Azole-Based Energetic Salts

Rachel Whittaker
March 28, 2012

Overview

- Background
- Tetrazole-Based
- Triazole-Based
- Imidazole/ Pyrazole Based
- Analysis of Energetic Properties
- Conclusions

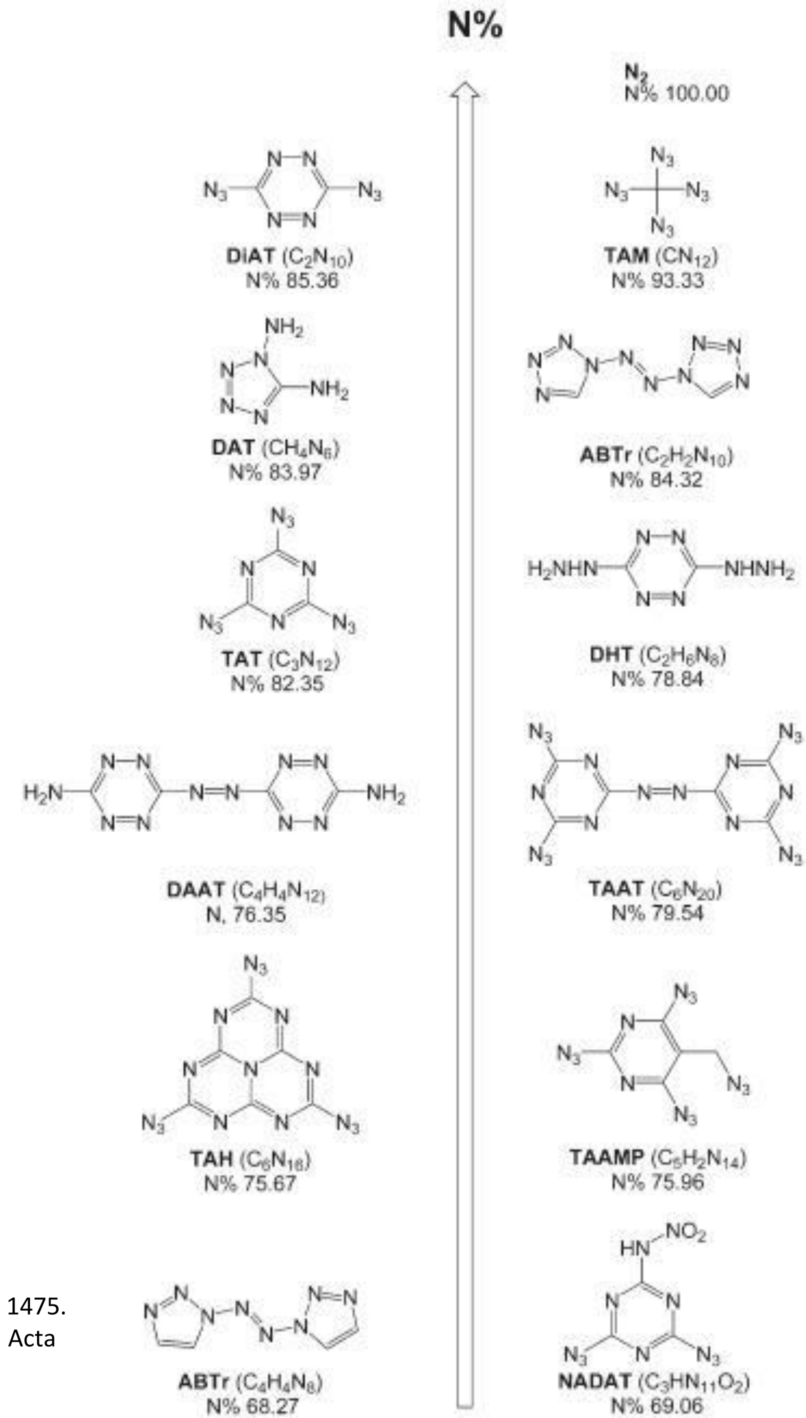
What Is Energetic Material?

that, when subjected to
ndergoes rapid, heat-
ion
propellants, and

tio
and pressure of surround
– Propellant- Combust in a
large volume of gas, raisi
enough to move an obje
– Pyrotechnics – Undergo
production of audiovisua

HEMDs

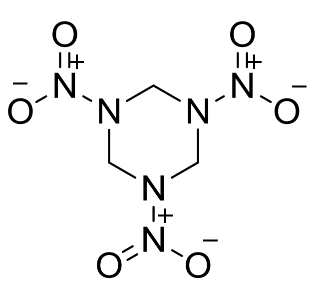
- High Energy Density Materials
- Traditional vs. High Nitrogen
  - Driving force: intramolecular oxidation vs. formation of N_2 triple bond
- Energetic Salts = newest development
  - Tend to have lower vapor pressures, higher densities, and be thermostable
- Azole salts show great promise

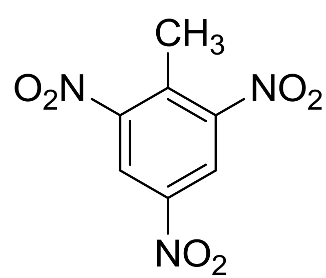


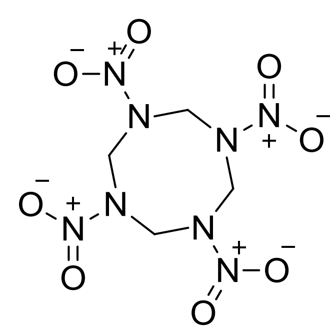
Steevens, J. A.; Duke, B.; Lotufo, G. R.; Bridges, T. S. Environ. Toxicol. Chem. 2002, 21, 1475.
Steinhauser, G.; Giester, G.; Leopold, N.; Wagner, C.; Villa, M.; Musilek, A. Helv. Chim. Acta 2010, 93 (2), 183.

RDX, TNT, HMX

- 1,3,5-trinitroperhydro- 1,3,5-triazine (RDX)
  - First synthesized in Germany in 1898 by nitrating hexamine nitrate and was used heavily in WWII
- Trinitrotoluene (TNT)
  - First made in 1863 in Germany as a yellow dye, then used during WWI
- 1,3,4,7-tetranitro- 1,3,5,7-tetrazocane (HMX)
  - First made from RDX in 1930 and also used heavily in WWII

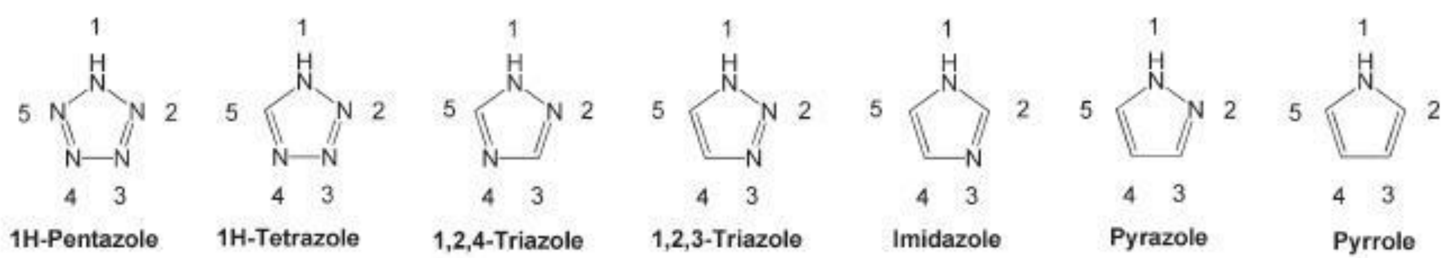






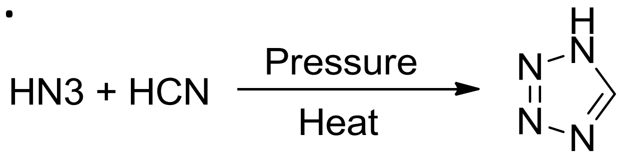
Azoles

- Class of 5-membered heterocyclic rings that contain at least one other non-carbon atom (N,S, or O)
  - Imidazole is well known example
- Very large role in many areas of synthesis
- When paired with energetic anions form energetic salts
  - Advantages: smokeless combustion, high heats of formation, high propulsive power, and high I_{sp}

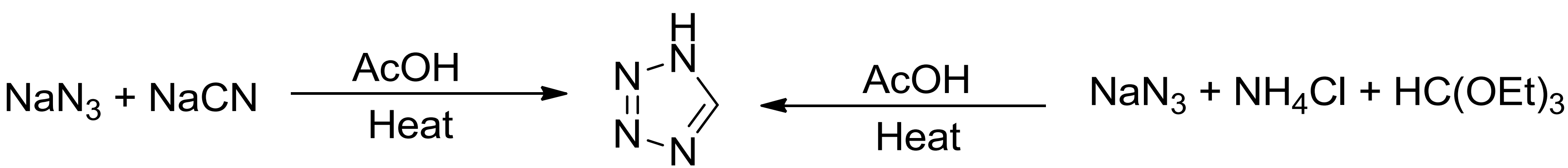


Tetrazole -Based

- Ring of 4 nitrogens and 1 carbon
- First prepared via:



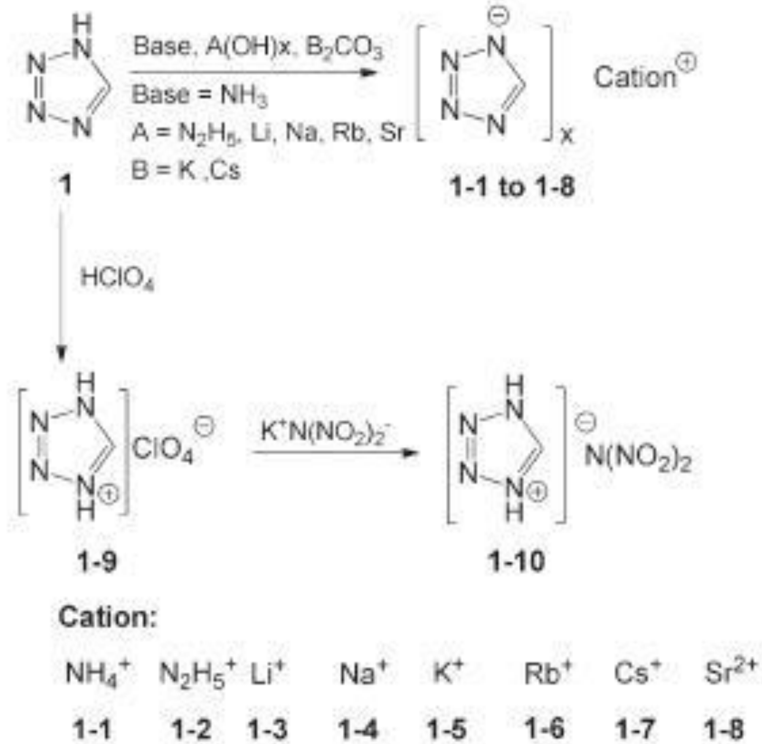
- Neutral molecule is quite stable, and deprotonation leads to extremely aromatic anion
- Addition of functional groups such as amine and nitro leads to new energetic properties
- Primarily used as high performance explosives



Klapotke, T. M.; Stein, M.; Stierstorfer, J. Z. Anorg. Allg. Chem. 2008, 634, 1711.

1H-Aminotetrazole Salts

- Simplest form

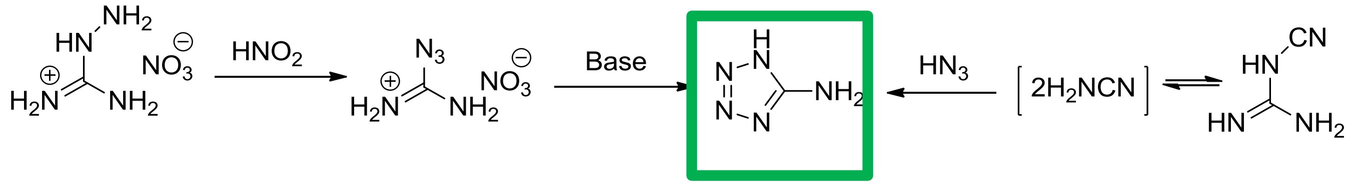


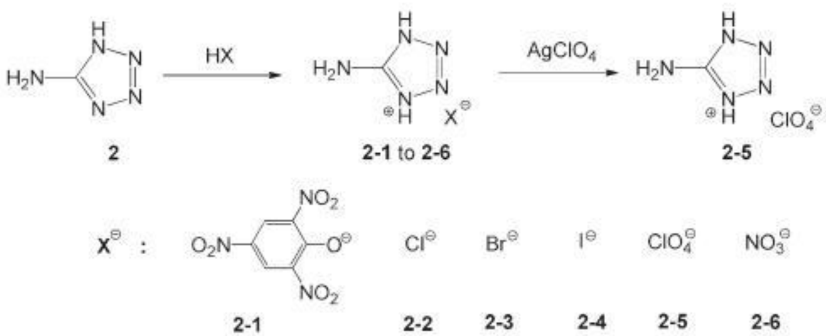
- Li^{+} and Sr^{2+} are the most promising candidates

Gao, H.; Shreeve, J. *Chem. Rev.* **2011**, *111*, 7377.

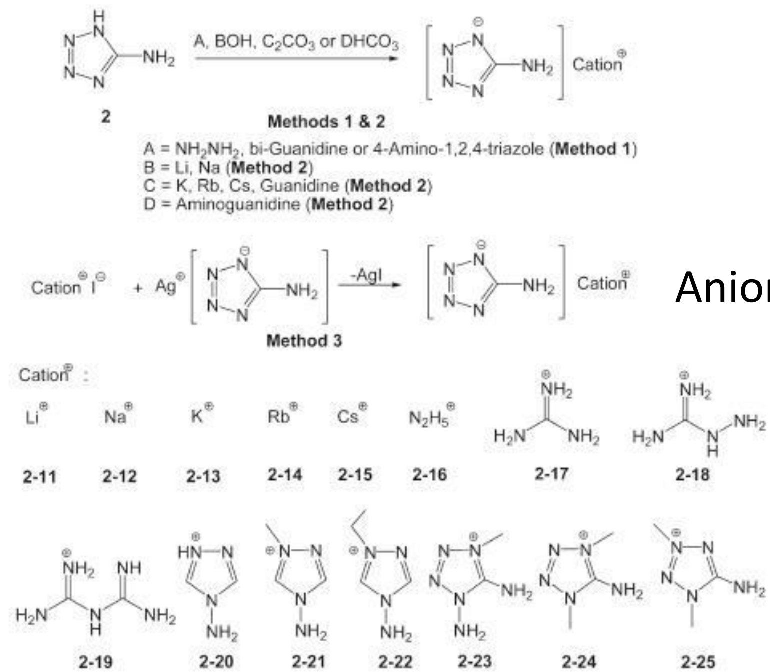
Tetrazole-Based

- 5-Amino





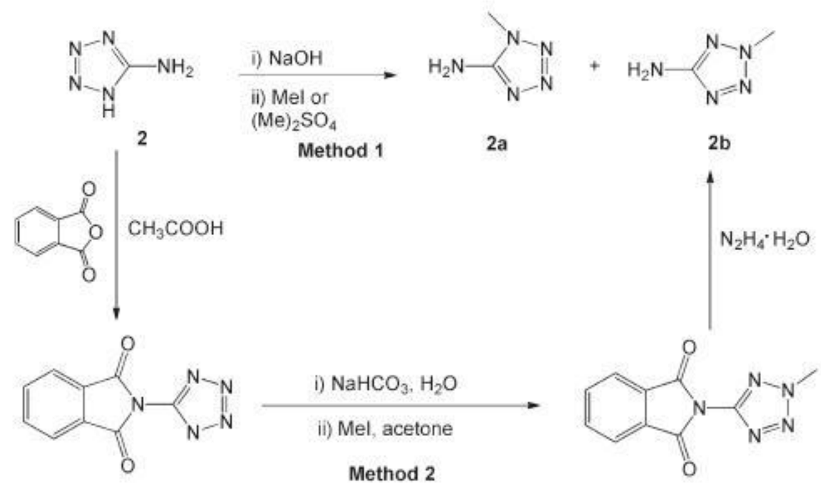
Cationic



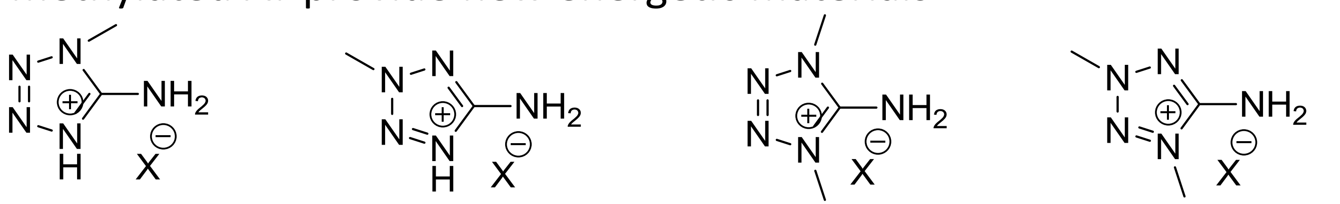
Anionic

Thiele, J. Liebigs Ann. 1892, 270, 1.
Stolle, R. Ber. Dtsch. Chem. Ges. 1929, 62, 1118.

Methylated 5-Aminotetrazole

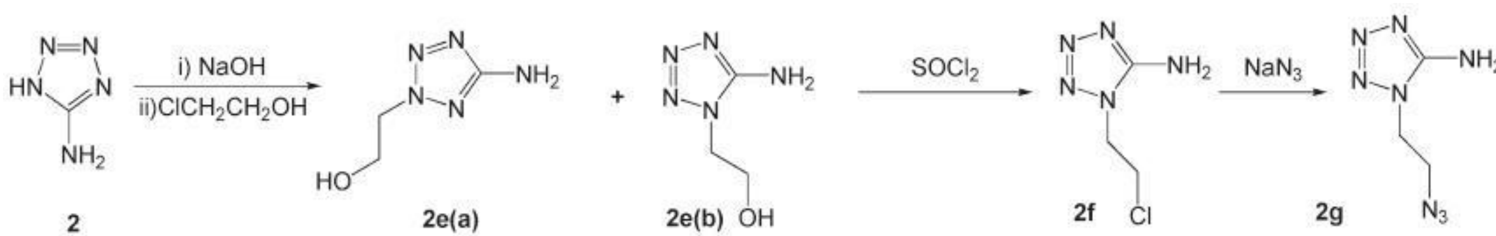


Salts of methylated AT provide new energetic materials



1-Methyl 2-Methyl 1,4-Dimethyl 1,3 Dimethyl

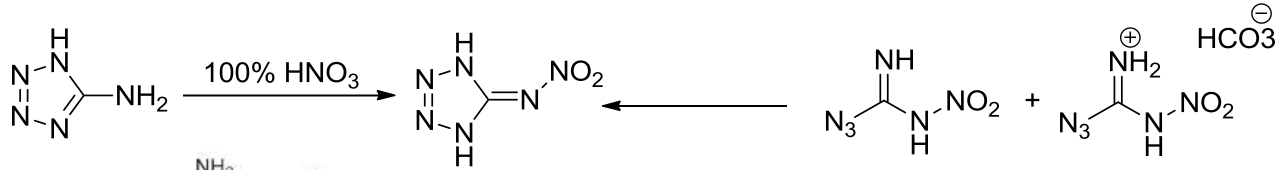
Alkylated Salts also show potential

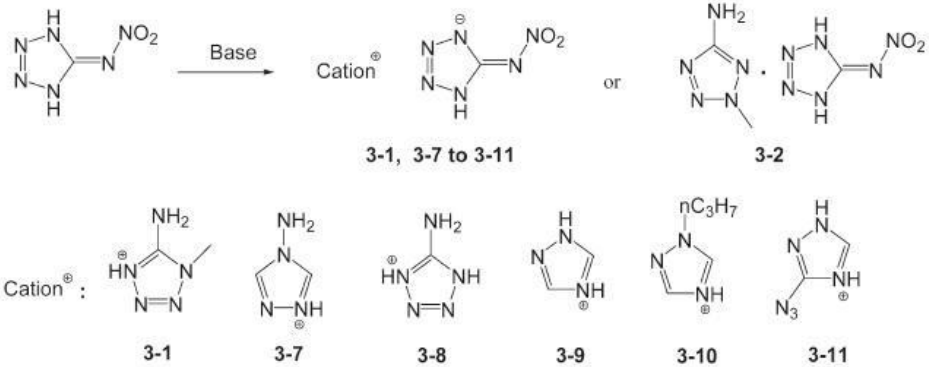


Klapotke, T. M.; Sabate, C. M.; Penger, A.; Rusan, M. Eur. J. Inorg. Chem. 2009, 880.
Stierstorfer, J.; Tarantik, K. R.; Klap€otke, T. M. Chem.—Eur. J. 2009, 15, 5775.

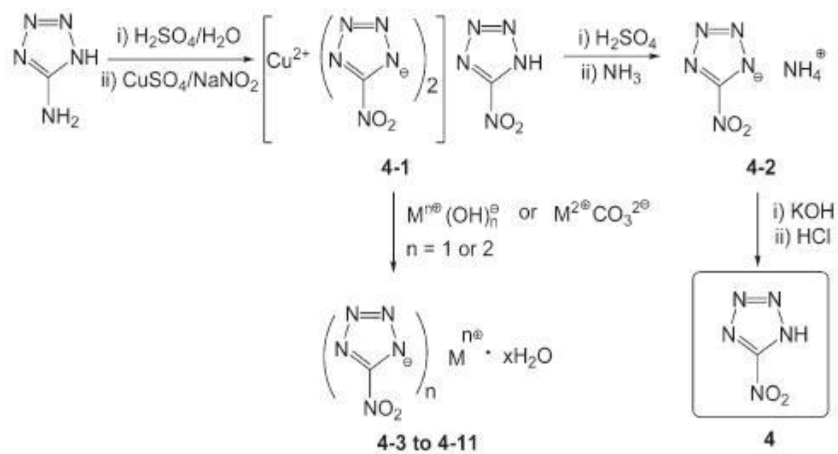
Tetrazole-Based

- 5-Nitroimino





- 5-Nitro

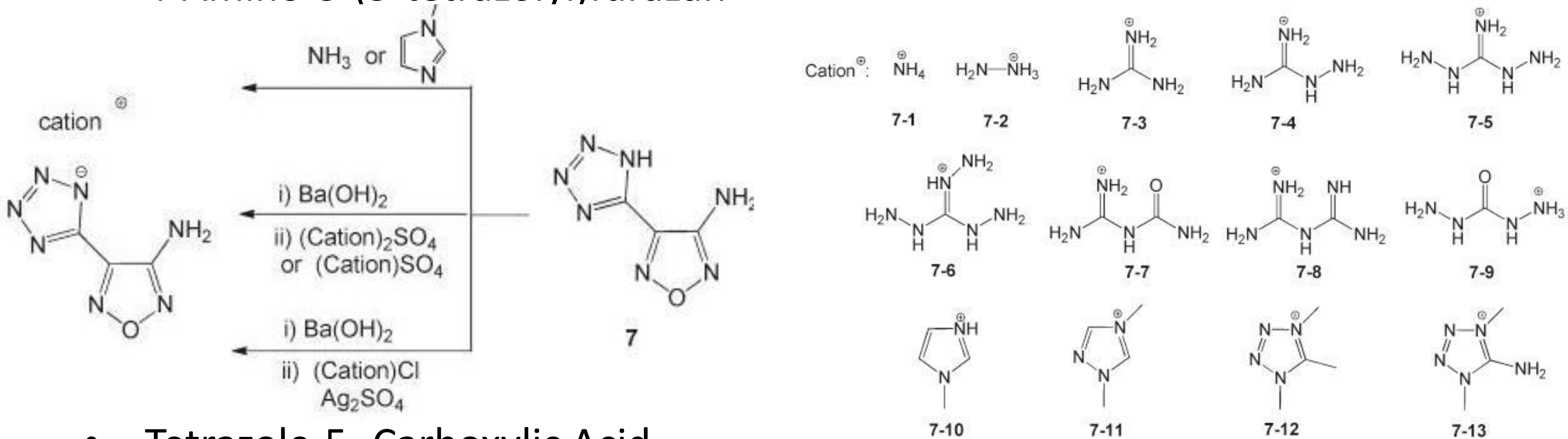


$M^{n\oplus}$	$Li^{\oplus}$	$Na^{\oplus}$	$K^{\oplus}$	$Rb^{\oplus}$	$Cs^{\oplus}$	$Mg^{2\oplus}$	$Ca^{2\oplus}$	$Sr^{2\oplus}$	$Ba^{2\oplus}$
x=	3	2	0	0	0	6	6	5	5
	4-3	**4-4**	**4-5**	**4-6**	**4-7**	**4-8**	**4-9**	**4-10**	**4-11**

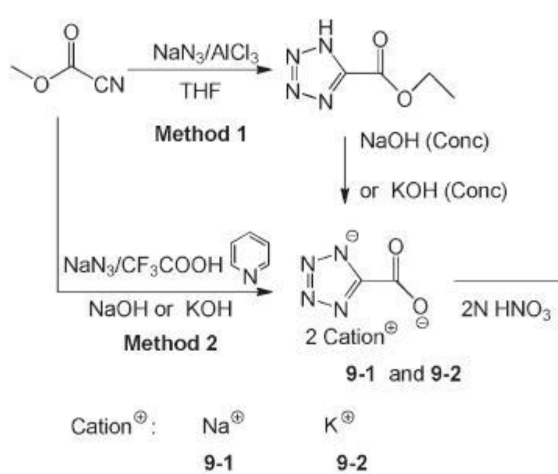
Lieber, E.; Sherman, E.; Henry, R. A.; Cohen, J. J. Am. Chem. Soc. 1951, 73, 2327.

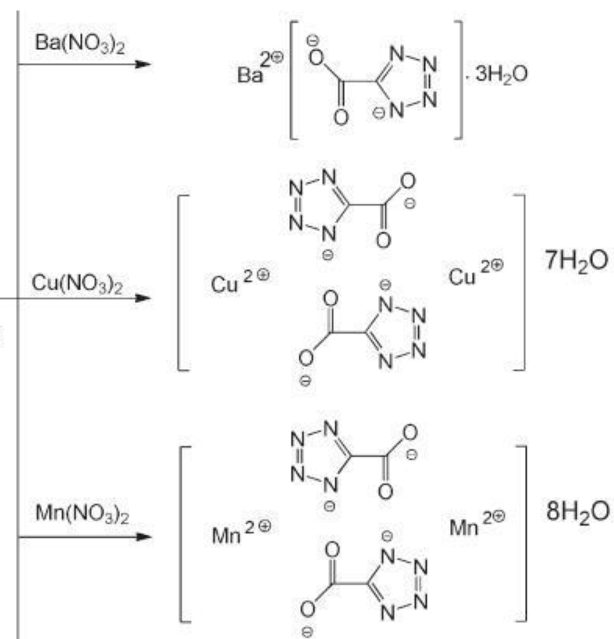
Tetrazole-Based

- 4-Amino-3-(5-tetrazolyl)furazan



- Tetrazole-5- Carboxylic Acid

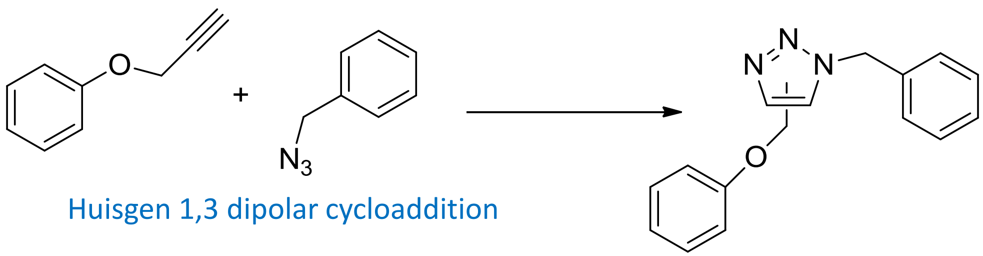




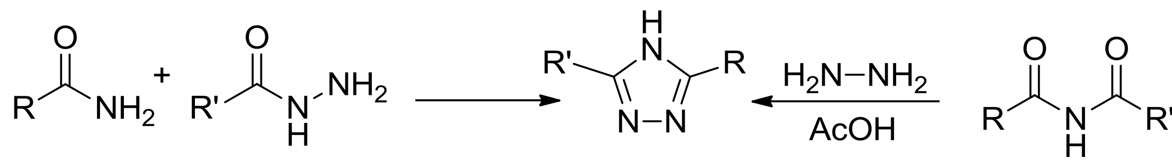
Wang, R.; Guo, Y.; Zeng, Z.; Twamley, B.; Shreeve, J. M. Chem.—Eur. J. 2009, 15, 2625.
Hartdegen, V.; Klap€otke, T. M.; Sproll, S. M. Inorg. Chem. 2009, 48, 9549.

Triazole-Based

- Heterocycle with 3 N’s and 2 C’s
- 2 isomers: 1,2,3 or 1,2,4



Huisgen 1,3 dipolar cycloaddition



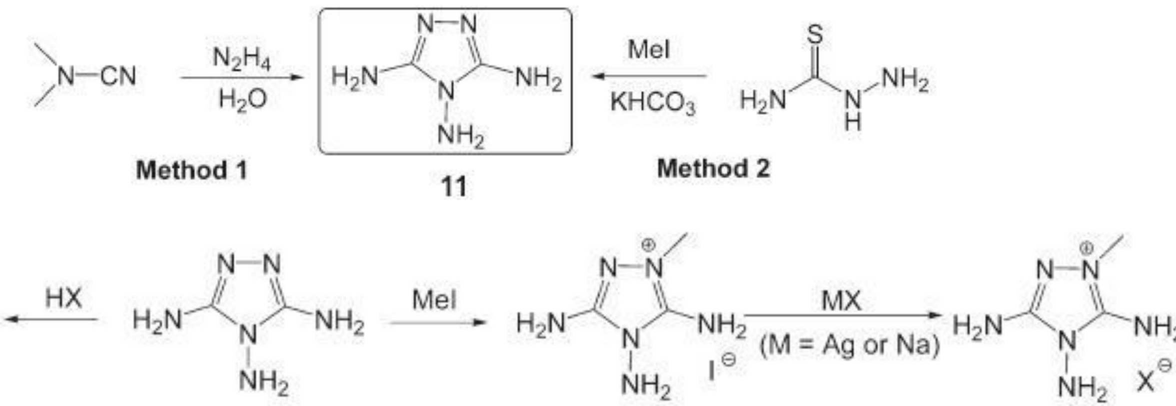
Pellizzari/ Einhorn-Brunner

- Why triazoles?
  - Derivative salts show great promise as energetic material

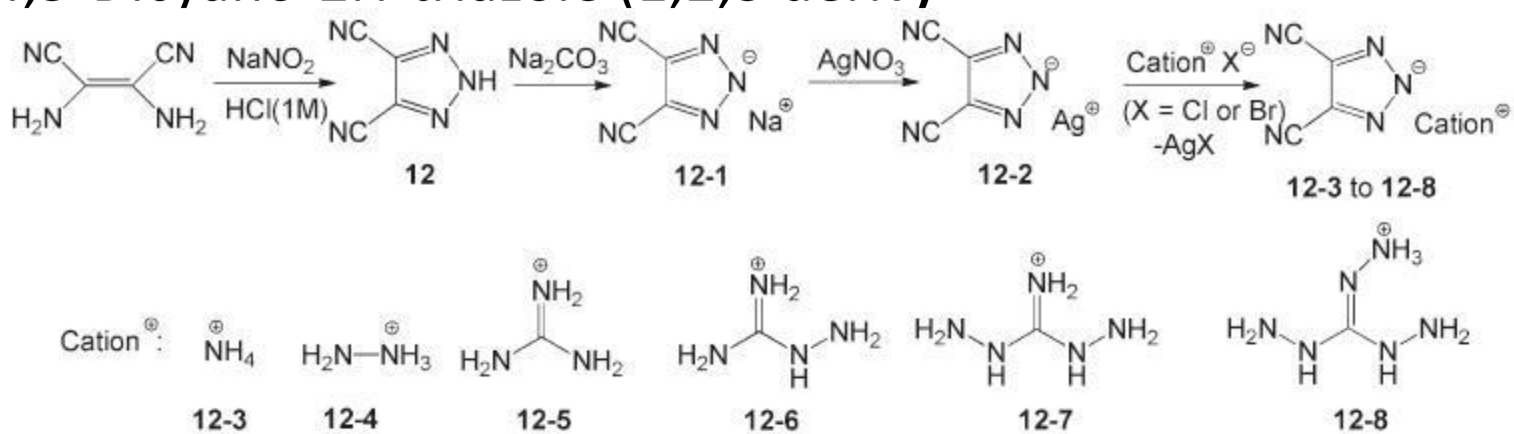
Potts, K. T. Chem. Rev. 1961, 61, 87.
Child, R. G. J. Heterocycl. Chem. 1965, 2, 98.

Triazole-Based

- 3,4,5-Triamino-1,2,4-triazole and its 1-methyl derivative show promise



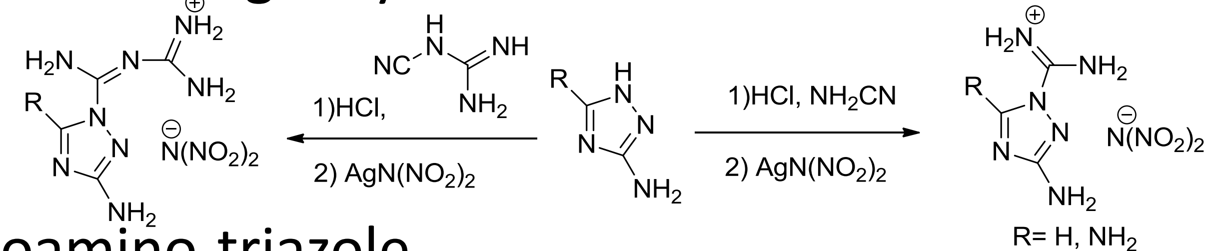
- 4,5-Dicyano-2H-triazole (1,2,3 deriv)



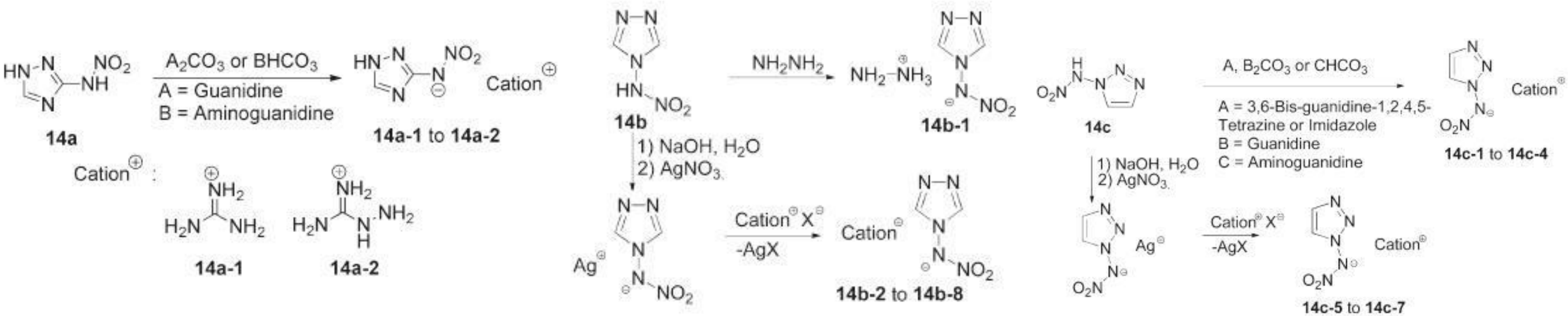
Darwich, C.; Klapotke, T. M.; Sabate, C. M. Chem.—Eur. J. 2008, 14, 5756.
Xue, H.; Gao, H.; Twamley, B.; Shreeve, J. M. Chem. Mater. 2007, 19, 1731.

Triazole-Based

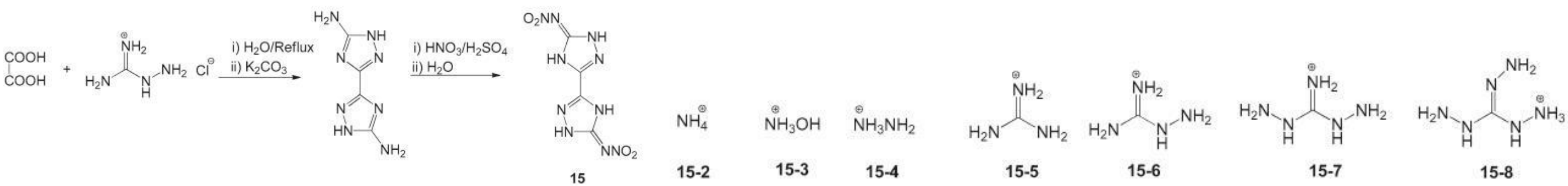
- Polyamino-1-guanyl-triazole

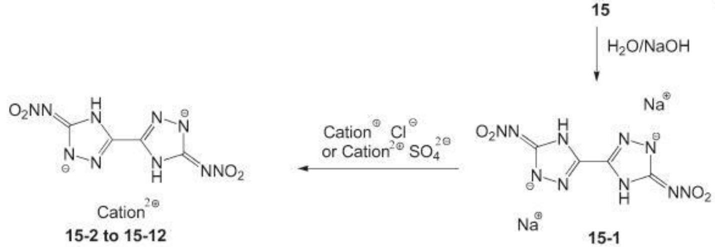


- Nitroamino-triazole



- Bis[3-(5-nitroimino-1,2,4-triazole)]

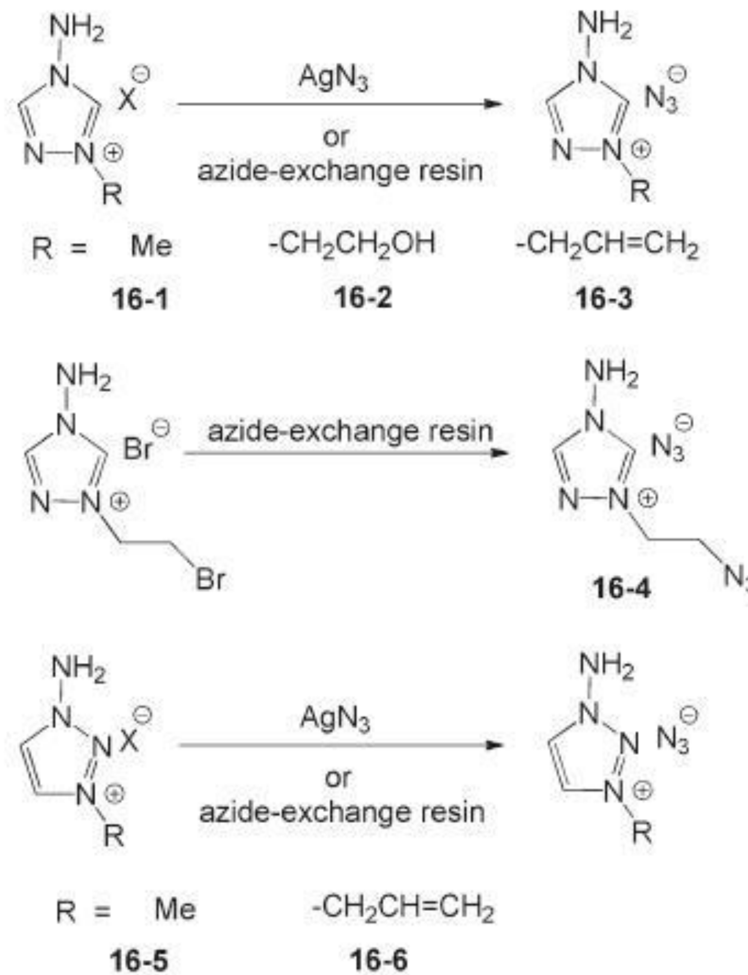




Zeng, Z; Wang, R.; Twamley, B.; Parrish, D. A.; Shreeve, J. M. Chem. Mater. 2008, 20, 6176.

Triazole-Based

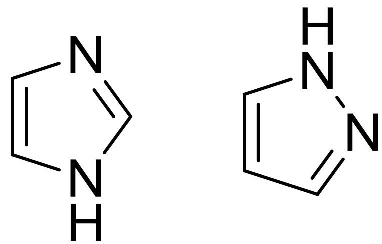
- Azide Ionic Liquids
- Ionic liquids: salt with melting temp < 100°C
- Liquid azides tend to be very volatile and thermally unstable
- 4° N corrects for both of these



Schneider, S.; Hawkins, T.; Rosander, M.; Mills, J.; Brand, A.; Hudgens, L.; Warmoth, G.; Vij, A. Inorg. Chem. 2008, 47, 3617.

Imidazole/Pyrazole-Based

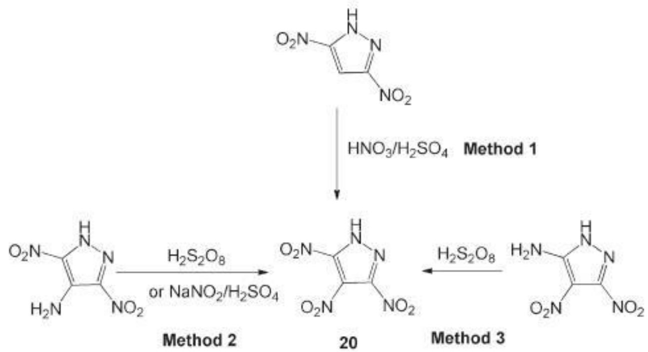
- Heterocycles with 2 N's and 3 C's
  - Pyrazole has nitrogen atoms next to one another

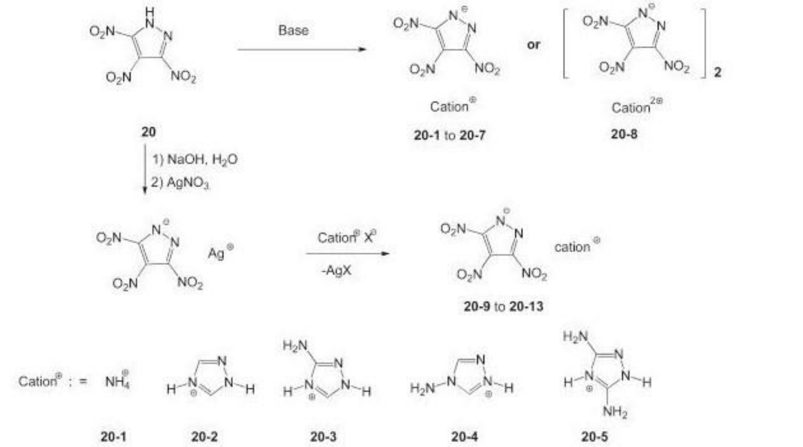


- Common molecules in synthesis and industry
  - Both anionic and cationic salts are common
- New energetic salts made via simple, cheap, safe methods
  - Show very interesting properties

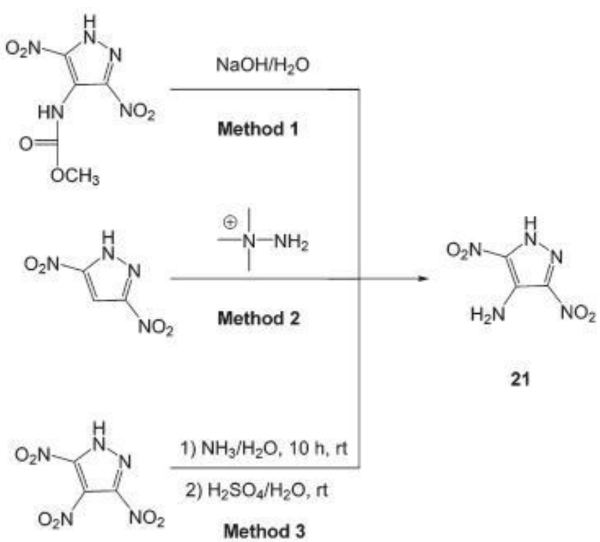
Imidazole/ Pyrazole-Based

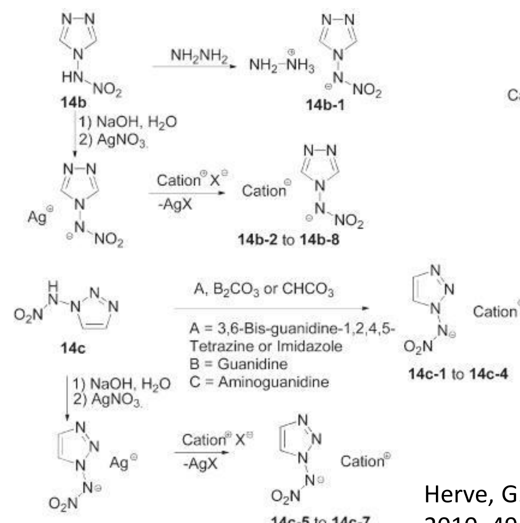
- 3,4,5-Trinitropyrazole

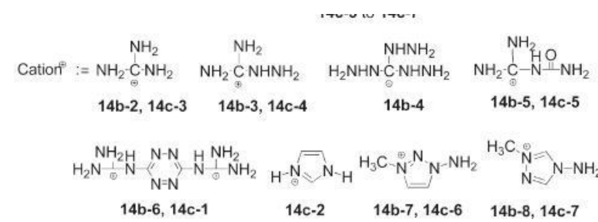




- 4-Amino-3,5-dinitro-pyrazole



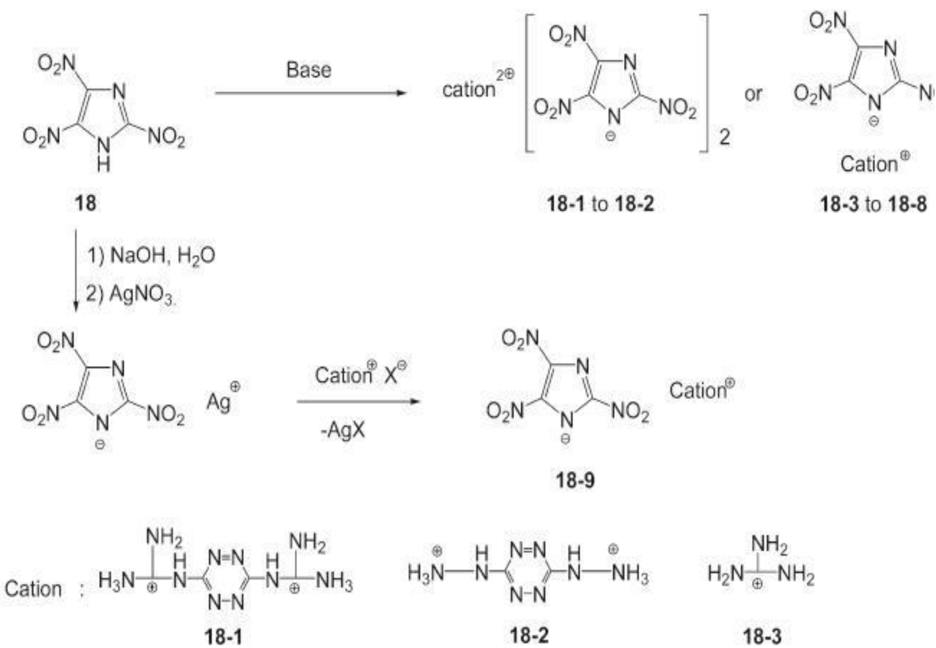




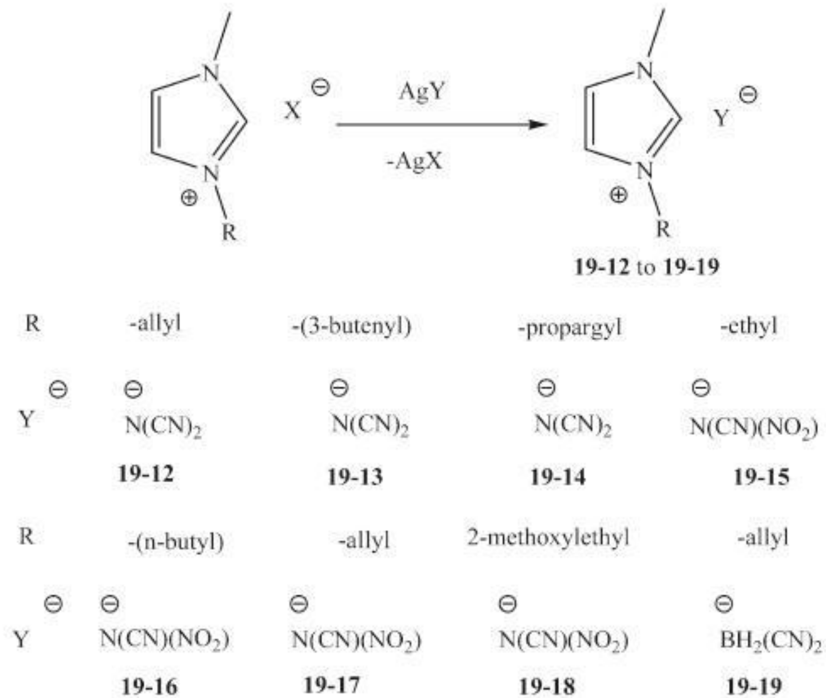
Herve, G.; Roussel, C.; Graindorge, H. Angew. Chem., Int. Ed. 2010, 49, 3177.
Zhang, Y.; Huang, Y.; Parrish, D. A.; Shreeve, J. M. J. Mater. Chem. 2011, 21, 6891.

Imidazole/ Pyrazole-Based

- 2,4,5-Trinitroimidazole



- Azole-Based Hypergolic Salts



- Hypergolic: Special propellants that consist of fuel + oxidizer

Gao, H.; Ye, C.; Gupta, O. D.; Xiao, J.-C.; Hiskey, M. A.; Twamley, B.; Shreeve, J. M. Chem.—Eur. J. 2007, 13, 3853.
Chambreau, S. D.; Schneider, S.; Rosander, M.; Hawkins, T.;Gallegos, C. J.; Pastewait, M. F.; Vaghjiani, G. L. J. Phys. Chem. A. 2008, 112, 7816.

Making Salts

- Clearly, both cation and anion matter
  - Enhanced performance, stability, etc
- How to decide which to use?
  - Time consuming/ costly/ potentially dangerous to screen everything
  - Instead can use computers and calcs to narrow field
    - Group Contribution Methods
    - Quantitative Structure- Property/Activity Relationships
- The ideal energetic salt:
  - Low melting point, thermostable, good O balance, high N content, high density, insensitive
- 3 Main Characterization Methods:
  1. Structure
  2. Thermal Stability
  3. Physiochemical Tests

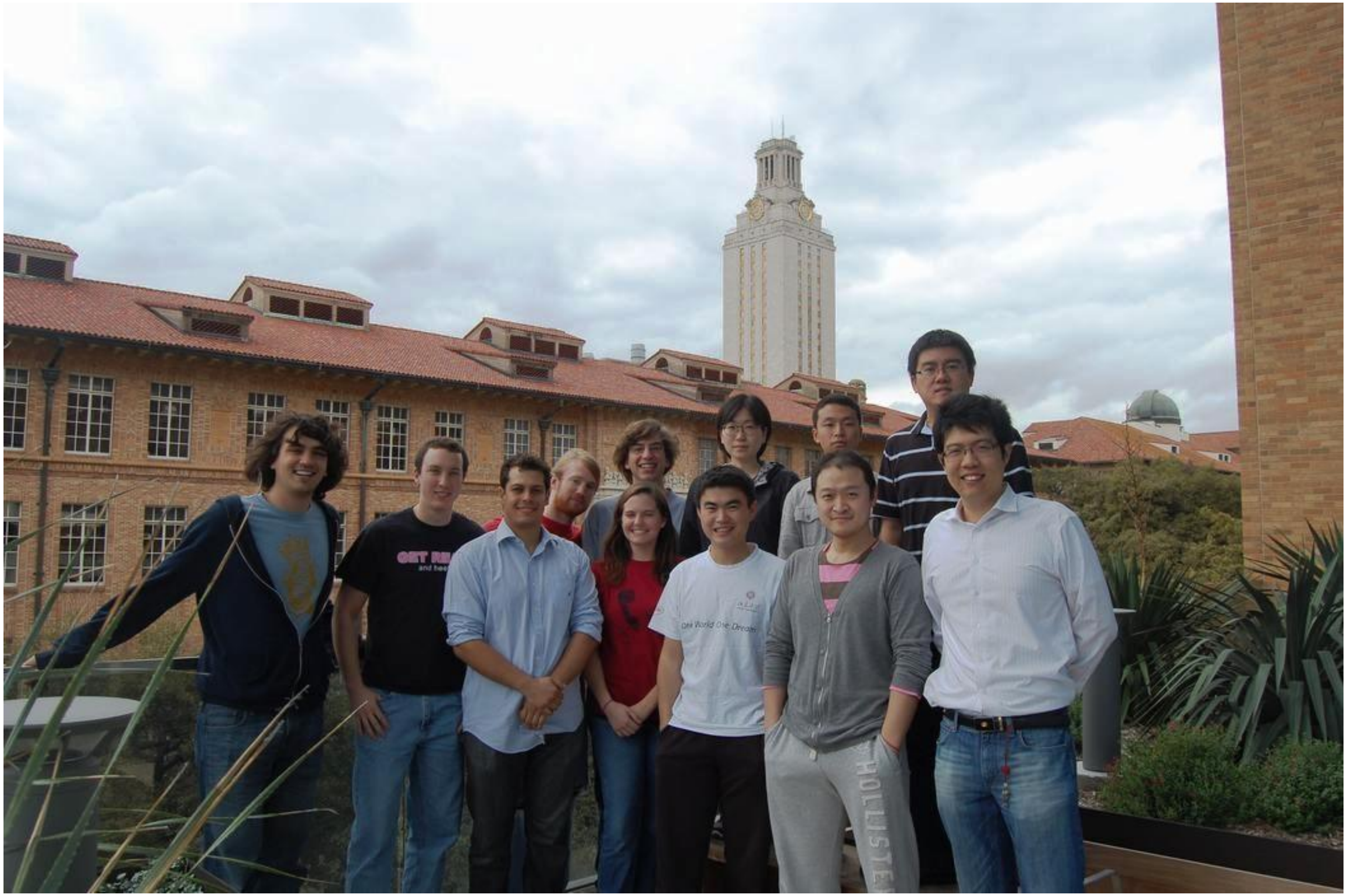
Green or Not So Much?

- Azole ionic salts and liquids touted as being more green
- Not necessarily true- compounds and degradation products can be very toxic
- Lower vapor pressure only criteria considered for “greeness”
- Little has been studied about ecological/biological effects

Conclusions

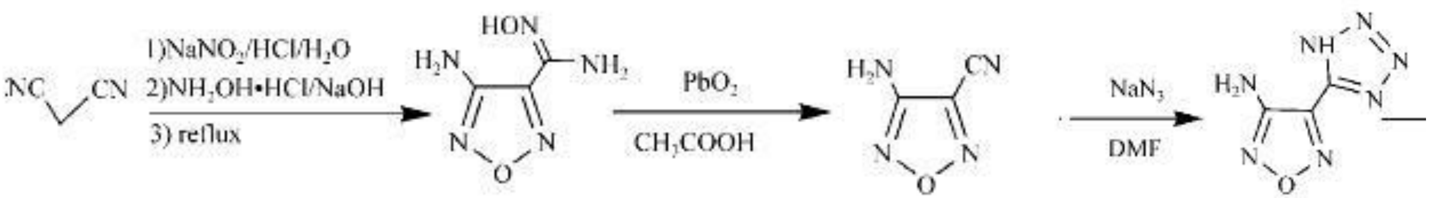
- Higher performance/ “Greener” = push for new types of energetic materials
- Azole-based salts show much promise
- Many have similar or better properties to known energetic materials
- Possibly better for the environment, but more needs to be done

THANK YOU!

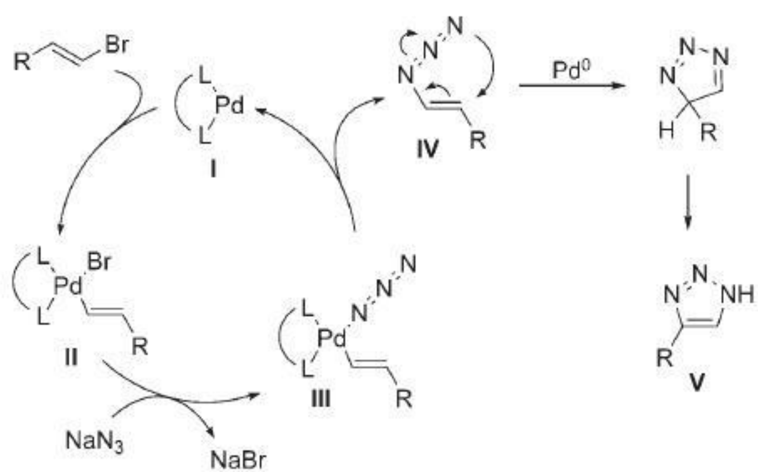


Questions:

1. Predict the products



2. Mechanism?



Questions:

3. Mechanism?