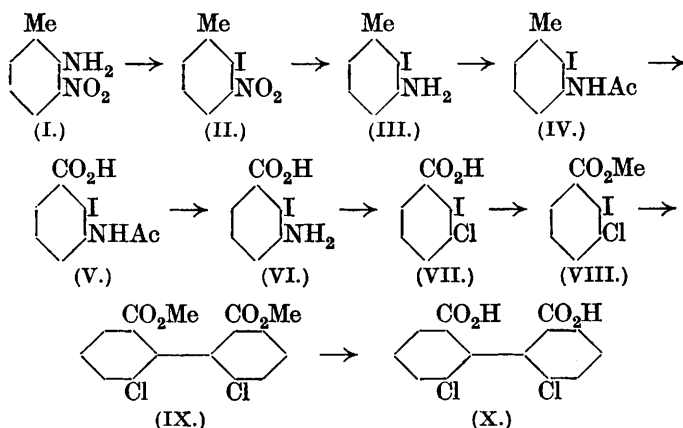


CCXIII.—*The Molecular Configurations of Polynuclear Aromatic Compounds. Part IV. 6:6'-Dichlorodiphenic Acid; its Synthesis and Resolution into Optically Active Components.*

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IN pursuing the inquiry into the nature of the configuration of diphenyl derivatives discussed in previous papers of this series (T., 1922, **121**, 614; this vol., p. 779), it is of importance to ascertain to what extent their resolvability into optically active components is affected by variation of the nature of the substituents or their orientation.

In connexion with the former of these questions, we have investigated 6:6'-dichlorodiphenic acid (X), of which the synthesis is represented by the following scheme :



The only difficulties encountered in this series of reactions arose from the mobility of the halogen atom in 2-iodo-*m*-toluidine (III) and in 2-iodo-*m*-aminobenzoic acid (VI). On this account, the preparation of the former from the corresponding nitro-compound must be carried out either by means of ferrous sulphate and ammonia (Wheeler and Liddle, *Amer. Chem. J.*, 1909, **42**, 441), or, if stannous chloride and hydrochloric acid be employed, only at a low temperature (compare Burton and Kenner, T., 1922, **121**, 675). Similarly, the hydrolysis of 2-iodo-3-acetylaminobenzoic acid (V) by means of hydrochloric acid must not be carried out above 100°, and even at this temperature iodine will be liberated if the reaction be too prolonged. Again, the amino-acid could not be prepared

by acid reduction of 2-iodo-3-nitrobenzoic acid owing to elimination of the iodine. In regard to the question as to whether the mobility of the halogen is favoured by salt formation (Burton and Kenner, *loc. cit.*) it may be noted that the iodotoluidine may be distilled in steam from alkaline solution without decomposition, and the hydrochloride of the amino-acid loses iodine at its melting point, whilst *iodoacetylaminobenzoic acid* (V) shows no tendency to decomposition under these conditions. This point is, however, one requiring further investigation.

The resolution of 6:6'-dichlorodiphenic acid was accomplished by fractional crystallisation of its brucine salts. The free acids respectively liberated from the two salts furnished sodium salts, solutions of which exhibited specific rotations of $+21.43^\circ$ and -20.18° , respectively.

These results confirm the correctness of the assumption that the cause of the stereoisomerism of the various nitrodiphenic acids previously investigated by two of us is not to be sought in any property peculiar to the nitro-group. It remains to be seen whether a racemic acid, isomeric with that now described, is obtainable from the corresponding dichlorophenanthraquinone.

EXPERIMENTAL.

2-Iodo-3-acetylaminobenzoic Acid.—2-Iodo-*m*-toluidine was prepared in good yield by gradual addition of a solution of 2-iodo-3-nitrotoluene (20 grams) in glacial acetic acid (134 grams) to a solution of stannous chloride (160 grams) in concentrated hydrochloric acid (160 c.c.) below 25° . The double tin salt which had separated after twelve hours was worked up in the usual manner.

A suspension of 2-iodoaceto-*m*-toluidide (10 grams) in boiling water (1200 c.c.), containing magnesium sulphate (9.3 grams), was oxidised by gradual addition of potassium permanganate (15.4 grams). The *2-iodo-3-acetylaminobenzoic acid* thus prepared formed colourless needles, m. p. 199° . It was hydrolysed by heating 20 grams with concentrated hydrochloric acid (80 c.c.) at 100° until vapours of iodine appeared in the flask; on cooling, the *hydrochloride* of *2-iodo-3-aminobenzoic acid* (7.5 grams), m. p. $262-263^\circ$ (with evolution of iodine), separated (Found: N = 4.76, equivalent = 145. $C_7H_6O_2NI \cdot HCl$ requires N = 4.68 per cent; equivalent = 149.5).

3-Chloro-2-iodobenzoic Acid.—This compound, prepared from the above amino-acid in the usual manner, separates from water in plates, m. p. $137-138^\circ$ (Found: C = 29.49; H = 1.58. $C_7H_4O_2ClI$ requires C = 29.78; H = 1.42 per cent.). The *methyl ester* (Found: C = 32.91; H = 2.00. $C_8H_6O_2ClI$ requires C = 32.38; H = 2.03

per cent.) boils at $182^{\circ}/28$ mm., and the *ethyl* ester at $175^{\circ}/15$ mm.

6 : 6'-*Dichlorodiphenic Acid*.—The methyl ester of this acid was prepared by gradual addition of copper powder to an equal weight of methyl chloriodobenzoate at 180° , and subsequent heating of the mixture at 230 – 240° for one hour. The *ethyl* ester is prepared in a similar manner.

r-6 : 6'-*Dichlorodiphenic acid*, $C_{12}H_6Cl_2(CO_2H)_2$, crystallises from alcohol in feathery clusters of needles, m. p. 288° (Found : C = 54.04; H = 2.16. $C_{14}H_8O_4Cl_2$ requires C = 54.02; H = 2.57 per cent.). The *methyl* ester separates from benzene in almost rectangular prisms, m. p. 156° , whilst the *ethyl* ester crystallises from alcohol in rhombic plates, m. p. 103 – 104° (Found : C = 58.88; H = 4.12. $C_{18}H_{16}O_4Cl_2$ requires C = 58.81; H = 4.36 per cent.).

Resolution of r-6 : 6'-Dichlorodiphenic Acid.

By repeated fractional crystallisation of the mixture of salts prepared from 2 grams of the racemic acid and 6 grams of hydrated brucine, 2.3 grams of the pure, less soluble salt, and 1.35 grams of the pure, more soluble salt were separated with moderate ease.

Brucine 1-6 : 6'-*dichlorodiphenate*, $C_{14}H_8O_4Cl_2 \cdot 2C_{23}H_{26}O_4N_2 \cdot 3H_2O$, consists of rectangular prisms, m. p. 235° , and is the less soluble of the two salts thus obtained. For a 1.23 per cent. solution in chloroform, $[\alpha]_D^{25} + 1.97^{\circ}$ (Found : $H_2O = 4.66$. $C_{60}H_{60}O_{12}N_4Cl_2 \cdot 3H_2O$ requires $H_2O = 4.68$ per cent. Found : for the anhydrous material dried at 120° , N = 5.18. $C_{60}H_{60}O_{12}N_4Cl_2$ requires N = 5.09 per cent.).

Brucine d-6 : 6'-*dichlorodiphenate*, $C_{14}H_8O_4Cl_2 \cdot 2C_{23}H_{26}O_4N_2 \cdot 1\frac{1}{2}H_2O$, forms rectangular plates, m. p. 163° (decomp.). For a 1.16 per cent. solution in chloroform, $[\alpha]_D^{25} - 58.62^{\circ}$ (Found : $H_2O = 2.43$. $C_{60}H_{60}O_{12}N_4Cl_2 \cdot 1\frac{1}{2}H_2O$ requires $H_2O = 2.40$ per cent. Found : for the anhydrous material dried at 120° , N = 5.17. $C_{60}H_{60}O_{12}N_4Cl_2$ requires N = 5.09 per cent.).

d-6 : 6'-*Dichlorodiphenic acid*, $C_{12}H_6Cl_2(CO_2H)_2$, from the brucine salt, forms rectangular plates, m. p. 259° . For a 0.69 per cent. solution of the sodium salt, $[\alpha]_D^{25} - 20.18^{\circ}$. The acid recovered from this solution furnished a dextrorotatory solution in ether, which, however, was too dilute for anything more than qualitative observation.

l-6 : 6'-*Dichlorodiphenic acid*, $C_{12}H_6Cl_2(CO_2H)_2$, rectangular plates, m. p. 259° , furnished a sodium salt for which $[\alpha]_D^{25} + 21.43^{\circ}$ in a 1.01 per cent. aqueous solution.

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