

Preparation of Di- and Polynitrates by Ring-Opening Nitration of Epoxides by Dinitrogen Pentoxide (N_2O_5)¹

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Abstract: Eighteen epoxides of various kinds were reacted with N_2O_5 in chlorinated hydrocarbon solvents (principally CH_2Cl_2) to give vicinal nitrate ester products by a novel ring-opening nitration reaction. The procedure offers easier temperature control and simpler isolation procedures compared with conventional mixed acid nitrations; it also enables selective nitration reactions to be carried out on polyfunctional substrates. The scope and limitations of the reaction, as well as those of an alternative route utilising N_2O_4 with *in situ* oxidation of an intermediate nitrite-nitrate, are discussed.

INTRODUCTION

The chemistry of nitrate esters (I), also known in the older literature as nitric esters or nitratoalkanes, has been reviewed³. They are an important family of compounds, finding applications, particularly when derived from polyols, in tonnage quantities in the field of military explosives and propellants as well as commercial explosives, but some, particularly nitroglycerine, are also used medicinally as vasodilators⁴. Other nitrate esters derived from sugars find use as intermediates in the synthesis of functional saccharides⁵.



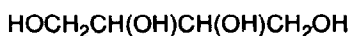
I

Nitrate esters are usually prepared from the corresponding alcohols by reaction with common nitrating agents such as mixtures of nitric acid with sulphuric acid, nitric acid with acetic anhydride, or pure nitric acid alone³. Routes of lesser importance using the action of more exotic nitrating agents on alcohol or alkyl halide precursors have been mentioned previously⁶ but are not regarded as suitable for large scale application. Therefore only the routes from alcohols, using conventional nitrating agents, will now be considered further.

Such methods suffer from several shortcomings. In the first instance the range of nitrate ester products which can be prepared is limited by the availability of suitable alcohols; this can be a problem with many polyols, particularly those derived from alkenes with chain length ≥ 4 , for instance erythritol (II) is a compound not commercially exploited owing to its scarcity, being extracted from certain seaweeds⁷. Secondly, nitrations using mixed acids or pure nitric acid are generally exothermic reactions, normally being carried out by adding the neat substrate to the nitrating medium. On commercial scale these frequently require

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special precautions to prevent thermal runaway, namely elaborate design of reactors to promote sufficient cooling, with remote handling and blastproof buildings to ensure adequate operator protection⁸. Product separation is often a problem due to contamination of the organic product by residual acid, and this necessitates additional clean-up steps to ensure stability of the product on storage. Conversely, the contamination of the spent acid stream by the polynitrate gives rise to stability problems in this medium also. Thus additional plant is required to remove the organic contaminants, usually by oxidation, so that the acid can be recycled. Lastly, the conventional nitration reaction is a relatively unselective reaction, such that the use of polyfunctional substrates frequently results in attack at undesired positions on the molecule, leading to problems during product separation and purification.

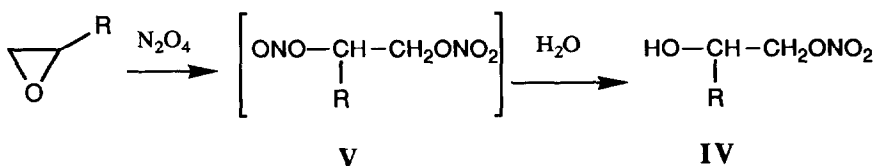


II



III

We sought a method of preparing polynitrates which would overcome many, if not all, of these drawbacks, and decided that a milder nitrating medium would offer many advantages. To this end, we surveyed the chemistry of the higher nitrogen oxides, N_2O_4 and N_2O_5 , which would offer mild, non-acidic nitrating media when dissolved in inert organic solvents, principally chlorinated hydrocarbons such as dichloromethane or chloroform⁹. Such reagents, particularly N_2O_4 , have only weak nitrating ability under these conditions¹⁰, and this, coupled with the problem of availability of polyols mentioned earlier, suggested that a switch to more reactive substrates would be advantageous. To this end, epoxides (alkene oxides, III) were investigated as substrates, and it was learned from the literature that nitrated products had been isolated from the reaction of ethylene oxide and propylene oxide with N_2O_4 (Eqn 1)¹¹. [In fact the product was originally erroneously described as 2-nitroethanol.] Hence the reaction of strained-ring heterocycles with oxides of nitrogen appeared to offer a route to nitrate ester products which could be worth exploiting, and further studies to this end are described below.



V

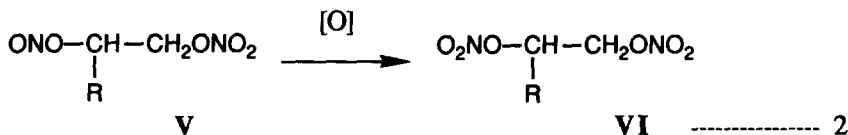
IV

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RESULTS AND DISCUSSION

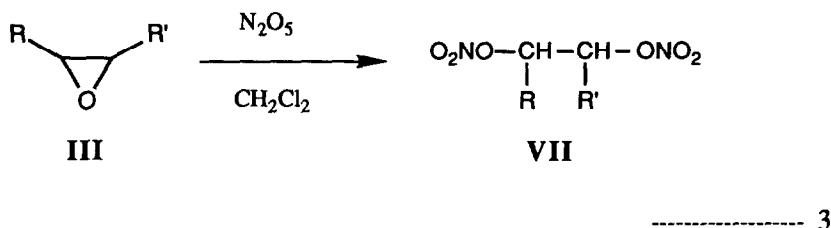
General

We considered employing the N_2O_4 -epoxide reaction (Eqn 1) as a route to our desired products, vicinal (1,2-) dinitrates, in two possible sequences: i) by nitration in a separate step of the hydroxy-nitrate (IV) isolated from the reaction shown in Eqn 1, or ii) by *in situ* oxidation of the unstable nitrite-nitrate (V) by a suitable oxidising agent to give the dinitrate (VI) as isolated product (Eqn 2). The first route was felt to be too



inconvenient, involving additional unnecessary manipulation of reagents and intermediates, and so attention was focused on the second route. Investigation of various oxidising agents showed ozone to be the most convenient for this purpose, but it was felt that this reagent was of limited value owing to its highly reactive nature and its incompatibility with many functional groups; such a methodology would therefore not provide the selectivity we had sought.

With this knowledge of the behaviour of N_2O_4 , we wondered if it might be possible to effect the functions of ring cleavage and oxidation using a single reagent, and N_2O_5 , the next higher oxide of nitrogen, appeared a likely candidate. We discovered that the reaction of many simple epoxides (III) with N_2O_5 did indeed lead to the formation of the corresponding dinitrates (VII) in excellent (>90%) yield in one step (Eqn 3; also see Table):



It was found advantageous to add the epoxide (as a solution in CH_2Cl_2) to the N_2O_5 solution and not vice-versa, in order to suppress undesired oligomer formation by cationic ring-opening polymerisation of the epoxide induced by traces of acid¹². With the simple (mono- and dialkyl) epoxides this is not a problem, but with some more complex substrates yields were somewhat reduced (see below).


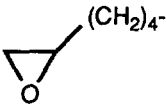
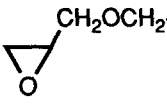
The procedure offers advantages compared with conventional nitrations since the reaction in Eqn 3 is a new type of nitration reaction, namely an addition nitration reaction where the whole N_2O_5 molecule is incorporated into the product. This compares favourably with a conventional substitutive nitration (such as the generation of a nitrate ester by attack of N_2O_5 on an alcohol, which releases one mol of HNO_3) in the following ways:- firstly, the whole of the nitrating agent is consumed in the reaction, thus minimising work-up since no acidic by-products are formed - in fact simple evaporation of solvent is often sufficient for product isolation, and secondly, this absence of acidic by-products results in the reaction being much less exothermic than normal nitration reactions, where the exotherm is believed to result largely from the heat of solution of the nitric acid evolved. Thus two of the problems of conventional nitrations - temperature control and disposal of waste acid - are solved at a stroke.

Before discussing the chemistry of particular substrates in more detail, it should be mentioned that N_2O_5 , far from being an exotic reagent, is in reality easily preparable from cheap precursors in high purity. It is essential that the purity be as high as possible, particularly with respect to nitric acid content, in order to suppress the undesired oligomerisation reactions mentioned above. Thus the commonly-employed¹³ dehydration reactions of nitric acid using P_2O_5 or acid anhydrides were avoided during the present work. Attention was instead concentrated on perfecting the gas phase oxidation¹⁴ of N_2O_4 , a readily available material,

Table: Reactions of Epoxides with N₂O₅

Entry	Heterocycle		Mol N ₂ O ₅ : substrate	Reaction time (min.)	Temp. °C	Yield %*	Ref.**	
A. Monoepoxides (III)								
	R	R'						
<i>i) Alkyl & cycloalkyl epoxides</i>								
1	a	H	H	1.1:1	5	10 to 15	96	3b
2	b	Me	H	1.1:1	5	10 to 15	96	3b
3	c	Me	Me	1.1:1	5	15 to 20	94	3b
4	d	Et	H	1.1:1	5	15 to 20	96	28
5	e	Et	Me	1.1:1	10	0 to 5	90	30
6	f	Et	Et	1.1:1	5	15 to 20	91	24
7	g	-(CH ₂) ₃ -		1.1:1	12	10±2	89	-
8	h	-(CH ₂) ₄ -		1.1:1	5	15 to 20	93	24
9	i	-(CH ₂) ₆ -		1.1:1	15	12±4	†	-
<i>ii) Epoxides bearing other functional groups</i>								
10	j	Ph	H	1.1:1	15	-5 to 5	96	22
11	k	Ph	Ph	1.1:1	15	-5 to 5	94	29a
12	l	CH ₂ OH	H	3.0:1	240	0 to 10	73	3b
13a	m	CH ₂ Cl	H	1.1:1	4 hr	10 to 15	38	3b
13b		"	"	1.1:1	60 hr	5	85	"

Table: Reactions of Epoxides with N_2O_5 (continued)

Entry	Heterocycle	Mol N_2O_5 : substrate	Reaction time (min.)	Temp. °C	Yield %*	Ref.**		
A. <u>Monoepoxides</u> ; ii) <i>Epoxides bearing other functional groups (contd.)</i> (III)								
	R	R'						
14	n	Bu ⁿ O	H	1.1:1	16 hr	0 to 5	74	33
15	o	Bu ^o O	H	1.1:1	16 hr	0 to 5	77	-
B. <u>Polyepoxides</u> (III)								
16	p		H	3.0:1	270	0 to 10	55	3b
17	q		H	2.2:1	30	10±2	91	-
18	r		H	2.15:1	270	5 to 15	31	25

* Entries 1- 8, 10-11 & 13-15: 1,2-dinitrates (VIIa-h & VIIj-o), R & R' as shown above;

Entry 12: trinitrate (VIII, nitroglycerine);

Entries 16-18: tetranitrates (VIIp-r), R & R' as shown above.

** I.e. literature where preparation by *other* route(s) of product in question is reported.

† Entry 9: 1,4-dinitrate (VIII; transannular reaction product) isolated in 77% yield.

Notes

i) All products were identical to authentic samples prepared by nitration of the corresponding polyols, where available (see text).

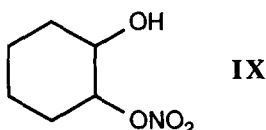
ii) All yields are isolated yields, after chromatographic purification, where necessary.

iii) Entries 12 & 16: anhydrous aluminium chloride (1 mol) was also added as catalyst.

using ozone, a reagent available on industrial scale. With suitable apparatus, solid N_2O_5 could be prepared in quantity and with essentially 100% purity, as evinced by its melting point, which was some 20 to 30°C higher than figures previously reported¹³. The reagent thus obtained could be stored for several months below -60°C without noticeable loss of purity.

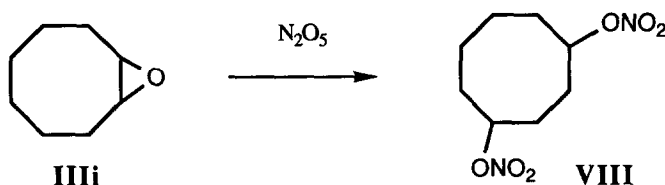
Alkyl and cycloalkyl epoxides

Nine mono- or dialkyl epoxides, including ethylene oxide itself, were studied (see Table) and, in all cases but one, the corresponding 1,2-dinitrates were obtained in high yield with only traces, if any, of oligomeric by-products, observed mainly with the terminal epoxides and ethylene oxide. The exception was cyclooctene oxide (**IIIi**), which yielded the 1,4-dinitrate (**VIII**), behaviour which will be commented upon below. Internal epoxides yielded relatively uncontaminated products, and in one instance, that of cyclohexene oxide, the cleanliness and quantitative nature of the reaction lent itself as a method for the chemical assay of N_2O_5 , since any nitric acid contaminant would yield the mononitrate (**IX**), which was readily monitored by GC. It is



notable also that the two dinitrates with chain length greater than four (entries 5 & 6 in table) would be accessible only with difficulty by conventional nitration routes, since none of the corresponding vicinal diols is commercially available. Moreover, preparation of the diols is more difficult than the epoxides, which can be generated by the facile epoxidation of the corresponding alkene (see experimental). Thus the novel nitration reaction offers further advantages with these substrates.

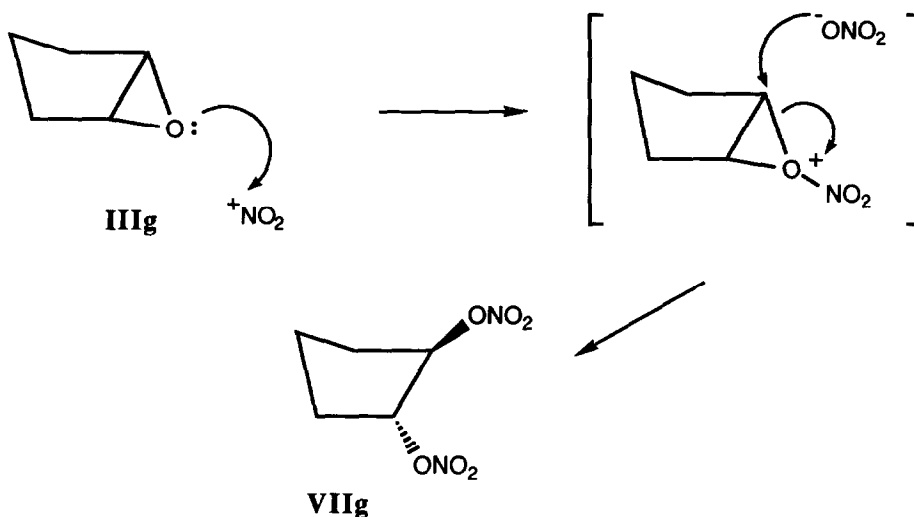
Before turning to functional epoxides, the behaviour of two cycloalkyl epoxides towards N_2O_5 requires explanation in more detail. Firstly, cyclooctene oxide (**IIIi**), as mentioned above, yielded the isomeric nitration product, cyclooctane-1,4-diol dinitrate (**VIII**, see Eqn 4). Such behaviour illustrates the propensity of large-



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ring (8-membered ring) compounds to undergo transannular reactions, and rearrangements in related systems under acid conditions have been well documented¹⁵; thus the formation of the 1,4- isomeric product in this reaction is hardly surprising. More interesting, however, was the reaction of cyclopentene oxide (**IIIg**) with N_2O_5 , where the product, cyclopentane-1,2-diol dinitrate (**VIIIg**) was found to consist almost entirely of the *trans*-isomer, by comparison with authentic samples (by hplc, i.r. and nmr). The formation of this product suggests that the reaction proceeds by a stepwise process via ionic intermediates with nitronium ion as the attacking species, along the lines shown in Scheme 1, rather than a radical pathway, which would be expected to yield the *cis*-isomer¹⁶. Such behaviour, on reflection, is not unexpected, given the strong propensity of

N_2O_5 to dissociate ionically and such dissociation under the influence of the polar epoxy group is readily explicable. It is hoped to present more detailed studies of N_2O_5 -epoxide mechanisms in future publications.



Scheme 1

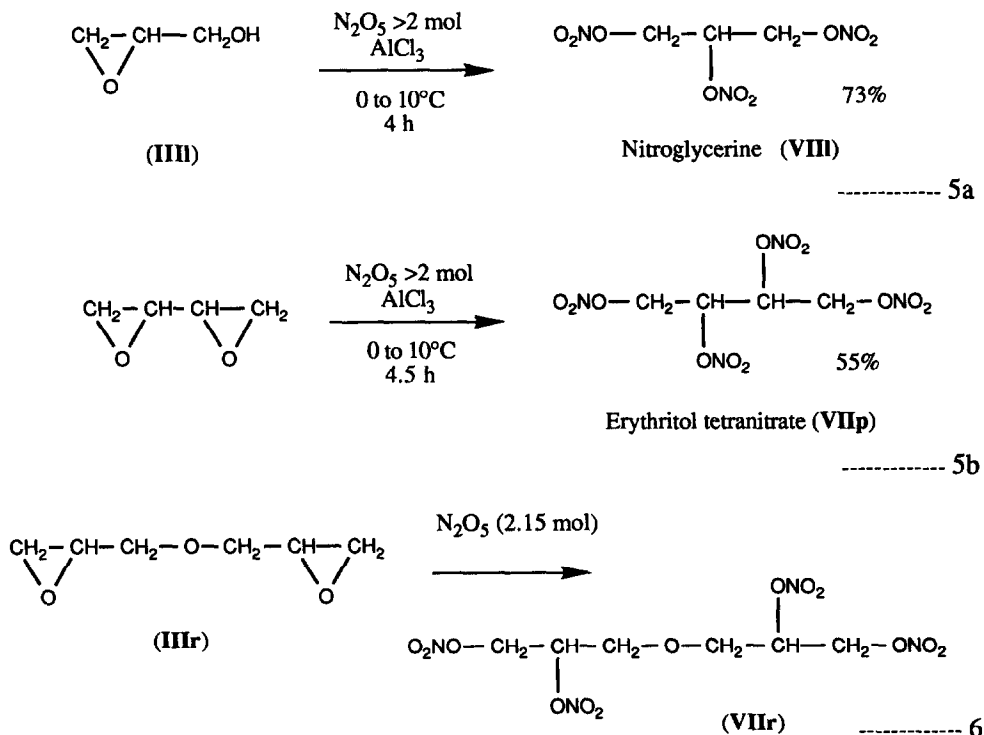
Epoxides bearing other functional groups and polyepoxides

Turning to the functional epoxides (entries 10 - 15) and polyepoxides (entries 16 - 18), in the case of the two aryl derivatives, styrene oxide and stilbene oxide, a further facet of the N_2O_5 ring opening nitration is seen, namely its selectivity, because in neither case was any aromatic nitration observed, as evinced primarily from the nmr spectrum of the products. The synthesis of the dinitrate derived from styrene oxide (**VIIj**) has only recently been reported²² (by a different route), evidently due to the non-availability of the diol and the lack of a selective nitration methodology.

Moving on to the epoxides bearing oxygen functions (entries 12, 14-16 & 18), a marked reduction in the reactivity of the epoxide function towards ring-opening nitration was observed, (with glycidol after initial rapid nitration of the hydroxyl group), with a concomitant increase in the propensity of the system to undergo oligomerisation reactions. Thus in the cases of glycidol (**IIIi**) and butadiene diepoxide (**IIIp**), it was necessary to enhance the reactivity of the N_2O_5 by introduction of an equivalent amount of a Lewis acid catalyst, $AlCl_3$. This resulted in optimum yields of the tri- and tetranitrates nitroglycerine (**VIII**) and erythritol tetranitrate (**VIIp**), of 73 and 55% respectively (Eqns 5a & 5b). By contrast, the non-glycidic diepoxide 1,2,7,8-diepoxyoctane (**IIIq**) gave a high (91%) yield of tetranitrate (**VIIq**), presumably because the separation of the epoxy functions by four methylene groups minimises neighbouring group interactions.

The other glycidic compounds (entries 14, 15 & 18) showed similar sluggishness to that encountered with **IIIi** and **IIIp**, although the alkyl glycidyl ethers **IIIn** and **IIIo** gave good (74 and 77% resp.) yields of the corresponding dinitrates, albeit after prolonged reaction periods (16 hr). On the other hand, the diglycidic compound diglycidyl ether (**IIIr**) appeared to give a high crude yield of product (*ca* 80%) but on closer

examination this was found to be heavily contaminated with oligomeric material (presumably formed from acid-catalysed polymerisation reactions favoured by presence of the second epoxy group), and subsequent chromatographic purification reduced the yield of pure tetranitrate (VIIr) to 30% (Eqn. 6).



Finally, study of a chloroalkyl epoxide, epichlorohydrin (III_m), indicated deactivation comparable to that of the glycidyl ethers, presumably due to the deactivating inductive effect of the chloro substituent, although steric factors could also be operating. This was evinced by a low (38%) yield of dinitrate (VII_m) after 4 hours under the "standard" conditions, which was raised to 85% after 60 hours, and is in accord with the behaviour of other epoxides bearing functional groups.

Conclusions

Thus it has been established that the ring-opening nitration of epoxides by N₂O₅ is a general reaction, providing the corresponding di- and polynitrates cleanly and efficiently with many variously substituted epoxides, the yields being highest and the reactions most rapid with simple monoepoxides, yields exceeding 90% being attainable in many cases. However, substitution with electron-withdrawing and/or sterically bulky groups (i.e. -OH, OR, -Cl) slows down the reaction, dramatically in some cases, and hence limits the synthetic utility of the reaction. Also larger amounts of oligomeric material are found in products from the reactions of epoxides so substituted, especially with polyepoxides, despite the use of catalysts to accelerate the nitration reaction in certain cases.

The scope of the N_2O_5 -epoxide ring-opening reaction has now been investigated and some limiting constraints on the substrate structure for efficient reaction identified. It remains, however, to investigate fully the mechanism of this novel nitration reaction, which appears at least superficially to differ greatly from the vast majority of nitrations in that it is an addition reaction rather than a substitution. In particular, the extent to which the N_2O_5 molecule is polarised when it approaches a substrate molecule is believed likely to influence strongly the course of the reaction, and studies on this topic have already commenced¹⁷. A more comprehensive study of the effect of catalysis upon the reaction is also in progress, and the results of these investigations will form the subject of future publications.

EXPERIMENTAL

1. Materials and apparatus

All materials were used as received unless otherwise stated. Commercially available epoxides except for propylene oxide (**IIIb**), glycidol (**III**), cyclooctene oxide (**IIIi**) and t-butyl glycidyl ether (**IIIo**) were supplied by Aldrich Chemical Co. Ltd (reagent or gold label grade); the latter two epoxides were supplied by Fluka Chemicals Ltd. Propylene oxide (**IIIb**) and glycidol (**III**) were supplied by BDH Ltd; the former was distilled prior to use and had b.pt. 35°C/760 mm. Butadiene diepoxide (**IIIp**) was distilled before use and had b.pt. 56-58°C/25 mm). Epoxides not commercially available were prepared by epoxidation of the corresponding alkenes using meta-chloroperbenzoic acid either in dichloromethane¹⁸ or glymes¹⁹ as solvents. Diglycidyl ether (**IIIq**) was prepared by reaction of diallyl ether (Aldrich) with hypochlorous acid followed by cyclisation of the bis-chlorohydrin thus formed with base, according to the method of Wittcoff *et al*²⁰ and had b.pt. 101°C/7 mm on a Fischer "Spaltrohr" apparatus. Other starting materials were supplied as follows:- alkenes (except but-2-ene and pent-2-ene), *trans*- and *cis*-cyclopentane-1,2-diol and cyclohexane-1,2-diol from Aldrich (alkenes were gold label grade), but-2-ene and propane-, butane- and 3-chloropropane-1,2-diols from BDH (reagent grade), and pent-2-ene from Fluka Chemicals (pract. grade).

Solvents and the remaining inorganic reagents were all supplied by BDH (reagent grade) with the following exceptions: dichloromethane was hplc grade (BDH); methanol and water used in hplc separations were Fisons hplc grade; 95% ethanol was supplied by Burroughs Ltd; $CDCl_3$ by Aldrich (99.5% isotopic purity); 99% HNO_3 by Royal Ordnance plc Bridgwater. 100% HNO_3 was freshly prepared from KNO_3/H_2SO_4 ²¹, and N_2O_5 by ozonation of N_2O_4 ¹⁴; both these materials were storable for short periods at -40 to -80°C. Dichloromethane was dried by passage through a column of chromatographic silica gel (BDH), and $CDCl_3$ was allowed to stand over 4A molecular sieves (BDH) before use. All other reagents were used as received.

¹H nmr spectra were recorded on a Varian Associates EM 360A nmr spectrometer equipped with an EM 3630 homonuclear lock-decoupler operating at 60 MHz. Chemical shifts are reported in ppm downfield from the tetramethylsilane (TMS) used as internal standard. Infra-red spectral measurements were carried out using either a Nicolet 5SX Fourier transform i.r. spectrometer operating in transmittance mode and equipped with DTGS detector, 1280 data processor and Zeta 8 plotter, or a Perkin-Elmer 157G i.r. spectrometer.

Glc analyses were carried out on a Pye Unicam 204 Series gas chromatograph equipped with a flame-ionisation detector, a temperature programmer and a Spectra-Physics 4100 computing integrator. Samples were run throughout this work on a 2.4 m x 3 mm i.d. glass column packed with 2-3% OV101 on Chromosorb, and conditions were chosen to provide optimum peak sharpness and separation whilst minimising peak tailing.

Hplc separations were performed on either a Kontron 600 Series gradient system controlled by a 205 series programmer with monitoring by Uvikon 720 or Pye-Unicam PU4021 u.v. spectrophotometers, or Waters-Millipore 600 multisolvent delivery system and WISP 710B autosampler attached to the detection system mentioned above. Output was to either a Uvikon Recorder 20 or a Pye-Unicam 4850 Video Chromatography Control Centre. Columns used measured 22 cm x 5 mm with Lichrosorb 10RP18 (Merck GmbH) packings, except Lichrosorb 10RP8 was used with VII, VIIp & VIIr. All columns were supplied pre-packed by HPLC Technology Ltd, Macclesfield or Merck (UK) Ltd. Conditions were as follows:- flow rate: 1.0 ml/min.; detector wavelength: 210 nm (except with methanol-based eluant - 215 nm); column temperature: 30°C (except with methanol-based eluant: 50°C); solvent composition ratios (acetonitrile:methanol: water) and internal standards used for quantitation (where applicable) are shown in parentheses (key: DPP = di-(n-propyl) phthalate, DBP = di-(n-butyl) phthalate) - VIIg (0:67:33, DPP), VIIi (70:0:30, DBP), VIIl (60:0:40), VIIm (60:0:40, DPP), VIIn (75:0:25), VIIo (75:0:25, DBP), VIIp (60:0:40), VIIq (33:33:34, DPP) and VIIr (65:0:35, DBP).

Melting points were determined in open capillaries on a Büchi 510 apparatus using a heating rate of 3°C/min. and are uncorrected. Refractive indices were measured at 20°C against the sodium D line using an Abbe "60" refractometer (Bellingham and Stanley Ltd, UK). Density measurements were carried out at 20°C using a Paar Model 46 density meter (Anton Paar KG, Graz, Austria).

CAUTION: Many of the products described herein are explosives; all reactions utilising N₂O₅ were therefore carried out in armoured cupboards.

2. Oxidation of 1-nitroethan-2-ol nitrate (V, R = H)

A solution of the title compound in CH₂Cl₂ was prepared as follows:- Ethylene oxide (0.1 mol) in CH₂Cl₂ (20 ml) was added to a solution of N₂O₄ (0.11 mol) in the same solvent (20 ml) at 0°C; a rapid reaction occurred.

Attempted oxidation of this intermediate by treatment, in CH₂Cl₂ solution, with the following oxidising agents resulted in isolation of the hydrolysis product (ethane-1,2-diol mononitrate, IV, R = H):- chromium trioxide, potassium dichromate, potassium permanganate, sodium peroxide, sodium perborate. Passage of ozonised oxygen through the solution, however, yielded the dinitrate (VI, R = H) quantitatively, based upon examination by spectroscopy (i.r. and ¹H nmr) and GC.

3. Reactions of epoxides with N₂O₅

A dry flask of appropriate size, fitted with a thermometer and a guard tube containing anhydrous calcium chloride, was placed in a constant temperature bath and a known weight of N₂O₅ (25 to 50 ml solution in dichloromethane) was added with magnetic stirring. When the solution was at the stated temperature (Table) sufficient dichloromethane solution of the oxygen heterocycle (ca 500 mg per ml) was added over 2 to 5 mins. to achieve the stated molar ratio. The mixture was then stirred for the appropriate time, agitated with saturated sodium hydrogen carbonate solution to remove any excess acidity, and the dichloromethane layer was separated, dried over anhydrous magnesium sulphate and filtered. Removal of solvent from the filtrate under reduced pressure (temperature <30°C) gave the product, generally in the form of a viscous oil.

The di-/polynitrates were characterised spectroscopically (i.r., ^1H nmr), by measurement of physical constants (refractive index, density) and by comparison of GC (entries 1-6 & 8) or hplc (entries 7,9,12 & 14-17) retention data with authentic samples, where available (see section 4). Where authentic samples could not be prepared owing to the inaccessibility of the corresponding diols or polyols (entries 5,6,10,11 & 17) products were characterised solely by their spectra; comparison with literature data was possible in some of these cases (entries 10 & 11)²²⁻²⁴. The following compounds were thus prepared by epoxide- N_2O_5 reactions:-

3.1 *Ethylene glycol dinitrate*, **VIIa** (from ethylene oxide, **IIIa**): δ (CDCl_3) 4.8 (s) ppm [lit.²⁵ 4.83 (s) ppm]; ν_{max} 1640 ($-\text{NO}_2$ asymm.), 1270 ($-\text{NO}_2$ symm.) cm^{-1} [lit.²⁶ 1640, 1270 cm^{-1}]; Dn^{20} 1.395 [lit.²⁷ 1.395]; ρ 1.490 gcm^{-3} [lit.²⁷ 1.492 gcm^{-3}].

3.2 *Propane-1,2-diol dinitrate*, **VIIb** (from propylene oxide, **IIIb**): δ (CDCl_3) 1.8 (d,3), 4.7 (m,2), 5.4 (m,1) ppm; ν_{max} 1640 ($-\text{NO}_2$ asymm.), 1260 ($-\text{NO}_2$ symm.) cm^{-1} [lit.²⁸ 1640, 1265 cm^{-1}]; Dn^{20} 1.427 [lit.²⁷ 1.427]; ρ 1.377 gcm^{-3} [lit.²⁷ 1.37 gcm^{-3}].

3.3 *Butane-1,2-diol dinitrate*, **VIIc** (from but-1-ene oxide, **IIIc**): δ (CDCl_3) 1.4 (t,3), 2.2 (qr,2), 4.6 (m,2), 5.3 (m,1) ppm; ν_{max} 1640 ($-\text{NO}_2$ asymm.), 1270 ($-\text{NO}_2$ symm.) cm^{-1} [lit.²⁸ 1638, 1270 cm^{-1}]; Dn^{20} 1.417; ρ 1.310 gcm^{-3} .

3.4 *Butane-2,3-diol dinitrate*, **VII d** (from but-2-ene oxide, **III d**): δ (CDCl_3) 1.4 (d,6), 5.4 (m,2) ppm [lit.²⁵ 1.43 (d,6), 5.39 (m,2) ppm]; ν_{max} 1635 ($-\text{NO}_2$ asymm.), 1265 ($-\text{NO}_2$ symm.) cm^{-1} ; Dn^{20} 1.428 [lit.²⁷ 1.4275]; ρ 1.306 gcm^{-3} [lit.²⁷ 1.306 gcm^{-3}].

3.5 *Pentane-2,3-diol dinitrate*, **VII e** (from pent-2-ene oxide, **III e**): δ (CDCl_3) 0.9-1.9 (m,8), 5.2 (m,2) ppm; ν_{max} 1638 ($-\text{NO}_2$ asymm.), 1274 ($-\text{NO}_2$ symm.) cm^{-1} .

3.6 *Hexane-3,4-diol dinitrate*, **VII f** (from hex-3-ene oxide, **III f**): δ (CDCl_3) 1.1 (t,6), 2.2 (m,4), 5.25 (m,2) ppm; ν_{max} 1638 ($-\text{NO}_2$ asymm.), 1270 ($-\text{NO}_2$ symm.) cm^{-1} ; Dn^{20} 1.445; ρ 1.411 gcm^{-3} .

3.7 *Trans-Cyclopentane-1,2-diol dinitrate*, **VII g** (from cyclopentene oxide, **III g**): δ (CDCl_3) 1.7-2.4 (m,6), 5.4 (m,2) ppm; ν_{max} 1639 ($-\text{NO}_2$ asymm.), 1282 ($-\text{NO}_2$ symm.), 866, 851 ($-\text{ONO}_2$) cm^{-1} . *Trans*-isomer showed signals at 2.2, 2.35 & 2.45(w) not present in ^1H nmr of *cis*-isomer, which had ν_{max} 1643 ($-\text{NO}_2$ asymm.), 1284, 1273 ($-\text{NO}_2$ symm.), 860 ($-\text{ONO}_2$) cm^{-1} , with extra bands esp. 1140(w), 1025 (m) & 972(w) not visible in the spectrum of *trans*-isomer.

3.8 *Cyclohexane-1,2-diol dinitrate*, **VII h** (from cyclohexene oxide, **III h**): δ (CDCl_3) 2.8 (m,8), 5.1 (s,2) ppm [lit.^{29c} δ (CCl_4) 1.33-2.53 (m,8), 4.82-5.55 (m,2)]; ν_{max} 1645 ($-\text{NO}_2$ asymm.), 1265 ($-\text{NO}_2$ symm.) cm^{-1} ; Dn^{20} 1.451; ρ 1.363 gcm^{-3} .

3.9 *Cyclooctane-1,4-diol dinitrate*, **VII i** (from cyclooctene oxide, **III i**): δ (CDCl_3) 1.4-2.2 (m,12), 5.3 (s,2) ppm; ν_{max} 1624 ($-\text{NO}_2$ asymm.), 1278 ($-\text{NO}_2$ symm.) 867 ($-\text{ONO}_2$) cm^{-1} .

3.10 *1-Phenylethane-1,2-diol dinitrate*, **VII j** (from styrene oxide, **III j**): δ (CDCl_3) 4.7 (d,2), 6.1 (t,1), 7.4 (s,5) ppm; ν_{max} 1645 ($-\text{NO}_2$ asymm.), 1265 ($-\text{NO}_2$ symm.) cm^{-1} [lit.²² (CHCl_3) 1640, 1280 cm^{-1}]; Dn^{20} 1.486; ρ 1.382 gcm^{-3} .

3.11 *1,2-Diphenylethane-1,2-diol dinitrate*, **VII k** (from stilbene oxide, **III k**): δ (CDCl_3) 6.5 (s,2), 7.4 (s,10) ppm [lit.^{29b} δ (CCl_4) 6.08 (s,2), 7.20 (m,10) ppm]; ν_{max} 1645 ($-\text{NO}_2$ asymm.), 1270 ($-\text{NO}_2$ symm.) cm^{-1} [lit.^{29b} ν_{max} (KBr) 1640, 1260, 1250 cm^{-1}]; Dn^{20} 1.492; ρ 1.474 gcm^{-3} .

3.12 *Nitroglycerine*, **VIII** (from glycidol (**III l**), in presence of AlCl_3): δ (CDCl_3) 4.9 (d,1), 5.8 (m,4) [lit.²⁵ 4.9 (d,1), 5.8 (m,4) ppm]; ν_{max} 1640 ($-\text{NO}_2$ asymm.), 1270 ($-\text{NO}_2$ symm.) cm^{-1} [lit.²⁶ 1640, 1270 cm^{-1}]; Dn^{20} 1.472 [lit.²⁷ 1.473]; ρ 1.593 gcm^{-3} [lit.²⁷ 1.593 gcm^{-3}].

3.13 *3-Chloropropane-1,2-diol dinitrate*, **VIIIm** (from epichlorohydrin, **IIIIm**): δ (CDCl₃) 4.2 (d,2), 5.1 (qr,1), 5.8 (m,2) ppm [lit.²⁵ 4.25 (d,2), 5.1 (qr,1), 5.8 (m,2) ppm]; ν_{\max} 1640 (-NO₂ asymm.), 1270 (-NO₂ symm.), 720 (-ONO₂) cm⁻¹; D_n^{20} 1.458 [lit.²⁵ 1.459]; ρ 1.532 gcm⁻³ [lit.²⁷ 1.532 gcm⁻³].

3.14 *3-(n-Butoxy)propane-1,2-diol dinitrate*, **VIIIn** (from n-butyl glycidyl ether, **IIIIn**): δ (CDCl₃) 0.9 (m,3), 1.5 (m,4) 3.55 (m,2), 3.70 (d,2), 4.7 (m,2), 5.45 (m,1) ppm; ν_{\max} 1650 (-NO₂ asymm.), 1272 (-NO₂ symm.) 850 (-ONO₂) cm⁻¹.

3.15 *3-(t-Butoxy)propane-1,2-diol dinitrate*, **VIIIo** (from t-butyl glycidyl ether, **IIIIo**): δ (CDCl₃) 1.2 (s,9), 3.67 (d,2) 4.7 (m,2), 5.4 (m,1) ppm; ν_{\max} 1651 (-NO₂ asymm.), 1288, 1271 (-NO₂ symm.) 846 (-ONO₂) cm⁻¹.

3.16 *Erythritol tetranitrate*, **VIIp** (from butadiene diepoxide (**IIIp**), in presence of AlCl₃): δ (CDCl₃) 4.7 (m,4), 5.5 (m,2) ppm; ν_{\max} 1656 (-NO₂ asymm.), 1278 (-NO₂ symm.), 838 (-ONO₂) cm⁻¹.

3.17 *Octane-1,2,7,8-tetrol tetranitrate*, **VIIq** (from octane-1,2,7,8-diepoxide, **IIIq**): δ (CDCl₃) 1.4-1.9 (m,8), 4.55 (m,4), 5.3 (m,2) ppm; ν_{\max} 1638 (-NO₂ asymm.), 1288,1272 (-NO₂ symm.), 854 (-ONO₂) cm⁻¹.

3.18 *Diglycerol tetranitrate*, **VIIr** (from diglycidyl ether, **IIIr**): δ (CDCl₃) 3.8 (d,2), 4.65 (m,2), 5.4 (m,1) ppm; ν_{\max} 1647 (-NO₂ asymm.), 1286, 1274 (-NO₂ symm.), 852 (-ONO₂) cm⁻¹. This product was purified by chromatography on neutral alumina using hexane-dichloromethane eluant.

4. Preparation of authentic di- and polynitrates

Commercially available diols were nitrated by the procedure given below [CAUTION: this procedure involves the generation of explosive materials and appropriate precautions should be taken]; diols unobtainable commercially were prepared by hydrolysis of the corresponding epoxides by the method of Swern *et al*³⁰. Authentic di-/ polynitrates were prepared for all anticipated products with the exceptions of entries 10,11 and 18 (compounds **VIIj**, **VIIk** and **VIIr** respectively), and the following compounds, which were available as archive samples:- nitroglycerine (**VIII**) and erythritol tetranitrate (**VIIp**).

A nitration medium (20 ml) was prepared by the slow addition of 99% HNO₃ to 98% H₂SO₄ at 0°C in the ratio of 1 part (wt.) HNO₃ to 3 parts (wt.) H₂SO₄. The mixture was stirred at 0°C and urea (0.2 to 0.3 g) was added to destroy nitrite. The diol was added dropwise at a rate which ensured that the reaction temperature did not exceed 5°C (a 10 mol% calculated excess of nitric acid was used to attain complete reaction). When addition was complete, the mixture was stirred for 5-10 minutes and then extracted with CH₂Cl₂. The extract was washed well with sodium hydrogen carbonate solution, dried over anhyd. MgSO₄ and the solvent removed on a rotary evaporator. The residual acid was carefully diluted and neutralised prior to disposal. The products were characterised by i.r. and ¹H nmr spectroscopy and, where appropriate, refractive index and density measurements. Thus prepared were compounds **VIIa-f**, **VIIh** and **VIIIm**.

An alternative procedure employing nitric acid in acetic anhydride was employed in certain cases (**VIIg**, **VIIi**, **VIIIn&o** and **VIIq**). Acetyl nitrate solution was prepared³¹ by dropwise addition of fuming nitric acid (0.55 ml, 11.25 mmol) with vigorous stirring at a temperature not exceeding 12°C (but >5°C) to acetic anhydride (3 ml). The resulting solution was kept at 12 to 15°C for 10 min., then the di-/polyol, as a neat liquid (3.5 mmol), was added dropwise over 1 min. with rapid stirring to the acetyl nitrate solution at 20±5°C (cardice-acetone cooling), and stirring was continued at 15 to 20°C for a further 20 min. The mixture was then poured into water (10 ml) and stirred vigorously for 1 hour at room temperature. The oil which separated was

transferred by pipette to a separating funnel containing ether (10 ml) and the ethereal solution was washed with saturated NaHCO_3 solution, dried over MgSO_4 and evaporated to yield the nitrate ester, which was characterised as indicated above.

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