NITROGUANIDINES[1]

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I. INTRODUCTION

Nitroguanidine is an important ingredient of flashless propellants; hence World War II gave to the study of this compound a stimulus which has continued unabated to the present. The investigations have provided many new derivatives of nitroguanidine and have resulted in the introduction of new methods for their preparation. In addition, the structure of nitroguanidine has attracted considerable attention along with the mechanisms of its reactions. Although the dearrangement mechanism (21, 23) offers a reasonable explanation for the transformation products of nitroguanidine, it has certain deficiencies. Some of these are discussed under specific reaction headings. An addition–elimination mechanism appears to offer a better interpretation of the reaction

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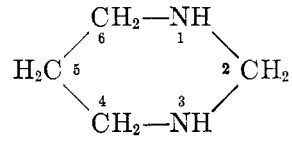
of amines with nitroguanidine and substituted nitrosonitroguanidines. The final decisions regarding these mechanisms must await further studies.

This review summarizes the published results on nitroguanidine chemistry to the early part of January 1952.[2]

II. NOMENCLATURE

The several systems used in naming compounds containing the $\rangle NNO_2$ group have been discussed (63, 82) previously. In the present paper the terms "nitramine" and "nitrimine" are used exclusively. Since the structures of nitroguanidine and some of its derivatives are being actively contested, the nitroguanidine derivatives are designated as *N*-substituted *N'*-substituted N"-nitroguanidines, in preference to the use of the more exact numbering system.

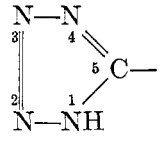
The heterocyclics referred to in this paper are numbered to give the hetero atoms the lowest possible values (82, 110). Thus, hexahydropyrimidine (I)



I

Hexahydropyrimidine

is referred to as 1,3-diazacyclohexane, while the tetrazole ring is numbered as in II.



II

III. NITROGUANIDINE

A. Preparation

Jousselin (57) in 1877 described a compound which he thought to be nitrosoguanidine. It was prepared by dissolving guanidine nitrate in fuming nitric acid through which nitrous oxide was bubbled. This solution was heated for a few minutes, after which it was poured into water to precipitate the product. Two years later Jousselin (58) gave an improved method of preparing this compound from guanidine nitrate and fuming nitric acid. He also prepared it by treating guanidine nitrate with sulfuric acid (59), but he still retained the mis-

[2] The patents pertaining to the preparation of metallic salts of nitroaminoguanidine and the silver salt of nitroguanidine have been omitted from this review. Some of these salts, especially the silver salt of nitroguanidine, are ill-defined and have contributed very little to the understanding of the chemistry of nitroguanidines.

conception that he was dealing with a nitroso compound. In 1891 both Pellizzari (111) and Franchimont (33) repeated the preparation described by Jousselin and proved the product to be nitroguanidine. The following year Thiele (132) produced nitroguanidine in 46.5 per cent yield by nitration of guanidine thiocyanate and by treating guanidine nitrate with a mixture of fuming sulfuric and nitric acids. Nitroguanidine also was obtained (133) as the main product when nitrosoguanidine was oxidized in nitric acid with potassium permanganate. Later Remsen and Garner (117) found that the benzenesulfonate and *p*-toluenesulfonate of guanylurea were converted to nitroguanidine in *ca.* 60 per cent yield on treatment with fuming nitric acid.

The above procedures of preparing nitroguanidine have evolved into two practical methods for its production, which have been also the most extensively studied. These methods are the nitration of guanidine sulfate (8, 22, 73, 127) and of guanidine nitrate (4, 19, 22, 30, 57, 58, 59, 60, 111, 122, 132). Marqueyrol and Loriette (73) claimed an 84 per cent conversion of dicyandiamide to nitroguanidine without isolation of the intermediate guanidine sulfate. Dicyandiamide is hydrolyzed to guanidine sulfate by heating with 61 per cent sulfuric acid to 135–140°C. Then the solution of guanidine sulfate is fortified with mixed acid to give a solution of the desired acid strength for nitration. The product is precipitated by pouring the acid solution into water. A lower yield of 65 per cent was obtained by Stettbacher (127) using this method. More recently Aubertein (8) has completed a systematic study of the preparation of nitroguanidine by the method of Marqueyrol and Loriette. The results of this study indicated that nitroguanidine may be obtained in 90 per cent yield from dicyandiamide when the best conditions are employed as follows: (*1*) The water content of the solution after the conversion of dicyandiamide to guanidine sulfate is complete must be below 11 per cent. The operating procedure during this step is regulated so that sufficient water evaporates during the heating to give the required concentration. (*2*) The temperature of nitration is held as nearly as possible at 25°C. (*3*) The maximum excess of nitric acid used in nitration is near 30 per cent.

The most important method of preparing nitroguanidine is the addition of guanidine nitrate to concentrated sulfuric acid. Ewan and Young (30) examined three methods of obtaining nitroguanidine from guanidine nitrate. These methods employed (*a*) concentrated sulfuric acid, (*b*) nitric acid, and (*c*) a mixture of sulfuric and nitric acids. Ewan and Young concluded that the action of 92–98 per cent sulfuric acid on guanidine nitrate for a period of 48 hr. gave the most satisfactory yields (87.1 per cent). The temperature was held below 30–40°C. High yields were obtained also by the use of 87–95 per cent sulfuric acid and a reaction time of 30 min. Davis (19) obtained a 75 per cent yield by dissolving guanidine nitrate in sulfuric acid at 20–25°C. and then pouring the solution into ice and water. It was found that a period of 15–20 hr. was required to dissolve the guanidine nitrate. This undoubtedly depended upon the small ratio of sulfuric acid to guanidine nitrate (1.65:1) used. Smith, Sabetta, and Steinbach (122) made a detailed study of this method and concluded that pure guanidine nitrate was necessary to obtain high-grade nitroguanidine. Also, by

increasing the ratio by weight of sulfuric acid to guanidine nitrate to 3:1, they were able to obtain nitroguanidine consistently in yields of 92 per cent. The reaction time was decreased to 30–60 min., while the reaction temperature was maintained below 0°C. This method of manufacturing nitroguanidine has been converted into a continuous process (4). Sulfuric acid (93.2–98 per cent) and guanidine nitrate in the ratio by weight of 2.35:1 are fed continuously into a system circulating a sulfuric acid solution of guanidine nitrate at 35°F. Part of the reaction mixture is continuously withdrawn for dilution to precipitate the nitroguanidine. The additions and withdrawals are maintained in balance once the run is started.

The use of substituted guanidine salts (III) for the preparation of *N*-alkyl-*N'*-nitroguanidines (IV) by nitration also has been reported (23).

$$\underset{\text{III}}{RNR'C(=NH)NH_2\cdot HNO_3} + H_2SO_4 \rightarrow \underset{\text{IV}}{RNR'C(=NH)NHNO_2} + H_2SO_4\cdot H_2O$$

RR' = alkyl or R' = H.

B. Quantitative estimation

Nitric oxide can be split off from nitroguanidine quantitatively upon the addition of sulfuric acid and mercury. The volume of nitric oxide liberated may then be measured in the Lunge nitrometer. This method has been used (16) to determine the purity of samples of nitroguanidine. The reaction yields only the nitrogen of the nitro group.

The ferrous sulfate method for the determination of nitrates has been adapted (17) to the quantitative analysis of nitroguanidine. The end-point of the titration is evidenced by the development of a brown color due to the formation of $FeSO_4\cdot NO$. This brown color develops on addition of a slight excess of the ferrous sulfate reagent. The use of this titration technique gave erratic results because of the indistinctness of the end-point. When, however, the titration was performed potentiometrically, excellent results were obtained. The latter method allowed the quantitative estimation of nitroguanidine with an accuracy of ± 0.2 per cent.

The only other technique developed for the assay of nitroguanidine was reduction with excess titanous chloride in acid solution (62, 138). The unreacted titanous chloride was determined by titration with standard ferric alum solution. This procedure gave variable results. One equivalent of nitroguanidine was found (138) to consume 3.75–4.21 equivalents of titanous chloride instead of the 6 equivalents required for conversion of nitroguanidine to aminoguanidine, as follows:

$$NH_2C(=NH)NHNO_2 + 6H \rightarrow NH_2C(=NH)NHNH_2 + 2H_2O$$

If 0.70–0.85 equivalent of ferrous ion is added to the nitroguanidine–titanous chloride solution before refluxing, then 6 equivalents of titanous chloride are consumed in the reaction. This modification could be used for the assay of nitroguanidine with an accuracy of 1.3–2.2 per cent, a result which compares favor-

ably with the Dumas nitrogen determination. The ferrous ion–titanous chloride method can be employed for the quantitative determination of other ammonocarbonic acids such as nitroaminoguanidine, *N*-methyl-N′-nitroguanidine, *N*-butyl-*N*′-nitroguanidine, etc. One disadvantage is that the concentration of ferrous ion required for consumption of 6 equivalents of titanous chloride reagent must be predetermined for each ammonocarbonic acid.

C. Physical properties

Nitroguanidine has been reported as decomposing at various temperatures between 220° and 257°C. As in the case of other compounds which decompose without melting, the decomposition point varies with the rate of heating. Davis, Ashdown, and Couch (22) described methods of preparing two crystalline modifications of nitroguanidine, which they called α- and β-nitroguanidine. Subsequent investigation (27) of these crystalline forms proved both to belong to the orthorhombic crystal system. The crystals are elongated rods having axial ratios $a:b:c$ of 0.708:1:0.144. Cleavage occurs parallel to the *c*-axis. X-ray diffraction data (27, 77, 124) showed the unit cell measurements to be a = 17.47 Å., b = 24.50 Å., and c = 3.59 Å. There are sixteen molecules (formula weights) of nitroguanidine per unit cell. The true density from x-ray data was found to be 1.78 (77). The refractive indices measured at 25°C., using light of 5893 Å. wave length, were $\alpha = 1.526 \pm 0.002$, $\beta = 1.694 \pm 0.002$, and $\gamma = 1.81 \pm 0.01$.

The heat of combustion of nitroguanidine at constant volume has been reported (74) as 210 kcal./mole.

Ultraviolet absorption spectra for nitroguanidine in various solvents have been reported by several workers (9, 56, 97, 118). In water it exhibits two absorption maxima in the ultraviolet region. The principal absorption maximum at 269 mμ has a molar extinction coefficient of 14,900. Infrared spectra of nitroguanidine and some of its derivatives have been published recently (64). Some twenty guanidine derivatives were found to give a strong absorption band in the region of 5.95–6.02 microns. This band is in the region of the spectrum characteristic of double bonds and was attributed to the C=NH group of the guanidines. Nitroguanidine itself gives a band at 6.0 microns. Another absorption band, which is assigned to the nitro group, occurs at 6.15 microns.

Jousselin (58) first observed that nitroguanidine crystallized from warm hydrochloric acid or nitric acid solution on cooling as the hydrochloride or nitrate salt, respectively. These salts were readily hydrolyzed by water, indicating that nitroguanidine has only weakly basic properties. Wood (137) determined the extent of dissociation of nitroguanidine hydrochloride in $N/25$ solution by its effect on the rate of hydrolysis of methyl acetate. This method showed that a $N/25$ solution of nitroguanidine hydrochloride is dissociated to the extent of 97.5 per cent. A 94 per cent dissociation was calculated for a $N/10$ solution and the dissociation constant of the base at 40.2°C. was calculated to be $2.1 \times 10.^{-14}$ This is just slightly less than the value for urea (3.7×10^{-14}) or acetamide (3.3×10^{-14}). The slight basicity of nitroguanidine is responsible for its increased solubility in acid solutions. Since in the final stage of the commercial production of

nitroguanidine it is precipitated by dilution of its sulfuric acid solution in water, this solubility factor becomes of practical importance. Davis (18) and Ewan and Young (30) have measured the solubility of nitroguanidine in dilute solutions of sulfuric acid. Some of the more important values are given in table 1.

Although a few values for the solubility of nitroguanidine in water have been reported (26, 132), the most detailed study was published in 1951 (75). This

TABLE 1

Solubility of nitroguanidine in dilute sulfuric acid solutions

H_2SO_4	GRAMS OF NITROGUANIDINE/100 G. OF ACID SOLUTION		
	0°C.*	13°C.†	25°C.*
per cent	*grams*	*grams*	*grams*
5.8		0.37	
17.0	0.399		0.623
17.2		0.65	
20.0		0.72	
20.9	0.577		1.113
24.8	0.640		1.525
28.2		1.37	
29.8	1.235		2.225
44.7	5.134		8.250

* The values given for 0°C. and 25°C. were calculated from data published by Davis (18).

† Ewan and Young (30).

recent work showed that in the range 30–70°C. the solubility can be expressed with an accuracy of 0.3 per cent by the equation

$$\text{Log (solubility in g./100 g. of water)} = -1963.2/T + 6.1255$$

while above 70°C. the solubility can be expressed with an accuracy of 1.3 per cent by the equation:

$$\text{Log (solubility in g./100 g. of water)} = -2167.0/T + 6.7215$$

In the higher temperature range autocatalytic hydrolysis of nitroguanidine occurs, increasing the alkalinity of the solution. Since nitroguanidine is amphoteric in nature, this effects an increase in solubility. The solubilities of nitroguanidine (in grams per 100 ml. of solvent) at 19°C. in nonaqueous solvents were determined (26) to be 0.050 in ethyl acetate, 0.267 in acetone, 0.166 in 96 per cent ethanol, 0.302 in methanol, and 1.750 in pyridine. Nitroguanidine is insoluble in benzene, chloroform, carbon tetrachloride, and toluene.

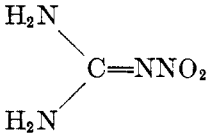
Another important physical property of nitroguanidine is its crystal habit. It crystallizes in slender needles, similar to those of phthalic anhydride, which mat into a felt-like mass. Thus, hand-packed nitroguanidine has a density of 0.3, while the true density is 1.78. This is unfavorable to the use of nitroguanidine as an explosive. The shattering effect of an explosive is dependent on its rate of detonation, which is, in turn, directly proportional to its packed density. At a density of 1.0 the rate of detonation of T.N.T. is 4870 m. per second, while that

of nitroguanidine is 5360 m. per second (114). The low density of hand-packed nitroguanidine is undoubtedly due in part to the formation of hollow crystals (15). If nitroguanidine is crystallized from dilute acetic acid, 70–80 per cent of the crystals have hollow cavities. When it is crystallized from water, only 10–20 per cent of the hollow aggregates are formed. Successful attempts (114) have been made to increase the bulk density of nitroguanidine by a change in crystallization technique. Nitroguanidine having a bulk density of 0.96 can be prepared by introduction of a hot saturated aqueous solution of the substance into methanol under controlled conditions. This material of higher bulk density can be slurried with T.N.T. for charging high-explosive shells. A detailed description of the preparation of nitroguanidine with high bulk density is given by Pritchard and Wright (114).

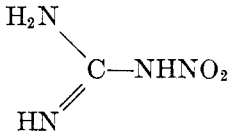
The main practical use of nitroguanidine is as an ingredient of flashless propellant mixes rather than as an explosive *per se*. Here again the crystallization habit of nitroguanidine is of tremendous importance. In order to prepare propellant mixes of desirable physical traits and containing high percentages of nitroguanidine, small crystals are required. A number of patents and papers (2, 3, 5, 6, 14, 28, 31, 32, 55, 107, 130, 135) have been published describing various procedures for obtaining nitroguanidine in fine crystals. This is accomplished by spraying a saturated aqueous solution of nitroguanidine into a countercurrent of dry air (2, 5, 6, 55, 107) or by adding the saturated solution to cold water (28, 130). The technique of rapid crystallization has been tried (14) with different solvents. Crystals of fine structure have been prepared also by the use of additives such as amines (3, 31, 32) or protective colloids (135) to affect the crystallizing habit of nitroguanidine. Tranchant (135) has reviewed the procedures used by the United States, Britain, and Germany and has investigated the use of protective colloids, e.g., carboxymethyl cellulose, starch, or dextrin, in the preparation of fine crystals.

D. Structure

Two structures have been considered for nitroguanidine: namely, the symmetrical (V) and the unsymmetrical (VI) forms. Although Pellizzari (111)



V



VI

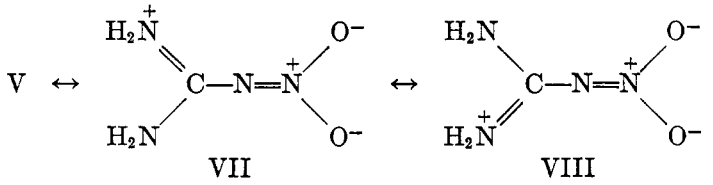
and Franchimont (33) used the symmetrical form, they presented no arguments in its favor. The first constructive arguments on the structure of nitroguanidine were presented by Thiele (132) in 1892. Thiele was unable to decide between the two forms on the basis of the behavior of nitroguanidine itself, but he concluded that its reduction product, aminoguanidine, possessed an unsymmetrical structure and that therefore nitroguanidine must exist in the nitramino form (VI). Furthermore, the formation of salts with acids and the dissolution of nitroguanidine in alkali were thought by Thiele to agree only with the unsymmetrical structure.

Since Thiele's publication this formula for nitroguanidine has been used almost exclusively.

Lieber, Sherman, and Patinkin (68) concluded from their ultraviolet studies that nitroaminoguanidine and nitroguanidine exist as "zwitterions." Earlier studies (42) of the oxidation–reduction potentials of nitroguanidine–nitrosoguanidine systems led to the same conclusion.

Recently Barton, Hall, and Wright (10) have questioned the nitramino form of nitroguanidine because it does not ordinarily act as an acid. They found that nitroguanidine in alkali changed on standing to give an acidic substance. Since they considered that the acidic properties could not be attributed to hydrolysis products alone, they stated that nitroguanidine exists in the nitrimino form and slowly changes over into the acidic nitramino form in alkali. However, this conclusion does not agree with the ultraviolet absorption spectra (56, 97) of nitroguanidine in neutral and basic media. These studies indicate that nitroguanidine changes immediately on addition to alkali to give a different species, responsible for an entirely new type of absorption in the ultraviolet region. Moreover, when a derivative of nitroguanidine, e.g., methylnitroguanidine or 2-nitramino-2-imidazoline, which gives the same type of absorption curve as nitroguanidine, is allowed to stand in alkali there is a steady decrease in E_{max}. The shape of the curve remains the same. This indicates that hydrolysis of the nitroguanidine derivatives begins immediately and continues during their contact with alkali (97). Although Barton, Hall, and Wright claim that the acidity observed by them was not due to hydrolysis products, their results do not exclude this possibility.

An extensive study (97) of the ultraviolet absorption spectra of nitroguanidine and its derivatives indicates that nitroguanidine exists as a resonance hybrid of several electronic structures, including V, VII, and VIII. Lamberton (63) has suggested that in theory no one bond of nitroguanidine is uniquely single or



double. At present, this seems to be the closest approach to the actual structures of nitroguanidine and its derivatives, e.g., 2-nitramino-2-imidazoline, capable of resonance.

E. Decomposition by acid and by heat

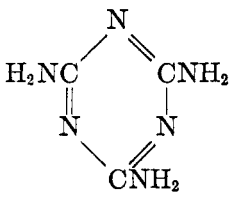
A solution of nitroguanidine in sulfuric acid on heating gives off nitrous oxide and carbon dioxide (18, 21). Ammonia also is produced quantitatively, in agreement with the equation:

$$NH_2C(=NH)NHNO_2 + HOH \rightarrow N_2O + 2NH_3 + CO_2$$

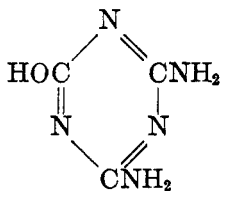
Davis and Abrams (21) showed that a solution of nitroguanidine in sulfuric acid

could be used to nitrate aniline, phenol, or aceto-*p*-toluide. They added an excess of aniline to a sulfuric acid solution of nitroguanidine and after completion of the reaction diluted with water. The dilute solution was made ammoniacal, and ammonium picrate was added, whereupon a precipitate of guanidine picrate formed. The authors used this as evidence for the presence of cyanamide. However, the presence of guanidine itself was not excluded.

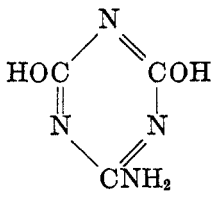
The decomposition of nitroguanidine by heat is more complex (21). Besides the simple products nitrous oxide, ammonia, carbon dioxide, cyanogen, cyanamide, urea, cyanic acid, and hydrogen cyanide, polymers of some of these products were formed. The polymeric substances identified were melamine (IX),



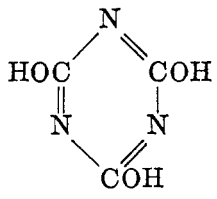
IX
Melamine



X
Ammeline



XI
Ammelide



XII
Cyanuric acid

ammeline (X), ammelide (XI), cyanuric acid (XII), melem, melam, melon, and paracyanogen. Probable structures for melem, melam, and melon have been described by Redemann and Lucas (116).

IV. REDUCTION OF NITROGUANIDINES

Pellizzari (111), in an attempt to reduce nitroguanidine to aminoguanidine, obtained ammonium chloride and guanidinium chloride. The following year Thiele (132) reported the preparation of aminoguanidine from nitroguanidine by reduction with zinc dust in acid solution. He also (133) isolated and identified the intermediate reduction product, nitrosoguanidine (XIII).

$$NH_2C(=NH)NHNO$$

XIII

Nitrosoguanidine

The yields of nitrosoguanidine were 40–60 per cent when the reductions were performed in an aqueous solution of ammonium chloride with zinc dust (119). Kerone (61) has described a similar method in which the acidity is provided by acetic acid, hydrochloric acid, ammonium chloride, ammonium sulfate, or calcium chloride. The oxidation potential of the nitroguanidine–nitrosoguanidine system has been measured (121). These results showed the reduction of nitroguanidine to nitrosoguanidine to be a reversible reaction. A practical inference from these studies was that it is not feasible to reduce nitroguanidine with hydrogen in strongly alkaline solution.

Davis and Rosenquist (25) have employed zinc dust in aqueous ammonium hydroxide to prepare *N*-methyl-*N'*-nitrosoguanidine, *N*-*n*-butyl-*N'*-nitrosoguan-

idine, and *N*-benzyl-*N'*-nitrosoguanidine from the respective nitroguanidines. *N*-Methyl- and *N*-ethyl-*N'*-nitrosoguanidines also have been prepared by the reduction of methyl- and ethylnitroguanidines in absolute methanol, using Raney nickel catalyst (72).

McGill (78) prepared aminoguanidine by the reduction of nitroguanidine with hydrogen in the presence of reduced nickel on kieselguhr. Other metallic catalysts were claimed to be effective. The hydrogenation was stated specifically to be carried out in the absence of substantial amounts of acids. Also, it has been claimed (138) that reduction may be carried out in aqueous solution with zinc in the presence of metallic acetates, e.g., zinc acetate. However, Lieber and Smith (70) found that the best yields of aminoguanidine were obtained when the catalytic reductions were conducted in an acid medium. At ratios of acid to nitroguanidine above 1, the formation of aminoguanidine was directly proportional to the uptake of hydrogen. When this reduction was carried out in 15 per cent acetic acid, the yield of aminoguanidine was 88.8 per cent. Furthermore, it was found that nitrosoguanidine was formed as an intermediate only on catalytic reduction in neutral and basic media, while in acid media aminoguanidine formed directly. This was considered one of the reasons for the higher yields on reduction in acid media. In confirmation of this it was observed (71) that the yields of aminoguanidine, beginning with nitrosoguanidine in acid medium, were very much lower than when the starting material was nitroguanidine. This is summarized in the following reaction scheme:

$NH_2C(=NH)NHNO_2$

$$+\ 3H_2 \xrightarrow{\text{catalyst}} \begin{cases} \xrightarrow{\text{neutral or basic media}} NH_2C(=NH)NHNO \\ \xrightarrow{\text{acid media}} NH_2C(=NH)NHNH_2 + 2H_2O \end{cases}$$

In addition, aminoguanidine has been produced in 60–70 per cent yield by adding a 1:1 mixture of sodium and ammonium chloride to a solution of nitroguanidine in liquid ammonia (36). When ammonium chloride was omitted, one mole-equivalent of nitrogen was evolved and cyanamide remained after evaporation of the ammonia.

Nitroguanidine has been reduced also by the use of electrolytic methods (120, 125, 129). It was converted to aminoguanidine in 75–80 per cent yield by using a tin cathode and stannous chloride in an electrolyte of 5 per cent sulfuric acid (125). Other cathodes used were lead, nickel, and cadmium. Nitrosoguanidine was identified as an intermediate reduction product.

Some substituted aminoguanidines, e.g., *N*-ethyl-*N'*-aminoguanidine, have been prepared by the catalytic reduction of the appropriate nitroguanidines (72). As a proof of the structure of nitroaminoguanidine (XIV) it was reduced (112) with zinc dust in 10 per cent acetic acid to the known *N*,*N'*-diaminoguanidine (XV), which was isolated as its hydrochloride (m.p. 176°C.).

$$NH_2NHC(=NH)NHNO_2 + 3H_2 \rightarrow NH_2NHC(=NH)NHNH_2 + 2H_2O$$

XIV — Nitroaminoguanidine

XV — *N*,*N*′-Diaminoguanidine

V. HYDRAZINOLYSIS OF NITROGUANIDINES

In 1928 Phillips and Williams (112) reported the preparation of nitroaminoguanidine (XIV) by the hydrazinolysis of nitroguanidine. They claimed that nitroaminoguanidine was formed in 50 per cent yield, but a repetition (48) of this work, using more precise methods of analysis, indicated that the yields were actually 30–35 per cent. Phillips and Williams noted that nitrous oxide and ammonia were produced on heating an aqueous solution of nitroguanidine and hydrazine. Thus they suggested the following reactions to account for the low yields of nitroaminoguanidine, although they were unable to find aminocyanamide (XVI) in the reaction liquors.

$$NH_2C(=NH)NHNO_2 + N_2H_4 \rightarrow NH_2\underset{\displaystyle NH_2}{\overset{\displaystyle NHNO_2}{\overset{|}{\underset{|}{C}}}}NHNH_2$$

$$\downarrow \qquad\qquad \downarrow$$

$$HN{=}C{=}NNH_2 + N_2O + NH_3 + H_2O \qquad NH_2NHC(=NH)NHNO_2 + NH_3$$

XVI — Aminocyanamide

XIV — Nitroaminoguanidine

Henry, Lewis, and Smith (48) reinvestigated the hydrazinolysis of nitroguanidine. They found the two principal by-products formed to be aminoguanidine (XVII) and diaminoguanidine (XV). It was estimated that approximately twice as much diaminoguanidine as aminoguanidine (on a weight basis) was produced when nitroguanidine was heated with an equivalent weight of hydrazine. The formation of these products may be explained by the "dearrangement mechanism" (21, 23), as follows:

$$NH_2C(=NH)NHNO_2 \rightleftharpoons \begin{cases} NH_3 + N{\equiv}CNHNO_2 \\ NH_2NO_2 + N{\equiv}CNH_2 \\ \quad\downarrow \\ N_2O + H_2O \end{cases}$$

$$N{\equiv}CNHNO_2 + N_2H_4 \rightleftharpoons NH_2NHC(=NH)NHNO_2$$

XIV

$$N{\equiv}CNH_2 + N_2H_4 \rightleftharpoons NH_2NHC(=NH)NH_2$$

XVII — Aminoguanidine

$$NH_2NHC(=NH)NHNO_2 \rightleftharpoons NH_2NO_2 + N{\equiv}CNHNH_2$$

$$\downarrow$$

$$N_2O + H_2O$$

$$N{\equiv}CNHNH_2 + N_2H_4 \rightleftharpoons NH_2NHC(=NH)NHNH_2$$

XV

Diaminoguanidine

Although this mechanism accounts for the products formed, it has the disadvantages outlined in Section VI,A. If one considers the reaction to occur by an addition–elimination mechanism (an intermediate may be formed or the addition–elimination reactions occur simultaneously), then the products could originate in the following manner:

Primary reaction:

$$NH_2C(=NH)NHNO_2 + N_2H_4 \rightarrow NH_2\overset{\displaystyle NH_2}{\underset{\displaystyle NHNO_2}{C}}NHNH_2$$

$$\downarrow \qquad\qquad\qquad \downarrow$$

$$NH_2C(=NH)NHNH_2 + NH_2NO_2 \qquad NH_2NHC(=NH)NHNO_2 + NH_3$$

XVII XIV

$$NH_2NO_2 \rightarrow N_2O + H_2O$$

Secondary reaction:

$$NH_2NHC(=NH)NHNO_2 + N_2H_4 \rightarrow NH_2NH\overset{\displaystyle NH_2}{\underset{\displaystyle NHNO_2}{C}}NHNH_2 \longrightarrow$$

XIV

$$NH_2NHC(=NH)NHNH_2 + N_2O + H_2O$$

XV

Recently (49) the yield of nitroaminoguanidine was increased by acidification of the reaction mixture at the end of the heating period. In this manner 40–50 per cent yields of nitroaminoguanidine of 96 per cent purity were obtained.

Nitroaminoguanidine decomposes at 190°C. Its lowest solubility in water occurs at about a pH of 7 and increases on either side of this pH in accordance with its amphoteric nature (76). Since it possesses a hydrazino group, it combines with aldehydes and ketones to form nitroguanylhydrazones:

$$NO_2NHC(=NH)NHNH_2 + CH_3CHO \rightarrow$$

$$NO_2NHC(=NH)NHN{=}CHCH_3 + H_2O$$

This latter reaction was first suggested by Phillips and Williams (112), but they did not report the properties of any of the hydrazones. Now, however, a number

of these derivatives have been described in the literature (52, 113, 115, 123, 128, 136); they are listed in table 11 along with their melting points.

The reaction (51) of methylhydrazine with *N*-methyl-*N*-nitroso-*N'*-nitroguanidine is of interest because the product formed was *N*-methyl-*N*-amino-*N'*-nitroguanidine (XVIII). None of the isomeric *N*-methylamino-*N'*-nitroguanidine (XIX) could be detected in the reaction mixture. When *N*-*n*-butyl-

$CH_3N(NH_2)C(=NH)NHNO_2$ XVIII

$CH_3NHNHC(=NH)NHNO_2$ XIX

N'-nitroguanidine was heated with hydrazine in aqueous solution (48), nitroguanidine, diaminoguanidine, and butylamine were formed. No *N*-*n*-butyl-*N'*-aminoguanidine was isolated. If, however, the reaction was run in ethyl alcohol, then the main products were *N*-*n*-butyl-*N'*-aminoguanidine and diaminoguanidine.

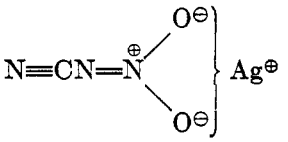
VI. AMINOLYSIS

A. Nitroguanidine

It has been suggested (21, 23) that nitroguanidine and *N*-alkyl-*N'*-nitroguanidines may react *via* two different routes:

$$RNHC(=NH)NHNO_2 \rightleftharpoons \begin{cases} RNH_2 + N{\equiv}CNHNO_2 & (A) \\ RNHC{\equiv}N + (NH_2NO_2 \rightarrow N_2O + H_2O) & (B) \end{cases}$$

When amines are heated with nitroguanidine, ammonia is liberated and *N*-substituted *N'*-nitroguanidines are formed. Therefore, nitroguanidine in aqueous amine solution was thought to decompose mainly by route A. This mechanism provides a satisfactory explanation for the products obtained when nitroguanidine or substituted nitroguanidines are employed in various reactions. There are, however, serious objections to the dearrangement theory, one of which was raised by Thiele (133) in 1893 with respect to the reaction of nitrosoguanidine with hydrazine. He noted that products formed in the latter reaction could be explained by assuming that nitrosoguanidine first splits into water, nitrogen, and cyanamide, the cyanamide then combining with hydrazine to give aminoguanidine. Thiele stated that his objection to the acceptance of this idea was based on the observation that the reaction of hydrazine with nitrosoguanidine proceeds at a low temperature which does not permit the splitting of nitrosoguanidine into cyanamide. In addition, amines combine with a substituted nitroguanidine, 1-nitro-2-nitramino-2-imidazoline, to give practically quantitative yields of linear-substituted nitroguanidines (92) (*cf.* Section VI,C). Such high yields would not be expected if dearrangement of any of the involved substituted nitroguani-



XX

dines occurred. Finally, several attempts (92) to prepare a substituted nitroguanidine by treating silver nitrocyanamide (XX) with one mole-equivalent of amine hydrochloride or potassium nitrocyanamide with an excess of an amine have failed.

The formation of *N*-alkyl-*N'*-nitroguanidines from amines and nitroguanidine can be explained by an addition–elimination mechanism. This reaction is accompanied by side reactions involving hydrolyses which result in the formation of ureas and nitrous oxide. Also, Davis and Elderfield (23) have shown that substituted nitroguanidines will combine with amines to give substituted guanidines and ureas. All these reactions may be expected to occur as follows:

$$NH_2C(=NH)NHNO_2 +$$

$$RNH_2 \rightleftharpoons NH_2\underset{\displaystyle RNH}{\overset{\displaystyle NH_2}{\overset{|}{\underset{|}{C}}}}NHNO_2 \rightarrow RNHC(=NH)NHNO_2 + NH_3(g)$$

$$\downarrow$$

$$RNHC(=NH)NH_2 + N_2O(g) + H_2O$$

$$NH_2C(=NH)NHNO_2 +$$

$$H_2O \rightleftharpoons NH_2\underset{\displaystyle OH}{\overset{\displaystyle NH_2}{\overset{|}{\underset{|}{C}}}}NHNO_2 \rightarrow NH_2CONH_2 + N_2O(g) + H_2O$$

$$RNHC(=NH)NHNO_2 +$$

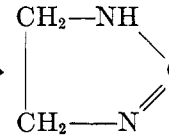
$$RNH_2 \rightleftharpoons RNH\underset{\displaystyle RNH}{\overset{\displaystyle NH_2}{\overset{|}{\underset{|}{C}}}}NHNO_2 \rightarrow RNHC(=NH)NHR + N_2O(g) + H_2O$$

$$RNHC(=NH)NHNO_2 +$$

$$H_2O \rightleftharpoons RNH\underset{\displaystyle OH}{\overset{\displaystyle NH_2}{\overset{|}{\underset{|}{C}}}}NHNO_2 \rightarrow RNHCONH_2 + N_2O(g) + H_2O$$

A number of *N*-substituted *N'*-nitroguanidines (see table 5) have been prepared by this method in 30–60 per cent yield. The yield of *N*-methyl-*N'*-nitroguanidine has been increased (101) from 30 per cent to 69–75 per cent by suspending nitroguanidine in 1 equivalent of aqueous potassium hydroxide solution and treating with methylamine hydrochloride at 59–61°C. This procedure has been used (102, 104) to prepare several cyclic nitroguanidine derivatives (XXI) (*cf.* table 7) from diamine salts and nitroguanidine. Later it was observed that it was not

$$NH_2CH_2CH_2NH_2 \cdot 2HCl + NH_2C(=NH)NHNO_2 + 2KOH \xrightarrow{H_2O}$$

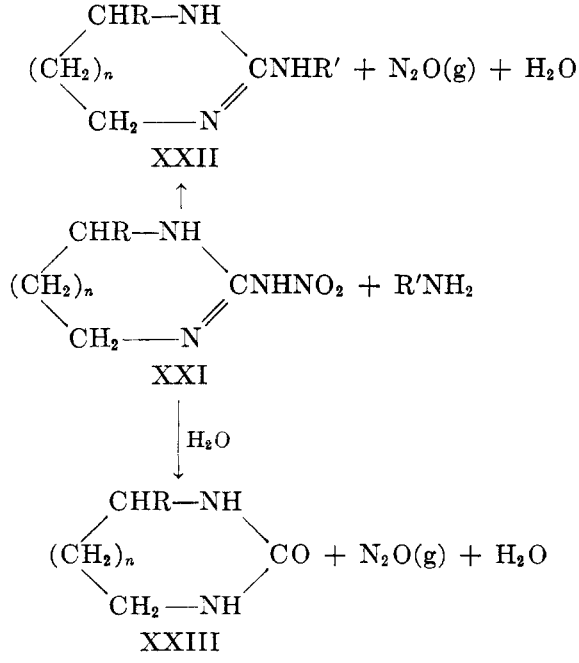


$$CNHNO_2 + 2NH_3(g) + 2KCl$$

XXI

necessary to use amine salts. Instead, if 0.2 mole-equivalent of an ammonium salt, e.g., ammonium sulfate, ammonium chloride, ammonium iodide, or ammonium phosphate, is added to an aqueous mixture of nitroguanidine and free amine before heating, equally high yields are obtained (126). These procedures of preparing *N*-substituted *N'*-nitroguanidines are successful with primary alkylamines, aralkylamines, and dimethylamine. An attempt (21) to use aniline and nitroguanidine to prepare *N*-phenyl-*N'*-nitroguanidine was unsuccessful. None of the higher secondary amines, e.g., diethylamine or di-*n*-propylamine, gave substituted nitroguanidines under these conditions.

As previously mentioned, substituted nitroguanidines heated with aqueous aliphatic amines (23) give *N*,*N'*-dialkylguanidines and substituted ureas. Thus, when cyclic nitroguanidine derivatives (XXI) were treated with amines (89, 90) to give 2-(substituted amino)-1,3-diaza-2-cycloalkenes (XXII), anhydrous conditions were used to avoid the formation of urea. However, the water generated in the reaction was sufficient to produce some (4–25 per cent) of the cyclic urea derivatives (XXIII).



$$CNHR' + N_2O(g) + H_2O$$

XXII

$$CNHNO_2 + R'NH_2$$

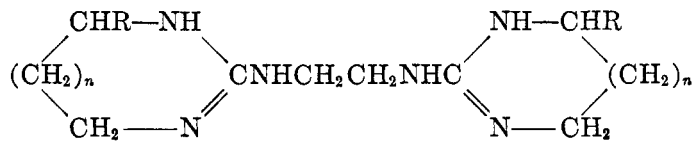
XXI

$$CO + N_2O(g) + H_2O$$

XXIII

R = H or CH_3; n = 0 or 1.

If aliphatic diamines are used, then both amino groups can replace nitramino groups of the cyclic nitroguanidine derivatives to give N,N'-disubstituted methylenediamines (XXIV). The diversity of cyclic products obtained in this



XXIV

reaction is shown in table 2. Some of the 2-alkylamino-2-imidazolines have been prepared (7) also by the reaction of alkylamines with 2-methylmercapto-2-imidazolinium iodide.

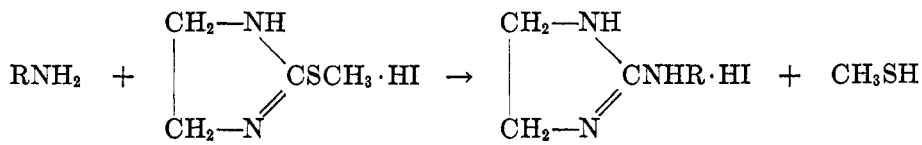


TABLE 2

2-(Substituted amino)-1,3-diaza-2-cycloalkenes

COMPOUND	MELTING POINT OF PICRATE	REFERENCE
	°C.	
2-*n*-Butylamino-1,3-diaza-2-cyclopentene	173–174	(89)
2-β-Phenylethylamino-1,3-diaza-2-cyclopentene	186.4–186.9	(89)
2-β-Phenylethylamino-1,3-diaza-2-cyclohexene	198.5–199.5	(89)
2-Cyclohexylamino-1,3-diaza-2-cyclopentene	227–228	(90)
2-Cyclohexylamino-4(or 5)-methyl-1,3-diaza-2-cyclopentene	197–198	(90)
N-2-(1,3-Diaza-2-cyclopentene)ethylenediamine	205–206.5	(90)
N,N'-2-(1,3-Diaza-2-cyclopentene)ethylenediamine	268–269 (dec.)	(90)

B. N-Alkyl-N-nitroso-N'-nitroguanidine

The first report on the reaction of amines with nitrosoamides was published by Davis and Rosenquist (25). They prepared monosubstituted guanidines in 16–37 per cent yield by adding amines to nitrosoguanidine in water. When N-alkyl-N'-nitrosoguanidines were used, N,N'-disubstituted guanidines were produced.

$$RNHC(=NH)NHNO + R'NH_2 \rightarrow RNHC(=NH)NHR' + N_2(g) + H_2O$$

R = H or alkyl; R' = alkyl.

No further results were reported on the reaction of amines with nitrosoamides until N-methyl-N-nitroso-N'-nitroguanidine (XXV) was prepared (101). The latter compound combines with amines to give generally good yields of N-substituted N'-nitroguanidines (XXVI) (46, 47, 65, 81, 86, 94, 99, 101) (see table

5). Henry (46) found that the methylnitrosoamino group replaced by the amine methylated part of the amine.

$$\underset{\text{XXV}}{CH_3N(NO)C(=NH)NHNO_2} + 2R'NH_2 \rightarrow \underset{\text{XXVI}}{R'NHC(=NH)NHNO_2} + CH_3R'NH + N_2 + H_2O$$

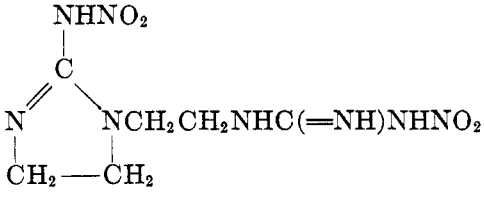
R′ = an alkyl, aralkyl, or aryl group.

This reaction is very useful in determining or verifying the structures of substituted nitroguanidines (82). It is used to prepare *N*-aryl-*N*′-nitroguanidines which cannot be obtained by the reaction of arylamines with nitroguanidine. It also has been used (88) to prepare 1-substituted 2-nitramino-2-imidazolines (XXVII).

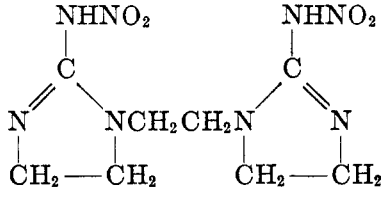
$$\underset{\text{XXV}}{CH_3N(NO)C(=NH)NHNO_2} + RNHCH_2CH_2NH_2 \rightarrow [RNHCH_2CH_2NHC(=NH)NHNO_2] + CH_3OH + N_2 + H_2O \rightarrow \underset{\text{XXVII}}{\text{1-substituted 2-nitramino-2-imidazoline}} + NH_3$$

R = CH_3, C_2H_5, or $HOCH_2CH_2$.

When polyamines such as 1,5-diamino-3-azapentane and 1,8-diamino-3,6-diazaoctane are used, compounds XXVIII and XXIX, respectively, are formed. The *N*-alkyl-nitroso-*N*′-nitroguanidines (81, 85), like nitroguanidine, do not give



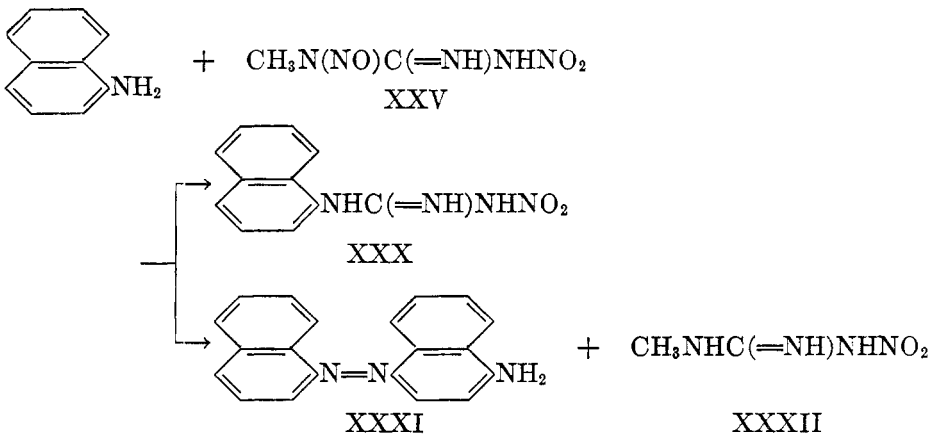
XXVIII



XXIX

substituted nitroguanidines with secondary linear aliphatic amines other than dimethylamine (101). If, however, the secondary nitrogen is a member of a ring system, as in piperidine and morpholine, substituted nitroguanidines are formed (46). Methylnitrosonitroguanidine upon being heated with 95 per cent solutions of methyl- or ethylaniline undergoes denitrosation to *N*-methyl-*N*′-nitroguanidine (81).

Lieber and Parker (65), in an attempt to prepare a polycyclic aromatic substituted nitroguanidine from methylnitrosonitroguanidine and α-naphthylamine, obtained only 25 per cent of the desired *N*-(α-naphthyl)-*N*′-nitroguanidine (XXX).



The other product consisted of brownish-green needles having dye properties and was identified as *p*-amino-α,α'-azonaphthalene (XXXI). This dye would be expected if partial denitrosation of methylnitrosonitroguanidine occurred during the reaction, since this would provide nitrous acid for diazotization of part of the naphthylamine, which could then couple with another portion of naphthylamine to produce the dye. β-Naphthylamine with methylnitrosonitroguanidine gave only the normal product, *N*-(β-naphthyl)-*N'*-nitroguanidine, in 65 per cent yield. On the other hand, β-naphthylamine hydrochloride under the same conditions gave a 95 per cent yield of 2-amino-α,β-azonaphthalene and methylnitroguanidine (XXXII).

C. 1-Nitroso-2-nitramino-2-imidazoline

The reaction of amines with 1-nitroso-2-nitramino-2-imidazoline (XXXIII) (83, 84, 96) is more complex than with the linear nitrosoamide *N*-methyl-*N*-nitroso-*N'*-nitroguanidine. The types of products obtained differed with aromatic and aliphatic or aralkyl amines. Aromatic amines gave 1-aryl-2-nitramino-2-imidazolines (XXXV), 1-nitro-2-arylamino-2-imidazolines (or the tautomeric 1-nitro-2-aryliminoimidazolidines) (XXXVIII), *N*-β-arylaminoethyl-*N'*-aryl-*N''*-nitroguanidines (XXXVI), *N*-aryl-*N'*-nitroguanidines (XXXIX), and *N*-(β-arylaminoethyl)-*N'*-arylureas (XL), while the aliphatic amines and aralkyl amines gave 1-substituted 2-nitramino-2-imidazolines (XXXV), *N*-substituted *N'*-nitroguanidines (XXXIX), *N*,*N'*-disubstituted *N''*-nitroguanidines (XXXVII), and 2-substituted amino-2-oxazolines (or the tautomeric 2-substituted iminoöxazolidines) (XLI). These reactions are outlined in chart I. An examination of the products obtained from the reaction of several amines with 1-nitroso-2-nitramino-2-imidazoline indicates that three generalizations may be made concerning the predictions of the types of products to be formed: (*1*) If one of the RNH groups of intermediate XXXIV is NH_2 or an aliphatic type of amine, i.e., methylamine, ethylamine (84), or benzylamine (83), then $\overset{\oplus}{C}H_2CH_2NH_2$ is lost; if both RNH groups are aromatic amino groups, then one of the RNH

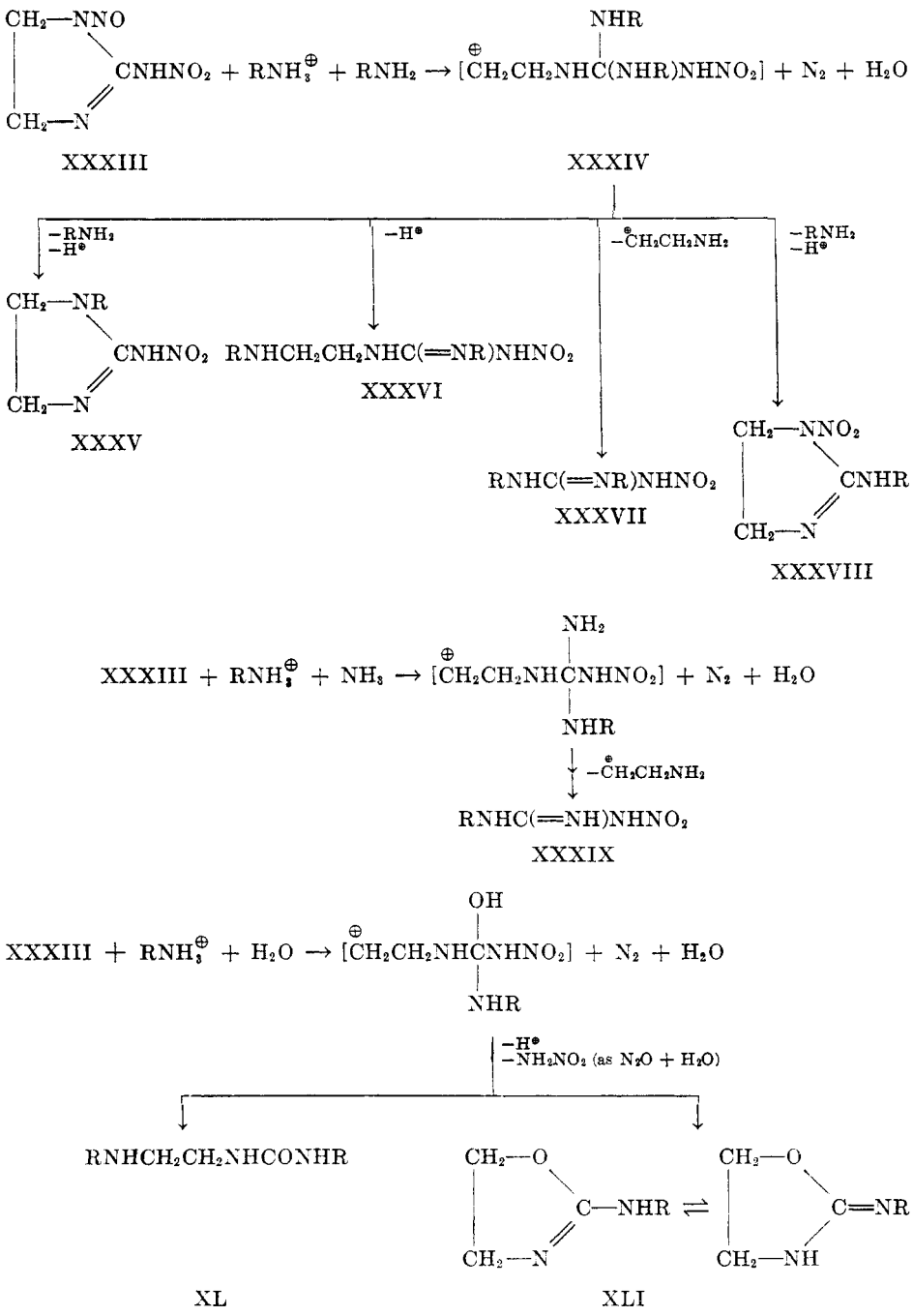

CH2—NNO
CNHNO2 + RNH3⊕ + RNH2 → [⊕CH2CH2NHC(NHR)NHNO2] + N2 + H2O
CH2—N
NHR
XXXIII
XXXIV
−RNH2
−H⊕
−H⊕
−⊖CH2CH2NH2
−RNH2
−H⊕
CH2—NR
CNHNO2
CH2—N
XXXV
RNHCH2CH2NHC(=NR)NHNO2
XXXVI
RNHC(=NR)NHNO2
XXXVII
CH2—NNO2
CNHR
CH2—N
XXXVIII
XXXIII + RNH3⊕ + NH3 → [⊕CH2CH2NHCNHNO2] + N2 + H2O
NH2
NHR
−⊖CH2CH2NH2
RNHC(=NH)NHNO2
XXXIX
XXXIII + RNH3⊕ + H2O → [⊕CH2CH2NHCNHNO2] + N2 + H2O
OH
NHR
−H⊕
−NH2NO2 (as N2O + H2O)
RNHCH2CH2NHCONHR
CH2—O
C—NHR
CH2—N
⇌
CH2—O
C=NR
CH2—NH
XL
XLI

CHART I

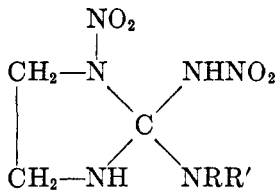
groups is eliminated to give linear products. (*2*) If one of the RNH groups of intermediate XXXIV is replaced by an —OH group then, in general, the group eliminated is NH_2NO_2. (*3*) Intermediate XXXIV may also rearrange to give cyclic products. On this basis *N*-substituted *N'*-nitroguanidines (XXXIX) could arise only through the presence of ammonia in the reaction mixture. Ammonia has been detected in the gases evolved during the reaction. The mechanism of the formation of ammonia is not known. However, one suggestion for the formation of ammonia is the following reaction:

$$RNH_3OH + NH_2NO \rightarrow RNH_2 \cdot HNO_2 + NH_3$$

A carbonium ion intermediate has been employed to explain these reactions, because it seemed the only logical explanation for the wide variety of compounds produced. It should be emphasized that the stepwise depiction of the reaction given in chart I is only for convenience of presentation. The fact that the rate of reaction is roughly proportional to the K_b of the amine used and to the dielectric constant of the medium (82) lends support to the participation of an ionic mechanism.

D. 1-Nitro-2-nitramino-2-imidazoline

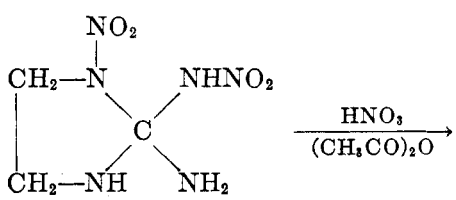
Amines combine with 1-nitro-2-nitramino-2-imidazoline to give products whose analyses indicate that the imidazoline has added one mole-equivalent of amine (43, 44, 92, 103). At first it was thought that the cyclic structure (XLII) was



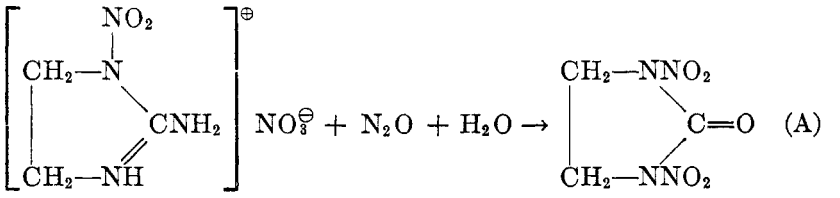
XLII

R,R′ = H or alkyl.

retained in these addition compounds. The main support of this contention was the formation of 1,3-dinitro-2-imidazolidone (XLV) on nitration of the ammonia addition compound (XLII: R,R′ = H) (103). However, nitration of either the cyclic form (XLIII) or the linear form (XLVI) of the ammonia addition product could give 1,3-dinitro-2-imidazolidone (XLV) by route A or B,



XLIII



XLIV XLV (A)

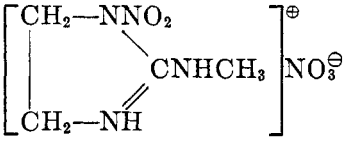
$O_2NNHCH_2CH_2NHC(=NH)NHNO_2 \xrightarrow[(CH_3CO)_2O]{HNO_3}$ *via* XLIV

XLVI

$NO_3CH_2CH_2NHC(=NH)NHNO_2 + N_2O + H_2O$ (B)

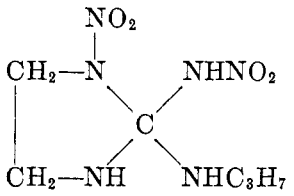
XLVII

respectively. Route A, if the ring structure remained intact, would give the higher yield of 1,3-dinitro-2-imidazolidone. 1-Nitro-2-amino-2-imidazolinium nitrate (XLIV), which represents an intermediate in both mechanisms, has been nitrated (94) to give compound XLV in 84 per cent yield. Intermediate XLVII would be expected to give several products, including the desired 1,3-dinitro-2-imidazolidone. The yield of the latter compound obtained in the nitration of the ammonia addition product was only 26 per cent. This would seem to favor mechanism B. It should be realized that one could also argue that the ammonia addition compound indeed had the cyclic structure (XLIII) to begin with but that rupture of the ring occurred during nitration, decreasing the yield of XLV. Perhaps the most that could be said for the nitration evidence is that it does not favor either structure on the basis of our present knowledge. An interesting confirmation of compound XLIV being an intermediate in this nitration reaction was obtained recently (92). When the methylamine addition product of 1-nitro-2-nitramino-2-imidazoline was nitrated, the nitration stopped at the intermediate stage and 1-nitro-2-methylamino-2-imidazolinium nitrate (XLVIII) was obtained.



XLVIII

Potentiometric titration data have been used (43, 44) as proof of the linear or cyclic nature of the amino addition compounds of 1-nitro-2-nitramino-2-imidazoline. If one considers only the case of the *n*-propylamine addition compound, it will be found that the data can be misleading. This compound was shown (44) by potentiometric titration to be a monobasic acid, and was therefore believed to have structure XLIX. This conclusion was in disagreement with the fact that the same potentiometric titration data were obtained after the



XLIX

compound had aged for one week in alkali. All known 1-nitro-2-imidazolines on standing in alkaline solution at room temperature for several hours have suffered ring opening to give linear compounds possessing aliphatic nitramino groups (44, 79, 83, 84). One would not expect a compound of structure XLIX to be more stable than 1-nitro-2-nitramino-2-imidazoline in alkaline solution. Therefore the only logical conclusion would appear to be that the *n*-propylamine addition product had originally the linear structure shown in formula XLIXa.

$$O_2NNHCH_2CH_2NHC(=NC_3H_7)NHNO_2$$

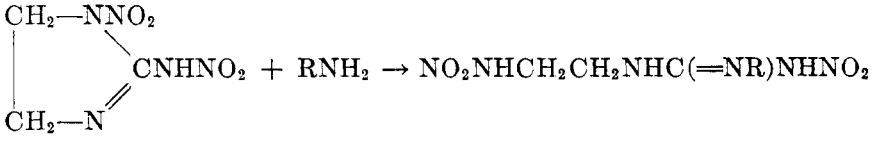
XLIXa

Other data available also point to a linear structure for these compounds; e.g., attempts to resolve them into optical antipodes have failed (103). Moreover, ultraviolet absorption studies (97, 98) show that all the amino addition products of 1-nitro-2-nitramino-2-imidazoline possess two absorption maxima at 232 mμ and 271 mμ, in agreement with the known linear compound *N*-β-nitramino-α-methylethyl-*N'*-nitrourea (L). The known 1-nitro-2-nitramino-2-imidazolines

$$NO_2NHCH_2CH(CH_3)NHCONHNO_2$$

L

have only one maximum at 269–273 mμ in this region of the spectrum. All of this evidence indicates that the reaction of amines with 1-nitro-2-nitramino-2-imidazoline (LI) is best represented by the equation:



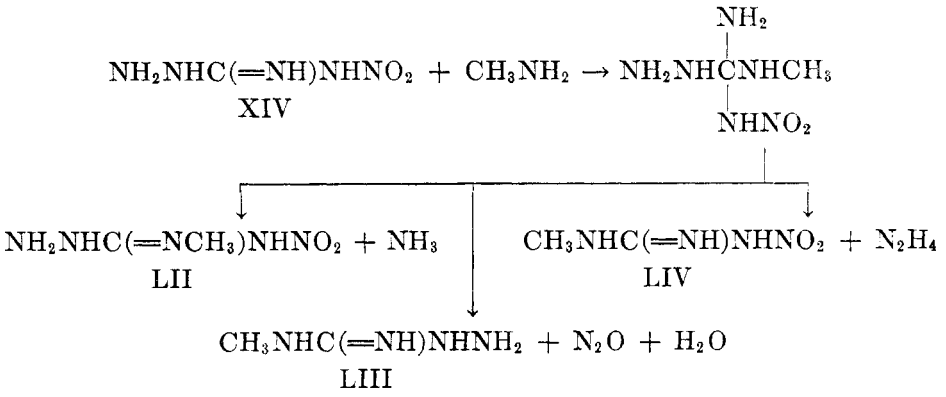
LI

R = H or alkyl.

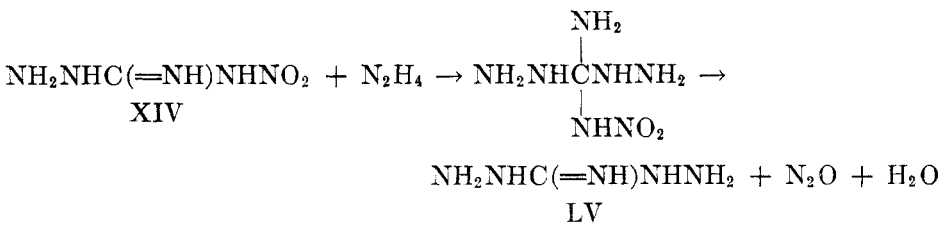
E. Nitroaminoguanidine

The products isolated (51) after heating nitroaminoguanidine (XIV) in aqueous methylamine solution were *N*-methyl-*N'*-nitroguanidine (LIV), *N*-methyl-*N'*-aminoguanidine (LIII), *N*,*N'*-diaminoguanidine (LV), and *N*-methyl-*N'*-amino-*N''*-nitroguanidine (LII). Small amounts of triaminoguanidine were isolated also as the tribenzal derivative (m.p. 227°C. with decomposition). These products can be accounted for by an addition–elimination mechanism.

Primary reaction:



Secondary reaction:



In a similar manner the products, hydrazine, guanidine, nitroguanidine, aminoguanidine, and diaminoguanidine, obtained by heating ammonium carbonate and nitroaminoguanidine in aqueous solution (50) can be explained.

VII. NITRATIONS

As previously mentioned, the crystalline structure of nitroguanidine detracted from its value as an explosive. Thus an effort was made to find a substitute for nitroguanidine having its desirable properties with none of its disadvantages. One phase of this investigation involved the preparation of dinitroguanidine or its derivatives.

A warm saturated solution of nitroguanidine in 70 per cent nitric acid deposits crystals of nitroguanidinium nitrate (m.p. 147°C.) on cooling. These crystals dissociate into nitric acid and nitroguanidine in water or on standing in air (20, 58). Some authors (60) consider that the melting point (147°C.) of nitroguanidinium nitrate is not a true melting point but the temperature at which nitroguanidine dissolves in the concentrated nitric acid.

The first attempts (101) to prepare the simple dinitroguanidine derivative, *N*-methyl-*N*,*N'*-dinitroguanidine (LVII), were abortive. When *N*-methyl-*N'*-

$$CH_3N(NO_2)C(=NH)NHNO_2$$

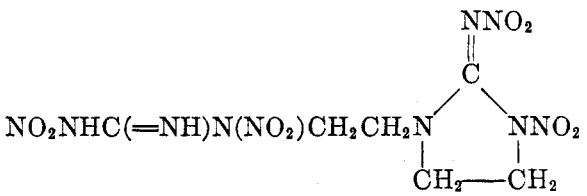
LVII

nitroguanidine was dissolved in absolute nitric acid and this solution poured into absolute ether, a solid precipitated. This solid melted indefinitely at 79–87°C. A similar preparation melted at 91°C. and gave analytical values in agreement with *N*-methyl-*N'*-nitroguanidinium nitrate. It now appears that the products obtained from these nitrations contained a small amount of the desired methyldinitroguanidine in spite of the analytical values. Recently Meen and Wright (105) have prepared both *N*-methyl- and *N*-*n*-butyl-*N*,*N'*-dinitroguanidines by the nitration of *N*-methyl- and *N*-*n*-butyl-*N'*-nitroguanidines in nitric acid–acetic anhydride medium. They also noted that nitration in absolute nitric acid gave a 95 per cent recovery of methylnitroguanidine, in agreement with the earlier work (101). Moreover, solution of *N*-methyl-*N*,*N'*-dinitroguanidine in absolute nitric acid gave a 59 per cent conversion to methylnitroguanidine. This equilibrium between methylnitroguanidine and methyldinitroguanidine, the relatively high solubility of methyldinitroguanidine in water (4 g./100 ml.), and its ease of hydrolysis undoubtedly explain in part the earlier failures to isolate it.

Prior to the work of Meen and Wright two linear dinitroguanidine derivatives, *viz.*, *N*-(β-nitroxyethyl)-*N*,*N'*-dinitroguanidine (LVIII) (94) and 1-(*N*-nitroguanyl-*N*-nitro-β-aminoethyl)-2-nitrimino-3-nitroimidazolidine (LIX) (88), had been

$NO_3CH_2CH_2N(NO_2)C(=NH)NHNO_2$

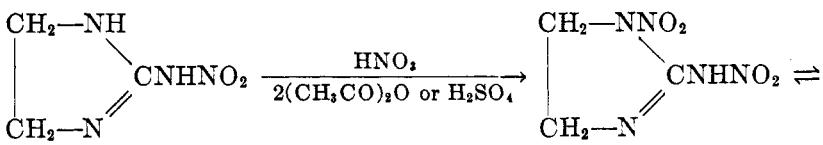
LVIII



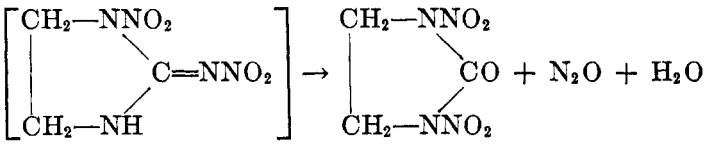
LIX

prepared. During these nitrations considerable quantities of colorless gas were evolved. This gas has been identified (105) as nitrous oxide.

Although the preparation of linear dinitroguanidines finally was achieved, the first successful preparation of a dinitroguanidine derivative resulted from a study (103) of the nitration of 2-nitramino-2-imidazoline (XXI). When 2-nitramino-2-imidazoline was nitrated with mixed acid or with one mole-equivalent of absolute nitric acid in acetic anhydride, 1-nitro-2-nitramino-2-imidazoline (LI) was obtained in good yield. If, however, a large excess of nitric acid in acetic anhydride was employed, gas was evolved and 1,3-dinitro-1,3-diaza-2-cyclo-

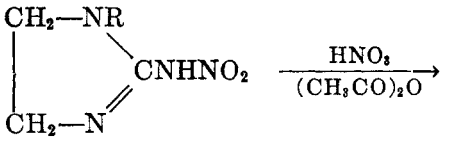


XXI LI

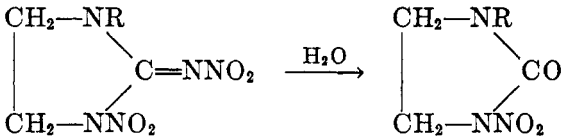


LX XLV

pentanone (XLV) was obtained. The latter compound was obtained also by the nitration of 1-nitro-2-nitramino-2-imidazoline under similar conditions. 1-Nitro-2-nitriminoimidazolidine (LX) was postulated as an intermediate in the formation of 1,3-dinitro-1,3-diaza-2-cyclopentanone. Evidence in support of this postulate was obtained in later studies (88) on the nitration of 1-substituted 2-nitramino-2-imidazolines (LXI). The substituent in position 1 stabilized the



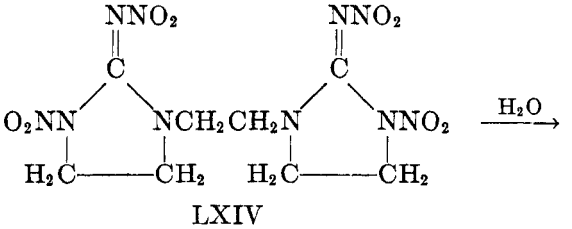
LXI



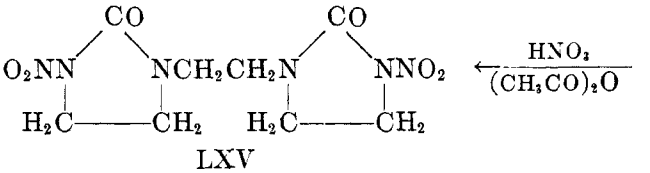
LXII LXIII

R = CH_3, C_2H_5, or $HOCH_2CH_2$.

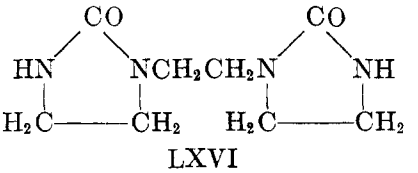
nitrimines and 1-methyl-, 1-ethyl-, and 1-(β-hydroxyethyl)-2-nitramino-2-imidazolines were converted in excellent yields (86–94 per cent) into the corresponding 1-substituted 2-nitrimino-3-nitroimidazolidines (LXII). 1-(β-Nitroxyethyl)-2-nitrimino-3-nitroimidazolidine (LXII: R = $NO_3CH_2CH_2$—) and 1,2-bis-1-(2-nitrimino-3-nitroimidazolidinyl)ethane (LXIV) were hydrolyzed in boiling water to 1-(β-nitroxyethyl)-3-nitro-2-imidazolidone (LXIII: R = $NO_3CH_2CH_2$—) and 1,2-bis-1-(3-nitro-2-imidazolidonyl)ethane (LXV), respectively. These two compounds also were prepared (91) by the nitration of 1-(β-hydroxyethyl)-2-imidazolidone and 1,2-bis-1-(2-imidazolidonyl)ethane (LXVI). They proved to be



LXIV



LXV

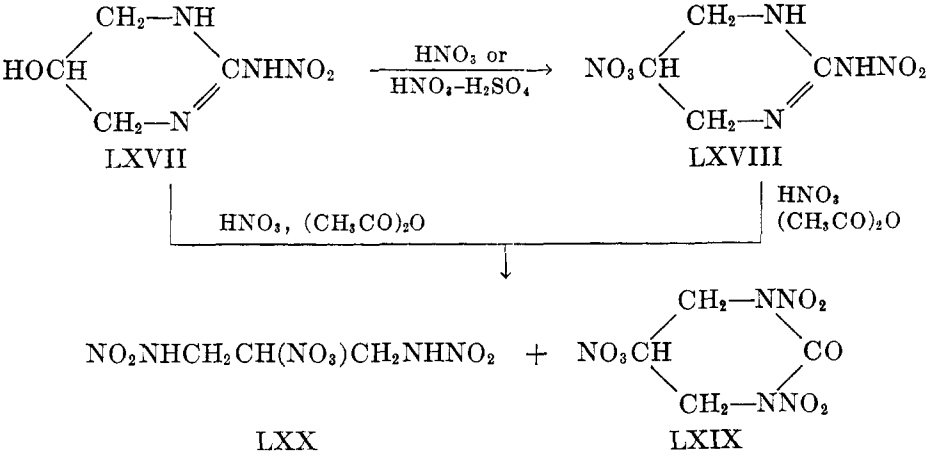


LXVI

identical with hydrolysis products from the corresponding nitrimines. This, together with the similarity of the ultraviolet absorption spectra (97) of the 1-methyl, 1-ethyl-, and 1-(β-nitroxyethyl)-2-nitrimino-3-nitroimidazolidines, served to confirm the structures of these nitrimines.

Although the five-membered ring compounds 2-nitramino-2-imidazoline and 2-nitramino-4(or 5)-methyl-2-imidazoline give 1-nitro derivatives, the higher homologs 1-nitro-2-nitramino-1,3-diaza-2-cyclohexene and 1-nitro-2-nitramino-1,3-diaza-2-cycloheptene could not be formed (93, 103).

The use of mixed acid and nitric acid–acetic anhydride media for the nitration of nitroguanidines led to apparent differences in nitration products. Thus, 1-(β-hydroxyethyl)-2-nitramino-2-imidazoline with mixed acid gave 1-(β-nitroxyethyl)-2-nitramino-2-imidazoline, while nitric acid in acetic anhydride yielded 1-(β-nitroxyethyl)-2-nitrimino-3-nitroimidazolidine (88). 2-Nitramino-5-hydroxy-1,3-diaza-2-cyclohexene (LXVII) with mixed acid or nitric acid alone formed 2-nitramino-5-nitroxy-1,3-diaza-2-cyclohexene (LXVIII), but with acetic anhydride–nitric acid solution it gave 1,3-dinitro-5-nitroxy-1,3-diaza-2-cyclohexanone (LXIX) and 1,3-dinitramino-2-nitroxypropane (LXX) (93). On the



LXVII LXVIII

LXX LXIX

other hand, 1-methyl- and 1-ethyl-2-nitramino-2-imidazolines yielded 1-methyl- and 1-ethyl-2-nitrimino-3-nitroimidazolidines on nitration with either mixed acid or nitric acid–acetic anhydride (88).

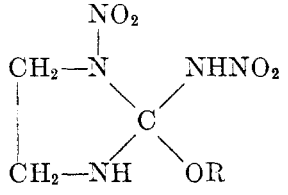
It has been well established that the nitronium ion is present in nitric acid–sulfuric acid solutions (39, 40, 54) and there exists good evidence that the $NO_2^{\oplus}$ ion is responsible for nitrations in mixed acid (11, 12, 13, 53). Recently Jones and Thorn (56) concluded from their ultraviolet studies of nitric acid–acetic anhydride solutions that the following equilibrium is displaced well to the right.

$$(CH_3CO)_2O + 2HNO_3 \rightleftharpoons N_2O_5 + 2CH_3COOH$$

This, together with the evidence that nitrogen pentoxide exists in equilibrium with nitrate and nitronium ions (11, 13, 56, 131), suggests that the same species, *viz.*, nitronium ion, is responsible for nitration in both mixed acid and acetic anhydride–nitric acid solutions (41). Further studies are necessary to establish whether the mechanisms of nitration in these two media are the same.

VIII. ALCOHOLYSIS OF 1-NITRO-2-NITRAMINO-2-IMIDAZOLINE

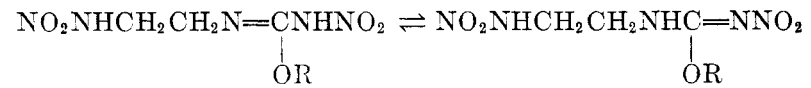
1-Nitro-2-nitramino-2-imidazoline on prolonged refluxing with absolute or aqueous alcohols is partly decomposed and partly converted to an alcohol addition product (45, 103). These addition products were assigned structure LXXI.



LXXI

R = alkyl.

Potentiometric titration data showed that 1-nitro-2-nitramino-2-*n*-propoxyimidazolidine (LXXI: R = C_3H_7) behaved as a monobasic acid with a K_a of approximately 1×10^{-6} (45). It was found that the behavior of this compound on potentiometric titration remained the same after the compound had stood in alkaline solution for one week. This last fact can only indicate that the substance under consideration has a linear structure (LXXII), because the ring of 1-nitro-2-imidazolines is readily opened in alkaline solution (*cf.* page 322, Section VI,D). At first the ultraviolet absorption spectrum (97) seemed to agree with a cyclic



LXXII

structure for the ethanol addition product of 1-nitro-2-nitramino-2-imidazoline. Now, however, the spectrum has been extended to shorter wave lengths and a second maximum observed (98). This additional spectroscopic evidence lends support to the linear structure (LXXII) for the alcohol addition products of 1-nitro-2-nitramino-2-imidazoline.

IX. HYDROLYSES OF NITROGUANIDINES

Pellizzari (111) reported that warming nitroguanidine in potassium hydroxide solution split it into carbon dioxide, ammonia, and nitrous oxide. He found that

approximately one mole of nitrous oxide was produced per mole of nitroguanidine. Thiele (132) suggested the following equation to represent this hydrolysis:

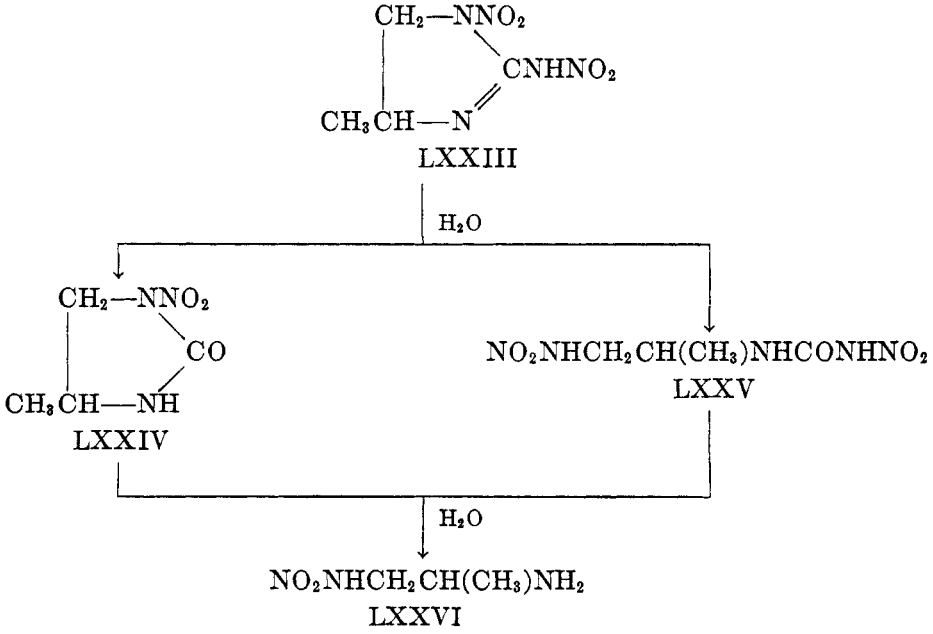
$$NH_2C(=NH)NHNO_2 + H_2O \rightarrow CO_2 + 2NH_3 + N_2O$$

A more detailed equation was presented by Franchimont (34).

$$NH_2C(=NH)NHNO_2 \begin{cases} \rightarrow NH_2CONH_2 \mid + H_2O \rightarrow 2NH_3 + CO_2 \\ \rightarrow NH_2NO_2 \mid \rightarrow N_2O + H_2O \end{cases}$$

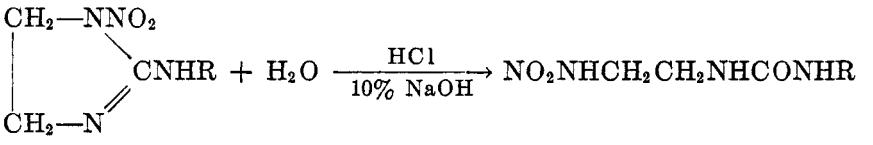
Neither of these workers confirmed the quantitative implications of these equations. Fry and Treon (35) conducted a more detailed study of the hydrolysis of nitroguanidine. Their results showed that nitroguanidine is hydrolyzed quantitatively into one mole-equivalent of carbon dioxide and two mole-equivalents of ammonia, in agreement with the above equation.

The substituted nitroguanidines vary in their ease of hydrolysis. 1-Nitro-2-nitramino-2-imidazoline is hydrolyzed rapidly (97 per cent in 5 min.) in boiling water (103). This and its high sensitivity (2.8 times as sensitive as cyclonite to impact) render it valueless as an explosive, even though it possesses high power (1.3 times trinitrotoluene in the ballistic mortar). The products of hydrolysis of 1-nitro-2-nitramino-2-imidazoline were not investigated but its 4-methyl derivative (LXXIII) was studied (100). The latter compound on hydrolysis yielded two intermediates: *N*-β-nitramino-α-methylethyl-*N'*-nitrourea (LXXV) and 1-nitro-4-methyl-2-imidazolidone (LXXIV). Both of these compounds gave 2-amino-3-nitraminopropane (LXXVI) on further hydrolysis.



The final hydrolytic product is readily soluble in water, difficultly soluble in the common organic solvents, and possesses a high melting point (240.9°C. with decomposition), as would be expected for a "zwitterion" structure.

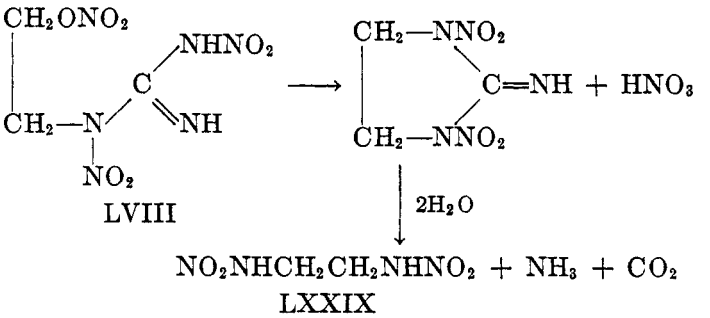
Cyclic nitroguanidines which have the nitramino group in the ring structure, e.g., 1-nitro-2-(substituted amino)-2-imidazoline (LXXVII), are readily hydrolyzed. When 1-nitro-2-propylamino-2-imidazoline (LXXVII: R = C_3H_7) (44) is dissolved in sodium hydroxide solution at ordinary temperatures, it is hydrolyzed in a short time to *N*-(β-nitraminoethyl)-*N'*-*n*-propylurea (LXXVIII: R = C_3H_7).



LXXVII LXXVIII

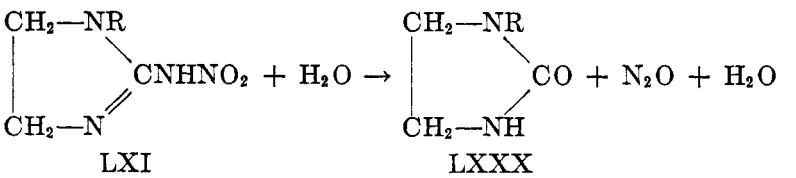
R = H, alkyl, or aryl.

It has been demonstrated (84) that solution of 1-nitro-2-*p*-acetamidophenylamino-2-imidazoline in either acid or basic solutions at room temperature hydrolyzes it to *N*-(β-nitraminoethyl)-*N'*-*p*-acetamidophenylurea. 1-(β-Nitroxyethyl)-*N*,*N'*-dinitroguanidine (LVIII) (94) should be included here, because the formation of 1,2-dinitraminoethane (LXXIX) on boiling with water must involve cyclization prior to hydrolysis, as follows:



LVIII LXXIX

There are many examples (83, 84, 89, 90, 96) of the hydrolysis of 2-nitramino-2-imidazolines (LXI) to the corresponding cyclic ureas (LXXX). This hydrolysis occurs within a few minutes on refluxing the nitramine in 10 per cent aqueous sodium hydroxide solution. The yields of cyclic ureas are excellent.



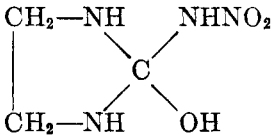
LXI LXXX

R = H, alkyl, or aryl.

Barton, Hall, and Wright (10) have found that 2-nitramino-2-imidazoline on standing in alkaline solution gives a compound melting at 137°C. This product gave analytical values in agreement with structures LXXXI, LXXXII, and LXXXIII.

$HOCH_2CH_2NHC(=NH)NHNO_2$ LXXXI

$NH_2CH_2CH_2NHCONHNO_2$ LXXXII



LXXXIII

Compound LXXXI had been prepared previously (94) and its properties differed from those of the crystals melting at 137°C. No attempt was made to distinguish between the remaining two structures, LXXXII and LXXXIII.

X. REACTION OF NITROGUANIDINE DERIVATIVES WITH NITROUS ACID

A number of linear-substituted nitroguanidines have been converted into their corresponding nitrosoamides (43, 81, 85, 88, 94, 95, 99, 103) by treatment with excess sodium nitrite in acid solution. This reaction does not occur when the

$$RNHC(=NH)NHNO_2 + HNO_2 \rightarrow RN(NO)C(=NH)NHNO_2 + H_2O$$

R = alkyl.

carbon attached to the nitrogen is secondary (95), as in *N*-isopropyl-*N'*-nitroguanidine and *N*-cyclohexyl-*N'*-nitroguanidine. These compounds will not undergo nitrosation under the usual conditions even with a large excess of nitrous acid. Some cyclic nitroguanidines, e.g., 2-nitramino-2-imidazoline, give a nitroso derivative by the same method (96). The nitroso derivatives of substituted nitroguanidines described in the literature are listed in table 10.

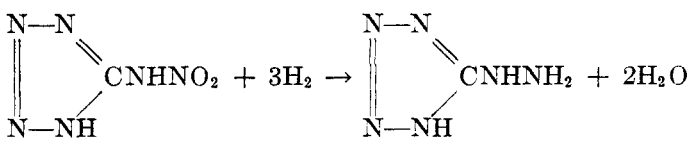
O'Connor, Fleming, and Reilly (108a) prepared nitroguanyl azide (LXXXIV)

$NO_2NHC(=NH)N_3$

LXXXIV

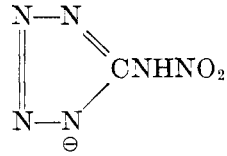
Nitroguanyl azide

by treating nitroaminoguanidine with nitrous acid. They found nitroguanyl azide to isomerize into 5-nitraminotetrazole (LXXXV) in the presence of alkalis. This new compound was identified by reduction with zinc dust in acetic acid to 5-hydrazinotetrazole (LXXXVI), which was isolated as its known (134) benzal derivative.

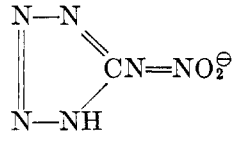


LXXXV LXXXVI

The yield of nitroguanyl azide from nitroaminoguanidine has been increased (67) to 77 per cent and several monobasic and dibasic salts (*cf.* table 13) of its isomer, 5-nitraminotetrazole, have been prepared. When nitroguanyl azide was treated with aniline, a 20 per cent yield of *N*-phenyl-*N'*-nitroguanidine was obtained, along with a 67 per cent yield of phenylammonium 5-nitraminotetrazole. The first acid hydrogen of 5-nitraminotetrazole was observed to act as a



LXXXVII



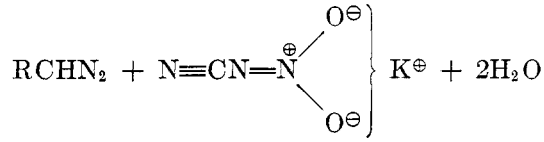
LXXXVIII

strong acid, while the second acidic dissociation constant was determined to be 9×10^{-7} (66). Two possible structures (LXXXVII and LXXXVIII) have been considered (68) for the anion of the monoacid salt. On the basis of the ultraviolet absorption spectra of 5-nitraminotetrazole and four of its salts, it was concluded that the initial proton removal is from the nitramino group. Thus the anion of the monoacid salt has structure LXXXVIII.

XI. REACTION OF ALKALI WITH *N*-ALKYL-*N*-NITROSO-*N'*-NITROGUANIDINES AND *N*-ALKYL-*N*,*N'*-DINITROGUANIDINES

Diazohydrocarbons are obtained from *N*-alkyl-*N*-nitroso-*N'*-nitroguanidines on treatment with strong aqueous alkali (80, 95). Potassium nitrocyanamide (LXXXIX) is obtained from the remaining fragment of the molecule.

$$RCH_2N(NO)C(=NH)NHNO_2 + KOH \rightarrow$$



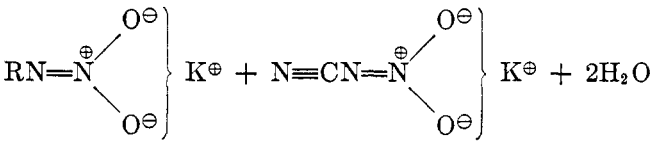
LXXXIX

R = H, CH_3, C_2H_5, C_3H_7, C_4H_9, or phenyl.

Diazomethane was prepared in 93 per cent yield by this method. The yields of diazoethane, diazo-*n*-propane, diazo-*n*-butane, diazo-*n*-pentane, and phenyldiazomethane are lower, but they are comparable with the yields obtained by other methods. The preparation of alkylnitrosonitroguanidines and their use in various reactions must be conducted in a good fumehood. The gases evolved during these reactions contain an ingredient which produces a skin irritation. In cases of severe contamination a vesicant action has been noted.

N-Alkyl-*N*,*N'*-dinitroguanidines behave similarly to alkylnitrosonitroguanidines in the presence of alkali. Meen and Wright (105) have demonstrated that *N*-methyl- and *N*-*n*-butyl-*N*,*N'*-dinitroguanidines combine with 2 equivalents of potassium hydroxide in aqueous solution to give the potassium salts of the corresponding alkylnitramines (XC) and nitrocyanamide (LXXXIX).

$$RN(NO_2)C(=NH)NHNO_2 + 2KOH \rightarrow$$

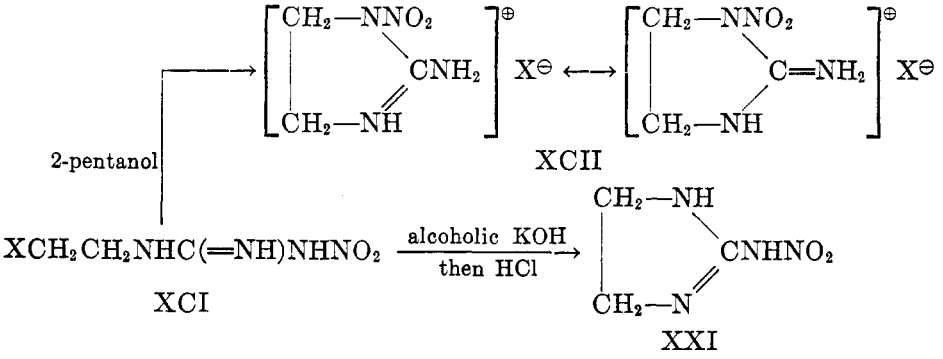


XC LXXXIX

R = CH_3 or n-C_4H_9.

XII. CYCLIZATION OF N-(β-SUBSTITUTED ETHYL)-N'-NITROGUANIDINES

In 1950 N-(β-chloroethyl)-, N-(β-bromoethyl)-, and N-(β-nitroxyethyl)-N'-nitroguanidines (XCI) were prepared (94). They all possessed double melting points. Further investigation disclosed that this property was dependent upon an intramolecular chemical transformation. This rearrangement could be induced also by heating these compounds in anhydrous solvents. The end-products were identified as salts of 1-nitro-2-amino-2-imidazoline (XCII).



XCII

XCI XXI

X = Cl, Br, or NO_3.

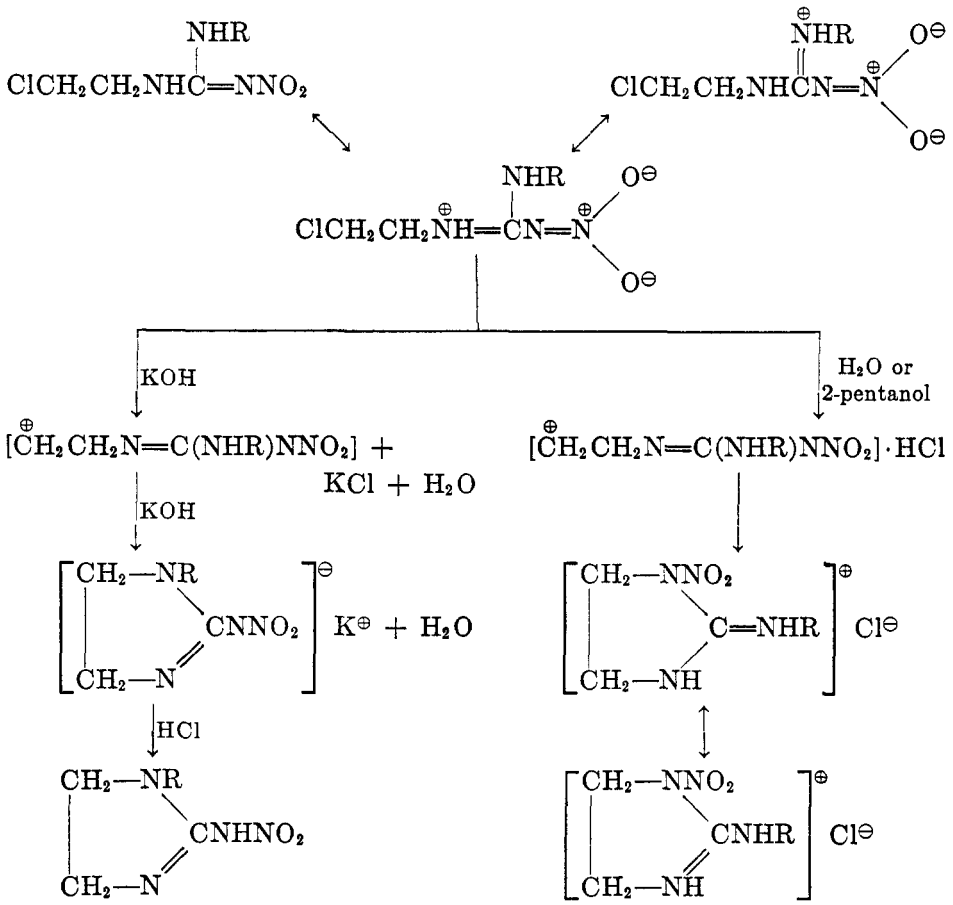
When N-(β-chloroethyl)-N'-nitroguanidine was heated for a short time in the presence of alcoholic potassium hydroxide, it cyclized to 2-nitramino-2-imidazoline (XXI) (43, 83).

Once this ease of cyclization was recognized, there was provided a reasonable explanation for the formation of 1,3-dinitro-2-imidazolidone through nitration of N-(β-nitraminoethyl)-N'-nitroguanidine (*cf.* page 320) (103). These rearrangements are not peculiar to nitroguanidine chemistry, for they occur with β-chloroethyl N-substituted carbamates (XCIII) (87, 108, 109), and N-(β-chloroethyl)-N'-substituted ureas (XCIV) (29, 37, 38, 87, 105). No kinetic

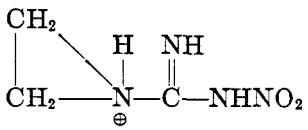
$ClCH_2CH_2OCONHR$ XCIII $\qquad$ $ClCH_2CH_2NHCONHR$ XCIV

studies have appeared on the cyclization of these compounds. Thus it may be premature to offer any mechanisms for these reactions. It has been suggested (87) that carbonium ion intermediates precede the cyclizations of N-(β-substituted ethyl)-N'-nitroguanidines. The evidence for this interpretation at present is not incontrovertible. It has been demonstrated (97) by ultraviolet absorption spectra

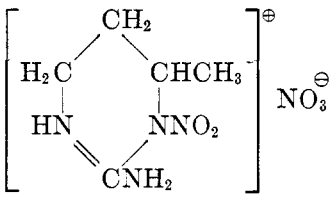
that nitroguanidine and many of its derivatives exist as resonance hybrids derived in part from electronic structures possessing charge separation. This, together with the ease of cyclization of *N*-(β-substituted ethyl)-*N'*-nitroguanidines in comparison with β-chloroethyl *N*-substituted carbamates and *N*-(β-chloroethyl)-*N'*-substituted ureas favors the following mechanism for rearrangements in neutral and basic solutions:



On the other hand, it may be that the interpretation given for alkylation by nitrogen mustards would be equally feasible here. The intermediate then would be

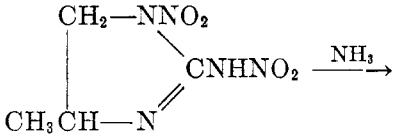


A six-membered ring compound also has been formed (99) by cyclizing *N*-(γ-nitroxybutyl)-*N'*-nitroguanidine to 1-nitro-2-amino-6-methyl-Δ^2-tetrahydropyridinium nitrate (XCV).

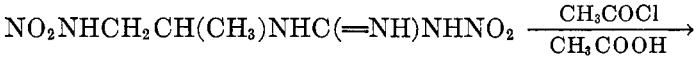


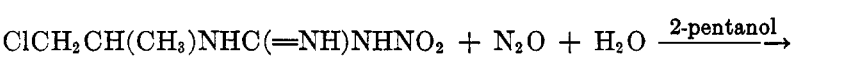
XCV

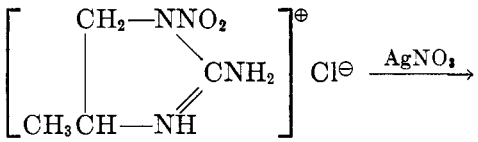
N-(β-Chloroethyl)-*N'*-substituted-*N''*-nitroguanidines are derived from *N*-(β-nitraminoethyl)-*N'*-substituted-*N''*-nitroguanidines by chlorination with acetyl chloride (*cf.* Section XIII) (43, 44, 92). This reaction has been used to determine the position of the methyl group in 1-nitro-4(or 5)-methyl-2-nitramino-2-imidazoline (LXXIII) (43). The latter compound was transformed to 1-nitro-2-amino-4(or 5)-methyl-2-imidazolinium nitrate (m.p. 150°C.) (XCVI) by the series of reactions given in chart II. This nitrate salt had different properties from those of the known 1-nitro-2-amino-5-methyl-2-imidazolinium nitrate (m.p. 115–116°C.) (XCVIII), previously (94) prepared from *N*-(β-nitroxypropyl)-*N'*-nitroguanidine (XCVII). Therefore, compound XCVI must have the methyl group at position 4, as written.

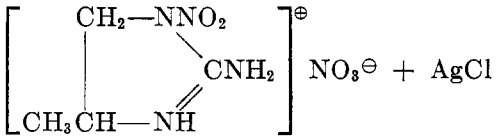


LXXIII

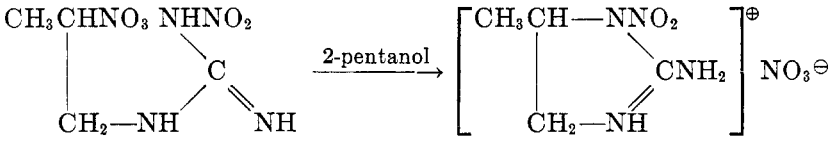








XCVI

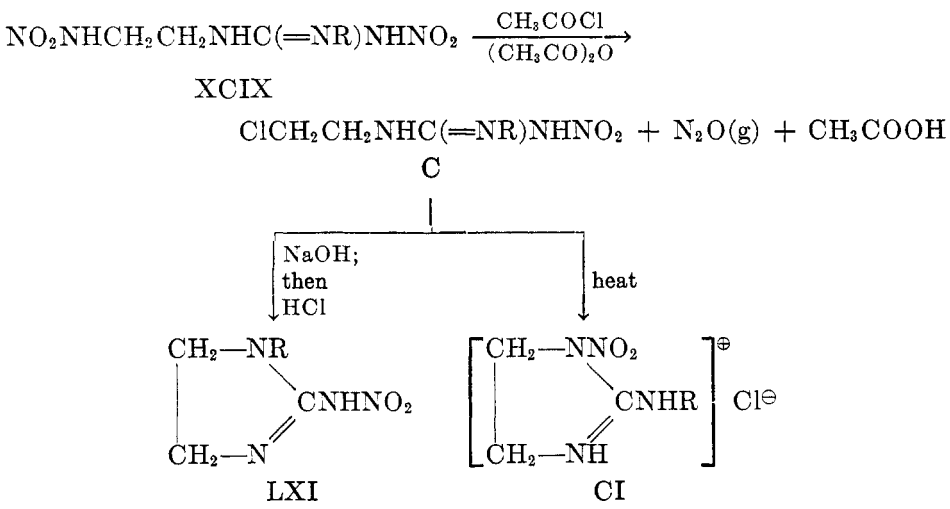


XCVII XCVIII

CHART II

XIII. REACTION OF ACETYL CHLORIDE WITH NITROGUANIDINE DERIVATIVES

The course of the reaction of acetyl chloride with the *n*-propylamino derivative of 1-nitro-2-nitramino-2-imidazoline, as described by Hall and Wright (44), is somewhat complicated. This is undoubtedly due to the fact that they considered the *n*-propylamino addition product to be cyclic, on the basis of their titration data. However, the compounds formed by the reaction of amines with 1-nitro-2-nitramino-2-imidazoline have been shown (97, 98) to be *N*-(β-nitraminoethyl)-*N'*-substituted-*N''*-nitroguanidines. Therefore the reaction is similar to the reaction of acetyl chloride with aliphatic nitramines (1). The primary reaction is simply a replacement of the nitramino group with chlorine. The other products are obtained because of the reaction conditions and manipulative procedures employed. It has been shown (94) that heating β-chloroethylnitroguanidine in an anhydrous solvent is sufficient to effect its cyclization to 1-nitro-2-amino-2-imidazoline. Thus the two products to be expected from the reaction of *N*-(β-nitraminoethyl)-*N'*-*n*-propyl-*N'*-nitroguanidine (XCIX: R = C_3H_7) with acetyl chloride are *N*-(β-chloroethyl)-*N'*-*n*-propyl-*N''*-nitroguanidine (C: R = C_3H_7) and 1-nitro-2-*n*-propylamino-2-imidazolinium chloride (CI: R = C_3H_7). When *N*-(β-nitraminoethyl)-*N'*-methyl-*N''*-nitroguanidine (XCIX: R = CH_3) was heated in an acetyl chloride–acetic acid–acetic anhydride medium and the products isolated without acidification or basification, *N*-(β-chloroethyl)-*N'*-methyl-*N''*-nitroguanidine (C: R = CH_3), 1-nitro-2-methylamino-2-imidazolinium chloride (CI: R = CH_3), and a small amount of oil were obtained



R = CH_3 or C_3H_7.

(92). Compounds of structure C give 1-substituted 2-nitramino-2-imidazolines (LXI) on treatment with alkali followed by acidification (83). This then explains the isolation of 1-*n*-propyl-2-nitramino-2-imidazoline (referred to in the literature (44) as 1-*n*-propyl-2-nitrimino-2-imidazolidone) from the reaction of acetyl chloride with *N*-(β-nitraminoethyl)-*N'*-*n*-propyl-*N''*-nitroguanidine.

Hall and Wright (45) found that 1-nitro-2-nitramino-2-*n*-propoxyimidazoli-

dine also combines with acetyl chloride in acetic acid. The product was *N*-(β-chloroethyl)-*N'*-nitro-*n*-propylisourea (51.7 per cent yield). Since the latest evidence (98) indicates that 1-nitro-2-nitramino-2-*n*-propoxyimidazolidine is quite likely the linear compound *N*-(β-nitraminoethyl)-*N'*-nitro-*n*-propylisourea, this

$$NO_2NHCH_2CH_2N{=}\overset{\displaystyle OC_3H_7}{\overset{|}{C}}NHNO_2$$

reaction would be similar to the one outlined above with *N*-(β-nitraminoethyl)-*N'*-methyl-*N''*-nitroguanidine.

TABLE 3

Franchimont nitramine color test

COMPOUND	COLOR WITH	
	Diethylaniline	Dimethylaniline
N-Methyl-*N'*-nitroguanidine	Light green	None
N-Allyl-*N'*-nitroguanidine	Light green	None
N-(*p*-Tolyl)-*N'*-nitroguanidine	None	Pink
N-(*m*-Tolyl)-*N'*-nitroguanidine	None	Pink
N-(*o*-Tolyl)-*N'*-nitroguanidine	Light green	Pink
N-(2,4-Dimethylphenyl)-*N'*-nitroguanidine	Light green	Pink
N-Phenyl-*N'*-nitroguanidine	None	Pink
1-(β-Nitroxyethyl)-2-nitrimino-3-nitroimidazolidine	Deep green	Deep green
1-Methyl-2-nitrimino-3-nitroimidazolidine	Green (fades)	Pink
1-Ethyl-2-nitrimino-3-nitroimidazolidine	Green (fades)	Pink
1-Methyl-2-nitramino-2-imidazoline	Pink	Pink
1-Ethyl-2-nitramino-2-imidazoline	Pink	Pink
1,3-Dinitro-2-imidazolidone	Deep green	Deep green
1,3-Dinitro-1,3-diaza-2-cycloheptanone	Deep green	Deep green
1-Nitro-2-nitramino-2-imidazoline	Greenish yellow to yellow	Reddish brown to pink
N-(β-Nitraminoethyl)-*N'*-methyl-*N''*-nitroguanidine	None	None
N-(β-Nitraminoethyl)-*N'*-ethyl-*N''*-nitroguanidine	Light green	None
N-(β-Nitraminoethyl)-*N'*-phenyl-*N''*-nitroguanidine	None	Pink

XIV. COLOR TESTS

Franchimont (34) noted that nitramines in glacial acetic acid give a pink color with α-naphthylamine and a green color with dimethylaniline on addition of zinc dust. The test is usually performed by adding to a few crystals of compound several drops of glacial acetic acid, after which several drops of a 1 per cent solution of the amine in glacial acetic acid and a pinch of zinc dust are added. This test has been extensively employed (82, 88) in nitroguanidine chem-

istry. Some of the color reactions obtained with dimethyl- and diethylanilines are given in table 3. Table 4 presents a summary of the observations on approximately one hundred nitroguanidine derivatives. The latter table shows that the use of both dimethyl- and diethylaniline permits a certain degree of differentiation among several groups of nitroguanidine derivatives. α-Naphthylamine is of

TABLE 4

Franchimont nitramine test

CLASS OF COMPOUNDS	COLOR WITH	
	Diethylaniline	Dimethylaniline
N-Alkyl-*N'*-nitroguanidines*	Light green	None
N-Aralkyl-*N'*-nitroguanidines	Light green	None
N-Aryl-*N'*-nitroguanidines	None or light green	Pink
1-Substituted 2-nitramino-2-imidazolines*	Pink	Pink
1,3-Dinitro-1,3-diaza-2-cycloalkanones	Deep green	Deep green
1-Nitro-2-amino-2-imidazolines	Deep green	Deep green

* Nitrate esters, e.g., 1-(β-nitroxyethyl)-2-nitramino-2-imidazoline and *N*-(β-nitroxyethyl)-*N'*-nitroguanidine, generally give deep green colors with both dimethyl- and diethylaniline.

no use in this respect, as it gives a red color with both primary and secondary amines. These tests cannot be taken as absolutely infallible, because sodium nitrite, some nitrate esters, and certain nitro compounds give positive results.

XV. TABLES OF NITROGUANIDINES

Tables 5 to 13 contain the derivatives of nitroguanidine described in the literature. A method of preparation of each of the compounds listed will be found in the references quoted. Some of the compounds, e.g., nitroguanidine and nitroaminoguanidine, adequately described in the text are omitted from the tables.

TABLE 5

N-Substituted-N'-nitroguanidines

COMPOUND	MELTING POINT	REFERENCES
	°C.	
N-Methyl-*N'*-nitroguanidine	160.5–161	(21, 24, 101)
N-Ethyl-*N'*-nitroguanidine	147–148	(21, 24)
N-(β-Hydroxyethyl)-*N'*-nitroguanidine	118 (dec.)	(94)
N-(β-Methoxyethyl)-*N'*-nitroguanidine	118.5–119.5	(94)
N-(β-Nitroxyethyl)-*N'*-nitroguanidine	92–93.5 (161)*	(94)
N-(β-Chloroethyl)-*N'*-nitroguanidine	116–117 (189)*	(43, 94)
N-(β-Bromoethyl)-*N'*-nitroguanidine	102–103 (180)*	(94)
N-Propyl-*N'*-nitroguanidine	98–98.5	(24)
N-Isopropyl-*N'*-nitroguanidine	154.8–155.6	(24)
N-Allyl-*N'*-nitroguanidine	107–108	(81)
N-(β-Hydroxypropyl)-*N'*-nitroguanidine	110–110.5	(94)
N-(β-Nitroxypropyl)-*N'*-nitroguanidine	129–129.5	(94)
N-Butyl-*N'*-nitroguanidine	84–85	(21, 24, 101)
N-Isobutyl-*N'*-nitroguanidine	121–121.5	(24, 101)
N-(γ-Nitroxybutyl)-*N'*-nitroguanidine	125–126	(99)
N-Amyl-*N'*-nitroguanidine	98.8–99.3	(24)
N-Isoamyl-*N'*-nitroguanidine	145.5–146.2	(24, 101)
N-*tert*-Amyl-*N'*-nitroguanidine	154.8–155.6	(24)
N-Heptyl-*N'*-nitroguanidine	115	(23)
N,*N*-Dimethyl-*N'*-nitroguanidine	193.6–194.5	(24, 101)
N-Cyclohexyl-*N'*-nitroguanidine	197–198	(81)
N-(γ-Diethylaminopropyl)-*N'*-nitroguanidine	135–136	(81)
N-(β-Nitraminoethyl)-*N'*-nitroguanidine	184.8–185.3	(43)
N-(α-Methyl-β-nitraminoethyl)-*N'*-nitroguanidine	172.7 (dec.)	(43)
N-Nitroguanylpiperidine	155–156	(46)
N-Nitroguanylmorpholine	188–189	(46)
1,2-Di(nitroguanylamino)ethane	248.5 (dec.)	(99)
1,3-Di(nitroguanylamino)propane	235 (dec.)	(99)
1,3-Di(nitroguanylamino)butane	230 (dec.)	(99)
1,4-Di(nitroguanylamino)butane	>265	(99)
N-Carbethoxymethyl-*N'*-nitroguanidine	153.5–154.5	(47)
N-Formamido-*N'*-nitroguanidine	191–192 (dec.)	(47)
N-Acetamido-*N'*-nitroguanidine	195 (dec.)	(47)
Ethyl *N*-nitroguanidinocarbonate	203–203.5	(47)
N-(2-Pyridyl)-*N'*-nitroguanidine	229 (dec.)	(47)
N-2-(5-Methylpyridyl)-*N'*-nitroguanidine	219	(47)
N-2-(6-Methylpyridyl)-*N'*-nitroguanidine	204–205	(47)
N-Benzyl-*N'*-nitroguanidine	183.5	(21, 24, 81)
N-*dl*-(α-Phenylethyl)-*N'*-nitroguanidine	117–118	(81)
N-(β-Phenylethyl)-*N'*-nitroguanidine	162–163	(81)
N-Phenyl-*N'*-nitroguanidine	152–153	(81, 101)
N-(*p*-Tolyl)-*N'*-nitroguanidine	165–166	(81)
N-(*m*-Tolyl)-*N'*-nitroguanidine	125–126	(81)
N-(*o*-Tolyl)-*N'*-nitroguanidine	203.5 (dec.)	(81)
N-(*p*-Anisyl)-*N'*-nitroguanidine	153–154	(81)
N-(*m*-Anisyl)-*N'*-nitroguanidine	154–155	(81)
N-(*o*-Anisyl)-*N'*-nitroguanidine	136–137	(81)

TABLE 5—*Concluded*

COMPOUND	MELTING POINT	REFERENCES
	°C.	
N-(*p*-Phenetyl)-*N'*-nitroguanidine	175–176	(81)
N-(*m*-Phenetyl)-*N'*-nitroguanidine	135–136	(81)
N-(*o*-Phenetyl)-*N'*-nitroguanidine	127–127.5	(81)
N-(*p*-Chlorophenyl)-*N'*-nitroguanidine	167.5–168.5	(81)
N-(*m*-Chlorophenyl)-*N'*-nitroguanidine	162.5–163.5	(81)
N-(*o*-Chlorophenyl)-*N'*-nitroguanidine	187–188	(81)
N-(*p*-Bromophenyl)-*N'*-nitroguanidine	189.2–190.2	(81)
N-(*m*-Bromophenyl)-*N'*-nitroguanidine	182–183	(81)
N-(*p*-Hydroxyphenyl)-*N'*-nitroguanidine	236 (dec.)	(99)
N-(*m*-Hydroxyphenyl)-*N'*-nitroguanidine	178 (dec.)	(99)
N-(*p*-Aminophenyl)-*N'*-nitroguanidine	220 (dec.)	(47)
N-(*o*-Aminophenyl)-*N'*-nitroguanidine	197 (dec.)	(47)
N-(*p*-*tert*-Amylphenyl)-*N'*-nitroguanidine	174–175	(81)
N-(*p*-Acetamidophenyl)-*N'*-nitroguanidine	223 (dec.)	(81)
N-(*p*-Dimethylaminophenyl)-*N'*-nitroguanidine	196–197	(81)
N-(*p*-Diethylaminophenyl)-*N'*-nitroguanidine	196 (dec.)	(99)
N-(2,5-Dimethylphenyl)-*N'*-nitroguanidine	161–162.7	(81)
N-(2-Methyl-5-isopropylphenyl)-*N'*-nitroguanidine	125–126	(81)
N-(3-Chloro-4-methylphenyl)-*N'*-nitroguanidine	170.5–172	(99)
N-(3-Ethoxy-4-methylphenyl)-*N'*-nitroguanidine	185.5–186	(99)
N-(3-Amino-4-methylphenyl)-*N'*-nitroguanidine	178–179.5	(99)
N-(4-Amino-3-methylphenyl)-*N'*-nitroguanidine	202 (dec.)	(99)
N-Anilino-*N'*-nitroguanidine	168	(47)
N-Benzoyl-*N'*-nitroguanidine	219.5 (dec.)	(47)
N-Benzamido-*N'*-nitroguanidine	197.5 (dec.)	(47)
N-(4-Nitrobenzamido)-*N'*-nitroguanidine	196.5 (dec.)	(47)
N-Benzenesulfonamido-*N'*-nitroguanidine	195 (dec.)	(47)
N-Nitroguanylbenzenesulfonamide	150.5 (dec.)	(47)
N-Methyl-*N*-amino-*N'*-nitroguanidine	171 (dec.)	(49)
N-(α-Naphthyl)-*N'*-nitroguanidine	214–216	(65)
N-(β-Naphthyl)-*N'*-nitroguanidine	195–196	(65)
Nitroguanyl azide	79 (dec.)	(67, 108a)
1-Nitroguanyl-3,5-dimethylpyrazole	126	(52)

* These compounds melt, then resolidify, and finally decompose at the higher temperatures.

TABLE 6

N,N'-Disubstituted-N"-nitroguanidines

COMPOUND	MELTING POINT	REFERENCES
	°C.	
N,N'-Diethyl-*N"*-nitroguanidine	115–116	(84)
N,N'-Dibenzyl-*N"*-nitroguanidine	166–167	(83)
N-(2-Phenylaminoethyl)-*N'*-phenyl-*N"*-nitroguanidine	145.6 (dec.)	(96)
N-(2-*p*-Tolylaminoethyl)-*N'*-*p*-tolyl-*N"*-nitroguanidine	163.5 (dec.)	(96)
N-(2-*p*-Anisylaminoethyl)-*N'*-*p*-anisyl-*N"*-nitroguanidine	181.3 (dec.)	(83, 96)
N-(2-*p*-Phenetylaminoethyl)-*N'*-*p*-phenetyl-*N"*-nitroguanidine	171.4 (dec.)	(96)
N-(β-Chloroethyl)-*N'*-*n*-propyl-*N"*-nitroguanidine	91–92 (163)*	(44)
N-(β-Nitraminoethyl)-*N'*-methyl-*N"*-nitroguanidine	182 (dec.)	(92)
N-(β-Nitraminoethyl)-*N'*-ethyl-*N"*-nitroguanidine	107.5–108.5	(92)
N-Methyl-*N'*-amino-*N"*-nitroguanidine (as benzalhydrazone)	176–177 (dec.)	(51)

* This compound possesses a double melting point.

TABLE 7

2-Nitramino-2-imidazolines

COMPOUND	MELTING POINT	REFERENCES
	°C.	
2-Nitramino-2-imidazoline	221 (dec.)	(102, 104)
2-Nitramino-4(or 5)-methyl-2-imidazoline	170.5	(102, 104)
2-Nitramino-1,3-diaza-2-cyclohexene	252 (dec.)	(102, 104)
2-Nitramino-4(or 6)-methyl-1,3-diaza-2-cyclohexene	147–148.5	(102, 104)
2-Nitramino-5-hydroxy-1,3-diaza-2-cyclohexene	233.5 (dec.)	(102, 104)
1-Methyl-2-nitramino-2-imidazoline	115–116	(88)
1-Ethyl-2-nitramino-2-imidazoline	86.5	(88)
1-Propyl-2-nitramino-2-imidazoline	104–104.2	(44)
1-(β-Hydroxyethyl)-2-nitramino-2-imidazoline	131.5–132	(88)
1-(β-Nitroguanylaminoethyl)-2-nitramino-2-imidazoline	197 (dec.)	(88)
2-Nitramino-5-nitroxy-1,3-diaza-2-cyclohexene	220.2 (dec.)	(93)
1-Benzyl-2-nitramino-2-imidazoline	147–148	(83)
1-Phenyl-2-nitramino-2-imidazoline	166–167	(96)
1-(*p*-Anisyl)-2-nitramino-2-imidazoline	169–169.5	(83, 96)
1-(*p*-Phenetyl)-2-nitramino-2-imidazoline	166.4–167.5	(96)
1-(β-Nitroxyethyl)-2-nitramino-2-imidazoline	114.8–115.2	(96)
1-(*p*-Acetamidophenyl)-2-nitramino-2-imidazoline	234 (dec.)	(84)
1,2-Bis-1-(2-nitramino-2-imidazolinyl)ethane	301 (dec.)	(88)

TABLE 8

Cyclic nitroguanidines with nitramino group in the ring

COMPOUND	MELTING POINT	REFERENCES
	°C.	
1-Nitro-2-amino-2-imidazoline	133.5	(94)
1-Nitro-2-amino-2-imidazolinium chloride	193.8 (dec.)	(43, 94)
1-Nitro-2-amino-2-imidazolinium bromide	180 (dec.)	(94)
1-Nitro-2-amino-2-imidazolinium nitrate	161 (dec.)	(94)
1-Nitro-2-amino-2-imidazolinium picrate	189.6	(43, 94)
1-Nitro-2-amino-4-methyl-2-imidazolinium chloride	187.5	(43)
1-Nitro-2-amino-4-methyl-2-imidazolinium nitrate	150	(43)
1-Nitro-2-*n*-propylamino-2-imidazolinium nitrate	148.8–149	(44)
1-Nitro-2-*n*-propylamino-2-imidazolinium styphnate	163.5 (dec.)	(44)
1-Nitro-2-amino-5-methyl-2-imidazolinium nitrate	115–116	(94)
1-Nitro-2-(*p*-anisylamino)-2-imidazoline	134.7 (dec.)	(83)
1-Nitro-2-(*p*-acetamidophenylamino)-2-imidazoline	172 (dec.)	(84)
1-Nitro-2-amino-6-methyl-1,3-diaza-2-cyclohexene nitrate salt	115	(99)
1-Nitro-2-amino-6-methyl-1,3-diaza-2-cyclohexene picrate	175–176	(99)

TABLE 9

Dinitroguanidines

COMPOUND	MELTING POINT	REFERENCES
	°C.	
N-Methyl-*N*,*N'*-dinitroguanidine	81.5–82.5	(105)
N-Butyl-*N*,*N'*-dinitroguanidine	71–72	(105)
N-(β-Nitroxyethyl)-*N*,*N'*-dinitroguanidine	84.5–85.3	(94)
1-Nitro-2-nitramino-2-imidazoline	151–152 (dec.)	(103)
1-Nitro-2-nitramino-4-methyl-2-imidazoline	123	(93)
1-Methyl-2-nitrimino-3-nitroimidazolidine	170 (dec.)	(88)
1-Ethyl-2-nitrimino-3-nitroimidazolidine	138 (dec.)	(88)
1-Propyl-2-nitrimino-3-nitroimidazolidine	125.2–125.5	(44)
1-(β-Nitroxyethyl)-2-nitrimino-3-nitroimidazolidine	116 (dec.)	(88)
1,2-Bis-1-(2-nitrimino-3-nitroimidazolidinyl)ethane	181 (dec.)	(88)
1-(*N*-Nitroguanyl-*N*-nitro-β-aminoethyl)-2-nitrimino-3-nitroimidazolidine	162 (dec.)	(88)

TABLE 10

Nitrosonitroguanidines

COMPOUND	MELTING POINT*	REFERENCES
	°C.	
N-Methyl-*N*-nitroso-*N'*-nitroguanidine	118	(81, 85, 101)
N-Ethyl-*N*-nitroso-*N'*-nitroguanidine	114.5	(81, 85)
N-Propyl-*N*-nitroso-*N'*-nitroguanidine	118	(95)
N-Butyl-*N*-nitroso-*N'*-nitroguanidine	113	(81, 85)
N-(β-Hydroxyethyl)-*N*-nitroso-*N'*-nitroguanidine	111.5	(94)
N-(β-Nitroxyethyl)-*N*-nitroso-*N'*-nitroguanidine	112.5	(94)
N-(β-Chloroethyl)-*N*-nitroso-*N'*-nitroguanidine	114.5	(94)
N-(γ-Nitroxybutyl)-*N*-nitroso-*N'*-nitroguanidine	87	(99)
N-Benzyl-*N*-nitroso-*N'*-nitroguanidine	118	(85, 95)
1-(*N*-Nitroguanyl-*N*-nitroso-β-aminoethyl)-2-nitramino-2-imidazoline	176	(88)
N-(γ-Hydroxybutyl)-*N*-nitroso-*N'*-nitroguanidine	100	(99)
1-Nitroso-2-nitramino-2-imidazoline	142	(96)

* All of these compounds decompose at the temperatures given.

TABLE 11

Nitroguanylhydrazones

ALDEHYDE OR KETONE	MELTING POINT OF NITROGUANYLHYDRAZONE	REFERENCE
	°C.	
Formaldehyde	169	(136)
Acetaldehyde	144–145	(52, 123)
Crotonaldehyde	175.5	(123)
Butyraldehyde	103–104	(52, 123)
Isobutyraldehyde	129.5–130.5	(52)
Heptanal	103–103.5	(52, 123)
Octanal	118	(123)
Citral	135–136.5	(136)
Decanal	112–113	(52)
Glyoxal	>300	(52)
Furfural	213–214	(52)
5-Nitrofurfural		(128)
Benzaldehyde	188	(136)
Phenylacetaldehyde	151–151.5	(52)
Hydrocinnamaldehyde	135	(52)
Cinnamaldehyde	186	(136)
4-Methylbenzaldehyde	179–180	(52)
4-Isopropylbenzaldehyde	187	(52)
2-Chlorobenzaldehyde	192	(52)
2,4-Dichlorobenzaldehyde	222–224	(52)
3,4-Dichlorobenzaldehyde	233–234	(52)
3-Nitrobenzaldehyde	239–240	(52)
2-Hydroxybenzaldehyde	213	(136)
4-Hydroxybenzaldehyde	253	(52)
2,4-Dihydroxybenzaldehyde	>300	(52)
2-Methoxybenzaldehyde	185.5	(52)
4-Methoxybenzaldehyde	200	(136)
3-Methoxy-4-hydroxybenzaldehyde	186–187	(136)
Piperonal	220	(136)
3,4-Dimethoxybenzaldehyde	195	(123)
3,4-Dimethoxy-5-bromo-6-nitrobenzaldehyde	243–244	(115)
d-Glucose	143–144	(52)
Acetone	164–165	(136)
2-Butanone	136.5	(136)
2-Pentanone	109–110	(136)
2-Hexanone	109–110	(136)
4-Methyl-2-pentanone	112.5	(123)
2-Heptanone	112–113	(52, 123)
2-Dodecanone	115–116	(52)
2-Methyl-5-decanone	78–79.5	(113)
2-Methyl-5-undecanone	84.5–86	(113)
Cyclohexanone	161.5	(136)
4-Methylcyclohexanone	122–123	(52)
Pyruvic acid	181.5	(136)
2,3-Butanedione	285–290	(52)
Acetoacetic ester	130–131	(136)
Acetophenone	161–162	(136)
Acetoacetanilide	184	(123)

TABLE 12

5-Nitramino-1,2,4-triazoles

COMPOUND	MELTING POINT	REFERENCE
	°C.	
5-Nitramino-1,2,4-triazole	217 (dec.)	(47)
3-Methyl-5-nitramino-1,2,4-triazole	213 (dec.)	(47)

TABLE 13

5-Nitraminotetrazole and its salts

COMPOUND	MELTING POINT	REFERENCES
	°C.	
5-Nitraminotetrazole	(195) 140*	(67, 108a)
Diammonium 5-nitraminotetrazole	220	(67)
Di(diethylammonium) 5-nitraminotetrazole	105 (dec.)	(67)
n-Butylammonium 5-nitraminotetrazole	161–163	(67)
Guanidinium 5-nitraminotetrazole	225–226 (dec.)	(67)
Phenylammonium 5-nitraminotetrazole	160	(67)
β-Naphthylammonium 5-nitraminotetrazole	175–177	(67)
Potassium 5-nitraminotetrazole	220*	(67)
Disodium 5-nitraminotetrazole	207*	(108a)

* These compounds explode at the recorded temperatures instead of melting.

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