

From DEPARTMENT OF BIOSCIENCES AND NUTRITION  
Karolinska Institutet, Stockholm, Sweden

# **NITRO COMPOUNDS FOR USE IN EXPLOSIVE CHARGES**

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**Karolinska  
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**FOI**

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## ABSTRACT

This first part of this thesis describes synthesis of and characterisation of energetic plasticisers. The general concepts and requirements of energetic plasticisers are introduced. The remainder of this part further describes the work published in three publications. The first paper included here outlines the work on derivatives of 2,2-dinitropropane-1,3-diol. The second paper contains information on synthesis attempts of other *gem*-dinitrodiols and the successful synthesis and characterisation of derivatives of 4,4-dinitroheptane-1,7-diol, *e.g.* 1,7-diazido-4,4-dinitroheptane. The third paper focuses on a new class of energetic plasticisers, namely derivatives of 3(5),4-dinitropyrazole. Two of the obtained compounds had satisfactory thermal properties to enable their use as energetic plasticisers. These two are the aforementioned 1,7-diazido-4,4-dinitroheptane and 1-allyl-3(5),4-dinitropyrazole.

This second part of this thesis describes synthesis of potentially low-sensitive explosives, *i.e.* 4-amino-3,5-dinitropyrazole in the fourth IV and 1,1-diamino-2,2-dinitroethene in the fifth paper. Both products are known. The work was directed towards process development to facilitate large scale synthesis. Four syntheses of the former were evaluated. Out of these, one was suitable for scale-up and 200 g per batch could be produced. For the latter, a new synthesis procedure without hazardous intermediated or by-products is suggested.

## LIST OF PUBLICATIONS

- I. Ek, S., Eldsäter, C., Goede, P., Holmgren, E., Tryman, R., and Latypov, N., C. Eur. J. Energ. Mater., *Synthesis and Characterisation of 2,2-Dinitro-1,3-propanediol-based Plasticisers*, 2005, 2(4), 33-45.
- II. Ek, S., Latypov, N., Goede, P., Lee, Y., and Yang, G., J. Energ. Mater., *Energetic Plasticizers Based on gem-Dinitrodiols*, 2012, 30:4, 324-334.
- III. Ek, S., Wahlström, L., and Latypov, N. J. Chem. Chem. Eng., *Derivatives of 3(5),4-Dinitropyrazole as Potential Energetic Plasticisers*, 2011, 5, 929-935.
- IV. Ek, S., and Latypov, N., J. Heterocycl. Chem., *Four syntheses of 4-amino-3,5-dinitropyrazole*, in print.
- V. Jalový, Z., Ek, S., Ottis, J., Dudek, K., Růžicka, A., Lyčka, A., and Latypov, N., J. Energ. Mater., *Scalable Synthesis of 1,1-Diamino-2,2-dinitroethene Without Hazardous Intermediates or by-Products*, 2013, 31:2, 87-99

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## LIST OF ABBREVIATIONS

ANFO	Ammonium Nitrate/Fuel Oil
BDNPA	Bis(2,2-dinitropropyl)acetal
BDNPF	Bis(2,2-dinitropropyl)formal
BFDNP	3,3-Bis(difluoroamino)-1,5-dinitratopentane
BTIN	Butanetriol trinitrate
CL-20	Hexanitrohexaazoisowurtzitane or 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0 <sup>5,9</sup> .0 <sup>3,11</sup> ]-dodecane)
DANPE	Diazidonitraminopentane
DEGBAA	Diethyleneglycol bis(azidoacetate)
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
DNDA	Dinitrodiazaalkyl
DNEB	Dinitroethylbenzene
DNMI	2-Dinitromethylideneimidazolidine-3,4-dion
DOA	Dioctyladipate
DSC	Differential scanning calorimetry
EGBAA	Ethylene glycol bis(azidoacetate)
EGDN	Ethyleneglycol dinitrate or nitroglycol
FEFO	2,2-Dinitro-2-fluoro-ethanol formal
FOI	The Swedish Defence Research Agency
FOX	FOI explosive
FOX-12	Guanylurea dinitramide
FOX-7	1,1-Diamino-2,2-dinitroethene
GAP	Polyglycidyl azide
GAPA	Azide-terminated glycidyl azide plasticiser
HMI	2-Hydroxy-2-methylimidazolidine-3,4-dion
HMX	1,3,5,7-Tetranitro-1,3,5,7-tetrazacyclooctane or octogen
HTPB	Hydroxy-terminated polybutadiene
K10	A mixture of dinitro- and trinitroethylbenzene
MMI	2-Methoxy-2-methylimidazolidine-3,4-dion
NENA	nitroxyethyl nitramine
NG	Nitroglycerine or glycerol trinitrate
NTO	Nitrotriazolone
PBX	Plastic-bonded explosive
PETKAA	Pentaerythritol tetrakis(azidoacetate)
PETN	Pentaerythritol tetranitrate
RDX	1,3,5-Trinitro-1,3,5-triazacyclohexane or hexogen
STANAG	Standard of the NATO group
TEGDN	Triethyleneglycol dinitrate
T <sub>g</sub>	Glass transition temperature
TMETN	Trimethylol ethane trinitrate
TMHI	Trimethylhydrazinium iodide
TMNTA	Trimethylol nitromethane tris(azidoacetate)
TNT	2,4,6-Trinitrotoluene
VNS	Vicarious nucleophilic substitution

# 1 INTRODUCTION – EXPLOSIVES AND CHARGES

Black powder – a mechanical mixture of charcoal, sulphur and saltpetre (potassium nitrate) – was the first explosive in use. In this case, charcoal and sulphur are the fuels and potassium nitrate is the oxidiser. It is still in use today, but mainly in pyrotechnical mixtures and not in conventional, explosive charges. Its explosive properties emanates from its capability to produce large volumes of gas on combustion. Black powder deflagrates. Deflagration is a combustion process from the edges towards the centre of a particle. The reaction propagates slower than the speed of sound in the material. If the reaction propagates faster than the speed of sound in the material and also along a front through the material, the reaction is referred to as a detonation.

Prior to Alfred Nobel's development of the mercury fulminate-based blasting cap, [1] only highly sensitive substances, so called primary explosives, could be used as main charges. Some examples are lead azide, mercury fulminate, lead styphnate and nitroglycerine, see Figure 1. There is no clear-cut definition of a primary explosive, but any substance more sensitive to mechanical stimuli and/or static electricity than pentaerythritol tetranitrate (PETN) is usually included in this group. Nobel is best known for his invention of dynamite, [2] but this would have been useless without the blasting cap, which could be considered his most important invention.

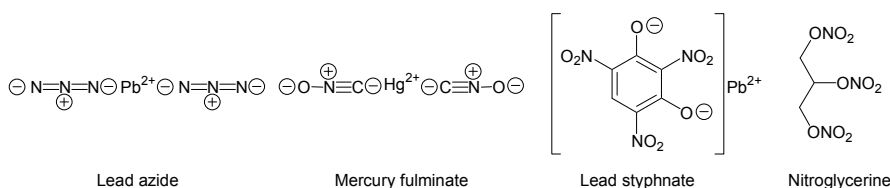


Figure 1. A selection of primary explosives

Nobel desensitised the highly sensitive nitroglycerine by mixing it with kieselguhr, a diatomaceous soil type found in the hills around Krümmel, the location of one of his factories. This process is also known as flegmatisation, or more humorously taming of the shrew. Flegmatisation with kieselguhr turned the primary explosive nitroglycerine into the secondary explosive dynamite. Once again, there is no clear-cut definition of the latter. One way to describe secondary explosives is that they include materials that can be initiated, *i.e.* made to detonate, by the use of practical quantities of primary explosives. Tertiary explosives, or blasting agents, can be described as products that can be initiated by the use of a booster, which is a charge of a secondary explosive. The most used blasting agent is ANFO (Ammonium Nitrate/Fuel Oil). The fuel is normally diesel oil or kerosene in commercial products, but any carbon source will do.

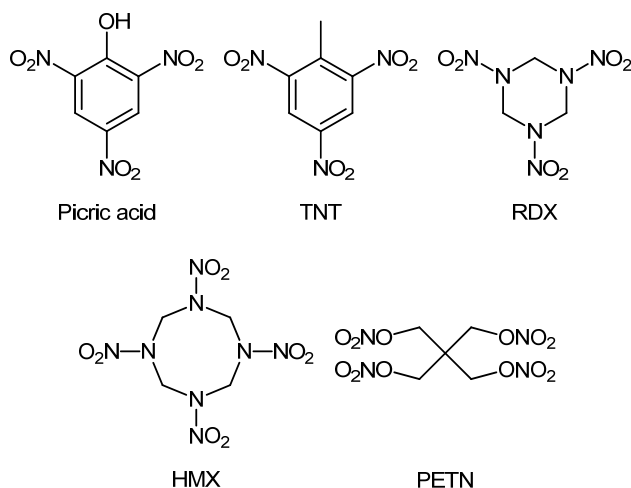


Figure 2. Common secondary explosives

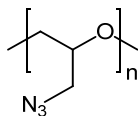
The most used secondary explosive is 2,4,6-trinitrotoluene (TNT). Other examples are picric acid, RDX, HMX, and PETN, see Figure 2. Picric acid was used in explosive charges in the late 19<sup>th</sup> and early 20<sup>th</sup> centuries.[3] It is highly acidic and forms salts with numerous metals, for instance the copper used in grenade shells. Picric acid itself is not very sensitive and can be handled safely. The salts on the other hand, are highly sensitive, which increases the risk for accidents. This was one of the reasons that picric acid was replaced by TNT before the Second World War. Another reason was that the production methods had to be sufficiently developed to allow production at low cost. This is true for most explosives. A compound can be a candidate to be an explosive as long as its density and energy content are sufficient. However, to come into practical use, its production must be cheap and simple. One example is RDX, which was first synthesised by Henning [4] in 1898 in Germany for medicinal applications. Herz [5, 6] patented its use as an explosive in the early 1920's, but it came into wide use only after extensive process development in the 1930's and 1940's. [7, 8]

The substitution of picric acid for TNT and RDX shows the two main trends in the development of new energetic materials. The first of these is the development of less sensitive substances. Lower sensitivity of an explosive charge does not only lead to safer handling, and thus fewer, or less severe, accidents; it also increases the survivability of ships, tanks and armoured vehicles. The explosive power carried by each so called platform is sufficient to destroy it completely, if the explosives are initiated. Unintentional ignition of ammunition should be impossible. The intentional ignition should follow a certain sequence and begin with a defined starting impulse in a so called ignition train. One way to attain these properties is the use of explosives with low sensitivity. The other trend is the development of energetic materials with higher performance. One reason is that higher detonation pressure will result in higher speed of metal shrapnels, which is crucial for their armour penetration capability. Another reason is higher energy density, *i.e.* more energy in a defined volume or weight. This could lead to longer range of a missile.





RDX and 40 % TNT (w/w). The RDX is added to increase the performance of the charge. A later example is Guntol, a mixture of TNT and FOX-12. This composition has very low sensitivity to mechanical stimuli. [14]



**Figure 5. Poly-glycidyl azide (GAP) - an example of an energetic binder**

The last example is plastic-bonded explosives (PBX). These charges contain a binder (a polymer, e.g. GAP, see Figure 5), a filler (an explosive, which can also be an oxidiser) and additives. Formulations of these components are prepared to obtain the desired properties of a charge. The aim of the additives is to enhance the performance as well as the mechanical properties of the PBX, in comparison with the current binders and/or plasticisers.

## 2 SYNTHESIS OF ENERGETIC PLASTICISERS

As mentioned above, a PBX contains a binder, a filler and additives. The inert binders, *e.g.* HTPB (hydroxy-terminated polybutadiene), currently in use have excellent mechanical properties. However, they contain little energy and require high solids loading, *i.e.* percentage of filler, to have a sufficient performance. The use of an energetic binder, *e.g.* GAP (poly-glycidyl azide), allows for lower solids loading, but many energetic binders have dissatisfactory mechanical properties. The polar groups in the molecular structure of these compounds render them increasingly viscous and elevate their glass transition temperatures. The rise in glass transition temperature downgrades the low temperature properties, which are especially important for missile propellants. The higher viscosity can result in processibility problems. Inert plasticisers, *e.g.* DOA (dioctyladipate), can be used to circumvent these problems, but the addition of an inert component will increase the demands on the solids loading. Therefore, energetic components are preferred. Hitherto, the known energetic plasticisers have inconveniences such as low thermal stability, low energy content, high migratory ability, and sometimes dissolution of the filler. The low thermal stability can be remedied with stabilisers, but finding a molecule that is stable as such is a very interesting area of research.

### 2.1 INTRODUCTION TO PLASTICISERS[15-17]

Plasticisation, in general, means a change in the thermal and mechanical properties of a given polymer and this effect can be achieved: (1) by compounding the given polymer with a low molecular weight compound or with another polymer: and (2) by introducing into the original polymer a co-monomer which reduces crystallisation and increases chain flexibility.

A plasticiser is usually defined in terms of the desired properties of a given polymer-plasticiser system. Thus, for coatings or films, it might be defined as a compound that gives flexibility, shock resistance, etc. For an elastomeric material a plasticiser changes the properties by reducing stiffness and permitting easier processing, *e.g.* milling, and mixing, or at least allows this at lower temperatures. For many moulded, extruded, and calendared plastics, it is a compound that imparts a desirable degree of flexibility over a broad range of use temperatures and lowers the temperature at which the material becomes brittle.

Unfortunately there seems to be no way at present to absolutely characterise the behaviour of a plasticiser in terms of some fundamental property. The reason is that the behaviour of a plasticiser is intimately tied up with the polymer to which it is added; moreover, properties of some polymers, in turn, depend greatly on their previous history (mainly semi-crystalline polymers). Whereas one can use molecular orbital calculations to predict, for instance, antioxidant behaviour (because oxidation involves electron transfer, and can therefore be put on a quantitative basis) there is no similarly well-defined quantitative description of the interaction with plasticisers.

There are two main groups of plasticisers: internal and external plasticisers. Internal plasticisers are actually a part of the polymer molecule, *i.e.* a second type of monomer is co-polymerised into the polymer structure, thereby making it less ordered, and therefore, more difficult for the chains to fit closely together. This softens the polymer, *i.e.* lowers the glass transition temperature ( $T_g$ ) or the modulus. The second monomer can either be incorporated in the main polymer chain or as side chains (substituents or grafted branches).

External plasticisers are the most important as far as commercial applications are concerned. The reason is that they provide more satisfactory combinations of properties

and allow the manufacturer more formulating flexibility than if the plasticiser were added during the polymerisation process. External plasticisers are compounds of low vapour pressure which, without chemical interaction, interact with the polymer, mainly at elevated temperature, by means of their solvent, or swelling power.

A distinction should be made between solvent plasticisers and non-solvent plasticisers. With an amorphous polymer, any plasticiser is a solvent plasticiser, i.e. under suitable conditions the polymer would eventually dissolve in the plasticiser. With a crystalline or semi crystalline polymer, there are some compounds, which enter both the crystalline (ordered), and the amorphous (disordered) regions. These are true plasticisers, sometimes being called primary plasticisers. If, on the other hand, only the amorphous regions are penetrated, the compound may be considered a non-solvent plasticiser, also known as a secondary plasticiser, or softener. Such softeners are used sometimes as diluents for the primary plasticiser.

Plasticisers represent a large family. There are more than 300 different plasticisers known, of which approximately one hundred are commercially produced - liquid, solid (low-melting), monomeric and polymeric. The majority of the commercial plasticisers is non-energetic and has been used and produced for a very long time. These have most often been used to plasticise non-energetic polymers. However, an example of a very old energetic polymer is nitrocellulose, which was plasticised with camphor to produce celluloid.

In general, non-energetic binders have excellent physical properties but they are inert, *i.e.* the binder dilutes the energetic composition, and reduces the overall energy output and the performance of the composition. To minimise the energy loss, one strategy is the use of fabrication methods, where the quantity of inert binder is kept low, *e.g.* axial pressing and extrusion. One problem with propellants and explosives produced by these methods is, however, that it is difficult to produce large items. Another problem associated with the large concentration of energetic filler within such an item is that it tends to be more sensitive. In order to produce larger items and less sensitive propellants and explosives cast-curing is preferred. Propellants and explosives produced with this method contain between 15-20% of binder. To maintain a high energy level in such a composition, the binder needs to be energetic. This is done by the inclusion of energetic functional groups, such as azido, nitro (C-nitro, O-nitro (nitrate esters) and/or N-nitro (nitramines)), and difluoroamino groups, along the polymer backbone and in the plasticiser. Incorporation of these functional groups increases the density of the polymer and thus the performance of the formulation, in addition to improving the overall oxygen balance.

### 2.1.1 Requirements on plasticisers[17]

An important reason for the difficulty in finding good energetic plasticisers is that the plasticiser is required for a number of different reasons. This places a large number of requirements on plasticisers, as shown in Table 1. Moreover, many of the properties are conflicting. For example, small molecules are good at lowering the glass transition temperature or reducing polymer viscosity. However, this is likely to give poor migration properties, as measured by diffusion rates or volatility. Similarly, a high energy contribution is often an important reason for choosing particular plasticisers, but this is often associated with poor hazard properties and stability. Compatibility issues can also be crucial. The choice for any particular application depends on which properties that are most important for that particular application, and is usually a compromise between different aspects.

**Table 1. Property requirements for plasticisers**

---

Plasticisation - lower $T_g$
Energy - often added to increase binder energy
Processing improvement - lower viscosity, increase solids loading
Migratory ability - diffusion, volatility
Chemical Compatibility
Chemical Stability - long term stability can be crucial
Hazard Properties - Sensitive materials inconvenient for processing
Availability
Cost
Purity
Toxicity

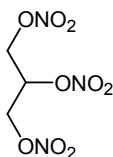
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## 2.1.2 Classes of Energetic Plasticisers

There is a large selection of different energetic plasticisers. These can be classified by the energetic moiety or moieties that they contain. In this section the different classes are briefly described and the most prominent members of each class illustrated.

### 2.1.2.1 Nitrate Esters

The first energetic plasticiser for commercial explosives was nitroglycerine (NG) or glycerol trinitrate, which is a high performance nitrate ester having the following structure:



**Figure 6. Nitroglycerine - a nitrate ester**

Major nitrate esters in use today include trimethylol ethane trinitrate (TMETN), triethyleneglycol dinitrate (TEGDN), ethyleneglycol dinitrate (EGDN or nitroglycol), and butanetriol trinitrate (BTIN). Being structurally similar to NG, they were developed to replace this material; most of these molecules possess some of NGs properties without the severe handling hazards of NG.

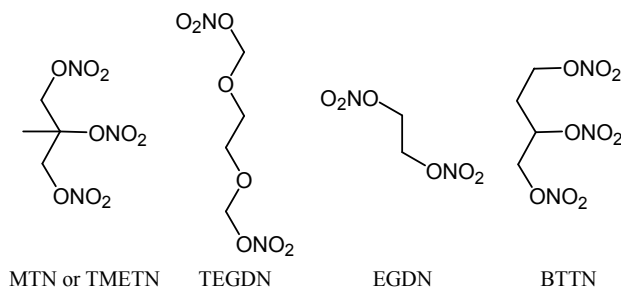


Figure 7. Example of nitrate esters used as plasticisers

The common drawback of nitrate esters is their propensity to autocatalytic decomposition. Therefore, munitions containing nitrate esters also require stabilisers in the formulations and monitoring of the properties of such formulations with time. Also, production hazards are well-known phenomena[18].

#### 2.1.2.2 *Gemdinitro*[17]

Plasticisers composed of bis(2,2-dinitropropyl)acetal (BDNPA) and bis(2,2-dinitropropyl)formal (BDNPF), developed in the USA, have found widespread application in energetic formulations there. BDNPA/F plasticisers are typically a 1:1 (w/w) mixture. BDNPF is a solid, whereas BDNPA is a liquid. A eutectic mixture of the two is used to lower the glass transition temperature of the formulation.

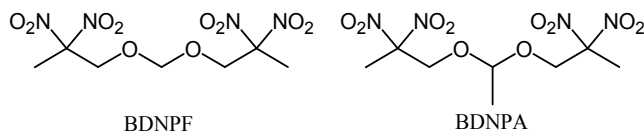


Figure 8. Plasticisers containing the *gem*-dinitro group

This composition, despite its extensive use in the USA, still has only limited applications, because of rather poor plasticising ability and, what is presumably more important, a very sophisticated production method.

#### 2.1.2.3 *Azido*[17]

Energetic plasticisers based on azido-acetate esters yield formulations with low  $T_g$ , good thermal stability and compatibility. Compounds described are ethylene glycol bis-(azidoacetate) (EGBAA), diethyleneglycol bis(azidoacetate) (DEGBAA), trimethylol nitromethane tris(azidoacetate) (TMNTA), pentaerythritol tetrakis (azidoacetate) (PETKAA). The general drawback of all these products is poor oxygen balance, relatively low density and also decreased enthalpy of formation, created by numerous carbonyls, which is only partly compensated by azido groups.

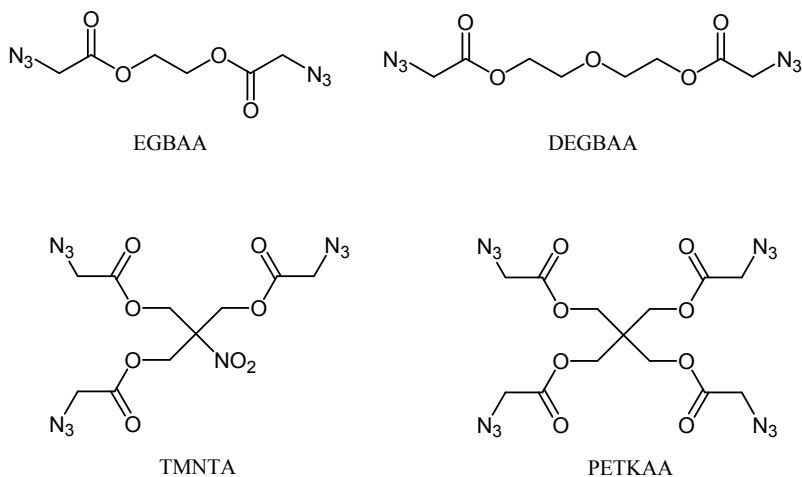


Figure 9. Plasticisers containing azido acetates

#### 2.1.2.4 Nitramine

Aliphatic nitramines, in the form of eutectic mixtures of 2,4-dinitrodiazapentane, 2,4-dinitrodiazahexane, and 3,5-dinitrodiazahexane (DNDA57)[19, 20], were suggested as a plasticiser for energetic binders in 1999. [21] This mixture, having good thermal stability and excellent plasticising ability, was shown to have rather high mobility in the polymer matrix.

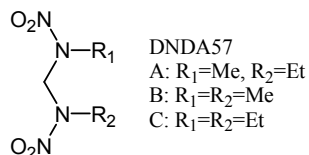


Figure 10. DNDA57 - a plasticiser containing a mixture of aliphatic nitramines

Moreover, the main draw-back of this, and possibly also other similar compositions, is their composite nature, creating long-term stability problems, due to different migratory ability of the ingredients. The exudation of one component could in extreme cases push the mixture out of its eutectic zone and thus increase the brittleness of a charge.

#### 2.1.2.5 Nitroaromatics[17]

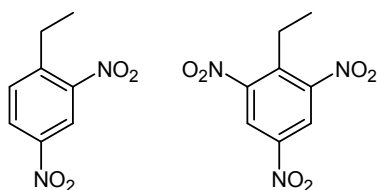


Figure 11. 2, 4-dinitro- and 2,4,6-trinitroethylbenzene - the two constituents of K10

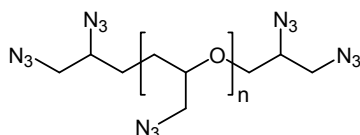
K10, also known as Rowanite 8001, is a nitro aromatic plasticiser consisting of a mixture of 2,4-dinitroethylbenzene and 2,4,6-trinitroethylbenzene (65%/35% w/w). 2,4-dinitroethylbenzene (DNEB) can be used as a plasticiser for good effect by itself[22].

Despite its excellent thermal stability and compatibility, Rowanite 8001 has only limited application, due to its poor oxygen balance (<-110 %) and a very high C/H ratio. The latter is undesired in propellant formulations, since it results in high average molecular weight of the combustion products.

#### 2.1.2.6 Oligomers[22]

Migration of the plasticiser is one of the major problems encountered with the use of energetic binder systems for explosive and propellant formulations. A recent approach has been to design plasticisers that resemble even more closely the polymer matrix, enhancing physical and chemical compatibility and, hopefully, minimizing migration.

Azide terminated glycidyl azide plasticiser (GAPA) is an oligomer of GAP having no reactive terminal hydroxyl groups which works as a plasticiser. GAPA is a liquid with low molecular weight, low  $T_g$  and good stability.

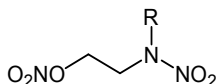


**Figure 12. GAPA - azide terminated GAP oligomer**

A strongly suspected serious draw-back of GAPA is its potential high sensitivity to mechanical stimuli, due to high loading of the structure by azido-groups<sup>B</sup>.

#### 2.1.2.7 Nitrate+nitramin[22]

The nitrooxyethyl nitramines (NENAs) are effective plasticisers in energetic formulations, particularly in nitrocellulose systems. NENAs contain both nitrate ester and nitramine functionalities



**Figure 13. General structure of NENA plasticisers**

The use of NENAs as plasticisers in gun and rocket propellants renders excellent properties such as high burning rates, reductions in flame temperature and low molecular weight of combustion products, and higher specific impulse. NENAs have good thermal stability, readily gelatinize nitrocellulose and other polymers, generate low molecular weight combustion gases, and have good impact sensitivity. While offering excellent initial plasticising effects, they are low molecular weight materials that are volatile and migrate readily from the polymeric binder system. Moreover, compatibility problems arising due to impurities in NENAs, has been observed. [23]

#### 2.1.2.8 Azide+nitramin

This combination of energetic ingredients has been considered. [24, 25] Properties such as high energy content, a wide range of burning rates and burning temperatures make them very attractive in the tailoring of the properties of composite propellants. However, it can be noted that the poor oxygen balance of these compounds considerably restricts their percentage in a propellant formulation. Moreover, one can expect both high volatility and migratory ability, given the relatively low molecular weight (150-250 g/mol) of the suggested candidates. [25]

<sup>B</sup> Personal experience in the research group



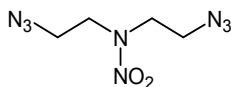


Figure 14. Typical example of an azide + nitramine plasticiser: DANPE

#### 2.1.2.9 Difluoramino

This is a relatively new type of energetic materials, which is also suitable for application as plasticisers. A typical example, 3,3-bis(difluoroamino)-1,5-dinitratopentane (BFDNP) appeared in an American patent. [26] The substance is presented as having high energy content and good plasticising properties. No other information could be found in the patent. Nonetheless, judging by the synthetic scheme, one can expect serious pollution problems in industrial scale production and an enormously high price for the product.

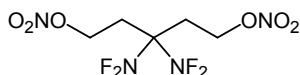


Figure 15. BFDNP

#### 2.1.2.10 gem-Dinitro + fluoro

An interesting compound in this series is the formal of 2,2-dinitro-2-fluoro-ethanol (FEFO), which was [27] suggested as a plasticiser in some formulations. This compound offers a very good set of properties for an energetic plasticiser. It has high density (1.60 g/cm<sup>3</sup>), good oxygen balance, excellent thermal stability etc. Unfortunately, it is a very poisonous compound<sup>c</sup>, causing severe skin irritation, which makes its use in a large scale seem dubious.

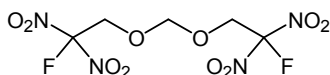


Figure 16. FEFO

#### 2.1.2.11 Selection of Target Molecules

As can be seen from this analysis, none of the available products can be considered as an ideal plasticiser, which is the reason to continue the research for new products, suitable for both explosive and propellant formulations. Since no reliable codes for the prediction of the properties of complex molecules – such as glass transition temperature and plasticising ability in different systems – are available to this date, our quest for new plasticisers was based on the analysis of the immense efforts of the scientists of the whole world in this area (*vide supra*).

Two main conclusions can be drawn from this analysis:

- Plasticisers, designed for propellants, may be structurally substantially different from those intended for explosive formulations. For explosive charges, the density is the most important factor, whereas the molecular weight of the combustion products – the lower, the better – is more important for propellants.
- Since different substituents impart different, or even sometimes contradictory, properties to complex molecules envisaged as potential plasticisers; it should be accepted that new plasticisers with good combination of properties are to be

<sup>c</sup> According to a colleague's personal communications with Russian researchers, there is no need to put such compounds into a charge. They are more effective as weapons if sprinkled over the enemy, even though this is against all conventions against chemical warfare.

tailored by the means of different functional groups, mentioned above. The introduction of different functional groups inevitably leads to multi-stage production methods and increased price for a new energetic plasticiser.

With these considerations in mind, our efforts were initially directed towards structures with *gem*-dinitro-, nitramine- and azido-substituents, since compounds with such groups in the structure are known for outstanding thermal stability and good compatibility with energetic materials.

## 2.2 RESULTS AND DISCUSSION

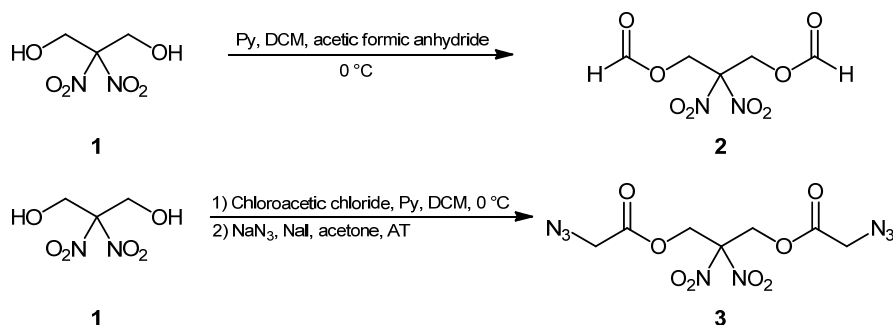
The first part of this chapter describes the efforts to synthesise energetic plasticisers based on dinitromethane. As mentioned above, a *gem*-dinitro carbon is a good oxygen carrier. Furthermore, dinitromethane is a by-product obtained in the production of FOX-7 [28, 29]. The dinitromethane is indeed a hazardous by-product, being thermally and chemically unstable, which has to be removed from the nitration mixture. A fruitful use of this compound would, besides providing plasticisers with good properties, reduce the production costs of FOX-7. My work in this area is described in Papers I and II.

An important criterion for an energetic plasticiser is its glass transition temperature. Even though unsymmetrical compounds generally have a lower melting point than symmetrical ones, the target molecules based on dinitromethane were all symmetrical. This was for the simple reason that it is very difficult to halt the reaction between a dinitromethane salt and for instance a Michael acceptor after only one addition. After the first such addition, the introduced chain acts as an en electron donor, which makes the product of the first step more reactive than the original dinitromethane salt.

### 2.2.1 2,2-Dinitropropane-1,3-diol and its derivatives

Other criteria are the heat of formation and the density of the plasticiser. In the beginning of this work, calculations were used to select suitable target molecules. There are methods to calculate these parameters for liquids [30] and solids [31], respectively. In my work to prepare plasticisers based on 2,2-dinitropropane-1,3-diol (**1**), see Scheme 1, the hypothesis that the latter method could be used also for liquids was evaluated, since the use of one single method for all substances would be simpler. This hypothesis proved to be erroneous, once the substances were characterised.

Furthermore, the experience of Wingborg *et al.* [32] showed that even symmetrical derivatives can have excellent low temperature properties. As **1** is unstable to bases in aqueous solution, pyridine (Py) in dichloromethane solution was used to derivatise this compound, see Scheme 1.



Scheme 1. Derivatisation of 2,2-dinitropropane-1,3-diol (**1**)

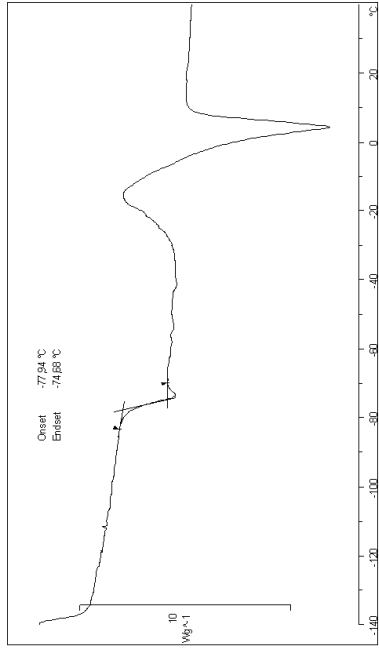


Figure 17. Glass transition temperature measurement of 2,2-dinitro-1,3-bis(formyloxy)propane

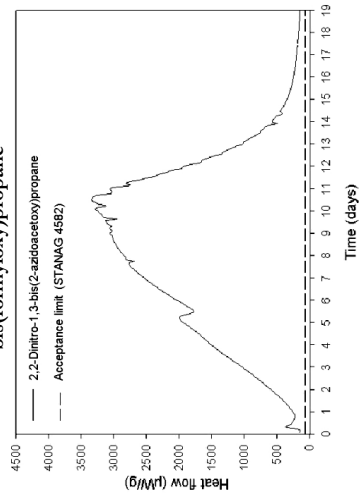


Figure 19. Heat flow calorimetry evaluation of 2,2-dinitro-1,3-bis(2-azidoacetoxy)propane at 75 °C

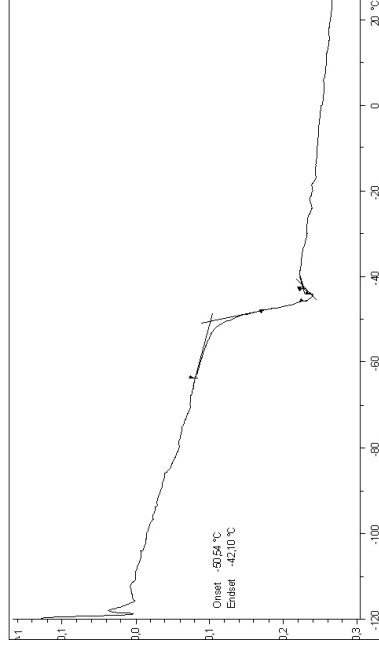


Figure 18. Glass transition temperature measurement of 2,2-dinitro-1,3-bis(2-azidoacetoxy)propane

The low temperature properties were evaluated with DSC and revealed that both compounds had excellent glass transition temperatures, -77 °C for the formyloxy compound **2** and -49 °C for the acidoacetoxy compound **3**, respectively. Though, heat flow calorimetry revealed that neither of these substances had sufficient thermal stability according to the requirements in STANAG 4582 [33], *i.e.* accelerated ageing at 75 °C for 19 days corresponding to ten years at 25 °C. It should be noted that this method is developed for the monitoring of the stability of nitrocellulose propellants and not for new energetic materials. However, treating the samples in this way will reveal autocatalytic decomposition or any other exothermal reaction. To avoid damage to the heat flow calorimeter, a sample is subjected to the same thermal regime in a standard metal heating block. Any discolouration or evolution of gas will disqualify the sample for more thorough evaluation in the heat flow calorimeter. This was the case of **2**, whereas **3** could be evaluated. The results showed that also this product was thermally unstable. Unfortunately, the images were misplaced in the printing procedure of Paper I. The correct graphs are shown below, see Figure 17-19.

### 2.2.2 3,3-Dinitropentane-1,5-diol

The discouraging results from the evaluation of the thermal stability of the esters of **1** reinforced the hypothesis that the close proximity of electron withdrawing groups might cause this undesired behaviour. The first step was to prolong the chain with one carbon on each side of the *gem*-dinitro carbon, *i.e.* to work with derivatives of 3,3-dinitro-1,5-pentanediol. Herzog *et al.* [34] prepared this compound *via* the Hunsdiecker reaction of 4,4-dinitropimelic acid (**4**) and further treatment to get the diol. Besides the fact that silver salts are expensive, it is also difficult to prepare sufficiently pure silver carboxylates for the Hunsdiecker reaction. In our hands, the reproducibility of Herzog's procedure was indeed low. The price of the chemicals involved and the trickiness of this reaction render it unsuitable for scale-up into industrial scale.

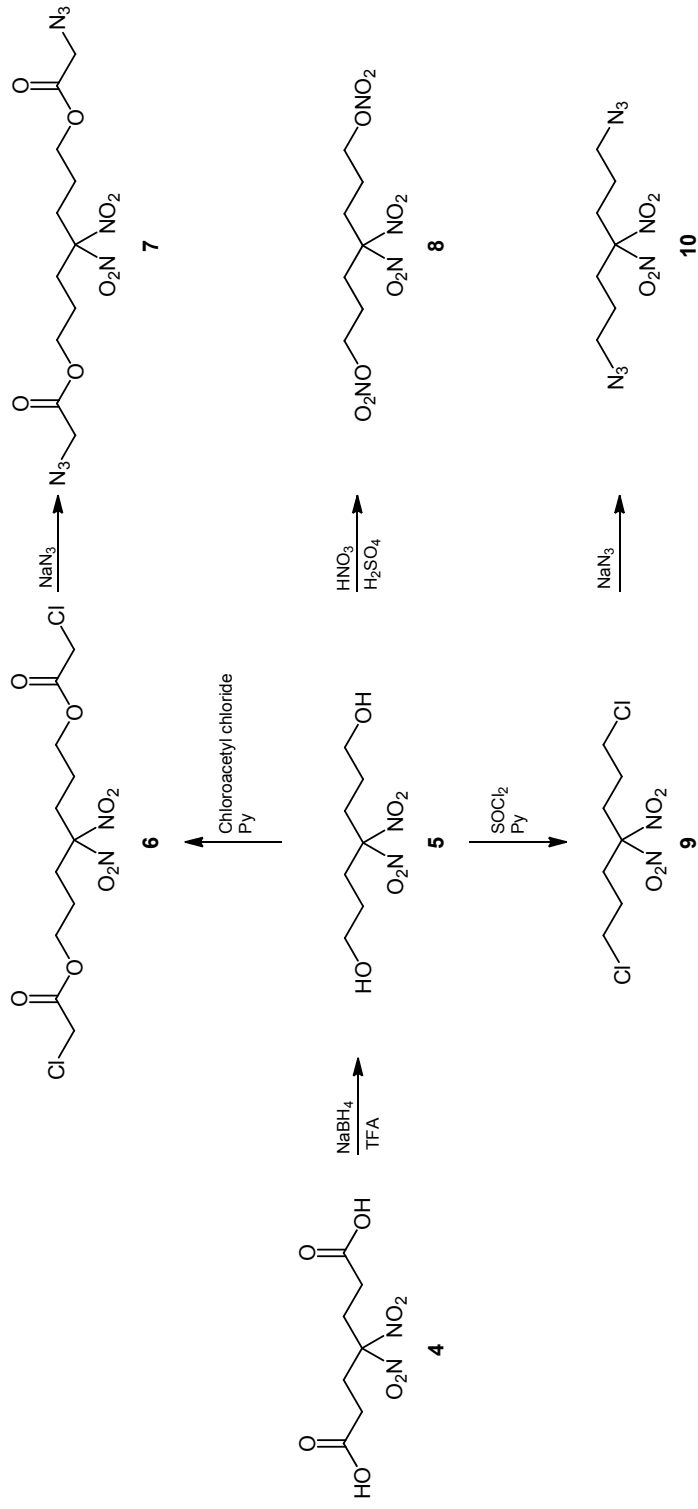
### 2.2.3 4,4-Dinitroheptane-1,7-diol and its derivatives

As Shevelev [35] showed, dinitromethane salts are very sluggish nucleophiles in alkylations with alkyl halides, even in a solvent such as DMF. This solvent is not suitable for scale-up, since it is toxic and difficult to recycle. Therefore, similar reactions were attempted in acetone. As all alkylations with different alkylating agent in this solvent failed, our efforts were then directed towards derivatives of the next diol in the series, *i.e.* 4,4-dinitro-1,7-heptanediol (**5**). The work on this substance and its derivatives is described in Paper II.

The mild conditions for the reduction of carboxylic acids into alcohols described by Suseela [36] were successfully applied on **4** to yield **5**. This compound was transformed into five different derivatives, out of which three were final products and two were intermediates, see Scheme 2.

Basic esterification of the diol with chloroacetyl chloride produced 4,4-dinitro-1,7-bis(2-chloroacetoxy)heptane (**6**), which was treated with sodium azide to provide 4,4-dinitro-1,7-bis(2-azidoacetoxy)heptane (**7**). This compound turned out to be a solid with a melting point of 83 °C and was not further evaluated as a plasticiser.

The case was the same for 4,4-dinitro-1,7-bisnitrooxyheptane (**8**), which was obtained by nitration of the diol **5**. This nitrate ester was a semi-solid with a melting point of 27-28 °C. Heat flow calorimetry showed that it, as expected for a nitrate ester, was thermally unstable.



Scheme 2. Derivatisation of 4,4-dinitro-1,7-heptanediol (5)

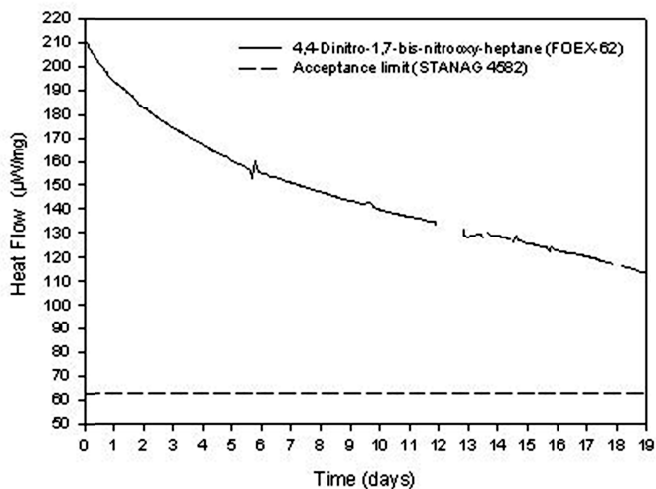


Figure 20. Heat flow calorimetry evaluation of 4,4-dinitro-1,7-bisnitrooxyheptane

After these discouraging results, the properties of 4,4-dinitro-1,7-diazidoheptane (**10**) were a breath of fresh air. The product was obtained by the reaction of the diol with thionyl chloride and pyridine to yield the intermediate 4,4-dinitro-1,7-dichloroheptane (**9**). The latter was treated with sodium azide to produce the desired product. DSC evaluation of this product revealed that it had an excellent glass transition temperature of -89.7 °C. Heat flow calorimetry evaluation of this compound according to STANAG 4582 showed that its thermal stability also was excellent, see Figure 21.

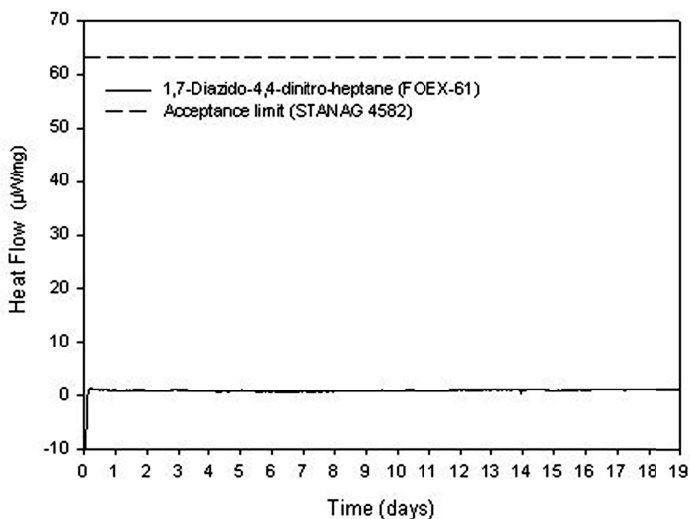


Figure 21. Heat flow calorimetry evaluation of 4,4-dinitro-1,7-diazidoheptane (**10**)

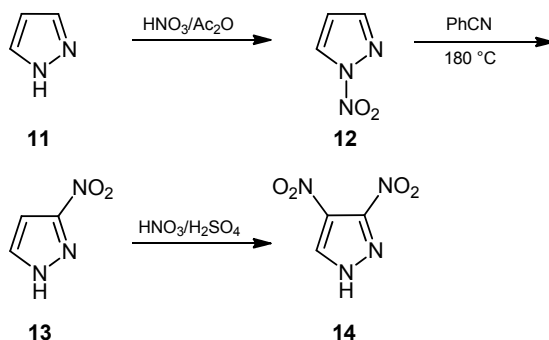
When **8** was reacted with sodium azide to produce **10**, the latter was indeed the major product. However, the purity was lower than in the synthesis via the chloro intermediate **9**. It seems that even trace amounts of water present in the last step caused hydrolysis of the nitrate ester.

The diazide **10** is a very interesting product. However, its synthesis cannot be scaled-up even into pilot plant scale in its present shape. The major obstacle is that it is too long with five steps. This would not be a problem for an expensive drug, but it is for an explosive. Five steps can be contrasted to one step for most of the nitrate esters and two steps for the NENAs [37]. Not only the number of steps is important, but also which steps that are required. In the synthesis of **10**, the reduction into the diol and the substitution in the last step must be developed to allow scale-up. The reduction produces hydrogen gas, which is risky unless proper safety measures are taken. The substitution is performed in DMSO, which is difficult to recycle. On the other hand, it is a waste of time and money to develop a perfect process prior to the evaluation of the properties of the product.

## 2.2.4 3(5),4-Dinitropyrazole and its derivatives

The complicated syntheses starting from potassium dinitromethane made us redirect our efforts towards supposedly simpler starting materials. My work on the synthesis of insensitive explosives is described, *vide infra*. This work included synthesis of different nitropyrazoles with the main goal to achieve a scalable synthesis of 4-amino-3,5-dinitropyrazole. However, one compound not included in that work proved to be an interesting and challenging starting material for energetic plasticisers, namely 3(5),4-dinitropyrazole.

As such, it could be interesting as a melt-cast explosive, since it has a melting point of 88 °C [38] and a decomposition temperature which is markedly higher (>300 °C). The development of an efficient synthesis of this product allowed investigation of the properties of some of its derivatives. This work is described in Paper III. The synthesis of 3(5),4-dinitropyrazole (**15**) was published by Janssen *et al.* in 1973 [38] in 58 % overall yield, see Scheme 3. Janssen's three-step procedure is a good chemical achievement, though it is unsuitable for larger scale synthesis.

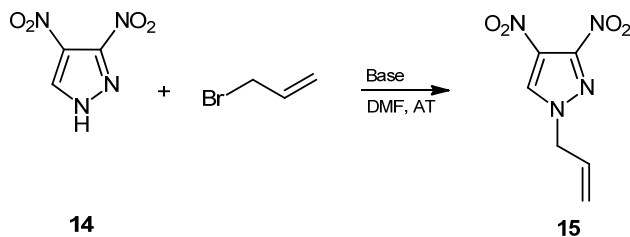


Scheme 3. Janssen's synthesis of 3(5),4-dinitropyrazole

The first intermediate (1-nitropyrazole, **12**) sublimates even at ambient temperature and atmospheric pressure. This explained the varying yield in my first attempts to synthesise this compound. Though, it must be dried prior to the thermal rearrangement into 3-nitropyrazole (**13**). An attempt to perform this rearrangement on the moist product obtained in the synthesis of **12** failed miserably, since the water hydrolysed the nitramine quicker than it could rearrange. Since the nitration of pyrazole (**11**) into **12** is performed

in acetic anhydride, which has a boiling point of 140 °C, the rearrangement was attempted in the nitrating mixture. However, the formation of water in the nitration produced acetic acid. This lowered the boiling point sufficiently to lower the rate of reaction sufficiently to prevent completion of the reaction within 48 hours. When the rearrangement was performed in the nitration mixture in a sealed vessel at 180 °C, the reaction was complete in four hours. The resulting suspension was diluted with water and evaporated to dryness. The residue was purified by nitration in mixed acids to produce **14** in 90 % total yield from pyrazole. Whether this is a one-pot or pseudo one-pot procedure is a matter of taste and depends on the reactors available. It should be noted that the *milieu* is very corrosive in the thermal rearrangement of **12** into **13**. So far, the only successful attempts were made in glass reactors. A Teflon bomb was used once, but this melted and wrought havoc to the heating system. When a steel reactor was submitted to the same treatment, the steel reacted with the reaction mixture. The reactor survived, but no product was obtained.

The use of **14** as the core of energetic plasticisers has several reasons: It has high energy, relatively high oxygen balance, excellent thermal stability and one acidic proton. The latter gives opportunities to derivatise it, which was the next step to obtain plasticisers. Methylation lowers the melting point to 20 °C for 1-methyl-3(5),4-dinitropyrazole, [39] compared to 88 °C for the parent compound. This is good, but not sufficient. On the other hand, allylation with allyl bromide and triethylamine in DMF, see Scheme 4, produced a liquid.



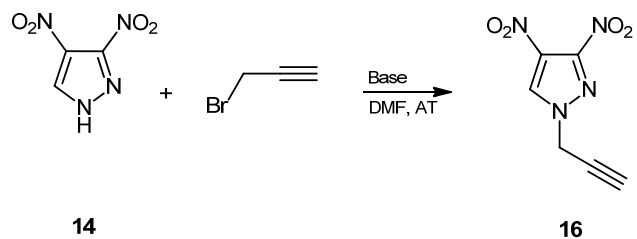
Scheme 4. Allylation of 3(5),4-dinitropyrazole into 1-allyl-3(5),4-dinitropyrazole (**15**)

DSC evaluation displayed that **15** had a decomposition temperature (onset) over 200 °C and a glass transition temperature of -72 °C. Repeated cooling and heating at controlled rates showed that the substance actually had a melting point of 5 °C, but that the cooling must be slow to give crystals in an ordered solid time to form. Rapid cooling produced an amorphous solid with the glass transition temperature stated above, *vide supra*. This behaviour has also been observed by Russian scientists<sup>4</sup> and is under current evaluation at FOI.

The same procedure was used to prepare 1-propargyl-3(5),4-dinitropyrazole (**16**), but propargyl bromide was used in this case, see Scheme 5. This substance turned out to be a solid with a melting point of 59 °C.

<sup>4</sup> Personal communications between Nikolaj Latypov and his former colleagues.





**Scheme 5. Propargylation of 3(5),4-dinitropyrazole into 1-propargyl-3(5),4-dinitropyrazole (16)**

Heat flow calorimetry evaluation of these two products showed now autocatalytic behaviour under the conditions stipulated in STANAG 4582[33].

## 3 SYNTHESIS OF EXPLOSIVES WITH LOW SENSITIVITY

### 3.1 INTRODUCTION

Nitroaromatics, such as picric acid and 2,4,6-trinitrotoluene (TNT), have been used as explosives throughout the last century. Nonaromatic explosives, mainly cyclic nitramines such as 1,3,5-triaza-1,3,5-trinitrocyclohexane (RDX) and 1,3,5,7-tetraaza-1,3,5,7-tetra-nitrocyclooctane (HMX) are also in use. The different classes of compound have their advantages and drawbacks, respectively. Compared to the nitramines, TNT has relatively low sensitivity to mechanic stimuli and thus to involuntary detonation, but relatively low oxygen content and heat of formation, which are important factors in the force of an explosive. RDX and HMX have higher energy and oxygen content, thanks to the carbons being replaced with nitrogen, but also higher sensitivity to mechanical stimuli.

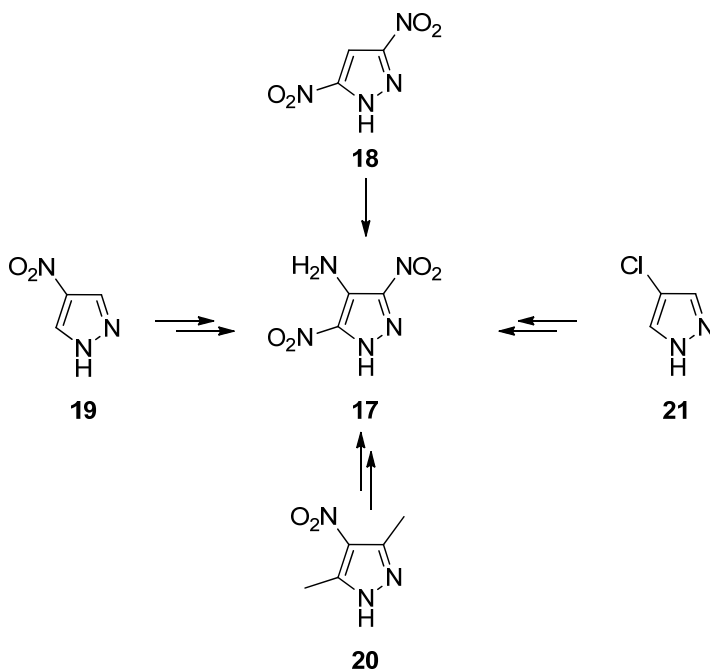
The combination of higher energy content and lower sensitivity is often desired. The former can be calculated [11-13, 31], whereas the latter is difficult to predict. Another way to phrase my scepticism against such calculations for a single substance is to compare to calculations of a lifetime of a person based on genetics. This will show the individual's potential for a long life or risk of premature death in comparison to a general population. However, the result of such a calculation will only be close to true for a person with a healthy lifestyle and the luck not to be involved in accidents or to contract diseases. Consequently, the calculations of sensitivity can be used as a relative guideline to avoid the worst substances. This is indeed the way that Cho *et al.* [30] use their calculation method. Though, the sensitivity of one specific sample cannot be predicted in a safe manner, even though such predictions have been attempted with the intent to reduce the heavy cost due to the extensive testing required by the REACH legislation. [40]

However, there are some features that seem to have a beneficial effect [41, 42]. One such is alternating electron donating groups and nitro groups, which can be found in energetic materials with low sensitivity, *e.g.* 1,3,5-triamino-2,4,6-trinitrobenzene (TATB)[43] and 1,1-diamino-2,2-dinitroethylene (DADNE, FOX-7)[44]. 5-Nitro-1,2,4-triazol-3-one (NTO)[45] is also a highly insensitive explosive, but it has no electron donating groups in its structure. Though, it has strong intermolecular hydrogen bonding, which appears to increase the stability towards thermal and mechanical stimuli. These inter- and intramolecular hydrogen bonds build up infinite flat or wavelike layers. These layers form a graphite-like structure, where the layers can slide on each other, since there are hydrogen bonds within the layers, but not between them. This sliding is a way to release energy, such as an impact, without breaking of any bonds. The latter would result in release of energy and possibly local overheating, which in turn could lead to initiation.

### 3.2 RESULTS AND DISCUSSION

#### 3.2.1 4-Amino-3,5-dinitro-1H-pyrazole

My efforts in the synthesis of potentially insensitive energetic materials are described in paper IV-V. The first of these deals with four different syntheses of 4-amino-3,5-dinitro-1H-pyrazole (**17**), see Scheme 6. Different syntheses of **17** are available in the literature[46-48], but they are all only suitable for laboratory scale.

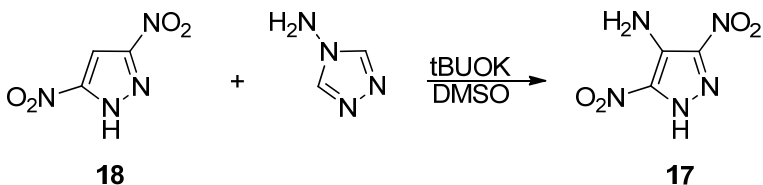


Scheme 6. A schematic view of the four syntheses of 4-amino-3,5-dinitropyrzazole

The heat of formation, the density and the performance of this product were calculated by the use of the method described by Jacob *et al.* [31]. The calculations suggested that it would have a performance slightly lower than that of RDX, but considerably higher than that of TNT. 4-Amino-3,5-dinitropyrzazole has alternating electron donating and electron withdrawing groups, which is the first of the two factors that seem to reduce the sensitivity. Schmidt *et al.* [48] investigated the 3D structure with X-ray crystallography and showed that the crystals are not constituted by infinite layers. Even though some data – *e.g.* pKa (3.42 [47]) and melting point (175-178 °C [49]) – were published, no information concerning the sensitivity towards mechanical stimuli was available. Once sufficient amounts to allow characterisation were obtained, it could be concluded that the sensitivity followed the trend of the performance, *i.e.* that it was slightly less sensitive to impact and shock than RDX. This can be contrasted to FOX-7, *vide infra*, which has the same performance as RDX, but markedly lower sensitivity. It thus seems that the 3D structure is indeed very important to the sensitivity.

#### 3.2.1.1 4-Amino-3,5-dinitropyrzazole via 3,5-dinitropyrzazole

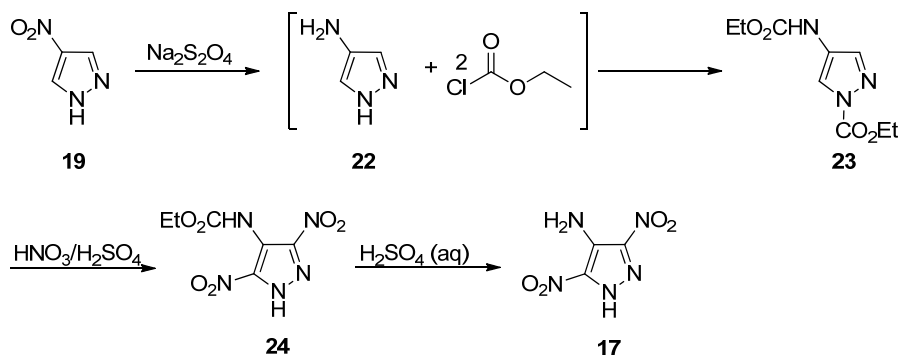
The first synthesis of **17** used 3,5-dinitropyrzazole (**18**) as its starting material, see Scheme 7. The synthesis looks deceptively short and efficient when drawn this way, since the four-step synthesis of **18** from pyrazole is omitted. [38] A very similar synthesis of **17** was published by Schmidt *et al.* [48] However, this group used trimethylhydrazinium iodide (TMHI) as the aminating agent. Besides not being commercially available, it is also highly toxic. Furthermore, the use of 4-amino-1,2,4-triazole also resulted in higher yield in this step (82 % in comparison with 67 % with TMHI). The modifications resulted in an overall yield of 21 % from pyrazole.



Scheme 7. 4-Amino-3,5-dinitropyrazole via VNS

### 3.2.1.2 4-Amino-3,5-dinitropyrazole via 4-nitropyrazole

The second synthesis of **17** started with 4-nitropyrazole (**19**), see Scheme 8, which was synthesised according to Hüttel *et al.* [50] through nitration of pyrazole in sulphuric acid. Reduction with sodium dithionite in basic, aqueous solution [51] produced 4-aminopyrazole (**22**), which had to be protected *in situ*, due to its propensity to oxidise in contact with air upon isolation.

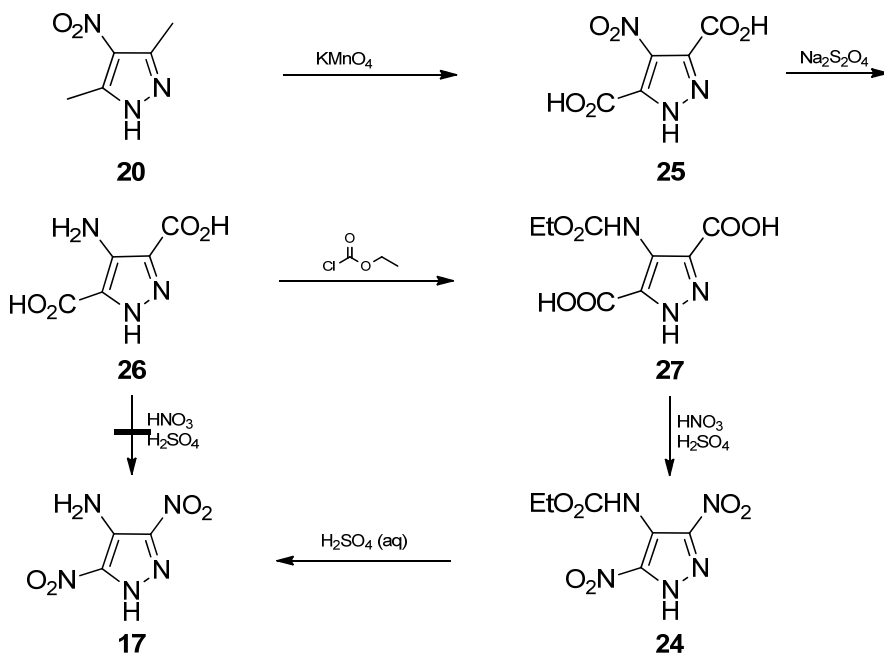


Scheme 8. 4-Amino-3,5-dinitropyrazole from 4-nitropyrazole

This reduction produces a lot of waste and can only be used on the laboratory scale. Product **23** was obtained once via catalytic hydrogenation of **19** over  $\text{Pd/C}$ , followed by protection *in situ*. The protection required concomitant addition of ethyl chloroformate and an aqueous solution of potassium hydroxide. This addition was too difficult to reproduce to allow its use in larger scale. Nonetheless, the work continued on the carbamate **23** obtained from dithionite reduction, followed by protection. Nitration of this carbamate produced 4-aminocarbonyloxy-3,5-dinitropyrazole (**24**), which was deprotected to yield **17**. The deprotection was first attempted in hydrochloric acid. This did indeed remove the protective group, but one or both of the nitrogroups were also substituted for chlorine. Deprotection in refluxing, aqueous potassium hydroxide solution also failed, whereas the reaction succeeded in 60 % aqueous sulphuric acid. The overall yield, from pyrazole into **17**, of this procedure was 40 %.

### 3.2.1.3 4-Amino-3,5-dinitropyrazole via 4-nitro-3,5-dimethylpyrazole

The main problem in this procedure is caused by the high sensitivity of **22** to air. One way to decrease its propensity towards oxidation is to have electron withdrawing groups on the ring, *e.g.* carboxylic acids. Another synthetic pathway based on this approach was developed, see Scheme 9.

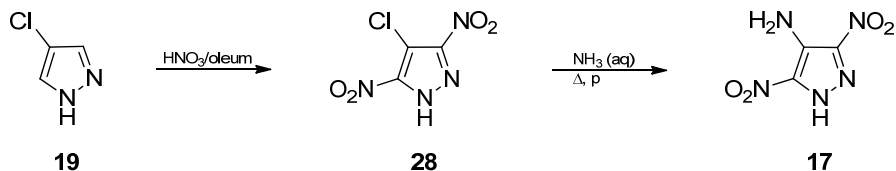


Scheme 9. 4-Amino-3,5-dinitropyrrole from 4-nitro-3,5-dimethylpyrrole

4-Nitro-3,5-dicarboxypyrazole (**25**) was prepared according to Latypov *et al.* [52] in two steps from 3,5-dimethylpyrazole (**20**). Reduction of this compound with the same dithionite method as described above produced 4-amino-3,5-dicarboxypyrazole (**26**), which was stable to air. Direct nitration of the latter was attempted, but to no avail. The unidentified products were bright red and probably arose from side reactions on the exocyclic amine. Protection of this amine, once again with ethyl chloroformate, produced 4-aminocarbethoxy-3,5-dicarboxypyrazole (**27**). Nitration of this compound in mixed acids produced **24**, *i.e.* the same intermediate as in the synthesis starting with 4-nitropyrrole. The same deprotection conditions could be used. The overall yield from 3,5-dimethylpyrazole to **17** was 37 %.

#### 3.2.1.4 4-Amino-3,5-dinitropyrrole from 4-chloropyrazole

None of the above syntheses are suitable for scale-up. However, the fourth synthesis is. This starts with the nitration of 4-chloropyrazole (**19**) into 4-chloro-3,5-dinitropyrrole (**28**), see Scheme 10. This product was subjected to nucleophilic aromatic substitution with ammonia at high temperature (130 °C) and pressure (15-20 atm).



Scheme 10. 4-Amino-3,5-dinitropyrrole from 4-chloropyrazole

The product from this reaction, *i.e.* the ammonium salt of the desired product, was recrystallised from acidic water to yield the hydrate of **17**, just as observed by Schmidt *et*

*al.* [48]. They removed the crystal water by recrystallisation from butyl acetate and heptane. This method proved difficult. Dissolution of the hydrate in ethyl acetate (solvent), addition of this solution to toluene (anti-solvent) and evaporation of the combined organic solution produced anhydrous **17**. The overall yield of this procedure was 52 % from **19**.

### 3.2.2 Conclusions

A detailed comparison of the four syntheses is given in paper IV. Table 2 shows the main points from this comparison.

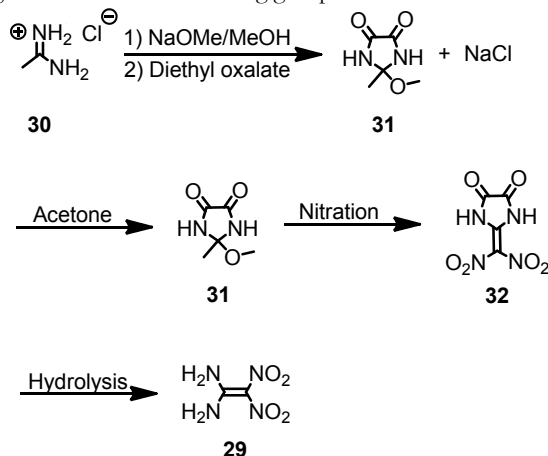
**Table 2. A brief comparison of the different synthetic procedures**

<i>Synthesis 1. Via 3,5-dinitropyrazole, see Scheme 7.</i>	<i>Synthesis 2. Via 4-nitropyrazole, see Scheme 8.</i>
Five steps Moderate amount of waste DMSO used in the last step Low overall yield: 21 % Average yield/step: 73 %	Four steps Moderate amount of waste No ill-favoured solvents required Moderate overall yield, 40 % Average yield/step: 80 %
<i>Synthesis 3. From 3,5-dimethylpyrazole, see Scheme 9.</i>	<i>Synthesis 4. From 4-chloropyrazole, see Scheme 10.</i>
Six steps High amount of waste No ill-favoured solvents required Moderate overall yield: 37 % Average yield/step: 85 %	Two steps Small amount of waste No ill-favoured solvents required Moderate overall yield: 46 % Average yield/step: 68 %

To conclude the study on **17**, it can be stated that four different syntheses of this product were developed and compared in terms of overall yield, number of steps, production of waste and price of the starting materials. One of them, namely the nitration of **19** followed by aromatic nucleophilic substitution with ammonia, was successfully transferred into small pilot plant scale. Batches of up to 200 g of the desired product could be obtained. **17** as such could be used as an explosive, or as a starting material for even more energetic and/or complex structures.

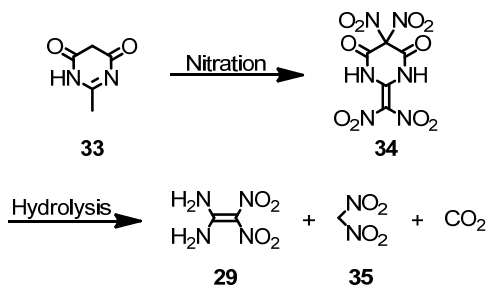
### 3.2.3 1,1-Diamino-2,2-dinitroethene (FOX-7, DADNE)

As mentioned above, FOX-7 (1,1-diamino-2,2-dinitroethene, **29**) is an explosive with very low sensitivity. It shows both features that seem to favour low sensitivity, *i.e.* alternating electron donating- and electron withdrawing groups and a 3D structure with layers. [42]



Scheme 11. Latypov's synthesis of FOX-7 from acetaminidinium chloride and diethyl oxalate

It was first synthesised by Latypov *et al.* in 1998 [44]. It has since attracted the interest of the research society for its high potential in diverse applications. This synthetic procedure to **29**, see Scheme 11, involved unstable intermediates and process steps that made it unsuitable for larger scale production. Another process, starting from 2-methylpyrimidine-4,6-dione (**33**), see Scheme 12, was presented by Astratev *et al.* [28] and optimised by Latypov *et al.* [29].



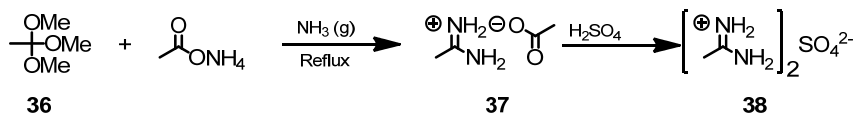
Scheme 12. Synthesis of FOX-7 from 2-methylpyrimidine-4,6-dione

This second procedure contains no steps that are directly unsuitable for scale-up. However, the tetranitro compound **34** obtained in the nitration is highly sensitive to mechanical stimuli. If it is isolated and dried, it is almost as sensitive as PETN, which means that it is close to being a primary explosive, *vide supra*. Its hydrolysis produces equimolar amounts of **29** and dinitromethane (**35**). The latter is thermally and chemically unstable and complicates the recycling of the spent acids, besides being risky to handle.

Therefore, it was interesting to study modifications of the original synthesis [44] to increase its suitability for production in larger scale. The combination of the use of acetaminidinium sulphate or acetate instead of the corresponding hydrochloride and neutralisation of the condensation mixture with sulphuric acid removed the tedious

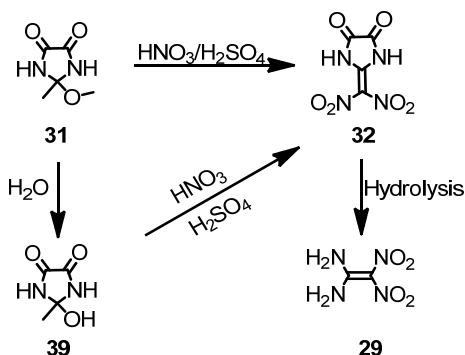
Soxhlet extraction from the procedure. The sodium sulphate that formed in this process is insoluble in the methanol used in the reaction and could be removed by filtration. However, the crystals were very small and the filtration required the use of the filtering aid Celite™. This is acceptable for desk scale and one kilogram of **29** was produced this way. Though, filtering aids must be avoided in industrial scale production. The work on **29** is presented in Paper V.

There are different ways to synthesise acetamidinium salts. The commercially available acetamidinium chloride used in Latypov's [44] original synthesis of **29** is obtained through a Pinner synthesis, where acetonitrile is treated with hydrogen chloride gas in an alcohol. The obtained imidoester is then treated with ammonia to produce the desired acetamidinium chloride. The rising price of acetonitrile and the problems involved in the handling of hydrogen chloride made us look deeper into the procedure of Taylor [53], who prepared acetamidinium acetate (**37**) and formate by reacting orthoacetates with ammonia in the presence of ammonium acetate or formate, respectively. For the synthesis of the acetate, see Scheme 13. Ion exchange provided acetamidinium sulphate (**38**). As mentioned above, either **37** or **38** could be used in the synthesis of **31**.



Scheme 13. Synthesis of acetamidinium salts

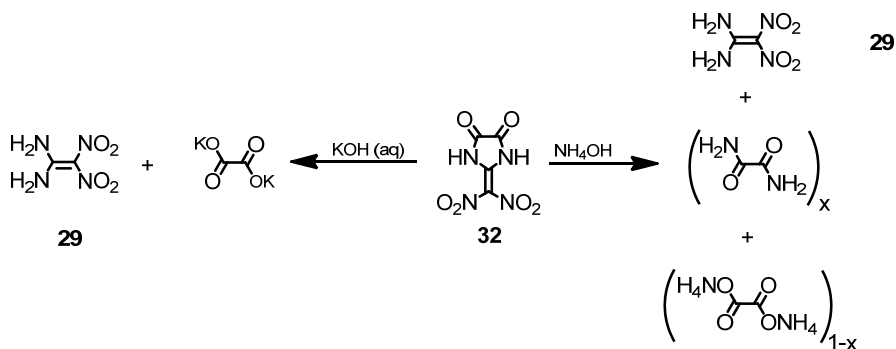
One of the problems in the original synthesis actually provided the solution. Our research group and others had observed that compound **31** was stable for an extended time only when stored in a dessicator with a drying agent. The first product in its hydrolysis is **39**, which could be obtained under gentle conditions. The product of its further hydrolysis has not been identified. Once obtained, **39** is stable to storage in air and could be nitrated into 2-dinitromethylideneimidazolidine-4,5-dione (**32**), which is the same intermediate as obtained from **31**, see Scheme 14.



Scheme 14. Synthesis of FOX-7 via 2-methoxy- (**32**) or 2-hydroxy-2-methylimidazolidine-4,5-dione (**39**)

The hydrolysis of **32** was further studied to avoid the problems with oxamide formation encountered when ammonia is used in this step. Potassium hydroxide was the base of choice to bring about the hydrolysis, thanks to the relatively high solubility of potassium oxalate.

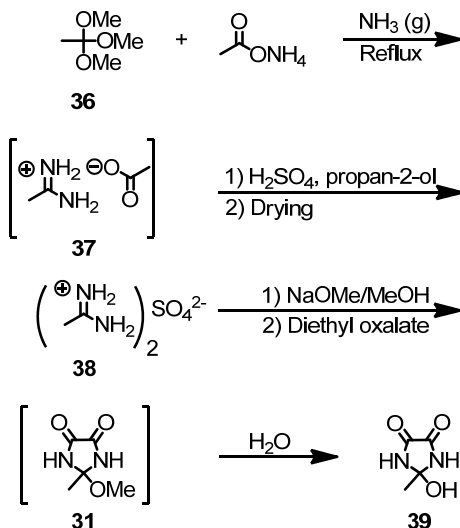




Scheme 15. Hydrolysis of 2-dinitromethylideneimidazolidine-4,5-dione (**32**) with different bases.

The pH must be monitored throughout the procedure. If it is too low, hydrogen potassium oxalate will precipitate and contaminate the **29**. Too high pH will lead to loss of product, since **29** is weak acid with a pKa of 11. [54]

The hydrolysis of **31** into **39** is still not fully understood. It is catalysed by acid and proceeds smoothly at pH 4-7. No product was obtained under basic conditions. Furthermore, attempted hydrolysis in an acetate buffer (pH 4.7) failed completely. An unidentified by-product was obtained. Even trace amounts of acetic acid seem to induce this side reaction. The hydrolysis of **31** into **39** was only occasionally reproducible when **31** prepared from **37** was used. Though, the synthesis was perfectly reproducible with **31** prepared from **38**. To our delight, it was possible to obtain **39** in a pseudo-one pot synthesis from **36**, see Scheme 16.



Scheme 16. Pseudo one-pot synthesis of 2-hydroxy-2-methylimidazolidine-4,5-dione (**39**) from trimethyl orthoacetate (**36**)

The work on the synthesis of acetamidineum salts described above is interesting regardless of the choice of starting material of **29**. As pointed out above, the presence of acetate ions will prevent the successful hydrolysis of **31** to **39**. The presence of chloride ions in **31** or **39** will cause the nitration into **32** to fail. In the case of **33**, acetamidineum

chloride works excellently and any traces of chloride can be washed off with water. When the same condensation was attempted with acetamidinium acetate, no product was obtained. The presence of acetate ions instead lead to a pink, porous solid, whose structure was not studied, but it was probably the result of a polymerisation.

#### **3.2.4 Conclusions**

It can be concluded that synthesis of **29** via **39** should be possible to scale up into at least pilot plant scale, since it has no unfavourable process steps. However, much work remains before this is done. Scale-up is an art of its own and it can spring many surprises that are difficult to predict from lab-scale syntheses. Though, this work should be done as soon as there is funding, since the increased safety and potentially lower price is beneficial to an existing and quite successful product.

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