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

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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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The Hammett Sigma Value for *m*-Phenyl

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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 $+1.32 \pm 0.06$ 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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