

heating to 250° for 1 hr. There was recovered 0.14 g. of starting material, m.p. 174.0–174.9°.

Preparation of cis-dibenzoylstilbene (III). Compound III may be prepared by the method of Zinin,⁸ or the following adaptation of his procedure may be used:

Tetraphenylfuran (1.0 g.) was heated to reflux for 1 hr. in 20 ml. of glacial acetic acid containing 0.2 g. of chromium trioxide. The resulting green solution was diluted with 50 ml. of water and washed three times with ether and once with chloroform. The combined extracts were washed twice with saturated aqueous sodium bicarbonate and once with water. The solvent was removed by distillation and replaced with ethanol. Crystallization gave 0.3 g. of III, as white needles, m.p. 216–217° (reported,⁸ 220°). The mixed melting point with I was 193–205°.

Anal. Calcd. for C₂₈H₂₀O₂: C, 86.57; H, 5.19. Found: C, 86.74; H, 5.37.

Infrared absorption bands are as follows (potassium bromide pellet): 3.26w, 6.02s, 6.22m, 6.31m, 6.71w, 6.90m, 7.57m, 7.70m, 7.91s, 8.06m, 8.38m, 8.47m, 9.08w, 9.19w, 9.61w, 9.71w, 9.82m, 9.98w, 10.90w, 11.68w, 11.87w, 12.14m, 12.96s, 13.40w, 13.61s, 14.40s, 14.68s, 15.60w.

Pyrolysis of cis-dibenzoylstilbene. Compound III (0.1 g.) was heated to 270° for 15 min. Crystallization of the melt from ethanol-chloroform gave a quantitative yield of the same lactone (II), m.p. 135.5–137.0°, as was obtained upon the pyrolysis of I. The identity of the compounds was established by comparison of their infrared spectra.

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[CONTRIBUTION FROM ORGANIC CHEMISTRY DEPARTMENT, NATIONAL RESEARCH CENTRE]

Carbonyl and Thiocarbonyl Compounds. II.¹ Reaction of Halogenated *o*-Quinones with Certain Hydrazones and Diazocompounds

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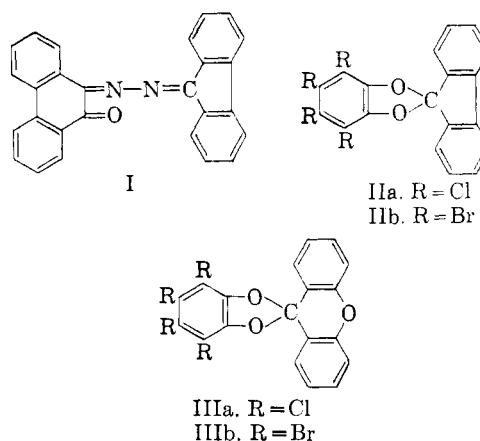
In contrast to other *o*-quinones, tetrachloro- and tetrabromo-*o*-benzoquinone react with fluorenone hydrazone at room temperature to give the cyclic ethers IIa and IIb respectively. With xanthone hydrazone the analogous products IIIa and IIIb are obtained. The mechanism proposed for this reaction suggests the formation of diazo derivatives as intermediate products.

The halogenated cyclic ethers IVa–IVf are obtained by the action of various diazomethane derivatives on tetrachloro- and tetrabromo-*o*-benzoquinone. 3,4-Dichloro-1,2-naphthoquinone reacts with 9-diazoxanthene giving the cyclic ether V. V is easily cleaved with hydrochloric acid in dioxane. An improved procedure for the preparation of 3,4-dichloro-1,2-naphthoquinone is described.

Gerhardt² has shown that aromatic ketohydrazones react with *o*-quinones to give ketazines of the type R₂C=N=N=R=O.³ For example, when warming phenanthraquinone with fluorenone hydrazone in dry benzene, a 45% yield of the deeply colored phenanthraquinofluorenone ketazine I was obtained. Acenaphthenequinone, camphorquinone, and thianaphthenequinone have been found to react similarly.

In an attempt to prepare analogous ketazines from halogenated *o*-benzoquinone derivatives, it has been found, however, that the reaction between ketohydrazones and these quinones proceeds in a different manner. Thus, when fluorenone hydrazone is added to a dry ethereal solution of tetrachloro-*o*-benzoquinone, a vigorous reaction with evolution of gas occurs and the colorless cyclic ether IIa is obtained together with tetrachlorocatechol. The reaction proceeds easily at room temperature and the product is obtained in excellent yield. Tetrabromo-*o*-benzoquinone reacts similarly with the formation of the bromo-analogue IIb. IIa and IIb have been previously obtained by

the action of 9-diazo fluorenone on the corresponding quinone:⁴



Xanthone hydrazone reacts similarly, but more vigorously, with these quinones with the formation of the analogous products IIIa and IIIb in almost quantitative yields. IIIa and IIIb have been obtained previously by the action of 9-diazo-xanthene on the corresponding quinones.¹ IIIa and IIIb are hydrolyzed easily when boiled with a solution of hydrochloric acid in dioxane to give xanthone and the corresponding tetrahalocatechol.

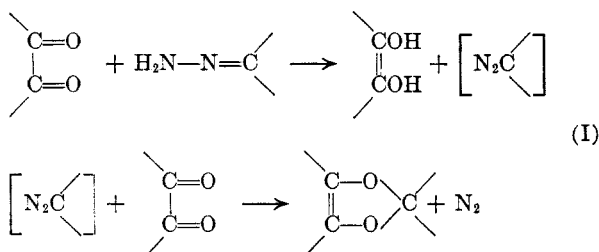
(1) Previous paper in this series, *Can. J. Chem.*, **37**, 863 (1959).

(2) O. Gerhardt, *Monatsh*, **42**, 70 (1921); *Chem. Abstr.*, **15**, 3834 (1921).

(3) G. Rieveschl and F. E. Ray, *Chem. Rev.*, **23**, 304 (1938).

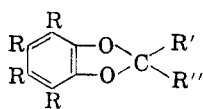
(4) A. Schönberg and N. Latif, *J. Chem. Soc.*, 446 (1952).

The mechanism of this reaction between the above-mentioned hydrazones and halogenated *o*-quinones involves the dehydrogenation of the hydrazone by the high-potential quinone to give the corresponding diazo derivative. The latter then reacts further with another molecule of the quinone forming the cyclic ether as shown in equation I.



Dehydrogenation reactions using high-potential *o*-quinones have been frequently studied.⁵ However, attention was directed mostly to the study of the dehydrogenation of hydroethylenic and hydroaromatic compounds. Similar dehydrogenations involving N—H linkages have not been described before.

Action of diazo-compounds on halogenated o-quinones. In the course of studies on the molluscicidal activity of halogenated cyclic ethers, the preparation of various methylenedioxy derivatives has been required for biological evaluation. (*p*-Chlorophenyl)phenyl-, bis(*p*-chlorophenyl)-, and (*p*-nitrophenyl)phenyl-diazomethane react with tetrachloro- and tetrabromo-*o*-benzoquinone at room temperature, forming the methylenedioxy derivatives IVa–IVf.

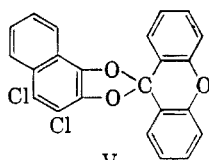


IV

- IVa. R = Cl; R' = phenyl; R'' = *p*-chlorophenyl.
 IVb. R = Br; R' = phenyl; R'' = *p*-chlorophenyl.
 IVc. R = Cl; R' = R'' = *p*-chlorophenyl.
 IVd. R = Br; R' = R'' = *p*-chlorophenyl.
 IVe. R = Cl; R' = phenyl; R'' = *p*-nitrophenyl.
 IVf. R = Br; R' = phenyl; R'' = *p*-nitrophenyl.

The constitution of the products is based on analogy,^{4,6} as well as on the fact that they are colorless and hydrolyzed by concentrated sulphuric acid at room temperature, as exemplified by IVa and IVb, to give the corresponding tetrahalocatechol.

In a previous article¹ the preparation of 9-diazoxanthene and its reaction with phenanthraquinone and *o*-benzoquinone derivatives have been described. 3,4-Dichloro-1,2-naphthoquinone reacts similarly with diazoxanthene to give the cyclic



V

ether V. Its constitution is based on analogy and on the fact that it is colorless and easily hydrolyzed by hydrochloric acid in dioxane to xanthone and 3,4-dichloro-1,2-dihydroxynaphthalene, as usually happens with analogous xanthene cyclic ethers (cf. IIIa). A modification of the method of preparation of the quinone⁷ to obviate the formation of resinous by-products⁸ is described.

EXPERIMENTAL⁹

Reaction of fluorenone hydrazone with: (a) *Tetrachloro-o-benzoquinone.* To a dry ethereal solution of the quinone (0.02 mole), the hydrazone (0.01 mol.) was added in portions at room temperature. After each addition a vigorous reaction with evolution of gas occurred. After all the hydrazone has been added, the red color of the quinone almost disappeared and on further standing for a few minutes a brownish solid separated. This was filtered off, washed with methyl alcohol and recrystallized from acetone when 9,9-(tetrachloro-*o*-phenylenedioxy) fluorene IIa was obtained in colorless crystals m.p. 281° (not depressed when admixed with an authentic sample prepared by the action of diazofluorene on the quinone), yield about 80%.

Anal. Calcd. for C₁₉H₉O₂Cl₄: C, 55.6; H, 1.9; Cl, 34.6. Found: C, 55.22; H, 2.16; Cl, 34.33.

The filtrate was evaporated to dryness, extracted with methyl alcohol and the extract poured onto ice and acidified with hydrochloric acid. The solid separated was dried and added to acetic anhydride and the mixture refluxed for 30 min., then poured onto ice. The solid separated was recrystallized from methyl alcohol and proved to be the diacetate of tetrachlorocatechol (m.p. and mixed m.p.).

(b) *Tetrabromo-o-benzoquinone.* The reaction was carried out as in the case of the chloro analog. The product separated was filtered off and recrystallized from xylene when IIb was obtained in colorless crystals m.p. 338°, yield about 80%.

Anal. Calcd. for C₁₉H₉O₂Br₄: C, 38.7; H, 1.3; Br, 54.4. Found: C, 38.39; H, 1.42; Br, 54.25.

Reaction of xanthone hydrazone with: (a) *Tetrachloro-o-benzoquinone.* To a dry ethereal solution of the quinone (0.02 mol.) the hydrazone was added in portions until the color of the quinone disappeared. A vigorous reaction with evolution of gas took place and a crystalline solid separated during the addition. This was filtered off, washed with hot methyl alcohol, and recrystallized from xylene when 9,9-(tetrachloro-*o*-phenylenedioxy) xanthene IIIa was obtained in colorless crystals m.p. 286° (undepressed when admixed with an authentic sample prepared by the action of diazoxanthene on the quinone).¹ Yield almost quantitative.

Anal. Calcd. for C₁₉H₉O₂Cl₄: C, 53.52; H, 1.87; Cl, 33.3. Found: C, 53.12; H, 2.13; Cl, 33.08.

Hydrolysis of IIIa. To a solution of concentrated hydrochloric acid (sp. gr. 1.19/1 ml.) in dioxane (5 ml.) was added IIIa (0.15 g.), the mixture boiled for 30 min. and left to cool. It was then poured onto ice and the colorless crystals separated were filtered off and dried. These were dissolved in the least amount of boiling methyl alcohol and the solution was left to cool when xanthone separated (m.p. and mixed m.p.). On addition of dilute hydrochloric acid to the mother liquor, a white precipitate was formed. This was filtered off, dried, and added to acetic anhydride. The mixture was then refluxed for 30 min., left to cool, then poured onto ice. The solid separated was recrystallized from methyl alcohol and proved to be the diacetate of tetrachlorocatechol (m.p. and mixed m.p.).

(5) L. Horner and H. Merz, *Ann.*, **570**, 89 (1950); E. A. Braude, L. M. Jackman, and R. P. Linstead, *J. Chem. Soc.*, 3564 (1954).

(6) A. Schönberg, W. I. Awad, and N. Latif, *J. Chem. Soc.*, 1358 (1951).

(7) Th. Zincke and Engelhardt, *Ann.*, **283**, 341 (1894).

(8) L. F. Fieser and J. T. Dunn, *J. Am. Chem. Soc.*, **59**, 1019 (1937).

(9) Melting points are not corrected.

TABLE I

Diazomethane ^a Derivative	<i>o</i> -Benzoquinone Derivative	Product M.p.	Analysis
(<i>p</i> -Chlorophenyl)- phenyl-	Tetrachloro-	IVa, 152°	<i>Anal.</i> Calcd. for C ₁₃ H ₉ O ₂ Cl ₅ : C, 51.12; H, 2.01; Cl, 39.68. Found: C, 51.65; H, 1.7; Cl, 39.34
(<i>p</i> -Chlorophenyl)- phenyl-	Tetrabromo-	IVb, 161°	<i>Anal.</i> Calcd. for C ₁₃ H ₉ O ₂ Br ₄ Cl: C, 36.53; H, 1.44. Found: C, 37.1; H, 1.44
bis(<i>p</i> -Chloro- phenyl)phenyl-	Tetrachloro	IVc, 174°	<i>Anal.</i> Calcd. for C ₁₅ H ₉ O ₂ Cl ₆ : C, 47.4; H, 1.66; Cl, 44.28. Found: C, 47.58; H, 1.63; Cl, 43.77
bis(<i>p</i> -Chloro- phenyl)phenyl-	Tetrabromo-	IVd, 170°	<i>Anal.</i> Calcd. for C ₁₅ H ₉ O ₂ Br ₄ Cl ₂ : C, 34.59; H, 1.21. Found: C, 34.42; H, 1.23
(<i>p</i> -Nitrophenyl)- phenyl-	Tetrachloro-	IVe, 190°	<i>Anal.</i> Calcd. for C ₁₅ H ₉ O ₄ NCl ₄ : C, 49.98; H, 1.97; N, 3.06; Cl, 31.07. Found: C, 50.35; H, 2.1; N, 3.18; Cl, 29.43
(<i>p</i> -Nitrophenyl)- phenyl-	Tetrabromo-	IVf, 208°	<i>Anal.</i> Calcd. for C ₁₅ H ₉ O ₄ NBr ₄ : C, 35.9; H, 1.41; N, 2.2; Br, 50.39. Found: C, 36.11; H, 1.37; N, 2.0; Br, 49.45

^a A. Schönberg, A. Fateen, and A. A. Sammour, *J. Am. Chem. Soc.*, **79**, 6020 (1957).

(b) *Tetrabromo-o-benzoquinone*. The reaction was carried out as in the case of the chloro quinone. The product separated during the reaction was filtered, washed with boiling acetone, and recrystallized from xylene (using charcoal) when the tetrabromo-analogue IIIb was obtained in almost colorless crystals m.p. 280° (decomp.). Its infrared spectrum is identical with that obtained by the action of diazoxanthene on the quinone.

Anal. Calcd. for C₁₃H₉O₂Br₄: Br, 52.98. Found: Br, 51.84.

Action of diazoalkanes on tetrachloro- and tetrabromo-o-benzoquinone. General procedure. The quinone (0.01 mol.) was added in portions to a dry ethereal solution of the diazoalkane (0.015 mol.). A vigorous reaction with evolution of gas occurred after each addition. After all the quinone has been added, the reaction mixture was left for 30 min. at room temperature when a crystalline solid separated. This was filtered off, washed with methyl alcohol, and recrystallized from alcohol. The methylenedioxy derivatives IVa-IVf were obtained in colorless crystals in almost quantitative yields (in the case of IVe and IVf, using charcoal was found necessary during crystallization). Results of the experiments are shown in Table I.

Hydrolysis of IVa. The substance (0.1 gm.) was mixed well with concentrated sulfuric acid (10 ml.), left overnight at room temperature then poured onto ice. The solid formed was filtered off, dried, refluxed for 30 min. with acetic anhydride, left to cool, and poured onto ice. The precipitate formed was recrystallized from methyl alcohol when the diacetate of tetrachlorocatechol was obtained (m.p. and mixed m.p.). When IVb was similarly treated the diacetate of tetrabromocatechol was obtained.

Preparation of 3,4-dichloro-1,2-naphthoquinone. Freshly prepared 1-amino-2-naphthol hydrochloride (2 gm.) was suspended in glacial acetic acid (20 ml.). A vigorous stream

of dry chlorine (free of HCl) was allowed to pass in the suspension until all the aminonaphthol went into solution with a red color. The solution was then poured onto ice, and the solid separated filtered off, washed with petroleum ether and recrystallized from benzene in orange red crystals m.p. 184° (undepressed when admixed with an authentic sample).⁷

Reaction of 3,4-dichloro-1,2-naphthoquinone with 9-diazoxanthene. The quinone (1 g.) was added in very small portions of a dry ethereal solution of diazoxanthene¹ (1.4 g.). A new portion was only added when the reaction from a previous addition had subsided. When all the quinone was added, the reaction mixture was kept at room temperature for 15 min. The yellowish product formed was filtered off, washed with hot acetone and recrystallized from benzene when 9,9-(3,4-dichloro-1,2-naphthylenedioxy)xanthene V was obtained in colorless crystals m.p. 268°, yield about 80%.

Anal. Calcd. for C₂₃H₁₂O₃Cl₂: C, 67.81; H, 2.94; Cl, 17.44. Found: C, 67.4; H, 2.90; Cl, 17.0.

Hydrolysis of V. Hydrolysis and separation of xanthone were carried out as in the case of IIIa. To the mother liquor left after the separation of xanthone, water (acidified with a few drops of hydrochloric acid) was added. The precipitate obtained was filtered, dried, added to acetic anhydride and the mixture refluxed for 30 min. then poured onto ice. The solid separated was recrystallized from methyl alcohol in colorless crystals m.p. 156° which are believed to be the diacetate of 3,4-dichloro-1,2-dihydroxynaphthalene.

Anal. Calcd. for C₁₄H₁₀O₄Cl₂: C, 53.67; H, 3.19. Found: C, 53.85; H, 3.24.

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