

Synthesis of Polynitrocompounds from Nitroguanidine*

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Synthese von Polynitroverbindungen bei Nitroguanidin als Ausgangssubstanz

Die Reaktionen von Nitroguanidin (NG) mit Urotropin oder Formaldehyd wurden untersucht. Folgende Verbindungen wurden synthetisiert mit NG als Ausgangssubstanz:

- 6-Nitroimino-1,3,5-trinitro-1,3,5-triazacyclohexan [2] und eine Anzahl seiner Derivate
- Bis(nitroguanidino)methan [9], ein wertvolles Zwischenprodukt zur Herstellung von Hochleistungssprengstoffen
- 1,5-Dinitro-2,4-dinitroimino-1,3,5-triazacyclohexan [10] und einige seiner Derivate über intramolekulare Cyclisierung von [9]
- 2-Nitroimino-1,3-diaza-5-oxacyclohexan [15], 1-(Nitroguanidinomethyl)-2-nitroimino-1,3-diaza-5-oxacyclohexan [14] und Bis(2-nitroimino-1,3-diaza-5-oxacyclohexyl)methan [16] durch Reaktion von [9] mit Formaldehyd.

Einige Detonationswerte dieser Verbindungen werden angegeben. Die Verbindungen [2] und [10] sind starke Sprengstoffe, aber thermisch sehr instabil und leicht hydrolysierbar. Dagegen besitzen die Verbindungen [14], [15] und [16] eine bessere Stabilität als triazacyclische Polynitroverbindungen mit Nitroiminogruppen, wie z. B. [2] oder [10].

Synthèse de composés polynitrés à partir de la nitroguanidine

On a étudié les réactions de la nitroguanidine (NG) avec l'urotropine et le formaldéhyde. On a ainsi réalisé la synthèse des substances suivantes à partir de la nitroguanidine:

- le 6-nitroimino-1,3,5-trinitro-1,3,5-triazacyclohexane [2] et une série de ses dérivés;
- le bis(nitroguanidino)méthane [9], un produit intermédiaire intéressant pour la préparation d'explosifs;
- le 1,5-dinitro-2,4-dinitroimino-1,3,5-triazacyclohexane [10] et quelques-uns de ses dérivées obtenus par cyclisation intramoléculaire de [9];
- le 2-nitroimino-1,3-diaza-5-oxacyclohexane [15], le 1-(nitroguanidinométhyl)-2-nitroimino-1,3-diaza-5-oxacyclohexane [14], et le bis(2-nitroimino-1,3-diaza-5-oxacyclohexyl)méthane [16] par réaction de [9] avec le formaldéhyde.

On indique quelques-unes des caractéristiques détonatives de ces composés. Les composés [2] et [10] sont des explosifs puissants mais thermiquement très instables et facilement hydrolysables. Les composés [14], [15] et [16] par contre sont plus stables que les composés polynitrés triazacycliques, comportant des groupes nitroimino, tels que par exemple les composés [2] ou [10].

Summary

The reactions of nitroguanidine (NG) with urotropine or formaldehyde have been studied. The following compounds are synthesized from NG:

- 6-nitroimino-1,3,5-trinitro-1,3,5-triazacyclohexane [2] and a number of its derivatives;
- bis(nitroguanidino)methane [9], a valuable intermediate for preparing some high explosives;
- 1,5-dinitro-2,4-dinitroimino-1,3,5-triazacyclohexane [10] and some of its derivatives via intramolecular cyclization of [9];
- 2-nitroimino-1,3-diaza-5-oxacyclohexane [15], 1-(nitroguanidinomethyl)-2-nitroimino-1,3-diaza-5-oxacyclohexane [14], and bis(2-nitroimino-1,3-diaza-5-oxacyclohexyl)methane [16] by reactions of [9] with formaldehyde.

Some detonation data of the above compounds are reported. Compounds [2] and [10] are powerful explosives but very unstable thermally and easily hydrolyzed. However, compounds [14], [15], and [16] possess a better stability than triazacyclic polynitrocompounds containing nitroimino groups, such as [2] and [10].

1. Introduction

NG is a well-known nitrocompound. It has been used not only in tribase propellants for many years but also as a potential insensitive explosive recently. The physical properties and detonation data of NG have been studied

extensively but its chemical reactivity on using it to synthesize high explosives has rarely been explored. The only published work concerned with this area is by McKay and Wright⁽¹⁾, who studied the reactions of NG with alkylamines in basic mediums and obtained some derivatives of NG^(2,3). The hydrazinolysis of NG was investigated by Henry⁽⁴⁾ and the research work on chemical reactions of NG was reviewed by McKay⁽⁵⁾ in 1952. Afterwards, some reports involving the use of NG as a component to prepare heterocyclic nitrogen compounds appeared, but none of these compounds are explosives.

Since there are two amino groups, one nitroimino group and one carbon atom in a molecule of NG, which may be used as an ideal "element" to form a desired explosive molecule. It does seem, however, a little surprising that the reactions of NG with urotropine or formaldehyde have been ignored for many years. Inspired by the fact as stated above we made an attempt to examine some reactions concerned with NG, which are described below.

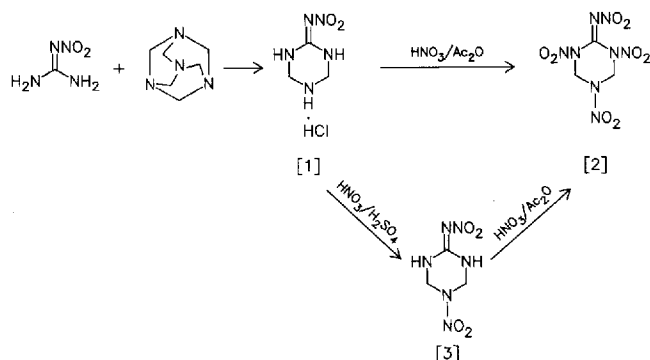
2. Results and Discussion

2.1 Reactions of NG with urotropine

The cyclization reaction of NG with fragments produced from urotropine gives compound [1], which can be subsequently nitrated in nitric acid/acetic anhydride to give compound [2], an explosive with zero oxygen balance.

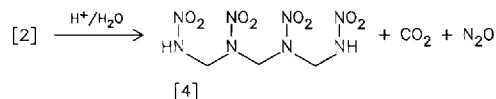
* This paper was read at the International Symposium of Pyrotechnics and Explosives, Beijing, China, 1987.

However, using nitric acid/sulfuric acid to nitrate [1] results in compound [3] instead of [2]. But [3] is converted to [2] when treated with nitric acid/acetic anhydride again.

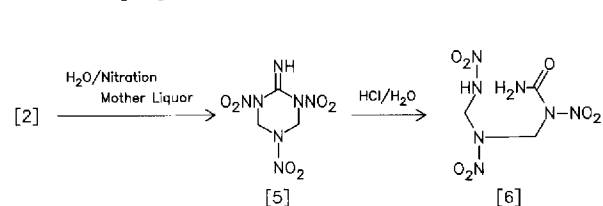


[2] may be regarded as a compound formed via replacement of two hydrogen atoms of CH_2 group in cyclotriethylene-trinitramine (RDX) by >=NNO_2 group. This makes [2] more powerful than RDX due to its favorable oxygen balance. Unfortunately [2] decomposes at low temperature (50°C).

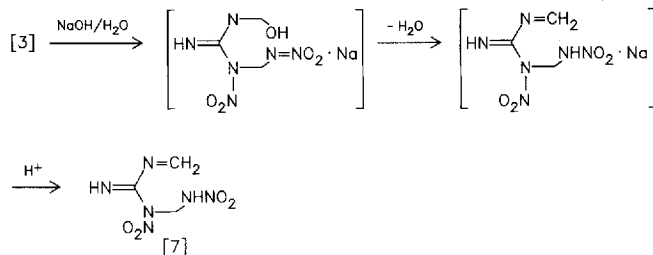
In acidic or basic medium [1] shows a relatively good hydrolytic stability, which is, however, lowered by introduction of nitro group into the ring. Since there is only one nitro group connected directly to the ring in [3], [3] does not hydrolyze under acidic conditions but does when treated with relatively strong bases. [2] consists of a nitroimino group >=NNO_2 and has the largest number of nitro groups among the above three compounds. This makes the carbon atoms of [2] behave like carbonium ions to some extent due to the effects of electron-withdrawing groups. In fact when treated with nucleophiles, such as OH^- , [2] is hydrolyzed easily and the ring is cleaved, yielding compound [4].



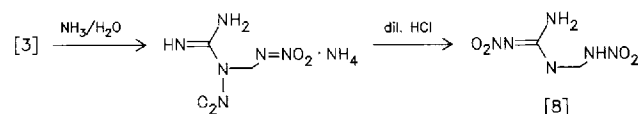
Methods for preparation of [4] were known in literature, while we prepared it by hydrolyzation of [2]. Recrystallization of the crude product from ethanol gave a purified sample as polyhedral crystals. The procedure used by us enables [2] to have a much better thermal stability than other known ones. Hydrolyzation of [2] also occurs in concentrated nitric acid because of the attack of proton on the nitrogen atom of >=NNO_2 group. For example, when water is dropped into the nitration mother liquor resulted from the preparation of [2], [2] is converted to [5].



[5] is analogous to [2] in properties and can be hydrolyzed to yield [6] when heated to 50°C – 60°C in hydrochloric acid. The hydrolyzation of [3] in high basic medium might take place via the following reaction route:

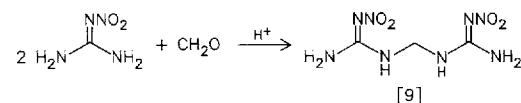


[7] is practically insoluble in water and common organic solvents but very soluble in bases. Treating [7] with aqueous ammonia gave an ammonium salt which is hardly soluble in water. This provides a way for purification of [7]. The hydrolyzation of [3] in aqueous ammonia occurs in a way similar to that in NaOH solution excepting that intramolecular dehydration does not occur in the former case. The reaction of [3] with ammonia proceeds through an intermediate bearing hydroxymethylene group, which can react with NH_3 to give an ammonium salt of [8] with taking off >CH_2 group. Neutralization of this salt with dilute hydrochloric acid results in [8].



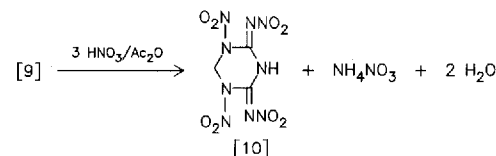
2.2 Reactions of NG with formaldehyde

We made a systematic investigation of the conditions of this reaction, which occurs readily in dilute hydrochloric acid and bis(nitroguanidine) methane [9] is formed in rather high yield.

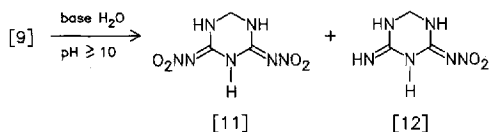


Although it is well known that NG reacts with formaldehyde, [9] has never been synthesized. We have considered it as an important intermediate for synthesizing heterocyclic nitrocompounds because there are >=NNO_2 , primary and secondary -NH_2 groups in its molecule.

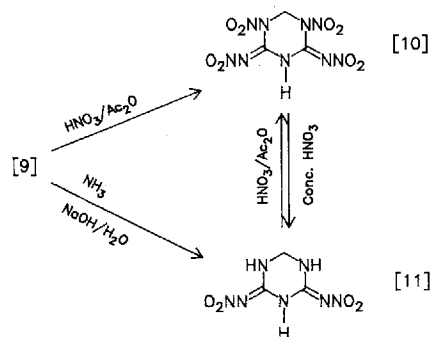
It is of interest to note that when [9] is treated with nitric acid/acetic anhydride, [10] is obtained. Namely, in this case, deamination cyclization and nitration of cyclized product proceed simultaneously.



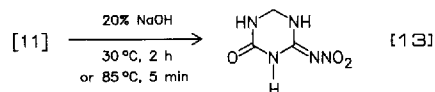
[10] is an explosive with slightly positive oxygen balance but very unstable. The deamination cyclization of [9] also takes place with evolution of ammonia gas in basic media at $\text{pH} > 10$. The cyclized product is [11] when the reaction goes at $< 8^\circ\text{C}$, [12] at $> 30^\circ\text{C}$, and a mixture of [11] and [12] at 8°C – 30°C .



[11] and [12] can be well separated from each other at different pH levels. Nitrating [11] with $\text{HNO}_3/\text{Ac}_2\text{O}$ gives [10], of which the active $-\text{NO}_2$ groups can be taken off in concentrated nitric acid and [11] is formed again. The reactions stated above are shown in the following scheme, which provides convincing evidence to demonstrate the structure of [10].



In high basic medium and at relatively elevated temperature [11] is subjected to further reaction and we found that in this type of reaction, it is [13] which is formed, not [12].

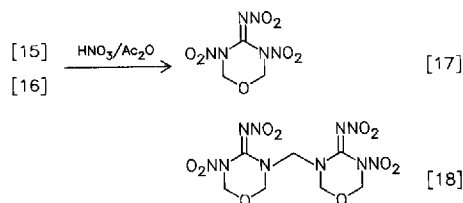


[13] is also a new intermediate used for synthesis of some useful compounds. Although [9] is the product of condensation of NG with formaldehyde, it is interesting to see if the primary and secondary amino groups in [9] are still reactive towards CH_2O . Results from our experiments give a positive answer to this question. Condensation between [9] and excess CH_2O in concentrated hydrochloric acid leads to the formation of a new class of polynitrocompounds: [14], [15], and [16], which have not been known in literature. Listed in Table 1 are the reaction conditions and structures of the above three compounds.

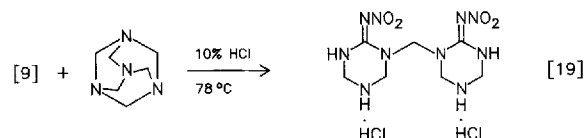
Table 1. Reaction Conditions

[9]: CH_2O mole ratio	Reaction temp. [$^\circ\text{C}$]	Product	
1:2.5	50–60		[14]
1:5	45		[15]
1:7	40		[16]

In the reaction of [9] with CH_2O either mono- or dicyclic compound is obtained depending on the amount of CH_2O used and either [15] or [16] is yielded according to whether the main chain of [9] is cleaved or not. Nitration of [15] and [16] with $\text{HNO}_3/\text{Ac}_2\text{O}$ gives [17] and [18] respectively.



By the action of [9] on urotropine in 10% hydrochloric acid and at 78°C compound [19] is synthesized, which can be subsequently nitrated to give its corresponding polynitroderivatives.



As has been stated before, we have prepared a series of new polynitro compounds which are either valuable intermediates or high explosives with zero or near zero oxygen balance and high density. Unfortunately most of them are unstable to heat and easy to hydrolyze mainly due to the existence of vicinal >=NNO_2 and >NNO_2 groups, which make up the weakest site in the molecules. But their stabilities can be improved considerably by introducing $-\text{O}-$ linkage to their rings.

Some performance parameters of compounds [1], [10], and [7] are summarized in Table 2.

Table 2. Performance Parameters

Compound	ρ [$\text{g} \cdot \text{cm}^{-3}$]	m.p. [$^\circ\text{C}$]	D [$\text{m} \cdot \text{s}^{-1}$]
[1]	1.95	102 (explode)	9000 ($\rho = 1.80$)
[7]	1.93	103–4 (dec.)	9020 ($\rho = 1.83$)
[10]	1.96	114 (dec.)	9250 ($\rho = 1.88$)

3. References

- (1) A. F. McKay and G. W. Wright, *J. Am. Chem. Soc.* 70, 430 (1948).
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(Received August 30, 1988; Ms 39/88)