

CCCVII.—*The Electrolytic Synthesis of
Tetramethyladipic Acids.*

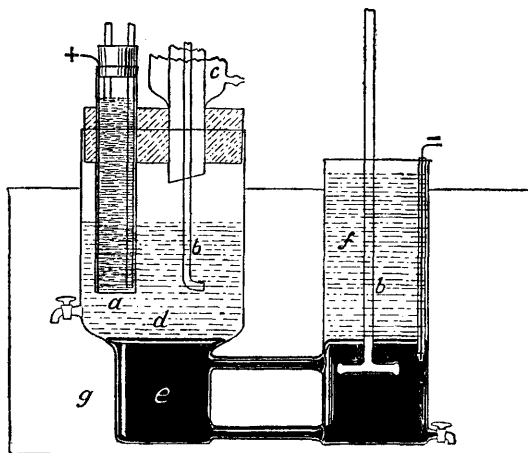
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THE preparation of $\beta\beta\beta'\beta'$ -tetramethyladipic acid by ordinary synthetic methods has been the subject of prolonged experiment. There are no naturally occurring substances from which this acid

may be derived and all attempts to synthesise it from substances such as *s*-tetramethylethylenedibromide, β -iodoisovaleric acid and $\beta\beta$ -dimethyl-lævulic acid have failed. No adipic acid containing two *gem*-dialkyl groups has hitherto been obtained, yet the interest attaching to these and other polyalkyladipic acids in connexion with the strain theory is such that experiment has been continued in the direction of synthesis by electrolysis.

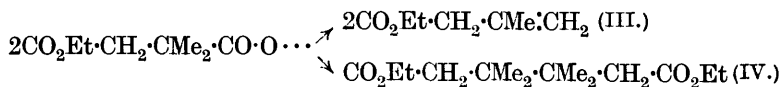
The ease with which adipic ester may be obtained electrolytically from ethyl sodium succinate rendered it probable that reasonable yields of the $\alpha\alpha\alpha'\alpha'$ -tetramethyladipic acid would be obtainable by

FIG. 1.



(a) Platinum anode sealed into glass tube provided with inflow and outflow tubes; (bb) stirrers; (c) water condenser provided above with mercury seal and side-arm for use when collecting more volatile products; (d) electrolyte; (e) mercury cathode; (f) alcohol; (g) water-bath.

employing the sodium salt, $\text{CO}_2\text{Et}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$ (I); consideration of the isomeric compound $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{Na}$ (II), would suggest, however, the great probability of degradation to β -methylisocrotonic ester (III), or the isomeric $\beta\beta$ -dimethylacrylic ester, rather than to a coupling of the residues to yield (IV):



Nevertheless, the electrolysis of the sodium salts of both ethyl hydrogen *as*-dimethylsuccinates has been effected, and in each case the appropriate tetramethyladipic acid has been obtained. The yields, however, were very different in the two cases.

In selecting an apparatus suitable for the continuous electrolysis

of large quantities of material, that of Bouveault (*Bull. Soc. chim.*, 1903, [3], 29, 1042) was taken as a pattern in designing the less expensive and more convenient form shown in the diagram. The requisite low temperature and high current density (50—100 amps./dcm.²) at the anode were readily obtained, and owing to the nature of the cathode and circulatory system (securing a continuously changing mercury surface), the anions were so efficiently removed that little hydrolysis occurred in the alcoholic electrolyte.

The products obtained from esters (I) and (II) are shown in Tables A and B respectively. A large proportion of the material suffered severe degradation leading to volatile products which were not investigated. This degradation was not due to unsuitable experimental conditions, since under similar conditions consistently good yields (over 70%) of adipic ester were obtained from methyl sodium succinate and only a very small portion of material suffered degradation.

TABLE A.

	%.
<i>aaa'a'</i> -Tetramethyladipic ester	32—35
Methoxypivalic ester (?) } <i>ββ</i> -Dimethylacrylic ester * }	3— 5
<i>as</i> -Dimethylsuccinic (neutral) ester	5— 7
<i>as</i> -Dimethylsuccinic (acid) ester	17
	<hr/> 62

TABLE B.

	%.
<i>βββ'β'</i> -Tetramethyladipic ester	5— 8
<i>β</i> -Methoxyisovaleric ester	8—10
<i>ββ</i> -Dimethylacrylic ester ...	30—35
<i>as</i> -Dimethylsuccinic (neutral) ester	Trace.
<i>as</i> -Dimethylsuccinic (acid) ester	11
	<hr/> 61

* Since the complete removal of the solid ester (II) from its liquid isomeride (I) could not be attained with certainty, the appearance of this substance is probably to be attributed to this cause.

The appearance of ethyl *ββ*-dimethylacrylate rather than of ethyl *β*-methylisocrotonate among the products from (II) affords another instance of the apparent inability of the latter to exist in a free state.

EXPERIMENTAL.

as-Dimethylsuccinic Anhydride.—Large quantities of dimethylsuccinic acid were obtained by the method of Thorpe and Higson (*J.*, 1906, 89, 1463), the yield of pure acid being 40—45%. Heating for 3 hours with acetyl chloride (three times theory) and subsequent distillation yielded the anhydride (b. p. 111°/16 mm.) in crystalline form.

Ethyl Hydrogen as-Dimethylsuccinate.—The anhydride was refluxed for 4 hours with twice the theoretical amount of alcohol. After removal of excess of alcohol the ester (II), m. p. 68°, crystal-

lised out and was removed by filtration and recrystallised from petroleum; the residual oil which yielded further small crops of crystals on dilution and strong cooling was freed from traces of neutral ester and distilled. It was obtained as a colourless oil, b. p. $147^{\circ}/15$ mm., which on long standing deposited a further small quantity of the crystalline isomeride. This substance was no doubt identical with de Rosanbo's acidic ester (*Ann. Chim.*, 1923, [ix], 19, 335) [Found: C, 54.6; H, 7.6; *M* (monobasic), 174. Calc. for $C_8H_{14}O_4$: C, 55.1; H, 8.0%; *M*, 174].

Electrolysis of Ester (II).—The ester (174 g.), dissolved in a small amount of methyl alcohol, was gradually added to a cold alcoholic solution of sodium hydroxide obtained by dissolution of sodium (23 g.) in methyl alcohol (230 g.) and addition of water (18 g.). The resulting fine suspension of sodium salt was electrolysed in two portions (*C.D.* about 70 amps./*dcm.*²). The temperature of the liquid rose appreciably but in the immediate neighbourhood of the anode it remained at 18° . After about 20 hours, the current fell to zero and the clear solution was removed. The methyl alcohol was distilled off and the residue poured into water. The precipitated oil was extracted with ether and the ethereal solution shaken with dilute alkali. The alkaline extract yielded the original acidic ester (15 g.); the ethereal solution contained a mixture of neutral oils which was carefully fractionated, the lower-boiling fractions being redistilled at atmospheric pressure. Ultimately three main fractions were obtained of b. p. 145 — 148° and 172 — 174° at atmospheric pressure, and 145 — $150^{\circ}/16$ mm., respectively. The products of the various electrolyses showed slight variations in the relative proportions of the different fractions, but the total yield did not vary appreciably.

$\beta\beta$ -Dimethylacrylic Acid.—The ester fraction, b. p. 145 — 148° , which possessed the characteristic odour of dimethylacrylic ester, was hydrolysed by boiling for $1\frac{1}{2}$ hours with the calculated amount of 50% aqueous potash to which sufficient alcohol had been added to bring the oil into solution. After removal of alcohol and traces of unchanged ester by ethereal extraction of the diluted alkaline product, the acid was obtained in almost pure condition on acidification and re-extraction. It was crystallised from water as long needles, m. p. 69° , and was in all respects similar to authentic $\beta\beta$ -dimethylacrylic acid.

β -Methoxyisovaleric Acid.—Hydrolysis of the ester fraction, b. p. 172 — 174° , under similar conditions yielded a syrupy acid, b. p. $118^{\circ}/14$ mm., which was readily soluble in water [Found: C, 55.1; H, 8.8; *M* (monobasic), 130. $C_6H_{12}O_3$ requires C, 54.5; H, 9.1%; *M*, 132]. The ester of this acid was not directly con-

vertible into $\beta\beta$ -dimethylacrylic acid by treatment with phosphorus trichloride, followed by hydrolysis. Estimation of the methoxyl group in the acid (Zeisel method) indicated the constitution assigned.

$\beta\beta\beta'\beta'$ -*Tetramethyladipic Acid*.—The ester fraction, b. p. 145—150°/16 mm., was boiled with 6 times its volume of concentrated hydrochloric acid until hydrolysis, which was effected slowly and with some charring, was complete. On cooling, the solution deposited crystals of a saturated acid, m. p. 207—208°. This substance was moderately soluble in benzene, ether and hot water, crystallising from the last in long prisms [Found : C, 59.3; H, 9.0; *M* (dibasic), 204. $C_{10}H_{18}O_4$ requires C, 59.4; H, 8.9%; *M*, 202]. This acid, unlike the $\alpha\alpha\alpha'\alpha'$ -acid, could readily be brominated by successive treatment with phosphorus pentachloride and bromine. The hydrolysis liquor on further evaporation yielded a small quantity of tetramethyladipic acid and some *as*-dimethylsuccinic acid.

Electrolysis of Ester (I).—Electrolysis was carried out as described above, the current density at the anode being almost identical in value with that employed for the ester (II). The time required was, however, considerably greater. The neutral oil isolated from the product was separated into fractions of b. p. (a) below 60°/15 mm., (b) 60—80°/15 mm., (c) 120°/15 mm., and (d) above 120°/15 mm. On hydrolysis with aqueous-alcoholic potash the fraction (a) yielded only $\beta\beta$ -dimethylacrylic acid, and (b) after redistillation at atmospheric pressure (b. p. 174—176°) yielded a mixture of *as*-dimethylsuccinic acid and a syrupy acid. Owing to the extreme difficulty of separating all the dimethylsuccinic acid from the syrupy acid, the identity of the latter is uncertain. It corresponded in composition and basicity approximately with *methoxyypivalic acid* and, on treatment with hydriodic acid, it yielded an acid, m. p. 112—115°, contaminated with a trace of dimethylsuccinic acid. After removal of the latter, as far as possible, the acid agreed approximately in composition and basicity with *hydroxyypivalic acid* (m. p. 124°). Hydrolysis of (c) yielded a mixture of the methoxy acid and dimethylsuccinic acid.

$\alpha\alpha\alpha'\alpha'$ -*Tetramethyladipic Acid*.—The high-boiling fraction (d) yielded, on prolonged hydrolysis with 10 times its volume of concentrated hydrochloric acid, large, colourless, hard crystals, m. p. 191°, which were deposited in the boiling solution. These were almost insoluble in cold and only slightly soluble in boiling water. In organic solvents this acid was much less soluble than its isomeride [Found : C, 59.1; H, 8.85; *M* (dibasic), 203. $C_{10}H_{18}O_4$ requires C, 59.4; H, 8.9%; *M*, 202]. The acid was saturated and, after prolonged heating of its acid chloride with bromine, yielded a bromine-free ester hydrolysable to the original acid.

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