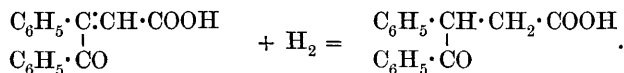


XI.—*Reduction of Desyleneacetic Acid, and the Constitution of Zinin's Pyroamaric Acid.*

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THE ease with which desyleneacetic acid may be prepared by the oxidation of anhydrazetonebenzil with sodium hypobromite led us to study some of the reactions of this compound. In the present communication, we give an account of its behaviour towards reducing agents.

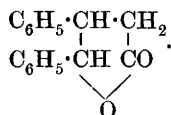
When dissolved in acetic acid and treated with zinc dust, desyleneacetic acid is converted into Victor Meyer and Oelkers's *desylacetic acid*,



By the limited action of sodium amalgam on an aqueous solution of sodium desyleneacetate, the same product is obtained. Excess of sodium amalgam, however, carries the reduction further, and $\beta\gamma$ -diphenyl- γ -

hydroxybutyric acid, $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{COOH} \\ | \\ \text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{OH} \end{array}$, is formed, which, when

liberated from its salts, speedily changes into the *lactone*



By boiling desyleneacetic acid for a few minutes with fuming hydriodic acid, it yields a mixture of *desylacetic acid* and *diphenylcrotonolactone*, behaving, in this respect, like desylenemalonic acid, except that, in the case of the latter compound, the reaction is attended with elimination of carbon dioxide (Japp and Davidson, Trans., 1895, 67, 136). By boiling desyleneacetic acid for some hours with hydriodic acid and amorphous phosphorus, the reaction is carried further, and both the primary products of the reduction are converted into $\beta\gamma$ -diphenylbutyric acid, $\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CH}(\text{C}_6\text{H}_5) \cdot \text{CH}_2 \cdot \text{COOH}$. Comparison of this substance with a specimen of *pyroamaric acid** showed that the two were identical. Pyroamaric acid was first obtained by Zinin (*Jahresbericht*, 1877, 813) by fusing amaric acid with caustic potash, and was regarded by him as an ethylbenzylbenzoic acid. Klingemann

* We were indebted for this specimen to Dr. Felix Klingemann, who prepared it by the fusion of β -dehydroamaric acid with caustic potash—a reaction discovered by him.

(*Annalen*, 1893, 275, 81) first suggested that it might be a diphenylbutyric acid, and showed that it was not identical with α -diphenylbutyric acid.

Incidentally, it was observed that when desyleneacetic acid is boiled with aqueous caustic potash it is hydrolysed, yielding deoxybenzoïn. Desylenemalonic acid is stable under these conditions.

EXPERIMENTAL.

Reduction of Desyleneacetic Acid with Zinc Dust and Acetic Acid.—Five grams of desyleneacetic acid were dissolved in glacial acetic acid, excess of zinc dust was added, and the whole was boiled for about an hour, after which the liquid was filtered and poured into water. The precipitated substance was recrystallised twice from benzene, from which it was deposited in the characteristic octahedra of desylacetic acid melting at 160° . It was stable towards permanganate in the cold, showing that it was free from desyleneacetic acid. Found: C = 75.57; H = 5.68. Calculated for $C_{16}H_{14}O_3$: C = 75.59; H = 5.51 per cent.

Reduction of Desyleneacetic Acid with Sodium Amalgam.—Five grams of desyleneacetic acid were dissolved in sodium carbonate and treated with 180 grams of 2.5 per cent. sodium amalgam, passing a current of carbon dioxide through the liquid during the entire process. On acidifying the solution, a gummy substance was precipitated, from which, by crystallisation from benzene, three substances were isolated: (1) unchanged desyleneacetic acid; (2) desylacetic acid, which formed colourless octahedra melting at 161° ; and (3) a substance crystallising in needles melting at 112 – 113° . The two former were deposited together and could be separated mechanically, the brownish colour of the crystals of impure desyleneacetic acid allowing of their being readily distinguished from the colourless octahedra of desylacetic acid. The third substance separated from the benzene mother liquor.

The experiment was repeated, using 400 grams of 2.5 per cent. sodium amalgam to 5 grams of desyleneacetic acid. This time, only the compound melting at 112 – 113° was obtained. It was purified by recrystallisation from a mixture of benzene and light petroleum. On analysis, it gave figures agreeing with the formula $C_{16}H_{14}O_2$.

0.1284 gave 0.3799 CO_2 and 0.0685 H_2O . C = 80.69; H = 5.92.

0.1214 „ 0.3586 CO_2 „ 0.0644 H_2O . C = 80.54; H = 5.89.

$C_{16}H_{14}O_2$ requires C = 80.67; H = 5.88 per cent.

This compound is, as already mentioned, the lactone

$$\begin{array}{c} C_6H_5 \cdot CH \cdot CH_2 \\ | \quad \quad | \\ C_6H_5 \cdot CH \quad CO \\ \quad \quad \diagdown \quad / \\ \quad \quad \quad O \end{array}$$

derived from $\beta\gamma$ -diphenyl- γ -hydroxybutyric acid. The acid, freshly precipitated from solutions of its salts, redissolves in sodium carbonate, but the crystallised lactone is apparently quite insoluble in sodium carbonate, and dissolves only with difficulty in a warm solution of sodium hydroxide.

Reduction of Desyleneacetic Acid with Fuming Hydriodic Acid.—Three grams of desyleneacetic acid were boiled with the strongest fuming hydriodic acid (sp. gr. 2.0) for 5 minutes. The product of the action was washed with water, dissolved in ether, and freed from iodine by treatment with sulphurous acid. From the ethereal solution, sodium carbonate extracted an acid which crystallised from benzene in octahedra melting at 160° , and was in all respects indistinguishable from desylacetic acid. The non-acid substance, which remained after expelling the ether, crystallised from benzene in tufts of needles melting at 151.5° and was identical with Klingemann's diphenylcroto-lactone (*Annalen*, 1892, 269, 134; cf. also Japp and Davidson, *loc. cit.*).

Reduction of Desyleneacetic Acid with Hydriodic Acid and Amorphous Phosphorus.—Five grams of desyleneacetic acid were boiled with 75 grams of hydriodic acid (sp. gr. 1.7) and 7 grams of amorphous phosphorus for 4 hours. The organic substance was extracted with ether, and, after the usual treatment of the ethereal solution with sulphurous acid, the organic acid was extracted twice with a solution of sodium carbonate. A small quantity of a neutral oil, which was not further examined, remained dissolved in the ether. Two organic acids were obtained. One of these, which was precipitated in a crystalline form from the first sodium carbonate extract, was sparingly soluble in ether and melted at $228-230^\circ$; the quantity was too small for further investigation. The second extract gave an acid which was oily when first precipitated, but speedily solidified. It was obtained in large crystals by spontaneous evaporation of its ethereal solution, and these were further purified by recrystallisation from a mixture of ethylic acetate and light petroleum, which deposited the compound in oblique plates melting constantly at $96-97^\circ$. Analysis gave figures agreeing with the expected formula of $\beta\gamma$ -diphenylbutyric acid,



0.1457 gave 0.4270 CO_2 and 0.0877 H_2O . C = 79.93; H = 6.68.

$\text{C}_{16}\text{H}_{16}\text{O}_2$ requires C = 80.00; H = 6.66 per cent.

A comparison of this substance with a specimen of Zinin's pyroamaric acid (*v. supra*) showed that the two substances were identical. Both crystallised from a mixture of ethylic acetate and light petroleum in the same oblique plates, and a simultaneous deter-

mination of the melting points, made in the same bath, gave 96—97° in both cases.

As already pointed out, the hitherto unknown constitution of pyroamaric acid is thus ascertained.

Action of Aqueous Caustic Potash on Desyleneacetic Acid.—In an experiment made with a different object, it was noticed that, when desyleneacetic acid was boiled with aqueous caustic potash, an oil, smelling like a benzenoid ketone, separated. Two grams of the acid were therefore boiled with excess of strong caustic potash for 4—5 hours. After extracting the oily substance with ether, the alkaline solution was acidified, but gave only a slight turbidity, showing that practically no desyleneacetic acid was left. The substance which remained on evaporating the ether solidified to a crystalline mass. It was purified by recrystallisation, first from benzene, and afterwards twice from alcohol, and was thus obtained in colourless leaflets, melting at 59°. Analysis gave figures agreeing with the formula $C_{14}H_{12}O$. Found: C = 85.38; H = 6.28. Calculated: C = 85.71; H = 6.12 per cent.

This is the formula of deoxybenzoin, which melts at 60°, and the other physical properties are also those of that compound. A cold, supersaturated alcoholic solution of the compound at once began to crystallise on adding a crystal of deoxybenzoin.

We did not attempt to isolate the other product of the hydrolysis.

As Japp and Davidson (*Trans.*, 1895, **67**, 135), in preparing desylenemalonic acid, heated it for a long time with caustic soda, it was of interest to know whether it was in any way decomposed by this treatment. We therefore heated desylenemalonic acid for many hours, both with caustic potash and with caustic soda, but no separation of neutral substance occurred, and the acid was recovered unchanged.

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