tracted twice with 150 ml. of carbon tetrachloride to recover the major portion of the dissolved bromoacetal. The carbon tetrachloride solutions were combined and distilled through a Whitmore–Fenske type column. Bromoacetaldehyde dimethyl acetal (124 g. or 83%) distils at 48–49° (14 mm.), $n^{20}\text{D}$ 1.4450; $d^{20}{}_4$ 1.430.

Preparation of Bromoacetaldehyde Diethyl Acetal.—The above procedure was repeated using 500 ml. of ethyl alcohol (99.5–100%) instead of 350 ml. of methyl alcohol. Distillation yielded bromoacetaldehyde diethyl acetal (151 g. or 77%), b. p. 64–65° (16 mm.), $n^{20}\text{D}$ 1.4418; $d^{20}{}_4$ 1.280. On using commercial 95% ethyl alcohol the yield was somewhat lower (142 g. or 72%).

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An Improved Method for the Synthesis of Quinone

By JOHN H. BILLMAN, BERNARD WOLNAK AND DAVID K. BARNES

In the course of another investigation it was necessary to prepare quinone in relatively large amounts. The procedure described in "Organic Syntheses"[1] requires vanadium pentoxide as a catalyst. Since there was no vanadium pentoxide available, we substituted an equivalent amount of ammonium metavanadate which worked equally well and gave comparable yields. In addition the reaction time was reduced to less than one third the time normally required. Other runs were made using increased amounts of ammonium metavanadate and warming the reaction mixture to 40° before adding the catalyst. It was found that the greater the amount of catalyst used the faster the reaction proceeded. Thus with 1.4 g. of ammonium metavanadate the reaction was complete in less than half an hour or about one-eighth the time normally required. The final procedure which was used is described in the experimental part.

Experimental

Quinone.—In a 2-liter round-bottom three-neck flask equipped with a mechanical stirrer and a thermometer were placed 1 liter of a 2% sulfuric acid solution, 110 g. of hydroquinone, and 60 g. of sodium chlorate. The mixture was vigorously stirred and warmed to 40°. At this temperature 1.4 g. of ammonium metavanadate was added. The flask was cooled from time to time, with tap water, so that the temperature did not rise above 42°. The reaction was over in less than thirty minutes. The mixture was cooled to 10°, then filtered with suction, and the quinone washed once with 100 ml. of cold water. After drying in a desiccator over calcium chloride the product weighed 97–99 g. and melted at 112–113°. Extraction of the filtrate and washings with three 100-ml. portions of warm benzene yielded 3–4 g. more of quinone, bringing the total amount to 101–103 g. (93–95% of the theoretical amount).

The quinone may be dried in about an hour in an oven at 100°. This should be done under a hood. There is about a 15% loss due to sublimation. Over calcium chloride, it takes from one to two days for the quinone to dry.

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(1) "Organic Syntheses," Coll. Vol. II, 1943, p. 553.

Preparation of *o*-Aminobenzyl and *β*-Aminoethyl Thiazolium Salts

BY HANS T. CLARKE

In view of the interesting observations recorded by Sealock and Goodland,[1] a description becomes necessary of the preparation of the thiazolium amino compounds which inhibit the enzymatic decomposition of the amine. After the recognition of the thiazole ring in thiamine,[2] these substances were synthesized early in 1936 for study as models, but they found useful application only after they had reached Dr. Sealock's Laboratory.

Experimental

3-*o*-Nitrobenzyl-4-methylthiazolium Chloride.—A mixture of 3.5 g. of *o*-nitrobenzyl chloride, 1 cc. of benzene and 2.0 g. of 4-methylthiazole was heated at 95–100° in a sealed tube for eighty to ninety hours. The crystalline product. well washed with ether and recrystallized from absolute alcohol, decomposed at 186.5–187°. The yield was 4.1 g. or 75%.

Anal. Calcd. for $C_{11}H_{11}O_2N_2SCl$: N, 10.4; Cl, 13.1. Found: N, 10.04; Cl, 13.1.

3-*o*-Aminobenzyl-4-methylthiazolium Chloride Hydrochloride.—A hot solution of 1.4 g. of the above nitro compound in 50 cc. of 2 *N* hydrochloric acid was boiled gently for an hour in the presence of 2.4 g. of granulated tin. As very little action had occurred, 3.4 g. of crystallized stannous chloride was added. The precipitate which formed slowly dissolved in the boiling mixture. The clear solution was warmed at 50° overnight, when most of the tin dissolved. The mixture was diluted, freed of tin salts with hydrogen sulfide and evaporated to dryness under reduced pressure. The residue was warmed with 4 cc. of absolute alcohol, when it rapidly became crystalline; it was filtered and washed with absolute alcohol. The product (about 0.9 g.) after recrystallization from aqueous alcohol decomposed over the range 204–212°.

Anal. Calcd. for $C_{11}H_{14}N_2SCl_2\cdot H_2O$: C. 44.8; H, 5.1; N, 9.5; Cl, 24.1. Found: C. 45.3; H, 4.9; N, 9.2; Cl. 24.4.

3-*β*-Phthalimidoethyl-4-methylthiazolium Bromide.—Equimolecular quantities of *β*-bromoethylphthalimide and 4-methylthiazole were heated in a sealed tube at 95–100° for ten days, when the mixture had completely solidified. The product was washed with ether, and recrystallized from water as platelets, m. p. 238° with slight darkening.

Anal. Calcd. for $C_{14}H_{13}O_2N_2SBr$: N, 7.9; Br, 22.7. Found: N, 7.9; Br, 22.4.

3-*β*-Aminoethyl-4-methylthiazolium Bromide Hydrobromide.—A solution of 2.5 g. of the phthalimide thiazolium bromide in 10 cc. of 48% hydrobromic acid was boiled under reflux for forty hours, and allowed to cool to room temperature. The phthalic acid (1.0 g., 85%) was filtered off and washed with water; the filtrate and washings were combined and evaporated nearly to dryness, the residue treated with absolute alcohol, and the crystalline product well washed with absolute alcohol. It shrank at 218.5–219.5° and melted with decomposition at 222.5–223.5°; yield 2.1 g.

Anal. Calcd. for $C_6H_{12}N_2SBr_2$: N, 9.2; S. 10.5; Br. 52.7. Found: N, 9.1; S, 10.7; Br, 52.8.

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(1) Sealock and Goodland, THIS JOURNAL, **66**, 507 (1944).

(2) Clarke and Gurin, *ibid.*, **57**, 1876 (1935).