

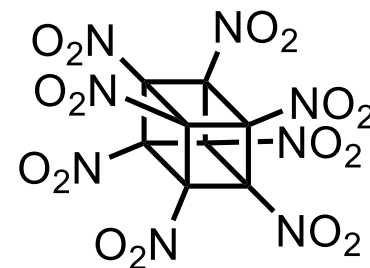
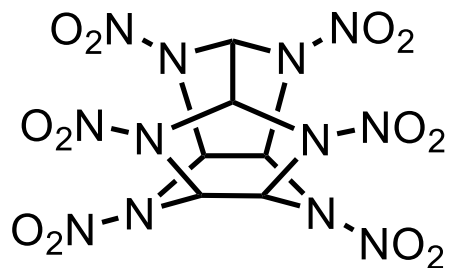


History & Chemistry of High Energy Materials

Jesse Panger

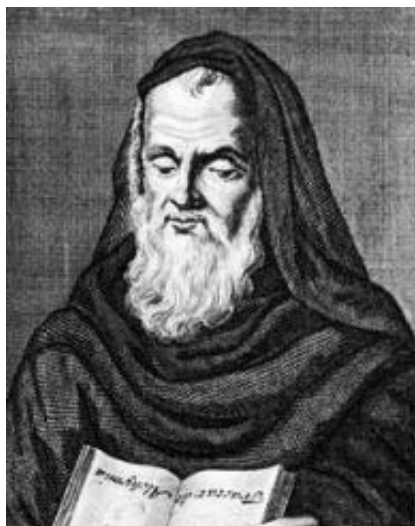
SED Group Meeting

18Jun2019



A Timeline of Brave Scientists

Roger Bacon



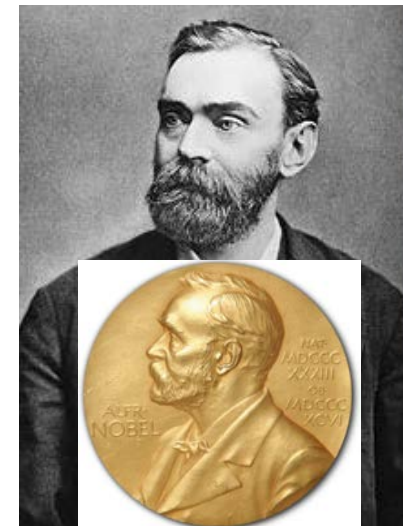
Berthold Schwarz



Ascanio Sobrero



Alfred Nobel

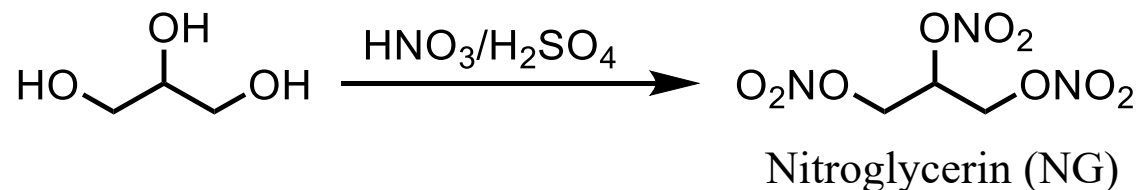


220 BC – 1425 AD

1846 - 1864



75% Saltpetre (KNO_3)
15% Charcoal (fuel)
10% Brimstone (exotherm)



1864: Emil Nobel died in an explosion at the NG factory

1866: Explosion destroyed the NG factory

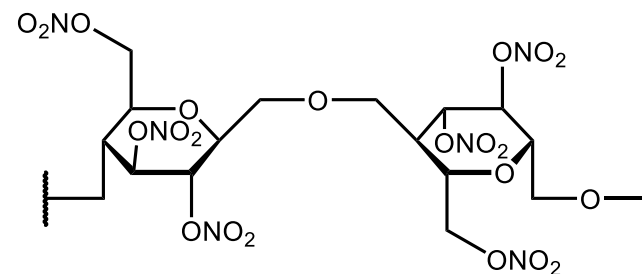
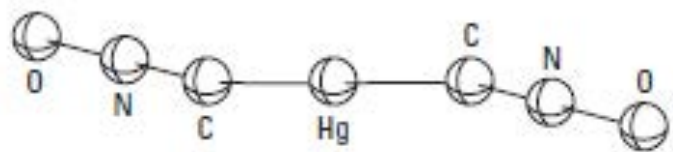
A Timeline of Brave Scientists



1864 (2007)

1867

1875

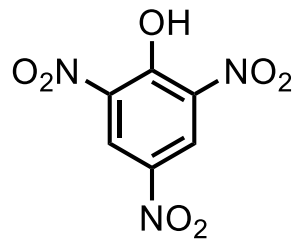


Mercury fulminate: Blasting cap
→ Primary explosive

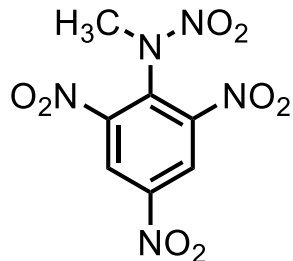
75% NG, 25% Kieselguhr

Nitrocellulose (NC)
→ Smokeless powder

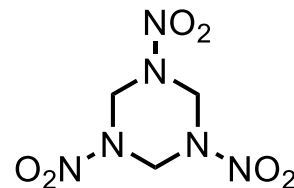
A Timeline of Brave Scientists



Picric acid

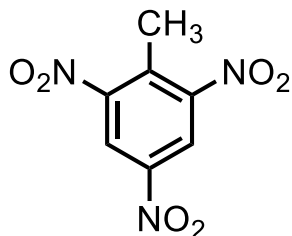


Tetryl

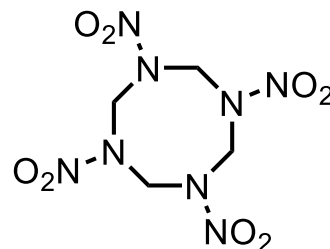


Hexogen (RDX)

- vasodilator to treat angina pectoris
- Torpedos, Semtex



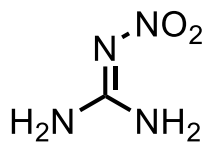
Trinitrotoluene: must be free of isomers (recrystallized from 62% nitric acid)



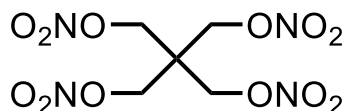
Octogen (HMX)

1877-1894

1920-1944



Nitroguanidine (NQ): reduced muzzle flash and decreased combustion temperature



Pentaerythritol tetranitrate (PETN):
Grenades in WWI

Name

Composition

Composition A 88.3% RDX, 11.7% non-energetic plasticizer

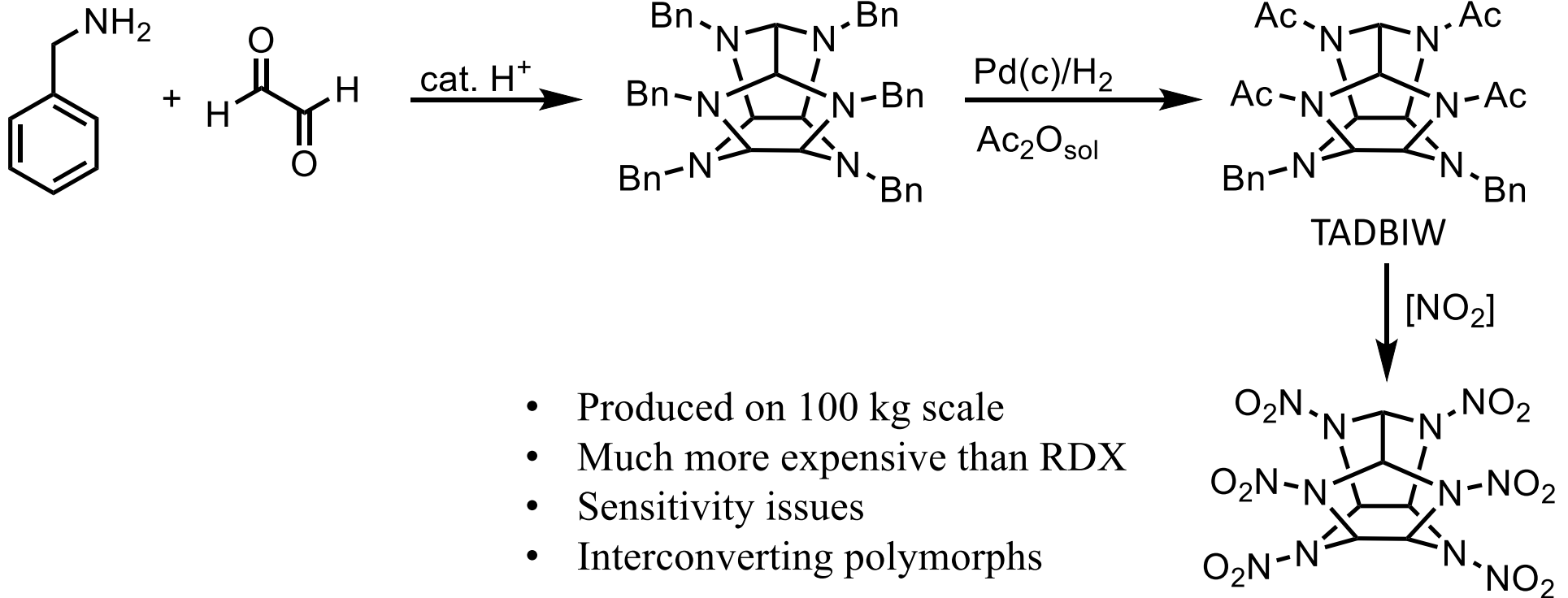
Composition B 60% RDX, 39% TNT, 1% binder

Composition C4 90% RDX, 10% polyisobutylene

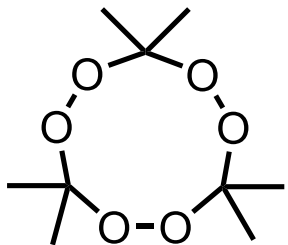
Octol 75% HMX, 25% RDX

Torpex 42% RDX, 40% TNT, 18% aluminum

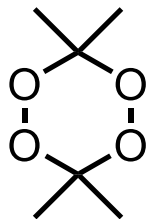
Modern Munitions



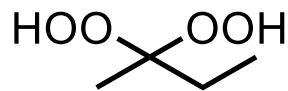
- Produced on 100 kg scale
- Much more expensive than RDX
- Sensitivity issues
- Interconverting polymorphs



TATP



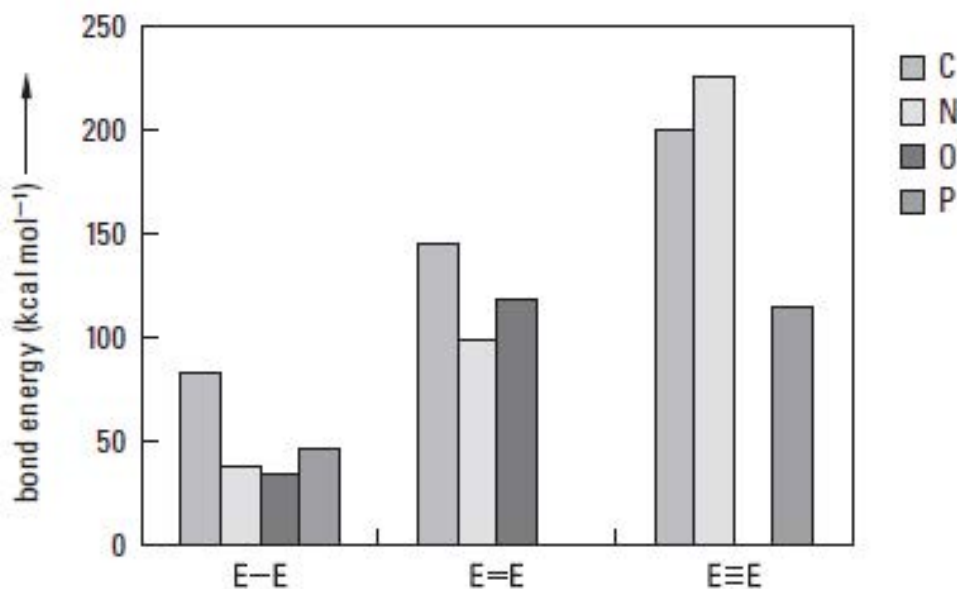
DADP



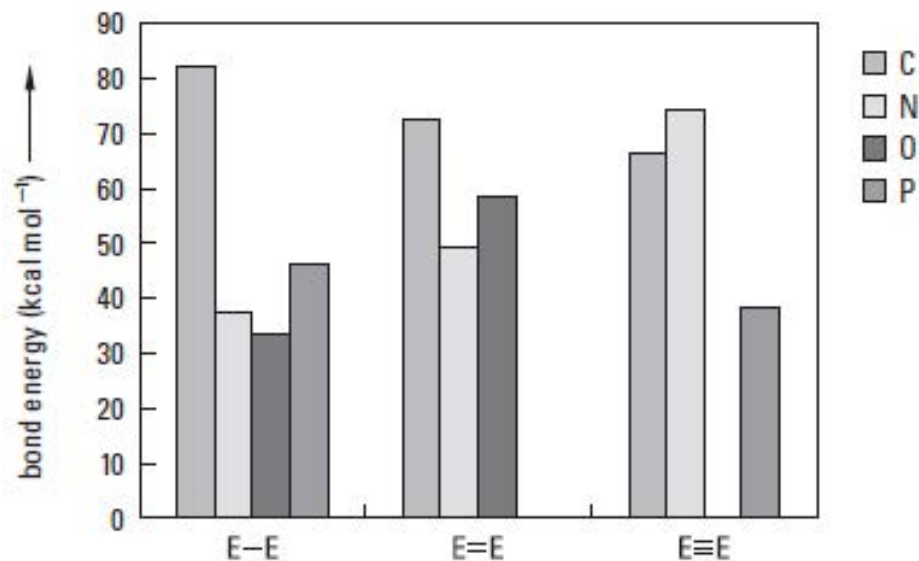
MEKP

Use by terrorist organizations as homemade explosives.

Special Topics in HEM: Bond Energies



Approximate bond energies for C-C, N-N, O-O, and P-P single, double, and triple bonds.



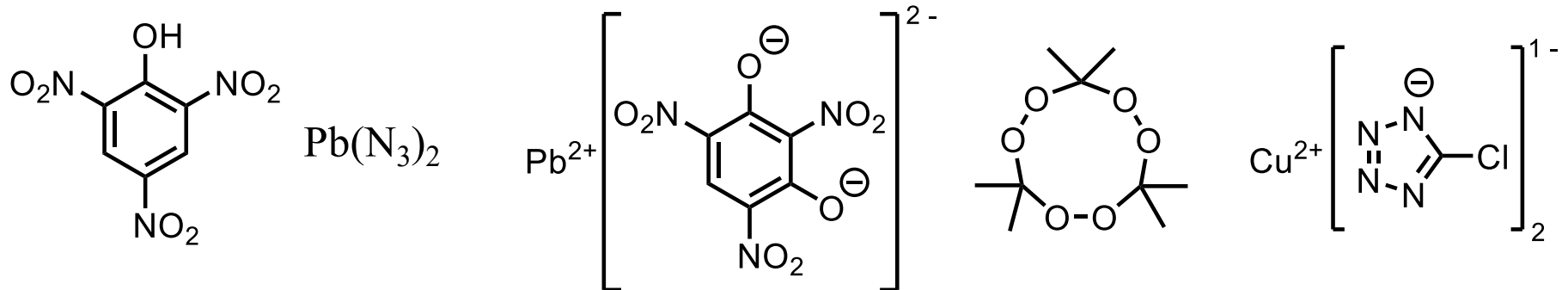
Average element-element bond energies per 2-electron bond.

New energetic materials with a high nitrogen content (>60%) and an N-N bond order of ≤ 2 will release large amounts of energy

A (Brief) Detour into Definitions

Primary Explosive: Show rapid transition from deflagration (combustion) to detonation

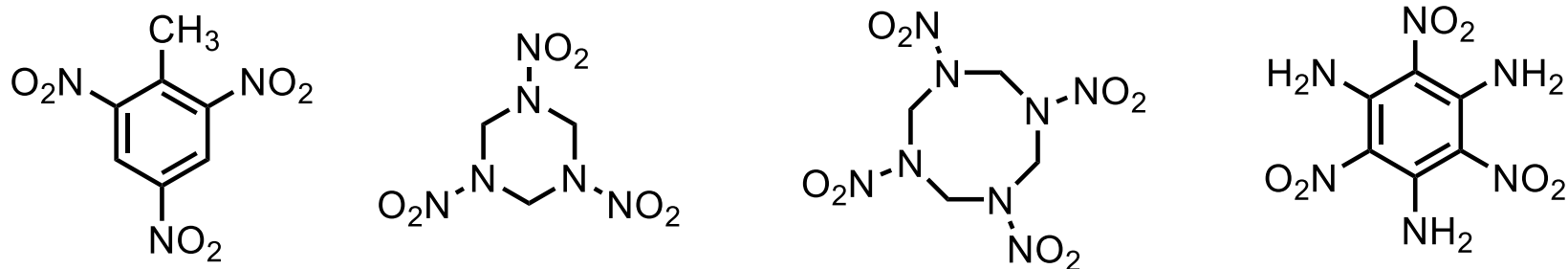
- Highly sensitive to generate large amounts of heat or a shockwave
- Generally lower detonation velocities, detonation pressures, and heats of explosions



Deflagration: Flame propagation is less than the speed of sound

Secondary (High) Explosive: cannot be initiated by heat or shock easily

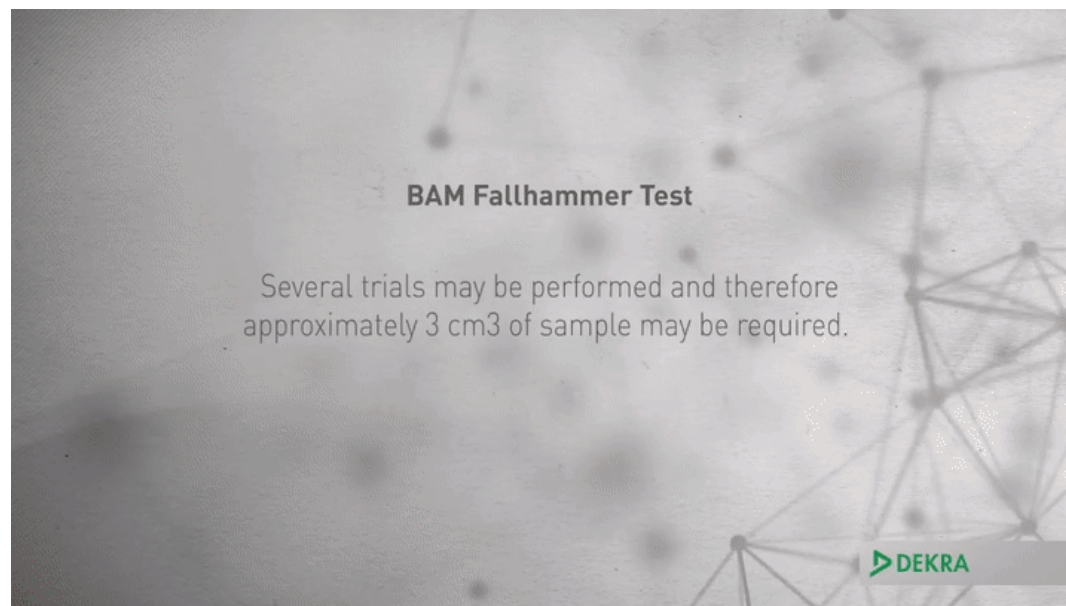
- Optimized for heat (kJ/kg), detonation velocity, and detonation pressure
- Lower toxicity and sensitivity



Experimental Characterization of Explosives

High energy materials need to be tested for 4 different sensitivities:

1. Impact: measured by the BAM drop hammer test; Energy = mass x acceleration x distance

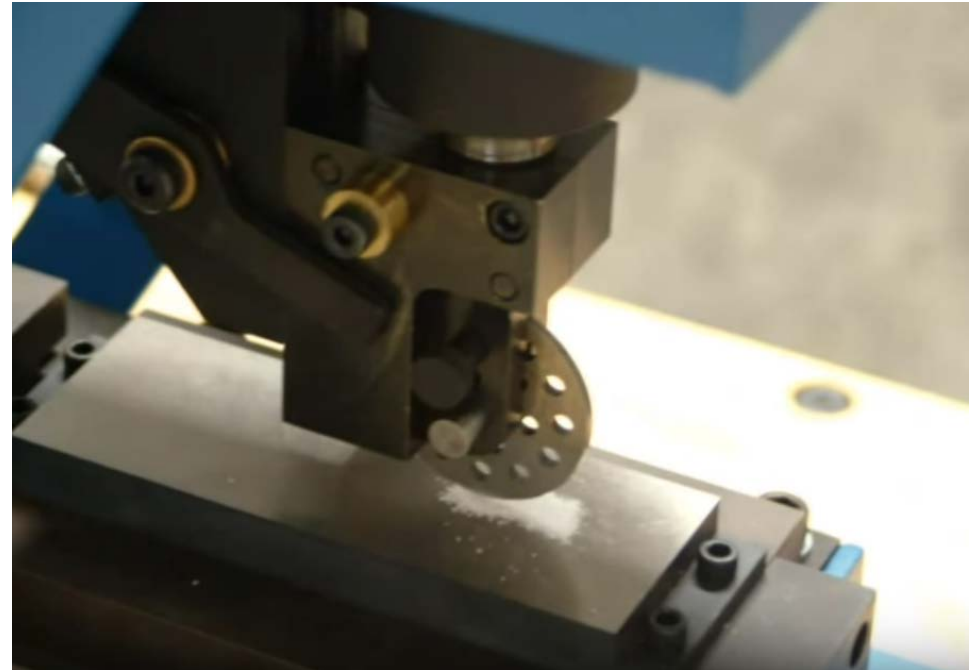
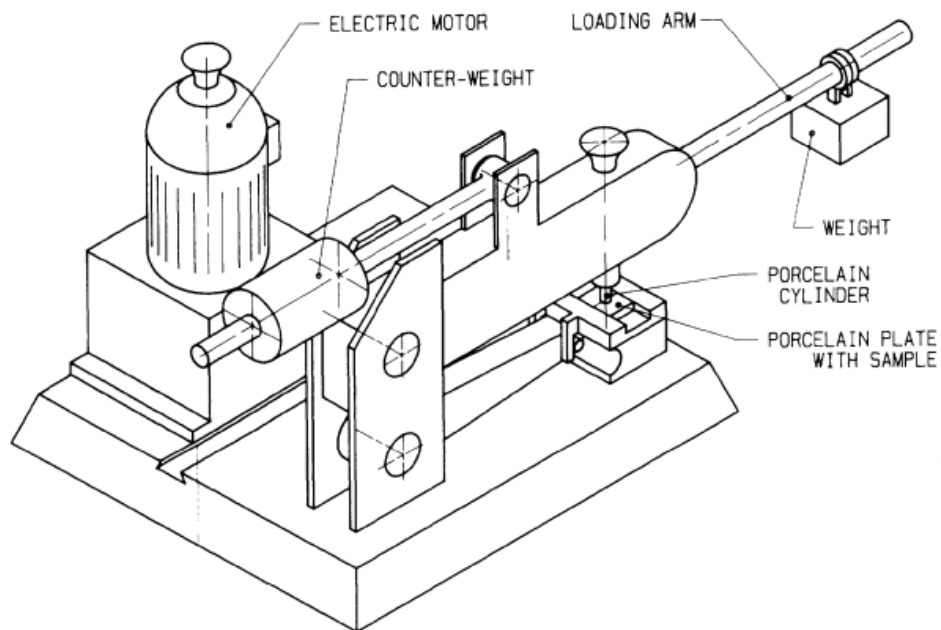


Sensitivity level	Explosive	% of Initiations with 10 kg weight
High	Nitroglycerine	100
Increased	RDX, HMX	72-80
Medium	Tetryl	44-52
Low	TNT	4-8
Nonsensitive	NH_4NO_3	0

Experimental Characterization of Explosives

High energy materials need to be tested for 4 different sensitivities:

1. Impact
2. Friction



A curve is established to determine F_0 , F_{50} , and F_{100} . Alternatively, the smallest weight used at which initiation is observed in at least 1/6 trials.

Experimental Characterization of Explosives

High energy materials need to be tested for 4 different sensitivities:

1. Impact
2. Friction
3. Electrostatic: <0.1 J classified as sensitive, >0.1 J are insensitive

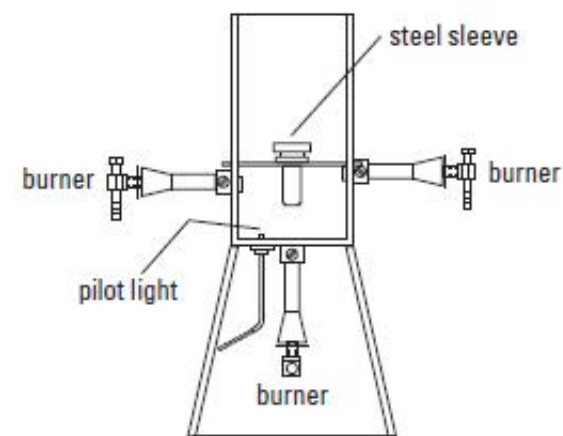
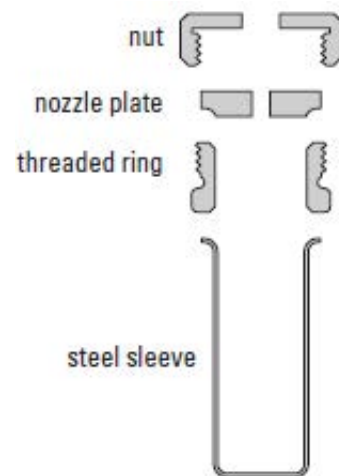
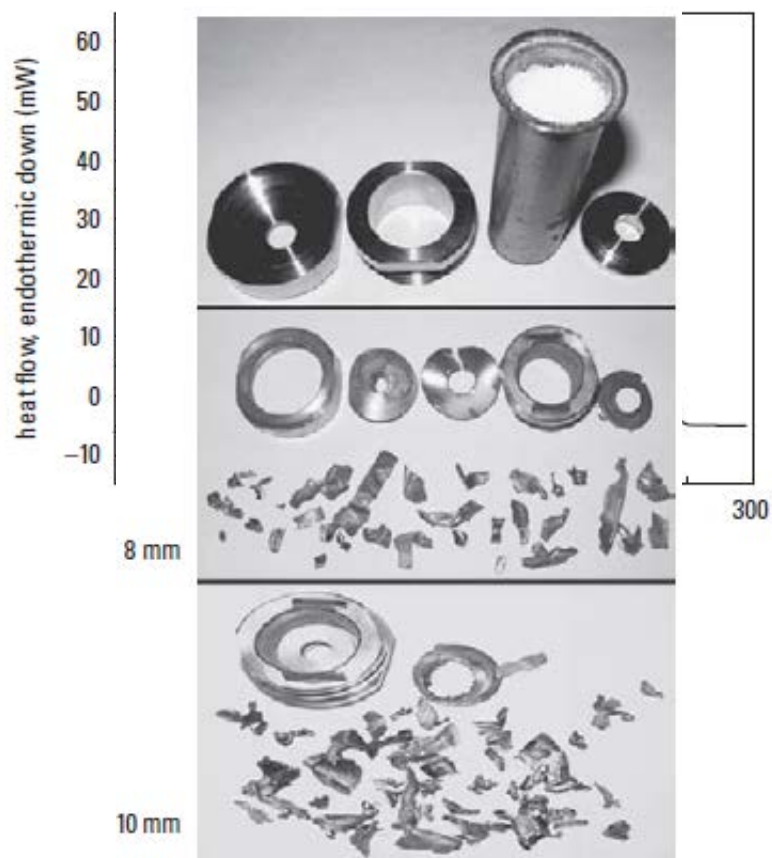
Human body can discharge 0.005 – 0.2 J

Explosive	Impact sensitivity (J)	Friction sensitivity (N)	ESD sensitivity (J)
Pb(N ₃) ₂	2.5-4	0.1-1	0.005
TNT	15	>353	0.46-0.57
RDX	7.5	120	0.15-0.20
β-HMX	7.4	120	0.21-0.23
PETN	3	60	0.19
NQ	>49	>353	0.60
TATB	50	>353	2.5-4.24

Experimental Characterization of Explosives

High energy materials need to be tested for 4 different sensitivities:

1. Impact
2. Friction
3. Electrostatic
4. Thermal: All tests are essential tests of thermal stability



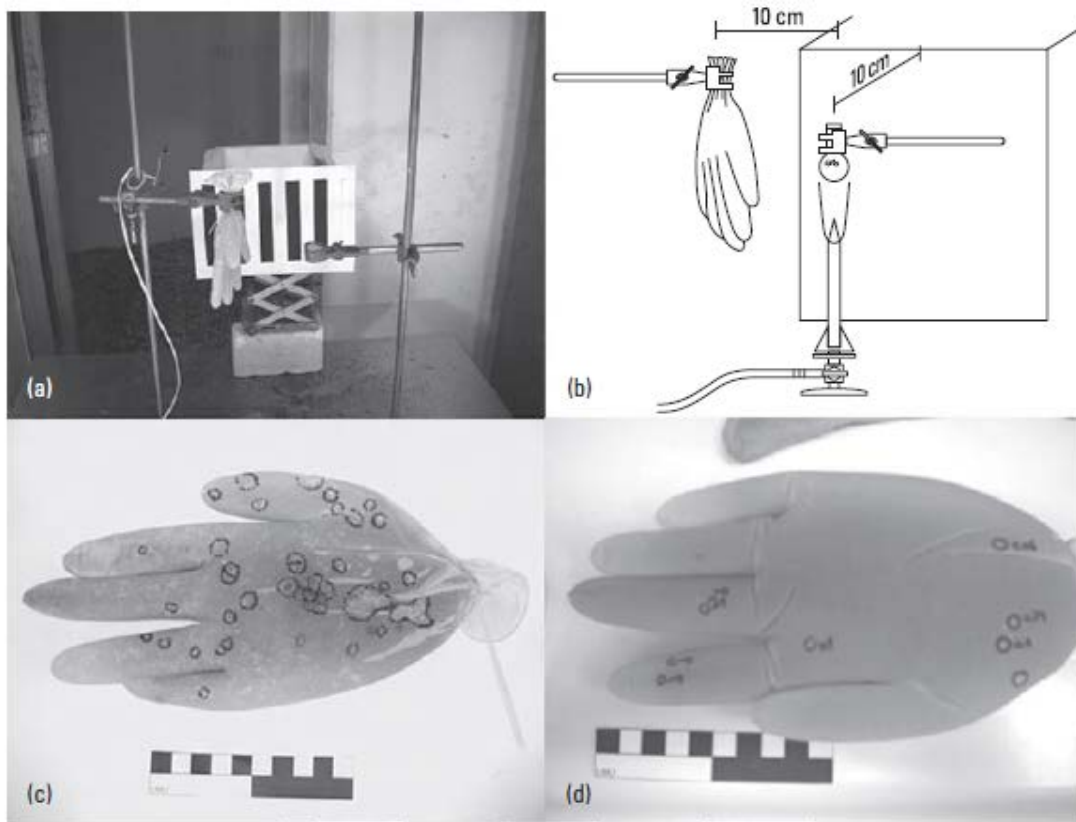
Safety Considerations of HEM: Lab Scale

Rule of Thumb for secondary explosives at large distances that offer a chance at survival:
Survival distance (D) $\approx 2(\text{mass of explosive in kg})^{0.33}$

- Use smallest possible quantities
- Keep maximum distance
- Mechanical manipulation
- Never encase vessel by hand

Protective Equipment:

- Wrist protectors
- Full-visor face shield
- Ear protectors
- Shoes with conducting soles & conducting/earthened floor
- Leather jacket



Unprotected hand

Kevlar-protected hand

Lastly, all equipment that contacts HEM must be plastic (spatula, beaker, stir bar) and humidity must be $\geq 60\%$ humidity

Applications of High Energy Materials: Propellants

Traditional propellants



Single-base propellants:

- Gunpowder
- Nitrocellulose

Double-base propellants:

- NC + NG in pistols and mortars
- Higher performance but high erosion

Triple-base propellants:

- NC + NG + RDX in tank and NAVY weapons
- Higher performance but high erosion

Rocket propellants: lower pressure, slower burn



$$\text{Thrust} = (\text{Impulse (s)} \times \Delta\text{mass propellant}) / \text{burn time}$$

Increasing specific impulse by 20 s effectively doubles the deliverable payload

Solid Rocket Propellants

Solid propellants can be double-base
(homogeneous) – based on NC - or composite
(heterogeneous) – ammonium perchlorate



May 4, 1988, Nevada

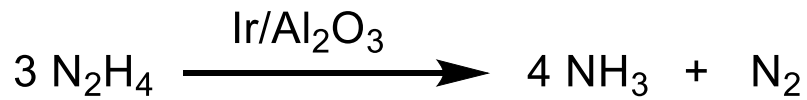
Perchlorate is known to decrease active transport of iodine into the thyroid

Current research into silanes as “air-breathing” machines (SiO_2 and Si_3N_4)

Liquid Rocket Propellants



Hydrazine as a monopropellant possesses relatively low energy and specific impulse and as such only used in small missiles/satellites for trajectory corrections.

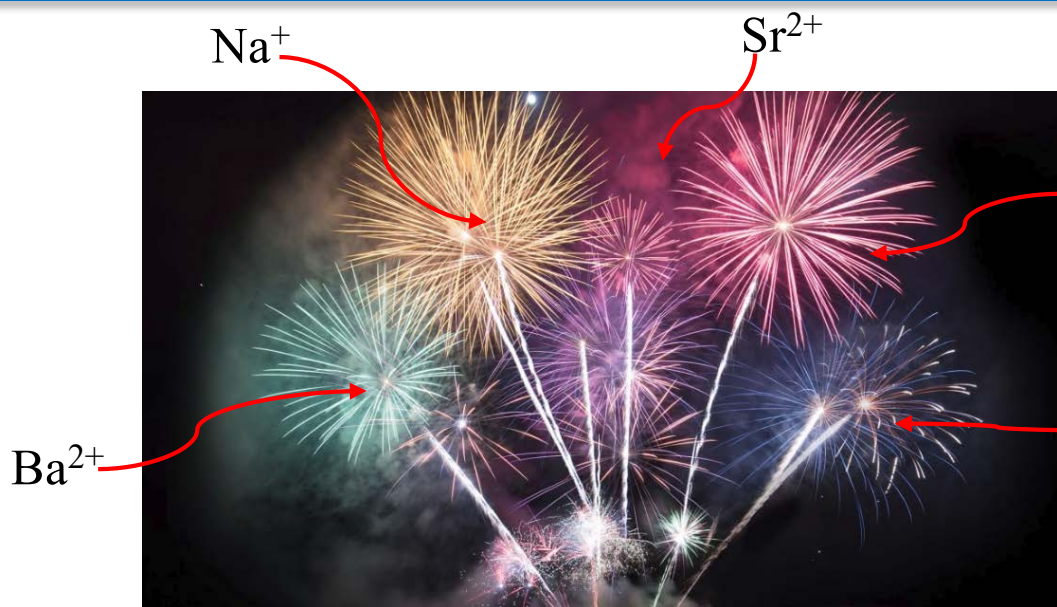


Bipropellant systems combine the oxidizer and fuel into combustion chamber

- Advantage in having more controlled burn

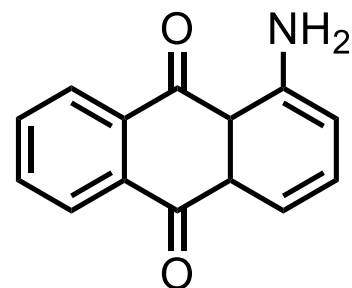
Oxidizer	Fuel
LOX	H ₂ , CH ₄ , B ₂ H ₆ , N ₂ H ₄
F ₂	N ₂ H ₄ , MMH
N ₂ F ₄	N ₂ H ₄
ClF ₅	MMH, N ₂ H ₄

Applications of High Energy Materials: Pyrotechnics

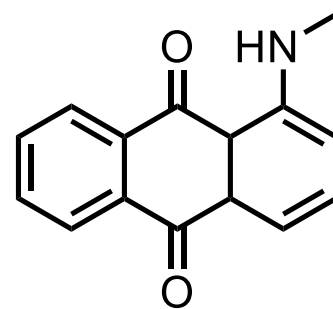


Lactose + KClO₃ + dye_(s)

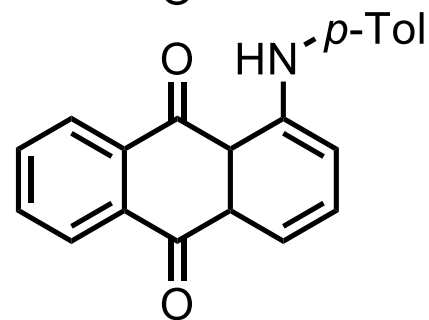
Sublimation T < Melt T



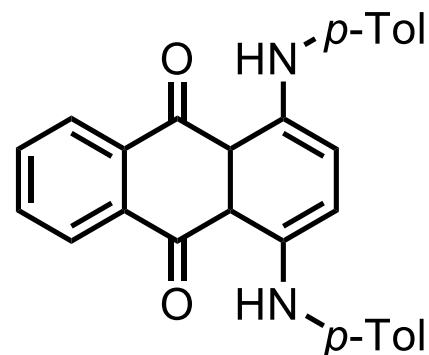
Orange



Red

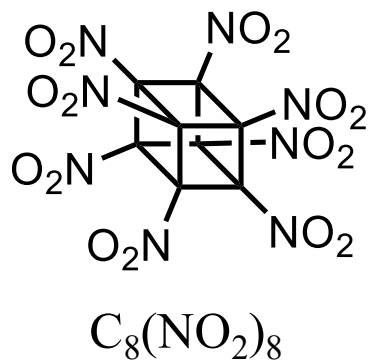


Blue



Bluish green

Octanitrocubane: A Pedagogic Model



How would a demolition expert view this molecule?

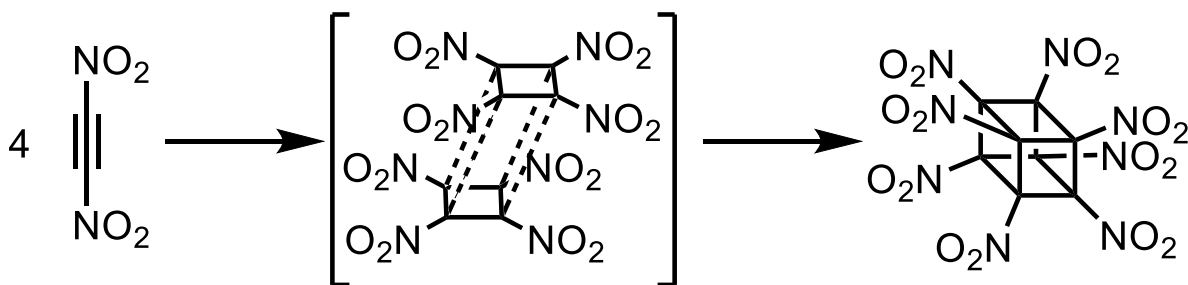
Great oxygen balance given $C_aH_bN_cO_d$: sufficient oxygen to burn all carbon

$$\Omega_{CO_2} = \frac{\left[d - (2a) - \frac{b}{2} \right] \times 1600}{M} = \frac{[16 - (16) - 0] \times 1600}{464.13} = 3.44\%$$

For comparison: NG = 3.5%; TNT = -74.0%

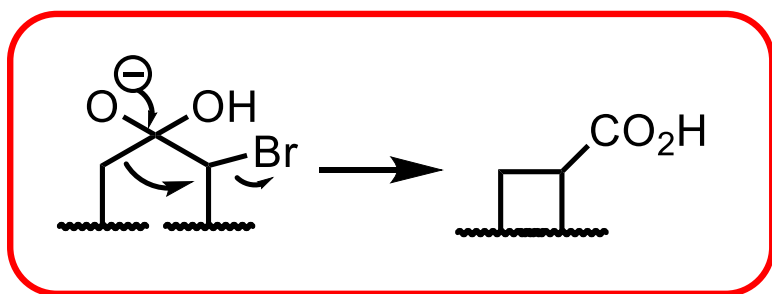
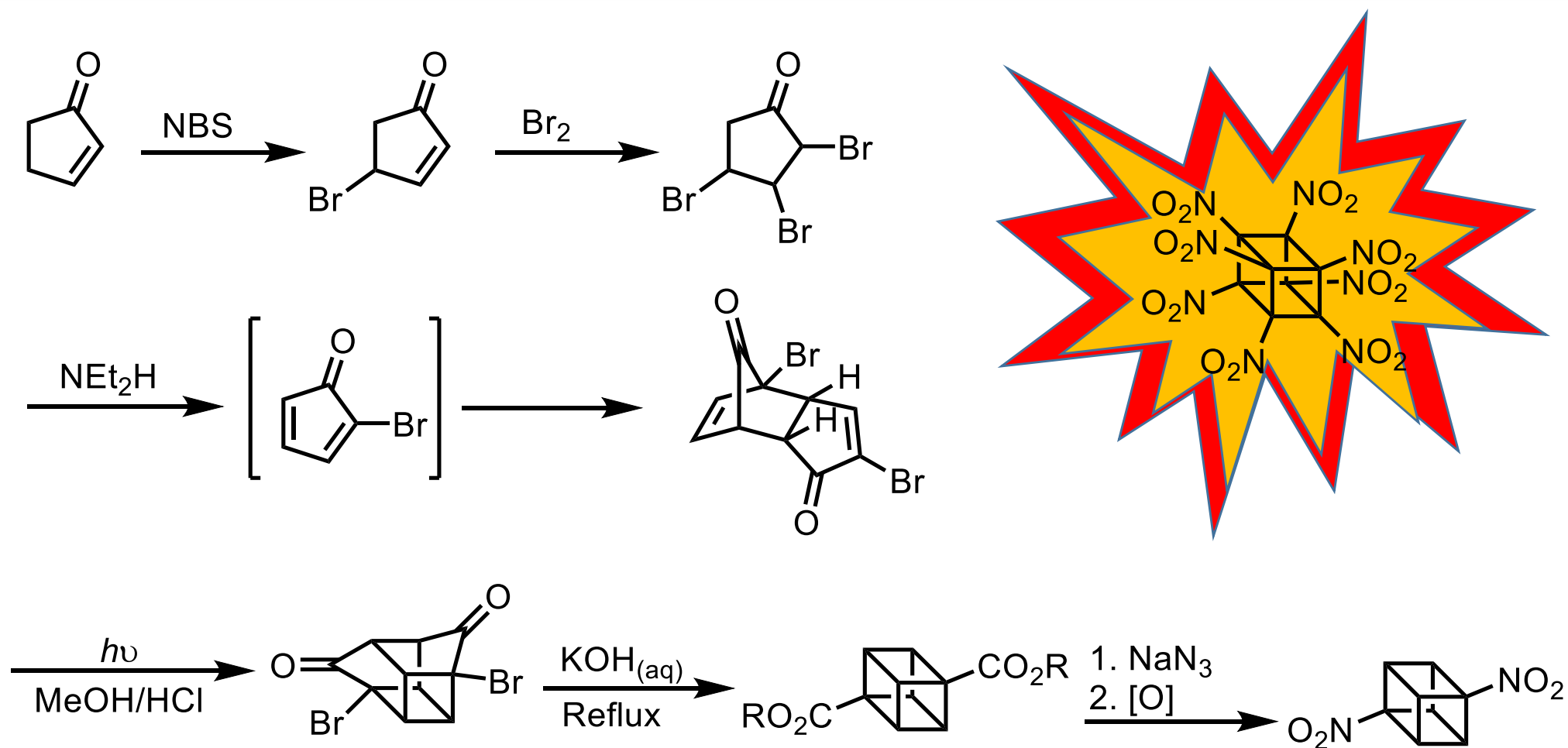
Projected density is 1.9-2.2 kg/L: velocity of propagation wave through explosive is proportional to its density squared

Strain energy of cubane alone is ~166 kcal/mol



Explosive	RE Factor
TNT	1 (definition)
C4 (90% RDX)	1.34
Nitroglycerin	1.54
CL-20 (HNIW)	1.85
ONC	2.38

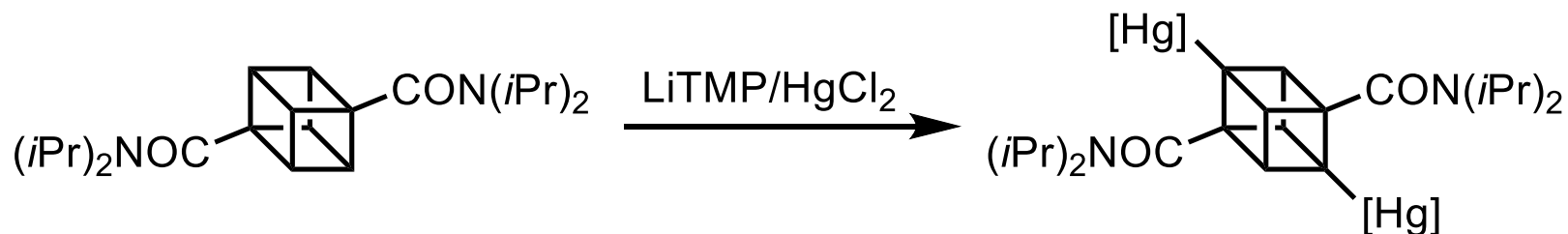
The Road to Octanitrocubane: A First Step



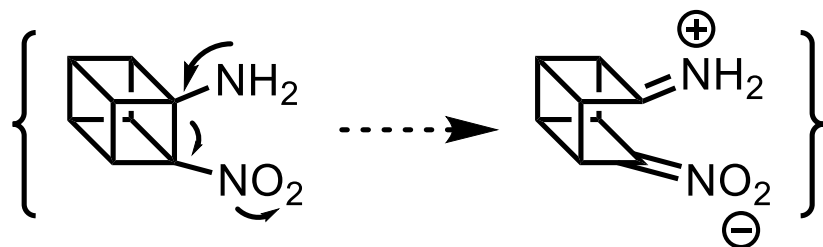
Eaton et al., *J. Am. Chem. Soc.* **1964**, *86*, 962-964.

Eaton et al., *J. Org. Chem.* **1984**, *49*, 185-186.

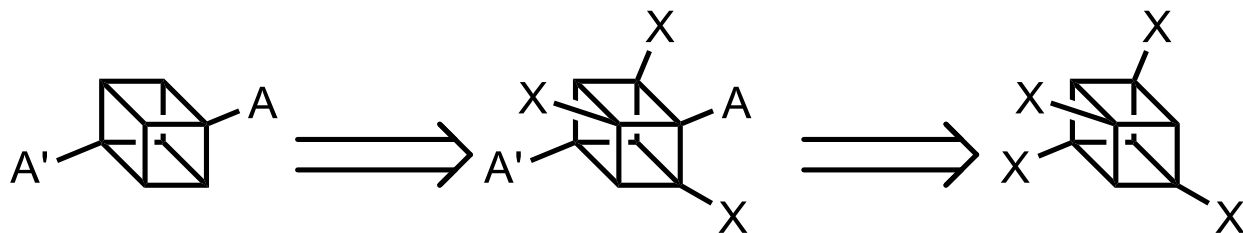
The Road to Octanitrocubane: Overcoming Barriers



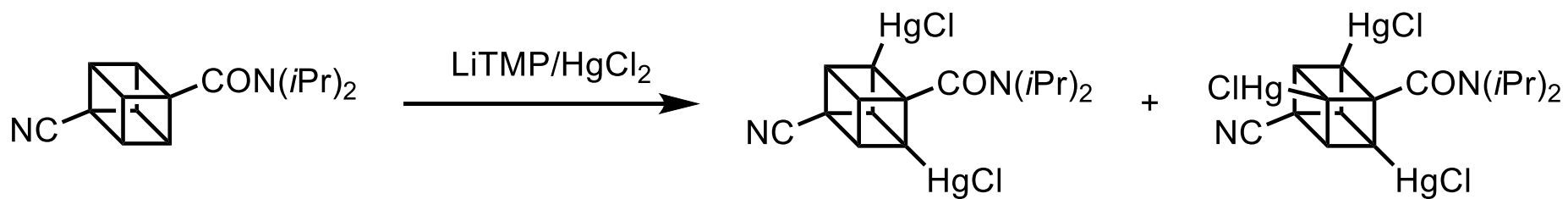
Problem: the approach for *ortho*-amination and oxidation was deemed not possible by unstoppable cage cleavage



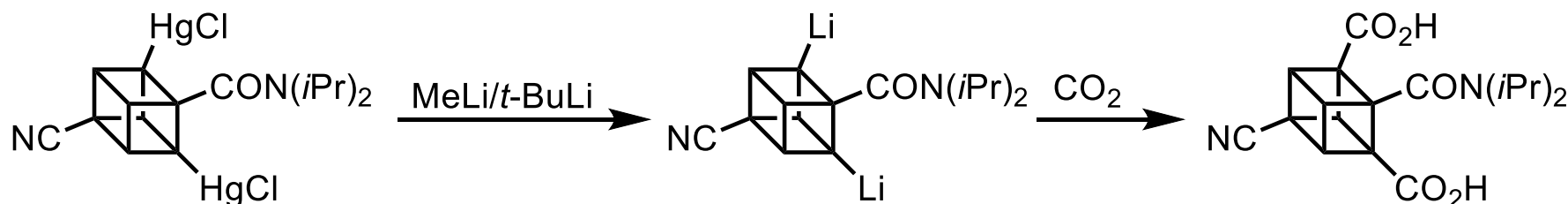
Temporary solution: generate non-vicinal nitrocubane



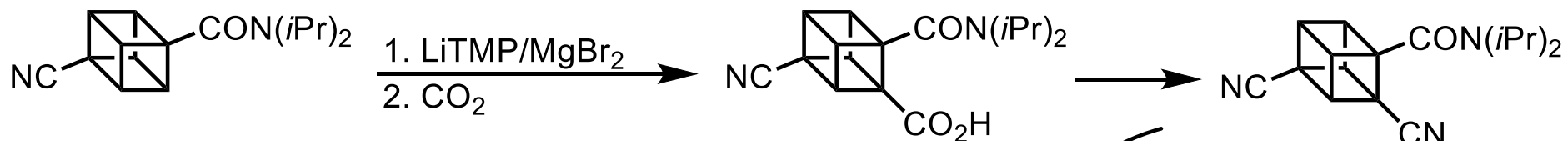
The Road to Octanitrocubane: Overcoming Barriers



Major



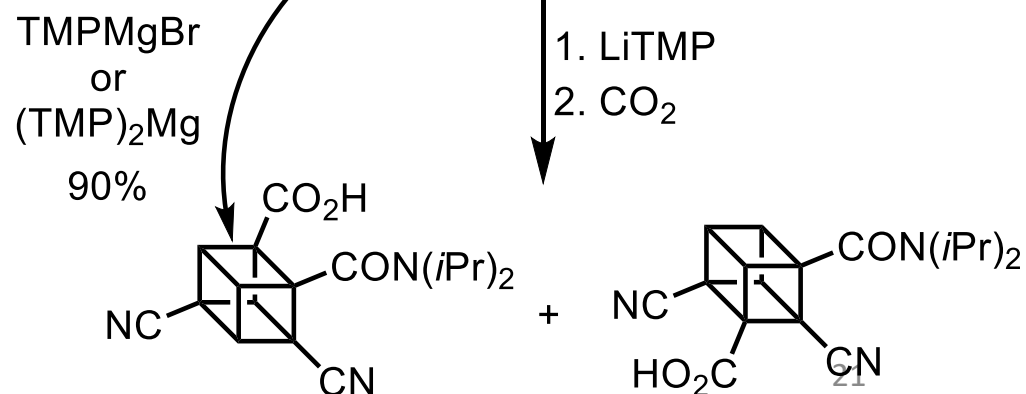
Progenitor to trinitrocubane



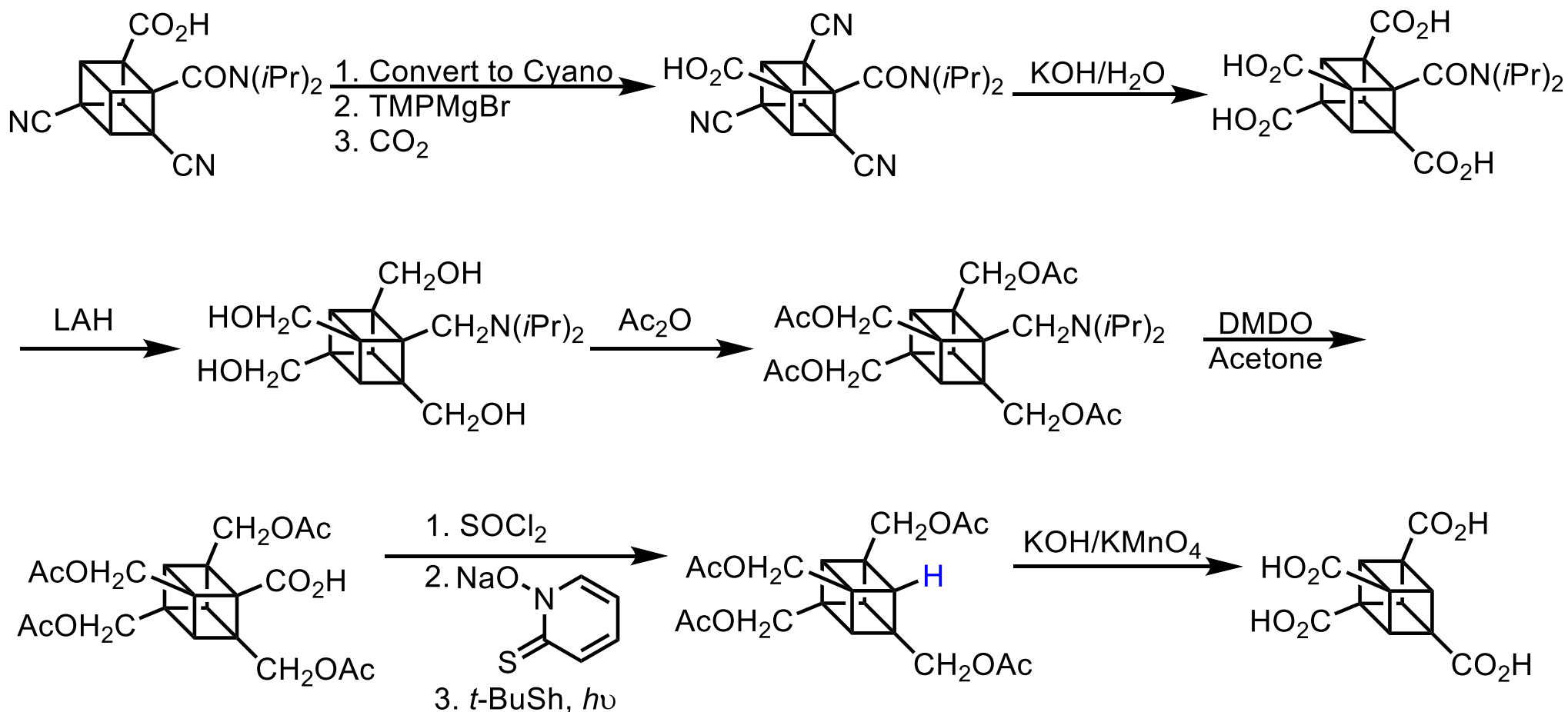
Point 1: One amide \approx Two cyano for *ortho*-directing.

Point 2: Magnesium amide bases are regioselective in strained aliphatic carbocycles.

Point 3: Cyano groups are ineffective activators for *ortho*-magnesiation.

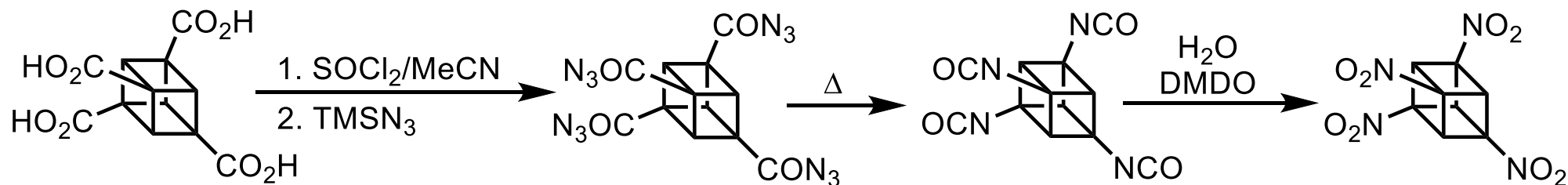


The Road to Octanitrocubane: Overcoming Barriers



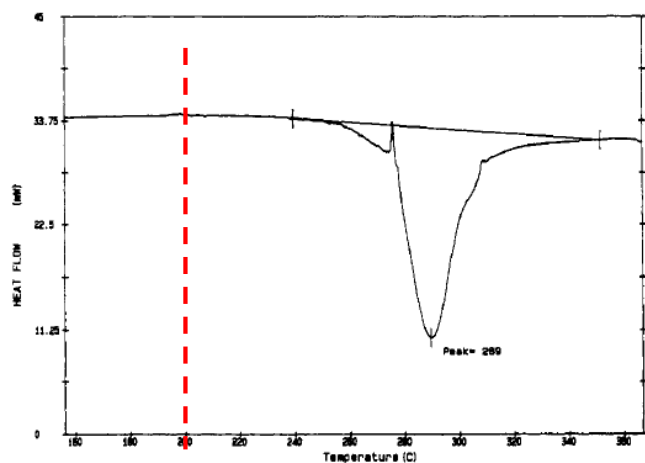
Point 4: Unusual oxidation of terminal, tertiary amine to carboxylic acid mediated by DMDO

The Road to Octanitrocubane: Overcoming Barriers

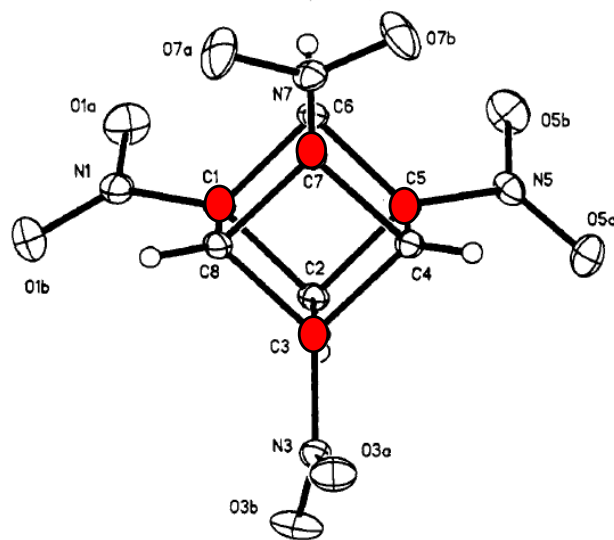


~18 steps

7 mg (30%) of final step



“We have learned (fortunately without serious incident) that cubane acyl azides are primary explosives, worthy of the greatest respect. Such compounds *cannot* be worked with safely unless *always* in dilute solutions.



Bond angles of nitro-bearing carbons are all $>90^\circ$

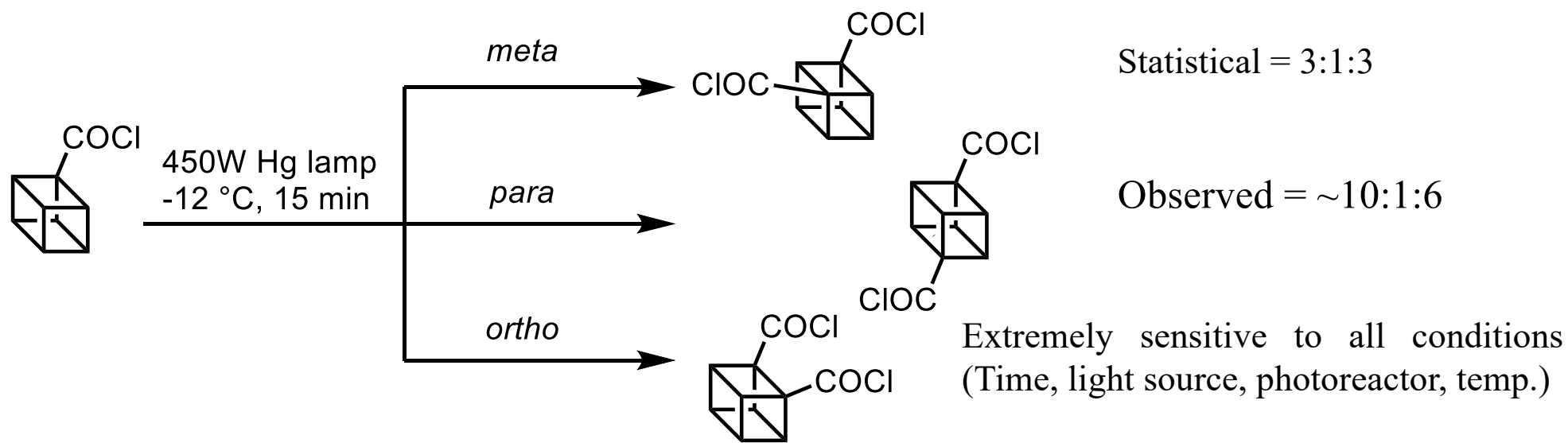
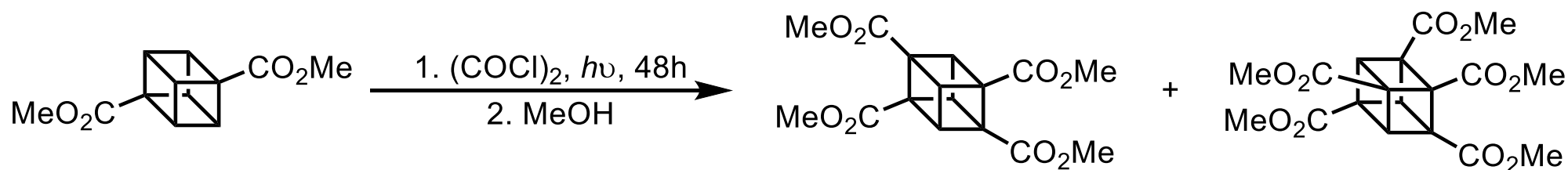
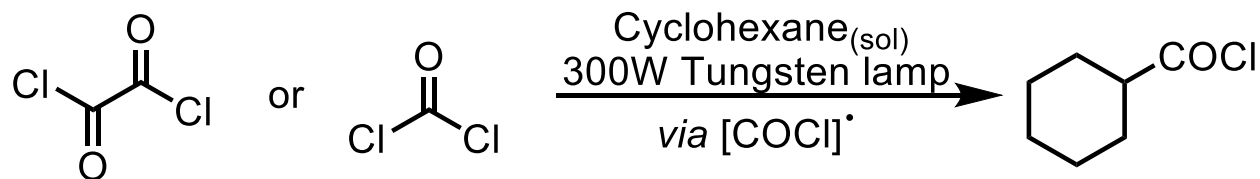
Odd-odd diagonals average 2.170 Å

Even-even diagonals average 2.235 Å

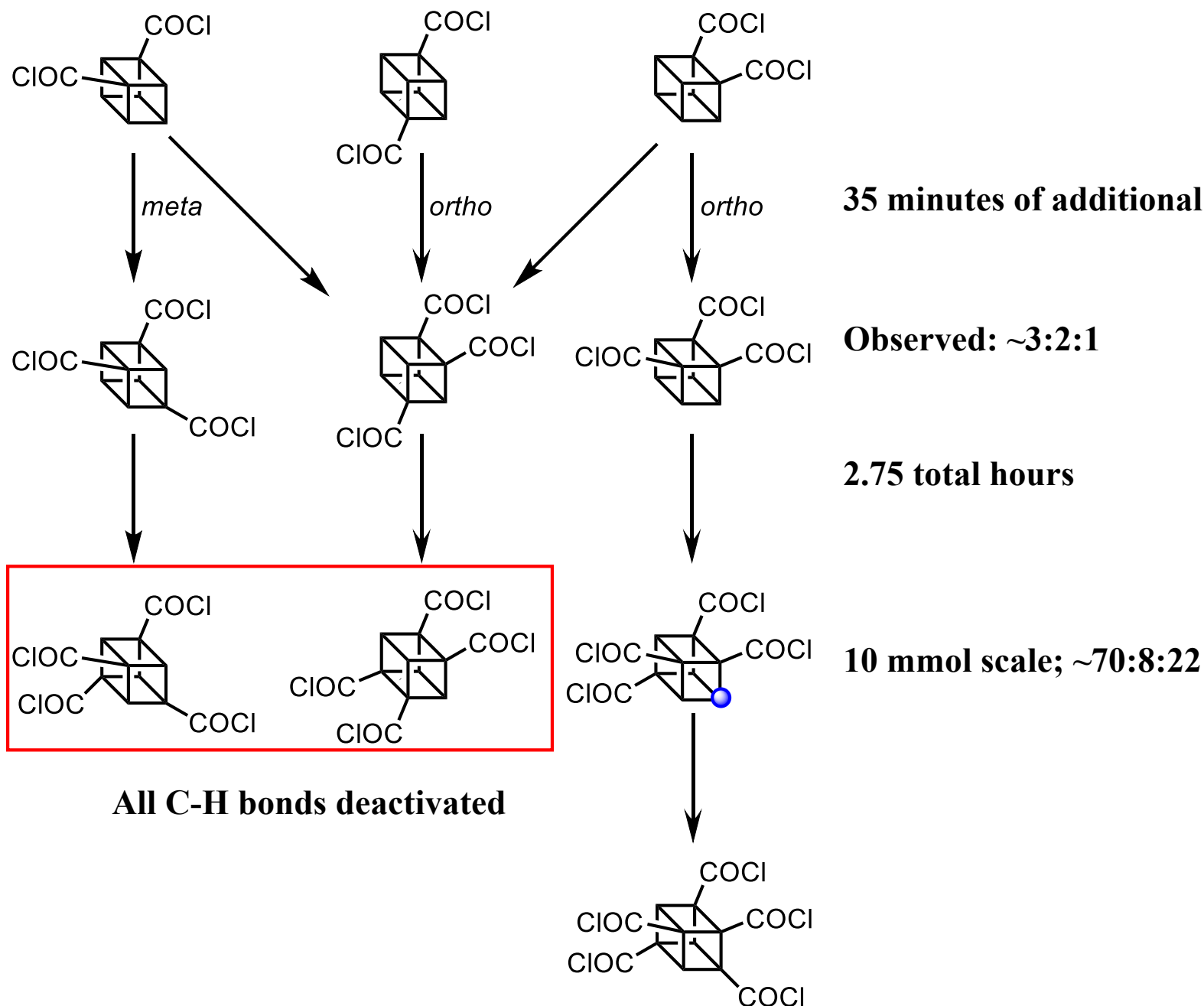


In short, a nitro group on a cube always displays one and only one C-C-N-O torsion angle in the -30 to 30° range, except in one case.

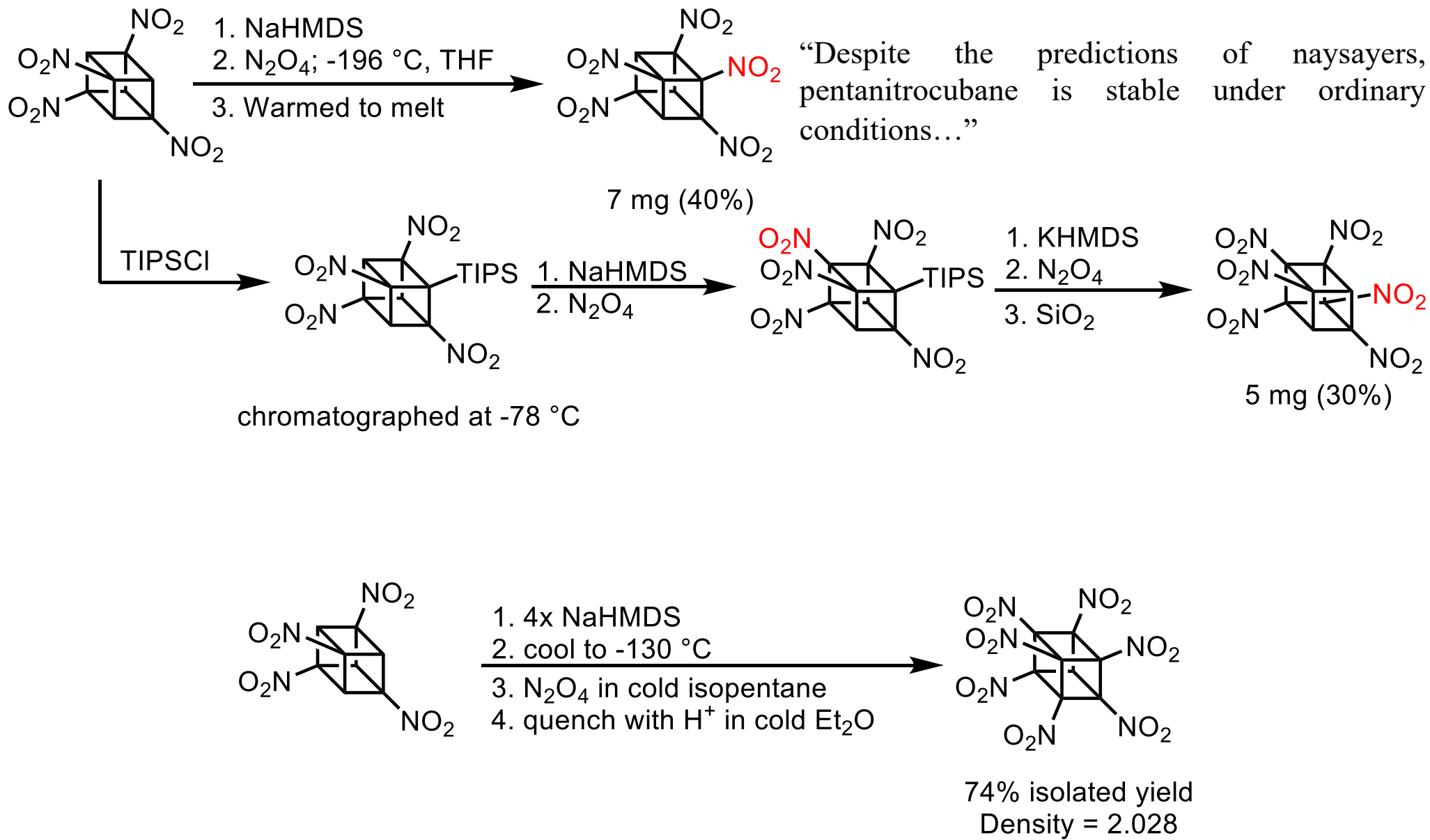
The Road to Octanitrocubane: A New Methodology



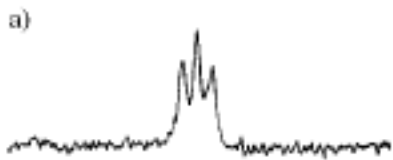
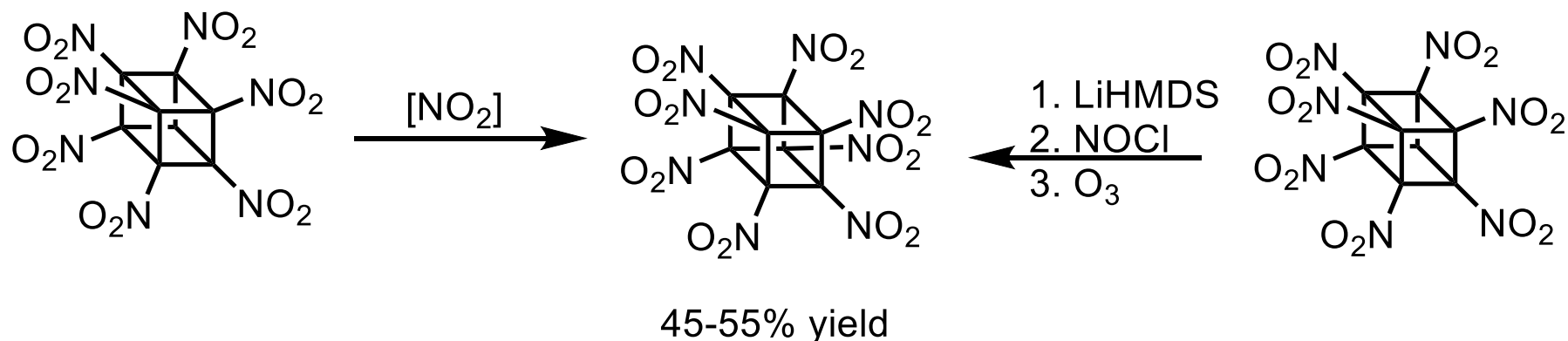
The Road to Octanitrocubane: A New Methodology



The Road to Octanitrocubane: Polynitration



The Road to Octanitrocubane: Endgame



Coupling to nitrogen explained in 2 ways:

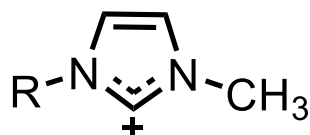
- 1) High symmetry about nitrogen nucleus (quaternary ammonium salts)
- 2) R group of RNO_2 is electronegative; in this case R = heptanitrocubyl

Break Time

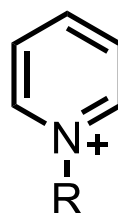
Ionic Liquids

IL: low-melting salt ($\leq 100\text{ }^\circ\text{C}$) normally composed of a large, asymmetric organic cation and an (in)organic anion.

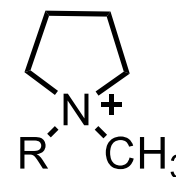
- Size and symmetry of participating ions prevents formation of a strong crystal lattice



1-alkyl-3-methylimidazolium



1-alkylpyridinium



1-alkyl-1-methylpyrrolidinium



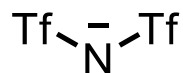
tetralkylammonium



tetralkylphosphonium



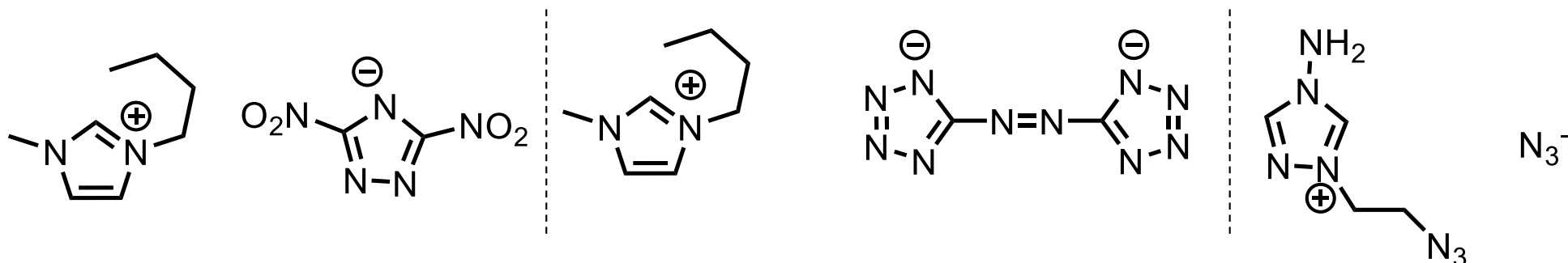
trialkylsulfonium



- Further applications in synthesis, electrochemistry, materials & energy, and analytical

Energetic Ionic Liquids

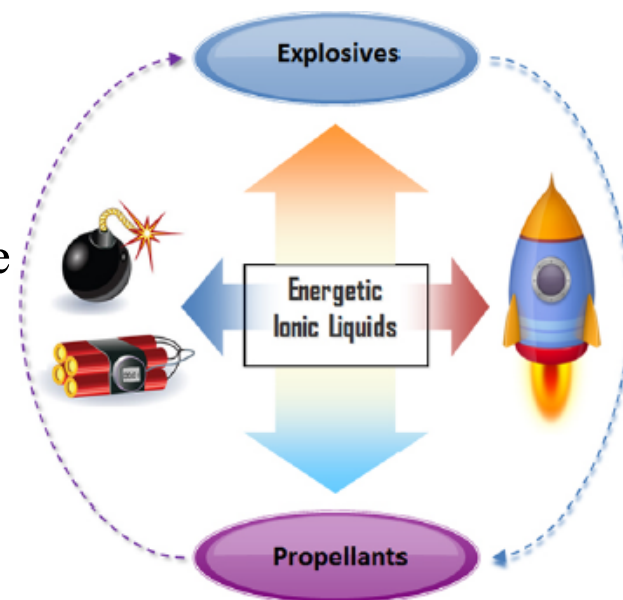
From the viewpoint of molecular structure, ionic liquids and HEMs share a key similarity: nitrogen-containing heterocycles are most often used as cations



Modular approach to tune physical properties

EILs as new-generation energetic materials due to:

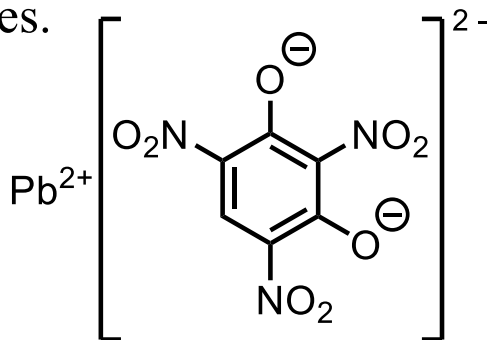
1. Low viscosity, high thermal stability, and broad liquid range
2. Negligible vapor pressure
3. Negates problems of polymorphism
4. Safer storage, handling, transportation and processing



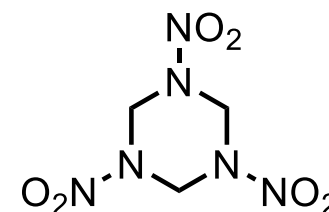
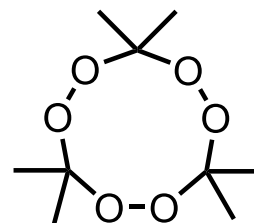
Energetic Ionic Liquids: A Greener Alternative?

Toxic Primers

Traditional energetic materials, specifically secondary explosives, still often use lead-based primary explosives.



Volatility



Toxic Inorganic Anions & Fuels

Perchlorate (ClO_4^-) water contamination from fireworks presents a health hazard for weeks and sometimes months afterwards



Waste Treatment

“TNT red water” refers to a complex mixture of dinitrotoluene sulfonates and incomplete nitration products.

The result is a difficult to handle, highly contaminated wastewater

Energetic Ionic Liquids: A Greener Alternative?

Toxic Primers

As a liquid, detonation initiated by addition of strong oxidant (100% HNO₃)

Shock and friction insensitive

Volatility

Negligible vapor pressure and low corrosivity

Can be stored, poured, and integrated into modern melt-pour facilities

Combustion products are CO₂ and N₂

Toxic Inorganic Anions & Fuels

EILs exist that leverage both benign and malignant anions.

The properties can be leveraged for each

Waste Treatment

Generally not as intensive but not without its own problems (perchlorates, azides, nitrates, etc.)

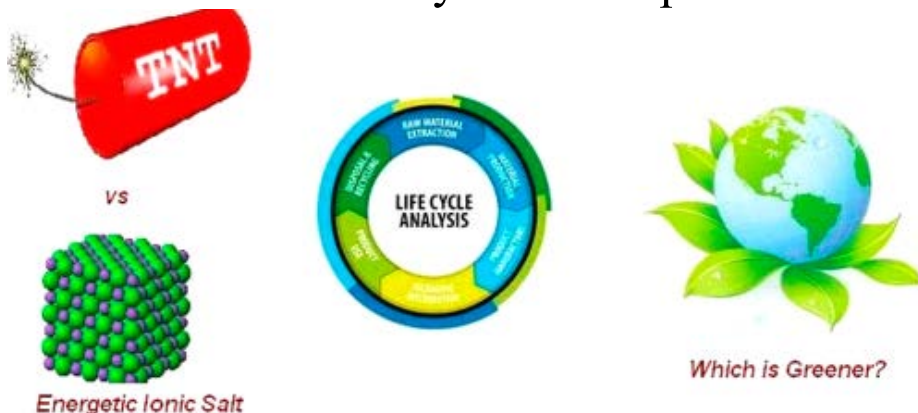
Energetic Ionic Liquids: A Greener Alternative?

The literature will lead you to believe EILs are a totally green alternative...
and if only considering volatility and combustion products then it's a reasonable assertion



No studies on bioaccumulation, biodegradation, and health impacts relevant to its production

Energetic groups ($-\text{NO}_2$, $-\text{CN}$, $-\text{N}_3$) and nitrogen-rich aromatic heterocycles have potential toxicity

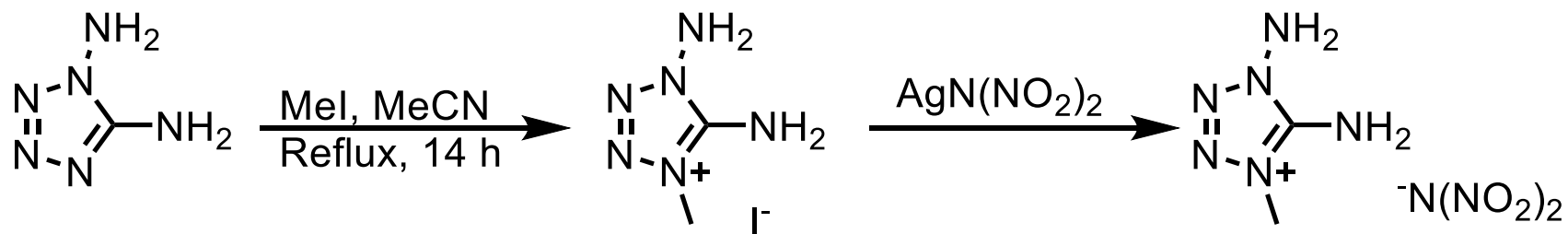


Cradle-to-gate life-cycle analysis revealed a **higher environmental impact** for 1,2,3-triazolium nitrate to TNT

- Climate change potential
- Acidification potential
- Eutrophication potential (excess nutrients)

Tetrazolium-Based EILs

High nitrogen content in cation (compared to imidazolium and triazolium) with the trade-off of more difficult syntheses.



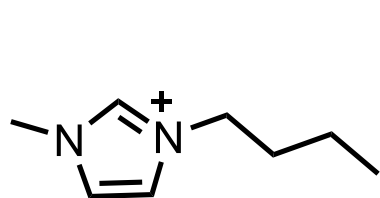
1,5-diamino-4-methyl-1H-tetrazolium dinitramide was too sensitive for further study



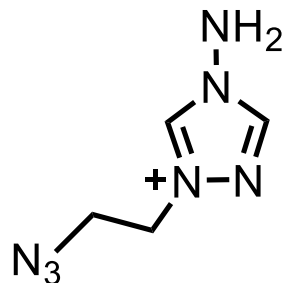
The 5-aminotetrazolium dinitramide analog exhibited excellent performance and was subjected to the “Koenen Test” steel sleeve apparatus.

- Detonation in < 1 ms
- Detonation velocity 9200 ± 500 m/s

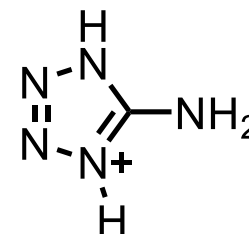
EILs; A Comprehensive View



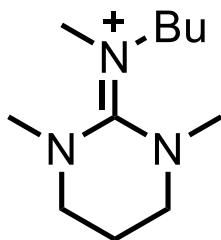
Imidazolium



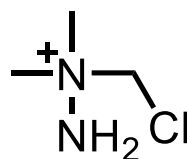
Triazolium



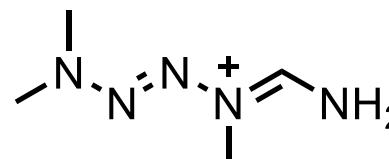
Tetrazolium



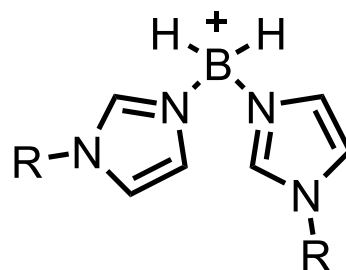
Guanidinium



Hydrazinium



Tetrazenium



Boronium

Special Topics in HEM: Detection

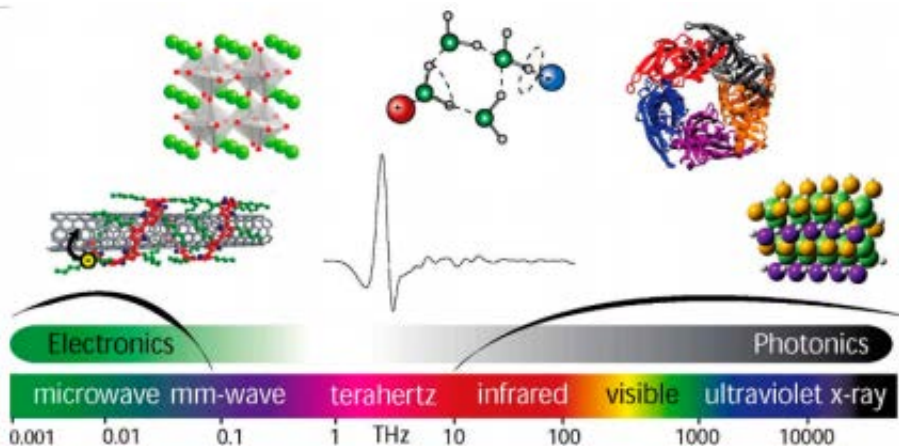


Radiography:

- ✓ Large scale detection
- ✓ Computer-aided
- X Must view directly
- X Item of minimum sizes

Bomb sniffing dogs:

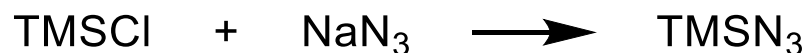
- ✓ Mobile detection
- ✓ Remarkably sensitive over distance
- X Extensive training
- X “Track-to-source” ability still under investigation



Terahertz spectroscopy:

- ✓ Transmit through packaging, clothes, etc.
- ✓ Chemical fingerprinting
- ✓ Mobile, rapid detection
- X Developing technology

Special Topics in HEM: Lab-Scale Detonations



What is a lab-safe scale to run this reaction on?

This was run on 200 g scale with no particular safety protocols



Rules of thumb for organic azides:

Walter Partlo sustained 2nd degree burns, injured eardrum, and glass fragmentation to the arm and side. "...though a synthetic procedure is well-documented in the literature, the inherent safety concerns may not be."



Spontaneous detonation inside fume hood



but no more concentrated than 1 M and a maximum of 5 g of material

3. If ≤ 1 then never isolated. Can be prepared if a transient intermediate AND limiting reagent AND limited to 1 g maximum

/stored

Special Topics in HEM: Lab-Scale Detonations



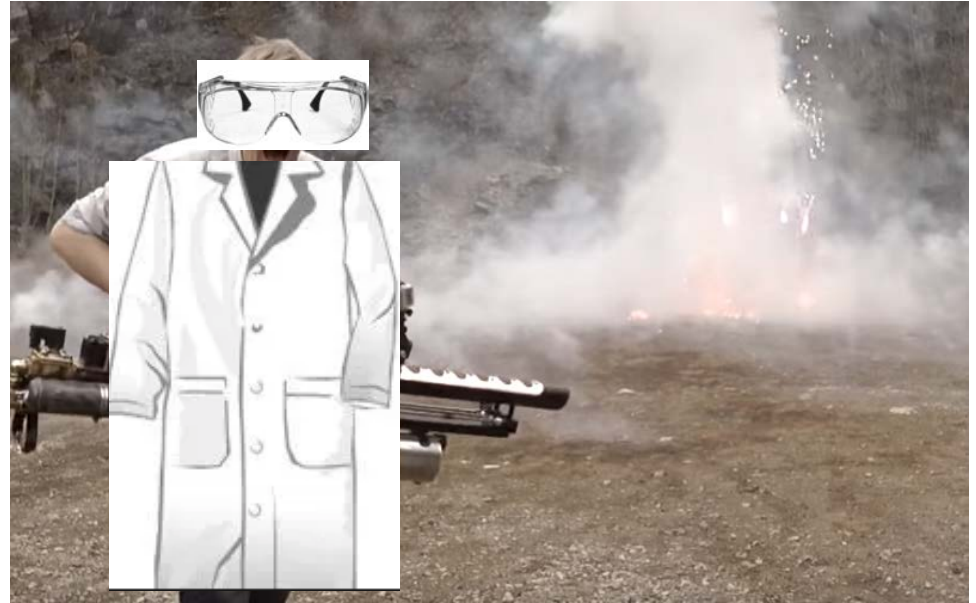
Shown (above) are remnants of $\text{Ni}(\text{N}_2\text{H}_4)_4\text{ClO}_4$
January 7, 2010



Brown placed a portion of the clumpy precipitate in a mortar and pestle, diluted with hexane, and ground the clumps. He walked away, removing safety glasses and lab coat then returned to mortar and “very gently, very, very gently” used a pestle to break up the chunks. The mortar detonated in his hands removing 3 fingers, an eye, and sustaining superficial cuts to other parts of his body.

Conclusions & Outlook

Explosions are cool!



But so is safety...

The development of environmentally friendly HEMs is a focus of ongoing research

The movement to more destructive, and sometimes more predictable, HEMs is inevitable

Diverse chemical sensors will be critical for HEM detection and deterrence

EILs may introduce much needed modularity of physical properties