GrIMEx: Development of a Novel, Green IM Comp B Replacement

Insensitive Munitions & Energetic Material Technology Symposium 2015

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Acknowledgements

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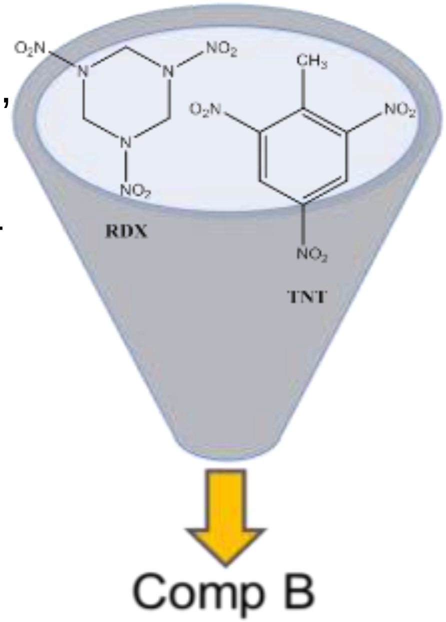
GrIMEx (Green IM Explosive)

Technology Focus

- To develop a novel IM Comp B replacement formulation containing novel, environmentally favorable TNT and RDX replacements.

Research Objectives

- The design and development of new synthesis routes for novel TNT <u>and</u> RDX replacements candidates that will be (relative to TNT or RDX):
    - Less sensitive to unplanned stimuli
    - Of comparable performance
    - Less toxic
    - Made through environmentally acceptable routes
- The design and development of new melt-pour Comp B replacement candidates that will be:
    - More IM-compliant than Comp B
    - Less toxic
    - Of comparable performance



What's wrong with Comp B?

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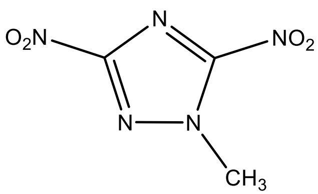
- **Environmental:**
  - DoD utilizes an large amount of Comp B in artillery and mortar rounds
  - RDX and TNT have known toxicity concerns and contaminate soil and groundwater
    - RDX has become an undesirable component of new munitions formulations because it causes neurological effects (i.e. convulsions) in personnel, and the U.S. EPA lists RDX as a possible human carcinogen.
    - RDX has also become an environmental contaminant of concern because of residues from its use in munitions and from manufacturing.
- **Performance:**
  - Comp B does not meet current "IM" (Insensitive Munitions) requirements mandated by DoD
    - Both RDX and TNT contribute to the lack of IM

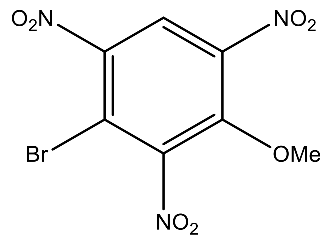
IM Test:	Fast Heating	Slow Heating	Bullet Impact	Fragment Impact	Sympathetic Reaction	Shaped Charge Jet Impact
Passing Criteria	V	V	V	V	III	III
120mm (Comp B)	II	I	I	I	(I)*	(I)*

VI	V	IV	III	II	I
No Sustained Reaction	Burn	Deflagration	Explosion	Partial Detonation	Detonation

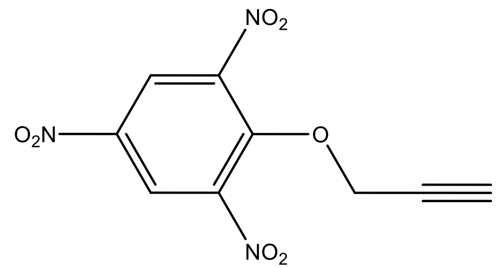
Potential TNT replacements



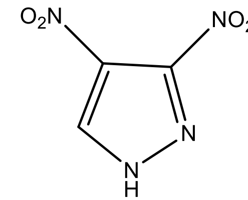
DNMT
Mp: 95C
Impact: 154 cm (2.5 kg wt)
Density: 1.7 g/cc
VOD: 7850 m/s (exp)
Pcj: 23.3 (exp)



TNBA
Mp: 95C
Density (calc): 1.85 g/cc
VOD: 7300 m/s (calc'd)



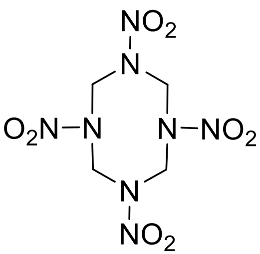
PiPE
Mp: 100C
Density (calc): 1.61 g/cc
VOD: 6950 m/s (calc'd)



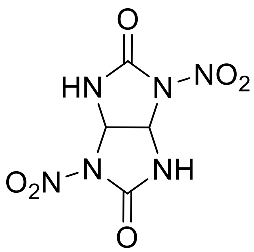
DNP
Mp:87C
Density: 1.77 g/cc
VOD: 8251 m/s

Compound	Pros	Cons
DNMT	Close to Comp B performance, Insensitive	Low synthetic yields, Use of methylhydrazine
PiPE	TNT performance, Predicted insensitivity	Immature synthetic route, insufficient characterization
TNBA	Reasonable maturity, Insensitive, One synthetic step	Density unknown, Effect of Bromide atom on performance unknown
DNP	> Comp B performance, synthesis alread developed	Acid proton?

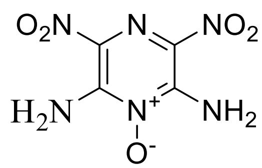
Potential RDX replacements



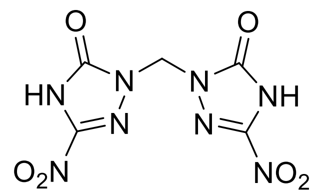
HMX



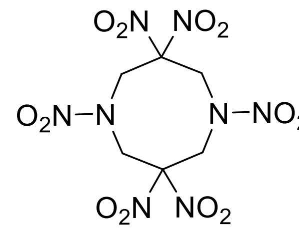
DNGU



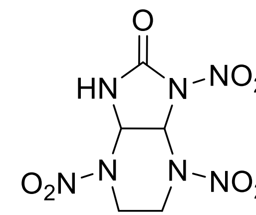
LLM-105



BiNTO



HCO



HK-56

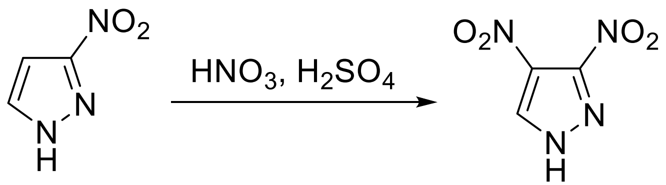
Compound	Pros	Cons
HMX	Less toxic and env. persistent than RDX, Higher power than RDX	Slightly more sensitive than RDX
DNGU	Low sensitivity, inexpensive	Unconfirmed performance
LLM-105	Insensitive, good performance	3-step synthesis, particle morphology
BiNTO/NANTO	Reduced water solubility, NTO as starting material	Unconfirmed performance and synthetic data
HCO	Similar to TNAZ, High density	Unconfirmed synthetic route
HK-56	Potential for low-cost and sensitivity	Unconfirmed performance, sensitivity and particle size issues

Small Scale Synthesis

- This project will begin with the small-scale laboratory synthesis (<25 g) of several novel RDX and TNT replacements to include:
  - Method development
  - Analytical methods
  - Particle shape and size (RDX replacements)
  - Sensitivity (impact and friction)
  - Thermal stability (DSC, TGA, VTS)

- It is the goal of the year one efforts to deliver 1-4 TNT replacement candidates and 1-4 RDX replacement candidates to USAPHC for second level (synthesis stage) environmental testing.

DNP Synthesis



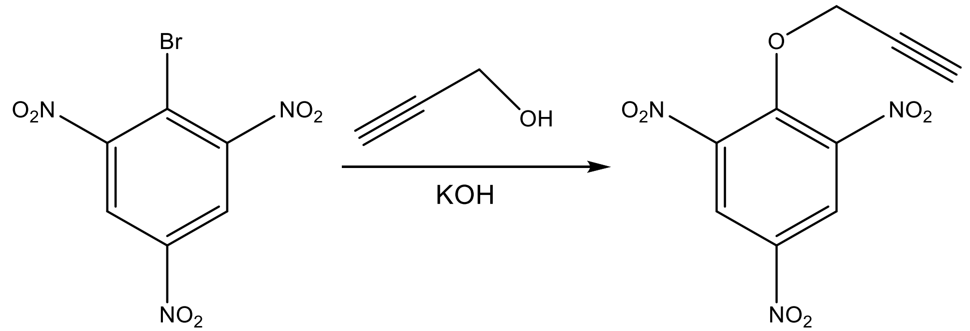
3NP DNP

- DNP (3,4-dinitropyrazole) is technically mature, and has been consistently synthesized on the 100-g scale with 65% crude yield and 99.9% HPLC purity but with ~5% remaining acids.
- Previous purification methods involved extractions and vacuum. Current efforts are focused on isolation and purification amenable to scale-up.
- Recrystallization in a solvent/antisolvent system currently shows the most potential of removing residual acid.

Other recrystallization ratios and solvents are also being evaluated.

▪**Technical Maturity:** Solid synthesis route, isolation and purification needs work

PiPE Synthesis

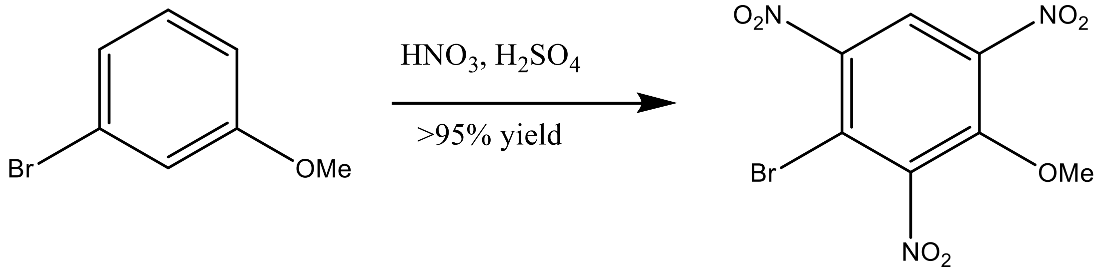


Material	Impact (cm)	Friction (N)	Purity (HPLC)	MP (°C)	% Yield
PiPE (1121-49)	56.7	>360	100%	100.2	54
Cl 5 RDX	50.8	144	N/A	N/A	N/A

- PiPE was easily synthesized on the small scale (approximately 5 g) from picryl bromide
- Very pure product
- Synthesis involves propargyl alcohol (potential toxicity concerns)

▪**Technical Maturity:** Synthetic route works nicely, some concerns over starting material toxicity

TNBA Synthesis

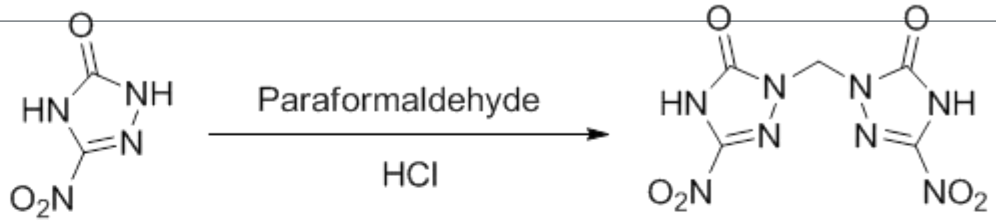


TNBA
$C_7H_4BrN_3O_7$
Mol. Wt.: 322.03

- Synthesis route is one step nitration
  - Crystalline solid precipitates from reaction in high yield
  - No sticky solid
- **Robust Process:**
  - 3 Synthesis chemists each performed 3 identical nitrations
  - Yields ranged from 96.5% to 100%
  - Purity ranged from 98.69% to 99.92%

▪**Technical Maturity:** Minimal optimization needed. Need to get preliminary performance testing to verify detonation velocity.

BiNTO Synthesis



BiNTO

BiNTO was predicted to be a water insoluble alternative to NTO and RDX but was eliminated for the following reasons:

(1) Solubility: Very water soluble. BiNTO could not be precipitated out of water and other reaction solvents (MeOH, EtOH) gave little to no reaction.

(2) Conversion: BiNTO reaches maximum conversion at 45 minutes, but NTO still present.

(3) Purity: TLC, recrystallization, or distillation gave no separation between NTO and BiNTO.

(4) Stability: In the presence of water, breaks down into NTO (determined by NMR and HPLC).

- **Technical Maturity:** Material was generated but shown to revert to starting material easily (labile)-Ingredient abandoned.

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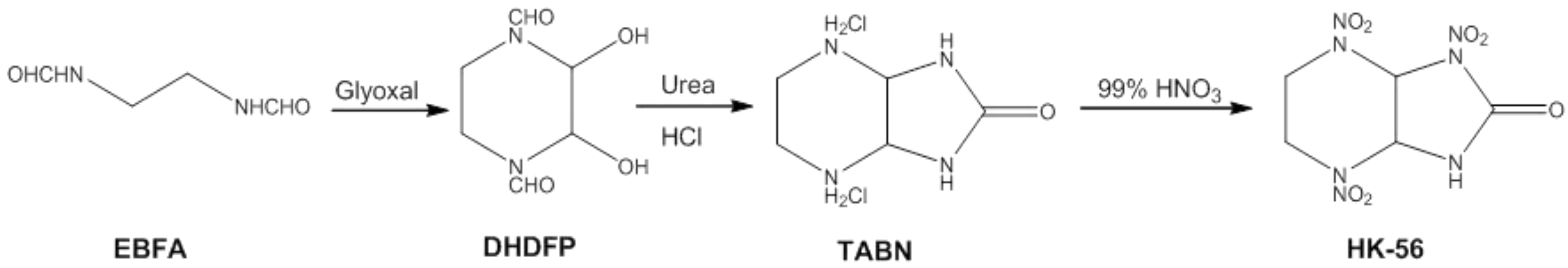
HK-56 Synthesis

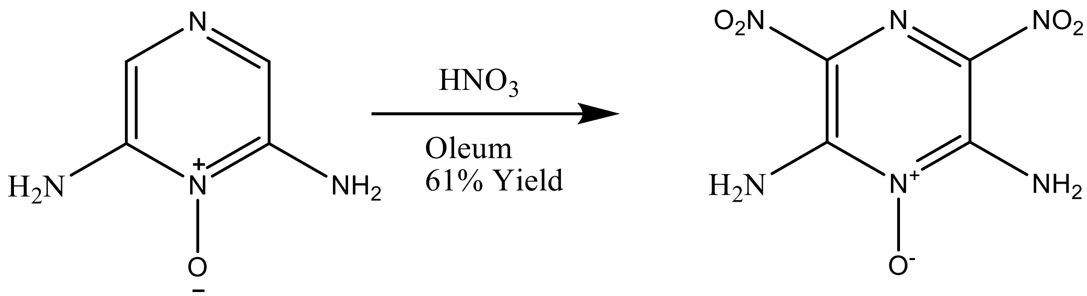


- Simple condensation to DHDFP (yields of 68%)
- TABN reaction completed up to the 2 L scale (yields of 68%)
- HK-56 for this program synthesized from TABN that had been previously generated under the US Army FREEDM program
- HK-56 yields of ~40%

- Particle size and shape of the HK-56 will be important for future formulation activities
  - HK-56 particle shape appears promising (no needles)
  - Particle size is approximately 5-10 microns
  - Adjusted quench conditions of the reaction did not increase particle size
  - Crystallization efforts will be conducted in order to generate a larger particle size

▪**Technical Maturity:** Leveraging work from FREEDM program, only small quantities generated

LLM-105 Synthesis



DAPO **LLM-105**

- Final stir in LLM-105 formation complicated by significant foaming.
- Off-gassing suggests consumption of the product or intermediates.
- Reduced HNO_3 loading and a reduced final stir temperature provides a modest yield improvement (4-5%).
- The reduced HNO_3 loading and reduced final stir temperature also results in less troublesome headspace foaming.
- Extensive robustness testing revealed reduced oleum loading and extended final stir temperatures above 30 ^oC as the only two major concerns affecting yield.
- Further reduction of HNO_3 loading results in lower yields and purity.

▪**Technical Maturity:** Robust synthesis process. Particle size is rather small.

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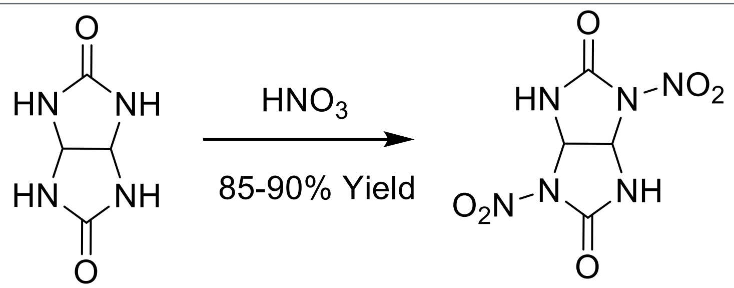
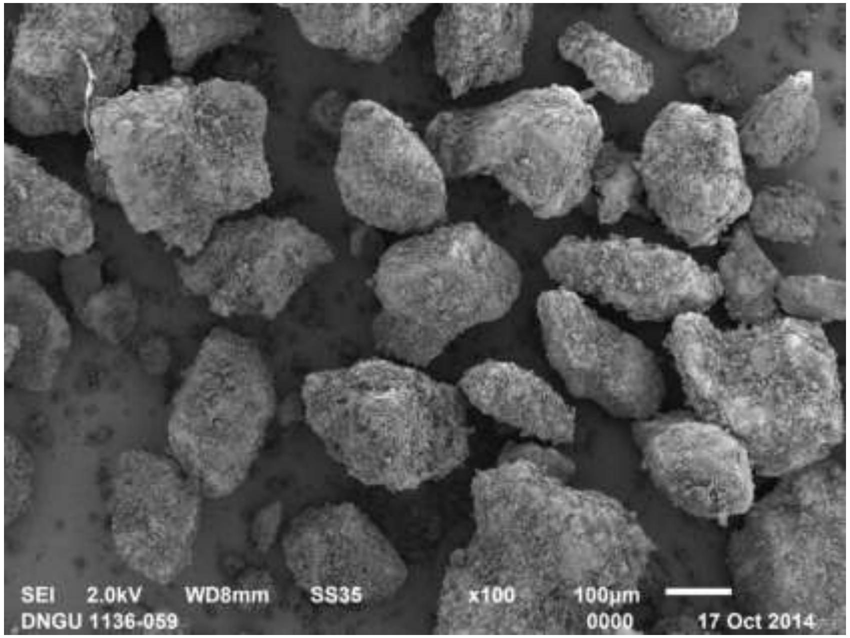
DNGU Particle Size Development



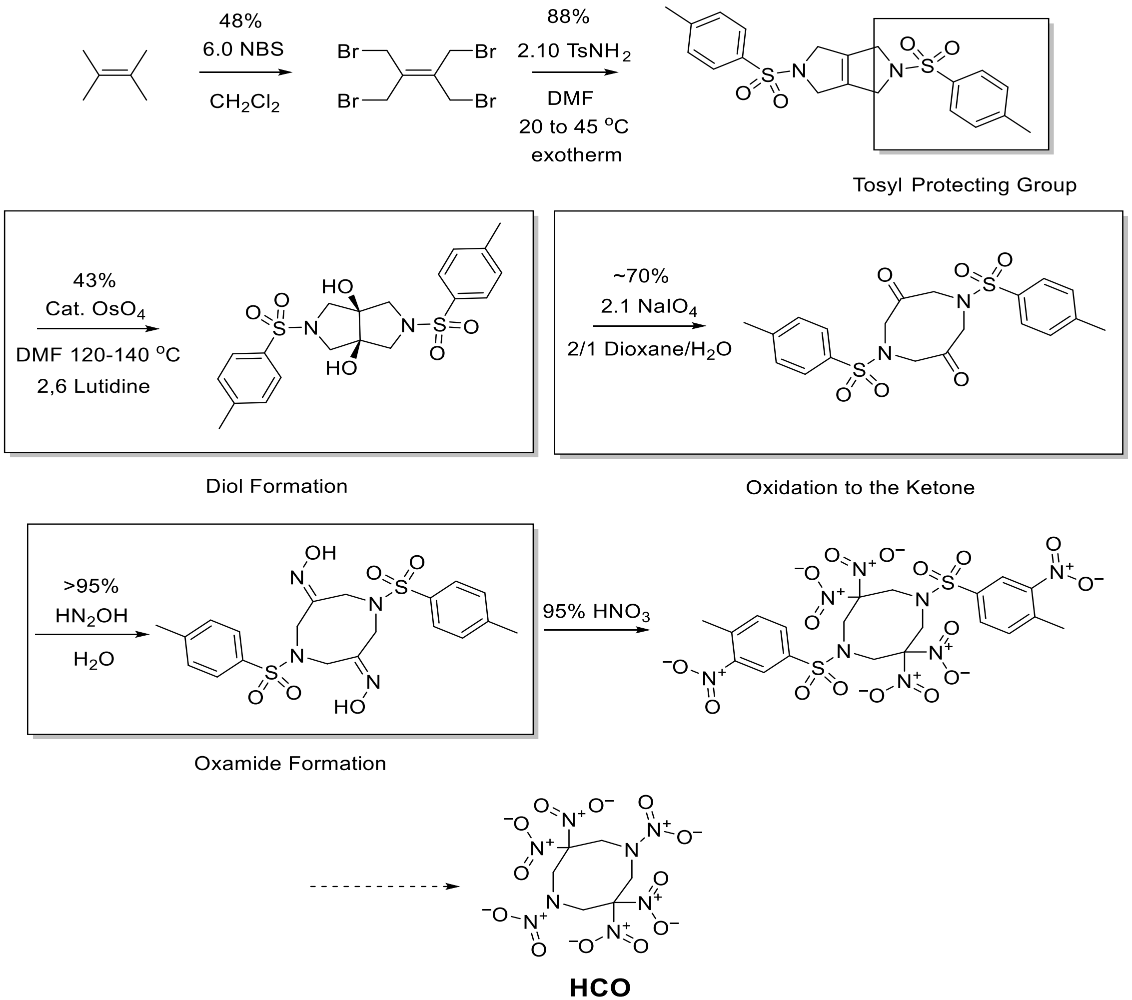
glycoluril DNGU

- Previous process afforded small particle size DNGU
  - <10 microns
- Specific nitration conditions needed to promote desired particle size growth.
- Higher temperature final stir contributes to larger particle size growth.
  - >100 microns



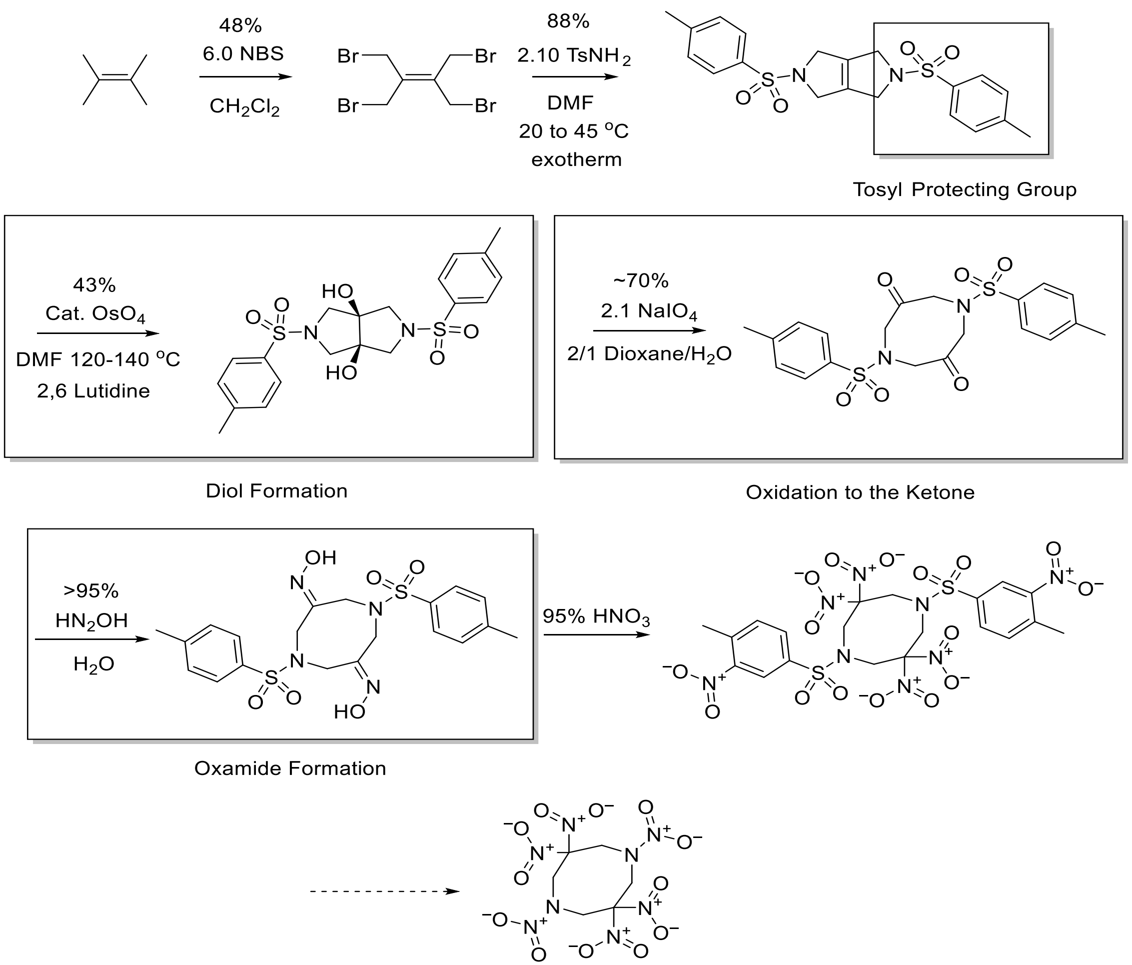
▪**Technical Maturity:** Larger particles generated with novel nitration process .

HCO Synthesis



- The Tosyl protecting group serves as a solubility ‘handle’. It’s lack of solubility allows reasonably high yields and clean product precipitation while leaving impurities in solution.
- The oxidation to the ketone proceeds as a solid to solid transformation.

HCO Synthesis-continued



HCO

- A more water soluble protecting group will allow the Diol Formation, Oxidation and Oxamide Formation to be performed in one pot, likely improving the overall yield.
- A more suitable protecting group will also allow complete nitration to the target **HCO**.
- HCO has not been synthesized yet via this route

▪**Technical Maturity:** Synthesis route almost completed.

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Results – VTS Compatibility

	NEAT	TNBA	DNMT	PiPE	DNP	DNGU	LLM-105	HK-56	HMX
NEAT		0.5273	0.785	2.8188	2.6083	0.4744	0.4348	0.2857	0.0699
TNBA	0.5273					0.4569	0.7201	0.4146	0.2323
DNMT	0.785					------	0.5184	0.1175	------
PiPE	2.8188					1.5223	1.7547	------	1.3033
DNP	2.6083					2.0563	1.6351	0.2971	------
DNGU	0.4744	0.4569	------	1.5223	2.0563		0.6147	0.4653	------
LLM-105	0.4348	0.7201	0.5184	1.7547	1.6351	0.6147		------	0.3372
HK-56	0.2857	0.4146	0.1175	------	0.2971	0.4653	------		0.226
HMX	0.0699	0.2323	------	1.3033	------	------	0.3372	0.226	

- STANAG 4147 Test 1B states that when 2.5 grams of material A is mixed with 2.5 grams of material B, the total gas evolved after 40 hrs at 100° C must be less than 5 cc in order to be deemed compatible.
- **All materials were compatible as tested.**

Results – Comparative Data

	TNT replacements					RDX replacements				
	TNBA	DNMT	PiPE	DNP	TNT	DNGU	LLM-105	HK-56	FEM-HMX	RDX
SEM	√	√	√	√		√	√	√	√	
Impact, cm	(Naval) 79.43	>85	56.7	55.0	88	(Naval) 112.20	50.0	35.0	30.7	45
Impact Std, cm	23.3	45.0	50.8	39.0		16.7	39.0	42.5	-	
Friction, N	70.0	166.0	>360	246.0	216	>360	>360	>360	183.5	144
Friction Std, N	144.0	142.7	144.0	164.0		164.0	164.0	-	-	
ESD, J	0.2900	0.0425	0.2113	0.2625	>0.25	0.0366	0.0366	0.0829	0.1050	<0.25
particle size	0	0	0	0		120	4	20	5	
det velocity	6.571	7932	6.929	8251	7180	8878	8667	8628	9246	8862
det pressure	23.98	25.97	21.96	29.24	20.02	35.64	32.72	32.82	37.19	33.46
V/V0 7.20	-5.87	-7.05	-5.91	-7.93	-5.42	-8.33	-7.56	-8.49	-9.66	-9.01
Oxygen balance	-44.72	-32.35	-80.85	-30.37	-73.96	-27.57	-37.02	-37.52	-21.61	-21.61
Density, g/cm3	1.948	1.66	1.612	1.773	1.654	1.941	1.881	1.85	1.91	1.816
melt temp	97	97	100	87		0	0	0	0	
heat of formation	18.88	122.8	227.4	120.5	-63.2	-41.54	-13	100.6	75	70

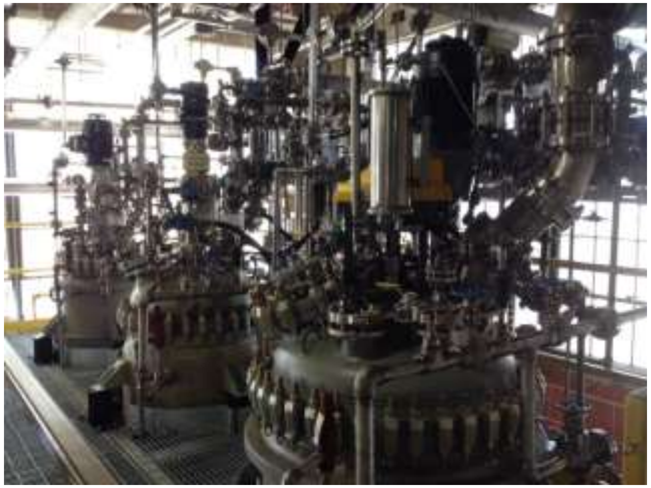
- This data was used in the downselect process for ingredients.
- Performance data was calculated using Cheetah 7.0.

Path Forward-Ingredients

- DNMT: Work on synthesis route development and improvements
- DNP: Continue to work on isolation/purification improvements
- DNGU: Scale up and refine method to maintain particle size and shape
- TNBA: No development needed, produce for formulation work efforts
- HK-56: Work to increase particle size and improve morphology
- LLM-105: No development needed, potentially produce for formulation efforts

Conclusions

- Lots of interesting synthesis development work
  - Different degrees of difficulty
  - Different attributes
  - Different ingredient maturities
- Down-select will help us focus on ingredients and formulations
- We are looking forward to scaling up ingredients and actual toxicity evaluations
- BAE Systems has commissioned a pilot plant at Holston which should better enable the scale up of these new materials



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Questions?