

8

Miscellaneous Explosive Compounds

The vast majority of organic compounds finding wide use as commercial or military explosives contain nitro functionality in the form of polynitroarylenes, nitramines and nitrate esters. These groups include important explosives like TNT, TATB, RDX, HMX and NG etc. Energetic compounds containing other 'explosophoric' groups tend to find only limited use because of poor thermal or chemical stability, high sensitivity to impact or friction, unsuitable physical properties or difficulty in synthesis. Some of these compounds include: azides, peroxides, diazophenols and numerous nitrogen-rich compounds derived from guanidine and its derivatives.

8.1 ORGANIC AZIDES

8.1.1 Alkyl azides

Dagley and Spear¹ noted that the introduction of an azido group into an organic compound increases its energy by ~ 355 kJ/mol and so its presence in energetic compounds is clearly favorable on thermodynamic grounds. However, many organic compounds containing azido groups have not found wide application as practical energetic materials because of their poor thermal stability and relatively high sensitivity to mechanical stimuli. The explosive properties of inorganic azides are well known, lead azide finding wide use as the initiating charge in detonators.

Alkyl azides are conveniently prepared from the reaction of alkali metal azides with an alkyl halide, tosylate, mesylate, nitrate ester or any other alkyl derivative containing a good leaving group. Reactions usually work well for primary and secondary alkyl substrates and are best conducted in polar aprotic solvents like DMF and DMSO. The synthesis and chemistry of azido compounds is the subject of a functional group series.²

Frankel and co-workers³ prepared a series of alkyl diazides from the reaction of dihaloalkanes with sodium azide in DMF at 95°C , including 1,3-diazidopropane, 1,4-diazidobutane and 1,3-diazido-2,2-dimethylpropane. Tris(azidomethyl)amine, an energetic fuel with potential for use in bipropellant propulsion systems, is synthesized from the reaction of tris(chloroethyl)amine with sodium azide.^{4,5}

334 Miscellaneous Explosive Compounds

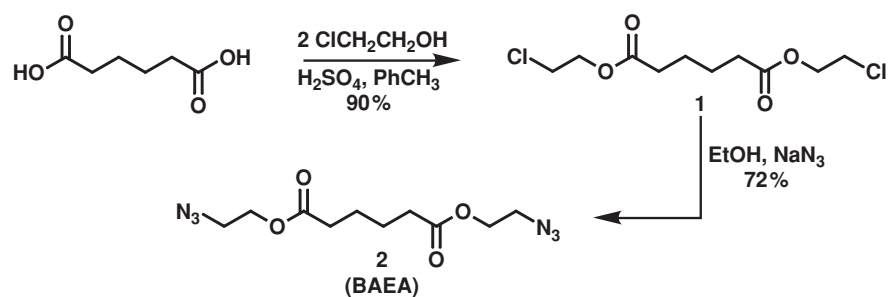


Figure 8.1

Agrawal and co-workers⁶ synthesized the energetic plasticizer bis(2-azidoethyl)adipate (2) (BAEA) from the reaction of bis(2-chloroethyl)adipate (1) with sodium azide in ethanol (72 %).

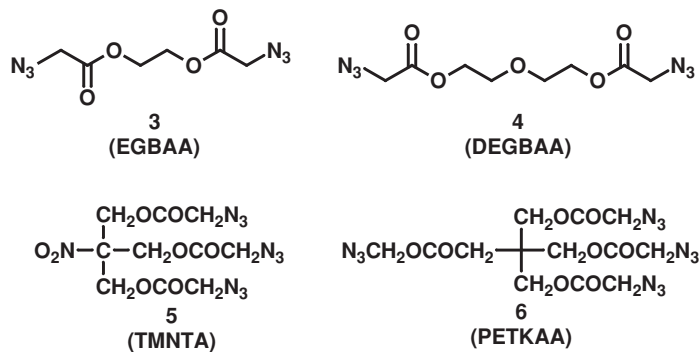


Figure 8.2

Drees and co-workers⁷ synthesized a number of energetic azido plasticizers whose structures are based on those of known nitrate ester plasticizers. EGBAA (3), DEGBAA (4), TMNTA (5) and PETKAA (6) are synthesized from the corresponding chloroacetate esters with sodium azide in DMSO.

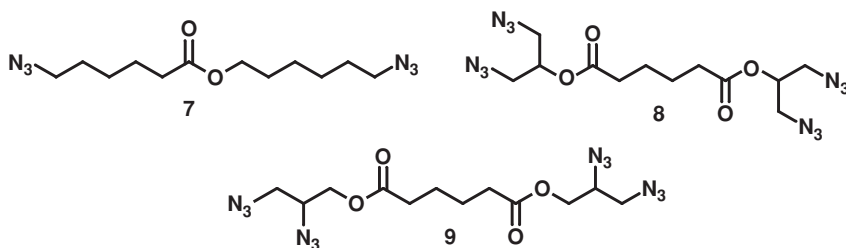


Figure 8.3

Several other azido esters has been reported, including (7),⁵ (8)⁸ and (9),⁹ which are synthesized along similar routes of ester formation followed by substitution of halogen with azide anion or in the reverse order.

Many energetic compounds have been reported where the azido group is in conjunction with another 'explosophore'. This has been a popular approach to new energetic materials. 2-Azidoethyl nitrate, an explosive resembling nitroglycerine (NG) in its properties, was synthesized some time ago from the reaction of 2-chloroethanol with sodium azide followed by *O*-nitration of the product, 2-azidoethanol, with nitric acid.¹⁰

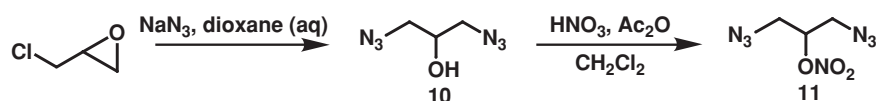


Figure 8.4

1,3-Diazido-2-propanol (10) has been synthesized from the reaction of epichlorohydrin with sodium azide in aqueous dioxane.¹¹ 1,3-Diazido-2-propanol (10) reacts with acetic anhydride–nitric acid to yield the nitrate ester (11),¹² whereas its reactions with polynitro derivatives of acid chlorides and alkyl chlorides has been used to synthesize a range of energetic materials.^{8,12,13}

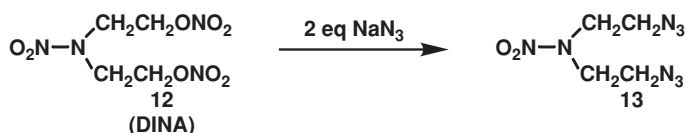


Figure 8.5

Displacements with azido anion are tolerant of many pre-existing 'explosophoric' groups but the nitrate ester group readily undergoes displacement as seen for the synthesis of bis(2-azidoethyl)nitramine (13) from *N*-nitrodiethanolamine dinitrate (12) (DINA).¹⁴

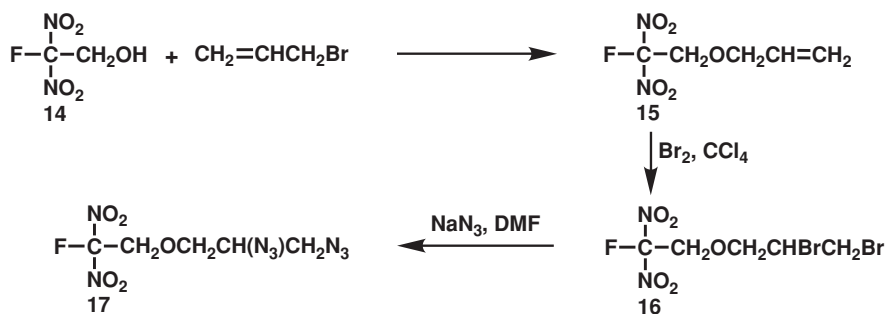


Figure 8.6

The diazide (17) is obtained from the reaction of the dibromide (16) with sodium azide in DMF.^{13,15} The fluorodinitrobutyrate ester (18) is synthesized from the corresponding allyl fluorodinitrobutyrate via a similar route of bromination and displacement with azide.¹⁶ The bis(fluorodinitroethyl)amine (19) is also obtained from the corresponding bromide.¹⁶

336 Miscellaneous Explosive Compounds

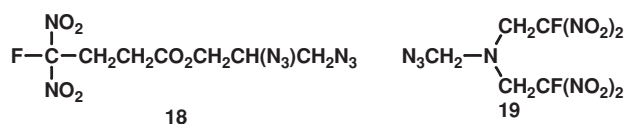


Figure 8.7

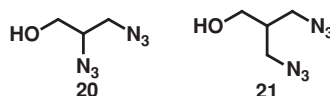


Figure 8.8

The azidoalcohols (20) and (21) have been reacted with acid chlorides and alkyl chloride to give esters containing both azido and fluorodinitromethyl functionality.^{16,17}

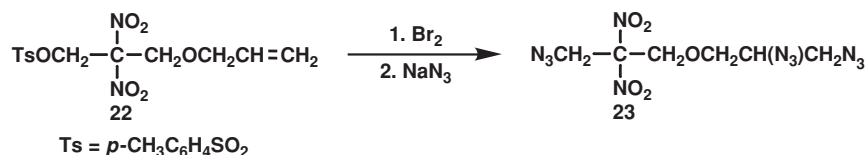


Figure 8.9

The triazide (23) has been synthesized from the bromination of the tosylate (22) followed by displacement of both bromide and tosylate functionality with sodium azide.¹⁶

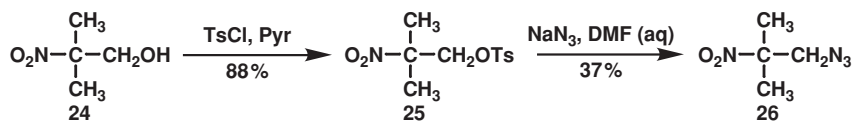


Figure 8.10

2-Methyl-2-nitro-1-azidopropane (26), synthesized from the tosylate (25), has been suggested for use as an energetic plasticizer.¹⁸

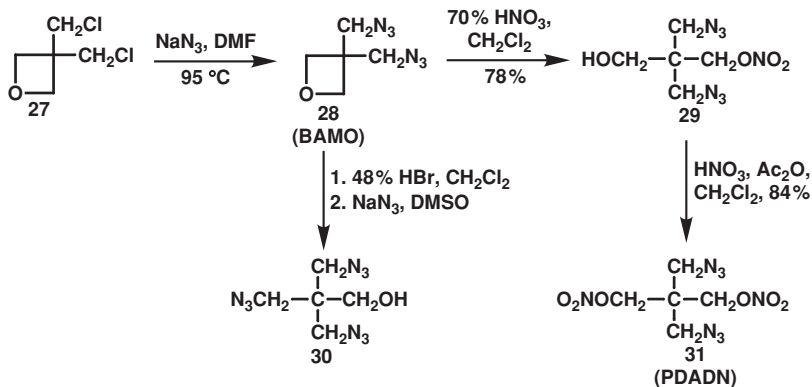


Figure 8.11

3,3-Bis(azidomethyl)oxetane (BAMO) (28), the product from treating 3,3-bis(chloromethyl)oxetane (27) with sodium azide in DMF,¹⁹ undergoes acid-catalyzed ring opening on reaction with 70 % nitric acid to give the nitrate ester (29).²⁰ Treatment of (29) with nitric acid in acetic anhydride yields 2,2-bis(azidomethyl)-1,3-propanediol dinitrate (PDADN) (31).²⁰ Reaction of BAMO (28) with aqueous hydrobromic acid in methylene chloride, followed by treatment of the resulting bromide with sodium azide in DMSO, yields the triazide (30).²⁰ The hydroxy groups of (29) and (30) have been reacted with acid chlorides like 4,4,4-trinitrobutyryl chloride for the synthesis of energetic plasticizers.²¹

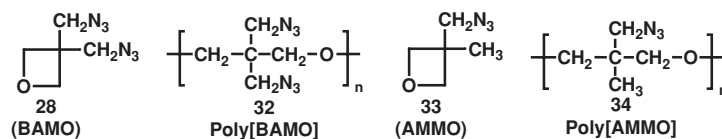


Figure 8.12

The energetic nature of the azido group makes its incorporation into energetic polymers and binders very desirable. 3,3-Bis(azidomethyl)oxetane (BAMO) (28) and 3-azidomethyl-3-methyloxetane (AMMO) (33) are energetic monomers which on polymerization result in the energetic polymers poly[BAMO] (32) and Poly[AMMO] (34), respectively, both of which are under evaluation as potential energetic alternatives to HTPB in composite propellant formulations.²²

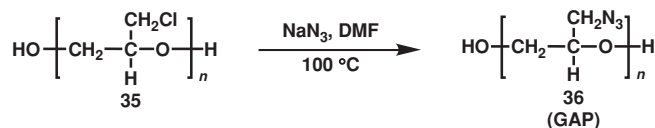


Figure 8.13

Glycidyl azide polymer (GAP) (36) is readily synthesized from the reaction of polyepichlorohydrin oligomers/polymers (35) with alkali metal azides in polar aprotic solvents.^{23,24} GAP oligomers prepared in this way are hydroxy-terminated polyethers with pendant azidomethyl groups and have densities of $\sim 1.3 \text{ g/cm}^3$ and positive heats of formation. GAP oligomers with number-average molar masses of 400–500 are used as plasticizers, whereas those between 3000 and 3500 are used as binders for propellants and undergo curing with isocyanates to give mixed polyether-carbamate energetic polymers. GAP is extremely insensitive to impact, even in the presence of additives like Pyrex powder and polycarbonate disc,²⁵ and has been used in the US in propellant formulations for a number of years. SNPE in France manufactures GAP for sale to European countries under licence from Rocketdyne in the US. Research at Fiat Avio in Italy and SNPE in France has focused on developing GAP-based propellants containing energetic nitrate ester plasticizers like MTN and BTTN, nitramines like RDX and CL-20, and energetic oxidizers like ammonium dinitramide (ADN) and hydrazinium nitroform (HNF).²² The use of GAP in propellants has been reviewed.²⁴

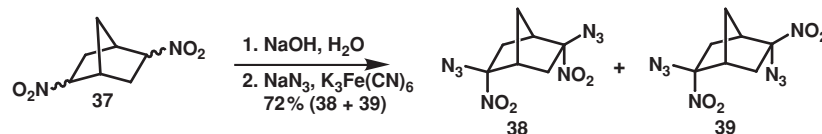


Figure 8.14

338 Miscellaneous Explosive Compounds

Bowman and co-workers²⁶ synthesized 2-azido-2-nitropropane by treating the sodium salt of 2-nitropropane with a mixture of sodium azide and potassium ferricyanide. Olah and co-workers²⁷ used the same methodology for the synthesis of alicyclic *gem*-azidonitroalkanes from secondary nitroalkanes. Isomeric azidonitronorbornanes (38) and (39) were synthesized from 2,5-dinitronorbornane (37). Some of the *gem*-azidonitroalkanes synthesized during this work have poor chemical and thermal stability.

1-Azido-1,1-dinitroalkanes have been synthesized from the electrolysis of 1,1-dinitroalkanes in alkaline solution containing sodium azide.²⁸ The reaction of trinitromethyl compounds²⁹ with lithium azide in DMF and DMSO, and the electrolysis of 1,1-dinitromethyl compounds³⁰ in the presence of azide anion, also generate 1-azido-1,1-dinitroalkanes.

8.1.2 Aromatic Azides

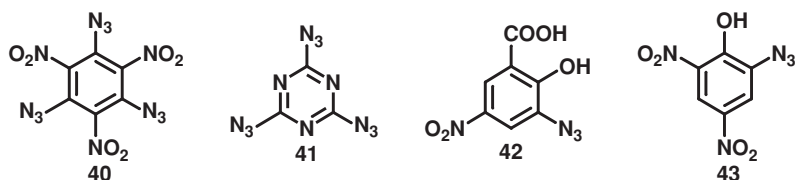


Figure 8.15

Azido groups are conveniently incorporated into aromatic rings via nucleophilic aromatic substitution of aryl halides containing nitro or other deactivating groups *o/p*- to the leaving group. 1,3,5-Triazido-2,4,6-trinitrobenzene (40), the product from the reaction of 1,3,5-trichloro-2,4,6-trinitrobenzene with excess sodium azide, is an explosive with VOD ~ 7500 m/s (at $d = 1.54$ g/cm³) and has some prospects of practical use as a primary explosive.³¹ Cyanuric triazide (41), prepared from cyanuric chloride and sodium azide, is a powerful initiator but must be considered a highly dangerous substance due to its high sensitivity to mechanical stimuli; large crystals of cyanuric triazide may detonate even on touch.³² Lead salts of the aryldiazides (42) and (43) have been explored for use in detonators but prove to be poor initiators.³³



Figure 8.16

Gilbert and Voreck³⁴ synthesized hexakis(azidomethyl)benzene (HAB) (45) from the reaction of hexakis(bromomethyl)benzene (44) with sodium azide in DMF. This azide has been comprehensively characterized for physical, thermochemical and explosive properties and stability. HAB is a thermally and hydrolytically stable solid and not highly sensitive to shock, friction or electrostatic charge but is sensitive to some types of impact. It shows preliminary

promise for possible use as a substitute for lead styphnate in less sensitive bridgewire detonators and also for tetrazene in percussion detonators. HAB contains 62 % nitrogen and belongs to the class of 'planar radial' compounds, which have compact, symmetrical, disc-like structures, resulting in high melting point, good stability and low solubility in solvents.

8.2 PEROXIDES

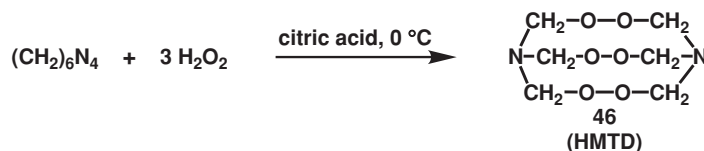


Figure 8.17

No peroxide has found practical use as an explosive, a consequence of the weak oxygen-oxygen bond leading to poor thermal and chemical stability and a high sensitivity to impact. Hexamethylenetriperoxidodiamine (HMTD) (46) is synthesized from the reaction of hexamine with 30 % hydrogen peroxide in the presence of citric acid.³⁵ HMTD is a more powerful initiating explosive than mercury fulminate but its poor thermal and chemical stability prevents its use in detonators.

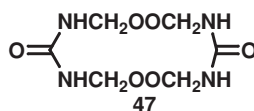


Figure 8.18

Another interesting dialkylperoxide explosive, which probably has the structure of (47), is synthesized by the addition of hydrogen peroxide and nitric acid to a solution of urea and formaldehyde.³⁶

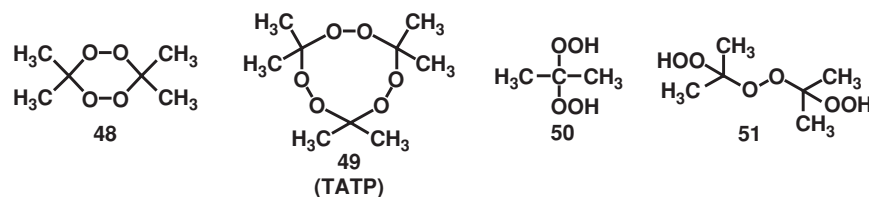


Figure 8.19

Some ketone-derived peroxides have explosive properties, of which the most interesting are obtained from acetone. Four acetone-derived peroxides have been synthesized. Acetone peroxide dimer (48) is obtained in 94 % yield by treating acetone with a slight excess of 86 % hydrogen peroxide in acetonitrile in the presence of concentrated sulfuric acid at subambient temperature.³⁷ The reaction of acetone with potassium persulfate in dilute sulfuric acid also yields acetone peroxide dimer (48).³⁸ Acetone peroxide trimer (49), also known as triacetone triperoxide (TATP), has been obtained as a by-product of these reactions or by the addition of

340 Miscellaneous Explosive Compounds

acetone to a cooled solution of 1.0 equivalent of 50 % hydrogen peroxide and 0.25 equivalents of concentrated sulfuric acid. The latter experiment yields a mixture containing 90 % TATP (49) which can be purified by low temperature recrystallization from pentane.³⁹ In the absence of mineral acid the hydroperoxides (50) and (51) can be obtained from these reactions.³⁹ Thus, a mixture of acetone and 50 % hydrogen peroxide stirred at 0 °C for 3 hours produces 2,2-bis(hydroperoxy)propane (50) as the sole product. Longer reaction times lead to the formation of (51), which is formed to the extent of approximately 20 % after ten days and is isolated by low temperature recrystallization from pentane.³⁹

Molecules such as TATP (49) possess explosive strength similar to TNT. Furthermore, TATP is extremely sensitive to heat and vibrational shock and can be ignited with an open flame or small electrical discharge i.e. does not need a primer unlike conventional explosives.

8.3 DIAZOPHENOLS

Diazophenols, also known as diazo oxides or diazonium phenolates, are thought to be zwitterions⁴⁰ with negative and positive charges localized on the oxo and diazo groups respectively, although tautomeric quinonoid⁴¹ structures have not been ruled out. Most diazophenols are sensitive to impact and exhibit properties which are characteristic of primary explosives, the nitro derivatives exploding violently on the application of heat or mechanical stimuli. Studies of these compounds have focused on the synthesis of various nitro-substituted diazophenols in an attempt to fine tune properties such as chemical stability, impact and friction sensitivity, and initiating potential.

8.3.1 Diazophenols from the diazotization of aminophenols

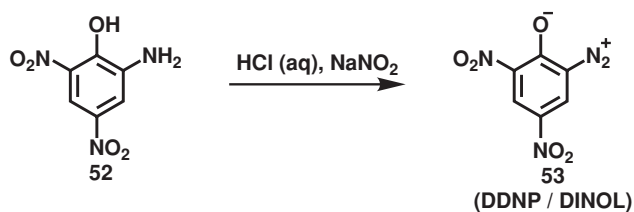


Figure 8.20

2-Diazo-4,6-dinitrophenol (DDNP or DINOL) (53) can be prepared from the diazotization of 2-amino-4,6-dinitrophenol (52) (picramic acid);⁴² the latter is obtained from the selective reduction of picric acid with ammonium sulfide.⁴³ 2-Diazo-4,6-dinitrophenol (53) is widely used as an initiating charge in detonators and caps.

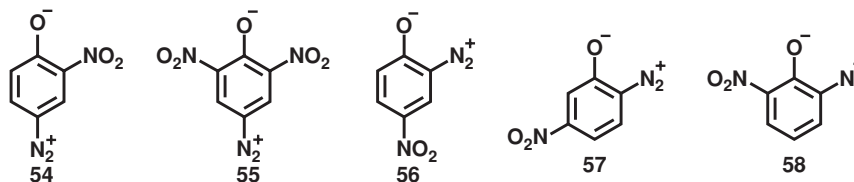


Figure 8.21

Vaughan and Phillips⁴⁴ prepared a number of nitro-substituted 4-diazophenol (54 and 55) and 2-diazophenol (56, 57 and 58) derivatives from the diazotization of the corresponding 4-amino- and 2-amino-phenols respectively. This work showed that nitro derivatives of 4-diazophenol are more stable than the corresponding 2-diazophenols and that the presence of a nitro group *o/p*- to the oxo group leads to higher stabilization compared to when the nitro group is positioned *m*- to the oxo group. Diazophenols containing two *o/p*- nitro groups to the oxo group show even higher stability; 2-diazo-4,6-dinitrophenol (53) and 4-diazo-2,6-dinitrophenol (55) falling into this category.

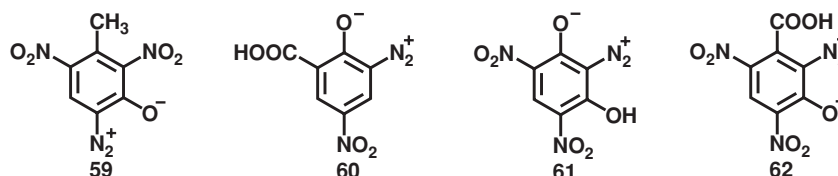


Figure 8.22

Glowiak⁴¹ studied the stability of the four diazophenols (59–62), which he prepared from the diazotization of the corresponding aminophenols. It was noted that (61) and (62) show higher chemical stability than (59) and (60); the latter compounds were postulated to have a quinonoid structure rather than a zwitterionic diazophenol structure.

8.3.2 Diazophenols from the rearrangement of *o*-nitroarylnitramines

The nitration of anilines frequently involves the formation of a nitramine which can sometimes be isolated or may undergo a spontaneous *N* → *C* nitro group rearrangement depending on the conditions of the nitration. This is the basis of the Bamberger rearrangement (Section 4.5). However, when an aromatic nitramine contains a nitro substituent in an *ortho* position, an electrocyclic rearrangement can occur with the formal displacement of HNO₃ from the molecule and the formation of a diazophenol; in effect, the *ortho* nitro group undergoes an intramolecular displacement by the adjacent nitramino functionality.⁴⁵ Studies have shown that rearrangement is favoured when the intermediate nitramine contains a nitro group *ortho* to the nitro group being displaced i.e. *meta* to the nitramino functionality, this arrangement activating the nitro group towards displacement.⁴⁵ More than often in these cases the formation of the diazophenol is so favourable (an intramolecular process) that the intermediate nitramine is not isolated and the diazophenol is the sole product.

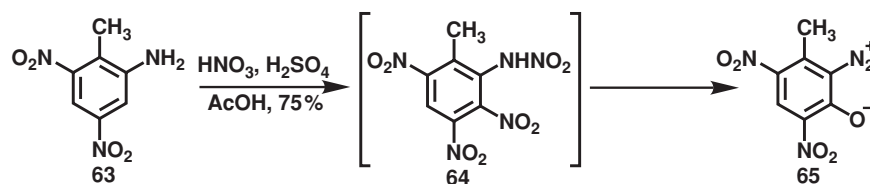


Figure 8.23

342 Miscellaneous Explosive Compounds

The nitration of 2-amino-4,6-dinitrotoluene (63) with a mixture of nitric acid in sulfuric and acetic acids yields 2-diazo-3-methyl-4,6-dinitrophenol (65) in 75 % yield without isolation of the intermediate nitramine (64).⁴⁶

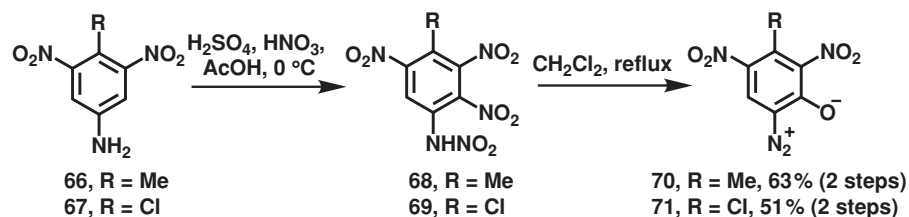


Figure 8.24

The nitration of both 4-methyl- and 4-chloro-2,6-dinitrotoluenes (66 and 67) with mixed acid in acetic acid at subambient temperature allows the isolation of the nitramines, (68) and (69), respectively. Thermolysis of (68) and (69) in refluxing methylene chloride yields the corresponding diazophenols, (70) and (71), respectively.⁴⁶ Scilly and co-workers⁴⁷ isolated 2-diazo-4,6-dinitrophenol (DINOL) (53) from the thermolysis of *N*,2,3,5-tetranitroaniline (73) in ethyl acetate at 60 °C.

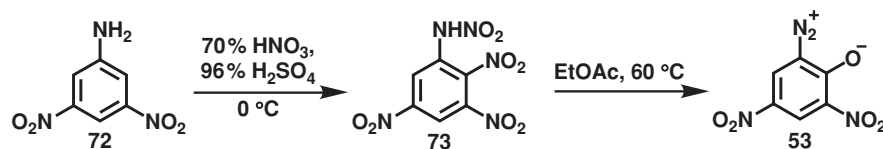


Figure 8.25

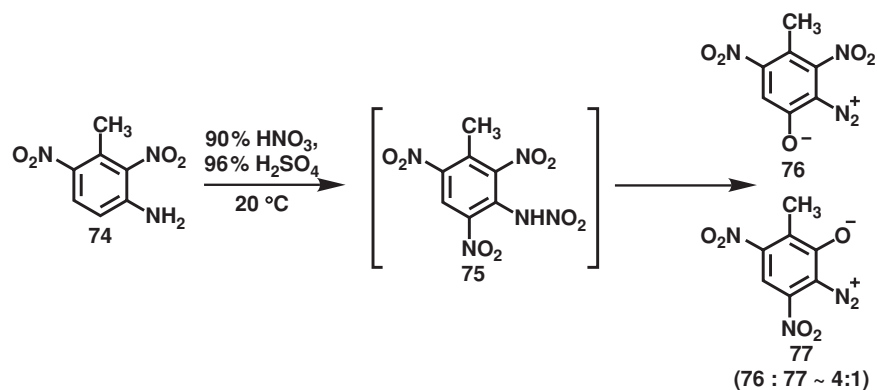


Figure 8.26

Unsymmetrical aryl nitramines with two nitro groups positioned *ortho* to the nitramino functionality can yield two isomeric diazophenol products. The diazophenols (76) and (77) were isolated in a 4:1 ratio from the nitration of 3-amino-2,6-dinitrotoluene (74) with mixed acid, the reaction proceeding via the intermediate nitramine (75).⁴⁵

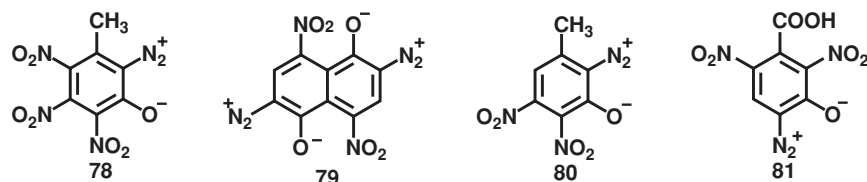


Figure 8.27

Chemists at the Naval Air Warfare Center (NAWC), China Lake, have conducted much research into the nitration of various substituted anilines as an indirect route to highly nitrated arylene hydrocarbons (Section 4.5). On numerous occasions these chemists found that diazophenols are formed as by-products and sometimes as the main or only product of a reaction. During these studies the diazophenols (65)⁴⁶ and (78–81)^{45,48–50} were isolated and characterized. These diazophenols were screened for use as explosive components of both percussion and stab-sensitive primary explosive compositions.⁴⁵

8.4 NITROGEN-RICH COMPOUNDS FROM GUANIDINE AND ITS DERIVATIVES

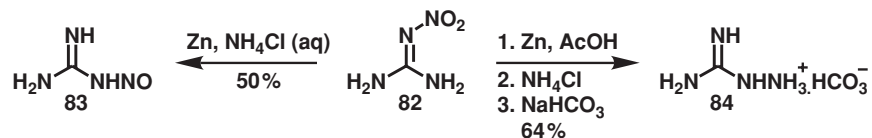


Figure 8.28

Nitroguanidine (82) is a starting material for the synthesis of a number of nitrogen-rich compounds of which many have explosive properties. Nitrosoguanidine (83) is prepared from the reduction of nitroguanidine (82) with zinc dust in the presence of aqueous ammonium chloride.⁵¹ Nitrosoguanidine is a primary explosive but its slow decomposition on contact with water limits its use. The reduction of nitroguanidine (82) with zinc dust in aqueous acetic acid yields aminoguanidine which is usually isolated as the sparingly soluble bicarbonate salt (84).⁵²

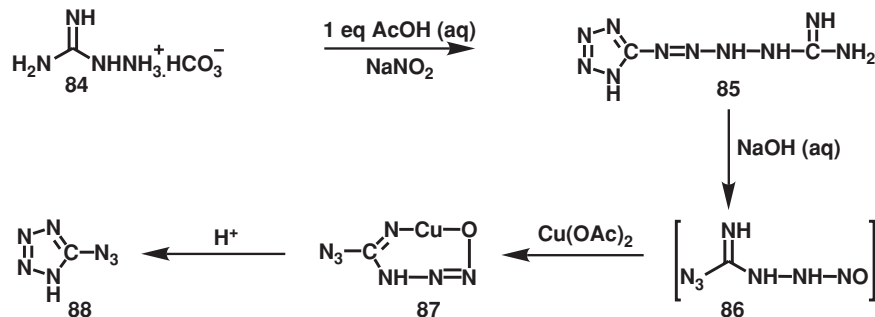


Figure 8.29

344 Miscellaneous Explosive Compounds

The reaction of aminoguanidine with sodium nitrite under neutral conditions yields tetrazolylguanilyltetrazene hydrate (85), a primary explosive commonly known as tetrazene.⁵³ Tetrazene (85) is only formed in the absence of free mineral acid and so a common method for its preparation treats the bicarbonate salt of aminoguanidine (84) with one equivalent of acetic acid followed by addition of aqueous sodium nitrite.⁵⁴ Tetrazene (85) is decomposed by aqueous alkali to form triazonitrosoaminoguanidine (86) which is isolated as the cuprate salt (87) on addition of copper acetate to the reaction mixture.^{55,56} Acidification of the copper salt (87) with mineral acid leads to the formation of 5-azidotetrazole (88) ($\text{CHN}_7 = 88\% \text{ N}$).^{55,56}

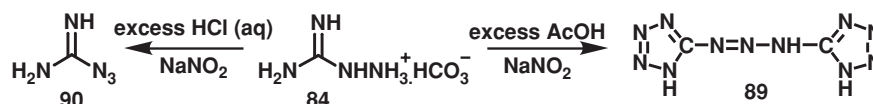


Figure 8.30

The reaction of aminoguanidine bicarbonate (84) with sodium nitrite in the presence of excess acetic acid produces 1,3-ditrazolyltriazine (89), another nitrogen-rich heterocycle ($\text{C}_2\text{H}_3\text{N}_{11} = 85\% \text{ N}$) which readily forms explosive metal salts.^{55,56} The reaction of aminoguanidine bicarbonate (84) with sodium nitrite in the presence of mineral acid yields guanyl azide (90), of which, the perchlorate and picrate salts are primary explosives.^{55,56} Guanyl azide (90) reacts with sodium hydroxide to form sodium azide, whereas reaction with weak base or acid forms 5-aminotetrazole.^{55,56}

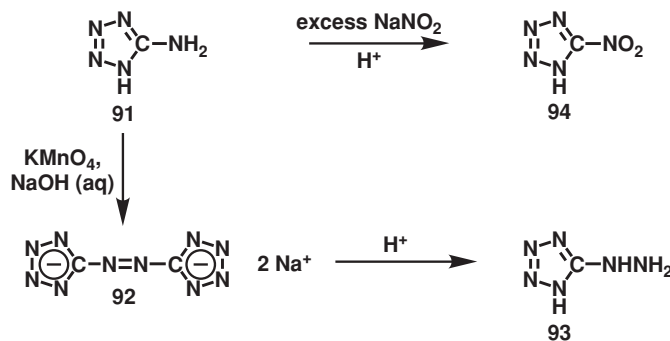


Figure 8.31

5-Aminotetrazole (91) reacts with potassium permanganate in excess aqueous sodium hydroxide to yield the disodium salt of 5-azotetrazole (92).⁵⁷ 5-Azotetrazole is unstable and attempts to isolate it by acidification yields 5-hydrazinotetrazole (93).⁵⁸ Diazotization of 5-aminotetrazole (91) in the presence of excess sodium nitrite yields 5-nitrotetrazole (94), a powerful explosive whose mercury and silver salts are primary explosives.⁵⁹

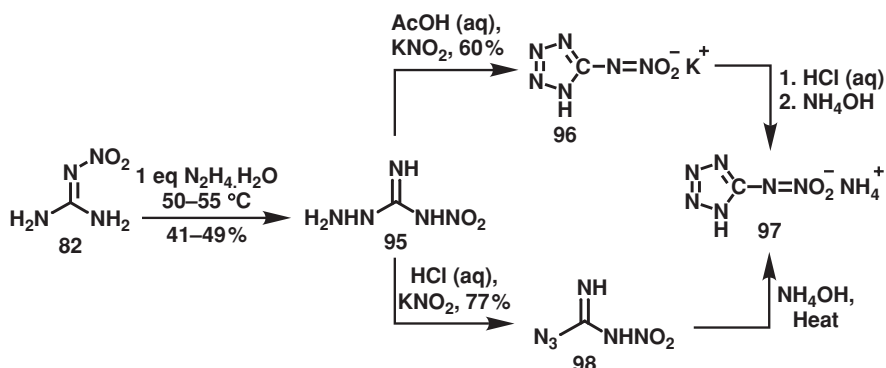


Figure 8.32

Nitroguanidine (82) undergoes hydrazinolysis on treatment with one equivalent of hydrazine hydrate to yield nitraminoguanidine (95), a compound which possesses explosive properties.^{60,61} Nitraminoguanidine (95) reacts with potassium nitrite in the presence of acetic acid to yield the potassium salt of 5-nitraminotetrazole (96), whereas the same reaction in the presence of mineral acid yields the azide (98), the latter yielding the ammonium salt of 5-nitraminotetrazole (97) on heating with aqueous ammonia.⁶² Reduction of nitraminoguanidine (95) with zinc dust in acetic acid yields diaminoguanidine (99).⁶⁰

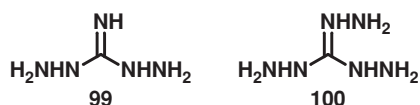


Figure 8.33

The salts formed between triaminoguanidine (100) and some oxidizing acids have attracted interest as potential components of energetic propellants. Triaminoguanidine (100) has been synthesized by treating dicyandiamide,⁶³ guanidine,⁶⁴ nitroguanidine⁶⁴ and diaminoguanidine⁶⁴ with an excess of hydrazine hydrate at reflux. The reaction between hydrazine hydrate and carbon tetrachloride at reflux is also reported to form triaminoguanidine (100).⁶⁵

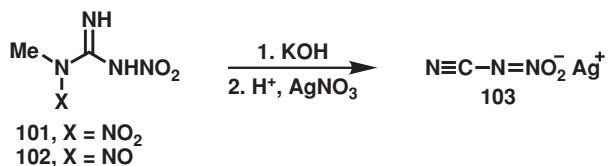


Figure 8.34

Hydrolysis of *N'*-nitro-*N'*-methylnitroguanidine (101) and *N'*-nitroso-*N'*-methylnitroguanidine (102) with aqueous potassium hydroxide results in the formation of potassium cyanamide.⁶⁶ Addition of acidic silver nitrate solution to these reaction mixtures leads to

346 Miscellaneous Explosive Compounds

the precipitation of the dangerously explosive silver salt (103) which has been used to prepare a variety of nitrocyanamide metal salts for testing as primary explosives.⁶⁷

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