Some Diacid Salts of Aminoguanidine and Methyl Aminoguanidine[1]

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There are some references in the literature to diacid salts of aminoguanidine. Lieber and Smith[4] mention aminoguanidinium dinitrate and aminoguanidinium dichloride, but give no details of the preparation. In another article, Thiele[5] also mentions the preparation of aminoguanidinium dinitrate. In this same article, Thiele also mentions the preparation of neutral aminoguanidine sulfate as well as diaminoguanidine sulfate. This present article reports a generalized method for the preparation of these and other diacid salts of aminoguanidine. This procedure is also applied in the preparation of a diacid salt α-methyl-γ-aminoguanidine. The melting points of the salts prepared are included.

Experimental

Aminoguanidinium bisulfate (0.1 mole) was dissolved in 100 ml. of hot water and to this was added a solution containing 0.1 mole of the barium salt of the acid corresponding to the diacid salt in preparation. To the above mixture was added a considerable excess of the corresponding concentrated acid. After one hour digestion on a hot plate, the barium sulfate was separated by filtration and the filtrate was evaporated on a steam-bath until crystallization started. The solution was then cooled and the crystals separated by filtration, dried *in vacuo*, and analyzed.

The methylaminoguanidine was prepared from methyl nitroguanidine by the method of Lieber and Smith.[6] Methylaminoguanidine bicarbonate was prepared by treating the methylaminoguanidine acetate obtained in the above reaction with potassium bicarbonate and carbon dioxide in isopropyl alcohol at a temperature of −10°. A 99% yield was obtained and the melting point of the bicarbonate was observed to be 151.5–152°.

To 6 g. of methylaminoguanidine bicarbonate (0.04 mole) in 60 g. of isopropyl alcohol was added 32 g. (0.32 mole) of 37% hydrochloric acid. The solution was treated with carbon black and filtered. After cooling to −18°, needle-like crystals separated out in clusters. These crystals were removed by filtration, washed with cold solvent, dried *in vacuo* for eighteen hours and analyzed. This material proved to be α-methyl-γ-aminoguanidinium dichloride.

TABLE I

		% N_2H_4		% Anion		Melting
		Found[a]	Calcd.	Found	Calcd.	point, °C.
AG.[b]	Dichloride	21.52	21.95	47.80	47.92	183–183.5
AG.	Dibromide	13.84	13.58	67.33	67.76	200–205
AG.	Diiodide	12.23	12.02	76.19	76.93	115–118
AG.	Dinitrate	16.02	16.34	61.97[c]	61.98	168 dec.
MAG.[d]	Dichloride	19.96	19.89	43.87	44.06	170.5–174

[a] By the method of Smith and Wheat.[7] [b] Aminoguanidinium. [c] By nitron precipitation. [d] α-Methyl-γ-aminoguanidinium.

Table I lists the diacid salts of aminoguanidine and α-methyl-γ-aminoguanidine prepared, their analyses and their melting points.

From these experiments it seems that aminoguanidine and α-methyl-γ-aminoguanidine will accept two protons in strongly acid solutions. Further work is in progress to gain more knowledge of the ionic species that exist in water solutions of these salts.

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[4] Lieber and Smith, *Chem. Rev.*, **25**, 217 (1939).

[5] Thiele, *Ann.*, **270**, 28 (1892).

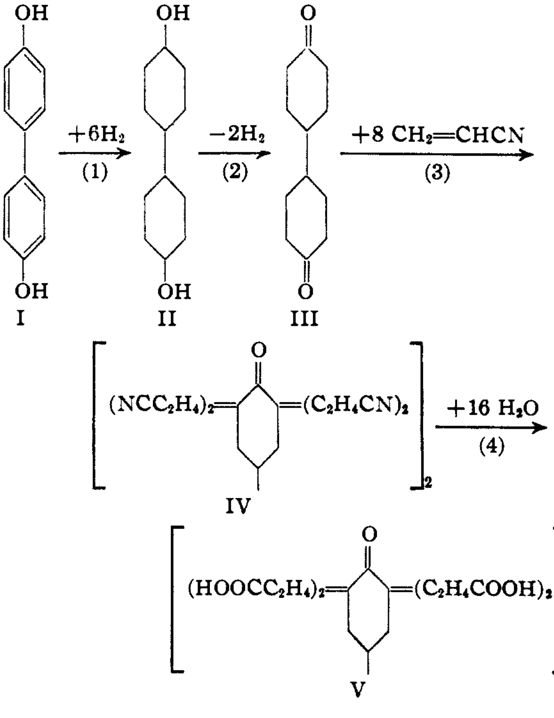
[6] Lieber and Smith, THIS JOURNAL, **59**, 2287 (1937).

[7] Smith and Wheat, *Ind. Eng. Chem., Anal. Ed.*, **11**, 200 (1939).

Synthesis of an Octabasic Carboxylic Acid

BY J. R. SCHAEFGEN AND P. J. FLORY

Dicyclohexanoneoctapropionic acid (V) has been prepared for use as the multifunctional reactant in the synthesis of octachain polymers.[1] This acid is of interest because, so far as we are aware, it is the first example of a stable octabasic carboxylic acid.[2] It has been synthesized from *p,p'*-diphenol (I) by the following series of reactions.



The over-all yield was about 6%. Complicating side reactions occurring in steps (1) and (2) are largely responsible for the low yield. Compounds III, IV and V are new.

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[1] J. R. Schaefgen and P. J. Flory, THIS JOURNAL, **70**, 2709 (1948).

[2] Beilstein, "Handbuch der organischen Chemie," IV ed., Vol. IX, 1st Suppl., Julius Springer, Berlin, 1932, p. 446, lists diphenyloctacarboxylic acid—(2,4,5,2',4',5,'x,x) which, however, loses carbon dioxide and water when heated to 110°.