CXCIX.—*Action of Monochloroacetic Acid on Thiocarbamide and Monoalkylated Thiocarbamides.*

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ONE of us (P., 1914, **30**, 140) has shown that whenever mercuric nitrite is treated with thiocarbamide or any other thio-compound which admits of the possibility of furnishing the thiol group (SH) by tautomeric changes, the primary reaction is of the type

It seemed to us that clearer light would be thrown on the mechanism of tautomeric changes by studying the reaction of thiocarbamide—a typical representative of this class of substances—and also its substituted alkyl derivatives with monochloroacetic acid. The expectation has been fully realised.

Volhard found that by the interaction of thiocarbamide and monochloroacetic acid, glycolylthiocarbamide was formed (*Annalen*, 1873, **166**, 385). This substance is now regarded as ψ - or *iso*-thiohydantoin, and it is now generally admitted that during its formation the parent substance, thiocarbamide, assumes the static configuration of iminothiocarbamic acid (compare Dixon and Taylor, T., 1912, **101**, 2502). As Volhard brought about the reaction by gentle heating, hydrogen chloride and water were simultaneously eliminated, resulting in the formation of the above cyclic compound. In the present paper it will be shown that by the interaction of the components in aqueous solution in the cold, condensation of the simple character represented by the following equation takes place:

If, however, the components are brought together in acetone solution in the cold, condensation of exactly the same type occurs, with this difference, that the hydrogen chloride which is eliminated is fixed by the base, with the formation of its hydrochloride. Glycine itself has feebly basic properties, and forms a hydrochloride; the present compound is evidently a stronger base, as it contains an amidine group. Monomethyl- and monoallyl-thiocarbamides also give rise to the corresponding condensation products in acetone solution, but no condensation takes place in aqueous solution. No sharp melting point of any of these compounds could be determined, as they all decompose, with slight charring, at about 200°. On examining the results of analysis, it

will be noticed that the purest products were obtained from the alkylated thiocarbamides.

The formation of these compounds throws some light on the constitution and reactions of thiocarbamides. Dixon and Taylor (*loc. cit.*) state that in the formation of isothiohydantoin "the parent thiocarbamide has behaved as a thiourea," but they add that a compound of the type $\text{H}_2\text{N}\cdot\text{C}(\text{:NH})\cdot\text{SX}$ "is essentially unstable, and there does not appear to be any reason why conjugation with a molecule of haloid acid should render it stable." They are further of the opinion that "mere dissolution in the cold by a non-hydrolysing solvent has no effect in producing hydrogen chloride; but this is eliminated in presence of various hydrolysts." The successful isolation of the hydrochlorides described in this paper, and that in a non-ionising solvent like acetone, disposes of this hypothesis.

Moreover, Werner has shown (T., 1912, **101**, 2166) that in the formation of formamidine disulphide,

by the interaction of iodine and thiocarbamide, a tautomeric change of the latter is involved; the halogen acid which is eliminated combines with the base, resulting in the formation of its hydriodide. It is evident that not only free halogen, but also a halogenated compound, which can readily part with its halogen, is equally effective in this respect. Another instance of the tautomerism of thiocarbamide is the formation of the compound

recently isolated by Sen (*Proc. Asiatic Soc. Bengal*, 1914) by the interaction of thiocarbamide and chloral hydrate (compare Coppin and Titherley, this vol., p. 32).

EXPERIMENTAL.

Formamidinethiolacetic Acid, $\text{NH}_2\cdot\text{C}(\text{:NH})\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$.

The components, dissolved separately in water, were mixed and allowed to remain overnight. A white, amorphous product was obtained, which was well washed with cold water and dried in a vacuum. The substance was sparingly soluble in hot water:

0.1849 gave 0.1831 CO_2 and 0.0747 H_2O . $\text{C}=27.00$; $\text{H}=4.59$.

0.0707 „ 12.8 c.c. N_2 at 34.5° and 760 mm. $\text{N}=19.64$.

0.1318 „ 0.2157 BaSO_4 . $\text{S}=22.47$.

$\text{C}_3\text{H}_6\text{O}_2\text{N}_2\text{S}$ requires $\text{C}=26.86$; $\text{H}=4.47$; $\text{N}=20.89$; $\text{S}=23.89$
per cent.

The slightly lower percentages of nitrogen and sulphur point to the fact that the compound was not obtained quite pure. Unlike

the compounds from the substituted thiocarbamides, it had a slight tendency to decompose.

The *hydrochloride* was obtained as a white, crystalline substance when the components were mixed in acetone solution as before and left for twenty-four hours. It was freely soluble in hot water, and moderately so in hot alcohol:

0.1551 gave 0.1248 AgCl and 0.2264 BaSO₄. Cl=19.90; S=20.04.

C₃H₆O₂N₂S.HCl requires Cl=20.80; S=18.77 per cent.

As the analysis indicates, this hydrochloride was also obtained in a somewhat impure state.

Methylformamidinethiolacetic Acid Hydrochloride,
NHMe·C(:NH)·S·CH₂·CO₂H.HCl.

The solvent used was acetone, as in the previous instance. Long, white needles were obtained, which were readily soluble in water:

0.0883 gave 0.0720 AgCl. Cl=20.16.

0.1406 „ 0.1802 BaSO₄. S=17.59.

0.0587 „ 8.2 c.c. N₂ at 31° and 760 mm. N=15.24.

C₄H₈O₂N₂S.HCl requires Cl=19.24; S=17.34; N=15.17 per cent.

The chlorine of this compound could also be estimated by directly precipitating it as silver chloride in aqueous solution by means of silver nitrate. The substance is therefore a true hydrochloride.

Allylformamidinethiolacetic Acid Hydrochloride,
C₃H₅·NH·C(:NH)·S·CH₂·CO₂H.HCl.

In this case, clusters of thin, white needles were obtained, which were soluble in water:

0.0608 gave 0.0744 CO₂ and 0.0346 H₂O. C=33.44; H=6.32.

0.092 „ 11.8 c.c. N₂ at 31° and 760 mm. N=14.12.

0.0718 „ 0.0518 AgCl. Cl=17.84.

0.0823 „ 0.0932 BaSO₄. S=15.55.

C₆H₁₀O₂N₂S.HCl requires C=34.20; H=5.22; N=13.30;
Cl=16.86; S=15.20 per cent.

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