This material is almost pure acetamide. If it is desired to obtain a sample free from all impurities, it may be recrystallized from a large volume of ether. If the sample is colored yellow, due to the charring of the corks, it can be obtained colorless and practically pure by distilling from a small retort. However, such distillation gives rise to a small amount of acetonitrile, which lowers the melting point of the crystals.

The yield is about 40 grams, or 85–90% of the theoretical amount calculated from the nitrogen content of the ammonium carbonate. The actual time required for the experiment is four hours.

This method has been used in the laboratories of organic chemistry at Cornell University for one year and has proven very satisfactory.

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A MODIFIED METHOD FOR THE PREPARATION OF TRIETHYLAMINE.

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Considerable difficulty has been experienced in the investigation of triethylammonium nitrite,[1] in the preparation of triethylamine. In order to obtain the base in a pure condition, it was thought feasible to prepare tetraethylammonium bromide by the method described by Scott;[2] next, to convert it into the quaternary hydroxide by the interaction with moist silver oxide, which on heating would decompose into triethylamine and ethylene. But, as has been already noticed,[3] the method was not found suitable for the purpose; the lack of success has been, reasonably enough, assigned to the higher atmospheric temperature of this tropical country. Next Hofmann's[4] method was tried; and in spite of the want of the indespensable details of this classical memoir, the base has been prepared by it. But the yield being comparatively poor, it was thought worth while investigating the exact condition under which the triethylamine can be conveniently prepared.

Of the two alkyl halides, ethyl iodide and bromide, the latter has been found easier to prepare, the former invariably yielding a mixture of all four bases under different circumstances. Seventy-five cc. of ethyl bromide and 50 cc. of strong ammonia (sp. gr. 0.88) were taken in a 750 cc. thick glass flask, sufficient absolute alcohol was then added to effect solution, and the flask immediately closed with a rubber cork and tied with wire. Next the flask was placed in a steam oven for three hours. After cooling, it was opened and the alcohol (which may be again used for the

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[1] Ray and Rakshit, *J. Chem. Soc.*, **101**, 216 (1912).

[2] *J. Chem. Soc.*, **95**, 1200 (1909).

[3] *Loc. cit.*

[4] *Phil. Trans.*, **1850**, Pt. L, 121.

same purpose after rectification) was distilled off. The residue was dissolved in a minimum quantity of water and distilled with an excess of caustic soda solution. The alkaline distillate was collected under dilute hydrochloric acid (1 in 3). This hydrochloric acid solution was evaporated on the water bath till there was no odor of the acid and the product, when removed from the water bath, solidified to a crystallin mass after a few minutes. If this solid mass be again placed on the water bath, it melts partially and remains as a mixture of fine, white crystals of ammonium chloride and a transparent liquid, which was expected to be a mixture of hydrochlorides of ethylamines. The ammonium chloride might have been quite efficiently eliminated by extraction with a mixture of ether and alcohol;[1] but, in dealing with larger quantities, the following method was found more convenient and less expensive.

A hot water funnel was filled with brine and heated to boiling. The funnel was fitted with a filtering flask, which was connected with a filter pump, and the molten mixture was rapidly filtered by suction. The residue was proved to be ammonium chloride. The filtrate, on cooling, solidified to a lustrous crystallin mass. A portion of it was converted into the chloroplatinate.

0.4580 gram gave 0.1786 gram Pt. Found: Pt = 38.99; theory for $(C_2H_5NH_3Cl)_2PtCl_4$: 38.93%.

It is thus seen that in this way practically pure primary ethylamine was obtained.

About 60 grams of sticks of caustic soda were taken in a 500 cc. distilling flask, fitted with a tap funnel and a condenser circulated by ice cold water. Sixty-two grams of ethylamine hydrochloride were dissolved in minimum quantity of water and put into the tap funnel for introducing into the flask drop by drop. The alkaline distillate was collected in a stout 500 cc. glass flask and cooled by freezing mixture. Finally it was heated to boiling for about five minutes. To the collected free base, 44 cc. of ethylbromide were added and the flask closed with a rubber cork and tied with wire. The mixture was then kept in a steam oven for three hours, after which time the contents of the flask formed two distinct layers. It was left in the over over night, slowly cooling with it. The next day the lower layer solidified to a crystallin mass, and the upper one remained as a slightly brownish, transparent liquid. When the flask was opened the odor of amine was noticeable and the amine product had a strongly alkaline reaction. The liquid was decanted off into a conical flask and cooled with ice and salt, then neutralized with dilute hydrochloric acid and evaporated on a water bath. The resulting product has been proved to be pure triethylamine hydrochloride. The yields in the first, second, and third experiments were 20, 18 and 18.6 grams, respectively.

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[1] THIS JOURNAL, 35, 444.

Substance I, 0.3534; II, 0.4628; III, 0.3842, gave I, 0.1122; II, 0.1473; III, 0.1221 gram Pt. Pt found = 31.76, 31.84 and 31.80%; calculated for $2\{(C_2H_5)_3NHCl\}PtCl_4$, 31.86%.

Sometimes the crude product obtained was brownish, but analyses proved that in such samples the quantity of foreign matter was not appreciable. The best way to purify this is by redistillation.

The solid lower stratum of the flask was taken out and distilled with caustic soda, and the alkaline liquid collected was carefully dried over caustic soda, when it distilled at 44–47°. But the boiling points of primary and secondary ethylamines are 16° and 56°, respectively. This fact is in conformity with the observations of Lea,[1] who found that these amines cannot be separated by fractional distillation, although there is a reasonable difference in boiling points for such possibility. The chloroplatinate of the mixed bases gave 37.82% of Pt. The primary and secondary bases contain 39.93% and 35.07%, respectively.

Discussion.

From the heats of neutralization of primary, secondary, and tertiary amines it is expected that the secondary one is more basic than the tertiary, and the primary more basic than either. On this hypothesis the intermediate steps of the reaction can be represented as:

$$EtNH_2 + EtBr = Et_2NH.HBr.$$

$$Et_2NH.HBr + EtNH_2 = Et_2NH + EtNH_2.HBr.$$

$$Et_2NH + EtBr = Et_3N.HBr.$$

$$Et_3N.HBr + EtNH_2 = Et_3N + EtNH_2.HBr.$$

$$Et_3NHBr + Et_2NH = Et_3N + Et_2NH.HBr.$$

The final products are hydrobromides of primary and secondary ethylamines, and free triethylamine. This is what was practically obtained. Calculated quantities of ethylamine and ethylbromide were taken so that the reaction may proceed according to the above equations, which when summed up are represented by

$$7EtNH_2 + 5EtBr = 2Et_3N + 4EtNH_2.HBr + Et_2NH.HBr.$$

Actually the reaction does not proceed directly according to this reaction, otherwise the yield would have been 29.8 grams, instead of 18–20. However, notwithstanding this shortcoming, the process is extremely convenient for the preparation of triethylamine.

I have great pleasure in expressing my thanks to Mr. R. L. Jenks for the interest he has taken in my work.

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[1] *Allen's Commercial Organic Analysis*, 1, 4th ed., 19 (1909).