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The Preparation of 1-Carbamoyl-3-cyanoguanidine and 1-Cyanobiuret from Cyanourea[1)]

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Synopsis. Cyanourea in an aqueous or organic solution which was allowed to stand at room temperature gave 1-carbamoyl-3-cyanoguanidine and 1-cyanobiuret. The reaction was promoted by a mixture of cyanourea and its alkali salt. 1-Cyanobiuret was also obtained quantitatively by the reaction of cyanourea with alkali cyanate.

It has previously been reported[2,3)] that 1-carbamoyl-3-cyanoguanidine (**1**) was obtained by the reaction of 2-methyl-1-carbamoylisourea with cyanamide, while 1-cyanobiuret (**2**) was obtained by the reaction of *S*-methyl 1-thioallophanate with cyanamide.

In this paper, the author will describe convenient methods of synthesizing **1** and **2** from cyanourea (**3**).

When **3** in a crystalline state had been kept for a long time in the atmosphere, the IR spectrum of **3** showed new absorptions at 2200 and 740 cm^{-1}. This fact was explained by the formation of **1**. Potassium, sodium, or copper(II) salt of **3** in the crystalline state, however, could be kept under the same conditions without any transformation. On the other hand, the formation of **1** was found in an aqueous solution of **3** or its alkali salt. The yield of **1** was enhanced by mixing **3** with its alkali salt; especially when their molar ratio was 3/1, **1** and alkali salt of **2** were obtained in 80 and 1% yields respectively when the solution was kept at 35 °C for a week. A similar reaction was also observed in organic solutions. Even if **3** and its alkali salt were slightly soluble in ethanol, dioxane and acetonitrile, **1** and the alkali salt of **2** were obtained in low yields. The yield of the alkali salt of **2** was enhanced by using DMF or sulfolane as a solvent. Only **3** in sulfolane, however, gave **1** and ammelide, which was the cyclic compound of **2**, in 11 and 14% yields respectively. This fact suggests that the free state of **2** was unstable and cyclized to ammelide, while the alkali salt of **2** was stable. **1**, the alkali salt of **2**, and ammelide were confirmed by comparing their IR spectrum and melting points with those of an authentic sample.[2,3)] These results are summarized in Table 1.

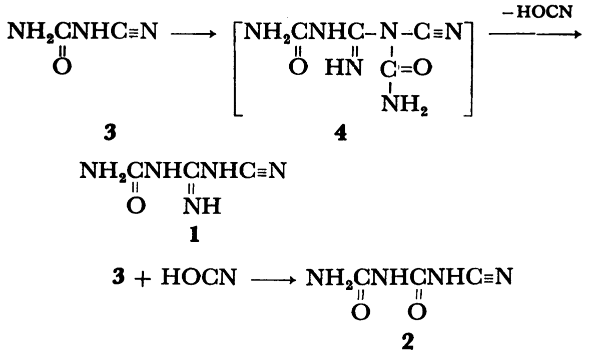
Table 1. Preparation of 1 and 2 from 3

3		Solvent	Products (Yield/%[b)])	
Free[a)]	K salt[a)]		1	2[c)]
1	0	H_2O	6	0
0	1	H_2O	11	0
1	1	H_2O	68	1
3	1	H_2O	80	1
1	1	EtOH	9	1
1	1	Dioxane	24	3
1	1	CH_3CN	22	4
1	1	DMF	28	30
1	1	Sulfolane	22	38
3	1	Sulfolane	31	27
1	0	Sulfolane	11	14[d)]

a) Molar ratio. b) Yield based on 2 $3 \rightarrow 1+2$. c) Yield of K salt of **2**. d) Yield of ammelide.

Though **1** could be constituted by the addition of cyanamide to **3**, cyanamide was not detected in any case and did not react with **3**. On the other hand, **2** was obtained quantitatively by the reaction of **3** with alkali cyanate in water, DMF, and sulfolane at room temperature. Ammonia was detected in the aqueous solution, but was not detected in organic solutions. It may be suggested that the decomposition of cyanic acid to ammonia and carbon dioxide caused the low yield of **2** in the aqueous solution.

These results suggest that **3** was dimerized to the labile intermediate (**4**), that **1** was formed by the elimination of cyanic acid from **4**, and that then cyanic acid reacted with the remaining **3** to form **2**.



Experimental

The melting points are uncorrected. The IR spectra were taken with a Hitachi EPI-2 spectrometer.

Materials. The **3** was prepared by the alkali hydrolysis of cyanoguanidine.[4)] The other reagents were commercially available and were used after purification if necessary.

Reaction of 3 in an Aqueous Solution. A mixture of **3** (1.70 g) and its potassium salt (2.46g) in water (10ml) was allowed to stand for a week at 35 °C. The precipitate was then filtered off and washed with a small amount of water to give 1.72 g (68%) of **1**;[2)] mp>360 °C. IR (KBr) 2200, 2100, 1700, 1650, 1595, 770, and 740 cm^{-1}. After the pH had been made 3.5—4.0 with 6 mol dm^{-3} of nitric acid, the filtrate was evaporated and extracted with DMF. The residue was dissolved in water, and copper(II) chloride was added to form copper(II) salt of **2** (0.1 g, 1%);[3)] mp>360 °C. Found: N, 28.41%. Calcd for $C_6H_6N_8O_4Cu \cdot 4H_2O$: N, 28.75%.

In the cases of ethanol, dioxane, and acetonitrile solutions, the method was similar to that described above.

Reaction of 3 in DMF Solution. A mixture of **3** (1.70 g) and its potassium salt (2.46 g) in DMF (10 ml) was allowed to stand for a week at 35 °C. The precipitate, potassium salt of **2**, was then filtered off and washed with methanol. The yield was 1.98 g (30%). The filtrate was evaporated under reduced pressure. The residue was dissolved in water, and the insoluble crystals, **1**, were filtered off. The yield was 0.70 g (28%).

In the case of the sulfolane solution, the method was similar to that described above.

Reaction of 3 with Potassium Cyanate. **3** (2.55g) and potassium cyanate (3.05g, as the purity was 80%) were dissolved in water (10ml). The reaction mixture was then kept at room temperature for 24 h. Potassium salt of **2** was subsequently deposited by the addition of 2-propanol. The yield was 4.46g (90%).

In the case of DMF and sulfolane, potassium salt of **2** was deposited quantitatively from the solution.

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