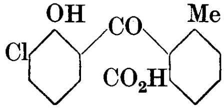
CXCIII.—*A New Isomerism of Halogenohydroxybenzoyltoluic Acids. Part III. 2-(3′-Chloro-4′-hydroxybenzoyl)-3(or 6)-methylbenzoic Acid.*

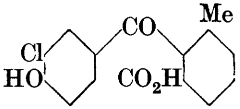
By Mosuke Hayashi.

The author has reported in preceding papers (J., 1927, 2516; this vol., p. 1513) that the action of concentrated sulphuric acid on halogenohydroxybenzoyltoluic acids which have the halogen in the *p*-position to the hydroxyl group gave rise to an isomeric change. He now submits the results of analogous studies with halogenohydroxybenzoyltoluic acids which have the halogen in the *o*-position to the hydroxyl group.

When 3-methylphthalic anhydride was condensed with *o*-chlorophenol or with *o*-chloroanisole in the presence of anhydrous aluminium chloride, only one chlorohydroxybenzoyltoluic acid (A), m. p. 198—199° (anhydrous), was obtained. On treatment of this acid with concentrated sulphuric acid at room temperature, an isomeric change occurred and chlorohydroxybenzoyltoluic acid (A′), m. p. 188·5—189°, was obtained. The (A) acid may have any of the formulæ (I), (II), (III), and (IV), in harmony with the rule which has been already mentioned in a previous paper (Part I, *loc. cit.*).

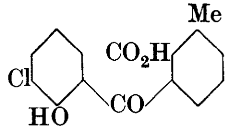
(I.)

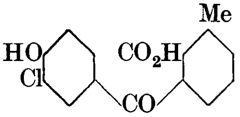




(II.)

(III.)





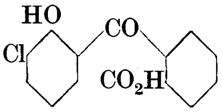
(IV.)

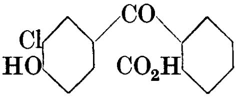
However, when phthalic anhydride was condensed with *o*-chlorophenol or with *o*-chloroanisole in the presence of anhydrous aluminium chloride, 2-(3′-*chloro*-4′-*hydroxybenzoyl*)*benzoic acid* only was obtained and 2-(3′-chloro-2′-hydroxybenzoyl)benzoic acid could not be isolated. The constitutional formula of the (A) acid may therefore be either (II) or (IV). The isomeric change should be the transformation of (II) into (IV) or *vice versa*, since it is improbable that the carboxytoluoyl group would migrate into the *o*-position to the hydroxyl group. This view receives important support from the great similarity of the ultra-violet absorption curves of the acids (A) and (A′) and of the 2-(3′-chloro-4′-hydroxybenzoyl)-benzoic acid.

A definite allocation of formulæ to the acids (A) and (A′) is not feasible, but, taking cognisance of the known influence of the methyl group in analogous reactions, it is highly probable that 2-(3′-chloro-4′-hydroxybenzoyl)-3-methylbenzoic acid (II) would be produced more easily than 2-(3′-chloro-4′-hydroxybenzoyl)-6-methylbenzoic acid (IV) when 3-methylphthalic anhydride is condensed with *o*-chlorophenol. Therefore, it seems probable that the chlorohydroxybenzoyltoluic acid (A) is 2-(3′-*chloro*-4′-*hydroxybenzoyl*)-3-*methylbenzoic acid* (II), and the chlorohydroxybenzoyltoluic acid (A′) is 2-(3′-*chloro*-4′-*hydroxybenzoyl*)-6-*methylbenzoic acid* (IV).

When phthalic anhydride was condensed with *o*-chlorophenol or with *o*-chloroanisole in acetylene tetrachloride solution in the presence of aluminium chloride, a chlorohydroxybenzoylbenzoic acid, m. p. 219·5—220°, was obtained (V or VI).

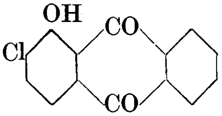
(V.)

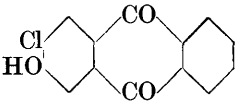




(VI.)

(VII.)





(VIII.)

When the chlorohydroxybenzoylbenzoic acid, m. p. 219·5—220°, was heated at 195° with a solution of boric acid in concentrated sulphuric acid, 2-chloro-3-hydroxyanthraquinone (VIII) was obtained (compare Tanaka, *Proc. Imp. Acad. Tokyo*, 1927, **3**, 82; or *Bull. Agr. Chem. Soc. Japan*, 1927, **3**, 17). Therefore, the chlorohydroxybenzoylbenzoic acid, m. p. 219·5—220°, is probably 2-(3′-chloro-4′-hydroxybenzoyl)benzoic acid (VI).

EXPERIMENTAL.

Condensation of 3-*Methylphthalic Anhydride with* o-*Chlorophenol or with* o-*Chloroanisole.* 2-(3′-*Chloro*-4′-*hydroxybenzoyl*)-3 (*or* 6)-*methylbenzoic Acid* (A).—Powdered aluminium chloride (25 g.) was gradually added with frequent shaking to a solution of 3-methylphthalic anhydride (10 g.) and *o*-chlorophenol (9 g.) in acetylene tetrachloride (50 c.c.). The mixture was then heated at 125—135° (oil-bath) and the product was mixed with ice-water and an excess of hydrochloric acid and distilled in steam. An ammoniacal extract of the residue was concentrated and then again diluted with water; the greyish-brown precipitate (4 g.) that separated was removed [m. p. 110—140° (decomp.); unidentified], and the filtrate, on acidification, afforded the crude acid (15 g.), m. p. 194—197°, in 83·6% yield.

After several recrystallisations from acetic acid, colourless microscopic needles were obtained (Found in air-dried material : loss at 105° in a vacuum, 5·9. $C_{15}H_{11}O_4Cl,H_2O$ requires H_2O, 5·8%. Found in anhydrous material : C, 61·9 ; H, 4·0 ; Cl, 12·15. $C_{15}H_{11}O_4Cl$ requires C, 61·95 ; H, 3·8 ; Cl, 12·2%).

The anhydrous *acid* melts at 198—199°. It is easily soluble in alcohol and hot acetic acid but very sparingly soluble in benzene or light petroleum. The solution in concentrated sulphuric acid is at first yellow, but gradually develops a red colour. The ultra-violet absorption curve of an alcoholic solution of this acid shows a band with head at λ 2840 Å.

2-(3′-*Chloro*-4′-*hydroxybenzoyl*)-6(*or* 3)-*methylbenzoic Acid* (A′).—After a solution of 2-(3′-chloro-4′-hydroxybenzoyl)-3(or 6)-methylbenzoic acid (A) (1 g.) in 98% sulphuric acid (6 c.c.) had been kept for one day at room temperature, the isolated product dissolved completely in aqueous sodium carbonate and, on acidification of the solution, an almost colourless substance was precipitated (0·95 g.), m. p. 187—189°. On crystallisation from acetic acid, colourless microscopic needles, m. p. 188·5—189°, were obtained (Found : C, 62·1 ; H, 4·1 ; Cl, 12·25. $C_{15}H_{11}O_4Cl$ requires C, 61·95 ; H, 3·8 ; Cl, 12·2%).

This *acid* closely resembles the isomeride (A), and the ultra-violet absorption curve of its alcoholic solution shows a band with head at λ 2850 Å.

When the acid (A) (1 g.) was heated with concentrated sulphuric acid (98%, 6 c.c.) at 120—130° for 1 hour, crude acid (A′) (0·9 g.), m. p. 186—188°, was obtained. And also, when a solution of the acid (A) in concentrated sulphuric acid was heated at 140° or 150—160° for 1 hour, crude acid (A′) only was obtained ; no anthraquinone derivative could be isolated.

3-Methylphthalic anhydride (5 g.) was condensed with *o*-chloroanisole (5 g.) (acetylene tetrachloride, 25 c.c. ; anhydrous aluminium chloride, 12·5 g.) under the same conditions as in the case of *o*-chlorophenol. In this case, crude 2-(3′-chloro-4′-hydroxybenzoyl)-3(or 6)-methylbenzoic acid (A) (7·2 g. ; 80·5%), m. p. 194—196° (anhydrous), was obtained, and no other substance was isolated.

2-(3′-*Chloro*-4′-*hydroxybenzoyl*)*benzoic Acid*.—Phthalic anhydride (5 g.) and *o*-chlorophenol (5 g.) were dissolved in acetylene tetrachloride (25 c.c.), powdered aluminium chloride (12·5 g.) was gradually added with shaking, and the mixture heated slowly. After 2 hours' heating at 120—130°, the product was cooled, mixed with ice-water and, after the addition of an excess of hydrochloric acid, distilled in steam. The residue was extracted with ether, the extract washed with sodium carbonate solution, and the *acid* regenerated (m. p. 219—220°; 9 g., 96·3%); it separated from glacial acetic acid in colourless crystals, m. p. 219·5—220° (Found: C, 60·7; H, 3·5; Cl, 12·8. $C_{14}H_9O_4Cl$ requires C, 60·75; H, 3·3; Cl, 12·8%).

This acid exhibited the usual properties of its class, and showed an absorption band with a head at λ 2840 Å. (solvent, alcohol). When a solution of this acid in concentrated sulphuric acid (98·25%, 6 vols.) was kept over-night at room temperature, the whole of the substance could be recovered unchanged.

Aluminium chloride (12·5 g.) was gradually added to a solution of phthalic anhydride (5 g.) and *o*-chloroanisole (5 g.) in acetylene tetrachloride (25 c.c.), and the subsequent treatment and the separation of the reaction product were carried out as in the case of *o*-chlorophenol. Crude 2-(3′-chloro-4′-hydroxybenzoyl)benzoic acid, m. p. 212—216°, only was obtained in 97% yield (9·1 g.).

2-(3′-*Chloro*-4′-*methoxybenzoyl*)*benzoic Acid*.—2-(3′-Chloro-4′-hydroxybenzoyl)benzoic acid (3 g.) was converted into its potassium salt, which was thoroughly dried and suspended in toluene (50 c.c.), methyl sulphate (6 g.) introduced, and the mixture gradually heated. After 2 hours' boiling, the product was mixed with 25% potassium hydroxide solution (20 c.c.) and distilled in steam. The residue was an almost colourless substance (3 g., 95·5%), m. p. 160—166°, which crystallised from acetic acid in microscopic pillars, m. p. 179—180° (Found: C, 62·25; H, 4·1; Cl, 12·2. $C_{15}H_{11}O_4Cl$ requires C, 61·95; H, 3·8; Cl, 12·2%).

The solubility and other properties were normal, and the alcoholic solution exhibited an absorption band with a head at λ 2810 Å.

2-*Chloro*-3-*hydroxyanthraquinone*.—The anthraquinone derivative was not obtained when 2-(3′-chloro-4′-hydroxybenzoyl)benzoic acid was heated even with 100% sulphuric acid at 195° for 1·5 hours.

2-(3′-Chloro-4′-hydroxybenzoyl)benzoic acid (1 g.) was heated with a solution of boric acid (1·5 g.) in 100% sulphuric acid (16 c.c.) at 195° for 1·5 hours, and the product poured into ice-water. The yellow precipitate was washed with boiling water and crystallised from alcohol (0·5 g.; 53·5%). The substance was purified by solution in and recovery from aqueous sodium carbonate, and crystallised from acetic acid in yellow feathery needles, m. p. 266·5—267° (Tanaka, *loc. cit.*, gives m. p. 258°) (Found: C, 65·0; H, 2·9; Cl, 13·7. Calc. for $C_{14}H_7O_3Cl$: C, 65·0; H, 2·7; Cl, 13·7%).

This chlorohydroxyanthraquinone exhibits two absorption bands with heads at λ 3120 and 2730 Å. (solvent, alcohol).

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