Dinitrobenzoate, m. p. 210–212°. *Anal.* Calcd. for $C_{22}H_{20}N_4O_{12}$: C, 49.62; H, 3.95. Found: C, 49.94; H, 4.11.

2-(1-Hydroxypropyl)-cyclohexanol.—B. p. 256–259°, n^{25}_D 1.4788, d^{25}_4 1.0060; M_D (calcd.) 44.61; M_D (found) 44.65. *Anal.* Calcd. for $C_9H_{18}O_2$: C, 68.35; H, 11.39. Found: C, 67.96; H, 11.42. 3,5-Dinitrobenzoate, m. p. 162.5–164°. *Anal.* Calcd. for $C_{23}H_{22}O_{12}N_4$: C, 50.54; H, 4.04. Found: C, 50.71; H, 4.48.

Summary

1. Alkylcyclohexanols are readily obtained by the hydrogenation of alkyl-, alkenyl- and acylphenols in the presence of Raney nickel.
2. The hydrogenation of di-ortho substituted phenols is promoted by small amounts of alkali.
3. The hydrogenation of alkenyl and acylphenols may be conducted at low temperatures to give good yields of alkylphenols.
4. The hydrogenation of acylphenols gives alkylphenols or alkylcyclohexanols depending upon the temperature. In the presence of alkali a mixture of alkylphenol and hydroxyalkylcyclohexanol is obtained at low temperatures and a mixture of alkylcyclohexanol and hydroxylalkylcyclohexanol at high temperatures.

Columbia, Missouri Received September 9, 1943

[Contribution from the Departments of Chemistry of the University of Texas and the University of Oklahoma]

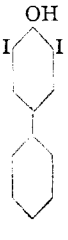
The Iodination of 4-Hydroxybiphenyl[1a]

By J. C. Colbert,[1b] H. W. Houghton,[1b] H. R. Schmidt[2] and J. L. Abernethy[2]

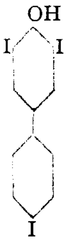
Although the chlorination[3] and bromination[4,5] of 4-hydroxybiphenyl have been investigated, the only iodine derivative of this phenol mentioned in the literature appears to be 4′-iodo-4-hydroxybiphenyl[6] obtained by use of the Sandmeyer reaction.

On the basis of the results of chlorination and bromination, it was anticipated that iodination of 4-hydroxybiphenyl would cause the first iodine atom to enter the 3-position, thereby yielding 3-iodo-4-hydroxybiphenyl (I); the second atom would enter the 5-position, with the resultant formation of 3,5-diiodo-4-hydroxybiphenyl (II); and, finally, the third atom would enter the 4′-position, giving rise to 3,5,4′-triiodo-4-hydroxybiphenyl (III).

I



II



III

Introduction of a solution of iodine dissolved in potassium iodide into a solution of 4-hydroxybiphenyl in sodium hydroxide[7] gave rise to I. However, when an attempt was made to diiodinate 4-hydroxybiphenyl using the same procedure, II could not be isolated from the reaction products. Instead, a compound which gave an analysis very close to a monoiodinated derivative was obtained. This substance decomposed at temperatures above 170°. Since it is known that on heating diiodinated phenols[8] with sodium hydroxide, two molecules undergo condensation with loss of hydrogen, *i. e.*, aristol formation takes place, it seemed plausible that a similar reaction had taken place during the attempted diiodination of 4-hydroxybiphenyl. Consequently a Rast molecular weight of this product was determined. This indicated that the molecular weight was approximately double that of a monoiodo-4-hydroxybiphenyl and suggested that aristol formation had taken place. No further attempt was made to prove its structure.

Iodination of 4-hydroxybiphenyl in an ammonium hydroxide solution gave rise to I. Further iodination introduced iodine in the 5-position, hence yielding II. This procedure is known to be more satisfactory than the procedure in which sodium hydroxide is used, in that in most instances very little aristol formation takes place with iodinated phenols.

Iodination with iodine monochloride gave rise to I, and further iodination gave rise to II. Attempts to triiodinate 4-hydroxybiphenyl were unsuccessful.

The benzoates of I and II were prepared by benzoylation of these substances with benzoyl chloride in pyridine. It was found that benzoylation of I took place readily, whereas benzoylation of II was somewhat more difficult. This latter

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[1a] In 1938 at the University of Oklahoma an attempt was made to apply the detailed method of iodination of a phenol used by Harington in the synthesis of thyroxin to the iodination of 4-hydroxybiphenyl. This method made use of a solution of iodine in potassium iodide which was added to the ammoniacal solution of the phenol. In work initiated independently at the University of Texas in 1942 an attempt was made to iodinate this substance in a sodium hydroxide solution. This was abandoned, however, in favor of iodination with iodine monochloride. Shortly after this latter work was under way it was learned through correspondence that the iodination had been accomplished at the University of Oklahoma. The present paper presents the results of the investigations conducted independently at both institutions.

[1b] University of Oklahoma, Norman, Oklahoma.

[2] University of Texas, Austin, Texas.

[3] Colbert, Meigs and Mackin, This Journal, **56**, 202 (1934).

[4] Raiford and Colbert, *ibid.*, **47**, 1456 (1925).

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

[6] Angelletti and Gatti, *Gazz. chim. ital.*, **58**, 630–635 (1929).

[7] Harington and Barger, *Biochem.*, **21**, 169 (1927); **22**, 1429 (1928).

[8] Bordeianu, *Chem. Abs.*, **30**, 1760 (1936).

finding is in accord with earlier investigations[9] involving diortho substituted phenols.

The introduction of one nitro group into 3-iodo-4-hydroxybiphenyl was accomplished by a method[4] previously used in the mononitration of 4-hydroxybiphenyl.

Acknowledgment.—The writers are indebted to Professor G. W. Watt of the University of Texas for a supply of liquid ammonia used in the analysis, and to the Research Institute of the University of Texas for a grant permitting the continuance of this work.

Experimental

3-Iodo-4-hydroxybiphenyl.—(a) 2.0 g. of 4-hydroxybiphenyl was dissolved in warm ammonium hydroxide and cooled as low as possible without causing the phenol to separate. The molecular equivalent (*i. e.*, three grams) of iodine was dissolved in a potassium iodide solution and diluted to the basis of 3.0 g. of iodine per 500 cc. of solution. The reagent was added at the surface of the solution with as rapid stirring as possible, the addition requiring one hour. Best results were obtained using only diffused light. Following filtration, which should be rapid, the filtrate was cooled in an ice-bath and the phenol precipitated by addition of a 10% solution of sulfuric acid. During addition of acid decomposition occurred unless the temperature were held below 35°. The white needle-like precipitate was filtered rapidly, care being taken to avoid drawing air through the residue, *i. e.*, the last of the filtrate was obtained by gravity filtration. The crystals were washed with water and air dried in a dark place. Final drying was completed *in vacuo*. The yield of crude material was 91.1% and the melting point 108–109°. Analysis for iodine was made by sodium peroxide fusion followed by titration with silver nitrate. Recrystallization from chloroform by addition of petroleum ether raised the melting point to 115–116°.

Anal. Calcd. for $C_{12}H_9OI$: I, 42.86. Found: I, 43.16.

(b) 4-Hydroxybiphenyl (17 g.) was dissolved in a solution of 35 g. of sodium hydroxide in 600 ml. of water. This solution was heated in order to dissolve the 4-hydroxybiphenyl completely and was subsequently cooled until the 4-hydroxybiphenyl began to precipitate. Iodine (25.4 g.) dissolved in 200 ml. of an aqueous solution of potassium iodide (25.4 g.) was then added over a period of two hours. At the end of this time the mixture was acidified with dilute hydrochloric acid, causing 27 g. of a white precipitate to separate. After several recrystallizations a small amount of pure 3-iodo-4-hydroxybiphenyl was obtained.

(c) Seventeen grams of 4-hydroxybiphenyl was dissolved in 40 ml. of glacial acetic acid upon being heated on a steam-bath. Iodine monochloride (20.4 g.), Eastman Kodak Co. grade, dissolved in glacial acetic acid (14 ml.) was added dropwise to the above solution over a period of twenty minutes. The reaction proceeded readily with the liberation of hydrogen chloride. Heat was also liberated as the reaction proceeded. After complete addition of the iodine monochloride solution the mixture was heated gently on a steam-bath with constant stirring for an additional two hours. At the end of this time the resultant solution was cooled to room temperature and poured into ice-water. The precipitate which separated was filtered and dissolved in chloroform. The chloroform solution was then washed with an aqueous solution of sodium bisulfite to remove the excess iodine. It was washed with water and dried over anhydrous sodium sulfate. The solution was filtered and approximately three-fourths of the chloroform was removed under reduced pressure. A white precipitate separated on cooling the solution in an ice-bath. After two recrystallizations from a mixed solvent of one-third chloroform and two-thirds petroleum ether (b. p. 30–35°), 18 g. of white needles was obtained which melted at 115–116°; yield of recrystallized material, 60.8%.

A more direct procedure for removal of the excess iodine from the iodinated product involved addition of an aqueous solution of sodium bisulfite directly to the acetic acid solution after iodination had taken place. Removal of the impure 3-iodo-4-hydroxybiphenyl by filtration followed by recrystallization from the mixed solvent named above yielded the pure substance in approximately the same quantity as by the other method.

Anal. Calcd. for $C_{12}H_9OI$: I, 42.86. Found: I, 42.75.

Benzoylation of 3-Iodo-4-hydroxybiphenyl.—To a cooled solution of 2 g. of 3-iodo-4-hydroxybiphenyl in 20 ml. of pyridine, 2 ml. of benzoyl chloride was added slowly, with shaking. The mixture was heated for one hour on a steam-bath. On cooling to room temperature, following which the mixture was poured into a large volume of ice-water, a precipitate separated. The precipitate was filtered and washed successively with 10% sodium hydroxide solution, a dilute hydrochloric acid solution and water. The product was recrystallized from ethanol. The white crystals were obtained in a yield of 1.2 g., or 44.4% and melted at 99.5–100°. The Schotten–Baumann method gave a 68.2% yield of the benzoate melting at 91–92°.

Anal. Calcd. for $C_{19}H_{13}O_2I$: I, 31.71. Found: I, 31.35.

Nitration of 3-Iodo-4-hydroxybiphenyl.—Two grams of 3-iodo-4-hydroxybiphenyl was dissolved in 20 cc. of glacial acetic acid and 0.43 cc. of concd. nitric acid dissolved in 5.0 cc. of glacial acetic acid added slowly to the cooled solution. Nitration occurred slowly and the product was recovered by pouring the solution into ice-water. Recrystallization from 50% alcohol gave a 62.4% yield of 3-iodo-5-nitro-4-hydroxybiphenyl; m. p. 95–100° with decomposition.

Anal. Calcd. for $C_{12}H_8O_3NI$: I, 37.21. Found: I, 37.24.

Attempted Diiodination of 4-Hydroxybiphenyl.—4-Hydroxybiphenyl (8.5 g.) was dissolved in 600 ml. of an aqueous solution containing 36 g. of sodium hydroxide. To this solution was added, dropwise, over a period of two hours, 200 ml. of an aqueous solution containing 25.4 g. of potassium iodide and 25.4 g. of iodine. At the end of the addition dilute hydrochloric acid was added to the resultant mixture until the solution was acid to litmus. A yellow precipitate (17.6 g.) separated which was thought to be 3,5-diiodo-4-hydroxybiphenyl. This material, upon recrystallization from an alcohol–water mixture, melted with decomposition at 170–171°.

An analysis of the above compound indicated that apparently a mono iodinated product was formed. It was assumed then that a second reaction had taken place with the formation of an aristol. A Rast molecular weight determination was then made on the compound. It was found that 0.0132 g. of the compound dissolved in 0.091 g. of camphor lowered the melting point of camphor 9°. This indicated a molecular weight of 637. The theoretical molecular weight of the aristol is 590.

Anal. Calcd. for $C_{24}H_{16}O_2I_2$: I, 43.01. Found: I, 42.08.

No further investigation was made on this compound.

3,5-Diiodo-4-hydroxybiphenyl.—(a) The ammonium salt of this phenol was obtained by dissolving 2.0 g. of 4-hydroxybiphenyl in 350 cc. of warm ammonium hydroxide followed by cooling as low as possible without precipitation. Six grams of iodine in one liter of potassium iodide solution was added with rapid stirring over a period of one hour. Upon the first appearance of a dark residue the dropwise titration was discontinued since otherwise the solution became dark. This appearance which is also mentioned by Harington appears after the addition of about 95% of the iodine. The white precipitate was filtered by gravity, light being excluded. Upon drying in a cool, dark place, a 79.5% yield of the ammonium salt of 3,5-diiodo-4-hydroxybiphenyl was obtained; m. p. for the white crystals, 95–97°. Upon standing the precipitate

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(9) Brazier and McCombie, *J. Chem. Soc.*, **101**, 970 (1912).

slowly turned yellow, the melting point falling to 92–93°. The yellow samples upon analysis appeared to have lost iodine.

Anal. Calcd. for $C_{12}H_8OI_2$: I, 57.86. Found: I, 55.10.

The 3,5-diiodo-4-hydroxybiphenyl set free from a sample of this ammonium salt gave white needles which readily decomposed.

(b) Seventeen grams of 4-hydroxybiphenyl was dissolved in 40 ml. of glacial acetic acid. To this mixture, 45 g. of iodine monochloride dissolved in 25 ml. of glacial acetic acid was added dropwise over a period of one-half hour. The mixture was then refluxed on a steam-bath for two hours. Hydrogen chloride gas was liberated freely during the reaction. After this treatment the mixture was cooled to room temperature and poured into a large volume of ice-water. A pale yellow solid and an oily, brown substance separated. Solid sodium bisulfite was added to the mixture in order to remove the iodine to some extent. The water soluble constituents of the mixture were decanted and the remaining portion extracted with carbon tetrachloride. The carbon tetrachloride solution was washed with sodium bisulfite solution which removed the remaining iodine and was then washed with water and dried over anhydrous sodium sulfate.

After the solution had dried, its volume was reduced to one-fourth the original volume by distillation under reduced pressure. Addition of petroleum ether to the remaining solution caused 21 g. of a white precipitate to separate. After dissolving the precipitate in chloroform and precipitating it from solution by the addition of petroleum ether several times and finally recrystallization from the mixed solvent of one-third chloroform and two-thirds petroleum ether (b. p. 30–35°), the yield was reduced to 4.8 g. The pure white solid melted at 86–87°.

Anal. Calcd. for $C_{12}H_8OI_2$: I, 60.15. Found: I, 60.07.

Benzoylation of 3,5-Diiodo-4-hydroxybiphenyl.—The procedure used to prepare 3,5-diiodo-4-benzoxybiphenyl was the same as given above for the preparation of 3-iodo-4-benzoxydiphenyl. The product was recrystallized from ethanol. The resulting white needles melted at 159–160°.

Anal. Calcd. for $C_{19}H_{12}O_2I_2$: I, 48.24. Found: I, 47.80.

Attempted Triiodination of 4-Hydroxybiphenyl.—Several attempts were made to prepare this compound in the manner described above for the mono- and diiodination of 4-hydroxybiphenyl by varying the solvent, the time of reaction and external heat applied. In each attempt, however, isolation of the desired product was unsuccessful.

Summary

4-Hydroxybiphenyl has been mono- and diiodinated forming 3-iodo-4-hydroxybiphenyl and 3,5-diiodo-4-hydroxybiphenyl, respectively. They were identified by analysis and analogy to the chlorination and bromination products of 4-hydroxybiphenyl.

Attempts to triiodinate 4-hydroxybiphenyl were unsuccessful.

The benzoate derivatives of the above mono- and diiodo-hydroxybiphenyls have been prepared. The mononitro derivative of 3-iodo-4-hydroxybiphenyl also has been obtained.

NORMAN, OKLAHOMA
AUSTIN, TEXAS

RECEIVED OCTOBER 1, 1943

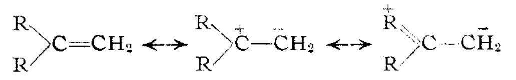
[CONTRIBUTION FROM THE MARIAN EDWARDS PARK LABORATORY OF BRYN MAWR COLLEGE]

The Condensation of Naphthoquinones with Polar Ethylenes

BY MARSHALL GATES

In 1939 Wizinger and Coenen[1] showed that a carbon–carbon bond could be established by displacement of chlorine from polynitro aromatic chlorides using as displacing agents certain unsymmetrically substituted ethylenes.

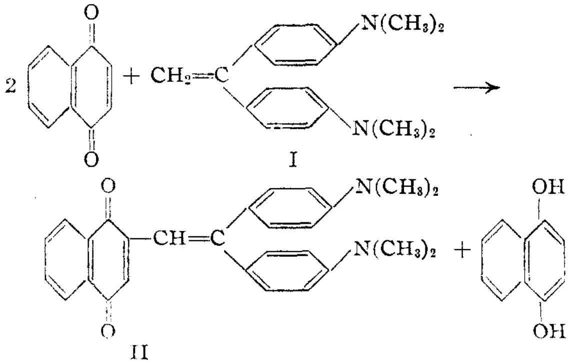
The ethylenes involved were of the type whose members readily form halochromic salts and show reactions with other types of electron acceptors.[2] Their reactions indicate large contributions from forms in which the ethylenic link is polarized



$$R_2C{=}CH_2 \longleftrightarrow R_2\overset{+}{C}{-}\overset{..}{C}H_2 \longleftrightarrow \overset{+}{R}{=}C(R){-}\overset{-}{C}H_2$$

Since many of the reactions of quinones involve the addition of a molecule with an unshared electron pair to the conjugated system of the quinone, it might be expected that a carbon–carbon bond could be established by the action of a polar ethylene of the above-mentioned type acting as an electron donor on a quinone acting as an electron accepting center. This expectation was fully realized and a number of condensations of this type were found to take place with ease.

To provide a trial free from the complicating side reactions which might be expected of benzoquinone, the action of 1,1-bis-(*p*-dimethylaminophenyl)-ethylene (I) on *α*-naphthoquinone was studied. On mixing these two reagents in benzene, acetone or dioxane, an intense deep purple color is produced immediately even at room temperature, and on standing the solution deposits beautiful fine purple needles of 2-(1′,4′-



I

II

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[1] Wizinger and Coenen, *J. prakt. Chem.*, **153**, 127 (1939).

[2] Pfeiffer and Wizinger, *Ann.*, **461**, 132 (1928).