

not inconsistent with the cyclic hydrogen-bonded complexes shown above.

It has been shown that systems containing the grouping N-C-C-O exert a similar catalytic effect on the ammonolysis and hydrolysis of methyl

acetate (Table I, 10). Only β -dimethylaminoethanol is reported here.¹⁰

(10) The work is being extended to other systems containing this grouping including compounds containing peptide linkages.

PHILADELPHIA 4, PENNSYLVANIA

[CONTRIBUTION FROM THE INORGANIC CHEMISTRY BRANCH, CHEMISTRY DIVISION, RESEARCH DEPARTMENT, U. S. NAVAL ORDNANCE TEST STATION]

The Hydrazinolysis of Nitroguanidine in Alcoholic Systems. Preparation and Reactions of 1,6-Dinitrobiguanidine^{1a,b}

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The hydrazinolysis of nitroguanidine in methanol or ethanol gives aminoguanidine in 50–70% yield; small amounts of nitroaminoguanidine (ca. 10%) and diaminoguanidine are formed. 1,6-Dinitrobiguanidine, $\text{NO}_2\text{NHC}(\text{NH})\text{NHNHC}(\text{NH})\text{NHNO}_2$, and 1,6-dinitro-2-(aminoguanyl)-biguanidine have also been isolated as their di-(aminoguanidinium) salts; the structure of each of these compounds has been elucidated and an extensive interrelationship between them has been established. 1,6-Dinitrobiguanidine can be prepared in 20–25% yield by the reaction of nitroaminoguanidine and 1-methyl-1-nitroso-3-nitroguanidine or in 55% yield by the hydrogen sulfide reduction of azobisnitroformamide. When 1,6-dinitro-2-(aminoguanyl)-biguanidine is diazotized, 5-aminotetrazole is eliminated in a ring closure which yields 3,5-di-(nitramino)-1,2,4-triazole (isolated as its monopotassium or ammonium salt).

The hydrazinolysis of nitroguanidine in aqueous systems has been shown to yield nitroaminoguanidine,² as the principal product and amino- and diaminoguanidine,³ as the by-products. In methanol or ethanol, however, the results are significantly different. In the first place, free nitroaminoguanidine can only be isolated with difficulty in small yields (10%), and in the second place, aminoguanidine is produced to the extent of 50–70% of theory. Small quantities of diaminoguanidine are also formed. Two new compounds, which are sparingly soluble in the alcohol, have also been isolated; the particular compound obtained depends on the alcohol employed for the solvent and on the other conditions of reaction.⁴

One of the compounds (IV) melts with decomposition at 146–147° and can be converted by refluxing in absolute methyl alcohol into the other compound (III), decomposing at 166–167°. Both of these compounds are readily soluble in water and give strongly basic solutions. Furthermore, they cannot be recovered or recrystallized from water because of extensive hydrolysis; from these aqueous solutions appreciable amounts of aminoguanidine can be isolated as suitable derivatives.

The chemical behavior and the elementary

(1) (a) Presented at the 116th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1949. This paper is published with the approval of the Office of Public Information, National Military Establishment. (b) For simplicity in naming and numbering certain of the derivatives in this paper, the parent compound $\text{NH}_2\text{C}(\text{NH})\text{NHNHC}(\text{NH})\text{NH}_2$, is named "biguanidine" rather than hy-

drazobisformamide or hydrazodicarbamide. This is consistent with the nomenclature used in *Chemical Abstracts*; thus, $\text{NH}_2\text{CONHNHC}(\text{NH})\text{NH}_2$, is biurea and $\text{HOOCNHNHC}(\text{NH})\text{COOH}$ is bicarbazic acid. Derivatives of $\text{NH}_2\text{C}(\text{NH})\text{N}=\text{NC}(\text{NH})\text{NH}_2$ are named as derivatives of azobisformamide; this is again consistent with the usage of *Chemical Abstracts*.

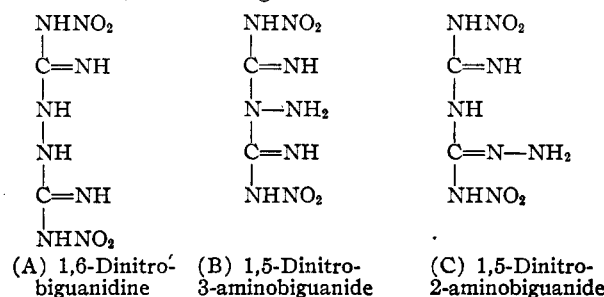
(2) R. Phillips and J. F. Williams, *THIS JOURNAL*, **50**, 2465 (1928).

(3) R. A. Henry, H. D. Lewis and G. B. L. Smith, *ibid.*, **72**, 2015 (1950).

(4) When anhydrous hydrazine is used instead of the hydrate, insignificant amounts of these compounds are formed and the nitroguanidine is converted almost exclusively to aminoguanidine.

analyses of these compounds are in agreement with the idea that they are di-(aminoguanidinium) salts of closely related nitramino derivatives and that they possess the formulas: compound III, $(\text{CH}_6\text{N}_4)_2\cdot\text{C}_2\text{H}_6\text{N}_8\text{O}_4$; compound IV, $(\text{CH}_6\text{N}_4)_2\cdot\text{C}_3\text{H}_9\text{N}_{11}\text{O}_4$. The compound, $\text{C}_2\text{H}_6\text{N}_8\text{O}_4$ (I), gives a positive Franchimont test with α -naphthylamine and very slowly reduces potassium iodate in the Jamieson hydrazine nitrogen determination⁵ which indicates the absence of a primary hydrazino group, but the presence of a protected hydrazino group which is liberated slowly through hydrolysis. Although this compound also reacts with both formaldehyde and glyoxal, the derivatives are not simple hydrazones; unlike nitroaminoguanidine, the compound does not yield a hydrazone with benzaldehyde.

Three probable structures, agreeing with the method of preparation and the empirical formula, $\text{C}_2\text{H}_6\text{N}_8\text{O}_4$, can be assigned



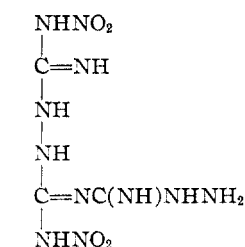
Formula (C) can be excluded immediately since this compound with a primary hydrazino group would be expected to reduce potassium iodate solution rapidly and to form a hydrazone with ease. Either of the other two tentative structures is in agreement with the observation that potassium iodate is only reduced slowly in the Jamieson hydrazine titration. However, 1,5-dinitro-3-am-

(5) G. S. Jamieson, *Am. J. Sci.*, **33**, 352 (1912); "Volumetric Iodate Methods," *Chemical Catalog Co.*, (Reinhold Publ. Corp.), New York, N. Y., 1926, p. 86.

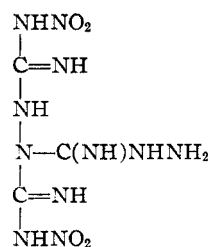
inobiguanide (B) can also be excluded since it should form a hydrazone, provided that there are no steric effects due to the two nitroguanyl groups.

Unambiguous proof that compound I was actually 1,6-dinitrobiguanidine was obtained by its synthesis from azobisnitroformamide,⁶ $O_2NNHC(NH)N=NC(NH)NHNO_2$. When the latter compound is treated with hydrogen sulfide under the same conditions used for the preparation of biguanidine dinitrate from the corresponding azo compound,⁷ it is rapidly reduced, with the precipitation of sulfur, to a colorless compound. The melting points, mixed melting point and X-ray powder diagrams are identical for the two materials. In addition, the di-(benzalamino-guanidinium) salts are identical.

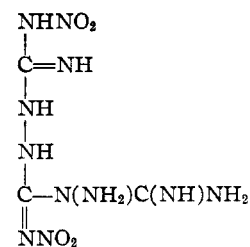
1,6-Dinitrobiguanidine (I) has also been synthesized in poor yield⁸ by the reaction of nitroaminoguanidine with 1-methyl-1-nitroso-3-nitroguanidine according to the method developed by McKay and Wright⁹ for the preparation of substituted nitroguanidine derivatives. However, by itself this synthesis did not serve to elucidate unambiguously the structure of compound I since there was no prior knowledge of the position of the nucleophilic center in nitroaminoguanidine under these particular reaction conditions and no way to predict definitely which one of the several possible isomeric compounds was actually formed. From this study it now appears that the nucleophilic center in nitroaminoguanidine for addition-elimination type reactions in either neutral or strongly basic medium is the terminal nitrogen in the hydrazino group. Nevertheless, the possibility of a very small amount of reaction at the other nitrogen atom in the hydrazino group should not be excluded entirely,¹⁰ but would probably be difficult to detect because of the low over-all conversions in these reactions. The formation of 1,6-dinitrobiguanidine in the reaction of hydrazine and nitroguanidine can be explained in the following manner: In the strongly



(D) 1,6-Dinitro-2-(aminoguanyl)-biguanidine



(E) 1,6-Dinitro-3-(aminoguanyl)-biguanidine



(F) 1,6-Dinitro-2-amino-2-guanylbiguanidine

basic solution of free aminoguanidine the nitroaminoguanidine, which arises from the hydrazinolysis of nitroguanidine, either adds to nitroguan-

idine followed by the elimination of ammonia, or adds to another molecule of nitroaminoguanidine, followed by the elimination of hydrazine.¹¹ The dinitrobiguanidine, when formed precipitates from the solution as the sparingly soluble di-(aminoguanidinium) salt and does not undergo extensive further reaction. This is probably one of the principal reasons why this compound has been isolated from the alcoholic systems but has not been detected in similar hydrazinolysis reactions performed in aqueous systems where the compound remains in solution.

The nitramino compound (II), derived from the aminoguanidinium salt IV, has the empirical formula $C_3H_9N_{11}O_4$ and differs from 1,6-dinitrobiguanidine by the elements of aminocyanamide. The behavior of compound II and its derivatives indicate that it is derived from dinitrobiguanidine by an ammonolysis-type reaction with aminoguanidine and that it retains the primary hydrazine group of the latter. For example, this compound forms a nitrate (VI) and readily forms a hydrazone with benzaldehyde (IX). In addition, one-half of its hydrazine nitrogen is rapidly and accurately titrated with potassium iodate under the conditions of the Jamieson method, whereas the balance can be titrated only very slowly. Compound II titrates potentiometrically as a very weak acid with a dissociation constant corresponding to a pK_a of approximately 9.3; its benzalhydrazone (IX) titrates potentiometrically as a dibasic acid ($pK_{a1} \cong 6.3$; $pK_{a2} \cong 8.6$).

Several structures can be proposed for compound II that agree with the empirical formula $C_3H_9N_{11}O_4$, the method of preparation, and the properties outlined above

However, only (D) is consistent with the behavior of the compound toward nitrous acid. When compound II is diazotized in *ca.* 2 *N* hydrochloric acid solution, an unstable azido compound can be obtained occasionally in impure form. The latter on reduction with hydrogen sulfide yields monoguanidinium 3,5-dinitramino-1,2,4-triazole. In general, however, the azido compound rearranges even in acid medium to an unstable tetrazole derivative since 5-aminotetrazole is subsequently eliminated by a cyclization which gives 3,5-dinitramino-1,2,4-triazole. The latter can be isolated from its aqueous solutions as either its sparingly soluble monopotassium or monoammonium

(11) An alternative explanation involves the addition of nitroaminoguanidine to nitrocyanamide which is hypothesized as a rearrangement product of nitroguanidine (T. L. Davis and A. J. J. Abrams, *Proc. Am. Acad. Arts and Sciences*, **61**, 487 (1926)) or nitroaminoguanidine (R. A. Henry and G. B. L. Smith, *THIS JOURNAL*, **71**, 1872 (1949)).

(6) G. F. Wright, *Can. J. Chem.*, **30**, 62 (1952).

(7) J. Thiele, *Ann.*, **270**, 1 (1892).

(8) Unsuccessful attempts to synthesize 1,6-dinitrobiguanidine included the nitration of biguanidine dinitrate in sulfuric acid, and the oxidation of nitroaminoguanidine in nitric acid solution with potassium permanganate according to the method of Thiele⁷ for the preparation of azobisformamide dinitrate from aminoguanidinium nitrate.

(9) A. F. McKay and G. F. Wright, *THIS JOURNAL*, **69**, 3028 (1947); A. F. McKay, *ibid.*, **71**, 1968 (1949).

(10) G. Pellizzari, *Gazz. chim. ital.*, **26**, II, 181 (1896), has shown that phenylhydrazine adds to cyanamide to give both 1-phenyl-1-aminoguanidine and 1-anilino-guanidine. A. H. Greer and G. B. L. Smith, *THIS JOURNAL*, **72**, 874 (1950), conclude that the nucleophilic center in methylhydrazine is on the nitrogen atom adjacent to the methyl group for addition-elimination reactions of this type; the same is true for the reaction of methylhydrazine and methylnitrosoguanidine (R. A. Henry and G. B. L. Smith, *ibid.*, **73**, 1858 (1951)). On the other hand when methylhydrazine and nitroguanidine react, some addition occurs at the terminal nitrogen of the hydrazino group (W. G. Finnegan, R. A. Henry and G. B. L. Smith, *ibid.*, **74**, 2981 (1952)).

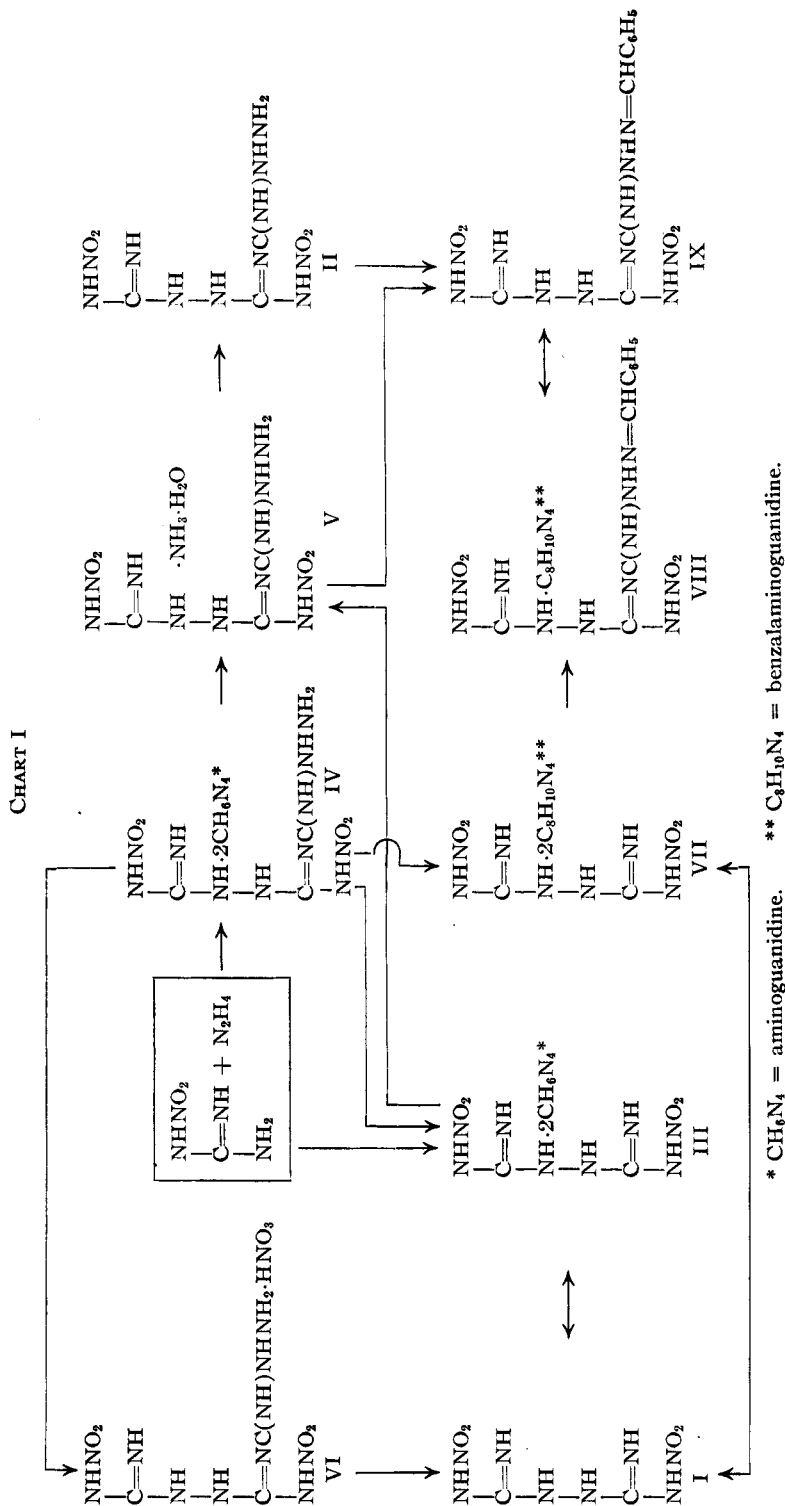
salt. Although the above reactions might suggest that compound II is actually the isomeric monoaminoguanidinium 3,5-dinitramino-1,2,4-triazole, rather than D, this is easily disproved. As indicated above, compound II' and its hydrazone are very weak acids; on the other hand, the acid salts of dinitraminotriazole all titrate sharply with sodium hydroxide solution and the second acid dissociation constant corresponds to a pK_a of 4.8.

Another property of 1,6-dinitro-2-(aminoguanyl)-biguanidine (II) and some of its derivatives is the relative ease with which they lose the elements of aminocyanamide with the regeneration of dinitrobiguanidine (I) or its derivatives. These interrelationships are summarized in Chart I.

When one mole of 1,6-dinitrobiguanidine (I) is treated with two moles of benzalaminoguanidine in cold methyl alcohol, its di-(benzalaminoguanidinium) salt (VII) is formed without loss of ammonia. The same salt results when the aminoguanidinium salt IV* is treated with benzaldehyde in cold aqueous solution; in this case an aminocyanamide group is lost. However, when benzalaminoguanidine (two moles) and 1,6-dinitrobiguanidine (I) (one mole) are refluxed in aqueous methyl alcohol, ammonia is evolved and the monobenzalaminoguanidinium salt (VIII) of the benzalhydrazone of 1,6-dinitro-2-(aminoguanyl)-biguanidine (IX) is formed. Only half of the starting amount of benzalaminoguanidine can be recovered upon acidifying an aqueous suspension of salt (VIII). The same benzalaminoguanidinium salt (VIII) can also be made by refluxing the aminoguanidinium salt (III) with excess benzaldehyde in aqueous methyl alcohol. When either the aminoguanidinium salt III or IV is refluxed with aqueous ammonium chloride, the monoammonium salt of 1,6-dinitro-2-(aminoguanyl)-biguanidine is recovered as the monohydrate (V) upon cooling.

The structure of the 3,5-dinitramino-1,2,4-triazole was established by catalytic hydrogenolysis of its ammonium salt to 3,5-diamino-1,2,4-triazole, which was isolated as the picrate and found to be identical with a known sample. Reduction of the potassium salt with zinc and acetic acid gave both 3,5-dihydrazino-1,2,4-triazole and 3-amino-5-hydrazino-1,2,4-triazole, which were isolated and

separated as their dibenzal derivatives. Reduction of 1,6-dinitrobiguanidine generally furnished the corresponding diamino compound; occasionally some 3-amino-5-hydrazino-1,2,4-triazole was also isolated as the dibenzal derivative. Dibenzal 1,6-diaminobiguanidine, as the free base, readily undergoes air oxidation to dibenzal azobisaminiformamide; on the other hand in acid solutions it undergoes partial hydrolysis to derivatives of $\text{NH}_2\text{NHCONHNHC(NH)NHNH}_2$.



Experimental^{12a,b}

Reaction of Equivalent Quantities of Hydrazine Hydrate and Nitroguanidine in Absolute Methyl Alcohol. Preparation of Di-(aminoguanidinium) 1,6-Dinitrobiguanidine (III).—The solution obtained by refluxing 42.9 g. of nitroguanidine, 23.7 g. of 87% hydrazine hydrate and 400 ml. of absolute methyl alcohol for 80 minutes was rapidly cooled to room temperature and filtered from the bright yellow material that had precipitated. When this precipitate had been washed with three 50-ml. portions of diethyl ether and dried, it weighed 3.4 g., m.p. 166–167° (dec.). Like compound IV, this compound was soluble in cold water giving an alkaline solution; it could not be recovered without decomposition because of hydrolysis. In contrast to compound IV, this compound was almost completely insoluble in hot methyl alcohol.

Anal. Calcd. for $2\text{C}_2\text{H}_5\text{N}_4\cdot\text{C}_2\text{H}_5\text{N}_5\text{O}_4$: C, 13.56; H, 5.12; N, 63.26. Found: C, 13.71; H, 5.00; N, 62.65, 62.90.

When the mother liquor from the above preparation was cooled overnight in the ice-box, 3.2 g. of the aminoguanidinium salt (IV), melting at 147–148° (dec.), was recovered. The melting point was unchanged after the compound was recrystallized from methyl alcohol; rosettes of yellow needles.

Anal. Calcd. for $\text{C}_2\text{H}_5\text{N}_5\text{O}_4\cdot 2\text{C}_2\text{H}_5\text{N}_4$: C, 15.15; H, 5.09; N, 63.62. Found: C, 15.17, 15.06; H, 5.18, 5.13; N, 64.36.

When 41.6 g. of nitroguanidine and 23.0 g. of 87% hydrazine hydrate in 400 ml. of absolute methyl alcohol were allowed to stand for six days at room temperature under a nitrogen atmosphere, 6.8 g. of compound IV, m.p. 146–147°, was obtained.

Prolonged refluxing of nitroguanidine and hydrazine hydrate in absolute methyl alcohol also gave largely compound IV rather than compound III.

Conversion of Di-(aminoguanidinium) 1,6-Dinitro-2-(aminoguanidyl)-biguanidine (IV) into Di-(aminoguanidinium) 1,6-Dinitrobiguanidine (III).—One gram of compound IV, m.p. 146°, was suspended and dissolved in 70 ml. of absolute methyl alcohol and the mixture refluxed for 3.5 hours. At the end of 1.5 hours, the melting point of the material had increased to 155–158° with preliminary shrinking at 150–152°. At the end of the heating period, the solution was cooled and the bright yellow powder removed by filtration. Its melting point was now 167° with shrinking and softening at 165–167°.

Reaction of Aminoguanidine with Nitroaminoguanidine.—A filtered aminoguanidine solution, obtained from a typical reaction of hydrazine hydrate and nitroguanidine (0.4 mole) in absolute ethyl alcohol, was refluxed for two hours with 8.0 g. of nitroaminoguanidine. A bright yellow precipitate began to appear within ten minutes. After cooling to room temperature, the precipitate was removed by filtration, washed with absolute methyl alcohol, and finally with ether. The yield amounted to 1.4 g., m.p. 167–168°. This material was identical with salt III obtained directly from hydrazine and nitroguanidine in absolute methyl alcohol.

1,6-Dinitrobiguanidine (I).—A solution of 1.66 g. of compound III in 50 ml. of water was acidified with 5 ml. of concentrated nitric acid. A yellowish-white precipitate appeared almost immediately. After standing ten minutes, this precipitate was removed by filtration and washed with water to remove excess acid. Air-drying left 0.65 g. of material melting at 184–185° with vigorous decomposition. One recrystallization from water (1 g. per 100 g.) furnished a pale yellow, granular crust of crystals, m.p. 186° (dec.). Further purification ultimately gave a white product decomposing vigorously at 193–195° when a sample in a capillary tube was plunged into a hot-bath held at this temperature. A mixed melting point with nitroaminoguanidine was 170–175° (dec.).

Anal. Calcd. for $\text{C}_2\text{H}_5\text{N}_5\text{O}_4$: C, 11.65; H, 2.94; N,

54.36; hydrazine nitrogen, 13.59. Found: C, 11.35; H, 2.91; N, 54.10, 54.18.

In the Jamieson titration for hydrazine nitrogen, the compound did not behave normally; an end-point could be reached at which all the iodine color would be discharged, but on standing, more iodine would be liberated slowly. In this case, after standing five days, the titration corresponded to a value of 10.66% hydrazine nitrogen. Because of this behavior, it is almost impossible to obtain reproducible or significant values.

X-Ray Data.—5.90 0.05; 4.46, 0.63; 3.93, 0.12; 3.25, 0.06; 3.17, 1.00; 3.07, 0.08; 2.954, 0.33; 2.317, 0.11; 2.272, 0.18; 2.239, 0.11.

1,6-Dinitrobiguanidine from Nitroaminoguanidine and 1-Methyl-1-nitroso-3-nitroguanidine.—A slurry of 1.19 g. (0.01 mole) of nitroaminoguanidine (99.4%), 1.47 g. (0.01 mole) of methylnitrosnitroguanidine,⁹ 10 ml. of water and 10 ml. of ethyl alcohol was allowed to stand in a stoppered flask at room temperature for two months. After chilling to 0°, the solid was removed by filtration and washed with 10 ml. of cold water. The yield of air-dried product was 1.47 g., m.p. 135–140°. A Jamieson hydrazine determination corresponded to a nitroaminoguanidine content of only 51%. All of the impure product was dissolved in 50 ml. of hot water; two drops of glacial acetic acid and 0.6 g. of benzaldehyde were then added with stirring. The resulting solution was evaporated to dryness under reduced pressure. When a dry cake was freed of the nitroguanidyl hydrazone of benzaldehyde by extraction with 90 ml. of hot ethyl alcohol, there was left 0.45 g. of insoluble material (20%) decomposing at 195–197° when plunged into a hot-bath.

This material was characterized as 1,6-dinitrobiguanidine by conversion into its di-(benzalamino-guanidinium) salt, m.p. 176° (dec.). A mixed melting point with compound VII was the same.

Nitroaminoguanidine and methylnitrosnitroguanidine also react in pyridine to give a 20–25% yield of 1,6-dinitrobiguanidine.

Reduction of Azobisnitroformamide. Preparation of 1,6-Dinitrobiguanidine.—Hydrogen sulfide was passed through a slurry of 2.0 g. of azobisnitroformamide⁶ in 100 ml. of water at 30° until the orange color was completely discharged. There was a rapid reduction with the formation of sulfur. The slurry was heated to 90° and filtered. The cake of sulfur was re-extracted with 50 ml. of boiling water and the two filtrates were combined and cooled to 0°. The product was removed by filtration, dried and extracted with carbon disulfide to remove final traces of sulfur. The yield was 1.1 g., m.p. 195–200° (dec.) when plunged into a hot-bath. An X-ray powder pattern was identical with that obtained on compound I.

The di-(benzalamino-guanidinium) salt obtained from 0.21 g. of the above compound and 0.4 g. of benzalamino-guanidine in 15 ml. of absolute methanol decomposed at 174–175°. A mixed melting point with compound VII was the same; X-ray powder patterns were also identical.

Azobisnitroformamide.—A saturated solution of calcium permanganate was added dropwise with stirring to a slurry of 1.0 g. of 1,6-dinitrobiguanidine in 25 ml. of 3.2 *N* nitric acid until there was no further decolorization. The temperature was held at 10–15°. Each drop of permanganate was allowed to react completely before adding the next. Some manganese dioxide separated near the end of the addition. When the oxidation was completed, solid sodium bisulfite was added in very small portions until the manganese dioxide had dissolved; an excess was avoided. The orange-yellow product was immediately removed by filtration and washed with ice-cold water until free of nitric acid. The yield was 1.0 g.; 0.65 g. was recrystallized rapidly from 110 ml. of nitromethane. The recovery of orange plates was 0.35 g., m.p. 171–172° (dec.). An X-ray powder pattern on the recrystallized material was identical with that obtained on an authentic sample of azobisnitroformamide made by the method of Wright.⁶ This compound also exists in a polymorphic form.

Anal. Calcd. for $\text{C}_2\text{H}_4\text{N}_5\text{O}_4$: C, 11.77; H, 1.97; N, 54.90. Found: C, 12.08; H, 1.92; N, 54.89.

X-Ray Data.—(A): 4.39, 0.18; 4.30, 0.25; 4.15, 0.18; 3.96, 1.00; 3.83, 0.50; 3.58, 0.75; 3.50, 0.21; 3.41, 0.26; 3.27, 0.18; 3.11, 0.26; 2.610, 0.18. (B): 4.87, 0.19; 4.16, 0.19; 3.80, 0.27; 0.81; 3.24, 0.47; 2.853, 1.00; 2.792, 0.08; 2.759, 0.12; 2.364, 0.11.

(12) (a) All melting points are uncorrected. (b) The X-ray data reported in this section were obtained either on a Norelco Recording Spectrogoniometer or on a Norelco Debye-Scherrer Camera (indicated by "photo" in parenthesis) using $\text{CuK}\alpha$ radiation through nickel filter. Data for the 10 strongest lines are recorded and repeated in the following order: $d(\text{\AA.}), I/I_0$.

Benzal Hydrazone of 1,6-Dinitro-2-(aminoguanyl)-biguanidine (IX) and its Benzalaminoguanidinium Salt (VIII).—A solution consisting of 2.0 g. of compound III, 2.0 g. of benzaldehyde and 200 ml. of absolute methyl alcohol was refluxed for two hours. The yellow salt had almost entirely dissolved after one hour; some ammonia was evolved. After three-quarters of the heating was completed, a white precipitate began to form. After cooling the reaction mixture to room temperature, the solid was removed by filtration and washed with a small volume of methyl alcohol. The yield amounted to 1.6 g. A second crop of 0.3 g. was obtained when the mother liquor was evaporated to 50 ml. and cooled. The impure material (VIII) melted at 185–190°. When it was recrystallized from a very large volume of methyl alcohol, or from a 50–50 water-ethyl alcohol mixture, it was obtained as white platelets, m.p. 193° (dec.). A mixed melting point with the isomeric di-(benzalaminoguanidinium) 3,5-dinitroamino-1,2,4-triazole was 181–182°. The X-ray powder pattern was also different.

Anal. Calcd. for $C_{18}H_{22}N_{10}O_4$: C, 42.10; H, 4.51; N, 40.92; benzalaminoguanidine, 31.6. Found: C, 42.31, 42.70; H, 4.31, 4.45; N, 40.66, 40.58; benzalaminoguanidine, 30.7.

X-Ray Data (Photo).—15.5, 1.0; 8.58, 0.6; 6.91, 0.4; 5.78, 0.1; 5.12, 0.3; 3.47, 0.3; 3.24, 0.6; 3.08, 0.1; 2.993, 0.1.

This same benzalaminoguanidinium salt (VIII) was prepared in 70% yield by refluxing for 8.5 hours 1.0 g. of 1,6-dinitrobiguanidine (I) with 1.65 g. of benzalaminoguanidine in 60 ml. of methyl alcohol and 5 ml. of water; m.p. 192–193° (dec.).

When 0.94 g. of salt VIII was suspended in 25 ml. of water at 50° and acidified with five drops of concentrated nitric acid, a white flocculent precipitate was formed. After standing four hours at 0°, this precipitate was filtered and dried; yield 1.05 g., m.p. 140–150° (dec.). By extraction with two 25-ml. portions of boiling 95% ethyl alcohol, this crude product was separated into two materials: (1) an alcohol-soluble material (0.40 g.), melting at 168–169° after one recrystallization from water; a mixed melting point with a sample of benzalaminoguanidinium nitrate was 170°; (2) an alcohol-insoluble fraction (0.65 g.), decomposing vigorously at 176°; recrystallization from 70 ml. of water gave rosettes of white needles decomposing at 180–181°. This material was identical with the benzal hydrazone of 1,6-dinitro-2-(aminoguanyl)-biguanidine (IX) described below.

Anal. Calcd. for $C_{10}H_{13}N_{11}O_4$: C, 43.19; H, 3.73; N, 43.86. Found: C, 43.15, 43.09; H, 3.61, 3.64; N, 43.78, 43.44.

When 0.14 g. of this hydrazone was heated under reflux for several hours with 0.13 g. of benzalaminoguanidine in 15 ml. of absolute methyl alcohol, it was reconverted to the starting benzalaminoguanidinium salt of the hydrazone (VIII), m.p. 190°.

Conversion of Di-(benzalaminoguanidinium) 1,6-Dinitrobiguanidine (VII) into the Benzalaminoguanidinium Salt of the Benzalhydrazone of 1,6-Dinitro-2-(aminoguanyl)-biguanidine (VIII).—A solution of 0.6 g. of the di-(benzalaminoguanidinium) salt VII in 55 ml. of methyl alcohol and 1 ml. of water was refluxed for two hours. Ammonia was evolved and a white precipitate began to appear after 30 minutes. After chilling the solution for one hour in an ice-bath, the precipitate was removed by filtration and washed with two small portions of ethyl alcohol; yield 0.4 g., m.p. 192–193°, a mixed melting point with compound VIII was 192°.

Anal. Calcd. for $C_{18}H_{23}N_{10}O_4$: N, 40.92. Found: N, 40.38, 40.43.

Ammonium Salt of 1,6-Dinitro-2-(aminoguanyl)-biguanidine (V).—A solution of 3.2 g. of compound III, 3.0 g. of ammonium chloride and 25 ml. of water was boiled for ten minutes and filtered. Cooling gave a crystalline material which decomposed at 178–179° after one recrystallization. A mixed melting point with the ammonium salt V (see below) made from compound IV was 178–179°.

Monobenzylammonium 1,6-Dinitrobiguanidine.—A slurry of 0.4 g. of 1,6-dinitrobiguanidine, 0.42 g. of benzylamine and 25 ml. of absolute methanol was allowed to stand several days at room temperature. The solution had a

deep yellow color; no ammonia was evolved. The solid had dissolved almost completely after two days and rosettes of yellow prisms began to crystallize after this same period of time. The salt was removed by filtration and washed several times with cold methanol; m.p. 166–167° (dec.).

Anal. Calcd. for $C_9H_{13}N_9O_4$: C, 34.50; H, 4.83; N, 40.24. Found: C, 34.77; H, 4.93; N, 40.03.

Dibenzal-1,6-diaminobiguanidine.—Seventy milliliters of 50% aqueous acetic acid was added with stirring during 95 minutes to a slurry of 8.0 g. of 1,6-dinitrobiguanidine and 20 g. of 90% zinc dust in 100 ml. of water. The temperature was maintained at 20–25°. The stirring was continued for one hour more at this temperature and finally for another hour at 45–50°. The unreacted zinc was removed by filtration and washed with two 30-ml. portions of hot water. After 60 g. of sodium acetate trihydrate in 80 ml. of water had been added to the combined filtrates, the solution was saturated with hydrogen sulfide until the zinc was completely precipitated. The zinc sulfide was removed by filtration and washed several times with cold water. The filtrate was acidified with 40 ml. of concentrated hydrochloric acid, heated to 50°, shaken with 15 ml. of benzaldehyde for 15 minutes and cooled to 0°. The white solid was removed by filtration and washed several times with cold water and with petroleum ether to remove excess benzaldehyde. The yield of dried product was 3.75 g., m.p. 220–230°. Several attempts to purify this hydrochloride by crystallization were not successful. The salt was dissolved in a minimum volume of 95% ethanol at room temperature and made alkaline to phenolphthalein with a 0.5 N solution of sodium hydroxide. A pale yellow precipitate began to separate almost immediately and was assisted by the addition of several volumes of water. The hydrazone was removed and washed with cold water until neutral. A portion (1.4 g.) of the dried product, after rapid recrystallization from one liter of a mixture consisting of 53% benzene and 47% absolute ethanol by volume, was recovered as white felted needles which decomposed sharply at 212°.

Anal. Calcd. for $C_{16}H_{18}N_8$: C, 59.61; H, 5.63; N, 34.76. Found: C, 59.41, 59.75; H, 5.38, 5.65; N, 34.65.

When this compound was heated with either picric acid or picrolonic acid in 95% ethanol, partial hydrolysis apparently occurred and the respective salts of the dibenzal derivative of $H_2NNHCONHNHC(NH)NHNH_2$ were recovered. The monopicrate after recrystallization from 95% ethanol, decomposed at 214–215°.

Anal. Calcd. for $C_{22}H_{30}N_{10}O_8 \cdot 3H_2O$: C, 43.56; H, 4.32; N, 23.10; H_2O , 8.9. Found: C, 43.43, 43.88; H, 4.21, 4.25; N, 23.03, 22.90; H_2O , 9.1.

The picrolonate decomposed at 248–249°.

Anal. Calcd. for $C_{26}H_{28}N_{11}O_6$: C, 53.15; H, 4.29; N, 26.23. Found: C, 52.89; H, 4.31; N, 26.09.

Dibenzal Azobisaminofornamidine.—When a hot, saturated alcoholic solution of dibenzal-1,6-diaminobiguanidine was cooled slowly while exposed to the air, purplish-red, flat needles, which decomposed sharply at 176–177°, were obtained rather than the white or pale yellow needles of starting compound.

Anal. Calcd. for $C_{16}H_{18}N_8$: C, 59.98; H, 5.03; N, 34.98. Found: C, 59.99; H, 4.99; N, 35.07.

Reaction of Equivalent Quantities of Hydrazine Hydrate and Nitroguanidine in Absolute Ethyl Alcohol. A. Preparation of Di-(aminoguanidinium) 1,6-Dinitro-2-(aminoguanyl)-biguanidine (IV).—A suspension of 41.6 g. of nitroguanidine (0.4 mole) in a solution of 23.0 g. of 87% hydrazine hydrate (0.4 mole) and 400 ml. of absolute ethyl alcohol was heated under reflux for 75 minutes. During this time ammonia was evolved and the white, sparingly soluble nitroguanidine gradually disappeared and was replaced by a fine yellow powder. After standing overnight at room temperature in a tightly stoppered flask, the yellow precipitate was removed by filtration and washed with two 50-ml. portions of absolute ethanol and two 50-ml. portions of diethyl ether. (The red colored mother liquors and the washings were saved for recovery of aminoguanidine.) In a series of experiments, the yield of dried product varied from 6.5 to 8.4 g.; the best samples melted at 146–148° with decomposition.

This compound was readily soluble in cold water giving

a strongly basic solution. It was sparingly soluble in boiling absolute methyl alcohol (slow decomposition on prolonged heating) and could be recovered as rosettes of yellow-orange needles; generally, the melting point remained unchanged at 147–148° (dec.).

Anal. Calcd. for $C_3H_9N_{11}O_4 \cdot 2CH_3N_4$: C, 14.60; H, 5.15; N, 64.70; hydrazine nitrogen, 20.43; amine value, 409.1; aminoguanidine, 36.0. Found: C, 14.66; H, 5.26; N, 63.97; hydrazine nitrogen, 20.41; amine value, 404.2. The per cent. aminoguanidine calculated from the yield of benzalaminoguanidine nitrate was: 33.3, 33.7, 36.5.

B. Recovery of Aminoguanidine from Mother Liquors.—Aminoguanidine was easily recovered from the alcoholic mother liquors of the above experiment by cooling and saturating with carbon dioxide. The yield of dried bicarbonate varied from 22.7 to 34.0 g. (41.8–62.2%), depending on the extent of loss of aminoguanidine through air oxidation. Hydrazine nitrogen determinations on the several impure salts varied as follows: 20.03, 20.03, 20.13, 21.44%, compared to a theoretical value of 20.58% for aminoguanidinium bicarbonate. Identification of the aminoguanidine was made by conversion into benzalaminoguanidinium nitrate, m.p. 160–161°, and comparison with an authentic sample.¹³

The aminoguanidine could also be isolated from the alcoholic solution as the nitrate or the bisulfate.

Another method for recovering the aminoguanidine, was to prepare and isolate benzalaminoguanidinium nitrate in the following manner: The alcohol solution was diluted with 400 ml. of water and acidified with 40 ml. of concentrated nitric acid. This solution was shaken vigorously with 40 g. of benzaldehyde for about one hour, then cooled at 0° for several hours. The material that separated was removed by filtration, washed with ether to remove benzalazine and excess benzaldehyde, and then with water to remove occluded acid; yield 9.9 g., m.p. 158–163°. Two recrystallizations from 95% ethyl alcohol gave soft felty clusters of needles, m.p. 195°; a mixed melting point with dibenzaldiaminoguanidinium nitrate (m.p. 204–205°) was 201–202°. This fraction was assumed to be dibenzaldiaminoguanidinium nitrate without further purification. By concentrating the aqueous alcoholic filtrate under reduced pressure to a volume of 200 ml. and cooling, 51.0 g. of benzalaminoguanidinium nitrate was obtained. The yield corresponds to a 56.7% conversion of the nitroguanidine to aminoguanidine.

Reactions of the Di-(aminoguanidinium) 1,6-Dinitro-2-(aminoguanyl)-biguanidine. **A. With Benzaldehyde in Acid Solution.**—A solution of 17.8 g. of the compound IV in 200 ml. of ice-cold water and 15 ml. of concentrated nitric acid was filtered, then shaken with 14.0 g. of benzaldehyde. After cooling in an ice-bath for five hours, the granular precipitate was removed by filtration and washed with cold water until neutral. The yield of dried product was 19.7 g., m.p. 140–145° (dec.). Several recrystallizations from water raised the melting point to 169–169.5°; a mixed melting point with benzalaminoguanidinium nitrate was 170°.

B. With Glyoxal in Acid Solution.—To a solution of 4.5 g. of 90% nitric acid in 50 ml. of water, cooled to 2°, was added 8.1 g. of compound IV. When the latter had dissolved completely, 5.7 g. of a 30.3% glyoxal solution in 20 ml. of water was added. A precipitate developed in a few minutes. The reaction was completed by heating to 60°. After standing 16 hours at 0°, the hydrazone was removed by filtration and washed twice with 15-ml. portions of ice-water. The yield of dried product was 5.52 g. Recrystallization from water containing a few drops of concentrated nitric acid gave clusters of orange-yellow, diamond-shape plates, decomposing at about 290°; Thiele and Dralle¹⁴ reported 292° for the dinitrate of glyoxal bis-guanylhydrazone.

Anal. Calcd. for $C_4H_{10}N_8 \cdot 2HNO_3$: N, 47.29. Found: N, 47.23, 47.35.

The free base, made from the dinitrate, crystallized from water in large, opaque plates or flat needles; m.p. 233–234°, reported¹³ 265–266°.

(13) J. Thiele and K. Heidenreich, *Ber.*, **26**, 2599 (1893), reported a melting point of 161° for benzalaminoguanidinium nitrate. We have found that this is a metastable form; the stable form melts at 170–171°.

(14) J. Thiele and E. Dralle, *Ann.*, **303**, 284, 288 (1898).

Anal. Calcd. for $C_4H_{10}N_8$: N, 65.85. Found: N, 65.77.

C. Hydrolysis in the Presence of Ammonium Chloride. Preparation of Ammonium 1,6-Dinitro-2-(aminoguanyl)-biguanidine (V).—From a solution of 7.0 g. of compound IV, 3.0 g. of ammonium chloride and 60 ml. of water, boiled for 15 minutes, there separated, on cooling, 2.5 g. of gray, warty clusters, decomposing at 180–181°. When recrystallized from water, the compound was obtained as hard, white spherulites or radiates, still decomposing at 181° when heated rapidly or plunged into a hot-bath. When the compound was heated slowly, it decomposed between 176–179°. A mixed melting point with nitroaminoguanidine was 172–175°. A mixed melting point with a sample of 1,6-dinitrobiguanidine (I), was 171–173°. This material is readily soluble in cold, dilute sodium hydroxide solution, yielding a deep yellow color.

Anal. Calcd. for $C_3H_9N_{11}O_6 \cdot NH_3 \cdot H_2O$: C, 12.08; H, 4.73; N, 56.36; H_2O , 6.04; $H_2O + NH_3$, 11.76; hydrazine nitrogen, 9.39. Found: C, 12.10; H, 4.37; N, 56.59; H_2O , 5.9; $H_2O + NH_3$, 12.5.

In the Jamieson determination of hydrazine nitrogen, two distinct stages were evident: (1) a rapid reduction of the potassium iodate, giving an end-point that corresponded to 9.15% hydrazine nitrogen; and (2) a very slow reduction of iodate solution which corresponded to 3.3% more of hydrazine nitrogen after five days.

D. With Nitric Acid. 1,6-Dinitro-2-(aminoguanyl)-biguanidine Nitrate (VI).—Three grams of compound IV was stirred into 40 ml. of ice-cold water and the pH adjusted to ca. 2 by the dropwise addition of concentrated nitric acid. The yellow color of the solution was discharged. A small quantity of insoluble material was removed by filtration and discarded and the filtrate was cooled for 16 hours at 0°. The white solid that crystallized during this time was collected on a filter and washed with three 5-ml. portions of cold water. A yield of 1.3 g. was obtained; m.p. 115–115.5° (dec.).

Anal. Calcd. for $C_3H_9N_{11}O_4 \cdot HNO_3$: N, 51.53; HNO_3 , 19.32; hydrazine nitrogen, one hydrazino group, 8.59; hydrazine nitrogen, two hydrazino groups, 17.18. Found: N, 51.86, 51.69; HNO_3 by nitron method, 18.95; hydrazine nitrogen by Jamieson method, first end-point, 8.62; after seven days, 10.57.

All attempts to purify this material by recrystallization from water were unsuccessful because of decomposition. The impure material as originally obtained was readily soluble in water; it was evidently a nitrate salt as the above analyses indicated. However, the recrystallized material was only sparingly soluble and it no longer contained nitrate. Frequently, two materials were isolated from the recrystallization; the principal one decomposed at 191–192° and was identical with 1,6-dinitrobiguanidine (I). The other product decomposed at 178–179° and was probably 1,6-dinitro-2-(aminoguanyl)-biguanidine (II).

E. With Benzaldehyde in Alkaline Solution. Preparation of Di-(benzalaminoguanidinium) 1,6-Dinitrobiguanidine (VII).—Benzaldehyde (4.2 g.) in 25 ml. of alcohol was shaken for two hours with 4.6 g. of compound IV dissolved in 75 ml. of water. An orange-colored, amorphous solid slowly collected on the sides of the flask. After the shaking was completed, the solid was removed by filtration, washed with two 50-ml. portions of water, two 30-ml. portions of cold 95% ethyl alcohol and finally with two 30-ml. portions of diethyl ether, yield 2.4 g. of an orange-powder; the impure product melted at 174–175°. By rapid recrystallization from a large volume of 95% ethyl alcohol, the melting point was raised to 176–177° and the compound obtained as small orange platelets. If heated for a prolonged time in 95% ethyl alcohol, the compound decomposed. In absolute ethyl or methyl alcohol, the compound could be refluxed for several hours without evidence of decomposition; it is only sparingly soluble in these solvents. It is readily soluble in hot water but undergoes decomposition.

Anal. Calcd. for $C_2H_6N_8O_4 \cdot 2C_3H_7N_4$: C, 40.73; H, 4.49; N, 42.28. Found: C, 40.50, 40.61; H, 4.87, 4.89; N, 42.62, 42.71.

X-Ray Data.—10.64, 0.37; 7.25, 0.10; 6.02, 0.10; 5.40, 0.11; 4.74, 0.19; 4.30, 0.48; 3.93, 0.12; 3.53, 0.19; 3.18, 1.00; 2.993, 0.12.

This benzalaminoguanidinium salt (VII) could also be

prepared as follows: When 0.41 g. of 1,6-dinitrobiguanidine (I), 0.66 g. of benzalaminoguanidine and 35 ml. of absolute methanol were shaken for one hour, and then allowed to stand at room temperature for 44 hours, the gray-white nitro compound gradually disappeared and was replaced by a bright orange powder. The yield was 0.61 g., m.p. 175–176° (dec.).

When 1.3 g. of this benzalaminoguanidinium salt (VII) was suspended in 25 ml. of water and made acid with concentrated nitric acid, the orange color disappeared and a white precipitate gradually appeared. There was recovered 1.2 g. of material after washing with water and drying; m.p. 150–151°. This material, although it was closely duplicated in several other experiments, was a mixture. By extraction with two 25-ml. portions of boiling 95% ethyl alcohol, separation into two components was effected. (1) An alcohol-insoluble fraction (about 0.4 g.) decomposing at 188–189° or at 192–193° after one recrystallization from water. This material was similar in appearance and behavior to 1,6-dinitrobiguanidine (I).

Anal. Calcd. for $C_2H_6N_6O_4$: N, 54.36. Found: N, 53.43, 53.29.

(2) An alcohol soluble fraction which proved to be identical with benzalaminoguanidinium nitrate after recrystallization from water.

The Benzaldehyde of 1,6-Dinitro-2-(aminoguanyl)-biguanidine (IX).—A solution of 0.6 g. of the ammonium salt VI in 20 ml. of water and five drops of concentrated nitric acid at 40–50° was shaken with 0.7 g. of benzaldehyde for several minutes. After cooling in an ice-bath to complete the precipitation, the white solid was removed by filtration and washed first with water to remove excess acid and then with petroleum ether to remove excess benzaldehyde. The yield of air-dried product was 0.75 g., m.p. 175–178° (dec.). A mixed melting point with benzalaminoguanidinium nitrate was below 150°. When recrystallized from 80 ml. of water, the product was obtained as white needles, decomposing at 178–180° when heated slowly from room temperature, or 181–183° if plunged in at 165–170° and heated.

Anal. Calcd. for $C_{10}H_{13}N_{11}O_4$: C, 34.19; H, 3.73; equiv. wt., 351.3. Found: C, 34.26; H, 3.80; equiv. wt., 354.4.

Potentiometric titration of 0.3803 g. in 100 ml. of water with 0.2006 *N* sodium hydroxide gave two small but definite inflections, one at 5.35 ml., the other at 10.7 ml. The first acid dissociation constant corresponds to a $pK_a \cong 6.3$; the second to a $pK_a \cong 8.6$.

1,6-Dinitro-2-(aminoguanyl)-biguanidine (II).—One gram of the ammonium salt V, suspended in 10 ml. of ice-cold water, was carefully acidified with concentrated nitric acid to a pH of 4.5. The cream-colored precipitate was removed by filtration and washed with two 25-ml. portions of ice-cold water. The yield of dried product, decomposing explosively at 180–182°, was 0.82 g. Recrystallization from water furnished rosettes of long, colorless needles, decomposing vigorously at 182°.

Anal. Calcd. for $C_8H_9N_{11}O_4$: C, 13.69; H, 3.45; N, 58.55; hydrazine nitrogen for one hydrazino group, 10.64; for two hydrazino groups, 21.29. Found: C, 13.65, 13.94; H, 3.32, 3.49; N, 58.54, 58.34; hydrazino nitrogen by Jamieson method, first end-point, 10.41.

X-Ray Data.—14.0, 0.54; 9.81, 0.17; 6.91, 0.14; 5.86, 0.18; 5.53, 0.11; 4.59, 1.00; 3.93, 0.12; 3.36, 0.11; 3.22, 0.13; 2.289, 0.10.

By treating an aqueous solution of this compound with benzaldehyde, the benzaldehyde (IX) was obtained.

Monopotassium 3,5-Di-(nitramino)-1,2,4-triazole.—A solution of 3.6 g. of potassium nitrite in 10 ml. of water was added slowly with good agitation to a slurry of 9.03 g. of 1,6-dinitro-2-(aminoguanyl)-biguanidine in 200 ml. of ice-cold 1.8 *N* hydrochloric acid. The temperature was maintained between 3 and 7°. Nitrite was rapidly consumed and the character of the suspended solid changed. After the nitrite had been added, the slurry was stirred for 20 minutes. The solid product was removed by filtration, washed twice with 10-ml. portions of cold water and reslurried in 200 ml. of ice-cold water. When 5 g. of anhydrous potassium carbonate was added, the solid dissolved completely to give a deep-yellow colored solution. The latter was filtered rapidly and the pH readjusted to about 3.5 with concentrated hydrochloric acid. After the solu-

tion had been chilled at 0° for several hours, the product was removed by filtration and washed carefully with cold water. The yield of dried product was 5.74 g., m.p. 199–200° (dec.). An additional 0.9 g. was recovered from the original aqueous filtrate by first adjusting the pH to 8.5 with 25 g. of anhydrous potassium carbonate, then re-adjusting to 3.5 with hydrochloric acid and finally cooling at 0° overnight. The total recovery amounted to 85.6%. This salt could be recrystallized from water; the melting point, however, did not change. The pK_a , calculated from a potentiometric titration with standard base, was approximately 4.8.

Anal. Calcd. for $C_2H_2N_7O_4K$: C, 10.57; H, 0.89; N, 43.16; K, 17.21; equiv. wt., 227.2. Found: C, 11.26, 11.54; H, 0.92, 0.94; N, 43.14, 43.27; K, 16.24; equiv. wt., 225, 229.

X-Ray Data.—4.09, 0.30; 3.73, 0.70; 3.32, 0.20; 3.08, 1.00; 2.917, 0.20; 2.702, 0.20; 2.504, 0.20; 2.312, 0.30; 2.077, 0.20.

Aminotetrazole was recovered from the reaction as follows: All of the aqueous filtrates were combined and evaporated to dryness on a steam-bath. The residue was extracted with three 70-ml. portions of hot absolute ethanol and the combined extracts were in turn evaporated to dryness. The yield of material, melting at 170–180°, was 2.4 g. Approximately 0.5 g. of this was ammonium chloride; the balance (66%) was 5-aminotetrazole. Recrystallization from a minimum volume of water raised the melting point to 203–204° (dec.); a mixed melting point with an authentic sample was the same.

Monoguanidinium 3,5-Di-(nitramino)-1,2,4-triazole.—A solution of 1.8 g. of sodium nitrite in 11 ml. of water was added during 20 minutes with stirring to a slurry of 5.26 g. of 1,6-dinitro-2-(aminoguanyl)-biguanidine in 120 ml. of 2 *N* hydrochloric acid. The temperature was held at 4 to 7°. When most of the nitrite had been added, the slurry suddenly became very thick with precipitate. Stirring was continued for 20 minutes more. The solid was removed by filtration and washed with four 15-ml. portions of cold water. The yield of dried product decomposing about 150° when plunged into a hot-bath was 2.55 g. Attempts to purify and recrystallize this material which was either impure 1,6-dinitro-2-(azidoguanyl)-biguanidine, or impure azidoguanidinium 3,5-dinitramino-1,2,4-triazole, were not successful. The impure material was dissolved in 195 ml. of 67% methanol heated to 65°; the solution was filtered rapidly, chilled to 0° and filtered from 0.5 g. of insoluble material. The filtrate was rewarmed to room temperature and saturated with hydrogen sulfide for 30 minutes; sulfur began to precipitate immediately. The solution was filtered and the filtrate concentrated to 25 ml. After an additional amount of free sulfur had been removed, the filtrate was cooled at 0° for several hours. The product was removed by filtration and dried; the yield was 0.69 g., m.p. 176–179° (dec.). Recrystallization from 25 ml. of water raised the decomposition temperature to 186–187°. The pK_a for this compound was also 4.8.

Anal. Calcd. for $C_8H_9N_{10}O_4$: C, 14.52; H, 3.25; N, 56.45. Found: C, 14.77; H, 3.01; N, 56.10.

When the filtrate and washings, remaining after the azido compound had been removed, were adjusted to pH 8 with anhydrous potassium carbonate, filtered, readjusted to pH 2 and cooled to 10°, there was recovered 1.8 g. of the monopotassium salt of di-(nitramino)-triazole, m.p. 198–199° (dec.).

Monoammonium 3,5-Di-(nitramino)-1,2,4-triazole.—Finely powdered 1,6-dinitro-2-(aminoguanyl)-biguanidine (5.26 g.) was shaken vigorously for several minutes with an ice-cold solution of 130 ml. of 2.8 *N* hydrochloric acid. The solution was rapidly filtered from a small amount of insoluble material and immediately diazotized with a solution of 1.5 g. of sodium nitrite in 10 ml. of water. The temperature was maintained between 0 and 5°. Nitrite was rapidly consumed. When the diazotization was completed, the solution was filtered again and then partially neutralized by adding 30 ml. of 8 *N* ammonium hydroxide. A white crystalline powder separated immediately; it was removed by filtration and washed three times with small volumes of cold water. The yield of vacuum dried product was 2.95 g.; the decomposition point varied from 183 to 192°. An additional 0.5 g. was obtained by adjusting the filtrate and washings to pH 8 with concentrated ammonium hydroxide,

readjusting to pH 2 with hydrochloric acid and cooling to 0°. The total recovery corresponded to an 84% yield. The compound could be recrystallized from water (0.5 g. per 25 ml.) without decomposition if the temperature did not exceed 70°; felted rosettes of fine, white needles, decomposing at 182–184°. A hot aqueous solution of the compound did not reduce hydrogen sulfide; this indicated the absence of an azido group. Ammonia was evolved when a warm solution was made alkaline.

Anal. Calcd. for $C_2H_8N_6O_4$: C, 11.65; H, 2.95; N, 54.36; equiv. wt., 206.13. Found: C, 12.19; H, 2.98; N, 54.18; equiv. wt., 207.

X-Ray Data.—6.41, 1.00; 5.09, 0.40; 4.35, 0.26; 4.24, 0.23; 4.13, 0.30; 3.42, 0.20; 3.12, 0.28; 3.06, 0.22; 2.993, 0.13; 2.862, 0.15.

Monoaminoguanidinium 3,5-Di-(nitramino)-1,2,4-triazole.—A solution of 0.4 g. of aminoguanidinium bicarbonate and 0.18 g. of ammonium di-(nitramino)-triazole (0.18 g.) in 10 ml. of water was heated to and maintained at the boiling point until the rapid evolution of ammonia ceased. The solution was cooled and adjusted to pH 3 with concentrated hydrochloric acid. There was an immediate formation of a white precipitate which was removed by filtration and washed with cold water. The product was recrystallized from 15 ml. of water; rosettes of needles, m.p. 180° (dec.). An X-ray powder pattern was different than that for either the starting material or the isomeric 2-amino-guanyl-1,6-dinitro-biguanidine.

Anal. Calcd. for $C_8H_9N_7O_4$: C, 13.69; H, 3.45; N, 58.55. Found: C, 13.31; H, 3.20; N, 59.1.

X-Ray Data (Photo).—15.2, 1.00; 5.53, 0.20; 5.15, 0.30; 4.59, 0.50; 4.09, 0.20; 3.81, 0.60; 3.41, 0.60; 3.24, 0.80; 3.08, 0.80; 2.633, 0.20.

Di-(benzalamino-guanidinium) 3,5-Di-(nitramino)-1,2,4-triazole.—A slurry of 0.22 g. of the ammonium salt of di-(nitramino)-triazole, 0.4 g. of benzalamino-guanidine and 15 ml. of absolute methanol was allowed to stand for three days at room temperature; any lumps which formed were occasionally broken apart. The solid was removed by filtration and weighed 0.56 g. (quantitative), m.p. 183–184°. Recrystallization from 175 ml. of absolute methanol did not change the melting point.

Anal. Calcd. for $C_{18}H_{23}N_{15}O_4$: C, 42.10; H, 4.51; N, 40.92. Found: C, 42.32; H, 4.63; N, 41.04, 40.66.

X-Ray Data (Photo).—15.5, 1.00; 13.8, 0.10; 8.49, 0.80; 6.80, 0.30; 5.15, 0.60; 4.03, 0.10; 3.53, 0.40; 3.26, 0.60; 3.03, 0.30; 2.871, 0.10.

Reduction of 3,5-Di-(nitramino)-1,2,4-triazole. A.—One gram of potassium di-(nitramino)-triazole and 4 g. of zinc dust were slurried in 25 ml. of water. Six milliliters of glacial acetic acid was added during 90 minutes with stirring; the temperature was held about 25°. The resulting mixture was warmed to 50°, filtered from unreacted zinc and treated with hydrogen sulfide for one hour. After the zinc sulfide had been removed by filtration, the filtrate was evaporated to dryness under reduced pressure at room temperature. The gummy solid was dissolved in 25 ml. of 95% ethanol, made alkaline to phenolphthalein with

piperidine and refluxed for two hours with 1.5 ml. of benzaldehyde. The solution gradually became brownish-yellow in color. The cooled solution was diluted with 20 ml. of water and chilled at 0° for 60 hours. The small lumps of crystals were removed (the filtrate was retained for A-1), the yield was 0.4 g.; m.p. 215–220°. After several recrystallizations from 95% ethanol, the melting point was raised to 230–231° and the compound was obtained as pale yellow, flat needles. A mixed melting point with dibenzal-3,4,5-triamino-1,2,4-triazole (m.p. 200°) was 181–186°. The analyses were consistent with those calculated for dibenzal-3-amino-5-hydrazino-1,2,4-triazole.

Anal. Calcd. for $C_{16}H_{14}N_6$: C, 66.19; H, 4.86; N, 28.95. Found: C, 66.27; H, 5.12; N, 28.63, 28.79.

The same compound was also isolated as one of the products in the zinc-acetic acid reduction of 1,6-dinitrobiguanidine.

When the dibenzal derivative was heated with picric acid in 95% ethanol, hydrolysis of one benzal group occurred and the picrate of monobenzal-3-amino-5-hydrazino-1,2,4-triazole was formed. Recrystallization from 95% ethanol gave orange needles which decomposed at 242–243°.

Anal. Calcd. for $C_{15}H_{13}N_6O_7$: C, 41.77; H, 3.04; N, 29.23. Found: C, 41.89; H, 3.20; N, 29.14, 29.34.

A-1.—By combining the reaction mother liquors and the first recrystallization liquors, diluting with more water to a permanent turbidity, and cooling the solution at 5° for several hours, a small quantity of another material melting at 245–250° was obtained. Recrystallization from 60% ethanol gave pale yellow platelets, m.p. 263–265° (dec.). The analyses agree with those calculated for dibenzal-3,5-dihydrazino-1,2,4-triazole.

Anal. Calcd. for $C_{16}H_{15}N_7$: C, 62.93; H, 4.95; N, 32.12. Found: C, 63.20; H, 4.62; N, 32.20.

B.—One gram of ammonium di-(nitramino)-triazole, slurried in 50 ml. of 50% aqueous acetic acid, was hydrogenated for 18 hours over 0.1 g. of Adams platinum oxide. The initial pressure was 50 p.s.i. Complete solution of the triazole was obtained. After the catalyst had been removed, the filtrate was diluted with 25 ml. of water, heated to boiling with 1.2 g. of picric acid and cooled. Orange-yellow, flat needles, m.p. 249–251° (dec.), were obtained; a mixed melting point with an authentic sample of 3,5-diamino-1,2,4-triazole picrate was the same; X-ray powder diagrams were also identical.

X-Ray Data.—5.21, 0.40; 4.92, 1.00; 4.03, 0.40; 3.84, 0.63; 3.78, 0.58; 3.61, 0.98; 3.33, 0.53; 3.06, 0.46; 2.907, 0.33; 2.702, 0.84.

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