Synthesis of New Energetic Melt-Pour Candidates

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Background

- TNT has been the backbone of melt-pour explosives for most of the 20th century.
  - Not IM enough for today's standards
- DNAN is:
  - quickly becoming the favored replacement for TNT due to its superior IM properties.
  - not very energetic and performance of DNAN-based explosives suffer as a result.
- Future melt-pour energetics need to have best of both worlds:
  - Superior IM properties
  - Good explosive performance

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Program Objectives

- Identify and Prepare New Melt Pour Ingredients with Inherent Comp B Performance
- Evaluate Candidates Using Small Scale Safety and Performance Testing
- Evaluate Scalability of Synthesis
- Evaluate Formulation Characteristics

Selection Criteria:

- Melting Point in Desired Range (80-120C)
- Sufficiently High Predicted Density
- Perceived Ease of Preparation

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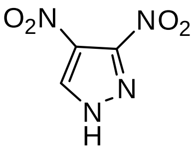
Candidates compounds

DNP
m.p. ~ 85°C
calc. dens. ~ 1.87 g/cm^3
energy out ~ 1961 cal/cm^3

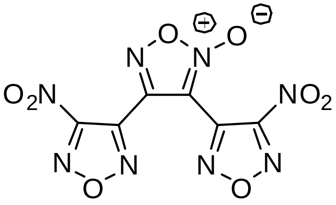
3 steps

MTNI
m.p. ~ 82°C
calc. dens. ~
energy out ~

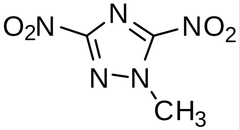
6 steps



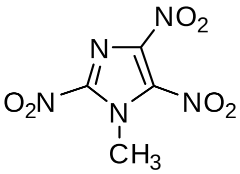
DNP



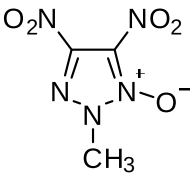
DNTF



DNMT



MTNI



DNMTO

DNMTO
m.p. ~ 130°C
calc. dens. ~
energy out ~

2 steps

DNTF
m.p. ~ 108 °C
calc. dens. ~ 1.95 g/cm^3
energy out ~ 2517 cal/cm^3

4 steps

DNMT
m.p. ~ 95 °C
calc. dens. ~ 2.10 g/cm^3
energy out ~ 1739 cal/cm^3

2 steps

Comp B energy out ~ 1837 cal/cm^3
LX-14 energy out ~ 2186 cal/cm^3

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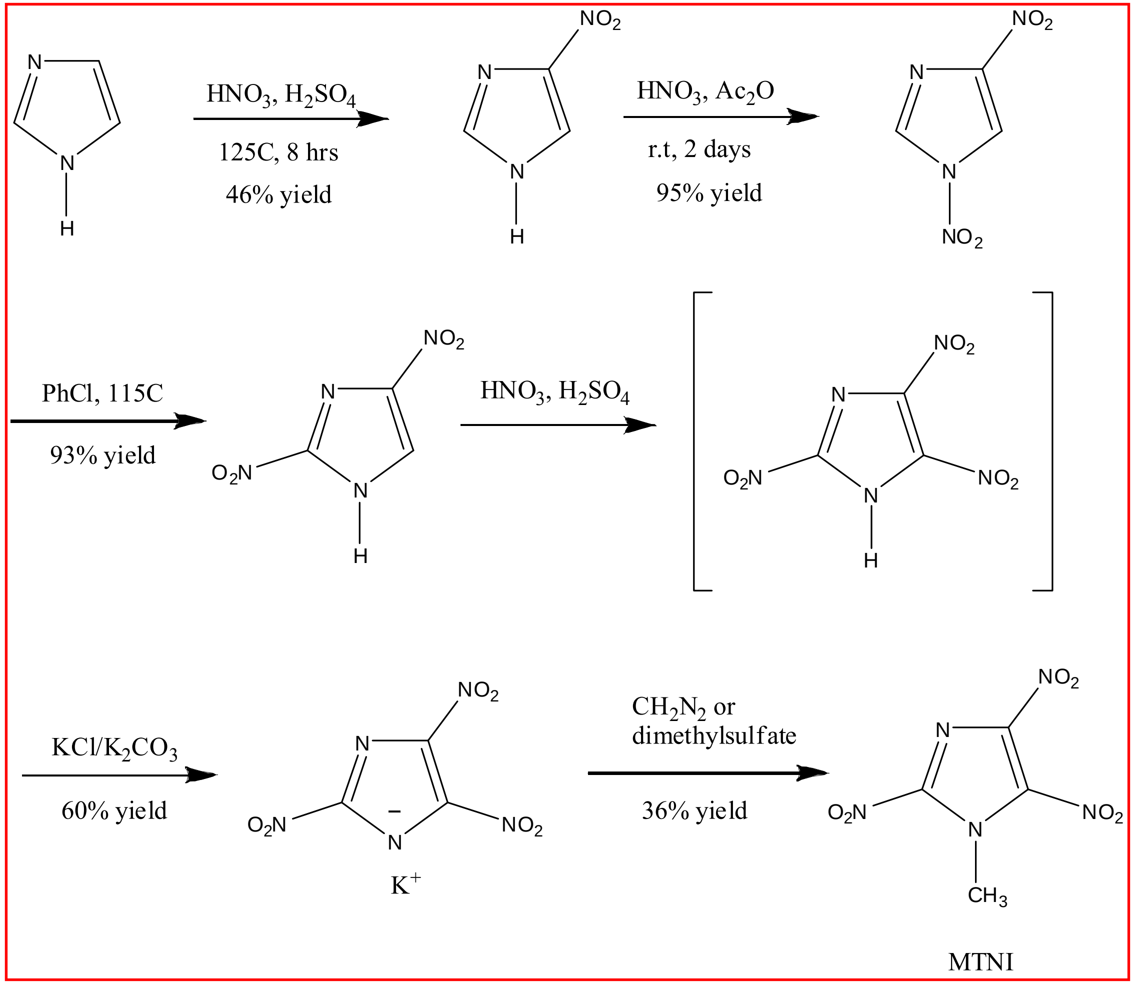
MTNI

- Original process:
  - Complicated (6 steps with methylation)
  - Low yielding (9% to 18%)
- Lots of effort on finding entirely new route to:
  - Avoid highly toxic chemicals
  - Minimize steps
  - Increase producibility
- Bottom line:
  - Didn't find a better way



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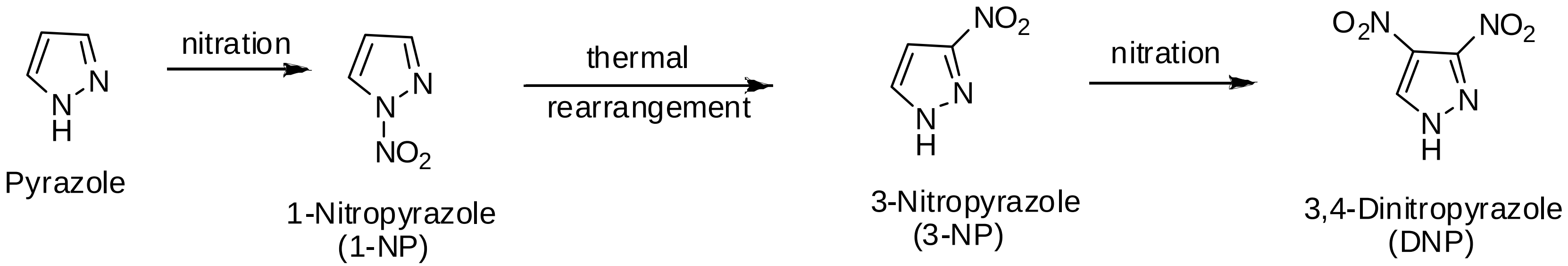
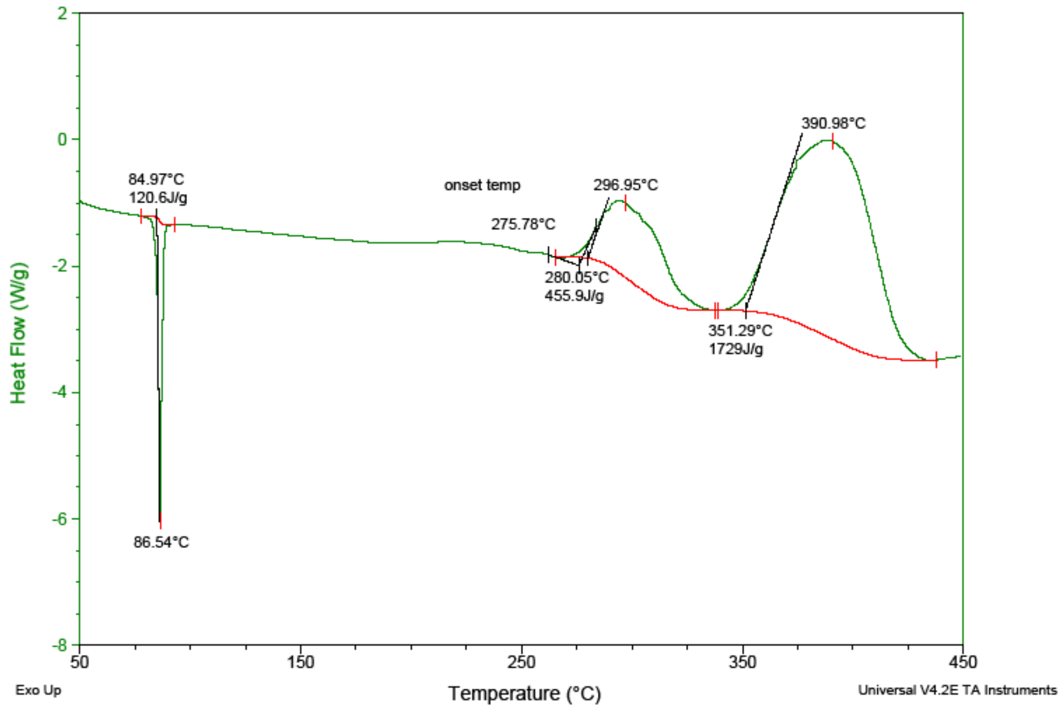
DNP



- Original process:
  - Used low concentration in thermal rearrangement
  - Used extraction in final work-up (not scale-up friendly)
  - Otherwise, not bad procedure



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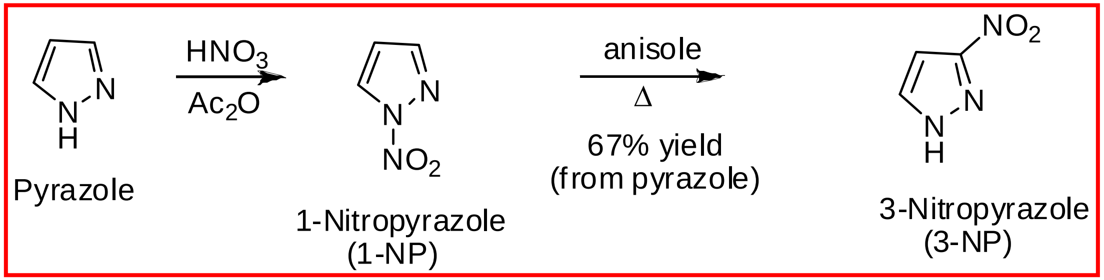
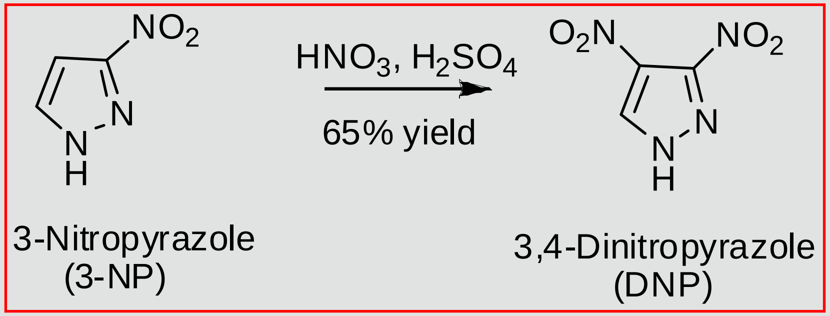
DNP Improvements





- Reduced H2SO4
  - Majority of DNP precipitates from solution
- Recrystallize with common inexpensive solvents
- 40% overall yield from pyrazole
- 5 lbs. produced

- 1st step:
  - Nitration; acetyl nitrate in situ
  - 1-NP sublimes at ambient pressure (difficulty drying)
- 2nd step:
  - Used anisole/water azeotrope to remove water
  - ARC studies confirmed safe range
  - <40% in anisole @ high temperature.
- 67% yield of 3-NP based on pyrazole

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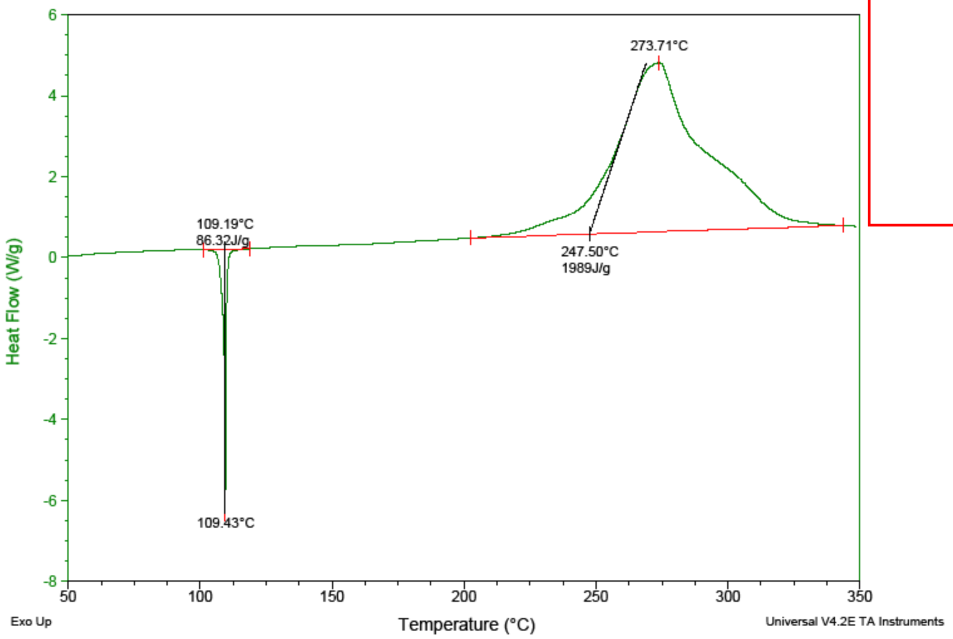
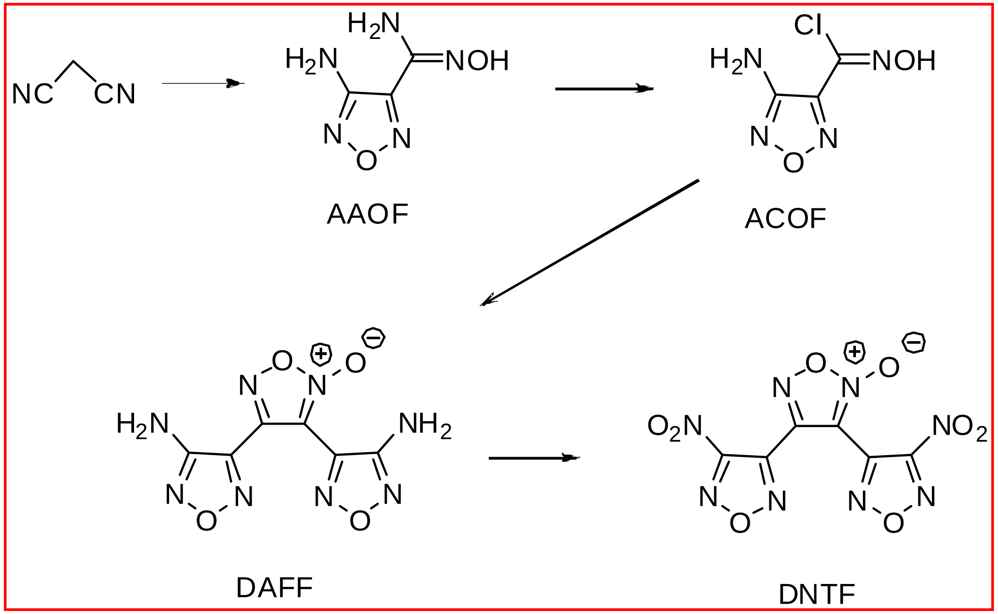
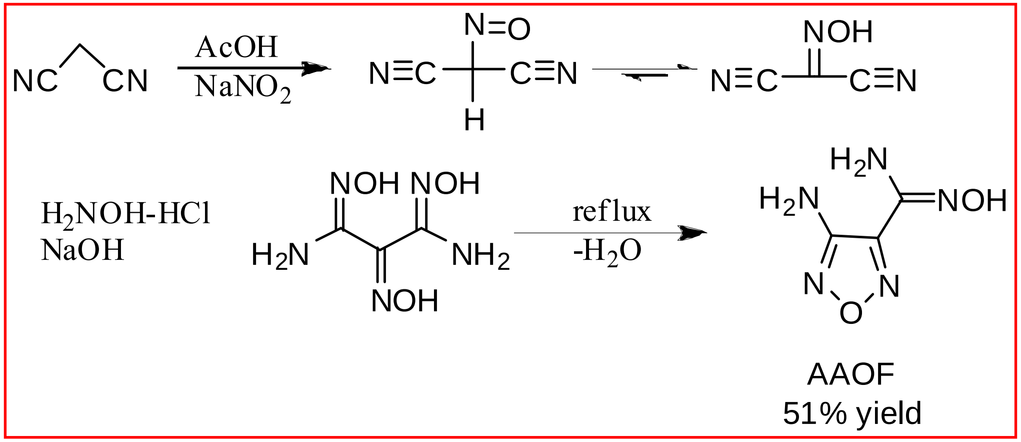
DNTF

- 4 step process
- Commercially available and affordable starting materials



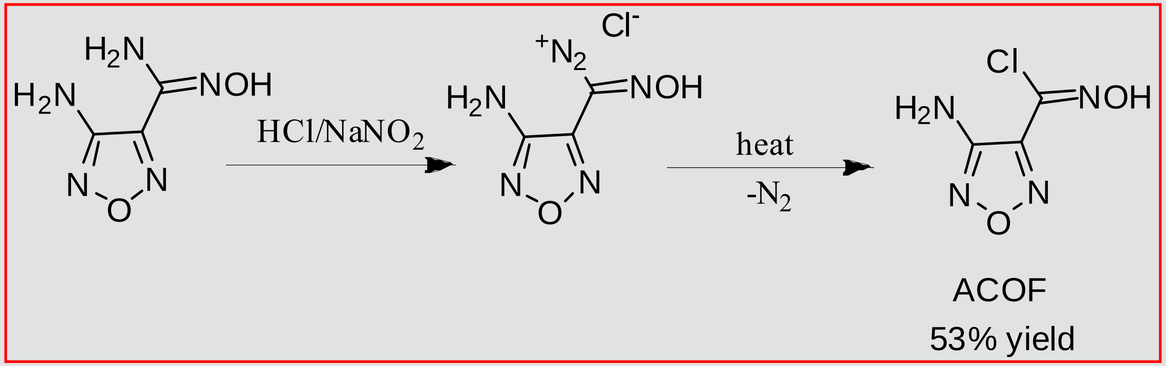


DNTF

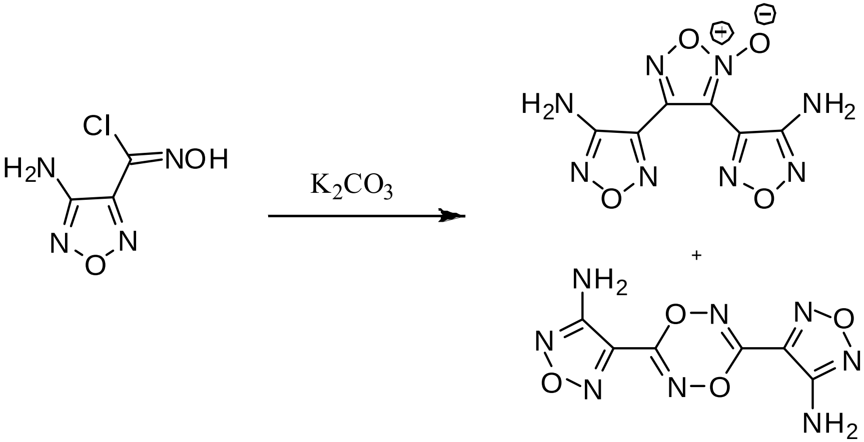


- Straightforward 3 step, 1 pot synthesis
- Scalable; several 1 kg batches
- 50% yields
- 90% yields reported when pH is tightly controlled during H2NOH-HCl addition

- Diazotization/substitution
- Stable diazonium salt intermediate
- Product a severe skin and respiratory irritant
- Transfer wet to next step; no isolation
- Scalable; ca. 1 kg produced
- 50% yields, unoptimized



DNTF



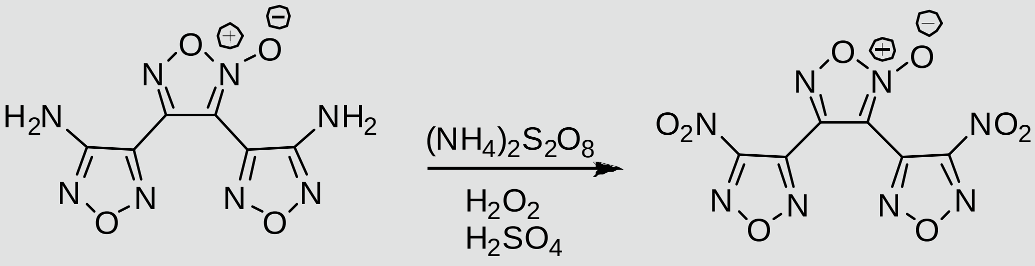
DAFF

45% yield

28% yield

- Heterogeneous; slurry in MTBE
- Low temperature
- Usually 2:1-DAFF:DAFD
- 50% yields of DAFF, not optimized
- Scalable with improved temperature control; 0.5 lbs produced

- Strong oxidation conditions required
- 24 hrs. @ ambient
- App. 50% isolated yield
- Isolation/purification problematic
- 99% yields reported by Dong, et al. using same reagents
- Optimization of conditions? Time and temperature?



DNTF

47% yield

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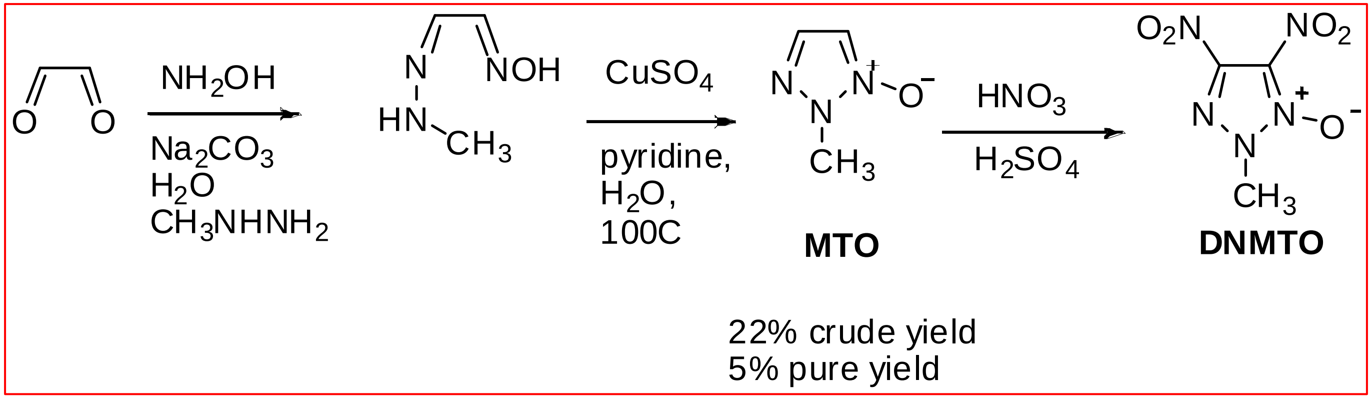
DNMTO



- MTO procedure from Prof. Begtrup, et al
  - Poor yield reproduced independently by Prof. Katritzky's group at UF
  - No improvements could be made
- Although reported nitration is high yielding, our efforts did not go that far

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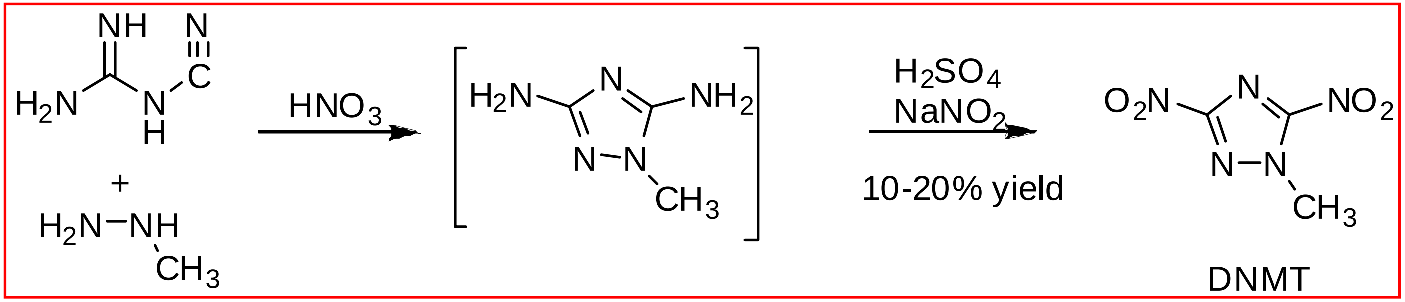
DNMT



- Original procedure:
  - Pseudo one pot reaction
  - Developed by Prof. Katritzky, et al.
  - DNMT soluble in acidic water
  - Extraction required
  - Synthesis/purification not optimized
  - 25 grams produced by this method

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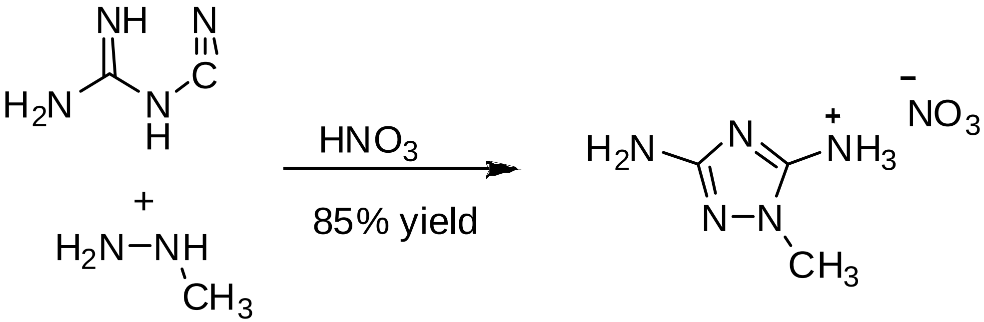
DNMT Improvements

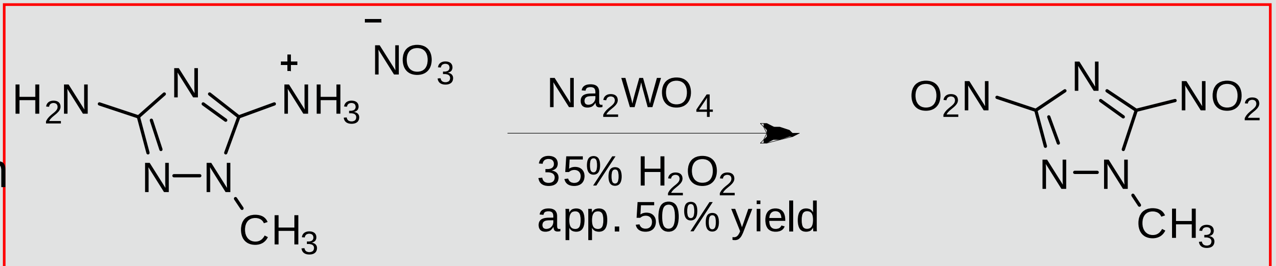


DAMT

- Moved from one-pot to two-pot sequence
- 1st step:
  - Isolation of DAMT enhanced by minimizing water in reaction
  - Product precipitates from reaction medium
  - Isolated by filtration

2nd step:

- Switching from diazotization to oxidation uses less reagents
  - DNMT precipitates from reaction medium
  - Product isolated by filtration



DAMT DNMT

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Safety Testing

ARDEC-Picatinny Arsenal

	ERL Impact (cm)	BAM Friction (N)	ESD (J)
DNP	67.4	>216	>0.25
DNTF	<15.8	>64	>0.25
DNMT	>100	>252	>0.25
RDX	25.4	>144	>0.25

OSI-Holston

Impact Sensitivity (cm), Navy Method		
	Pre-melt	Post-melt
DNP	54.1	146.9
DNTF	~17	<8
DNMT	92.7	171.0

- Melt-recrystallization might provide amorphous character
- Potentially remove crystalline defects/hot spots
- Appears valid for DNP, DNMT
- DNTF-long recrystallization time; highly crystalline

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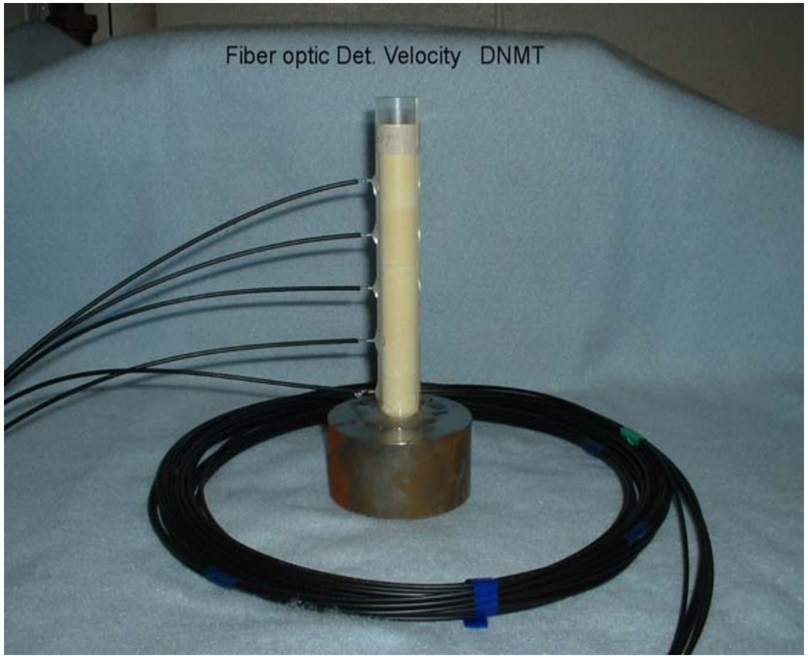
Performance-Rate Stick/Plate Dent

	Pcj, calc. (GPa)	Pcj, exp. (GPa)	Energy out, calc. (cal/cc)	VOD, exp. (Km/s)
DNP	28.8	29.4	1961	8.104
DNMT	25.4	23.3	1739	7.850
Comp B	27.7	~27.6	1837	~7.960
DNTF	35.9		2517	
LX-14	35.1	~37	2186	~8.800



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Compatibility Evaluations

- 1:1-Mass:Mass Physical Mixtures of HSAAP Formulation Ingredients
- DSC @ 5 °C/min. from 50 to 450 °C
- Observe Changes in Exotherm Onset and Peak for Lowest Value Component
- Negative Deviations ≥10 °C Indicate "Fail"; Invoke VTS

Compatibility Matrix

	DNP			DNTF			DNMT		
	MP	Exo Onset	Exo Max	MP	Exo Onset	Exo Max	MP	Exo Onset	Exo Max
NEAT	86.5	275.8	296.9	107.5	230.2	270.7	95.7	260.6	280.0
RDX: MP 203.6, Exo Onset 205.8, Exo Max 227.9	83.8	202.6	234	106.6	204.6	227.2	88.2	204.3	230.9
HMX: MP 187.2, Exo Onset 276.3, Exo Max 284.2	86.7	203.3	221.2	108.1	239.3	260.1	93.7	223.4	252.8
NTO: MP N/A, Exo Onset 262.3, Exo Max 273.4	86.4	175.7	237.7	108.2	253.9	257.9	97.7	176.9	231.4
TATB: MP N/A, Exo Onset 366.56, Exo Max 373.8	86.7	193.3	273.7	108.4	234.6	267.8	97.6	227.1	243.5
DNAN: MP 94.2, Exo Onset 326.9, Exo Max 342.9	57.9	203.9	302.9	68.9	241.8	271.9	54.8	301.6	322.3
NQ: MP N/A, Exo Onset 195.2, Exo Max 202.8	84.2	182.5	222.7	108.5	182.8	225.5	95.3	182.7	222.8
DNP: MP 86.5, Exo Onset 275.8, Exo Max 296.9				78.3 /102.1	208.5	248.7	46.25	285.4	345.6
DNTF: MP 107.5, Exo Onset 230.2, Exo Max 270.7							81.1/92.5	233.8	268.7

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Conclusions

- DNP was optimized and scaled to produce 5 lbs of material
- MTNI was discontinued due to complicated synthetic route (not easily scalable, costly)
- DNMT was discontinued although not before showing some promise of scalability and affordability
- DNMTO was discontinued due to terrible yields in first synthetic step
- DNTF was discontinued due to sensitivity concerns with final product

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