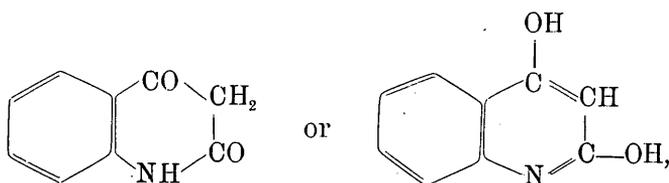


Formation of γ -Oxycarbostryl from *o*-Nitrobenzoylacetic Acid.

By

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γ -Oxycarbostryl or 2:4-dihydroxyquinoline,



the inner anhydride of *o*-aminobenzoylacetic acid, was first obtained by BAEYER and BLOEM (Ber., 1882, 15, 2151), by heating *o*-aminophenylpropionic acid with concentrated sulphuric acid to 145°, in their attempt to prepare *o*-aminobenzoylacetic acid. Owing to the close relationship which exists between *o*-aminobenzoylacetic acid and several members of the indigo group, many other investigators have attempted to prepare this acid. All these attempts have, however, been unsuccessful, the product being always found to be γ -oxycarbostryl, which can also be obtained in other ways. Thus it was obtained by FRIEDLANDER and WEINBERG (Ber., 1882, 15, 2683) by the potash-fusion of γ -chloro- or γ -bromo-carbostryl; by BISCHOFF (Ber., 1889, 22, 387; Ann., 1889, 251, 377), by the reduction of ethyl *o*-nitrobenzoylacetate

in alcoholic solution with tin and hydrochloric acid; by CAMPS (D. R. P., 1898, 102894; Ber., 1899, 32, 3228; Arch. Pharm., 1899, 237, 690; 1901, 239, 601) by treating an absolutely dry solution of ethyl acetanthranilate in toluene with metallic sodium, and also by boiling *o*-acetophenyl urethane with an aqueous alcoholic solution of caustic soda for several hours. ERDMANN (Ber., 1899, 32, 3570) obtained it by the action of metallic sodium on a mixture of ethyl anthranilate and ethyl acetate, ethyl acetanthranilate which is first formed giving off alcohol spontaneously or more easily on acidification. The BADISCHE ANILIN- UND SODA-FABRIK (D. R. P., 1900, 117167) patented a method of preparing it by heating an alkali or alkaline earth salt of acetanthranilic acid with dry alkali or alkaline earth to 150°.

During the course of some experiments with *o*-nitrobenzoyl-acetic acid, it was observed that this acid gave γ -oxycarbostyryl on reduction with ferrous sulphate and ammonia. The use of ferrous sulphate and an alkali as a reducing agent is not new. WÖHLER in 1828 (Pogg. Ann., 13, 448) had already used ferrous sulphate in presence of baryta to reduce picric acid and obtained picramic acid. BAEYER and BLOEM (Ber., 1882, 15, 2147) reduced ethyl *o*-nitrophenylpropionate by pouring its solution in ammonia into a saturated solution of ferrous sulphate, and obtained ethyl *o*-aminobenzoylacetate. Many other examples of the application of this salt with one or other alkali as a reducing agent can be found in the literature of the subject.

o-Nitrobenzoyl-acetic acid was prepared according to the method described by NEEDHAM and PERKIN (Jour. Chem. Soc., 1904, 85, 148). After recrystallising from benzene, in which

it dissolves slightly, its melting point was found to be 122°. NEEDHAM and PERKIN give 117°–120° as its melting point.

Ferrous sulphate (8 grams) was dissolved in water (20 c.c.) and an excess of ammonia was added to it. *o*-Nitrobenzoylactic acid (1 gram) dissolved in ammonia was then added. The reaction took place at once in the cold, the greenish coloured ferrous hydroxide changing into the reddish coloured ferric hydroxide, which was filtered off. On neutralising the filtrate with hydrochloric acid, a colourless precipitate separated out, which was collected on a filter and drained on a porous porcelain plate. This precipitate does not dissolve in most of the ordinary organic solvents. It can be dissolved in a solution of sodium carbonate and is reprecipitated from this solution on acidification. It does not melt at 300°. All these properties correspond to those of γ -oxycarbostryl or 2:4-dihydroxyquinoline, which is the inner anhydride of *o*-aminobenzoylactic acid, the reduction-product.

A sample recrystallised from glacial acetic acid gave the following percentage of nitrogen on analysis:

0.1663 gr. substance gave 12.2 c.c. nitrogen at	
16° and 750.6 m.m.	N = 8.44%,
C ₉ H ₇ O ₂ N requires	N = 8.70%.

