[JOINT CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF OKLAHOMA AND THE LABORATORIES OF THE MONSANTO CHEMICAL COMPANY]

Derivatives of the Hydroxydiphenyls. III. 4-Nitro-3-hydroxydiphenyl

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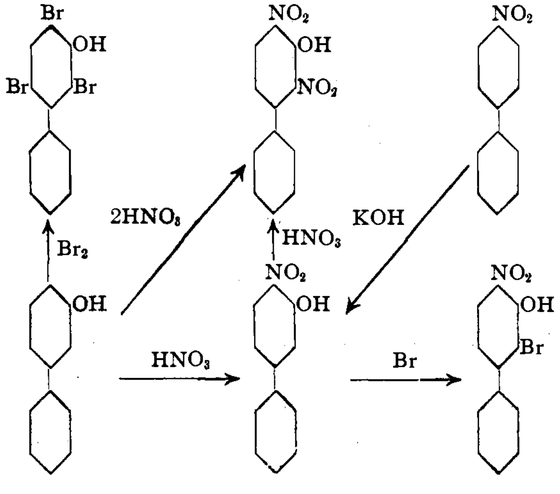
In the 4-hydroxydiphenyl molecule the usual orienting effect of the hydroxyl group should open positions 3,5,4′ to substitution. That substitution does follow the normal course, namely, (1) mono-ortho, (2) di-ortho, and (3) di-ortho-*p*′ has been demonstrated by Bell and Robinson[1] for nitration, and by Colbert and others[2] for chlorination. The substitution reactions of 2-hydroxydiphenyl, in which postions 3,5 are open, have been investigated by Borsche and Scholten.[3]



Very little work has been reported for the less readily obtainable 3-hydroxydiphenyl. This latter phenol presents an interesting case since positions 2,4,6 are open on the same ring with the hydroxyl group—a circumstance which should lead to the preparation of phenyl substituted picric acid as well as like compounds.

Nitration and Bromination of 3-Hydroxydiphenyl.—When 3-hydroxydiphenyl is treated in acetic acid solution with one molar proportion of nitric acid, the solution warms up, turns a deep red, and when added to boiling water throws down a crystalline precipitate of mononitro-3-hydroxydiphenyl. Further dilution of the mother liquor leads to precipitation of a dark colored oil, the nature of which is still under investigation. Nitration with two or more molar proportions of nitric acid yields a dinitro derivative. This is the highest nitration product it has yet been possible to obtain by the direct nitration of 3-hydroxydiphenyl. Since this dinitro derivative does not form a diphenyl ether, or a benzoate, reactions given readily by the mononitro-3-hydroxydiphenyl, it is thought to be a di-ortho derivative and is tentatively assigned the structure 2,4-dinitro-3-hydroxydiphenyl. It should be pointed out that this lack of reactivity is also found in the case of 3,5-dinitro-4-hydroxydiphenyl as we have often observed in this Laboratory. The nitration of mononitro-3-hydroxydiphenyl forms the same dinitro derivative as that obtained by use of a double portion of nitric acid upon 3-hydroxydiphenyl.

Bromination in carbon disulfide of 3-hydroxydiphenyl yields oils save when three or more molar proportions of bromine are added. In the latter case a crystalline tribromo derivative results. The formula 2,4,6-tribromo-3-hydroxydiphenyl is assigned tentatively although it has not yet been possible to degrade to recognizable products. While mononitro-3-hydroxydiphenyl brominates readily in acetic acid solution, only one bromine atom enters the ring. Henkel and Hey[4] report the preparation of 5-bromo-3-hydroxydiphenyl and 4,5-dibromo-3-hydroxydiphenyl, but not by direct bromination of the corresponding phenol.

Proof of Structure for 4-Nitro-3-hydroxydiphenyl.—Wohl[5] has shown that when nitrobenzene is allowed to stand in contact with finely powdered potassium hydroxide an intermolecular oxidation–reduction reaction occurs which gives rise to *o*-nitrophenol as one of the principal products of the reaction. It has also been shown[6] that on the large scale and with special care to avoid the presence of moisture the principal reaction comprises the interaction of five moles of nitrobenzene in the presence of the potassium hydroxide to form three moles of nitrophenol, in the form of the potassium salt, and one mole of azoxybenzene. A relatively small amount of the *p*-nitrophenol is produced at the same time.

The reaction appears to be fairly general, hav-

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[1] Bell and Robinson, *J. Chem. Soc.*, **130**, 1128 (1927).

[2] Colbert and others, THIS JOURNAL, **56**, 202 (1934).

[3] Borsche and Scholten, *Ber.*, **50**, 596 (1917).

[4] Henkel and Hey, *J. Chem. Soc.*, **131**, 1200 (1928).

[5] Wohl, *Ber.*, **32**, 3486 (1899).

[6] Wohl and Aue, *ibid.*, **34**, 2444, footnote (1901).

ing been used to convert nitrotoluene, *m*-nitrochlorobenzene and nitronaphthalene to the corresponding *o*-nitrophenols[7] but it has not, so far as we are aware, been applied to a nitrodiphenyl.

When 4-nitrodiphenyl is heated on the water-bath with an excess of powdered potassium hydroxide, the medium being benzene, a nitrophenol is obtained. The melting point as well as the microscopic appearance of this phenol is in agreement with the mononitrophenol obtained by the direct nitration of 3-hydroxydiphenyl. A mixed melting point confirms this conclusion. Since introduction of the hydroxyl group into 4-nitrodiphenyl yields the same phenol as that obtained by introducing the nitro group into 3-hydroxydiphenyl, the nitrophenol must be 4-nitro-3-hydroxydiphenyl.

The nature of the oil formed in the mononitration of 3-hydroxydiphenyl is still under investigation. The oil may contain the 2-nitro, the 5-nitro or a mixture of such mononitro derivatives. Preliminary experiments indicate that when 2-nitrodiphenyl is treated with potassium hydroxide, a mononitrophenol is formed. This compound may be found identical with a component of the oil.

Experimental Part

4-Nitro-3-hydroxydiphenyl from 3-Hydroxydiphenyl.—Seven grams of 3-hydroxydiphenyl was dissolved in 100 cc. of glacial acetic acid, the solution cooled to 10–15° and 2.6 cc. of concd. nitric acid in 20 cc. of glacial acetic acid added. The solution became a dark red within two minutes and after standing for thirty minutes at room temperature was precipitated by pouring with stirring into an equal volume of boiling water. The solution was allowed to cool and the rather small precipitate of irregular yellow plates filtered. The yield varied from 15.6 to 24.4%, the larger figure being obtained by permitting the nitration mixture to stand overnight before precipitation. The larger yields were darker colored and somewhat tarry. Recrystallization from 80% alcohol gave a product melting from 102.5–103.5°.

Anal. Calcd. for $C_{12}H_9NO_3$: N, 6.52. Found: N, 6.80.

4-Nitro-3-hydroxydiphenyl from 4-Nitrodiphenyl.—Two hundred and eighty-four grams of potassium hydroxide, previously ground in a corn mill, 112 g. of benzene and 112 g. of 4-nitrodiphenyl were well mixed and heated on the water-bath at 72–76° for seventy-two hours. At the end of that time a small amount of water and benzene was added with good agitation and the mixture filtered. It was finally pulped twice with fresh benzene and the benzene filtered off after each pulping. Weight of air-dried precipitate was 45 g.

The precipitate was dissolved in 500 cc. of hot water, the solution filtered hot and allowed to cool slowly. The deep red, crystalline, precipitate was filtered off, washed with a little cold water, and dried in a desiccator; weight 18.1 g.

A small portion (4 g.) of this material was dissolved in water and the solution acidified with hydrochloric acid, whereupon a greenish-yellow crystalline solid precipitated. After being filtered off, washed and dried, the material weighed 3.0 g. and melted at 103.1 to 103.2°. It was recrystallized from 20 g. of Skellysolve E. The recrystallized material occurred in the form of glistening greenish-yellow plates, weighed 2.5 g. and melted at 103.1 to 103.3°.

When a sample of this material was mixed with that obtained by direct nitration of 3-hydroxydiphenyl, the m. p. was 102.7 to 103.2°. When crystallized from 80% alcohol and examined under the microscope the crystals from the two sources appeared identical.

Dinitro-3-hydroxydiphenyl.—Seven grams of 3-hydroxydiphenyl was dissolved in 20 cc. of glacial acetic acid and 7.8 cc. of concd. nitric acid added. This was sufficient nitric acid for the formation of a trinitro derivative. The solution became red and boiled vigorously. Upon cooling coarse yellow, prismatic crystals precipitated and 2.95 g. of product was obtained, or a yield of 27.5%. Evaporation of the mother liquor to half volume led to the further crystallization of less pure material. Recrystallization from 95% alcohol gave a lemon-yellow product melting at 172.5–173°. This compound is very inert chemically and forms neither benzoate, bromo derivative, nor diphenyl ether.

Dinitro-3-hydroxydiphenyl from 4-Nitro-3-hydroxydiphenyl.—Six-tenths gram of 4-nitro-3-hydroxydiphenyl was dissolved in 8 cc. of glacial acetic acid and 0.25 cc. of concd. nitric acid in 3.0 cc. of glacial acetic acid added. After standing a few minutes the solution was heated to boiling, cooled to 15° and precipitated by pouring over ice. The precipitate weighed 0.54 g., m. p. 165°. Recrystallization from 95% alcohol raised the m. p. to 170°. A mixed melting point confirmed the identity of the product from the two sources.

Anal. Calcd. for $C_{12}H_8N_2O_5$: N, 10.76. Found: N, 10.30.

Tribromo-3-hydroxydiphenyl.—When 28.2 g. (8.9 cc.) of bromine was added to 10.0 g. of 3-hydroxydiphenyl in 100 cc. of carbon disulfide, the ensuing reaction was quite vigorous. After standing for five days the solution was washed with sodium carbonate solution, acidified, separated, and dried over calcium chloride. The carbon disulfide was distilled off and crystals obtained after long standing. The product was light brown, slightly gummy, and formed in 86.1% yield, *i. e.*, 20.62 g. Recrystallization was accomplished with difficulty from 200 cc. of 80% acetic acid; m. p. 92°.

Anal. Calcd. for $C_{12}H_7OBr_3$: Br, 58.93. Found: Br, 58.10.

Other Derivatives of 3-Hydroxydiphenyl.—Ethers and other derivatives have been obtained by methods similar to those reported in a preceding paper.

3′-Phenyl-2,4-dinitrodiphenyl ether, $C_6H_5C_6H_4OC_6H_3(NO_2)_2$, from potassium hydroxide, pyridine, $C_6H_3Cl(NO_2)_2$; m. p. 100°; yield 90.0%; calcd. N, 8.33; found: N, 8.53.

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[7] German Patent 116.790 (1899).

3′-Phenyl-2,4,6′-trinitrodiphenyl ether, $C_6H_5C_6H_3(NO_2)$-$OC_6H_3(NO_2)_2$, from potassium hydroxide, pyridine, C_6H_3Cl-$(NO_2)_2$; m. p. 131°; yield 95.7%; calcd. N, 11.03; found: N, 10.99.

3′-Phenyl-2,4,6-trinitrodiphenyl ether, $C_6H_5C_6H_4OC_6H_2$-$(NO_2)_3$, from potassium hydroxide and picryl chloride; m. p. 143°; yield 92.4%; calcd. N, 11.03; found: N, 11.80.

?-Bromo-4-nitro-3-hydroxydiphenyl, $C_6H_5C_6H_2Br(NO_2)$-OH; m. p. 109°; yield 40.0%; calcd. Br, 27.18; found: Br, 26.62.

Summary

1. When 3-hydroxydiphenyl is nitrated the first compounds formed are probably isomeric mononitro derivatives. One of these isomers has been isolated in pure form.

2. The structure of the mononitro derivative isolated has been proved by preparation from 4-nitrodiphenyl by the use of powdered potassium hydroxide.

3. While with bromine 3-hydroxydiphenyl yields a tribromo derivative, with nitric acid only a mono and a dinitro compound have been prepared. Due to the reduced activity of the hydroxy group the dinitrophenol is believed to be 2,4-dinitro-3-hydroxydiphenyl.

4. Work is continuing in an effort to obtain higher nitro derivatives, bromo derivatives containing less than three bromine atoms, and in the expectation of obtaining definite compounds from the oily by-product obtained in the mononitration of 3-hydroxydiphenyl.

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Crystalline Acetal Derivatives of *d*-Arabinose[1]

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Solutions of methyl glycoside acetates of the pyranose type, such as β-methyl glucoside tetraacetate, in a mixture of acetic acid and acetic anhydride, upon catalysis by sulfuric acid, have been shown to be transformed to α-acetates of the pyranose type,[2] while those possessing a furanoside linkage are changed under the same conditions to form either aldehydo acetates[3] or ring acetates probably of furanoid structure. It seemed of interest to investigate the course of this reaction in the case of an acetylated methyl glycoside of arabinose, in which the ring, while pyranoid in structure, involves the hydroxyl group of the terminal carbon atom. The results obtained were so novel that it seemed desirable to extend the investigation to include observations upon the catalytic effect of zinc chloride; here again, a novel change was disclosed.

A solution of triacetyl-β-methyl-*d*-arabinoside (I) in a mixture of three volumes of acetic acid and seven volumes of acetic anhydride (hereafter called the acetylating mixture), containing 4% by weight of sulfuric acid, reached an equilibrium rotation (−17°)[4] in three minutes at 20°, in contrast to the behavior of tetraacetyl-β-methyl glucoside, which required forty-eight hours under the same conditions. The crystalline reaction products that were isolated from the pentose derivative included 56% of an open chain compound, aldehydo-*d*-arabinose hexaacetate (II), but there was present only 11% of the expected ring compound, β-*d*-arabinose tetraacetate (III); under similar conditions β-methyl glucoside tetraacetate yielded 92% of the ring compound, α-glucose pentaacetate.

The fact that this concentration of sulfuric acid thus led largely to rupture of the pentopyranoside ring, removal of the methyl group, and peracetylation, suggested the substitution of zinc chloride or a weaker sulfuric acid concentration as milder catalytic agents. The zinc chloride (8%) caused a decided shift in the equilibrium value (+30°) of the acetylating solution and resulted in *complete* rupture of the lactonyl ring, *but without removal of the methyl group,* the elements of acetic anhydride being added to yield a mixture of two pentaacetyl-*d*-arabinose methyl hemi-acetals (IV and V), which were isolated in high (86%) yield. No ring compound could be isolated and the rotations of the pure hemi-acetal pentaacetates, +25° and +32° (in the acetylation mixture), compared to the equilibrium rotation of +30°, indicated the

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[1] Publication authorized by the Surgeon General, U. S. Public Health Service.

[2] Hann and Hudson, THIS JOURNAL, **56**, 2465 (1934).

[3] Montgomery and Hudson, *ibid.*, **56**, 2463 (1934).

[4] All rotations are specific rotations at 20° in sodium light.