

XCVII.—*The Action of Hydrogen Peroxide on Secondary and Tertiary Aliphatic Amines. Formation of Alkylated Hydroxylamines and Oxamines.*

By WYNDHAM R. DUNSTAN, F.R.S., and ERNEST GOULDING, B.Sc.

IN a recent paper (Trans., 1899, **75**, 792), the authors have given an account of the reaction of alkyl haloids with hydroxylamine. They have shown that methylic iodide and hydroxylamine react, forming *trimethylamine oxide*, or *trimethyloxamine*,  $(\text{CH}_3)_3\text{N}\cdot\text{O}$ , whilst ethylic iodide forms at first  $\beta$ -*diethylhydroxylamine*,  $(\text{C}_2\text{H}_5)_2\text{N}\cdot\text{OH}$ , and, by further action, *triethyloxamine*,  $(\text{C}_2\text{H}_5)_3\text{N}\cdot\text{O}$ . Similarly,  $\beta$ -*dipropylhydroxylamine* and  $\beta$ -*di-isopropylhydroxylamine* are formed by the reaction of hydroxylamine with propylic and isopropylic iodide respectively; the corresponding oxamines have not yet been obtained by this method. The constitution assigned by us to these oxamines, as isomerides of the trialkylated hydroxylamines, suggested the possibility that they might be produced by the direct oxidation of the corresponding trialkylated amines, of which they may be regarded as the oxides. Moreover, it seemed likely that even substituted hydroxylamines might be produced by the direct oxidation of primary and secondary amines. The authors have shown ground for the supposition that the production of trialkylated oxamines,  $\text{R}_3\text{N}\cdot\text{O}$ , is probably preceded by the formation of the corresponding trialkylated hydroxylamines,  $\text{R}_3\text{N}\cdot\text{OR}$ , which, being unstable, at once change into the isomeric oxamines. Moreover, they have proved that the first product of the action of ethylic iodide on hydroxylamine is not diethyloxamine, but diethylhydroxylamine.

Experiment has shown that this direct oxidation of the amines may be effected by means of hydrogen peroxide. In this way, trimethylamine, triethylamine, and tripropylamine have been converted into the

## PEROXIDE ON SECONDARY AND TERTIARY ALIPHATIC AMINES. 1005

corresponding oxamines, whilst diethylamine has been converted into  $\beta$ -diethylhydroxylamine, an example of the direct oxidation of a residue of ammonia into one of hydroxylamine, and, similarly, dipropylamine has been directly oxidised into  $\beta$ -dipropylhydroxylamine.

The method is, doubtless, capable of further extension to the direct oxidation of other nitrogen compounds, and the authors have already made a number of preliminary experiments in this direction. It has not been found possible, however, by direct oxidation to convert a primary amine into a mono-alkylated hydroxylamine, and all experiments made with the view of directly converting ammonia into hydroxylamine have failed. So far, it appears that hydrogen peroxide is capable of adding one atom of oxygen to the nitrogen of tertiary amines, and of converting the hydrogen atom of secondary amines into a hydroxyl group.

As has been pointed out in a previous paper (*loc. cit.*), the alkylated oxamines closely resemble in their properties the dimethylaniline oxide which has been recently prepared by Bamberger and Tschinner (*Ber.*, 1899, **32**, 3421), by acting on dimethylaniline with hydrogen peroxide. On the other hand, they differ considerably from the alkylpiperidine oxides described by Wernick and Wolfenstein (*L. r.*, 1898, **31**, 1553; 1899, **32**, 688) as resulting from the action of hydrogen peroxide on alkylated piperidines, which are stated to liberate iodine from potassium iodide.

A close analogy may be traced between these oxamines and the alkylated oxyphosphines, oxyarsines, and oxyturbines.

The method now described for the preparation of the oxamines is very easy to carry out and gives an excellent yield. It is on this account to be preferred to the process by which the authors prepared the first member of this series of compounds, namely, by the action of methylic iodide on hydroxylamine, inasmuch as this involves a troublesome separation of the oxamine from the salts of hydroxylamine which accompany it.

*Action of Hydrogen Peroxide on Trimethylamine. Formation of Trimethyloxamine,  $(\text{CH}_3)_3\text{N}:\text{O}$ .*

An aqueous solution of trimethylamine containing about 3 grams of the base was mixed with the calculated quantity of hydrogen peroxide (60 c.c. of a 3 per cent. solution, previously freed from sulphuric acid by shaking with barium carbonate) and the mixture was allowed to stand for 24 hours at the ordinary temperature. The ammoniacal smell of the trimethylamine gradually disappeared.

The solution was concentrated to a small volume (about 20 c.c.) by distillation under reduced pressure. On the addition of dilute hydro

## 1006 DUNSTAN AND GOULDING: THE ACTION OF HYDROGEN

chloric acid in slight excess, some evolution of nitrous fumes occurred, indicating the presence of a nitrite. The acidified solution was evaporated on the water-bath until the volume was reduced to about 5 c.c. On cooling, a salt crystallised out which closely resembled the hydrochloride of trimethyloxamine. The crystals were removed, washed with ethylic alcohol, and recrystallised from hot methylic alcohol. On concentrating the mother liquor, more of the same salt was obtained and purified in the same manner. The whole of the purified material was then again recrystallised from hot methylic alcohol, washed with ethylic alcohol, drained on a porous tile, and dried in the water-oven. The properties of this salt were precisely those of the *trimethyl-oxamine hydrochloride* previously described by the authors.

0.2522 furnished 0.3228 AgCl. Cl = 31.7.

$(\text{CH}_3)_3\text{NO}, \text{HCl}$  requires Cl = 31.8 per cent.

The *platinichloride* was prepared and recrystallised from methylic alcohol. Its properties agreed with those of the trimethyloxamine salt.

0.1401 gave, on ignition, 0.0486 Pt. Pt = 34.6.

$[(\text{CH}_3)_3\text{NO}]_2, \text{H}_2\text{PtCl}_6$  requires Pt = 34.8 per cent.

The *aurichloride* crystallised from hot water in yellow octahedra.

0.0995 of a recrystallised specimen gave 0.0471 Au. Au = 47.3.

$(\text{CH}_3)_3\text{NO}, \text{HAuCl}_4$  requires Au = 47.5 per cent.

The hydrated base,  $(\text{CH}_3)_3\text{N}:\text{O} + 2\text{H}_2\text{O}$ , was prepared by the addition of moist silver oxide to a solution of the hydrochloride in just sufficient quantity to remove the whole of the chlorine. The solution was filtered and evaporated nearly to dryness on the water-bath. On cooling, the base crystallised rapidly in radiating needles in the manner characteristic of trimethyloxamine.

This substance was strongly alkaline to litmus, and possessed all the properties of trimethyloxamine, showing the same reactions with silver nitrate, cupric sulphate, and ferrous sulphate.

The action of hydrogen peroxide on an aqueous solution of trimethylamine constitutes the best method of preparing trimethyloxamine, which was first obtained by the authors by the action of hydroxylamine on methylic iodide.

*Action of Hydrogen Peroxide on Triethylamine. Formation of Triethyloxamine,  $(\text{C}_2\text{H}_5)_3\text{N}:\text{O}$ .*

Three grams of triethylamine were mixed with 34 c.c. of a 3 per cent. solution of hydrogen peroxide (these quantities being in approximately molecular proportion) and allowed to stand with occasional agitation

## PEROXIDE ON SECONDARY AND TERTIARY ALIPHATIC AMINES. 1007

for 24 hours. The oily base completely disappeared. When the solution was evaporated on the water-bath, a thick, colourless liquid was obtained, which was strongly alkaline to litmus, and crystallised after remaining for several days in a vacuous desiccator. This substance exhibited all the reactions of the triethyloxamine obtained by the action of ethylic iodide on diethylhydroxylamine. It formed an apple-green precipitate with solution of cupric sulphate, which, on warming, subsided as a pale blue powder. With solution of silver nitrate, a white precipitate was produced, reduced to metallic silver on heating. When a solution of the base was added to solution of ferrous sulphate, it immediately became reddish-brown, and ferric hydroxide separated.

In a second experiment, the triethylamine was mixed with 6 per cent. solution of hydrogen peroxide. After shaking for a few minutes, the solution became quite warm, and the layer of triethylamine rapidly grew smaller and finally disappeared. On evaporating the solution, the triethyloxamine remained as a thick, colourless liquid.

In order to completely characterise the oxamine, the following salts were prepared :

The *hydrochloride*,  $(C_2H_5)_3NO, HCl$ , was obtained as a sticky liquid, which crystallised in the desiccator in deliquescent needles.

The *platinichloride*,  $[(C_2H_5)_3NO]_2, H_2PtCl_6$ , is very soluble in water and methylic alcohol, slightly soluble in cold ethylic alcohol, but more soluble in hot. After recrystallising twice from hot ethylic alcohol, the platinum was determined by ignition.

0.1231 gave 0.0372 Pt. Pt = 30.2.

0.0549 „ 0.0167 Pt. Pt = 30.4.

$[(C_2H_5)_3NO]_2, H_2PtCl_6$  requires Pt = 30.3 per cent.

The *aurichloride*,  $(C_2H_5)_3NO, HAuCl_4$ , separates as an oil when auric chloride is added to a solution of the hydrochloride. It is somewhat soluble in hot, but very sparingly soluble in cold water.

The *picrate*,  $(C_2H_5)_3NO, C_6H_2(NO_2)_3OH$ , is obtained as a pale yellow precipitate when a cold saturated solution of picric acid is added to an aqueous solution of triethyloxamine. This salt is soluble in hot water and crystallises on cooling in fine, yellow needles which soften above  $160^\circ$  and melt at  $164^\circ$ .

0.3355 gave 0.5098  $CO_2$  and 0.1587  $H_2O$ . C = 41.44; H = 5.26.

$(C_2H_5)_3NO, C_6H_2(NO_2)_3OH$  requires C = 41.62; H = 5.20 per cent.

The following experiment was made in order to ascertain the extent to which the formation of triethyloxamine takes place.

One gram of triethylamine was mixed with 6 c.c. of 6 per cent. solution of hydrogen peroxide. After standing for about 24 hours, cold saturated aqueous picric acid solution was added in excess. The

## 1008 DUNSTAN AND GOULDING: THE ACTION OF HYDROGEN

precipitate was collected on a tared filter, dried, and weighed. 2.5 grams were thus obtained. It was found that triethyloxamine picrate is soluble to about the extent of 0.6 gram in 100 c.c. of water at the temperature at which the experiment was carried out; hence the filtrate (which measured 150 c.c.) contained about 0.9 gram of the picrate in solution. The total weight of picrate formed was therefore 3.4 grams, which is exactly that required by the equation  $(C_2H_5)_3N + O = (C_2H_5)_3NO$ , so it may be concluded that the reaction takes place quantitatively.

*Action of Hydrogen Peroxide on Tripropylamine. Formation of Tripropyloxamine,  $(C_3H_7)_3N \cdot O$ .*

Owing chiefly to its insolubility, tripropylamine is scarcely at all attacked by an aqueous solution of hydrogen peroxide. If, however, the base is dissolved in alcohol, it can be readily oxidised and converted into its oxamine. The following plan has been found to answer best.

About 4 grams of tripropylamine are dissolved in 30 c.c. of ethylic alcohol, 16 c.c. of hydrogen peroxide (6 per cent.) are added, and the mixture is warmed for about 12 hours at 60°. The liquid is distilled under reduced pressure until about two-thirds have passed over. The syrupy residue, if placed in a vacuum desiccator, soon becomes very thick, and finally crystallises in radiating needles, which dissolve readily in water and alcohol, but are insoluble in ether.

As thus obtained, tripropyloxamine is a very hygroscopic substance which acts as a strong base; it is alkaline to litmus, and combines energetically with acids, forming well-defined salts. It has a bitter taste.

The *hydrochloride*,  $(C_3H_7)_3NO \cdot HCl$ , may be obtained by adding hydrochloric acid to a solution of the base and evaporating to dryness. The gummy residue soon crystallises on standing. The salt is readily soluble in water, alcohol, and chloroform, but is insoluble in ether. It is best purified by precipitating it by the addition of ether to an alcoholic solution. When heated, it gradually softens, and is completely melted at about 90°.

The *picrate*,  $(C_3H_7)_3NO \cdot C_6H_2(NO_2)_3OH$ , is a characteristic salt which is precipitated when an aqueous solution of picric acid is added to a solution of the base. It is remarkable in being nearly insoluble in cold water. Hot water dissolves it, and crystals separate on cooling which melt at 129°.

The *platinichloride*,  $[(C_3H_7)_3NO]_2 \cdot H_2PtCl_6$ , is nearly insoluble in cold water, but crystallises readily from hot water in orange-red

## PEROXIDE ON SECONDARY AND TERTIARY ALIPHATIC AMINES. 1009

prisms melting at 174—175°. This salt, recrystallised from water, was analysed with the following result :

0·1377 gave 0·0368 Pt. Pt = 26·73.

$[(C_3H_7)_3NO]_2, H_2PtCl_6$  requires Pt = 26·76 per cent.

The *aurichloride*,  $(C_3H_7)_3NO, HAuCl_4$ , is precipitated as an oil when auric chloride is added to a solution of the hydrochloride. From warm water, it crystallises in golden spangles. This salt is slightly soluble in cold water, rather more soluble in hot water, and readily dissolved by alcohol. On analysis, a specimen dried at 100° furnished the following result :

0·0871 gave 0·0342 Au. Au = 39·3.

$(C_3H_7)_3NO, HAuCl_4$  requires Au = 39·5 per cent.

Tripropyloxamine exhibits generally the same properties and reactions as the trimethyl- and triethyl-oxamines already described. With copper sulphate, it furnishes a pale blue precipitate, with ferrous sulphate, it produces ferric hydroxide, undergoing reduction, whilst it readily reduces solution of silver nitrate. It does not liberate iodine from potassium iodide or show any other evidence of being a powerful oxidising agent.

*Action of Hydrogen Peroxide on Dimethylamine.*

Two grams of dimethylamine (in 33 per cent. aqueous solution) were mixed with 25 c.c. of hydrogen peroxide (6 per cent. solution). After standing for a short time, the solution became warm and smelt of formaldehyde ; small quantities of oxygen were continuously evolved. After 24 hours all the hydrogen peroxide had disappeared, but it was found that only about half of the dimethylamine had been attacked. The chief products of oxidation appeared to be nitrous acid, formic acid, and formaldehyde. No  $\beta$ -dimethylhydroxylamine, corresponding to the products of the action of hydrogen peroxide on diethylamine and dipropylamine, could be detected. The solution contained a small quantity of a substance which, after boiling with dilute acid, reduced Fehling's solution in the cold, but it was present in too small amount to be identified.

*Action of Hydrogen Peroxide on Diethylamine. Formation of  $\beta$ -Diethylhydroxylamine,  $(C_2H_5)_2N \cdot OH$ .*

Diethylamine was dissolved in the calculated quantity of solution of hydrogen peroxide (6 per cent.) and the mixture allowed to stand at the ordinary temperature for 24 hours. The whole of the hydrogen peroxide had then disappeared, and the solution had become slightly

## 1010 ACTION OF HYDROGEN PEROXIDE ON ALIPHATIC AMINES.

yellow, and had acquired the characteristic odour of  $\beta$ -diethylhydroxylamine,  $(C_2H_5)_2N \cdot OH$ . The liquid was shaken with ether, the ethereal solution dried with calcium chloride, and the ether carefully distilled off. The residue was a very basic liquid, having all the properties of  $\beta$ -diethylhydroxylamine, and giving the same reactions with solutions of cupric sulphate, silver nitrate, and mercuric chloride.

When an ethereal solution of anhydrous oxalic acid was added to an ethereal solution of the base, the *oxalate* of  $\beta$ -diethylhydroxylamine,  $[(C_2H_5)_2N \cdot OH]_2, H_2C_2O_4$ , was precipitated, which, after recrystallisation, melted at  $136-137^\circ$ , and exhibited the crystalline form and properties characteristic of that salt, as described in a previous paper (*loc. cit.*). A determination of the oxalic acid gave the following result :

0.2143 of salt gave 0.0443 CaO.  $H_2C_2O_4 = 33.2$ .

$[(C_2H_5)_2N \cdot OH]_2, H_2C_2O_4$  requires  $H_2C_2O_4 = 33.6$  per cent.

The yield of  $\beta$ -diethylhydroxylamine furnished by this reaction is probably not more than about 50 per cent. of that required by the equation  $(C_2H_5)_2NH + O = (C_2H_5)_2N \cdot OH$ .

*Action of Hydrogen Peroxide on Dipropylamine. Formation of  $\beta$ -Dipropylhydroxylamine,  $(C_3H_7)_2N \cdot OH$ .*

Dipropylamine was mixed with the calculated quantity of hydrogen peroxide (6 per cent.) and allowed to stand for 24 hours with occasional agitation. It was found that no hydrogen peroxide remained, and that a substance had been produced which reduced Fehling's solution in the cold and possessed the curious odour characteristic of  $\beta$ -dipropylhydroxylamine. The mixture was extracted with ether, and the ethereal solution dried with calcium chloride. The ether was distilled off and an oily residue remained.

To 1 gram of this residue a strong, warm, aqueous solution of 1 gram of oxalic acid was added. The solution was concentrated on the water-bath, and on cooling a salt crystallised out in rosettes of plates. The crystals were removed from the mother liquor, washed with a little cold water and alcohol, and recrystallised from warm alcohol. The recrystallised salt melted at  $139^\circ$ , was acid to litmus, and exhibited all the characters of the acid oxalate of  $\beta$ -dipropylhydroxylamine,  $(C_3H_7)_2N \cdot OH, H_2C_2O_4$ . A determination of the oxalic acid gave the following result :

0.3430 gave 0.0928 CaO.  $H_2C_2O_4 = 43.5$ .

$(C_3H_7)_2N \cdot OH, H_2C_2O_4$  requires  $H_2C_2O_4 = 43.5$  per cent.

The free base exhibited the reactions with cupric sulphate, mercuric

chloride, and silver nitrate which have been described for  $\beta$ -dipropylhydroxylamine in the authors' previous paper (*loc. cit.*).

The yield was only about 50 per cent. of that required by the equation  $(C_3H_7)_2NH + O = (C_3H_7)_2N \cdot OH$ .

In conclusion, we may remark that we have tried a number of experiments on the action of hydrogen peroxide, under different conditions, on ammonia and its salts, in the hope of effecting the production of hydroxylamine. All these experiments have, however, been unsuccessful. It has not been possible in any case to detect the presence of hydroxylamine in the product.

With regard to the possibility of producing monosubstituted hydroxylamines by the oxidation of primary amines, all experiments have been unsuccessful, the primary amine being completely decomposed, forming nitrous acid among other products. It has been observed also that primary amines are not rapidly attacked by hydrogen peroxide at the ordinary temperature. Experiments have also been made with numerous other amines and amino-derivatives, as a rule with little or no result. Ethylenediamine, however, is vigorously decomposed by hydrogen peroxide, and the products of the change are now under investigation.

SCIENTIFIC DEPARTMENT,  
IMPERIAL INSTITUTE, S. W.

---