# 649. *Anodic Syntheses.* Part I. New Syntheses of Stearic, Myristic, and Other Acids.*

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Mixtures of half esters of adipic, sebacic, and hexadecane-1 : 16-dicarboxylic acids with various monocarboxylic acids have been electrolysed. Both symmetrical and unsymmetrical coupling occurred, giving mixtures of a hydrocarbon, a diester, and a monoester. The formation of the last, by unsymmetrical coupling of the two components, constitutes a very convenient synthesis of fatty acids.

Stearic acid, for example, has been synthesised from three different pairs of components.

Hitherto, applications of the well-known Kolbe electrolytic synthesis † have been largely restricted to the electrolysis of the sodium salts of either saturated carboxylic acids or half

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* This work was begun at Teddington in 1947—1948 by Dr. Thomas and Mr. Greaves and continued at the Imperial College by Dr. Weedon and Mr. Shephard.—R. P. L.

† The formation of carbon dioxide and a hydrocarbon (R·R) on electrolysis of an alkali-metal carboxylate ($R{\cdot}CO_2M$) was first observed by Kolbe (*Annalen*, 1849, **69**, 257), after whom the reaction is named. In this series, the term " Kolbe synthesis " will be used generally to include all other related anodic coupling reactions : for example, that sometimes referred to as the Crum Brown and Walker synthesis, which involves the electrolysis of a half ester of a dicarboxylic acid (*ibid.*, 1891, **261**, 107 ; *Trans. Roy. Soc. Edin.*, 1891, **36**, 291).

esters of αω-dicarboxylic acids. These reactions provide convenient synthetic routes to many hydrocarbons and diesters which are otherwise rather inaccessible in a pure state (see Swann, "Technique of Organic Chemistry," New York, 1948, Vol. II, p. 195; *Trans. Amer. Electrochem. Soc.*, 1936, **69**, 289, 339; 1940, **77**, 460; 1945, **88**, 104).

$$2R\cdot CO_2^- \longrightarrow R\cdot R + 2CO_2 + 2e$$
$$2MeO_2C\cdot[CH_2]_n\cdot CO_2^- \longrightarrow MeO_2C\cdot[CH_2]_{2n}\cdot CO_2Me + 2CO_2 + 2e$$

The electrolyses are usually carried out in either aqueous or anhydrous methanolic solutions. Different mechanisms probably operate in the two media (Glasstone and Hickling, *ibid.*, 1939, **75**, 333). In aqueous solutions, optimum yields are obtained by the use of a smooth platinum anode, a high anode current density, an acid medium maintained at low temperature, and a high concentration of sodium salt (*idem, loc. cit.*; *J.*, 1934, 1878; Hickling and Westwood, *J.*, 1938, 1039). When these conditions are fulfilled, side reactions, leading in particular to the formation of alcohols (Hofer and Moest, *Annalen*, 1902, **323**, 284) and olefins, are reduced to a minimum. Although electrolyses in methanol have received no systematic study (cf. Glasstone and Hickling, *Trans. Amer. Electrochem. Soc.*, 1939, **75**, 333), the conditions for optimum yields appear to be less critical than in aqueous media.

The yields of coupled products obtained in the Kolbe reaction depend to a large extent on the structure of the carboxylic acid employed as well as on the experimental conditions. Although good yields are generally obtained from straight-chain saturated aliphatic acids and half esters, only small, or even negligible, yields of coupled products have been reported from α-substituted carboxylic acids (see, *e.g.*, Farmer and Kracovski, *J.*, 1926, 2318; Swann, *Trans. Amer. Electrochem. Soc.*, 1929, **56**, 457; Fichter *et al.*, *Helv. Chim. Acta*, 1932, **15**, 698; 1934, **17**, 1218; 1938, **21**, 141; *Trans. Amer. Electrochem. Soc.*, 1939, **75**, 319; Murray and Taylor, *J.*, 1937, 1450), αβ- and βγ-unsaturated acids (Fichter and Holbro, *Helv. Chim. Acta*, 1937, **20**, 333), and benzoic acid (Fichter and Stenzl, *ibid.*, 1939, **22**, 970).

The electrolysis of a mixture of two carboxylic acids ($R\cdot CO_2H$ and $R'\cdot CO_2H$) would be expected to give rise to products ($R\cdot R$, $R\cdot R'$, and $R'\cdot R'$) by both symmetrical and unsymmetrical ("crossed") coupling. Although this extension of the Kolbe reaction has numerous potentialities for the synthesis of unsymmetrical molecules, only a few isolated examples of its use have so far been recorded (see, for example, Miller and Hofer, *Ber.*, 1895, **28**, 2427; Hofer, *Ber.*, 1900, **33**, 650; Carmichael, *J.*, 1922, **121**, 2545; Ruzicka *et al.*, *Helv. Chim. Acta*, 1932, **15**, 1459; Kitaura, *Bull. Inst. Phys. Chem. Res. Japan*, 1937, **16**, 765; *Chem. Abstr.*, 1938, **32**, 4523; Offe, *Z. Naturforsch.*, 1947, **26**, 182; Gunstbée and Stenhagen, *Svensk Kem. Tidskr.*, 1942, **54**, 243; Hunsdiecker, *Ber.*, 1942, **75**, 447, 460, 1197). Preparatory to the application of this modified Kolbe reaction to the synthesis of branched-chain fatty acids, potentially of biological interest, the scope of the method has been examined by electrolysing mixtures of a saturated carboxylic acid and a half-ester of an αω-dicarboxylic acid. The results of these investigations are described in the present communication.

The methyl hydrogen esters of adipic, sebacic, and hexadecane-1 : 16-dicarboxylic acids (I; $n = 4$, 8, and 16) were selected for study, and each was electrolysed in the presence of various fatty acids (see Table). In all cases the expected mixture of three products (hydrocarbon, mono- and di-carboxylates) was obtained, and in general the separation of the required unsymmetrical product (II) presented no difficulty. Crossed coupling was found to occur in both aqueous and anhydrous methanolic media. In the latter, however, not only were rather higher yields obtained, but side reactions leading to the formation of unsaturated materials were much less in evidence. Only in those experiments employing acetic acid as the monocarboxylic acid component were the products of mixed coupling, isolated by distillation, liable to be contaminated with small amounts of an unsaturated ester, presumably (III), derived from the half-ester (I). As was to be expected, an increase in the molar proportion of the monocarboxylic acid component effected a marked improvement in the conversion of the half-ester into the required unsymmetrical product.

$$R\cdot CO_2H + \underset{\text{(I.)}}{HO_2C\cdot[CH_2]_n\cdot CO_2Me} \longrightarrow R\cdot R + \underset{\text{(II.)}}{R\cdot[CH_2]_n\cdot CO_2Me} + MeO_2C\cdot[CH_2]_{2n}\cdot CO_2Me$$
$$\underset{\text{(III.)}}{CH_2{:}CH\cdot[CH_2]_{n-2}\cdot CO_2Me}$$

A wide difference between the sizes of the coupling units can be tolerated. For example, stearic acid has been made by coupling a $C_5$ to a $C_{13}$ residue, a $C_9$ to a $C_9$, and a $C_{17}$ to a $C_1$ (see Table).

| Half-ester. | Acid. | Molar ratio.* | Product. | Yield, %.† in absolute MeOH. | Yield, %.† in aqueous MeOH. |
|---|---|---|---|---|---|
| $HO_2C{\cdot}[CH_2]_4{\cdot}CO_2Me$ | $CH_3{\cdot}CO_2H$ | 1 : 6 | $CH_3{\cdot}[CH_2]_4{\cdot}CO_2H$ | 40 | 29 |
| ,, | $CH_3{\cdot}[CH_2]_2{\cdot}CO_2H$ | 1 : 1 | $CH_3{\cdot}[CH_2]_6{\cdot}CO_2H$ | 31 | — |
| ,, | ,, | 1 : 2 | ,, | 40 | — |
| ,, | ,, | 1 : 6 | ,, | — | 42 |
| ,, | $CH_3{\cdot}[CH_2]_4{\cdot}CO_2H$ | 1 : 1 | $CH_3{\cdot}[CH_2]_8{\cdot}CO_2H$ | 36 | 12 |
| ,, | ,, | 1 : 2 | ,, | 49 | 39 |
| ,, | ,, | 1 : 6 | ,, | 58 | 48 |
| ,, | $CH_3{\cdot}[CH_2]_8{\cdot}CO_2H$ | 1 : 2 | $CH_3{\cdot}[CH_2]_{12}{\cdot}CO_2H$ | 38 | — |
| ,, | $CH_3{\cdot}[CH_2]_{12}{\cdot}CO_2H$ | 1 : 2 | $CH_3{\cdot}[CH_2]_{16}{\cdot}CO_2H$ | 28 | — |
| $HO_2C{\cdot}[CH_2]_8{\cdot}CO_2Me$ | $CH_3{\cdot}CO_2H$ | 1 : 2 | $CH_3{\cdot}[CH_2]_8{\cdot}CO_2H$ | 34 | — |
| ,, | ,, | 1 : 6 | ,, | 51 | — |
| ,, | ,, | 1 : 15 | ,, | — | 50 |
| ,, | $CH_3{\cdot}[CH_2]_4{\cdot}CO_2H$ | 1 : 2 | $CH_3{\cdot}[CH_2]_{12}{\cdot}CO_2H$ | 44 | — |
| ,, | $CH_3{\cdot}[CH_2]_8{\cdot}CO_2H$ | 4 : 3 | $CH_3{\cdot}[CH_2]_{16}{\cdot}CO_2H$ | 18 | — |
| ,, | ,, | 1 : 3 | ,, | — | 21 |
| $HO_2C{\cdot}[CH_2]_{16}{\cdot}CO_2Me$ | $CH_3{\cdot}CO_2H$ | 1 : 4 | $CH_3{\cdot}[CH_2]_{16}{\cdot}CO_2H$ | 25 | — |

* This column gives the molar ratio of reagents, the half-ester being given first.

† Calculated on the half-ester present.

In addition to its simplicity, this method for the synthesis of fatty acids has the advantage that, by suitable choice of starting materials, a product is obtained which is uncontaminated by substances of the same, or very similar, molecular weight. In consequence, acids may readily be prepared and isolated in a state of high purity. By a suitable modification in apparatus, comparatively large runs can be handled on the laboratory scale involving batches of a total of 200—300 g. of reagents. The fatty acids actually synthesised during the present investigation were hexanoic, octanoic, decanoic, myristic, and stearic.

## EXPERIMENTAL.

(Yields are calculated on the total amount of half-ester introduced.)

*Intermediates.*—Butyric and hexanoic acids were obtained by catalytic hydrogenation of crystalline crotonic and sorbic acids, respectively. Methyl hydrogen adipate and methyl hydrogen sebacate were prepared by half esterification of the corresponding dicarboxylic acids (cf. Fichter and Lurie, *Helv. Chim. Acta*, 1933, **16**, 887; Swann, Oehler, and Buswell, *Org. Synth.*, Coll. Vol. II, p. 276; Hunsdiecker and Hunsdiecker, *Ber.*, 1942, **75**, 297), and methyl hydrogen hexadecane-1 : 16-dicarboxylate by half hydrolysis of the diester (cf. *idem, ibid.*).

*Electrolyses.*—The electrolyses were in general performed by one of the following methods :

*Method* A (aqueous methanol). A mixture of the half-ester and monocarboxylic acid was dissolved in 50% aqueous methanol to which sufficient sodium had been added to neutralise about one-twelfth of the total acids used. The solution was placed in a cell consisting of a boiling tube (2″ diameter) fitted with a platinum spiral anode (from 20 cm. of 24 s.w.g. wire; surface area 3·51 sq. cm.) and a platinum plate cathode (total surface area 4 sq. cm.). Sufficient light petroleum (b. p. 60—80°) was added to the cell to form a layer above the aqueous methanol, in order to dissolve the products which otherwise separated on the electrodes. The cell was cooled by immersion in an ice-bath (internal temperature of cell about 30°), and a current of 2 amps. was passed until the electrolyte became slightly alkaline. This usually required *ca.* 15—20% longer than the time calculated on the basis of the current and the amounts of acids employed.

The products were isolated by dilution of the cell contents with water and extraction with light petroleum. The extract was washed with sodium hydroxide solution (2%) to remove small amounts of starting materials, dried, and evaporated. The residue was hydrolysed by heating it with aqueous methanolic alkali (10%), and the neutral and acidic fractions were separated in the usual manner.

*Method* B1 (absolute methanol). The half-ester, or a mixture of the half-ester and monocarboxylic acid, was electrolysed in methanol to which sufficient sodium had been added to neutralise 2% of the total acids used. The temperature of the electrolyte was maintained at 40—50° by external cooling. The electrodes consisted of two parallel plates (4 × 2·5 cm.) placed about 1—2 mm. apart. A current of 1·5—2·0 amps. was passed until the electrolyte became slightly alkaline, which usually took about 20—40% longer than the calculated time.

After termination of the electrolysis, the methanolic solution was neutralised with glacial acetic acid and evaporated. The residue was dissolved in ether, and the ethereal solution washed with sodium hydrogen carbonate solution, dried, and evaporated. The crude products thus obtained were either fractionally distilled or, alternatively, hydrolysed, and the neutral and acidic fractions separated in the usual way.

*Method* B2 (absolute methanol). This procedure differed from (*B*1) solely in the size and design of the apparatus. This consisted of a tall, flat-bottomed, cylindrical, glass vessel (14 × 3″) fitted with two parallel platinum plate electrodes (2·5 × 2 × 0·002″), placed about 2—3 mm. apart, and two spiral cooling coils (10 × 1″) through which ice-water was passed. A current of 7—8 amps. was employed, and by surrounding the cell with an ice-bath the internal temperature was maintained at about 40°.

### *Electrolyses with Methyl Hydrogen Adipate.*

*Hexanoic Acid.*—(*a*) Electrolysis of the half-ester (9·6 g., 1 mol.) and acetic acid (21·6 g., 6 mols.) in 50% aqueous methanol (36 c.c.) by method *A* gave crude hexanoic acid (3·9 g.), b. p. 97—100°/13 mm.; iodine value, 56. The unsaturated material was destroyed by shaking the product with a slight excess of a neutral aqueous potassium permanganate. Distillation of the product gave hexanoic acid (2·0 g., 29%), b. p. 96°/13 mm., f. p. −5°, $n_D^{20}$ 1·4179 (Garner, Madden, and Rushbrooke, *J.*, 1926, 2499, give f. p. −3·6°). The *p*-bromophenacyl ester crystallised from alcohol in plates, m. p. 72·5° undepressed on admixture with an authentic specimen (Moses and Reid, *J. Amer. Chem. Soc.*, 1932, **54**, 2101, give m. p. 72·0°).

(*b*) Electrolysis of methyl hydrogen adipate (40·0 g., 1 mol.) and acetic acid (90·0 g., 6 mols.) in methanol (200 c.c.) by method *B*2 gave: (i) Crude methyl hexanoate (18·0 g.), b. p. 42—45°/30 mm., which was dissolved in carbon tetrachloride and treated with bromine until the latter was no longer rapidly absorbed. Evaporation of the solution and distillation of the residue gave methyl hexanoate (14·0 g.), b. p. 150°, which was hydrolysed, yielding hexanoic acid (11·5 g., 40%), b. p. 118°/28 mm., f. p. −5° to −6°, $n_D^{23}$ 1·4155. The *p*-bromophenacyl ester had m. p. 72·3°, undepressed on admixture with an authentic specimen. (ii) Methyl sebacate, which was hydrolysed to sebacic acid (3·0 g., 10%).

*Octanoic Acid.*—(*a*) Electrolysis of methyl hydrogen adipate (4·8 g., 1 mol.) and butyric acid (15·8 g., 6 mols.) in 50% aqueous methanol (36 c.c.) by method *A* gave octanoic acid (1·8 g., 42%), b. p. 123°/11 mm., m. p. 8° (Halde and Gentner, *Ber.*, 1925, **58**, 1422, give m. p. 16·3°). The *p*-bromophenacyl ester crystallised from aqueous methanol in plates, m. p. 65·5° undepressed on admixture with an authentic specimen (Moses and Reid, *loc. cit.*, give m. p. 67·4°).

(*b*) (With J. C. Lunt). The half-ester (68·0 g., 1 mol.) and butyric acid (74·0 g., 2 mols.) were electrolysed in methanol (270 c.c.) by method *B*2. The products were: (i) Octanoic acid (24·7 g., 40%), b. p. 136—137°/22 mm., f. p. 15·6—15·3°, $n_D^{27}$ 1·4251. The *p*-bromophenacyl ester had m. p. 66° undepressed on admixture with an authentic specimen. (ii) Sebacic acid (13·6 g., 32%).

Electrolysis of equimolar quantities of the same reagents by method *B*1 gave octanoic acid in 31% yield.

*Decanoic Acid.*—(*a*) Electrolysis of methyl hydrogen adipate (4·8 g., 1 mol.) and hexanoic acid (21·0 g., 6 mols.) in 50% aqueous methanol (36 c.c.) by method *A* gave: (i) Decane (4·0 g.), b. p. 57°/10 mm. (ii) Decanoic acid (2·5 g., 48%), b. p. 147°/10 mm., f. p. 29° (Garner and Randall, *J.*, 1924, **125**, 887, give m. p. 31·2°) (Found: equiv., 170. Calc. for $C_{10}H_{20}O_2$: equiv., 172). The *p*-bromophenacyl ester crystallised from aqueous methanol in plates, m. p. 69° undepressed on admixture with an authentic specimen (Moses and Reid, *loc. cit.*, give m. p. 67·0°). (iii) Sebacic acid (0·3 g., 10%).

Similar electrolyses of the half-ester and hexanoic acid with molar ratios of 1 : 2 and 1 : 1, gave decanoic acid in yields of 39 and 12%, respectively, and sebacic acid in yields of 25 and 50%, respectively.

(*b*) A solution of methyl hydrogen adipate (9·6 g., 1 mol.) and hexanoic acid (14·0 g., 2 mols.) in methanol (30 c.c.) was electrolysed by method *B*1 and gave: (i) Decane (1·8 g.), b. p. 30°/1 mm. (ii) Decanoic acid (5 g., 49%), b. p. 146°/10 mm., m. p. 30°, which was crystallised once from methanol, yielding the pure acid as plates, m. p. 31° (Found: equiv., 171. Calc. for $C_{10}H_{20}O_2$: equiv., 172). The *p*-bromophenacyl ester had m. p. 69·5° undepressed on admixture with an authentic specimen. (iii) Sebacic acid (1·6 g., 26%).

Electrolysis of the half-ester and hexanoic acid in molar proportions 1 : 1 and 1 : 6 gave decanoic acid in 36 and 58% yields, respectively.

*Tetradecanoic Acid.*—Electrolysis of methyl hydrogen adipate (6·4 g., 1 mol.) and decanoic acid (13·8 g., 2 mols.) in methanol (30 c.c.) by method *B*1 gave: (i) Octadecane (2·7 g.), m. p. 27·5° (Heilbron and Owens, *J.*, 1928, 945, give m. p. 28—29°). (ii) Tetradecanoic acid (3·5 g., 38%), b. p. 184°/4 mm., m. p. 57·5° (Found: equiv., 227. Calc. for $C_{14}H_{28}O$: equiv., 228). One recrystallisation from methanol gave the pure acid in plates, m. p. 58·5° (Levene and West, *J. Biol. Chem.*, 1914, **18**, 463, give m. p. 57·5—58·0°). The *p*-bromophenacyl ester crystallised from aqueous methanol in plates, m. p. 81·0° (Moses and Reid, *loc. cit.*, give m. p. 81·0°). (iii) Sebacic acid (0·75 g., 19%).

*Octadecanoic Acid.*—Methyl hydrogen adipate (1·6 g., 1 mol.) and tetradecanoic acid (4·6 g., 2 mols.) were electrolysed in methanol by method *B*1. The crude product was hydrolysed and separated into neutral and acidic fractions. The former consisted of hexacosane (1·6 g.), m. p. 56° (Levene and West, *J. Biol. Chem.*, 1915, **20**, 529, give m. p. 59—60°). The acidic portion was converted into the lead salts, and the latter were extracted first with ether and then with hot chloroform. The insoluble residue was treated with 2N-nitric acid and gave sebacic acid (0·2 g., 20%). The chloroform extract was shaken with 2N-nitric acid, then with water, dried, and evaporated. Crystallisation of the residue from methanol gave octadecanoic acid (0·8 g., 28%) as plates, m. p. 69·6° undepressed on admixture with a highly purified specimen of natural stearic acid, m. p. 69·0° (Guy and Smith, *J.*, 1939, 615, give m. p. 69·6°) (Found: equiv., 281. Calc. for $C_{18}H_{36}O_2$: equiv., 284). The *p*-bromophenacyl ester crystallised from aqueous methanol in plates, m. p. 89° undepressed on admixture with an authentic specimen (Moses and Reid, *loc. cit.*, give m. p. 90·0°).

### *Electrolyses with Methyl Hydrogen Sebacate.*

*Decanoic Acid.*—(*a*) A mixture of the half-ester and acetic acid was electrolysed by the following modification of method *A* in which the electrolysis was carried out in a continuous-extraction apparatus.

A solution of the half-ester (2·16 g., 1 mol.) and acetic acid (9·0 g., 15 mols.) in methanol (10 c.c.) was neutralised with sodium hydroxide (6·4 g.) in water (20 c.c.) and electrolysed for 8 hours. During the experiment a mixture of the half-ester (5·85 g.) and acetic acid (24·5 g.) was added. Throughout the electrolysis the cell contents were subjected to continuous extraction with light petroleum (b. p. 40—60°). Evaporation of the petroleum extract and distillation of the residue gave methyl decanoate, b. p. 100—105°/12 mm., which was hydrolysed to decanoic acid (3·2 g., 50%), m. p. 30° undepressed on admixture with an authentic specimen. The *p*-toluidide crystallised from benzene–light petroleum (b. p. 60—80°) in plates, m. p. 74° undepressed on admixture with an authentic specimen (Robertson, *J.*, 1919, **115**, 1210, gives m. p. 78°).

(*b*) Methyl hydrogen sebacate (54 g., 1 mol.) and acetic acid (90 g., 6 mols.) in methanol (200 c.c.) were electrolysed by method *B*2 and gave: (i) Crude methyl decanoate (30·0 g.), b. p. 130°/23 mm., which was dissolved in carbon tetrachloride and treated with bromine until the latter was no longer rapidly absorbed. Evaporation of the solution and distillation of the residue gave methyl decanoate (26·0 g.), b. p. 130°/25 mm., which was hydrolysed to decanoic acid (22·0 g., 51%), b. p. 160°/17 mm., f. p. 30·5—31·0°. (ii) Methyl hexadecane-1 : 16-dicarboxylate (5·6 g., 13%).

Electrolysis of the half ester and acetic acid in the molar proportions of 1 : 2 gave decanoic acid in 34% yield. The *p*-bromophenacyl ester had m. p. 69° undepressed on admixture with an authentic specimen.

*Tetradecanoic Acid.*—Methyl hydrogen sebacate (21·6 g., 1 mol.) and hexanoic acid (23·2 g., 2 mols.) in methanol (90 c.c.) were electrolysed by method *B*1 and gave: (i) Decane (5 g.), b. p. 30°/1 mm. (ii) Methyl tetradecanoate (11·0 g.), b. p. 63°/1 mm., which on subsequent hydrolysis gave tetradecanoic acid (10·0 g., 44%), m. p. 55·5° (Found: equiv., 226. Calc. for $C_{14}H_{28}O_2$: equiv., 228). The *p*-bromophenacyl ester had m. p. 81° undepressed on admixture with the specimen described above. (iii) Dimethyl hexadecane-1 : 16-dicarboxylate (1·0 g., 6%), b. p. 196°/1 mm., m. p. 57° (Chuit, *Helv. Chim. Acta*, 1926, **9**, 276, gives m. p. 60°), which on hydrolysis gave the dicarboxylic acid which crystallised from chloroform in prisms, m. p. 124° (*idem, loc. cit.*, gives m. p. 124·6—124·8°).

*Octadecanoic acid.*—(*a*) A mixture of methyl hydrogen sebacate and decanoic acid was electrolysed by the following modification of method *A* in which the electrolysis was carried out in a continuous-extraction apparatus.

The half-ester (1·0 g., 1 mol.) and decanoic acid (2·58 g., 3 mols.) were added to a solution of sodium hydroxide (0·8 g.) in water (10 c.c.) and methanol (5 c.c.). The solution was electrolysed for 2 hours by using a spiral of platinum wire (2·65 sq. cm. surface area) as anode, and an anodic current density of 0·57 amp./sq. cm. During the electrolysis, a mixture of the half-ester (3·24 g.) and decanoic acid (7·74 g.) was slowly added, and throughout the experiment the cell contents were subjected to continuous extraction with light petroleum (b. p. 40—60°). The petroleum extract was washed with dilute sodium hydroxide solution and evaporated. The residue was hydrolysed by heating it with alcoholic sodium hydroxide, the resulting mixture was diluted with water, and the alcohol removed by distillation. The non-hydrolysable material was extracted with light petroleum, and the sparingly soluble sodium salt was separated and acidified. One crystallisation of the crude product from light petroleum (b. p. 60—80°) gave octadecanoic acid (1·2 g., 21%) as plates, f. p. 68·4° undepressed on admixture with an authentic specimen.

Repetition of the preceding experiment with an anodic current density of 1·0 amp./sq. cm. resulted in no significant change in the yield of octadecanoic acid.

(*b*) Electrolysis of methyl hydrogen sebacate (8·6 g., 4 mols.) and decanoic acid (5·2 g., 3 mols.) in methanol (30 c.c.) by method *B*1 gave: (i) Octadecane (4·4 g.), b. p. 100—105°/0·15 mm., which solidified and was recrystallised from acetone, yielding needles, m. p. 28° (Heilbron and Owens, *J.*, 1928, 945, give m. p. 28—29°). (ii) Methyl octadecanoate (2·6 g.), b. p. 136°/0·3 mm., which on subsequent hydrolysis yielded octadecanoic acid (2·0 g., 18%). This crystallised from methanol in plates, m. p. 68·8° undepressed on admixture with an authentic specimen. The *p*-bromophenacyl ester had m. p. 89·5° undepressed on admixture with the specimen described above.

*Dimethyl Hexadecane*-1 : 16-*dicarboxylate.*—Methyl hydrogen sebacate (31·5 g.) in methanol (70 c.c.) was electrolysed by method *B*1 and gave: (i) An unsaturated ester (2·5 g.), b. p. 54°/0·8 mm. (ii) Dimethyl hexadecane-1 : 16-dicarboxylate (16·5 g., 66%) (cf. Swann, Oehler, and Pinkey, *Org. Synth.*, 1941, **21**, 48).

*Octadecanoic Acid.*—Methyl hydrogen hexadecane-1 : 16-dicarboxylate (3·6 g., 1 mol.), m. p. 78° (Found: C, 69·7; H, 11·4. Calc. for $C_{19}H_{36}O_4$: C, 69·5; H, 11·1%), and acetic acid (2·6 g., 4 mols.) were added to a solution of ammonia (0·017 g.) in methanol (40 c.c.), and the resulting solution was electrolysed in the cell described under method *B*1. (The ammonium rather than the sodium salts were used on account of the low solubility of the sodium salt of the half-ester in methanol.) A current of 1·4 amps. was passed for 85 minutes, the temperature being maintained at 40°. The solvent was removed under reduced pressure, and the residue dissolved in ether (300 c.c.) and washed with 2N-potassium hydroxide solution. The alkaline solution was concentrated to a small volume and then acidified, hexadecane-1 : 16-dicarboxylic acid (0·6 g.), m. p. 124°, being precipitated. Evaporation of the ethereal solution and distillation of the residue gave methyl octadecanoate (0·85 g.), b. p. 110°/0·1 mm., which on subsequent hydrolysis yielded octadecanoic acid (0·77 g., 25%), m. p. 68·9° undepressed on admixture with an authentic specimen. The *p*-bromophenacyl ester had m. p. 89·0° undepressed on admixture with an authentic specimen.

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