[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

3-NITRO-4-HYDROXYDIPHENYL AND SOME OF ITS DERIVATIVES

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Of the five possible mononitro derivatives of *p*-hydroxydiphenyl indicated below, three have thus far been reported in the literature. The structure of V was established by Schmidt and Schultz,[1] and that of III

I. $C_6H_5.C_6H_3(NO_2)(OH)(3,4)$
II. $C_6H_5.C_6H_3(NO_2)(OH)(2,4)$
III. $(2)NO_2C_6H_4.C_6H_4OH(4)$
IV. $(3)NO_2C_6H_4.C_6H_4OH(4)$
V. $(4)NO_2C_6H_4.C_6H_4OH(4)$

by Schultz, Schmidt and Strasser.[2] When Latschinoff[3] nitrated *p*-hydroxydiphenyl he obtained two nitro compounds melting at 67° and 154°, respectively. The first was identified as a mononitro compound by means of a nitrogen determination, while the study of the potassium salt of the second indicated that it was a dinitro derivative. Each is reported in Richter's "Lexikon" as having an unknown configuration.

The melting point of Latschinoff's mononitro compound is much lower than that (170°) of the isomer proved to have the 4,4′-relationship, which suggested that the product in question might be an ortho[4] derivative. It had additional interest for us, for it furnished an instance where the migration of acyl from nitrogen to oxygen might be used to assist in establishing the structure of a compound.

The first consideration was to secure a supply of 4-hydroxydiphenyl. Diphenyl was first nitrated by a modification of Schultz's method,[5] the isomeric nitro compounds were separated as explained below (Experimental Part), the *para* compound was reduced to the corresponding amine, the latter diazotized and converted into the required phenol. The yield was disappointing. Better results were obtained by following the directions of Norris and collaborators.[6] In this way we obtained a product that melted[7] at 163°. Our product was further characterized by the prepa-

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[1] Schmidt and Schultz, *Ann.*, **207**, 347 (1881).

[2] Schultz, Schmidt and Strasser, *Ann.*, **207**, 351 (1881).

[3] Latschinoff, *J. Russ. Chem. Soc.*, **5**, 58 (1873).

[4] Carnelley [*Phil. Mag.*, [5] **13**, 116 (1882)] noted that of two isomeric compounds, the one having the more symmetrical structure shows the higher melting point. But Smiles ["The Relations between Chemical Constitution and Some Physical Properties," Longmans, Green and Co., London, **1910**, p. 201] has pointed out that the exceptions to such a rule are so numerous that the analogies should always be supported by direct evidence.

[5] Schultz, *Ann.*, **174**, 210 (1874).

[6] Norris, Macintire and Corse, *Am. Chem. J.*, **29**, 120 (1903).

[7] Latschinoff [(a) Ref. 3, p. 52] found 164–165°, while Hübner [(b) *Ann.*, **209**, 349 (1881)] reported a value as low as 151–152°. Subsequent work by Kaiser [(c) *Ann.*, **257**, 101 (1890)] indicates that Hübner's figures are probably erroneous.

ration of the acetyl and benzoyl derivatives, which are known and a dibromo substitution product which has not been recorded. The positions probably taken by bromine in this compound may be inferred from the behavior of *p*-cresol under similar conditions, in which case the bromine atoms are found *ortho* to hydroxyl.[8] Our product should, therefore, be 3,5-dibromo-4-hydroxydiphenyl. The behavior of the bromo derivative of *p*-cresol toward nitrating agents[9] suggested examination of the diphenyl derivative under similar conditions. With the small amount of material available only a preliminary study could be made; nevertheless, the results obtained indicate a marked difference in the behavior of the two compounds. In the diphenyl derivative the nitro radical replaced hydrogen instead of bromine.

The phenol was next nitrated by following, in general, Latschinoff's directions with the modifications indicated below. From the resulting mixture[10] there was isolated a nitrophenol that melted at 66°, and which agreed in properties with Latschinoff's mononitro compound. Reduction of our product gave an aminophenol that melted at 208°, and which does not appear to have been reported in the literature. On the assumption that this product might be an *ortho* compound its acyl derivatives were examined. The diacetylated compound[11] melted at 141°. Hydrolysis of the product gave an N-acyl compound, m. p. 176°, phenolic in character. Treatment of the latter, in pyridine solution, with benzoyl chloride gave an acetyl-benzoyl derivative; m. p., 167°. Hydrolysis of this product with alcoholic potassium hydroxide gave an acylaminophenol melting at 238°, not identical with that used in the preparation of the acetyl-benzoyl derivative. The identity of the phenolic compound here in question was established by going back to the aminophenol, the hydrochloride of which was readily converted into the O-benzoyl-N-benzoyl compound. Hydrolysis of this substance gave a phenolic compound, m. p. 238°, identical with that obtained by hydrolysis of the acetyl-benzoyl derivative indicated above. The phenolic compound must, therefore, be 3-benzoylamino-4-hydroxydiphenyl. Acetylation of this substance gave the acetyl-benzoyl derivative melting at 167°, whose structure was in question. Apparently, the rearrangement occurred when the acetylaminophenol was

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[8] Schall and Dralle, *Ber.*, **17**, 2532 (1884).

[9] Thiele and Eichwede [*Ann.*, **311**, 374 (1900)] found that this product undergoes nitration, when treated with ethyl nitrite, whereby one bromine atom is replaced by the nitro radical. Zincke obtained the same result [*Ann.*, **341**, 310 (1905)] with nitrous acid. Work in this Laboratory has shown [THIS JOURNAL, **46**, 2248 (1924)] that when the position *para* to hydroxyl is available, the Zincke reaction leads to isomeric nitro compounds.

[10] We isolated, also, Latschinoff's dinitro compound, the structure of which has not been established.

[11] Dimroth, Friedemann and Kämmerer, *Ber.*, **53**, 482 (1920).

benzoylated. The yield of diacylated product obtained by treatment of the N-acetyl derivative with benzoyl chloride was 97%, which renders it improbable that any steric influence was exerted by the unsubstituted nucleus of diphenyl. Both results agree with our previous experience with similar substances.

Experimental Part

4-Hydroxydiphenyl.—Seventy-seven g. of Eastman's purest diphenyl was dissolved in 155 cc. of glacial acetic acid, and a mixture of 50 g. of fuming nitric acid and 20 g. of ordinary concd. acid was added.[12] This mixture was boiled under a reflux condenser for 12 hours, and then poured into 500 cc. of cold water. After 24 hours the liquid was decanted, and unchanged diphenyl was removed by steam distillation. The non-volatile portion, which solidified upon cooling and consisted of the *ortho* and *para* isomers,[13] was collected on a suction filter, and well pressed down with a pestle. The low-melting *ortho* isomer was drawn through as an oil. Crystallization of the remaining solid from alcohol gave yellow needles, m. p. 113°, which agrees with the literature; yield,[14] 47% of pure material. Reduction by Schlenk's[15] method gave a light yellow solid, m. p.[16] 50°, that was not further purified. The amine was diazotized as directed by Kaiser[7c] and the mixture boiled to convert the diazonium salt into the phenol, and allowed to cool. Potassium hydroxide solution was next added and the mixture filtered. Hydrochloric acid was added to the filtrate until precipitation almost commenced, after which carbon dioxide was passed in until the hydroxydiphenyl was precipitated, thus separating the phenol from any nitro compound that might have been formed. Crystallization from 20% alcohol gave colorless leaflets; m. p., 163°. Most of our material was prepared according to the general directions of Norris[6] and co-workers, with the modifications indicated, though we did not obtain as high a yield as they reported. The black oil obtained by pouring phenyldiazonium sulfate solution into hot phenol was separated from the aqueous solution, heated in an oil-bath between 150° and 170°, and distilled with superheated steam that entered at 140–160°. After the unchanged phenol had passed over, a gummy-looking material[17] collected in the condenser tube. After removal of this product, the tube rapidly filled with material of a different appearance which was mainly the *para* compound. The entire mass was dried and extracted with petroleum ether (40–60°) which readily dissolves the *ortho* compound in the cold while it dissolves but little of the *para* isomer even at the boiling point. The residue gave colorless leaflets, m. p. 163°, from 20% alcohol.

This product was further characterized by conversion into its acetyl derivative, m. p. 88°, and a benzoyl derivative which we found to melt[18] at 121°. Repeated crystallization did not change this. Treatment of a carbon disulfide solution of the phenol with 2.5 molecular proportions of bromine and allowing the mixture to stand for two days gave a 73% yield of dibromo derivative. Purification by filtration of its ligroin solution through Norite and evaporation to a small bulk gave a nearly colorless solid on standing.

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[12] Schultz (Ref. 5) used concd. nitric acid alone, and allowed the mixture to stand at room temperature.

[13] Ref. 7b, p. 341.

[14] Neither Schultz nor Hübner reported a yield.

[15] Schlenk, *Ann.*, **368**, 303 (1909).

[16] Various workers have reported 49° to 52°.

[17] This was probably the 2-hydroxydiphenyl identified by Norris and collaborators but which was disregarded in our work.

[18] Kaiser (Ref. 7c) reported 150° as the melting point of the benzoate.

Recrystallization gave prisms; m. p., 96°. Analysis for halogen showed that the product was not entirely pure, but indicated clearly that it is a dibromo compound.

Anal. Calcd. for $C_{12}H_8OBr_2$: Br, 48.78. Found: 49.45.

Five g. of the product was nitrated according to Zincke's method. A nitro compound was obtained which was crystallized in yellow needles from a mixture of chloroform and ligroin; m. p., 171°, with apparent decomposition. Analysis for halogen left little doubt that both bromine atoms remained after nitration.

Anal. Calcd. for $C_{12}H_8O_3NBr$ and $C_{12}H_7O_3NBr_2$: Br, 27.21 and 42.89. Found: 41.18.

3-Nitro-4-hydroxydiphenyl.—Latschinoff's directions were first tried in nitration of the phenol. Both mono- and dinitro products were obtained, the last-named in largest amount. Better results were secured by dissolving 8.5 g. of the phenol in 500 cc. of glacial acetic acid, and adding 5% more than the calculated amount of nitric acid (d., 1.2) which was run in from a buret. The mixture was shaken well and heated on a water-bath until the liquid became dark red. The cooled mixture was poured slowly during stirring into 1.5 liters of a mixture of water and cracked ice, and the whole allowed to stand for two hours. The yellow solid that formed was collected on a filter, washed and dried. Repetition of this process gave 80–88% yields. The product was distilled with superheated steam in order to obtain the mononitro compound free from the disubstitution product which is not volatile under the conditions of operation. The solid recovered from the distillate was crystallized by slow evaporation of its ether solution; m. p., 66°; Latschinoff recorded 67°.

Hydrochloride of 3-Amino-4-hydroxydiphenyl.—A solution of 8 g. of the nitro compound in 25 cc. of alcohol was treated gradually with a concd. hydrochloric acid solution of twice the calculated amount of stannous chloride and the mixture refluxed for half an hour; yield, 75%.

Anal.[19] Calcd. for $C_{12}H_{12}ONCl$: N, 6.32; Cl, 16.02. Found: N, 6.37; Cl, 15.79.

3-Amino-4-hydroxydiphenyl.—This base was obtained by treatment of a watery paste of the hydrochloride with the calculated amount of ammonium carbonate solution; yield, 96%. The substance is readily soluble in alcohol, ether, benzene and other organic solvents. From chloroform it gave nearly colorless scales; m. p., 208°.

Anal. Calcd. for $C_{12}H_{11}ON$: N, 7.56. Found: 7.22.

3-Acetylaminodiphenyl-4-acetate.—Acetylation in the usual way[20] gave a mixture of di- and tri-acylated products and separation was difficult. The diacetyl derivative was finally prepared as directed by Dimroth, Friedemann and Kämmerer,[11] in 95% yield. This was soluble in the usual organic solvents but insoluble in aqueous alkali except on long standing. From ligroin (100–110°) it crystallized in colorless plates; m. p., 141°.

Anal. Calcd. for $C_{16}H_{15}O_3N$: N, 5.20. Found: 5.49.

3-Diacetylaminodiphenyl-4-acetate.—When the amino-hydrochloride was heated with sodium acetate and acetic anhydride and the mixture poured into water, an oil separated. This was removed, dried and dissolved in the smallest possible quantity of warm chloroform, after which two volumes of low-boiling ligroin were added. The diacetyl derivative, m. p. 141°, crystallized. Concentration of the filtrate gave the triacetylated product; m. p., 87°.

Anal. Calcd. for $C_{18}H_{17}O_4N$: N, 4.50. Found: 4.42.

3-Acetylamino-4-hydroxydiphenyl.—This compound was obtained in 95% yield

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[19] We are indebted to Mr. C. N. Owen for the halogen determination.

[20] Liebermann and Hörmann, *Ber.*, **11**, 1619 (1878). See also Raiford and Couture, THIS JOURNAL, **44**, 1794 (1922).

by hydrolysis of the diacetyl derivative. Crystallization from a mixture of one volume of toluene and two volumes of ligroin gave nearly colorless needles; m. p., 176°. This substance was soluble in most organic solvents and in aqueous alkali.

Anal. Calcd. for $C_{14}H_{13}O_2N$: N, 6.16. Found: 6.11.

Action of Benzoyl Chloride on the Acylaminophenol.—A yield of 97% of acetyl-benzoyl derivative was obtained. It was purified by filtering its absolute alcoholic solution through Norite to remove the color, evaporation of the filtrate and addition of two volumes of petroleum ether. Cooling gave crystals; m. p., 167°.

Anal. Calcd. for $C_{21}H_{17}O_3N$: N, 4.23. Found: 4.22.

Hydrolysis of the diacyl derivative just described gave a phenolic compound which, after crystallization from toluene, melted at 238°. Analysis agreed with the presence of a benzoyl radical.

Anal. Calcd. for $C_{19}H_{15}O_2N$: N, 4.84. Found: 4.67.

3-Benzoylaminodiphenyl-4-benzoate.—This was obtained by benzoylation of the amino hydrochloride in the presence of pyridine; yield, 95%. From toluene it crystallized in irregular plates; m. p., 234°. It was insoluble in cold, dil. aqueous alkali.

Anal. Calcd. for $C_{26}H_{19}O_3N$: N, 3.56. Found: 3.61.

Hydrolysis of this product gave a phenolic compound that, after crystallization from toluene, melted[21] at 238°, and which is identical with that obtained by hydrolysis of the acetyl-benzoyl derivative melting at 167°. The latter was easily obtained when the phenolic product here in question was acetylated.

Summary

1. A new aminophenol has been prepared and its acetyl-benzoyl derivatives have been studied.

2. The observations here recorded agree with similar ones made on known *ortho* compounds, and indicate that the structure of Latschinoff's compound is 3-nitro-4-hydroxydiphenyl.

3. It has been shown that the presence of the phenyl radical as a *para* substituent in an *o*-aminophenol neither prevents nor hinders to a noticeable degree the migration of acetyl from nitrogen to oxygen.

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[21] Although this product dissolved readily in alkali, and gave analytical data which indicated that it could not be identical with the dibenzoyl derivative, m. p. 234°, from which it was obtained, a mixture of the two melted at about 236°, without showing the expected depression.