Ross Miller

Approaches to the Synthesis of Energetic Heterocyclic Compounds Suitable for Use in Insensitive Explosive and Propellant Compositions

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Outline of Presentation

- Introduction
- Reappraisal of Insensitive High Explosives (IHEs)
- Selection Method for Candidate Compounds
- Discussion of Syntheses of Selected Candidates
- Other Properties of Selected Candidates
- Conclusions
- Acknowledgements

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Insensitive explosives/propellants

- Create insensitive composition by desensitisation of high energy compounds (e.g. HMX)
- Synthesise intrinsically insensitive HE compounds

Rationale Behind IHE Research

- Previous types of IHE compounds
  - Amino-nitro aromatics e.g. TATB, DATB
    - Known since 1880s
    - Insensitive to ignition
    - Large critical diameter
    - PBX developments overcame these issues
    - Nuclear applications
  - Picrylated aromatics (carbo-/heterocyclic) e.g. 2,6-di-(picrylamino)-3,5-dinitropyridine (PYX)
    - Behaved more like nitoraromatics
    - Low sensitivity
    - But low performance

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Newer Types of IHEs

- Increased nitrogen content
  - Heterocyclic nuclei instead of carbocyclic *(O Balance)*
  - More amino groups and fewer nitro groups *(H bonding)*
  - Replace nitro groups by N-oxide *(Sensitiveness)*
- Increased density
  - Heterocyclics
  - Unsymmetrical molecules
- Both these changes lead to increased power output with maintained or improved insensitivity

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Objective

- Reassessment as
  - Cheaper sources of chemicals may make then viable
  - Newer applications (e.g. initiators, explosive trains) need smaller amounts
- Examine molecules made on lab scale
- Assess feasibility of scaling up to Kg scale
  - Availability of raw materials
  - Cost of raw materials
  - Practicality of synthesis
  - Safety of scale up

Selection Criteria for new IHEs

- Power (Pcj) greater than TATB (i.e. >25 GPa)
- Impact sensitivity acceptable (not <70 cm [US $h_{50\%}$])
- Density >1.75 gcm^{-3}
- Thermally stable (DSC exotherm >200^{o}C)

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Structural Classes of New IHEs

- 1,2,5-Oxadiazoles (Furoxans)
- 1,2,4-Triazoles (including ANTA derivatives)
- 1,2,3-Triazoles
- Pyrazoles
- Other monocyclic heterocycles
- Non-heterocycles
- >50 compounds considered originally

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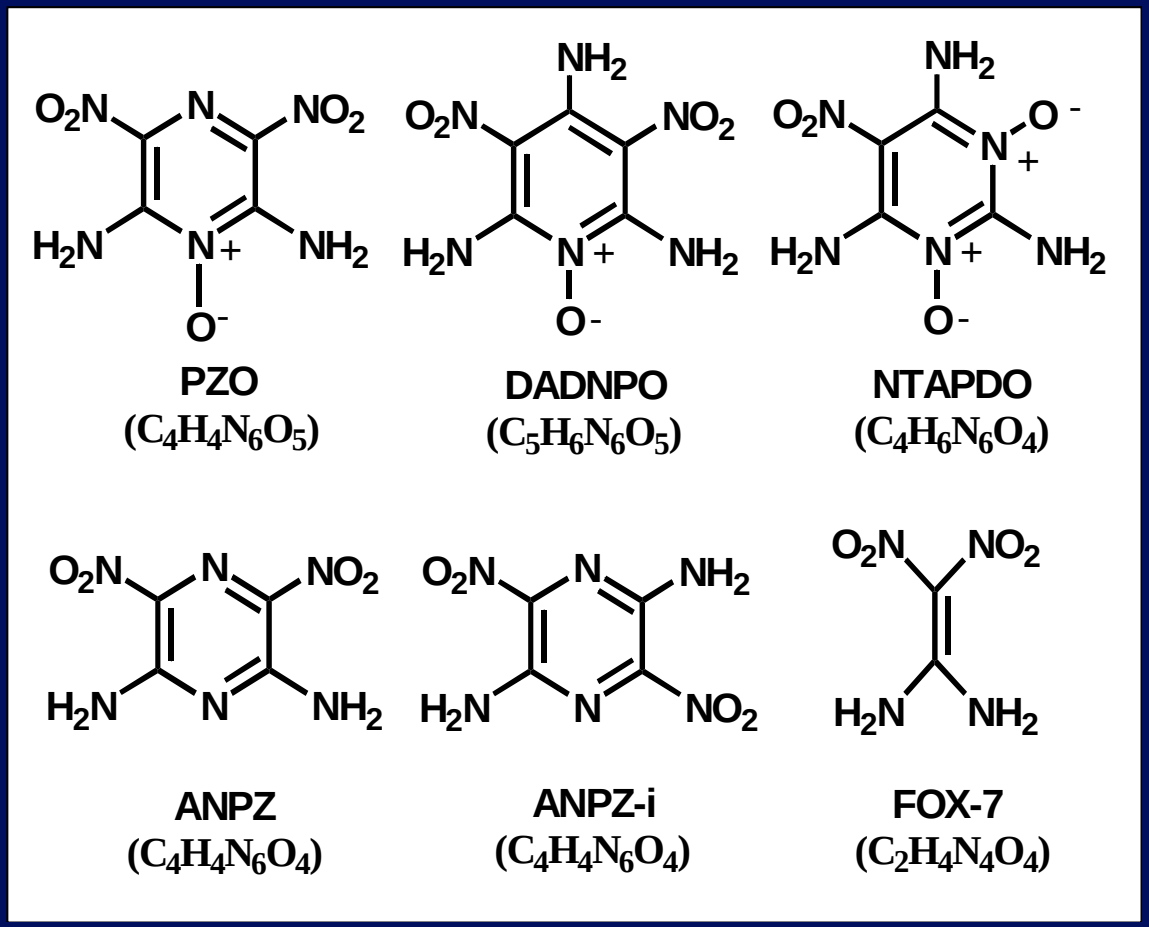
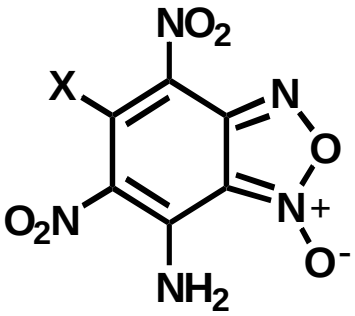
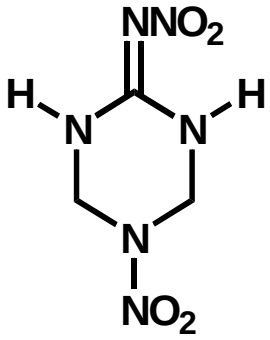
IHE Structures (Selection)



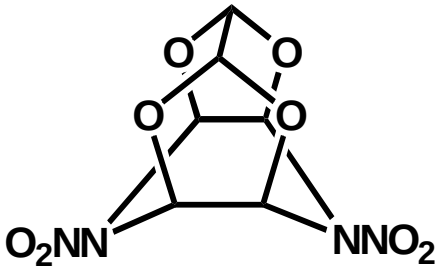
IHE Structures (Selection) - continued



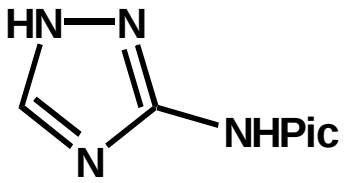
X=NH_2: CL-14 ($C_6H_4N_6O_6$)
X=H : ADNBF ($C_6H_3N_5O_6$)



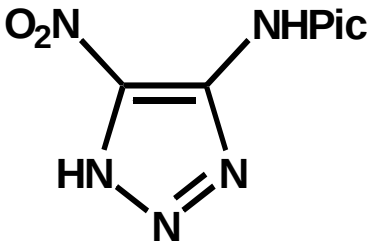
NNHT
($C_3H_6N_6O_4$)



TEX
($C_6H_4N_4O_8$)



PATO
($C_8H_5N_7O_6$)



PANT
($C_8H_3N_8O_8$)

Downselection

- FOX-7, TEX, DADNPO commercially available
- PATO – low density
- PZO – question over sensitiveness
- ANPZ – precursor to PZO
- ADNBF – lower performance than Cl-14
- Left 5 candidates

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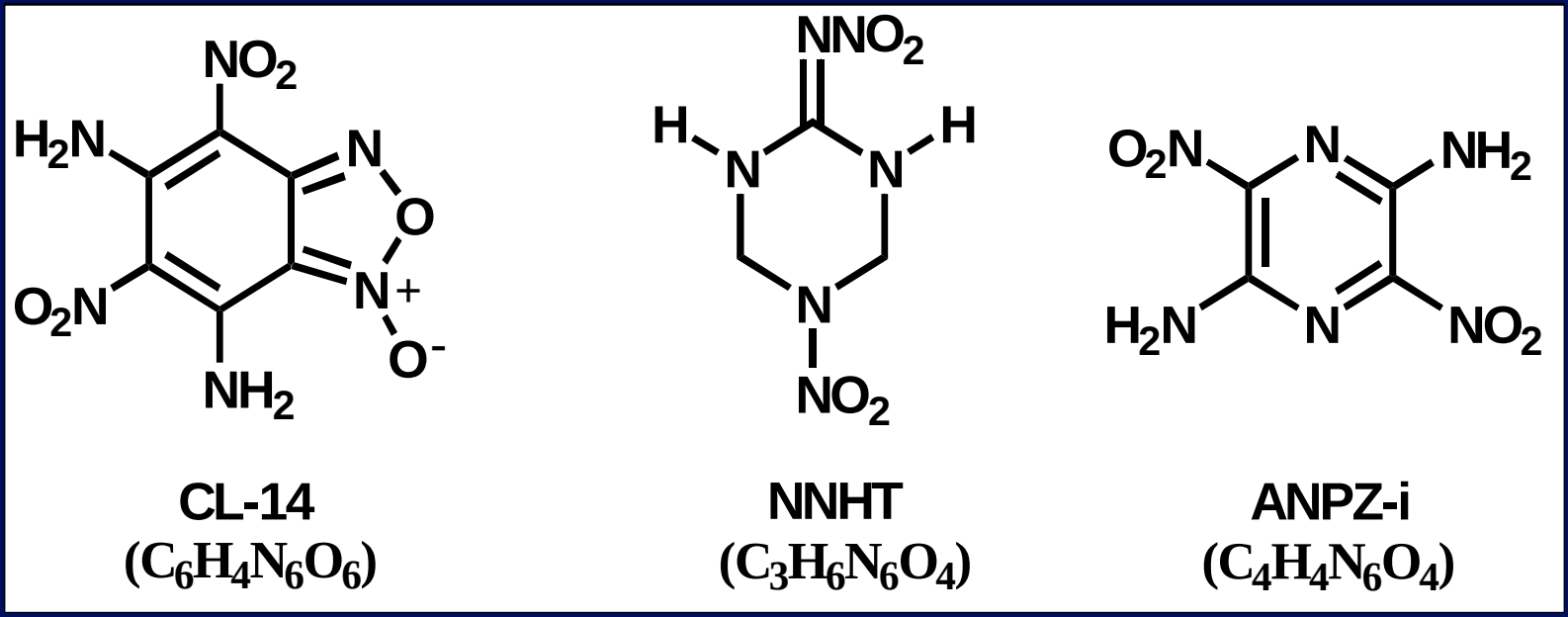
Further Downselection

- NTAPDO – N oxidation could not be achieved
- PANT – safety (p-toluenesuphonyl azide) and cost
- Left 3 candidates – NNHT, CL-14 and ANPZ-i

Structures of Selected IHE Candidates



CL-14 ($C_6H_4N_6O_6$)

NNHT ($C_3H_6N_6O_4$)

ANPZ-i ($C_4H_4N_6O_4$)

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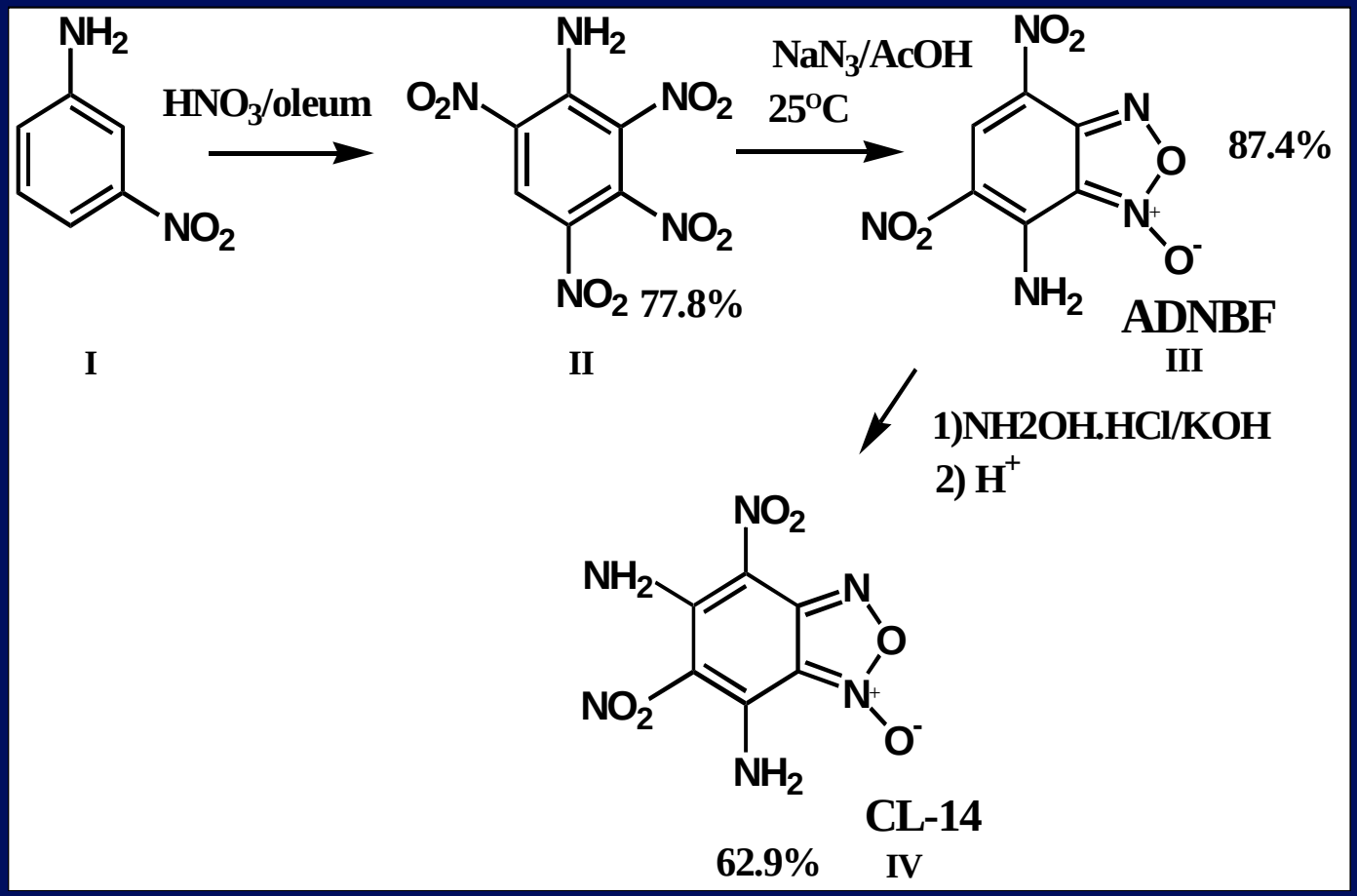
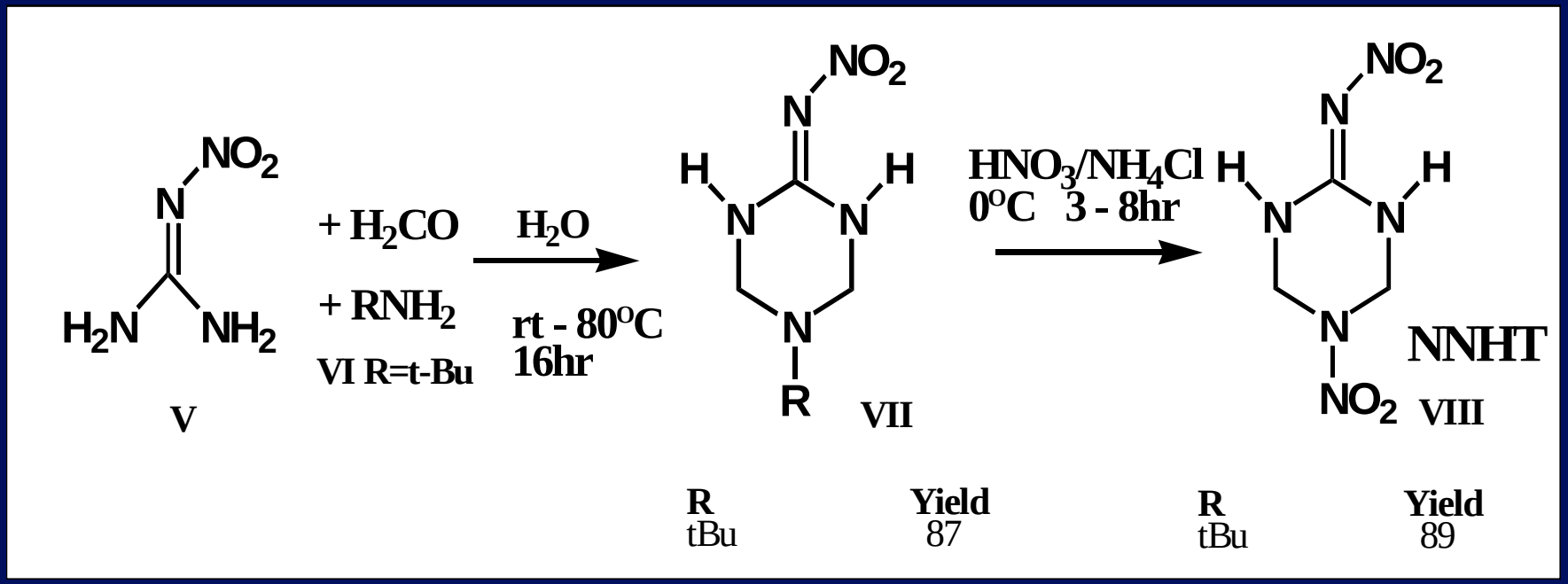
Synthesis of CL-14



CL-14

- 1st stage nitration
  - Possible problem with sensitiveness of tetranitroaniline
  - possible with N_2O_5/sulphuric acid at lower temp.
- Waste streams being analysed
- Reported applications
  - Pressable compositions with EVA binder (for boosters)
  - Melt-castable explosive compositions with either:
    - Carnauba waxes
    - Ozokerite waxes

Synthesis of NNHT



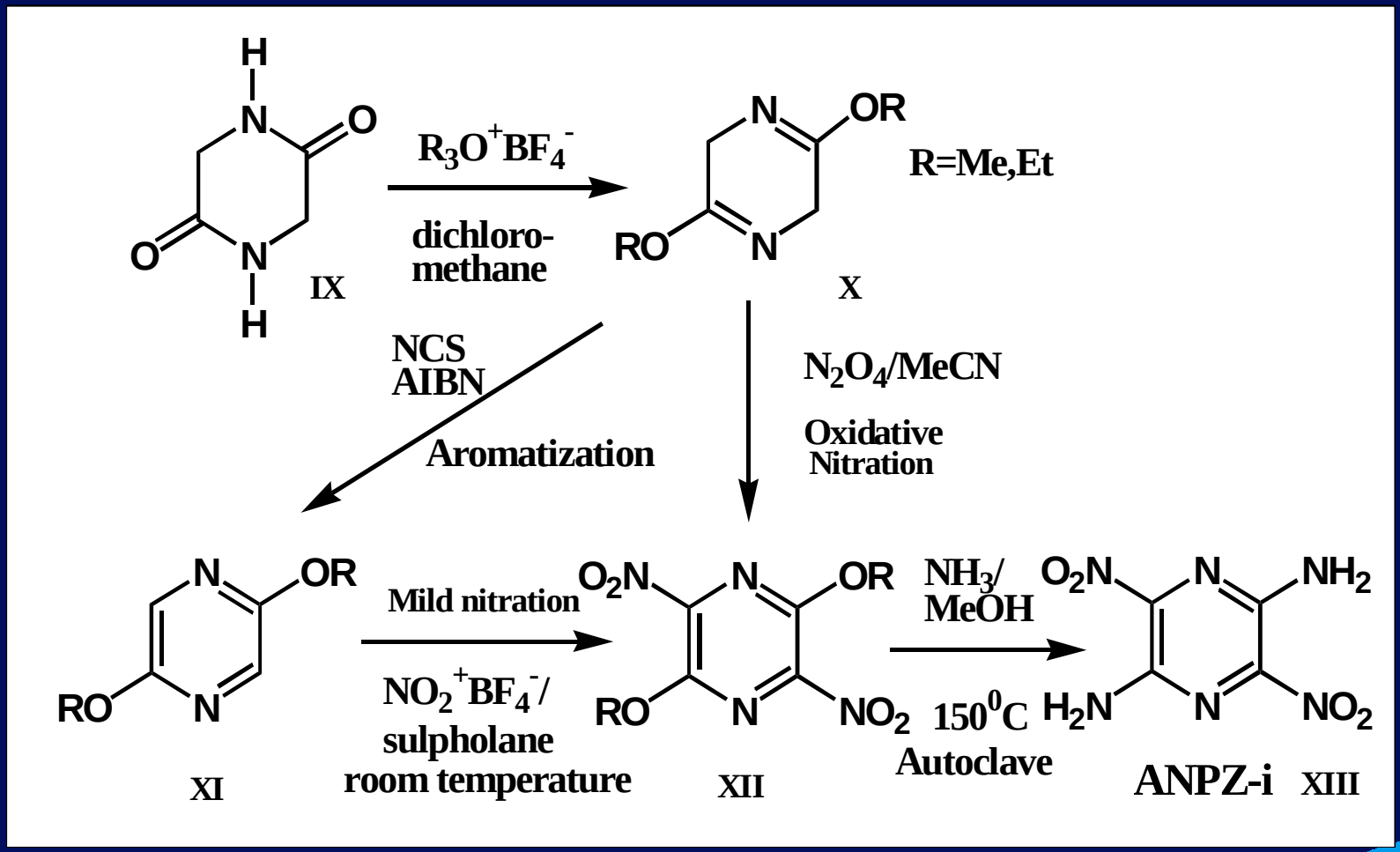
R	Yield
tBu	87

R	Yield
tBu	89

NNHT

- First synthesised by Aerojet, also studied in Russia and Australia
- 1st step is 16 hour reaction
- 2nd is 8 hour reaction
- Working to reduce these
- Reported application as oxidizer for gun propellants

Synthesis of ANPZ-i



ANPZ-i

- First reported in Russia
- Synthesis improved in QinetiQ
- Complex synthesis
- Working to improve by use of 2-amino-5-chloro, 2-amino-5-bromo or 2,5-dichloro-pyrazines
- No reported uses

Explosive Performance

Compound	Formula	Exptl. Density gcm^{-3}	Calc. Density gcm^{-3}	ΔH_f $kcalmol^{-1}$	P_{cj} from exptl. Density GPa	P_{cj} from calc. Density GPa
CL-14	$C_6H_4N_6O_6$	1.91	1.94	21	32.4	33.3
ANPZ-i	$C_4H_4N_6O_4$	n/k	1.88	23.2	n/k	34.9
NNHT	$C_3H_6N_6O_4$	1.75	1.764	16.3	29.9	29.3

Enthalpies of formation (ΔHf) were calculated using the software MOPAC Version 6.00 with the PM3 semi-empirical method, density calculations were carried out using the MOLPAK 2.0 software – the results obtained are the highest theoretical densities calculated by this program – and Cheetah 2.0 was used for detonation pressure (Pcj) calculations.

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Conclusions

- Explosive compounds exist which:
  - Possess high performance yet exhibit low sensitivity
  - And can be synthesised in quantity
- Downselected against a number of criteria
- Three candidate compounds are currently undergoing evaluation (one will be recommended for scale up)
- Should be suitable for EIDS category compositions (UN 1.6)

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Acknowledgements

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