Procedure.—One-hundredth mole of ester was dissolved in 35–50 cc. of methanol and the catalyst added. After standing for twenty-four hours at room temperature (sixty hours in the case of α-naphthyl acetate) the solution was evaporated at 25–40° under the vacuum of a good water-pump. The residual alcohol or phenol had the correct melting point and was frequently of exceptional purity. As catalyst, 5 cc. of concentrated hydrochloric acid may be used. However, ethanolic hydrogen chloride is preferable, 0.5 g. of 38% solution (wt./wt.) being effective.

Catechol diacetate, β-naphthyl acetate, pentaerythritol tetraacetate and hydroquinone dipropionate were found to be completely cleaved under very mild conditions. α-Naphthyl acetate was also cleaved but required a longer time. Benzoyl and carbethoxy groups appear to react more slowly.

When low fatty acid esters of relatively nonvolatile alcohols are concerned, the method offers the advantage that all other components of the solution can be removed under reduced pressure, at or near room temperature, permitting the isolation of the product without further manipulation.

From the foregoing it is evident that considerable caution is necessary in working with alcoholic solutions of esters, particularly acetyl compounds, when small amounts of strong acid are present.

BURROUGHS WELLCOME & CO. U. S. A.
EXPERIMENTAL RESEARCH LABORATORIES
TUCKAHOE, N. Y.
RECEIVED MAY 9, 1941

Methylanilines by Demethylation of Dimethylanilines

BY WILLIAM S. EMERSON

Since dimethyl-2,4,6-trisubstituted anilines are readily obtained,[1] they offer a convenient starting point for the preparation of the corresponding monomethyl derivatives. We have found that when three of these compounds are treated with nitrous acid the N-nitroso derivative of the secondary amine is produced in each case in quantitative yield in contrast to dialkylanilines where not all of the active positions are blocked.[2] The nitroso group is easily removed by one of the standard methods employed when secondary amines are purified through this derivative.[3] Since it has been shown that a methyl group is removed less readily with nitrous acid than an ethyl group,[2] this method should be capable of extension to other dialkyl-2,4,6-trisubstituted anilines.

Experimental

N-Nitroso-N-methyl-2,4,6-tribromoaniline.—2,4,6-Tribromoaniline was reductively alkylated with formaldehyde and formic acid by the method of Clark, Gillespie and Weisshaus.[1a] In this way 10 g. (92%) of N,N-dimethyl-2,4,6-tribromoaniline, b. p. 134–138° (15 mm.), was obtained from 10 g. of the primary amine. Its physical properties, which have never been reported, are n^{20}_{D} 1.6244, d^{20}_{20} 1.998, M^{20}_{D} calcd. 64.3, M^{20}_{D} found 63.5. Its perbromide melted at 123–124° (124°).[4]

After 5.5 g. of N,N-dimethyl-2,4,6-tribromoaniline had been dissolved in 30 cc. of concentrated hydrochloric acid and 20 cc. of water, a solution of 7 g. of sodium nitrite in 10 cc. of water was added over a one-half hour period. During the addition the mixture was cooled in ice and shaken occasionally. It was then allowed to stand sixteen hours at room temperature before the N-nitroso-N-methyl-2,4,6-tribromoaniline was collected on a filter, washed with water and dried; yield 5.7 g. (100%) of practically pure material. After two crystallizations from aqueous alcohol an analytical sample melted at 91.5–92.0°.

Anal.[5] Calcd. for $C_7H_5ON_2Br_3$: N, 7.50. Found: N, 7.62.

N-Methyl-2,4,6-tribromoaniline.—When 5.7 g. of the N-nitroso-N-methyl-2,4,6-tribromoaniline was treated with stannous chloride and hydrochloric acid essentially according to the procedure for N-ethyl-*m*-toluidine,[3] 4.5 g. (85%) of N-methyl-2,4,6-tribromoaniline was obtained. It boiled at 178–179° (30 mm.) and melted at 36–37° (39°).[4] Its acetyl derivative melted at 97.5–98.5° (101°)[4] after one crystallization from aqueous alcohol.

N-Nitroso-N-methyl-2,4,6-trichloroaniline.—N,N-Dimethyl-2,4,6-trichloroaniline was prepared from 2,4,6-trichloroaniline by reductive alkylation with formaldehyde and formic acid.[1a] The 10 g. of tertiary amine obtained from 10 g. of the primary represented a yield of 83%. It boiled at 128–138° (20 mm.); n^{20}_{D} 1.5649 (1.5660).[6] The perbromide prepared by Fries' method[4] melted at 112–113°.

Anal. Calcd. for $C_8H_9NCl_3Br_3$: C, 20.6; H, 1.93. Found: C, 20.9; H, 1.93.

Treatment of 7.5 g. of the N,N-dimethyl-2,4,6-trichloroaniline with nitrous acid as described above yielded 8.0 g. (100%) of practically pure N-nitroso-N-methyl-2,4,6-trichloroaniline. An analytical sample melted at 66.5-67.0° after two crystallizations from aqueous alcohol and one from aqueous methyl alcohol.

Anal. Calcd. for $C_7H_5ON_2Cl_3$: N, 11.7. Found: N, 11.5.

N-Methyl-2,4,6-trichloroaniline was prepared by the reduction of 7.5 g. of the nitroso derivative with stannous chloride and hydrochloric acid. The yield of 6 g. (90%)

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(1) (a) Clark, Gillespie and Weisshaus, THIS JOURNAL, **55**, 4571 (1933); (b) Emerson, Neumann and Moundres, *ibid.*, **63**, 972 (1941).

(2) Crowley, Milton, Reade and Todd, *J. Chem. Soc.*, 1286 (1940).

(3) Buck and Ferry, "Organic Syntheses," Vol. 18, 1938, p. 40.

(4) Fries, *Ann.*, **346**, 128 (1906).

(5) The analyses in this paper are microanalyses and were carried out by Mr. L. G. Fauble and Miss Mary S. Kreger.

(6) Emerson, Dorf and Deutschman, THIS JOURNAL, **62**, 2159 (1940).

boiled at 134–137° (25 mm.). Its acetyl derivative melted at 88–89° (89–90°).[7]

N-Nitroso-N-methylmesidine.—N,N-Dimethylmesidine was prepared from nitromesitylene by the method of Emerson, Neumann and Moundres.[1b] It was converted to N-nitroso-N-methylmesidine by the above procedure, 6 g. (100%) of the latter being obtained from 5.5 g. of the tertiary amine. A sample distilled at 113–117° (3 mm.): n^{20}_D 1.5344, d^{20}_{20} 1.047, M^{20}_D calcd. 53.7, M^{20}_D found 52.8.

N-Methylmesidine.—Six grams of the nitroso derivative was reduced with stannous chloride and hydrochloric acid yielding 2.5 g. (50%) of N-methylmesidine: b. p. 107–118 (30 mm.), n^{20}_D 1.5248, d^{20}_{20} 0.951, M^{20}_D calcd. 49.4, M^{20}_D found 48.0. The *p*-toluenesulfonamide melted at 147.0–147.5° (145–146°)[8] after one crystallization from aqueous alcohol.

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(7) German Patent 176,474, *Chem. Zentr.*, **78**, I, 142 (1907).

(8) Hey, *J. Chem. Soc.*, 1581 (1931).

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RECEIVED FEBRUARY 27, 1941

Antimony Electrode. A Correction

BY FRANK HOVORKA AND G. H. CHAPMAN

Dr. Duncan A. MacInnes has kindly called our attention to the fact that there is a simple explanation for the difference of the *p*H values for 0.05 *M* potassium acid phthalate that he recommends[1] and the other values quoted in our paper on the "Antimony Electrode."[2] His value is based on the *p*H scale proposed by MacInnes, Belcher and Shedlovsky,[3] and our value is obtained by using Sörensen's value for E_0, and the two values are not comparable. The difference between the two values is about 0.02 *p*H unit. When our value is recalculated on this proposed scale, the agreement is excellent and is within the experimental error.

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(1) MacInnes, "Principles of Electrochemistry," Reinhold Publishing Corporation, New York, N. Y., 1939.

(2) Hovorka and Chapman, THIS JOURNAL, **63**, 955 (1941).

(3) MacInnes, Belcher and Shedlovsky, *ibid.*, **60**, 1094 (1938).

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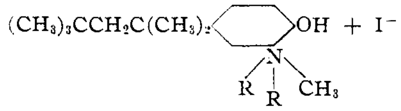
RECEIVED MAY 23, 1941

Phenolic Invert Soaps

BY JOSEPH B. NIEDERL AND FRANK A. ABBRUSCATO[1]

Since none of the previously reported capillary active and water soluble "invert soaps"[2,3] contain a free phenolic hydroxyl group, it was thought desirable to prepare and study such types of compounds. For this purpose *p*-$\alpha,\alpha,\gamma,\gamma$-tetramethobutylphenol (diisobutylphenol)[4] was condensed with formaldehyde and a series of secondary amines. The resulting tertiary amines were then converted into the respective phenolic invert soaps upon treatment with methyl iodide. These quaternary ammonium salts possess the structure



Experimental Procedure

To a solution of 20 g. of diisobutylphenol and 0.1 mole of the secondary amine in 35 cc. of methanol was added with stirring 10 g. of 30% aqueous formaldehyde solution.[5] The reaction mixture was then allowed to stand at room temperature until two layers had formed. The tertiary amine, the bottom layer, was separated and either crystallized (morpholine, piperidine) or subjected to further purification by precipitation with ammonia of the amine from its filtered solution in dilute acetic acid. The crystalline methiodides were prepared by dissolving the purified amine in an equal amount of methyl iodide and allowing the reaction mixture to stand at room temperature until the quaternary salt crystallized out.

TABLE I

Compounds	Formulas	M. p., °C. (uncor.)	Nitrogen anal., Calcd.	Nitrogen anal., Found
N-(2-Hydroxy-5-$\alpha,\alpha,\gamma,\gamma$-tetrametho-butyl)-benzyl-				
Morpholine	$C_{19}H_{31}NO_2$	44–45	4.59	4.45
Methiodide	$C_{20}H_{34}NIO_2$	176–177.5	3.13	3.03
Piperidine	$C_{20}H_{33}NO$	92–93	4.62	4.73
Methiodide	$C_{21}H_{36}NIO$	162–163.5	3.15	3.00
Ammonium iodides				
Methyl-diethyl	$C_{20}H_{36}NIO$	124–125	3.23	3.41
Methyl-di-*n*-propyl	$C_{22}H_{40}NIO$	135–136.6	3.06	3.04
Methyl-di-*n*-butyl	$C_{24}H_{24}NIO$	132–133	2.86	2.88

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(1) Abstracted from the thesis presented by Frank A. Abbruscato to the Graduate School of New York University in partial fulfillment of the requirement for the degree of Master of Science, June, 1941.

(2) R. Kuhn and D. Jercbel, *Ber.*, **73**, 1100 (1940).

(3) J. B. Niederl and co-workers, THIS JOURNAL, **63**, 945, 1475 (1941).

(4) J. B. Niederl, *Ind. Eng. Chem.*, **30**, 1269 (1938).

(5) H. A. Bruson, U. S. Patents 2,031,557, 2,033,092 (1936).

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RECEIVED MAY 14, 1941

Indole Preparation

BY FLOYD T. TYSON

The author has found that the intramolecular condensation of *o*-formotoluide is a convenient method for the preparation of indole. Verley[1] used sodium amide as the condensing agent. No yields or details with respect to indole preparation were given by Verley although this author describes a procedure for the preparation of 2-

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(1) Verley, *Bull. soc. chim.*, **35**, 1039 (1924).