

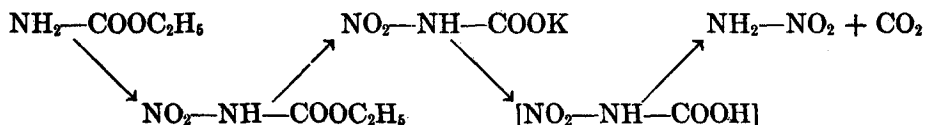
CHAPTER VIII

NITROAMINES AND RELATED SUBSTANCES

The nitroamines are substituted ammonias, substances in which a nitro group is attached directly to a trivalent nitrogen atom. They are prepared in general either by the nitration of a nitrogen base or of one of its salts, or they are prepared by the splitting off of water from the nitrate of the base by the action of concentrated sulfuric acid upon it. At present two nitroamines are of particular interest to the explosives worker, namely, nitroguanidine and cyclotrimethylenetrinitramine (cyclonite). Both are produced from synthetic materials which have become available in large commercial quantities only since the first World War, the first from cyanamide, the second from formaldehyde from the oxidation of synthetic methyl alcohol.

Nitroamide (Nitroamine)

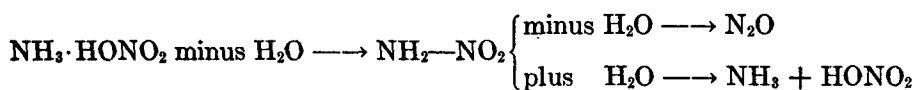
Nitroamide, the simplest of the nitroamines, is formed by the action of dilute acid on potassium nitrocarbamate, which itself results from the nitration of urethane and the subsequent hydrolysis of the nitro ester by means of alcoholic potassium hydroxide.



Nitroamide is strongly acidic, a white crystalline substance, melting at 72–73° with decomposition, readily soluble in water, alcohol, and ether, and insoluble in petroleum ether. It explodes on contact with concentrated sulfuric acid. The pure material decomposes slowly on standing, forming nitrous oxide and water; it cannot be preserved for more than a few days. When an aqueous solution of nitroamide is warmed, gas bubbles begin to

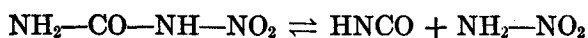
come off at about 60–65°, and decomposition is complete after boiling for a short time.

The solution which results when ammonium nitrate is dissolved in a large excess of concentrated sulfuric acid evidently contains nitroamide.¹ If the solution is warmed directly, no nitric acid distils from it but at about 150° it gives off nitrous oxide which corresponds to the dehydration of the nitroamide by the action of the strong acid. The nitroamide moreover, by the action of the same acid, may be hydrated to yield nitric acid, slowly if the solution is digested at 90° to 120°, under which conditions the nitric acid distils out, and rapidly at ordinary temperature in the nitrometer where mercury is present which reacts with the nitric acid as fast as it is formed.



The two reactions, hydration and dehydration, or, more exactly, the formation of nitrous oxide and of nitric acid, are more or less general reactions of the substituted nitroamines. The extent to which one or the other occurs depends largely upon the groups which are present in the molecule. Thus, tetryl on treatment with concentrated sulfuric acid forms nitric acid, and it gives up one and only one of its nitro groups in the nitrometer, but the reaction is not known by which nitrous oxide is eliminated from it. Methylnitramine, on the other hand, gives nitrous oxide readily enough but shows very little tendency to produce nitric acid.

Solutions of nitrourea and nitroguanidine in concentrated sulfuric acid contain actual nitroamide, and these substances give up their nitro group nitrogen in the nitrometer. Nitroamide has been isolated² both from an aqueous solution of nitrourea and from a solution of the same substance in concentrated sulfuric acid.



The reaction is reversible, for nitroamide in aqueous solution combines with cyanic acid to form nitrourea.

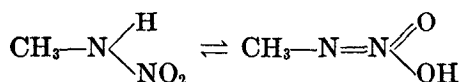
¹ Davis and Abrams, *J. Am. Chem. Soc.*, **47**, 1043 (1925).

² Davis and Blanchard, *J. Am. Chem. Soc.*, **51**, 1790 (1929).

Methylnitramine

Methylnitramine is produced when aniline reacts with tetryl in benzene solution, and when ammonia water or barium hydroxide solution acts upon dinitrodimehydroxamide. The structure of tetryl was first proved by its synthesis from picryl chloride and the potassium salt of methylnitramine.

Methylnitramine is a strong monobasic acid, very readily soluble in water, alcohol, chloroform, and benzene, less soluble in ether, and sparingly soluble in petroleum ether. It crystallizes from ether in flat needles which melt at 38°. It is not decomposed by boiling in aqueous solution even in the presence of an excess of alkali. On distillation it yields dimethylnitramine, m.p. 57°, methyl alcohol, nitrous oxide and other products. Methylnitramine owes its acidity to the fact that it is tautomeric.



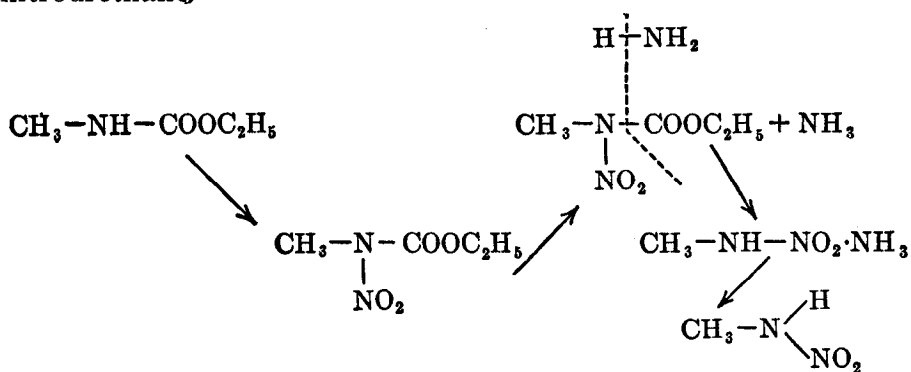
Dimethylnitramine, in which there is no hydrogen atom attached to the atom which carries the nitro group, cannot tautomerize, and is not acidic.

Methylnitramine decomposes explosively in contact with concentrated sulfuric acid. If the substance is dissolved in water, and if concentrated sulfuric acid is added little by little until a considerable concentration is built up, then the decomposition proceeds more moderately, nitrous oxide is given off, and dimethyl ether (from the methyl alcohol first formed) remains dissolved in the sulfuric acid. The same production of nitrous oxide occurs even in the nitrometer in the presence of mercury. If methylnitramine and a small amount of phenol are dissolved together in water, and if concentrated sulfuric acid is then added little by little, a distinct yellow color shows that a trace of nitric acid has been formed. The fact that methylnitramine gives a blue color with the diphenylamine reagent shows the same thing.

Methylnitramine is conveniently prepared³ by nitrating methylurethane with absolute nitric acid, drowning in water, neutralizing with sodium carbonate, extracting with ether, and

³ Franchimont and Klobbie, *Rec. trav. chim.*, 7, 354 (1887).

then passing ammonia gas into the ether solution of methyl-nitrourethane,



A white crystalline precipitate of the ammonium salt of methyl-nitramine is deposited. This is dissolved in alcohol, and the solution is boiled—whereby ammonia is driven off—and concentrated to a small volume. The product is procured by completing the evaporation in a vacuum desiccator over sulfuric acid.

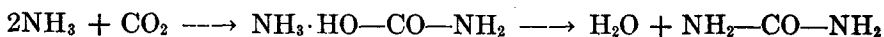
The heavy metal salts of methylnitramine are primary explosives, but have not been investigated extensively.

Urea Nitrate

Although urea has the properties of an amide (carbamide) rather than those of an amine, it nevertheless acts as a monoacid base in forming salts among which the nitrate and the oxalate are noteworthy because they are sparingly soluble in cold water, particularly in the presence of an excess of the corresponding acid. The nitrate, white monoclinic prisms which melt at 152° with decomposition, is procured by adding an excess of nitric acid (1.42) to a strong aqueous solution of urea. The yield is increased if the mixture is chilled and allowed to stand for a time. Urea nitrate is stable and not deliquescent. It has interest as a powerful and cool explosive, but suffers from the disadvantage that it is corrosively acidic in the presence of moisture.

Pure urea is manufactured commercially by pumping ammonia and carbon dioxide into an autoclave where they are heated together under pressure while more of each gas is pumped in. Ammonium carbamate is formed at first, this loses water from its molecule to form urea, and the autoclave finally becomes

filled with a strong solution of urea which is drawn off and crystallized.



Urea is sometimes incorporated in blasting explosives for the purpose of lowering the temperature of explosion. Its use as a stabilizer has already been mentioned.

Nitrourea

Nitrourea is a cool but powerful explosive, and would be useful if it were not for the fact that it tends to decompose spontaneously in the presence of moisture. The mechanism of its reactions is the same as that of the reactions of nitroguanidine, which differs from it in containing an $>\text{NH}$ group where nitrourea contains a $>\text{CO}$, but the reactions of nitrourea are very much more rapid. The nitro group promotes the *urea dearrangement*, so that nitrourea when dissolved in water or when warmed breaks down into cyanic acid and nitroamide much more readily than urea breaks down under like conditions into cyanic acid and ammonia. The imido group in place of the carbonyl hinders it; guanidine dearranges less readily than urea, and nitroguanidine is substantially as stable as urea itself.

Nitrourea is prepared by adding dry urea nitrate (200 grams) in small portions at a time with gentle stirring to concentrated sulfuric acid (1.84) (300 cc.) while the temperature of the mixture is kept below 0° . The milky liquid is poured without delay into a mixture of ice and water (1 liter), the finely divided white precipitate is collected on a filter, sucked as dry as may be, and, without washing, is immediately dissolved while still wet in boiling alcohol.⁴ The liquid on cooling deposits pearly leaflets of nitrourea. It is chilled and filtered, and the crystals are rinsed with cold alcohol and dried in the air. The product, which melts at 146° to 153° with decomposition, is sufficiently pure for use in synthesis, and may be preserved for several years unchanged in hard glass bottles. If slightly moist nitrourea is allowed to stand in contact with soft glass, that is, in contact with a trace

⁴The product at this point contains acid enough to prevent it from decomposing in boiling alcohol. For a second recrystallization it is unsafe to heat the alcohol above 60° .

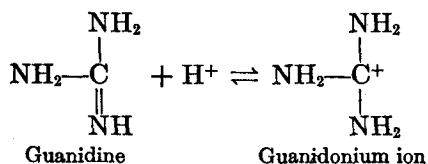
of alkali, it decomposes completely within a short time forming water, ammonia, nitrous oxide, urea, biuret, cyanuric acid, etc. Pure nitrourea, recrystallized from benzene, ether, or chloroform, in which solvents it is sparingly soluble, melts with decomposition at 158.4–158.8°.

In water and in hydrophilic solvents nitrourea rearranges rapidly into cyanic acid and nitroamide. Alkalis promote the reaction. If an aqueous solution of nitrourea is warmed, bubbles of nitrous oxide begin to come off at about 60°. If it is allowed to stand over night at room temperature, the nitrourea disappears completely and the liquid is found to be a solution of cyanic acid. Indeed, nitrourea is equivalent to cyanic acid for purposes of synthesis. It reacts with alcohols to form carbamic esters (urethanes) and with primary and second amines to form mono- and *unsym*-di-substituted ureas.

Guanidine Nitrate

Guanidine nitrate is of interest to us both as an explosive itself and a component of explosive mixtures, and as an intermediate in the preparation of nitroguanidine. All other salts of guanidine require strong mixed acid to convert them to nitroguanidine, but the nitrate is converted by dissolving it in concentrated sulfuric acid and pouring the solution into water.

Guanidine is a strong monoacid base, indistinguishable from potassium hydroxide in an electrometric titration. There is considerable evidence⁵ which indicates that the charge of the guanidonium ion resides upon its carbon atom.

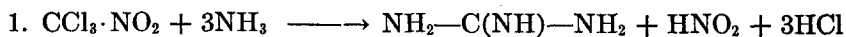


Guanidine itself is crystalline, deliquescent, and strongly caustic, and takes up carbon dioxide from the air.

Guanidine was first obtained by Strecker in 1861 by the oxidation with hydrochloric acid and potassium chlorate of guanine (a substance found in guano and closely related to uric acid).

⁵ Davis, Yelland, and Ma, *J. Am. Chem. Soc.*, **59**, 1993 (1937).

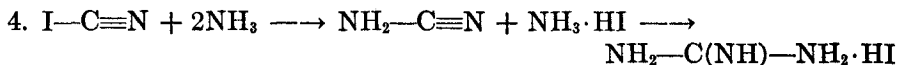
Guanidine or its salts may be prepared, among other ways, by the interaction (1) of orthocarbonic ester or (2) of chloropicrin



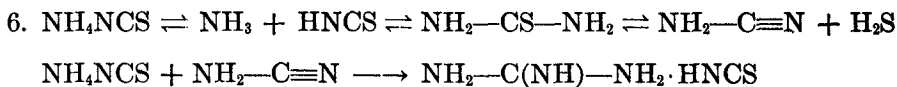
with aqueous ammonia at 150°, by the interaction (3) of carbon tetrabromide with alcoholic ammonia in a sealed tube at 100°,



by the interaction (4) of cyanogen iodide with alcoholic ammonia in a sealed tube at 100°, whereby cyanamide and ammonium iodide are formed first and then combine with one another to



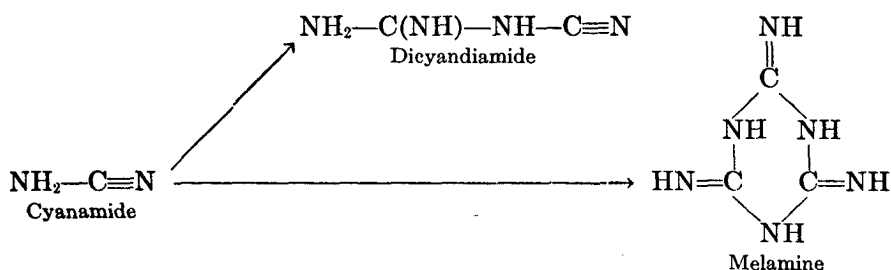
form guanidine iodide, by the combination (5) of cyanamide, already prepared, with an ammonium salt by heating the materials with alcohol in a sealed tube at 100°, and (6) by heating



ammonium thiocyanate at 170–190° for 20 hours, or until hydrogen sulfide no longer comes off, whereby the material is converted into guanidine thiocyanate. The reaction depends upon the fact that the ammonium thiocyanate is in part converted into thiourea, and that this breaks down into hydrogen sulfide, which escapes, and cyanamide which combines with the unchanged ammonium thiocyanate to form the guanidine salt. The yield from this process is excellent.

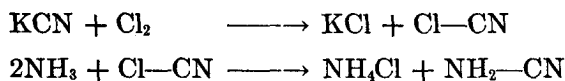
For many years guanidine thiocyanate was the most easily prepared and the most commonly used of the salts of guanidine. Other salts were made from it by metathetical reactions. Nitroguanidine, prepared from the thiocyanate by direct nitration with mixed acids, was found to contain traces of sulfur compounds which attacked nitrocellulose and affected the stability of smokeless powder, and this is one of the reasons why nitroguanidine powders did not come into early use. Guanidine thiocyanate is deliquescent. Strong solutions of it dissolve filter paper.

Cyanamide itself is not a suitable raw material for the preparation of guanidine salts, for it is difficult to prepare and to purify, and it polymerizes on keeping. The evaporation of an aqueous solution of cyanamide yields the dimer, dicyandiamide, and the heating, or even the long keeping, of the dry substance produces the trimer, melamine.

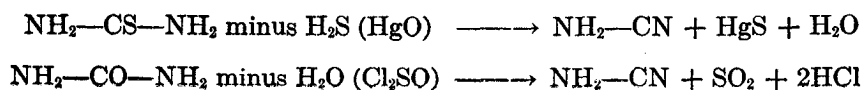


Cyanamide, colorless crystals, m.p. 40°, is readily soluble in water, alcohol, and ether. An aqueous solution of cyanamide gives a black precipitate of copper cyanamide with ammoniacal copper sulfate solution, and a yellow precipitate of silver cyanamide with ammoniacal silver nitrate. The precipitates are almost unique among the compounds of copper and silver in the respect that they are insoluble in ammonia water.

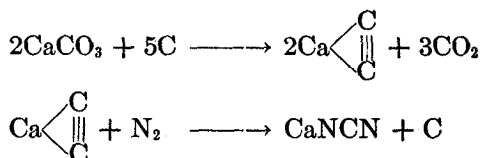
Before the development of the cyanamide process for the fixation of nitrogen, cyanamide was prepared by the interaction of cyanogen chloride or bromide (from the action of the halogen on potassium cyanide) with ammonia in water or ether solution.



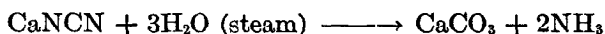
If the reaction, say, with cyanogen chloride, is carried out in ether solution, ammonium chloride precipitates and is filtered off, and the cyanamide is procured as a syrup by allowing the ether solution to evaporate spontaneously and later as crystals by allowing the syrup to stand over sulfuric acid in a desiccator. Cyanamide may also be prepared by removing the component atoms of hydrogen sulfide from thiourea by means of mercuric oxide. Thionyl chloride effects the corresponding removal of water from urea.



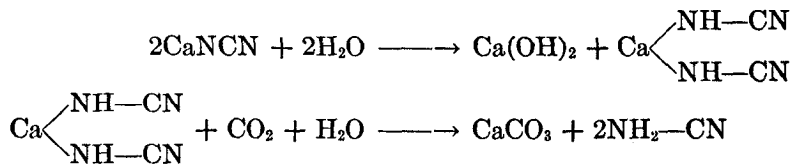
The cyanamide process has made cyanamide and its derivatives more easily available for commercial synthesis. Coke and limestone are heated together in the electric furnace for the production of calcium carbide. This substance, along with a small amount of calcium chloride which acts as a catalyst, is then heated at 800–1000° in a stream of nitrogen gas.



The resulting dark-colored mixture of calcium cyanamide and carbon is known as *lime nitrogen* (*Kalkstickstoff*) and is used in fertilizers. If steam is passed through it, it yields ammonia.



Water, whether cool or warm, produces some cyanamide, which is readily soluble, and some calcium hydrogen cyanamide, white, microcrystalline, and sparingly soluble, but water plus acid for the removal of the calcium (sulfuric acid, oxalic acid, or carbon dioxide) yields a solution of cyanamide which is directly applicable for use in certain reactions.

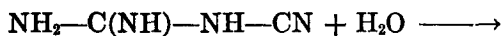


On hydrolysis with dilute sulfuric acid it yields urea. On treatment with ammonium sulfide it prefers to react with the hydrogen sulfide part of the molecule to form thiourea, not with the ammonia part to form guanidine, and the reaction is the commercial source of many tons of thiourea for the rubber industry. On evaporation for crystals, the solution yields dicyandiamide which constitutes a convenient source for the preparation of guanidine nitrate.

Dicyandiamide crystallizes from water in handsome flat needles or plates which melt at 208.0–208.1° and decompose if heated slightly above the melting point. A saturated aqueous solution contains—

TEMPERATURE, °C.	GRAMS PER 100 CC. OF SOLUTION
0	1.3
10	2.0
20	3.4
30	5.0
40	7.6
50	11.4
60	16.1
70	22.5
80	30.0
90	37.9
100	46.7

The preparation of guanidine nitrate from dicyandiamide by the action of aqua regia has been patented,⁶ but the reaction evidently depends solely upon the hydrolysis of the cyan group and does not require the use of a vigorous oxidizing agent. Marqueyrol and Loriette in a French patent of September 26, 1917, described a process for the preparation of nitroguanidine direct from dicyandiamide without the isolation of any intermediate products. The process depends upon the hydrolysis of the dicyandiamide by means of 61% sulfuric acid to form guanylurea or dicyandiamidine (sulfate) which is then further hydrolyzed to form carbon dioxide, which escapes, and guanidine and ammonia, which remain in the reaction mixture in the form of sulfates.



Dicyandiamide



Guanylurea



Guanidine

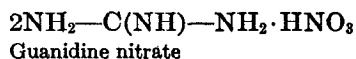
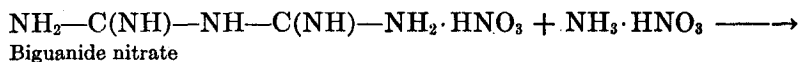
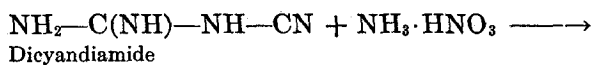
The guanidine sulfate, without removal from the mixture, is then nitrated to nitroguanidine.⁷ The process yields a nitroguanidine which is suitable for use in nitrocellulose powder, but it suffers from the disadvantages that the dicyandiamide, which corresponds after all to two molecules of cyanamide, yields in theory

⁶ Ulpiani, Ger. Pat. 209,431 (1909).

⁷ The procedure, under conditions somewhat different from those described in the patent, is illustrated by our process for the preparation of β -nitroguanidine; see page 383.

only one molecular equivalent of guanidine, that the actual yield is considerably less than the theory because of the loss of guanidine by hydrolysis to carbon dioxide and ammonia, and that the final nitration of the guanidine sulfate, which is carried out in the presence of water and of ammonium sulfate, requires strong and expensive mixed acid.

Werner and Bell⁸ reported in 1920 that dicyandiamide heated for 2 hours at 160° with 2 mols of ammonium thiocyanate gives 2 mols of guanidine thiocyanate in practically theoretical yield. Ammonium thiocyanate commends itself for the reaction because it is readily fusible. The facts suggest that another fusible ammonium salt might work as well, ammonium nitrate melts at about 170°, and, of all the salts of guanidine, the nitrate is the one which is most desired for the preparation of nitroguanidine. When dicyandiamide and 2 mols of ammonium nitrate are mixed and warmed together at 160°, the mixture first melts to a colorless liquid which contains biguanide (or guanylguanidine) nitrate, which presently begins to deposit crystals of guanidine nitrate, and which after 2 hours at 160° solidifies completely to a mass of that substance.⁹ The yield is practically theoretical. The reaction consists, first, in the addition of ammonia to the cyan group of the dicyandiamide, then in the ammoniolytic splitting of the biguanide to form two molecules of guanidine.



The nitric acid of the original 2 mols of ammonium nitrate is exactly sufficient for the formation of 2 mols of guanidine nitrate. But the intermediate biguanide is a strong diacid base; the ammonium nitrate involved in its formation supplies only one equivalent of nitric acid; and there is a point during the early part of the process when the biguanide mononitrate tends to attack the unchanged ammonium nitrate and to liberate ammonia from it. For this reason the process works best if a small excess of

⁸ *J. Chem. Soc.*, 118, 1133 (1920).

⁹ Davis, *J. Am. Chem. Soc.*, 43, 2234 (1921); Davis, U. S. Pat. 1,440,063 (1922), French Pat. 539,125 (1922).

ammonium nitrate is used. The preparation may be carried out by heating the materials together either in the dry state or in an autoclave in the presence of water or of alcohol.

Guanidine nitrate is not deliquescent. It is readily soluble in alcohol, very readily in water, and may be recrystallized from either solvent. The pure material melts at 215–216°.

Preparation of Guanidine Nitrate. An intimate mixture of 210 grams of dicyandiamide and 440 grams of ammonium nitrate is placed in a 1 liter round-bottom flask, and the flask is arranged for heating in an oil bath which has a thermometer in the oil. The oil bath is warmed until the thermometer indicates 160°, and the temperature is held at this point for 2 hours. At the end of that time the flask is removed and allowed to cool, and its contents is extracted on the steam bath by warming with successive portions of water. The combined solution is filtered while hot for the removal of white insoluble material (ammelime and ammelide), concentrated to a volume of about a liter, and allowed to crystallize. The mother liquors are concentrated to a volume of about 250 cc. for a second crop, after the removal of which the residual liquors are discarded. The crude guanidine nitrate may be recrystallized by dissolving it in the least possible amount of boiling water and allowing to cool, etc., or it may be dried thoroughly and used directly for the preparation of nitroguanidine. A small amount of ammonium nitrate in it does not interfere with its conversion to nitroguanidine by the action of concentrated sulfuric acid.

Nitroguanidine

Nitroguanidine exists in two forms.¹⁰ The α -form invariably results when guanidine nitrate is dissolved in concentrated sulfuric and the solution is poured into water. It is the form which is commonly used in the explosives industry. It crystallizes from water in long, thin, flat, flexible, lustrous needles which are tough and extremely difficult to pulverize; $N_\alpha = 1.518$, $N_\beta =$ a little greater than 1.668, $N_\gamma =$ greater than 1.768, double refraction 0.250. When α -nitroguanidine is decomposed by heat, a certain amount of β -nitroguanidine is found among the products.

β -Nitroguanidine is produced in variable amount, usually along with some of the α -compound, by the nitration of the mixture of guanidine sulfate and ammonium sulfate which results from the hydrolysis of dicyandiamide by sulfuric acid. Conditions have

¹⁰ Davis, Ashdown, and Couch, *J. Am. Chem. Soc.*, 47, 1063 (1925).

been found, as described later, which have yielded exclusively the β -compound in more than thirty trials. It crystallizes from water in fernlike clusters of small, thin, elongated plates; $N_\alpha = 1.525$, N_β not determined, $N_\gamma = 1.710$, double refraction 0.185. It is converted into the α -compound by dissolving in concentrated sulfuric acid and pouring the solution into water.

Both α - and β -nitroguanidine, if dissolved in hot concentrated nitric acid and allowed to crystallize, yield the same nitrate, thick, rhomb-shaped prisms which melt at 147° with decomposition. The nitrate loses nitric acid slowly in the air, and gives α -nitroguanidine when recrystallized from water. Similarly, both forms recrystallized from strong hydrochloric acid yield a hydrochloride which crystallizes in needles. These lose hydrogen chloride rapidly in the air, and give α -nitroguanidine when recrystallized from water. The two forms are alike in all their chemical reactions, in their derivatives and color reactions.

Both forms of nitroguanidine melt at 232° if the temperature is raised with moderate slowness, but by varying the rate of heating melting points varying between 220° and 250° may be obtained.

Neither form can be converted into the other by solution in water, and the two forms can be separated by fractional crystallization from this solvent. They appear to differ slightly in their solubility in water, the two solubility curves lying close together but apparently crossing each other at about 25° , where the solubility is about 4.4 grams per liter, and again at about 100° , where the solubility is about 82.5 grams per liter. Between these temperatures the β -form appears to be the more soluble.

Preparation of α -Nitroguanidine. Five hundred cc. of concentrated sulfuric acid in a 1-liter beaker is cooled by immersing the beaker in cracked ice, and 400 grams of well-dried guanidine nitrate is added in small portions at a time, while the mixture is stirred with a thermometer and the temperature is not allowed to rise above 10° . The guanidine nitrate dissolves rapidly, with very little production of heat, to form a milky solution. As soon as all crystals have disappeared, the milky liquid is poured into 3 liters of cracked ice and water, and the mixture is allowed to stand with chilling until precipitation and crystallization are complete. The product is collected on a filter, rinsed with water for the removal of sulfuric acid, dissolved in boiling water

(about 4 liters), and allowed to crystallize by standing over night. Yield 300–310 grams, about 90% of the theory.

The rapid cooling of a solution of α -nitroguanidine produces small needles, which dry out to a fluffy mass but which are still too coarse to be incorporated properly in colloided powder. An



FIGURE 89. α -Nitroguanidine (25 \times). Small crystals from the rapid cooling of a hot aqueous solution.

extremely fine powder may be procured by the rapid cooling of a mist or spray of hot nitroguanidine solution, either by spraying it against a cooled surface from which the material is removed continuously, or by allowing the spray to drop through a tower up which a counter current of cold air is passing.

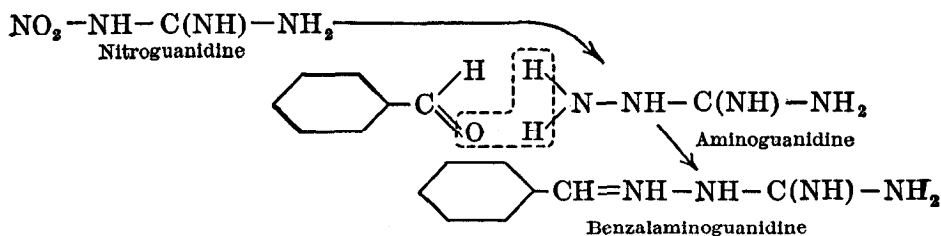
Preparation of β -Nitroguanidine. Twenty-five cc. of 61% aqueous sulfuric acid is poured upon 20 grams of dicyandiamide contained in a 300-cc. round-bottom flask equipped with a reflux condenser. The mixture warms up and froths considerably. After the first vigorous reaction has subsided, the material is heated for 2 hours in an oil bath at 140° (thermometer in the oil). The reaction mass, chilled in a freezing

mixture, is treated with ice-cold nitrating acid prepared by mixing 20 cc. of fuming nitric acid (1.50) with 10 cc. of concentrated sulfuric acid (1.84). After the evolution of red fumes has stopped, the mixture is heated for 1 hour in the boiling-water bath, cooled, and drowned in 300 cc. of cracked ice and water. The precipitate, collected on a filter, rinsed with water for the removal of acid, and recrystallized from water, yields about 6 grams of β -nitroguanidine, about 25% of the theory.

Saturated solutions of nitroguanidine in sulfuric acid of various concentrations contain ¹¹ the amounts indicated below.

CONCENTRATION OF SOLVENT SULFURIC ACID, %	NITROGUANIDINE (GRAMS) PER 100 cc.	
	at 0°	at 25°
45.....	5.8	10.9
40.....	3.4	8.0
35.....	2.0	5.2
30.....	1.3	2.9
25.....	0.75	1.8
20.....	0.45	1.05
15.....	0.30	0.55
0.....	0.12	0.42

Nitroguanidine on reduction is converted first into nitroso-guanidine and then into aminoguanidine (or guanylhydrazine). The latter substance is used in the explosives industry for the preparation of tetracene. In organic chemical research it finds use because of the fact that it reacts readily with aldehydes and ketones to form products which yield crystalline and easily characterized nitrates.



Preparation of Benzalaminoguanidine Nitrate (Benzaldehyde Guanylhydrazone Nitrate). Twenty-six grams of zinc dust and 10.4 grams of nitroguanidine are introduced into a 300-cc. Erlenmeyer flask, 150 cc. of water is added, then 42 cc. of glacial acetic acid at such a rate that the temperature of the mixture does not rise above 40°. The liquid at first turns yellow because of the formation of nitrosoguanidine but

¹¹ Davis, *J. Am. Chem. Soc.*, 44, 868 (1922).

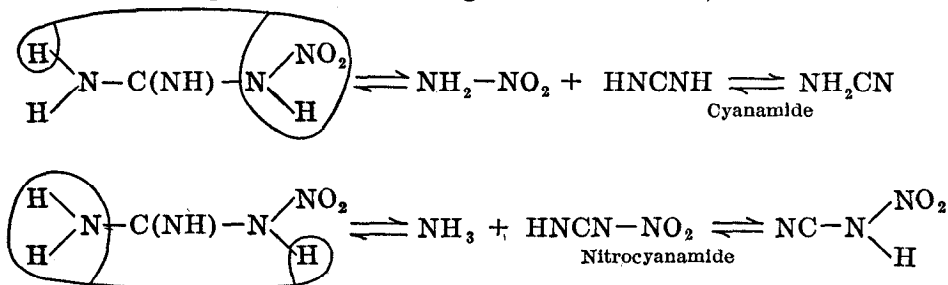
becomes colorless again when the reduction is complete. After all the zinc has disappeared, 1 mol of concentrated nitric acid is added, then 1 mol of benzaldehyde, and the mixture is shaken and scratched to facilitate the separation of the heavy granular precipitate of benzalaminoguanidine nitrate. The product, recrystallized from water or from alcohol, melts when pure at 160.5°.

Nitroguanidine and nitrosoguanidine both give a blue color with the diphenylamine reagent, and both give the tests described below, but the difference in the physical properties of the substances is such that there is no likelihood of confusing them.

Tests for Nitroguanidine. To 0.01 gram of nitroguanidine in 4 cc. of cold water 2 drops of saturated ferrous ammonium sulfate solution is added, then 1 cc. of 6 *N* sodium hydroxide solution. The mixture is allowed to stand for 2 minutes, and is filtered. The filtrate shows a fuchsine color but fades to colorless on standing for half an hour. Larger quantities of nitroguanidine give a stronger and more lasting color.

One-tenth gram of nitroguanidine is treated in a test tube with 5 cc. of water and 1 cc. of 50% acetic acid, and the mixture is warmed at 40–50° until everything is dissolved. One gram of zinc dust is added, and the mixture is set aside in a beaker of cold water for 15 minutes. After filtering, 1 cc. of 6% copper sulfate solution is added. The solution becomes intensely blue, and, on boiling, gives off gas, becomes turbid, and presently deposits a precipitate of metallic copper. If, instead of the copper sulfate solution, 1 cc. of a saturated solution of silver acetate¹² is added, and the solution is boiled, then a precipitate of metallic silver is formed.

Many of the reactions of nitroguanidine, particularly its decomposition by heat and the reactions which occur in aqueous and in sulfuric acid solutions, follow directly from its dearrangement.¹³ Nitroguanidine dearranges in two modes, as follows.



¹² Two grams of silver acetate, 2 cc. of glacial acetic acid, diluted to 100 cc., warmed, filtered, and allowed to cool.

¹³ Davis and Abrams, *Proc. Am. Acad. Arts and Sciences*, 61, 437 (1926).

A solution of nitroguanidine in concentrated sulfuric acid comports itself as if the nitroguanidine had dearranged into nitroamide and cyanamide. When it is warmed, nitrous oxide containing a small amount of nitrogen comes off first (from the dehydration of the nitroamide) and carbon dioxide (from the hydrolysis of the cyanamide) comes off later and more slowly. Long-continued heating at an elevated temperature produces ammonia and carbon dioxide quantitatively according to the equation,



The production of nitrous oxide is not exactly quantitative because of secondary reactions. A solution of nitroguanidine in concentrated sulfuric acid, after standing for some time, no longer gives a precipitate of nitroguanidine when it is diluted with water.

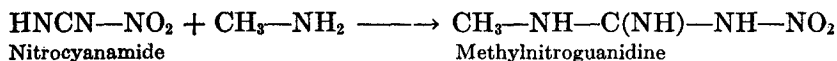
A freshly prepared solution of nitroguanidine in concentrated sulfuric acid contains no nitric acid, for none can be distilled out of it, but it is ready to produce nitric acid (by the hydration of the nitroamide) if some material is present which will react with it. Thus, it gives up its nitro group quantitatively in the nitrometer, and it is a reagent for the nitration of such substances as aniline, phenol, acet-*p*-toluide, and cinnamic acid which are conveniently nitrated in sulfuric acid solution.

In aqueous solution nitroguanidine dearranges in both of the above-indicated modes, but the tendency toward dearrangement is small unless an acceptor for the product of the dearrangement is present. It results that nitroguanidine is relatively stable in aqueous solution; after many boilings and recrystallizations the same solution finally becomes ammoniacal. Ammonia, being alkaline, tends to promote the decomposition of nitroamide in aqueous solution. Also, because of its mass action effect, it tends to inhibit dearrangement in the second mode which produces ammonia. If nitroguanidine is warmed with aqueous ammonia, the reaction is slow. But, if it is warmed with water and a large excess of ammonium carbonate, nitrous oxide comes off rapidly, the ammonia combines with the cyanamide from the dearrangement, and guanidine carbonate is formed in practically quantitative amount.

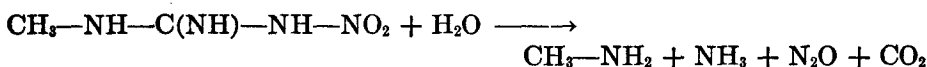
Preparation of Guanidine Carbonate from Nitroguanidine. Two hundred and eight grams of nitroguanidine, 300 grams of ammonium carbonate, and 1 liter of water are heated together in a 2-liter flask in the

water bath. The flask is equipped with a reflux condenser and with a thermometer dipping into the mixture. When the thermometer indicates 65–70°, nitrous oxide escapes rapidly, and it is necessary to shake the flask occasionally to prevent the undissolved nitroguanidine from being carried up into the neck. The temperature is raised as rapidly as may be done without the reaction becoming too violent. After all the material has gone into solution, the flask is removed from the water bath and the contents boiled under reflux for 2 hours by the application of a free flame. The liquid is then transferred to an evaporating dish and evaporated to dryness on the steam or water bath. During this process all the remaining ammonium carbonate ought to be driven off. The residue is taken up in the smallest possible amount of cold water, filtered for the removal of a small amount of melamine, and the filtrate is stirred up with twice its volume of 95% alcohol which causes the precipitation of guanidine carbonate (while the traces of urea which will have been formed remain in solution along with any ammonium carbonate which may have survived the earlier treatment). The guanidine carbonate is filtered off, rinsed with alcohol, and dried. The filtrate is evaporated to dryness, taken up in water, and precipitated with alcohol for a second crop—total yield about 162 grams or 90% of the theory. The product gives no color with the diphenylamine reagent; it is free from nitrate and of a quality which would be extremely difficult to procure by any process involving the double decomposition of guanidine nitrate.

In the absence of ammonia and in the presence of a primary aliphatic amine, nitroguanidine in aqueous solution dearranges in the second of the above-indicated modes, ammonia is liberated, and the nitrocyanamide combines with the amine to form an alkylnitroguanidine.



The structure of the N-alkyl,N'-nitroguanidine is demonstrated by the fact that it yields the amine and nitrous oxide on hydrolysis, indicating that the alkyl group and the nitro group are attached to different nitrogen atoms.



The same N-alkyl,N'-nitroguanidines are produced by the nitration of the alkyl guanidines.¹⁴

¹⁴ Davis and Elderfield, *J. Am. Chem. Soc.*, **55**, 731 (1933).

Nitroguanidine, warmed with an aqueous solution of hydrazine, yields N-amino,N'-nitroguanidine,¹⁵ white crystals from water, m. p. 182°. This substance explodes on an iron anvil if struck with a heavy sledge hammer allowed to drop through a distance of about 8 inches. It may perhaps have some interest as an explosive.

Flashless colloid powder containing nitroguanidine produces a considerable amount of gray smoke made up of solid materials from the decomposition of the substance. The gases smell of ammonia. The powder produces more smoke than the other flashless powders which are used in this country.

Nitroguanidine decomposes immediately upon melting and cannot be obtained in the form of a liquid, as can urea, dicyandiamide, and other substances which commence to decompose when heated a few degrees above their melting points. A small quantity heated in a test tube yields ammonia, water vapor, a white sublimate in the upper part of the tube, and a yellow residue of mellon which is but little affected if warmed to a bright red heat. The products which are formed are precisely those which would be predicted from the rearrangements,¹⁶ namely, water and nitrous oxide (from nitroamide), cyanamide, melamine (from the polymerization of cyanamide), ammonia, nitrous oxide again and cyanic acid (from nitrocyanamide), cyanuric acid (from the polymerization of cyanic acid), ammeline and ammelide (from the co-polymerization of cyanic acid and cyanamide) and, from the interaction and decomposition of these substances, carbon dioxide, urea, melam, melem, mellon, nitrogen, prussic acid, cyanogen, and paracyanogen. All these substances have been detected in, or isolated from, the products of the decomposition of nitroguanidine by heat.

There is no doubt whatever that nitroguanidine is a cool explosive, but there appears to be a disagreement as to the temperature which it produces. A package of nitroguanidine, exploded at night by means of a blasting cap, produces no visible flash. If 10 or 15% of the substance is incorporated in nitrocellulose powder, it makes the powder flashless. Vieille¹⁷ found that the gases from the explosion of nitroguanidine were much less erosive

¹⁵ Phillips and Williams, *J. Am. Chem. Soc.*, **50**, 2465 (1928).

¹⁶ Davis and Abrams, *Proc. Am. Acad. Arts and Sciences*, **61**, 443 (1926).

¹⁷ *Mém. poudres*, **11**, 195 (1901).

than those from other explosives of comparable force, and considered the fact to be in harmony with his general conclusion that the hotter explosives are the more erosive. In his experiments the explosions were made to take place in a steel bomb equipped with a crusher gauge and with a removable, perforated, steel plug through the perforation in which the hot gases from the explosion were allowed to escape. They swept away, or eroded off, a certain amount of the metal. The plug was weighed before and after the experiment, its density had been determined, and the number of cubic millimeters of metal lost was reported as a measure of the erosion. Some of Vieille's results are indicated in the following table.

EXPLOSIVE	CHARGE (Grams)	PRES- SURE		EROSION PER GRAM	FORCE	
		(Kg./sq. cm.)	EROSION			
Poudre BF	3.45	2403	20.3	5.88	6.4	9,600
	3.50	2361	22.7	6.58		
	3.55	2224	24.7	6.96		
	3.55	2253	25.5	7.19		
	3.55	2143	20.1	5.66		
Cordite	3.55	2500	64.2	18.1	10,000	
Ballistite VF	3.47	2509	84.5	24.3	24.3	10,000
	3.51	2370	83.2	23.7		
	3.55	2542	90.2	25.4		
	3.55	2360	85.9	24.2		
	3.55	2416	84.5	23.8		
Black military	10.00	2167	22.3	2.2	3,000	
Black sporting	8.88	1958	40.0	4.5	3,000	
Blasting gelatin	3.35	2458	105.0	31.4	10,000	
Nitromannite	3.54	2361	83.5	23.6	10,000	
Nitroguanidine	3.90	2019	8.8	2.3	9,000	

These experiments¹⁸ were carried out in a bomb of 17.8 cc. capacity, which corresponds, for the example cited, to a density of loading of 0.219 for the nitroguanidine which was pulverulent

¹⁸ The cordite used in these experiments was made from 57% nitroglycerin, 5% vaseline, and 38% high nitration guncotton colloided with acetone; the ballistite VF of equal amounts by weight of nitroglycerin and high nitration guncotton colloided with ethyl acetate. The black military powder was made from saltpeter 75, sulfur 10, and charcoal 15; the black sporting powder from saltpeter 78, sulfur 10, and charcoal 12. The blasting gelatin contained 94% nitroglycerin and 6% soluble nitrocotton.

material "firmly agglomerated in a manner to facilitate the naturally slow combustion of that substance."

An experiment with 18.11 grams nitroguanidine in a bomb of 75.0 cc. capacity (density of loading 0.241) showed an erosion of 2.29 per gram of explosive.

The temperature (907°) which Vieille accepted as the temperature produced by the explosion of nitroguanidine had been determined earlier by Patart¹⁹ who published in 1904 an account of manometric bomb experiments with guanidine nitrate and with nitroguanidine. The explosives were agglomerated under a pressure of 3600 kilograms per square centimeter, broken up into grains 2 or 3 mm. in diameter, and fired in a bomb of 22 cc. capacity. Some of Patart's experimental results are tabulated below. Calculated from these data, Patart reported for guanidine

DENSITY OF LOADING	PRESSURE, KILOGRAMS PER SQUARE CENTIMETER	
	Guanidine Nitrate	Nitroguanidine
0.15.....	1128	1304
	1038	1584
	...	1416
0.20.....	1556	2060
	1416	2122

0.25.....	2168	3092
	2028	3068

0.30.....	3068	4118
	2814	4038

0.35.....	3668	...
	3730	...

nitrate, covolume 1.28, force 5834, and temperature of explosion 929°; for nitroguanidine, covolume 1.60, force 7140, and temperature of explosion 907°. He appears to have felt that these calculated temperatures of explosion were low, for he terminated his article by calling attention to the extraordinary values of the covolume deduced from the pressures in the closed vessel, and subpended a footnote:

It may be questioned whether the rapid increase of the pressure with the density of loading, rather than being the consequence of a constant reaction giving place to a considerable covolume, is not due simply to the mode of de-

¹⁹ *Mém. poudres*, 13, 153 (1905-1906).

composition being variable with the density of loading and involving a more and more complete decomposition of the explosive. Only an analysis of the gases produced by the reaction can determine this point, as it also can determine the actual temperature of the deflagration.

The later studies of Muraour and Aunis²⁰ have shown that the temperature of explosion of nitroguanidine may be much higher than Patart calculated, and have given probability to his hypothesis that the density of loading has an effect upon the mode of the explosive decomposition. These investigators found that a platinum wire 0.20 mm. in diameter, introduced into the bomb along with the nitroguanidine, was melted by the heat of the explosion—a result which indicates a temperature of at least 1773°C. They pointed out that nitroguanidine, if compressed too strongly, may take fire with difficulty and may undergo an incomplete decomposition, and hence at low densities of loading may produce unduly low pressures corresponding to a covolume which is too large and to a temperature of explosion which is too low. The pressure of 3600 kilograms per square centimeter, under which Patart compressed his nitroguanidine, is much too high. Nitroguanidine compressed under 650 kilograms per square centimeter, and fired in a manometric bomb of 22 cc. capacity, at a density of loading of 0.2, and with a primer of 1 gram of black powder, gave a pressure of 1737 kilograms per square centimeter; compressed under 100 kilograms per square centimeter and fired in the same way nitroguanidine gave a pressure of 1975 kilograms per square centimeter, or a difference of 238 kilograms. In an experiment with a bomb of 139 cc. capacity, density of loading 0.2, Muraour and Aunis observed a pressure which, correction being made for various heat losses, corresponded to a temperature of 1990°.

Assuming that nitroguanidine explodes to produce carbon dioxide, water, carbon monoxide, hydrogen, and nitrogen,²¹ assuming that the equilibrium constant for the reaction, $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$, is 6, and that the molecular heat of formation at con-

²⁰ *Annales des Mines*, **9**, 178, 180 (1920); *Comp. rend.*, **190**, 1389, 1547 (1930); *Mém. poudres*, **25**, 91 (1932–1933).

²¹ This assumption however is not true, for powder which contains nitroguanidine produces a gray smoke consisting of solid decomposition products and yields gases which smell of ammonia.

stant volume of nitroguanidine is 17.9 Calories, and taking the values of Nernst and Wohl for the specific heats of the various gases, Muraour and Aunis calculated the following values for the explosion of nitroguanidine, temperature 2098°, covolume 1.077, force 9660, and pressure (at density of loading 0.20) 2463 kilograms per square centimeter. They have also calculated the temperature of explosion of ammonium nitrate 1125°;²² of "explosive NO" (ammonium nitrate 78.7, trinitrotoluene 21.3) 2970°, and of explosive N4 (ammonium nitrate 90, potassium nitrate 5, trinitronaphthalene 5) 1725°, and have found by experiment that the last named of these explosives, fired at a density of loading of 0.30, did not fuse a platinum wire (0.06-mm. diameter) which had been introduced along with it into the bomb.

Nitroguanidine detonates completely under the influence of a detonator containing 1.5 gram of fulminate. According to Patart²³ 40 grams exploded on a lead block 67 mm. in diameter produced a shortening of 7 mm. Picric acid under the same conditions produced a shortening of 10.5 mm., and Favier explosive (12% dinitronaphthalene, 88% ammonium nitrate) one of 8 mm. Muraour and Aunis²⁴ experimented with nitroguanidine compressed under 100 kilograms per square centimeter and with trinitrotoluene compressed under 1000 kilograms per square centimeter, in a manometric bomb of 22-cc. capacity and at densities of loading of 0.13, 0.20, 0.25, and 0.30, and reported that the two explosives gave the same pressures.

During the first World War the Germans used in trench mortar bombs an explosive consisting of nitroguanidine 50%, ammonium nitrate, 30%, and paraffin 20%.

Nitrosoguanidine

Nitrosoguanidine is a cool and flashless primary explosive, very much more gentle in its behavior than mercury fulminate and lead azide. It is a pale yellow crystalline powder which explodes on contact with concentrated sulfuric acid or on being heated in a melting point tube at 165°. It explodes from the blow of a car-

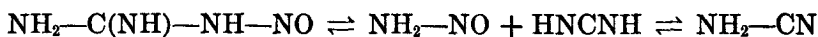
²² The temperature of 1121° was calculated by Hall, Snelling, and Howell, "Investigations of Explosives Used in Coal Mines," *U. S. Bur. Mines Bull.* 15, Washington, 1912, p. 32.

²³ *Mém. poudres*, 13, 159 (1905-1906).

²⁴ *Ibid.*, 25, 92-93, footnote (1932-1933).

penter's hammer on a concrete block. Its sensitivity to shock, to friction, and to temperature, and the fact that it decomposes slowly in contact with water at ordinary temperatures, militate against its use as a practical explosive. It may be kept indefinitely in a stoppered bottle if it is dry.

The reactions of nitrosoguanidine in aqueous solution are similar to those of nitroguanidine except that nitrogen and nitrous acid respectively are formed under conditions which correspond to the formation of nitrous oxide and nitric acid from nitroguanidine. It dearranges principally as follows.



If it is warmed in aqueous solution, the nitrosoamide breaks down into water and nitrogen, and the cyanamide polymerizes to dicyandiamide. The evaporation of the solution yields crystals of the latter substance. A cold aqueous solution of nitrosoguanidine acidified with hydrochloric acid yields nitrous acid, and may be used for the introduction of a nitroso group into dimethylaniline or some similar substance which is soluble in the acidified aqueous liquid.

*Preparation of Nitrosoguanidine.*²⁵ Twenty-one grams of nitroguanidine, 11 grams of ammonium chloride, 18 grams of zinc dust, and 250 cc. of water in an 800-cc. beaker are stirred together mechanically while external cooling is applied to prevent the temperature from rising above 20–25°. After 2 hours or so the gray color of the zinc disappears, the mixture is yellow, and on settling shows no crystals of nitroguanidine. The mixture is then cooled to 0° or below by surrounding the beaker with a mixture of cracked ice and salt; it is filtered, and the filtrate is discarded. The yellow residue, consisting of nitrosoguanidine mixed with zinc oxide or hydroxide and basic zinc chloride, is extracted with 4 successive portions of 250 cc. each of water at 65°. The combined extracts, allowed to stand over night at 0°, deposit nitrosoguanidine which is collected, rinsed with water, and dried at 40°. Yield 8.0–9.2 grams, 45–52% of the theory.

The flashlessness of nitrosoguanidine may be demonstrated safely by igniting about 0.5 gram of it on the back of the hand. The experiment is most striking if carried out in a darkened room. The sample being poured out in a conical heap on the back of the left hand, a match held in the right hand is scratched and allowed to burn until the mate-

²⁵ Davis and Rosenquist, *J. Am. Chem. Soc.*, **59**, 2114 (1937).

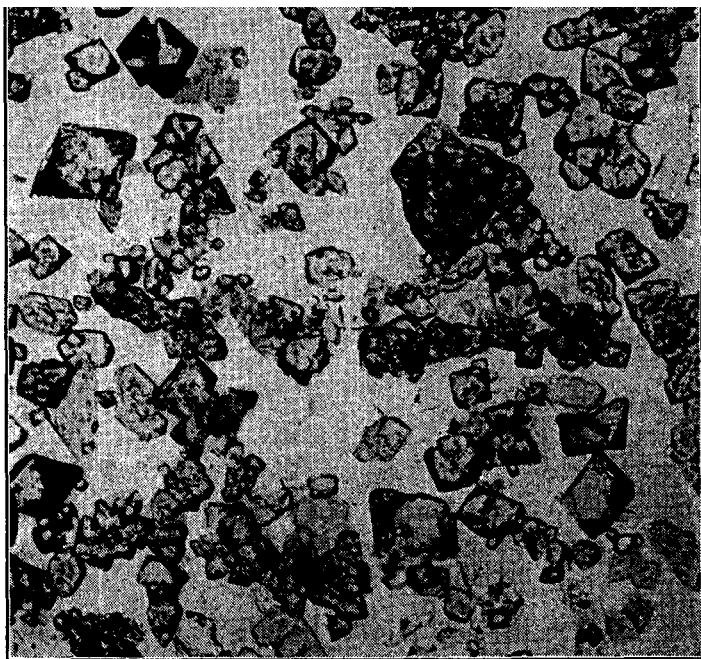


FIGURE 90. Ethylenedinitramine Crystals (60 \times).

may be prepared directly, without isolating this intermediate, by the nitration of ethyleneurea with mixed acid.

²⁶ Franchimont and Klobbie, *Rec. trav. chim.*, 7, 17, 244 (1887).

