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Synthesis of 4-Amino-N-Ethyl-N-β-Hydroxyethylanilin Hemi-Sulfate Hydrate

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4-Amino-N-ethyl-N-β-hydroxyethylaniline hemi-sulfate hydrate was synthesized by nitrosation of N-ethyl-N-β-hydroxyethylaniline, then reduced with zinc powder/hydrochloric acid, without isolating of the nitroso compound. The amine salt so formed was basified with ammonia, then extracted with chloroform and the free base converted its hemi-sulfate hydrate directly, by adding a sufficient amount of sulfuric acid in ethanol.

INTRODUCTION

4-Amino-N-ethyl-N-β-hydroxyethylaniline and its salts are used in colour photography as colour developing agents. This is a patented compound [1], [2], [3]. There are no details of its synthesis in the literature. Julian and Ruby [4] have determined its reduction potantials at different pH, but they did not mention any literature reference for the synthesis. Bent et al. [5] have made the compound by means of reduction of corresponding nitroso compound, 4-nitroso-N-ethyl - N -β-hydroxyethylaniline whose hydrochloride salt is highly soluble in water. For this reason, the compound has been made in low yield [5].

In this paper, synthesis of 4-amino-N-ethyl-N-β-hydroxyethyaniline hemisulfate hydrate, starting from N-ethyl-N-β-hydroxyethylaniline, without isolation of the intermediate nitroso compound and free base, is described.

N-ethyl-N-β-hydroxyethlaniline was first nitrosated then the nitroso compound so formed was reduced directly with zinc

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powder/hydrochloric acid to 4-amino-N-ethyl-N-β-hydroxyethylaniline hydrochloride. In order to liberate the base, ammonia was added to the solution and sodium hydrogensulfite solution also added to prevent air oxidation of free base, the base was then extracted with chloroform. The solvent was removed by distillation, and the residue was dissolved in ethanol (% 96) and an equivalent amount of sulfuric acid in ethanol was added to convert the free base into its hemi-sulfate hydrate. In the reaction sequence, two steps, that is isolating of nitroso compound and vacuum distillation of the free base, were eliminated. The overall yield was as high as the direct convertion of the free bas into its hemi-sulfate hydrate which is a one step reaction [5].

EXPERIMENTAL SECTION

In a three neck, one liter flask, equipped with a mechanical stirrer, dropping funnel and a thermometer, chilled in an ice bath, was introduced a mixture of 160 ml of water and 50 ml of conc. hydrochloric acid. Into this mixture, 33 g (0.2 moles) of N-ethyl-N-β-hydroxyethylaniline was added, which dissolved slowly; the mixture was cooled to 0°C. 14 g (0.2 moles) of sodium nitrite was dissolved in 50 ml of water, cooled and introduced into the dropping funnal. The mechanical stirrer was started and the nitrite solution was added such a rate that temperature did not exceed 5°C (this takes about one hour). The reaction mixture was stirred for one hour more, then 100 ml of conc. Hydrochloric acid was added and 40 g (0.6 gramatom) of zinc powder was added in small portions in such a way that temperature did not exceed 20°C (each portion was abut 5 grams). After the addition of the last portion, mixture was stirred for 15 minutes more and orange colour of the solution was disappeared. The reaction mixture was decanted into a 2 liter flask, 100 ml of chloroform was added and a sufficient amount of ammonia (20 %) added to make the solution basic against litmus (abut 150 ml of ammonia). Then 50 ml of sodium hydrogensulfite solution (40 %) was added and the mixture was transferred to a 2 liter separatory funnel, shaken well and the chloroform phase separated, the aqueous layer was extracted three times with chloroform (each 50 ml), the chloro-

form extracts were combined, dried over anhydrous potassium carbonate. Most of the solvent was removed by distillation and a light brown residue remained. This was dissolved in 75 ml of ethanol (96 %), and cooled in an ice bath. Into this cold mixture, a chilled solution of 50 ml of ethanol and 6 ml of conc. sufuric acid was added slowly while stirring. The resulting solution was allowed to crystallize in the refrigerator overrnight. Solid material was filtered by means of a fritted glass funnel by suction, washed twice with cold ethanol (each 50 ml) and dired in a vacuum dessicator, containing $CaCl_2$ 35 g (0.14 mmoles, 72 %) of light yellow crystalline 4-amino-N-ethyl-N-β-hydroxyethylaniline hemisulfate hydrate was obtained. A small amount of material was crystallized from ethanol and gave rise to a colourless crystalline compound which melted at 179–180° [5]. No depression was observed in melting point with an admixture of an authentic sample.

REFERENCES

[1] British patent 460.580 (1937).

[2] Canadian patent 369.777 (1737).

[3] U. S. Patent 1.108.243 (1938) (I.G.).

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[5] Bent et al., J. Amer. chem. Soc., **73**, 3100 (1951).

ÖZET

Bu çalışmada, renkli fotoğrafçılıkta bir renk developörü olarak kullanılan 4-amino-N-etil-N-β-hidroksietil anilin hemi-sülfat hidratın, N-etil-N-β- hidroksietil anilinden çıkarak ve reaksiyon ara basamakları olan 4-nitrozo-N-etil-N-β-hidroksietil anilin ve hemi-sülfat hitrata tekabül eden serbest baz izole edilmeden iyi bir verimle elde edilişi gösterilmiştir.

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