treated with gramine methiodide and sodium ethoxide in ethanol.

The synthesis of 1-phenyl-3-ethyl-3,4-dihydro-β-carboline is effected by alkylation of 1-nitropropane with gramine, reduction of the product, and cyclization of the benzoyl derivative of the resulting amine.

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NOTES

The Chlorination of Anthranilic Acid

BY EDWARD R. ATKINSON AND PARKER B. MITTON

The extension to a larger scale[1] of our earlier synthesis[2] of the resolvable *d,l*-4,6,4′,6′-tetrachlorodiphenic acid required the preparation of large amounts of 3,5-dichloro-2-aminobenzoic acid. The present paper describes the conditions we found best for the direct chlorination of anthranilic acid in either glacial acetic acid or in dilute hydrochloric acid. We have also identified three of the polychloro by-products which are formed in acetic acid solution, and which have not been isolated from this reaction mixture in previous work. The most interesting of these is 2,3,4,4,5,6-hexachloro-2,5-cyclohexadiene-1-one which has previously been prepared by the chlorination of a number of other aromatic substances and which recently has been introduced as an insecticide and fungicide.[3]

Experimental

Chlorination in Glacial Acetic Acid.—The method of Elion[4] did not give satisfactory results when used with 200 g. of anthranilic acid until important modifications were introduced. At least 25 cc. of commercial glacial acetic acid was used per gram of anthranilic acid; no change in results was noted when chlorination was performed under completely anhydrous conditions. When stirring of the reaction mixture was vigorous, the rate at which chlorine gas was introduced was not a critical factor. Dilution of chlorine with air prior to use did not increase the yield of the desired product. The reaction mixture was maintained at 15–20°. Chlorination was continued until the reaction mixture gained 1.0 g. to 1.4 g. per gram of anthranilic acid used. Further chlorination led to a marked diminution in yield with a corresponding increase in polychloro by-products. In all experiments these could be removed by leaching the crude with benzene as previously described[1] but we preferred to filter the solid mixture of crude mono- and dichloroanthranilic acids directly from the reaction mixture, the by-products remaining dissolved in the acetic acid filtrate. Their isolation and identification is described below.

The crude product was dried at temperatures under 40° then leached with boiling 15% hydrochloric acid, using 20 cc. of this acid per gram of crude. The insoluble portion was the desired 3,5-dichloro-2-aminobenzoic acid, m. p. 224–226°, obtained in over-all yields of 41–50%. 5-Chloro-2-aminobenzoic acid was recovered from the hydrochloric acid solution by raising the *p*H to 6.

Chlorination in Dilute Hydrochloric Acid.—Anthranilic acid was dissolved in 15% hydrochloric acid (20 cc. per gram) and chlorinated at 15–20° as above until the reaction mixture gained 1.0 to 1.2 g. per gram of anthranilic acid used. The crude product was filtered from the reaction mixture. It melted at 210–220° and was obtained in yields of 80%. In this method the 5-chloro-2-aminobenzoic acid by-product remained dissolved in the acidic reaction mixture. After appropriate dilution with water this acid solution could be used as solvent for a subsequent chlorination reaction.

Identification of Polychloro By-products.—These were easily isolated by pouring the filtrate from chlorinations in acetic acid into a large volume of water. For example when 20 g. of anthranilic acid was chlorinated until the reaction mixture had gained 38 g. in weight very little mono- and dichloroanthranilic acids were obtained. The filtrate was poured into 2 liters of water and a colorless emulsion was obtained. After four days a mass of yellow crystals imbedded in a red tar was separated by decantation. From this material there was isolated 5 g. of 2,3,4,4,5,6-hexachloro-2,5-cyclohexadiene-1-one,[5] 1 g. of chloranil, 0.5 g. of pentachlorophenol and a red oil which must have consisted chiefly of the hexachlorocyclohexadienone since it gave 2 g. of pentachlorophenol on reduction with stannous chloride in acetic acid.[5]

In his original work on the chlorination of anthranilic acid in acetic acid solution Elion[4] poured the entire reaction mixture into a large volume of aqueous sulfite solution. No explanation for the use of sulfite was given. We have observed that if sulfite is used, hexachlorocyclohexadienone is not isolated, for this material is easily reduced by aqueous bisulfite to pentachlorophenol at room temperature.

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[1] Atkinson, Morgan, Warren, Manning, THIS JOURNAL, **67**, 1513 (1945).

[2] Atkinson and Lawler, *Ibid.*, **62**, 1704 (1940).

[3] (a) Swingle, Phillips and Gahan, U. S. Dept. Agri., Bureau Entomol. Plant Quarantine E-621 (1944); (b) Wolcott, *Caribbean Forester*, **6**, 245 (1945); (c) Ter. Horst, U. S. Patent 2,378,597 (1945).

[4] Elion, *Rec. trav. chim.*, **44**, 1106 (1925).

[5] Biltz, *Ber.*, **37**, 4009 (1904).

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Extractives of Douglas Fir and Douglas Fir Lignin Residue

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The appearance of wax-like materials of high boiling point in the hydrogenation product of lignin residue from the dilute acid hydrolysis of Douglas fir led to an investigation at the Forest Products Laboratory of the extractives present in this lignin residue and in the original wood-bark mixture. The lignin used was a residue of the Madison wood-sugar process[1] which treats sawmill waste with 0.5% sulfuric acid at 150°.

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[1] E. E. Harris and E. Beglinger, *Ind. Eng. Chem.*, **38**, 890–895 (1946).