reacted *O*-ethylisourea.[8] The insoluble residue consisted of melamine whose melting point was 349°. The yield was 6.2 g., 19% based on reacted *O*-ethylisourea. Both yields based on guanidine were almost quantitative.

Anal. (Biguanide monohydrochloride). Calcd. for $C_2H_8N_5Cl$: N, 50.91, Cl, 25.77. Found: N, 51.13, Cl, 25.53.

To the mother liquor were added 67.0 g. of *O*-ethylisourea and 39.6 g. of guanidine hydrochloride and the resulting solution was heated for 3 hr. at 60°–65° and worked up as described above. As a result, 71.1 g. of pure biguanide monohydrochloride and 6.7 g. melamine were obtained. The yields were 58% and 12%, respectively, based on reacted *O*-ethylisourea.

Another run was carried out using 400 cc. of a methanolic solution of 74.1 g. of *O*-methylisourea, 59.1 g. of guanidine, and 191 g. of guanidine hydrochloride. The solution was heated at 60°–65° for 3 hr. and worked up as described above. As a result, 54.5 g. of pure biguanide monohydrochloride, melting at 224°–225°, and 6.0 g. of melamine, melting at 349°, were obtained. The yields were 54% and 19%, respectively, based on *O*-methylisourea consumed. To the mother liquor were added 55.0 g. of *O*-methylisourea and 38.0 g. of guanidine hydrochloride; the reaction was again carried out in the same manner as described above. As a result, 69.0 g. of pure biguanide monohydrochloride and 6.5 g. of melamine were obtained. The yields were 56% and 17%, respectively, based on *O*-methylisourea consumed. Both yields based on guanidine were almost quantitative.

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Cyanamide Derivatives. LVIII.[1] Formation of Formoguanamine and Guanidine Salt by the Reaction of Formamidine Salt with Dicyandiamide[2]

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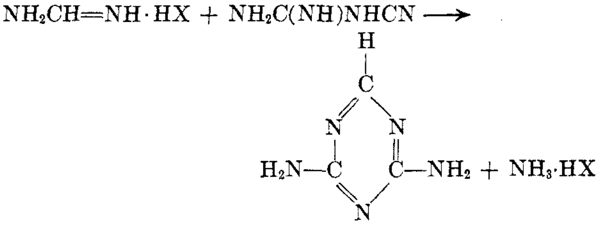
We discovered that the reaction of formamidine with dicyandiamide gave good yields of formoguanamine and guanidine salt.



$$0.5\ NH_2C(NH)NHCN + NH_3\cdot HX \longrightarrow NH_2C(NH)NH_2\cdot HX$$

As a simple method for the preparation of formamidine has been devised by us,[3] we have obtained a convenient route to prepare pure formoguanamine.

EXPERIMENTAL

A sample of 4.03 g. of formamidine hydrochloride and 6.30 g. of dicyandiamide was thoroughly mixed and heated in an oil bath at 150°–160° for 1.5 hr. The mixture melted at 70° and heat evolution was observed at about 160°. Therefore, attention is required to keep the reaction temperature at the desired region by a suitable method. Crystals of the products began to separate during the reaction and a solidification of the total mixture was observed at the end. The reaction products were pulverized, extracted with 30 cc. of water, and filtered. After the residue was washed with 5 cc. of ethanol and dried, it was recrystallized from hot water. A 4.90-g. sample (88%) of formoguanamine was obtained, m.p. 316°. It showed no depression on admixture with an authentic sample.[4] Melting point of the picrate[4] was 247°.

The water extract, combined with ethanol wash, was concentrated to dryness and then extracted with 20 cc. of ethanol.[5] Evaporation of the extract gave 3.71 g., 78% of guanidine hydrochloride, m.p. 184°; m.p. of picrate, 315°.

Better results were obtained by using phenol as a solvent. Here is an example.

An 8.05-g. sample of formamidine hydrochloride and 12.60 g. of dicyandiamide were mixed with 20 g. of phenol and the mixture was heated in an oil bath at 200° for 1 hr. After the reaction, the solvent was removed by distillation and the residue was worked up as described above. A 10.28-g. sample, 93%, of formoguanamine and 8.40 g., 89%, of guanidine hydrochloride were obtained.

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