3,4-Dimethyl-(*d*-ribityl)-aniline, V.—The hydrolysis of IV is best carried out by catalytic *trans*-esterification procedures using barium methylate or sodium methylate in methanol. In a typical experiment, 5 g. of IV in 15 cc. of methanol containing 0.1 g. of sodium methylate is gently heated to reflux for one hour. On cooling the product separates in essentially pure form melting at 142–143° (wt. 2.3 g.). On diluting the filtrate with an equal volume of water, 0.5 g. of somewhat less pure product is obtained.

Summary

N-(*d*-Ribityl)-3,4-dimethylaniline was prepared by two methods without the use of *d*-ribose. In one method, 3,4-dimethyl-(tetraacetyl-*d*-ribonyl)-anilide is converted to the chloroimine and the latter is reduced and then deacetylated. In the second procedure 3,4-dimethylaniline and tetraacetyl-*d*-ribonitrile are subjected to catalytic reductive coupling and the resulting acetylated amine deacetylated.

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[CONTRIBUTION FROM THE SCHOOL OF PHARMACY, UNIVERSITY OF GEORGIA]

The Hydrolysis of Some Quinone Oximes

BY W. T. SUMERFORD AND D. N. DALTON

Compounds of the *p*-benzoquinone series have recently become of more than academic interest due to their vitamin K activity,[1] their use as intermediates in the synthesis of tocopherols,[2] and their potent fungicidal properties.[3]

Quinones may be obtained in varying yields by oxidizing under stated conditions the appropriate: (1) hydrocarbon, (2) dihydric phenol, (3) aromatic amine, (4) aminophenol, or (5) aromatic diamine with: (1) chromium trioxide, (2) ceric sulfate, (3) sodium dichromate, (4) ferric chloride, and (5) manganese dioxide, respectively.

The hydrolysis of quinone monoximes to the corresponding quinones and hydroxylamine would seem to offer an attractive route to the production of quinones since the tautomeric nitrosophenols can usually be prepared conveniently and in good yields. In fact this method has not been entirely overlooked. Henrich, Taubert and Birkner[4] obtained 2-chloro-5-hydroxy-tolu-3,6-quinone in an unstated yield by treating the monoxime of this compound with diluted sulfuric acid and potassium dichromate. More recently Karrer and Hoffmann[5] used a 30% solution of hydrogen peroxide to destroy the hydroxylamine in a similar reaction, and thereby were able to hydrolyze 2,6-dimethyl-3-ethylbenzoquinone-1-oxime to obtain a 70% yield of the corresponding quinone.

Lapworth[6] found that certain aldehydes aid in the hydrolysis of oximes by removing hydroxylamine from the sphere of the reaction. Tseng[7] claims to have hydrolyzed three quinone monoximes by refluxing them with 8% hydrochloric acid and formaldehyde to obtain yields of the corresponding quinones up to 90% of the theoretical. Attempts to duplicate the results of Tseng[7] with thymoquinone monoxime were unsuccessful, but a 36% yield of the quinone was obtained with the use of acetone in place of the formaldehyde.[8]

Since Tseng's results fell far short of duplication, and the Karrer and Hoffmann method[5] was found to be inapplicable to some homologous oximes, other oxidizing agents known to react with hydroxylamine were tried in this reaction. Preliminary trials showed that ferric chloride and cupric sulfate could be used advantageously here, but cuprous salts, which were tried because of the relative position of Cu^{++} and Cu^{+} in the electromotive series, proved superior to anything used in the reaction. A method using cuprous chloride and a carbonyl compound for the hydrolysis of quinone oximes was worked out, and applied to a series of tautomeric *p*-nitrosophenols ⇄ quinone monoximes. The results are given in Table I, and are compared there with the results obtained by subjecting the same oximes to the Karrer and Hoffmann method.

Experimental Part

Preparation of the Oximes.—All of the quinone oximes listed in Table I except 2-methylnaphthoquinone monoxime were prepared by treating the appropriate phenol with sodium nitrite and hydrochloric acid as described by Kremers and Wakeman.[9] The 2-methylnaphthoquinone monoxime was obtained by heating equivalent amounts of the quinone and hydroxylamine hydrochloride in ethanol containing hydrochloric acid. The thymoquinone dioxime was prepared by refluxing 2-methyl-5-isopropylbenzoquinone-1-oxime with hydroxylamine hydrochloride in ethanol.

Hydrolysis of the Oximes. Method I.—A mixture of 0.01 mole of the quinone oxime, 20 ml. of diluted hydrochloric acid (1 to 5), and 3 ml. of Superoxol (assay 26%) was refluxed for one and one-half hours. The mixture was then steam distilled, the distillate extracted with diethyl ether, the ether extract dried over Drierite, and finally allowed to evaporate spontaneously with the aid of a small electric fan. In one or two instances it was necessary to complete the drying process by placing the quinone in a desiccator over phosphorus pentoxide for an hour or

(1) Fieser, Campbell and Fry, THIS JOURNAL, **61**, 2206 *et seq.* (1939).

(2) Smith, Opie, Wawzonek and Prichard, *J. Org. Chem.*, **4**, 318 (1939).

(3) Ter Horst and Felix, *Ind. Eng. Chem.*, **35**, 1255 (1943).

(4) Henrich, Taubert and Birkner, *Ber.*, **45**, 303 (1912).

(5) Karrer and Hoffmann, *Helv. Chim. Acta*, **22**, 654 (1939).

(6) Lapworth, *J. Chem. Soc.*, **91**, 1133 (1907).

(7) Tseng, Hu and Chu, *J. Chinese Chem. Soc.*, **2**, 136 (1934).

(8) Sumerford and Hartung, *J. Am. Pharm. Assoc.*, **29**, 65 (1940).

(9) Kremers and Wakeman, "Organic Syntheses," Coll. Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 511.

two. The yields obtained by this method are listed in column 3 of Table I.

Method II.—One hundredth mole of the quinone oxime was dissolved in 15 ml. of methyl cellosolve and 1.5 ml. of acetone. To this was added 1.4 g. (0.01 mole) of cuprous oxide (Merck commercial grade) and 4.7 ml. of hydrochloric acid previously diluted with 6 ml. of water. The solution was refluxed for forty-five minutes, and then steam distilled. The quinone was isolated by the procedure described in Method I, and was thus easily obtained in a high state of purity. In the case of thymoquinone dioxime the quantity of the reagents was doubled, and the refluxing time increased to two and one-half hours.

A Modification of Method II.—The conditions described in Method II are too severe for hydrolyzing 3-methylbenzoquinone 1-oxime and 2-methylbenzoquinone-1-oxime, but the following modification of Method II gave fair yields with these oximes. To 1.37 g. (0.01 mole) of the oxime, contained in a glass mortar, was added 2 ml. of acetone and 4.7 ml. of hydrochloric acid. To this mixture was added 1.4 g. (0.01 mole) of cuprous oxide in divided portions with trituration after each addition. The entire mixture was diluted with 20 ml. of water, shaken mechanically for forty-five minutes, and then steam distilled. The quinone was isolated in the usual manner. The yields obtained with this procedure are given in Table I.

TABLE I

RESULTS OBTAINED FROM THE HYDROLYSIS OF THE OXIME

Oxime			Quinone		
	Yield, %	M. p. (uncor.)	Yield Method I, %	Yield Method II, %	M. p., °C. (uncor.)
Benzoquinone-1-					
2-Methyl-	70	135 dec.	Trace (oily)	55[a]	67
3-Methyl	81	157 dec.	Trace	20[a]	67
2,6-Dimethyl-	88	175 dec.	18	78	73
3,5-Dimethyl-	91	172 dec.	26	87	73
2,5-Dimethyl-	90	173 dec.	28	92	125
2,3,6-Trimethyl-	90	172 dec.	7	92	32
2,3,5,6-Tetramethyl-	80	89 dec.	33	66	107
2-Isopropyl-5-methyl-	90	155 dec.	Trace	88	45
2-Methyl-5-isopropyl-	85	162	None	85	45
Thymoquinone dioxime	66	235 dec.	None	80	45
2-Methylnaphthoquinone monoxime	79	165 dec.	45	45	105

[a] These two compounds were hydrolyzed by the Modification of Method II.

Discussion.—Methyl cellosolve was used as a solvent in these reactions because it provided homogeneity and a suitable boiling range of from 97 to 101°. Methyl cellosolve was also tried in the Karrer and Hoffmann method,[5] but in each instance the yield was poorer than with the regular procedure.

Four controlled experiments disclosed that an 85% yield of thymoquinone was obtained from its monoxime by Method II with the use of cuprous oxide and acetone while the same procedure without the acetone gave a 79% yield, and without the cuprous oxide gave a 15% yield, and without either gave only a trace of thymoquinone.

It is evident from the data in Table I that *p*-nitrosophenol $\rightleftharpoons$ quinone monoxime tautomers in which both the nitroso and hydroxyl groups are hindered are more difficult to hydrolyze than those in which only one of these groups is hindered. It appears also that the reaction is slightly favored in those tautomers in which the nitroso group is partially hindered.

The method described here for hydrolyzing quinone oximes has not been applied to *p*-aminophenols, but a similar procedure to Method II using cupric sulfate was found to give an 80% yield of thymoquinone from *p*-aminothymol.

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Summary

A method for hydrolyzing *p*-quinone oximes with the aid of cuprous chloride has been described, and the results obtained with eleven oximes have been given in a tabular form.

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Some Glycol Complexes of the Light Transition Metals

BY ROBERT GOMER AND G. N. TYSON, JR.

In the course of some studies on the complex-forming behavior of the light transition elements, it has been found possible to synthesize and partially characterize by means of magnetic susceptibility measurements the following glycol complexes: $CuSO_4 \cdot 2$ glycol (I), $CuSO_4 \cdot 1$ glycol (II), $NiSO_4 \cdot 4$ glycol (III), $NiSO_4 \cdot 3$ glycol $\cdot 1H_2O$ (IV), $NiSO_4 \cdot 2$ glycol $\cdot 1H_2O$ (V), $CoCl_2 \cdot 3$ glycol (VI), $CoCl_2 \cdot 3$ glycol $\cdot 1H_2O$ (VII), $CoCl_2 \cdot 2$ glycol $\cdot 1H_2O$ (VIII), $FeSO_4 \cdot 1$ glycol $\cdot 2H_2O$ (IX), $FeSO_4 \cdot 3$ glycol (X), $FeSO_4 \cdot 3$ glycol $\cdot 1H_2O$ (XI), $MnCl_2 \cdot 2$ glycol $\cdot 1H_2O$ (XII). Of these (I), (IV), (V), (VI), (VII), (VIII) have been reported previously by Grün.[1,2] The duplication of some of the syntheses requires rigid adherence to all conditions and these experimental procedures have been given in detail.

Experimental

Synthesis.—In the following syntheses J. T. Baker and Co. C. P. salts were used as the source of the metal ions, and the glycol and pyridine were obtained from Eastman Kodak Company.

(I) is prepared by adding 3.7 g. of $CuSO_4 \cdot 5H_2O$ to 5 g. of glycol on the water-bath. The decanted solution crystallizes after several days of standing in the cold. The

(1) Grün and Bockisch, *Ber.*, **41**, 3465–3478 (1908).

(2) Grün and Boedecker, *ibid.*, **43**, 1051–1062 (1910).