

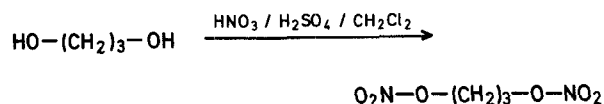
A Low Hazard Procedure for the Laboratory Preparation of Polynitrate Esters

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We would like to report a convenient, low hazard procedure for the laboratory preparation of nitrate esters of polyols. This method provides product in high yield and of analytical purity without resorting to physical methods of purification. This procedure has been utilized to prepare from 24 g up to 450 g of nitrate ester. Our method involves the nitration of the polyol with mixed nitric-sulfuric acid in the presence of dichloromethane. The reaction conditions are monitored by an Ingold Type 488 redox potential probe¹.

Dichloromethane solvent is present in these reactions primarily to reduce the safety hazards associated with the preparation and the products. This is done in three ways: (a) the solvent decreases the impact sensitivity of the nitrate ester; (b) it removes the nitrate ester from the nitration medium so that side reactions are minimized; and (c) it serves as a heat sink in case of too rapid heat generation.



The Ingold redox probe is present in the nitrating acid to monitor the nitrite ion formation, which could generate unstable nitrite esters. The theoretical aspects of the utilization of these probes in the nitroglycerine manufacturing process have been described by Öhman². The nitrite anion can be minimized by starting with pure polyol and can be kept at a reduced level by using the probe to control the addition rate of the polyol. The polyol is added to the nitrating acid at a rate which keeps the potential nearly

constant. In a typical addition, the initial probe reading will be near -0.01 volt and when the addition is complete the potential should be near -0.07 volt, with a temperature near 20° . If the potential nears -0.20 volt the reaction may be out of control and at -0.35 volt it may undergo rapid and violent decomposition³.

An additional procedure required to reduce the nitrite anion concentration involves the careful preparation of the nitrating acid solution. This is easily achieved by the slow addition of freshly prepared anhydrous nitric acid to an equal volume of cooled fuming sulfuric acid while maintaining a constant temperature. The nitrite concentration of this nitrating acid is determined by a permanganate titration technique⁴. The initial value should be near 0.016%, as nitrous acid and this material should no longer be used for nitration after the nitrous acid concentration reaches 0.05%.

With the use of these techniques on a laboratory scale, several polynitrate esters could be easily prepared (see Table) with the minimum of hazard and in high yield and purity. The additional advantages of this method, as previously mentioned, include desensitization of the product by diluting in the solvent, maintaining stable reaction conditions with the redox probe, and the avoidance of unstable side products such as nitrite esters.

CAUTION: These nitrate esters should be prepared behind safety shields in an isolated laboratory, since the products are highly explosive materials. As a further safety precaution to minimize transfer of hazardous materials and to maintain temperature control, we recommend the use of a jacketed, three-neck flask with a bottom discharge, Teflon stopcock. All glass to glass joints should be Teflon tape wrapped. All washings should be done in the reaction flask. Experience with these reactions should be gained on a small scale before attempting them on a larger scale. The following procedure is typical.

Table. Nitration of Polyols

Polyol	Yield ^a [%]	m.p.	Lit. m.p.	Refractive Index $n_D^{22.5}$	Lit. Refractive Index $n_D^{21.5}$	Molecular formula ^c
$\text{HO}-\text{CH}_2-\overset{\text{OH}}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{OH}$	90	—	—	1.4725	1.4725 ^b	$\text{C}_3\text{H}_5\text{N}_3\text{O}_9$ (227.1)
$\text{HO}-\text{CH}_2-\overset{\text{HO}}{\underset{ }{\text{CH}}}-\overset{\text{OH}}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{OH}$	89	59–60.5°	61° ^d	—	—	$\text{C}_3\text{H}_4\text{N}_4\text{O}_{12}$ (288.1)
$\text{HO}-\text{CH}_2-\overset{\text{OH}}{\underset{ }{\text{CH}}}_2-\overset{\text{OH}}{\underset{ }{\text{CH}}}_2-\text{CH}_2-\text{OH}$	23 ^{e,f}	112–113° ^f	112–113° ^g	—	—	$\text{C}_6\text{H}_8\text{N}_6\text{O}_{18}$ (452.2)
$(\text{HO}-\text{CH}_2-\text{CH}_2)_2\text{O}$	69	—	—	1.4503	1.4505 ^b	$\text{C}_4\text{H}_8\text{N}_2\text{O}_7$ (196.1)
$\text{HO}-(\text{CH}_2)_3-\text{OH}$	86	—	—	1.4482	1.4483 ^b	$\text{C}_3\text{H}_6\text{N}_2\text{O}_6$ (166.1)

^a The I.R. spectra of the product nitrate esters are identical to those of authentic samples.

^b Ref. 5, page 3.

^c All products gave satisfactory nitrogen analyses ($\text{N} \pm 0.07\%$); values were determined on samples as isolated by removing reaction solvent under reduced pressure.

^d Ref. 5, page 166.

^e For safety reasons, considerable material was discarded since the mannitol hexanitrate was insoluble in the dichloromethane.

^f Mannitol hexanitrate was recrystallized from ethanol before determination of nitrogen analysis.

^g Ref. 5, page 169.

Preparation of 1,3-Propanediol Dinitrate:

The nitrating acid is prepared by slowly adding freshly prepared anhydrous nitric acid (200 ml, 4.86 mol) to fuming sulfuric acid (200 ml) while stirring and maintaining a temperature of less than 15°. After the addition of distilled dichloromethane (1,500 ml) the mixture is cooled to 12° and the initial potential reading of the Ingold Type 488 redox probe is 0.006 volt. The 1,3-propanediol (76.0 g, 1.00 mol) is slowly added to the stirred nitrating mixture at a rate which will keep the potential as steady as possible with a temperature less than 12°. After the 1,3-propanediol addition is completed, the redox potential is -0.045 volt at 10°. The spent acid is immediately removed through the bottom discharge stopcock and the dichloromethane phase is washed in the reaction flask with water (500 ml \times 1), 10% aqueous sodium carbonate solution (400 ml \times 3), 10% aqueous urea solution (500 ml \times 1), and water (500 ml \times 3). This organic phase is dried over anhydrous sodium sulfate followed by 4-A molecular sieves. The solvent is removed under reduced pressure to give the 1,3-propanediol dinitrate: yield: 144.0 g (86%).

$C_3H_6N_2O_6$	calc.	N 16.86
(166.1)	found	16.79

I.R. (neat): $\nu_{\max} = 2990, 2905, 1640, 1288 \text{ cm}^{-1}$.

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- ¹ These redox probes are available from Chemapec, Inc. Hoboken, New Jersey.
- ² V. Öhman, *Sven. Kem. Tidskr.* **78**, 20 (1966) and references cited therein. To our knowledge utilization of these probes on a laboratory scale and with polyols other than glycerine and diethylene glycol has not been reported.
- ³ P. Mosher and W. O. Brimijoin, Naval Ordnance Station, Indian Head, Maryland: personal communication.
- ⁴ I. M. Kolthoff, E. B. Sandell, E. J. Meehan, S. Brukenstein, *Quantitative Chemical Analysis*, 4th Edit., The Macmillan Company, 1969, p. 834.
- ⁵ T. Urbański, *Chemistry and Technology of Explosives*, Pergamon Press, Oxford, 1965.