tially solidified. Following evaporation of the ammonia, the mass again became fluid. The mixture was gently refluxed for 3 hours and then a solution of 24.0 g. (0.154 mole) of ethyl iodide in 35 ml. of dry benzene was added dropwise over a period of 2.5 hours. The refluxing with stirring was continued for an additional hour. The hot mixture was then filtered and the residue washed with warm benzene; the total volume of the solution was about 350 ml. The cold solution was chromatographed on a 38 × 180 mm. column of alumina (Alcoa, F-20) giving 16 g. (70%) of crude 10-ethylphenothiazine and some phenothiazine (mixed melting point). Two recrystallizations of the crude product gave 8.1 g. (36%) of yellow needle-like prisms, m.p. 102.5–103°.

(B) **Preparation in Liquid Ammonia.**—Forty-seven grams (0.236 mole) of phenothiazine was added with stirring to a suspension of 0.26 mole of sodamide[6] in 1600 ml. of liquid ammonia giving a dark red mixture. The stirring was continued for 2.5 hours and then 39 g. (0.354 mole) of ethyl bromide was added dropwise over a period of 45 minutes. During the addition of the ethyl bromide, the color of the mixture gradually became lighter and a gray-brown solid separated. The ammonia was allowed to evaporate and the residue was refluxed with 500 ml. of petroleum ether (b.p. 60–70°) and benzene (1:2). The inorganic material was filtered off and washed with 3 small portions of hot benzene. The golden brown filtrate was concentrated to 150 ml. by distillation. On standing, 19.6 g. of light green, cubic crystals, m.p. 103–104°, separated. The mother liquor was chromatographed on a 38 × 180 mm. column of alumina[7] giving 32.2 g. of light green crystals, m.p. 102–103°. The total yield of pure 10-ethylphenothiazine was 51.8 g. (97%).

In a second preparation of 10-ethylphenothiazine, 19.9 g. (0.1 mole) of phenothiazine was added to a 0.11 mole of sodamide[6] in 650 ml. of liquid ammonia. The resulting mixture was treated with 16.5 g. (0.15 mole) of ethyl bromide in the same manner as in the preceding reaction. After evaporation of the ammonia, the residue was extracted with a solution of benzene and petroleum ether (b.p. 60–70°) (4:1). The solution was chromatographed on a 38 × 200 mm. column of alumina[7] to give 21 g. (92%) of the desired product, m.p. 103–104°, and 0.3 g. (1.5%) of phenothiazine (mixed melting point).

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2-β-Aminoethylquinoline

BY REUBEN G. JONES

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Although a number of N-substituted derivatives of 2-β-aminoethylquinoline have been prepared from quinaldine using the Mannich reaction,[1,2] there appears to be some confusion concerning 2-β-aminoethylquinoline itself. Kermak and Muir[1] were unable to obtain the compound by the reaction of β-2-quinolinepropionhydrazide with nitrous acid; however, Hupe and Schramme[3] had previously reported its preparation by hydrogenation of what they believed to be 2-quinolineacetaldehyde oxime. 2-β-Aminoethylquinoline was synthesized in this Laboratory for testing as an analog of histamine.[4] The sample was obtained by the reaction of hypochlorite on β-2-quinolinepropionamide and was isolated as the dihydrochloride. This salt did not melt at 212° as reported by Hupe and Schramme,[3] but decomposed without melting at about 195–200°.

Recently Woodward and Kornfeld[5] have shown that the so-called 2-quinolineacetaldehyde[6] as used by Hupe and Schramme in their synthesis, is, in reality, 3-acetylquinoline. Therefore, it appears that the previously reported 2-β-aminoethylquinoline[3] was in fact 3-α-aminoethylquinoline.

Experimental

2-β-Aminoethylquinoline Dihydrochloride.—A mixture was prepared by absorbing 3.3 g. of chlorine in a solution of 8.7 g. of sodium hydroxide in 25 ml. of water. To this was added 45 g. of chipped ice followed by 8.5 g. of β-2-quinolinepropionamide.[6] After stirring for one hour at room temperature the solution was heated for one-half hour on the steam-bath and then cooled. The mixture was extracted with five 100-ml. portions of ethyl acetate, and the dried extract was treated with ethereal hydrogen chloride. The product was recrystallized by solution in hot methanol followed by the addition of three volumes of ethyl acetate. It did not melt but turned black at 195–200°. The yield was 7.5 g. (71%).

Anal. Calcd. for $C_{11}H_{12}N_2 \cdot 2HCl$: N, 11.42. Found: N, 11.12.

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[1] W. O. Kermak and W. Muir, *J. Chem. Soc.*, 3089 (1931).

[2] Tseou Heou-Feo, *Bull. soc. chim.*, **2**, 96 (1935).

[3] R. Hupe and A. Schramme, *Z. physiol. Chem.*, **177**, 315 (1928).

[4] H. M. Lee and R. G. Jones, *J. Pharmacol.*, **95**, 71 (1949).

[5] R. B. Woodward and E. C. Kornfeld, THIS JOURNAL, **70**, 2508 (1948).

[6] A. Einhorn and P. Sherman, *Ann.*, **287**, 26 (1895).

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The Hammett Sigma Value for *m*-Phenyl

BY NORMAN N. LICHTIN AND HARRY P. LEFTIN

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It has recently been pointed out[1] that the σ-value assigned to the *m*-phenyl group by Hammett[2] is based on unreliable data. A study of the effect of one *m*-phenyl substituent on the ionization equilibrium in liquid sulfur dioxide of triphenylchloromethane[1] has produced data which can be interpreted as resulting from a small fundamental electron attracting influence. Alternative explanations, however, are possible, namely, that the *m*-phenyl group complexed with sulfur dioxide[3] may be responsible rather than the group itself, or that the presence of a positive charge localized in one ring of a biphenyl group decreases the resonance interaction of the two rings. It therefore became of interest to carry out measurements which would provide a more reliable σ-value for the *m*-phenyl group and provide information on its electronic influence subject to less ambiguous interpretation. Berliner and Blommers[4] have recently provided a direct route to these objectives by establishing a ρ-value of +1.32 ± 0.06 for the dissociation of substituted benzoic acids in 50% aqueous butyl cellosolve at 25° and an ionic strength of 0.05. The (non-thermodynamic) pK_A values for benzoic acid and *m*-phenylbenzoic acid have been determined under the conditions employed by these workers and have been employed together with their ρ-value

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[1] N. N. Lichtin and H. Glazer, THIS JOURNAL, **73**, 5537 (1951).

[2] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 188.

[3] L. J. Andrews and R. M. Keefer, THIS JOURNAL, **73**, 4169 (1951).

[4] E. Berliner and E. A. Blommers, *ibid.*, **73**, 2479 (1951).

to calculate a σ-value for the *m*-phenyl group by means of Hammett's equation.[5] The data are summarized in Table I.

TABLE I

APPARENT IONIZATION CONSTANTS IN 50% AQUEOUS BUTYL CELLOSOLVE AT 25° AND IONIC STRENGTH 0.05

Acid	pK_A	No. of determinations
Benzoic[a]	5.66 ± 0.024	5
m-Phenylbenzoic	5.58 ± 0.018	4

[a] Berliner and Blommers[3] give pK_A = 5.65 ± 0.01 for this compound.

The resulting σ-value is +0.06 ± 0.03. Interpretation of this result is simpler than for the triphenylchloromethanes. No steric factors can be involved. The absence of any complexing or specific interaction of the solvent with the *m*-phenyl group can be deduced from the fact[6] that the ultraviolet spectrum of benzene in solution in water, ethanol or diethyl ether, resembles its spectrum in the gas phase even more closely than does its spectrum in cyclohexane solution, the differences in all these cases being very small. It is not possible, however, to distinguish between the remaining two possibilities. The results can readily be explained in terms of phenyl having a small fundamental electron attracting influence relative to hydrogen. The possibility that resonance interaction between the two phenyl groups is reduced by the presence of a positive charge in one of them is also in accord with the facts. Symbolic structures in which such a charge is distributed to the ortho and para positions of the disubstituted ring are more important in the un-ionized acid than in the anion and might lead to a greater decrease in interaction of the benzene rings and a consequent small destabilization of the acid.

Experimental

Materials.—The benzoic acid was National Bureau of Standards Acidimetric and Calorimetric Standard No. 39-f. The *m*-phenylbenzoic acid was prepared by carboxylation of the corresponding Grignard reagent. Eastman Kodak Co. Practical *o*-aminobiphenyl was converted to *m*-bromobiphenyl by the method of Huber, *et al.*,[7] modified by deaminating with hypophosphorous acid[8] instead of ethanol and copper bronze. A 42.5% over-all yield of bromide with $n^{24}D$ 1.6394 and a b.p. of 104° at 0.2 mm. was obtained.

This compound was converted to the Grignard reagent by reacting with Dow Corporation "Super Pure" magnesium.[9] The reaction proceeded very slowly in dry ether (at 1 molar concn.) and was accompanied by formation of a white precipitate. On addition of about 7% by volume of dry benzene the precipitate dissolved and the reaction proceeded smoothly. Hydrolysis and acid titration of an aliquot indicated a 94% yield after one hour. The product obtained after treating the Grignard solution with gaseous CO_2 dried by passage through concentrated sulfuric acid was recrystallized four times from hot approximately 50% aqueous ethanol to give a 44% yield of purified material, m.p. 165.4–166.0°.[10]

Howe and French Co. technical grade butyl cellosolve was purified by the method of Halford[11] to yield material boiling at 106–107° at 70 mm. pressure.

Measurements.—The pK_A values were determined with essentially the same procedures and conditions as those of Berliner and Blommers.[3] The temperature was 25.10 ± 0.25°. Each sample was maintained under a nitrogen atmosphere throughout its titration. A Leeds and Northrup No. 7662 *p*H meter and glass electrode sensitive to ±0.01 *p*H unit were employed. Asymmetry of the glass electrode was corrected using Coleman Certified buffer tablets of *p*H 4.00, 5.00, 6.80 and 7.00. Individual pK_A values were 5.70, 5.68, 5.65, 5.64, 5.63 for benzoic acid and 5.57, 5.57, 5.61, 5.56 for *m*-phenylbenzoic acid.

Acknowledgment.—One of us (H. P. L.) wishes to express his gratitude to the Research Corporation for a fellowship provided by a Frederick Gardner Cottrell grant.

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[5] Reference 2, p. 186.

[6] K. Lauer and R. Oda, *Ber.*, **69**, 851 (1936).

[7] W. F. Huber, M. Renoll, A. G. Rossow and D. T. Mowry, THIS JOURNAL, **68**, 1109 (1946).

[8] N. Kornblum in "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 296–297.

[9] Spectroscopically pure magnesium, finely turned immediately before use.

[10] Capillary melting point with Anschütz type total immersion thermometer.

[11] J. O. Halford, THIS JOURNAL, **53**, 2944 (1931).

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Phenol Alcohols in the Ammonia-Catalyzed Phenol–Formaldehyde Reaction

BY R. W. MARTIN

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It has been shown that di- and tri-(hydroxybenzyl)-amines are formed on heating phenols with hexamethylenetetraamine.[1–4] It is possible that similar amines are formed in phenol–aldehyde resins where ammonia has been used as catalyst. As the quantity of ammonia normally employed in preparing these resins is not sufficient to give amine derivatives with all the phenol and formaldehyde present other reactive intermediates must also be formed. The most logical products, in addition to the hydroxybenzylamines, are the mono- and polynuclear phenol alcohols. However, because of the rapid loss of water solubility in ammonia-catalyzed phenol–formaldehyde resins, the formation of phenol alcohols has been much debated.[4,5]

It has now been shown that at least at room temperature both phenol monoalcohols and phenol dialcohols may be separated from ammonia-catalyzed phenol–formaldehyde reaction products. The phenol alcohols, *p*-hydroxybenzyl alcohol and 2,4-di-(hydroxymethyl)-phenol, were separated from the phenol–formaldehyde reaction mixture according to a procedure previously described by Martin.[6]

Experimental

Phenol, 282 g. (3 moles), 362 g. of 37.2% formalin (4.5 moles) and 14.1 g. of 28% ammonia were mixed and held at 25–30° for 6 days. The reaction mixture was then dehydrated, treated with trimethylchlorosilane and the trimethylsilyl derivatives (662 g.) separated into twelve fractions by fractional distillation according to the procedure previously described.[6] Hydrolysis of Fraction III (b.p. 117–121° (1–2 mm.); weight, 104 g.) gave *p*-hydroxybenzyl alcohol and of Fraction VII (b.p. 106–121° (0.2–0.3 mm.); weight, 47.4 g.) gave 2,4-di-(hydroxymethyl)-phenol.

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[1] A. Zinke, F. Hanus and H. Pichelmayer, *Monatsh.*, **78**, 311 (1948).

[2] G. Zigeuner and O. Gabriel, *ibid.*, **81**, 952 (1950).

[3] K. Hultzsch, *Chem. Ber.*, **82**, 16 (1949).

[4] K. Hultzsch, "Chemie Der Phenolharze," Springer-Verlag, 1950, p. 122–123.

[5] K. B. Goldblum, *Ind. Eng. Chem.*, in press.

[6] R. W. Martin, THIS JOURNAL, **74**, 3024 (1952).