

## XX.—*Preparation of Adipic acid and some of its Derivatives.*

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IN the course of an investigation of some derivatives of adipic acid and their condensation products, large quantities of the acid were required, but as Wislicenus' method (*Annalen*, 1867, **144**, 221) of preparing it, namely, heating  $\beta$ -iodopropionic acid with silver, was found to be tedious and unsatisfactory, other methods were investigated. According to Laurent (*Ann. Chim. Phys.*, [2], **66**, 166), Bromeis (*Annalen*, 1840, **35**, 105), and Malaguti (*Ann. Chim. Phys.*, 1846, [3], **16**, 84), adipic acid is easily prepared by oxidising fats with nitric acid, sebaccic acid being formed as an intermediate product; in fact, a method of obtaining adipic acid from sebaccic acid by oxidising the latter with nitric acid is given in detail by Arppe (*Zeit. f. Chem.*, 1865, 300). The following is an account of my attempts to prepare adipic acid by these methods.

*Action of Nitric acid on Sebaccic acid.*—Witt's method (*Ber.*, 1874, **7**, 220) for preparing sebaccic acid gives very satisfactory results. Castor oil is saponified with sodium hydroxide, and the soap obtained is heated until the evolution of octylic alcohol ceases; it is then dissolved in water, and the acid precipitated by means of hydrochloric acid.

Arppe (*loc. cit.*) states that he oxidised sebaccic acid by heating it with nitric acid, expelled the excess of the latter, and crystallised the residue from hot water. The crystals, after being dried and heated until they fused, were powdered when cold and then shaken with ether, which readily dissolves the adipic acid, but not the succinic acid, as the latter is insoluble in ether.

On heating sebaccic acid on a water bath for four hours with a

mixture of equal parts of nitric acid (sp. gr. 1.5) and water, driving off the nitric acid, and shaking the dried, powdered residue with a small amount of ether, part of it was dissolved, and the residue left on evaporating the solution to dryness was purified by recrystallisation from water. It formed colourless plates melting at 127°. On adding more ether, the remainder of the product dissolved, and from this solution crystals were obtained identical in appearance and crystalline form with the first fractions and with the original acid; and they all melted at 127°. Nitric acid, therefore, of this strength has no action on sebacic acid.

The same specimen of sebacic acid was now heated on a water bath for four hours with a more concentrated acid, namely, nitric acid diluted with half its volume of water. In this case, also, no oxidation took place.

Sebacic acid was then heated on a water bath for 48 hours with fuming nitric acid; on allowing the liquid to cool, flat, colourless plates were deposited which were collected and washed first with dilute nitric acid and then with water, and finally recrystallised from hot water; the flat crystals which were deposited melting at 127°. The strongly acid mother liquor was then evaporated to dryness, and the residue dissolved in boiling water and allowed to crystallise; these crystals also melted at 127°. Their identity with sebacic acid was established by a combustion.

0.2578 gave 0.5598 CO<sub>2</sub> and 0.2095 H<sub>2</sub>O. C = 59.2; H = 9.03.

C<sub>10</sub>H<sub>18</sub>O<sub>4</sub> requires C = 59.41; H = 8.91 per cent.

It was thus shown that sebacic acid is not oxidised by boiling with nitric acid, but crystallises out unchanged.

*Oxidation of Sebacic acid by Potassium Permanganate.*—Sebacic acid is slowly oxidised by potassium permanganate in neutral, alkaline, and acid solutions; the yield, however, was so small in each case as to preclude investigation. With neutral permanganate, a faintly acid substance was obtained melting at 104–112°. The silver salt prepared by precipitating a neutral solution of the ammonium salt with silver nitrate, gave 28.8 per cent. of silver on analysis. (Adipic acid requires Ag = 60.0 per cent.) With acid and alkaline permanganate, faintly acid substances were obtained which gave no sharp melting point.

#### *Preparation of Adipic acid from Beef Suet.*

Malaguti (*loc. cit.*) states that adipic acid may be easily obtained by heating beef suet with ordinary nitric acid in a flask fitted with a reflux condenser, until the oily layer disappears. The contents of the flask are then concentrated on a water bath until the liquid solidifies

on cooling, and the crystals are collected, washed first with nitric acid and then with water, and finally recrystallised from water; the crystals, said to consist of adipic acid, melt at  $130^{\circ}$ , whereas adipic acid melts at  $148-149^{\circ}$ . In repeating this experiment, 500 grams of clarified beef suet were treated with about 200 c.c. of fuming nitric acid; the action, which at first was very violent, quickly subsided, and the flask was then heated on a sand bath, nitric acid being added from time to time to replace loss by evaporation; after 32 hours digesting the oily layer had disappeared. The contents of the flask were evaporated on the water bath to remove the excess of nitric acid, and the viscid residue was dissolved in boiling water; on evaporating the solution to the consistence of a syrup, and leaving it for a week, the whole solidified to a gritty, crystalline mass. This, according to Malaguti, should consist of nearly pure adipic acid, but I found that, after recrystallisation from water, it melted at  $109-112^{\circ}$ . The acid is readily soluble in ammonia, and is reprecipitated by hydrochloric acid. The silver salt, obtained as a white amorphous precipitate on adding silver nitrate to a neutral solution of the ammonium salt, was analysed.

0.7542 gave 0.4172 AgCl. Ag = 55.14 per cent.

A combustion of the recrystallised acid gave results which agreed neither with the formula of sebacic acid nor with that of adipic acid, and, judging from this and from the ill-defined melting point, it cannot be regarded as a simple acid but must be a mixture of two or more acids. An attempt was made to separate the various constituents by treating the dried and powdered product with successive small quantities of anhydrous ether, and in this way two fractions of definite melting point were isolated. The first ethereal extract, on evaporation, left a white, crystalline residue, which separated in colourless plates on slow evaporation of its alcoholic solution; the crystals melted at  $122-129^{\circ}$ . The crystalline residue from the second ethereal extract melted at  $124-125^{\circ}$ , and that from the third and fourth at  $127-128^{\circ}$ . The first two fractions were too small to deal with. The third and fourth were mixed, dissolved in dilute ammonia, the excess of ammonia driven off, and silver nitrate added; the white, amorphous precipitate which was thrown down gave the following result on analysis.

0.2544 gave 0.1317 Ag. Ag = 51.72 per cent.

The substance is evidently sebacic acid, as this melts at  $127-128^{\circ}$ , and its silver salt contains 51.92 per cent. of silver.

The residue left after the product had been extracted 10 times successively with ether melted at  $100-112^{\circ}$ ; and on crystallisation

from alcohol yielded colourless plates melting at 105—107°. On analysis it gave the following results.

0.1228 gave 0.2581 CO<sub>2</sub> and 0.0937 H<sub>2</sub>O. C = 57.32; H = 8.47.

Azelaic acid, C<sub>7</sub>H<sub>14</sub>(COOH)<sub>2</sub>, melts at 106°, and contains C = 57.45 and H = 8.51 per cent.

The silver salt gave the following results on analysis.

0.226 gave 0.1216 Ag = 53.8 per cent. of silver.

This acid appears to be azelaic acid.

The action of ordinary nitric acid on beef suet was next tried. 50 grams of purified beef suet were heated on a water bath for 48 hours with 250 c.c. of nitric acid, sp. gr. 1.42, the excess of acid driven off, and the whole evaporated to dryness. The viscid, semi-crystalline residue was boiled with water, in which it nearly all dissolved, and the solution concentrated; on standing for three days, hard, gritty crystals were deposited, which, after recrystallisation from hot water, melted at 95—96°. The amorphous, white silver salt yielded the following result on analysis.

0.372 gave 0.1861 Ag. Ag = 50.2 per cent.

The acid was again carefully recrystallised from water, and analysed.

0.1085 gave 0.2422 CO<sub>2</sub> and 0.0905 H<sub>2</sub>O. C = 60.88; H = 9.28.

0.2722 ,, 0.6065 ,, 0.2312 ,, C = 60.78; H = 9.43.

The results are in accord with those which would be furnished by a dibasic acid, C<sub>11</sub>H<sub>20</sub>O<sub>4</sub>; this requires C = 61.1; H = 9.26 per cent.; and its silver salt Ag = 50.7 per cent.

It is evident, from the foregoing results,

1. That the action of nitric acid on beef suet is a complex one.
2. That the products vary with the concentration of the acid used.
3. That sebacic acid and azelaic acid are amongst the products of the action of fuming nitric acid on beef suet, whilst ordinary nitric acid gives an acid having the formula C<sub>11</sub>H<sub>20</sub>O<sub>4</sub>.
4. That adipic acid is not formed by the oxidation of sebacic acid.

The adipic acid used in the preparation of the derivatives subsequently described was obtained by a modification of V. Meyer's process (*Ber.*, 1887, **19**, 3244, and *Ber.*, 1888, **21**, 24). Glycerol was converted into glyceric acid by slow oxidation with nitric acid, the excess of nitric acid driven off by heating the products on a water bath, and the crude glyceric acid diluted with water until it had a sp. gr. of 1.26. 176 grams of iodine were then gradually added to 100 c.c. of the solution of the crude acid, previously mixed with

22 grams of red phosphorus, and the viscid, brown liquid which remained after the action was over was well cooled; the crystalline scales of  $\beta$ -iodopropionic acid, which separated, were collected on a vacuum filter and recrystallised from carbon bisulphide. The  $\beta$ -iodopropionic acid was converted into adipic acid by heating it with finely-divided copper at  $160^\circ$ .

*$\alpha$ -Monobromadipic acid*,  $\text{COOH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{COOH}$ .—This acid was obtained by Gal and Gay-Lussac (*Annalen*, 1870, **155**, 250), but not in a pure state. Adipic acid (1 mol.) was heated with bromine (2 mols.) at  $160^\circ$  in a sealed tube for two hours. When cold, the contents of the tube, which consisted of a nearly colourless, crystalline mass, were extracted with anhydrous ether, and the residue left on the evaporation of the ether was recrystallised from absolute alcohol; the colourless crystals obtained melted at  $131^\circ$ .

0.1196 gave 0.7994 AgBr. Br = 35.98.

0.1146 „ 0.1356  $\text{CO}_2$  and 0.0434  $\text{H}_2\text{O}$ . C = 32.2; H = 4.2.

$\text{C}_6\text{H}_9\text{O}_4\text{Br}$  requires C = 32.0; H = 4.0; Br = 35.55 per cent.

*$\alpha$ -Hydroxyadipic acid*,  $\text{COOH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{COOH}$ .— $\alpha$ -Bromadipic acid was warmed for a few minutes with a dilute solution of potash, acidified with hydrochloric acid, and shaken with ether; the ethereal solution, on evaporation, left a nearly colourless oil, which solidified almost entirely on standing. The crystals, when drained on a porous tile and recrystallised from ether, melted at  $151^\circ$ , and sublimed undecomposed. They are easily soluble in alcohol, ether, and water.

The following results were obtained on analysis.

0.2021 gave 0.3282  $\text{CO}_2$  and 0.0117  $\text{H}_2\text{O}$ . C = 44.5; H = 6.4.

$\text{C}_6\text{H}_{10}\text{O}_5$  requires C = 44.4; H = 6.1 per cent.

Monobromadipic acid, when heated with water, yields the hydroxy-acid, but the product is contaminated with large quantities of uncrystallisable bye-products, which render its purification difficult.

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