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Anodic Oxidation. Part VII.¹ Electrolysis of Sodium 2,2-Dimethylcyclopropanecarboxylate

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The main products from the electrolysis of sodium 2,2-dimethylcyclopropanecarboxylate in methanol at a platinum anode are 1,1-dimethylcyclopropane, 2-methylbuta-1,3-diene, 3-methoxy-3-methylbut-1-ene, 1-methoxy-3-methylbut-2-ene, 3-methylbut-2-en-1-al, 2,2-dimethylcyclopropylmethanol, 1,1-dimethylprop-2-envl and 3-methylbut-2-enyl 2,2-dimethylcyclopropanecarboxylates, 2-methoxy-2,7-dimethylocta-4,7-diene, and 2,7-dimethoxy-2,7-dimethyloct-4-ene.

In continuation of our studies ^{1,2} on the anodic oxidation of substituted cyclopropanecarboxylic acids we now report the identificaton of 10 products from the electrolysis of sodium 2,2-dimethylcyclopropanecarboxylate in methanol with a platinum anode.

3-Methylbut-2-enal (XIV), 2,2-dimethylcyclopropylmethanol (X), 1,1-dimethylprop-2-enyl 2,2-dimethylcyclopropanecarboxylate (VII), 2-methoxy-2,7-dimethylocta-4,7-diene (XII) and 2,7-dimethoxy-2,7-dimethyloct-4-ene (XIII), which were present in comparable amounts, were isolated by preparative g.l.c., and a mixture of 1,1-dimethylcyclopropane (IX) and 2-methylbuta-1,3-diene (III) was isolated by distillation. 3-Methoxy-3-methylbut-1-ene (V), 1-methoxy-3-methylbut-2-ene (IV), and 3-methylbut-2-enyl 2,2-dimethylcyclopropanecarboxylate (VI) were identified by g.l.c. Two other products were identical (g.l.c.) with the major products of the anodic methoxylation of 2-methylbuta-1,3-diene,³ and there were further unidentified minor products. A quantitative analysis of the total electrolysis products was not attempted.

The isolated products were identified spectroscopically; this approach was not entirely satisfactory for the aldehyde (XIV), which was rapidly oxidised by air to 3-methylbut-2-enoic acid, and so (XIV) was further characterised as the 2,4-dinitrophenylhydrazone.⁴ Three previously unknown compounds (VI), (VII), and (X) were synthesised by standard methods (see Experi-

¹ Part VI, R. Brettle and G. B. Cox, J. Chem. Soc. (C), 1969,

1227. ² T. D. Binns, R. Brettle, and G. B. Cox, J. Chem. Soc. (C), 1968, 584. ³ G. B. Cox, Ph.D. Thesis, Sheffield, 1968.

mental section); the structures of the other two new compounds (XII) and (XIII) were assigned on the basis of the following results. Catalytic hydrogenation of (XIII) gave 2,7-dimethoxy-2,7-dimethyloctane, the structure of which was established by synthesis. Glaser coupling of 3-methoxy-3-methylbut-1-yne⁵ gave 2,7-dimethoxy-2,7-dimethylocta-3,5-diyne (XV; R = Me), which on catalytic hydrogenation with Adams catalyst gave 2,7-dimethoxy-2,7-dimethyloctane, identical (i.r., n.m.r., g.l.c.) with the product from (XIII). We were unable to prepare (XIII) by the partial hydrogenation of (XV; R = Me); the reduction of (XV; R = H) to the ene-diol corresponding to (XIII) has been reported,⁶ but in our hands this reaction gave a mixture of saturated and unsaturated products. The i.r. spectrum of (XIII) showed absorption at 970 cm.⁻¹ due to a disubstituted double-bond, and the n.m.r. spectrum showed absorptions due to vinyl protons (m, τ 4.62), methoxy-groups (s, τ 6.88), methylene protons (m, τ 7.88) and methyl groups (s, τ 8.93) with integrated intensities in the ratio of 1:3:2:6. The position of the absorption due to the methylene groups established the symmetrical position of the double bond, since in the alternative unsymmetrical structure the methylene groups would have different chemical shifts with one absorbing at higher field (cf. the signal from the methylene protons in 2,7-dimethoxy-2,7-dimethyloctane at τ 8.67). The i.r. spectrum of (XII) revealed the presence of both a disubstituted

⁴ T. Takeshima, J. Sci. Research Inst. (Tokyo), 1951, **45**, 211 (Chem. Abs., 1953, **47**, 6864). ⁵ Kh. V. Balyan, J. Gen. Chem. U.S.S.R., 1951, **21**, 803 (Chem.

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double-bond (970 cm.⁻¹) and a terminal methylene group (890 cm.⁻¹). The n.m.r. spectrum showed very marked similarities to that of (XIII), with absorptions at $\tau 4.61$, 6.89, 7.87, and 8.91 but with integrated intensities in the ratio of 2:3:2:6. In addition there were absorptions attributable to a terminal methylene group (2H m, τ 5.35), a doubly allylic methylene group (2H, m, τ 7.35) and a methyl group on a double-bond (3H, m, τ 8.31). Compound (XII) is thermally unstable and the molecular ion, the exact mass of which agreed with that required by (XII), could be observed only in the mass spectrometer when the sample was introduced into a watercooled source. Compound (XII), pure by g.l.c., gave

methanol (X) is believed to arise by combination of a 2,2-dimethylcyclopropyl radical (VIII) with a hydroxymethyl radical formed by hydrogen abstraction from methanol. By carrying out the electrolysis in a divided cell we have demonstrated that (X) is formed only in the anode compartment, thus ruling out the possibility that (X) arises by cathodic reduction of (I). We cannot at present rationalise the formation of the other identified monomeric product (XIV).

Compounds (XII) and (XIII) represent novel types of dimeric products of a kind not previously encountered in the anodic oxidation of substituted cyclopropanecarboxylic acids. Their close similarity suggests that



consistently low microanalytical figures; we have already reported ¹ similar behaviour by other olefinic tertiary ethers.

The two-electron oxidative decarboxylation of the 2,2-dimethylcyclopropanecarboxylate ion (I) gives the unsymmetrical allylic cation (II) which on nucleophilic attack by (I) or methanol gives the pairs of esters (VI) and (VII) and ethers (IV) and (V). Elimination of a proton from (II) gives 2-methylbuta-1,3-diene (III). 1,1-Dimethylcyclopropane (IX) arises by hydrogen abstraction, probably from the methanol solvent, by a 2,2-dimethylcyclopropyl radical (VIII). Examples of processes analogous to each of these reactions have previously been reported,^{1,2} though not all in connection with a single electrolysis. 2,2-Dimethylcyclopropyl-⁷ A. J. Baggaley and R. Brettle, J. Chem. Soc. (C), 1968, 2055.

they are derived from a common precursor, the cation (XI), and their dimeric nature probably implies that a radical coupling reaction is involved in their formation; we cannot at present define a pathway from (VIII) to (XI).

EXPERIMENTAL

General directions have been given in earlier parts of this series.1,7,8

Starting Materials and Reference Samples.-2,2-Dimethylcyclopropanecarboxylic acid, b.p. 89-91°/9 mm., $n_{\rm D}^{21}$ 1.4394 (lit., 83–84°/5 mm., $n_{\rm D}^{20}$ 1.4405), $\tau = 2.14$ (1H, s, CO₂H), 8.72 and 8.80 (each 3H, s, Me) and 8.41–9.23 (3H, complex, ring protons) was prepared from 2,2-dimethylpropane-1,3-diol 9 via 2,2-dimethylcyclopropanecarbonitrile, b.p. 46—47°/15 mm., $n_{\rm D}^{20}$ 1·4280 (lit., 9 154·5—

⁸ T. D. Binns and R. Brettle, J. Chem. Soc. (C), 1966, 336.
⁹ E. Nelson, M. Maienthal, L. Lane, and A. Benderley, J. Content of the source of the so Amer. Chem. Soc., 1957, 79, 3467.

155°, $n_{\rm D}^{23}$ 1·4261), τ 8·69 and 8·84 (each 3H, s, Me) and 8.76-9.2 (3H, complex, ring protons). 3-Methoxy-3-methylbut-1-ene (V), b.p. 82° (lit., 5 82-83°) v_{max} 2950, 1370, 1355, and 1087 cm.⁻¹, τ 4·15 (1H, m, CH=C), 5·0 (2H, m, $CH_2=C^{-}$), 6.95 (3H, s, MeO), and 8.77 and 8.81 (each 3H, s, Me) and 1-methoxy-3-methylbut-2-ene (IV), b.p. 102—105° (lit., ¹⁰ 104—105°), ν_{max} . 2910, 1690, and 1095 cm.⁻¹, $\div 4.73$ (1H, m, J 7 c./sec., J' 1 c./sec., CH=C), 6.18 (2H, d, J 7 c./sec., CH2O), 6.78 (3H, s, MeO), and 8.27 and 8.35 (each 3H, d, J 1 c./sec., Me) were prepared 10 from 2-methylbut-3-en-2-ol. 3-Methylbut-2-en-1-al (XIV), b.p. 133-135° (lit., 4 133—135°) $\nu_{\rm max}$ 2990, 2750, 1680, and 1200 cm. $^{-1}$, τ 0.03 (1H, d, J 8 c./sec., CHO), 4.13 (1H, m, J 8 c./sec., J' 1.3 c./sec., CH=C) and 7.83 and 8.01 (each 3H, m, J' 1.3 c./sec., Me) [2,4-dinitrophenylhydrazone, m.p. 176-178° (lit.,4 177-178°], was obtained from 2-methylbut-3-en-2-ol with 90% formic acid containing hydroquinone.4 3-Methylbut-2-en-1-ol, b.p. 48-50°/18 mm., n_p¹⁶ 1.4441 (lit.,¹¹ 141°, $n_{\rm D}^{20}$ 1·4433), $\nu_{\rm max}$ 3300 and 1670 cm.⁻¹, τ (H⁺) 4·68 (1H, cm, CH=C), 5·56 (1H, s, OH), 6·02 (2H, d, J 7 c./sec., CH_2O), 8.28 (3H, m, J 0.5 c./sec., Me) and 8.35 (3H, s, Me) was prepared from 2-methylbut-3-en-2-ol via 3-methylbut-2-envl acetate.¹¹ 1,1-Dimethylcyclopropane (IX), b.p. 20–21° (lit., ¹² 20.6°), τ 8.95 (4H, s, CH₂) and 9.80 (6H, s, Me) was prepared from 2,2-dimethylpropane-1,3-diol via 1,3-dibromo-2,2-dimethylpropane.

2,2-Dimethylcyclopropyl Carbinol (X).-Reduction of 2,2-dimethylcyclopropanecarboxylic acid with lithium aluminium hydride in ether gave 2,2-dimethylcyclopropylmethanol, b.p. 78–80°/43 mm., ν_{max} 3300, 2940, 1450, and 1030 cm.⁻¹, τ 6.50 (2H, m, CH₂O) 7.23 (1H, s, OH) 8.85– 9.95 (3H, c, CH) and 8.90 and 8.93 (each 3H, s, Me) (Found: C, 72.1; H, 12.1. C₆H₁₂O requires C, 72.0; H, 12.0%).

1,1-Dimethylprop-2-enyl and 3-Methylbut-2-enyl 2,2-Dimethylcyclopropanecarboxylates .- Crude 2,2-dimethylcyclopropanecarbonyl chloride (4 g.), b.p. 110-140° (from the acid and thionyl chloride) was added to stirred and cooled (ice) 2-methylbut-3-en-2-ol (3.2 g.) in pyridine (10 ml.); the mixture was heated at 100° for 10 min. Isolation of the product with ether gave 1,1-dimethylprop-2-enyl 2,2-dimethylcyclopropanecarboxylate (VII), b.p. 80° (bath)/11 mm., $n_{\rm p}^{23}$ 1.4399, $v_{\rm max}$ 1720 and 1630 cm.⁻¹, τ 3.92 (1H, m, CH=C), 4.93 ($CH_2=C$, m, 2H), 8.51 (6H, s, Me_2CO) 8.83 (6H, s, ring Me), and 8.6-9.5 (3H, complex ring CH) (Found: C, 72.9; H, 9.6. C₁₁H₁₈O₂ requires C, 72.5; H, 9.9(5)%).

3-Methylbut-2-enyl 2, 2-dimethylcyclopropanecarboxylate (VI), b.p. 101—103°/20 mm., $n_{\rm D}^{20}$ 1.4545, $\nu_{\rm max}$ 1730 and 1670 cm.⁻¹, τ 4.70 (1H, complex multiplet, *CH*=C), 5.52 (2H, d, J 7 c./sec., $-CH_2O$) 8.26 (6H, s + d, J 0.5 c./sec., Me₂C=), 8.81 and 8.84 (each 3H, s, ring Me-) and 8.48---9.4 (3H, complex, ring CH) (Found: C, 73.0; H, 9.8%) was prepared similarly.

3-Methoxy-3-methylbut-1-yne.-2-Methylbut-3-yn-2-ol (16.8 g., 0.2 mole) was added to a stirred suspension of sodium hydride (4.8 g., 0.2 mole) in ether (200 ml.). After 15 hr. dimethyl sulphate (27.7 g., 0.22 mole) in ether (100 mole)ml.) was added. An aqueous work-up gave 3-methoxy-3-methylbut-1-yne (10.1 g.), b.p. 80° (lit., 5 79-80°).

2,7-Dimethoxy-2,7-dimethyloctane. 3-Methoxy-3-methylbut-1-yne (4.5 g., 0.05 mole), methanol (5 ml.), pyridine

(1 ml.), and cuprous chloride (60 mg.) were stirred together under oxygen until absorption ceased. The mixture was poured into saturated aqueous ammonium chloride (25 ml.) and the aqueous mixture was extracted with ether. The ethereal extracts were washed successively with 2n-hydrochloric acid, water, saturated aqueous sodium hydrogen carbonate, and water; the extract was then dried and distilled to give crude 2,7-dimethoxy-2,7-dimethylocta-2,5diyne (3.0 g., 68%), b.p. 116-119°/15 mm. The crude diyne (1.2 g.) in ethyl acetate (30 ml.) was hydrogenated over platinic oxide (2 \times 60 mg.) and gave 2,7-dimethoxy-2,7-dimethyloctane, b.p. (bath) $140^{\circ}/14$ mm., ν_{max} 2930, 1375, 1360, and 1080 cm.⁻¹, τ 6.92 (6H, s, MeO), 8.67 (8H, bs, CH₂), and 8.93 (12H, s, Me) (Found: C, 71.5; H, 12.8. C₁₂H₂₆O₂ requires C, 71.3; H, 12.9%).

Electrolysis of Sodium 2,2-Dimethylcyclopropanecarboxylate.—(a) Sodium 2,2-dimethylcyclopropanecarboxylate (13.6 g., 0.1 mole) in methanol (500 ml.) was electrolysed at 15-35° for 8 hr. in an undivided cell of the type described earlier.⁸ The current, initially 3.5 A at 46 v fell to 0.2 A at 100 v. Distillation gave material b.p. 20° containing 1,1-dimethylcyclopropane (IX) and 2-methylbuta-1,3-diene (III) (n.m.r., g.l.c., D6 50% silicone, 48°; 10% dinonyl phthalate, 42°) and b.p. 20-66° (mostly methanol) containing 3-methoxy-3-methylbut-1-ene (V) (g.l.c., D6 10% dinonyl phthalate, 60°; 50% silicone, 40°) and 1-methoxy-3-methylbut-2-ene (IV) (g.l.c., D6 15% silicone, 60°; F. and M, 10% Apiezon L 60°). The residues from four such electrolyses were taken up in ether and the ethereal solution was washed with saturated aqueous sodium hydrogen carbonate [which removed 2,2-dimethylcyclopropanecarboxylic acid (6.0 g.)] and water; the extract was then dried. Preparative g.l.c. (A-700, 30% silicone 80-145°) gave 3-methylbut-2-enal (XIV) having n.m.r. and i.r. spectra identical with an authentic sample (2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 175-177°) 2,2-dimethylcyclopropylmethanol (X), and 1,1-dimethylprop-2-enyl 2,2-dimethylcyclopropanecarboxylate (VII) having n.m.r. and i.r. spectra identical with authentic samples, 2-methoxy-2,7-dimethylocta-4,7-diene (XII), m/e 168, 153, 139, 114, 97, 83, 73, and 41 (Found: M, 168.1505; C11H22O requires M, 168.1515) and 2,7-dimethoxy-2,7-dimethyloct-4-ene (XIII) (Found: C, 72.3, H, 11.9. C₁₂H₂₄O₂ requires C, 72.0; H, 12.0%). Hydrogenation of 2,7-dimethoxy-2,7-dimethyloct-4-ene (50 mg.) in ethanol (10 ml.) over platinic oxide (10 mg.) gave 2,7-dimethoxy-2,7-dimethyloctane identical (n.m.r., i.r., g.l.c., D6 10% silicone, 125°) with an authentic sample. One of the minor products had the same retention times (D6, 20% silicone, 110°; F and M, 10% Apiezon L, 60°) as 3-methylbut-2-enyl 2,2-dimethylcyclopropanecarboxylate.

(b) A similar electrolysis was conducted in a divided cell in which the anode and cathode compartments were separated by a glass sinter. The electrolyte was divided between the compartments and at the conclusion of the electrolysis the anolyte and catholyte were separately worked up. 2,2-Dimethylcyclopropylmethanol was present (g.l.c., D6, 10% silicone oil, 85°) in the anolyte but not in the catholyte.

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