XXX.—*A Synthesis of para-Urazine from Carbamide.*

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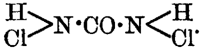
THE author has recently shown that two of the hydrogen atoms of carbamide can be replaced by chlorine, a dichlorocarbamide being formed. Although this compound, as might be expected, is very readily hydrolysed, it can be obtained by passing chlorine through a saturated aqueous solution of carbamide, when it crystallises out in small, transparent plates. It is safe to handle, and can be preserved for a considerable time in a dry atmosphere.

Its composition shows that it has the formula $CH_2ON_2Cl_2$, and having regard to its mode of formation as well as to the structure of carbamide itself, its constitution is undoubtedly represented by the formula  $\mathrm{{}^{H}_{Cl}\!>\!N\cdot CO\cdot N\!<^{H}_{Cl}}$. As dichlorocarbamide thus contains two chlorine atoms, each attached to a nitrogen atom not otherwise linked to any complex organic group, and as it is a stable solid compound easily prepared and isolated and soluble in many common solvents, it promises to be of considerable use in organic synthesis.

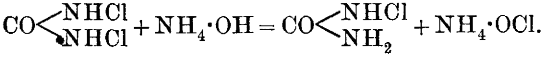
When dichlorocarbamide is acted on by ammonia, a reaction takes place which is of interest, as it not only affords the first synthesis of *p*-urazine from carbamide itself, but adds another to the limited number of reactions by which nitrogen atoms can be made to link together.

When dichlorocarbamide is added to a strong aqueous solution of ammonia, hydrolysis occurs accompanied by liberation of nitrogen and formation of ammonium carbonate, but, in addition, *p*-urazine,

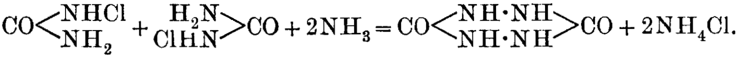
$$\mathrm{CO}{<}\begin{matrix}\mathrm{NH{\cdot}NH}\\ \mathrm{NH{\cdot}NH}\end{matrix}{>}\mathrm{CO},$$

is produced, and separates out in considerable quantity as a sparingly soluble, crystalline powder.

The formation of *p*-urazine from dichlorocarbamide in this reaction may be explained by assuming that by interaction with ammonium hydroxide one of the chlorine atoms is replaced by hydrogen [*] and a monochlorocarbamide produced, two molecules of which condense under the influence of the ammonia with elimination of hydrogen chloride, thus :



$$\mathrm{CO}{<}\begin{matrix}\mathrm{NHCl}\\ \mathrm{NHCl}\end{matrix} + \mathrm{NH_4{\cdot}OH} = \mathrm{CO}{<}\begin{matrix}\mathrm{NHCl}\\ \mathrm{NH_2}\end{matrix} + \mathrm{NH_4{\cdot}OCl}.$$



$$\mathrm{CO}{<}\begin{matrix}\mathrm{NHCl}\\ \mathrm{NH_2}\end{matrix} + \begin{matrix}\mathrm{H_2N}\\ \mathrm{ClHN}\end{matrix}{>}\mathrm{CO} + 2\mathrm{NH_3} = \mathrm{CO}{<}\begin{matrix}\mathrm{NH{\cdot}NH}\\ \mathrm{NH{\cdot}NH}\end{matrix}{>}\mathrm{CO} + 2\mathrm{NH_4Cl}.$$

Curtius has shown that *p*-urazine, which he prepared from hydrazine hydrate,[†] can be heated on a water-bath with a mixture of equal parts of concentrated sulphuric acid and water for many hours without alteration. He found, however, that it could be converted into hydrazine and carbon dioxide by heating it with concentrated hydrochloric acid in a sealed tube to 150°.

This hydrolysis can be much more easily effected by heating *p*-urazine with concentrated sulphuric acid to about 120—130°. Carbon dioxide is rapidly evolved, and hydrazine sulphate formed.

[*] This replacement of chlorine by hydrogen very frequently takes place when substituted nitrogen chlorides are treated with ammonia, ammonium hypochlorite or products of its decomposition being produced. That this replacement actually takes place in the reaction between dichlorocarbamide and ammonia is shown by the reconversion of a small amount of the dichlorocarbamide used into carbamide itself.

[†] *p*-Urazine was prepared by Curtius (*J. pr. Chem.*, 1895, [ii], **52**, 481) by acting on ethyl chloroformate in alcoholic solution with hydrazine hydrate, and then heating the ethyl hydrazinedicarboxylate, $N_2H_2(CO_2Et)_2$, formed with two molecules of hydrazine hydrate for some hours in a sealed tube at 100°.

The latter crystallises out in a pure state on cooling and adding a little water to the product :

$$CO{<}\begin{matrix}NH\cdot NH\\NH\cdot NH\end{matrix}{>}CO + 2H_2O + 2H_2SO_4 = 2CO_2 + 2NH_2\cdot NH_2,H_2SO_4.$$

Dichlorocarbamide can be prepared from carbamide and converted into *p*-urazine so easily, and the latter can be so quickly hydrolysed, that the reactions afford a synthesis of hydrazine more adapted to prepare a small quantity of the pure sulphate than any yet described. The operations involved are simple, and excellently suited for showing the synthesis of hydrazine as a lecture experiment.

Preparation of p-*Urazine.*

In order to prepare *p*-urazine, it is not necessary to dry the dichlorocarbamide. The crude product, free from all adhering mother liquor, is dissolved in from ten to twenty times its weight of water and rapidly added to excess of concentrated ammonia, the mixture being thoroughly stirred. A vigorous evolution of nitrogen takes place, and a white, crystalline powder separates, a little more crystallises out on keeping, and a still further small quantity on evaporating the mother liquor after neutralising with hydrochloric acid. In the reaction nothing appears to be formed except nitrogen, ammonium carbonate, ammonium chloride, and *p*-urazine, but a small quantity of the dichlorocarbamide used is reconverted into carbamide. The yield of *p*-urazine is about 20 per cent. of the theoretical.

The *p*-urazine thus obtained as a white, crystalline powder can be crystallised from boiling water, in which it is sparingly soluble; on cooling, it separates in small, colourless crystals, which melt, when rapidly heated, in the neighbourhood of 270°. The exact melting point of the pure substance cannot be determined, as the temperature at which liquefaction occurs varies considerably with the rate of heating, decomposition appearing to commence about 260°.

For analysis, the compound was recrystallised once from water:

0·1014 gave 41·8 c.c. N_2 (moist) at 12° and 755 mm. $N = 48{\cdot}62$.

$C_2H_4O_2N_4$ requires $N = 48{\cdot}28$ per cent.

Hydrolysis of p-*Urazine and Preparation of Hydrazine Sulphate.*

When *p*-urazine is mixed with about five times its weight of concentrated sulphuric acid and warmed to about 80°, it dissolves apparently without change; on heating the solution to about 95—100°, hydrolysis slowly takes place, with evolution of carbon dioxide. On raising the temperature still higher, the rate of evolution of carbon dioxide increases, until at about 120—130° it is very rapidly liberated;* at this temperature hydrolysis is soon complete, and a clear, colourless liquid is obtained, which deposits crystals of hydrazine sulphate on cooling. It is best, however, to add to the cooled liquid its own bulk of water, when pure hydrazine sulphate at once separates as a white, crystalline powder. To ascertain its purity, a specimen was prepared as above, washed a few times with distilled water, dried, and analysed:

0·2406 gave 0·4298 $BaSO_4$. $H_2SO_4 = 75·06$.

N_2H_4,H_2SO_4 requires $H_2SO_4 = 75·37$ per cent.

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