ride, 0.8 g. of aluminum chloride and 5 ml. of carbon disulfide; the product was hydrolyzed, washed and dried. The 2,4-dinitrophenylhydrazone of the ketone melted at 181°.

Anal. Calcd. for $C_{21}H_{23}N_4O_4$: C, 63.79; H, 5.83; N, 14.17. Found: C, 63.31; H, 6.00; N, 13.83.

The product remaining from the distillation solidified, it consisted of dicycloalkylated benzene, amounting to 22% based on methylcyclohexene reacted. On recrystallization from alcohol it melted at 70–71°. The probable structure of this compound was *p*-di-(1-methylcyclohexyl)-benzene.

Anal. Calcd. for $C_{20}H_{30}$: C, 88.89; H, 11.11. Found: C, 88.36; H, 11.06.

Dehydrogenation.—Eight grams of the compound corresponding to 1-methyl-1-phenylcyclohexane was dehydrogenated by passing it over 20 ml. of chromia-on-alumina,[4] promoted with cerium and potassium, catalyst at 435° and an hourly liquid space velocity of 0.10. The product began to solidify at the outlet when half the material had been passed; recovery, 7.0 g.

The solid material was recrystallized from Skellysolve "A"; melting point and mixed melting point with a known sample of biphenyl, 69–70°.

The gaseous product was composed of 30% methane and 70% hydrogen.

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RECEIVED JUNE 22, 1949

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pK Values of Methyl Red Indicator in Alcohol–Water Mixtures[1]

BY W. D. LARSON AND W. J. TOMSICEK

Data on the ionization constant of *o*-methyl red in mixtures of methanol and water cannot be found in the literature. In order to interpret polarographic data on methyl red it became desirable to have this information. It was obtained by a spectrophotometric method which had been used by Reimers[2] for determining the *pK* for this indicator in ethanol–water mixtures.

A Coleman model 11 spectrophotometer was used for the absorption measurements. No temperature control was used. All measurements were made between 27 and 30°. A sample of *o*-methyl red was prepared according to directions given in "Organic Syntheses,"[3] and purified by a recrystallization from toluene.[4] Its melting point was 182–184° (cor.). For comparison, the measurements of Reimers[2] in ethanol–water mixtures were repeated. Ethanol was commercially available absolute alcohol (U.S.I.); methanol was a synthetic product, dried by the method of Lund and Bjerrum.[5] Standard solutions of the dye were prepared in the dry solvents, with adequate protection from moisture. The working solutions were prepared from these standard solutions by diluting with weighed amounts of water and either pure ethanol or pure methanol to give a solvent of the desired composition. The dye was approximately 2×10^{-5} molar in each case.

The composition of the solvent is given in volume per cent. so as to be comparable to Reimers[2] results, and so that the *pK* values for benzoic acid in ethanol–water mixtures given by Michaelis[6] could be used. Nevertheless, the solvent mixtures were prepared by weight, and the weight per cent. is given in each case. The *p*H of the methanol–water solutions containing benzoate buffers was measured with a Beckman type G glass electrode. Measured *p*H values in ethanol–water mixtures agreed with those of Michaelis[6] to within 0.02 *p*H. An aqueous buffer 0.01 molar in sodium benzoate and in benzoic acid had a measured *p*H of 4.21, in satisfactory agreement with the *pK* for benzoic acid given by Harned and Owen.[7] The dye was converted to the yellow form by addition of sufficient sodium hydroxide or potassium hydroxide to give a *p*H of 11.6, calculated on the assumption that these bases are completely ionized and have unit activity coefficients in all the solvent

TABLE I

pK VALUES OF *o*-METHYL RED IN ETHANOL–WATER MIXTURES

Vol. % ethanol	Wt. % ethanol	*pK* (Reimers)	*pK* (this study)
10	8.02	..	5.38
30	25.13	5.75	5.90
50	43.92	6.26	6.35
70	64.65	6.75	6.80
90	87.59	..	7.46

TABLE II

pK VALUES OF *o*-METHYL RED IN METHANOL–WATER MIXTURES

Vol. % methanol	Wt. % methanol	*pK*
10	8.04	5.37
30	25.17	5.54
50	43.96	5.83
70	64.65	6.12
90	87.63	6.66

TABLE III

*p*H OF 0.01 MOLAR BENZOIC ACID + 0.01 MOLAR SODIUM BENZOATE SOLUTION IN WATER AND IN MIXTURES OF METHANOL OR ETHANOL AND WATER

Vol. % alcohol	*p*H methanol	*p*H ethanol
0	4.21	4.21
10	4.30	4.31[a]
30	4.72	4.83[a]
50	5.38	5.62[a]
70	5.88	6.30[a]
90	6.48	7.03[a]

[a] Data of Michaelis and Mizutani, ref. 6.

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[1] This work was supported by a grant from the Research Corporation, which we gratefully acknowledge. The experimental work reported was done by Mr. George N. Sausen.

[2] Reimers, *Z. anorg. allgem. Chem.*, **228**, 33 (1936).

[3] "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, New York, N. Y., 1932, p. 366.

[4] Livingston and Pariser, THIS JOURNAL, **70**, 1510 (1948).

[5] Lund and Bjerrum, *Ber.*, **64**, 210 (1931).

[6] Michaelis and Mizutani, *Biochem. Z.*, **147**, 7 (1924).

[7] Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1943, p. 210.

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

BY ROBERT F. MILLIGAN

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.