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GrIMEx (Green IM Explosive): Development of Novel IM Comp B Replacements Based on Green TNT and RDX Replacements

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Abstract

Comp B is an explosive formulation consisting of TNT, RDX and wax and has been used for many years in bomb fills, grenades and anti-personnel mines. Although Comp B has performed well over the years, the environmental impact of the formulation warrants concern. With the recent development of IMX-101 and IMX-104, invented by BAE Systems Ordnance Systems' scientists, IM replacements for TNT and Comp B were created. However, although IMX-104 is considered and accepted to be a Comp B replacement, some performance data of IMX-104 indicates it is lower than that of Comp B. There is a need for IM melt-pour formulations with performance equivalent to or above Comp B while retaining the IM properties of the IMX family of explosive formulations and also containing non-toxic and environmentally-benign ingredients produced through synthetic methods of low environmental impact. This project combines the capabilities of the US Army Public Health Command and BAE Systems, Ordnance Systems Inc and is funded by the DoD's Strategic Environmental Research and Development Program or SERDP.

The objective of this project is to address the following: 1) Develop environmentally acceptable synthesis methods to scale-up environmentally sustainable, insensitive secondary explosives as alternatives to cyclotrimethylenetrinitramine (RDX), 2, 4, 6-trinitrotoluene (TNT), and ammonium perchlorate (AP); and 2) Develop novel formulations utilizing the alternative materials to replace Composition B (Comp B).

This paper describes initial lab scale synthesis of all the ingredients including justifications and rationale for evaluating these materials, technical challenges encountered with the synthesis efforts, and preliminary analytical results.

Background

Technology Focus

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

Research Objectives

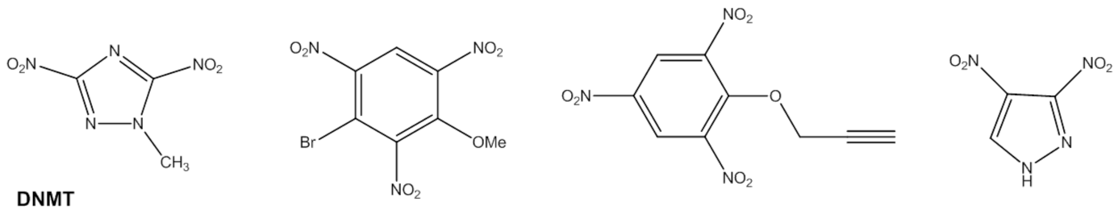
- The design and development of new synthesis routes for novel TNT <u>and</u> RDX replacements candidates that will be (relative to TNT or RDX):
  - Less sensitive to unplanned stimuli
  - Of comparable performance
  - Less toxic
  - Made through environmentally acceptable routes
- The design and development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

- **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



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

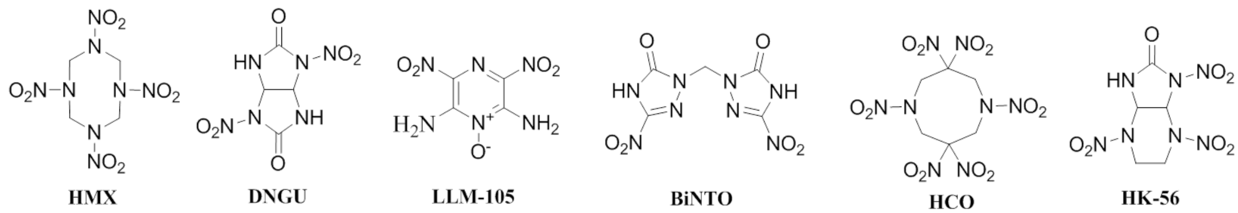
TNBA
Mp: 95C
Density (calc): 1.85 g/cc
VOD: 7300 m/s (calc'd)

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?

Figure 1: Potential TNT Replacements



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

Figure 2: Potential RDX Replacements

Results and Discussion

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.

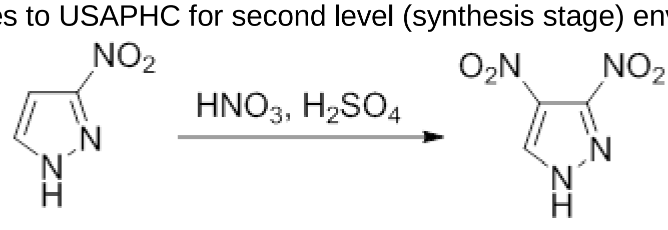


Figure 3: DNP Synthesis Route

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 a solvent/antisolvent system currently shows the most potential of removing residual acid. Other recrystallization ratios and solvents are also being evaluated.

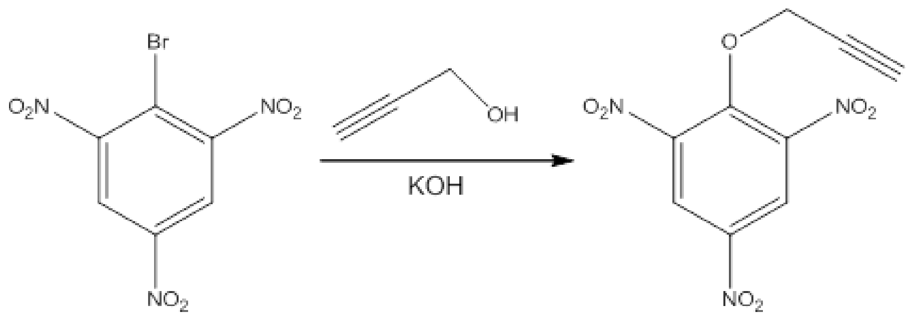


Figure 4: PiPE Synthesis

PiPE was easily synthesized on the small scale (approximately 5 g) from picryl bromide resulting in a very pure product. The synthesis involves propargyl alcohol (potential toxicity concerns)

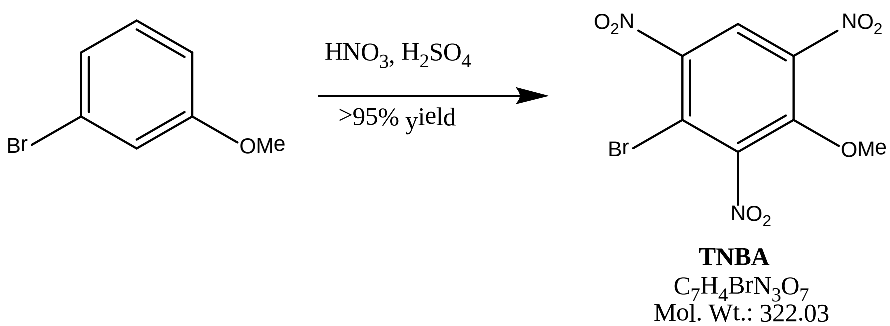


Figure 5: TNBA Synthesis

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%

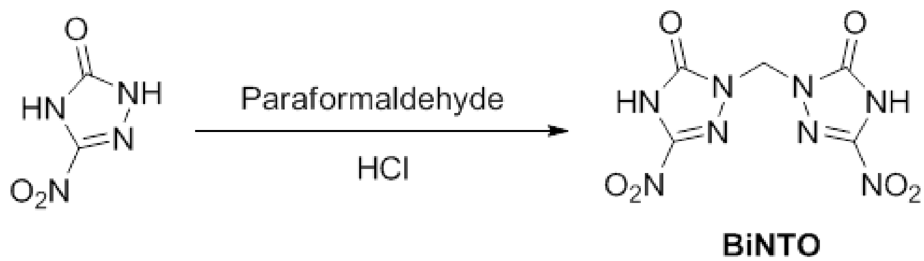


Figure 6: BiNTO Synthesis

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).

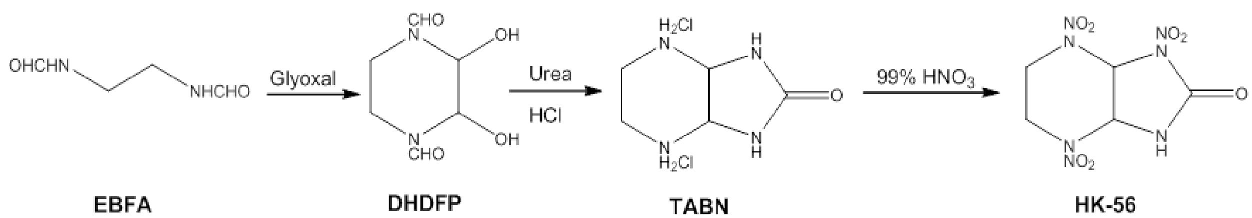


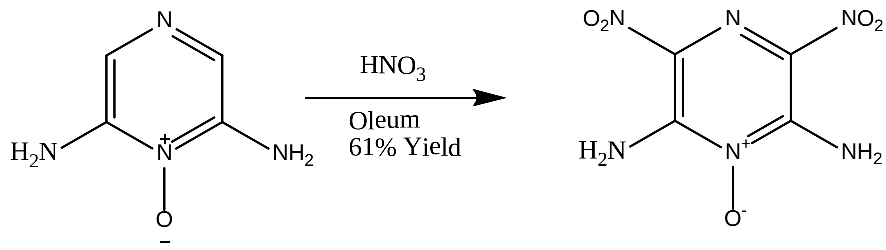
Figure 7: HK-56 Synthesis

- 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

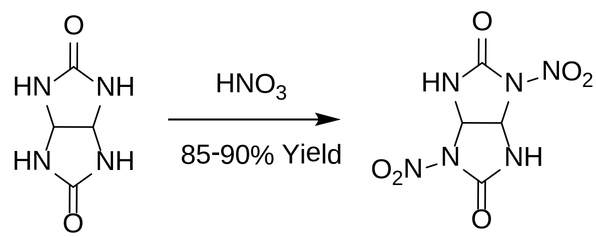
- Crystallization efforts will be conducted in order to generate a larger particle size



DAPO **LLM-105**

Figure 8: LLM-105 Synthesis

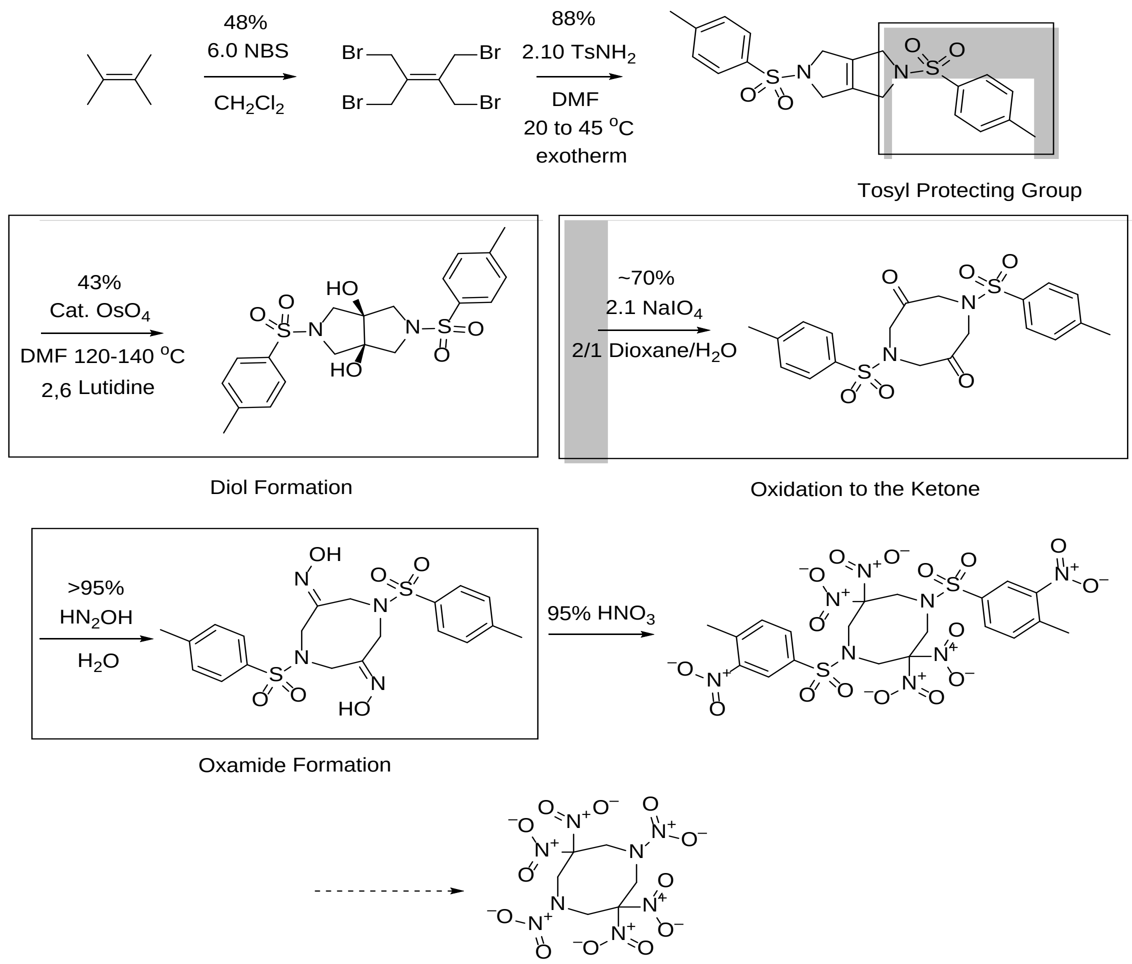
- Final stir in LLM-105 formation complicated by significant foaming.
- Off-gassing suggests consumption of the product or intermediates.
- Reduced HNO_3 loading and a reduced final stir temperature provides a modest yield improvement (4-5%).
- The reduced HNO_3 loading and reduced final stir temperature 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.



glycoluril **DNGU**

Figure 9: DNGU Synthesis

- 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



HCO

Figure 10: 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.

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

	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	

Figure 11: Compatibility Testing Results

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.

	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

Figure 12: Sensitivity and Performance Data

Future Work

- 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

BAE Systems is also currently commissioning a Pilot Scale R&D Facility with 50, 100, & 200 gallon glass-lined reactors (figures 8 and 9). This facility will enable a better transition from lab scale to Agile Facilities (particularly for ingredient synthesis). Commissioning is scheduled to be completed by Q4 2013. Several ingredient scale-up programs are already lined up (DoD, DoE, commercial) with Class 1 NTO to be produced in our pilot plant in 2013. A nominal 100 lb batch size is currently planned for Class 1 NTO with further scale up to full scale production later (3000 lb batch size (nominal)).

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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