Analysis. Subs., 0.2030, 0.1716; AgBr, 0.2902, 0.2456. Calc. for $C_6H_{12}OBr_2$: Br, 61.5. Found: 60.8. 60.9.

Summary.

γ,γ'-Dichloro- and dibromo-dipropyl ethers have been prepared and their physical properties recorded.

URBANA, ILL.

[CONTRIBUTION FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, LABORATORY OF ORGANIC CHEMISTRY.]

THE ACTION OF AMMONIA WATER ON DICYANDIAMIDE.[1]

BY TENNEY L. DAVIS.

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Dicyandiamide hydrolyzed with sulfuric acid produces one molecule of guanidine sulfate and one of ammonium sulfate, and guanidine sulfate may be obtained in satisfactory yields by this process.[2] But dicyandiamide is most readily prepared from Lime-nitrogen, from which ammonia may be produced more readily by simpler methods—and the production of ammonia from dicyandiamide in a process where guanidine is the object might well be regarded as the virtual loss of one quarter of the nitrogen which has earlier been "fixed" in the form of Lime-nitrogen and of dicyandiamide. We[1] have studied the reaction of ammonia on dicyandiamide with the expectation that it would lead to the formation of guanidine or of guanidine carbonate without the agency of mineral acid, and in the hope that it might perhaps lead to the formation of two molecules of guanidine from one of dicyandiamide.

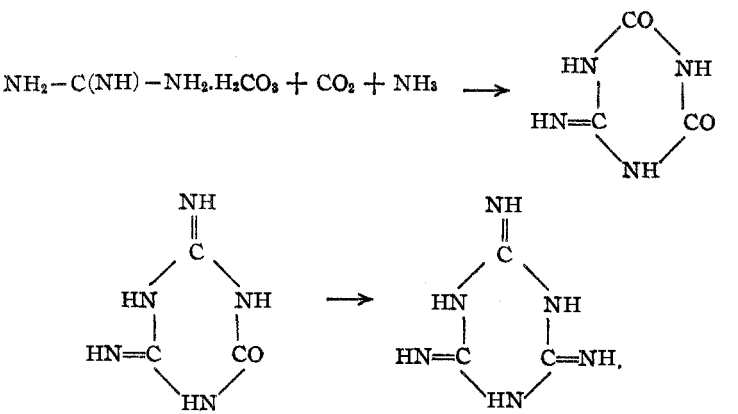
We find that the action of ammonia water on dicyandiamide when the materials are heated together in a sealed tube is simple hydrolysis, water only being effectively involved and the dicyandiamide being converted first into guanylurea and later into guanidine carbonate. We have followed the progress of the reaction by precipitating the solution with ammonium picrate and have been able to judge from the melting point whether the precipitate consisted of picrate of guanidine or of picrate of guanylurea. After relatively short durations of heating at 150°, guanylurea was found in the product and the reaction mixture contained no appreciable amount of insoluble material. When the reaction was of longer duration or at a higher temperature, guanidine was formed and the reaction mixture contained considerable quantities of ammeline and ammelide. When the reaction was carried on for a still longer time, no guanidine was found and

[1] This investigation was carried out in connection with a contract between the Ordnance Department and the Massachusetts Institute of Technology, and the present paper is published by permission of the Chief of Ordnance. In this work I have been assisted by William S. Johnson. T. L. D.

[2] THIS JOURNAL, 43, 669 (1921).

a large quantity of melamine was isolated along with the ammeline and ammelide.

Bamberger[3] reports that dicyandiamide heated with water at 160–170° yields carbon dioxide, ammonia and ammelide. He reports also the formation of ammelide by heating dicyandiamide with ammonium carbonate at 120°. Either reaction would account for the formation of ammelide under the conditions of our experiments. The formation of melamine in our experiments and the disappearance of the guanidine carbonate which is first formed would seem to indicate that the melamine is produced from the guanidine salt. Smolka and Friedreich[4] report that guanidine carbonate at 180–190° gives carbon dioxide, ammonia and melamine, and that dicyandiamide and ammonium carbonate at 160° give the same products. We find that guanidine carbonate heated with ammonia water at 160° for 2 hours gives melamine—and believe that the formation of the mono-, di-, and tri-imides of cyanuric acid in our experiments is plausibly explained by supposing that guanidine carbonate reacts with carbon dioxide and ammonia to form first ammelide (the mono-imide), then ammeline (the di-imide), and finally melamine (the tri-imide), as follows.



When Lime-nitrogen is leached with hot water and the solution is evaporated, dicyandiamide is formed, but more or less ammonia is always produced, and the tailings from the crystallization of dicyandiamide are strongly basic, viscous and caustic liquids which deposit insoluble white materials. The foregoing considerations help to explain the genesis of these products.

Discussion of Experiments.

Effect of Ammonia Water.—A systematic series of sealed tube experiments, with 4 g. of dicyandiamide and 7.5 cc. of ammonia water (sp. gr. 0.90) was carried out.

[3] Bamberger, *Ber.*, **16**, 1074, 1703 (1883).

[4] Smolka and Friedreich, *Monatsh.*, **10**, 91, 93 (1889).

After the heating, the contents of the tubes were rinsed out, filtered, and precipitated by the addition of ammonium picrate solution. The precipitated picrate was washed and dried, and its melting point was determined. Guanylurea picrate turns deep red at 235° and at 265° it turns black and decomposes but does not melt. Guanidine picrate melts with decomposition at 310–320°. The results were as follows:

Temperature. ° C.	Time. Hours.	Weight of picrate. G.	Melting point. ° C.
100	2	0	——
	4	0	——
	6	0	——
	8	0	——
150	1	0	——
*	2	trace	——
*	3	0.4	265 decomp.
*	4	1.1	
*	5	1.6	
*	6	1.4	
*	7	0.9	
*170	8	0.7	310–320
*	9	0.6	
180	0.5	0.8	
*	1	1.8	
*	1.5	1.8	
*	1	2.2	
*200	10 min.	0.4	
*	20	—— exploded	——
	1 hour	3.2	
	1.5	1.6	310–320
	2	0.6	
	2.5	—— exploded	——

In the experiments which are marked with an asterisk (*) a white insoluble compound was obtained. This was filtered off before precipitating with ammonium picrate, and was later identified as a mixture of ammelide and ammeline. Since the yields of guanidine were poor, it was judged that too much ammonia water had perhaps been used, so making the reaction mixture too dilute in dicyandiamide, and another series of experiments was carried out to test this point. Four g. of dicyandiamide was used in each experiment.

Volume of ammonia water (0.90). Cc.	Time. Hours.	Temperature. ° C.	Weight of picrate. G.	Melting point. ° C.
*3	1	160	3.5	310–320
*4			3.4	
*5			4.1	
*4		170	2.5	
*4		180	2.4	
5			1.1	265
5	2	150	—— exploded	——
5	3		3.9	265

Since the best yield was obtained by heating 4 g. of dicyandiamide with 5 cc. of ammonia water at 160° for 1 hour, an experiment with the materials in the same relative proportion was tried on a larger scale. Fifty g. of dicyandiamide and 62.5 cc. of ammonia water (0.90) were heated in an autoclave at 160° for 1 hour, but the autoclave was heavy and required several hours to cool before it could be opened, and the high temperature was actually maintained for much more than 1 hour. The reaction mixture contained no guanidine; it yielded a considerable quantity of the familiar insoluble white material, together with 13.2 g. of a substance which crystallizes from water in white glistening leaflets or in thick rhomb-shaped plates, which does not melt below 360°, and which has been identified as melamine by its properties and by analysis.

Guanidine Carbonate and Ammonia Water.—To test the hypothesis that the melamine was produced by the secondary reaction of ammonia on the guanidine carbonate first formed 1.5 g. of guanidine carbonate (from the thiocyanate) and 5 cc. of 6 *N* ammonia water were heated together in a sealed tube at 160° for 6 hours. The reaction mixture yielded about 1 g. of melamine, identified by its reactions and properties. It contained not more than traces of ammelide and ammeline.

Action of Sodium Carbonate.—To confirm the idea that the conversion of dicyandiamide to guanidine by the action of ammonia water might be due to the action of hydroxyl ions rather than to that of the ammonia itself, a tube containing 2 g. of dicyandiamide and 6.5 cc. of 3 *N* sodium carbonate solution was heated for 1 hour at 160°. The precipitated picrate weighed 1.9 g. and melted with decomposition at 310-320°.

Summary.

Ammonia water acts on dicyandiamide in the same way that other hydrolytic agents do, converting it first into guanylurea and later into guanidine carbonate. The guanidine carbonate enters into a secondary reaction with the ammonia, and is converted finally into melamine.

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