CXXVII.—*n-Decanedicarboxylic Acid.*

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THE following research was begun by us more than two years ago, and was then completed as far as the electrosynthesis of *n*-decanedicarboxylic acid from pimelic acid. The properties of the electrosynthetic acid differed, however, in so many particulars from those of the acid prepared by Nördlinger from his bromundecylic esters (*Ber.*, 1890, 23, 2357; compare preceding paper), that, notwithstanding their general resemblance, we were uncertain of the identity of the two acids, and were compelled to undertake a revision of Nördlinger's work. In the

meantime, an abstract of a paper by Komppa appeared (*Chem. Centr.*, 1899, ii, 1016 ; from *Festschrift. Polyt. Institut. Helsingfors*, April, 1899), in which it was stated that he had prepared the electrosynthetic acid, and found its properties to be identical with those of the acid described by Nördlinger. We were at a loss to account for this divergence from our own results, and awaited the details of Komppa's research. These have now been published (*Ber.*, 1901, 34, 895), and as we have, meantime, prepared *n*-decanedicarboxylic acid from ω -bromundecylic acid, we are at present in a position to make a direct comparison of this with our electrosynthetic acid, and also to compare both of these with the acids of Nördlinger and Komppa.

As Komppa performed the electrolysis of ethyl potassium pimelate with a comparatively small quantity (6.5 grams) of material, and investigated none of the intermediate and subsidiary products, we here give a brief account of the preparation and electrolysis of ethyl potassium pimelate, as carried out by ourselves.

Preparation of n-Pimelic Acid from Salicylic Acid.

When salicylic acid is reduced by sodium in amyl alcohol, a considerable proportion of it is converted into *n*-pimelic acid according to the empirical equation,

(Einhorn and Lumsden, *Annalen*, 1895, 286, 257). This reaction forms a convenient method of preparing *n*-pimelic acid when carried out according to the following directions.

Salicylic acid is boiled for 2 hours with five times its weight of dried fusel oil and half its weight of sulphuric acid. By this means, it is mostly converted into esters, which are more readily reducible than the acid itself. After cooling, the sulphuric acid is washed out from the oil with water, and finally with dilute sodium carbonate solution (which also removes a little untransformed salicylic acid), and the residual liquid is then dried over anhydrous sodium sulphate. The solution is diluted with fusel oil until it occupies 100 c.c. for each 7 grams of salicylic acid originally taken.

The reduction is then effected as follows. A litre flask of Jena glass is fitted with a ∇ -shaped adapter of half-inch bore, the sloping limb of which is attached to a reflux condenser. A dropping-funnel is fitted by means of a cork into the upright limb, and can be removed as required for the introduction of pieces of sodium. Ten grams of sodium in large pieces and 50 c.c. of fusel oil are heated in the flask on an asbestos air-bath to the boiling point of the alcohol, and the solution of salicylic esters is then dropped in slowly from the tap funnel until 150 c.c. have been added. When the first charge of sodium is reduced

to a small bulk, a second charge of 10 grams is added, and the heating continued until all the sodium disappears. The operation lasts about 3 hours, and during this time the flask must be occasionally shaken, to prevent the sodium compounds which separate out from hardening on the walls of the flask.

When the sodium has disappeared, the contents of the flask are cooled to a little below 100° , and an equal bulk of water is added to decompose the sodium amyloxyde and dissolve out the sodium salts produced by the reduction. The aqueous layer is separated from the oil, which is subsequently washed out twice with its own bulk of water, the aqueous extracts being added to the original aqueous solution. The aqueous liquid is then boiled to reduce its bulk and to remove the fusel oil which it retains in solution. After cooling, the liquid is strongly acidified with hydrochloric acid. An oily acid separates at once, and some salicylic acid crystallises out on standing. These are removed by filtration and rejected. The filtrate is then boiled down until sodium chloride begins to separate, when it is cooled and thrice extracted with ether. The ether is distilled off from the extract, and the residue dissolved in a little boiling water, any oil which remains undissolved being filtered off. On cooling, a little salicylic acid usually separates. This is removed by filtration, and the filtrate concentrated by evaporation until pimelic acid begins to crystallise out. The average yield of pimelic acid is 4.5—5 grams from 10.5 grams of salicylic acid.

It is inadvisable to work with pure amyl alcohol, or with larger quantities than those given. As three or four reductions, however, can be carried on simultaneously, and the products worked up together, the preparation of a quantity of pimelic acid is not so tedious as might appear from the above description.

Preparation and Electrolysis of Ethyl Potassium Pimelate.

Pimelic acid (100 grams) was converted into the diethyl ester (103 grams obtained) by means of ethyl alcohol and hydrochloric acid. The diethyl ester thus prepared was dissolved in twenty-five times its weight of ethyl alcohol, and half saponified at the ordinary temperature by treatment with the calculated quantity of potassium hydroxide in four successive portions (compare Walker, Trans., 1892, 51, 710). Ten grams of the ester were recovered unchanged, so that 10 grams had been converted into the dipotassium salt, and 80 grams into the ethyl potassium salt.

Ethyl Hydrogen Pimelate, $\text{CO}_2\text{H} \cdot [\text{CH}_2]_5 \cdot \text{CO}_2\text{Et}$.—A small quantity of the aqueous solution of the mixed potassium salts was acidified with hydrochloric acid, and the liberated acids extracted with ether. The acids were then converted into the corresponding calcium salts by

warming with water and precipitated calcium carbonate until the aqueous solution became neutral. Ethyl calcium pimelate is freely soluble in water (less so at the boiling point than at the ordinary temperature), whereas calcium pimelate is sparingly soluble. The calcium salts were thus to a large extent separated from each other. Ethyl hydrogen pimelate, separated from the solution of ethyl calcium pimelate by acidification, is a colourless oil which does not solidify at 0° . In this respect it resembles ethyl hydrogen adipate, and differs from ethyl hydrogen suberate and ethyl hydrogen sebate, which are solids melting at 18° and 38° respectively (Walker, *loc. cit.*, p. 713). It is easily miscible with the ordinary organic solvents, but only sparingly soluble in water.

0.1 gram required 10.9 c.c. *N*/20 HCl for neutralisation; replaceable $H = 0.54$ per cent.; calculated for $\text{CO}_2\text{Et} \cdot [\text{CH}_2]_5 \cdot \text{CO}_2\text{H}$ replaceable $H = 0.53$ per cent. The substance was therefore nearly free from pimelic acid.

A solution which contained 75 grams of ethyl potassium pimelate, together with dipotassium pimelate as impurity, was dissolved in 100 c.c. of water, and electrolysed with a stout platinum wire as anode, the current averaging 10 amperes and the temperature being kept below 30° . In this way, 26 grams of an oil were obtained which consisted mainly of the ethyl esters of two acids formed at the anode in the normal manner as follows:

The esters were dissolved out in ether, washed, dried with calcium chloride, and after evaporation of the ether distilled under reduced pressure. As usual, the esters separated roughly on fractionation into a low boiling and a high boiling portion, which were saponified separately with alcoholic potash. On acidification, the portion of lower boiling point yielded an oily acid containing a little solid, and that of higher boiling point a solid acid contaminated with a little oil.

n-Pentenecarboxylic Acid, $\text{CH}_2 \cdot \text{CH} \cdot [\text{CH}_2]_3 \cdot \text{CO}_2\text{H}$.—The liquid acid, which was only obtained in small quantity, was found to be easily volatile with steam, and was therefore separated from the solid acid by steam distillation. The oil thus obtained boiled between 215° and 220° , and did not solidify in a good freezing mixture. It mixed readily with the ordinary organic solvents, but was comparatively slightly soluble in water. It absorbed bromine in chloroform solution, and its sodium salt at once decolorised potassium permanganate in aqueous solution at the ordinary temperature.

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0.1264 gave 0.2942 CO₂ and 0.1016 H₂O. C = 63.5; H = 8.9.C₆H₁₀O₂ requires C = 63.2; H = 8.8 per cent.

The small quantity at our disposal precluded further purification, but the above data are sufficient to show that the acid is *n*-pentene-carboxylic acid, a normal product of the electrolysis.

n-Decanedicarboxylic Acid, CO₂H·[CH₂]₁₀·CO₂H.—The solid acid obtained from the fraction of higher boiling point, which constituted by far the larger proportion of the mixed esters, was freed from the liquid acid by steam distillation. It was finally dissolved in much boiling water, from which it separated on cooling in the form of pearly scales melting at 126.5—127°. Komppa gives 125.5—127° as the melting point of his electrosynthetic acid.

0.1551 gave 0.3555 CO₂ and 0.1320 H₂O. C = 62.52; H = 9.46.C₁₂H₂₂O₄ requires C = 62.61; H = 9.56 per cent.0.1428 barium salt gave 0.0902 BaSO₄. Ba = 37.2.C₁₂H₂₀O₄Ba requires Ba = 37.5 per cent.

The acid is thus the normal product of the electrosynthesis.

Preparation of n-Decanedicarboxylic Acid from ω-Bromundecylic Acid.

Nördlinger states that Brunner's bromundecylic acid cannot be converted by the action of potassium cyanide into the corresponding cyanundecylic acid. He consequently employed for this transformation the methyl and ethyl esters obtained by the addition of hydrogen bromide to the corresponding esters of undecylenic acid (see preceding paper). In view, however, of the comparative stability of the ω-bromo-acid, we considered it probable that replacement of bromine by cyanogen could be effected in a neutral salt of the acid; this we found to be the case.

5.3 grams of ω-bromundecylic acid were dissolved in 20 c.c. of normal caustic soda solution, 1.6 grams of potassium cyanide were added, and the liquid was then made up to 100 c.c. The solution was heated on the water-bath for 12 hours, during which time a considerable amount of a brownish, flocculent precipitate was deposited. This was removed by filtration, and the filtrate saturated with hydrogen chloride. An oily cyano-acid separated, which partially solidified on cooling. After heating the mixture on the water-bath in a reflux apparatus for 3 hours, the oil was completely transformed into a cake of small crystals. The mixture on cooling deposited more crystals, which were filtered off together with the original cake, washed, and recrystallised from boiling water. The substance obtained melted at 123—124°, but on subsequent recrystallisation, the melting point rose to 126.5°.

Nördlinger gives 124.5—125.5° for his acid. 1.65 grams of the pure substance were thus obtained.

0.0900 gave 0.2060 CO₂ and 0.0776 H₂O. C = 62.42; H = 9.58.

C₁₂H₂₂O₄ requires C = 62.61; H = 9.56 per cent.

0.1458 required 25.1 c.c. *N*/20 NaOH for neutralisation. Replaceable H = 0.861. Calculated for C₁₀H₂₀(CO₂H)₂ replaceable H = 0.869.

On direct comparison, the acid was found to be identical in every respect with the electrosynthetic acid. This fact is conclusive evidence of the normal structure of undecylenic acid, and affords additional confirmation of the formulæ ascribed to the various substances mentioned in the preceding paper.

Nördlinger obtained a very impure product from the esters which he employed, and consequently a very small yield of the purified decanedicarboxylic acid. On the other hand, the yield from the sodium salt of ω -bromundecylic acid is equal to 40 per cent. of the theoretical, and the substance is at once obtained in a state approximating to purity.

Solubility of n-Decanedicarboxylic Acid.—The chief point in which Nördlinger and Komppa have obtained results in absolute discordance from ours is the solubility of the acids in water. This point is of importance, as it affords the only available numerical means (besides the melting point) for a comparison of their acid with ours. The solubility of our electrosynthetic acid is exactly that of the acid we prepared from ω -bromundecylic acid, and yet it is entirely divergent from the solubility of the acids obtained in similar ways by Nördlinger and Komppa, as the following numbers show:

	Nördlinger.	Komppa.	W. and L.
100 parts of water dissolve at 23°.....	0.005	0.0059	0.003
" " " 100°.....	0.113	0.105	0.368

It thus appears that our acid is less soluble at 23°, and more soluble at 100°, than Nördlinger's and Komppa's acids. The difference in solubility at the lower temperature need not, however, be insisted on, as the magnitude measured is very small. On the other hand, the difference at 100° is far too great to be explained by any ordinary experimental error. Thus Komppa states that 100 c.c. of the solution saturated at 100° required 9.2 c.c. of decinormal soda solution for neutralisation, whilst a similar quantity of the saturated solution of our acid would require more than 30 c.c.

As we found the solubility of the acid near the boiling point varied very rapidly with the temperature, we determined the solubility at different intermediate temperatures, with the following results:

Temperature.	Parts dissolved by 100 parts of water.
23°	0·003
28	0·005
54	0·027
84	0·120
98	0·306
100	0·368

In each case, the solubility was determined by titrating a weighed quantity of the saturated solution by means of a twentieth-normal solution of caustic soda which had been standardised against the acid itself, phenolphthalein being used as indicator. At 54° and above, the filtration was conducted by means of a small suction filter immersed in the liquid itself.

The accompanying curve shows that our acid has a solubility at 82° equal to that given by Komppa and Nördlinger for 100°.

Solubility curve of normal decanedicarboxylic acid.

It is well known that the solubility of the members of the series of normal saturated dibasic acids with an even number of carbon atoms is smaller than the solubility of the members with an odd number of carbon atoms. This regularity persists with the higher members of the series, as we see from the following table, which incorporates the solubility results for the ordinary temperature given in this and the preceding paper.

Acid (even).		Solubility (parts in 100 of water).		Acid (odd).	
Adipic	$C_6H_{10}O_4$	1·5	4·5	$C_7H_{12}O_4$	Pimelic
Suberic	$C_8H_{14}O_4$	0·14	0·12	$C_9H_{16}O_4$	Azelaic
Sebacic	$C_{10}H_{18}O_4$	0·01	0·014	$C_{11}H_{20}O_4$	Nonanedicarboxylic
Decanedicarboxylic...	$C_{12}H_{22}O_4$	0·003	0·004	$C_{13}H_{24}O_4$	Brassylic

Salts of n-Decanedicarboxylic Acid.—The description given by Nördlinger of the salts of his acid differs in many points of detail from what we found with the acid we had prepared, although there is a general resemblance in behaviour. For our experiments, we used a solution containing 0.64 gram of sodium salt in 100 c.c. With calcium nitrate, this gave a flocculent precipitate which settled readily; no further precipitate appeared when the clear liquid was boiled. Nördlinger states that both the calcium and barium salts are less soluble in boiling than in cold water. This is certainly the case to a slight extent with the barium salt, but we were unable to detect, in the case of the calcium salt, any appreciable difference in solubility at the ordinary temperature and at the boiling point. Strontium nitrate gave no precipitate at the ordinary temperature with the above solution, but gave a very slight precipitate on boiling. Magnesium nitrate gave no precipitate at any temperature; but a solution containing four times as much sodium salt gave a precipitate with this reagent on standing. Mercuric chloride gave a bulky, finely divided, precipitate, which did not coagulate readily on heating. Nördlinger states that his acid gave no precipitate with mercuric chloride, but only a slight opalescence.

Notwithstanding these differences, we are inclined to think that both Nördlinger and Komppa had *n*-decanedicarboxylic acid in their hands, Nördlinger's acid having been derived from a quantity of ω -bromundecylic ester, which must have been contained in the ester he prepared from undecylenic ester.

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