NOTES

Characterization of 2-Hydroxy-2′-nitrobiphenyl

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2-Hydroxy-2′-nitrobiphenyl[1] has been obtained in the form of an oil through diazotization and hydrolysis of the partial reduction product from 2,2′-dinitrobiphenyl. The methyl ether of 2-hydroxy-2′-nitrobiphenyl[2] has been prepared using a mixed Ullmann reaction. Solid 2-hydroxy-2′-nitrobiphenyl has not been reported. This phenol has now been prepared in crystalline form by repetition and modification of these two methods. The mixed Ullmann reaction, followed by hydrolysis of the resultant 2-methoxy-2′-nitrobiphenyl, gives an over-all yield of 24% of 2-hydroxy-2′-nitrobiphenyl compared with 5% by the first method. This phenol has been characterized by the preparation of a number of derivatives.

Infrared spectra indicate that some association exists in solutions of this phenol. It is probably intermolecular since the phenol is not volatile in steam as would be true of an *o*-nitrophenol such as 2-hydroxy-3-nitrobiphenyl.[3] While the combined radii of the substituents in the *o,o′*-positions are sufficiently great to somewhat restrict rotation about the pivotal bond of biphenyl[4] chelation is probably inhibited since planarity is impossible without straining the bond angle between the rings.

Experimental

Infrared Spectra of 2-Hydroxy-2′-nitrobiphenyl.—Infrared spectra for chloroform solutions of 2-hydroxy-2′-nitrobiphenyl were determined using a Perkin–Elmer recording spectrophotometer.[5] An absorption peak occurs in the –OH region as well as at higher wave lengths where dipole interaction between groups would be indicated.

Table I

O–H and O–H—O Absorption in Chloroform

Molal concn.	2.80 mμ	3.08 mμ
0.15	11.5%	11.5%
.10	5.0	7.0
.05	1.0	2.3

1. **Preparation of 2-Hydroxy-2′-nitrobiphenyl from 2,2′-Dinitrobiphenyl.**—Hydrogen sulfide was passed for 1.5 hours through 600 ml. of 95% ethanol at 60° to which 10 g. (0.04 mole) of 2,2′-dinitrobiphenyl and six molar proportions of ammonium hydroxide had been added. Following acidification with hydrochloric acid unchanged 2,2′-dinitrobiphenyl was extracted with benzene and the aqueous portion filtered through charcoal to remove free sulfur and highly colored impurities. Concentration and cooling gave 5 g. of the light yellow hydrochloride (49%) of 2-amino-2′-nitrophenyl. The neutral equivalent was 249 (calcd. 250.7).

A 3.75-g. portion of the hydrochloride of 2-amino-2′-nitrobiphenyl was diazotized in the usual manner and added to boiling 50% sulfuric acid. The phenol was recovered by making the solution alkaline, extracting with benzene to remove non-phenolic material, acidifying and extracting the aqueous portion with benzene. Evaporation of the benzene extract gave a tarry residue which was taken up with alkali, acidified and permitted to stand. Pale yellow needles, 0.32 g. (10% or 5% if based upon 2,2′-dinitrobiphenyl), m.p. 139–140°, were obtained.

Anal. Calcd. for $C_{12}H_9O_3N$: C, 67.0; H, 4.2; N, 6.5. Found: C, 66.8; H, 4.0; N, 6.4.

2. **Preparation of 2-Hydroxy-2′-nitrobiphenyl by Mixed Ullmann Reaction.**—Twelve grams (0.048 mole) of *o*-iodonitrobenzene, 10 g. of *o*-bromoanisole (0.053 mole) and 10 g. of activated copper bronze,[6] were placed in a long-necked flask fitted with a mechanical stirrer. Efficient stirring was accomplished by entangling copper-wool in the stirring rod. The reactants were held just short of reflux temperature for 1.5 hours, cooled, flushed out with benzene and centrifuged. The benzene was evaporated and the residue steam distilled to remove unreacted *o*-iodoanisole. The undistilled portion was taken up with benzene, dried and evaporated to a thick oil. Twenty-five ml. each of acetic anhydride and 48% hydrobromic acid were added to the oil and the mixture heated for 48 hours. The hydrolysate was diluted to 300 ml. with water, made alkaline with 10% sodium hydroxide and extracted with benzene. The remaining solution was acidified with hydrochloric acid. Pale yellow needles superimposed upon a darker colored matte formed upon standing overnight. The yield of 2-hydroxy-2′-nitrobiphenyl was 2.48 g. (24%). The melting point was 139–140°.

A benzene extract, following hydrolysis of the methyl ether, when evaporated to dryness, gave 2.94 g. (50%) of 2,2′-dinitrobiphenyl. This by-product, melting at 128°, was used in the preparation of 2-hydroxy-2′-nitrobiphenyl by the first method described.

2-Methoxy-2′-nitrobiphenyl.—This substance was prepared by refluxing a reaction mixture from the previously described mixed Ullmann with several 30-ml. portions of benzene, uniting these extracts, filtering through sintered glass to remove cuprous iodide, and concentrating on a water-bath. The addition of petroleum ether (37–45°) caused separation of a dark oil. Upon standing, crystals of 2,2′-dinitrobiphenyl separated. The supernatant liquid was decanted, concentrated on the water-bath and distilled under atmospheric pressure for removal of excess *o*-iodoanisole. The residue was taken up with benzene and petroleum ether added to precipitate the remaining 2,2′-dinitrobiphenyl. The remaining liquid was concentrated and petroleum ether added. Pale yellow crystals weighing 3.2 g. (27%) and melting at 70–72° were obtained. Recrystallization from chloroform and petroleum ether raised the melting point to 82° which agrees with that previously recorded.[2]

Nitration of 2-Hydroxy-2′-nitrobiphenyl.—To 0.5 g. of 2-hydroxy-2′-nitrobiphenyl in 5 ml. of acetic acid, 0.45 ml. of concd. nitric acid was added dropwise. After 15 minutes standing the reaction mixture was refluxed for one hour. Upon addition of water the trinitrophenol precipitated. Two crystallizations from 95% alcohol gave 0.49 g. (70%). The melting point was 123°. 2-Hydroxybiphenyl yields 2-hydroxy-3,5-dinitrobiphenyl,[7] hence it is assumed that the present product is 2-hydroxy-3,5,2′-trinitrobiphenyl.

Anal. Calcd. for $C_{12}H_7O_7N_3$: N, 13.8. Found: N, 13.9.

Bromination of 2-Hydroxy-2′-nitrobiphenyl.—A 100% excess of brominating solution (made by dissolving 15 g. of potassium bromide in 100 ml. of water and adding 10 g. of bromine) was added to 1 g. of 2-hydroxy-2′-nitrobiphenyl in 20 ml. of acetone. After 30 minutes standing with occasional shaking, water was added to precipitate the bro-

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(1) L. Mascarelli and D. Gatti, *Atti acad. Lincei*, **13**, 887 (1931).

(2) L. Mascarelli and D. Gatti, *Atti IV Cong. naz. chim. pure applicata*, 503 (1933).

(3) Voroscov and Troscenko, *J. Gen. Chem.* (*U. S. S. R.*), **8**, 432 (1938).

(4) Roger Adams and H. C. Yuan, *Chem. Revs.*, **12**, 284 (1933).

(5) Infrared spectra were determined by Ralph S. Shank through the courtesy of the Phillips Petroleum Company, Research Division, Bartlesville, Oklahoma.

(6) E. C. Kleiderer and Roger Adams, This Journal, **55**, 4219 (1933).

(7) Borche, *Ann.*, **312**, 266 (1900).

TABLE II

DERIVATIVES OF 2-HYDROXY-2'-NITROBIPHENYL

Derivative, 2-(2-nitrophenyl)-phenyl-	Formula	Yield, %	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Benzoate	$C_{19}H_{13}O_4N$	50	116	71.5	71.3	4.1	3.9	4.4	4.4
4-Nitrobenzoate	$C_{19}H_{12}O_6N_2$	70	116	62.6	62.5	3.3	3.2	7.7	7.8
3,5-Dinitrobenzoate	$C_{19}H_{11}O_8N_3$	70	180					10.3	10.2
4-Nitrobenzene sulfonate	$C_{18}H_{12}O_7N_2S$	90	147					7.0	6.9
3-Nitrobenzene sulfonate	$C_{18}H_{12}O_7N_2S$	50	161	54.0	54.2	3.0	2.8	7.0	7.0
4-Methylbenzene sulfonate	$C_{19}H_{15}O_5NS$	40	100					3.8	3.7
2,4-Dinitrophenyl ether	$C_{18}H_{11}O_7N_3$	10	118					11.0	11.1

minated product. The crystals were filtered, dissolved in chloroform, the solution dried over sodium sulfate, concentrated and precipitated by addition of petroleum ether. The light yellow material melted at 149°. Since 2-hydroxybiphenyl readily yields 3,5-dibromo-2-hydroxybiphenyl[8] the present product is assumed to be 2-hydroxy-3,5-dibromo-2'-nitrobiphenyl. A yield of 1.2 g. (70%) was obtained.

Anal. Calcd. for $C_{12}H_7O_3Br_2N$: Br, 42.9. Found: Br, 42.7.

This procedure was repeated using 1 g. of 2-methoxy-2'-nitrobiphenyl. The dibrominated ether weighed 1.25 g. (70%) and melted at 108° following recrystallization from chloroform and petroleum ether.

Anal. Calcd. for $C_{13}H_9O_3Br_2N$: Br, 41.3. Found: Br, 41.0.

Hydrolysis of the dibrominated ether was accomplished by heating 0.2 g. of the ether for two days at 90° with 2 ml. each of acetic anhydride and hydrobromic acid. Fifteen milligrams of 2-hydroxy-3,5-dibromo-2'-nitrobiphenyl was isolated. This hydrolysis product melted at 149° when mixed with that obtained by bromination of 2-hydroxy-2'-nitrobiphenyl. The dibromoether is assumed to be 2-methoxy-3,5-dibromo-2'-nitrobiphenyl.

Derivatives of 2-Hydroxy-2'-nitrobiphenyl.—Seven derivatives involving the -OH group of 2-hydroxy-2'-nitrobiphenyl were prepared. All were prepared by well known methods. In general, the phenol was dissolved in pyridine and the acid chloride added in slight excess. Refluxing for 30 minutes was followed by pouring the reaction mixture over ice or into cold water. The precipitate was dissolved in a suitable solvent such as chloroform or alcohol and a crystalline product obtained. Table II supplies details.

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(8) Auwers and Wittig, *J. prakt. Chem.*, **108**, 99 (1924).

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Colored Complexes with Inorganic Salts Mounted on Silica Gel

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Jura, Grotz and Hildebrand[1] have reported that mesitylene reacts with the salts of 19 metals on a silica gel surface to form colored complexes, and attributed the color formation to a generalized acid–base interaction between mesitylene and the respective cations. Evidence is listed below, however, which shows that the colors reported by these investigators can be attributed to the presence of an as yet unidentified trace impurity in mesitylene. This evidence does not, of course, exclude the possibility of the existence of genuine mesitylene complexes that have characteristic absorption bands outside of the visible spectrum.

Sulfates of four of the 19 ions reported to give colored mesitylene complexes—Cu^{++}, Zn^{++}, Mg^{++} and Al^{+++}—were mounted on silica gel. When mesitylene from two different sources was added to these salts, two types of reactions were observed. Mesitylene from the first source, which we will denote mesitylene I, produced an intense red-purple color with each of the above four salts. A sample of mesitylene used by Jura, *et al.*,[2] gave a red-purple color that was not as intense as was the case for mesitylene I. However, mesitylene from the second source (denoted as mesitylene II) produced no color change of any kind with these same salts. A mixture of I and II gave the red-purple color reaction. These results were already strong evidence for the presence of a color-producing impurity in mesitylene I that was absent from mesitylene II.

The attempts to isolate and identify the color-producing impurity—henceforth denoted as X—in mesitylene I can be summarized as follows: (1) Simple distillation or chromatographic treatment with silica gel did not remove impurity X. (2) Ten equal fractions were obtained by distillation of mesitylene I through a 60-plate fractionating column at a reflux ratio of *ca.* 60:1. Since impurity X did not appear in the first nine fractions, but was found in the higher boiling residue (fraction 10), a tenfold concentration of impurity X was effected. (3) After learning that mesitylene I was probably synthesized from acetone, two of the possible higher boiling by-products of this synthesis—phorone and isophorone—were added to the mounted salts. No color reaction was observed. (4) Chromatographic treatment using copper sulfate mounted on silica gel as the adsorbent completely removed impurity X, as was evidenced by the appearance of an extremely intense red-purple zone localized at the top of the chromatographic column. Attempts to remove impurity X from the colored adsorbent by sublimation in high vacuum resulted in decomposition of the adsorbed material. In this respect, the adsorption seemed irreversible. (5) Ultraviolet analysis of mesitylene I revealed no absorption peaks other than those characteristic of mesitylene itself. (6) The above-mentioned mesitylene samples were analyzed mass-spectrometrically at each stage of purification and isolation. In making an intercomparison of the mass spectra of these samples, it was assumed (because of the results described in 2) that impurity X had a molecular weight higher than that of mesitylene. Although it was not possible to assign

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[1] G. Jura, L. Grotz and J. H. Hildebrand, American Chemical Society Meeting Abstracts, September, 1950, p. 56Q.

[2] The writer gratefully acknowledges the coöperation of Professor George Jura, who kindly supplied this sample of mesitylene.