LXVI.—*The Supposed Existence of Two Isomeric Triethyloxamines.*

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IN a previous paper on the "Action of Alkyl Haloids on Hydroxylamine" (Trans., 1899, 75, 792), we showed that by the action of ethyl iodide on an ethereal solution of diethylhydroxylamine a salt of triethyloxamine, $(C_2H_5)_3NO$, is produced. We obtained this base in a crystalline state and gave an account of its properties and those of its principal salts, and showed by the study of its reactions that it was to be regarded as a true oxamine, $(C_2H_5)_3N:O$, and not as the isomeric triethylhydroxylamine, $(C_2H_5)_2N \cdot OC_2H_5$. Later (Trans., 1899, 75, 1006), we obtained the same compound by the direct oxidation of triethylamine with hydrogen peroxide.

We also proved that this triethyloxamine is not identical with the compound which Bewad (*J. Russ. Phys. Chem. Soc.*, 1888, 20, 125) had obtained by acting on nitroethane with zinc ethyl. Bewad regarded this substance as the isomeride of a true triethylhydroxylamine and assigned to it the formula $(C_2H_5)_3NO$, on account of its having apparently furnished triethylamine on reduction. As the properties of this compound differed so markedly from ours, it seemed

possible that Bewad had obtained the isomeric triethylhydroxylamine which we had been unsuccessful in producing by any method we had tried. The properties of the substance described by Bewad were, however, not such as would be expected from a substituted hydroxylamine of the formula $(C_2H_5)_2N \cdot OC_2H_5$. As the question was one of some theoretical importance, we prepared a quantity of Bewad's material. In the meantime, however, Lachman (*Ber.*, 1900, 33, 1022) published an account of an investigation of this question. He prepared β -diethylhydroxylamine by the action of zinc ethyl on diphenylnitrosamine. The properties of the substance obtained by this method agree with those of the compound prepared by us by acting on hydroxylamine with ethyl iodide. Having been struck by the remarkable isomerism which apparently existed between the triethyloxamine prepared by us and that obtained by Bewad, Lachman proceeded to compare their properties.

In general, Lachman's account of the properties of triethyloxamine correspond with ours. He has, however, been unsuccessful in crystallising the base and is inclined to regard the crystallisation we observed as due to an impurity. This, however, is a mistake, for we have satisfied ourselves of the purity of the crystalline substance described in our previous paper. If the concentrated aqueous solution of the pure base is left in a vacuum desiccator with phosphoric oxide, it gradually becomes crystalline. These crystals are extremely hygroscopic.

After an examination of the properties of Bewad's compound, Lachman confirms our conclusion that the two substances are not identical and leaves to us the further determination of the question, but we now need only refer to it briefly, since Bewad (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 455) has shown that his supposed triethylhydroxylamine is really β -ethyl-*sec*-butylhydroxylamine,

which satisfactorily accounts for its properties. Bewad concludes that the action of zinc alkyls on primary or secondary nitroparaffins always results in the formation of β -disubstituted hydroxylamines.

Although Bewad himself does not discuss the supposed isomerism, any further investigation of the matter by us is unnecessary, for the conclusion reached by Bewad is entirely in accordance with our own, but we may point out that the additive compound, which Lachman describes as resulting from the action of methyl iodide on Bewad's compound, cannot possess the constitution or undergo the reactions which he attributes to it. Instead of being represented by the formula $(C_2H_5)_3N(OCH_3)I$, it is probably a hydriodide of methylethyl-*sec*-butyloxamine,

This being the case, it is clear that it could not undergo the decompositions described by Lachman into formaldehyde and triethylamine and other products.

Bewad has also shown (*loc. cit.*) that β -diethylhydroxylamine results from the action of zinc ethyl on *isopropyl* or *isoamyl* nitrite, and that β -dipropylhydroxylamine may be obtained by the action of zinc propyl on propyl nitrite. These compounds are identical with those we have prepared by the action of ethyl and propyl iodides on hydroxylamine.

We take this opportunity of replying to the complaint made by Mamlock and Wolfenstein (*Ber.*, 1900, 33, 159) that we have worked on the action of hydrogen peroxide on aliphatic amines, although Wolfenstein had previously stated that he was engaged in the study of the action of hydrogen peroxide on organic bases. Wolfenstein previously had taken similar exception to the work of Bamberger and Tschirner (*Ber.*, 1899, 32, 342). In the paper referred to above, these authors proceed to describe the properties of β -dipropylhydroxylamine and tripropyloxamine without any allusion to the fact that these compounds have already been prepared by us. As a matter of fact, we commenced the investigation of the action of alkyl haloids on hydroxylamine so long ago as 1894 (*Proc.*, 1894, 10, 138), and in 1899 (*Trans.*, 1899, 75, 792; *Proc.*, 1899, 15, 58) showed that the reaction previously described was a general one by means of which, not only trimethyl, but other alkylated oxamines and hydroxylamines could be prepared. In this paper, we stated that we were attempting to produce these new compounds by the action of hydrogen peroxide on the amines in order to settle their constitution. When Wolfenstein, whose previous investigations had been restricted to the oxidation of pyridine and quinoline derivatives—in which field Merling (*Ber.*, 1892, 25, 3123) had also worked—announced that he intended to extend his work to the aliphatic amines, our experiments were nearly completed.

In any case, our study of the action of hydrogen peroxide on certain aliphatic amines was undertaken merely to confirm the constitution of the oxides of the amines (oxamines) which we had already prepared by an entirely distinct reaction.

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