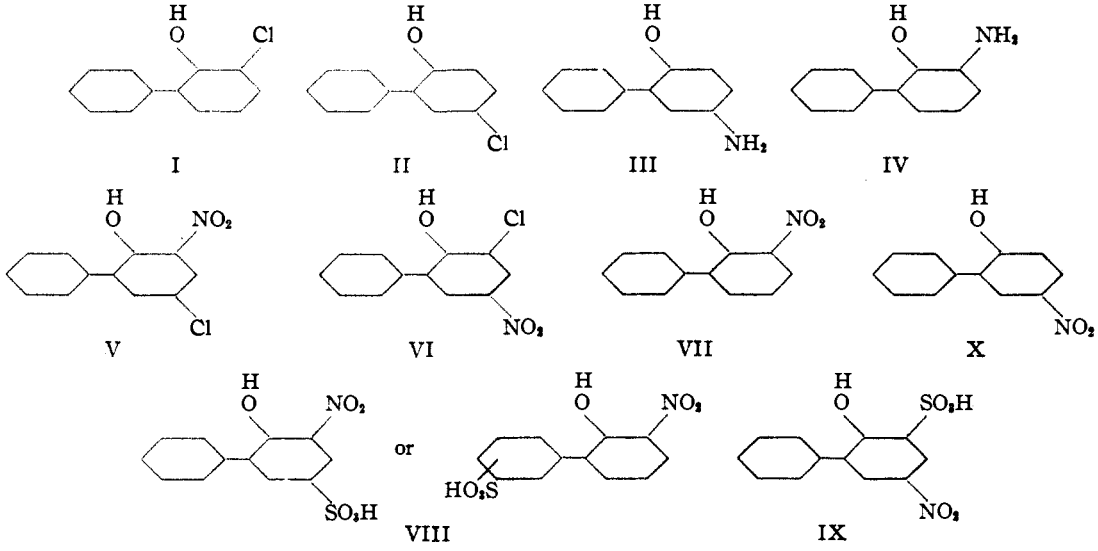
[COMMUNICATION NO. 992 FROM THE KODAK RESEARCH LABORATORIES]

The Identity of 3- and of 5-Monochloro-2-hydroxydiphenyl

BY A. WEISSBERGER AND I. F. SALMINEN

By passing chlorine into 2-hydroxydiphenyl, in an amount less than that theoretically required to convert the latter completely into the monochloro compounds, Britton and Bryner[1] obtained two monochloro derivatives melting at 11 and 72°, respectively. The structure of 2-hydroxy-3-chlorodiphenyl, I, was assigned to the lower-melting, that of 2-hydroxy-5-chlorodiphenyl, II, to the higher-melting compound. Chlorohydroxydiphenyls are of interest in color photography,[2] but their behavior as dye-forming couplers casts doubt on the validity of the just-mentioned assignment of formulas.[3] As shown below, these formulas should be reversed.



The structures of 2-hydroxy-5-aminodiphenyl, III, and of 2-hydroxy-3-aminodiphenyl, IV, can be considered as firmly established. III is obtained by reduction of one of the two mononitro products obtained in the nitration of 2-hydroxydiphenyl under mild conditions,[4] and also by reduction of the product formed in the condensation of *p*-nitrosophenol with diazotized aniline with elimination of nitrogen.[5] IV is obtained by reduction of the other mononitro derivative obtained from 2-hydroxydiphenyl. The circumstances under which this nitro derivative is formed and its yellow color and volatility with steam[6] all show that the nitro group and, therefore, the amino group in IV are attached in position 3. This is confirmed by the formation of a benzoxazole from IV with benzoyl chloride.[4] When the amino group in III and IV was replaced by chlorine via the diazonium compounds, monochlorohydroxydiphenyls were obtained which are identical with the (purified) commercial products mentioned above. However, reversing the structure assigned in the literature, the compound melting at 71° derives from IV and, therefore, is I, while the compound melting at 11° derives from III and, therefore, is II.

Nitration of the lower melting chlorohydroxydiphenyl gives a yellow mononitro derivative melting at 57–58°, not described in the literature. This compound, in accordance with the newly assigned structure of the parent substance II, is 2-hydroxy-3-nitro-5-chlorodiphenyl, V. The yellow color of the new compound corroborates this assignment of structure in analogy with the yellow color of 2-nitro-4-chlorophenol and of other *o*-nitrophenols. The mononitration product of the higher-melting chlorohydroxydiphenyl, prepared by Vorozhtsov and Troshchenko,[7] which melts at 127° cannot be V, therefore, but is 2-hydroxy-3-chloro-5-nitrodiphenyl, VI. This structure agrees with the fact that the compound is colorless in analogy with the colorless 2-chloro-4-nitrophenol and with other *p*-nitrophenols.

Certain other results reported by Vorozhtsov and Troshchenko[7] require further discussion. These authors treated 2-hydroxydiphenyl with hot concentrated sulfuric acid and nitrated the

(1) Britton and Bryner, U. S. Patent 1,969,963, assigned to The Dow Chemical Company, 1930.

(2) Mannes and Godowsky, U. S. Patent 2,039,730, assigned to Eastman Kodak Company, 1935.

(3) P. W. Vittum, private communication.

(4) Vorozhtsov and Troshchenko, *J. Gen. Chem.* (U. S. S. R.), **8**, 431 (1938).

(5) Borsche, *Ann.*, **312**, 211 (1900).

(6) Sidgwick, Taylor and Baker, "Organic Chemistry of Nitrogen," 2nd ed., Oxford, 1937, p. 268.

(7) Vorozhtsov and Troshchenko, *J. Gen. Chem.* (U. S. S. R.), **9**, 59 (1939).

resulting oil. The sodium salt of the reaction product was freed from unsulfonated nitrohydroxydiphenyl by extraction with ether and recrystallized from water. It was considered to be the 2-hydroxy-3-nitrodiphenyl-5-sulfonate. The purified salt, when desulfonated with hot sulfuric acid, formed 2-hydroxy-3-nitrodiphenyl, VII, as should be expected of a 2-hydroxy-3-nitro-sulfonic acid, VIII. However, when an aqueous solution of the salt was treated with chlorine, replacing SO_3H by Cl, a chloronitro-2-hydroxydiphenyl, melting at 127°, was obtained which, according to the revised formulas, is VI. Obviously VI cannot be formed by substituting Cl for SO_3H in a 2-hydroxy-3-nitro-sulfonic acid, VIII. The anomalous result would be explained if the salt used in the chlorination experiment contained either the 2-hydroxy-5-nitro-3-sulfonic acid, IX, or 2-hydroxy-5-nitrodiphenyl, X. The latter alternative is improbable because the analysis for sodium given by Vorozhtsov and Troshchenko does not permit of the presence of appreciable amounts of an unsulfonated product.

We repeated the experiments of Vorozhtsov and Troshchenko, heating the sulfonation mixture for six hours to 120°, as stated by these authors. After the treatment with nitrate, the sodium salt was extracted with ether and recrystallized from water, although it was very soluble even in cold water. The purified salt, on heating with 50% sulfuric acid, did not give VII, *i. e.*, a steam-volatile product, nor was a precipitate of V or VI formed when chlorine was introduced into the aqueous solution of the salt. However, by cutting the heating period of the sulfonation mixture to fifteen minutes, we obtained after nitration and extraction with ether a sodium salt which appears to be that described by Vorozhtsov and Troshchenko. It is readily recrystallized from water, gives VII on hydrolysis with sulfuric acid and, on chlorination of the aqueous solution, forms a precipitate of VI. The reduction in the heating time of the sulfonation mixture used in our experiments may be necessary because the sulfuric acid is more concentrated, or for some other reason. Analysis of the sodium salt for C, H, N, S, and Na confirms the composition stated by Vorozhtsov and Troshchenko. The suggestion that the sodium salt contains a 2-hydroxy-3-nitrodiphenyl sulfonate together with 2-hydroxy-5-nitrodiphenyl-3-sulfonate is at present the most probable explanation for the formation of VI or VII in the treatment with chlorine or sulfuric acid, respectively.

Experimental

2-Hydroxy-3-chlorodiphenyl, I.—Five and one-half grams of 2-hydroxy-3-aminodiphenyl hydrochloride[4] (m. p. 220–222°) was dissolved in 125 ml. of hot glacial acetic acid, and cooled to 17° with stirring. The suspension of fine platelets was added[8] in portions to nitrosyl sulfuric acid, from 2.28 g. of sodium nitrite and 20 ml. of concd. sulfuric acid. The clear amber solution was added at 17° to cuprous chloride, from 18 g. of copper sulfate,[9] in 100 ml. of concd. hydrochloric acid. The clear dark solution, diluted with 250 ml. of water, was heated at 80–90° for one hour. Droplets of oil separated. After cooling to 15°, the solid was filtered, washed with water, and dissolved moist in 300 ml. of petroleum ether at room temperature. After decanting, the solution was washed twice with 200-cc. portions of water, dried with calcium chloride, stirred with 0.3 g. of Darco, and filtered through Darco. Evaporated to dryness, 2.3 g. (45%) colorless flat needles, m. p. 73–74°.

2-Hydroxy-5-chlorodiphenyl, II.—To a solution of 18.5 g. of 2-hydroxy-5-aminodiphenyl[4] in 25 ml. of water and 12.5 ml. of concd. hydrochloric acid was added 27.5 ml. of concd. hydrochloric acid and 100 g. of ice. To the mixture was added all at once 7.2 g. of sodium nitrite in 30 ml. of water. The filtered solution was added to cuprous chloride,[9] from 30 g. of copper sulfate in 50 ml. of water and 38 ml. of concd. hydrochloric acid. The tan-colored complex changed, on heating, to a dark oil. After heating for one hour, the mixture was cooled to 10°, decanted, the oil dissolved in 300 ml. of ethyl ether, dried with calcium chloride, stirred with 1 g. of Darco, and filtered through Darco. On evaporation, 13 g. of dark oil was obtained, twice distilled *in vacuo*, 5.5 g. (27%) of straw-colored liquid, b. p. 128–130° (2 mm.).

2-Hydroxy-3-nitro-5-chlorodiphenyl, V.—To 2.0 g. of 2-hydroxy-5-chlorodiphenyl in 10 ml. of glacial acetic acid was added dropwise 1.0 g. of concd. nitric acid at 15–20°. The clear brown solution was warmed to 27° and diluted with 5 cc. of water, precipitating an oil which solidified. This was filtered, washed with water, dissolved in ether, and dried with calcium chloride. After evaporation of the solvent to dryness, the mononitro compound was extracted from the mixture of mononitro and dinitro compounds with 15 cc. of ether at room temperature. The residue of about 0.1 g. of crude dinitro compound melted at 160–170°. The ether solution was diluted with an equal volume of petroleum ether, filtered after three hours from some dinitro compound, and shaken with Darco. On evaporation of the clear brown filtrate to 5 cc., the mononitro compound crystallized in orange hexahedra; recrystallized from petroleum ether, 1.2 g. (48%); m. p. 57–58°.

Anal. Calcd. for $C_{12}H_8O_3NCl$: C, 57.71; H, 3.21; N, 5.61. Found: C, 57.94; H, 3.12; N, 5.55.

2-Hydroxy-5-nitro-3-chlorodiphenyl, VI.—(1) To a solution of 20.5 g. of commercial "4-chloro-2-phenylphenol" (m. p. 71–72°), which is actually 2-hydroxy-3-chlorodiphenyl, in 100 ml. of glacial acetic acid was added in forty-five minutes with stirring and cooling in ice 10 g. of concd. nitric acid (d. 1.42) at 15–19°. The product was filtered and washed with 10 ml. of acetic acid followed by 150 ml. of petroleum ether, 11 g. of pale violet platelets; m. p. 128–129°. These were dissolved in 250 ml. of ether, the solution was shaken with Darco, the pale yellow filtrate concentrated to 50 cc., and precipitated with an equal volume of petroleum ether, 7.58 g. (31%) of fine tan needles, m. p. 130–131°.

(2) Chlorine was passed for five to seven minutes into a suspension of 5 g. of the 2-hydroxynitrodiphenyl sodium sulfonate obtained by method 2 (below) in 30 ml. of water, the temperature rising from 18 to 25°. The mixture was extracted twice with 100-ml. portions of ether. The solution was dried with calcium chloride and concentrated to dryness. The crude product, 2.5 g., was extracted with 50 ml. of hot hexane. The residue (0.8 g.), m. p. 115–123°, was combined with the solid (0.3 g.) m. p. 115–126° which crystallized from the hexane and dissolved in 100 ml. of ether. After shaking with Darco, the pale yellow filtrate was concentrated to 5 ml. and precipitated with 10 ml. of hexane; 0.5 g. (11%) tan needles; m. p. 128–129°.

Sulfonation, Nitration, and Hydrolysis of 2-Hydroxydiphenyl.—(1) Method of Vorozhtsov and Troshchenko[7]: one hundred and seventy grams of *o*-hydroxydiphenyl was added to 200 ml. of concd. sulfuric acid. The temperature rose to 52°, and the mixture was heated at 115–120° for

(8) Hodgson and Walker, *J. Chem. Soc.*, 1620 (1933).

(9) Gilman and Blatt, Org. Syn. Coll., Vol. I, 2nd ed., 1941, p. 163.

six hours. After cooling, the sirup was diluted with 200 ml. of water, at a temperature below 60°, and 85 g. of sodium nitrate in 250 ml. of water was added, at 30–42°. The temperature rose to 48°. The mixture, standing at room temperature, crystallized after one and a half hours. After eighteen hours, it was filtered, the cake washed with 100 ml. of water at 4°, and the ground, air-dried product (82 g.) extracted with ether in a Soxhlet for twenty-four hours; residue, 70 g., crystallized from 50 ml. of water 31 g. of yellow needles.

A solution of 2 g. of the crystalline yellow needles in 10 ml. of 50% sulfuric acid boiled (154°) under reflux for three hours gave no trace of 2-hydroxy-3-nitrodiphenyl even when the solution was distilled with superheated steam up to a temperature of 190° in the distilland.

(2) VIII.—One hundred and thirty-six grams of *o*-hydroxydiphenyl was added to 160 ml. of concd. sulfuric acid, the temperature rising from 21 to 52°. The sirup heated at 115–120° for fifteen minutes and worked up as in (1) gave 101 g. (40%) of a product which differed from that of method (1) by being soluble in six parts of hot water instead of one and by giving 14% of 2-hydroxy-3-nitrodiphenyl on addition of 50% sulfuric acid and distillation with superheated steam.

(3) The same result was obtained less tediously, as follows: thirty-four grams of *o*-hydroxydiphenyl was added to 40 ml. of concd. sulfuric acid. The temperature rose from 21 to 52°. The sirup was stirred for ten minutes, heated to 60°, and poured on 40 g. of crushed ice. The violet suspension was nitrated at 30–40° with 17 g. of sodium nitrate in 50 cc. of water. A yellow solid crystallized while the temperature rose to 47°. The mixture was filtered at 30°, the cake washed with 20 ml. of water, 50 ml. of alcohol and ether (1:1), and 50 ml. of ether, stirred for ten minutes in 200 cc. of alcohol and ether (1:1), filtered, and washed with 200 ml. of ether; 30.5 g. (48%) of yellow needles. Further extraction of a sample with ether did not remove anything. Twenty-two grams, recrystallized from six parts of water, yielded 15.2 g. of yellow needles.

Anal. Calcd. for $C_{12}H_8O_6NNaS$: C, 45.42; H, 2.52; N, 4.41; Na, 7.26; S, 10.09. Found: C, 45.43; H, 2.52; N, 4.36; Na, 7.23; S, 10.10.

Summary

1. 2-Hydroxy-3-chlorodiphenyl, m. p. 72°, and 2-hydroxy-5-chlorodiphenyl, m. p. 11°, were prepared from the corresponding amino-2-hydroxydiphenyls.

2. The structures given in the literature for the compounds of m. p. 11 and 72°, respectively, should be reversed.

3. 2-Hydroxy-3-nitrodiphenyl was prepared as a yellow steam-volatile compound.

4. Nitration of 2-hydroxy-3-chlorodiphenyl gave the colorless 2-hydroxy-5-nitro-3-chlorodiphenyl melting at 127°, which, in the literature, is erroneously listed as 2-hydroxy-3-nitro-5-chlorodiphenyl. Nitration of 2-hydroxy-5-chlorodiphenyl gave the true 2-hydroxy-3-nitro-5-chlorodiphenyl melting at 57°.

5. The "3-nitro-2-hydroxydiphenyl-5-sulfonate" which, according to the literature, gives 2-hydroxy-3-nitrodiphenyl on hydrolysis, and gives the chloronitro-2-hydroxydiphenyl melting at 127° on chlorination, appears to contain 2-hydroxy-5-nitrodiphenyl-3-sulfonate, together with a 2-hydroxy-3-nitrodiphenyl sulfonate.

ROCHESTER 4, NEW YORK RECEIVED AUGUST 25, 1944

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

Studies in the Pyridazine Series. The Absorption Spectrum of Pyridazine[1]

BY RICHARD CASTLEMAN EVANS AND F. Y. WISELOGLE

Studies in this Laboratory on simple compounds containing the N—N bond[2] have led to speculations concerning the modifications of such a bond when incorporated in a resonating system. An unusually interesting type of resonance is found in the aromatic nucleus of which the simplest representative is pyridazine. The pyridazine ring is unique in that the two "Lewis Structures," (A) and (B), need not have the same

(A)

(B)

energy and hence need not make equal contributions in the simplified quantum mechanical representation for the state of the pyridazine molecule. It is of interest to determine whether one of the two structures may be associated predominantly with the physical properties and chemical reactions of pyridazine and simple pyridazine derivatives.

Pyridazine itself was first obtained by Ernst Täuber[3] in 1895 by the oxidation of 3,4,5,6-dibenzopyridazine to pyridazine tetracarboxylic acid and subsequent decarboxylation.

Gabriel and Colman[4,5] used hydrazine to close a ring in substituted γ-keto acids and removed the substituent groups by oxidation and decarboxylation.

Gabriel[5] obtained pyridazine in 2-g. quantities in a seven-step synthesis starting with diethyl oxalate and diethyl succinate. Condensation of these esters using sodium yielded diethyl-β-carbethoxy-α-oxoglutarate from which α-oxoglutaric acid was obtained on hydrolysis and decarboxylation. Condensation of this ketoacid with hydrazine gave 1,4,5,6-tetrahydro-6-oxopyridazine-3-carboxylic acid. Dehydrogenation with bromine followed by decarboxylation gave 3(2)-

(1) From a dissertation submitted by R. C. Evans in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Johns Hopkins University. We are indebted to the Hynson, Westcott and Dunning Research Fund for a Grant-in-Aid covering a part of the cost of this research.

(2) Buhle, Moore and Wiselogle, THIS JOURNAL, **65**, 29 (1943).

(3) Täuber, *Ber.*, **28**, 451 (1895).

(4) Gabriel and Colman, *ibid.*, **32**, 395 (1899).

(5) Gabriel, *ibid.*, **42**, 654 (1909).