

Some Diacid Salts of Aminoguanidine and Methyl Aminoguanidine¹

BY JOHN J. PITHA,² HARRY HUGHES, JR., AND G. B. L. SMITH³

There are some references in the literature to diacid salts of aminoguanidine. Lieber and Smith⁴ mention aminoguanidinium dinitrate and aminoguanidinium dichloride, but give no details of the preparation. In another article, Thiele⁵ 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.

TABLE I

		% N ₂ H ₄		% Anion		Melting point, °C.
		Found ^a	Calcd.	Found	Calcd.	
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.

(1) This paper is abstracted from the theses submitted to the Graduate Faculty of the Polytechnic Institute of Brooklyn by Mr. Pitha and Mr. Hughes in June, 1942, and June, 1944, in partial fulfillment of the requirements for the degree of Master of Science in Chemistry.

(2) Present address: Kedzie Chemical Laboratories, Michigan State College, East Lansing, Mich.

(3) Present address: Inorganic Chemistry Section, Science Department, U. S. Naval Ordnance Test Station, Inyokern, California.

(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).

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

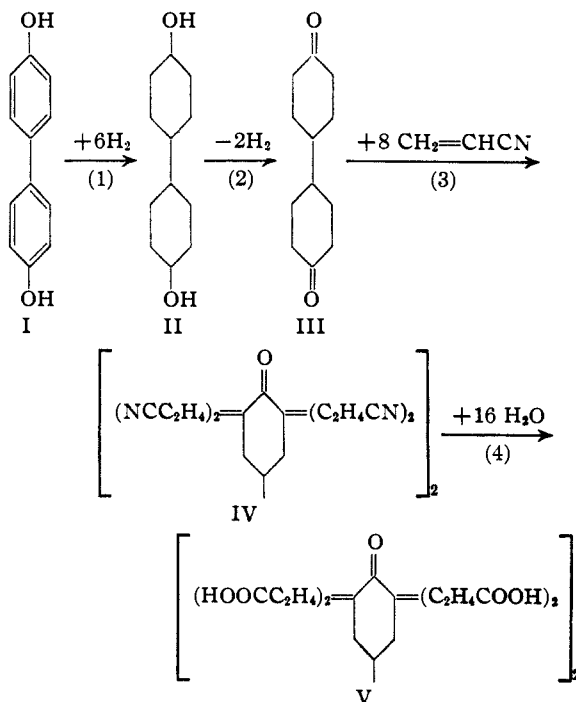
From these experiments it seems that aminoguanidine and α -methyl- γ -aminoguanidine will accept two protons in strongly acid solutions. Further work is in progress to gain more knowledge of the ionic species that exist in water solutions of these salts.

DEPARTMENT OF CHEMISTRY
POLYTECHNIC INSTITUTE OF BROOKLYN
BROOKLYN, NEW YORK RECEIVED FEBRUARY 5, 1948

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.

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

(2) Beilstein, "Handbuch der organischen Chemie," IV ed., Vol. 1X, 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° .

Experimental

4,4'-Diketodicyclohexyl (III).—Crude 4,4'-dihydroxydicyclohexyl (II), prepared from *p,p'*-diphenol (I) by high pressure hydrogenation over Raney nickel catalyst by the method of Adkins,³ was converted to (III) as follows. A mixture of 50 g. of (II), 50 ml. of diphenyl ether, and 13 g. of copper chromite catalyst was heated for three hours at 260–270°. During this time 70% of the theoretical quantity of hydrogen necessary for complete conversion to the diketone (III) was evolved. The reaction mixture was cooled and dissolved in chloroform. The solution was filtered to remove catalyst, and the filtrate was distilled. The fraction boiling from 144–170° (1 mm.) (which solidified on cooling) contained the product. Several crystallizations from mixtures of acetone and *n*-hexane gave a 16.5% yield of diketone (III); m. p. 116.5–118°. The purest material melted from 118–119°.

*Anal.*⁵ Calcd. for C₁₂H₁₈O₂: C, 74.18; H, 9.33. Found: C, 74.62; H, 9.53.

The diketone formed a dioxime; m. p. ca. 290° (copper block). The dioxime was practically insoluble in all ordinary organic solvents.

Anal. Calcd. for C₁₂H₂₀O₂N₂: C, 64.26; H, 8.98. Found: C, 64.82; H, 9.60.

bis-[3,3,5,5-Tetra-(β-cyanoethyl)-4-ketocyclohexyl] (IV).—To a solution of 18.4 g. of 4,4'-diketodicyclohexyl (III) in 80 ml. of dioxane containing 1.3 ml. of Triton B (38% aqueous solution of trimethylbenzylammonium hydroxide) there was added dropwise 41.5 g. of acrylonitrile (3% excess). The reaction mixture was vigorously stirred and maintained at room temperature by use of a water-bath during the addition. Yellow crystals were deposited as the reaction proceeded. After stirring overnight, the mixture was diluted with water and filtered, and the precipitated product was washed with acetone. Two or three crystallizations from formamide-nitromethane mixtures (ca. 80–20) gave 39 g. (66%) of white crystalline "octanitride" (IV); m. p. 280–287°.

Anal. Calcd. for C₃₆H₄₂O₂N₈: C, 69.86; H, 6.83; N, 18.11. Found: C, 69.86; H, 7.16; N, 18.05.

bis-[3,3,5,5-Tetra-(β-carboxyethyl)-4-ketocyclohexyl] (V) (Dicyclohexanoneoctapropionic Acid).—A suspension of 6.83 g. of the "octanitride" (IV) in 35 ml. of 85% aqueous phosphoric acid was heated for forty-eight hours on the steam-bath. Suspended matter dissolved as the hydrolysis proceeded, after which the clear solution gradually changed to a semi-solid mass. When hydrolysis was substantially complete, the reaction mixture was diluted with water, cooled and filtered. The precipitate was dissolved in alkali and the solution filtered. The filtrate on acidification gave fine white needles of the desired acid which, after recrystallization from water, weighed 5.82 g. (66% yield). Further purification consisting of (1) treating the acid with activated charcoal, (2) boiling in dilute hydrochloric acid solution (to hydrolyze any remaining nitrile groups) and (3) crystallizing from water followed by drying at 110° under reduced pressure was found necessary to secure a pure product; m. p. 274–277°, neutral equivalent 96.6, calcd. 96.3. On standing for several months in a desiccator, the melting point rose to 286–288°, probably due to a change in crystalline form.

Anal. Calcd. for C₃₆H₅₀O₁₈: C, 56.08; H, 6.54. Found: C, 56.05; H, 6.47.

RESEARCH LABORATORY

GOODYEAR TIRE AND RUBBER CO.

AKRON 16, OHIO

RECEIVED DECEMBER 29, 1947

(3) H. Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, 1937, p. 58.

(4) All melting points are corrected.

(5) Analyses by Mr. Carl Parks of this Laboratory.

Preparation of Triethylacetonitrile and Triethylacetic Acid

BY CONRAD SCHUERCH, JR.,^{1,2} AND ERNEST H. HUNTRESS

Synthetic methods for the preparation of tertiary aliphatic acids or their simple relatives have not been correlated in the prior literature. They include, however, alkylation of aliphatic nitriles with alkyl bromides or chlorides in presence of sodamide,³ and the carbonation of RMgX compounds.⁴

For tertiary acids above dimethylethylacetic, carbonation of the appropriate RMgX compounds is not generally utilizable since the Grignard reagents prepared from higher halides usually react abnormally, yielding mixtures of alkanes and alkenes. Furthermore, the required carbinols are not commercially available and simple distillation is somewhat inadequate for removal of residual traces of the carbinols from their chlorides.

Our experience (Table I) in attempting to prepare tertiary acids by carbonation of tertiary-alkyl magnesium chlorides with either gaseous or solid carbon dioxide indicates that the yields of acids become progressively more unsatisfactory. The reactions were run on Grignards derived from 200–300 g. of alkyl chloride using the usual precautions^{4d}; yields are not necessarily optimal.

TABLE I

Acid	This work		Published work		Ref.
	Carbonylation with CO ₂ as	Yield, %	Carbonylation with CO ₂ as	Yield, %	
A. Trimethylacetic	Gas	67	Gas	61–70	4d
B. Dimethylethylacetic	Gas	40	Gas	60	4c
				Lower than (A)	4e
C. Methyl-diethylacetic	Solid	17	Not reported	42	4a
D. Triethylacetic	Solid	7	Not reported	Not reported	4a
E. 1-Methylcyclohexanecarboxylic	Solid	15	Gas	<25	4b

A better preparative process for triethylacetic acid was found in Ziegler's method³ for the alkylation of acetonitrile followed by subsequent purification and hydrolysis of the resultant triethylace-

(1) This paper is constructed from part of a dissertation submitted in June, 1947, by Conrad Schuerch, Jr., to the Faculty of the Massachusetts Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Present address: Division of Cellulose and Industrial Chemistry, McGill University, Montreal 2, Canada.

(3) (a) Ziegler (to Schering-Kahlbaum, A. G.) U. S. Patent 1,958,653, May 15, 1933; C. A., **28**, 4435 (1934); British Patent 393,955, 394,087; C. A., **27**, 5755 (1933); German Patent 581,728, 583,561; C. A., **28**, 1057 (1934); French Patent 728,241; *Chem. Zentr.*, **104**, I, 1197–1198 (1933); C. A., **26**, 5573 (1932); (b) Ziegler and Ohlinger, *Ann.*, **495**, 84–112 (1932).

(4) (a) Whitmore and Badertscher, *THIS JOURNAL*, **55**, 1559–1567 (1933); (b) Gutt, *Ber.*, **40**, 2069 (1907); (c) Corson, Thomas and Waugh, *THIS JOURNAL*, **51**, 1950–1951 (1929); (d) Gilman, Kirby, "Organic Syntheses," Coll. Vol. 1 (2nd ed.), 361–364 (1941); (1st ed.) 353–356 (1932); Gilman and Parker, *ibid.*, **5**, 75–77 (1925); (e) Degnan and Shoemaker, *THIS JOURNAL*, **68**, 104 (1946).