Anodic Oxidation. Part II.[1] The Electrolysis of Dialkyl Sodiomalonates

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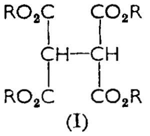
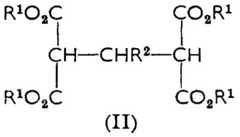
The electrolysis of diethyl sodiomalonate in ethanol gives tetraethyl ethane-1,1,2,2-tetracarboxylate, hexaethyl propane-1,1,2,2,3,3-hexacarboxylate, and tetraethyl 2-methylpropane-1,1,3,3-tetracarboxylate. In *NN*-dimethylacetamide the products are tetraethyl ethane-1,1,2,2-tetracarboxylate and tetraethyl propane-1,1,3,3-tetracarboxylate. The electrolysis of diethyl sodiomethylmalonate gives tetraethyl butane-2,2,3,3-tetracarboxylate and tetraethyl butane-1,1,3,3-tetracarboxylate.

IN continuation of our studies on the electrolysis of ethyl sodioacetoacetate in ethanolic systems we have investigated the electrolysis of diethyl sodiomalonate, and of diethyl sodiomethylmalonate in ethanol and in *NN*-dimethylacetamide.

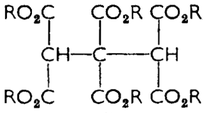
Two major products, tetraethyl ethane-1,1,2,2-tetracarboxylate (I; R = Et) and tetraethyl 2-methylpropane-1,1,3,3-tetracarboxylate (II; R^1 = Et, R^2 = Me), which contains a two-carbon fragment derived from the solvent, are produced when diethyl sodiomalonate is electrolysed in ethanol; only the former product has previously been reported.[2,3] The formation of (II; R^1 = Et, R^2 = Me) is analogous to the formation of products derivable from diethyl 4-methyl-2,6-dioxoheptane-3,5-dicarboxylate in the electrolysis of ethyl sodioacetoacetate in ethanol,[1] and the ester (II; R^1 = Et, R^2 = Me) presumably results in a similar way from the condensation of the starting material with acetaldehyde derived from the solvent. Acetaldehyde, previously suggested as a product of the electrolysis,[3] was characterised as its 4-nitrophenylhydrazone The electrolysis of dimethyl sodiomalonate in methanol gives similar results: formaldehyde is produced and the two major products are tetramethyl ethane-1,1,2,2-tetracarboxylate (I; R = Me) and tetramethyl propane-1,1,3,3-tetracarboxylate (II; R^1 = Me, R^2 = H). An attempt to electrolyse di-isopropyl sodiomalonate in propan-2-ol was frustrated by the insolubility of the sodio-derivative in the alcohol.



(I)



(II)



(III)

The mixtures of tetraesters formed in these electrolyses were investigated by vapour phase chromatography (v.p.c.). Confirmation of their structures was obtained by hydrolysis and decarboxylation of the electrolysis mixtures, and a study of the behaviour of the resultant dicarboxylic acids on paper chromatography and of the derived dimethyl esters on v.p.c. These operations also revealed that a hexaester (III; R = Me or Et) is a minor electrolysis product in each case. Such oxidative trimers have occasionally been reported before in radical reactions.[4] One pathway by which the hexaester (III; R = Et) may arise from the primary electrolysis product (I; R = Et) is as follows:

$$\underset{\text{(IV)}}{(EtO_2C)_2\dot{C}H} + \underset{\text{(V)}}{(EtO_2C)_2\dot{C}{-}CH(CO_2Et)_2} \longrightarrow \text{(III; R = Et)}$$

The radical (V) may arise either by hydrogen abstraction from the primary electrolysis product (I; R = Et) by some other radical [*e.g.*, (IV)] or by the anodic oxidation of the corresponding carbanion, formed from (I; R = Et) by proton transfer to the carbanion of diethyl malonate. Alternatively, the hexaester (III; R = Et) may arise by the addition of diethyl malonate to tetraethyl ethylene-1,1,2,2-tetracarboxylate, formed, together with (I; R = Et) by the disproportionation of the radical (V). Since there is only evidence for one hexaester in each of the electrolysis mixtures, we conclude that the second primary electrolysis product in each case (II; R^1 = Me or Et, R^2 = H or Me, respectively) does not undergo this type of secondary reaction.

When a solution of diethyl sodiomalonate in an excess of diethyl malonate was electrolysed, tetraethyl ethane-1,1,2,2-tetracarboxylate (I; R = Et) could easily be isolated (37%).† In attempts to find more suitable solvents for the preparation of the oxidative dimers of dialkyl malonates we have investigated the electrolysis of diethyl sodiomalonate in a number of dipolar aprotic solvents. The highest yield of the oxidative dimer (I; R = Et) was obtained in dimethyl sulphoxide, in which a very concentrated solution of diethyl sodiomalonate could be obtained, but the major product was in fact the hexaester (III; R = Et), which could be isolated directly by distillation. The separation and purification of the products was hampered by persistent malodorous by-products. We therefore investigated in detail the electrolysis in *NN*-dimethylacetamide, where the yield of (I; R = Et) was greater than that in either *NN*-dimethylformamide or *N*-methylpyrrolidone. In *NN*-dimethylacetamide two products were obtained, in

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† Based on the amount of diethyl malonate initially converted into its sodio-derivative.

[1] Part I, T. D. Binns and R. Brettle, *J. Chem. Soc.* (*C*), 1966, 336.

[2] S. P. Mulliken, *Amer. Chem. J.*, 1893, **15**, 523.

[3] T. Okubo and S. Tsutsumi, *Technol. Reports Osaka Univ.*, 1963, **13** (589), 495.

[4] M. S. Kharasch, H. C. McBay, and W. H. Urry, *J. Amer. Chem. Soc.*, 1948, **70**, 1269; H. B. Henbest, J. A. W. Reid, and C. J. M. Stirling, *J. Chem. Soc.*, 1964, 1217.

roughly equal amounts, the expected tetraester (I; R = Et) and tetramethyl propane-1,1,3,3-tetracarboxylate (II; R^1 = Et, R^2 = H). The latter, on hydrolysis and decarboxylation, gave glutaric acid. The one-carbon fragment incorporated into (II; R^1 = Et, R^2 = H) presumably arises from the solvent. The same two products were obtained when diethyl sodiomalonate was electrolysed in *NN*-dimethylformamide, but the insolubility of the sodio-derivative prevented a study of the electrolysis in *NN*-dimethylpropionamide or *NN*-diethylformamide.

We believe that the one-carbon fragment originates as one of the *N*-methyl groups of the solvent, and that the immediate precursor of the tetraester (II; R^1 = Et, R^2 = H) is diethyl methylenemalonate (VII). The latter probably arises by the condensation of formaldehyde with diethyl malonate; although we have attempted to perform our electrolyses under anhydrous conditions, only a catalytic amount of water would be needed for the production of diethyl methylenemalonate (VII) from a cation (VI) produced by oxidation of the solvent. The cation (VI) may arise either by a direct two-electron transfer from the solvent to the anode, or by attack on the solvent by the malonic ester radical (IV), followed by a second one-electron transfer to the anode. These steps, for which close analogies have recently been reported from studies of other electrolytic oxidations in *NN*-dimethylamide solvents,[5] are summarised in the Scheme.

$$\text{(IV)} + CH_3{\cdot}CO{\cdot}NMe_2 \longrightarrow CH_3{\cdot}CO{\cdot}NMe{\cdot}\dot{C}H_2 \xrightarrow{-1e} \underset{\text{(VI)}}{CH_3{\cdot}CO{\cdot}NMe{\cdot}\overset{+}{C}H_2}$$

or

$$CH_3{\cdot}CO{\cdot}NMe{\cdot}CH_3 \xrightarrow{-2e,\ -H^+} CH_3{\cdot}CO{\cdot}NMe{\cdot}\overset{+}{C}H_2$$

$$\left.\begin{array}{l} CH_3{\cdot}CO{\cdot}NMe{\cdot}\overset{+}{C}H_2 + H_2O \xrightarrow{-H^+} CH_3{\cdot}CO{\cdot}NMe{\cdot}CH_2OH \\ CH_3{\cdot}CO{\cdot}NMe{\cdot}CH_2OH \longrightarrow CH_3{\cdot}CO{\cdot}NHMe + CH_2{:}O \\ CH_2{:}O + (EtO_2C)_2CH_2 \longrightarrow \underset{\text{(VII)}}{CH_2{:}C(CO_2Et)_2} + H_2O \end{array}\right\}$$

$$(EtO_2C)_2CH_2 + CH_2{:}C(CO_2Et)_2 \longrightarrow \text{(II; } R^1 = \text{Et, } R^2 = \text{H)}$$

When a solution of diethyl sodiomethylmalonate in either ethanol or *NN*-dimethylacetamide was electrolysed, the two products were the expected product of oxidative dimerisation, tetraethyl butane-2,2,3,3-tetracarboxylate (VIII), and tetraethyl butane-1,1,3,3-tetracarboxylate (IX). An authentic sample of the hitherto unknown tetraester (IX) was prepared by the catalytic reduction of tetraethyl but-1-ene-1,1,3,3-tetracarboxylate, which is accessible from diethyl malonate in two steps. The structures of the two products [(VIII) and (IX)] were confirmed by degradation to dicarboxylic acids in the way described for the tetraesters [(I) and (II)]. An analysis by v.p.c. of the derived dimethyl esters led to the definition of conditions (see Experimental section) for the separation of dimethyl *meso*- and (±)-αα′-dimethylsuccinates.

$$\underset{\text{(VIII)}}{(EtO_2C)_2{\cdot}CMe{\cdot}CMe{\cdot}(CO_2Et)_2} \qquad \underset{\text{(IX)}}{(EtO_2C)_2CMe{\cdot}CH_2{\cdot}CH(CO_2Et)_2}$$

We believe that both the products [(VIII) and (IX)] are derived from the radical (X) produced by the anodic oxidation of diethyl sodiomethylmalonate. The self-coupling of (X) gives the symmetrical product (VIII), and its disproportionation gives diethyl methylenemalonate and diethyl malonate, which combine in a Michael condensation to give the unsymmetrical product (IX).

$$\underset{\text{(X)}}{(EtO_2C)_2\dot{C}Me} \qquad \underset{\text{(XI)}}{(EtO_2C)_2CH\dot{C}H_2}$$

Eberson has reported[6] that the dominating side reaction in the Kolbe anodic synthesis with alkyl hydrogen mono- and di-alkylmalonates is the disproportion of the intermediate radicals, and the production of the hexaester (III; R = Et) in the electrolysis of diethyl sodiomalonate may, as described above, also involve an analogous disproportionation of a radical derived from a monosubstituted malonic ester. Any mechanism involving the intervention of the radical (XI), which could only arise indirectly by hydrogen abstraction from the methyl group of the starting material, would lead to a second symmetrical tetraester amongst the electrolysis products, and no evidence for the presence of a second such tetraester was obtained.

An early study[7] of the electrolysis of diethyl sodiomethylmalonate was vitiated by the use of impure starting material. The electrolysis of diethyl methylmalonate in acetonitrile or *NN*-dimethylformamide containing potassium iodide has recently been reported,[8] but full details of the characterisation of the products were not given.

EXPERIMENTAL

Electrolyses with a mercury cathode were performed in the cell previously described[1] and were continued until the current dropped to a low steady value. Other electrolyses were performed in a similar cell with a platinum anode and a nickel cathode. A d.c. power unit supplying 100 v was used. Tetra- and hexa-carboxylic acid esters were hydrolysed and decarboxylated by heat under reflux with moderately concentrated hydrochloric acid; the alcohol produced was occasionally distilled off, and at the end of the reaction the water was evaporated off under reduced pressure. Acids were esterified with diazomethane. Paper chromatography of di- and tri-basic acids was carried out with the butyl acetate system of Šandu, Prochazka, and Le Moal.[9] Analytical v.p.c. was performed on an F. and M. 720 instrument using a 10% Apiezon column, and preparative separations were effected on a Wilkens-Aerograph A-700 instrument using a 20% Apiezon column. For other general directions, see Part I.[1]

Reference Compounds.—Tetraethyl ethane-1,1,2,2-tetracarboxylate (I; R = Et), m. p. 73·5—75·5°, was prepared

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[5] S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Org. Chem.*, 1966, **31**, 128; *J. Amer. Chem. Soc.*, 1966, **88**, 4657; L. Eberson and K. Nyberg, *ibid.*, p. 1686.

[6] L. Eberson, *J. Org. Chem.*, 1962, **27**, 2329.

[7] J. B. Weems, *Amer. Chem. J.*, 1894, **16**, 569.

[8] T. Okubo and S. Tsutsumi, *J. Electrochem. Soc. Japan*, 1965, **33**, 637.

[9] V. Šandu, Ž. Prochazka, and H. Le Moal, *Coll. Czech. Chem. Comm.*, 1959, **24**, 420.

by the method of Bailey and Sorensen.[10] Tetraethyl 2-methylpropane-1,1,3,3-tetracarboxylate (II; R^1 = Et, R^2 = Me), b. p. 142—146°/0·4 mm., n_D^{20} 1·4370 was prepared by the method of Goss, Ingold, and Thorpe.[11] Diethyl 2,3-diethoxycarbonylbut-2-enedioate[12] was prepared from diethyl bromomalonate[13] and converted into hexaethyl propane-1,1,2,2,3,3-hexacarboxylate (III; R = Et), b. p. 186—190°/1 mm., n_D^{24} 1·4470, by the method of Ruhemann and Cunnington.[14] Tetramethyl ethane-1,1,2,2-tetracarboxylate (I; R = Me), m. p. 136—137°, was prepared by the method of Walker and Appleyard.[15] Tetramethyl propane-1,1,3,3-tetracarboxylate (II; R^1 = Me, R^2 = H), m. p. 46·5—48·5°, was prepared by the method of Meerwein and Schurmann.[16] Tetraethyl propane-1,1,3,3-tetracarboxylate (II; R^1 = Et, R^2 = H), b. p. 195—199°/13 mm., n_D^{20} 1·4392, was prepared by Welch's method.[17] Tetraethyl butane-2,2,3,3-tetracarboxylate (VIII), b. p. 190—194°/16 mm., n_D^{25} 1·4442 (lit.,[18] n_D^{20} 1·4459), was prepared from diethyl methylmalonate[19] by the method of Bischoff and Rach.[20] Tetraethyl sodioprop-1-ene-1,1,3,3-tetracarboxylate was prepared by the method of Ingold and Perren[21] and converted into tetraethyl but-1-ene-1,1,3,3-tetracarboxylate, b. p. 153—158°/0·3 mm., n_D^{23} 1·4528 (lit.,[22] n_D^{20} 1·4530), τ 2·59 (C=C*H*), by the method of Ruhemann.[23]

Electrolysis of Diethyl Sodiomalonate in Ethanol.—Diethyl malonate (50 g., 1 mol.) was added to sodium ethoxide [from sodium (3 g., 0·42 mol.)] in ethanol (150 ml.) and the solution was electrolysed with a nickel cathode. A current of 0·45—0·2 A was passed for 32 hr. The pH of the solution was then adjusted to 7 with acetic acid. Distillation gave ethanol containing acetaldehyde, from which acetaldehyde 4-nitrophenylhydrazone, m. p. and mixed m. p. 125—126°, was isolated. The material remaining after most of the ethanol had been distilled off was taken up in ether, washed twice with water, and dried. Distillation gave diethyl malonate (5·6 g.) and higher-boiling fractions: (i) b. p. 88—128°/0·9 mm., n_D^{25} 1·4310 (4·0 g.); (ii) b. p. 130—136°/0·11 mm. (10·5 g.); (iii) b. p. 134—138°/0·14 mm. (7·1 g.); (iv) b. p. 140—164°/0·12 mm., n_D^{25} 1·4402 (5·0 g.); and (v) b. p. 164—200°/0·53 mm., n_D^{25} 1·4494 (3·15 g.). Fractions (i)—(iii), when cooled at 0° overnight, partly crystallised. Recrystallisation gave tetraethyl ethane-1,1,2,2-tetracarboxylate (5·0 g.), m. p. and mixed m. p. 73·5°. The liquid portions of fractions (i)—(iii) were combined, hydrolysed, and decarboxylated. Paper chromatography then showed the presence of acids, R_F 0·14, 0·35, and 0·76. (R_F values of tricarballylic, succinic and β-methylglutaric acids were, respectively, 0·15, 0·35, and 0·77.) Crystallisation of the acids from water gave succinic acid, m. p. and mixed m. p. 182—183°. Evaporation of the aqueous filtrate, followed by repeated crystallisation of the residue alternately from chloroform and benzene, gave β-methylglutaric acid, m. p. and mixed m. p. 83—86°. The acids obtained by the hydrolysis and decarboxylation of fractions (iv) and (v) were esterified to give only dimethyl succinate, dimethyl β-methylglutarate and trimethyl carballylate [v.p.c. (170°)].

Similar results were obtained in a number of electrolyses carried out using a mercury cathode, in which equivalent amounts of sodium and diethyl malonate were taken.

Electrolysis of Dimethyl Sodiomalonate in Methanol.—Dimethyl malonate (66 g., 0·5 mole) was added to sodium methoxide [from sodium (11·5 g., 0·5 mol.)] in methanol (350 ml.) and the solution was electrolysed with a mercury cathode. The amalgam was then removed and a grey precipitate of tetramethyl ethane-1,1,2,2-tetracarboxylate was collected, m. p. and mixed m. p. 135·5—136·5° (from benzene). The pH of the methanolic solution was adjusted to 7 with acetic acid, and the solution was distilled to give dimethyl malonate (14·5 g.) and a high-boiling oil. The latter was dissolved in chloroform (250 ml.) and the solution was washed with water (2 × 50 ml.), dried, and combined with the mother-liquors from the crystallisation of the crude tetramethyl ethane-1,1,2,2-tetracarboxylate. The solvents were distilled off to leave a semi-solid residue (43 g.) which consisted (v.p.c., temperature programmed from 170—245° at 7·5°/min.) mainly of tetramethyl propane-1,1,3,3-tetracarboxylate (II; R^1 = Me, R^2 = H) together with tetramethyl ethane-1,1,2,2-tetracarboxylate (I; R = Me) and a compound with a considerably longer retention time, presumed to be hexamethyl propane-1,1,2,2,3,3-hexacarboxylate (III; R = Me). Hydrolysis and decarboxylation of the residue (43 g.) gave a mixture of acids (19 g.) shown by paper chromatography to contain tricarballylic, succinic, and glutaric acids (R_F values 0·12, 0·36, and 0·57, respectively). A part of the acid mixture (5 g.) was esterified, to give a mixture of methyl esters (5·6 g.), b. p. 70—130°/2·5 mm., which contained (v.p.c., temperature programmed from 115—210° at 5°/min.) only dimethyl succinate, dimethyl glutarate, and trimethyl carballylate (retention times 2·25, 4·0, and 10·9 min., respectively).

Methanol distilled from the electrolysis mixture at the conclusion of a duplicate electrolysis contained formaldehyde, characterised as its 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 166—167°.

Electrolysis of Diethyl Sodiomalonate in Diethyl Malonate.—Sodium (4·6 g., 0·2 mol.) was dissolved in diethyl malonate (160 g., 1 mol.) and the solution was electrolysed with a mercury cathode. The resultant solution was separated from the amalgam and poured into an excess of 2N-hydrochloric acid at 0°. Organic material was collected in ether, and the ethereal solution was washed with saturated aqueous sodium hydrogen carbonate and twice with water, and then dried. Distillation gave diethyl malonate (135 g.) followed by a fraction (14·6 g.), b. p. 120—140°/0·08 mm., which solidified. Crystallisation gave tetraethyl ethane-1,1,2,2-tetracarboxylate (11·8 g.), m. p. and mixed m. p. 73—74·5°.

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[10] W. J. Bailey and W. R. Sorensen, *J. Amer. Chem. Soc.*, 1956, **78**, 2287.

[11] F. R. Goss, C. K. Ingold, and J. F. Thorpe, *J. Chem. Soc.*, 1923, **123**, 3342.

[12] B. B. Carson and W. L. Benson, *Org. Synth.*, *Coll. Vol. II*, 1943, 273.

[13] C. S. Palmer and P. W. McWherter, *Org. Synth.*, *Coll. Vol. I*, 1941, 245.

[14] S. Ruhemann and A. V. Cunnington, *J. Chem. Soc.*, 1898, **73**, 1006.

[15] J. Walker and J. R. Appleyard, *J. Chem. Soc.*, 1895, **67**, 768.

[16] H. Meerwein and W. Schurmann, *Annalen*, 1913, **398**, 196.

[17] K. N. Welch, *J. Chem. Soc.*, 1931, 673.

[18] F. Weygand and H. G. Peine, *Rev. Chim.* (*Roumania*), 1962, **7**, 1379.

[19] F. B. Cox and S. M. McElvain, *Org. Synth.*, *Coll. Vol. II*, 1943, 272, 279.

[20] C. A. Bischoff and C. Rach, *Ber.*, 1884, **17**, 2781; *Annalen*, 1886, **234**, 54.

[21] C. K. Ingold and E. A. Perren, *J. Chem. Soc.*, 1921, **119**, 1582.

[22] B. S. Gidvani, G. A. R. Kon, and C. R. Wright, *J. Chem. Soc.*, 1932, 1027.

[23] S. Ruhemann, *J. Chem. Soc.*, 1893, **63**, 874.

The material in the mother-liquors from this crystallisation, on hydrolysis and decarboxylation, gave a mixture of tricarballylic and succinic acids (paper chromatography).

Electrolysis of Diethyl Sodiomalonate in Dimethyl Sulphoxide.—Diethyl malonate (80 g., 0·5 mol.) was added dropwise, with stirring and occasional cooling, to a suspension of sodium hydride (12 g., 0·5 mol.) in dimethyl sulphoxide (200 ml.) under a slow stream of nitrogen, and the solution was then stirred for 1 hr. at 70°. The resultant solution was electrolysed, with a mercury cathode, the amalgam was separated, and the solution (pH 2) was poured into water (200 ml.) and extracted 3 times with ether. The ethereal solution was washed twice with water, with aqueous sodium hydrogen carbonate, and again with water, dried, and the ether was distilled off. Further distillation gave diethyl malonate (28·2 g.) and three more fractions: (i) b. p. 98—168°/0·42 mm., (24·7 g.); (ii) b. p. 168—182°/0·38 mm., n_D^{26} 1·4472 (2·6 g.); and (iii) b. p. 184—210°/0·33 mm., n_D^{26} 1·4549 (11·0 g.). Fraction (i) partly solidified at 0° during 12 hr.; crystallisation of the solid portion from ethanol gave tetraethyl ethane-1,1,2,2-tetracarboxylate (9·5 g.), m. p. and mixed m. p. 73·5—74·5°. Refractionation of the combined fractions (ii) and (iii) gave pure hexaethyl propane-1,1,2,2,3,3-hexacarboxylate (III; R = Et) (3·8 g.), b. p. 172—178°/0·13 mm., n_D^{30} 1·4576 (Found: C, 53·2; H, 6·9. Calc. for $C_{21}H_{32}O_{12}$: C, 52·9; H, 6·7%). Hydrolysis and decarboxylation of the rest of fractions (ii) and (iii) gave tricarballylic acid (0·5 g.), m. p. and mixed m. p. 156—158° (from dioxan).

Electrolysis of Diethyl Sodiomalonate in NN-*Dimethylacetamide.*—Diethyl sodiomalonate [from sodium hydride (2·5 g., 0·1 mol.) and diethyl malonate (50 g., 0·31 mol.)] in *NN*-dimethylacetamide (200 ml., dried by azeotropic distillation with benzene) was electrolysed, with a nickel cathode. A current of 0·6—0·2 A was passed for 39 hr. The pH of the electrolysis mixture (pH 12) was adjusted to 7 by the addition of acetic acid (8 ml.) and the solution was poured into water (50 ml.). The resultant solution was extracted 4 times with ether and the ethereal layer was washed with water and dried. The ether was distilled off. Further distillation gave diethyl malonate (11·5 g.) and three more fractions: (i) b. p. 146—163°/0·33 mm. (3·3 g.); (ii) b. p. 163—170°/0·5 mm. (9·4 g.); and (iii) b. p. 170—230°/0·1—0·5 mm. (10·0 g.). Analysis by v.p.c. (232°) of fractions (i) and (ii) showed the presence of tetraethyl ethane-1,1,2,2-tetracarboxylate (I; R = Et) and tetraethyl propane-1,1,3,3-tetracarboxylate (II; R^1 = Et, R^2 = H) (retention times 2·7 and 4·2 min., respectively). Hydrolysis and decarboxylation of fractions (i) and (ii) together gave a mixture of tricarballylic, succinic, and glutaric acids (R_F values 0·11, 0·25, and 0·43, respectively) and an unidentified acid (R_F value 0·67). The three major components of the derived methyl ester mixture were dimethyl succinate, dimethyl glutarate, and trimethyl tricarballylate (v.p.c.). Preparative v.p.c. gave dimethyl glutarate, n_D^{20} 1·4244 (lit.,[24] 1·4242), identified by comparison of its infrared spectrum with that of an authentic sample.

A similar electrolysis in *NN*-dimethylformamide gave two fractions: (i) b. p. 140—160°/0·35 mm., and (ii) b. p. 160—210°/0·35 mm., each of which contained the tetra-esters (I; R = Et) and (II; R^1 = Et, R^2 = H) (v.p.c.).

Tetraethyl Butane-1,1,3,3-*tetracarboxylate* (IX).—Platinum oxide (880 mg.) was added to a solution of tetraethyl but-1-ene-1,1,3,3-tetracarboxylate (10·4 g.) in ethyl acetate (100 ml.), and the mixture was hydrogenated until hydrogen uptake ceased. The solution was filtered and distilled, to give the *tetracarboxylate* (IX), b. p. 157—159°/1 mm. (10 g., 96%). A redistilled sample had b. p. 146—148°/0·4 mm., n_D^{25} 1·4375, $\nu_{max.}$ 2970, 1740, 1460, and 1440 cm.$^{-1}$ (Found: C, 55·7; H, 7·2. $C_{16}H_{26}O_8$ requires C, 55·5; H, 7·5%), τ 8·73 (ester CH_3, triplet 12H), 5·83 (ester CH_2, quartet 8H), 8·65 (C–CH_3, singlet 3H), 7·57 (CH_2, doublet 2H), and 6·6 (CH, triplet 1H).

Electrolysis of Diethyl Sodiomethylmalonate.—Diethyl methylmalonate[19] (40 g., 0·25 mol.) was added, dropwise with stirring, to a suspension of sodium hydride (5·5 g., 0·23 mol.) in *NN*-dimethylacetamide (200 ml.) cooled in ice–water. The solution was then stirred at 60—70° for 0·5 hr. until hydrogen evolution ceased, and then electrolysed with a mercury cathode. The amalgam was separated, and the solution (pH 7) was poured into water (500 ml.) and extracted 3 times with ether. The ethereal solution was washed with water, dried, and distilled, to give diethyl methylmalonate (13·6 g.) and several higher-boiling fractions: (i) b. p. 180—188°/15 mm., n_D^{20} 1·4412 (1·2 g.); (ii) b. p. 188—192°/15 mm., n_D^{28} 1·4410 (3·3 g.); (iii) b. p. 192—200°/15 mm., n_D^{29} 1·4408 (3·0 g.); (iv) b. p. 170—180°/0·6 mm., n_D^{30} 1·4366 (4·2 g.); (v) b. p. 180—196°/1 mm., n_D^{30} 1·4524; (vi) b. p. 196—236°/1 mm., n_D^{30} 1·4560 (2·3 g.). Fractions (ii)—(vi) each contained (v.p.c., temperature programmed from 146—270° at 5°/min.) tetraethyl butane-2,2,3,3-tetracarboxylate (VIII) (retention time 18·2 min.) and tetraethyl butane-1,1,3,3-tetracarboxylate (IX) (19·7 min.). The former was the major component in fractions (ii)—(iv) and the latter in fractions (v) and (vi). Fractions (ii) and (iii) were combined, hydrolysed, and decarboxylated, to give a mixture of acids from which *meso*-αα′-dimethylsuccinic acid, m. p. and mixed m. p. 212—214°, was isolated by crystallisation from water and then concentrated hydrochloric acid. Paper chromatography on the acids recovered from the mother-liquors of the crystallisation from water showed a single broad spot, R_F 0·81. The R_F values of *meso*- and (±)-αα′-dimethylsuccinic, α-methylglutaric, and adipic acids under the same conditions were 0·82, 0·81, 0·79, and 0·69, respectively. Analysis by v.p.c. (150°) of the derived dimethyl esters showed two major peaks (retention times 3·75 and 4·4 min.) and one minor peak (6·0 min.) due to dimethyl *meso*-αα′-dimethylsuccinate, dimethyl (±)-αα′-dimethylsuccinate, and dimethyl α-methylglutarate, respectively. Fractions (iv)—(vi) were similarly combined, hydrolysed, and decarboxylated. Analysis by v.p.c. (132°) of the derived dimethyl esters showed the presence of dimethyl *meso*-αα′-dimethylsuccinate (retention time 3·75 min.), dimethyl (±)-αα′-dimethylsuccinate (4·5 min.) and (major component) dimethyl α-methylglutarate (6·1 min.), together with a trace of material with a retention time of 8·4 min. A pure sample of dimethyl α-methylglutarate was isolated by preparative v.p.c. (140°) and had an infrared spectrum identical with that of an authentic sample.

Similar results were obtained when the electrolysis of diethyl sodiomethylmalonate was conducted in ethanol in a cell with a mercury cathode.

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