48 (2 H, q, CH$_2$), and 2.7 (4 H, br, CH$_2$); ν_{max} 2 890, 1 720, 1 410, 1 370, 1 170, and 1 115 cm^{-1}.

2,3-*Dimethylcyclopentenone.*—Hepta-2,5-dione (10.6 g, 0.08 mol) was added to aqueous NaOH (2%; 160 cm^3) and methanol (20 cm^3) and the mixture was refluxed for 3 h. Extraction (ether), followed by distillation gave the product (8.8 g, 41%), b.p. 47–48 °C at 1 Torr (lit.,[13] 90–92 °C at 25 Torr); m/z 110 (M^+); δ 1.66 (3 H, s, Me), 2.08 (3 H, s, Me), and 2.35 (2 H, br s, CH$_2$); ν_{max} 2 950, 1 720, 1 670, 1 400, 1 340, 1 190, and 1 070 cm^{-1}.

1,2,3-*Trimethylcyclopenta*-1,3-*diene* (**3**).—A Grignard reagent was prepared from iodomethane (10 g) in ether. The reagent solution was cooled to −5 °C and 2,3-dimethylcyclopentanone (3.5 g, 0.032 mol) dissolved in ether (40 cm^3) was added. After being stirred for 30 min, the solution was quenched with ice–water and acidified to pH 4 with dil. HCl. Ether extraction and evaporation yielded the diene, which polymerised rapidly and so was used immediately; δ 1.86 (3 H, s, Me), 1.87 (3 H, s, Me), 1.91 (3 H, s, Me), 2.8 (2 H, br s, CH$_2$), and 5.85 (1 H, br s, =CH).

5-*Methylhex*-5-*en*-2-*ol.*—Acetyl acetone (75 g, 0.75 mol), 3-chloro-2-methylpropene (63.4 g, 0.7 mol) and anhydrous potassium carbonate (96.8 g, 0.7 mol) were refluxed for 16 h in dry ethanol (500 cm^3). Work-up gave the ketone (36 g) (47%), b.p. 148 °C, lit.,[14] 148–150 °C. Reduction of the product (7.6 g, 0.067 mol) with $LiAlH_4$ followed by work-up gave the hexenol (6.3 g) (82%), b.p. 90 °C at 25 Torr (lit.,[15] 73–74 °C at 27 Torr); m/z 114 (M^+); δ 1.18 (3 H, d, Me), 1.55 (2 H, m, $\mathrm{C}H_2\mathrm{COH}$), 1.7 (3 H, s, CH$_3$), 2.1 (2 H, m, $\mathrm{C}H_2$–C=), 2.4 (1 H, br s, OH), 3.77 (1 H, m, CH), and 4.7 (2 H, s, =CH$_2$); ν_{max} 3 400, 3 100, 2 950, 1 650, 1 380, 1 150, and 880 cm^{-1}.

Norbornene Oxide (**5**).—Norbornene oxide was prepared according to the literature, m.p. 124 °C (lit.,[16] 125 °C).

1-*Methylcyclohexene Oxide* (**7**).—This was prepared according to the literature, b.p. 118–120 °C (lit.,[17] 137–138 °C); m/z 112; δ 1.3 (3 H, s, Me), 1.4–1.9 (8 H, m, ring CH$_2$), and 2.95 (1 H, br s, O–C–H).

1,2-*Dimethylcyclohexene Oxide* (**9**).—This was prepared according to the literature, b.p. 150–152 °C (lit.,[17] 150–150.5 °C).

Geraniol 2,3-oxide [(*E*)-3,7-*Dimethyl*-2,3-*epoxyocta*-2,6-*dien*-1-*ol*] (**11**).—Geraniol was purified by complexation with calcium chloride[18] to give a product 99.5% pure by g.l.c. To purified geraniol (15.3 g, 0.1 mol) and vanadium acetylacetonate (0.7 g, 2 × 10^{-3} mol) was added benzene (150 cm^3), and the resulting solution was stirred and heated to reflux. When the solvent, initially brown, turned bright green, t-butyl hydroperoxide (12.6 g, 0.1 mol; 72% solution) was added dropwise over a period of 20 min. The solution was refluxed for 30 min, washed with aqueous NaHCO$_3$, then water, dried, and the solvent evaporated. The resulting yellow oil was purified by column chromatography using silica gel H and diethyl ether to give a colourless oil; δ_H 1.24 (3 H, s, CH$_3$), 1.60 (3 H, s, CH$_3$), 1.66 (3 H, s, CH$_3$), 2.05 (4 H, m, $\mathrm{C}H_2$–$\mathrm{C}H_2$), 2.82 (1 H, t, $\mathrm{C}H_2$OH), 3.65 (2 H, m, CH$_2$OH), and 6.05 (1 H, m, CH=); ν_{max} 3 420, 2 960, 2 910, 2 850, 1 670, 1 497, 1 380, 1 230, 862, and 752 cm^{-1}.

Reaction of Geraniol 2,3-*Oxide with* FSO_3H/SO_2.—Geraniol 2,3-oxide (12 g) in CS$_2$ (40 cm^3) was cooled to −78 °C and added over a period of 20 min to a stirred mixture of fluorosulphuric acid (43 cm^3) and liquid sulphur dioxide (43 cm^3) maintained at −78 °C under a dry atmosphere of nitrogen. After being stirred for 30 min the clear yellow acid layer, contained in a dropping funnel maintained at −78 °C, was allowed to run slowly (over 25 min) down the inside wall of a vessel containing a rapidly stirred slurry of potassium carbonate (120 g, added in 20 g portions), methanol (250 cm^3) and ice (30 g) cooled to −78 °C. After completion of the addition, followed by warming to room temperature, water (700 cm^3) was added, and the mixture filtered. The aqueous phase was extracted with ether (75 cm^3) and hexane (3 × 20 cm^3), following saturation with $(NH_4)_2SO_4$. The ether and hexane extracts were combined, and removal of the solvent gave a red-brown oil (9.6 g, 80%).

Analytical g.l.c. showed it to contain two volatile components. The oil was distilled at 45–50 °C (2.5 Torr) to give a yellow oil (3.4 g, 36% overall).

Identification of Products of Reaction of Geraniol 2,3-*Oxide with* FSO_3H/SO_2.—The mixture consisted of two components in the ratio 2.5:1. The major and minor components had slightly longer and slightly shorter g.l.c. retention times, respectively, than geraniol. They were separated by preparative g.l.c.

Major component (**12**). (Found: C, 70.3; H, 10.3. $C_{10}H_{18}O_2$ requires C, 70.6; H, 10.6%); ν_{max} at 3 415br, 2 950s, 2 870s, 1 450m, 1 380m, 1 365m, 1 270s, 1 025w, 1 000s, 960w, and 850m, 790; δ_H(100 MHz) 0.97 (3 H, d, *J* 6 Hz), 1.11 (3 H, s), 1.27 (3 H, s), 1.1–1.8 (5 H, complex m), 3.07 (1 H, dd, *J* 12 and 3 Hz), 3.29 (1 H, br s, disappears with D_2O), and 4.54 (AB system, *J* 12 Hz). On adding 0.1 g of $Eu(fod)_3$ to a 10% solution in $CDCl_3$, the ^1H n.m.r. spectrum showed δ 1.85 (3 H, d), 2.46 (3 H, s), 2.64 (3 H, s), 5.67 (1 H, d), and 6.61 (1 H, d) with the multiplet remaining unresolved. The ^{13}C n.m.r. spectrum is given in the Table; *m*/*z* 170 (M^+, 0.25), 155 (16), 140 (8), 125 (27), 119 (6), 112 (14), 97 (23), 91 (12), 81 (15), 79 (15), 70 (24), 69 (23), 67 (21), 59 (12), 55 (21), 53 (22), 43 (100), 42 (17), and 41 (72). The parent ion was confirmed by an $M - Si(CH_3)_3$ derivative, M^+, 242.

Minor component (**13**). (Found: C, 70.4; H, 10.5. $C_{10}H_{18}O_2$ requires C, 70.6; H, 10.6%); ν_{max} 3 395br, 2 955s, 2 870s, 1 380s, 1 365s, 1 200s, 1 050s, 960w, 860s, 825w, and 790w cm^{-1}; δ_H(100 MHz) 0.94 (3 H, d, *J* 6 Hz), 1.08 (3 H, s), 1.27 (3 H, s), 1.1–1.8 (5 H, complex m), 2.04 (1 H, m), 2.68 (1 H, br s, disappears with D_2O shake), and 3.66 (2 H, AB system, *J* 12 Hz). On addition of $Eu(fod)_3$ (0.15 g) to a 10% solution in $CDCl_3$, the ^1H n.m.r. spectrum showed δ 2.35 (3 H, d), 3.15 (2 H, m), 3.36 (3 H, s), 3.38 (3 H, s), 4.50 (2 H, m), 5.25 (2 H, m), 7.10 (1 H, d), and 7.78 (1 H, d). The ^{13}C n.m.r. spectrum is given in the Table; *m*/*z* 170 (M^+, 0.25), 155 (28), 140 (14), 125 (45), 112 (16), 97 (27), 95 (26), 91 (17), 81 (28), 79 (26), 70 (30), 69 (34), 67 (32), 59 (14), 55 (33), 53 (23), 43 (100), 42 (16), and 41 (65). The parent ion was confirmed by an $M - Si(CH_3)_3$ derivative, M^+, 242.

Limonene 1,2-*Oxide* (**16**) (4-*Isopropenyl*-1-*methyl*-1,2-*epoxycyclohexane*).—(+)-Limonene was epoxidised using monoperphthalic acid, which was generated as needed by adding 30% hydrogen peroxide (62.5 cm^3) to finely powdered phthalic anhydride (37.5 g) dissolved in ether (250 cm^3). After 24 h, the ether layer was washed with 40% ammonium sulphate solution (3 × 45 cm^3) and dried over sodium sulphate, then titrated using potassium iodide to liberate iodine. The required quantity of limonene was then added dropwise with stirring at 0 °C, then left to stand in the refrigerator until titration showed the reaction to be complete. Work-up followed by chromatography on a silica gel H column, eluting with ether, gave limonene 1,2-oxide (mixture of *cis* and *trans* isomers), 98% pure (g.l.c.); δ_H 1.22 (3 H, s), 1.5–2.05 (10 H, complex m), 2.85 (1 H, m), and 4.61 (2 H, s); ν_{max} 3 140, 2 980, 1 660, 1 460, 1 445, 1 380, 1 045, 850, 810, and 765 cm^{-1}.

Reaction of Limonene 1,2-*Oxide with* FSO_3H/SO_2.—Limonene 1,2-oxide (10 g) was treated in the same way as geraniol 2,3-oxide, yielding a red-brown oil (6 g, 60%). The oil was distilled at 40–45 °C at 2.5 Torr, to yield a yellow oil (5.1 g, 51%) which was shown by g.l.c. to consist of *ca.* 20 components. Four of these were isolated by preparative g.l.c. and their physical properties examined.

First fraction (**19**). (Found: C, 78.5; H, 10.3. $C_{10}H_{16}O$ requires C, 78.9; H, 10.5%); ν_{max} at 2 850s, 2 700m, 1 730s, 1 460br d, 1 375s, 1 235w, 1 150s, 1 135m, 1 020w, 940m, 880m, 828w, 790, and 743 cm^{-1}; δ_H(100 MHz) 1.09 (3 H, s), 1.63 (6 H, br s), 1.85–2.65 (6 H, m), and 9.43 (1 H, s). The ^{13}C n.m.r. spectrum is given in the Table; *m*/*z* 152 (M^+, 73), 138 (17), 137 (100), 123 (25), 119 (20), 109 (50), 107 (27), 105 (18), 95 (23), 93 (28), 91 (44), 82 (64), 70 (39), 77 (37), 69 (28), 67 (41), 65 (23), 55 (18), 53 (28), 51 (14), 43 (20), and 41 (58).

Second fraction (**18**). (Found: C, 78.7; H, 10.2. $C_{10}H_{16}O$ requires C, 78.9; H, 10.5%); ν_{max} 3 020w, 2 830s, 1 710s, 1 640w, 1 445s, 1 380s, 1 220m, 895br, and 790m cm^{-1}; δ_H 1.05 (3 H, d, *J* 8 Hz), 0.9–1.5 (6 H, complex m), 1.74 (3 H, s), 2.0–2.54 (2 H, m), and 4.74 (2 H, s). The ^{13}C n.m.r. spectrum is given in the Table; *m*/*z* 152 (M^+, 22), 137 (12), 110 (18), 109 (29), 108 (19), 95 (74), 82 (52), 81 (55), 69 (33), 68 (79), 67 (100), 55 (47), 53 (28), 41 (78), and 39 (34).

Third fraction (**17**). (Found: C, 78.6; H, 10.4. $C_{10}H_{16}O$ requires C, 78.9; H, 10.5%); ν_{max} 3 020w, 2 910s, 2 850s, 1 710w, 1 670s, 1 630s, 1 460m, 1 385s, 1 370s, 1 330w, 1 210s, 1 105w, and 955w cm^{-1}; δ_H(100 MHz) 1.02 (3 H, d, *J* 8 Hz), 1.10 (6 H, d, *J* 8 Hz), 1.2–2.5 (6 H, complex m), and 5.68 (1 H, s). The ^{13}C n.m.r. spectrum is given in the Table; *m*/*z* 152 (M^+, 31), 137 (3), 124 (2), 110 (100), 109 (13), 96 (5), 95 (89), 91 (6), 81 (13), 79 (10), 77 (8), 67 (42), 58 (18), 51 (12), and 41 (39).

Fourth fraction (**20**). (Found: C, 78.5; H, 10.7. $C_{10}H_{16}O$ requires C, 78.9; H, 10.5%); ν_{max} 3 480br d, 3 030w, 2 950s, 2 870s, 1 650m, 1 600m, 1 450m, 1 370m, 1 210s, 885m, and 790m cm^{-1}. The ^{13}C n.m.r. spectrum is given in the Table; *m*/*z* (M^+, 18), 134 (24), 121 (20), 119 (75), 107 (10), 105 (15), 93 (100), 92 (37), 91 (52), 79 (24), 77 (38), 67 (10), 65 (16), 64 (17), 53 (14), 48 (13), 43 (25), and 41 (27).

Generation of Carbocations with FSO_3H.—Sulphur dioxide (1 cm^3) was condensed into a 10 cm^3 round-bottomed flask and FSO_3H (2.5 cm^3) was added. The solution was cooled to −70 °C using a solid CO_2/acetone bath. The substrate (500 mg) was dissolved in SO_2 (1 cm^3) and cooled to −78 °C then added dropwise, down the inside of the cooled flask, to the stirred FSO_3H/SO_2 mixture. After being stirred for 10 min the solution was added to a 12 mm n.m.r. tube cooled to −78 °C. The n.m.r. tube was sealed with Parafilm, removed from the cooling bath, and cleaned of any residual acetone before the spectrum was measured.

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