[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Tetramethyl-*o*-benzoquinone

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Simple *o*-benzoquinones have not been studied very extensively, no doubt chiefly because they are difficult to prepare in good yields and are not stable substances, except when halogen atoms are present in the ring.[1]

In continuation of the work on duroquinone in progress in this Laboratory,[2] it was desired to study analogous reactions of a substituted *o*-benzoquinone containing no halogen, and to compare these results with those obtained using duroquinone. It seemed likely that the stabilizing action of halogen atoms on these ortho quinones was due, not particularly to the nature of the substituent, but to the fact that little or no hydrogen was left attached directly to the ring; consequently, the completely methylated *o*-benzoquinone was selected for study. This quinone was accordingly prepared, but the preparation was very difficult and the product has been found to be a very unstable substance, decomposing in a few hours on standing in air or in an inert atmosphere, or *in vacuo*. Because of this, the original purpose of the research could not be realized, but enough of the quinone was obtained so that its properties could be studied and several derivatives of it made.

Experimental Part

Because it was necessary to use prehnitene as starting material and the dinitro compound was the only easily obtainable derivative of this hydrocarbon which seemed promising for our purpose, it was unavoidable that the diamine should be an intermediate in the synthesis. Many oxidizing agents were tried in the hope of converting this diamine directly to the quinone and thus avoiding the troublesome direct chlorination as used by Zincke. In every case, however, the result was a complicated mixture consisting largely of colored condensation products from which no quinone could be isolated, and we reluctantly turned to the original procedure of Zincke in which an ortho diamine is chlorinated, the crude reaction product reduced with stannous chloride to the dihydroxy compound, and the latter then carefully oxidized to the quinone.

Dinitroprehnitene.—This was prepared in 80% yield from prehnitene by the method previously used for the nitration of durene.[3] The product is almost white and melts at 176°.

Diaminoprehnitene.—The dinitro compound (22 g.), suspended in hot alcohol (100 cc.) is poured rapidly into a boiling solution of stannous chloride (170 g.) in concentrated hydrochloric acid (195 cc.) contained in a large flask. As soon as the vigorous reaction subsides, the flask is cooled and the resulting white solid is filtered. It weighs 24 g. and is the hydrochloride and not the stannichloride, as is the case with diaminodurene. The product always contains a little tin, but is pure enough to use in the next step. The free diamine, isolated from the hydrochloride in the usual way, is white and melts at 144°, but it soon darkens in the air.

Dihydroxyprehnitene.—Diaminoprehnitene hydrochloride (10 g.) is suspended in a mixture of 100 cc. of glacial acetic acid and 10 cc. of hydrochloric acid, and a slow current of chlorine is passed in for ten to twelve hours. The mixture becomes momentarily pink, then bright yellow, and as the hydrochloride gradually dissolves, ammonium chloride precipitates out. After the reaction is complete, the ammonium chloride (3.8 g.) is filtered off and the excess chlorine removed from the filtrate by applying suction. From 8 to 10 g. of a bright yellow viscous oil may be obtained by diluting the solution with water and extracting with ether, but it is not necessary to isolate the product at this point. The chlorinated solution is treated directly with a boiling solution of 50 g. of stannous chloride in 90 cc. of concentrated hydrochloric acid. The color becomes a bright red, slowly fading to orange after warming on the steam-bath for five to eight hours. An equal volume of 6 *N* hydrochloric acid is added and the solution is cooled in ice and salt. The precipitate is filtered and washed with cold 6 *N* hydrochloric acid. Recrystallization from the 6 *N* acid or from aqueous alcohol gives from 4.0 to 5.2 g. of long white needles, m. p. 111°, which gradually darken in the air.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.2; H, 8.5. Found: C, 72.1, 72.2; H, 8.3, 8.4.

The dihydroxy compound gives a momentary blue color with alkali, which is very delicate and may be used for detecting traces of it.

Diacetate.—Acetylation with acetyl chloride in acetic acid, followed by recrystallization from alcohol, gives long white needles of the diacetate, m. p. 175°.

Anal. Calcd. for $C_{14}H_{18}O_4$: C, 67.2; H, 7.2. Found: C, 67.0, 67.1; H, 7.2, 7.1.

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(1) Zincke, *Ber.*, **20**, 1776 (1887); **21**, 2720 (1888); *Ann.*, **290**, 359 (1896); **417**, 217 (1918); Zincke and Schwarz, *ibid.*, **307**, 46 (1899); Zincke and Janney, *ibid.*, **398**, 351 (1913); Willstätter and Müller, *Ber.*, **41**, 2581 (1908); Willstätter, *ibid.*, **44**, 2174 (1911); Diepolder, *ibid.*, **42**, 2921 (1909); Prenntzell, *Ann.*, **296**, 185 (1897); Bergmann and Francke, *ibid.*, **296**, 163 (1897); Francke, *ibid.*, **296**, 206 (1897); Hodes, *ibid.*, **296**, 218 (1897); Jackson and co-workers have dealt with the halogenated *o*-benzoquinones in a series of papers beginning with *Am. Chem. J.*, **26**, 10 (1901), and ending with *Am. Chem. J.*, **47**, 197 (1912).

(2) Smith and Dobrovolny, THIS JOURNAL, **48**, 1693 (1926); Smith and Crawford, *ibid.*, **50**, 869 (1928); Smith, *ibid.*, **56**, 475 (1934).

(3) Smith and Dobrovolny, *ibid.*, **48**, 1420 (1926).

Dibenzoate.—Benzoylation in the usual way followed by digestion of the product with petroleum ether and recrystallization from alcohol gives white needles of the dibenzoate, m. p. 157°.

Anal. Calcd. for $C_{24}H_{22}O_4$: C, 75.6; H, 6.2. Found: C, 75.2, 75.2; H, 6.1, 6.2.

Dimethyl Ether.—The dihydroxy compound (2 g.) is dissolved in 25 cc. of methyl alcohol and 38 g. of dimethyl sulfate, and to the solution is added slowly a solution of 40 g. of potassium hydroxide in 200 cc. of methyl alcohol. The reaction mixture is heated to boiling for a few minutes, and then steam distilled. The distillate is cooled to 0° and the white solid filtered off. It melts at 21°.

Anal. Calcd. for $C_{12}H_{18}O_2$: OCH_3 (two), 31.9. Found: OCH_3, 32.1, 32.1.

Prehnitenequinone; tetramethyl-*o*-benzoquinone.—Two grams of the pure dihydroxy compound in 125 cc. of anhydrous ether was shaken for an hour with 10 g. of dry silver oxide.[4] The bright red solution was filtered, about half the ether evaporated, and then cooled. The quinone crystallizes in beautiful bright red needles, m. p. 110–111° with darkening at 80°; yield, 1.6 g. It is odorless. Reduction with sulfur dioxide yields the hydroquinone.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.1; H, 7.4. Found: C, 73.0, 73.3; H, 7.3, 7.4.

After about four hours the quinone begins to decompose, becoming reddish-brown, and the decomposition is not retarded appreciably even in an inert atmosphere at low temperatures. The decomposition product is apparently a mixture, for although it can be recrystallized from ether, it gives no constant melting point, nor can concordant analyses be obtained.

1,2,3,4-Tetramethylphenazine.—To the ethereal solution of the quinone obtained from 2 g. of the dihydroxy compound is added 1.5 g. of *o*-phenylenediamine dissolved in a very little acetic acid and the solution allowed to stand in a stoppered flask for two days. Most of the ether is then evaporated and the brownish-yellow solid filtered. The filtrate is then washed with sodium hydroxide, dilute sulfuric acid, water and dilute ammonium hydroxide and the ether evaporated. The residue is added to the main product, and the whole recrystallized from benzene; bright yellow needles, m. p. 217°, slightly soluble in alcohol, moderately soluble in ether.

Anal. Calcd. for $C_{16}H_{16}N_2$: C, 81.3; H, 6.8. Found: C, 81.2, 81.2; H, 6.9, 6.8.

Octamethylphenazine.—A similar procedure using diaminoprehnitene instead of *o*-phenylenediamine gave bright yellow needles of octamethylphenazine, m. p. 279°.

Anal. Calcd. for $C_{20}H_{24}N_2$: C, 82.1; H, 8.3. Found: C, 81.8, 81.8; H, 8.2, 8.1.

Summary

1. Tetramethyl-*o*-benzoquinone (prehnitenequinone) and several of its derivatives have been prepared and characterized.

2. The quinone is not a stable substance, decomposing after standing about four hours in air or in an inert atmosphere.

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[4] Willstätter, *Ber.*, **37**, 4744 (1904).

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Synthesis with β,β'-Dichloroethyl Ether. Morpholine Derivatives

BY W. NELSON AXE AND CHARLES FREEMAN

The formation of morpholine derivatives by the action of β,β'-dichloroethyl ether on primary amines has been extended to phenylhydrazine, benzidine and *p*-phenylenediamine. The last two named are the first diamino compounds to be used in this type of condensation. With *m*-phenylenediamine the condensation could not be effected. Repeated attempts with the latter compound yielded nothing but resinous material.

$$C_6H_5—NH—NH_2 + RCl_2 \longrightarrow C_6H_5—NH—N < R + 2HCl \quad (1)$$

$$H_2N—C_6H_4—NH_2 + 2RCl_2 \longrightarrow R > N—C_6H_4—N < R + 4HCl \quad (2)$$

$$H_2N—C_6H_4—C_6H_4—NH_2 + 2RCl_2 \longrightarrow R > N—C_6H_4—C_6H_4 < R + 4HCl \quad (3)$$

(R represents the ether residue $—CH_2—CH_2—O—CH_2—CH_2—$)

Chemical Behavior of Condensation Products

(a) **N-Phenylaminomorpholine.**—This compound does not possess the properties of ordinary amines, but rather those of the morpholine compounds. The product cannot be acylated by acetic anhydride or benzenesulfonyl chloride under the conditions at which these reactions are usually carried out.

(b) **N,N′-Phenylene-1,4-dimorpholine.**—It is a well-known fact that tertiary aromatic amines do not form salts, while mixed aryl alphyl tertiary amines do. This compound presents an interesting example of a substance that might be considered as a tertiary aromatic amine or a mixed amine. It is readily soluble in acids, indicating the formation of a salt. On the other