The development of an alternative route to triaminotrinitrobenzene

J. Hanks, T. Highsmith, A. Sanderson, and S. Velarde
Acknowledgements

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• Anthony Bellamy, RMCS and Peter Golding, AWE
Why TATB Synthesis?

- Current production method produces undesirable waste
- TCB is no longer readily available
- Presence of ammonium chloride is a concern in TATB from traditional process
New TATB Synthesis objectives

• Develop a viable sustainable route to TATB
  • Reasonable cost
  • Acceptable waste streams
  • TATB meets current specifications
  • Scaleable
  • Avoids chlorides
Possible TATB routes

- Need to cleanly have 1,3,5 nitration
  - Mild conditions
  - High yield
  - Acceptable waste
  - Intermediate that can be undergo aminolysis/amination

- Aminolysis/amination should be simple
  - High yield
  - Mild conditions
  - Available aminating agent
  - Acceptable waste
**Phloroglucinol Route**

- **Phloroglucinol is ubiquitous**
  - In bark of fruit trees as glycoside derivative
  - Free form in the acacia tree and the kino gum of the eucalyptus tree
  - Worldwide, approximately 140-200 metric tons of phloroglucinol are produced each year
  - Numerous synthetic industrial routes (including demil of TNT)
- **Route developed by Bellamy, Golding and Ward**

\[ \text{NaNO}_2, \text{NaOH/ dilute HNO}_3, 5-15^\circ C/ 70\% \text{ HNO}_3, 45-50^\circ C \]

or

\[ 1.\text{Ac}_2\text{O}, \text{NaOAc, 130}^\circ \text{C 2.HNO}_3, \text{H}_2\text{SO}_4, -5^\circ \text{C} \]

\[
\begin{align*}
\text{RO} & \rightarrow \text{NO}_2 \\
\left(\text{RO}\right)_3\text{CH} & \rightarrow 85-90^\circ \text{C}
\end{align*}
\]

\[
\text{NH}_3, \text{solvent} \rightarrow \text{H}_2\text{N} \text{NO}_2, \text{NH}_2
\]
Phloroglucinol route assessment

- What is the best route and optimum conditions?
- Is route scaleable?
  - Safety
  - Processing
  - Product quality
  - Reproducibility
  - Waste
  - Cost (Materials, labour and waste disposal at production scale)
**Synthesis of TNPG**

- **Acetylation hard to scale**
  - Lower yield as scale increased
- **Extra step over nitrosation**
  - **Higher temperatures**
  - **Easy to scale**
    - Higher yields at bigger scales
- **Moderate yield**

**Phloroglucinol**

\[
\begin{align*}
&\text{Phloroglucinol} \\
\rightarrow &\text{Ac}_2\text{O/NaOAc} \\
&130^\circ\text{C} \\
\rightarrow &95\% \\
&\text{(95%)}
\end{align*}
\]

\[
\begin{align*}
&\text{HNO}_3/\text{H}_2\text{SO}_4 \\
&-5 - 0^\circ\text{C} \\
\rightarrow &90\% \\
&\text{(97%)}
\end{align*}
\]

**Steps**

1. \(\text{NaNO}_2, \text{NaOH}\)
2. dilute \(\text{HNO}_3, 5\text{-}15^\circ\text{C}\)
3. \(70\% \text{ HNO}_3, 45\text{-}50^\circ\text{C}\)

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&-5 - 0^\circ\text{C} \\
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&\text{(97%)}
\end{align*}
\]
• Reasonable exotherms
• Addition rate controls heat evolution
• Easily controllable in 1700l reactor
Synthesis of TETNB

- Used triethylorthoformate due to cost
- Maximized reaction concentrations
- Increased isolated yield

\[
\text{Reaction: } \text{OEt} \quad \text{C}_2\text{H}_5\text{O} \quad 85-90^\circ\text{C} \quad 95\% \quad (90\%)
\]
Reaction Calorimetry Data for Alkylation

- Not exothermic reaction
- Very exothermic crystallization
  - Needs to be controlled for viable scale-up
Safety Data of Intermediates

- No special hazards
- TNPG is very acidic

<table>
<thead>
<tr>
<th></th>
<th>TNPG</th>
<th>TETNB</th>
<th>Acceptable limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABL impact (cm)</td>
<td>13</td>
<td>51</td>
<td>≥3.5</td>
</tr>
<tr>
<td>ABL friction (lbs @ ft/s)</td>
<td>800 @ 8</td>
<td>800 @ 8</td>
<td>=50 @ 3</td>
</tr>
<tr>
<td>DSC onset/peak (°C)</td>
<td>219/223</td>
<td>307/318</td>
<td>--</td>
</tr>
<tr>
<td>VTS, 100°C, 48 h (ml gas/g substrate)</td>
<td>0.189</td>
<td>0.450</td>
<td>&lt;2.0</td>
</tr>
<tr>
<td>TC ESD unconfined (J)</td>
<td>8, no mass ignition</td>
<td>0.6, no mass ignition</td>
<td>no mass ignition</td>
</tr>
<tr>
<td>TC impact (in)</td>
<td>27.7</td>
<td>45</td>
<td>&gt;4</td>
</tr>
<tr>
<td>TC friction (lbs)</td>
<td>&gt;64</td>
<td>&gt;64</td>
<td>&gt;10</td>
</tr>
<tr>
<td>SBAT onset (°F)</td>
<td>297</td>
<td>391</td>
<td>&gt;225</td>
</tr>
<tr>
<td>Russian deflagration-to-detonation (500 psi)</td>
<td>GO</td>
<td>NO GO</td>
<td>NO GO</td>
</tr>
<tr>
<td>IHE mini-card gap (zero cards)</td>
<td>GO</td>
<td>NO GO</td>
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</tr>
</tbody>
</table>
# Aminolysis Results

<table>
<thead>
<tr>
<th>Solvent System</th>
<th>Particle Size-Micron (10%, 50%, 90%)</th>
<th>Temperature (°C)</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>1.9, 5.5, 11.4</td>
<td>-5</td>
<td>97.8</td>
</tr>
<tr>
<td>EtOH</td>
<td>3.9, 8.2, 13.8</td>
<td>-5</td>
<td>98</td>
</tr>
<tr>
<td>DMF</td>
<td>1.8, 8.8, 20.0</td>
<td>-5</td>
<td>99.1</td>
</tr>
<tr>
<td>EtOH/DMSO (2/1)</td>
<td>4.5, 9.6, 15.8</td>
<td>0</td>
<td>99.4</td>
</tr>
<tr>
<td>i-PrOH</td>
<td>4.7, 15.6, 28.8</td>
<td>-5</td>
<td>99.1</td>
</tr>
<tr>
<td>Dimethoxydiethylether</td>
<td>6.1, 12.0, 19.8</td>
<td>-5</td>
<td>97.5</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>4.1, 14.6, 35.9</td>
<td>-5</td>
<td>97.8</td>
</tr>
<tr>
<td>Pyridine</td>
<td>4.9, 13.7, 25.1</td>
<td>-7</td>
<td>99</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>8.8, 22.9, 45.4</td>
<td>-5</td>
<td>99.8</td>
</tr>
<tr>
<td>Toluene</td>
<td>16.6, 30.4, 53.0</td>
<td>-5</td>
<td>95.3</td>
</tr>
<tr>
<td>Navy TATB (Included for comparison)</td>
<td>26.0, 62.6, 114.5</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

- Bubbled ammonia into reaction solution
- Simple and reproducible
**TATB Analysis**

- Analysis (purity) is difficult due to TATB insolubility
- Quantitative HPLC method developed but needs standard

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<td>&lt;2</td>
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<td>0.8, no mass ignition</td>
<td>2.66, no mass ignition (at 8 J)</td>
<td>no mass ignition (at 8 J)</td>
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<td>TC impact (in)</td>
<td>&gt;46</td>
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TATB Processing

- Made moulding powder
- Processed and safety properties as standard TATB
Conclusions

- Synthesis of TATB from phloroglucinol as described by Bellamy et al has been found to be reproducible and scaleable
- Each step has been run under different conditions multiple times at the 500g to 1kg scale and high purity material obtained
- Reagents are all readily available and of reasonable cost
- Significant reaction optimization has been completed
- There appear to be few reaction scale issues that would prevent this chemistry from being further scaled up