Preparation of Common Nitrate Esters by Mild Nitration of Polyols

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Outline

• Background

• Targeted Nitrate Esters

• Synthesis Optimization and Results

• Summary
Nitrate esters are common explosives widely used in both commercial and military applications – typically as plasticizers.

Nitroglycerine (NG) was first discovered in 1846 by Italian chemist Ascanio Sobrero who warned against using it as an explosive due to sensitivity issues.

Alfred Nobel developed useful NG based explosives after discovering that it can be absorbed onto porous materials.

The high oxygen content of the $\text{NO}_3$ group offers easily overoxidized potential. Nitrate esters can be mixed with carbonaceous (oxygen deficient) explosives like nitrocellulose.

Facile preparation by nitration of alcohols.

Nitrate Ester Applications

General Nitrate Ester Usage
• Widely used in production of gun propellants, rocket propellants, and explosives
• These materials provide the ability to manipulate key formulation parameters:
  ➢ Density
  ➢ Oxygen balance
  ➢ Sensitivity
• Techniques and procedures have been developed allowing nitrate esters to be safely processed and handled

Examples

PETN
• Most stable and least reactive of the common nitrate ester explosives
• Mixed with phlegmatizers for use in detonation cord
• Can be mixed with synthetic polymers to form PBXs
• Pentolite = 1:1 PETN and TNT; used as a military explosive and in booster charges

TMETN, TEGDN, BTTN
• Investigated near the time of NG discovery for use as a freezing point depressant and desensitizer for NG.
Synthetic Targets

Triethylene Glycol Dinitrate (TEGDN)

O₂NO₃O-ONO₂

Pentaerythritol Tetranitrate (PETN)

O₂NO₃O-ONO₂

Diglycerol Tetranitrate (DGTN)

O₂NO₃O-ONO₂

1,1,1-(Trimethylol)ethane Trinitrate (TMETN)

O₂NO₃O-ONO₂

1,2,4-Butanetriol Trinitrate (BTTN)

O₂NO₃O-ONO₂

Nitroglycerin (NG)

O₂NO₃O-ONO₂
Nitration Conditions - Generalizations

**Drawbacks**

- Strongly acidic
- Oxidizing
- Selectivity
- Exothermic
  - Thermal runaway
  - Explosions
- *Product separation – Hazardous waste streams*

**Countermeasures**

- Remote operations
- Strict control
- Elaborate equipment
- Blast/explosion proof shielding and buildings
- Multiple extractions and washings

Albright, L. F.; Hanson, C. *Industrial and Laboratory Nitrations* (ACS Symposium Series 22); American Chemical Society: Washington, DC, 1976; (a) Ross, D. S.; Kirshen, N. A. Chapter 7, 114–131; (b) Hanson, C.; Kaghazchi, T.; Pratt, M. W. T. Chapter 8, 132–155; (c) Deno, N. C. Chapter 9, 156–159.
Nitration Considerations

Nitration

Solubility

Undernitration

Overnitration

Oxidation

Decomposition

Separation

Purification

Waste Stream

Isolation

Recycle

Disposal

Explosion
Typical O-Nitrating Agents

Nitric Acid (HNO₃)
- Fuming (86-95% HNO₃)
- Commercial (68-70% HNO₃)

Mixed Acid (H₂SO₄/HNO₃)
- Mixed acid/CH₂Cl₂

Nitric Acid/Acetic Anhydride

N₂O₄
R−OH + N₂O₄ → R−ONO₂ + HNO₂
R−O⁻Na⁺ + N₂O₄ → R−ONO₂ + NaNO₂

N₂O₅
R−OH + N₂O₅ → R−ONO₂ + HNO₃

Many others....

Mild Nitrating Mixture – Nitrate Salt/$\text{H}_2\text{SO}_4$

\[
\begin{align*}
\text{XNO}_3 &\xrightarrow{\text{H}_2\text{SO}_4} \text{HNO}_3 + \text{XHSO}_4 & \xleftarrow{\text{H}_2\text{SO}_4} \text{NO}_2^+ + \text{H}_2\text{O} + \text{HSO}_4^- \\
\text{X} &= \text{K}^+, \text{Na}^+, \text{NH}_4^+ \\
\end{align*}
\]

**Advantages Over Mixed Acid**

- Nitrate salts are stable with long shelf lives
- Nitrate salts are less hazardous than $\text{HNO}_3$
- Mild exotherm of mixing nitrate salts with $\text{H}_2\text{SO}_4$
- Simple stoichiometric control of $\text{NO}_2^+$ group
- Limits $\text{NO}_x$ vapors
- Partial neutralization of $\text{H}_2\text{SO}_4$ in the nitration process
- Limits the amount of nitric acid in the waste stream
  - Limits the amount of nitrate esters in the waste stream
Triethylene Glycol Dinitrate (TEGDN)

\[
\text{HO-} \quad \text{O-} \quad \text{O-} \quad \text{OH} \quad + \quad 4 \text{NH}_4\text{NO}_3 \quad \xrightarrow{\text{H}_2\text{SO}_4} \quad \text{2 h ambient} \quad \text{O}_2\text{NO-} \quad \text{O-} \quad \text{O-} \quad \text{ONOO}_2
\]

Triethylene Glycol Dinitrate (TEGDN)
64% yield

98% TEGDN

2%
Pentaerythritol Tetranitrate (PETN)

\[
\text{Pentaerythritol} + 8 \text{NH}_4\text{NO}_3 \xrightarrow{\text{H}_2\text{SO}_4, 2 \text{h}} \text{ambient} \Rightarrow \text{Pentaerythritol Tetranitrate (PETN)}
\]

62% yield

94% PETN
Diglycerol Tetranitrate (DGTN)

\[
\text{HO} \overset{\text{OH}}{\text{O}} \overset{\text{OH}}{\text{O}} \overset{\text{OH}}{\text{O}} \overset{\text{OH}}{\text{O}} + 8 \text{NH}_4\text{NO}_3 \xrightarrow{\text{H}_2\text{SO}_4 \text{ ambient}} \text{O}_2\text{NO} \overset{\text{ONO}_2}{\text{O}} \overset{\text{ONO}_2}{\text{O}} \overset{\text{ONO}_2}{\text{O}} \overset{\text{ONO}_2}{\text{O}}
\]

Diglycerol

Diglycerol Tetranitrate (DGTN)
(56% yield)

Graph: Response Units vs. Acquisition Time (min)
- 96% DGTN
- 2.5%
- 1.5%
1,1,1-Tris(methylol)ethane Trinitrate (TMETN)

Trimethylol Ethane

\[
\text{HO-} \quad \text{OH} \quad + \quad 6 \text{NH}_4\text{NO}_3 \quad \xrightarrow{\text{H}_2\text{SO}_4} \quad 4 \text{ h} \quad 0 \degree \text{C} \quad \text{O}_2\text{NO}_2\text{ONOO}_2
\]

1,1,1-Tris(methylol) Ethane Trinitrate (TMETN) 51% yield

93% TMETN

7%
1,2,4-Butanetriol Trinitrate (BTTN)

\[
\text{HO} - \xrightarrow{\text{H}_2\text{SO}_4 \text{ ambient}} \xrightarrow{3 \text{ h}} \text{ONO}_2 - \xrightarrow{6 \text{ NH}_4\text{NO}_3} \text{OH} \\
1,2,4-\text{Butanetriol} + 6 \text{NH}_4\text{NO}_3 \rightarrow 1,2,4-\text{Butanetriol Trinitrate (BTTN)} \ (80\% \text{ yield})
\]

Graph showing the response units vs. acquisition time (min) with peaks at 4.952 and 6.118 minutes, indicating 97% BTTN and 3% other compounds.
Nitroglycerine (NG)

\[
\text{HO-\hspace{0.5cm}OH-\hspace{0.5cm}OH} + 6 \text{NH}_4\text{NO}_3 \xrightarrow{\text{H}_2\text{SO}_4, \text{3 h ambient}} \text{O}_2\text{NO-\hspace{0.5cm}ONOO}_2
\]

Glycerin

Nitroglycerin (NG) (96% yield)
Summary

- 6 Common nitrate esters prepared by mild nitration method

- Preliminary results suggest that nitrate salt/H$_2$SO$_4$ is:
  - Equally effective as mixed acid
  - Less hazardous than mixed acid
  - More controllable than mixed acid
  - Practical for lab- or large-scale batch synthesis of nitrate esters
  - Potentially adaptable to continuous processing
  - Worthy of additional investigation as nitrating agent for other energetic materials

<table>
<thead>
<tr>
<th>Nitrate Ester</th>
<th>Crude % Yield (unoptimized)</th>
<th>% Purity (HPLC/UV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEGDN</td>
<td>64</td>
<td>98</td>
</tr>
<tr>
<td>PETN</td>
<td>62</td>
<td>94</td>
</tr>
<tr>
<td>DGTN</td>
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<td>96</td>
</tr>
<tr>
<td>TMETN</td>
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<td>93</td>
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<tr>
<td>BTTN</td>
<td>80</td>
<td>97</td>
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<tr>
<td>NG</td>
<td>96</td>
<td>96</td>
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