XLVIII.—*The Preparation of Diacetoneamine.*

By ARTHUR ERNEST EVEREST.

THE methods for the preparation of diacetoneamine which are described in the literature are laborious and by no means satisfactory, and this applies whether the preparation is through mesityl oxide or by the direct action of ammonia on acetone.

Having need of considerable quantities of the compound, as the starting point for synthetic work, the author tried to find a method which would be both simple in action and satisfactory in respect of yield. The process described below, which was the result of the work, is successful in both respects, and furthermore eliminates almost completely the laborious recovery of mixtures of alcohol and acetone which are formed in the usual process of preparation from acetone and ammonia (see the table below). It enables considerable quantities of diacetoneamine to be prepared with ease and comparative rapidity, and thereby makes this product much more available as a starting point for synthetic work.

One of the chief difficulties in the production of diacetoneamine from acetone and ammonia is the comparatively small amount of ammonia which acetone will dissolve, a fact that necessitates several slow re-saturations being resorted to at intervals of five to seven days. Even when this course is adopted, a large proportion of the acetone remains unchanged. The author has made use of anhydrous calcium chloride to obviate this difficulty. By this means, the whole of the ammonia required can be passed into the reaction mixture in quite a short time, and, moreover, not only does the calcium chloride store up the requisite ammonia, but the water formed as the reaction proceeds is taken up by it, whereby a concentrated solution is formed which separates as a distinct layer and can be removed when the reaction is completed.

EXPERIMENTAL.

Acetone (1160 grams) and anhydrous calcium chloride (200 grams) were introduced into a vessel fitted with a reflux condenser (to prevent loss of acetone during the introduction of ammonia) and an inlet for ammonia. The vessel was then placed in cold water and ammonia (from a cylinder) blown into the mixture as rapidly as the liquid would absorb it (100 grams of ammonia were introduced in quite a short time without any appreciable loss).

Much heat was developed during the addition of the ammonia, but with an effective condenser no loss resulted from this. The introduction of ammonia was continued until the amount absorbed was equal to the weight of the calcium chloride used (200 grams). If it was found that the liquid became nearly saturated before the requisite amount of ammonia had been added (this was rarely the case), the addition of ammonia was stopped, the vessel allowed to remain some eight to ten hours (say overnight), and a further amount of ammonia then added. Before the whole of the ammonia had been introduced, water had usually commenced to separate, a fact that had no detrimental effect on the result.

When 200 grams of ammonia had been blown in, the vessel was allowed to remain at the ordinary temperature for eight to nine days. It was found to be advantageous to shake well once a day during this period. As the reaction proceeded, the compound of calcium chloride and ammonia decomposed, and the products dissolved in the water formed by the reaction, the calcium chloride solution thus produced forming the lower layer in the vessel. Towards the end of the reaction, the upper layer became quite viscous and developed a pale yellow colour, whilst the odour of the amine became noticeable alongside that of ammonia.

When the reaction was completed, the layers were separated, care being taken that all the calcium chloride was removed, as when this was not done, considerable trouble was caused in the filtrations later by the calcium oxalate formed in working up the product. The aqueous layer when extracted with ether yielded a small additional quantity of amine, but in general it was not considered profitable to carry out this operation, and the yields stated below do not include such extractions.

After separation, the amine layer (top) was placed in a vessel and dry air drawn rapidly through it for several hours, whereby a large proportion of the excess of ammonia was removed. The liquid thus obtained possessed a strong odour of the amine. The amount of oxalic acid required for the formation of the hydrogen oxalate was determined (by titration with standard oxalic acid), this was dissolved in alcohol, three times the volume of the reaction mixture being used, and the amine then poured slowly into the alcoholic solution, the whole being kept well agitated. Rectified spirit (B.P.) gave with this process as good results as absolute alcohol had given with other processes, this being due to the fact that the water produced in the reaction was removed, whilst in the older methods it remained in the reaction mixture.

When all the amine had been added, the product, without filtration, was placed in a distilling flask and distilled up to 75°, during

590 EVEREST: THE PREPARATION OF DIACETONAMINE.

which process a small amount of a mixture of acetone and alcohol passed over (from 1160 grams of acetone, only about 45 grams remained unacted on and passed over in this mixture). At 75°, the distillation was discontinued, and the contents of the distilling flask were rapidly filtered hot. The filtrate, on cooling, deposited diacetoneamine hydrogen oxalate in crystalline condition, which was collected, washed with alcohol, and dried. The solid residue from the hot filtration yielded a small additional quantity of the product when extracted with fresh hot alcohol. From the total mother liquors, a considerable further quantity of pure product was obtained by distilling them on a water-bath until nothing further passed over, allowing the residue to remain for about twenty-four hours in the cold, collecting the crystals which separated, and washing them with alcohol. A certain amount of syrup remained as a by-product, and in this a small amount of triacetoneamine was detected.

By the above method, 800 grams of diacetoneamine hydrogen oxalate (m. p. 125—127°), containing about 1 per cent. of ammonium hydrogen oxalate (see note at end of paper), could be regularly obtained. Of this yield, about 600 grams were obtained from the first deposition and about 200 grams from the liquors and by extraction of the solid residues.

The following table gives comparative results as obtained with the method described above (*a*), and by the direct action of ammonia on acetone without the use of calcium chloride (*b*).

	(<i>a</i> .)	(<i>b</i> .)
Acetone taken	1045 grams	2100 grams
„ recovered	45 „	1100 „
„ used	1000 „	1000 „
Acetone-alcohol mixture fractionated to recover acetone and alcohol ...	100 c.c.	2250 c.c.
Alcohol used	3 litres (rectified spirit, B.P.)	2½ litres (absolute).
„ recovered	All; somewhat diluted.	All; considerably diluted.
Oxalic acid used	1050 grams.	1060 grams.
Time of keeping	8½—10 days.	24—28 days.
Number of saturations with ammonia	One.	4, at intervals of 5—7 days.
Ammonia used (anhydrous)	190 grams.	210 grams.
Yield	724 „	434 „
By-product: ammonium hydrogen oxalate	340 „	440 „

The work described above was carried out in the chemical laboratories of University College, Reading, in February, 1916, and the author desires to thank the Sectional Chemical Committee

of the Royal Society, at whose request the preparation of the diacetoneamine was undertaken, for permission to publish the results.

APPENDIX.

Note on Diacetoneamine Hydrogen Oxalate and Vinylacetoneamine Oxalate.

By ARTHUR ERNEST EVEREST and HAROLD ROGERSON.

In connexion with the work on the new process for the preparation of diacetoneamine described above, it was desirable that a ready means of checking the purity of samples of diacetoneamine hydrogen oxalate and of vinylacetoneamine oxalate should be available. It was further necessary to prove the identity of the products obtained.

In view of the fact that no melting points have been recorded in the literature for these substances, previous workers have at times resorted to the expedient of converting either of the above compounds into a salt of vinylacetonealkamine, liberating the free base, and determining the melting point of this. The fact that this method is obviously unsatisfactory, and that time did not permit of ultimate analysis, led one of us (A. E. E.) to test pure specimens of the above compounds for melting point. It was found that both could be identified by this means. At the same time, the other (H. R.), who was also preparing quantities of these compounds, had quite independently observed that they had sharp melting points. The determinations were therefore mutually confirmed by exchange of specimens.

EXPERIMENTAL.

(a) *Diacetoneamine Hydrogen Oxalate.*

A pure specimen of diacetoneamine hydrogen oxalate melts fairly sharply at 126—127° to a clear, colourless liquid which, on cooling, sets to a mass of crystals, which again melt at 126—127°. The presence of ammonium hydrogen oxalate in the product causes opalescence in the liquid that results on melting, but has little effect on the melting point. Thus:

Pure diacetoneamine hydrogen oxalate melts to a clear liquid at 126—127°.

Pure diacetoneamine hydrogen oxalate + 1 per cent. of ammonium hydrogen oxalate melts at 125·5—127°.

Pure diacetoneamine hydrogen oxalate + 5 per cent. of ammonium hydrogen oxalate softens then melts at $124\cdot5$ — 126° .

Pure diacetoneamine hydrogen oxalate + 10 per cent. of ammonium hydrogen oxalate softens more noticeably then melts at 124 — $125\cdot5^{\circ}$.

If much ammonium hydrogen oxalate is present in the sample, no melting point is observed, only a softening taking place. This may account for the fact that no melting point has been recorded previously.

A rough approximation of the amount of ammonium hydrogen oxalate in a sample of diacetoneamine hydrogen oxalate may be obtained by observation of the degree of opalescence shown when it melts, but for more accurate determinations an extraction of the diacetoneamine salt from the sample by boiling absolute alcohol and weighing of the residue is recommended.

(b) *Vinyldiacetoneamine Oxalate.*

When this compound is prepared from diacetoneamine hydrogen oxalate which contains ammonium hydrogen oxalate, the latter passes through into the product. The presence of ammonium hydrogen oxalate has the same effect on the melting point of vinyl-diacetoneamine oxalate as it has on that of the diacetoneamine salt. If sufficient of the ammonium salt is present, no melting point can be observed, mere shrinkage and change of colour taking place.

Pure vinyldiacetoneamine oxalate, prepared from pure diacetoneamine hydrogen oxalate and freed from the latter and from oxalic acid by twice boiling with a fairly large quantity of absolute alcohol, filtering hot, and finally washing with boiling absolute alcohol and drying in a vacuum over concentrated sulphuric acid, melts sharply at 184 — 185° with the evolution of gas and development of a yellow colour. The presence of diacetoneamine hydrogen oxalate in the vinyl compound affects the melting point of the latter considerably and makes it less sharp.

These observations were made at University College, Reading, and at Guy's Hospital Medical School, in February, 1916.

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