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.

MINNEAPOLIS, MINN. RECEIVED NOVEMBER 2, 1933

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

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WESTMINSTER COLLEGE]

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 hand, it is known that true aromatic tertiary amines often form highly colored addition products with salts of heavy metals, acids and halogens. These addition products are unstable and have been isolated in only a few instances. Deeply colored addition products of this type were observed with this compound. Brilliantly colored blue solutions were instantly obtained when small amounts of the base were added to solutions of the following substances: sulfuric acid, chromic acid, hydrogen peroxide, silver nitrate, bromine, iodine, mercuric nitrate and ferric chloride. In no case did very much of the base take part in the reaction because of its slight solubility in water; however, the color was very intense. In all cases, a few minutes of boiling sufficed to destroy the color. The color also gradually fades when the solutions are allowed to stand for several hours at room temperature.

(c) **N,N'-Biphenylene-4,4'-dimorpholine.**—This substance forms salts with acids, but does not exhibit the color reactions of the preceding compound.

TABLE I

PROPERTIES AND ANALYTICAL DATA OF MORPHOLINE DERIVATIVES

Morpholine	Yield, %	M. p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
1	20–30	107.5	$C_{10}H_{14}N_2O$	67.42	67.29	7.91	8.04	15.72	15.48
2	55–65	196	$C_{14}H_{20}N_2O_2$	67.69	67.53	8.12	8.00	11.28	11.00
3	35–40	228.5	$C_{20}H_{24}N_2O_2$	74.02	73.94	7.46	7.35		

Experimental Part

The improved method for the preparation of morpholine compounds described by Cretcher[1] was tried and found to be unsatisfactory with the materials used in this work. In general the original method of Kamm and Waldo[2] was followed with modifications.

Procedure.—Gram molecular proportions of the reactants were refluxed in the presence of sufficient 40% potassium hydroxide to take care of the hydrogen chloride formed. The reactions are slow, four to six hours of refluxing being necessary in the case of the diamines and at least ten hours in the case of phenylhydrazine. The solid portion in each instance is filtered off and washed thoroughly with a suitable solvent. Acetone and alcohol are very suitable for washing out unchanged reactants in the diamine condensations, while 20% alcohol was used in washing the phenylaminomorpholine. For recrystallization, 50% alcohol was used for the phenylaminomorpholine and both isoamyl alcohol and xylene were used for the dimorpholines. The color of the biphenylenedimorpholine can be improved by dissolving it in hydrochloric acid and boiling in decolorizing charcoal.

The molecular weights of the morpholines were estimated by the cryoscopic method using both camphor and naphthalene as solvents.

	Mol. wt. Calcd.	Mol. wt. Found (av.)
(1) N-Phenylaminomorpholine	178	179
(2) N,N'-Phenylene-1,4-dimorpholine	248	232
(3) N,N'-Biphenylene-4,4'-dimorpholine	324	325

Summary

1. β,β'-Dichloroethyl ether has been condensed with phenylhydrazine, *p*-phenylenediamine and benzidine to give N-phenylaminomorpholine, N,N' - phenylene -1,4 - dimorpholine and N,N'-biphenylene-4,4'-dimorpholine, respectively. These compounds have not hitherto been described in the literature.

2. Interesting color reactions were observed when N,N'-phenylene - 1,4 - dimorpholine was treated with solutions of salts of heavy metals, halogens and acids.

NEW WILMINGTON, PA. RECEIVED NOVEMBER 6, 1933

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[1] Cretcher, Koch and Pittenger, THIS JOURNAL, **47**, 1173 (1925).

[2] Kamm and Waldo, *ibid.*, **43**, 2223 (1921).