

228. Studies on Hydrogen Cyanide. Part XV. The Action of Hydrogen Chloride on Methyl Cyanide.

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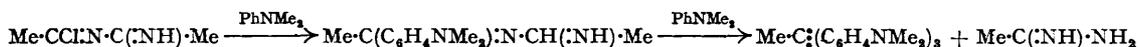
Hydrogen chloride readily combines with methyl cyanide at low temperatures forming a crystalline acetamido dichloride. The latter compound is unstable and is readily dissociated into its two components by water or by bases such as dimethylaniline. The dichloride melts at 6° and in the liquid state undergoes partial decomposition into acetimido chloride, methyl cyanide and hydrogen chloride; further changes slowly occur yielding α -chloroethylidene acetamidine and its hydrochloride. The latter compound is the chief product of heating the dichloride under pressure.

GAUTIER (*Ann. Chim. Phys.*, 1869, 17, 174) saturated methyl cyanide with hydrogen chloride at 0° and obtained a small quantity of a crystalline substance. Since the liquid had absorbed almost one equivalent of hydrogen chloride Gautier concluded that the compound had the formula $\text{CH}_3\text{CN}\cdot\text{HCl}$. He was not able to obtain a stable compound since the crystals readily redissolved in the liquid.

If Gautier's experiment be repeated at -17°, two molecules of hydrogen chloride are readily absorbed and crystals rapidly form, the liquid becoming a solid crystalline mass consisting of acetamido dichloride, $\text{Me}\cdot\text{CCl}_2\cdot\text{NH}_2$. This compound is unstable at ordinary temperatures and melts at 6° with partial decomposition in the first instance into a mixture of methyl cyanide, acetimido chloride, $\text{Me}\cdot\text{CCl}\cdot\text{NH}$, and hydrogen chloride. This liquid on being recooled to -17° deposits the dichloride but when left at room temperature it gradually undergoes further changes in which union takes place between two molecules of acetimido chloride and at the same time a molecule of acetimido chloride combines with a molecule of acetamido dichloride yielding in the first case α -chloroethylidene acetamidine (I) and in the second case its hydrochloride (II).



The hydrochloride (II) is readily converted into α -chloroethylidene acetamidine (I) by solution in alcohol and both compounds react with dimethylaniline in a manner similar to that of chloromethylene formamidine (cf. Hinkel and Dunn, J., 1930, 3343) yielding α -tri(dimethylaminophenyl)-ethane.



Actamido dichloride when heated in a sealed tube at 100° is converted almost entirely into the hydrochloride of α -chloroethylidene acetamidine (II). Acetamido dichloride is completely dissociated into methyl cyanide and hydrogen chloride by water. It does not react with resorcinol in ether in presence of zinc chloride at 0° but readily does so at room temperature yielding resacetophenone, due to its partial decomposition into acetimido chloride. It reacts slowly with well-cooled alcohol yielding crystals of the hydrochloride of acetimido ethyl ether, $\text{Me}\cdot\text{C}(\text{:NH},\text{HCl})\cdot\text{OEt}$.

Acetamido dichloride reacts vigorously with dimethylaniline even at low temperatures liberating methyl cyanide, and a small quantity of α -tri(dimethylaminophenyl)-ethane. Under reduced pressure the dichloride may be heated to 90° without liquefaction, but it loses its crystalline form and gradually dissociates into its two components leaving a small residue of α -chloroethylidene acetamidine.

EXPERIMENTAL.

Methyl cyanide was purified as described by Koch (J., 1927, 648), being finally distilled over phosphorus pentoxide and boiling at 81.6°/760 mm.

Acetamido Dichloride.—Dried hydrogen chloride was passed into well-cooled (ice and salt) methyl cyanide with the rigid exclusion of moisture. After a short latent period the absorption of the hydrogen chloride was rapid, the liquid increased in volume and colourless crystals began to separate. The passage of hydrogen chloride was continued until all the methyl cyanide was converted into the dichloride. The crystals were placed in a well-cooled desiccator under slightly reduced pressure for a short time to remove adhering hydrogen chloride (Found: N, 12.0; Cl, 62.7. $\text{C}_2\text{H}_5\text{NCl}_2$ requires N, 12.3; Cl, 62.3%). *Acetamido dichloride* melts at 6° with partial decomposition, some hydrogen chloride being evolved. Considerable recrystallisation occurs on cooling the resulting liquid to -17°. The crystals are insoluble in the cold in ether, benzene, chloroform, and esters.

In the subsequent experiments the solid acetamido dichloride was directly prepared from the calculated quantity of methyl cyanide dissolved in dry well-cooled ether, the ether being subsequently decanted from the crystals of the dichloride.

Decomposition of Acetamido Dichloride.—(a) *Under reduced pressure.* Methyl cyanide (10 c.c.) was converted into the dichloride as described above. The vessel was then connected to a well-cooled U-tube and this in turn to a water pump to maintain an internal pressure of 11 mm. The vessel containing the dichloride was then gradually warmed. At 40° the solid dichloride lost its crystalline structure and as the temperature rose it gradually disintegrated until at 90° decomposition with effervescence began, leaving a small quantity of a liquid which solidified on cooling. The liquid which condensed in the U-tube yielded methyl cyanide on distillation.

(b) *Slow decomposition at room temperature.* The solid dichloride was allowed to attain room temperature in a flask to which access of moisture was prevented and the resulting liquid left for several months. The liquid became pink and viscous and was then transferred to a vacuum desiccator to remove free methyl cyanide and hydrogen chloride. The white solid residue was extracted with dry ether. The ether solution on concentration yielded transparent needles which, when purified by dissolution in the minimum of alcohol and precipitated with ether, gave colourless plates, m. p. 174—175° (Found: N, 23.8; Cl, 30.3. $\text{C}_4\text{H}_7\text{N}_2\text{Cl}$ requires N, 23.7; Cl, 30.0%). *α -Chloroethylidene acetamidine*

was a hygroscopic solid, stable in dry air, readily soluble in alcohol and sparingly soluble in ether but insoluble in many other solvents. The residue from the ether extraction was insoluble in most solvents but was sparingly soluble in methyl cyanide from which it separated in colourless rosettes, m. p. 80° (decomp.) (Found: N, 17.8; Cl, 45.8. $C_8H_8N_2Cl_2$ requires N, 18.1; Cl, 45.7%). *α*-Chloroethylidene acetamidine hydrochloride was a very hygroscopic solid. It was soluble in alcohol from which solution excess of ether precipitated the above *α*-chloroethylidene acetamidine. These two acetamidine derivatives were obtained more readily, though in lesser yield, from the above-mentioned pink viscous liquid by the addition of dry ether until no further turbidity occurred. The upper ether layer on standing slowly deposited transparent needles of *α*-chloroethylidene acetamidine. The lower layer similarly on standing for several hours deposited the hydrochloride in colourless rosettes.

(c) *Heating under pressure.* Methyl cyanide (15 c.c.) was converted at 16° into the dichloride in a thick-walled tube sealed at one end. The tube with its contents was then sealed and heated at 100° for 6 hours. The resulting viscous liquid which did not yield any crystals on being cooled to -16° was slightly warmed and rapidly transferred to a basin and placed over solid sodium hydroxide in a vacuum desiccator. The resulting crude yellowish solid (14 g., 62%) consisted of *α*-chloroethylidene acetamidine hydrochloride and, after washing with dry ether, had m. p. 78°. It was not further purified but converted into the free chloroethylidene acetamidine by dissolution in alcohol and precipitation with ether as previously described.

Action of Alcohol on Acetamido Dichloride.—Well-cooled absolute alcohol (5 c.c.) was added to the dichloride, obtained from methyl cyanide (4.5 c.c.), and the mixture maintained at -16°. The crystals gradually changed their structure and, after a few hours, became transparent prismatic crystals of the hydrochloride of acetimido ethyl ether. These were removed and a further yield obtained by adding ether to the mother liquor (total, 7.1 g., 58%) (Found: N, 11.5; Cl, 28.9. Calc.: N, 11.3; Cl, 28.8%).

Action of Water on Acetamido Dichloride.—The dichloride obtained from methyl cyanide (20 c.c.) was slowly added to water at 0° in which it gradually dissolved yielding a colourless solution which was immediately fractionally distilled. The portion distilling below 90° was collected and after standing over fused calcium chloride yielded, on distillation, methyl cyanide (14 c.c.), b. p. 82°.

Action of Dimethylaniline on Acetamido Dichloride.—Well-cooled dimethylaniline (50 g.) was added slowly to the dichloride obtained from methyl cyanide (7 c.c.) at -16°. A brisk reaction occurred, methyl cyanide was evolved and a small quantity of a dark blue solid remained. The solid was dissolved in water, made alkaline and steam-distilled. The solid residue, after crystallisation from alcohol, yielded colourless plates of *α*-tri(dimethylaminophenyl)-ethane, m. p. 87° (Found: C, 80.5; H, 9.1; N, 10.0. Calc.: C, 80.6; H, 8.6; N, 10.9%).

Action of Dimethylaniline on α-Chloroethylidene Acetamidine.—A solution of *α*-chloroethylidene acetamidine (14 g.) in dimethylaniline (43 g.) was heated on a water-bath for several hours during which time the mixture became violet in colour. The reaction mass was dissolved in water, made alkaline and distilled in steam. The solid residue after several crystallisations from alcohol yielded crystals of *α*-tri(dimethylaminophenyl)-ethane, m. p. 87° (24.3 g., 53%). A similar result was obtained from the hydrochloride of the above *α*-chloroethylidene acetamidine.

Reaction with Resorcinol.—A well-cooled solution of resorcinol (12 g.) in ether (40 c.c.) together with powdered zinc chloride (4.5 g.) was added to acetamido dichloride prepared from methyl cyanide (7 c.c.) in ether. No reaction occurred at 0° even after several hours. A reaction, however, set in as soon as the mixture attained room temperature, a light brown precipitate being formed. The mixture was poured into water, the ether removed by evaporation and the solution heated to boiling. On cooling crystals of resacetophenone were obtained, m. p. 145° (3.2 g.).

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