mixtures used. This *p*H was chosen because, in all the solvent mixtures used, it assures conversion of the methyl red to the alkaline form.

We present in Tables I and II our results (with those of Reimers for comparison). In Table III are given the *p*H values as read from the *p*H meter for benzoate buffers at various methanol–water concentrations. In each case the benzoic acid and sodium benzoate were 0.01 molar. It is realized that these are not true *p*H readings, since aqueous standard buffers were used as references.

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Some Higher Members of the Wurster Salts Series

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Interest in the oxidation products of aromatic *p*-diamines was aroused in this laboratory when Kuhn and Beinert[1] reported the di- and tetra-N-methyl derivatives of *p*-phenylenediamine to be enzyme poisons. Previously Stevenson, Dobriner and Rhodes[2] had demonstrated that *p*-dimethylaminoazobenzene, one of the most potent carcinogenic dyes, was cleaved *in vivo* at the azo bond to yield among other products *p*-phenylenediamine and some of its derivatives. Kensler, and co-workers[3] concluded from their work that the free radicals, Wurster salts, formed by the oxidation of these diamines are the true enzyme poisons and possibly the real carcinogenic substances.

Knowing that N-methyl-*p*-phenylenediamines undergo oxidation, it was desirable to determine whether the reaction was general for structurally related compounds.

In the previous work on Wurster type compounds most of the data were obtained from solutions of the salts and in only a few cases was the material isolated and analyzed.

Michaelis and Granick[4] investigated thoroughly the various N-methyl and N-ethyl substitution products and gave methods for preparing some of the compounds in crystalline form. The oxidation was accomplished by the slow addition of bromine to a solution of the diamine in cold methyl alcohol–acetic acid and allowing the reaction product to precipitate. When we applied this method to compounds other than N-methyl it was found that oxidation, which was indicated by the development of intensely colored solutions, was rapidly followed by decomposition. By substituting dioxane for methyl alcohol and modifying the amount of bromine the reaction proceeded smoothly and gave good yields of the desired products.

The freshly prepared compounds dissolve in water to yield highly colored solutions which vary in stability. For example the Wurster salt of *p*-aminodiethylaniline shows no change after boiling two hours, whereas the oxidation product of benzidine gives a blue solution which fades on warming or standing.

In the solid state, even when protected from light and moisture, these products undergo progressive decomposition with loss of color. At the end of six months they dissolve in water to give straw-colored solutions.

Experimental

A. N-Substituted *p*-Phenylenediamines.—With the exception of *p*-aminodiethylaniline, which was obtained from Eastman Kodak Co., all the N-substituted *p*-phenylenediamines were prepared in the laboratory by methods previously reported.

***p*-Aminodipropylaniline.**—By treating dipropylaniline according to Jacobs and Heidelberger[5] a product pure enough for further use was obtained, providing it was not allowed to stand too long.

***p*-Aminodi-*n*-butylaniline.**—By a method substantially the same as outlined above, Reilly and Hickinbottom[6] aminated dibutylaniline. This product was found satisfactory for the work undertaken here.

N-(*p*-Amino-phenyl)-morpholine.—This material was obtained by condensing *p*-chloronitrobenzene with morpholine[7] and reducing the resulting nitro compound to the amine with tin and hydrochloric acid.

N,N'-Phenylene-1,4-dimorpholine.—This was obtained directly by the condensation of morpholine with β,β'-dichloroethyl ether.[8]

B. Primary Diamines Related to *p*-Phenylenediamine.—Benzidine and dianisidine were found to undergo oxidation to yield products characteristic of the Wurster salts and for this reason they are included in this report. They were of technical grade and were used without further purification.

C. Oxidation Products.—Michaelis and Granick[4] employed a system of nomenclature to distinguish the free radical from the polymer by the use of the prefix s or π before the name of the diamine from which the compound was derived. When no distinction is made the prefix σ is used. In the present work no effort was made to determine this property and therefore the latter prefix is used throughout.

σ-1-Amino-4-diethylaminobenzene Bromide.—To 8.2 g. of *p*-aminodiethylaniline dissolved in 80 cc. of dioxane + 40 cc. acetic acid, cooled to 0°, a mixture of 1 cc. of bromine and 40 cc. of dioxane was added dropwise over one-half hour. The solution which is at first a deep purple turns green with the deposition of a black precipitate. The solid is collected at once on a buchner funnel, washed with 150 cc. of ether and dried *in vacuo* at room temperature; yield 7 g., m. p. 145–155° uncor.[9] *Anal.* Calcd. for $C_{10}H_{16}N_2Br$: Br, 32.73. Found: Br, 32.59. A sample of the dried material in water gave a bluish-red solution which could be boiled for two hours without any apparent change. The dried material on standing for three months turned brown and gave a straw colored solution in water.

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(1) Kuhn and Beinert, *Ber.*, **76B**, 904 (1943).

(2) Stevenson, Dobriner and Rhodes, *Cancer Research*, **2**, 160–167 (1942).

(3) Kensler, *et al.*, *J. Biol. Chem.*, **143**, 465 (1942); *Cancer Research*, **2**, 1 (1942).

(4) Michaelis and Granick, THIS JOURNAL, **65**, 1747 (1943).

(5) Jacobs and Heidelberger, *J. Biol. Chem.*, **21**, 116 (1915).

(6) Reilly and Hickinbottom, *J. Chem. Soc.*, **113**, 107 (1918).

(7) Kremer, Meltsner and Greenstein, THIS JOURNAL, **61**, 2552 (1939).

(8) Axe and Freeman, *ibid.*, **56**, 478 (1934).

(9) In all cases here reported the compounds give melting point ranges and seem to undergo thermal decomposition prior to the true melting point temperature.

σ-1-Amino-4-di-*n*-propylaminobenzene Bromide.—Oxidation in this and the following two experiments were conducted as in the example above. Quantities of reagents and degree of temperature were kept constant and only the amount of the amine varied. In this case 9.6 g. of di-*n*-propylaniline was treated; yield 6.2 g. of brilliant green micro crystals. The product in water gives a bright bluish-red solution; m. p. turns brown at 100°, and melts from 190–195° uncor. *Anal.* Calcd. $C_{12}H_{20}N_2Br$: Br, 29.36. Found: Br, 28.80.

σ-1-Amino-4-di-*n*-butylaminobenzene Bromide.—Eleven grams of di-*n*-butylaniline was oxidized to give 9.2 g. of brilliant green crystals. Solution is similar to the dipropyl compound; m. p. 111–119° uncor. *Anal.* Calcd. $C_{14}H_{24}N_2Br$: Br, 26.61. Found: Br, 26.60.

σ-1-Amino-4-morpholinebenzene Bromide.—From 8.9 g. of *p*-aminophenylmorpholine, after oxidation with the bromine solution, 8 g. of deep olive green crystals was obtained which gave a deep purple-red solution in water, m. p. 130° uncor. *Anal.* Calcd. $C_{10}H_{14}ON_2Br$: Br, 30.95. Found: Br, 31.20.

σ-1,4-Bis-(dimorpholine)-benzene Bromide.—To 12.4 g. of 1,4-phenylenedimorpholine dissolved in 160 cc. of dioxane + 80 cc. of acetic acid and cooled to 30°, a mixture of 1.2 cc. of bromine in 80 cc. of dioxane + 24 cc. of acetic acid was added dropwise. A slate gray precipitate formed which when dried weighed 14 g. and gave an intense blue-violet solution in water; m. p. 266°, uncor. *Anal.* Calcd. $C_{14}H_{20}O_2N_2Br$: Br, 24.35. Found: Br, 24.15.

σ-4,4′-Diaminodiphenyl Bromide.—In a mixture of 50 cc. of dioxane + 40 cc. of acetic acid 4.6 g. of benzidine was dissolved and cooled to 5°. Six-tenths cc. of bromine in 40 cc. of dioxane + 12 cc. of acetic acid were added over one-half hour and the dark blue precipitate collected at once. After washing with 200 cc. of ether the solid was dried *in vacuo* and weighed 4.75 g. The dried material was dark green and gave a blue solution in water; m. p. turns gray at 160° and does not melt below 300°. *Anal.* Calcd. $C_{12}H_{12}N_2Br$: Br, 30.25. Found: Br, 30.64.

σ-3,3′-Dimethoxy-4,4′-diaminodiphenyl Bromide.—Six and one-tenth grams of dianisidine was dissolved in 80 cc. of dioxane + 40 cc. of acetic acid, cooled to 0°, and treated with a mixture of 0.6 cc. of bromine dissolved in 40 cc. of dioxane + 12 cc. of acetic acid. After standing one hour the blue-green precipitate was collected, washed with 200 cc. of ether and dried *in vacuo;* yield 6.6 g. In water the compound gives a blue-green solution; m. p. turns gray above 140° and melts at 254°. *Anal.* Calcd. $C_{14}H_{16}O_2N_2Br$: Br, 24.65. Found: Br, 24.33.

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The Properties of Hydroxylamine. I. The Reduction of Hydroxylammonium Salts by Arsenite

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In an effort to extend the work of Gutman[3] on the reaction between salts of hydroxylamine and sodium arsenite, data have been obtained for (1) decomposition of hydroxylammonium salts in the presence of sodium hydroxide and (2) reduction of hydroxylammonium salts by arsenite.

Experimental

From 10 to 15 ml. of water was added to a definite amount of hydroxylammonium salt present in the Kjeldahl flask of an ammonia distillation apparatus. Forty-five ml. of the sodium hydroxide solution, which did or did not contain primary-standard quality arsenic(III) oxide, was then added to the fairly concentrated salt solution. Gradual mixing of the solutions was effected, after which the ammonia formed was distilled over into excess standard acid in the usual manner. Residual solutions were all diluted to one-liter volumes and separate series of aliquots analyzed for arsenite and arsenate. Arsenite, in a medium properly buffered with sodium bicarbonate, was determined by titration with standard iodine solution. For the determination of arsenate, iodate-free potassium iodide was added to aliquots made highly acidic with sulfuric acid. The iodine liberated was titrated with sodium thiosulfate. Unreacted hydroxylamine was never found, after distillation, in either the reaction flask or in the receiver.

TABLE I

DECOMPOSITION OF HYDROXYLAMMONIUM SALTS IN THE PRESENCE OF SODIUM HYDROXIDE

Salt, g. $NH_2OH \cdot HCl$	Salt, millimoles	% NaOH, 45 ml.	Total NH_3 absorbed, millimoles	Ratio, total NH_3/salt, millimoles
1.4848	21.362	15	7.189	0.337
1.5112	21.740	15	7.472	.344
1.4546	20.927	15	7.017	.335
			Av.	.339
1.3150	18.920	30	6.492	.343
1.6604	23.888	30	7.889	.330
1.5192	21.857	30	7.543	.344
			Av.	.339
$NH_2OH \cdot {}^1/_2H_2SO_4$				
3.0498	37.962	15	10.951	.295
2.8304	34.432	15	10.157	.295
2.3462	28.540	15	8.122	.284
			Av.	.291
2.3079	28.066	30	9.797	.349
2.4712	30.064	30	10.112	.336
2.3482	28.566	30	9.802	.343
			Av.	.343

Hydroxylamine decomposes, in alkaline solution, according to the equation

$$3NH_2OH \longrightarrow NH_3 + 3H_2O + N_2 \qquad (1)$$

The data of Table I indicate that the amounts of ammonia resulting from the decomposition of the chloride and sulfate salts of hydroxylamine are essentially the same for 15 and 30% sodium hydroxide. Too, three moles of salt produce one mole of ammonia in accordance with (1). The yield of ammonia from the sulfate salt with 15% sodium hydroxide differs from the other data by about twelve per cent. despite the fact that the concentration of alkali in the final mixture is the same as for the chloride salt. A discrepancy of this sort is not uncommon for reactions of hydroxylammonium salts which are not carried out

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[1] Reported at the meeting of the Washington Section of the American Chemical Society, November 10, 1949.

[2] A part of the work reported herein was done under a contract between the Office of Naval Research and Howard University.

[3] A. Gutman, *Ber.*, **55B**, 3010 (1922).