A Chemical Exploration of

Explosives

Engle Lab Group Meeting
22 June 2017
Andrew M Romine

Brief Overview

China Lake – US Navy
Adelphi Laboratory Center – US Army
Los Alamos National Labs – DoE
Intitut fur Chemie der Treib und Explosivstoffe in Karlruhe-Berghausen – Germany
High Energy Materials Research Laboratory – India
Energy Materials Laboratory – UK

Brief Overview

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Energy Materials Laboratory – UK

University Lab Accident Under Investigation

Lab Safety: Texas Tech examination is first for chemical safety board

3 hurt in explosion at top DRDO unit, one critical

An inquiry has been ordered to probe the causes of the incident, officials said.

BRISTOL UNIVERSITY EVACUATED AFTER STUDENT ACCIDENTALLY MAKES EXPLOSIVE CHEMICAL USED IN TERROR ATTACKS

Brief Overview

"I suspect that almost all chemists are fascinated by explosives. Not only do explosives produce the most spectacular chemical reactions, they have also had an enormous impact on human history, for both good and evil. Gunpowder and its modern descendants have been instruments of destruction in guns and bombs, and of construction in mining and road building. Much can be learned about the history of chemistry and its relationship to society by studying the history of explosives..."

-Jeffrey Kovac, Department of Chemistry, University of Tennessee

Brief Overview

1. History of the entire world up until 1850
    - Fire, chemists, and gunpowder
2. Basics of High Energy Materials
    - Pyrotechnics
    - Pressurized Fluids
    - Nuclear
3. High Explosives
    - Primary
    - Tertiary
4. Secondary High Explosives
    - Nitrate-esters
    - Aromatic C-Nitro compounds
    - N-Nitro compounds
    - C-Nitro compounds
    - Cage compounds
    - The future

Where to start?

Fire

Assyrian Fire Pots, 900 BC

British Museum bas-reliefs of besieged city

Tow-tipped Arrows, 480 BC

Herodotus; Battle of Salamis

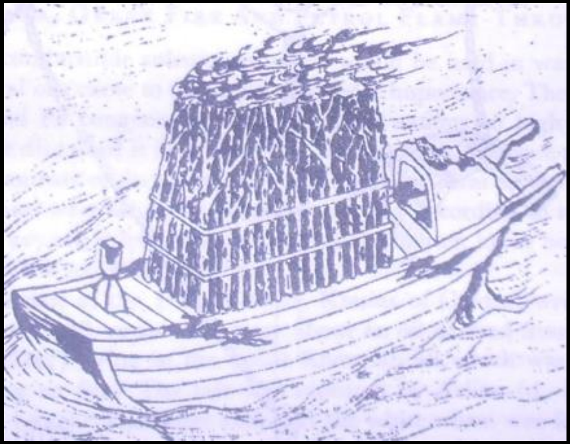
Pitch Flamethrower, 424 BC

Thucydides; Siege of Delium

Fire Ships, 332 BC

Arrian; Siege of Tyre

Painting by Andrew Howat



From Wujing Zongyao military manuscript

The Big Bang: A History of Explosives.
G.I. Brown. Sutton Publishing (1998)

Introducing the Chemists

Greek Fire

- Brought from Heliopolis to Constantinople by Kallinikos – 673 AD
- Protected Rome for eleven centuries (until 1453)

From the Madrid Skylitzes

Liver of Sulfur: K_2S, $K_2S_2SO_3$	Tartar: $KC_4H_5O_6$	Sarcocolla: 	Pitch: Petrochemicals

Boil

↓

Ignite

13th century,
Liber Ignium ad Comburendos Hostes

The Big Bang: A History of Explosives.
G.I. Brown. Sutton Publishing (1998)

A History of Greek Fire and Gunpowder
J.R. Partington. Heffer & Sons (1960)

(can only be extinguished by urine, vinegar, or sand)

The Gunpowder Monopoly

The first explosive composition: blackpowder (220 BC)

- Western alchemists focused on transmutation
- Eastern alchemists focused on elixers of imortality
  - Found *huo yao*, “fire drug”
  - It was used as a weapon in eastern wars
    - Bombs of 1231 defense of Kaifeng
- Brought an end to the Greek Fire wielding Byzantines in 1453 due to Turkish cannons

Dardanelles gun
(1464 – 1807)

The Chemistry of Explosives.
J Akhavan. RSC Paperbacks (2004)

A History of Greek Fire and Gunpowder
J.R. Partington. Heffer & Sons (1960)

Gunpowder as the Fourth Power, East and West.
J Needham. HK UP (1983)

Gunpowder. J Kelly
Basic Books (2004)

The Gunpowder Monopoly

Gunpowder

- The only explosive used for propulsion and blasting from until 1850

XX%

XX%

XX%

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The Gunpowder Monopoly

Gunpowder

- The <u>only</u> explosive used for propulsion and blasting from until 1850

Charcoal: From smoldering wood, removing impurities	Brimstone: Sulfur, which lowers the mixtures ignition temp.	Saltpetre: Oxygen source now known to be potassium nitrate
15%	10%	75%

$$C + S + KNO_3 \longrightarrow$$

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$$8C + 3S + 10KNO_3 \longrightarrow 2K_2CO_3 + 3K_2SO_4 + 6CO_2 + 5N_2$$

3 megajoules per kilogram

10-25% of your yearly phone energy consumption

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The Gunpowder Monopoly

Gunpowder

- The only explosive used for propulsion and blasting from until 1850

Charcoal: From smoldering wood, removing impurities	Brimstone: Sulfur, which lowers the mixtures ignition temp.	Potassium Chlorate: Contains lower % of oxygen, but releases it at a lower temperature

Usefulness discovered in 1786 by Berthollet, who held a party to celebrate its his first new batch of gunpowder being stamped that day in 1786. On return to the mill from breakfast, the guests were met with a violent explosion throwing the two leaders "a great distance" killing them.

~12 megajoules per kilogram

when stabilized with tan and sawdust (Kellow & Short, 1862)

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Gunpowder

- The only explosive used for propulsion and blasting from until 1850

Charcoal:	Brimstone:	Potassium Chlorate:
From smoldering wood, removing impurities	Sulfur, which lowers the mixtures ignition temp.	Contains lower % of oxygen, but releases it at a lower temperature

Kellow & Short were simply better businessmen; their mill demolished an entire block of building upon detonation in July 1865

~12 megajoules per kilogram

when stabilized with tan and sawdust (Kellow & Short, 1862)

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The Gunpowder Monopoly

Gunpowder

- The only explosive used for propulsion and blasting from until 1850

Charcoal: From smoldering wood, removing impurities	Brimstone: Sulfur, which lowers the mixtures ignition temp.	Sodium Nitrate: Stabilized to moisture by Lammot duPont in 1857

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Wait, what is an explosive?

Fuel

"A substance capable of reaction with atmospheric oxygen and oxygen carriers (oxidizers) with the evolution of heat"

Explosive

"A substance which, when suitably triggered, releases a large amount of heat and pressure by way of a very rapid self-sustaining exothermic decomposition reaction"

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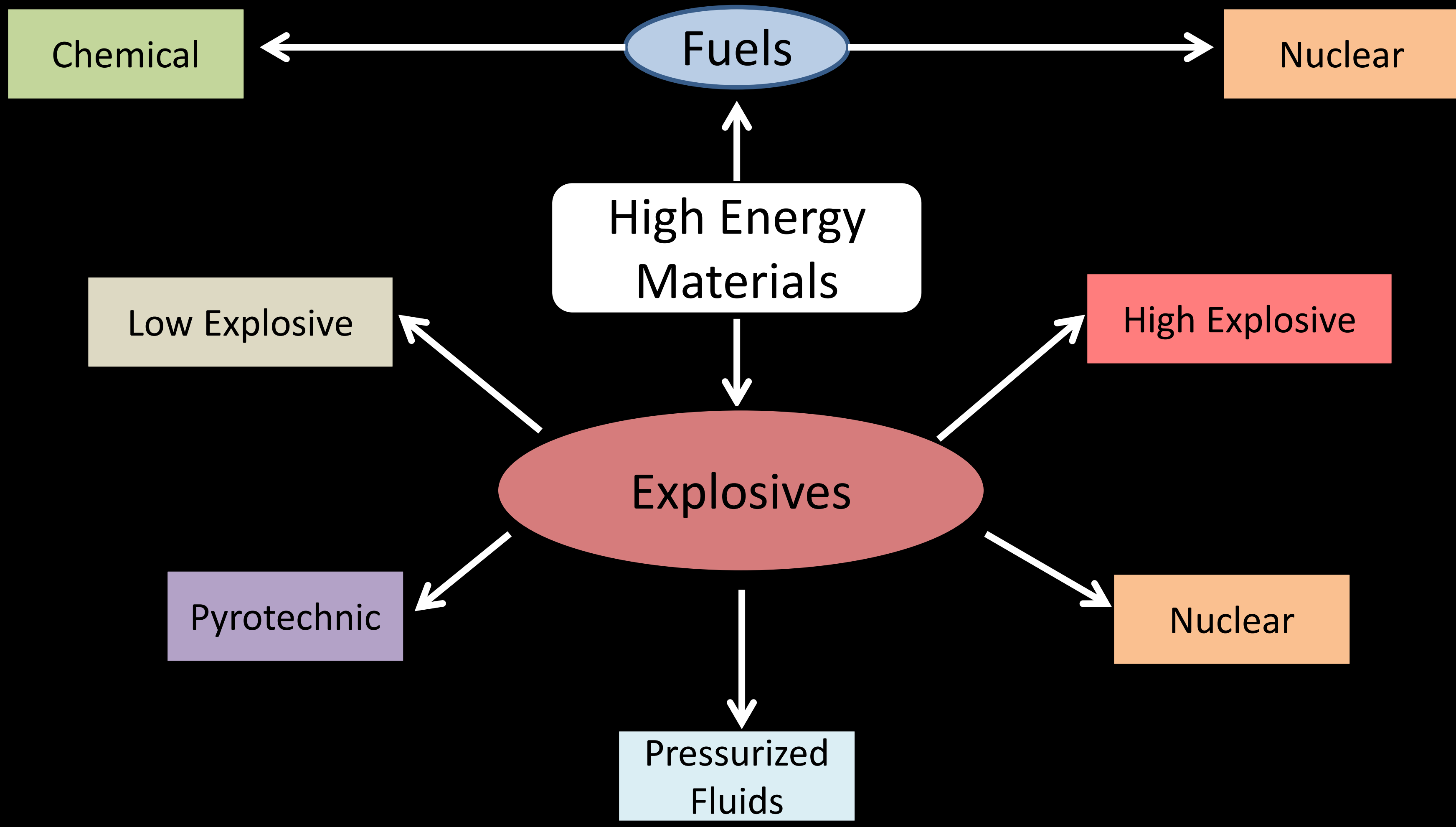

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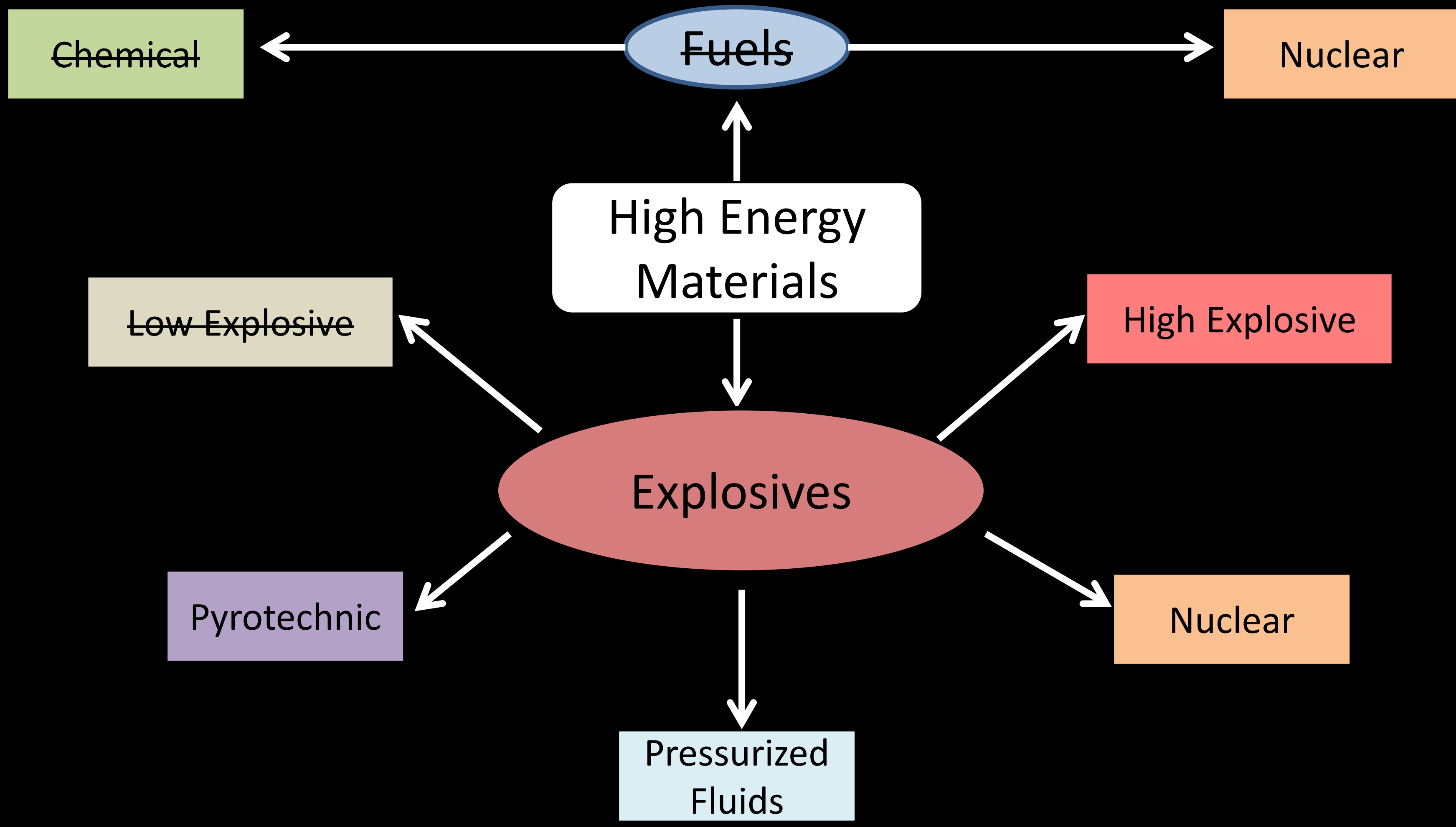

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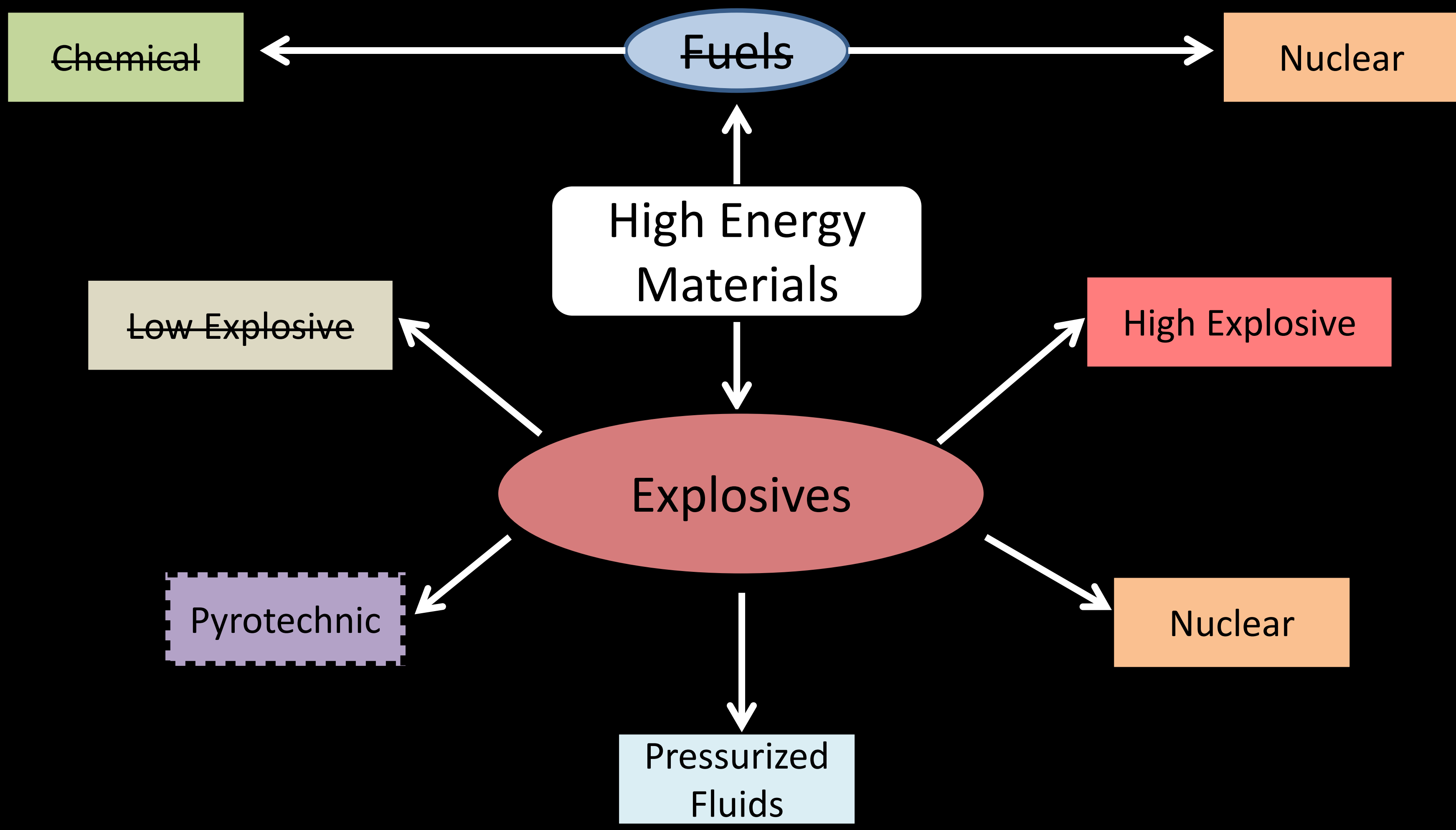

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Pyrotechnic

Thermite

$$Fe_2O_3 + 2\ Al \longrightarrow 2\ Fe + Al_2O_3$$

Fireworks: Gunpowder + Metals

Li_2CO_3
$SrCO_3$

$CaCl_2$

NaCl

$BaCl_2$

CuCl

Sr+Cu

Al/Ti/Mg

Unstable under heat!

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CuCl

Sr+Cu

Al/Ti/
Mg

Magnesium-aluminum alloy (magnalium) provides an okay alternate

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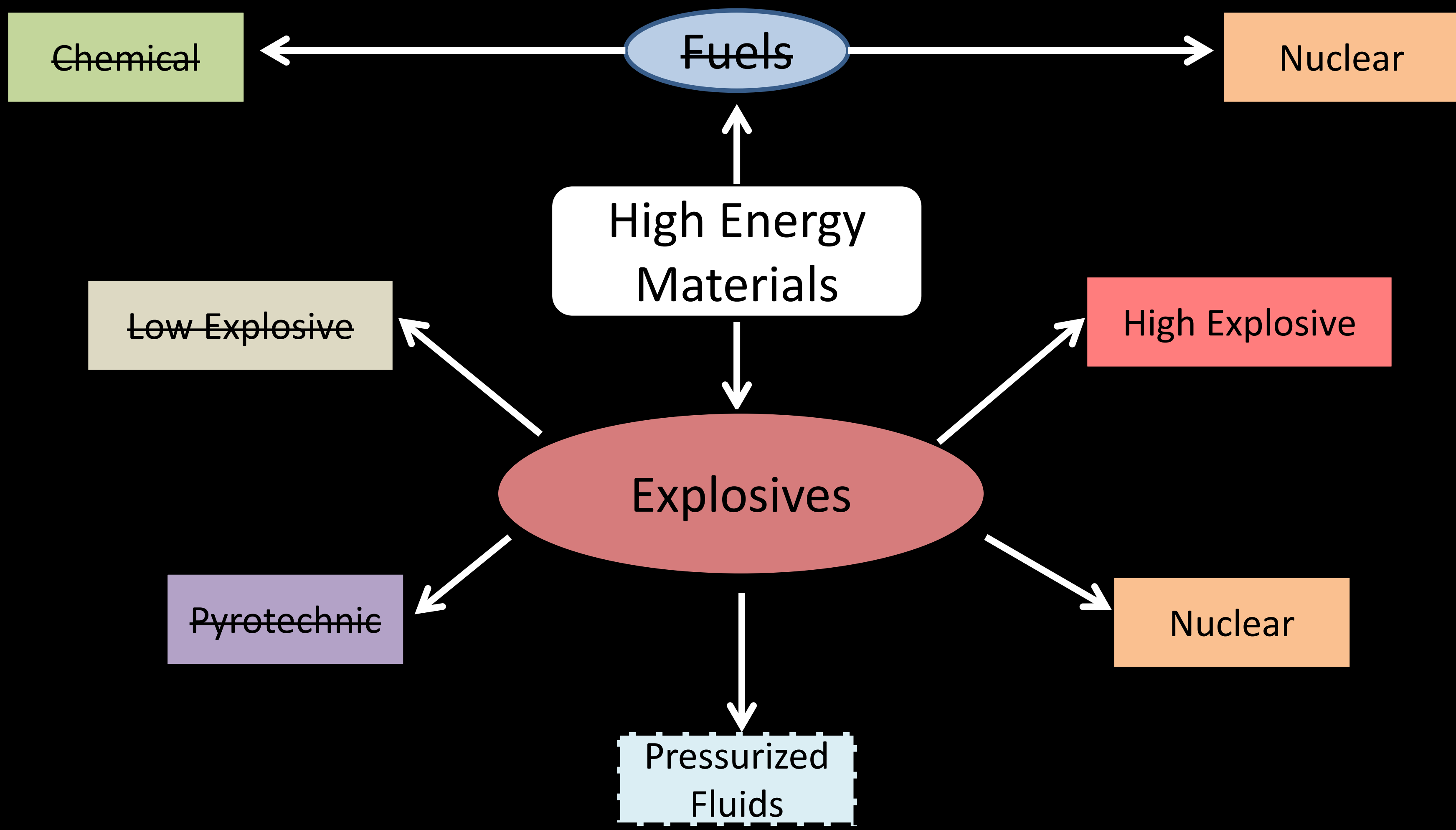
Wait, what is an explosive?



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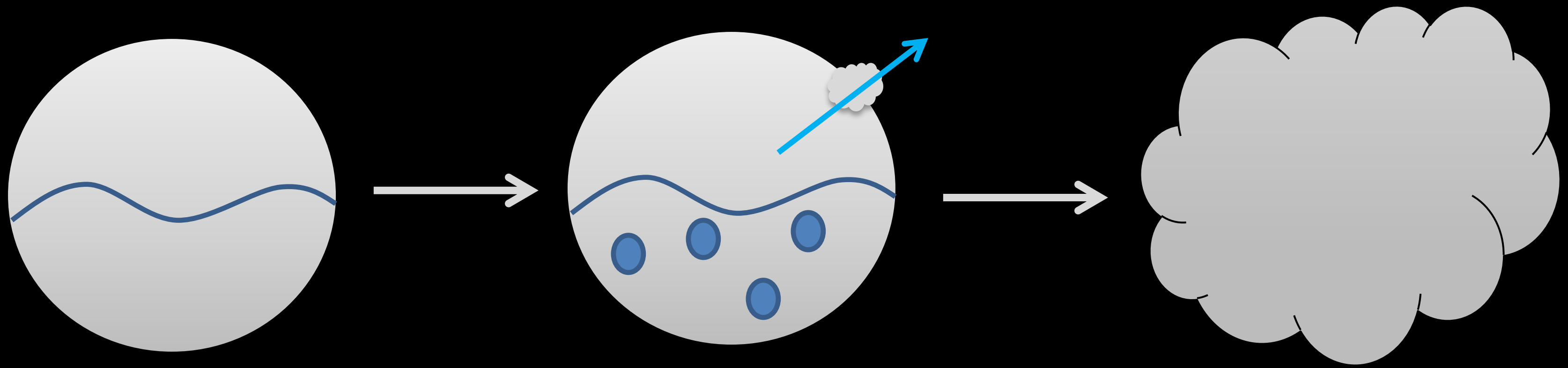
Pressurized Fluids

B.L.E.V.E. – Boiling Liquid Expanding Vapor Explosion

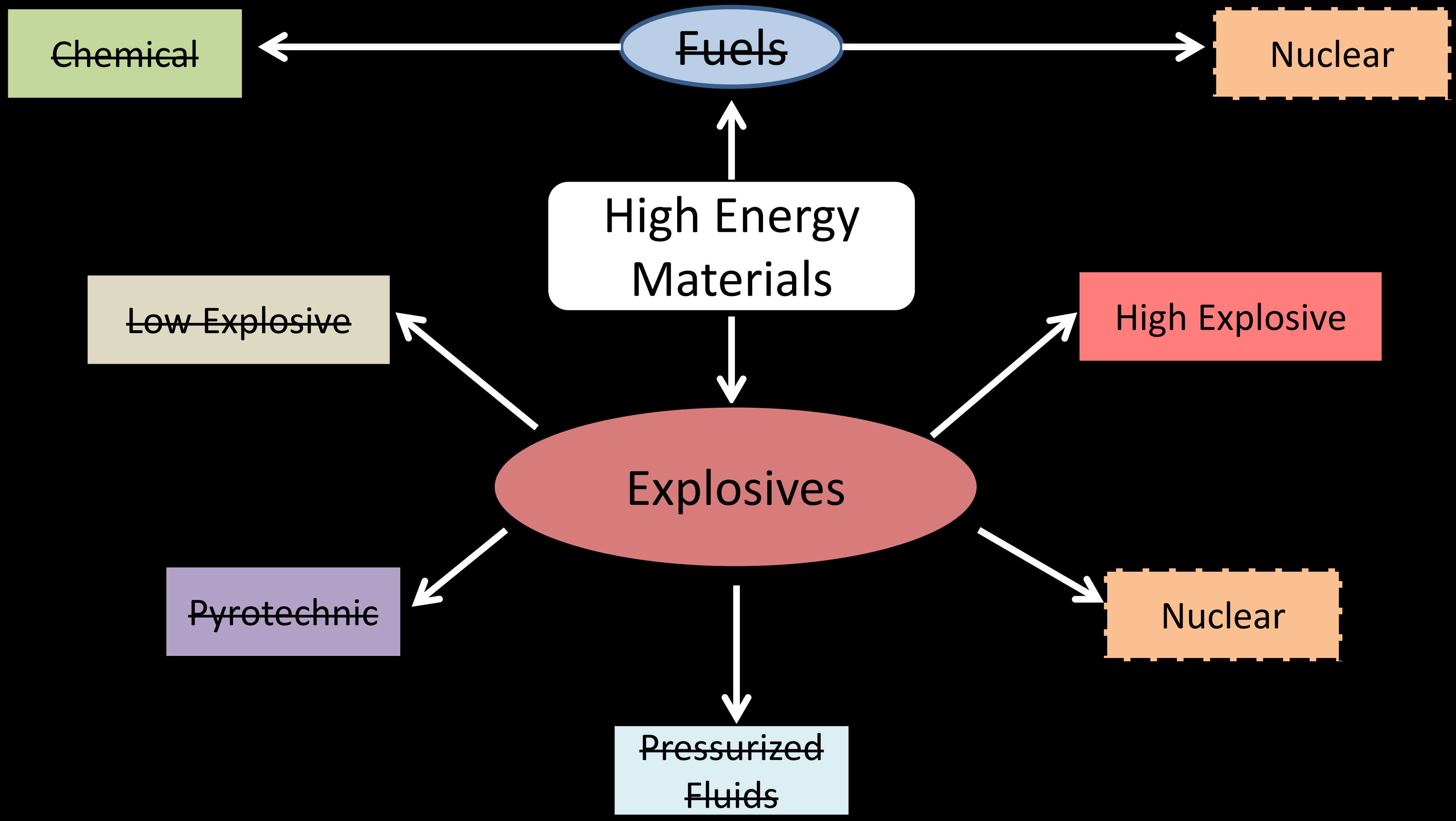
A BLEVE occurs due to catastrophic failure of a vessel holding liquefied gas fails



Can be caused by flammable (propane, gas, etc.) and nonflammable (LN2, H_2O, etc.) liquids alike.

Birk A. M., Cunningham, M., Liquid Temperature Stratification and its Effect on BLEVEs and their Hazards, Journal of Hazardous Materials, 48 (1996) pp 219-237.

Wait, what is an explosive?



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Nuclear

Fusion (atomic reactors / atomic bombs)

$$^{1}_{0}N + ^{235}_{92}U \longrightarrow ^{141}_{56}Ba + ^{92}_{36}Kr + 3\ ^{1}_{0}N + 3.2x10^{-11}J$$

Fission (sun / hydrogen bombs)

$$^{2}H + ^{3}H \longrightarrow ^{4}He + ^{1}N + 5.6x10^{-13}J$$

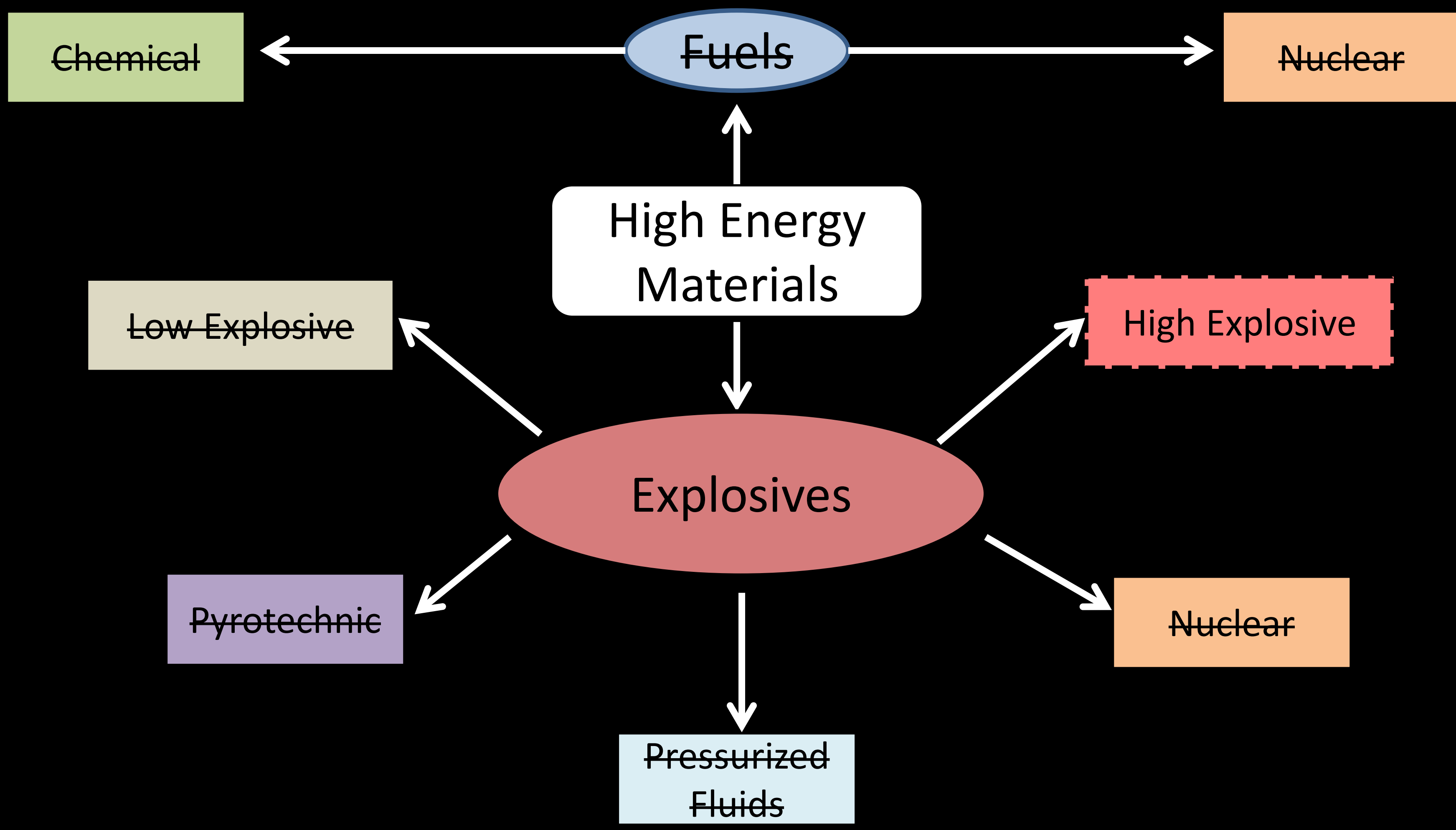
Largest detonation reported:

Tsar Bomba
1961; Soviet Union
57 Megatons of TNT equivalent

The Big Bang: A History of Explosives.
G.I. Brown. Sutton Publishing (1998)

Principles of Nuclear Chemistry
McPherson P.A. Belfast (2017)

Wait, what is an explosive?



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High Explosive

Low Explosive

Deflagration: self-sustaining decomposition slower than the speed-of-sound

Rate of deflagration measured using linear burning rate eq.:

$r = \beta P^{\alpha}$,
β=burning rate coefficient
P=pressure at surface
α=burning rate index

Gunpowder:

$5 \text{mm s}^{-1} = \beta(10\text{e-}2 \text{ N mm}^{-2})^{0.5}$

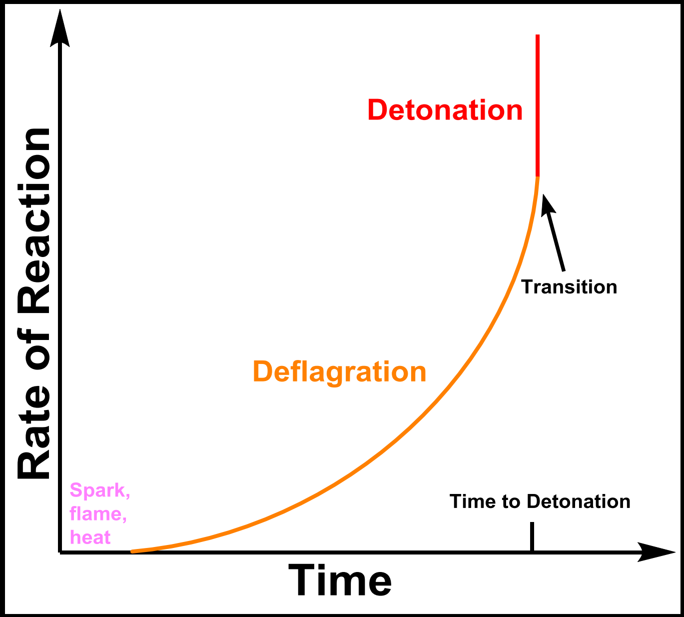
β=17

In a tube (at 4000x pressure):

$r = 17 \times (4000 \times 10\text{e-}2)^{0.5} = 399 \text{mm/s}$

High Explosive

Detonation: decompose through shockwave transfer rather than thermal transfer at supersonic speeds (1500 to 9000 m/s)



The Chemistry of Explosives. J Akhavan. RSC Paperbacks (2004)

High Explosive

Deflagration

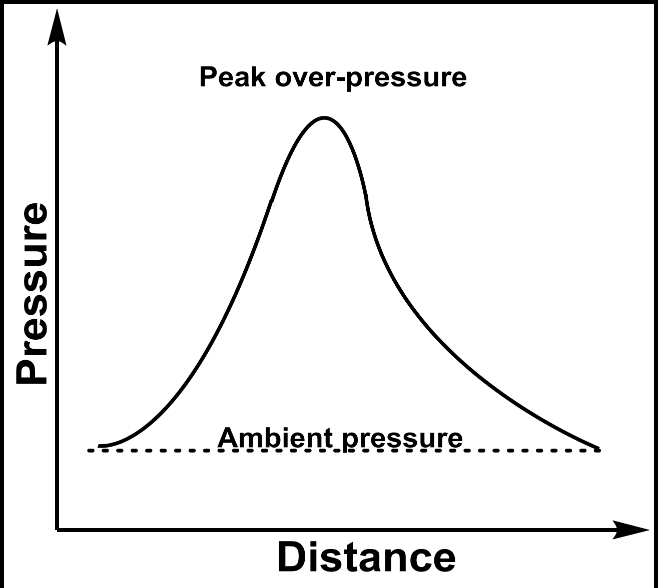
Decomposed mass moves a *different* direction from the explosion

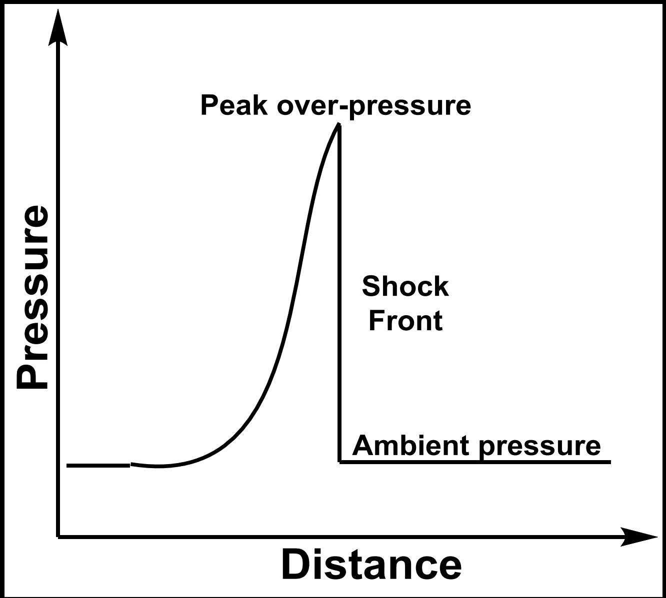
propellant

Detonation

Decomposed mass moves the *same* direction as the explosion

bombs





Important Terms

Heat of Explosion: ΔH_e (Joules/kg)

Energy released per mass

Oxygen Balance: OB% (mass)

Positive if more than needed; negative if less

Not extremely useful, but can be a rule of thumb (TNT=-74%)

Used in creating mixtures (ammonium nitrate=20%); AN/TNT = 80/20

Velocity of Detonation: VOD (m/s)

Rate of travel of the shockwave front

Relative Effectiveness: R.E. (TNT eq.)

TNT provides a useful benchmark; height of explosion can be estimated

Brisance: $\alpha(\text{R.E. x VOD}^2)$

Measure of detonation pressure useful for estimating fragmentation

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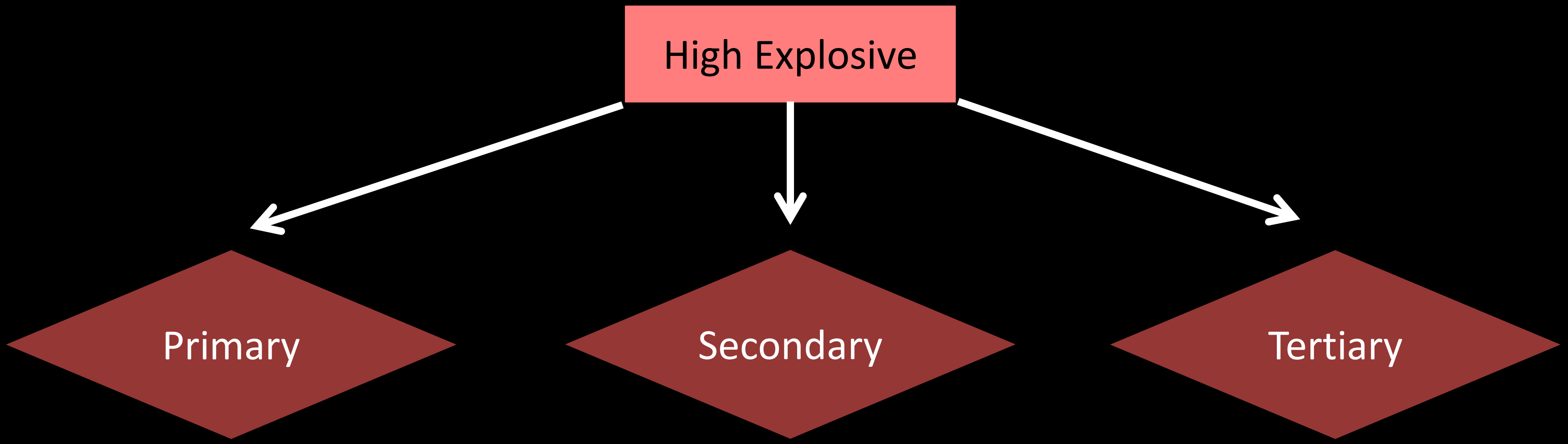
High Explosive



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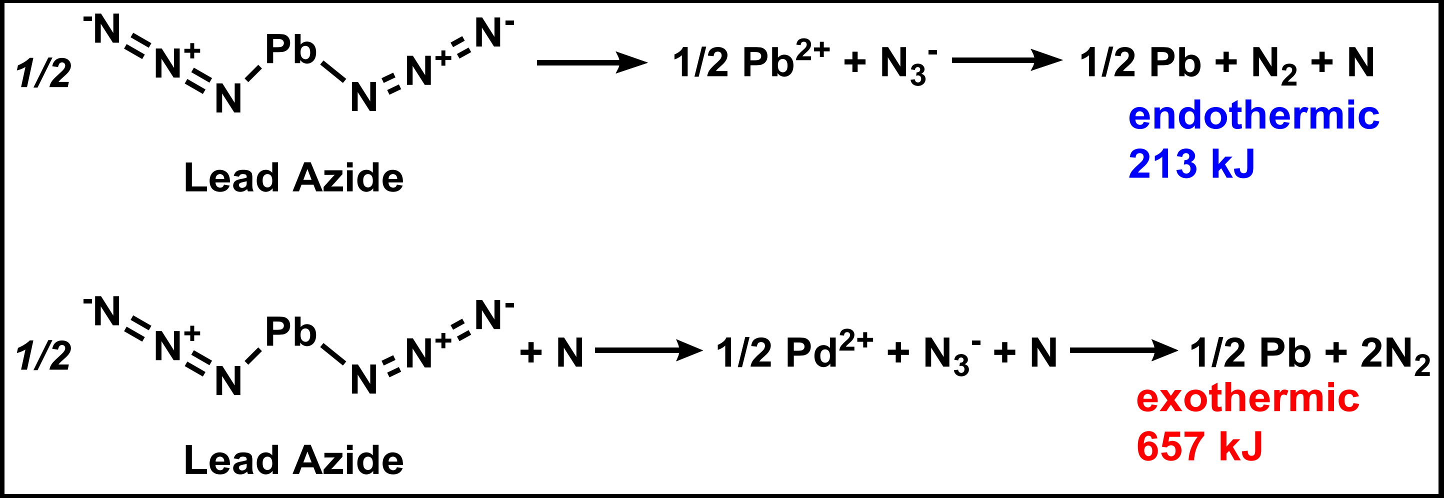
Primary Explosives

Undergo a very rapid transition from burning to detonating

- Contact explosive
- Detonate due to heat or shock
- Initiate with an explosive dissociation followed by a stable explosion



Explosives Meyer R.
Verlag Chem (1977)

The Chemistry of Explosives.
J Akhavan. RSC Paperbacks (2004)

Primary Explosives

Mercury Fulminate

Creation: Dissolve mercuric nitrate in nitric acid and *slowly* add ethanol

$$Hg(NO_3)_2 + HNO_3 + EtOH \longrightarrow {}^{-}O-N^{+}\equiv C-Hg-C\equiv N^{+}-O^{-}$$

$$(CNO)_2Hg \longrightarrow 2CO + N_2 + Hg$$

Oxygen Balance:	11.2%
Nitrogen amount:	9.84%
Heat of explosion:	1486 kJ/kg
Deflagration point:	165 ^{o}C
Impact sensitivity:	1-2 J

100,000kg produced per year in early 20th century Germany

Necessary for early dynamite

Explosives Meyer R. Verlag Chem (1977)

Beck et al. (2007). The Crystal and Molecular Structure of Mercury Fulminate. DOI:10.1002/zaac.200700176

The Chemistry of Explosives. J Akhavan. RSC Paperbacks (2004)

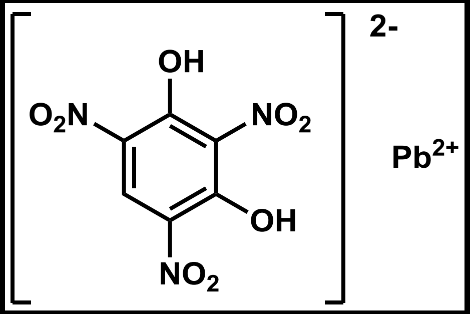
Primary Explosives

Lead Styphnate

Creation: Dissolve magnesium styphnate in nitric acid and add lead acetate and precipitate out product

$$\{C_6N_3O_8\}MgH_2O + Pb(CH_3CO_2)_2 \longrightarrow \{C_6N_3O_8\}PbH_2O + Mg(CH_3CO_2)_2$$

Oxygen Balance:	18.8%
Nitrogen amount:	8.97%
Heat of explosion:	1549 kJ/kg
Deflagration point:	275 °C
Impact sensitivity:	5 J



Used in explosive caps in combination with lead azide to decrease shock sensitivity and reduce static sensitivity of unadulterated compound

Explosives Meyer R. Verlag Chem (1977)

The Big Bang: A History of Explosives. G.I. Brown. Sutton Publishing (1998)

The Chemistry of Explosives. J Akhavan. RSC Paperbacks (2004)

Primary Explosives

Silver Azide

Creation: Precipitates upon mixing of sodium azide and silver salts

$$NaN_3 + AgNO_3 \longrightarrow AgN_3 + NaNO_3$$

$$2AgN_3 \longrightarrow 3N_2 + 2Ag$$

Nitrogen amount:	28.03%
Volume of gas:	224L/kg
Deflagration point:	273 °C
Impact sensitivity:	<1 J

Initiates reaction better than lead azide, but not used due to extreme sensitivity to friction and unsatisfactory physical characteristics (cheesy & amorphous)

Explosives Meyer R.
Verlag Chem (1977)

The Big Bang: A History of Explosives.
G.I. Brown. Sutton Publishing (1998)

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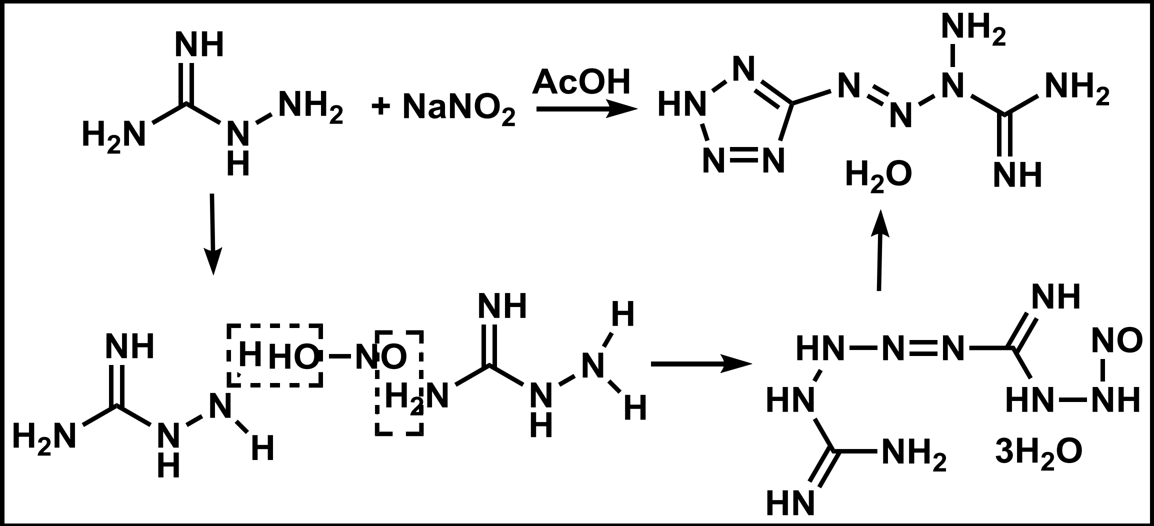
Primary Explosives

Tetrazene (tetrazole guanyltetrazene hydrate)

Creation: Precipitates from reaction of aminoguanidine and sodium nitrate



Explosives Meyer R. Verlag Chem (1977)

Organic Chemistry of Explosives. Agrawal J.P. Wiley (2007)

The Big Bang: A History of Explosives. G.I. Brown. Sutton Publishing (1998)

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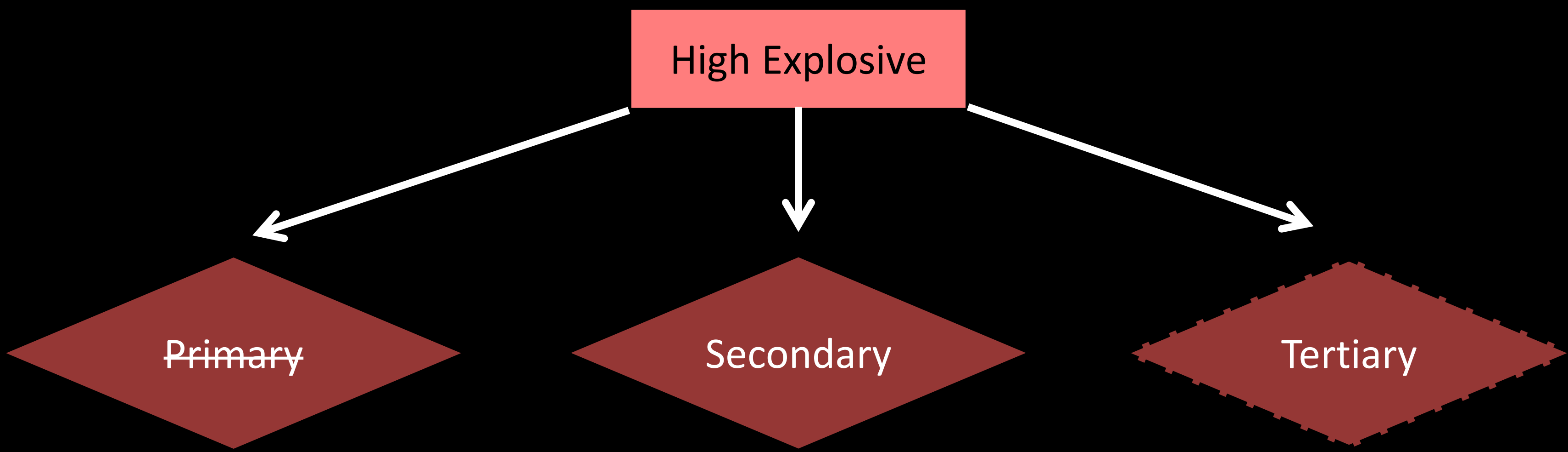
High Explosive



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Tertiary Explosives

Extremely shock insensitive and much safer to handle

- Blasting agents
- Do not reliably detonate with primer
- Require booster comprised of secondary explosives

$$3NH_4NO_3 + 2CH_3NO_2 \longrightarrow 4N_2 + 2CO_2 + 9H_2O$$

Nitrogen amount:	35%
Oxygen balance:	20%
Volume of gas:	980L/kg
Heat of explosion:	1601 kJ/kg
Deflagration point:	273 ^{o}C
Impact sensitivity:	>49 J

Ammonium nitrate & nitroethane (ANNM) or AN & fuel oil (ANFO) make up 80% of commercial explosives and often use TNT (a secondary explosive) as a booster

Explosives Meyer R. Verlag Chem (1977)

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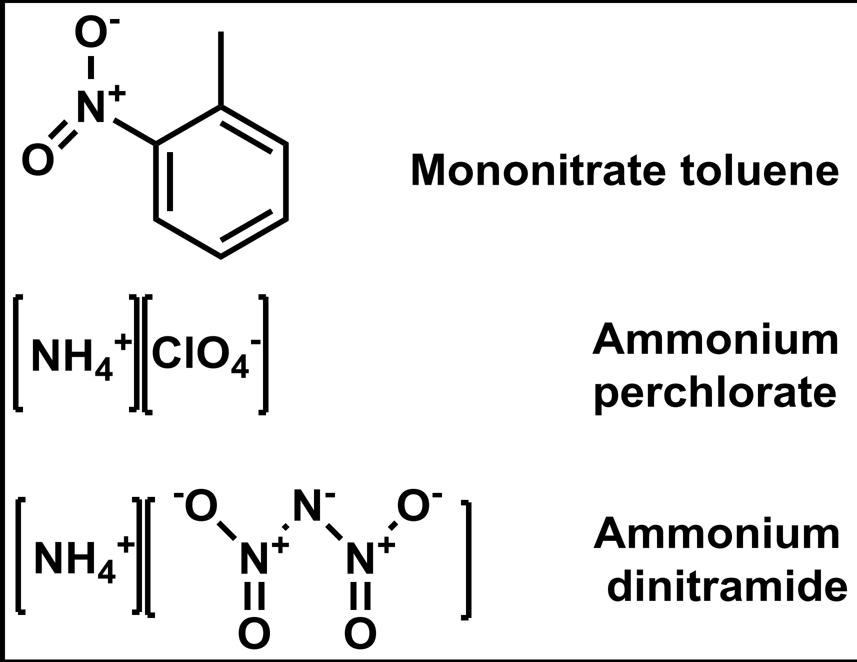
Tertiary Explosives

Don’t let them fool you!



In 1988, PEPCON plant caught fire (cause unknown) and caused the 4500 metric tons of ammonium perchlorate to explode, killing 2 and injuring 372 with an estimate damage of $100m USD.

Explosives Meyer R. Verlag Chem (1977)

Reed, Jack W. (November 1988). Sandia National Laboratories

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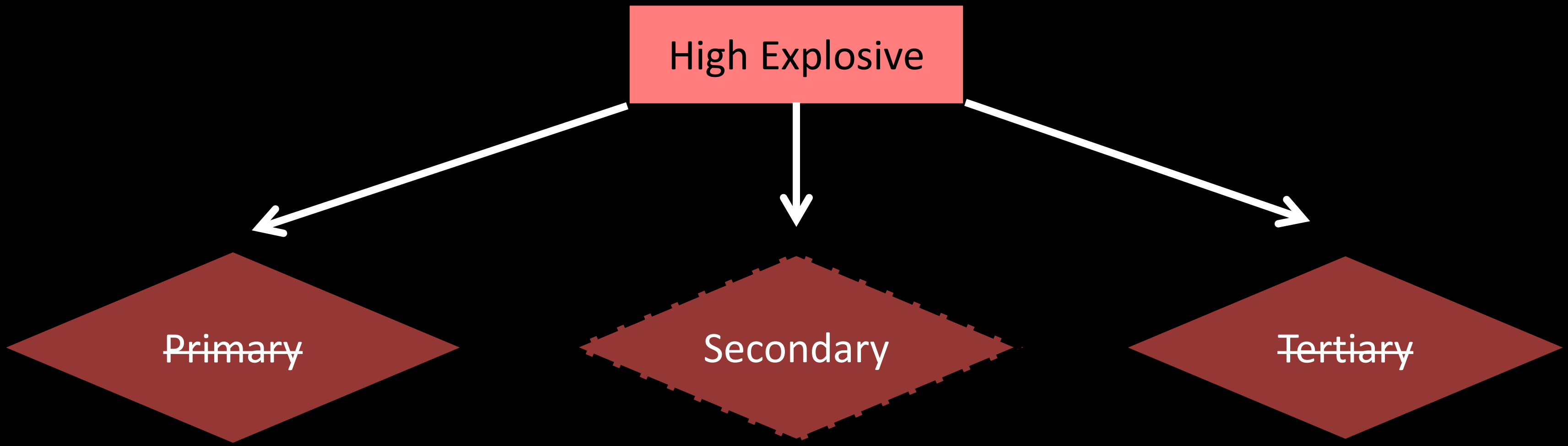
High Explosive



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Nitroglycerine

First real explosive discovered after gunpowder

- Developed by Italian, Ascanio Sobrero, to treat angina pectoris
- Violently exploded sending glass into his hands

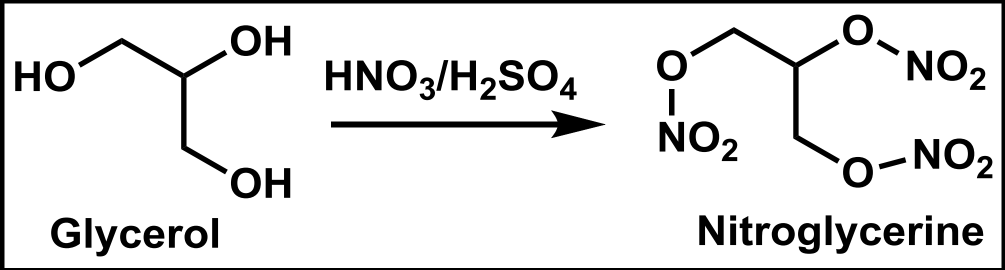
It has a sharp sweet, aromatic taste. It is advisable to take great care in testing this property. A trace of nitroglycerine placed upon the tongue, but not swallowed, gives rise to a most pulsating, violent headache, accompanied by great weakness of the limbs. A dog was given a few centigrams of nitroglycerine. It soon began to foam at the mouth and then vomited. Despite the fact that the greater part of the nitroglycerine had thus been eliminated from the system, within seven or eight minutes the animal had fallen down and almost ceased breathing. A dose of olive oil and ammonia was administered. The animal revived somewhat, and remained for some two hours whining, trembling violently, and beating its head on the wall. A post-mortem examination showed that the vessels of the brain and heart were suffused with blood and much distended. Similar results were obtained with rats and guinea-pigs. The violence of the decomposition has prevented me, up to the present, making an analysis of the body.

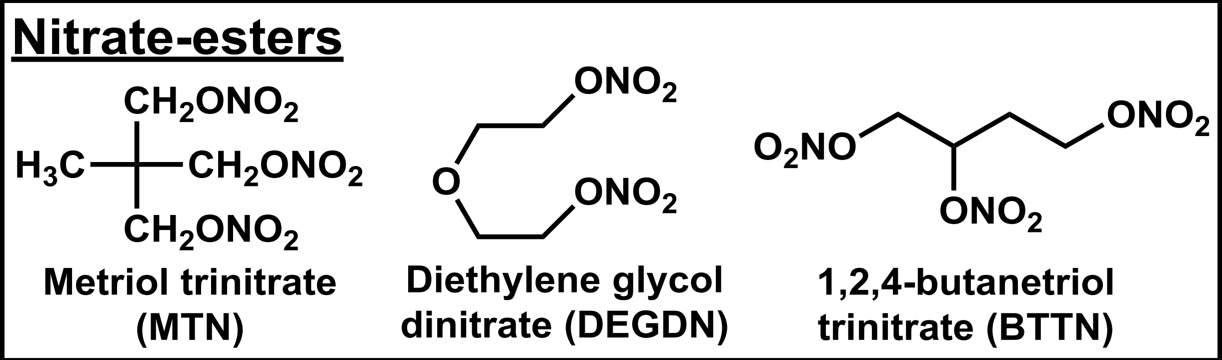
The Big Bang: A History of Explosives.
G.I. Brown. Sutton Publishing (1998)

Nitroglycerine

First real explosive discovered after gunpowder

- Stabilized by Nobel as dynamite
- Lead to the Haber-Bosch process





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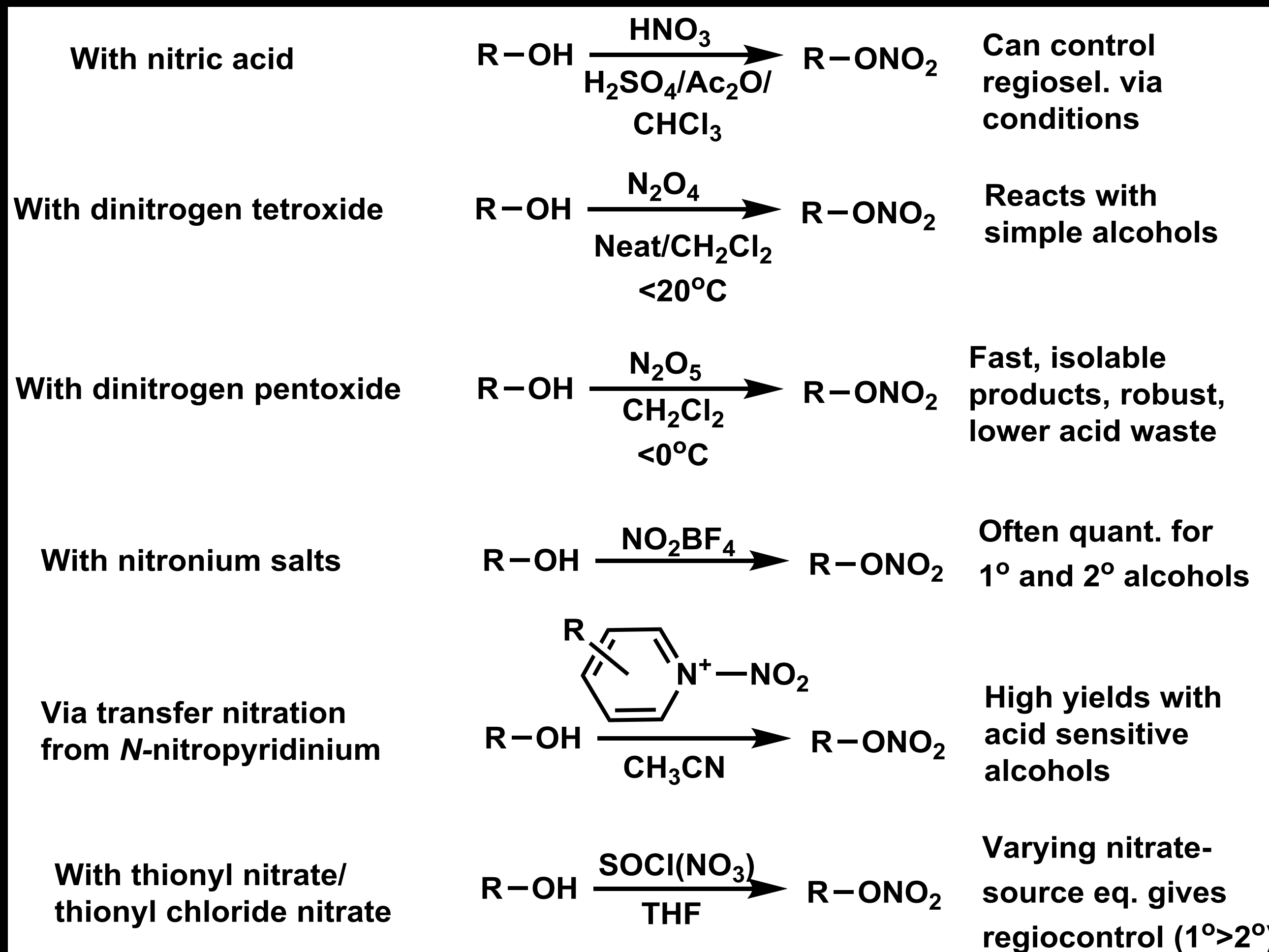
Nitrate-esters

Common *O*-nitration routes:



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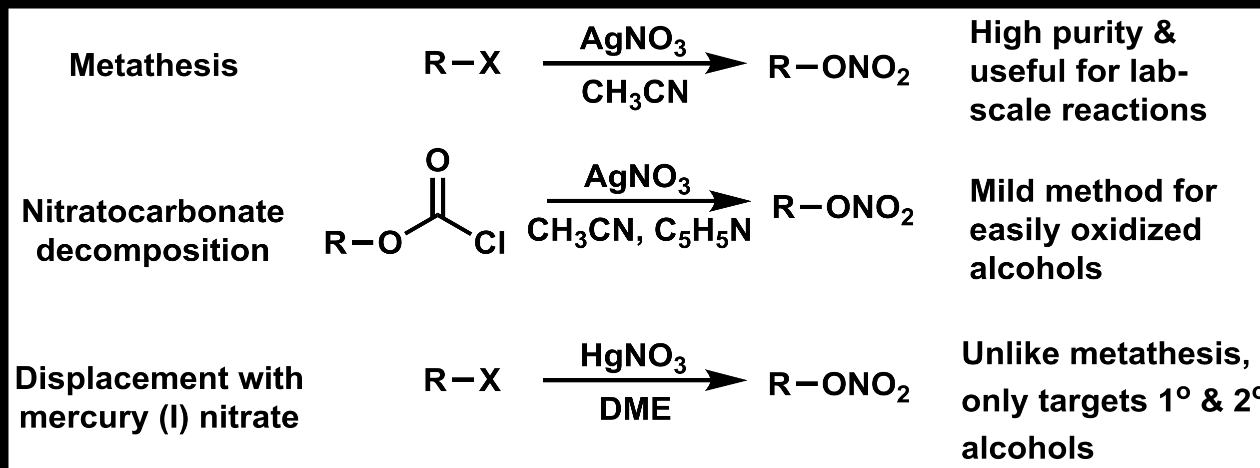
Nitrate-esters

Nucleophilic displacement routes:



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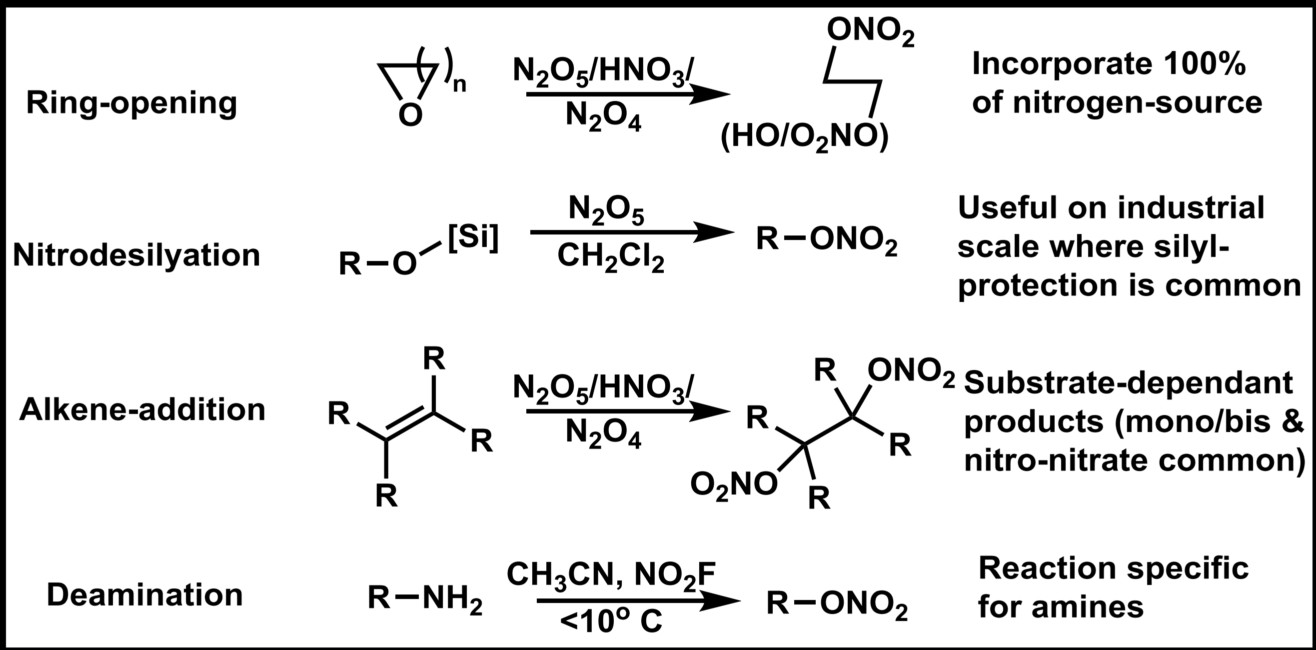
Nitrate-esters

Other common routes:



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Reed, Jack W. (November 1988). Sandia National Laboratories

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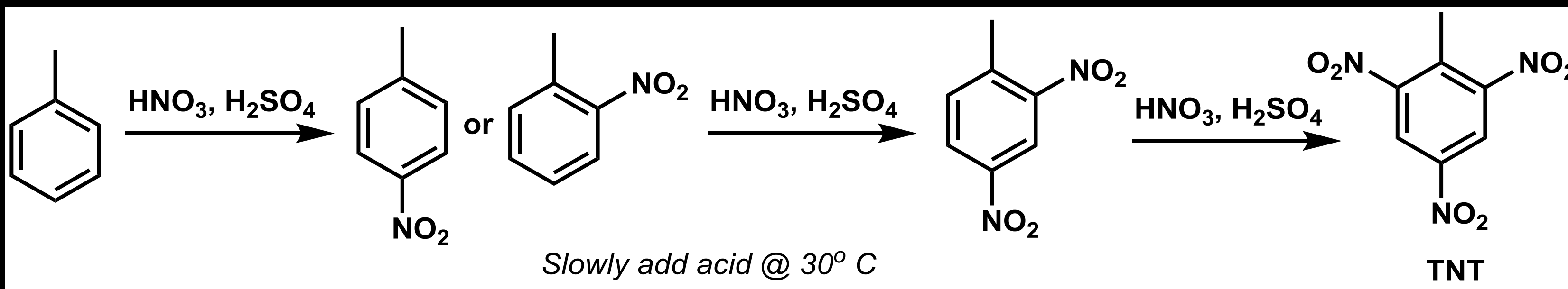
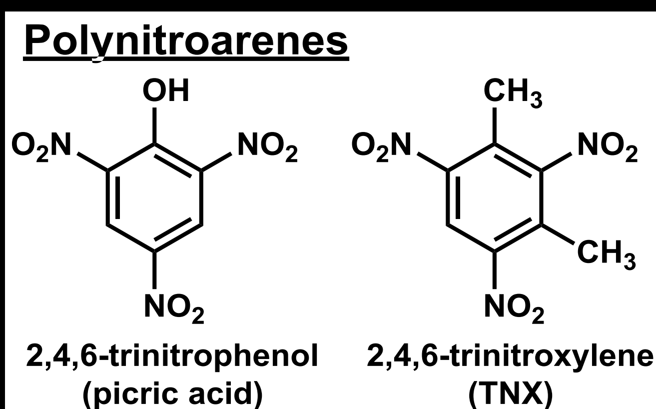
Trinitrotoluene

Ideal properties

- Developed in 1863
- Cheap, raw reactants
- High stability (resistance to impact and friction)





Mainly confined to history due to moderate performance & frequent formation of primary explosives when coordinated to metals (such as lead/picric acid salt)

Recent resurgence in oil due to thermal stability and impact stability

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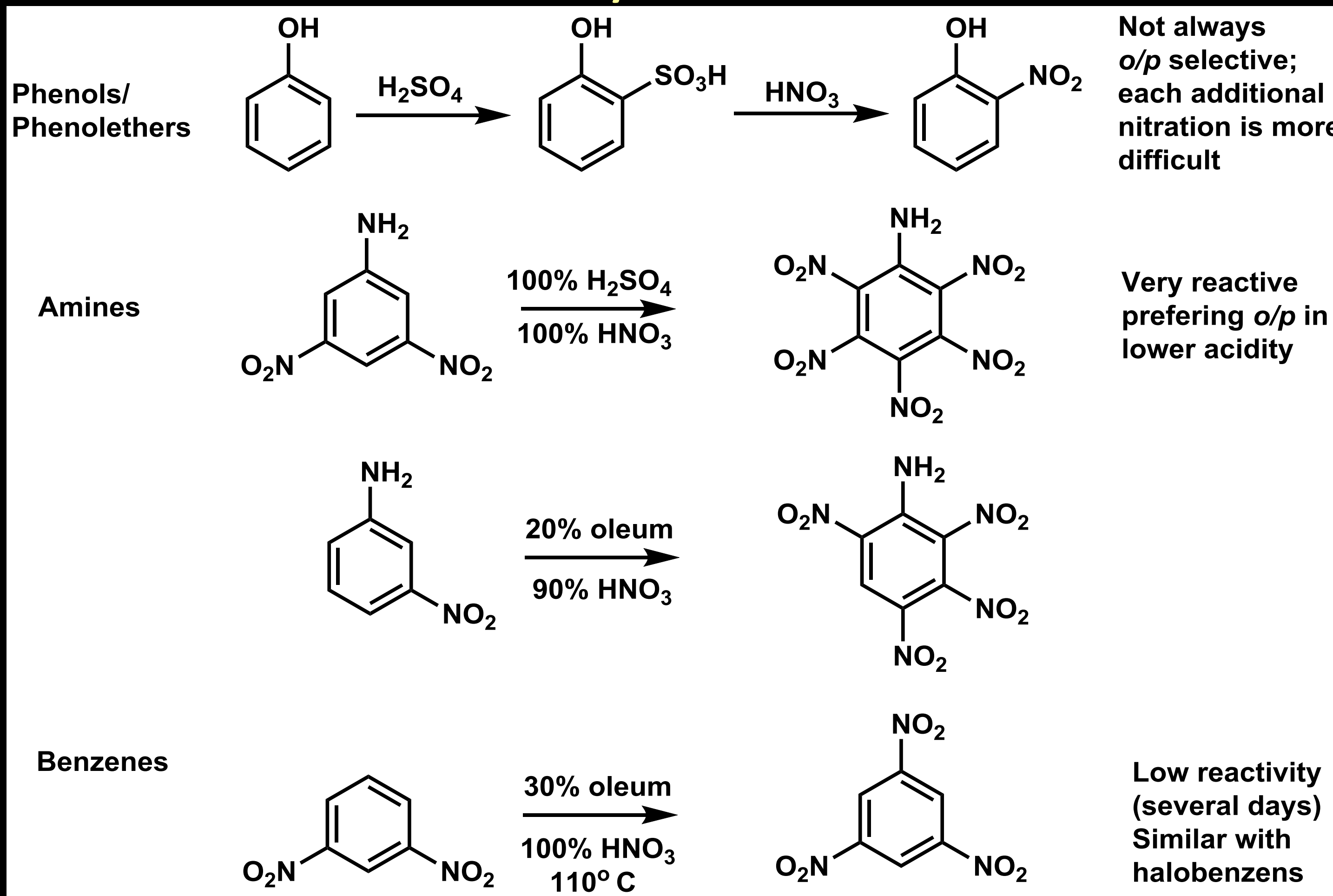
Aromatic *C*-nitro compounds

Substrate-derived reactivity



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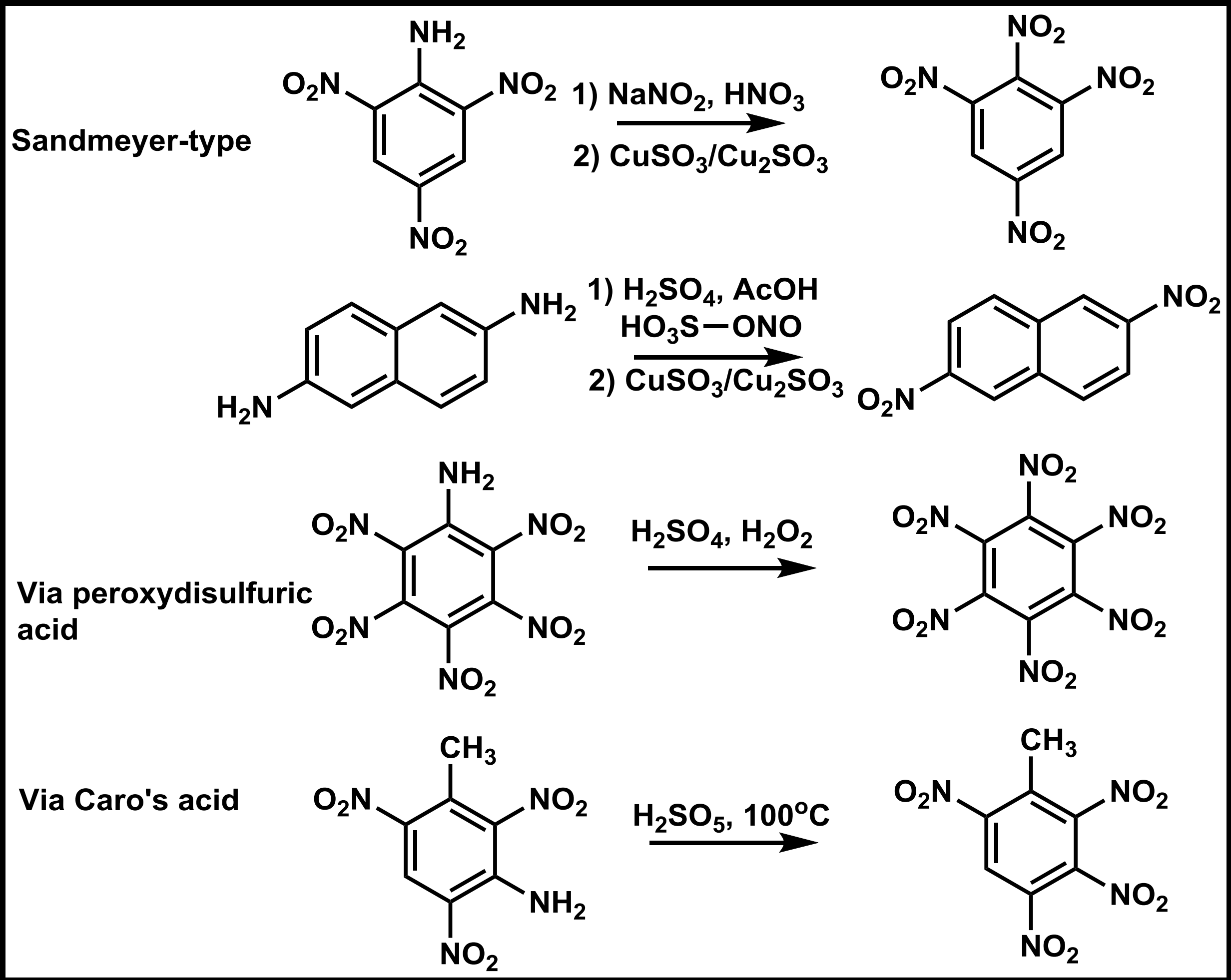
Aromatic *C*-nitro compounds

Nitration via oxidation of arylamines



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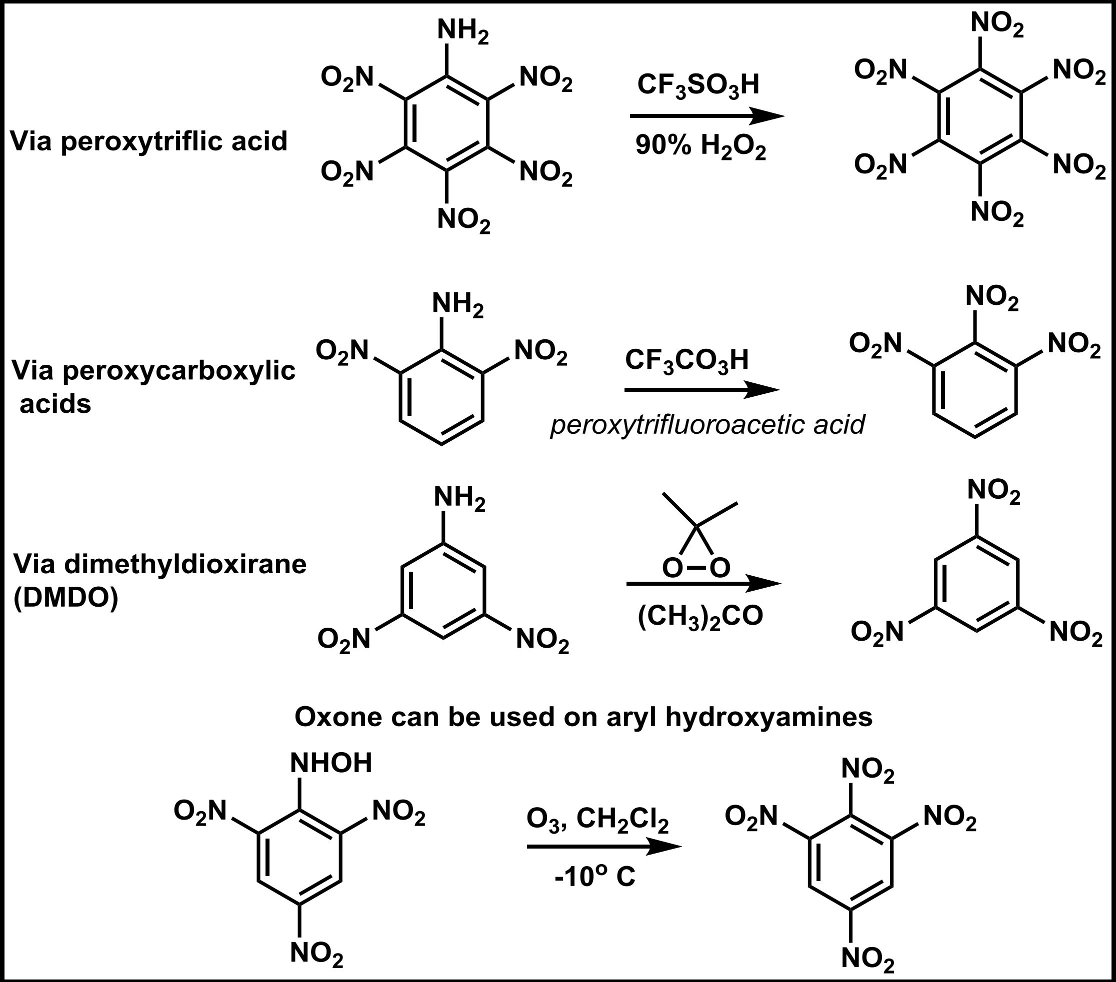
Aromatic *C*-nitro compounds

Nitration via oxidation of arylamines



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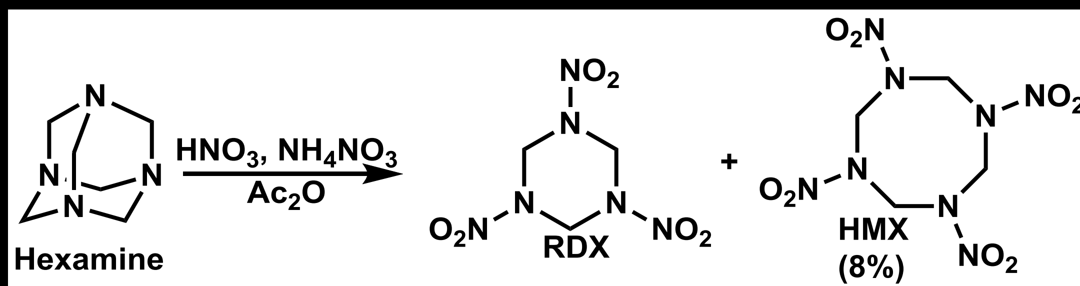
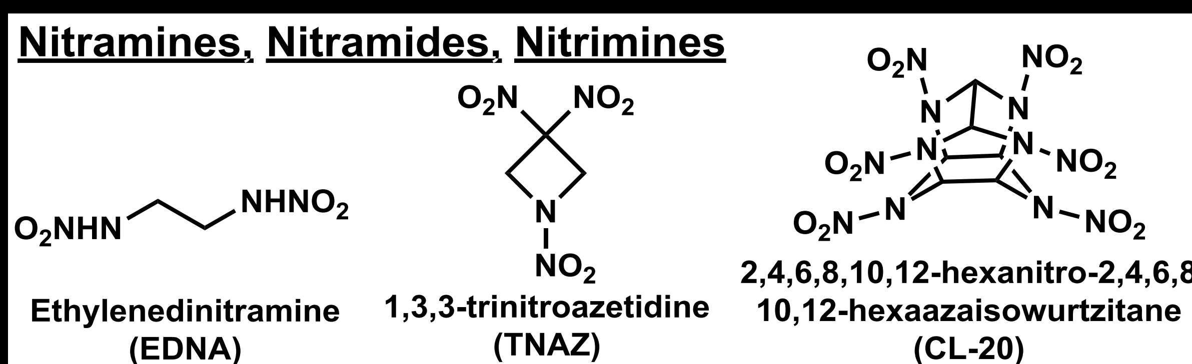
Cyclotrimethylenetrinitramine

Research Development Explosive

- Developed by Henning in 1899 (German patent: 104280) for med. use
- More than >20k tons made per month in WW2 by US & Germany alone
- Main ingredient in Compositions A, B, C, D ; HBX; H-6; PBX etc.
- More stable than TNT; one of the primary explosives in the military





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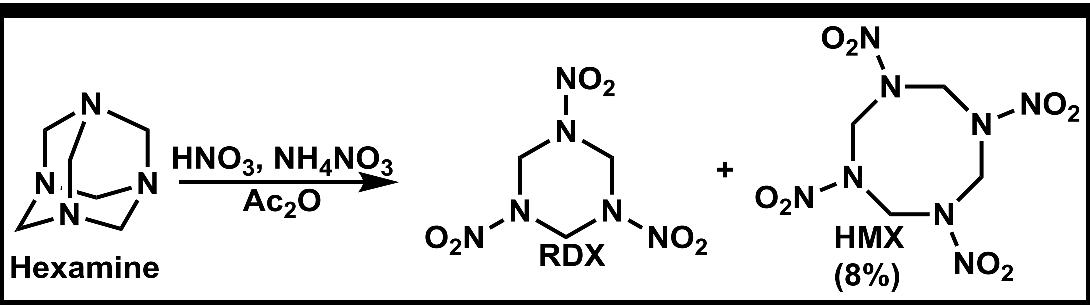
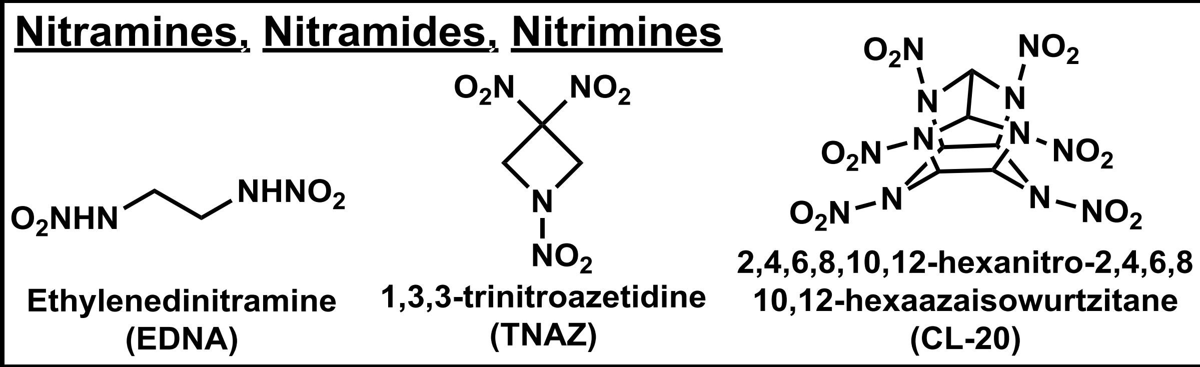
Cyclotrimethylenetrinitramine

Type	Abbreviation	D. Vel. (m/s)	Density (g/cm^2)
N-nitro (Ali)	CL-20	9,500	2.04
N-nitro (Ali)	HMX	9,400	1.91
N-nitro (Ali)	RDX	8,750	1.76
C-nitro (Ar)	TNT	6,900	1.60





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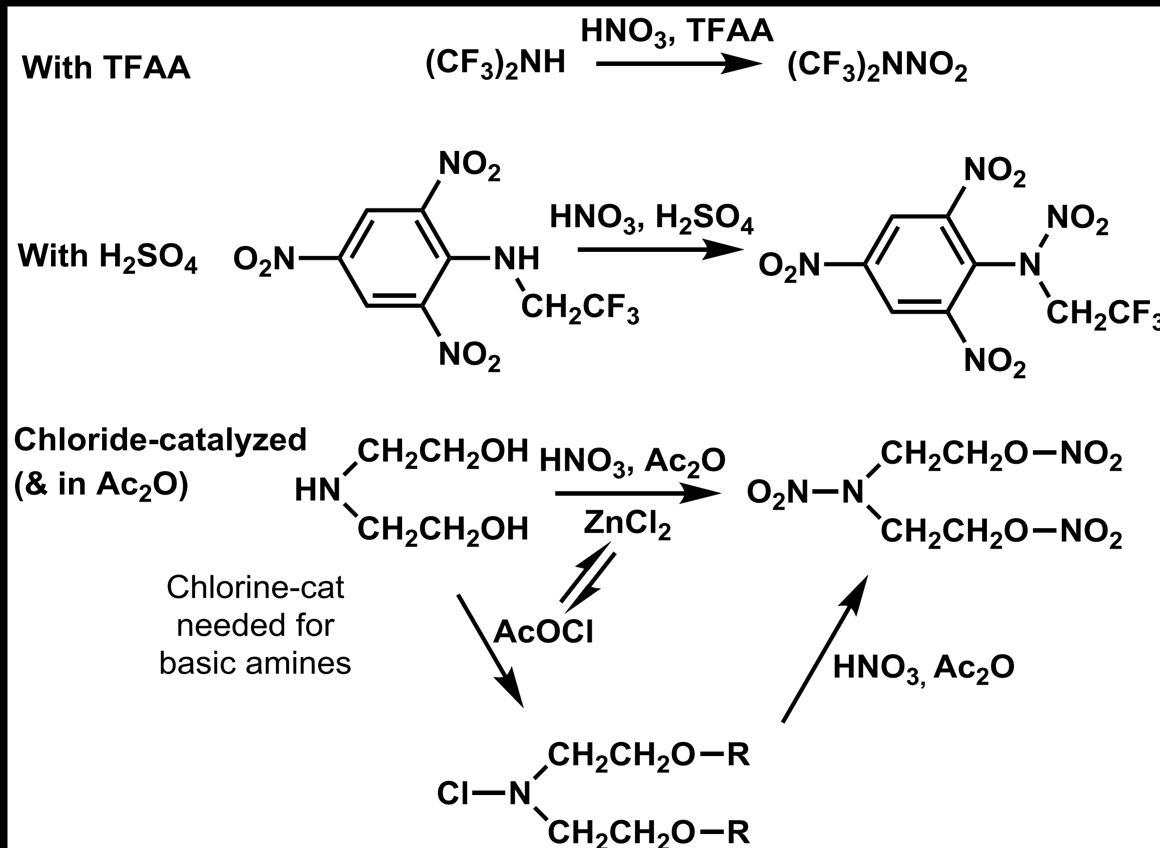
N-Nitro Compounds

Acidic nitration



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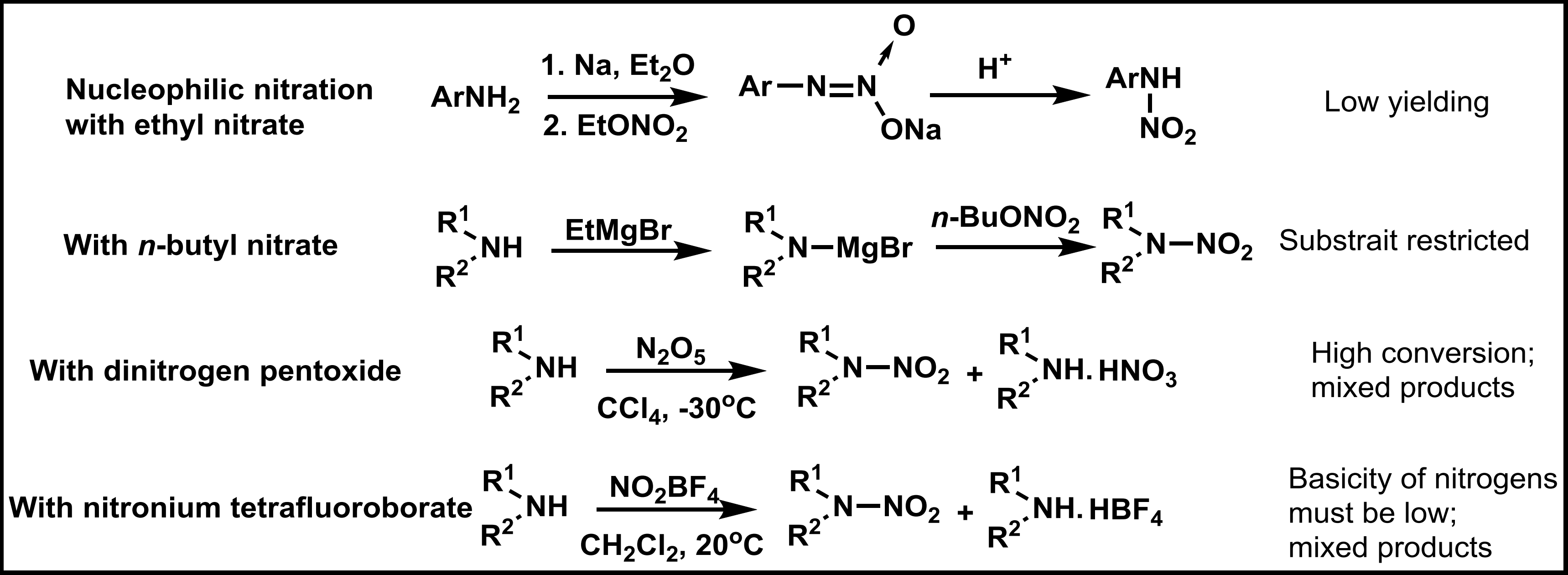
N-Nitro Compounds

Nonacidic nitration: Allows for nitration of primary & secondary amines



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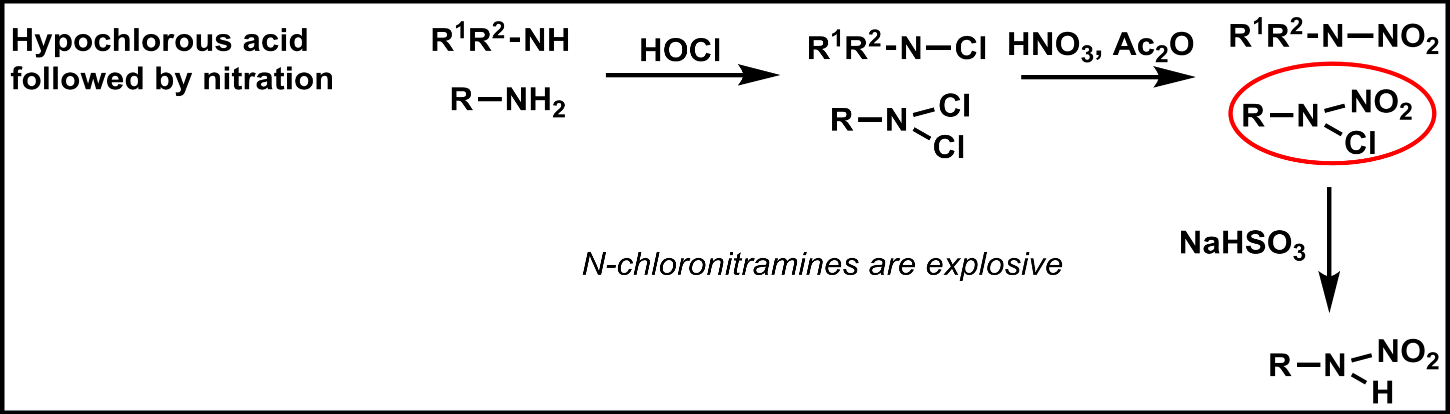
N-Nitro Compounds

Nitration of chloroamines



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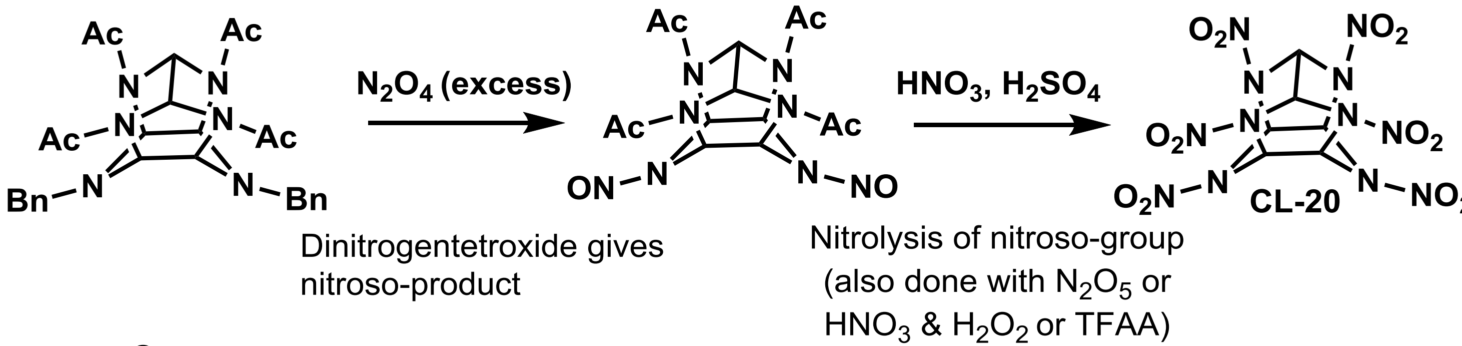
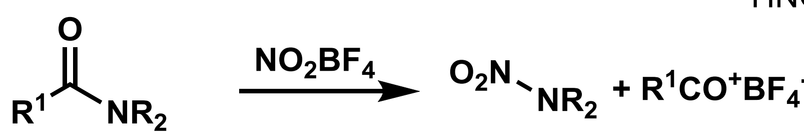
N-Nitro Compounds

Nitration via nitrolysis

Nitrolysis with acidic reagents

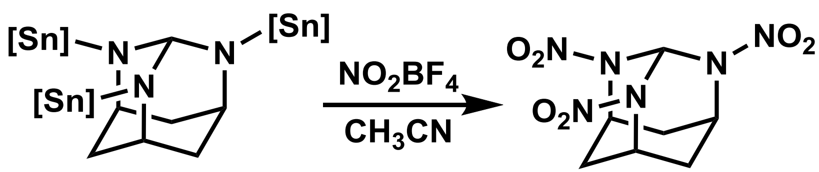


Nitrolysis with nonacidic reagents



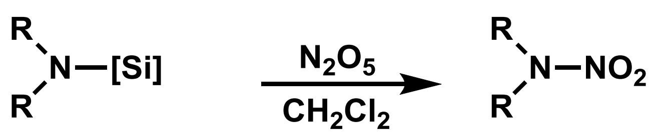
Nitronium salts give high yield, but products are limited in scope

Nitrolysis on stannylamines



High yielding, but produce toxic products

Nitrolysis on silylamines



High yielding and clean, but difficult precursors

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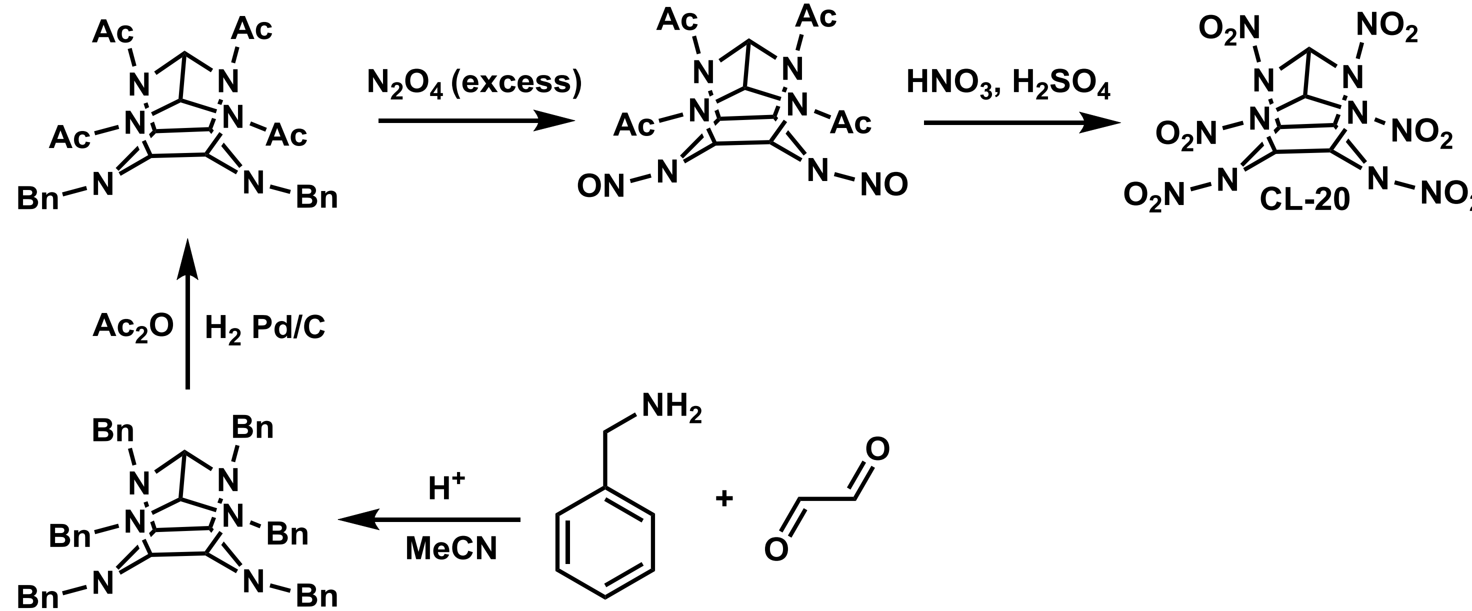
N-Nitro Compounds

Nitration via nitrolysis

Nitrolysis with acidic reagents



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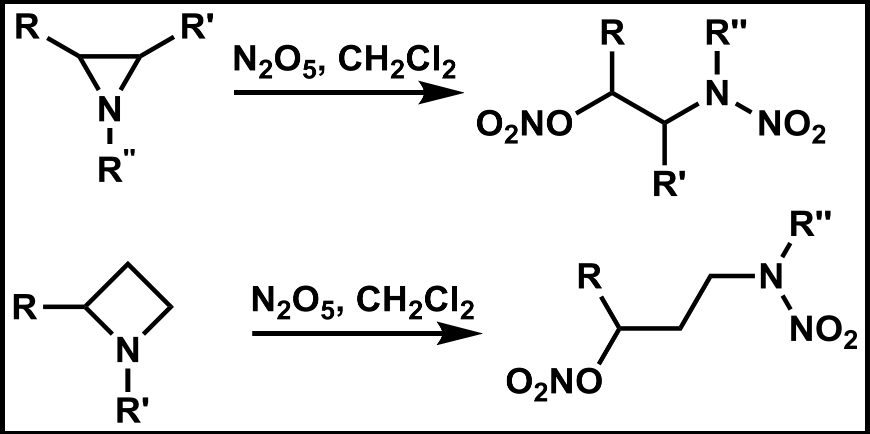
N-Nitro Compounds

Nitration through ring-opening



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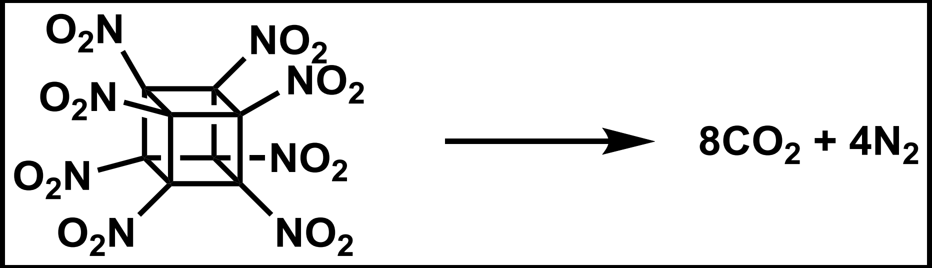
Octonitrocubane

Type	Abbreviation	D. Vel. (m/s)	Density (g/cm²)	R.E.
C-nitro (Ali)	ONC	10,100	2.00	2.38
N-nitro (Ali)	CL-20	9,500	2.04	1.80
N-nitro (Ali)	HMX	9,400	1.91	1.70
N-nitro (Ali)	RDX	8,750	1.76	1.60
C-nitro (Ar)	TNT	6,900	1.60	1.00



Volume expansion: 1150 fold @ STP
Energy release: 7.5 kJ/g

Low shock and friction sensitivity
However, more valuable gram per gram than gold

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Eaton, P.E., et al. *Angew. Chem Int. Ed.*, 401-404, 39, 2 (2000)

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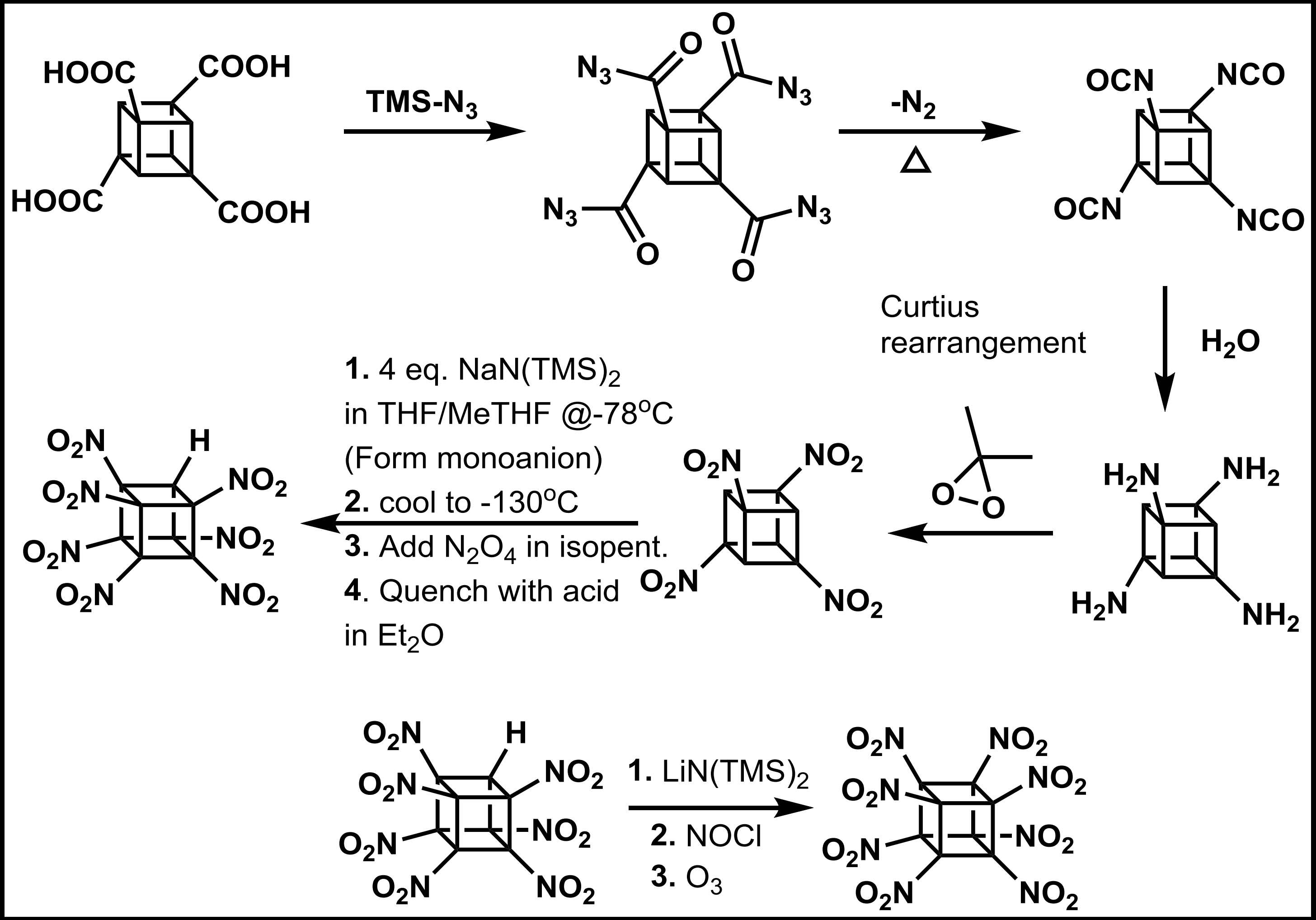
Octonitrocubane



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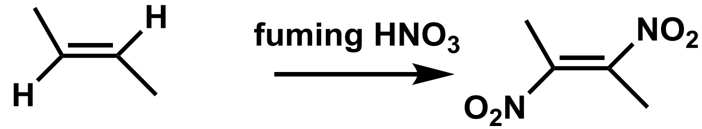
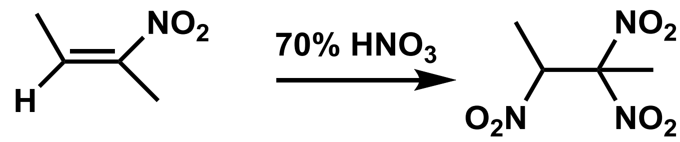
C-Nitro Compounds

Addition to unsaturated bonds

With nitric acid

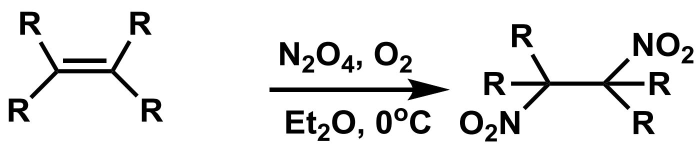


Low yielding



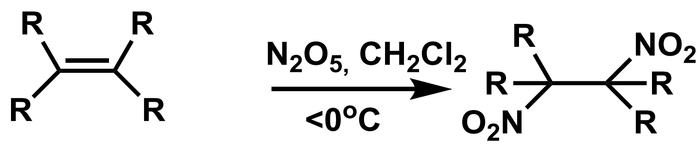
Low yielding; mixture of products

With dinitrogen tetroxide



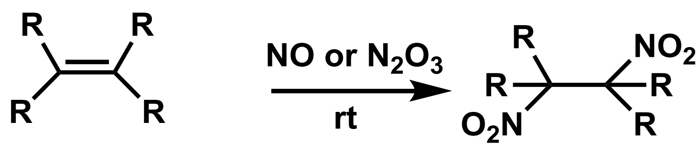
High yielding for e-deficient olefins but often provides nitro/nitrite mixtures

With dinitrogen pentoxide



Broadly high yielding but gives nitro/nitroso or nitro/ester mixtures

With nitrous oxide or dinitrogen trioxide



Moderate yield giving nitro/nitroso mixtures; excess can push to dinitro

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Eaton, P.E., et al. *Angew. Chem Int. Ed.,* 401-404, 39, 2 (2000)

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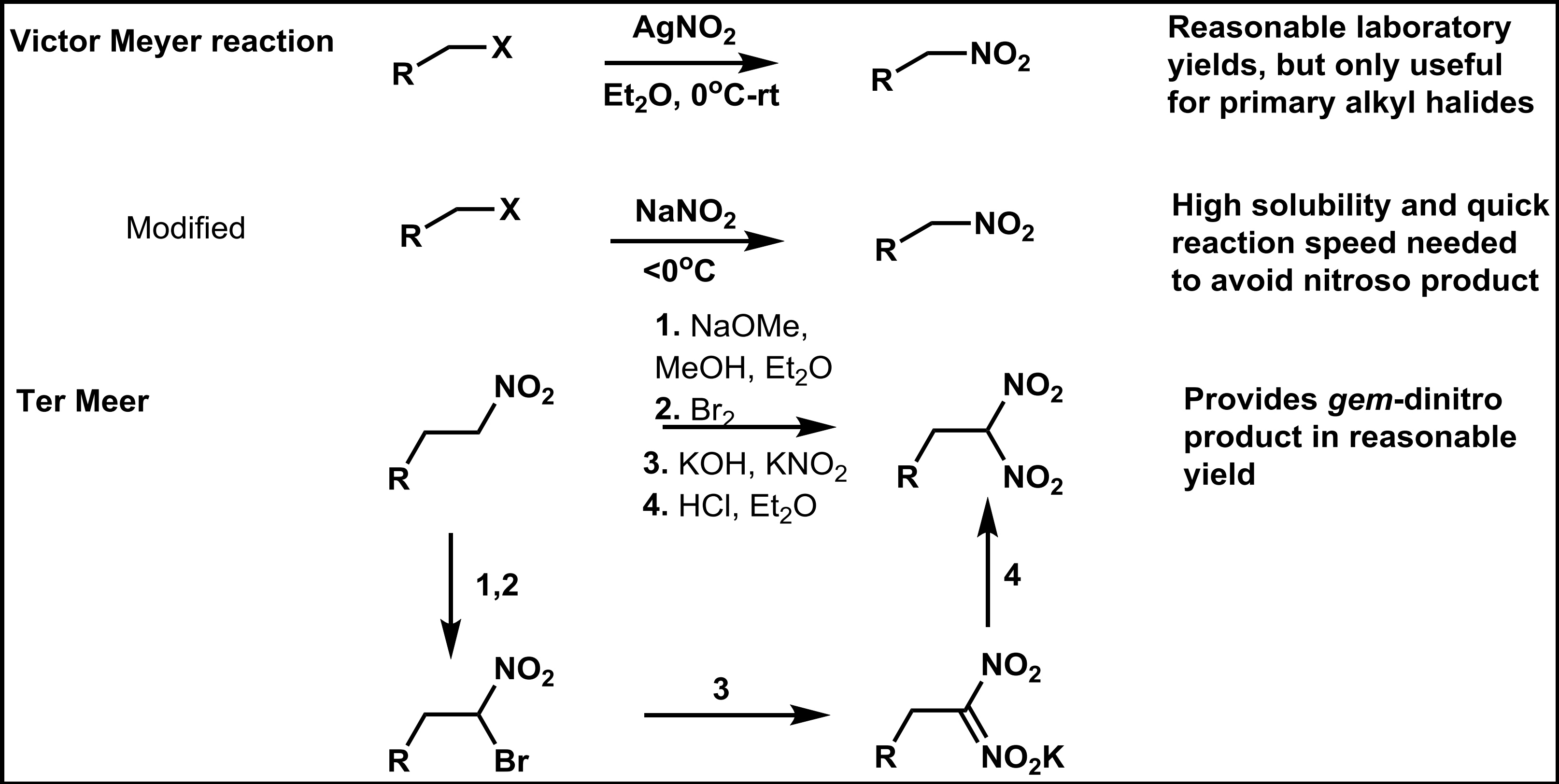
C-Nitro Compounds

Halide displacement



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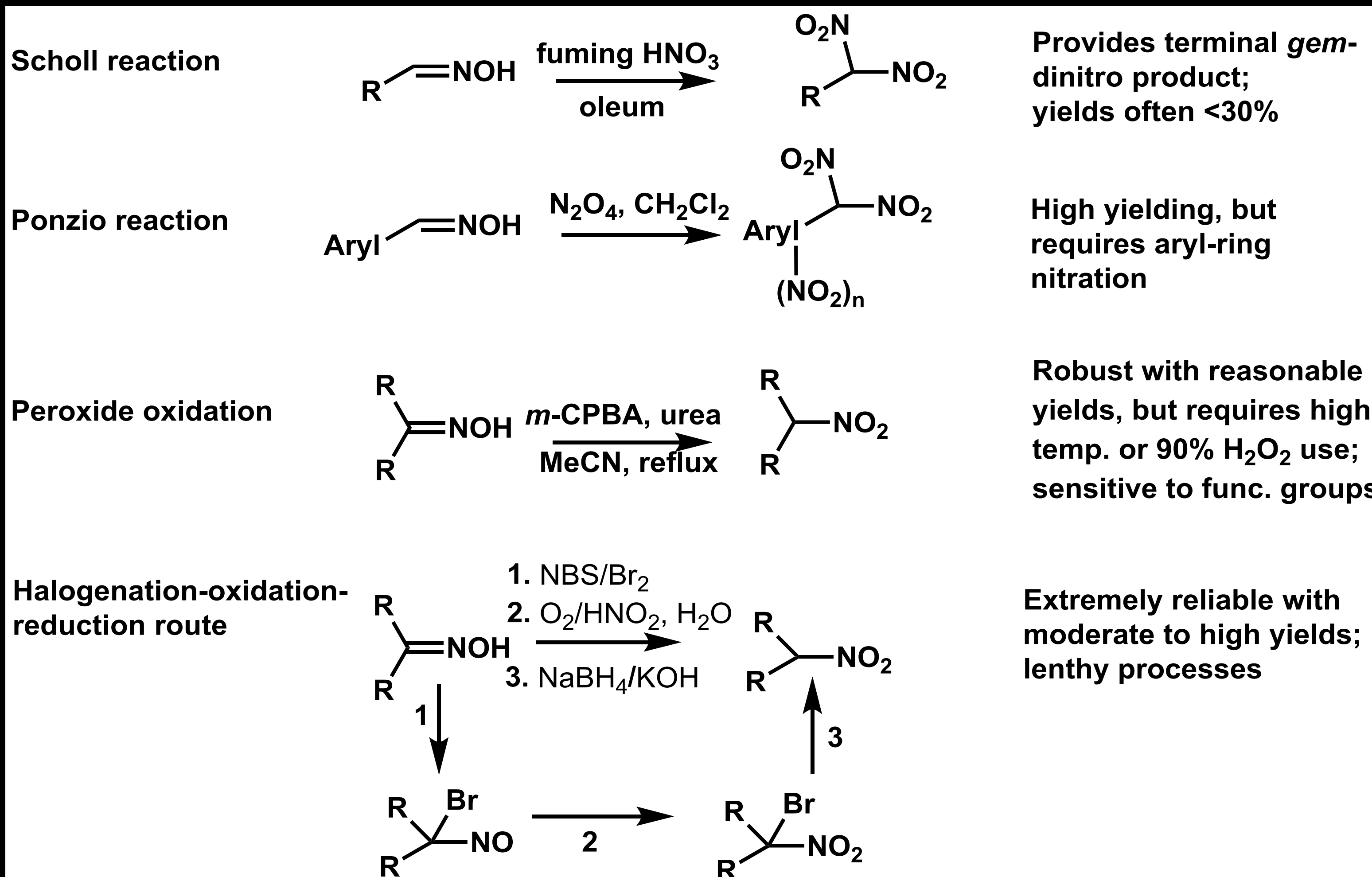
C-Nitro Compounds

Oxidation of oximes



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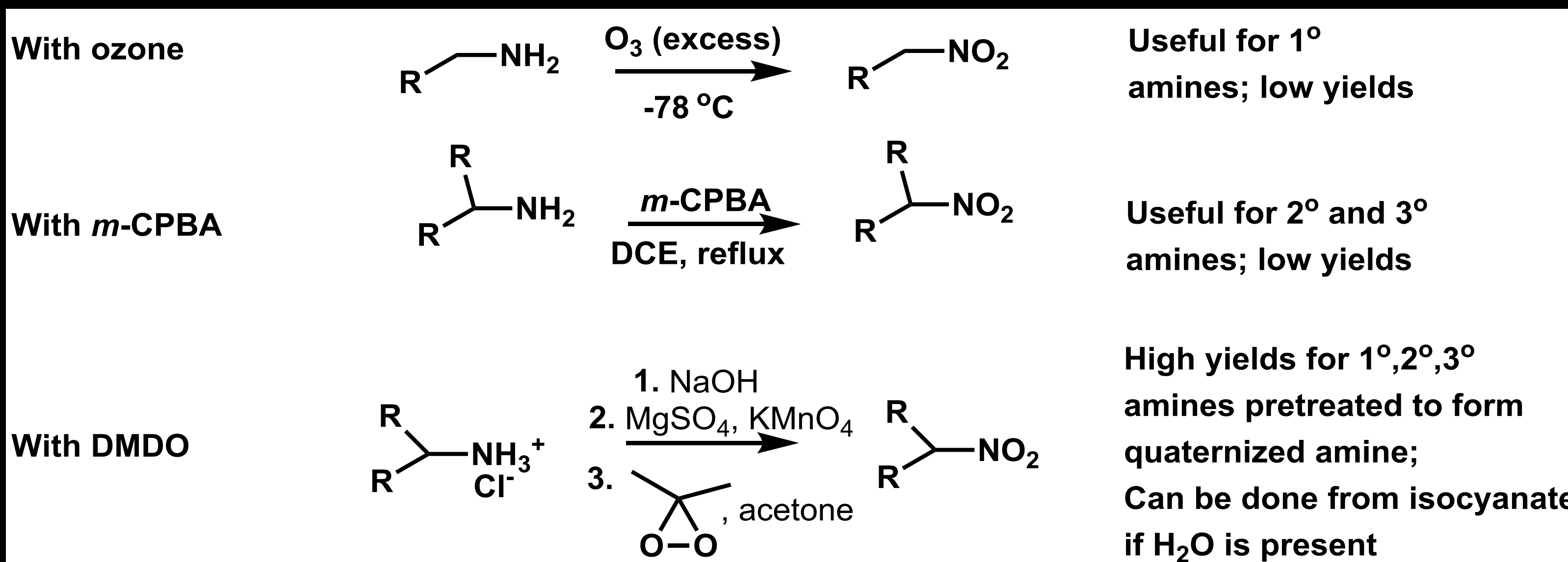
C-Nitro Compounds

Oxidation of amines



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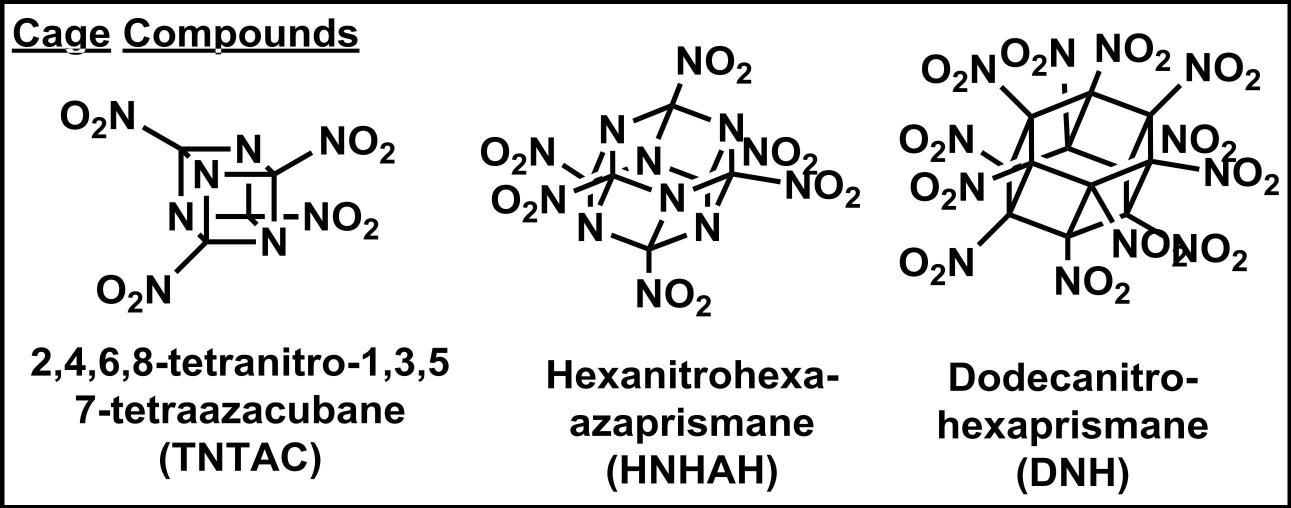
Cage Compounds

1) Oxygen balance of <u>zero</u> (no water)
2) Extremely persistent
3) High symmetry
4) Very powerful (strain)



Difficult to develop routes on a large scale for products that exceed the performance of CL-20, HMX, or RDX.

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Eaton, P.E., et al. *Angew. Chem Int. Ed.*, 401-404, 39, 2 (2000)

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New High Explosives

P: Detonation pressure (Kpa)
D: Detonation velocity (km/s)
N: Moles of gas released (mol/g)
M: Average MW of gas (g/mol)
Q: Energy of explosion (Joules)
p: Density of crystalline solid (g/cm^3)

$$D=1.01(N\text{x}M^{1/2}\text{x}Q^{1/2})^{1/2}\,(1+1.30p)$$

$$P=1.558p^2N\text{x}M^{1/2}\text{x}Q^{1/2}$$

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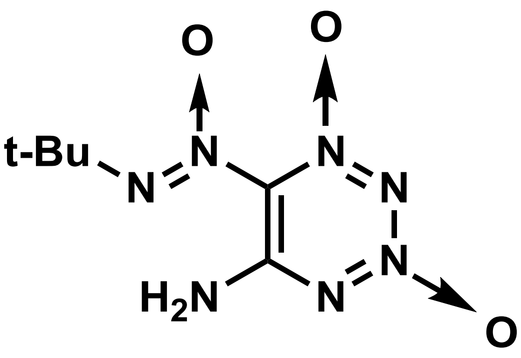
New High Explosives

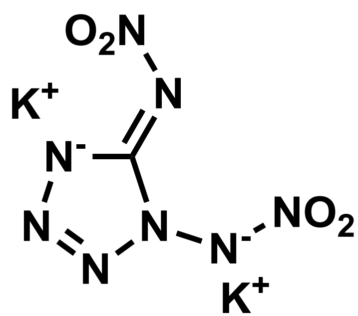
Some non-cage compounds being explored

- Still hard to beat HMX or RDX
- Often have long syntheses
- Provide an alternative route away from complex cages



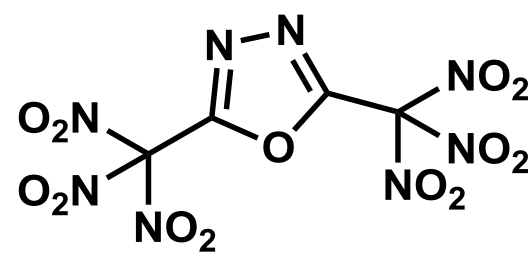
10 steps
~HMX

Tartakovsky, V. A.
DOI: 10.1002/anie.201605611



Very sensitive!
V_{det}=10,011 ms^{-1}

Fischer D.
DOI: 10.1002/anie.201502919



More sensitive than RDX or HMX

Yu Q.
10.1021/jacs.7b05158

Thank you!

Useful resources

Books:

- *Organic Chemistry of Explosives*. Agrawal J.P & Hodgson R.D. (2007)
- *Chemistry of High-Energy Materials*. Klapotke T.M. (2012)
- *The Chemistry of Explosives.* Akhavan J. (2004)
- *The Big Bang: A History of Explosives*. Brown G.I. (1998)
- *Explosives*. Meyer R. (1977)
- *The Science of High Explosives*. Cook M.A. (1958)
- *LASL Explosive Property Data*. Gibbs T.R. & Popolato A. (1980)
- *Gunpowder.* Kelly J. (2004)
- *Design Considerations for Toxic and Explosive Facilities.* Doemeny & Scott (1987)
- *The Chemistry of Powder & Explosives.* Davis T.L. (1943)
- *Gunpowder as the Fourth Power, East and West*. Needham J. (1983)

Papers:

- Eaton, P.E. et al. *Angew. Chem. Int. Ed., 401-404, 39, 2 (2000)*
- Eaton, P.E. et al. *Advanced Materials, 12, 1143-8* (2000)
- Wang, F. et al. *J Phys. Chem. A., 115, 11788-11795* (2011)
- Qiong, W., et al. *RSC Advances, 4, 3789-3797* (2014)