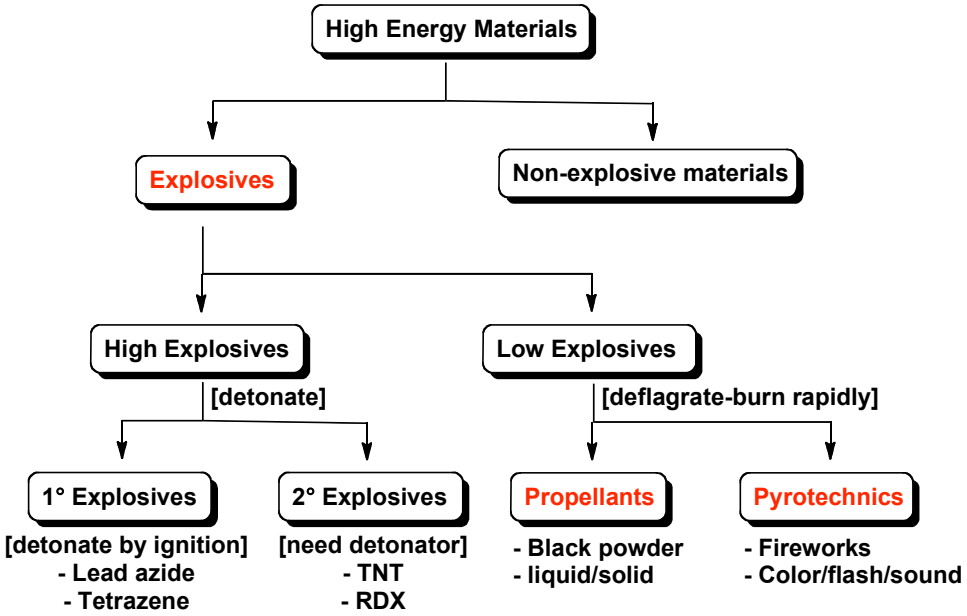
R.A. Rodriguez

Chemistry of High Energy Materials

Baran GM
2012-08-18



Organic Chemistry of Explosives by J.P. Agrawal and R.D. Hodgson

Prof. Thomas Klapotke - Ludwig-Maximilians-Universität München - Germany
Chair of inorganic chemistry

Dr. Michael A. Hiskey - Los Alamos National Laboratory

What makes an explosion?

Exothermic chemical reaction comprised of an oxidant and fuel, which releases energy (gas and heat) in a given time interval.

Whats the difference between explosive, propellants and pyrotechnics?

Rate at which it burns (Flamming gummy bear vs. rocket booster vs. TNT)
Speed of reaction will determine subsonic vs. supersonic blast pressure waves

History of Explosives

7th century A.D.- "Greek Fire" petroleum distillate used by Byzantines of Constantinopole

13th century - black powder (aka gunpowder) Chinese alchemists

18th century - black powder composition became standardized: KNO_3/charcoal/sulfur (75/15/10 w/w)

19th century - NH_4NO_3 replacement for KNO_3 in black powder

1846 - Italian Chemist Ascanio Sobrero invented nitroglycerin (NG)

1863 - German chemist Julius Wilbrand invented 2,4,6-trinitrotoluene (TNT) originally used as a yellow dye. Potential as an explosive not appreciated due to difficulty to detonate (insensative).

1866 - Mixing of NG with silica (PBX) to make malleable paste (dynamite)

late 19th century - nitration chemistry on common materials (resins,cotton, etc.)

1910 - military use of TNT for artillery shells and armour-piercing shells

1939-1945 - World War II - Research on explosives intesified (nitration chemistry) Developlment of cyclotrimethylenetrinitramine (RDX) and cyclotetramethylenetetranitramine (HMX).

Introduction to high energy materials terminology

Brisance: Shattering capabiliy of explosive. Measure of rate an explosive develops its maximum pressure.

Relative effectiveness factor (R.E. factor): Measurement of an explosive's power for military purposese. It is used to compare an explosive's effectiveness relative to TNT by weight (TNT equivalent/kg or TNTe/kg).

Detonation velocity (VoD): The velocity at which the shock wave front travels through a detonated explosive. Difficult to measure in practice so use gas theory to make prediction.

Specific impulse (I_{sp}): The force with respect to the amount of propellant used per unit time. Used to calculate propulsion performance.

Oxygen balance (OB%): Expression used to indicate degree to which explosive can be oxidized. If explosive contains just enough oxygen to form carbon dioxide from carbon, water from hydrogen molecules and all metal oxides from metals with no excess, the explosive is said to have zero oxygen balance.

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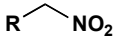
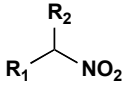
Chemical types/class of organic explosives

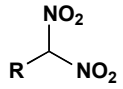
Aliphatic *C*-nitro compounds



1° nitroalkane

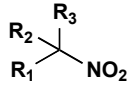


2° nitroalkane

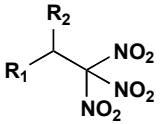


Terminal *gem*-dinitroalkane

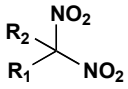
acidic protons (condensation chemistry)



3° nitroalkane



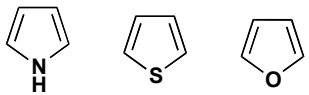
Trinitromethyl

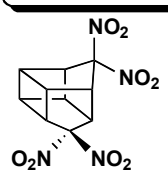


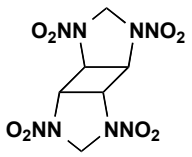
Internal *gem*-dinitroalkane

high explosive with high thermal and chemical stability

heterocycles

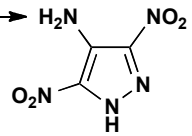




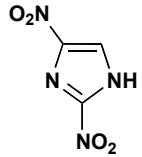


Nitro derivatives of pyrroles, thiopenes, and furans are not practical explosives:
1. heat of formation offers no benefits over standard arylene hydrocarbons
2. during nitration, these heterocycles are much more prone to oxidation and acid cat. ring opening compared to arenes

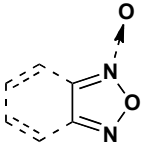
H-bonding reduction in sensativity



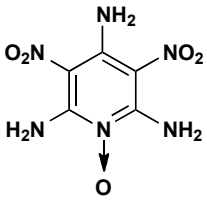
4-amino-3,5-dinitropyrazole (LLM-116)



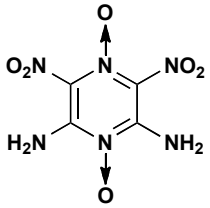
2,4-dinitroimidazole (2,4-DNI)



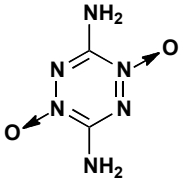
furazans/benzofurazans furoxans/benzofuroxans



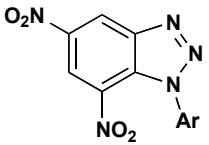
pyridine N-oxide



pyrazine N-oxide

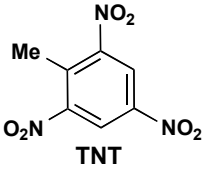


tetrazine N-oxide

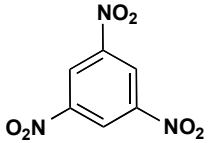


benzotriazoles

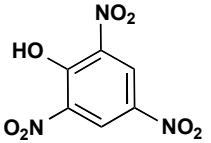
Aromatic *C*-nitro compounds



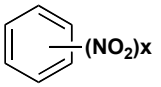
TNT



1,3,5-trinitrobenzene (TNB)

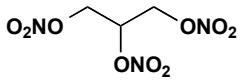


2,4,6-trinitrophenol (picric acid)

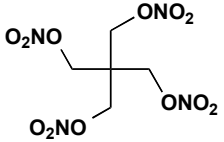


x ≥ 4
poor chemical stability

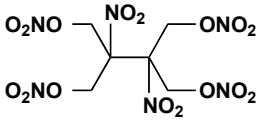
Aliphatic *O*-nitro compounds



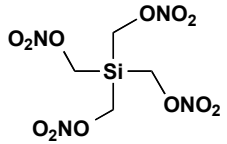
Nitroglycerin (VOD=7750 m/s)



Pentaerythritol tetranitrate (PETN) (VOD=8310 m/s)

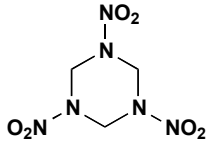


novel energetic nitrate eseter

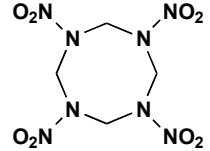


Si-PETN

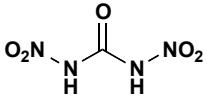
Aliphatic *N*-nitro compounds



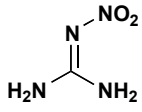
RDX (VOD=8440 m/s)



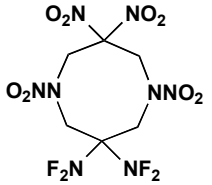
HMX (VOD=9110 m/s)



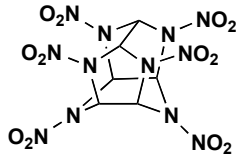
N,N'-dinitrourea (DNU)



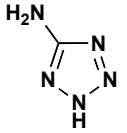
nitroguanadine



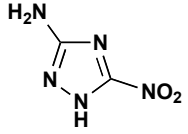
3,3-bis(difluoroamino) octahydro-1,5,7,7-tetranitro-1,5-diazocine (TNFX)



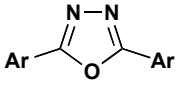
Hexanitrohexa-azaisowurtzitane (HNIW or CL-20) (VOD=9380 m/s)



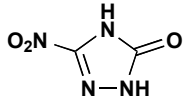
tetrazoles



1,2,4 triazoles



1,3,4-oxadiazoles



3-nitro-1,2,4-triazol-5-one (NTO)

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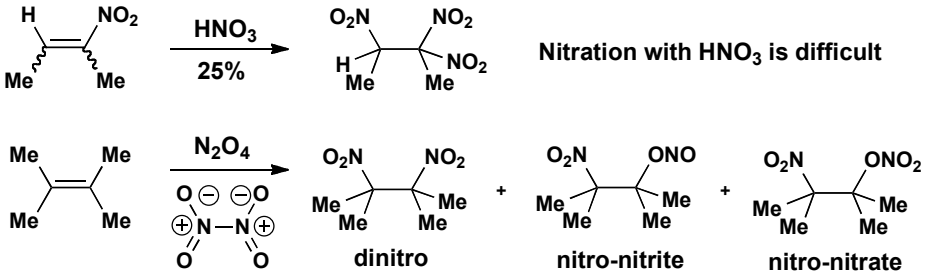
Nitration chemistry

The nitro gorup whether attached to aromatic or aliphatic carbon, is probably the most widely studied of the functional groups and this is in part attributed to its use as an 'explosophore' in many energetic materials.

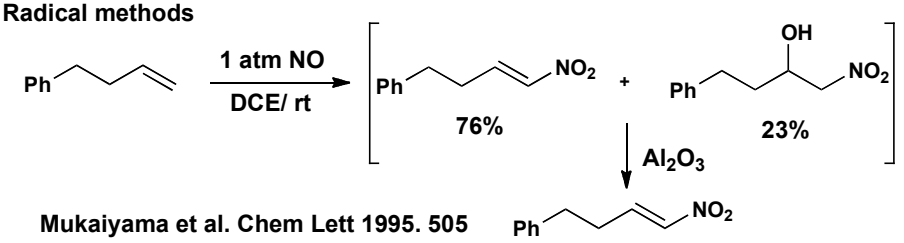
Borgardt et al. Chem Rev 1964. 64, 19 (polynitro functionality)

Routes to C-Nitro functionality

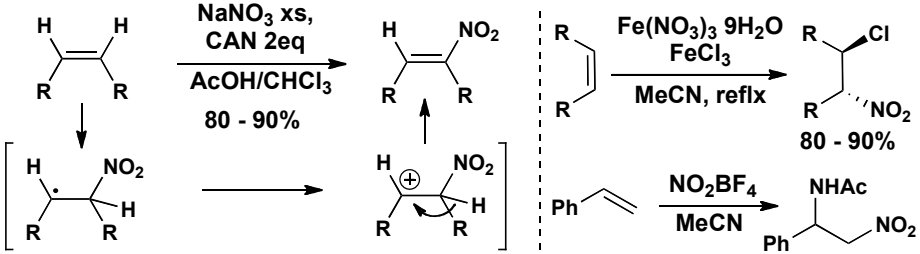
Direct nitration of aliphatic and alicyclic hydrocarbons possible in the vapor phase using HNO_3 or NO_2 (toxic redish-brown gas) at elevated temperatures.



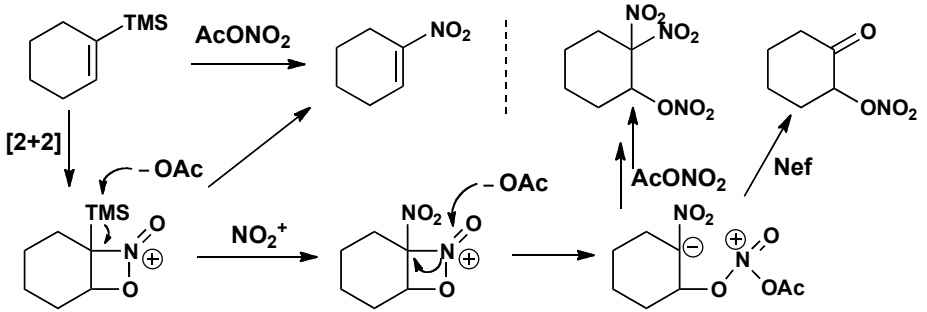
Radical methods



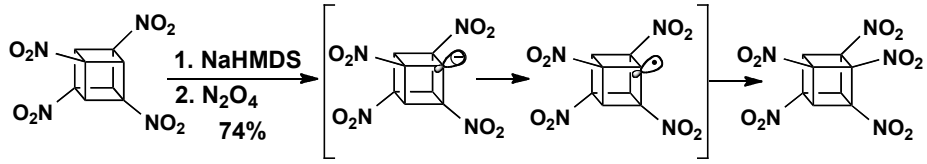
Mukaiyama et al. Chem Lett 1995. 505

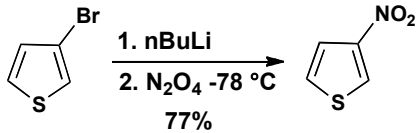


Hwu et al. J Chem Soc Chem Commun 1994. 1425
Taniguchi et al. JOC 2010. 75, 8126

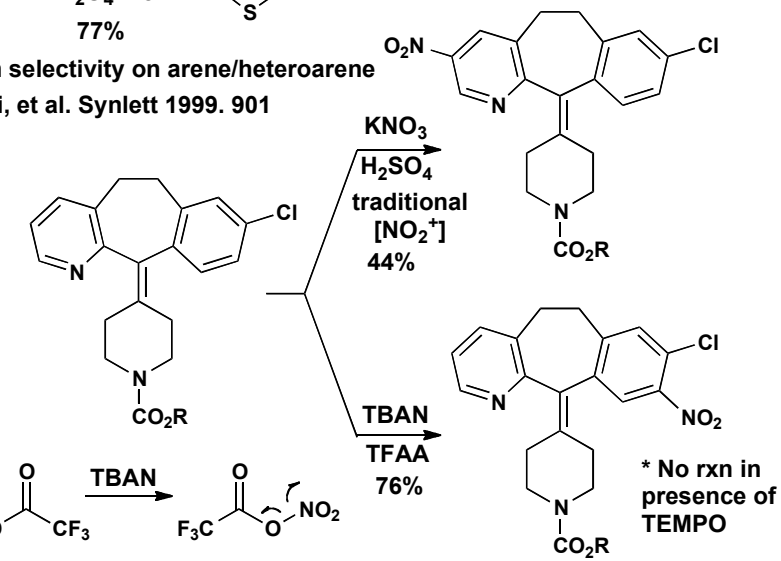


alkaline nitration





NItration selectivity on arene/heteroarene
Kakiuchi, et al. Synlett 1999. 901



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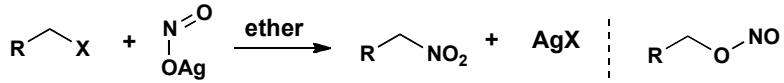
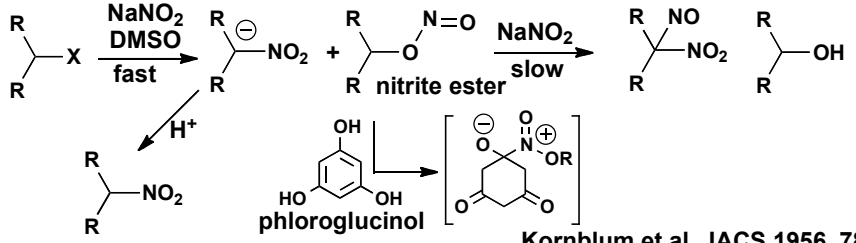
1° and 2° nitro compounds

Victor Meyer rxn
- **alkyl chlorides too slow**
- **only good for 1° (2° alkyl halide gives nitrate ester)**
- **nitrate ester arises from desproportionation of silver nitrate acc. by heat/light**

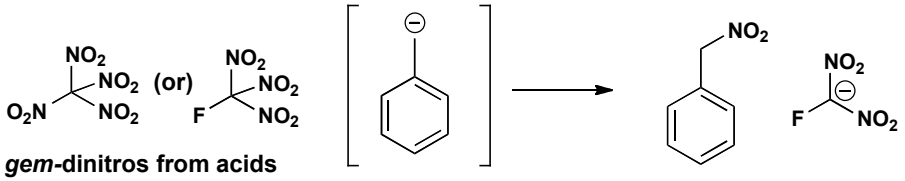


modified VM (alkali metal nitrites e.g. $NaNO_2$) time and solubility is VIMP

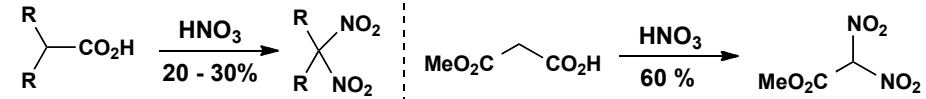


Kornblum et al. JACS 1956. 78, 1497

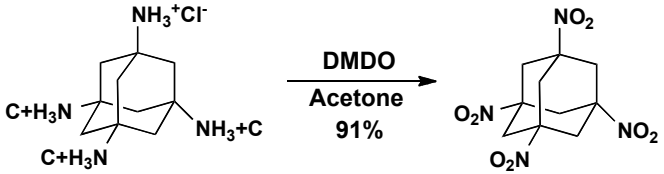
Fluorotrinitromethane



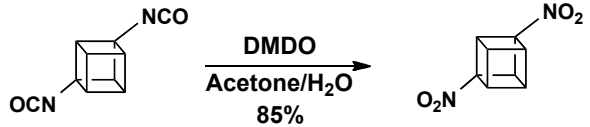
***gem*-dinitros from acids**



oxidation of amines

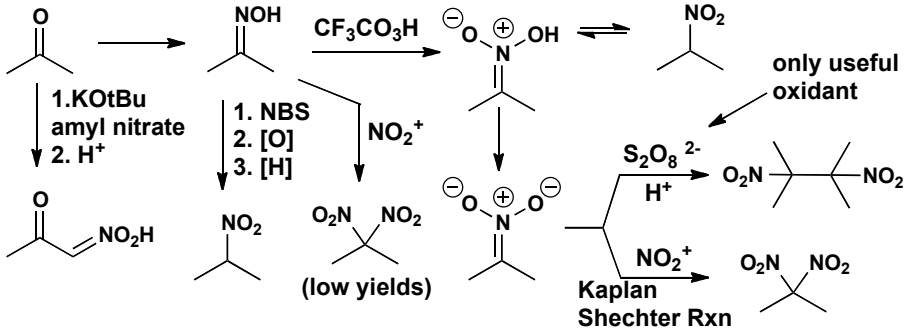


oxidation of isocyanates



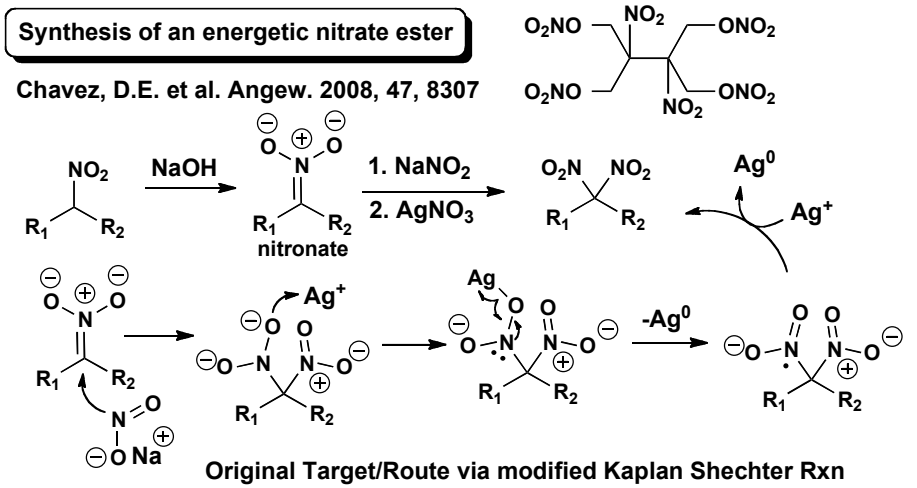
via amine thus H_2O essential

Eaton et al. JOC 1988. 5353

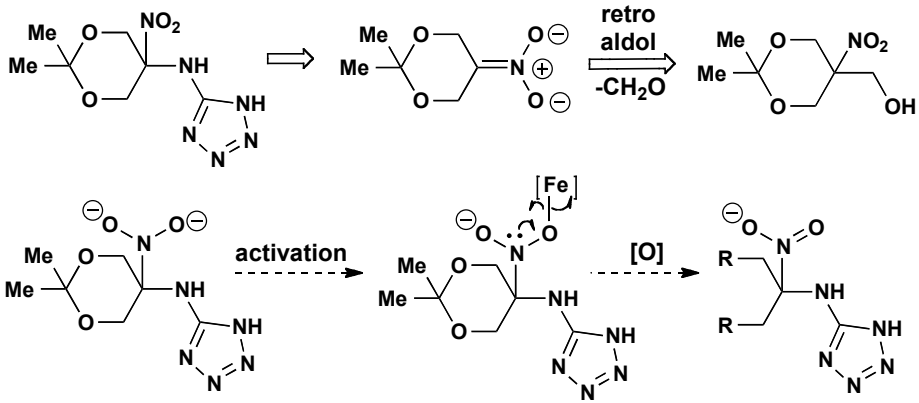


Synthesis of an energetic nitrate ester

Chavez, D.E. et al. Angew. 2008, 47, 8307



Original Target/Route via modified Kaplan Shechter Rxn



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Initial Results: homocoupled product

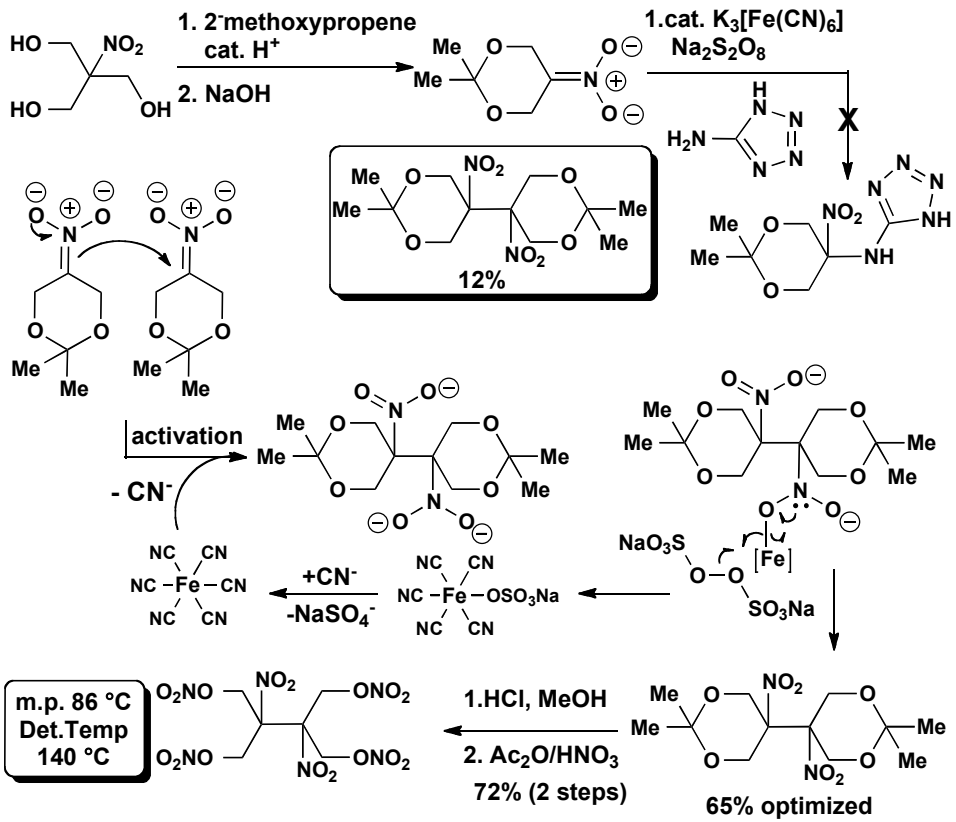


Table 1: Sensitivity properties of **1**.

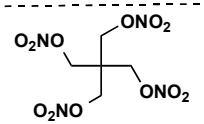
	Impact[a]	Spark[b]	Friction[c]	DSC[d]
1	2.7 J	0.625 J	74.5 N	140 °C
PETN	2.9 J	0.625 J	56.8 N	160 °C

[a] LANL type 12, 50% drop height, 2.5 kg. [b] ABL spark threshold initiation level (TIL). [c] 50% load Bruceton up/down method. [d] 10 °C

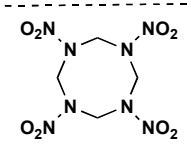
Table 2: Predicted performance properties of **1**.

	$V_{Det.}$ [km s^{-1}]	P_{CJ} [GPa]
1[a]	9.1 ← **20,164 MPH!!**	40
HMX[b]	9.1	39

[a] Cheetah 5.0 calculation. [b] Livermore Explosives Handbook.



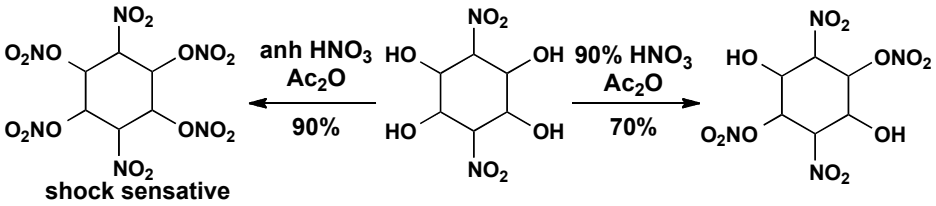
comparable stability to PETN



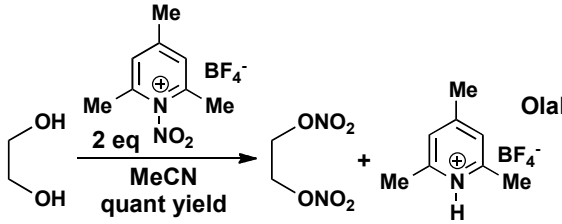
CHEETAH calculates as powerful as HMX

Routes to O-Nitro functionality

- Use of mixed acids (esterification) and nitrogen oxides described for C-Nitraion
Key points:
1. **fuming (anhydrous) HNO_3 prep: dry air bubbled through anhydrous HNO_3 to remove any oxides of nitrogen present, followed by addition of trace urea to remove any nitrous acid present. AKA "white nitric acid"**
2. **Urea destruction of nitrous acid important to avoid violent fume-off**
3. **O-nitrations with mixed acids of "white nitric acid" above ambient temperatures is dangerous and has increase risk of explosion**
4. **anhydrous HNO_3/Ac_2O- Acetyl nitrate is generally a weak nitrating agent but in the presence of a strong acid like HNO_3, ionization to nitronium ion occurs**



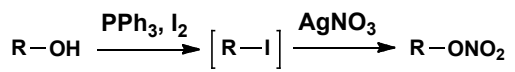
Transfer nitration (neutral conditions - good for acid sensative alcohols)



Olah G.A. et al JOC, 1965. 30, 3373

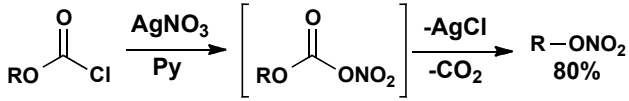
works for 1°, 2°, 3° alcohols

***in situ* halide displacement with $AgNO_3$**

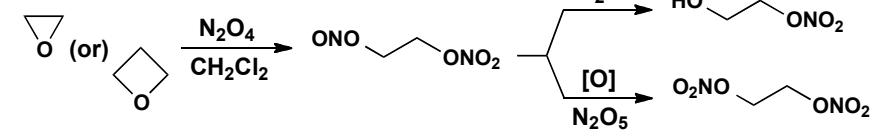


Low yields for 2°
$HgNO_3$ can be used for 2° and 3° alkyl halide displacements

decomposition of nitrocarbonates (very mild, rt or reflux MeCN)



ring opening of strained oxygen heterocycles



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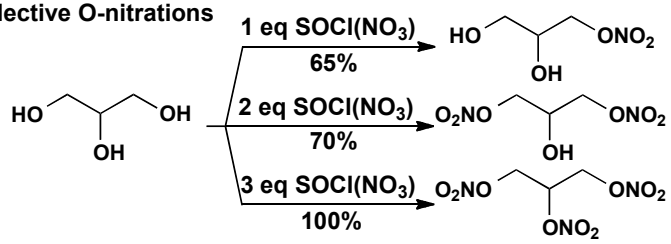
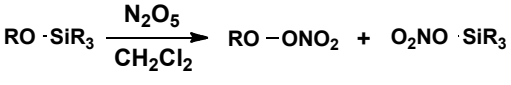
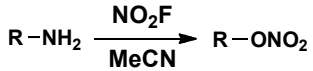
selective O-nitrations



nitrodesilylation



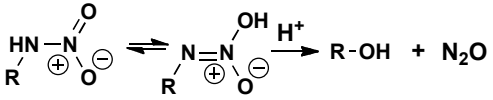
deamination



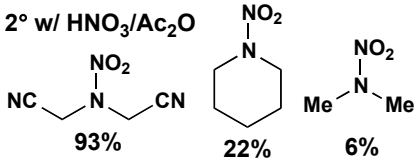
Routes to N-Nitro functionality

- Compounds resulting from nitration of nitrogen are of far less use for mainstream organic synthesis. However the N-NO_2 group is an important 'explosophore' and is present in many enrgetic materials

- Direct nitration of a 1° amine to a nitramine using HNO_3/mixed acids is not possible due to instability of the tautomeric isonitramine in strongly acidic conditions. 2° amines are more stable and can undergo electrophilic nitration using HNO_3/Ac_2O



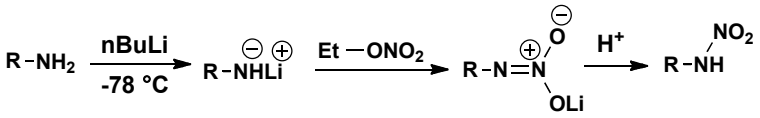
2° w/ HNO_3/Ac_2O

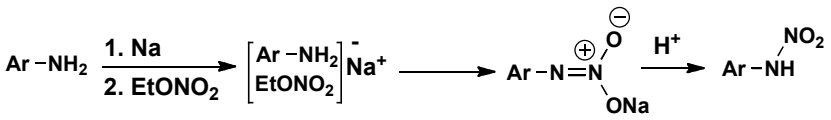


anilines - must contain one or more nitro groups on the aromatic ring

How to get around this problem??
- synthesis via condensation chemistry (Mannich, 1,4 addition, etc)

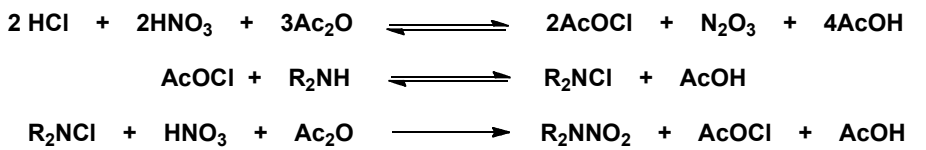
What about if need more direct method??
-non-acidic nitrating reagents (nucleophilic nitration)



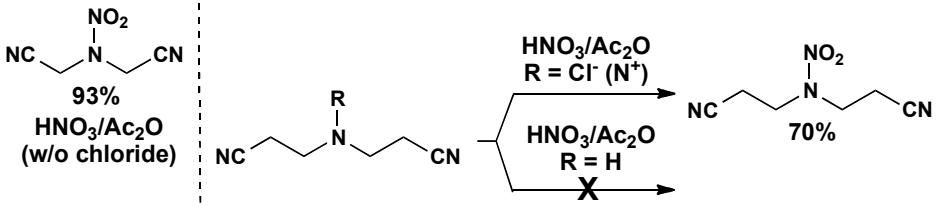


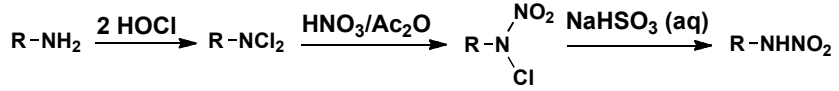
-chloride ion catalysis

anhydrous $ZnCl_2$, hydrochloride salt of amine, or dissolved HCl(g) can serve as a source of electropositive chloride under the oxidizing conditions of nitration



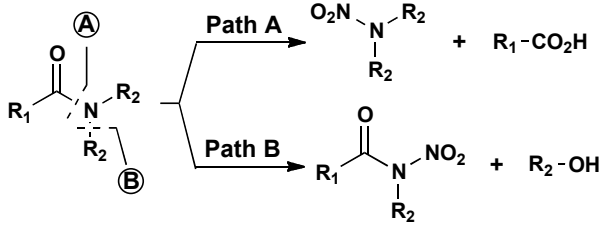
Wright et al. Can. J. Res. 1948. 26B, 294



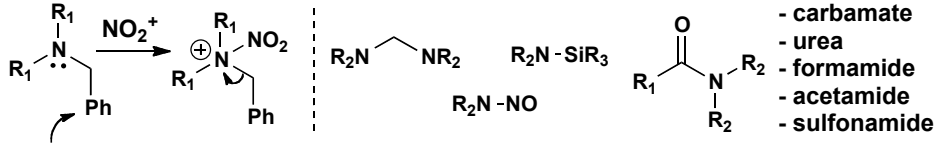


- Nitrolysis of fully substituted nitrogen

rupture of C–N bond leading to formation on N–NO_2



Nitramine formation via nitrolysis possible from:



Ease of alkyl nitrolysis depends on stability of the resulting cation: benzyl, tertiary (t-Bu), etc...

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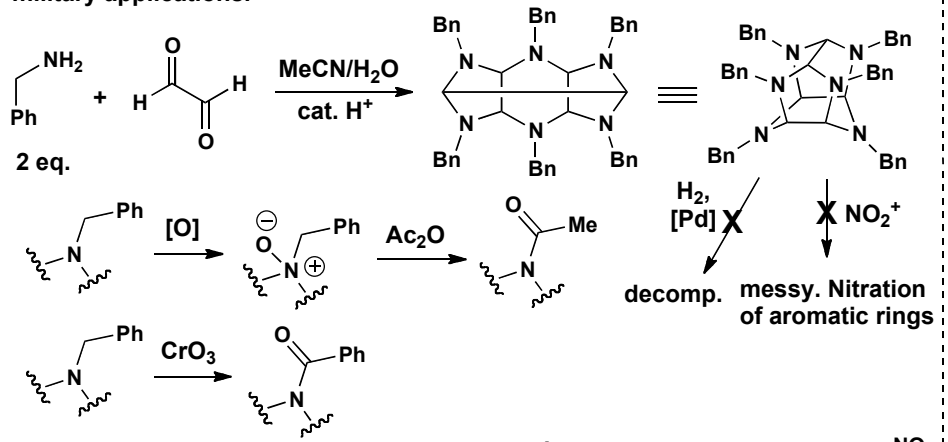
Synthesis of Hexanitrohexaazaisowurtzitane (HNIW)

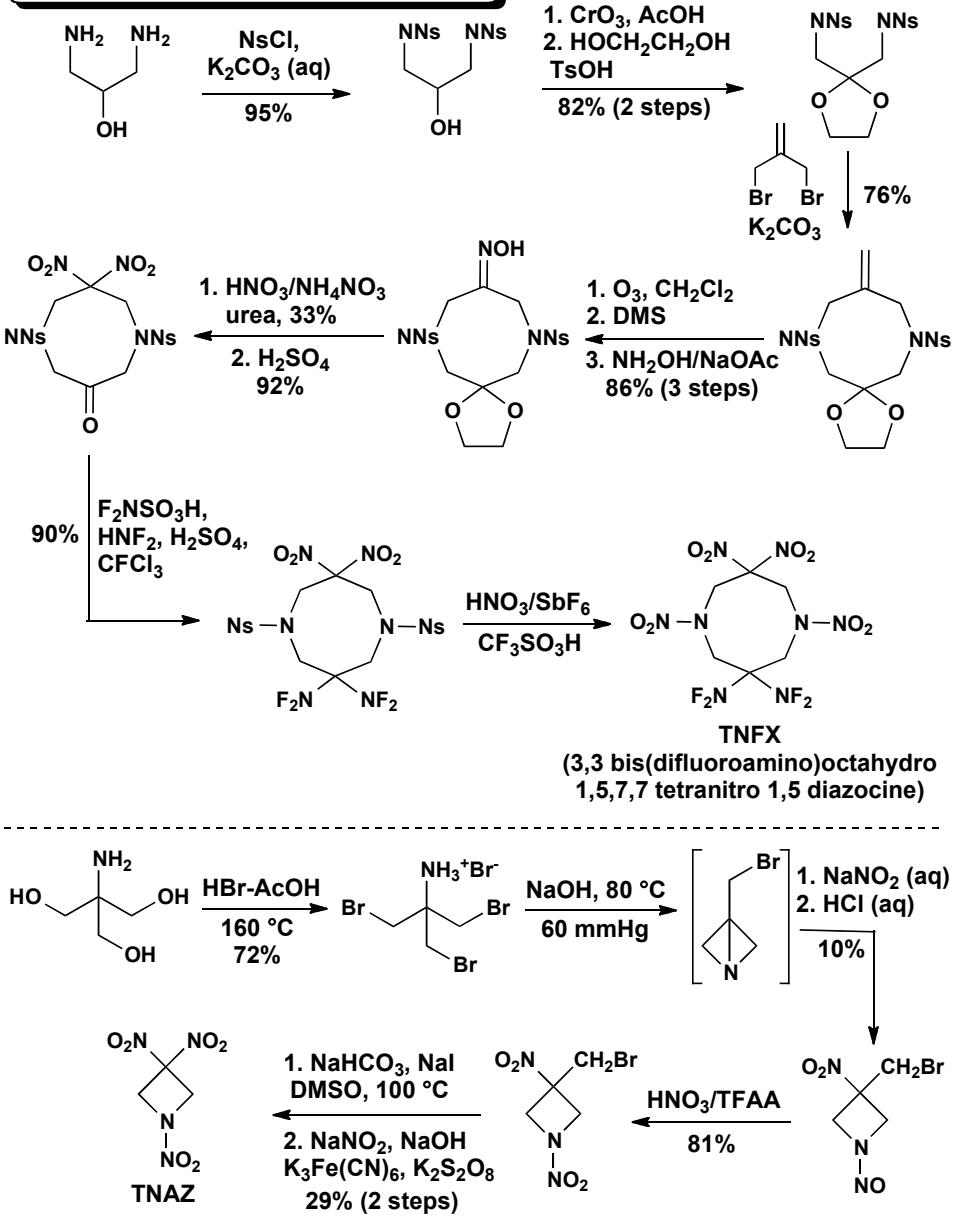
- Many nitramines are more powerful than aromatic C-nitro compounds and have high brisance and high chemical stability and low sensativity to impact and friction compared to nitrate ester explosives. This is why they are of interest to military applications.



HNIW aka CL-20

- explosive/propellant (low smoke-emission)
- most powerful to date (better oxidizer-to-fuel than RDX/HMX)
- first prep by Nielsen 1987 Naval Air Warefare
- pilot plant in 1990 for 200 kg in China Lake facility
- unmatched performance in specific impulse, burn rate, detonation velocity (9.38 km/s = 21,000 MPH!!)
- highest density than any other explosive (d = 2.044 g/cm^3)
- thermally stable (250 -260 °C) but sensative to mechanical stress still greater stability than nitrocellulose, PETN and others.
- 4 different polymprphs with different densities/properties

Syntheses of some nitramine explosives



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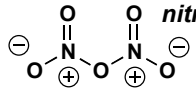
N_2O_5 No single nitrating agent is as diverse and versatile
It is considered as the future for energetic materials synthesis

non-acidic nitrating reagents (neutral)

1° amines/nitramines leads to deamination and formation of nitrate ester by-product but analines are successful.

N_2O_5 ≡  ⇌ $[NO_2^+][NO_3^-]$ *nitronium nitrate* salt

- adopts two structures depending on condition

sublime slightly above rt	polar
condition: chlorinated solvents	condition: anhyd. HNO_3
- clean and selective	- powerful but acidic and non-selective
- non-oxidizing &n non-acidic	

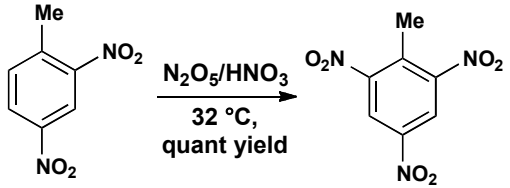
- 1st prepared over 150 years ago but due to difficult prep and low thermal stability (require -60 °C long term storage) received little attention.
- Environmental restrictions and push for green chemistry sparked interest

Advantage: ***Rxns are very clean***

- faster and less exothermic (due to absence of oxidation byproducts)
- high yields
- simple isolation
- non-acidic conditions possible with this reagent (compared to mixed acids)

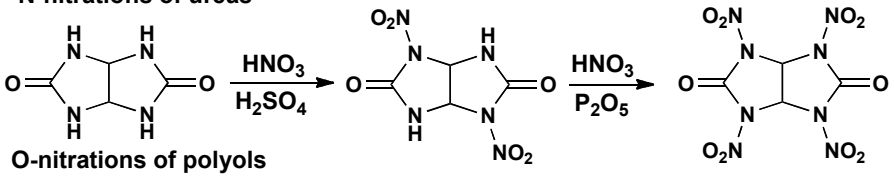
$N_2O_5 \xrightarrow{rt} 2\ N_2O_4 + O_2$ Stable for 2 weeks at -20 °C; Stable for up to 1 yr at -60 °C

synthesis of TNT under mild conditions

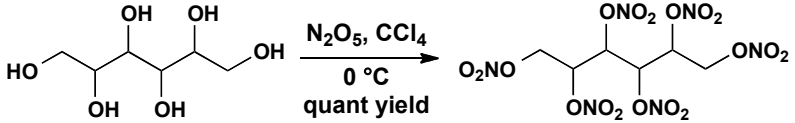


No explosion hazard

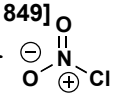
N-nitrations of ureas



O-nitrations of polyols



Preparation of N_2O_5 [Deville 1849]

$AgNO_3 + Cl_2\ (g) \longrightarrow$  $+ AgNO_3 \longrightarrow N_2O_5$

Dehydration of nitric acid

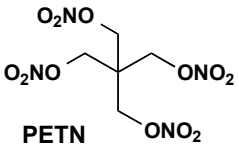
$HNO_3 + P_2O_5 \longrightarrow N_2O_5 + H_3PO_4$

$N_2O_5 \xrightarrow{\Delta} N_2O_4 \xrightarrow{O_3} N_2O_5$

- isolation by sublimation and collection trap at -78 °C
- stream of ozone needed to avoid collection on N_2O_4
- if don't care about acidity, can use HNO_3/P_2O_5 mixture directly (no ozone stream)

Process chemist at Defense and Evaluation Research Agency (DERA) in the UK
Development of a flow process: Using commercial ozonizer to generate 5 - 10% mix of ozone in oxygen and mixed in flow with N_2O_4. N_2O_5 is trapped in solid condenser tubes (cooled by dry ice/acetone).

Explosives in JACS: Sila explosives — Klapotke T.M. JACS 2007. 129, 6908

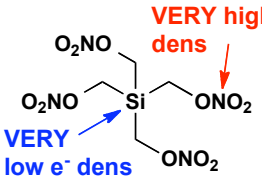


PETN

- Used in WW I
- One of most high energy explosives known
- more shock sensative than TNT. used as booster mix
- Europe marketed as lentonitrat (vasodilator) like NG

- Det. Velocity 8,400 m/s
- d= 1.7 g/cm^3

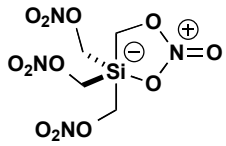
Silicon analogue of PETN



$\Rightarrow Si(CH_2OAc)_4 \Rightarrow Si(CH_2Cl)_4$

"The crystalline compound exploded on every occasion upon contact with Teflon spatula... Solutions in diethyl ether exploded upon the slighest evaporation of the solvent."

Why does Si-PETN have drastically increased sensativity?

Theoretical: electrostatic potential:

1. Surface electrostatic potential, in general, is related to the sensitivity of the bulk
2. The more evenly distributed the electrostatic potential is over the surface of a molecule, the more stable it is to impact.