

Reactions of Terpenoids in Strong Acids. Part 2.¹ Novel Cyclisations of Citronellol and the Isomers of Citral

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Treatment of citronellol (3,7-dimethyloct-6-en-1-ol) with fluorosulphonic acid at -78°C led to recovery of 2,2,5-trimethyl- and 2-ethyl-2,5-dimethyl-oxacycloheptane (40%; 1:1 w/w). The former resulted from an unexpected fragmentation, and ^{14}C tracer studies revealed that a methyl group was lost from C-7 of the substrate. Similar treatment of citral (3,7-dimethylocta-*trans*-2,6-dienal and its *cis*-isomer; 7:3 w/w) or α -cyclocitral (2,6,6-trimethylcyclohex-2-enecarbaldehyde) gave low (*ca.* 17%) yields of the novel products 1,5-dimethyl-2-oxabicyclo-[3.3.1]non-3-ene and 7-methoxy-2,2,8-trimethyl-6-oxabicyclo[3.2.1]octane. β -Cyclocitral (2,6,6-trimethylcyclohex-1-enecarbaldehyde) was largely unchanged. ^1H N.m.r. spectra of all substrates in fluorosulphonic acid or fluorosulphonic acid-antimony pentafluoride at -78 to $+27^{\circ}\text{C}$ revealed carbocations or derived species that corresponded to some of the isolated products and were essentially uncontaminated by the tars that in most cases predominated after quenching.

RECENT studies of the reactions of geraniol (3,7-dimethylocta-*trans*-2,6-dien-1-ol) and related compounds¹ have confirmed scattered observations²⁻⁵ that treatment of monoterpenes with super acids (ref. 6: liquid acids shown by indicator measurements to be stronger than anhydrous sulphuric acid) gives completely different products from those of conventional acid-catalysed processes. We now report an extension of these studies to citronellol (I) (3,7-dimethyloct-6-en-1-ol) and the citrals (IX) and (X) (3,7-dimethylocta-*trans*-2,6-dienal and its *cis*-isomer) and their cyclic isomers. Again a novel pattern of products was found and the glycols, menthadienes, *etc.* that are formed on treatment with aqueous mineral and organic acids⁷⁻¹⁰ did not occur.

Cyclisation of Citronellol.—Treatment of citronellol with fluorosulphonic acid diluted with sulphur dioxide-carbon disulphide at -78°C and quenching under carefully controlled conditions resulted in two cyclic ethers (40%; 1:1) and an uninvestigated mixture of diols and olefins (30%) derived from these; the balance was high-boiling polymer. The ethers were shown by

^1H n.m.r., fragmentation under electron impact (*cf.* ref. 11), and degradation to the characterized products (IV)—(VIII) to be 2,2,5-trimethyl- (II) and 2-ethyl-2,5-dimethyl-oxacycloheptane (III). Products (VI)—(VIII) are formed by rearrangements that are well known¹²⁻¹⁴ under the reaction conditions. ^1H and ^{13}C n.m.r. spectra showed (III) to be the expected mixture of diastereoisomers.

The loss of a methyl group to form the C_9 ether (II) is unprecedented with fluorosulphonic acid as catalyst, although similar fragmentations have been reported for other substrates that had been treated with stronger super acids,^{15,16} *e.g.* fluorosulphonic acid-antimony pentafluoride and fluorosulphonic acid-hydrogen fluoride. These last reactions involve formation of methane; presumably a proton from the acid medium abstracts CH_3^- to generate a carbocation in a manner analogous to the well established¹⁵ abstraction of a hydride ion under similar conditions. In our case there was ^1H n.m.r. evidence [τ 5.70 (s)] for the formation of methyl fluorosulphonate in the acid solution, and we suggest a sequence as in Scheme 2 whereby the methyl group is

¹ Part 1, D. V. Banthorpe, P. A. Boullier, and W. D. Fordham, *J.C.S. Perkin I*, 1974, 1637.

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³ E. Huang, K. Ranganayakulu, and T. S. Sorenson, *J. Amer. Chem. Soc.*, 1972, **94**, 1780.

⁴ K. E. Hine and R. F. Childs, *J. Amer. Chem. Soc.*, 1971, **93**, 2323.

⁵ M. Kurbanov, A. V. Semenovskii, V. A. Smit, and V. F. Kucherov, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1971, **11**, 2541.

⁶ R. J. Gillespie, *Accounts Chem. Res.*, 1968, **1**, 202.

⁷ R. Locquin and P. Barbier, *Compt. rend.*, 1913, **157**, 114.

⁸ O. Zeitschel and R. Schmidt, *J. prakt. Chem.*, 1932, (ii) **133**, 370.

⁹ R. Horiuchi, H. Otsuki, and O. Okudo, *Bull. Chem. Soc. Japan*, 1939, **14**, 501.

¹⁰ E. Whalley, *Canad. J. Chem.*, 1958, **36**, 228.

¹¹ R. Smakman and J. de Boer, *Org. Mass Spectrometry*, 1968, **1**, 403.

¹² F. Johnson in 'Friedel-Crafts and Related Reactions,' ed. G. A. Olah, Interscience, New York, 1965, vol. IV, p. 12.

¹³ C. D. Nenitzescu and A. T. Balaban in ref. 12, vol. III, p. 1033.

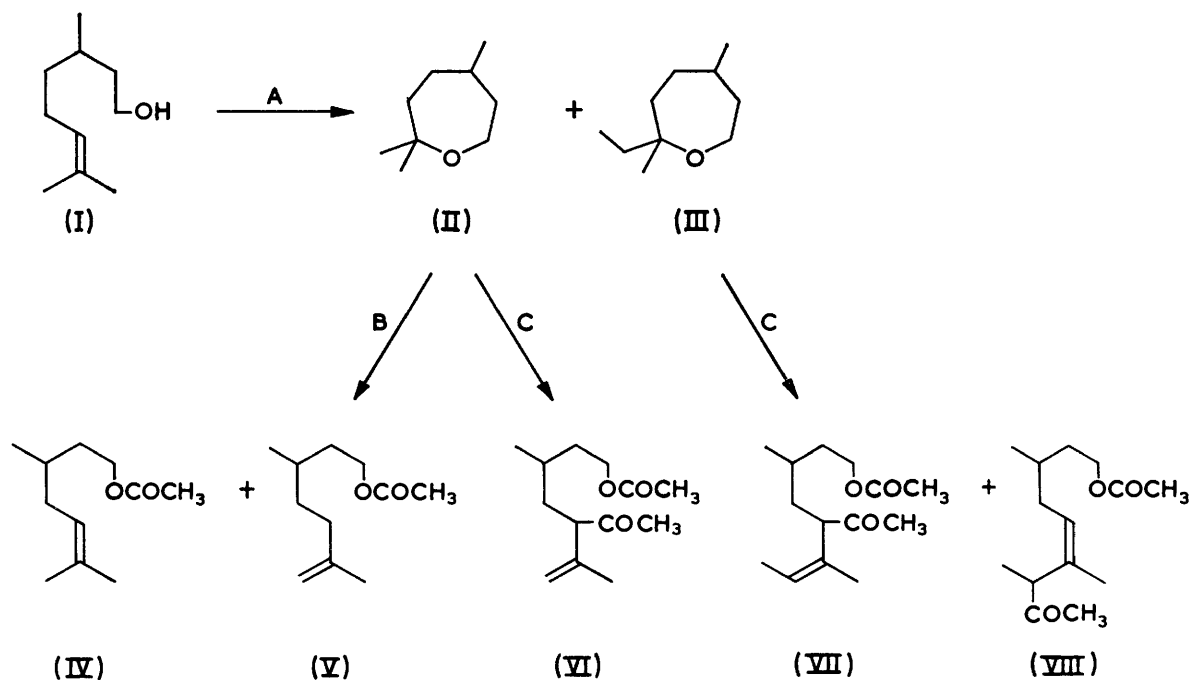
¹⁴ P. Arnaud, *Compt. rend.*, 1957, **244**, 1785.

¹⁵ D. M. Brouwer and H. Hogeveen, *Progr. Phys. Org. Chem.*, 1972, **9**, 179.

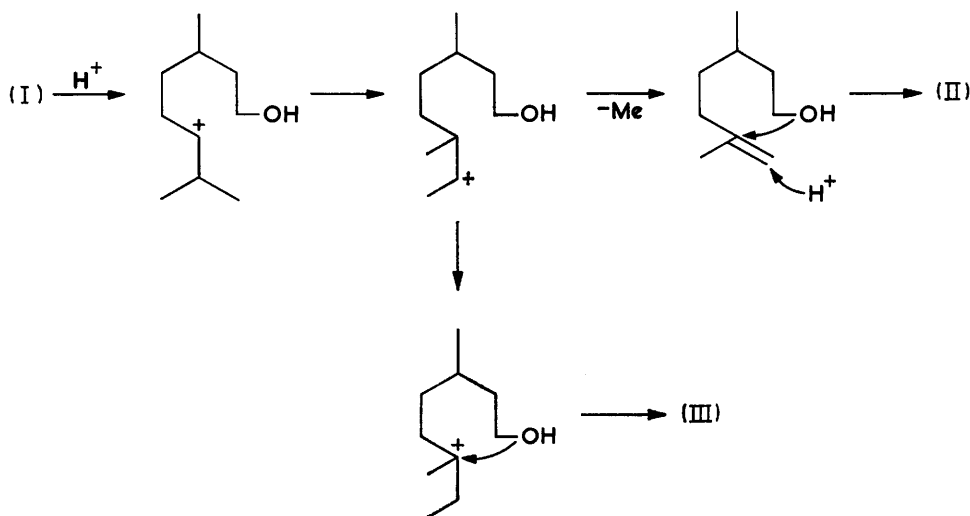
¹⁶ R. J. Gillespie and J. E. Peel, *J. Amer. Chem. Soc.*, 1973, **95**, 5173.

lost as CH_3^+ . The cleavage was confirmed and the absence of deep-seated rearrangement was demonstrated by the finding that $[8,9\text{-}^{14}\text{C}_2]$ citronellol yielded an oxacycloheptane with $49 \pm 3\%$ of the original specific radioactivity: thus a methyl group was lost from C-7 of the substrate.

in different proportions, *viz.* *p*-cymene 11 and 3; 1-isopropenyl-4-methylbenzene 10 and 6; α -cyclocitral 5 and 23; β -cyclocitral 13 and 7; and two novel products (XIII) 21 and 3 and (XIV) 19 and 53%, respectively. Compound (XIII) was identified by its ^1H n.m.r. spectrum and fragmentation pattern under electron



SCHEME 1 A, HFSO_3 at -78° ; B, AcOH-BF_3 at 25° ; C, $\text{Ac}_2\text{O-BF}_3$ at 0°



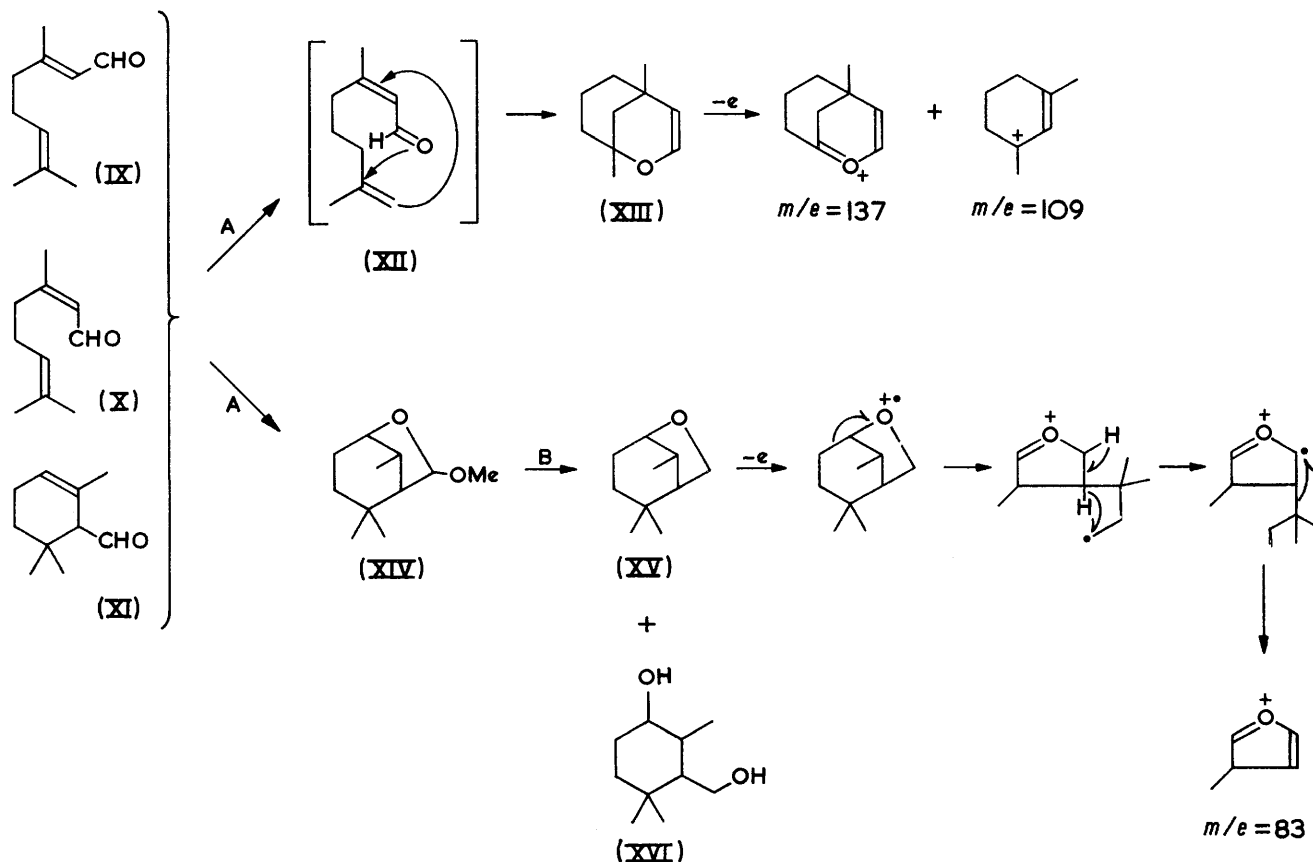
SCHEME 2

Reactions of Citral and its Cyclic Isomers.—Treatment of citral [(IX) and (X), 70 : 30 w/w] or of α -cyclocitral (XI) (2,6,6-trimethylcyclohex-2-enecarbaldehyde) with fluorosulphonic acid under the same conditions gave much high-boiling material and low (15–33% at most) recoveries of monoterpenoids. The latter fraction comprised the same products from the two substrates

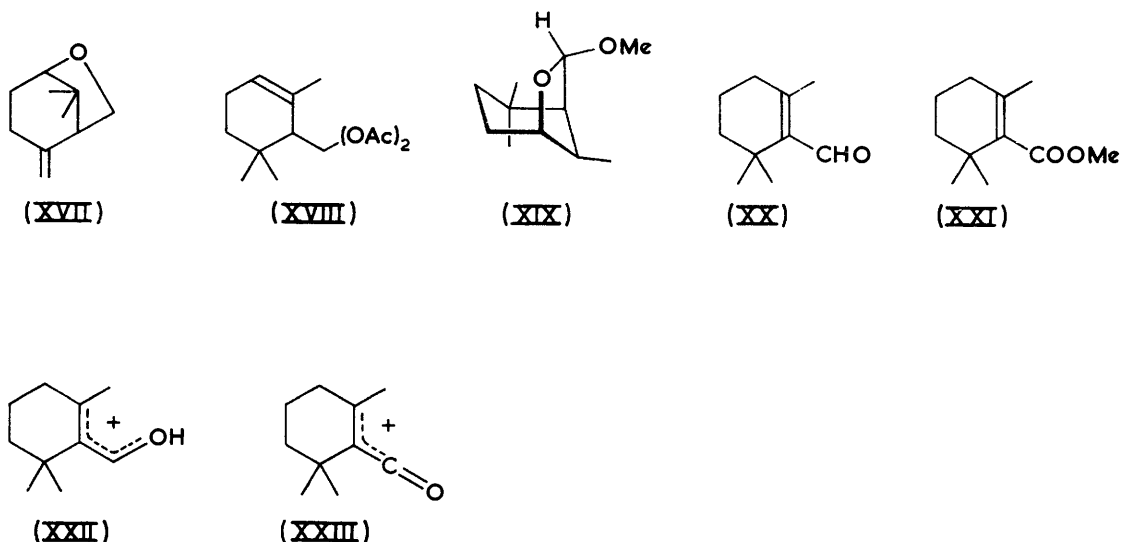
impact as 1,5-dimethyl-2-oxabicyclo[3.3.1]non-3-ene, presumably formed *via* cyclisation of (XII) (Scheme 3). Compound (XIV) was reduced to an ether (XV) and a diol (XVI) and was similarly characterized spectrally as 7-methoxy-2,2,8-trimethyl-6-oxabicyclo[3.2.1]octane. The latter identification was supported by the similarity of the ^1H n.m.r. and mass spectra to those of karahana

ether (XVII) from hop oil;¹⁷ by the recovery in excellent yield (>80%) of α -cyclocitral on heating (XIV) with toluene-*p*-sulphonic acid in methanol; and by formation

methyl groups as illustrated in (XIX), which is the isomer expected if *anti*-addition to the double bond in the presumed intermediate is followed by attack of



SCHEME 3 A, HFSO₃ at -78°; B, (a) Ac₂O at 138°; (b) AlCl₃-LiAlH₄ at 35°



SCHEME 4

of α -cyclogeranyl diacetate (XVIII) after cleavage with boron trifluoride-acetic anhydride. The ¹H n.m.r. couplings suggest the orientation of the methoxy and

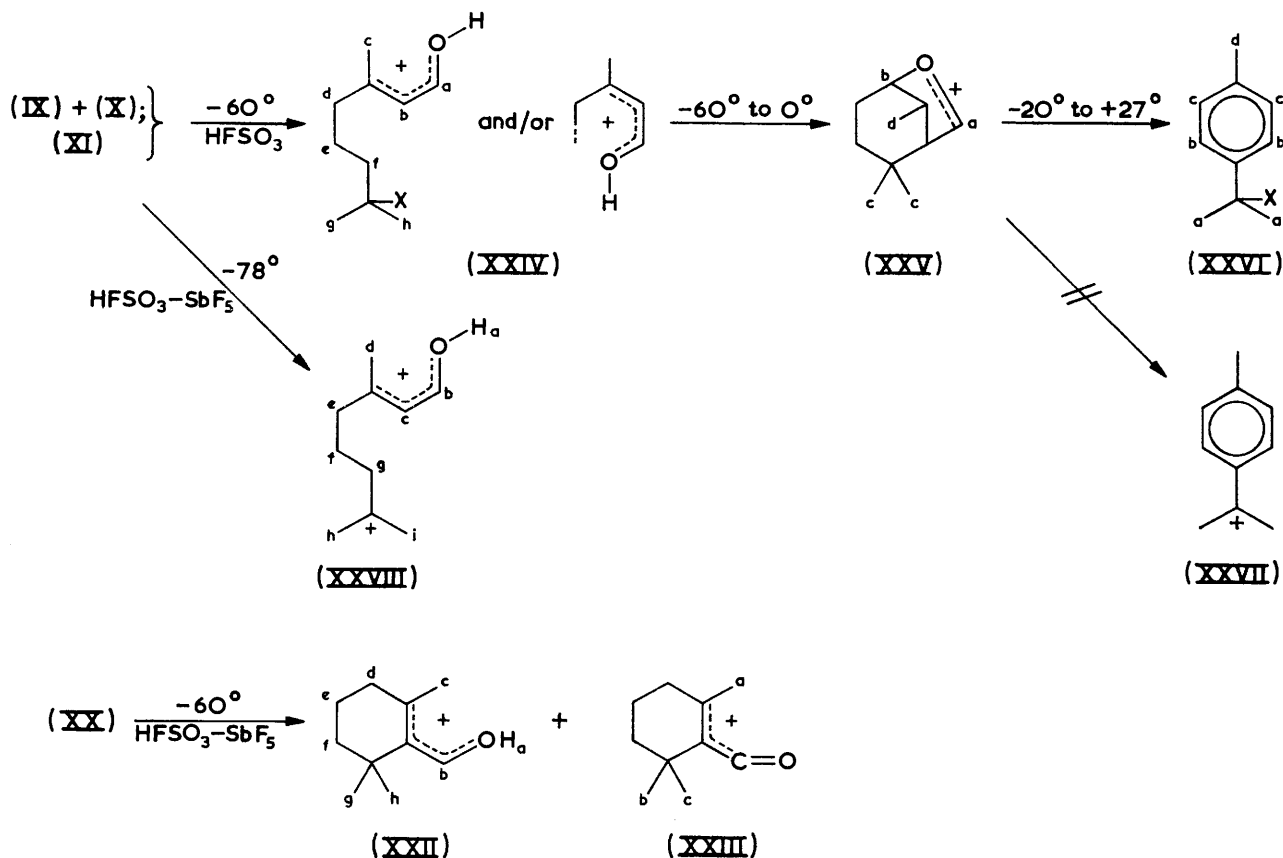
methoxide (from the quenching medium) from the less hindered side.

¹⁷ Y. Naka and M. Kotake, *Tetrahedron Letters*, 1968, 1365.

The Wagner–Meerwein shifts and ring contractions to form cyclopentyl systems that are characteristic of geraniol and its relatives in similar conditions¹ do not occur in the above examples presumably because protonation of the oxygen of $\alpha\beta$ -unsaturated aldehyde systems (known to be favoured in super acids^{18–21}) gives a delocalised cation. An extreme example of this is β -cyclocitral (XX) (2,2,6-trimethylcyclohex-1-enecarbaldehyde), which was recovered (73%) together with methyl β -cyclogeranate (XXI) (23%) after treatment with fluorosulphonic acid at -78°C ; here the cation (XXII) is extremely stable (see next section) but can

latter being diastereoisomeric): characteristic signals were at τ 5.26 (m, $\cdot\text{CH}_2\cdot\text{OH}^+$) and 8.2–8.4 (m, $\text{CH}_3\cdot\text{C}^+\cdot\text{OH}$). The ^{13}C n.m.r. spectra also varied little over the temperature range and confirmed the presence of the protonated ether structure (δ 80; $\cdot\text{C}^+\cdot\text{OH}$).

The ^1H n.m.r. spectra of acidic solutions of the citral isomers were more complicated but could be elucidated reasonably by comparison with spectra of isolated products dissolved in fluorosulphonic acid or fluorosulphonic acid–antimony pentafluoride. Citral [(IX) + (X)] and α -cyclocitral (XI) in fluorosulphonic acid gave



SCHEME 5

nevertheless split off an α -hydrogen atom to form (XXIII), which reacts with methanol in the quenching medium to give (XXI).

Carbenium and Oxonium Ions in Acidic Systems.—N.m.r. spectroscopy of solutions of geraniol (I) and certain bicyclic monoterpenes^{2,3,22,23} in super acids has revealed the existence of various interconverting carbenium and oxonium ions. Solutions of citronellol in fluorosulphonic acid had nearly identical ^1H n.m.r. spectra throughout the temperature range -78 to $+25^\circ\text{C}$ which indicated the presence of essentially only the protonated oxacycloheptanes (II) and (III) (the

very similar spectra. At -60°C the species (XXIV) (lettering refers to ^1H n.m.r. assignments; see Experimental section) was predominant ($>90\%$). The hydroxy-proton did not give a signal (rapid exchange) and J_{ab} (~ 10 Hz) indicated these hydrogen atoms were *cisoid*. The signal from the *gem*-dimethyl protons (τ 8.65; s) showed that this system was not located at a tertiary carbon atom or a cationic centre and a further group X must be present. Presumably this is fluorosulphonate, as this anion is known sometimes to

¹⁸ H. Hogeveen, *Rec. Trav. chim.*, 1967, **86**, 696.

¹⁹ D. M. Brouwer, *Rec. Trav. chim.*, 1967, **86**, 879.

²⁰ D. H. O'Brien, *J. Amer. Chem. Soc.*, 1967, **89**, 3586.

²¹ G. A. Olah and M. Calin, *J. Amer. Chem. Soc.*, 1968, **90**, 938.

²² C. M. Holden and D. Whittaker, *J.C.S. Chem. Comm.*, 1974, 353.

²³ T. S. Sorenson, *J.C.S. Chem. Comm.*, 1976, 45.

neutralise carbenium ions in this medium.²⁴ At higher temperatures the species (XXV), characterized by signals at τ 0.61 and 3.53 (a, b; cf. refs. 25 and 26) came into prominence but this was replaced by (XXVI) when the solution had warmed to ca. 0 °C. In the range 0 to +27 °C, (XXVI) was increasingly accompanied (up to 10% of total) by unidentified species. Species (XXVI) was another neutralised carbenium ion whose spectra differed from that of (XXVII); the latter was readily observed on dissolution of 1-isopropenyl-4-methylbenzene in fluorosulphonic acid-antimony pentafluoride; cf. ref. 27. Quenching at -78 °C of solutions made up at 0-27 °C which contained predominantly (XXVI) yielded 1-isopropenyl-4-methylbenzene (<20%) as the only non-polymeric product.

Citral or α -cyclocitral in fluorosulphonic acid-antimony pentafluoride at -78 °C yielded essentially only the carbenium ion (XXVIII), characterized by the signals of the *gem*-dimethyl protons (τ 6.06; t, *J* 4 Hz) split by 1,3-coupling through the cationic centre. The hydroxy-proton signal was also observed (τ -2.46) as is usual in this acidic medium.²⁵

β -Cyclocitral (XX) retained its skeleton in fluorosulphonic acid alone or with antimony pentafluoride added and signals due to a hydroxy-proton were observed from both solutions at -60 °C. The ion (XXII) persisted in the range -60 to +27 °C, but above 0 °C in fluorosulphonic acid the signal due to H_a broadened and that of H_b became a singlet (τ 0.65), and a cation (XXIII) [ca. 15% total; H_a , τ 7.35 (s)] was formed. The H_a signal did not broaden until above +25 °C in fluorosulphonic acid-antimony pentafluoride and (XXII) was stable for several days at +27 °C.

These experiments revealed the existence of ions in the super acid solutions that could lead directly to the products that were found after quenching. The spectra revealed that the polymers and tar that predominated in the quenched products did not exist to any significant extent in the acidic solutions. Despite all precautions to ensure rapid, intimate mixing of the acid and the quenching medium at the lowest possible temperature, these polymers and tar were always formed as secondary products of the isolation procedure.

EXPERIMENTAL AND RESULTS

G.l.c., t.l.c., ¹H n.m.r. and mass spectrometric techniques, and criteria for purity of products were as previously described in detail.¹ ¹³C n.m.r. data were obtained by Dr. D. Whittaker (Liverpool University) using a Varian XL-100-15 spectrometer at 25.2 MHz on ca. 1.0M-solutions in CDCl₃ or the appropriate acid. Fourier transform spectra were obtained with ¹H-noise decoupling and an accumulation time of 0.4 s with up to 10⁴ transients: this gave a spectrum with 2 048 real data points, i.e. ± 2.5 Hz (± 0.1 p.p.m.). Standard off-resonance spectra were obtained by using single frequency decoupling at δ -15. ¹H n.m.r. spectra of ions in acidic media were obtained with

²⁴ G. A. Olah, J. Nuhimura, and Y. K. Mo, *Synthesis*, 1973, 661.

²⁵ G. A. Olah, Y. Halpern, Y. K. Mo, and G. Liang, *J. Amer. Chem. Soc.*, 1972, **94**, 3554.

the tubes sealed under nitrogen: traces of water gave a singlet at τ -0.2.

Materials.—Sulphuryl chlorofluoride was obtained from Ozark-Mahoning Co., Tulsa, Oklahoma; and methyl fluorosulphonate from Aldrich Chem. Co., London. Other reagents were as before.¹ Citronellol (from geranium oil) was distilled; b.p. 114° at 12 mmHg; $[\alpha]_D^{18}$ -3.8°; and contained the α - and β -isomers (15:85 v/v). Citral (*trans*:*cis* 70:30 v/v) was obtained from Bush Boake Allen and Co. Ltd., London. α - and β -Cyclocitral were prepared by cyclisation of a Schiff's base of citral.²⁸ All substrates were >99% pure by g.l.c. and t.l.c. (cf. ref. 1).

Oxacycloheptanes from Citronellol.—Citronellol (20 g) in carbon disulphide was treated with sulphur dioxide-fluorosulphonic acid at -78 °C and the mixture was quenched with triethylamine (1 l) and methanol (500 ml) in three batches by a standard procedure.¹ After work up (cf. ref. 1) an oil (69%) was recovered that comprised two cyclic ethers (ca. 40%; 1:1), a complex mixture of derived diols (45%; as indicated by g.l.c.-mass spectrometry), and citronellol (15%). This was distilled (71-80 °C and 22 mmHg) to give a fraction containing the ethers, and these were purified by preparative g.l.c. on Carbowax 20M at 120 °C: relative retention times with respect to geraniol (t_R 100) were 102 and 167.

2,2,5-Trimethyloxacyclohexane (II) (>99% pure by g.l.c. and t.l.c.; cf. criteria in ref. 1) was a liquid (Found: C, 75.9; H, 12.2. C₉H₁₈O requires C, 76.1; H, 12.5%); *m/e* 142 (*M*⁺, 1%), 127 (47), 59 (100), and 43 (80); ν_{\max} 2 820m (CH₂-O), 1 387-1 371ds (*gem*-Me₂), 1 150s, 1 100s, and 1 073s cm⁻¹ (C-O); τ (100 MHz) 9.07 (3 H, d, virtual coupling), 8.88-8.20 (7 H, ms), 8.86 (6 H, s), 6.48 (2 H, m) [Eu(fod)₃ (0.5 mole fraction) caused the transpositions τ 9.07 (3 H, d) \rightarrow 8.99 (3 H, d), 8.86 (6 H, s) \rightarrow 8.46 (3 H, s), and 8.22 (3 H, s) and 6.48 (2 H, m) \rightarrow 5.94 (1 H, dd, *J* 6 and 13 Hz), and 5.78 (1 H, dd, *J* 2.8 and 13 Hz)].

The ether (II) (170 mg) was degraded by stirring with acetic acid (1.5 ml), boron trifluoride-ether (1.5 ml), and ether (3.0 ml) for 3 days at 25 °C. Work-up gave two monoacetates (76 and 9%) and unchanged ether (II) (12%). The main product, 3,6-dimethylhept-5-enyl acetate (IV) was purified by g.l.c. on Carbowax 20M (t_R 89.3) (Found: C, 71.6; H, 10.8. C₁₁H₂₀O₂ requires C, 71.7; H, 10.9%); *m/e* 184 (*M*⁺, 1.2%), 124 (15), 96 (44), 82 (59), and 43 (100); ν_{\max} 2 950s (\cdot O-CH₂) and 1 735s cm⁻¹ (\cdot CO- \cdot); τ (100 MHz) 9.11 (3 H, d, *J* 6 Hz), 8.39 (3 H, s), 8.28 (3 H, s), 7.96 (3 H, s), 8.5-7.7 (5 H, ms), 5.90 (2 H, t, *J* 6.5 Hz), and 4.89 [1 H, tq, *J*_{HH} 7.0, *J*_{H,HC} (*trans*) 1.5 Hz]. The minor product, 6-methylene-3-methylheptyl acetate (V) had similar properties and was characterised by a ¹H n.m.r. signal at τ 5.33br (2 H, s). The ether (II) (170 mg) was also degraded by treatment (1.5 h; 0 °C) with acetic anhydride (1 ml), ether (0.5 ml), and boron trifluoride-ether (1 ml) to give 5-isopropenyl-3-methyl-6-oxoheptyl acetate (VI) (85%) (Found: C, 68.9; H, 9.8. C₁₃H₂₂O₃ requires C, 69.0; H, 9.7%); *m/e* 124 (10) and 43 (100); ν_{\max} 2 955s and 2 930m cm⁻¹ (\cdot O-CH₂); τ (100 MHz) 9.08 (3 H, d, *J* 6 Hz), 8.7-8.2 (5 H, ms), 8.35 (3 H, s), 7.97 (3 H, s), 7.87 (3 H, s), 6.74 (1 H, t, *J* 6 Hz), 5.91 (2 H, t, *J* 6.5 Hz), and 5.04br (2 H, s).

²⁶ D. M. Brouwer, C. F. Roobeck, J. A. van Doorn, and A. A. Kitten, *Rec. Trav. chim.*, 1973, **92**, 563.

²⁷ G. A. Olah, M. B. Comisarow, and C. J. Kim, *J. Amer. Chem. Soc.*, 1969, **91**, 1458.

²⁸ L. Colombi, A. Borshard, H. Schinz, and C. F. Seidal, *Helv. Chim. Acta*, 1951, **34**, 265.

The second ether, 2-ethyl-2,5-dimethylloxacycloheptane (III) (Found: C, 77.0; H, 12.7. $C_{10}H_{20}O$ requires C, 76.9; H, 12.8%), showed m/e 156 (M^+ , 0.1%), 127 (100), and 109 (45); ν_{\max} 2 820s ($\cdot CH_2 \cdot O$), 1 380s (*gem*-alkyls), 1 149, 1 135, and 1 105s cm^{-1} (C-O); τ (100 MHz) 9.15 (3 H, t, J 7 Hz), 9.07 (3 H, d, J 6.5 Hz), 8.94 (3 H, s), 8.7–8.1 (9 H, ms), and 6.48 (2 H, m) [$Pr(fod)_3$ (0.01 mole fraction) caused the transposition τ 9.15 (t) \rightarrow 9.25 (t) to reveal the doublet at τ 9.07; use of $Eu(fod)_3$ was limited owing to line broadening, but the appropriate proton resonances were observed to split in a manner consistent with the presence of diastereoisomers; this effect was also clear in the ^{13}C n.m.r. spectrum]. Attempts to cleave (III) with acetic acid-boron trifluoride led to a mixture of eight products. Cleavage [as for (II)] with acetic anhydride gave two acetyl acetates (60%). One, 5-acetyl-3,6-dimethyloct-6-enyl acetate (VII) (20%) (Found: C, 69.7; H, 10.1. $C_{14}H_{24}O_3$ requires C, 69.7; H, 10.0%) showed m/e 240 (M^+ , 0.1%) and 137 (41); ν_{\max} 2 945s cm^{-1} ($\cdot O \cdot CH_2$); τ (100 MHz) 9.11 (3 H, d, J 6 Hz), 8.49 (3 H, s), 8.36 (3 H, d, J 7 Hz), 8.6–8.1 (5 H, ms), 7.97 (3 H, s), 7.90 (3 H, s), 6.85 (1 H, t, J 6.5 Hz), and 4.53 (1 H, q, J 7.0 Hz) [the protons resonating at τ 6.85 (t) and 8.47 (m) were coupled to those at 4.53 (q) and 8.36 (d)]. The other product, 3,6,7-trimethyl-8-oxonon-5-enyl acetate (VIII) (48%) (Found: C, 70.3; H, 10.0. $C_{14}H_{24}O_3$ requires C, 70.0; H, 10.0%) showed m/e 137 (36%) and 109 (27); ν_{\max} 2 955 and 2 925s cm^{-1} ($\cdot O \cdot CH_2$); τ (100 MHz) 9.08 (3 H, d, J 6.5 Hz), 8.87 (3 H, d, J 7 Hz), 8.45 (3 H, s), 7.96 (3 H, s), 7.90 (3 H, s), 8.6–7.7 (5 H, ms), 6.85 (1 H, q, J 7 Hz), 5.89 (2 H, t, J 6.5 Hz), and 4.63 (1 H, t, J 7 Hz) [the protons resonating at τ 6.85 (q) and 8.87 (d) were coupled].

Investigation of Methyl Loss to form the Ether (II).— 1H N.m.r. spectra of acidic solutions of citronellol at $-78^\circ C$ revealed a signal at τ 5.70 (s) superimposed on that of methyl fluorosulphonate in the same media. Integration showed this corresponded to decomposition of $20 \pm 5\%$ of the substrate by methyl loss. The location of the lost methyl was revealed by tracer experiments. Citronellol was converted into its tetrahydropyranyl ether (90%) and this was ozonised in methanol at $-70^\circ C$. The aldehyde system (15%) was then coupled in a Grignard reaction with $[1,3-^{14}C_2]$ isopropyl bromide and the crude product was refluxed with acetic acid²⁹ to give $[8,9-^{14}C_2]$ citronellol (5% overall yield), which after recrystallisation as its 3,5-dinitrobenzoate, showed an activity of $5.31 \pm 0.12 \times 10^3$ disint. $min^{-1} mmol^{-1}$. When a sample of this was converted into the ether (II), the latter after rigorous purification (g.l.c. and t.l.c.) had an activity of 2.60 ± 0.16 disint. $min^{-1} mmol^{-1}$.

Reactions of Citrals.—Citrals and its α - and β -cyclic isomers were treated in fluorosulphonic acid with carbon disulphide-sulphur dioxide as solvent, as for citronellol. Work-up and distillation gave yields of ca. 15, 33, and 96% of non-polymeric product. Preparative g.l.c. yielded, *inter alia*, 1,5-dimethyl-2-oxabicyclo[3.3.1]non-3-ene (XIII) and 7-methoxy-2,2,8-trimethyl-6-oxabicyclo[3.3.1]octane (XIV) in 21 and 3% yields from citral and 19 and 53% from α -cyclocitral. Compound (XIII), t_R 39.5 (Found: C, 78.8; H, 10.6. $C_{10}H_{16}O$ requires C, 78.9; H, 10.5%), showed m/e 152 (M^+ , 42%), 137 (60), and 109 (100); ν_{\max} 2 910s cm^{-1} (C-O); τ (100 MHz) 9.00 (3 H, s), 8.79 (3 H, s), 8.8–8.1 (8 H, ms), 5.69 (1 H, d, J 6.0 Hz), and 3.56 (1 H, d, J 6.0 Hz) (the protons resonating at τ 5.69 and 3.56 were

coupled). Compound (XIV), t_R 113.5 (Found: C, 71.7; H, 10.5. $C_{11}H_{20}O_2$ requires C, 71.7; H, 10.9%), showed m/e 184 (M^+ , 1%) and 109 (100); ν_{\max} 2 920s cm^{-1} (C-O); τ (100 MHz) 9.03 (3 H, s), 9.01 (3 H, s), 8.89 (3 H, d, J 7 Hz), 8.90–8.21 (5 H, ms), 7.95 (1 H, q, J 7 Hz), 6.63 (3 H, s), 5.88 (1 H, d, J 4 Hz), and 5.14 (1 H, s) [the protons resonating at τ 8.89 (d) and 7.95 (q) were coupled, as were those at 5.88 (d) and 8.39br (s)]. Compound (XIV) was refluxed with acetic anhydride (24 h) to give 7-acetoxy-2,2,8-trimethyl-6-oxabicyclo[3.2.1]octane (80%), t_R 137.4 (Found: C, 67.5; H, 9.7. $C_{12}H_{20}O_3$ requires C, 67.9; H, 9.4%); m/e 153 (100%) and 109 (38); ν_{\max} 2 925s cm^{-1} (C-O); τ (100 MHz) 9.01 (3 H, s), 8.95 (3 H, s), 8.87 (3 H, d, J 7 Hz), 8.8–8.1 (5 H, ms), 7.97 (3 H, s), 7.86 (1 H, q, J 7 Hz), 5.78 (1 H, d, J 4 Hz), and 3.84 (1 H, s). This (200 mg) was then converted (1 h; $35^\circ C$) with aluminium trichloride (140 mg) and lithium aluminium hydride (20 mg) in ether (1.0 ml) into a mixture of the ether (XV) (70%) and the diol (XVI) (20%). The ether (XV) showed m/e 154 (M^+ , 12%) and 83 (100); τ (100 MHz) 9.11 (3 H, s), 9.02 (3 H, s), 9.06 (3 H, d, J 7 Hz), 7.87 (1 H, q, J 7 Hz), 6.31 (1 H, m), and 6.13 (2 H, m). The diol showed m/e 172 (M^+ , 10%); ν_{\max} 3 340s (OH), and 1 390 and 1 370 s cm^{-1} (*gem*-Me₂).

Acidic treatment of β -cyclocitral in the conditions used for the other isomers resulted in a 73% recovery of substrate, together with methyl β -geranate (XXI) (23%), t_R 210.0 (Found: C, 72.6; H, 9.9. $C_{11}H_{18}O_2$ requires C, 72.5; H, 9.9%); m/e 182 (M^+ , 26%), 167 (61), and 135 (100); ν_{\max} 1 357 and 1 368 (m) cm^{-1} (*gem*-Me₂); τ (100 MHz) 8.92 (6 H, s), 8.55 (2 H, m), 8.40 (2 H, m), 8.35 (3 H, s), 8.02 (2 H, m), and 6.28 (3 H, s).

1H N.m.r. Spectra of Acidic Solutions.—The technique was as before.¹ Under the conditions outlined in the Discussion section the following ions and related compounds were characterized (see formulae for proton lettering): (XXIV), τ (100 MHz) 8.65 (6 H, s, g + h), 8.7–8.1 (6 H, ms, d + e + f), 7.28 (3 H, s, c), 3.01 (1 H, d, J 10 Hz, b), and 0.61 (1 H, d, J 10 Hz, a); (XXV) τ 8.94 (3 H, d, J 7 Hz, d), 8.65 (6 H, s, c), 3.53 (1 H, d, J 4 Hz, b), and 0.61 (1 H, s, a); (XXVI) 7.41 (6 H, s, a), 7.30 (3 H, s, d), 2.88 (2 H, d, J 8 Hz, c), and 1.09 (2 H, d, J 8 Hz, b); (XXVIII) 7.7–7.1 (2 H, ms, f), 7.20 (3 H, s, d), 6.87 (2 H, m, e), 6.06 (6 H, t, J 4 Hz, h + i), 5.8–5.1 (2 H, ms, q), 2.88 (1 H, d, J 9.5 Hz, c), 0.38 (1 H, m, b), and -2.46 (1 H, d, J 8 Hz, a) (a and b were coupled, as were b and c); (XXII) [in (a) $HfSO_3 \cdot SbF_5$, (b) $HfSO_3$] τ 8.32, 8.72 (6 H, s, g + h); 7.97, 8.35 (4 H, m, e + f); 7.08, 7.42 (3 H, s, c); 6.75, 7.11 (2 H, m, d); 0.38, 0.62 (1 H, d, J 8.3 Hz, b); -1.70 , -2.22 (1 H, d, J 8.3 Hz, a) (at $-60^\circ C$, the signal due to H_a was overlapped by a broad peak of the fluorosulphonic acid-antimony pentafluoride system; at $-30^\circ C$, the acid peak centred on τ -0.73 moved to τ -0.43 to reveal the peak previously at τ -1.70 , but the rest of the spectrum was insignificantly shifted by this temperature change); (XXIII) τ 8.62 (6 H, s, b + c) and 7.35 (3 H, s, a).

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²⁹ W. G. Dauben and L. H. Bradlow, *J. Amer. Chem. Soc.*, 1952, **74**, 559.