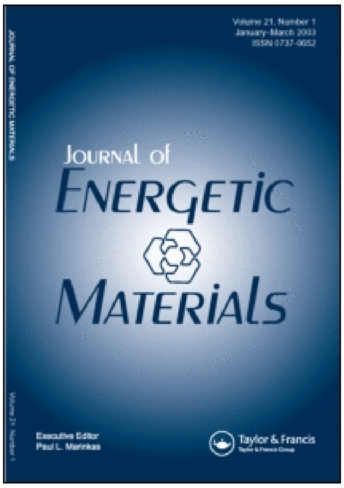

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Recent approaches to the synthesis of high explosive and energetic materials: A review

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RECENT APPROACHES TO THE SYNTHESIS OF HIGH EXPLOSIVE AND ENERGETIC MATERIALS: A REVIEW

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ABSTRACT

The synthesis of energetic materials over the past 10-15 years has been reviewed. The areas in which most activity has occurred embrace six different classes of compounds: polynitroaliphatics, dinitrofluoromethyl compounds, difluoramines, azido compounds, polynitroaromatics and heterocyclic compounds. Each class is treated within a single section covering the synthesis of the basic "building-block" materials, the strategies for transforming these into the final products and the scope and limitations of the reactions carried out. Most of the literature covered deals with new compounds but new or improved syntheses of compounds already known to possess useful properties are also described. Finally, developments in the prediction of explosive properties from molecular structure/composition are dealt with more briefly.

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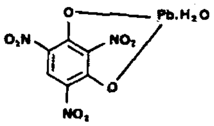
INTRODUCTION

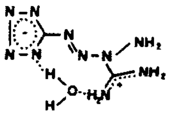
Military high explosives are conventionally categorised as primary, secondary and tertiary explosives on the basis of their sensitivities and uses. Primary explosives are the most sensitive to mechanical and electrical initiation and are used in small quantities in the initiatory segment of explosive trains, ie, in detonators and fuzes. Typical examples are lead azide, lead styphnate and tetrazene. Secondary explosives are less sensitive (but generally more powerful) and are used as the main explosive filling in bombs, shells and other munitions, as well as in commercial applications. Common examples are nitroglycerine (NG) (in formulations such as dynamite), 2,4,6-trinitrotoluene (TNT) and cyclotrimethylenetrinitramine (RDX). Tertiary explosives are even less sensitive yet still energy-rich materials; they are not generally regarded as explosives, but can detonate under

$Pb(\dot{N}=\dot{N}=\dot{N})_2$

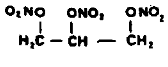
LEAD AZIDE



LEAD STYPHNATE

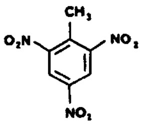


TETRAZENE

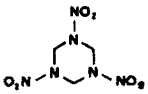


$$\begin{matrix} O_2NO & ONO_2 & ONO_2 \\ | & | & | \\ H_2C & -\ CH\ - & CH_2 \end{matrix}$$

NG



TNT



RDX

certain conditions. The usual example is the fertilizer ammonium nitrate (AN) which forms the basis of most explosives used in the mining and construction industries.

Since the First World War explosive fillings for shells and bombs have been based on TNT, eked out at that time by the inclusion of AN to give the amatols. The major development of the Second World War was the incorporation of RDX into TNT to give the more powerful cyclotols, of which Composition B (RDX/TNT/Beeswax 60/40/1) is the most common. The vast majority of explosive fillings for military use by all countries are still of this type, sometimes with aluminium added to enhance blast and underwater effects. The sensitivities and performances of these compositions are well documented and well understood. It should not be inferred, however, that cyclotols are the ideal fillings. Such explosive compositions are weak, brittle materials subject to cracking, and are prone to exudation and dimensional instability in response to thermal cycling. Furthermore, the explosive performance and insensitivity of Composition B are only adequate for use in shells for the current generation of guns, and appear to be at best marginal for use in the newer high performance/high velocity large caliber guns in which the larger set-back forces on firing increase the probability of premature detonations. Alternatives to RDX/TNT compositions include pressed or extruded explosives, which consist of explosives such as RDX with a binder/desensitiser, and polymer bonded explosives (PBX's) which consist of explosive materials suspended in a matrix of binder which is cured in situ. While these compositions overcome some of the deficiencies of melt-cast RDX/TNT, they have practical limitations of their own, particularly in the areas of cost and ease of processing. Even if satisfactory alternatives to the melt-cast RDX/TNT technology were available, a likely estimate for the time to introduction into service stores would be 20 years. As a result efforts are constantly being made to improve the performance, sensitivity and material properties of existing RDX/TNT formulations.

In parallel with this developmental approach directed towards modification of the properties of existing formulations, considerable attention has been devoted to the synthesis of new energetic compounds with the potential to overcome the shortcomings of the traditionally used materials. Earlier workers largely used ad hoc approaches in selection and synthesis of new candidate materials based on their knowledge of existing compositions. The synthesis of new explosive materials in this way generated an increasing data base which ultimately enabled enunciation and proof of structure/property relationships. Exploitation of these relationships coupled with computer codes to predict explosive properties (such as detonation velocities) from molecular structure has led to the development of new explosives, propellants and energetic binders.

In this report, the synthesis of energetic materials over the last 10-15 years has been reviewed. In particular, our aim has been to elucidate recent trends and to assess what classes of compounds have provided the most promising candidate explosives. The major concern of this review is with secondary explosives because they are the most common explosives, in terms of sheer bulk, used in military applications.

GENERAL DISCUSSION OF APPROACHES TO SYNTHESIS OF NEW ENERGETIC MATERIALS

It has long been recognised that the presence of certain atomic linkages such as N=O, N=N and O-Cl conferred potential explosiveness and, by analogy with the chemical theory of colour, such functional groupings were dubbed explosophores. Taylor, in the first modern review of explosive materials[1], identified four classes of explosive compounds:

(i) compounds containing nitrogen-oxygen bonds, which included nitrates and nitric esters, nitroaliphatics and nitroaromatics

(ii) peroxides and ozonides

(iii) chloroderivatives including chloroamines and oxychloroacids and their salts

(iv) self-linked nitrogen compounds including hydrazines, nitramines and azo, diazo and azido compounds

A further class may be added from the results of more recent research:

(v) fluoroderivatives including difluoramines and fluoronitro compounds.

The best general sources of information on the explosive properties and chemistry of specific compounds contained in these five classes of materials can be found in the three volume set by Urbanski[2] and the "Encyclopedia of Explosives and Related Items" from Picatinny Arsenal (now ARRADCOM)[3].

The principal objective of research into new energetic materials is the synthesis of new compounds with increased explosive performance (ie increased available energy), reduced sensitivity to stimuli such as impact and shock, and/or enhanced chemical and thermal stability. The explosive performance of a compound is a thermodynamic property and should primarily depend on the number and type of explosophores present. If this were the only criterion for selection, principal attention would be centred on building more explosophores into existing molecular frameworks. However, sensitivity and stability are kinetic properties in that they depend largely on the weakest bond in the molecule; this bond need not (but usually does) form part of the explosophore(s) but may well be influenced electronically or sterically by its (their) presence. Thus the factors which increase the explosive performance often also increase sensitivity and decrease stability so that a compromise must often be reached.

In the period between about 1950 and 1965 the principal research goal was increased explosive performance. A very large number of trinitromethyl [R-C$(NO_2)_3$] and related compounds, which were considered at that time to be the most promising class of new high explosive molecules, were synthesised during this period. However, though certainly energetic, most of these materials tended to be far too sensitive for practical application. Attention has subsequently been directed towards materials such as dinitrofluoromethyl derivatives [R-CF$(NO_2)_2$] which have somewhat lower explosive performance but much decreased sensitivity compared with the corresponding trinitromethyl compounds. Considerable effort was also devoted to the synthesis of hexanitrobenzene. This compound proved to have both high density and high velocity of detonation, but rather poor chemical stability.

Another area of considerable interest has been explosives of enhanced thermal stability. Rates of thermal decomposition may be as much as 50-100 times faster in the melt or solution than in the solid state at comparable temperatures, due to enhanced molecular mobility. One approach to the synthesis of thermally stable explosives has therefore been to prepare compounds of ever-increasing molecular weight (and therefore increasing melting point); in general these compounds have been polynitro polycyclic aromatics. Another approach has been to consider intrinsically more stable heterocyclic ring systems substituted with nitro and/or picryl (2,4,6-trinitrophenyl) groups, while a third avenue has been the synthesis of compounds stabilised by the presence of resonance structures or by inter- and intramolecular hydrogen bonding in the crystal lattice. Since initiation by mechanical stimuli such as impact and friction is a thermal process, these thermally stable explosives also tend to be relatively insensitive.

This review is set out in two sections. The principal section is a discussion of the synthesis of new energetic materials, and new or improved syntheses of materials already known to have useful properties. This section is subdidivided into six parts, representing the six classes of materials in which the most intense activity has occurred or which have provided the most promising candidate materials: polynitroaliphatics, dinitrofluoromethyl compounds, difluoramines, azido compounds, polynitroaromatics, and heteroaromatic and heterocyclic compounds. No specific part has been allocated to nitramines or nitrate esters: although such materials have been studied extensively throughout this century, most materials which have been synthesised recently incorporate other explosophores and examples of these can be found throughout the six principal parts. The second and shorter section is a discussion of research on the prediction of explosive properties from molecular structure/composition.

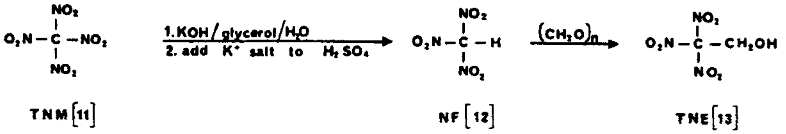
In general no attempt has been made to indicate explosive properties of specific compounds but we have tried to give a general feel for the properties of specific classes of materials. Earlier review articles in 1971[4] and 1974[5] have been useful but they have been of quite limited scope. A comprehensive review of the reactions involved in explosive synthesis[6] has also been useful. Biannual reports in "Reports on the Progress of Applied Chemistry"[7] usually provide an adequate coverage of recent literature, particularly patents. Some partial duplication of these earlier review articles has been unavoidable for the aim of giving an overall impression of the process of development over the entire field.

CLASSES OF ENERGETIC MATERIALS

Polynitroaliphatics

The general approach of increasing the energy content of existing structural units has led to the synthesis of a very large number of polynitroaliphatic compounds. A number of these materials display promise as explosives, propellants or energetic binders although the sensitivity is in general too great for practical use. The most intense period of activity on this class of compounds occurred before 1965 and has largely been covered by a symposium proceedings in 1963[8] and a subsequent review article[9]. The synthesis of trinitromethyl compounds was reviewed in 1970[10]. Although activity on this class of energetic materials has diminished in favour of more promising materials, there has still been a substantial number of new compounds reported over the last decade and examples shown below were chosen mainly from this data. Not all reaction types are described: a complete listing can be obtained from references[8-10].

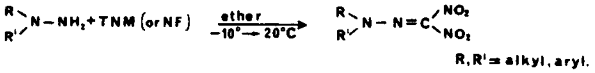
The synthesis of polynitroaliphatic compounds can be achieved by two basic strategies. In one approach, small highly nitrated molecules are added to suitable substrates to construct larger molecules containing a number of nitro groups. An alternative method involves the stepwise nitration of a built-up skeleton initially containing some nitro groups to ultimately yield a highly nitrated system. The first approach has been by far the most widely used and requires, as the basic building blocks, tetranitromethane (TNM)[11], trinitromethane (or nitroform, NF)[12] and 2,2,2-trinitroethanol (TNE)[13]. NF and TNE are synthesised successively from TNM as shown in scheme 1. TNE can also be synthesised directly from TNM without isolation of NF [14].



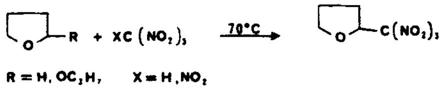
$$C(NO_2)_4 \xrightarrow[\text{2. add } K^+ \text{ salt to } H_2SO_4]{\text{1. KOH/glycerol/}H_2O} (O_2N)_3C\text{-}H \xrightarrow{(CH_2O)_n} (O_2N)_3C\text{-}CH_2OH$$

(1)

TNM has limited synthetic uses. Condensation with hydrazines to form dinitromethylhydrazones (scheme 2)[15] and reaction with tetrahydrofuran and related substrates by a radical process to give α-trinitromethyl derivatives (scheme 3)[16] are two recent examples. However both these reactions can be achieved with NF.

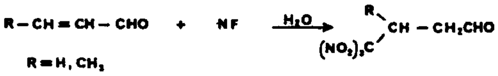


(2)



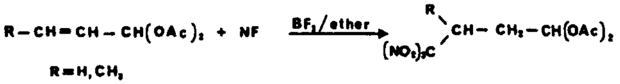
(3)

NF is sufficiently nucleophilic to add directly to a wide range of substrates and sufficiently acidic that an acid catalyst is not normally required. Examples of such additions are the Michael reactions to unsaturated aldehydes (scheme 4)[17] and esters (scheme 5)[18]. Addition to the unsaturated acylals shown in scheme 6 required BF_3 as a catalyst[17]. The attempted addition to ketene failed because the ketene reacted with acetone prior to NF addition (scheme 7)[19].

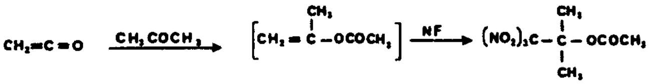


(4)

(5)

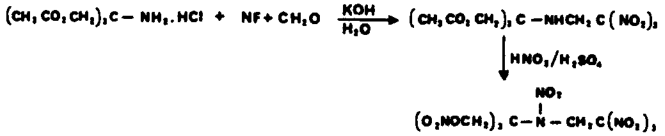


(6)

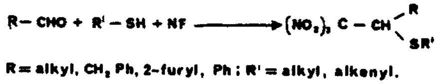


(7)

The nucleophilicity and acidity of NF are ideal for the Mannich reaction which has been used extensively[8-10]. A recent example can be seen as the first step in the preparation of the nitramine tris(nitric ester) shown in scheme 8[20]. A related reaction is the condensation of NF with aldehydes in the presence of thiols to give trinitromethyl sulfides (scheme 9)[21].

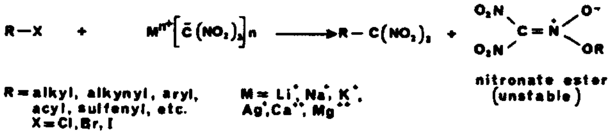


(8)



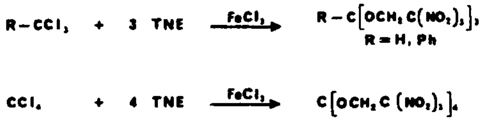
(9)

Reactions of salts of NF with electrophilic reagents have been studied extensively[22-25]. Reaction can occur either at carbon or oxygen, the latter course giving unstable nitronate esters (scheme 10). The preference for attack at carbon or oxygen is dependent both upon the particular metal salt and the electrophilic reagent. For example, silver[22,23] and magnesium salts[24] largely give nitronate esters while potassium, sodium and lithium salts favour reaction at carbon[22]. Alkylation[22] and reaction with sulfenyl halides[25] usually occurs at carbon while acylation[24] occurs on oxygen.



(10)

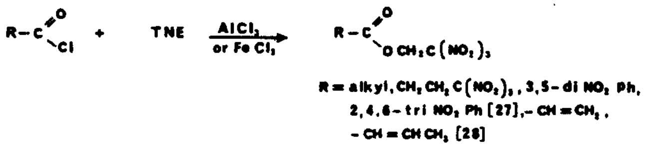
The main area of experimental interest has been compounds prepared from TNE. TNE readily condenses with halides[26] and acid chlorides[27,28] in the presence of Lewis acid catalyst (schemes 11, 12). Reaction with bis(acid chlorides) proceeds similarly to give diesters[27,28].



$$R{-}CCl_3 + 3\ TNE \xrightarrow{FeCl_3} R{-}C[OCH_2C(NO_2)_3]_3 \quad R = H, Ph$$

$$CCl_4 + 4\ TNE \xrightarrow{FeCl_3} C[OCH_2C(NO_2)_3]_4$$

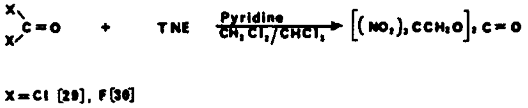
(11)



$$R{-}COCl + TNE \xrightarrow[\text{or } FeCl_3]{AlCl_3} R{-}COOCH_2C(NO_2)_3$$

(12)

TNE condenses readily with phosgene[29] or carbonyl fluoride[30] in the presence of pyridine to give bis(2,2,2-trinitroethyl)carbonate (scheme 13). However if sodium fluoride is employed as the base, reaction with carbonyl fluoride affords the fluoroformate which can be further reacted with SF_4 to the trifluoromethyl ether (scheme 14)[30].



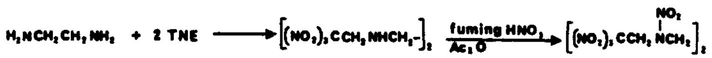
$$X_2C{=}O + TNE \xrightarrow[CH_2Cl_2/CHCl_3]{Pyridine} [(NO_2)_3CCH_2O]_2C{=}O$$

X=Cl [29], F[30]

(13)

$$F_2C{=}O + TNE \xrightarrow[100\ psi]{NaF} (NO_2)_3CCH_2OCOF \xrightarrow[90°,700psi]{SF_4/HF} (NO_2)_3CCH_2OCF_3 \qquad (14)$$

TNE also condenses with amines, an example of which can be seen in the first step of the bis(nitramine) preparation detailed in scheme 15[31].



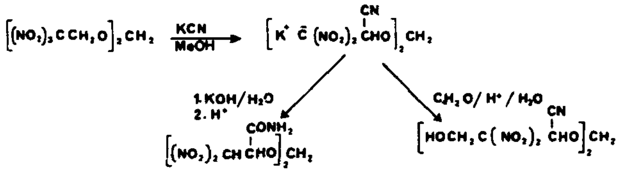
$$H_2NCH_2CH_2NH_2 + 2\ TNE \longrightarrow [(NO_2)_3CCH_2NHCH_2{-}]_2 \xrightarrow[Ac_2O]{\text{fuming } HNO_3} [(NO_2)_3CCH_2N(NO_2)CH_2{-}]_2$$

(15)

Treatment of trinitromethyl compounds with potassium iodide followed by acidification produces the corresponding dinitromethyl derivatives (scheme 16)[32]. An interesting variation can be seen in scheme 17, where bis(2,2,2-trinitroethyl)formal reacted with KCN to give bis(1-cyano-2,2-dinitroethyl)formal which could be further hydrolysed to the diamide or reacted with formaldehyde to give the hydroxypropyl derivative (scheme 17)[33].

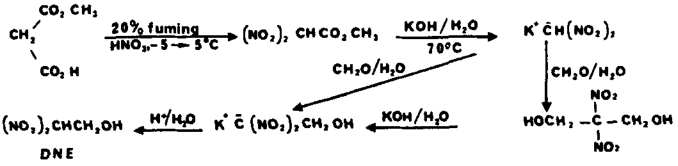
$$R-CH_2C(NO_2)_3 \xrightarrow[H_2O]{KI} RCH_2\bar{C}(NO_2)_2\,K^+ \xrightarrow{H^+} R-CH_2CH(NO_2)_2 \qquad (16)$$

$R = H, CH_2NO_2, CH_2COCH_3, CH_2COPh, CH_2CONH_2$



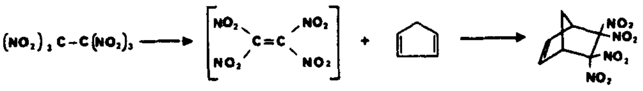
(17)

Terminal dinitromethyl derivatives can also be prepared from 2,2-dinitroethanol (DNE). An improved synthesis of the key intermediate, the potassium (or sodium) salt of dinitromethane, has recently been reported (scheme 18)[34]. This salt is readily converted to an extremely useful compound, 2,2-dinitropropan-1,3-diol[14,35] and thence to DNE[35], or directly to DNE[34] (scheme 18). DNE undergoes an analogous series of reactions to TNE[9].



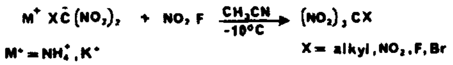
(18)

Another reagent which has recently been reported is tetranitroethene[36], presumed to be generated in situ when hexanitroethane[14] is reacted with dienes. The reaction with cyclopentadiene is shown in scheme 19. The reagent also reacts with anthracenes[36].



(19)

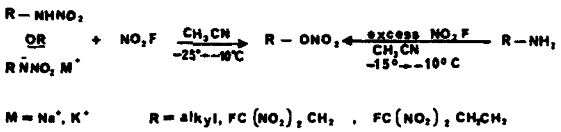
The alternative approach of building up polynitroaliphatics has not often been used due to the lack of a general procedure for conversion of dinitromethyl groups to trinitromethyl groups. A brief summary of earlier methods such as the Ter Meer reaction and nitration with TNM can be found in earlier references[9,10]. One reagent which has shown promise is nitroxylfluoride (NO_2F) which readily nitrates substituted dinitromethyl salts to trinitromethyl compounds (scheme 20)[37,38]. In contrast, reaction of NO_2F with nitramines yields the corresponding nitrates by rearrangement (scheme 21)[37,39]. This same result can be achieved directly from the amines using two mole equivalents of NO_2F[39]. Bis(nitramines) react correspondingly to give the bis(nitrate esters)[37,39].



$$M^+ X\bar{C}(NO_2)_2 + NO_2F \xrightarrow[-10^\circ C]{CH_3CN} (NO_2)_3CX$$

$M^+ = NH_4^+, K^+$ $\quad$ $X = \text{alkyl}, NO_2, F, Br$

(20)

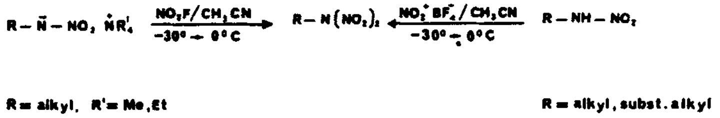


$$\begin{matrix} R-NHNO_2 \\ \underline{OR} \\ R\bar{N}NO_2\,M^+ \end{matrix} + NO_2F \xrightarrow[-25^\circ\to-10^\circ C]{CH_3CN} R-ONO_2 \xleftarrow[\substack{CH_3CN \\ -15^\circ\to-10^\circ C}]{\text{excess } NO_2F} R-NH_2$$

$M = Na^+, K^+$ $\quad$ $R = \text{alkyl}, FC(NO_2)_2CH_2, FC(NO_2)_2CH_2CH_2$

(21)

N-Nitration of nitramines can be effected with NO_2F by using nitramine salts of bulky tetraalkyl ammonium cations (scheme 22)[40] but the products, N,N-dinitramines, are more readily synthesised by reaction of nitramines with nitronium tetrafluoroborate (scheme 22)[41]. Methyldinitramine, synthesised accordingly, has been shown to be an efficient reagent for conversion of primary aliphatic nitro compounds to the corresponding gem-dinitro derivatives, isolated as the potassium salts (scheme 23)[42]. The interesting coupling reaction shown in scheme 24 is also initiated by methyldinitramine[42].



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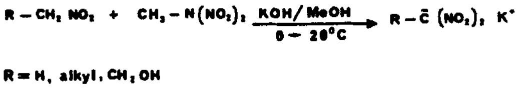

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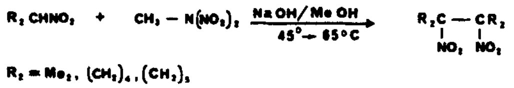
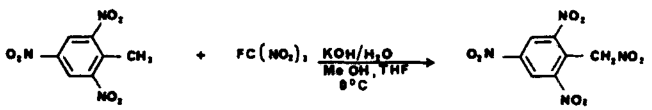


(24)

Fluorotrinitromethane has also been used to nitrate potassium 2,4,6-trinitrobenzylide to the α-nitro derivative (scheme 25)[43].

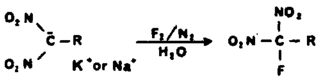


(25)

Dinitrofluoromethyl Compounds

Kamlet[44] proposed in 1959 that the (unacceptably) high sensitivity of trinitromethyl compounds resulted from restriction of rotation about the individual C-NO_2 linkages. This is the bond most likely to be broken in the rate-determining step to initiation. Kamlet's proposal was based on the knowledge that concentration of energy within a particular molecular fragment leads to a distribution of energy between bonded atom vibrations and rotations. Thus when rotational modes are restricted, more energy goes into the potentially bond breaking vibrational modes and processes beginning with bond breaking are more likely. Kamlet predicted that the replacement of one nitro group by the much smaller fluorine atom would substantially decrease the C-NO_2 rotational barrier, hence ease of bond breaking and consequently sensitivity would be substantially decreased. Furthermore, since the fluorine atom bestows quite a high energy content on molecules in which it forms a part, a $-CF(NO_2)_2$ compound should be only slightly less energetic than its $-C(NO_2)_3$ analogue. Kamlet's prediction has been verified from data for the many hundreds of dinitrofluoromethyl compounds which have been synthesised over the last 10-15 years. Kamlet and Adolph[45] have recently reviewed the performance characteristics of this class of energetic materials.

Two basic strategies have been used for the synthesis of dinitrofluoromethyl compounds. One approach has been the preparation of the corresponding trinitromethyl or dinitromethyl compounds, conversion to the dinitromethyl anion (see scheme 16) and subsequent fluorination. The usual fluorination reagent is a dilute stream of fluorine in nitrogen. A very large number of dinitrofluoromethyl compounds have been prepared using this procedure, which has been named the Grakauskas Reaction[46]. A selection of examples can be seen in schemes 26 and 27.



$$(O_2N)_2\bar{C}-R \;\; K^+ \text{ or } Na^+ \xrightarrow[H_2O]{F_2/N_2} O_2N-\underset{F}{\overset{NO_2}{C}}-R$$

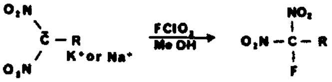
R = H [34], alkyl [47], $CH_2CH_2CO_2Me$,
CO_2Et, OMe, [48], $CH_2C(NO_2)_2CH_2OMe$,
$CH_2C(NO_2)_2CH_2OAc$ [48], 4-NO_2-, 3-NO_2-,
2,4-diNO_2-, 2,4,6-triNO_2Ph [49], CN [50]

(26)

$$\left[(NO_2)_2\bar{C}CH_2\right]_2 X.2K^+ \xrightarrow[H_2O]{F_2/N_2} \left[(NO_2)_2CFCH_2\right]_2 X \qquad (27)$$

X = -OCH_2O- [46,51] —NHCONH— [46]

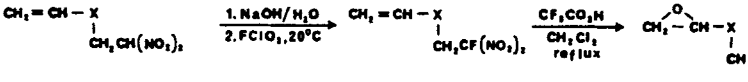
Perchloryl fluoride ($FClO_3$) has also been used as a fluorination reagent, but much less extensively because of its lower reactivity and the hazardous chlorate byproducts which hinder product isolation. Some examples of syntheses using this reagent are shown in scheme 28. The lower reactivity of $FClO_3$ can be used to advantage for fluorination of substrates containing functional groups which would react with fluorine. The lack of reaction with double bonds is of particular interest and has been exploited in the epoxide synthesis shown in scheme 29[54].



$$(O_2N)_2\bar{C}-R \;\; K^+ \text{ or } Na^+ \xrightarrow{FClO_3 / MeOH} O_2N-\underset{F}{\overset{NO_2}{C}}-R$$

R = NO_2, H [52], alkyl, Ph [46,52],
CH_2Ph, $CH_2CH=CH_2$ [52], CN, $CONH_2$,
CONHEt, CH_2CH_2COMe etc [53]

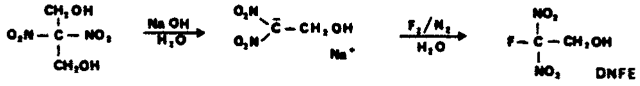
(28)



(29)

X = CH_2, CH_2O

The alternative synthetic approach is to build up larger energetic compounds by the addition of small molecules containing the dinitrofluoromethyl group. The most widely used reagent of this category is 2,2-dinitro-2-fluoroethanol (DNFE) which can be synthesised from a variety of precursors. The usual procedure is to react 2,2-dinitropropan-1,3-diol[14,35] (see scheme 18) with aqueous sodium hydroxide then fluorinate the resulting anion (scheme 30)[47]. An alternative synthesis is fluorination of NF[46] or its sodium salt[47] to fluorotrinitromethane and condensation with formaldehyde in the presence of alkaline hydrogen peroxide (scheme 31)[46]. Although fluorotrinitromethane can be synthesised by reaction of TNM with potassium fluoride (scheme 31)[55], such displacement reactions appear to be of limited synthetic utility.



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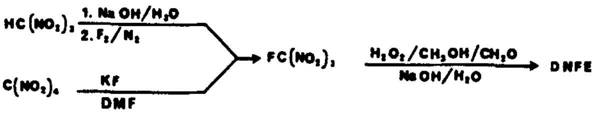
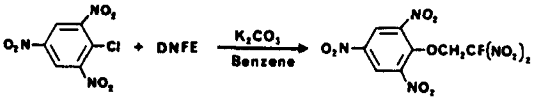


(31)

DNFE will react with an extremely wide range of substrates. It readily undergoes nucleophilic displacement and condensation reactions; examples include reaction with alkyl chlorides in the presence of $FeCl_3$ catalyst (scheme 32)[56] and reaction with picryl chloride (scheme 33)[57].

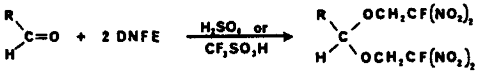
$$HCCl_3 + 3\,DNFE \xrightarrow{FeCl_3} HC[OCH_2CF(NO_2)_2]_3$$

$$CCl_4 + 4\,DNFE \xrightarrow{FeCl_3} C[OCH_2CF(NO_2)_2]_4 \qquad (32)$$



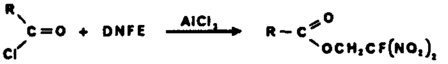
(33)

Substrates which will undergo condensation reactions with DNFE include aldehydes, which give formals as products (scheme 34), acid chlorides in the presence of $AlCl_3$ to give esters (schemes 35 and 36) and isocyanates where the products can be further nitrated to more energetic derivatives (scheme 37)[59]. DNFE does not readily esterify directly with carboxylic acids, but this problem can be overcome by initially reacting with chlorosulfonic acid to give 2,2-dinitro-2-fluoroethanesulfate (scheme 38)[61]. This intermediate readily reacts with carboxylic acids, and their salts, esters, anhydrides and acid chlorides to give esters[62].



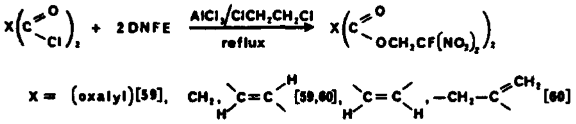
R = H [51,57], CCl3, CF3, CO2H [58]

(34)



R = CH3, SO2Ph, 3,5-di NO2Ph, 2,4,6-tri NO2Ph [57]

(35)



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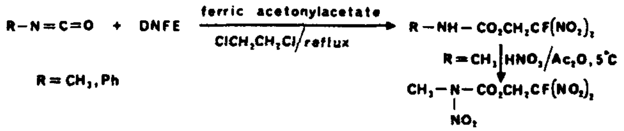
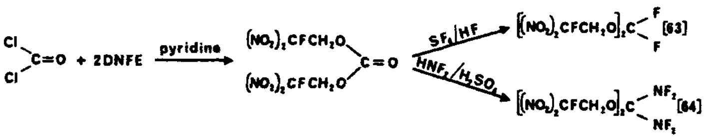


(37)

$$\text{DNFE} + \text{ClSO}_3\text{H} \xrightarrow{10^\circ-40^\circ\text{C}} (\text{NO}_2)_2\text{CFCH}_2\text{OSO}_3\text{H} \qquad (38)$$

DNFE readily condenses with phosgene in the mole ratio 2:1 to give the explosive bis(2,2-dinitro-2-fluoroethyl)carbonate[63] which can subsequently be converted to the bisfluoro[63] and bis(difluoramino)[64] derivatives (scheme 39). However under carefully controlled conditions equimolar quantities react to give 2,2-dinitro-2-fluorochloroformate[65] which is an intermediate for the preparation of a further series of energetic materials (scheme 40)[65,66].



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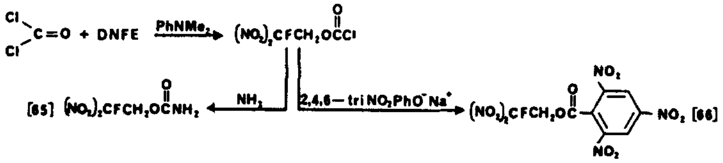
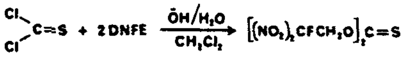


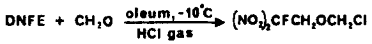
(40)

Thiophosgene also condenses with DNFE to give the thioncarbonate which is a useful explosive (scheme 41)[67].



(41)

The condensation between DNFE and formaldehyde is another reaction of great potential. In conc. H_2SO_4, the reaction product is the substituted formal (scheme 34, R=H), but at -10°C under conditions of chloromethylation using gaseous HCl, the chloromethyl ether results (scheme 42)[51]. This very useful intermediate reacts with a wide range of nucleophiles including alcohols (scheme 43)[51,68] and metal salts (scheme 44)[69].



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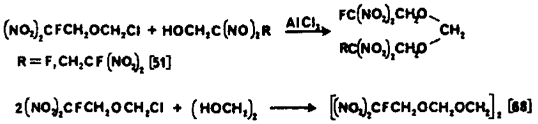

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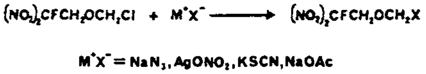
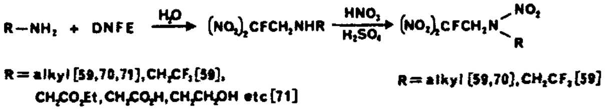


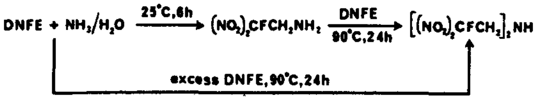
(44)

One of the most active areas of research has been the reaction of DNFE with amines to give 2,2-dinitro-2-fluoroethanamine derivatives which can often be further functionalised to more energetic materials. Examples of the preparation of such compounds, including further nitration to nitramines, can be seen in scheme 45[59,70,71].



(45)

Reaction of DNFE with aqueous ammonia affords either 2,2-dinitro-2-fluoroethanamine, a rather unstable, hazardous material, or the more stable bis(2,2-dinitro-2-fluoroethan)amine, depending upon the reaction conditions (scheme 46)[57]. Tris(2,2-dinitro-2-fluoroethan)amine is prepared by fluorination of the dipotassium salt shown in scheme 47[72]. The N-nitro-bis(amine) can also be prepared by this procedure (scheme 47, $R=NO_2$)[72].



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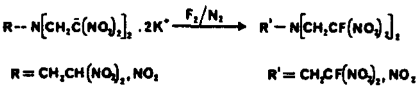
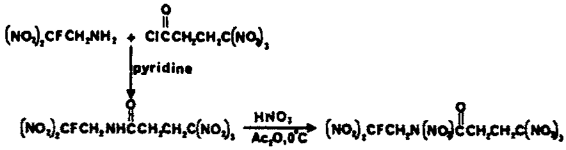


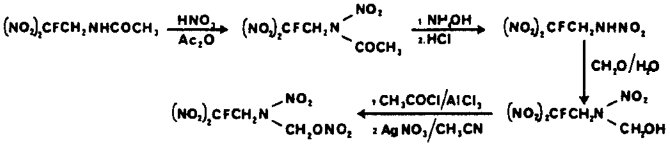
(47)

Both mono- and bis(2,2-dinitro-2-fluoroethan)amine are relatively unreactive but can be induced to form amides under forcing conditions. An example of acylation of the mono(amine) can be seen in scheme 48; the amide product can be further nitrated as shown[73]. Amides of the bis(amine) are prepared by reaction with the appropriate acid in trifluoroacetic anhydride[74].



(48)

Acetylation is used in the first step of the preparation of 2,2-dinitro-2-fluoroethylnitramine (scheme 49)[75], which cannot be prepared by direct nitration of the amine. This nitramine undergoes formylation readily and the product can be further transformed to the nitrate ester (scheme 49)[75]. In contrast, the bis(amine) readily nitrates directly[72] as well as nitrosating to the interesting N-nitroso explosive[76] which can subsequently be oxidized to the nitramine (scheme 50).



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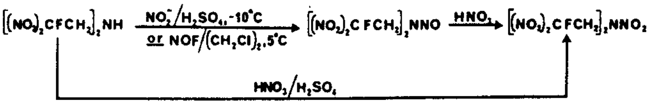
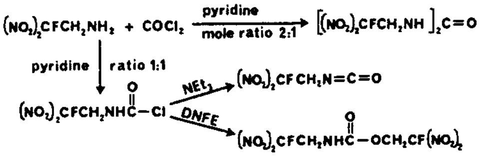


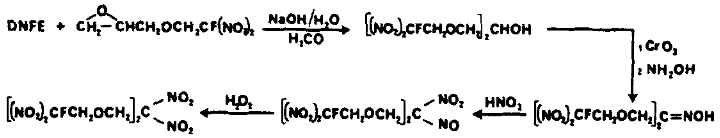
(50)

2,2-Dinitro-2-fluoroethanamine condenses with phosgene to give either the urea, a promising explosive, or the carbamoyl chloride as products (scheme 51)[77]. The latter can be further reacted to carbamates or the isocyanate, from which can be prepared other energetic materials (scheme 51)[77].



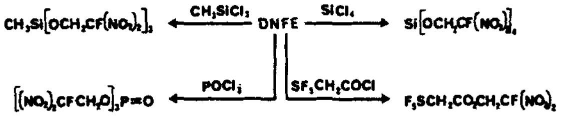
(51)

DNFE undergoes addition to epoxides in the presence of formaldehyde. A good example can be seen as the first step of the sequence depicted in scheme 52[78]. Note the last step of the sequence where the oxime initially reacts with HNO_3 to give the nitro-nitroso compound which is subsequently oxidized to the final product with H_2O_2[78].



(52)

Other energetic compounds of potential use which have been prepared from DNFE include silicates[79], the phosphate[80] and the pentafluorothioacetate[81] (scheme 53). 2,2-Dinitro-2-fluoroethanthiol, which is prepared from DNFE via the triflate (scheme 54), has shown promise as a propellant additive[82].



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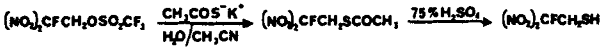
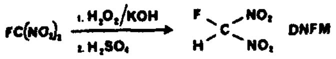


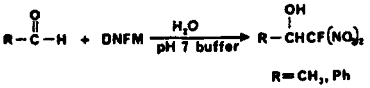
(54)

Another building block which has been used with some success for constructing larger molecules containing dinitrofluoromethyl groups is dinitrofluoromethane (DNFM). DNFM can be most easily synthesised by fluorination of potassium dinitromethanide (see schemes 18 and 28)[34] or alternatively from fluorotrinitromethane (scheme 55)[46] or DNFE[57].



(55)

DNFM readily adds to aldehydes (the Henry reaction) to form stable adducts (scheme 56)[83], in marked contrast to NF where TNE (from formaldehyde, scheme 1) is the only stable addition compound. This is believed to result from the very poor stability of the $\overline{C}F(NO_2)_2$ ion formed in the reverse reaction, while the $\overline{C}(NO_2)_3$ ion is much more stable[83]. Addition to α,β - unsaturated aldehydes and ketones (scheme 57)[84] and esters (scheme 58)[18] occurs preferentially at the β-carbon.



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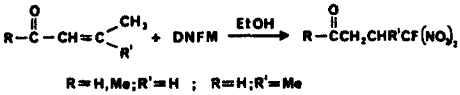

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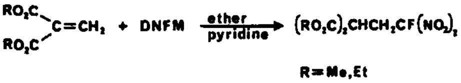
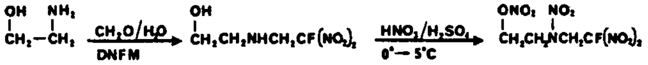


(58)

DNFM will also undergo a Mannich condensation with amines in the presence of formaldehyde, depicted as the first step in scheme 59. This product can subsequently be nitrated to the nitramine-nitrate ester[85]. Bis(2,2-dinitro-2-fluoroethan)alkylamines can be prepared by reaction of DNFM with the correpending bis(alkoxyethan)amines (scheme 60)[86].



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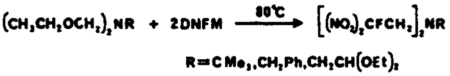
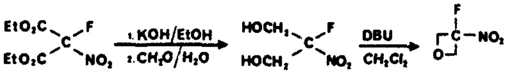


(60)

A compound which has recently been reported is 3-fluoro-3-nitrooxetane, synthesised in the sequence shown in scheme 61[87]. This compound readily polymerises and undergoes ring opening reactions and might find use in the future as a synthetic intermediate.

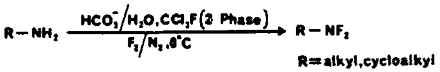


(61)

Difluoramines

Although synthesis of an alkyldifluoramine was first reported as early as 1936, this class of compounds remained little more than an experimental curiosity until stimulus for further research came from the expansion of the aerospace industry in the 1950's. More energetic oxidizers and fuels were required and difluoramines were considered to be attractive because they were a source of fluorine yet potentially circumvented many of the problems inherent in handling elemental fluorine. A considerable number of these materials were subsequently synthesised and although many were found to be sensitive and/or unstable, a new area of chemistry had been opened up. An extensive review on nitrogen fluoride derivatives was published in 1967[88] covering mainly inorganic chemistry with some organic chemistry of these species.

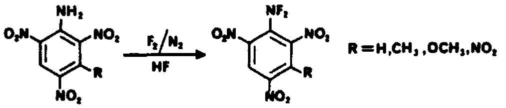
A number of methods can be used to prepare fluoramines. All involve extremely hazardous reagents and unexpected explosions are not uncommon. The direct method, ie., fluorination of amines, was not successful until Sharts[89] employed a buffered two phase system which enabled the product to be extracted before decomposition via secondary reactions could occur (scheme 62).



$$R-NH_2 \xrightarrow[F_2/N_2,\,0^\circ C]{HCO_3^-/H_2O,\,CCl_3F\,(2\ Phase)} R-NF_2 \quad R=alkyl,cycloalkyl$$

(62)

The fluorination of aromatic amines is much more straightforward for both monocyclic (scheme 63)[90] and bicyclic (scheme 64)[91] derivatives using either HF or acetonitrile as solvents (see also scheme 120). A severe limitation is that ring fluorination occurs if the position ortho to the amino group is unsubstituted (scheme 65)[90]. Very highly substituted systems such as 2,4-diamino-1,3,5-trinitrobenzene (DATB) or 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) react but give mainly fluorinated decomposition products and very little of the desired difluoramines[90].



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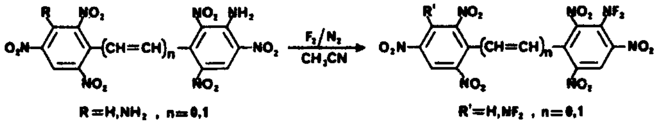

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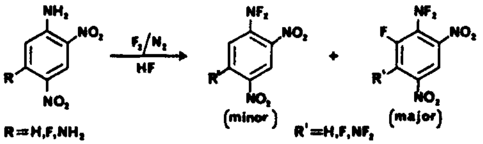
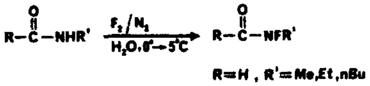


(65)

A number of types of organic nitrogenous compounds have been fluorinated and a comprehensive reivew was published in 1971[92]. Amides (scheme 66)[93], ureas (scheme 67)[94,95] and carbamates (scheme 68)[96] are readily fluorinated. In the latter reaction, the N,N-difluorocarbamate is unstable in H_2O where it readily decomposes to difluoramine and other products, but can easily be isolated from acetonitrile. These reactions are usually characterised by low to moderate yields of the desired products accompanied by lower molecular weight decomposition products resulting from bond ruptures. The fluorination of terminal amides (scheme 69)[93] is an example of such a reaction. A much more comprehensive list of reactions can be found in references[88,92].



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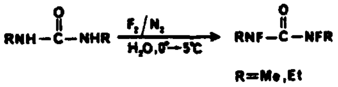

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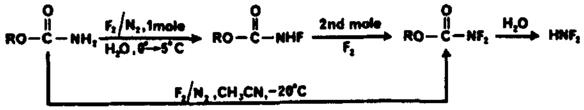

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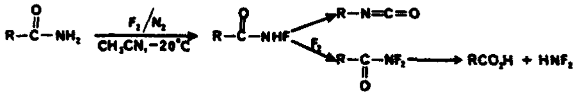
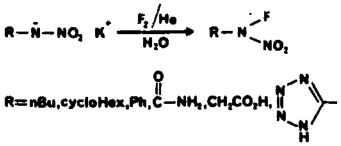


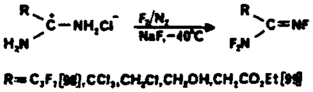
(69)

A related synthesis which has been reported is the fluorination of the potassium salts of nitramines, shown in scheme 70[97].



(70)

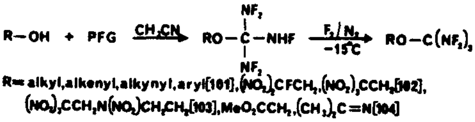
Amidine salts are readily fluorinated to the trifluoroamidines (scheme 71)[98,99] which are very useful intermediates for the preparation of energetic materials. The member of this series which has been most extensively studied is pentafluoroguanidine (PFG) which is synthesised by fluorination of guanidinium fluoride (scheme 72)[100].



(71)

(72)

PFG is an extremely explosive, hazardous material which readily undergoes addition reactions with a wide range of nucleophiles. The most important are alcohols where the initial addition product can subsequently be fluorinated to give tris(difluoramino) derivatives (scheme 73)[101-104]. An interesting addition is that of isocyanic acid where the intermediate product undergoes a number of reactions such as further addition of alcohols or fluorination in the presence of NaF to give tetrakis(difluoramino)methane (scheme 74)[105].



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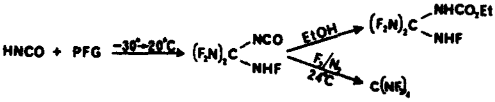
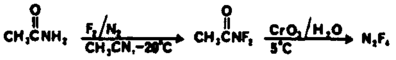


(74)

The vast majority of difluoramines have been prepared either from tetrafluorohydrazine (N_2F_4) or difluoramine (HNF_2). N_2F_4 is normally prepared by reaction of the commercially available nitrogen trifluoride with a fluorine acceptor such as copper (scheme 75)[106]. N_2F_4 can also be prepared by fluorination of a terminal amide followed by in situ oxidation (scheme 76)[93], or analogously by oxidation of N,N-difluorocarbamates with CrO_3[92]. N_2F_4 is now available commercially in the US (Air Products).

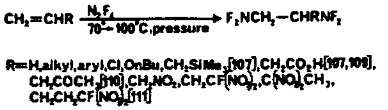
(75)



$$CH_3C(=O)NH_2 \xrightarrow[CH_3CN,-20°C]{F_2/N_2} CH_3C(=O)NF_2 \xrightarrow[5°C]{CrO_3/H_2O} N_2F_4$$

(76)

N_2F_4 is in facile equilibrium with the difluoramine radical ($\dot{N}F_2$)[88] and most of the reported reactions of N_2F_4 probably involve the radical. The most important reaction of N_2F_4 is addition to alkenes at moderate temperatures and pressures to give vicinal bis(difluoramines). Note that explosions of alkene/N_2F_4 mixtures are not uncommon. Despite the hazards, a large number of compounds have been synthesised by addition to acyclic (scheme 77)[107-111] and cyclic[107,108,112] alkenes. α,β-Unsaturated aldehydes, ketones, acids and acid chlorides (scheme 78)[107,109,110] and esters (scheme 79)[113] add across the double bond leaving the carbonyl group untouched. Poly(difluoramino) compounds can be prepared similarly (scheme 80)[114].



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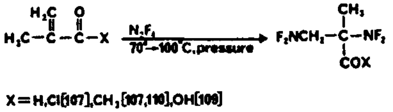

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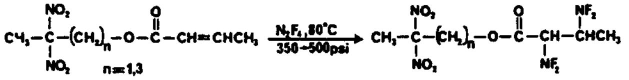

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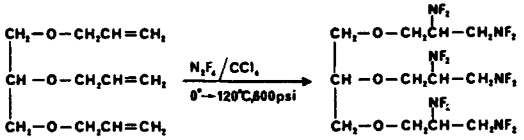
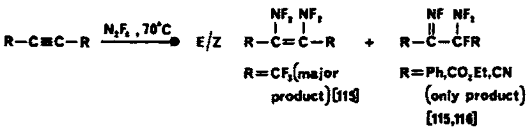


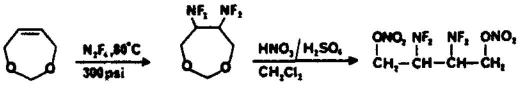
(80)

N_2F_4 will also add to alkynes but usually the product results from thermal rearrangment of the initially formed addition product (scheme 81)[115-116].



(81)

Difluoramino groups are moderately unreactive[117] and functionalisation by additional explosophores can often be achieved. Examples include the nitrative ring opening of the product obtained by addition to the unsaturated diether (scheme 82)[118], hydrolysis and nitration of the ester addition product (scheme 83)[119] and 1,4-addition to butadiene followed by addition of N_2O_5 (scheme 84)[120].



(82)

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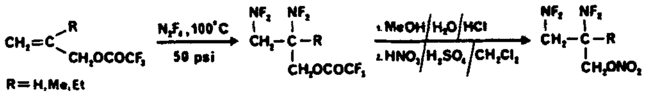

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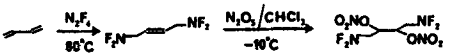
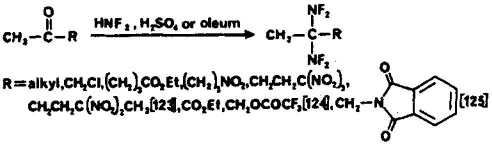


Difluoramine (HNF_2) is the other reagent from which a large number of difluoramines have been prepared. HNF_2 is prepared from N_2F_4 by reaction with thiophenol (scheme 85)[121] or alternatively by aqueous hydrolysis of difluorocarbamates (cf. scheme 68) using 25% H_2SO_4 at 70°C[96]. HNF_2 is particularly hazardous and unexpected detonations have been recorded in both the liquid and solid phases at temperatures as low as -196°C, particularly during phase changes. Although less hazardous reagents which generate HNF_2 in situ are available, eg., difluorosulphamic acid (see scheme 93)[68], they do not appear to have been widely used.

$$F_2NNF_2 + 2PhSH \xrightarrow{50^\circ C} 2HNF_2 + PhSSPh \qquad (85)$$

Reactions of HNF_2 are normally conducted in the presence of a strongly dehydrating but weakly oxidizing acid such as conc. H_2SO_4 or oleum. Any substrate capable of forming a carbocation in this strongly acidic media will react with HNF_2. An extensive review on such alkylation reactions of HNF_2 was published in 1971[122]. The most widely studied substrates have been carbonyl compounds which give geminal bis(difluoramines) under these conditions. A considerable number of acyclic (scheme 86)[123-5] (see also scheme 39) and cyclic[123] aliphatic and aromatic carbonyl compounds (schemes 87, 88)[126,127] have been used as substrates.



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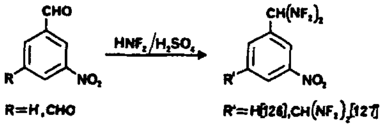

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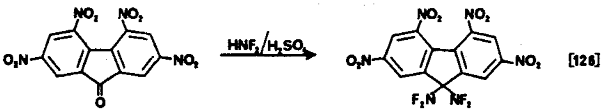
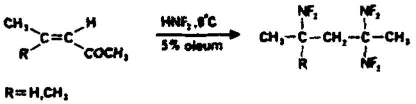


(88)

Benzylic halides and alcohols[122,124] and substituted alkenes[122,124,128] also readily form difluoramines.

α,β- Unsaturated carbonyl compounds react both at the double bond and carbonyl group to give tris(difluoramine) derivatives (scheme 89)[129]. Since the intermediates in these reactions are carbocations, additions of HNF_2 to carbonyl compounds containing other oxygen functional groupings often result in cyclised products rather than simple addition (scheme 90)[123].



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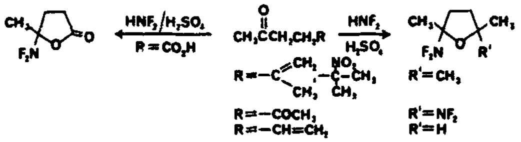
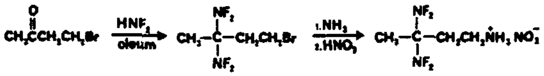


(90)

1,1-Bis(difluoramino)alkanes, formed by addition of HNF_2 to aliphatic aldehydes, will eliminate HF in the presence of pyridine to form trifluoroamidines (scheme 91; cf. scheme 71)[98]. In general geminal bis(difluoramino) groups are relatively unreactive[117] and additional explosophores can subsequently be introduced. Three such examples are shown in schemes 92-94; reaction with NH_3 then HNO_3 to give the amine nitrate salt (scheme 92)[130], reaction with azide to the bis(azido) compound (scheme 93)[68] and hydrolysis of the acinitro salt to the ketone (scheme 94)[131]. An example of an explosive containing both nitramino and difluoramino explosophores, synthesised by addition of the difluoramino groups in the last step, can be seen in scheme 95[132].

(91)



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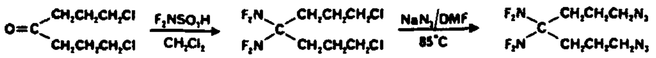

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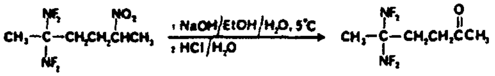

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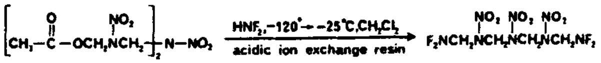
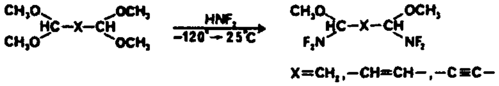


(95)

HNF$_2$ will react with some substrates in the absence of an acid catalyst, such as shown in scheme 96[133] where one methoxy of each acetal is replaced. This could have potential for substrates which would not be stable under the strongly acidic conditions normally used.

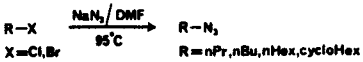


(96)

Azido Compounds

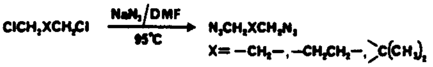
The azido group has a very high heat of formation, 85 kcal/unit, and consequently bestows a high energy content on molecules in which it forms a part. Many compounds containing this explosophore have been prepared, the best known being the lead and silver salts which have found extensive use in initiating compositions. Organic azides have been found to be of little practical use because, with the exception of 1,3,5-triazido-2,4,6-trinitrobenzene, they possess insufficient stability or are too sensitive. A comprehensive account of the chemistry of the azido group has been published[134].

In general, unsaturated azides are very sensitive and much of the published material in the last decade has been concerned with saturated azides, usually with additional explosophores present. Saturated azides are readily prepared via displacement of a good leaving group by azide ion in a strongly solvating solvent such as DMF. A series of mono and diazido aliphatics have been prepared using this approach (schemes 97, 98)[135]. These structurally related materials display a wide range of sensitivities[135].



$$\underset{X=Cl,Br}{R{-}X} \xrightarrow[95^\circ C]{NaN_3/DMF} \underset{R=nPr,nBu,nHex,cycloHex}{R{-}N_3}$$

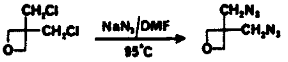
(97)



$$ClCH_2XCH_2Cl \xrightarrow[95^\circ C]{NaN_3/DMF} \underset{X=-CH_2-,\,-CH_2CH_2-,\,{>}C(CH_3)_2}{N_3CH_2XCH_2N_3}$$

(98)

There has been considerable interest in the synthesis of azido containing monomers for preparation of polymers as potential high energy binders. Two such materials are the oxetane (scheme 99)[136] and the glycidyl ether produced by the long synthetic sequence shown in scheme 100[136]. Both materials are readily polymerised.



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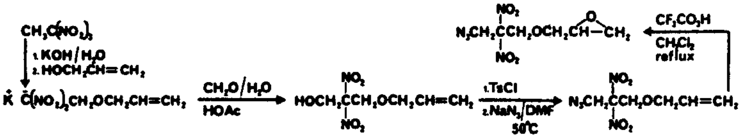
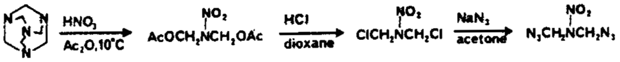


(100)

The azide displacement has considerable synthetic utility as reaction does not usually occur with other explosophores which may be present. Examples of such syntheses can be seen below where nitramine (scheme 101)[137] and fluoronitromethyl groups (schemes 102-104)[87,137] can be incorporated with azido groups into the same molecule by nucleophilic displacement using sodium azide in the last step of the synthetic sequences. A related synthesis with difluoramino groups can be seen in scheme 93.



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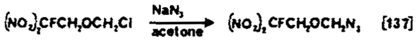

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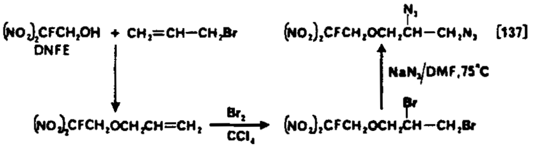

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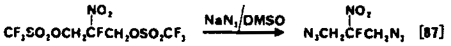
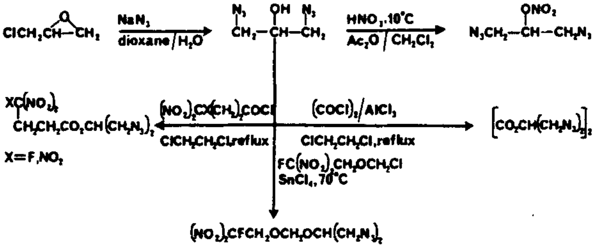


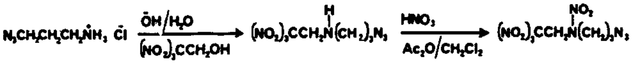
(104)

A number of energetic materials have been prepared from 1,3-diazido-2-propanol, readily synthesised by reaction of epichlorohydrin with sodium azide (scheme 105)[138]. This useful intermediate can be nitrated to the nitric ester[68] or reacted with acid chlorides[68,139] and aliphatic chlorides[68,137]; all these reactions are shown in scheme 105.



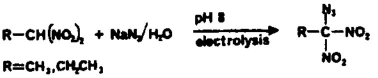
(105)

3-Azidopropanamine has been used as an intermediate for the preparation of the novel 3-aza-6-azido-1,1,1,3-tetranitrohexane (scheme 106)[138].



(106)

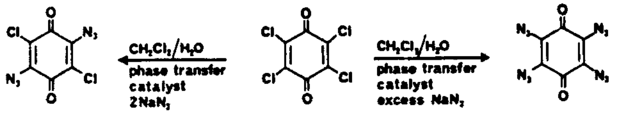
Electrolysis of 1,1-dinitroalkanes with 5% aqueous NaN_3 at pH8 has been reported to yield the corresponding 1-azido-1,1-dinitroalkanes (scheme 107)[140].



(107)

Very few new aromatic azides have been prepared. A series of pyridyl azides were prepared by reaction of the corresponding pyridyl chloride with sodium azide (scheme 108) and were reported to have useful explosive properties[141]. The reaction of chloranil with sodium azide was re-examined and improved by the use of a two phase system with a phase transfer catalyst. Either the tetraazido- or 2,5-diazido-3,6-dichloro-1,4-benzoquinone can be obtained depending on reagent ratios (scheme 109)[142]. Tetraazido-1,4-benzoquinone is described as an extremely dangerous explosive.

(108)

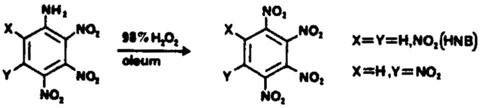


(109)

Polynitroaromatics

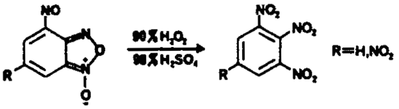
The main direction of research in the field of polynitroaromatic compounds has been towards the synthesis of less sensitive, more thermally stable materials. A number of strategies have been employed to achieve this goal, particularly the synthesis of polycyclic aromatic skeletons where the increased molecular weight leads to enhanced thermal stability, and aromatic compounds containing adjacent NO_2 and NH_2 groupings which greatly diminishes the sensitivity. Whereas this approach mainly involves the design and synthesis of new energetic materials, there has been an equally concerted effort directed to improvements in the synthesis of materials already studied or used. Both these approaches will be discussed. Heat resistant explosives have recently been reviewed[143].

However, the most exciting development in this general field has been the discovery that polynitroarylamines can be oxidized to polynitroaromatics using peroxydisulphuric acid[144]. A number of previously unreported compounds such as hexanitrobenzene (HNB), pentanitrobenzene and 1,2,3,4-tetranitrobenzene have accordingly been prepared (scheme 110)[144], as well as other polycyclic derivatives (see schemes 114 and 127). The objective of this research was to prepare HNB because it was predicted to have a very high density and detonation velocity. Although HNB was found to be extremely powerful and of only moderate sensitivity, its hydrolytic stability was poor; exposure to moisture afforded trinitrophloroglucinol[144].



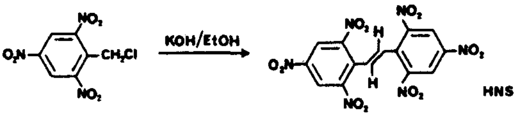
(110)

Polynitrobenzenes can also be prepared by oxidation of nitrobenzofurazan 1-oxides (nitrobenzofuroxans) with the related reagent monoperoxysulphuric acid (scheme 111)[145].



(111)

The general strategy of increasing the molecular weight to increase thermal stability while maintaining energy content has largely involved synthesis of molecules containing picryl (2,4,6-trinitrophenyl = Pi) groups. The simplest heat resistant explosives which fall into this category have the general formula Pi-X-Pi and a substantial number of such derivatives have been prepared. One of the most important target molecules has been 2,2',4,4',6,6'-hexanitrostilbene (HNS) which was first synthesised in 1964 by reaction of 2,4,6-trinitrobenzylchloride with alcoholic KOH (scheme 112)[146]. HNS has subsequently been prepared directly from TNT by oxidative coupling using sodium hypochlorite[147] or metal catalysts such as copper sulfate/pyridine[148] or sodium naphthenate[149] (scheme 113). These reactions proceed via the intermediacy of hexanitrobibenzyl (HNBB) which can easily be isolated by short-stopping the reactions[147-150]. The oxidation of HNBB to HNS by quinones has also been studied[151].



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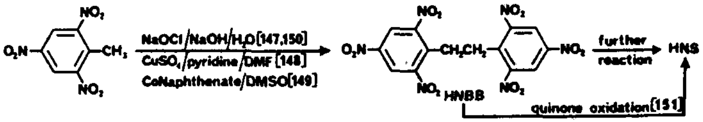
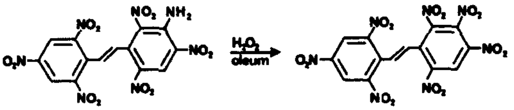


(113)

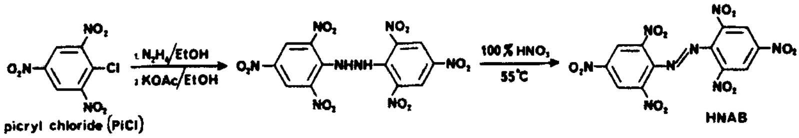
The further nitrated 2,2',3,4,4',6,6'-heptanitrostilbene has been synthesised by peroxydisulfuric acid oxidation of 3-aminoHNS (scheme 114)[144].



(114)

A related material which has been synthesised and found to have promising explosive properties is 2,2',4,4',6,6'-hexanitroazobenzene (HNAB). HNAB is readily prepared by reaction of picryl chloride with hydrazine followed by oxidation of the intermediate bis(picryl)hydrazine (scheme 115)[152]. 2,2',4,4',6,6'-

Hexanitrobenzophenone (scheme 116)[153], bis(picryl)carbonate (scheme 117)[154] and bis(picryl)amine (scheme 118)[155] have similarly been synthesised and found to have useful explosive properties.



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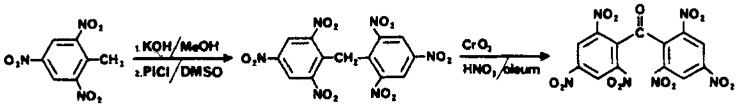

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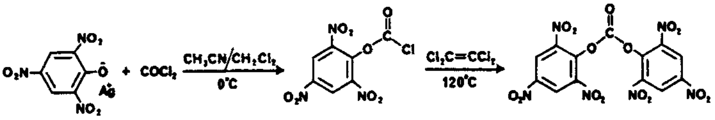

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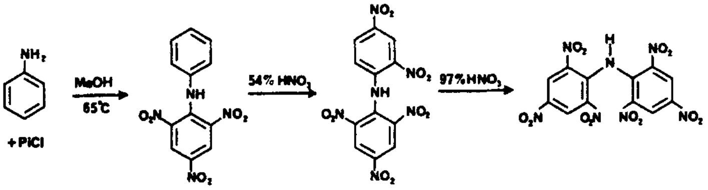
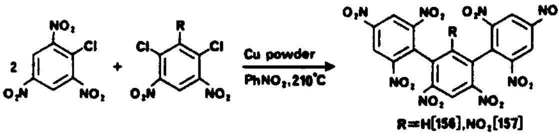


(118)

A number of higher melting (mp > 400°C) terphenyl derivatives have been synthesised using mixed Ullman reactions. 2,2",4,4',4",6,6',6"-Octanitro-[156] and 2,2',2",4,4',4",6,6',6"-nonanitro-m-terphenyl[157] have been synthesised as shown in scheme 119. 3,3"-Diamino-2,2",4,4',4",6,6',6"-octanitro-m-terphenyl has similarly been synthesised[158] and subsequently reacted with fluorine to give the 3,3"-bis(difluoramino) derivative[91] and oxidized using peroxydisulfuric acid to 2,2",3,3",4,4',4",6,6',6"-decanitro-m-terphenyl[144] (scheme 120).



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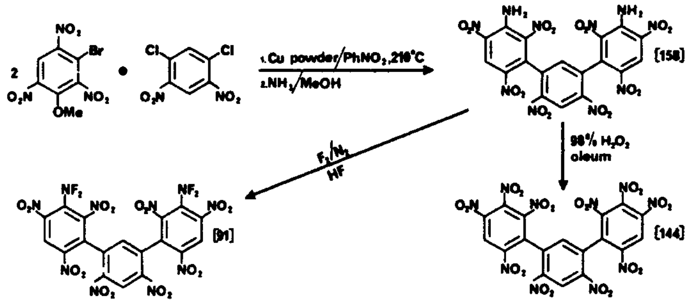
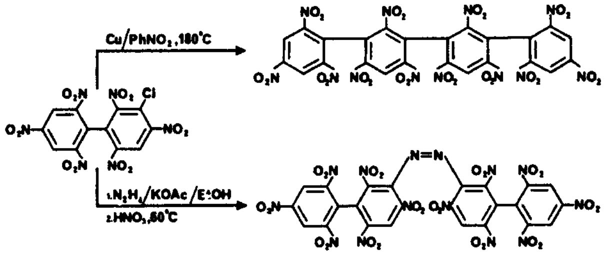


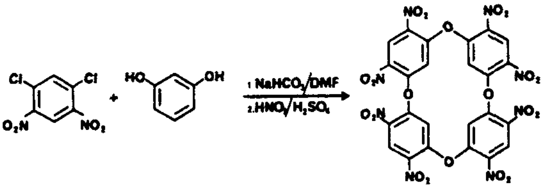
(120)

An even higher molecular weight member of this series, 2,2',2",2"',4,4',4",4"',6,6',6",6"'-dodecanitroquaterphenyl, has been prepared by coupling of 3-chloro-2,2',4,4',6,6'-hexanitrobiphenyl using copper (scheme 121)[159]. Another heat resistant explosive, azobis(2,2',4,4',6,6'-hexanitrobiphenyl) has also been prepared from this starting material by reaction with hydrazine followed by oxidation with nitric acid (scheme 121)[160].



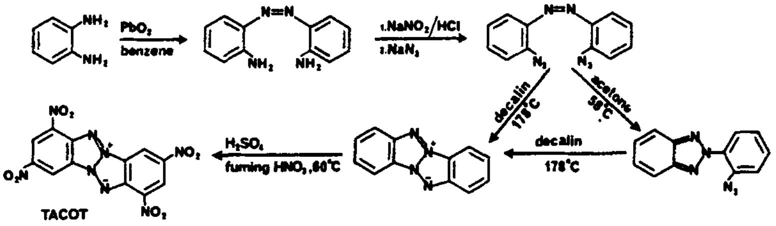
(121)

A series of thermally stable macrocylic compounds have been synthesised by reaction of dichlorodinitrobenzenes with diphenols and subsequent nitration of the products (scheme 122)[161].



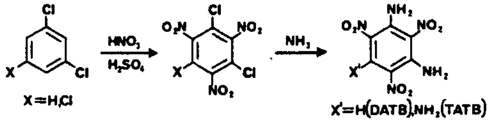
(122)

An extremely interesting heat resistant explosive discovered in the early 1960's was 2,4,8,10-tetranitrodibenzo-1,3a,4,6a-tetraazapentalene (TACOT), synthesised from 1,2-diaminobenzene by the sequence shown in scheme 123[162,163]. TACOT has been developed commercially as a component of a number of heat resistant explosive compositions.



(123)

The requirement for high explosives exhibiting very low sensitivity to initiation has prompted examination of compounds containing adjacent NO_2 and NH_2 groups. This atomic arrangement has been found to confer a substantial decrease in sensitivity relative to the corresponding material where the NH_2 group is replaced by an H atom. The two most important members of this series are 1,3-diamino-2,4,6-trinitrobenzene (DATB) and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). Both DATB and TATB were prepared last century by nitration of intermediates such as the halides, followed by displacement with ammonia (scheme 124). Large scale preparation of TATB still uses this basic sequence[164] but DATB can be prepared much more readily from styphnic acid via the pyridinium salt (scheme 125)[165]. The preparation of TATB from TNT via selective reduction, exhaustive nitration then displacement by ammonia has recently been reported (scheme 126)[166].



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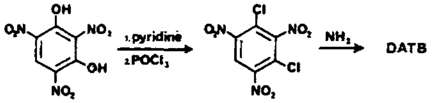

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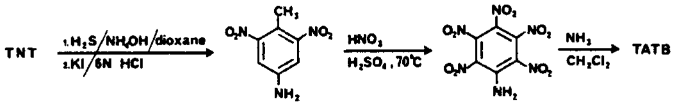
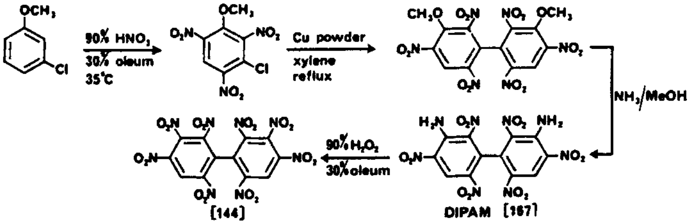


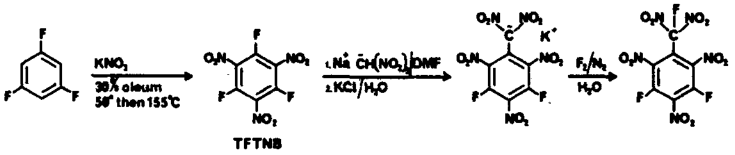
(126)

Higher molecular weight analogues have also been examined. One material which has been found to be particularly promising is 3,3'-diamino-2,2',4,4',6,6'-hexanitrobiphenyl (DIPAM). DIPAM has been synthesised by a number of synthetic routes all involving nitration and Ullman coupling at some stage. A typical sequence is shown in scheme 127[167]. DIPAM has been further oxidized with peroxydisulphuric acid to 2,2',3,3',4,4',6,6'-octanitrobiphenyl (scheme 127)[144].



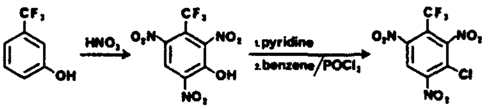
(127)

An area of recent interest is the synthesis of fluorinated analogues of energetic materials. These materials normally have higher crystal density (e.g, 1,3,5-trinitrobenzene (TNB), $\rho = 1.69\ g/cm^3$; 1,3,5-trifluoro-2,4,6-trinitrobenzene (TFTNB), $\rho = 2.00\ g/cm^3$) hence higher detonation velocities and explosive power. The synthesis of TFTNB[168] and 3,5-difluoro-1-dinitrofluoromethyl-2,4,6-trinitrobenzene[169] are shown in scheme 128.



(128)

A related area has been the synthesis of trifluoromethyl (CF_3) derivatives which are often more powerful but less heat sensitive than the corresponding non-fluorinated derivatives. A number of energetic materials have been synthesised from 3-chloro-2,4,6-trinitrotrifluoromethylbenzene, which is readily available via nitration of 3-trifluoromethylphenol followed by formation of the pyridinium salt and subsequent reaction with $POCl_3$ (scheme 129)[170]. This intermediate has subsequently been dechlorinated[170], reacted with methylamine[171], 3-trifluoromethylaniline[172] and phenol[173] followed by nitration to give a range of energetic materials containing trifluoromethyl groups (scheme 130). The same authors reacted picryl fluoride with 2,2,2-trifluoroethylamine and nitrated the product to give the nitramine (scheme 131)[171].



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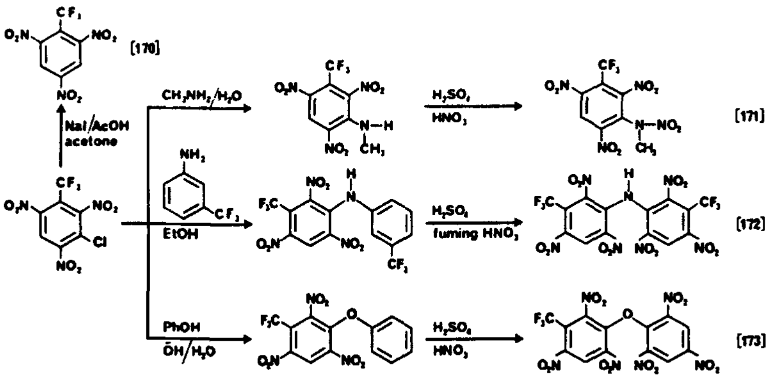

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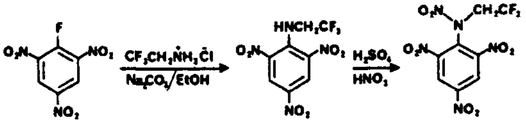
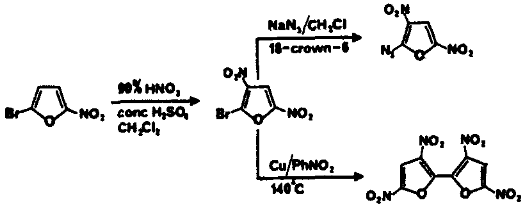


(131)

Heterocyclic Compounds

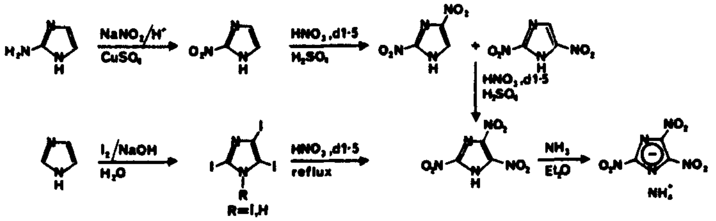
The synthesis of energetic heterocyclic compounds over the last 10-15 years can be divided into three broad areas. One objective has been the synthesis of new heteroaromatic compounds substituted by nitro groups, picryl groups or polynitro sidechains. Another major area of interest has been the preparation of metal salts of heterocyclic systems such as tetrazoles and their assessment as primary (initiating) explosives: a full discussion of this work is outside the scope of this review. A third area has been the investigation of improved syntheses of compounds which are currently used in explosive or propellant formulations or which have shown promise for such use.

The synthesis of nitro-substituted heteroaromatics can be achieved by two strategies. The direct method, ie. nitration of the heteroaromatic ring, is of only limited use. One system where it has been successfully employed is the nitration of 2-bromo-5-nitrofuran to 2-bromo-3,5-dinitrofuran, from which new energetic materials can subsequently be prepared by reaction with azide or Ullman coupling (scheme 132)[174]. Another related preparation is that of 1-methyl-3,4-dinitropyrazole[175].



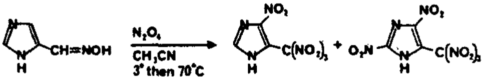
(132)

2,4,5-Trinitroimidazole can be synthesised by successive nitration of 2-nitroimidazole (scheme 133)[176]; direct nitration of imidazole gives 4,5-dinitroimidazole which cannot be further nitrated[176]. A better synthesis is initial iodination of imidazole to a mixture of 2,4,5-triiodo- and 1,2,4,5-tetraiodoimidazole followed by nitrolysis (scheme 133)[176,177]. The ammonium salt, prepared by reaction with ammonia (scheme 133), is significantly more stable than the free acid and is reported to possess interesting explosive properties[177].



(133)

An interesting reaction is the nitration of imidazole-5-aldoxime with N_2O_4 to give 2,4-dinitro-5-(trinitromethyl)imidazole as the major product accompanied by some 4-nitro-5-(trinitromethyl)imidazole (scheme 134)[178]. Thiophene-2-aldoxime reacts in an analogous manner (scheme 135)[179].



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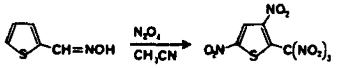
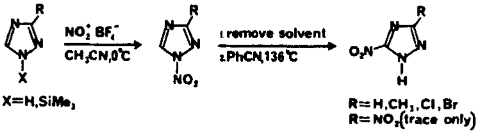


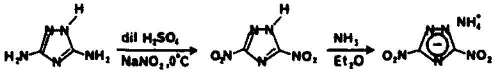
(135)

Triazoles cannot be nitrated under acidic conditions since the ring is protonated. Nitronium salts will nitrate triazoles via the intermediate N-nitrotriazoles which rearrange thermally to the C-nitro isomer (scheme 136)[180]. The reaction gives a higher yield when the triazole is initially trimethylsilylated. When $R=NO_2$, 3,5-dinitrotriazole is only obtained in very poor yield (scheme 136)[180].



(136)

A reaction of wider application to nitroheterocyclic synthesis is the diazotization of aminoheterocyclics in the presence of a large excess of sodium nitrite, an example of which can be seen as the first step in the reaction sequence in scheme 133. Aminoheterocyclics are readily obtained by cyclisation or condensation reactions. One extremely useful material which can be prepared in this manner is 3,5-dinitro-1,2,4-triazole (cf. scheme 136), from commercially available 3,5-diamino-1,2,4-triazole (scheme 137)[181]. 3,5-Dinitro-1,2,4-triazole reacts with ammonia to give the ammonium salt (scheme 137) which is an interesting explosive in that it forms a eutectic with ammonium nitrate[181], or can be methylated to 3,5-dinitro-1-methyl-1,2,4-triazole (scheme 138)[182]. This latter compound, which can alternatively be synthesised by diazotization of the 3,5-diamine[182], reacts with phenylhydrazine and then nitric acid to give the coupled azoxy derivative (scheme 138)[183]. It also undergoes an unusual reaction with acetyl hydrazine to give 5-azido-1-methyl-3-nitro-1,2,4-triazine (scheme 138)[183].



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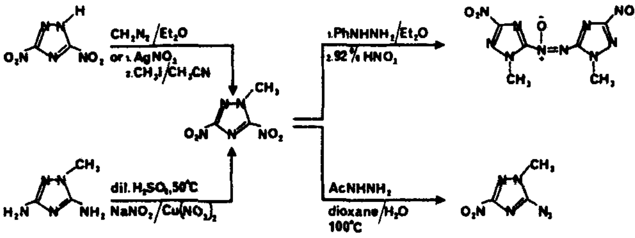
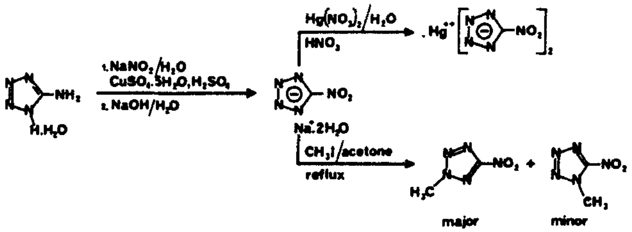


(138)

There has been considerable interest in derivatives of 5-nitrotetrazole. The free acid is explosively unstable and the most important intermediate for synthesis is sodium 5-nitrotetrazole dihydrate (NaNT.$2H_2O$), prepared via the complex copper salt from diazotisation of 5-aminotetrazole in the presence of excess nitrite (scheme 139)[184]. NaNT.$2H_2O$ can be used for the preparation of mercuric bis(5-nitrotetrazole), a detonating primary explosive, but a better route to this material is via the intermediate bis(ethylenediamine) copper bis(5-nitrotetrazole) which is much easier to process[184]. Reaction of NaNT.$2H_2O$ with methyl iodide gives 2-methyl-5-nitrotetrazole contaminated by a small amount of the 1-methyl isomer (scheme 139)[185] while dehydration followed by reaction with picryl chloride gives 2-picryl-5-nitrotetrazole[186]. All possess interesting explosive properties. 2-Methyl-5-nitrotetrazole can alternatively be prepared by diazotisation of the corresponding amine (scheme 140)[185].



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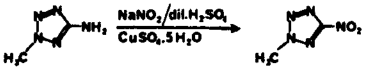
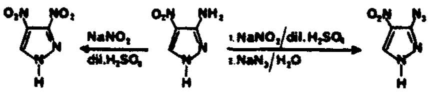


(140)

The intermediate diazo compounds can also be reacted with azide ion to give azido compounds. For example, 3-amino-4-nitropyrazole gives 3,4-dinitropyrazole in the presence of excess nitrite ion or 3-azido-4-nitropyrazole if azide is added (scheme 141)[187]. In an analogous manner the diazonium salts of C-amino-

1,2,4-triazoles give azides (scheme 142)[188] while reaction with trinitromethane gives the unusual 1,2,4-triazoyl-3-azotrinitromethane (scheme 143)[189].



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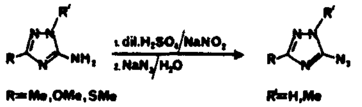

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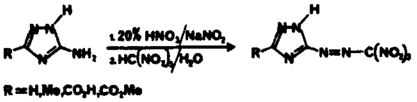
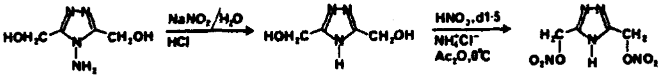


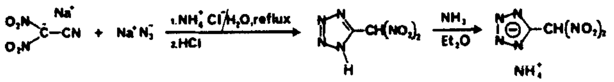
(143)

Reductive diazotisation has also frequently been used. An example can be seen in the triazole dinitrate preparation (scheme 144), where the N-aminotriazole formed by cyclisation in the Mannich reaction is converted to the triazole[190]



(144)

Heterocycles with polynitro sidechains can also be synthesised by cyclisation reactions. For example, reaction of sodium dinitroethanitrile with sodium azide gave 5-dinitromethyltetrazole in low yield, isolated as the ammonium salt (scheme 145)[191]. Synthesis of the related 5-trinitromethyltetrazole and 5-dinitrofluoromethyltetrazole from trimethylsilyl azide with the corresponding nitrile (scheme 146)[192] has recently been reported. Both compounds were isolated as their ammonium salts[192].



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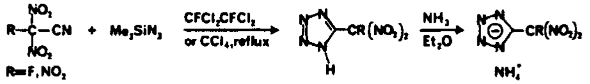
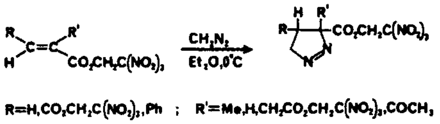


(146)

Another cyclisation route which has been explored is the reaction of diazomethane with trinitroethyl esters of unsaturated carboxylic acids to give the corresponding pyrazoline carboxylic esters (scheme 147)[193]. The related reaction of aliphatic diazo compounds with 1,2-dinitroethanes also yields pyrazolines but only as the minor products; the major products are 4-nitroisoxazoline N-oxides (scheme 148)[194].



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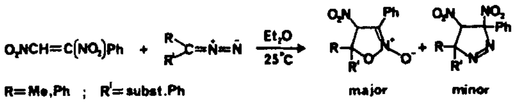
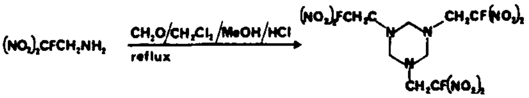


(148)

The preparation of s-triazines, which have been very extensively studied, involve different types of cyclisation reactions. In the simplest case, an amine is condensed with formaldehyde to give a hexahydro-1,3,5-trisubstituted-1,3,5-triazine (scheme 149)[195]. A modification is condensation in the presence of a polynitromethane salt, which gives 1,3-diazacyclohexanes or 1,5-diaza-3-oxacyclooctanes, depending upon the reaction conditions (scheme 150)[196]. The trimerisation of nitriles under pressure has also been applied to energetic materials: trimerisation of dinitrofluoroethanitrile initially gave 2,4,6-tris(dinitrofluoromethyl)-1,3,5-triazine but it could not be isolated due to displacement by the solvent (scheme 151)[197].



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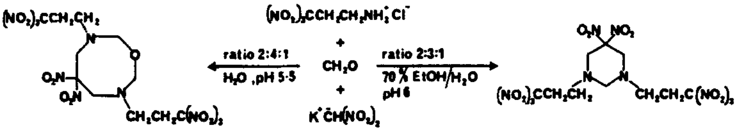

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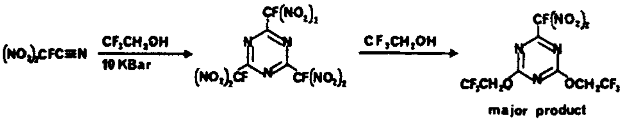
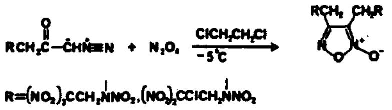


(151)

Furazanoxides (furoxans) are a class of energetic materials which have yielded promising explosives. A number of procedures can be used to construct the heterocyclic ring. Reaction of diazoketones with dinitrogen tetroxide gives 3,4-disubstituted furazanoxides (scheme 152)[198] while 2-methylpropenoic acid reacts with nascent nitrous anhydride to give 3-methyl-4-nitrofurazan 2-oxide (scheme 153)[199] and cyanoacetic acid reacts with nitric acid to give the interesting explosive 3,4-dicyanofurazan 2-oxide (scheme 154)[200]. The explosive properties of these latter two compounds have been investigated[199,200].



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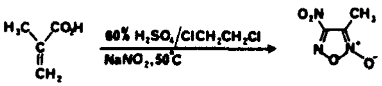

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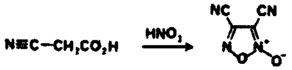
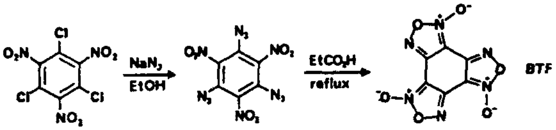


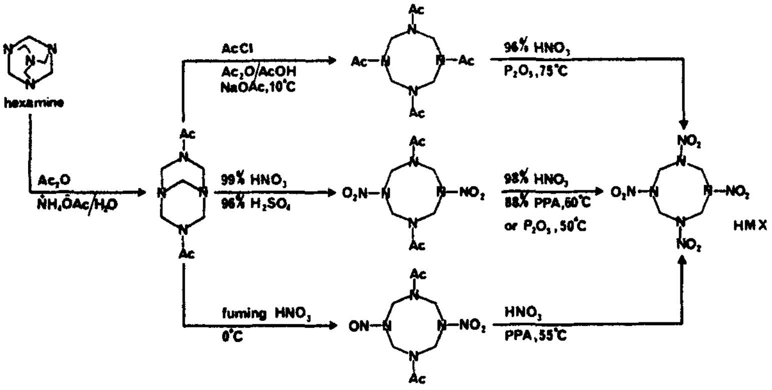
(154)

Benzotrifurazanoxide (benzotrifuroxan, BTF) has been known for over 50 years but was often found to be unduly sensitive. This high sensitivity has been shown to be due to the presence of small amounts of the intermediate 1,3,5-triazido-2,4,6-trinitrobenzene (scheme 155)[201], which can be removed by recrystallisation from benzene which gives the benzene complex of BTF. BTF regenerates upon evacuation at 80°C[201].



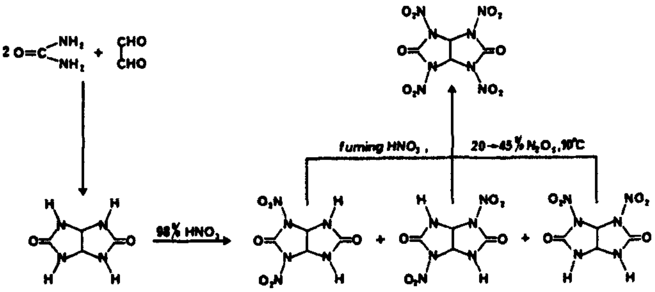
(155)

Another important energetic material whose preparation has been extensively reinvestigated is 1,3,5,7-tetranitro-1,3,5,7-tetraazacylooctane (HMX). HMX is the most powerful of the currently used military explosives and is also widely used as a propellant ingredient. No new synthetic routes have been uncovered but yields have been markedly improved by superior reagents[202]. Three routes from hexamine via the bicyclic diacetate have been examined and are shown below as scheme 156[202]; all give very good yields of high purity products. The route via 1,5-diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane was selected as the most promising and was developed on a pilot plant scale[202]. Very recently the preparation of 1,3,5,7-tetraacetyl-1,3,5,7-tetraazacyclooctane directly from hexamine in high yield has been reported[203].



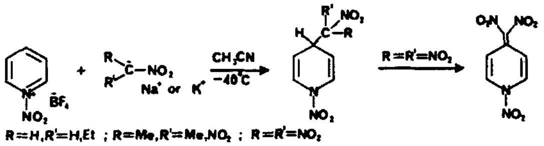
(156)

Two explosives derived from glycoluril have been extensively studied[204]. Glycoluril is readily synthesised by condensation of 2 moles of urea with glyoxal and can be nitrated to a mixture of the dinitro isomers with 98% HNO_3 (scheme 157)[204]. Tetranitroglycoluril is subsequently prepared by nitration of the mixed dinitro isomers with fuming nitric acid containing 20-45% N_2O_5[204]. Both dinitro- and tetranitroglycoluril have high densities and detonation velocities but poor hydrolytic stability.



(157)

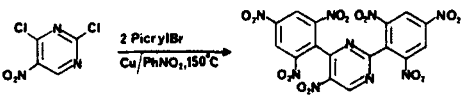
An interesting intermediate which has been subjected to limited study is N-nitropyridinium tetrafluoroborate. This material readily adds salts of polynitroalkanes to form 1,4-dihydropyridines and, in the case of trinitromethane salts, further elimination occurs to the 4-(dinitromethylene) derivative (scheme 158)[205].



(158)

The theme so far in this section has been the synthesis of relatively low molecular weight highly energetic compounds. An alternative aim has been to synthesise new energetic materials of high thermal stability. Again the basic strategy has been to synthesise higher molecular weight, higher melting materials, usually by attaching picryl groups directly to the heterocyclic ring or a sidechain.

C-Picrylheterocycles have been mainly prepared by the Ullman reaction. Pyrimidinyl (schemes 159, 160) and 1,3,5-triazinyl (scheme 160) derivatives have been synthesised by reaction between picryl bromide and the corresponding halides[206]. Tripicryl-1,3,5-triazine shows excellent promise as a heat resistant explosive. Dipicryl furans, thiophenes and thiazoles have been prepared similarly, but here more energetic materials can subsequently be made by nitration of the heterocyclic ring (schemes 161, 162)[206].



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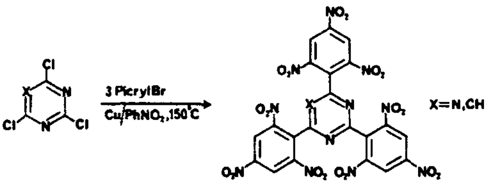

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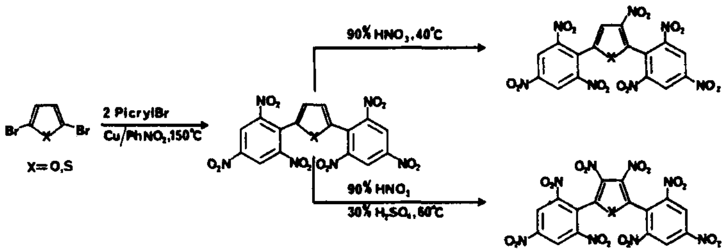

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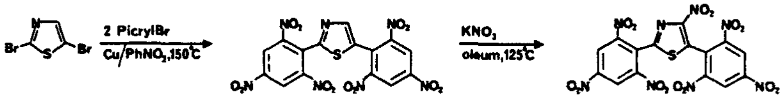
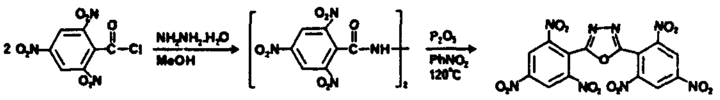


(162)

An alternative synthetic strategy can be seen for 2,5-bis(picryl)-1,2,4-oxadiazole, prepared by reaction of picroyl chloride with hydrazine followed by cyclisation (scheme 163)[206] The related 2,5-bis(3'-amino-2',4',6'-trinitrophenyl)-1,3,4-oxadiazole and -1,3,4-thiadiazole are synthesised by yet another route whereby the heterocyclic ring is constructed first, the nitro groups are then introduced, and the amino groups are inserted in the last step (scheme 164)[206].



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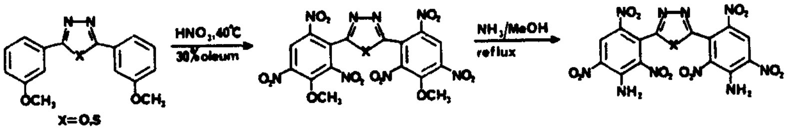
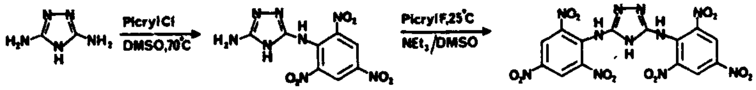


(164)

Quite a number of heterocycles substituted by picrylamino groups have been synthesised by reaction of picryl chloride or fluoride with the corresponding amine. Examples are the compounds based on the 1,2,4-triazole system whose syntheses are depicted in schemes 165-167[207]. 3,5-Bis(picrylamino)-1,2,4-triazole (scheme 165) will not undergo further reaction with picryl fluoride[207].



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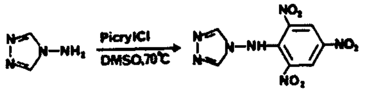

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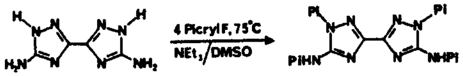
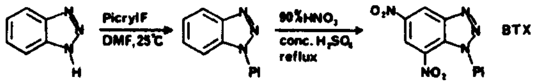


(167)

Yet another heterocyclic system from which a number of useful enegetic materials have been prepared is benzotriazole. Reaction with picryl fluoride followed by nitration gives 5,7-dinitro-1-picrylbenzotriazole (BTX, scheme 168)[208] which is a heat resistant initiating explosive. The 4,6-dinitro isomer can be synthesised by a different route whereby the triazole ring is not formed until the last step (scheme 169)[208]. The heat resistant explosive 2,6-bis(picrylamino)-3,5-dinitropyridine (PYX) is synthesised similarly by picrylation of 2,6-diaminopyridine followed by nitration (scheme 170)[209].



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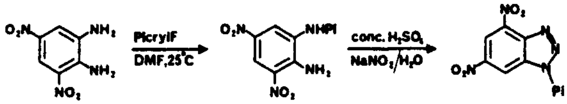

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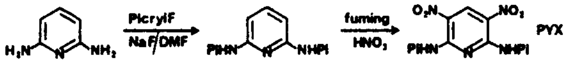
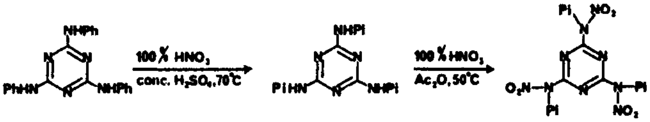


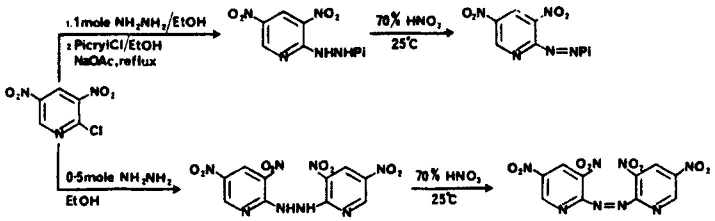
(170)

2,4,6-Tris(picrylamino)-1,3,5-triazine, which also has promising explosive properties, has been synthesised by reaction of cyanuric chloride with aniline followed by nitration (scheme 171)[210]. Further nitration to the tris(nitramino) derivative can be achieved but this product is unstable.



(171)

Picrylhydrazino compounds are yet another variation on this very useful theme. Reaction of 2-chloro-3,5-dinitropyridine with an equimolar quantity of hydrazine followed by reaction with picryl chloride gave 2-picrylhydrazino-3,5-dinitropyridine, while mole ratios of 2:1 gave 1,2-bis(3',5'-dinitro-2'-pyridyl)hydrazine (scheme 172)[211]. Both hydrazines can be oxidized to their azo derivatives using 70% HNO_3 (scheme 172)[211]. 2,6-Bis(picrylhydrazino)-3,5-dinitropyridine and the corresponding bis(azo) derivative can be synthesised by a similar process (scheme 173)[211]. Both materials exhibit promising explosive properties.



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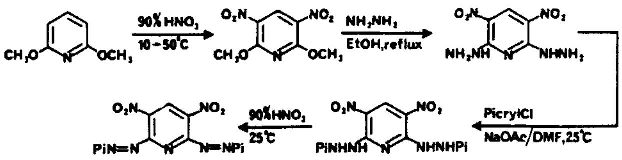


(173)

THE PREDICTION OF EXPLOSIVE PROPERTIES FROM MOLECULAR STRUCTURE/COMPOSITION

The search for new high explosive and energetic materials relies heavily on the ability of scientists working in this field to predict which compounds might offer significant advantages over currently used explosives. This "predictive capability" would be vastly improved if it were possible to accurately compute detonation properties from a given molecular formula, or to quantitatively estimate such properties from structurally related materials whose properties have already been determined. New and possibly complicated, expensive syntheses could then be restricted to compounds predicted to have desirable explosive properties.

At present there is a large and increasing literature base of calculations of ballistic properties and detonation performance. The earlier literature was reviewed in 1959[212] while a general feel for more recent developments can be obtained from the article by Finger et al[213]. An up to date summary of this output would require a review in itself. We have therefore confined this section to two areas: a discussion of structure/reactivity relationships for explosive materials, and the calculation of crystal density and detonation velocity from structural formulae.

That structure/reactivity relationships exist for explosive properties in the same manner that they exist (say) for solution reactions of organic molecules has been shown beyond doubt. Kamlet, in a series of three papers[45,214,215], has investigated the relationship between structure and sensitivity for a wide range of high explosives. As a measure of sensitivity, Kamlet chose critical impact heights, $H_{50\%}$, the height (in cm) at which a 2.5 kg mass impacting the confined sample has a 50% probability of causing an explosion. The structural parameter chosen for comparison was oxidant balance, OB_{100}, defined as "the number of equivalents of oxidant per hundred grams of explosive above the amount required to burn all hydrogen to water and all carbon to carbon monoxide[214]". For a C-H-N-O-(F) explosive,

$$OB_{100} = \frac{100}{MW} (2n_O + n_F - n_H - 2n_C - 2n_{COO})$$

where n_O, n_F, n_H, n_C are the number of the respective atoms in the molecule, n_{COO} is the number of carboxyl groups (which are considered "dead weight") and MW is the molecular weight of the compound.

A plot of log $H_{50\%}$ against OB_{100} for all the explosives for which data was available revealed, not unexpectedly, a broad band of increasing log $H_{50\%}$ with decreasing OB_{100}. However, within classes of explosives excellent correlations (high correlation coefficients) of the general type

$$\log H_{50\%} = a - b.OB_{100}$$

were observed. The classes of explosive studied by Kamlet and correlations obtained were:-

Polynitroaliphatic compounds[214]:

(i) with at least one $-C(NO_2)_3$ group, 28 compounds,

$a = 1.753$, $b = 0.233$

(ii) with at least one $>N-NO_2$ group, 45 compounds,

$a = 1.372$, $b = 0.168$

Polynitroaromatic compounds[215]:

(i) with at least one α C-H atom, 11 compounds,

$a = 1.33$, $b = 0.26$

(ii) with no α C-H linkage, 24 compounds,

$a = 1.73$, $b = 0.32$

Fluorodinitromethyl compounds[45]:

18 compounds, $a = 2.15$, $b = 0.303$

Kamlet concluded from this data that the existence of structure-sensitivity relationships was confirmed and that "mechanisms" of initiation exist in the same manner as, for example, reaction mechanisms in solution. Specifically, Kamlet proposed that there is a "trigger linkage" which is the weak bond in particular classes of explosive which breaks preferentially in the initiation process. As a generalisation, if an explosive compound contains more than one trigger linkage, its sensitivity is best approximated by predictions for the most sensitive grouping. For example, polynitroaliphatics containing a $>N-NO_2$ group are more sensitive than those containing $-C(NO_2)_3$ groups, and if both explosophores are present sensitivity is typical of a nitramine. Kamlet also identified steric factors which lead to an increase in sensitivity.

A complementary approach has been adopted by Delpuech and Cherville[216-218] in that they have attempted to introduce a more theoretical basis for structure-explosive property relationships. Delpuech and Cherville investigated the relationships between the molecular electronic structure (calculated by molecular orbital programmes) and the shock sensitivity of secondary explosives. The families of explosives which were studied were nitroaromatics[216], nitramines[216], nitric esters[217], tetrazoles[218] and picryltriazoles[218]. The calculations were specifically directed at the electronic structure of the molecules in the ground state and the manner of distributing absorbed energy within the molecular framework. In this way they derived a molecular theory of the mechanism of shock initiation which fully complements Kamlet's ideas. It was found that in each class of explosive there was a privileged bond (cf. Kamlet's trigger linkage) which governs sensitivity to shock. For example, energy absorbed by a nitramine tends to concentrate energy within the $>N-NO_2$ bond, leading to a high sensitivity, whereas in less sensitive systems such as nitroaromatics there is a more even distribution of energy.

The explosive properties considered by both Kamlet and Delpuech and Cherville were sensitivities to impact and shock initiation, and this data can be used to predict the sensitivity of new explosives projected for synthesis. However, if new explosives with increased power output are required, the detonation property of most interest is the Chapman - Jouguet pressure, P_{CJ}, given by

$$P_{CJ} = \rho_o \text{ (V of D)}^2/(K + 1)$$

where ρ_o is the density of the explosive, V of D is the detonation velocity and K is the adiabatic expansion coefficient of the chemical reaction product gases. Both V of D and K are linear functions of density. Therefore if more powerful explosives are to be developed, energetic molecules with very high densities must be identified.

The calculation of the density of organic compounds directly from structural formulae is an area of considerable recent activity. The least empirical approach is that of Cady[219] who used the method of Kitaigorodsky[220] to calculate molecular volume (V) directly from the volume of each atom defined by an empirically determined van der Waal's radius. V was then related to density (ρ) by

$$\rho = \frac{MW}{V} . k$$

where MW is the molecular weight and k is the packing coefficient, ie. the ratio of molecular to crystal volume. Cady determined k empirically by regression analysis of data from 183 compounds to have the form

$$k = 0.7686 - 0.1280\,\underline{a}$$

where $\underline{a}$ is the atom fraction of hydrogen atoms directly bonded to carbon atoms. This method gives calculated densities reliable to within 2-4% of measured values.

The remaining purely empirical methods[221-224] are concerned with estimating the total molar volume (V_{total}) of a compound by regression analysis of published structural data, density being calculated from the equation

$$\rho = MW/V_{total}$$

The methods differ only in the means by which V_{total} is determined. Tarver[221] estimated V_{total} from summation of individual group molar volumes. Immirzi and Perini[222] determined what are basically atom molar volumes and included ring contributions while Cichra et al[223] independently derived a similar method but restricted their basis set to explosives and explosives-related compounds. The most recent publication, by Stine[224], again uses the approach of calculating atom molar volumes followed by summation but uses a very much larger "basis set" of 2051 "error-free" compounds.

All these empirical approaches[221-224] are extremely easy to use, which is a considerable advantage over Cady's method[219]. However, Tarver's group values were determined from quite a small data set and Cady has stated[219] that Tarver's method[220] "did not work well in his hands." Cady found the atom molar volume methods[222,223] to be "reliable" and gave similar calculated densities to his technique, with Cichra et al's method[223] being the better of the two for calculating densities of explosive materials. Presumably Stine's method[224] represents the current state-of-the-art, being based on a very large data base and giving predicted densities with an expected error of less than 3%. Further improvement should follow since the data base is constantly being upgraded, and consequently more reliable empirical atom molar volumes can be derived. Similarly a larger data base would permit further refinement of the physical model which forms the basis of Cady's method. More theoretically based methods of density prediction could follow in the near future.

Detonation velocity (V of D) is also an extremely useful parameter to know for a high explosive molecule whose synthesis is being considered. In a recent article, Rothstein and Petersen[225] have described an empirical method for predicting high explosive V of D's from composition and structure for C-H-N-O type explosives. This work has very recently been extended by Rothstein[226] to include fluorine containing explosives. In this method, V of D is empirically related to a factor F which is expressed as

$$F = \frac{100}{MW}\left[nO + nN + nF - \left(\frac{nH - nHF}{2nO}\right)^{*} + \frac{A}{3} - \frac{nB/F}{1.75} - \frac{nC}{2.5} - \frac{nD}{4} - \frac{nE}{5}\right] - G$$

where nO, nN, nF and nH are the number of the respective atoms in the molecule, nHF is the number of hydrogen fluoride molecules that can possibly form from available hydrogen, nB/F is the number of oxygen atoms in excess of those available to form CO_2 and H_2O and/or the number of fluorine atoms in excess of those available to form HF, nC is the number of oxygen atoms in $>C=O$ linkages, nD is the number of oxygen atoms in C-O-R linkages where R=H, $-NH_4$, -C etc, and nE is the number of nitrato groups either in nitrate esters or nitrate salts. A=1 for an aromatic compound or 0 otherwise, and G=0.4 for a liquid explosive and 0 for a solid. The term *=0 if nHF > nH or nO=0. F was related to V of D by linear regression analysis and found to be:-

$$\text{V of D (mm/}\mu\text{s)} = \frac{F - 0.26}{0.55}$$

For the 80 explosives which were evaluated, 95% had calculated V of D within 5% and 99% within 7% of experimentally reported values. The absolute error was ± 2.4%. The detonation pressure (P_{CJ}) was also related empirically by

$$P_{CJ} = 93.3 \text{ (V of D)} - 456 \quad \text{(kbar)}$$

but the number of data points (11) was quite low.

The chief advantage of this method is that it is simple to use, is derived solely from molecular formulae and structures and requires no prior knowledge of any measured, estimated or calculated physical, chemical or thermochemical properties other than to know or to predict whether an explosive is a liquid or solid. The compositional terms in F are obviously simplistically related to thermochemical properties such as heat of formation, and the structural elements A, C, D, E and G are related to physical properties such as density, but none of these properties are explicitly calculated.

Mention should be made of Kamlet and co-workers[227] who derived a method for calculation of V of D and P_{CJ} for C-H-N-O explosives provided that elemental composition, heat of formation and density were known or could be estimated. Aizenshtadt[228] also developed an empirical set of simple formulae for calculating V of D : again chemical formulae, enthalpy of formation and density must be known or estimated. Kamlet has recently extended this earlier work[227] to an improved method for calculating detonation pressures, which he has called the "rule for gamma"[229]. A comment on Kamlet's methods plus earlier reports can be found in a very recent paper by Andersen[230].

Research into the prediction of explosive properties is still in a developing stage and considerable advances can be expected over the next few years. However, it cannot be stressed too strongly that consideration of a single predicted property can serve only as a guideline for assessing new candidate molecules for synthesis. Physical, explosive and chemical properties should all be considered since a material which performs well in one respect may be inferior in another.

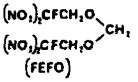
Consider for example the synthesis of new explosive analogues in which H atoms are replaced by F atoms, a subject discussed briefly in a preceding section. Replacement of H by F has the desirable effect of increasing density but simultaneously decreases melting point, which may or may not be desirable. Examples are given below. Total energy usually increases slightly but sensitivity changes are extremely variable. For example DFF is very much less sensitive than FEFO (see below) and this desensitizing effect extends to a smaller degree for other formals, ethers and nitrates[231]. However, nitramines show no change and though 1,3,5-trinitrobenzene is more sensitive than picryl fluoride replacement of further H atoms by F results in sensitization (see below)[231]. There is consequently considerable current interest in zero hydrogen compounds but our understanding of why such properties vary is at present far from complete.

$CH_3CH(NO_2)_2$

ρ1·35 g/cm³, mp 37°C

$CH_3CF(NO_2)_2$

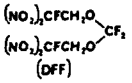
ρ1·40, mp < 25°C



$(NO_2)_2CFCH_2O-CH_2-OCH_2CF(NO_2)_2$

(FEFO)

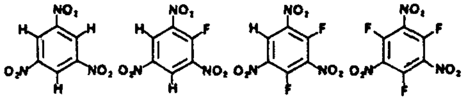
ρ1·59, mp 14°
sensitivity 6kg-cm



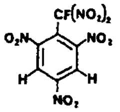
$(NO_2)_2CFCH_2O-CF_2-OCH_2CF(NO_2)_2$

(DFF)

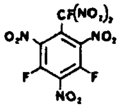
ρ1·87, mp −17°
sensitivity 135 kg-cm [229]



ρ	1·69			2·00
mp	122°	130°	147°	82°
sensitivity	103cm	138	48	84 [229]

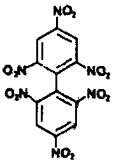


ρ1·87, mp 130°
sensitivity 13cm

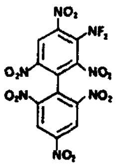


ρ1·98, mp 71°
sensitivity 8cm [169]

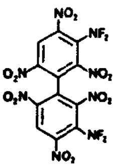
Replacement of H by the explosophore NF_2 has a similar effect to replacement by F in that densities increase (but to a smaller degree) and melting points decrease. Examples are given below. However, these changes are accompanied by substantial decreases in thermal stability and an even more dramatic increase in sensitivity to impact: sensitivies approaching those of primary explosives are observed.



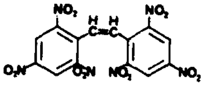
ρ1·80, mp 263°



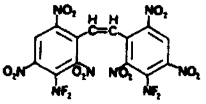
ρ1·83, mp 204°



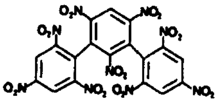
ρ1·82, mp 237°



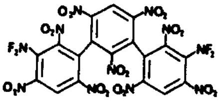
ρ1·74, mp316°



ρ1·76, mp 208°



ρ1·78, mp440°



ρ1·81, mp 240°

In summary, selection of candidate energetic materials projected for synthesis to satisfy performance criteria is still something of an "art" but is becoming with every year more of a "science". Developments over the next few years promise to lead to new materials with interesting and useful properties, as well as improved methods for prediction of these properties prior to practical realisation.

GLOSSARY OF ABBREVIATIONS OF COMPOUNDS

AN	Ammonium nitrate
BTF	Benzotrifurazan N-oxide (benzotrifuroxan)
BTX	5,7-Dinitro-1-picrylbenzotriazole
DATB	1,3-Diamino-2,4,6-trinitrobenzene
DFF	Bis(2,2-dinitro-2-fluoroethyl)difluoroformal

DIPAM	3,3'-Diamino-2,2',4,4',6,6'-hexanitrobiphenyl
DNE	2,2-Dinitroethanol
DNFE	2,2-Dinitro-2-fluoroethanol
DNFM	Dinitrofluoromethane
FEFO	Bis(2,2-dinitro-2-fluoroethyl)formal
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane
HNAB	2,2',4,4',6,6'-Hexanitroazobenzene
HNBB	2,2',4,4',6,6'-Hexanitrobibenzyl
HNS	2,2',4,4',6,6'-Hexanitrostilbene
NF	Trinitromethane (nitroform)
NG	Nitroglycerine
PFG	Pentafluoroguanidine
Pi	2,4,6-Trinitrophenyl (or picryl) group
PiCl	Picryl chloride
PYX	2,6-Bis(picrylamino)-3,5-dinitropyridine
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazacyclohexane
TACOT	2,4,8,10-Tetranitrodibenzo-1,3a,4,6a-tetraazapentalene
TATB	1,3,5-Triamino-2,4,6-trinitrobenzene
TFTNB	1,3,5-Trifluoro-2,4,6-trinitrobenzene
TNB	1,3,5-Trinitrobenzene
TNE	2,2,2-Trinitroethanol
TNM	Tetranitromethane
TNT	2,4,6-Trinitrotoluene

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