CCL.—*The Molecular Configurations of Polynuclear Aromatic Compounds. Part VII. 5 : 5′-Dichlorodiphenyl-3 : 3′-dicarboxylic Acid.*

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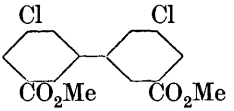
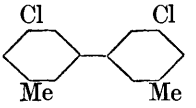
FOR reasons which have been fully set out elsewhere (Kenner, *Chem. and Ind.*, 1927, **46**, 218), it was of importance to synthesise and examine a diphenyldicarboxylic acid isomeric with one of the 6 : 6′-diphenic acids, of which the asymmetry has been demonstrated (J., 1922, **121**, 614; 1923, **123**, 779, 1948; 1926, 470, 671), and carrying its substituents in the 3-, 3′-, 5-, and 5′-positions. 5 : 5′-Dinitrodiphenyl-3 : 3′-dicarboxylic acid having been found to be inaccessible by the usual method of synthesis, attention was directed to the corresponding dihalogenated acids. In this direction the facility with which 3-bromo-5-nitro-*p*-toluidine is available (Neville and Winther, *Ber.*, 1880, **13**, 968) suggested 5 : 5′-dibromodiphenyl-3 : 3′-dicarboxylic acid as the most suitable objective. However, bromine as well as iodine was eliminated when either *-bromo-5-iodotoluene* or *methyl 3-bromo-5-iodobenzoate* was heated with copper powder, so that no definite diphenyl derivative could be synthesised from either of them.

Finally, therefore, the more laborious preparation of *3-chloro-5-iodotoluene* and of *methyl 3-chloro-5-iodobenzoate* was undertaken, and from each of these compounds the desired diphenyl derivative was obtained. Even in the latter case, however, the *methyl* 5 : 5′-*dichlorodiphenyl*-3 : 3′-*dicarboxylate* (I) underwent decomposition, so that the compound could only be obtained in poor yields under carefully regulated conditions, and, although, on the other hand, 5 : 5′-*dichloro*-3 : 3′-*ditolyl* (II) was readily isolated, it proved to be

of no value for the present purpose since it could not be readily oxidised to the corresponding dicarboxylic acid.

(I.) 



(II.)

The *brucine*, *quinine*, and *acid morphine* salts of 5 : 5′-*dichlorodiphenyl*-3 : 3′-*dicarboxylic acid* were each found to be uniform, and the solutions of ammonium 5 : 5′-dichlorodiphenyl-3 : 3′-dicarboxylate prepared from them were in each case optically inactive. It would therefore appear that the acid has not the asymmetry of its 2 : 2′-6 : 6′-structural isomeride.

EXPERIMENTAL.

5-Iodo-3-nitrobenzoic Acid. (Experiments carried out by F. Allsop in the University of Sheffield.)—The usual procedure for the replacement of the amino-group by iodine yielded unsatisfactory results in this instance, but excellent yields were obtained in the following way. An intimate mixture of 5-nitro-3-aminobenzoic acid (5 g.) with potassium metabisulphite (3 g.) was slowly added to fuming nitric acid (12 c.c.) below −2°. After 2 hours, the solution was diluted with ice (60 g.) and then gradually treated with a solution of potassium iodide (8 g.) and iodine (4 g.) in water (8 c.c.). After 12 hours, the mixture was heated on the steam-bath, and the excess of iodine destroyed by addition of sodium bisulphite. By crystallisation from light petroleum, the *acid* was obtained in long prisms, m. p. 166—167° (Found: N, 4·8. $C_7H_4O_4NI$ requires N, 4·8%). The *ethyl* ester consisted of long prisms, m. p. 59—60° (Found: N, 4·4. $C_9H_8O_4NI$ requires N, 4·4%). Repeated attempts to prepare a diphenyl derivative from the ester in the usual manner were unsuccessful.

3-Bromo-5-iodotoluene.—When a solution of potassium iodide (24 g.) in water (40 c.c.) was gradually added to a diazonium salt solution prepared from 5-bromo-*m*-toluidine (18 g.), sulphuric acid (12 c.c.), water (120 c.c.), and sodium nitrite (8 g.), the violence of decomposition of the resultant diazonium iodide was such as to project the material from the containing vessel. In subsequent preparations, this difficulty was overcome by carrying out the mixing of the respective solutions, and the subsequent decomposition, in small aliquot proportions. *3-Bromo-5-iodotoluene* boiled at 150°/29 mm. and melted at 23° (Found: X,* 141·6. C_7H_6BrI requires X, 142·4).

* X denotes weight of mixed silver halides expressed as a percentage of the weight of material analysed.

3-*Bromo*-5-*acetamidobenzoic acid*, prepared by the oxidation of 5-*bromoaceto*-m-*toluidide*, m. p. 171—172° (33·5 g.), with a solution of potassium permanganate (72 g.) and hydrated magnesium sulphate (48 g.) in water (6000 c.c.), melted at 279—281° (Found : N, 5·5. $C_9H_8O_3NBr$ requires N, 5·4%).

5-*Bromo*-3-*aminobenzoic acid* was obtained in the form of its hydrochloride by boiling a solution of the acetyl derivative (5 g.) in concentrated hydrochloric acid (50 c.c.) for one hour and then evaporating it. The acid, liberated by means of sodium acetate, separated from dilute alcohol in colourless needles, m. p. 220—222° after softening at 194° (Found : N, 6·5. $C_7H_6O_2NBr$ requires N, 6·5%).

3-*Bromo*-5-*iodobenzoic acid* was prepared from the hydrochloride of 5-bromo-3-aminobenzoic acid in the usual manner and melted at 209—211° (Found : X, 128·6. $C_7H_4O_2BrI$ requires X, 129·3). The *methyl* ester separated from benzene in small orange prisms, m. p. 59—61° (Found : X, 123·1. $C_8H_6O_2BrI$ requires X, 124·0).

3-*Chloro*-5-*iodotoluene*, prepared with the precautions explained in the case of the corresponding bromo-derivative, boiled at 138—140°/26 mm. and melted at 0° (Found : X, 149·4. C_7H_6ClI requires X, 149·5).

5 : 5′-*Dichloro*-3 : 3′-*ditolyl* was readily prepared by gradually adding copper powder during ½ hour to an equal weight of 3-chloro-5-iodotoluene at 250—260°, finally raising the temperature to 290°, and then allowing the product to cool. After crystallisation from alcohol, it melted at 101—102° (Found : Cl, 27·8. $C_{14}H_{12}Cl_2$ requires Cl, 28·4%). Experiments on its oxidation with dilute nitric acid (Cohen and Dakin, J., 1901, **79**, 1124) or neutral or alkaline permanganate led to no satisfactory result.

3-*Chloro*-5-*acetamidobenzoic acid*, m. p. 265—267° (Found : N, 6·55; *M*, 213·9. $C_9H_8O_3NCl$ requires N, 6·6%; *M*, 214·5), and 3-*chloro*-5-*aminobenzoic acid hydrochloride*, m. p. 118—121° (Found : N, 6·65. $C_7H_7O_2NCl_2$ requires N, 6·7%), were prepared in the manner adopted for the bromo-derivatives. In place, however, of the ordinary procedure, the following was a much more satisfactory method of preparing 3-*chloro*-5-*iodobenzoic acid* : A finely ground mixture of 3-chloro-5-aminobenzoic acid hydrochloride (30 g.) with potassium metabisulphite (16·2 g.) was gradually added below 0° to nitric acid (78 c.c.; *d* 1·5). After 4 hours, the mixture was poured on ice (240 g.) and gradually treated with a solution of iodine (22·2 g.) and potassium iodide (43·2 g.) in water (40 c.c.). The acid crystallised from dilute alcohol in reddish-yellow needles, m. p. 190—191° (Found : X, 133·5; *M*, 281. $C_7H_4O_2ClI$ requires X, 134·2; *M*, 282·4). Its *methyl* ester crystallised from methyl

alcohol in orange needles, m. p. 43—44° (Found: X, 127·0. $C_8H_6O_2ClI$ requires X, 127·9).

Methyl 5 : 5′-*dichlorodiphenyl*-3 : 3′-*dicarboxylate* was obtained when copper powder was gradually added to an equal weight of methyl 3-chloro-5-iodobenzoate at 265—270°, and the mixture was then heated for 10 minutes at 270°. For the success of the preparation the copper powder must be added as quickly as possible consistent with the maintenance of the temperature within the limits indicated, since prolonged or over-heating causes decomposition. Even in the most favourable circumstances the yield could not be raised above 25%. The ester separated from benzene in small cubical crystals, m. p. 156° (Found: Cl, 21·5. $C_{16}H_{12}O_4Cl_2$ requires Cl, 21·2%).

5 : 5′-*Dichlorodiphenyl*-3 : 3′-*dicarboxylic acid*, prepared from its ester by means of aqueous sodium hydroxide, was practically insoluble in the ordinary solvents and was sparingly soluble in glacial acetic acid. From this it crystallised in nodules, m. p. 358—360° (Found: Cl, 23·2. $C_{14}H_8O_4Cl_2$ requires Cl, 23·1%).

The *brucine* salt crystallised from methyl alcohol in radiate clusters of small prisms, m. p. 178—179°, decomp. 191—193° (Found: N, 5·1. $C_{60}H_{60}O_{12}N_4Cl_2$ requires N, 5·1%). For a 0·78% solution in chloroform, $[\alpha]_D = -5·2°$.

The *quinine* salt separated from methyl alcohol in small prisms, m. p. 170—172°, decomp. 174° (Found: N, 5·8. $C_{54}H_{60}O_4N_4Cl_2$ requires N, 5·85%). They were insoluble in acetone, chloroform, and ether, and only sparingly soluble in methyl or ethyl alcohol. For a 0·18% solution in absolute alcohol, $[\alpha]_D = -132°$.

The *acid morphine* salt crystallised from methyl alcohol in small nodules, m. p. 218—219°, decomp. 223—225° (Found: N, 2·4. $C_{31}H_{27}O_7NCl_2$ requires N, 2·4%). The salt was almost insoluble in benzene, chloroform, acetone, and ether, and sparingly soluble in methyl or ethyl alcohol. For a 0·20% solution in ethyl alcohol, $[\alpha]_D = -30°$.

Solutions of the ammonium salt were prepared from both the brucine and the quinine salt by shaking them with chloroform and dilute ammonia solution, but in the case of the acid morphine salt dilute ammonia alone was employed, the bulk of the morphine being then removed by filtration, and the last traces by means of chloroform. In each case the solutions obtained were optically inactive. The quinidine salt was an oil, easily soluble in methyl alcohol and acetone, sparingly in ether or benzene. The cinchonine salt was a gum, readily soluble in chloroform, water, and methyl alcohol, but very sparingly soluble in benzene or ether, and could not be obtained in the solid condition.

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