Summary

1. The preparation of 2,4,8,10-tetranitrodiphenyl ether by the nitration of diphenyl ether has been described.

2. In connection with the reduction of 2,4,8,10-tetranitrodiphenyl ether by stannous chloride and concd. hydrochloric acid, the formation of diaminophenazine and 2,4,8,10-tetraminodiphenyl ether has been observed.

TOKYO, JAPAN

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF WASHINGTON]

SOME REACTIONS OF QUINOL AND A CONTRIBUTION TO THE CONSTITUTION OF QUINHYDRONE

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When an iodate reacts with quinol,[2] quite diverse effects are produced when the solutions are acid, neutral or alkaline. In general, quinhydrone or a dye or a mixture of these two is obtained.

In equal aqueous solutions the following products were obtained

Quinol, g.	$NaIO_3$, g.	CH_3COOH, g.	NaOH, g.	Product
10	6	5	0	7 g. of quinhydrone
10	6	0	0	9 g. of quinhydrone
10	6	0	5	Only the dye
40	25	0	0	39 g. of quinhydrone

Preparation of Quinhydrone.—The following is the most convenient and satisfactory method for the preparation of quinhydrone. To 40 g. of quinol suspended or dissolved in 200 cc. of water, add a cold saturated solution of 25 g. of sodium iodate. The mixture is shaken and kept cold by tap water. Almost immediately long glistening prisms begin to separate and in less than one-half hour a 90% yield and in 2–3 hours practically a quantitative yield can be filtered off as brassy black prisms melting at 171°. The reaction is in accordance with

$$6C_6H_6O_2 + 2NaIO_3 \longrightarrow 3C_6H_4O_2 \cdot C_6H_6O_2 + 2NaI + 6H_2O$$

Since hydriodic acid[3] reduces quinone to quinol, acid solutions give smaller yields.

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[1] The material presented in this paper is from part of a thesis submitted by Theodore W. Evans, du Pont fellow for 1929–1930, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1930.

[2] For the oxidation of quinol to oxalic acid, see Hesse, *Ann.*, **114**, 300 (1860); nitrogen oxides to nitranilic acid, Nietzki, *ibid.*, **215**, 138 (1883); silver sulfate and persulfuric acid to maleic and formic acid, Kempf, *Ber.*, **39**, 3717, 3726 (1906); by other oxidants, Wöhler, *Ann.*, **51**, 151 (1844).

[3] Wöhler, Ref. 2. For the reaction of iodine in $KHCO_3$ solutions, see Valeur, *Ann. chim.*, [7] **21**, 529 (1900).

QUINHYDRONE BY OTHER OXIDATIONS

Oxidant	Quinol, g.	Yield of quinhydrone, etc., g.
29 g. $KMnO_4$ + 3.2 g. acetic acid	10	3
30 g. $K_3Fe(CN)_6$ + 5.5 g. KOH	10	6
5 g. $KClO_3$	10	0
13 g. $K_2S_2O_8$	10	9
10 g. $NaBO_3 \cdot 4H_2O$	10	Dye
20 g. $KBrO_3$	40	25

The persulfate[4] method gives beautiful crystals in practically quantitative yields, but requires many hours of standing for complete reaction. The bromate required one to two weeks to complete the reaction.

Quinone by the Iodate Method.—Varied conditions were employed and the mixtures were distilled with steam to separate the quinone.

Manner of treatment	Reactions	Yield of quinone,[5] %
Quinhydrone + $^1/_3$ mole $NaIO_3$	Neutral	41
Quinol to hot mole $NaIO_3$	Alkaline	0
Quinol to hot mole $NaIO_3$	Neutral	36
Quinol to hot mole $NaIO_3$	Neutral	40
$^1/_3$ Mole of $NaIO_3$ to hot quinol	Neutral	40

Here and elsewhere it is observed that alkaline solutions give little or no quinone; when alkaline oxidants react, a dye which yields a brown color on silk was formed. This dye can be salted from its solutions and is easily soluble in ammonium hydroxide. It will be investigated.

It is usually held that quinhydrone is first formed and is then completely oxidized to quinone. Whereas this is substantially true when aniline or quinhydrone is oxidized by chromate[6] solutions it was found that quinhydrone, by further oxidation with sodium iodate, did not yield additional quinone, but the quinol portion was oxidized to the dye. Since, on the one hand, numerous experiments with different aqueous reagents, even with water alone, directed to splitting quinhydrone into its constituent molecules, always gave less than 50% of quinone and no residual quinol but only the dye; and since, on the other hand, anhydrous solvents such as chloroform, toluene, etc., do produce dissociation into quinone and quinol, it seems that hot water and quinone have a profound effect on quinhydrone. These observations may bear upon the question of quinhydrone constitution. However, a more important contribution to this problem is the formation of the following compound.

[4] Compare Kempf, *Ber.*, **39**, 3717 (1906),

[5] Notwithstanding that only 40% yields are obtainable by the iodate method, it is very convenient for the preparation of quinone, since the materials need only be mixed and distilled with steam to obtain a pure product. The yields reported above did not include additional quinone which was contained in the aqueous filtrates.

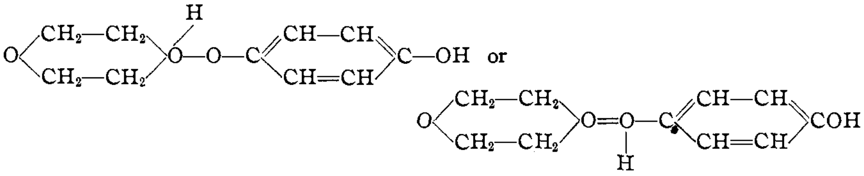
[6] Nietzki, *Ber.*, **19**, 1468 (1886).

Quinoldioxane.—When 1–2 equivalents of dioxane are added to a saturated solution of quinol in dry ether, a precipitate of thick, transparent glistening rectangular plates, or the same with one, or with two opposite truncated corners, is formed.

Anal. Calcd. loss (of dioxane), when heated to 100°, from $C_6H_4(OH)_2 \cdot C_4H_4O_2$: 44.45. Found: loss, 44.48, 44.49.

The residue of quinol melted at 170°. Quinoldioxane melts in a sealed capillary at 93–100°. It is soluble in most organic solvents, difficultly soluble in chloroform and insoluble in petroleum ether, benzene and other hydrocarbons. A sample kept for six months in a stoppered vial lost 4%. It is soluble in water; such solutions precipitate quinhydrone when treated with quinol. A rapid method for the preparation of quinoldioxane is as follows. Dissolve quinol in a small volume of hot dioxane and then carefully add dry ether or petroleum ether.

Since all the atoms of dioxane are saturated, except its oxonium valencies, it seems very probable that Richter's formulas[7] as applied to the quinhydrones are the most valid. Thus quinoldioxane can be formulated



The second formula seems the more probable because the compound decomposes readily, and if these formulas are valid for quinoldioxane, then the analogous oxonium formulas depicted by Richter are the most probable for quinhydrone. Numerous experiments by the above method, with dioxane and phenols, amino derivatives, etc., to obtain other dioxane additive compounds were strictly negative; hence it is concluded that dioxane and quinol bear a unique structural or affinity relation in quinoldioxane, and it seems probable that a similar relation exists between quinol and quinone in quinhydrone. The uniqueness of this compound also makes it useful as an extremely characteristic test for quinol and dioxane.

Summary

Some new oxidations of quinol to quinhydrone and quinone are given. The additive compound of dioxane and quinol contributes to the theory of constitution of the quinhydrones.

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[7] See *Ber.*, **43**, 3603 (1910). For other formulas for quinhydrone see Wichelhaus, *ibid.*, **12**, 1500 (1879); Jackson and Oenslager, *ibid.*, **28**, 1614 (1895); Valeur, *Ann. chim.*, [7] **21**, 560 (1900); Posner, *Ann.*, **336**, 85 (1904); Urban, *Monatsh.*, **28**, 299 (1907); Willstätter and Piccard, *Ber.*, **41**, 1463 (1908).