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ORGANIC AZIDO COMPOUNDS AS ENERGETIC MATERIALS

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Azido compounds suitable for propellants are described with respect to their particular application as energetic materials. General synthetic methods are briefly described. Physical properties, sensitivity and thermal stability characteristics of the compounds are summarized.

Contents

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1 Introduction

Organic azido compounds are important substances in the chemistry of energetic materials. The main area for their use is in various types of propellants, both energetic fillers and plasticizers. The aim of these compounds is to enhance the performance and the mechanical properties of propellants in comparison with the currently used materials.

Introduction of azido group into the molecule significantly enhances the enthalpy of formation of the material. The explosive reaction of organic azido compounds produces large amounts of nitrogen and hydrogen, which decrease the average molecular weight of combustion products and increase the combustion rate. Moreover, nitrogen is inert and non-toxic.

The azido group itself does not need oxygen for explosive reaction. Oxygen in the molecule is necessary for the reaction with hydrogen and carbon from the rest of the molecule producing carbon dioxide or carbon monoxide and water. A combination of both the azidogroup and the nitrogroup in one molecule is very effective, with the resulting compounds usually possessing high enthalpy of formation, high nitrogen content and a proper oxygen balance.

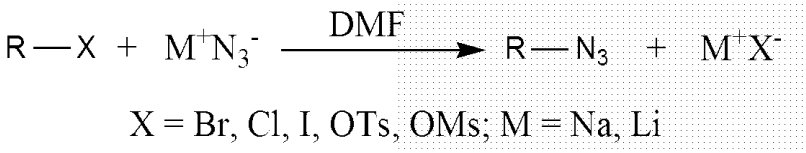
On the other hand, it needs saying that some energetic azido compounds may possess inconvenient properties, such as low thermal stability and/or high sensitivity. The potential presence of these characteristics must be taken into account in the handling, storage and use of such compounds.

2 General Synthetic Methods

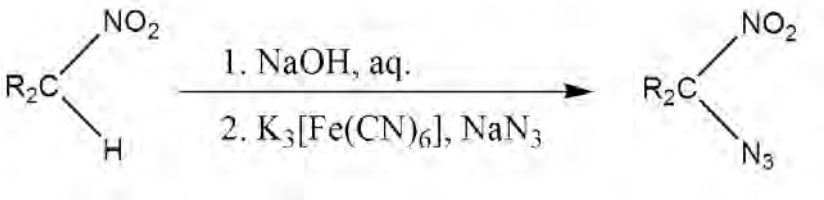
Most syntheses of azidocompounds use nucleophilic substitution of a halogen or nitroxy group by an azido group. Tosyl and methanesulfonyl are also often chosen. Sodium azide is the most widely selected nucleophile [1]. Sometimes, lithium azide is used [2] (Scheme 1).

Polar aprotic solvents (dimethyl sulfoxide, dimethylformamide) are most often employed. The yields are generally between 37 % and 95 %. To avoid rather laborious isolation from dimethyl sulfoxide or dimethylformamide, phase transfer catalysis may be used [3-8]. The use of microwave or ultrasound has also been

reported [9,10]. Anodic oxidation [11,12] or oxidative azidation [13] are suitable for geminal azido-nitrocompounds (Scheme 2).



Scheme 1



Scheme 2

3 Comparison of Known Materials

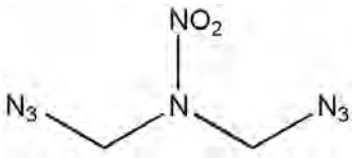
In this chapter, a literature survey of azido compounds with respect to their particular application as energetic materials is presented. Impact and friction sensitivity, thermal stability and comparison with commonly used explosives are summarized in Tables I-IV in Chapter 4.

3.1 Azidonitramines Derived from Hexamethylenetetramine

The first group of compounds represents those that can be synthesized from hexamethylenetetramine, which is the usual precursor for cyclic nitramines like 1,3,5-trinitro-1,3,5-triazinane (RDX) and 1,3,5,8-tetranitro-1,3,5,8-tetrazocane (HMX). It is possible to prepare various linear acetoxy-terminated nitramines simply by changing the sequence of addition of reactants and the reaction conditions. These acetoxy-derivatives can be re-esterified using nitric acid into nitroxy-derivatives which can then be azidated [14].

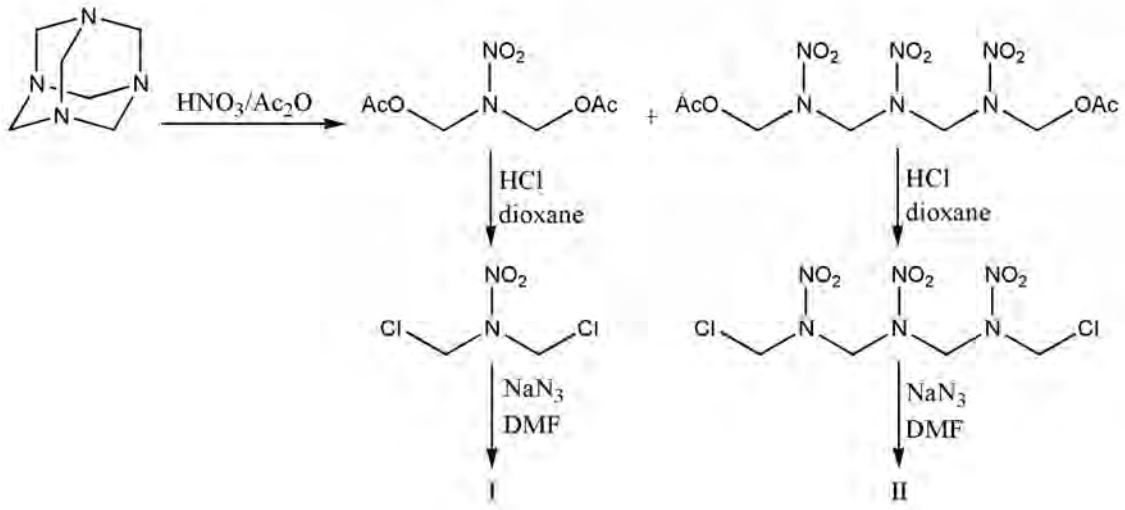
1,3-Diazido-2-nitro-2-azapropane (**I**)

1,3-Diazido-2-nitro-2-azapropane (Fig. 1) possesses the highest nitrogen content and enthalpy of all known azidonitramines. It has enough oxygen to react with carbon to form carbon monoxide with the products of its decomposition being ideally CO, N_2 and H_2.



Double base smokeless powder based on nitroglycerine has been compared with the same composition with **I** by Flanagan and Frankel [15]. The azidonitramine based powder shows a higher impulse while having a flame temperature at the same level as nitroglycerine powder. Simmons [16] compares compositions containing **I** with other usual and potential propellant components. Most of these mixtures have a force of up to 1450 J g^{-1}, but flame temperatures reach over 4000 K. Klapötke *et al.* [17] consider (**I**) quite sensitive, having an impact sensitivity of < 1 J and a friction sensitivity of 20 N.

Compound **I** was synthesized by Flanagan and Frankel [15] using a multistep procedure starting from hexamethylenetetramine (Scheme 3). The yield of the last azidation step was 85.7 %. The synthesis has been recently repeated and new data have been introduced [17].

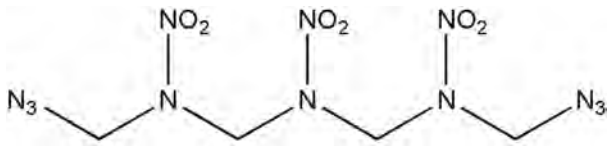


Scheme 3

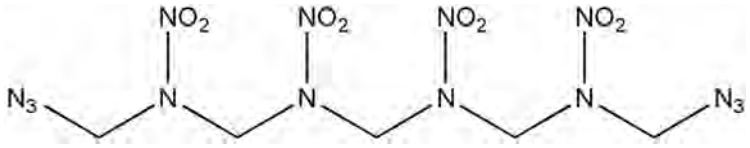
1,7-Diazido-2,4,6-trinitro-2,4,6-triazaheptane (**II**)

Compound **II** (Fig. 2) is prepared in the same way as **I** according to Klapötke *et al.* [17] (Scheme 3). The azidation of its dinitroxy-derivative may be used as well. In both cases, hexamethylenetetramine is a precursor in the synthesis.

Compound **II** is a potential energetic filler providing, as it does, a high enthalpy of formation of 1916 kJ kg^{-1}. Binary mixtures containing **II** were examined by Simmons [18,19]. The impact sensitivity is <1 J and friction sensitivity 20 N [17].



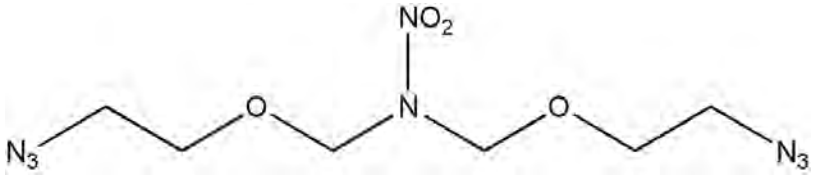
1,9-Diazido-2,4,6,8-tetranitro-2,4,6,8-tetraazanonane (**III**)



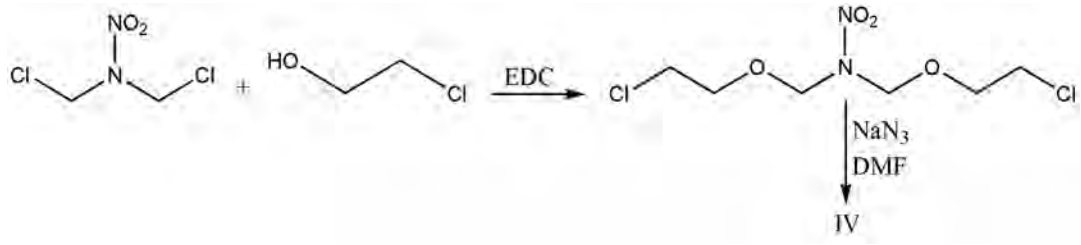
The enthalpy of formation of **III** is the lowest from all linear azidonitramines (1404 kJ kg^{-1}) and impact sensitivity is lower as well, reaching 19 cm / 2.5 kg. Uncontrolled crystallization of **III** was found by Zigmund [20]; it was accompanied by a sensitivity increase from 45 to 10 cm / 2 kg.

Henry and Norris [21] described the preparation of **III** starting from the 1,9-dinitroxy-derivative and the 1,9-dichloro-derivative of **III** with yields of 84 % and 77 %, respectively. The dinitroxy-derivative can be obtained from hexamethylenetetramine in a slightly modified method from that used for precursors of **I** and **II** [14].

1,9-Diazido-5-nitro-3,7-dioxa-5-azanonane (**IV**)



The low melting point (< –78 °C) and low impact sensitivity of **IV** make this compound a potential energetic plasticizer. Witucki and Flanagan [22] suggest **IV** as a flame reducing plasticizer for solid rocket propellants based on HMX with polyester binder. The synthesis of **IV** has been described by Witucki *et al.* [23]. 1,3-Dichloro-2-nitro-2-azapropane is condensed with 2-chloroethanol in 1,2-dichloroethane (EDC) and the product is azidated (Scheme 4). Overall yield of the synthesis is 47.5 %.

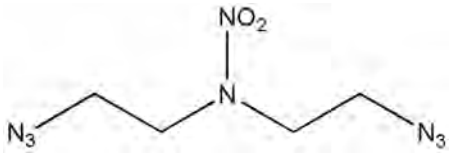


Scheme 4

3.2 Azidonitramines Derived from Aminoalcohols

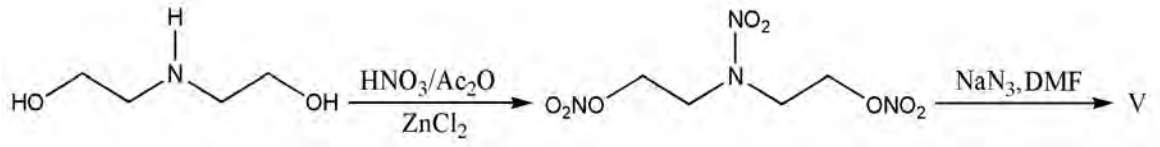
This group of materials is derived from nitroxyethylnitramines (NENA). Synthesis of NENAs start from aminoalcohols, which are alkylated and then nitrated and esterified with nitric acid. This synthetic route is presently used even on a large scale to prepare 1-nitroxy-3-nitro-3-azaheptane (BuNENA), which is used as a propellant plasticizer. Azido substituted NENAs possess higher enthalpy of formation.

1,5-Diazido-3-nitro-3-azapentane (**V**)



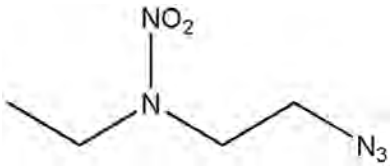
Synthesis of **V** is facilitated by the availability of its precursor. Simmons and Young [24] described preparation starting from diethanolamine where the first step is its nitration and esterification to the well known 1,5-dinitroxy-3-nitrazapentane (DINA) with a 76 % yield. Using better catalysts, Blomquist and Fiedorek [25] obtained a yield in this step as high as 94 %. The second step is the azidation using sodium azide in dimethyl sulfoxide. The azidation step produces a yield of 86 %, so the overall yield can reach 81 % (Scheme 5).

Simmons *et al.* [16,19,24] discussed the influence of **V** on the properties of smokeless propellants. Most of compositions give higher burning rates and lower flame temperatures compared to those with common plasticizing additives. Zigmund [20] states high impact sensitivity (10 cm / 2 kg), lower thermal stability (exotherm starts at 147 °C), and also lower density (1.196 g cm^{-1}) in contrast with Simmons. A way of improving safety while handling **V** was suggested by Frankel and Witucki [26]. The product of the synthesis is solvent transferred from the dimethyl sulfoxide based reaction mixture into ethyl acetate. The resulting solution can be used directly in propellant manufacture.



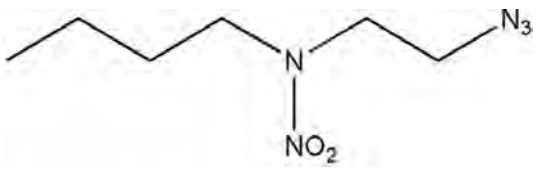
Scheme 5

1-Azido-3-nitro-3-azapentane (**VI**)



This is mentioned by Simmons [16] as a low energetic liquid potentially useful as an ingredient of eutectic mixtures with other azido compounds. Preparation of **VI** can be carried out from 1-nitroxy-3-nitro-3-azapentane [25].

1-Azido-3-nitro-3-azaheptane (**VII**)

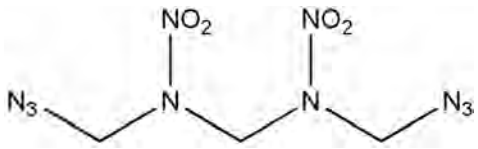


Azidation of 1-nitroxy-3-nitro-3-azaheptane (BuNENA) with a yield of 83 % has been described by Witucki *et al.* [23].

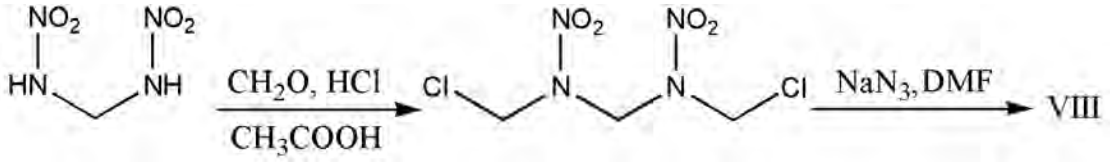
3.3 Other azidonitramines

Large numbers of azidonitramine precursors can be prepared from chloromethylnitramines prepared by the reaction of primary nitramines with formaldehyde and subsequent chlorination of the methylolnitramines formed. The most suitable starting primary nitramine is 1,4-dinitro-1,4-diazabutane (ethylenedinitramine, EDNA), which was used for several years as a military explosive; therefore, its synthesis has become routine. Another starting primary nitramine, 1,3-dinitro-1,3-diazapropane (methylenedinitramine) has been examined by Mikšovský *et al.* [27].

1,5-Diazido-2,4-dinitro-2,4-diazapentane (**VIII**)

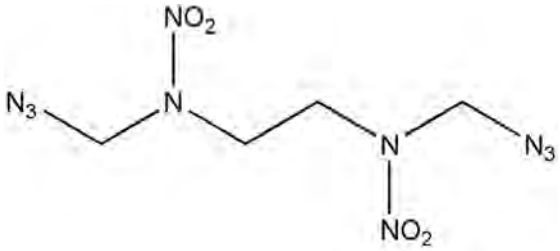


Compound **VIII** can be prepared by chloromethylation of 1,3-dinitro-1,3-diazapropane (methylenedinitramine) and subsequent azidation according to Rosher (Scheme 6). [28]. The yield of the azidation step is 60 %.
The product has a melting point of 80 °C, density of 1.70 g cm^{-3} and enthalpy of formation of 3055 kJ kg^{-1} [16].



Scheme 6

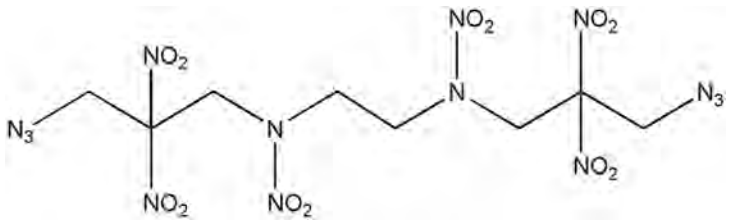
1,6-Diazido-2,5-dinitro-2,5-diazahexane (**IX**)



In a similar way to **VIII**, Rosher [28] prepared **IX** starting with chloromethylation of the well known 1,4-dinitro-1,4-diazabutane (ethylenedinitramine, EDNA). The overall yield reaches 63.8 %.

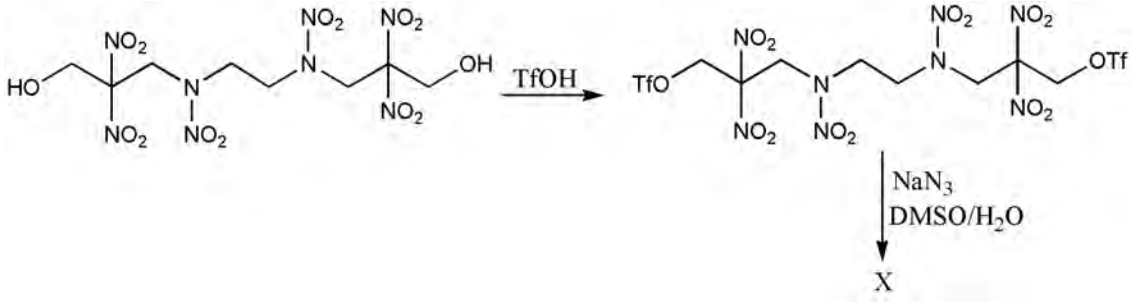
Simmons [16] states the density of 9 to be 1.61 g cm^{-3} with an enthalpy of formation of 2772 kJ kg^{-1}. Simmons and Walsh [19] also described dependencies of constant force on the burning temperature for RDX-based binary mixtures with various azidonitramines. Similarly, Flanagan and Gray [29] describe burning temperature and force variation caused by addition of **II**, **III** and **IX** into propellant composition containing nitrocellulose, nitroisobutylglycerol trinitrate (NIBTN) and **V**.

1,10-Diazido-2,2,4,7,9,9-hexanitro-4,7-diazadecane (**X**)



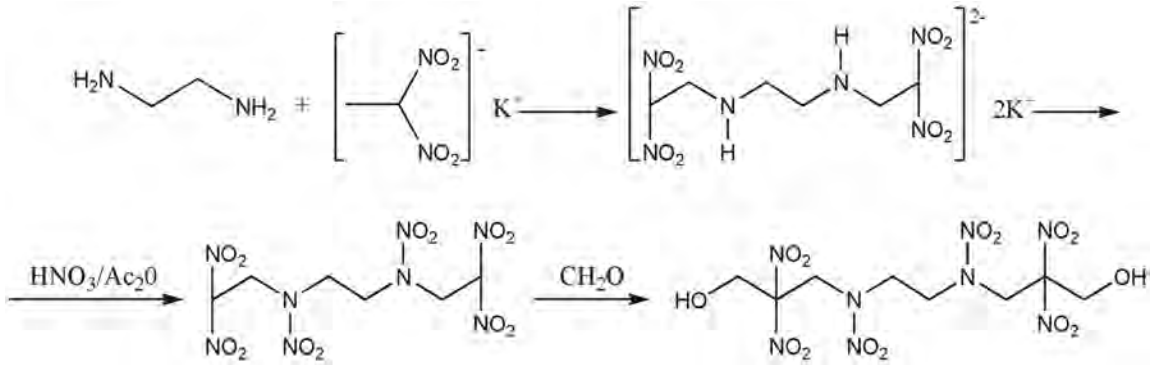
Compound **X** has been described by Yan *et al.* [30] as a high density azidonitramine (1.722 g cm^{-3}) with highly positive enthalpy of formation (974 kJ kg^{-1}). The presence of the geminal dinitro groups is said to be preferable to 1,1,1-trinitroalkyl group from the standpoint of impact sensitivity.

Preparation of **X** starts from its hydroxy derivative which is then esterified with trifluoromethanesulfonic acid followed by azidation in a DMSO-water mixture (Scheme 7) [30].



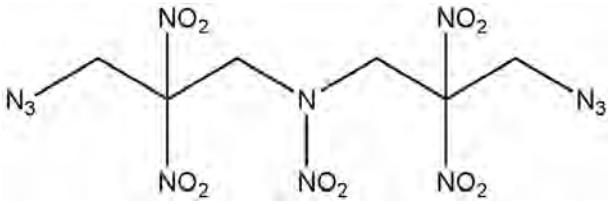
Scheme 7

The required hydroxy derivative was synthesized by Hang *et al.* [31]. The potassium salt of 2,2-dinitroethanol reacts with 1,2-diaminoethane and the resulting product is nitrated and formylated (Scheme 8).



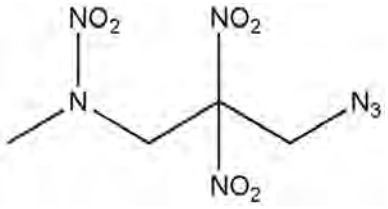
Scheme 8

1,7-Diazido-2,2,4,6,6-pentanitro-4-azaheptane (**XI**)



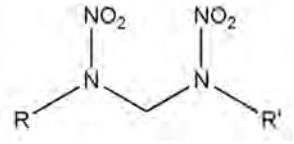
This compound is stated by Yan *et al.* [30] to have the highest density (1.835 g cm^{-3}) of all azidonitramines. It has zero oxygen balance calculated to CO and high enthalpy of formation — 1356 kJ kg^{-1}. The synthesis of **XI** is analogous to that of **X** and preparation of its hydroxy derivative has been described by Hang *et al.* [31] as well.

1-Azido-2,2,4-trinitro-4-azapentane (**XII**)



Compound **XII** has only been mentioned by Yan *et al.* [30]. The molecule resembles one half of the compound **X** and its synthesis is analogous. After extraction and purification, a colourless oily liquid is obtained with the last (azidation) step giving a yield of 85.7 %.

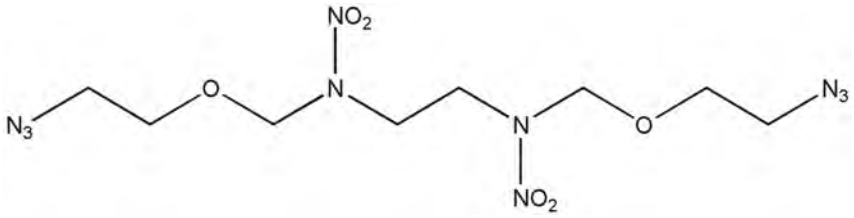
Substituted 1,3-dinitro-1,3-diazapropane (**XIII**)



Tartakovskii *et al.* [32] described plasticizers based on a mixture of various azidonitramines **XIII** (R,R´ = methyl, 2-azidoethyl, 3-azidopropyl or 2-azidopropyl). All of these compounds possess high enthalpy of formation (over 800 kJ kg^{-1}), high nitrogen content and a proper oxygen/carbon ratio. The melting point of triple based mixtures can be lower than 0 °C.

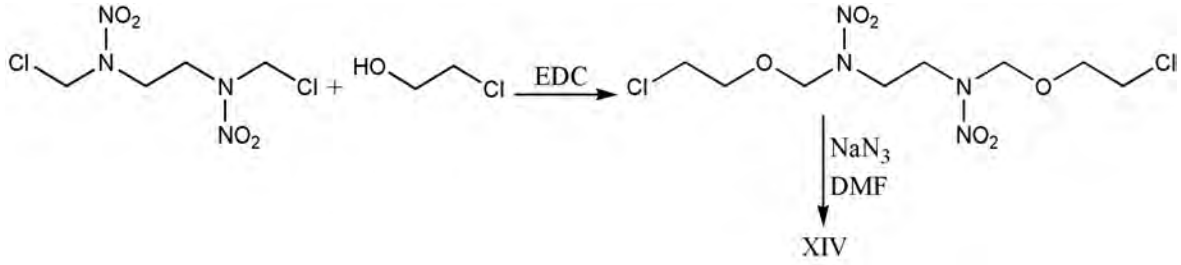
Reference [32] only describes the last synthetic step, i.e., azidation of nitroxy-derivatives in the presence of $CaCl_2$. The yield can be between 67 and 81 % depending on the substrate composition.

1,12-Diazido-3,10-dioxa-5,8-dinitro-5,8-diazadodekane (**XIV**)



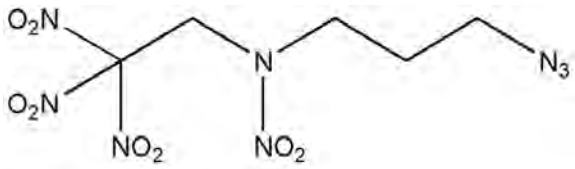
Compound **XIV** possesses a melting point of –15 °C and is almost insensitive to impact. Witucki [22] patented its use as a flame reducing plasticizer in solid rocket propellants with a polyester based binder.

The preparation of **XIV** was published by Frankel *et al.* [23]. 1,6-Dichloro-2,5-dinitro-2,5-diazahexane is condensed with 2-chloroethanol, and the resulting 1,12-dichloro-3,10-dioxa-5,8-dinitro-5,8-diazadodecane is azidated (Scheme 9). The yield of the azidation reaches 87 %.

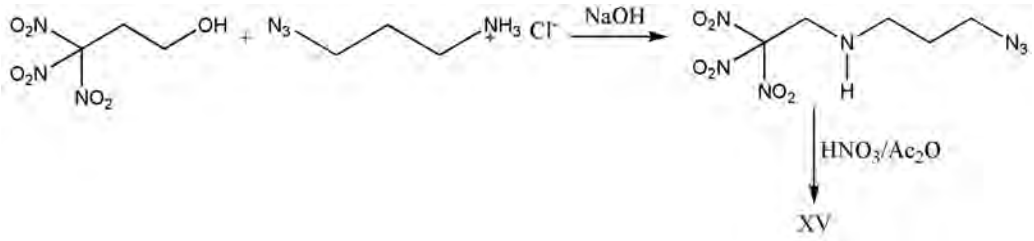


Scheme 9

6-Azido-1,1,1,3-tetranitro-3-azahexane (**XV**)

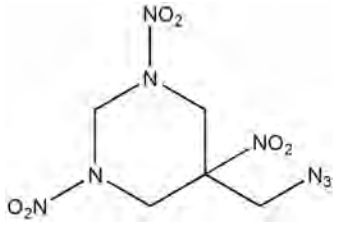


Witucki and Frankel [33] described condensation of 2,2,2-trinitroethanol with 3-azidopropylamin hydrochloride in the presence of sodium hydroxide giving 6-azido-1,1,1-trinitro-3-azahexane, which is nitrated using nitric acid in acetic anhydride to give **XV** as a yellowish oily liquid with a yield of 26.6 % (Scheme 10). Density of 15 is 1.52 g cm^{-3}.



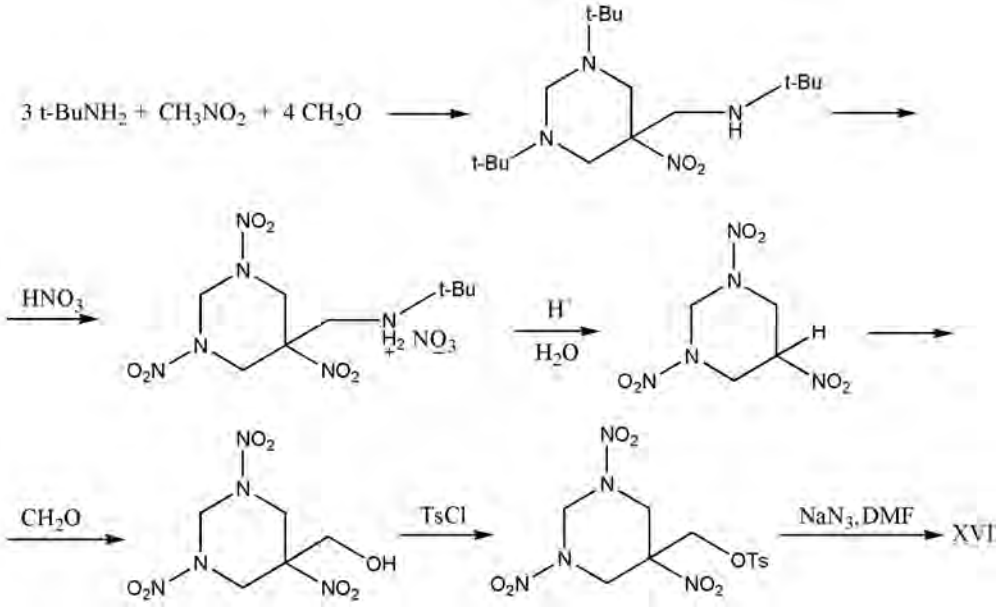
Scheme 10

5-Azidomethyl-1,3,5-trinitrohexahydropyrimidine (**XVI**)



Compound **XVI** is one of a few heterocyclic azidonitramines discussed in recent literature. Licht and Ritter [34] suggested **XVI** as a potential energetic filler with the density of 1.74 g cm^{-3} and enthalpy of formation equal to 998 kJ kg^{-1}. Thermal stability is remarkably better than that of analogous 5-nitroxymethyl-1,3,5-trinitrohexahydropyrimidine.

Synthesis is briefly summarized in [34]. *tert*-Butylamine, formaldehyde and nitromethane react to give 5-hydroxymethyl-1,3,5-trinitrohexahydropyrimidine which is then transformed to its tosyl derivative and finally azidated (Scheme 11).



Scheme 11

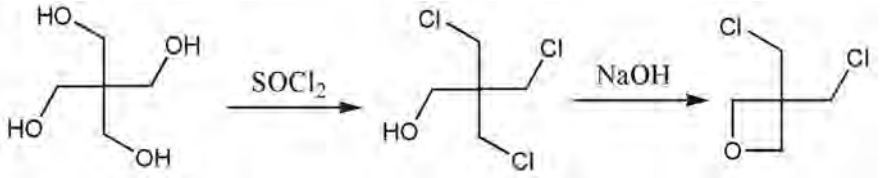
Medvedeva *et al.* [35] prepared several six- and seven-membered heterocyclic azidonitramines.

3.4 Azido compounds from 3,3-bis(chloromethyl)oxetane

3,3-bis(Chloromethyl)oxetane is a precursor for a modern energetic binder, poly(3,3-bis(azidomethyl)oxetane) (polyBAMO), and for preparation of various other azidocompounds. Its synthesis starts from pentaerythritol which is chlorinated to pentaerythritol trichlorohydrine and cyclized using a strong base (Scheme 12) [36].

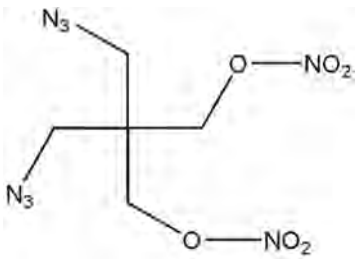
3,3-bis(Chloromethyl)oxetane can be azidated easily to 3,3-bis(azidomethyl)oxetane (BAMO). Treated with acids, the oxetane ring is opened and derivatives of pentaerythritol are formed. Nitroxy-, bromo- and azido-derivatives are accessible via this route. Opening in sulfuric acid forms the hydroxy derivative which is useful for preparation of various esters and ethers containing the azidogroup [37,38].

Frankel and Wilson [37] described classical azidation to produce BAMO in DMF with a 76 % yield. Optimization of phase transfer catalyzed azidation was discussed by Malik and Manser [5]. The use of 2.5-10 mol % of phase-transfer catalyst (TBAB) gives yields of 95 %.



Scheme 12

2,2-bis(Azidomethyl)-1,3-dinitroxypropane (**XVII**)

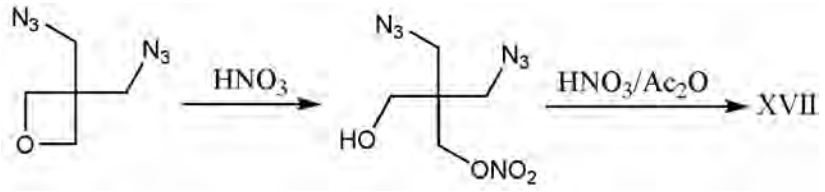


The synthesis of **XVII** is described by Wilson and Frankel [38]. 3,3-bis(Azidomethyl)oxetane is ring opened and esterified using 70 % nitric acid at ambient temperature. 2,2-bis(Azidomethyl)-3-nitroxypropan-1-ol is formed and

further esterified using a nitric acid/acetic anhydride mixture (Scheme 13). The overall yield of a colourless oily liquid is 65 %.

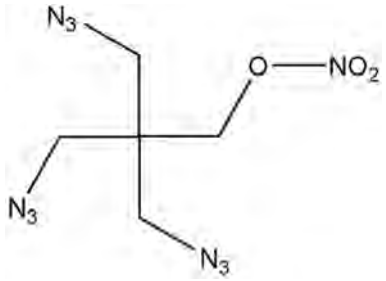
Zhang *et al.* [39] published an easier method starting from pentaerythritol. It is twice brominated, azidated to obtain the diazido derivative and then esterified with nitric acid. The yield reaches 82 % calculated for the dibromo derivative.

Properties of **XVII** were summarised by Guo *et al.* [40]. In comparison with common nitrate esters, it possesses slightly lower impact sensitivity than nitroglycerine and much higher enthalpy of formation — equal to 2952 kJ kg^{-1}.



Scheme 13

3-Azido-2,2-bis(azidomethyl)-1-nitroxypropane (**XVIII**)



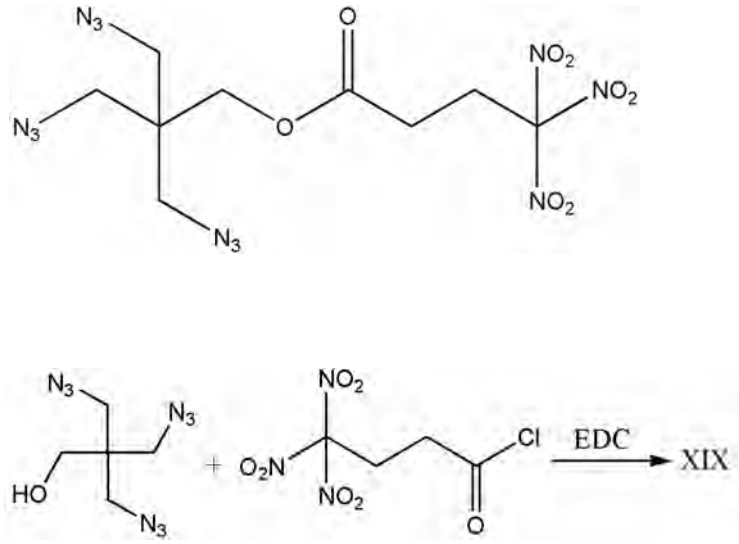
This derivative of pentaerythritol is prepared by ring opening of 3,3-bis(azidomethyl)oxetane with HBr followed by azidation to the triazido-derivative and esterification in the same manner as in the case of **XVII** as described by Wilson and Frankel [38]. An overall yield of 66 % is obtained. According to Malik and Manser [5], the triazido-derivative is also obtained by reaction of 3,3-bis(azidomethyl)oxetane with sodium azide in an acidic solution.

Compound **XVIII** is prepared in the form of a colourless liquid having a solidification point in the range from –15 to –18 °C [41].

3-Azido-2,2-bis(azidomethyl)propyl-4,4,4-trinitrobutyrate (**XIX**)

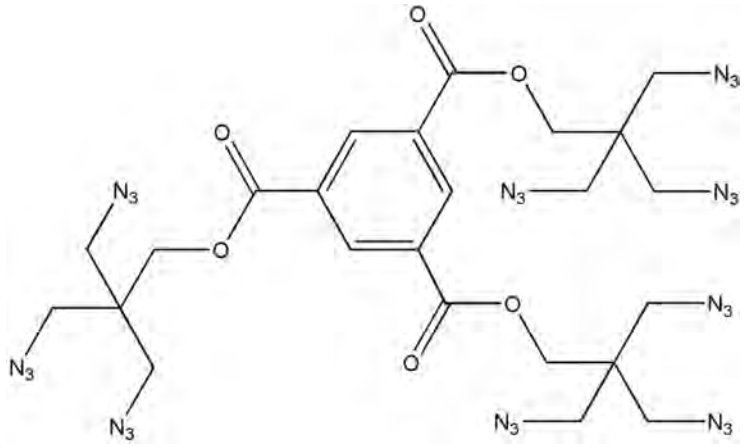
Compound **XIX** (Fig. 19) is an example of a potential ester-based plasticizer as stated by Wilson and Frankel [38]. It can be prepared by a simple reaction of 4,4,4-trinitrobutyryl chloride with 3-azido-2,2-bis(azidomethyl)propan-1-ol in 1,2-

dichlorethane (Scheme 14). The yield reaches 94 %. Similarly, the same reaction can be carried out starting with 3-nitroxy-2,2-bis(azidomethyl)propan-1-ol.



Scheme 14

1,3,5-tris[3-Azido-2,2-bis(azidomethyl)propyl]benzentricarboxylate (**XX**)

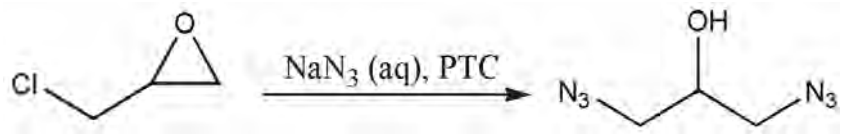


Compound **XX** is an example of a plasticizer's molecular weight enhancement. Wilson and Frankel [38] prepared **XX** similarly to **XIX** by reaction of 3-azido-2,2-bis(azidomethyl)propan-1-ol with benzene-1,3,5-tricarboxylic acid chloride. An oily liquid is obtained with a yield of 80 %. Crystallization from a methanol-chloroform mixture gives a solid product with the melting point of 65-68 °C.

3.5 Azido compounds from epichlorohydrin

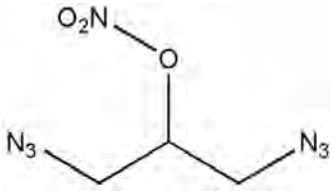
Epichlorhydrin (1-chloro-2,3-epoxypropane) is an important precursor for various azidocompounds. On a large scale, azidation of epichlorohydrin or poly epichlorohydrin is used for preparation of a high-molecular-weight polyglycidyl azide, which is a modern binder.

According to Vander Werf *et al.* [42], epichlorohydrin is azidated in dioxane to yield 1,3-diazidopropan-2-ol. This method involves a rather dangerous vacuum distillation of the product, eliminating polymeric impurities. A more convenient method using an aqueous solution of sodium azide with phase-transfer catalyst (Scheme 15) is described by Caubere and Forconi [3].



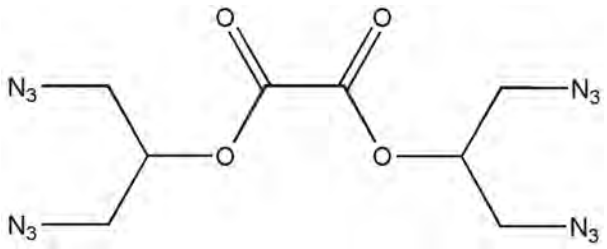
Scheme 15

1,3-Diazido-2-nitroxypropane (**XXI**)



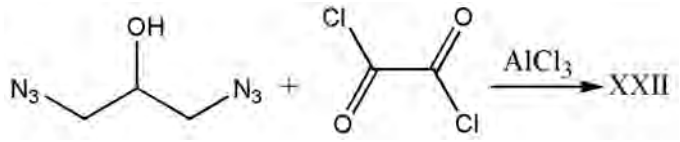
This partial "azido-analogue" of nitroglycerine was described by Witucki and Frankel [33]. 1,3-Diazidopropan-2-ol is carefully esterified with nitric acid in acetic anhydride and then extracted from the reaction mixture with dichloromethane.

bis(1,3-Diazido-2-propyl)oxalate (**XXII**)



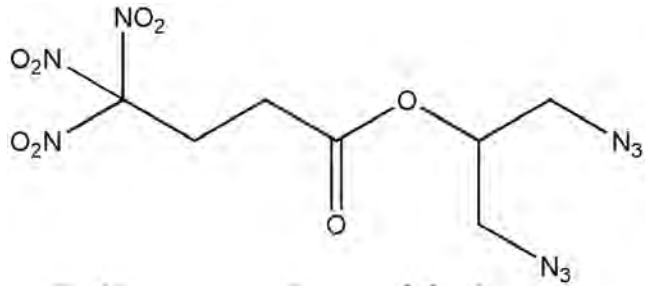
Witucki and Frankel [33] prepared **XII** by the reaction of 1,3-diazidopropan-2-ol with oxalyl chloride in the presence of aluminum(III) chloride (Scheme 16). The yield of the purified low melting solid was 59 %.

Properties of some other bis(diazidopropyl) esters of dicarboxylic acids were summarized by Frankel *et al.* [43].



Scheme 16

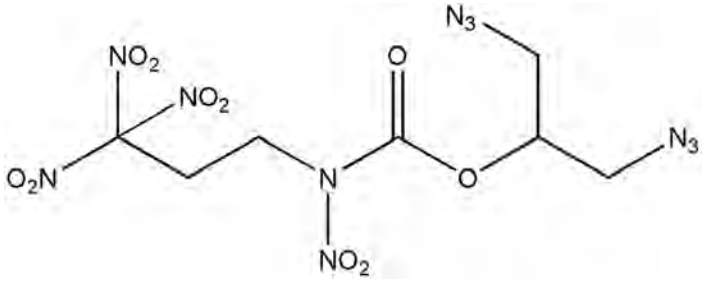
1,3-Diazido-2-propyl-4,4,4-trinitrobutyrate (**XXIII**)



The last step of the synthesis of this compound was described by Witucki and Frankel [33]. 4,4,4-Trinitrobutyryl chloride is heated with 1,3-diazidopropan-2-ol in 1,2-dichlorethane, similarly to the preparation of **XIX**. After purification, the yield of (23) is 66 %. Unfortunately, 4,4,4-trinitrobutyryl chloride is not easy to obtain. One way uses the reaction of trinitromethane with acrolein followed by oxidation and chlorination.

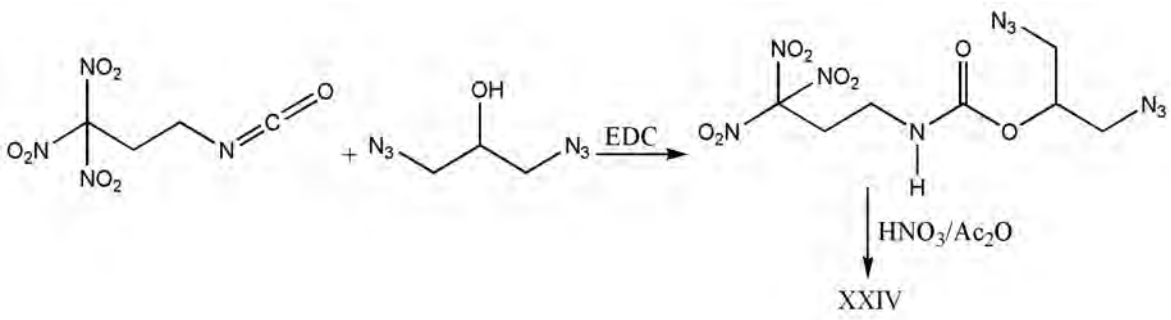
Compound **XXIII** is a liquid with the density of 1.464 g cm^{-3} and enthalpy of formation equal to 326 kJ kg^{-1}.

1,3-Diazido-2-propyl-*N*-nitro-*N*-(3,3,3-trinitropropyl)carbamate (**XXIV**)



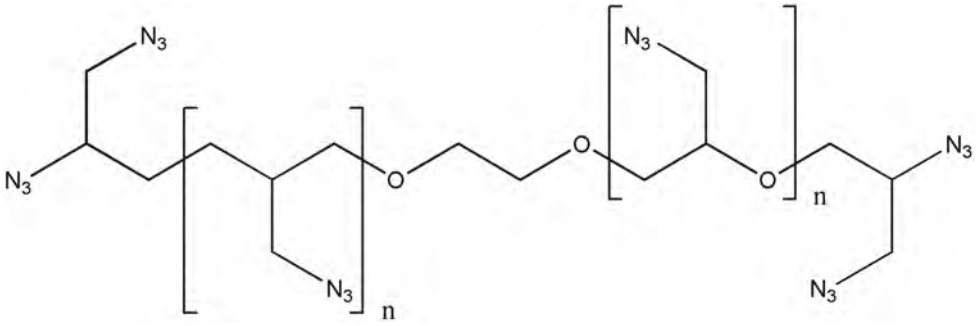
The preparation of compound **XXIV** was mentioned by Witucki and Frankel [44]. 1,3-Diazido-2-propyl-*N*-(3,3,3-trinitropropyl)carbamate is prepared by the reaction of 3,3,3-trinitropropyl isocyanate with 1,3-diazidopropan-2-ol in 1,2-dichloroethane under reflux, followed by nitration using a nitric acid/acetic anhydride mixture (Scheme 17).

Frankel and Witucki [45] published some properties of **XXIV** which suggest this compound as an energetic plasticizer for polyester-bonded solid rocket propellants. Compound **XXIV** has a melting point of 7 °C.



Scheme 17

Polyglycidyl azide azido-terminated (**XXV**)



Glycidyl azide polymer (GAP) with M_W = 2000-5000 g mol^{-1} is a known modern binder for propellants and pyrotechnic compositions. Unbranched GAP is a liquid, having M_W = 400-800 g mol^{-1}. It is suitable for plasticizing of nitrocellulose bonded mixtures as well as compositions using high molecular weight GAP. In this last case, plasticizing GAP should not be hydroxy-terminated, because terminal hydroxy-groups are easily joined in the crosslinking process, and the plasticizing effect is lost. This is why it is advantageous to prepare the azido-terminated compound **XXV** [46].

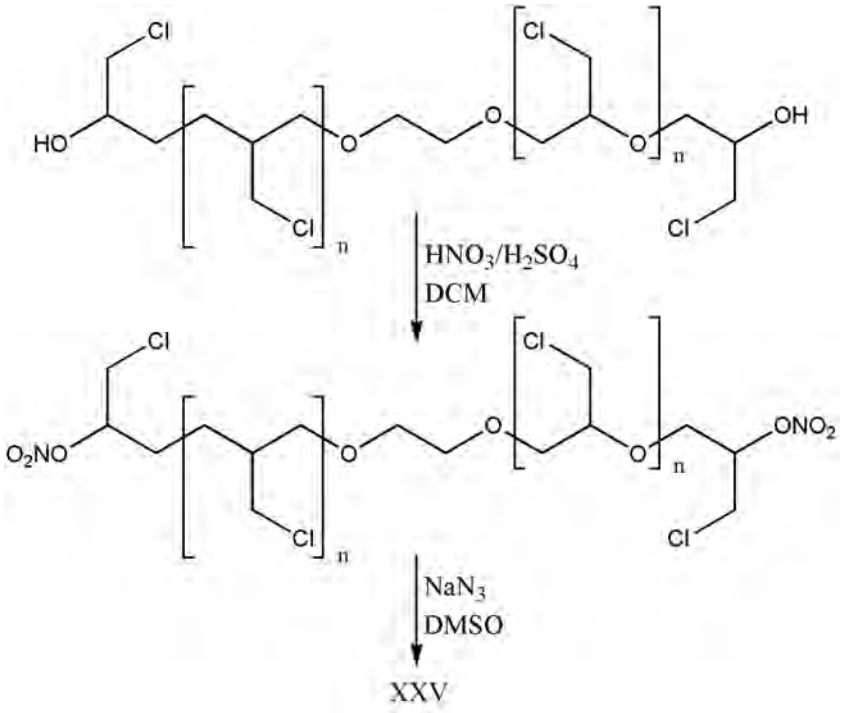
Compound **XXV** has a high enthalpy of formation (2322 kJ k^{-1}) and high nitrogen content (48.4 %). It has moderate impact sensitivity and glass transition temperature of about –56 °C, which makes it suitable for plasticizing of propellant

compositions [46]. Hunter and Manzara [47] summarized the compatibility data for mixtures of **XXV** with various polymers.

Wilson and Frankel [48] described the preparation of **XXV** starting from polyepichlorohydrin in dichloromethane which was then esterified using a nitration mixture. Subsequent azidation in dimethyl sulfoxide gives a 43.8 % yield after 8 hours (Scheme 18). If the reaction is carried out in aqueous solution in the presence of PTC, the yield reaches 75 % after 88 hours according to Wilson and Weber [8].

At present, compound **XXV** is commercially available from MACH I, Inc. under GAP-0700 trademark [49].

The propellant compositions containing RDX, TAGN, NC and **XXV** were discussed by Damse *et al.* [50]. These mixtures exhibit a higher force at similar sensitivity to mechanical stimuli and have more convenient burning rate characteristics in comparison with those plasticized with dioctyl phthalate. The main disadvantages of the mixtures are worse mechanical properties and, in mixtures without TAGN, also higher flame temperature.



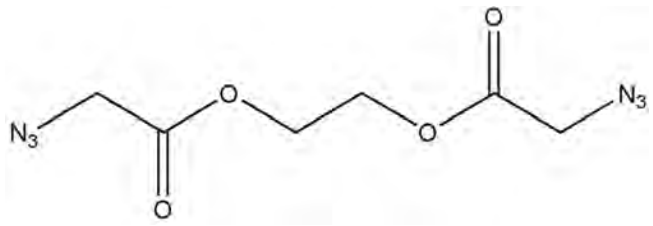
Scheme 18

3.6 Azidoacetates

Almost all known esters of azidoacetic acid are potential plasticizers. Their syntheses can be accomplished by esterification of alcohols using chloroacetic acid and subsequent azidation of the chloroacetate. The main advantages of these

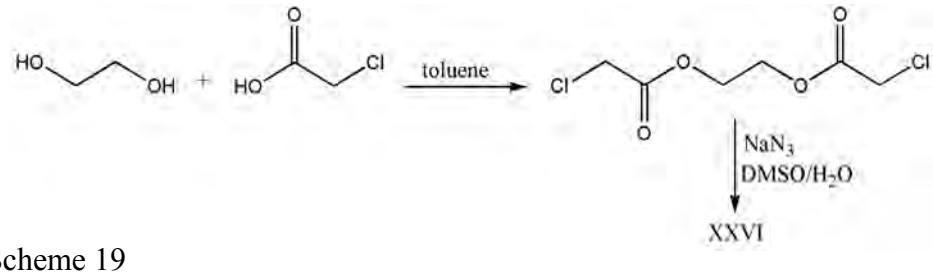
materials are low glass transition temperature and sufficient thermal stability. However, they possess lower enthalpy of formation than other azidocompounds.

2-(Azidoacetoxy)ethyl azidoacetate (**XXVI**)



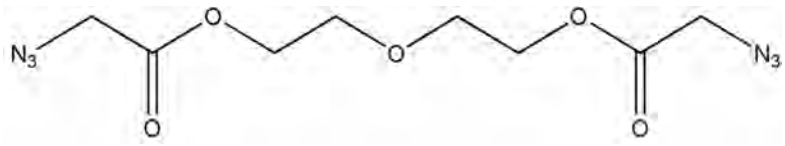
Compound **XXVI** was studied by Drees *et al.* [51]. The synthesis is started with azeotropic distillation of ethyleneglycol with chloroacetic acid in toluene. The resulting azidoacetate is azidated in a water/DMSO system to obtain a yield of 70 % (Scheme 19).

Low glass transition temperature of –70.8 °C and high temperature of decomposition (232 °C) enables **XXVI** to be a valuable plasticizer. Damse and Singh [52] reported slightly higher sensitivity to mechanical stimuli for **XXVI**-based propellants.



Scheme 19

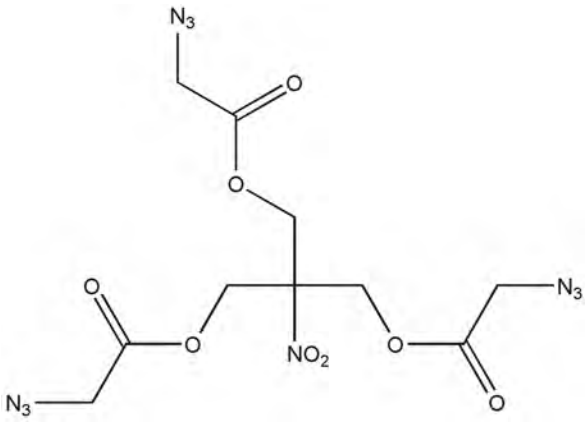
5-(Azidoacetoxy)-3-oxopentyl azidoacetate (**XXVII**)



Preparation of **XXVII** proceeds in almost the same way as that of **XXVI**. The yield of the corresponding chloroacetate is nearly quantitative and azidation gives a yield of 85 %.

The compound is characterized by low density (1.0 g cm^{-3}) and lower impact sensitivity in comparison to **XXVI**. Thermal stability (215 °C) is sufficient. The enthalpy of formation is the lowest of all known azidoacetates (–1209 kJ kg^{-1}) [51].

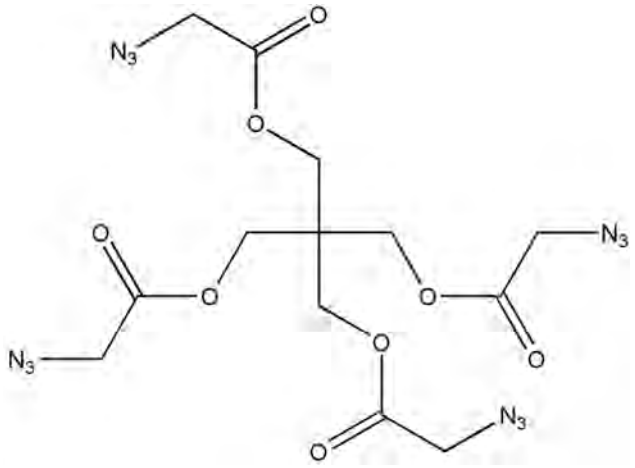
3-(2-Azidoacetoxy)-2-(azidoacetoxymethyl)-2-nitropropyl azidoacetate (**XXVIII**)



This azidoacetate has a proper oxygen/carbon ratio and density of 1.45 g cm^{-3}. Compared to other azidoacetates, it has the lowest decomposition temperature of 214 °C.

Azidation of the corresponding chloroacetate proceeds with more difficulty giving a yield of 50 % after 70 hours [51].

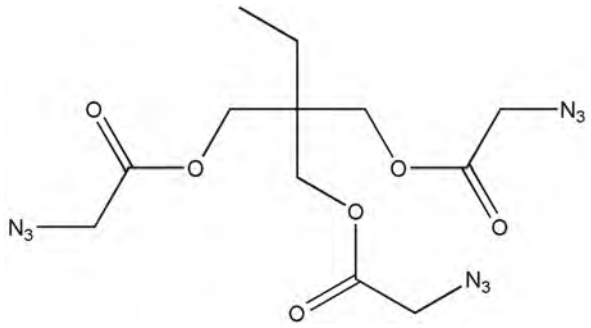
3-(Azidoacetoxy)-2,2-bis(azidoacetoxymethyl)propyl azidoacetate (**XXIX**)



Compound **XXIX** has twice the viscosity of glycerol. Compared to **XXVI** and **XXVII**, it possesses a higher glass transition temperature of –34.1 °C and also superior impact sensitivity and thermal stability.

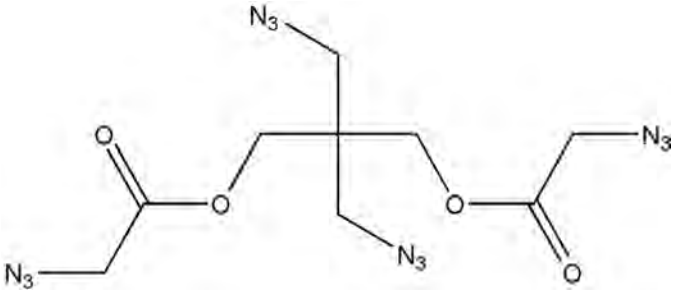
The yield of pentaerythritol esterification is almost quantitative, while the azidation yields 75-95 % of XXIX after 24 hours [51].

2,2-bis(Azidoacetoxymethyl)butyl azidoacetate (**XXX**)



Pant *et al.* [53] described the preparation of **XXX** by esterification of 2,2-bis(hydroxymethyl)butan-1-ol with chloroacetic acid and subsequent azidation. The overall yield reaches 81 %. Glass transition temperature of **XXX** is –47 °C.

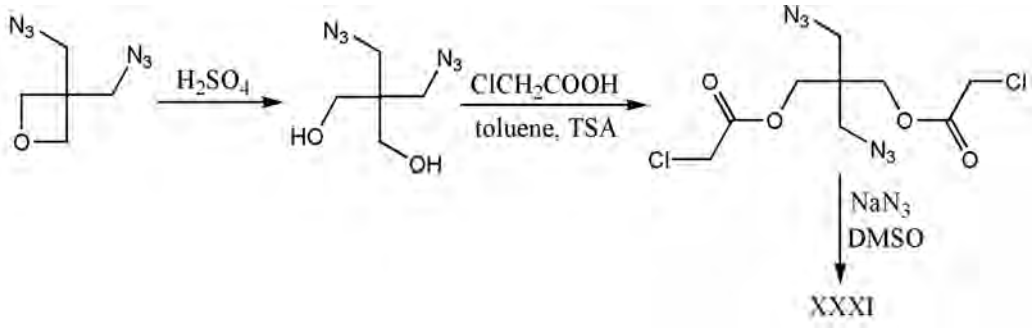
3-Azidoacetoxy-2,2-bis(azidomethyl)propyl azidoacetate (**XXXI**)



Compound **XXXI** was suggested by Shaojun *et al.* [54] as a plasticizer for solid rocket propellants bonded with azidopolymers. Good thermal stability and high nitrogen content are emphasized.

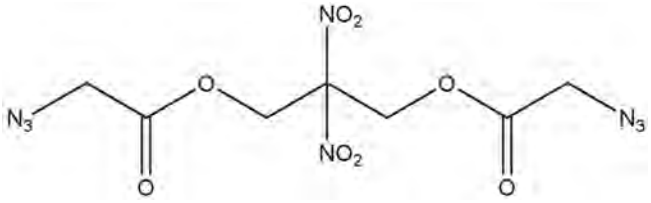
Pant *et al.* [53] described the preparation of **XXXI** starting from 3,3-bis(azido-methyl)oxetane. The oxetane ring is opened during boiling with diluted sulfuric acid and the resulting 2,2-bis(azidomethyl)propan-1,3-diol is esterified with chloroacetic acid in toluene in the presence of *p*-toluenesulfonic acid (TSA) and then azidated (Scheme 20). The overall yield is 80 %. Also the preparation of **XXXI** from 2,2-bis(bromomethyl)propan-1,3-diol was described [54].

Triple-base smokeless propellants with minor amounts of **XXX** or **XXXI** were discussed by Ghosh *et al.* [55]. If phthalates in a propellant are substituted by these azido compounds, there follows a slight increase in force, improved mechanical properties and decreased sensitivity to mechanical stimuli.

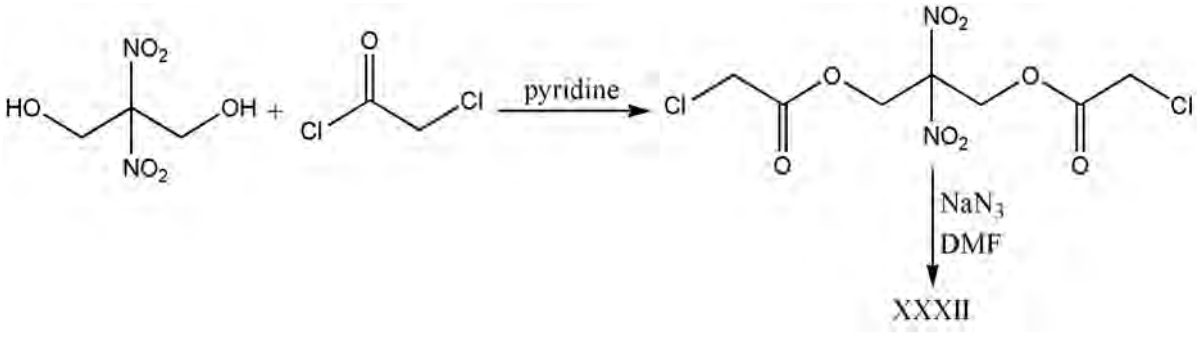


Scheme 20

3-(3-Azidoacetoxy)-2,2-dinitropropyl azidoacetate (**XXXII**)



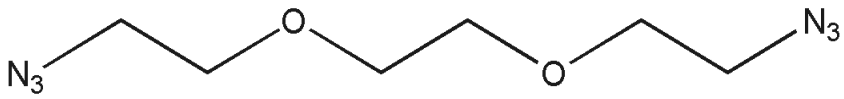
The synthesis of **XXXII** was described by Ek *et al.* [56]. 2.2-Dinitropropane-1,3-diol is treated with chloroacetyl chloride to yield 2,2-dinitro-1,3-bis(2-chloroacetoxy)propane, which is azidated with sodium azide to yield **XXXII** (Scheme 21). The product has a density of 1.46 g cm^{-3}, acceptable glass transition temperature of –49 °C, but low thermal stability. The thermal stability was estimated by heat flow calorimetry. Calculated explosive properties are also reported in the paper [56].



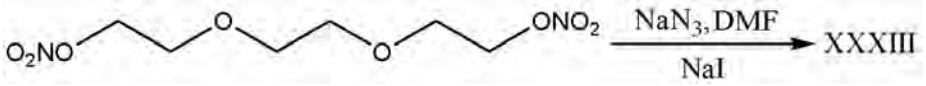
Scheme 21

3.7 Other azidocompounds

1,8-Diazido-3,6-dioxaoctane (**XXXIII**)

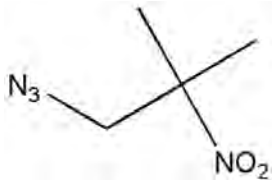


Alvarez *et al.* [57] described the preparation of **XXXIII** starting from triethyleneglycol dinitrate (TEGDN). The azidation proceeds in dimethylformamide in the presence of sodium iodide gives a yield of 67 % (Scheme 22). Alternatively, azidation can be done in an aqueous solution in the presence of a phase transfer catalyst with a yield of 72 %. Compound **XXXIII** has a density of 1.15 g cm^{-3} and is almost impact insensitive. Compatibility with liquid nitric acid esters is good as well as its plasticizing ability. Frankel and Wilson [43] described the preparation and some properties of other azido derivatives of polyethylene-glycols.



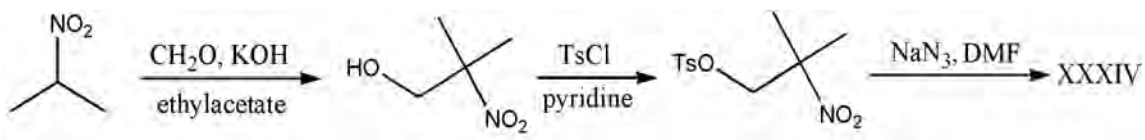
Scheme 22

2-Methyl-2-nitro-1-azidopropane (**XXXIV**)



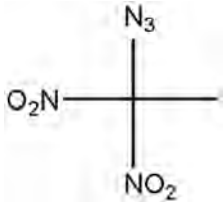
Wang *et al.* [58] prepared **XXXIV** by the reaction of 2-nitropropane with formaldehyde in the presence of potassium hydroxide followed by tosylation and azidation (Scheme 23). The last step yield is 37 %.

Compound (34) melts at –18 °C and decomposes above 206 °C.



Scheme 23

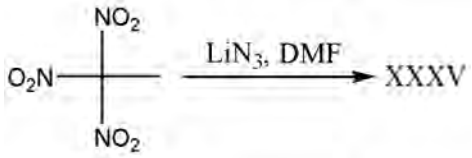
1-Azido-1,1-dinitroethane (**XXXV**)



Compound **XXXV** was suggested by Wright [12] as a plasticizer for insensitive propellants. These propellants exhibit the same force but have a lower impact sensitivity (80 cm / 2 kg) than those with nitroglycerine. In addition, 1-azido-1,1-dinitropropane is known to have an even lower sensitivity than **XXXV** [12].

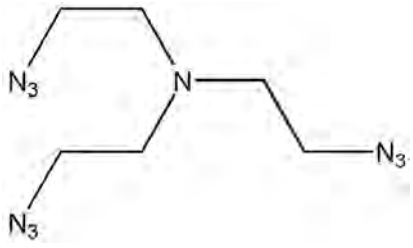
Synthesis of **XXXV** is based on electrochemical oxidation of potassium dinitroethane salt in the presence of sodium azide. After 1.5 hours, the starting material is consumed and the yield of the product was 27 %. Electrochemical azidation of some other geminal nitro compounds is also discussed by Frankel in [11].

The second method for preparing compound **XXXV** uses 1,1,1-trinitroethane as a precursor which is treated with lithium azide in anhydrous dimethylformamide (Scheme 24). In this case, the yield reaches 28 % [2].



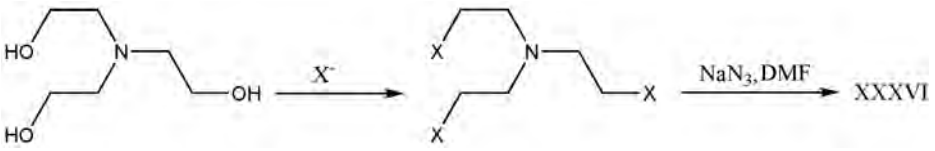
Scheme 24

tris(2-Azidoethyl)amine (**XXXVI**)



Frankel and Wilson [59] patented the preparation of **XXXVI** by azidation of tris(2-chloroethyl)amine (Scheme 25) and suggested the use of the material in ternary hypergolic mixtures with nitrogen(IV) oxide and nitric acid. In scheme 25, component X can be halide, nitrate or tosylate. Compound **XXXVI** possesses low

impact sensitivity and a melting point of –19 °C. The high nitrogen content of **XXXVI** minimizes smoke formation during its combustion.



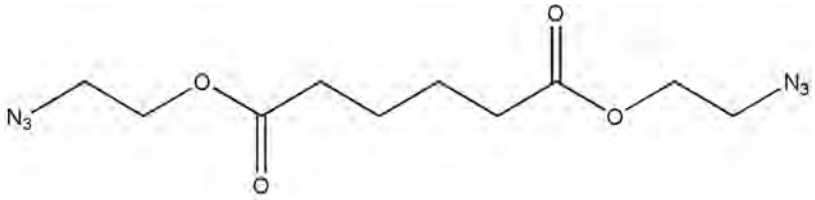
Scheme 25

1-Azidoethyl nitrate (**XXXVII**)

Compound **XXXVII** was described by Simmons [16] as a liquid having a density of 1.34 g cm^{-3} and positive enthalpy of formation of 1657 kJ kg^{-1}. Fedoroff *et al.* [60] described the synthesis of **XXXVII** by esterification of 2-chloroethan-1-ol with a nitrating mixture followed by azidation (Scheme 26). Unfortunately, the impact sensitivity of **XXXVII** is stated to be three times higher in comparison with nitroglycerine.

Scheme 26

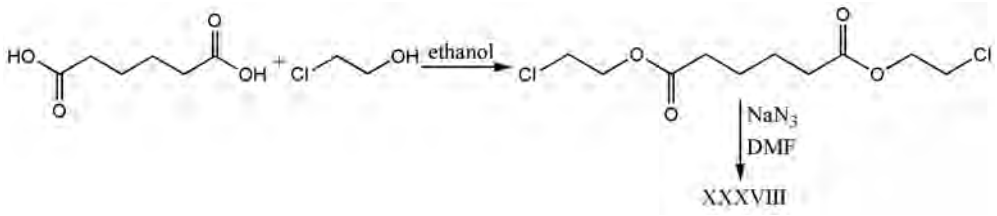
bis(2-Azidoethyl)adipate (**XXXVIII**)



Compound **XXXVIII** is produced according to Agrawal *et al.* [61] by condensation of 2-chloroethanol with adipic acid and subsequent azidation in ethanol with an overall yield of 65 % (Scheme 27).

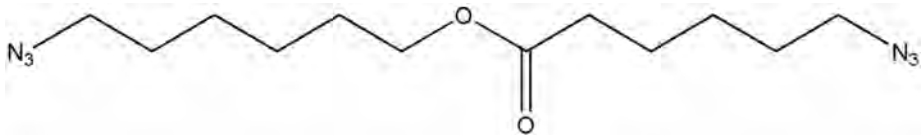
This compound exhibits acceptable thermal stability (exotherm starts at 197 °C) and ability to plasticize nitrocellulose; therefore, it is suggested as a co-plasticizer in mixtures with nitroglycerine. However, the sensitivity must be controlled

by addition of diethyl phthalate. The optimum mixture, reported in [61], contains compound **XXXVIII**, diethyl phthalate and nitroglycerine in 5:15:80 ratio.



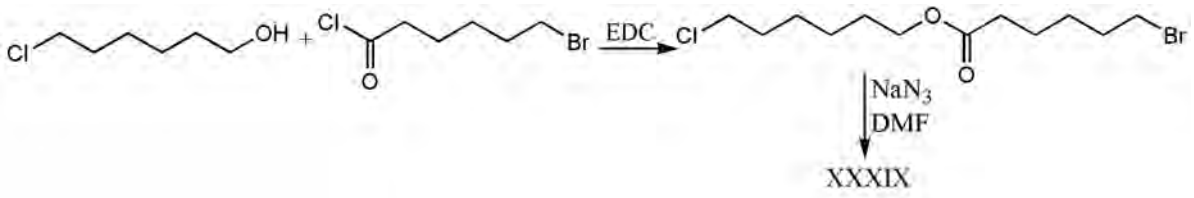
Scheme 27

6-Azidohexyl-6-azidohexanoate (**XXXIX**)



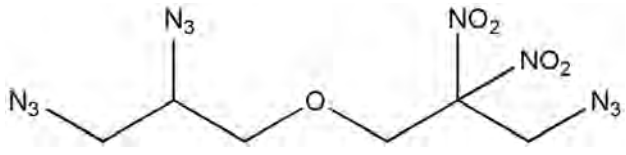
Frankel and Wilson [23] described the preparation of **XXXIX** by condensation of 6-bromohexanoylchloride with 6-chlorohexanol in 1,2-dichloroethane followed by azidation (Scheme 28). The overall yield of the synthesis reaches 69 % after purification.

Compound **XXXIX** is almost impact insensitive and possesses a melting point below –78 °C.



Scheme 28

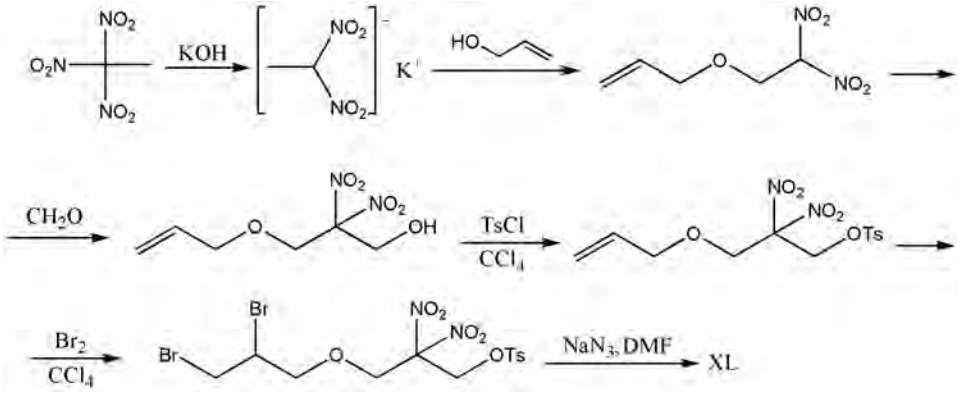
3-Azido-2,2-dinitropropyl-2,3-diazidopropylether (**XL**)



Helmy [62] suggested **XL** as a rocket propellant plasticizer due to its highly

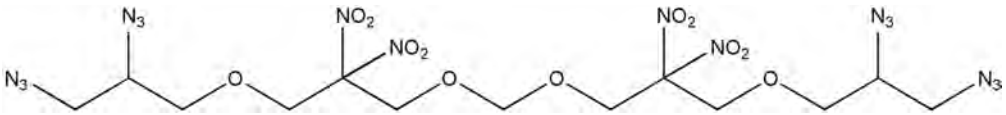
positive enthalpy (2099 kJ mol^{-1}).

Witucki & Frankel [44] and Frankel & Wilson [37] described a multistep synthesis of **XL**. First, 1,1,1-trinitroethane is converted to the potassium salt of 1,1-dinitroethane using potassium hydroxide. Addition of prop-2-en-1-ol and subsequent methylolation result in the formation of 3-hydroxy-2,2-dinitropropyl-2-propenylether. Bromination and tosylation are then carried out forming 3-tosyl-2,2-dinitropropyl-2,3-dibromopropylether (Scheme 29). The last azidation step is carried out in dimethylformamide with a 70 % yield.



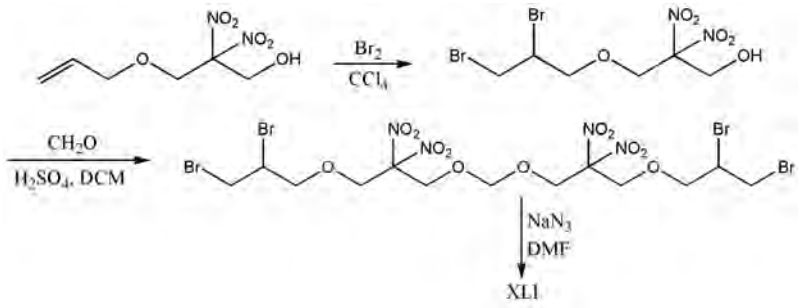
Scheme 29

bis(1,2-Diazido-4-oxa-6,6-dinitroheptyl)formal (**XLI**)



Preparation of **XLI** was described by Witucki and Frankel [44]. 3-Hydroxy-2,2-dinitropropyl-2-propenylether is brominated to 3-hydroxy-2,2-dinitropropyl-2,3-dibromopropylether and then formylation is carried out. The last azidation step gives a 50 % yield after purification (Scheme 30).

Compound **XLI** has less than half the enthalpy of formation of **XL**.



Scheme 30

4 Summary of Properties

Properties of the described azidocompouds are summarised (Tables I and II) and compared with common explosives (Tables III and IV).

Table I Basic properties of azido compounds

No.	*M* g mol^{-1}	Nitrogen content %	Enthalpy of formation kJ kg^{-1}	Density g cm^{-3}	References
I	172.1	65.1	4330	1.432	[15,17]
II	320.2	52.5	1916	1.720	[16]
III	394.2	49.7	1404	1.670	[20,21]
IV	260.2	43.1			[23]
V	200.2	56.0	3416	1.33 (1.196)	[20,24]
VI	159.2	44.0	1288		[16,63]
VII	187.2	37.4	1476	1.210	[23,63]
VII	246.1	56.9	3055	1.70	[12,16]
IX	260.2	53.8	2772	1.610	[12,16]
X	496.3	39.5	974	1.722	[30]
XI	408.2	41.2	1356	1.835	[30]
XII	249.1	39.4	884		[30]
XIIIa	219.2	44.7	963	1.400	[32,63]
XIIIb	233.2	42.1	837	1.390	[32,63]
XIIIc	233.2	42.1	837	1.390	[32,63]
XIV	348.3	40.2			[23]
XV	308.2	36.4		1.520	[33]
XVI	276.2	40.6	998	1.740	[34]
XVII	276.2	40.6	2952		[38,40,63]
XVIII	256.2	54.7			[38,63]
XIX	416.3	40.4	966		[64]
XX	789.7	47.9			[64]
XXI	187.1	52.4		1.379	[33]
XXII	338.2	49.7	3127	1.272	[33,63]
XXIII	347.2	36.3	326	1.464	[33]
XXIV	407.2	37.8	401	1.563	[44,63]
XXV	607.6	48.4	2322	1.270	[8,48]
XXVI	228.2	36.8	–734	1.340	[51]
XXVII	272.2	30.9	–1209	1.000	[51]
XXVIII	400.3	35.0	–576	1.450	[51]
XXIX	468.3	35.9	–460	1.390	[51]
XXX	383.3	32.9	–411		[55]
XXXI	352.3	47.7	1719		[55]
XXXII	332.2	33.7		1.46	[56]
XXXIII	200.2	42.0	1199	1.150	[57]
XXXIV	144.1	38.9			[58]
XXXV	161.1	43.5	1219	1.456	[12,63]
XXXVI	224.2	62.5	3960	1.162	[59]

Table I – Continued

No.	*M* g mol^{-1}	Nitrogen content %	Enthalpy of formation kJ kg^{-1}	Density g cm^{-3}	References
XXXVII	132.1	42.4	1657	1.340	[16]
XXXVIII	284.3	29.6		1.154	[61]
XXXIX	282.3	29.8			[23]
XL	315.2	48.9	2099	1.406	[44,62]
XLI	592.4	37.8	721	1.418	[44]

Table II Sensitivity and decomposition temperature of azido compounds

No.	Melting point[a] °C	Mechanical sensitivity[b]	Decomposition temperature[c]	References
I	–57	imp. < 1 J; fric. 20 N		[15,17]
II	130.85	imp. < 1 J; fric. 144 N		[16]
III	176	imp. 19 cm/2,5 kg; (10-45 cm kg^{-1})	173 °C*; 195.7 °C*	[20,21]
IV	< –78 *	imp. > 150 in lb		[23]
V	–20*	imp. 10 cm/2 kg	147 °C*	[20,24]
VI	< 15			[16,63]
VII	< –78*	imp. > 150 in lb		[23,63]
VII	80			[12,16]
IX	76			[12,16]
X	137.4		203.5 °C (10 °C min^{-1})	[30]
XI	105.5		196.3 °C (10 °C min^{-1})	[30]
XII			186.1 °C (10 °C min^{-1})	[30]
XIIIa	< 0			[32,63]
XIIIb	< 0			[32,63]
XIIIc				[32,63]
XIV	–15*	imp. > 150 in lb		[23]
XV				[33]
XVI	128		225 °C	[34]
XVII	39.6	imp. 15.4 cm/2 kg; (NG 12.1 cm)	189 °C	[38,40,63]
XVIII	–15*			[38,63]
XIX				[64]
XX	65-68			[64]
XXI				[33]
XXII	54-55			[33,63]
XXIII		imp. 12 in lb		[33]
XXIV	7	imp. 5 inlb		[44,63]
XXV	–56*; –67*	imp. 40 in lb; fric. < 36 kg	224 °C, 187 °C*	[8,48]
XXVI	–70.8**	imp. 5.5 N m; fric. 165 N	232 °C* (5 °C min^{-1})	[51]
XXVII	–63.3**	imp. > 10 N m; fric. 160 N	235 °C* (5 °C min^{-1})	[51]
XXVIII	–34.1**	imp. 16 N m; fric. 192 N	214 °C* (5 °C.min^{-1})	[51]
XXIX	–35.4**	imp. 60 N m; fric. 360 N	234 °C* (5 °C.min^{-1})	[51]
XXX	–47	imp. > 170 cm/2 kg; fric. 36 kg	254.5 °C	[55]
XXXI	–52	imp. > 170 cm/2 kg; fric. 36 kg	245.8 °C	[55]

Table II – Continued

No.	Melting point[a] °C	Mechanical sensitivity[b]	Decomposition temperature[c]	References
XXXII	–49**			[56]
XXXIII	–21; –79.8*	imp. 50 J; fric. 0 %, 360 N	225 °C*	[57]
XXXIV	–18*		206 °C	[58]
XXXV		imp. 80 cm/2 kg		[12,63]
XXXVI	–19*	imp. 60-65 in lb		[59]
XXXVII	–20			[16]
XXXVIII			197 °C*(10 °C min^{-1})	[61]
XXXIX	< –78*	imp. > 150 in lb		[23]
XL		imp. 8 in lb		[44,62]
XLI				[44]

Table III Basic properties of selected common explosives

Common name	*M* g mol^{-1}	Nitrogen content %	Enthalpy of formation kJ kg^{-1}	Density g cm^{-3}	References
Nitroglycerine	227.1	18.5	–1632	1.593	[63,65]
1,3,5,7-Tetranitro-1,3,5,7-tetraazocane (HMX)	296.2	37.8	284	1.91	[63,65]
1,3,5-Trinitro-1,3,5-triazinane (RDX)	222.1	37.8	271	1.816	[65]
2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane	438.2	38.4	849	2.044	[63,65]
Nitrocellulose (13 % N)	278.4	13.0	–2494	1.66	[63,65]
Trimethylolethane trinitrate (TMETN)	255.1	16.5	–1666	1.47	[63,65]

Table IV Sensitivity and thermal stability of selected common explosives

Common name	Melting point [a] °C	Mechanical sensitivity [b]	Thermal stability [c]	References
Nitroglycerine		imp. 0.2 N m		[63,65]
1,3,5,7-Tetranitro-1,3,5,7-tetraazocane (HMX)	240 (dec.)	imp. 7.4 N m fric. 120 N	287 °C	[63,65]
1,3,5-Trinitro-1,3,5-triazinane (RDX)	201	imp. 7.5 N m fric. 120 N	204 °C*	[65]
2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane	~200 (dec.)	imp. 4 N m fric. 48 N	228 °C*	[63,65]

Table IV – continued

Common name	Melting point [a] °C	Mechanical sensitivity [b]	Thermal stability [c]	References
Nitrocellulose (13 % N)	170 (dec.)	imp. 3 N m		[63,65]
Trimethylolethane trinitrate (TMETN)		imp. 0.2 N m	182 °C*	[63,65]

Notes to tables

[a] Freezing point is marked with an asterisk, double asterisk means glass transition temperature.

[b] Sensitivity is given/stated in original units, 1 J = 1 N m ≈ 8.851 in lb.

[c] Peak of exotherm is listed. Onset of exotherm is marked with an asterisk. The method used were mostly DSC or DTA with milligram quantities of the samples

5 Conclusion

As energetic fillers, azidonitramines 1,7-diazido-2,4,6-trinitro-2,4,6-triazaheptane (**II**) and 1,9-diazido-2,4,6,8-tetranitro-2,4,6,8-tetraazanonane (**III**) are very promising materials, because the starting material for their synthesis is hexamethylene-tetramine, with the advantage that the technology for production of 1,3,5-trinitro-1,3,5-triazinane (RDX) may be used. Compound **III** has moderate sensitivity to mechanical stimuli, but compound **II** must be desensitised before further use.

1,5-Diazido-3-nitro-3-azapentane (**V**) is suitable as an energetic plasticizer, 1-azido-3-nitro-3-azaheptane (**VII**) and 1,8-diazido-3,6-dioxooctane (**XXXIII**) are suitable as insensitive plasticizers for LOVA propellants.

The starting material for synthesis is an alcohol or, in general, a hydroxy compound. Esterification of alcohols to produce nitrate esters is a well known and highly developed process in energetic materials chemistry and technology. It is extremely important to take great care in handling, and to follow all safety procedures during the process and during recycling of spent acid after esterification. In addition, the subsequent azidation step is characterized by the use of the highly toxic sodium azide, and polar aprotic solvents such as dimethyl sulfoxide or dimethylformamide. To avoid the laborious isolation of the products from solvents, phase transfer catalysis in two phases (water/organic solvent) may be used.

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