# Synthesis of Propyl Nitroguanidine (PrNQ)

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# Background

- GP bombs traditionally filled with sensitive tritonal or H-6
- Current GP bomb fills still do not pass all IM requirements
  - Novel formulations that meet all IM criteria are needed
- Novel PrNQ based IM formulations are being evaluated for use in GP bombs

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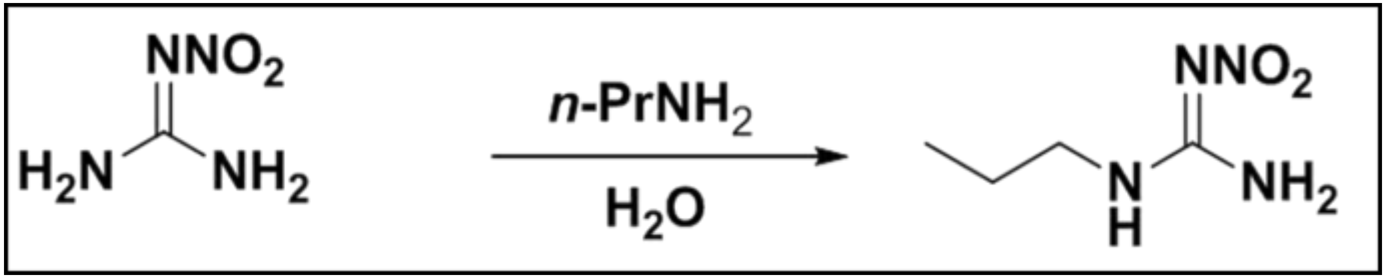
# Why PrNQ?

- 99 °C melt is perfect for melt-pour formulations
- Based on inherently insensitive explosive: NQ
  - NQ has large critical diameter (SCJ)
  - NQ is extremely insensitive to shock (SR)
  - Mild response to SCO
- PrNQ synthesized in one step
  - Inexpensive/readily available starting materials
  - Mild processing conditions
  - Crystallization from inexpensive solvent
- PrNQ possesses TNT like performance

# PrNQ Synthesis Background

- First synthesized in 1927 by Davis & Luce
- US ARL completed limited optimization of the known process
- Process involves heating NQ & $PrNH_2$ in water followed by crystallization
- Transitioned to ARDEC for laboratory scale (kg quantities) production
  - ARDEC provided over 24 kg to ARL for further testing at ARL
  - ARDEC scientists identified areas for improvement
- ARL contracted BAE Systems, OSI for further development
  - Full optimization program followed by pilot scale synthesis



# Project Overview

**Phase I: Laboratory scale optimization**

Optimization Goals:

1. Reduce overall cost
2. Develop robust process

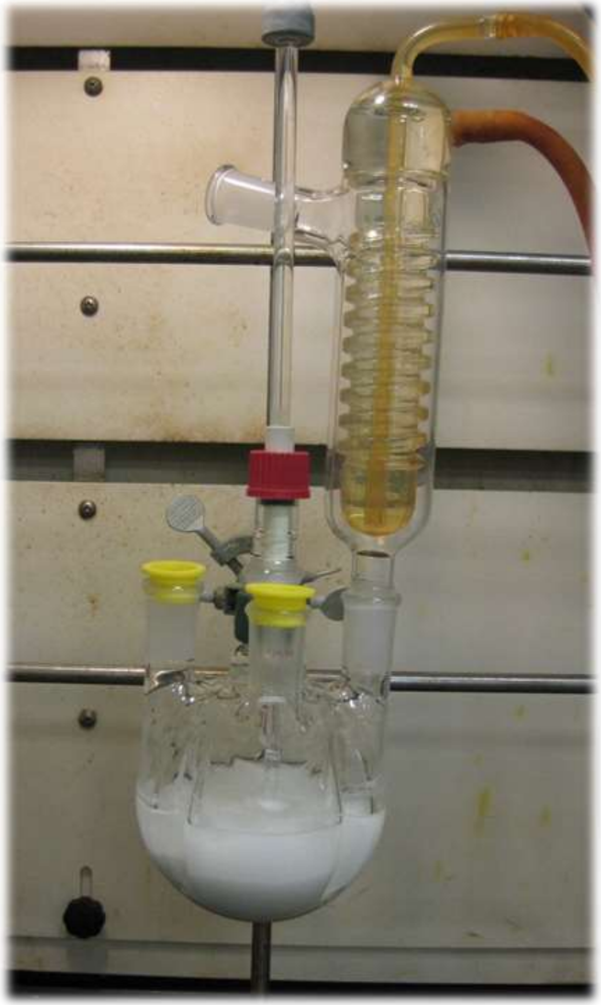
Parameters Evaluated:

1. Reaction solvent content
2. Reaction Temperature
3. Reagent Ratio ($PrNH_2$:NQ)
4. Reaction Time
5. Reaction Neutralization conditions
6. Crystallization Solvent

**Phase II: Large laboratory scale synthesis**

Goal: Identify scale up concerns/issues

**Phase III: Pilot scale synthesis**



# Phase I: Reaction Solvent Content Evaluation

| $H_2O$:NQ Ratio | Temp. (°C) | Yield | Purity |
|---|---|---|---|
| Original | Original | 44 | 100.0 |
| Original | Optimal | 46 | 97.9 |
| Original x 2 | Optimal | 51 | 97.4 |
| Original x 3 | Optimal | 56 | 98.9 |
| Original x 4 | Optimal | 52 | 98.0 |

- Concerns about adequate stirring using original process
- Increased water solved stirring concerns, increased yield
  - Yield and purity increase with original x 3
  - Original x 4 decreases yield and purity
  - Original x 3 determined to be optimal ratio

**Increased solvent = increased yield & purity**

# Phase I: Temperature Evaluation

| Temperature | % Yield @ 1 h | % Yield @ 2 h | % Yield @ 3 h | % Yield @ 4 h |
|---|---|---|---|---|
| Temp A | 74 | 74 | 68 | 65 |
| Temp B | 73 | 63 | 55 | 52 |
| Temp C | 59 | 45 | 31 | 26 |

*Note: All times given are post-dissolution of NQ

- All reactions employed improved water ratio
- Yields for 1 h-4 h samples are in-situ yields determined via HPLC analysis of the reaction solution
- Temperature B determined to be optimal temperature
  - Balances yield vs. reaction time
  - Cooling at reaction end quicker than with higher temperatures
  - Reaction robust enough to address any potential upsets

**Temp B balances labor time with yield**

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# Phase I: Reagent Ratio Evaluation

| $PrNH_2$:NQ | Temp. | Yield | Purity |
|---|---|---|---|
| Original | Temp B | 56 | 98.9 |
| Original – 12.5% | Temp A | 58 | 99.5 |
| Original – 25% | Temp A | 60 | 98.7 |
| Original – 25% | Temp B | 65 | 99.1 |
| Original – 37.5% | Temp B | 64 | 94.7 |

- Evaluated at two different temperatures
- Initial evaluation indicated 25% reduction gives highest yield and purity
- Later work indicated 37.5% reduction viable with change in water content

**Reagent reduction = cost reduction**

# Phase I: Quench Conditions Evaluation

| Acid | pH | Yield | Purity |
|---|---|---|---|
| Acid A | 6.4 | 56 | ND |
| Acid A | 3.6 | 57 | ND |
| Acid A | 3.1 | 57 | ND |
| Acid A | 1.8 | 58 | ND |
| Acid A | 1.1 | 56 | ND |
| Acid A | 1.1 | 60 | ND |
| Acid B | ~3.0 | 59 | 97.6 |
| Acid C | ~3.0 | 63 | 99.5 |
| Acid A | 6.5 | 56 | 98.9 |

- Samples from a single reaction quenched at various pH levels to test effects on yield
  - pH at quench has minimal effect on yield
- pH must be below 7
  - $PrNH_2$ must be in salt form
- pH above 3 preferable
  - pH <3 = hazardous waste
- pH of 6.5 optimal for cost and yield
- Alternate acids: Acid C optimal
  - Acid C increased yield & purity
  - Acid B lowered purity

**Acid C maximizes yield & purity**

# Phase I: Crystallization Conditions Evaluation

| Solvent : PrNQ ratio | % Recovery |
|---|---|
| Original | 92 |
| Original x 1.5 | 88 |
| Original x 2.5 | 86 |

- Crystallizations completed on dry, clean PrNQ
- Original crystallization solvent used
  - Most economical of possible choices
- Same sample used for all iterations
- Even large increases did not greatly impact product recovery

# Phase II: Large Laboratory Scale Synthesis of PrNQ

- 56% Yield
  - In agreement with small scale work
- 99.9% pure PrNQ
- Completed in Holston style 18 L still
- Reaction proceeded as expected: no unusual occurrences
- Reaction and crystallization solutions analyzed for waste disposal purposes
  - No waste disposal issues identified

# Phase III: Pilot Scale Production of PrNQ

| Avg. Rxn Yield | Avg Cryst. Yield | Avg. Purity |
|---|---|---|
| 69% | 87% | 99.5% |

- ~5000 lbs. PrNQ produced
  - no surprises/issues
- PrNQ was first synthesis campaign in pilot plant
  - 50, 100 & 200 gallon reactors
  - Remote monitoring and control of reactors
  - Rated for 3,000 lbs of explosives
  - Stainless steel filter press
  - Chiller with capacity to -5 °C

# Summary

- PrNQ is of interest as a melt-pour explosive in GP bombs
  - Low sensitivity, suitable melting point for current melt-pour infrastructure
  - PrNQ may also be suitable for other explosive purposes
- Earlier work by ARL resulted in an initial PrNQ synthesis process
  - One step synthesis from inexpensive & readily available reagents
- ARL synthesis process optimized to yield a cost-effective, robust synthesis process
- Optimized process completed on pilot scale to yield 5,000+ lbs of analytically pure product

**PrNQ is a cost-effective melt-pour explosive for future applications**

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