# LXXXII.—*The Preparation of Ethylamine and of Diethylamine.*

By EMIL ALPHONSE WERNER.

IN the preparation of ethylamine and of diethylamine by the interaction of ethyl bromide and ammonia, it has been the usual practice, so far as hitherto recorded, to submit the whole of the alkyl haloid to the action of ammonia in a single operation.

This is a faulty procedure, since it conduces largely to the formation of the less useful triethylamine, with consequent loss in the yields of the primary and secondary bases. Whether the change is promoted by heat or is allowed to proceed at the ordinary temperature, the tertiary amine has been present in largest amount in the final product (compare Garner and Tyrer, T., 1916, **109**, 174).

The author has found that when ethylamine is added to an alcoholic solution of diethylammonium chloride, the displacement of the secondary amine by the primary is quantitative; thus diethylamine only was obtained on distillation of the mixture after it had remained for an hour, whilst under similar conditions the displacement of triethylamine from its hydrochloride by diethylamine was likewise quantitative (Expts. I, II).

A fair separation of all three amines, in the same order, has been effected by fractional treatment of a solution of their salts with sodium hydroxide; the tertiary amine was first liberated, the secondary next, and the primary amine last (Expt. III).

It must be admitted that these results go to show, contrary to the commonly accepted view, that triethylamine is the weakest base of the three amines.

Reasoning on this basis, and bearing in mind the relative tendency to dissociation* of the respective 'amine' salts, a procedure has been adopted whereby the formation of triethylamine has been almost completely suppressed. Thus, from the product of two experiments, in which 2090 grams of ethyl bromide were used, only 27 grams of triethylamine were obtained, whilst the yield of ethylamine was 33·8 per cent. and of diethylamine 57·5 per cent. of the theoretical.

The influence of the proportion of ammonia to ethyl bromide on the yield of ethylamine is shown by the following results:

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|---|---|---|---|---|---|
| Molecular ratio $EtBr : NH_3$ ............... | 1 : 1 | 1 : 4 | 1 : 6 | 1 : 8 | 1 : 16 |
| Percentage yield of $NH_2Et$ on theoretical ...... ... | 11·3 | 24·4 | 26·7 | 28·1 | 34·2 |

The necessity of maintaining a good excess of ammonia throughout the progress of the reaction is indicated by theory.

## EXPERIMENTAL.

### *Preparation of Ethylamine and of Diethylamine.*

Five litres of 90 per cent. alcohol were saturated with ammonia (compare this vol., p. 698) until 490 grams of the gas had been dissolved, 200 grams of ethyl bromide were added (ratio EtBr to $NH_3$ approximately 1 to 16), after which, at successive intervals of two days, fresh quantities of the alkyl haloid were added in the following amounts: 180, 170, 150, 130, 110, 100, 80, and, finally, 66 grams. Preliminary experiments had shown that with the above ratio of ammonia the whole of the ethyl bromide was decomposed after two days, hence the successive quantities were regulated

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* The term as used here does not refer to ionisation or electrolytic dissociation.

so as to maintain the desired excess of ammonia throughout the progress of the change. In all, 1186 grams of ethyl bromide were used; ammonium bromide began to separate on the twelfth day, and on the sixteenth day the preparation was stopped. Test experiments on a small scale with pure alcohol had shown that when ammonium bromide separated in quantity in the early stage of the process, the formation of triethylamine was promoted when the reaction was prolonged. The reason is fairly obvious when the probable mechanism of the process is considered, hence it was found advantageous to use alcohol containing 10 per cent. of water.

The alcoholic solution, separated from ammonium bromide, was concentrated by distillation (the ammonia evolved was used to charge more alcohol) until nearly all the ammonium bromide formed had separated, 362 grams of which were recovered.

The solution of the hydrobromides of the mixed amines was distilled until the temperature reached 130°, in order to remove the last traces of alcohol. Where it was not found convenient to liberate the entire quantity of the mixed amines by the addition of aqueous sodium hydroxide to the residue, chloroform was used as a solvent for their separation.

Ethylammonium bromide is dissolved by chloroform to the extent of only 0·163 gram in 100 c.c. at 14°, whilst the same volume of chloroform dissolves 42 grams of diethylammonium bromide. By this means, 465 grams of pure ethylammonium bromide and 510 grams of diethylammonium bromide, containing slightly more than 5 per cent. of triethylammonium bromide, were obtained. After the separation of triethylamine (14 grams) by treatment with the requisite proportion of sodium hydroxide, 226 grams of diethylamine, collected at 56—57·5° and dried over potassium hydroxide, were obtained.

### (a) *Displacement of Diethylamine by Ethylamine, and of* (b) *Triethylamine by Diethylamine.*

*Expt. I.*—(*a*) Nine grams of pure ethylamine were added to 12 grams of diethylammonium chloride dissolved in 30 c.c. of alcohol. After an hour, all free amine was removed by distillation. The hydrochloride prepared from the distillate gave $Cl = 32·33$, whilst $NHEt_2,HCl$ requires $Cl = 32·42$ per cent. The displacement of the secondary amine from its salt was therefore complete.

*Expt. II.*—(*b*) Eight grams of pure diethylamine were added to 15 grams of triethylammonium chloride dissolved in 35 c.c. of alcohol. The mixture was distilled as in the previous experiment. The hydrochloride prepared from the distillate gave Cl = 25·78, whilst $NEt_3,HCl$ requires Cl = 25·81 per cent. The displacement of the tertiary amine by the secondary was therefore complete.

### *Separation of the Three Amines by Sodium Hydroxide.*

*Expt. III.*—To a solution which contained 13·8 grams of triethylammonium chloride, 11 grams of diethylammonium chloride, and 9 grams of ethylammonium chloride dissolved in 60 c.c. of water, 4 grams of sodium hydroxide were added. The solution was well shaken, and after twenty hours the liberated amine was distilled off.

The hydrochloride prepared from it gave Cl = 26·04, whilst $NEt_3,HCl$ requires Cl = 25·81 per cent. The amine was therefore almost pure triethylamine.

To the remaining solution, when cold, 4 grams of sodium hydroxide were added, and a similar treatment was applied.

The hydrochloride prepared from the liberated amine gave Cl = 34·44, which corresponds with a mixture, in round numbers, of diethylamine = 85 and ethylamine = 15 per cent. The residual solution was directly distilled after a final addition of sodium hydroxide. The hydrochloride prepared from the distillate gave Cl = 41·12; the liberated amine had, therefore, the approximate composition, ethylamine = 75 and diethylamine = 25 per cent. These results indicate that this method of procedure for the separation of the amines may prove useful on a larger scale, and the subject is under investigation in connexion with certain of the higher aliphatic amines.

UNIVERSITY CHEMICAL LABORATORY,
TRINITY COLLEGE,
DUBLIN.

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