

Detail of the Preparation of Dihydroxy-dihydroquinone.—A mixture of 100 g. of hydroquinol, 400 cc. of water, 150 g. of sodium chlorate, 50 cc. of *N* hydrochloric acid and 10 cc. of a 1% osmium tetroxide solution is made in a 1-liter flask. The change to quinhydrone is observed to occur rapidly and it is found necessary to cool the mixture. After the evolution of heat has ceased, the flask is closed with a stopper carrying a tube equipped with a Bunsen valve (slit rubber tube closed at the outer end) so that the carbon dioxide which forms during the change may escape. The mixture is then shaken during about 54 hours. By this time all quinone will have disappeared and abundant white crystals will have formed. These are removed, washed with water, alcohol and finally with ether. The yield is better than 50%. The product may be recrystallized from boiling water. Oxalic acid and at least one other product not yet fully identified are present in the water solution left from the preparation.

Summary

A new oxidation product of quinone is reported. Its molecular formula is $C_6H_6O_4$. Tentatively it is called dihydroxy-dihydroquinone. Its preparation and representative reactions are described.

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THE EFFECT OF SUBSTITUENTS IN THE FORMATION AND REACTIONS OF CERTAIN ETHERS¹

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RECEIVED JUNE 14, 1926

PUBLISHED OCTOBER 6, 1926

Though chloro- and bromobenzenes do not give up halogen readily by double decomposition,² the nitro radical in the *ortho* or *para* position increases the activity.³ Thus, Heumann⁴ and Laubenheimer⁵ found that

¹ An abstract of part of a thesis presented by James C. Colbert to the Graduate College of the State University of Iowa in partial fulfilment of the requirements for the degree of Doctor of Philosophy. Reported in abstract at the Tulsa meeting of the American Chemical Society, April, 1926.

² Fittig, *Ann.*, **133**, 49 (1865). Jungfleisch, *Ann. chim. phys.*, [4] **15**, 224 (1868). Weber and Wolf, *Ber.*, **18**, 335 (1885). Blau, *Monatsh.*, **7**, 621 (1886).

³ Fry [THIS JOURNAL, **38**, 1329 (1916)] heated the three isomeric chloronitrobenzenes in separate sealed tubes with sodium methylate for five hours at 100°. Chlorine was removed from the *ortho* and *para* positions, but the *meta* isomer did not react. The activating effect of the *ortho* nitro group may sometimes fail, for Borsche found [*Ber.* **50**, 1343 (1917)] when 1,3-dichloro-4,6-dinitrobenzene was heated with potassium phenolate, that it gave 2,4-dinitro-5-chlorodiphenyl ether instead of the expected triphenyl ether.

⁴ Heumann, *Ber.*, **5**, 910 (1872).

⁵ Laubenheimer, *Ber.*, **8**, 1626 (1875); Ger. pat. 140,133, 1903.

p-nitrochlorobenzene reacted with alcoholic potassium hydroxide to give dichloroazoxybenzene, and that 2,5-dichloronitrobenzene⁶ gave other products in addition to the azoxy compound. Later, Willgerodt⁷ showed that when *p*-chloronitrobenzene was heated with alcoholic potassium hydroxide in a sealed tube between 100° and 130°, chiefly the azoxy compound was formed; from 150–200°, the azo derivative was obtained. When the alcoholic solution was diluted and the mixture refluxed, *p*-nitrophenylethyl ether was the chief product. Brand⁸ obtained similar results with the *o*-nitro derivative. Neither author recorded the yield. Jackson and Carlton⁹ found that 2,6-dinitro-1,3,4,5-tetrachlorobenzene reacted with sodium ethylate (slightly more than four molecular proportions) to give a triethyl ether in which the halogen atoms *ortho* and *para* to the nitro groups were replaced.¹⁰ More recently Blom¹¹ studied the reaction between *p*-chloronitrobenzene and methyl and ethyl alcohols quantitatively, and found that a temperature of 70° and a low concentration of alcohol gave over 80% of the ether. Higher temperatures caused the formation of azoxy derivatives. In the case of allyl alcohol, experiments made at 50°, 60°, 70° and 85°, respectively, gave only the azoxy derivative.

The activity of the halogen toward several reagents is much increased by the presence of two nitro groups.¹² Austen¹³ found that sodium and an alcoholic solution of 2,4-dinitrochlorobenzene gave only the corresponding dinitrophenyl alkyl ether, while the mononitro derivative gave nothing but the chloro-azoxybenzene.

Preliminary experiments in this Laboratory¹⁴ indicated that when *p*-bromonitrobenzene was treated with methyl alcohol by Blom's method, about one-fourth of it was converted into the ether and the remainder was unchanged.¹⁵ Somewhat similar results were obtained with the chlorine compound. To test this behavior further it was proposed to repeat Gordon's work and to study the action of the chloro and bromo compounds on other alcohols. It seemed interesting, also, to examine the behavior of

⁶ Laubenheimer, *Ber.*, **7**, 1601 (1874).

⁷ Willgerodt, *Ber.*, **15**, 1002 (1882).

⁸ Brand, *J. prakt. Chem.*, [2] **67**, 145 (1903).

⁹ Jackson and Carlton, *Am. Chem. J.*, **31**, 376 (1904).

¹⁰ Kehrman [J. *prakt. Chem.*, [2] **40**, 368 (1889); **43**, 260 (1891)] found that there is a fundamental difference, in some cases, between the behavior of alcoholic and water solutions of alkali toward halogenated derivatives of this type.

¹¹ Blom, *Helvetica Chim. Acta*, **4**, 297, 510, 1029 (1921).

¹² Clemm, *Ber.*, **3**, 126 (1870). Leymann, *Ber.*, **15**, 1233 (1882). Einhorn and Frey, *Ber.*, **27**, 2457 (1894).

¹³ Austen, *Ber.*, **8**, 666 (1875).

¹⁴ Gordon, *Thesis*, State University of Iowa, 1923.

¹⁵ Though Blom reported a yield of more than 80% of *p*-nitro-anisol from the chlorine derivative by this method, he usually did not isolate the ether but calculated the yield in terms of the chloride ion found by titration of the reaction mixture.

compounds containing more than one halogen atom or nitro radical, respectively. 2,5-Dichloronitrobenzene and 2,4-dinitrochlorobenzene were selected for these tests. The general results are indicated in Table I.

TABLE I
THE INTERACTION OF HALOGENATED NITROBENZENES AND ALCOHOLS TO GIVE: (A) ETHERS; (B) AZOXY DERIVATIVES

Benzene derivative	Alcohols employed			
	Methyl	Ethyl	Propyl	Allyl
<i>p</i> -Nitrochloro	Mixture	Mixture
<i>p</i> -Nitrobromo	Mixture	Mixture	Mostly azoxy derivative	40% of azoxy derivative
2,5-Dichloro-nitro	92% of ether	33.9% of ether	Azoxo derivative only
2,5-Dibromo-nitro	85.7% of ether ^a	49.0% of ether ^a
2,4-Dinitro-chloro	94.7% of ether	68.8% of ether	65.8% of ether

^a Bren's work, now in progress in this Laboratory.

A second point of interest was to determine the behavior of the halogenated nitrobenzenes when the alcohol is replaced by phenol in the experiments indicated above. The work of Maikopar,¹⁶ Willgerodt and co-workers,¹⁷ and Haeussermann and Teichmann¹⁸ showed that if phenol is substituted for the alcohol mentioned above, the corresponding diphenyl ethers are generally obtained. Yields are not given, and nothing is said, regarding the possible effect of different substituents in the phenol employed.¹⁹ The present report contains data obtained by studying that question.

The first experiments were made with *p*-chloro- and *p*-bromonitrobenzenes, respectively, on potassium phenolate. It was desired to prepare 4-nitrodiphenyl ether by this method in order to determine the yield because Haeussermann and Teichmann,¹⁸ who first obtained it, gave no yield and, also, to test the peculiar results recorded by Jones and Cook.²⁰

¹⁶ Maikopar, *Ber.*, **6**, 564 (1873).

¹⁷ Willgerodt, (a) *Ber.*, **12**, 762 (1879); (b) **13**, 887 (1880); (c) **17**, 1764 (1884).

¹⁸ Haeussermann and Teichmann, *Ber.*, **29**, 1446 (1896).

¹⁹ A German patent (216,642, 1909) gives data regarding the reduction products of certain ethers obtainable from 2,5-dichloronitrobenzene and various potassium phenolates, but does not describe the ethers.

²⁰ Jones and Cook [THIS JOURNAL, **38**, 1543 (1916)] claim to have prepared *p*-nitrodiphenyl ether by heating *p*-bromonitrobenzene with potassium phenolate without a solvent for 14 hours on a boiling water-bath. Their evidence, however, is far from convincing. To begin with, the product which they regarded as the ether sublimed upon the walls of the flask, and melted at 123.5°. It has been observed in this Laboratory that *p*-bromonitrobenzene, m. p. 125°, behaves in exactly that way under the circumstances described. They purified their reaction product by distillation under reduced pressure, and recrystallized the distillate seven times, until crystals melting sharply at 123° were obtained, although they state that they obtained crystals melting all the

A good yield of ether was obtained from the chlorine compound, but the bromine compound, for reasons given above, was not suitable.

The formation of an ether by the "wet method" from a halogenated nitrobenzene and an alkali phenolate is influenced by the substituents present. When *o*- or *p*-nitrochlorobenzene was heated with potassium phenolate, a good yield of the corresponding ether was obtained; if the phenolate radical contained a nitro group as substituent, no ether was formed. When, however, 2,4-dinitrochlorobenzene was used, an ether was always obtained regardless of the substituents in the phenol, which suggests the activating effect of the second nitro radical in the starting material (chlorobenzene). Table II shows the behavior when the radicals are "reversed."

TABLE II
EFFECT OF "REVERSING" RADICALS IN THE PREPARATION OF CERTAIN DIPHENYL ETHERS

Halogenated benzene derivative	Phenol	Ether formed	Yield, %
2,4-Dinitrochloro	Phenol	2,4-Dinitrodiphenyl	92.0
Chloro	2,4-Dinitro		None
2,4-Dinitrochloro	2-Nitro-4-chloro	2,4,2'-Trinitro-4'-chloro-diphenyl	87
2,5-Dichloronitro	2,4-Dinitro		None
2,4-Dinitrochloro	2-Nitro	2,4,2'-Trinitrodiphenyl	90.5
2-Nitrochloro	2,4-Dinitro		None
2,4-Dinitrochloro	4-Nitro	2,4,4'-Trinitrodiphenyl	97.0
4-Nitrochloro	2,4-Dinitro		None
2,4-Dinitrochloro	2-Nitro-4-bromo	2,4,2'-Trinitro-4'-bromo-diphenyl	94.9
2,5-Dibromonitro	2,4-Dinitro		None ^a

^a Prediction based on previous work

way from 65° up, and that they accepted the highest melting material, 123.5°, as *p*-nitrodiphenyl ether. Our experience has shown that this ether is more soluble in cold alcohol than is *p*-bromonitrobenzene, which latter would probably be the product isolated if a mixture of the two were subjected to the method of purification Jones and Cook describe. Furthermore, although the melting points of certain derivatives of the nitrodiphenyl ethers do show some irregularities, it seems very unlikely that *p*-nitrodiphenyl ether can melt as high as 123.5°. Thus, 2-nitro-4'-chlorodiphenyl ether melts at 45.5°, while 4-nitro-4'-chlorodiphenyl ether melts at 76.5°. This order is reversed in the case of bromine derivatives, for it is found that 2-nitro-4'-bromodiphenyl ether melts at 71°, and 4-nitro-4'-bromodiphenyl ether at 65-66°. Nevertheless, none of the derivatives of *p*-nitrodiphenyl ether indicated in the tables in this paper shows a melting point so high as that recorded by Jones and Cook. Finally, they argue that their results are supported by an analysis of their product for nitrogen, in which they record 12.21% as found, compared with 12.3% calculated. They gave no data from which their results could be recalculated, and they did not prove that their product was free from bromine. However, calculation shows that the formula requires but 6.51% of nitrogen for the ether in question, and 6.93% for *p*-bromonitrobenzene. Haeussermann and Teichmann found 61° for the melting point of this ether and their results are checked by analysis for carbon, hydrogen and nitrogen, of which latter they found 6.71%. The present work (see experimental part) is in good agreement with this.

A third point of interest was the behavior of the ethers toward bromine. Cahours,²¹ and Reinecke²² found that anisole gave a 2,4,6 derivative when treated with bromine, but Lippman²³ showed that only two bromine atoms could be introduced into phenetole in this way, while *p*-nitrophenetole gave a monobromo product only.²⁴ Diphenyl ether has been studied very little in this respect. Mailhe and Murat²⁵ obtained a mono and a dibromo compound of known structures, while Cook²⁶ obtained a tetrabromo derivative that is listed by Stelzner as of unknown structure. In the present work, attempts were made to brominate a number of ethers and to determine the configuration of the products. The results thus far obtained are summarized in Table III.

TABLE III
ACTION OF BROMINE ON VARIOUS MIXED ETHERS

Ether	Action	Ether	Action
2-Nitro-4-chlorophenyl-methyl	None	2,4-Dinitrodiphenyl	Bromine entered the <i>p'</i> position
2-Nitro-4-chlorophenyl-ethyl	None	4-Nitrodiphenyl	Two atoms of bromine entered ^a
2,4-Dinitrophenyl-methyl	None	2,4,2'-Trinitrodiphenyl	None
2-Nitro-4-chlorophenyl-allyl	Allyl radical saturated	2,4,3'-Trinitrodiphenyl	None
2,4-Dinitrophenyl-allyl	Allyl radical saturated	2-Nitro-4'-bromodiphenyl	None
2-Nitro-4-chlorophenyl-benzyl	90% decomposed in acetic acid soln.	4-Nitro-4'-chlorodiphenyl	Mixture, not yet identified ^a
2,4-Dinitrophenyl-benzyl	10% decomposed in chloroform soln.		
2-Nitro-4-chlorodiphenyl	Bromine entered the <i>p'</i> position		

^a Will be studied further to determine configuration.

The behavior of these ethers toward hydrogen bromide is also important. Stoermer²⁷ obtained 75% of the corresponding phenol by heating *p*-

TABLE IV
DECOMPOSITION OF MIXED ETHERS BY HYDROBROMIC ACID

Ether	Decomposition	Ether	Decomposition
2-Nitro-4-chlorophenyl-methyl	About 15%	2,4-Dinitrophenyl-allyl	Almost quantitative
2,4-Dinitrophenyl-methyl	About 35%	2,4-Dinitro-4'-bromodiphenyl	No change
2,4-Dinitrophenyl-ethyl	About 25%		

²¹ Cahours, *Ann.*, **52**, 331 (1844).

²² Reinecke, *Z. Chem.*, **2**, 366 (1866).

²³ Lippman, *Jahresber.*, **23**, 739 (1870).

²⁴ Hallock, *Am. Chem. J.*, **3**, 20 (1881).

²⁵ Mailhe and Murat, *Compt. rend.*, **154**, 601 (1912).

²⁶ Cook, *THIS JOURNAL*, **32**, 1286 (1910).

²⁷ Stoermer, *Ber.*, **41**, 321 (1908).

bromo-anisole and *p*-bromophenetole with hydrobromic acid (d., 1.49), for two hours under a reflux condenser, but ethers containing the nitro radical seem not to have been studied. The observations made on this reaction in the present work are summarized in Table IV.

Experimental Part

A. Derivatives of Mixed Ethers

2-Amino-4-chloro-anisole.—Reduction of the corresponding nitro compound²⁸ with stannous chloride and hydrochloric acid gave a poor yield. Aluminum amalgam²⁹ was more successful. Ten g. of ether dissolved in 150 cc. of 80% alcohol was refluxed for one hour with 5 g. (a large excess) of amalgam and the mixture allowed to stand overnight. It was then filtered, the residue washed with hot alcohol, the combined filtrate and washings were heated to boiling and diluted with water until the amine could just be brought into solution by further heating; the mixture was then filtered hot to remove a small amount of red material that was insoluble under the conditions,³⁰ and this filtrate allowed to crystallize. The crystals were collected, dissolved in dil. hydrochloric acid, the solution was boiled with Norite, filtered, and the filtrate made alkaline with aqueous ammonia. Crystallization of the precipitate from 40% alcohol gave a 51.6% yield of colorless needles; m. p., 82–83°.

The benzoyl derivative of this base was obtained in 85% yield by treatment of 3 g. with slightly more than one molecular proportion of benzoyl chloride by the Einhorn³¹ method. Crystallization from dil. alcohol gave shining needles; m. p., 77.5°.

Anal. Subs., 0.2661, 0.2849: 9.97 cc. of 0.1 *N* acid; AgCl, 0.1591. Calcd. for C₁₄H₁₂O₂NCl: N, 5.35; Cl, 13.55. Found: N, 5.25; Cl, 13.81.

2-Nitro-4-chlorophenetole.—This ether, though known,³² had not previously been prepared by hydrolysis³³ of the chloronitrobenzene. The method described above for the methyl compound gave here a yield of 41.8%. Crystallization from alcohol gave small, nearly colorless needles, m. p. 61°, which agrees with the literature.

Three g. of the phenetole dissolved in 30 cc. of glacial acetic acid was mixed with

²⁸ Previously prepared by Reverdin and Eckhard [*Ber.*, **32**, 2623 (1899)] and by Badische Anilin und Soda-Fabrik (Ger. pat., 140,133, 1903), but no yield reported. Following the German patent, we obtained a 92% yield, and found that when the compound was exposed in a glass bottle or a celluloid container to direct sunlight for a portion of the day for several weeks, a thin layer in immediate contact with the container became pink. This color did not disappear when the bottle was kept in the dark. It was partly decomposed by boiling with hydrobromic acid [Graebe and Martz, *Ann.*, **340**, 220 (1905)].

²⁹ Wislicenus and Kaufmann, *Ber.*, **28**, 1323 (1895).

³⁰ This was always present, but in appreciable quantities only when the yield of the base was low. In one experiment 25.8% of base and 9.2% of red product (calculated as azoxy derivative) were obtained. After crystallization from alcohol, the azoxy derivative melted at 117–118°. Gordon [*Thesis*, State University of Iowa, 1921], who prepared this compound by another method, found 116–117°. The product here in question gave a dark red color with concd. sulfuric acid [Wallach and Belli, *Ber.*, **13**, 525 (1880)].

³¹ Einhorn and Hollandt, *Ann.*, **301**, 99 (1898).

³² Faust and Saame, *Z. Chem.*, **6**, 451 (1869). Hallock, *Am. Chem. J.*, **2**, 258 (1880).

³³ Gordon (Ref. 14) made a single experiment with this method, but reported a very poor yield.

three molecular proportions of bromine and a few crystals of iodine and the whole allowed to stand at 40° for 15 hours. From this mixture 77% of the starting material was recovered and no bromine derivative could be isolated.

Reduction of this compound as described above gave, apparently, a tin double salt from which the pure base was not secured. Two g. of this material was benzoyleated, the product boiled with a mixture of equal volumes of glacial acetic acid and alcohol, filtered and the filtrate allowed to cool. Colorless, silky needles, m. p. 119°, were obtained.

Anal. Subs., 0.1411, 0.2267: 5.41 cc. of 0.1 *N* acid, 8.12 cc. of 0.1 *N* AgNO₃. Calcd. for C₁₆H₁₄O₂NCl: N, 5.08; Cl, 12.84. Found: N, 5.37; Cl, 12.70.

2-Nitro-4-chlorophenyl-allyl Ether.—Attempts were made to prepare this compound by Blom's method at temperatures of 50°, 60°, 70° and 85° in four separate experiments. The first two gave only the starting material and the last two, dark colored mixtures from which was isolated a yellow solid that after crystallization from alcohol melted at 145°. This gave a crimson color with concd. sulfuric acid and was analyzed as tetrachloro-azoxybenzene.³⁴

Anal. Subs., 0.1038, 0.0897: 6.09 cc. of 0.1 *N* acid; AgCl, 0.1543. Calcd. for C₁₂H₆ON₂Cl₄: N, 8.34; Cl, 42.22. Found: N, 8.23; Cl, 42.55.

To 15 g. of the silver salt of the nitrophenol³⁵ in a suitable flask surrounded by ice water and provided with an efficient reflux condenser, 20 cc. of ether was added. From a separatory funnel a mixture of 7.5 cc. of allyl iodide and 40 cc. of ether was dropped slowly³⁶ into the flask. When the red color of the salt had disappeared, the flask was shaken and warmed to the boiling point of the solvent and the mixture cooled and filtered. The residue was twice extracted with a 10cc. portion of hot absolute alcohol, and the extract added to the ethereal solution. Norite was added, the liquid filtered, most of the ether distilled and the mixture allowed to cool and crystallize. A 77.2% yield of light yellow crystals was obtained. Recrystallization from alcohol gave needles; m. p., 46°; analysis indicated the ether.

Anal. Subs., 0.2305, 0.1829: 10.56 cc. of 0.1 *N* acid; AgCl, 0.1216. Calcd. for C₉H₆O₃NCl: N, 6.55; Cl, 16.63. Found: N, 6.43; Cl, 16.45.

2-Amino-4-nitrophenetole.—This was obtained by reduction of 2,4-dinitrophenetole,³⁷ in 48.5% yield. It was identified by preparation of a benzoyl derivative; yield, 93.9%. Crystallization from absolute alcohol gave short, yellow needles; m. p., 135–136°.³⁸

Anal. Subs., 0.1667: 11.62 cc. of 0.1 *N* acid. Calcd. for C₁₁H₁₄O₄N₂: N, 9.79. Found: 9.77.

2,4-Dinitrophenyl-allyl Ether.—Both Willgerodt³⁹ and Fairbourne and Toms⁴⁰ ³⁴ Laubenheimer (Ref. 6) reported this behavior for 2,5,2',5'-tetrachloro-azoxybenzene, for which he found a melting point of 141°.

³⁵ Faust and Saame, *Ann. Chem. Pharm. Suppl.*, 7, 190 (1870).

³⁶ Without these precautions the reaction cannot be controlled.

³⁷ Previously obtained by Willgerodt (Ref. 17a) who gave no yield. Blom's method gave mainly 2,4-dinitrophenol. The ether was prepared here in 68.8% yield by refluxing a mixture of 34 g. of 2,4-dinitrochlorobenzene in 315 cc. of 95% alcohol and 12 g. of potassium hydroxide in 50 cc. of water, with the addition of 25 cc. of ethyl iodide. Treatment of this ether with hydrobromic acid gave the corresponding phenol to the extent of about 25%.

³⁸ Cahours [*Ann.*, 74, 316 (1850)] obtained a product that may be identical with this one, but he did not record yield, melting point or analysis.

³⁹ Ref. 17 a, p. 765.

⁴⁰ Fairbourne and Toms, *J. Chem. Soc.*, 119, 1038 (1921).

obtained this ether, but neither recorded a yield nor did they test its behavior toward hydrobromic acid. Twenty-five g. of the 2,4-dinitrochlorobenzene was dissolved in 100 cc. of allyl alcohol, and the calculated amount of potassium hydroxide in 25 cc. of water was added. Though the reaction was rapid and much potassium chloride was precipitated at once, the mixture was refluxed for four hours. The salt was removed by filtration, the filtrate concentrated to half its volume and a second portion of salt separated from the hot mixture. Cooling the final filtrate gave a mass of yellow needles which were filtered off; addition of cracked ice to the filtrate gave more of the ether. This was dissolved in hot 95% alcohol, the solution boiled with Norite, filtered and water added to the hot filtrate, during shaking, until precipitation began, then alcohol until the liquid was clear. Repetition of this procedure until the temperature was brought below where two layers tend to separate, and allowing to cool, gave long, nearly colorless needles.⁴¹ A yield of 65.8% of pure material, m. p. 46–47°, was obtained. Treatment with bromine gave an addition product that melted at 108.5°, evidently identical with that recorded by Fairbourne and Toms who found 110°. Hydrobromic acid decomposed the ether almost quantitatively.

2-Nitro-4-chlorophenyl-benzyl Ether.—According to a German patent,⁴² this product may be obtained by the action of benzyl chloride on the corresponding phenol, but details of manipulation and yield are not given. In the present work, treatment of the silver salt of the phenol with alkyl halide gave a yield of about 10%. When 20.4 g. of the potassium salt of the phenol, 25 cc. of water and 13 g. of benzyl chloride were heated under a reflux condenser⁴³ for two hours on an oil-bath between 125° and 160°, and the mixture distilled for an hour, about 1 g. of the free phenol, which was isolated and identified, was driven over with the steam. The residue, which solidified on cooling, was extracted with water to remove potassium salt, and crystallized from alcohol; yield, 51%; m. p., 85–86°.

Treatment of 5 g. of this ether with five molecular proportions of bromine in the presence of iodine gave 4.2 g. or 91.2% of a product that melted at 123–124°, and was identified as 2-nitro-4-chloro-6-bromophenol.

2,4-Dinitrophenyl-benzyl Ether.—Kumpf⁴⁴ did not record his yield of this product obtained by the silver salt method, which in our work gave 36.4%. A mixture of 20 g. of 2,4-dinitrochlorobenzene, 11 cc. of benzyl chloride and 25 cc. of water was heated for ten hours at about 150°. The solid that separated on cooling was powdered and extracted with hot dilute alkali solution to remove phenol. Crystallization of the residue from glacial acetic acid gave large plates; m. p., 149.5°; yield, 51.8%. Heating for four hours gave 43.4%.

B. Derivatives of Diphenyl Ether

The ethers included in this group were prepared by slight modifications of the general method, which will be indicated for the first one only.

Ten g. of *p*-nitrochlorobenzene was added to a solution of potassium phenolate prepared by dissolving 7.5 g. of phenol in 15 cc. of a water solution containing 4.25 g. of the alkali. The mixture was heated under a reflux condenser on an oil-bath at about 150° for six hours. Most of the water was then evaporated and the residue steam-distilled for an hour to remove unchanged chloronitrobenzene. The ether was collected

⁴¹ The yield of pure material can be increased considerably by placing the flask in a freezing mixture after crystallization at room temperature has ceased.

⁴² Ger. pat. 142,899, 1903; *Friedländer*, 7, 466 (1902–1904).

⁴³ Gomberg and Buchler, *THIS JOURNAL*, 42, 2060 (1920).

⁴⁴ Kumpf, *Ann.*, 224, 128 (1884).

TABLE V
DERIVATIVES OF DIPHENYL ETHER

Ether	Yield, %	Solvent	Crystal form	M. p., °C.	Analysis						
					Subs., G.	0.1 N acid, cc.	N, %		0.1 N AgNO ₃ , cc.	Halogen, %	
							Calcd.	Found		Calcd.	Found
4-Nitrodiphenyl	66.4	Alcohol	Nearly colorless tablets	60-61	0.1915	8.95	6.51	6.55
2,4-Dinitrodiphenyl ^a	92.6	Alcohol	Leaflets	70
2,4-Dinitro-4'-bromo- diphenyl ^b	Quant.	Alcohol-acetic acid (1:2)	Colorless needles	138.5	.2112	11.06	8.25	8.31
					.3446	10.23	23.59	23.60
2,4-Dinitro-4'-chloro- diphenyl	96.6	Alcohol-acetic acid (1:2)	Yellow tablets	123	.2116	14.51	9.50	9.61
					.3796	12.78	12.05	11.94
2,4,2'-Trinitrodiphenyl	89.4	Alcohol-acetic acid	Yellow needles	137.5 ^c	.1723	16.96	13.77	13.79
2,4,3'-Trinitrodiphenyl ^d	76.8	Alcohol-acetic acid	Yellow tablets	135	.2424	23.95	13.77	13.84
2,4,4'-Trinitrodiphenyl	97	Alcohol-acetic acid (1:1)	Yellow tablets	116 ^e
2,4-Dinitro-2',4',6'- tribromodiphenyl	27.7	Acetic acid (1:1)	Nearly colorless flakes	130.5	.2104	8.48	5.63	5.65
					.2163	12.91	48.29	47.90
2,4,2'-Trinitro-4'- chlorodiphenyl	86.9	Acetic acid	Yellowish plates	154	.1836	16.13	12.37	12.32
					.3060	8.86	10.45	10.27
2,4,2'-Trinitro-4'- bromodiphenyl	94.9	Alcohol-acetic acid (1:4)	Nearly colorless needles	148.5	.2004	15.53	10.93	10.85
					.2010	5.19	20.83	20.65
2-Nitro-4'-chloro- diphenyl	72.2	Alcohol		45.5	.2060	8.21	5.61	5.58
					.2846	11.3	14.21	13.95
2-Nitro-4'-bromo- diphenyl	70.0	Alcohol-acetic acid (1:2)	Yellowish-green needles	71	.1705	5.71	4.76	4.69
					.1772	5.98	27.21	26.97
4-Nitro-4'-chloro- diphenyl	81.0	Alcohol-acetic acid (1:1)		76.5	.2064	8.25	5.61	5.60
					.1616	6.42	14.21	14.08
4-Nitro-4'-bromo- diphenyl	81.3	Alcohol-acetic acid (1:1)	Brownish plates	65-66	.1998	6.82	4.76	4.78
					.2556	9.05	27.21	27.25

TABLE V (Concluded)

Ether	Yield, %	Solvent	Crystal form	M. p., °C.	Analysis						
					Subs., G.	0.1 N acid, cc.	N, %		0.1 N AgNO ₃ , cc.	Halogen, %	
							Calcd.	Found		Calcd.	Found
2-Nitro-4-chloro- diphenyl	67.5	Alcohol ^f	Lemon-yellow plates	36-37	0.2040	8.28	5.61	5.60
					.1594	0.0954	14.21	14.68
2-Nitro-4-chloro-4'- bromodiphenyl ^g	91.2	Alcohol	Pale yellow needles	93-94	.1862	5.86	4.26	4.41
					.1103	6.70	35.15	35.04
2-Nitro-4,4'-dichloro- diphenyl ^h	84.4	Alcohol	Pale yellow needles	79	.1718	6.20	4.92	5.06
					.2170	15.19	24.96	24.84
2-Nitro-4,4'-dibromo- diphenyl	91.9	Alcohol-acetic acid (5:1)	Yellow granules	94.5	.1946	5.0	3.75	3.60
					.1798	9.60	42.89	42.69
2-Nitro-4-bromo-4'- chlorodiphenyl	91.9	Alcohol-acetic acid (5:1)	Lemon-yellow needles	100.5	.2149	6.37	4.26	4.11
					.1616	9.85	35.15	35.17

^a Obtained previously by Maikopar¹⁶ in impure form, and by Willgerodt (Ref. 17 a, p. 767), neither of whom recorded a yield. Analytical data have been published.

^b Prepared by the action of five molecular proportions of bromine with iodine as a carrier on 2,4-dinitrodiphenyl ether in glacial acetic acid solution. When smaller amounts of bromine were used, some unchanged material was recovered. The structure of this product was proved by preparing it from 2,4-dinitrochlorobenzene and 4-bromophenol in the presence of a solution of potassium hydroxide.

^c Willgerodt and Hüetlin [*Ber.*, 17, 1765 (1884)] reported 119° for an ether they regarded as having the composition and structure of ours, but they gave no yield.

^d Though general directions for the preparation of this product are given in Ger. pat. 281,053, 1914 [Friedländer, "Fortschritte der Teerfarbenfabrikation," Springer, Berlin, 12, 165 (1914-1916)], neither yield nor analysis is recorded.

^e Willgerodt and Hüetlein (Ref. c, above) found 114° for a product that analyzed satisfactorily for this ether, but no yield is recorded.

^f An oil was obtained from the reaction mixture. This was extracted with ether, dried over calcium chloride, the ether evaporated and the oil distilled under reduced pressure. The fourth distillation gave an oil boiling at 201°, at 12 mm., which crystallized after several days' standing.

^g This product was also obtained by the action of bromine on 2-nitro-4-chlorodiphenyl ether, as described above in Ref. b.

^h Mentioned indirectly in Ger. pat. 216,642, 1909 [Friedländer, "Fortschritte der Teerfarbenfabrikation," Springer, Berlin, 9, 322 (1908-1910)], but without details of process or yield.

and crystallized from alcohol; m. p., 60–61°. ⁴⁵ Table V gives the data for other ethers prepared in a similar way.

Summary

1. The formation of phenyl alkyl ethers by treatment of halogenated nitrobenzene with aqueous alcoholic potassium hydroxide is dependent upon the number and relative positions of the nitro radicals, the reducing action of the alcohol, the concentrations of the reacting components and temperature.

2. The reaction between a halogenated nitrobenzene and a phenol is influenced most noticeably by the substituents in the phenol. When the latter contains a nitro radical, the reaction will fail unless the halogenated benzene contains more than one nitro group.

3. Bromine does not readily substitute in the phenyl radical of phenyl alkyl ethers when two of the three possible positions are occupied by substituents other than hydrogen. When alkyl is represented by allyl, the latter will be saturated by bromine. Phenyl-benzyl ethers are decomposed into the corresponding brominated phenol and benzyl bromide, which suggests that substitution in the phenyl nucleus occurs first, and that the resulting hydrogen bromide decomposes the ether.

4. The presence of a nitro radical in diphenyl ether hinders the entrance of bromine, regardless of the solvent used.

5. The decomposition of phenyl alkyl ethers by hydrobromic acid under the conditions specified is not complete and appears to be influenced by substituents in the phenyl nucleus. When alkyl is represented by allyl, the splitting is nearly quantitative.

6. Diphenyl ethers are unaffected by hydrobromic acid under the conditions of these experiments.

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⁴⁵ In view of the peculiar results reported by Jones and Cook in their attempts to prepare this ether from *p*-bromonitrobenzene, previously referred to in this paper, it was deemed necessary to analyze our product. The results are in complete agreement with Haeussermann and Teichmann's observations (see Table V).