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).

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
UNIVERSITY OF NEW HAMPSHIRE
DURHAM, NEW HAMPSHIRE
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Extractives of Douglas Fir and Douglas Fir Lignin Residue

BY IRA L. CLARK, J. R. HICKS AND E. E. HARRIS

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).

TABLE I

WAX FROM DOUGLAS FIR AND DOUGLAS FIR LIGNIN RESIDUE

Material	M. p., °C.	Sp. gr., 20 per 20	Sapon. value,	Acid value,	Ester value,	Acetyl value	Iodine (Hanus), I_2 per 100 g.	Reichert Meissl, ml. 0.1 *N* KOH per 5 g.
			mg. KOH per g.					
Hogged woodbark	53	1.05	176.8	46.1	130.7	76.8	42.3	0.43
Bark	55	1.05	194.9	46.8	148.1	80.6	37.4	.14
Lignin	61	1.05	170.4	74.2	96.2	77.1	27.8	6.7

Extraction of dried lignin residue with benzene yielded 3.9% extractives. A similar extraction with acetone yielded 7.1% extractives of which 3.6% (dry lignin basis) was benzene-soluble, the rest being soluble lignin and other materials. Extraction of wet lignin residue with acetone yielded 10.8% extractives, of which 6.9% (dry lignin basis) was benzene-soluble. Increased yields by acetone extraction of wet lignin may be attributed to improved solvent diffusion into undried cellular structure.[2] Benzene extraction of the original dried, hogged Douglas fir waste, which contained approximately 30% bark yielded 1.5% extractives. Similar extraction of sapwood alone yielded 1.1% extractives.

Benzene-soluble extractives obtained were wax-like brown and black substances. They consisted of a mixture of long chain aliphatic acids, alcohols, esters, and unidentified materials. The customary values for waxes were determined for Douglas fir wax (Table I). A petroleum ether separation of benzene extractive yielded a light brown petroleum ether-soluble fraction having lower acetyl and saponification values and a petroleum ether-insoluble fraction of higher melting point and saponification value.

A separation of a sample of 180 g. of benzene extractives by saponification and subsequent solvent extraction of the salts yielded 66% wax-saponifiable materials, 12% water-soluble materials, and 22% unsaponifiable material.

Behenic acid, lignoceric acid, and a C_{15} alcohol have been identified in the hydrogenation product from the lignin residue. These are believed to have been present originally as extractives. Further separation and characterization of the extractives is now in progress to check this.

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[2] A. J. Stamm and L. A. Hansen, *Ind. Eng. Chem.*, **38**, 413–416 (1946).

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The Homogeneous Reaction of Nitric Oxide and Carbon Monoxide

BY CHARLES P. FENIMORE

Although the interaction of carbon monoxide and nitric oxide has been studied in the neighborhood of 900°,[1] no homogeneous gas phase reaction of these compounds is reported in the literature.

$$2NO + 2CO \longrightarrow N_2 + 2CO_2 \qquad (1)$$

At 1380 to 1580° and one atmosphere pressure, a slow homogeneous reaction has been found to occur. The reaction is first order with respect to carbon monoxide and second order with respect to nitric oxide. This dependence on composition is the same as that which characterizes all other known homogeneous reactions of nitric oxide.

$$dNO/dt = -k[NO]^2[X] \quad X = Cl_2, O_2, Br_2, H_2 \qquad (2)$$

The temperature required is so high that no great accuracy in temperature measurement can be claimed. The data obtained are best correlated by

$$k = 2 \times 10^{10} e^{-49,600/RT} \text{ sec.}^{-1} \text{ mole}^{-2} \text{ liter}^2$$

Nitric oxide and carbon monoxide were prepared by reduction of nitrite ion and dehydration of formic acid, respectively.[3] The gases, either alone or sometimes with added nitrogen, were stored briefly over an aqueous sodium hydroxide solution, then by displacement of the solution forced to flow through a train consisting of calcium chloride drying tube, flowmeter and reaction tube. A sample of the unreacted gas was analyzed for nitric oxide by absorption in a dilute sulfuric acid solution of ferrous sulfate and for carbon monoxide by subsequent combustion with excess oxygen. After a steady flow rate had been established through the reaction tube and a volume of gas had been passed equal to at least ten times the volume of the tube, the extent of reaction was determined by absorption of carbon dioxide in ascarite from a known volume of gas. Before using the ascarite, air was displaced from the absorption bulb by nitrogen.

The reaction tube was of clay, ten inches long, one inch inside diameter, heated in a glowbar furnace. Temperature was measured with platinum-platinum rhodium thermocouple, uncalibrated in the temperature region of interest, using e. m. f. values from tables.[4]

The residence time of the gas in the reaction tube was calculated by dividing the volume of the tube by the volume of gas at the prevailing temperature and pressure. Inasmuch as a volume change accompanies the reaction, an average was struck between the volumes of the unreacted and the reacted gas for this calculation. Between 1000 and 1300° only a zero order surface reaction was observed. At 1317°, the reaction velocity was

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[1] Musgrave and Hinshelwood, *J. Chem. Soc.*, **56** (1933).

[2] Schumacher, "Chemische Gasreaktionen," Edwards Bros., Ann Arbor, Michigan, 1943, p. 311.

[3] Farkas and Melville, "Experimental Methods in Gas Reactions," The Macmillan Co., New York, N. Y., 1939, chapt. III.

[4] Lange, "Handbook of Chemistry," 5th ed., p. 845.