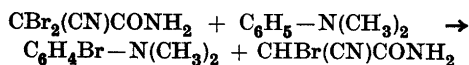


On the Synthesis of Monobromocynoacetamide

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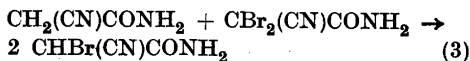
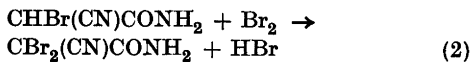
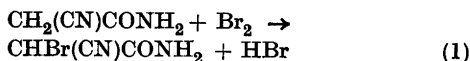
Although dibromocynoacetamide was prepared by Hesse¹ as early as 1896, the monobromoderivative was not prepared until 1922 by Gupta and Thorpe². They prepared monobromocynoacetamide by partial debromination of dibromocynoacetamide by means of dimethylaniline:



A solution of dibromocynoacetamide and dimethylaniline in benzene was kept at 80° for five hours. In this way monobromocynoacetamide and *p*-bromoaniline were obtained in a yield of 55 per cent of the theoretical amount.

Dibromocynoacetamide is obtained in a simple way by bromination of cyanoacetamide in aqueous solution in the presence of sodium acetate at low temperature. The dibromo-product separates during the reaction. Gupta and Thorpe stated, that all attempts to prepare monobromocynoacetamide by direct bromination were fruitless.

However, a more careful study of the bromination reaction indicates, that the following three competitive reactions take place:

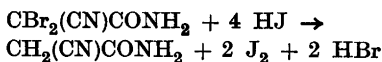
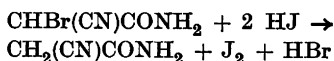


At a low temperature the reactions (1) and (2) are very fast; reaction (3) is evidently slow. At a higher tempe-

ature, however, reaction (3) is also fast. On bromination of cyanoacetamide in the cold, the formation of the dibromoderivative is also favoured by the fact, that it is less soluble than the monobromoderivative and thus quickly separates from the solution. It is likely, that a bromination of cyanoacetamide at a high temperature would lead mainly to the monobromoderivative, when equimolar parts of amide and bromine are used.

The best method for preparing monobromocynoacetamide is, however, to make use exclusively of reaction (3). Thus, on heating equimolar parts of cyanoacetamide and dibromocynoacetamide in aqueous solution, a good yield of the monobromo-product is obtained.

Both mono- and dibromocynoacetamide are quantitatively debrominated by an acidified potassium iodide solution:



These reactions are useful for the analytical determination of bromocynoacetamides, since the liberated iodine can be titrated with sodium thiosulfate.

Experimental. 6.3 g (0.075 mole) of cyanoacetamide and 18.2 g (0.075 mole) of dibromocynoacetamide were dissolved in 50 ml of hot water, and the solution was boiled for about two minutes, treated with some decolorizing charcoal and filtered hot. On cooling, monobromocynoacetamide separated as white needles. Yield 20 g (80 %). The product may be recrystallized from hot water or preferentially from alcohol. M.p. 121–122°.

0.1929 g: 23.30 ml 0.1018 N Na₂S₂O₃.
0.2009 g: 24.19 » 0.1013 » HCl (Kjeldahl)
C₃H₃ON₂Br = 163.0. Calc. N 17.19, Br 49.03
Found » 17.09, » 49.12

1. Hesse, B. *Am. Chem. J.* **18** (1896) 723.
2. Gupta, B. M., and Thorpe, J. F. *J. Chem. Soc.* **121** (1922) 1896.

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