THE ACTION OF DICHLOROCARBAMIDE ON AMINES. THE SYNTHESIS OF 2,4-DIBENZYL-3-PHENYL-6-KETO-3-HYDROXYHEXAHYDRO-1,2,4,5-TETRAZINE.

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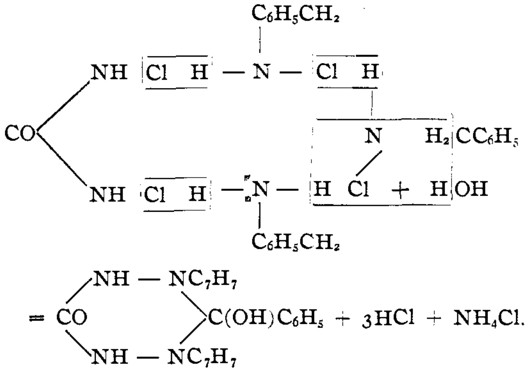
The action of dichlorocarbamide on amines was studied by one of us[1] when it was shown that dichlorocarbamide is essentially a chlorinating agent, resulting in the production of chloroamines—accompanied by hydrolysis with the lower members but proceeding quantitatively with the higher members, especially with benzylamine. It was also noted that both monochloro- and dichlorobenzylamines could be prepared by its means and incidentally some interesting decompositions of the said chloroamines were studied, showing that the side groups —CH_2NHCl and —CH_2NCl_2 of monochloro- and dichlorobenzylamines undergo hydrolysis into —CHO and —COOH groups, respectively, which points to the fact that the hydrogen atoms directly connected with carbon in the above groups are easily brought into interaction and which, as will be shown later, makes possible the synthesis of the tetrazine derivative in question.

It was previously pointed out that chloroamines are the only products of the interaction between dichlorocarbamide and amines, but it has now been found that, by varying the condition of interaction, other products besides chloroamines could be isolated from the reaction mixture.

Thus, when a solution of dichlorocarbamide is added to a large excess of a well-cooled allylamine solution, besides the formation of the chloroamine, *p*-urazine is precipitated in small quantities. Again, from a similar interaction with benzylamine, a mixture of *p*-urazine and 2,4-dibenzyl-3-phenyl-6-hydroxyhexahydro-1,2,4,5-tetrazine is precipitated. The formation of the latter compound takes place according to the following scheme:



Monochlorobenzylamine is first formed by the action of the chlorourea on an excess of benzylamine, two molecules of which and a molecule of free

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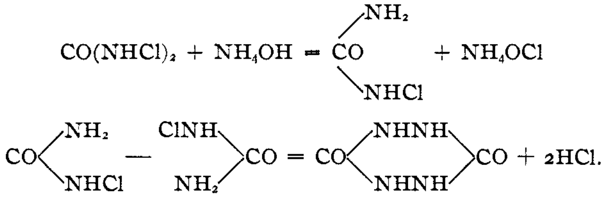
[1] *J. Chem. Soc.*, 101, 166 (1912); This Journal, 34, 1613 (1912).

amine condense with dichlorocarbamide, with the elimination of hydrochloric acid and ammonium chloride, to form the tetrazine derivative. The ready abstraction of hydrochloric acid is facilitated by the fact that the reaction has to be carried out with a very large excess of concentrated benzylamine solution and in fact this is the essential condition of the reaction.

The formation of *p*-urazine can be explained by assuming that the amine snatches away the chlorine atoms of dichlorocarbamide, leaving the urea residue $\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH}-\\ \mathrm{NH}-\end{matrix}\right.$, which unites with itself to form *p*-urazine. Chattaway[1] prepared *p*-urazine by adding dichlorourea to a concentrated solution of ammonia and he explained the reaction by assuming that two molecules of monochlorocarbamide are first produced, which condense together in the presence of a large excess of ammonia to form *p*-urazine, thus:



$$\mathrm{CO(NHCl)_2} + \mathrm{NH_4OH} = \mathrm{CO}\left\langle\begin{matrix}\mathrm{NH_2}\\ \mathrm{NHCl}\end{matrix}\right. + \mathrm{NH_4OCl}$$

$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH_2}\\ \mathrm{NHCl}\end{matrix}\right. - \left.\begin{matrix}\mathrm{ClNH}\\ \mathrm{NH_2}\end{matrix}\right\rangle\mathrm{CO} = \mathrm{CO}\left\langle\begin{matrix}\mathrm{NHNH}\\ \mathrm{NHNH}\end{matrix}\right\rangle\mathrm{CO} + 2\mathrm{HCl}.$$

But it is evident, from the formation of *p*-urazine by the interaction of dichlorocarbamide on amines that the above explanation given by Chattaway of the formation of *p*-urazine is untenable. It is most likely, as has been pointed out before, that ammonia or amine removes the chlorine atoms of dichlorocarbamide, itself being chlorinated and leaving the urea residue to unite with itself to form *p*-urazine.

Experimental.

The Action of Dichlorocarbamide on Allylamine.—An excess of a strong aqueous solution of allylamine (50–60%) is cooled in a freezing mixture and to it is gradually added a well-cooled saturated solution of dichlorourea, when a small quantity of a white crystallin precipitate is produced and at the same time most of the amine undergoes hydrolysis with the evolution of gas—a part also getting chlorinated. The yield obtained is very poor but it can be improved a little by allowing the reaction mixture to stand overnight. The precipitate thus obtained is taken on a filter paper, washed with water, acidified with hydrochloric acid and finally with pure water. The dried salt had a melting point 265°–266° and is evidently *p*-urazine, which was further proved by a nitrogen determination.

Found: N, 47.89; calculated for $C_2N_4H_4O_2$: N, 48.27.

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[1] *J. Chem. Soc.*, **95**, 235 (1909).

The Action of Dichlorocarbamide on Benzylamine.—A strong solution of benzylamine, preferably 60%, is cooled in ice as before and to it a well-cooled solution of dichlorocarbamide is gradually added, with shaking, taking care that no considerable amount of hydrolysis takes place. Care must be taken to use only a small quantity of the chlorourea, keeping the amine in considerable excess. Within a very short time of the addition, the liquid becomes thick with a mass of flocculent precipitate. The precipitate thus obtained is filtered, washed repeatedly with hydrochloric acid to free it from the excess of benzylamine and another basic substance, which is under examination. The substance thus obtained does not give a definit melting point, since it is a mixture of *p*-urazine and the tetrazine derivative, the latter being present in much greater quantity than the former. To effect a separation, the crystallin mass is warmed with a small quantity of acetone when the *p*-urazine derivative remains undissolved, the tetrazine derivative passing into solution. On evaporating the acetone solution and effecting a second recrystallization from the same solvent, the substance is found to melt sharply at 146°. It was analyzed with the following results:

Sample I. Found: C, 70.32; N, 14.93; H, 6.12.
Sample II. Found: C, 70.21; N, 14.98; H, 5.97.
Calculated for $C_{22}H_{22}N_4O_2$: C, 70.58; N, 14.97; H, 5.88.

The residue left on the filter is washed with acetone and is found to be *p*-urazine, giving a melting point, 264°–266°. (Found, N = 48.01; calc. N = 48.27.)

Further researches on the application of dichlorocarbamide as a synthetic agent are being continued.

Our thanks are due to Prof. P. C. Rây for his encouragement in carrying on the above investigation.

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IODOPLATINATES OF SUBSTITUTED AMMONIUM AND SULPHONIUM BASES.

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In continuation of the researches on the double iodides, several of which with platinum and copper have already been described,[1] it was thought advisable to prepare other double platinic iodides, especially of the heavily substituted ammonium bases and also to determin clearly the condition of the precipitation of such salts. The method of preparation by double decomposition is also extended to the double platinic iodides of the sulfonium bases.

It has been pointed out in my previous paper, that double platinic iodides

[1] Datta, *J. Chem. Soc.*, **103**, 426 (1913).