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Some Ammonolytic Reactions[1]

BY EDWARD C. FRANKLIN

Ammono Carbonic Acid Esters. Esters of Cyanamide.—It has been shown that cyanamide is an ammono carbonic acid, which is to say that it is a derivative of ammonia in the same sense that ordinary carbonic acid may be said to be a derivative of water.[2] Such being the case it follows that the alkyl and aryl derivatives of cyamamide are to be regarded as ammono carbonic acid esters.

The methods for the preparation of diethylcyanamide, for example, and its behavior toward hydrolyzing agents are in accordance with the assumption that it is a diethyl ammonocarbonate. It has been prepared by the action of disodium cyanamide on ethyl iodide, $C_2H_5I + Na_2NCN = (C_2H_5)_2NCN + 2NaI$, by the interaction of cyanogen bromide, a carbonic acid bromide, and diethylamine, $NCBr + (C_2H_5)_2NH = (C_2H_5)_2NCN + HBr$, and is hydrolyzed by the action of aqueous hydrochloric acid to diethylamine, carbon dioxide and ammonia, $(C_2H_5)_2NCN + H_2O = (C_2H_5)_2NH + HOCN \xrightarrow{+H_2O} CO_2 + NH_3$. Looked upon as an ammono carbonic acid ester diethylcyanamide should undergo ammonolytic decomposition under the action of potassium amide in liquid ammonia solution by the equation $(C_2H_5)_2NCN + 2KNH_2 = (C_2H_5)_2NH + K_2NCN + NH_3$, which represents a reaction closely analogous to the hydrolytic reaction involved in the conversion of ethyl aquocarbonate into aquo ethyl alcohol and potassium aquocarbonate under the action of aqueous potassium hydroxide, $OC(OC_2H_5)_2 + 2KOH = K_2CO_3 + 2C_2H_5OH$.

Accordingly Griswold accomplished the ammonolysis of the following esters of cyanamide by warming them, at 35°, in liquid ammonia solution with potassium amide. The percentage yields of the ammonolytic products are given under K_2CN_2 and R_2NH.

Ester	Formula	K_2CN_2		R_2NH		
Diethylcyanamide	$(C_2H_5)_2NCN$	100		64	72	75
Di-*n*-propylcyanamide	$(C_3H_7)_2NCN$	99	98	86	78	
Diisobutylcyanamide	$(C_4H_9)_2NCN$	101	100	75	67	

Since dipotassium cyanamide is insoluble in liquid ammonia, its quantitative separation from the reaction mixture was easily accomplished. The quantitative recovery of the soluble amines from a large excess of ammonia is not a simple matter.

Esters of Guanidine.—The alkyl and aryl derivatives of guanidine, like those of cyanamide, are ammono carbonic acid esters and as such

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(1) The laboratory work upon which this report is based was done by Christian W. Niemann, Thesis, Stanford University, 1926, Gale G. Griswold, Thesis, Stanford University, 1926, and by Faw Yap Chuck.

(2) Franklin, THIS JOURNAL, **44**, 490 (1922).

should be susceptible to ammonolytic decomposition in a manner resembling the hydrolytic decomposition of the aquocarbonates. But one such compound has been studied in respect to its ammonolytic behavior in liquid ammonia solution.

N,N′,N″-Triphenylguanidine, $C_6H_5N{=}C(NHC_6H_5)_2$.—Beyond the formation of a dipotassium salt[3] potassium amide is without action on triphenylguanidine even when the solution is heated. When, however, the ester is heated at 200° in liquid ammonia solution with hydrochloric acid (ammonium chloride), it is ammonolyzed to guanidine and aniline as represented by the equation

$$C_6H_5N{=}C(NHC_6H_5)_2 + 3NH_3 = HN{=}C(NH_2)_2 + 3C_6H_5NH_2$$

A typical experiment gave 82% of the calculated amount of aniline based on the preceding equation, and an abundant yield of guanidine isolated in the form of its picrate. N,N′,N″-Triphenylguanidine, it may be recalled, is hydrolyzed by the action of aqueous hydrochloric acid at 250° to aniline, carbon dioxide and ammonia.

Metallic Salts of Acid Guanidine Esters.—Several metallic salts of N,N′,N″-triphenylguanidine, which is an acid ester of an ammono carbonic acid, have been prepared.[3]

When potassium amide and dialkylcyanamides are brought together in cold liquid ammonia solution, products are formed as represented by the equation $R_2NCN + KNH_2 = R_2NC(NH)NHK$. The following named and formulated potassium salts of dialkylguanidines have been prepared.

		Analyses, %			
		Metal		Nitrogen	
Ester-salt	Formula	Calcd.	Found	Calcd.	Found
K-Dimethylguanidine	$(CH_3)_2NC(NH)NHK$	31.2	31.6	33.6	34.4
			31.5		34.0
K-Diethylguanidine	$(C_2H_5)_2NC(NH)NHK$	25.5	25.6	27.4	27.0
			25.2		27.2
K-Diisopropylguanidine	$(C_3H_7)_2NC(NH)NHK$	21.5	21.5	23.2	23.1
			21.4		23.3
			21.2		
K-Diisobutylguanidine	$(C_4H_9)_2NC(NH)NHK$	18.7	18.4	20.1	20.1
			18.9		19.4
			18.6		20.0
K-Diisoamylguanidine	$(C_5H_{11})_2NC(NH)NHK$	16.5	16.1	17.7	18.0
			16.7		17.8
Na-Diethylguanidine	$(C_2H_5)_2NC(NH)NHNa$	16.4	16.2	30.0	30.5
			16.5		30.3
Na-Diisobutylguanidine	$(C_4H_9)_2NC(NH)NHNa$	11.9	11.6	21.8	21.3
			12.0		21.4

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(3) Franklin, THIS JOURNAL, **44**, 490 (1922).

Unfortunately nothing is known concerning these compounds beyond the facts that they are formed by the direct addition of the alkali metal amides to the respective dialkylcyanamides, that they have been obtained well crystallized and of sharply definite composition and that they are fairly soluble in liquid ammonia. Circumstances brought an end to Griswold's work before he had determined definitely whether or not these compounds are derivatives of guanidine. That they are, however, is highly probable.

Aquo-Ammono-Carbonic Acid Esters.—Urea is an aquo-ammono carbonic acid of which O-esters and N-esters are known. The ammonolytic behavior of two urea esters has been observed.

N-Methylurea, $H_2NCONHCH_3$.—Methylamine, urea and guanidine have been identified as products of the ammonolytic decomposition of methylurea.

N,N′-Diphenylurea, $OC(NHC_6H_5)_2$.—In accordance with the equation $OC(NHC_6H_5)_2 + 2NH_3 = OC(NH_2)_2 + 2C_6H_5NH_2$, Niemann[4] obtained a 77% yield of aniline together with undetermined amounts of urea when he heated this phenyl aquo-ammono-carbonate in liquid ammonia solution with ammonium chloride. Guanidine was formed at the same time as the result of the ammonolysis of a portion of the urea formed.[5] Ammonia in alcoholic solution at 150° ammonolyzes diphenylurea to aniline and urea. Under the action of aqueous hydrochloric acid the ester is hydrolyzed to aniline, carbon dioxide and ammonia.

Carbazylic Acid Esters and Carboxazylic Acid Esters.—As is well known ammonium acetate when heated is partly converted into acetamide. An aquo acetic acid is thereby ammonolyzed to an aquo-ammono acetic acid. Chuck found that when either ammonium acetate or acetamide is heated in liquid ammonia solution with ammonium chloride, liberal yields of acetamidine are formed. Inversely, acetamidine, which is an ammono acetic acid, is readily hydrolyzed first to acetamide and thence to acetic acid. The reversible reactions involved are represented by the equation

$$CH_3COOH \xrightarrow[-H_2O]{+NH_3} CH_3CONH_2 \xrightarrow[-H_2O]{+NH_3} CH_3C(NH)NH_2.$$

Niemann found that diphenylacetamidine and diphenylbenzamidine, when heated with ammonium chloride in liquid ammonia solution, are ammonolyzed, the one to acetamidine and aniline, $CH_3C(NC_6H_5)NHC_6H_5 + 2NH_3 = CH_3C(NH)NH_2 + 2C_6H_5NH_2$, the other to benzamidine and aniline, and that acetanilide under similar treatment gives abundant yields of acetamidine and aniline. That acetamidine was obtained instead of acetamide is accounted for by the above-noted observation by Chuck to the effect that acetamide is ammonolyzed to acetamidine under the condi-

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(4) Niemann, Thesis, Stanford University, 1926.

(5) Blair, THIS JOURNAL, **48**, 87 (1926).

tion of Niemann's experiments. By the action of dilute aqueous acids or alkalies, acetanilide is hydrolyzed to aquo acetic acid and aniline.

Acid Chlorides.—Benzotrichloride, $C_6H_5COCl_3$, is hydrolyzed by the action of water at 150° to aquo benzoic acid. It is simultaneously hydrolyzed and ammonolyzed by the action of aqua ammonia at 130° to aquo benzoic acid, aquo-ammono-benzoic acid (benzamide) and benzoic anammonide (benzonitrile). Niemann obtained a 75% yield of benzonitrile by allowing a liquid ammonia solution of benzotrichloride to stand at laboratory temperatures for some time. When he heated such a solution for a time at 100°, good yields of monomolecular and trimolecular benzonitrile were obtained.

Summary

An account is given of the ammonolytic behavior of three dialkylcyanamides, of triphenylguanidine, of two N-esters of urea, of acetic acid and acetamide, of diphenylacetamidine and diphenylbenzamidine, of acetanilide and of benzotrichloride.

It is shown that the dialkylcyanamides unite with alkali metal amides at low temperatures in liquid ammonia solution to form metallic salts of dialkylguanidines.

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Metallic Salts of Carboxazylic Acids[1]

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In this Laboratory we have come to use the general name carbylic acids to include the closely related carboxylic acids, the acid amidines and the acid amides and to speak of the three classes of compounds as carboxylic acids, carbazylic acids and carboxyazylic acids, respectively. Acetic acid, acetamidine and acetamide are examples of the three classes of compounds. Acetic acid and acetamidine we regard as acetic acids belonging, respectively, to an oxygen system and a nitrogen system of compounds.[2] The first acid, as a derivative of water, is an aquo acetic acid, the second, as a derivative of ammonia, is an ammono acetic acid, while acetamide, which may be said to be derived at the same time from water and ammonia, is an aquo-ammono acetic acid.

In many ways the acid amidines and the acid amides closely resemble the carboxylic acids. For example, Franklin and Stafford[3] showed that

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(1) The laboratory work upon which this report is based was done by Ruth V. Fulton, Thesis Stanford University, 1925.

(2) Franklin, *Am. Chem. J.*, **47**, 285 (1912); Fernelius and Johnson, *J. Chem. Educ.*, **5**, 664, 828 (1928); **7**, 1291, 1602, 1850 (1930).

(3) Franklin and Stafford, *Am. Chem. J.*, **28**, 83 (1902).