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

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Abstract: Ten oxetanes bearing various substituents were reacted with N_2O_5 in chlorinated hydrocarbon solvents to yield 1,3-dinitrate esters (I) by ring-opening nitration. The yields ranged from 73 to 88% for di-/trinitrates derived from oxetanes unsubstituted in the 2-position, to only 15 to 21% for oxetanes bearing such substituents. Although selective ring cleavage of oxetanes bearing non-hydroxylic substituents (epoxy (oxiranyl), spiro-oxetane and alkene) was not, in general, possible, selective nitration of hydroxyalkyloxetanes was achievable under the conditions employed to yield nitrato-methyloxetanes useful as precursors for energetic polyethers. A semi-quantitative reactivity comparison with representative epoxides indicated that the reactivity of oxetanes towards N_2O_5 was lower, as expected on account of their lower ring strain.

INTRODUCTION

Recently we have shown that ethylene oxide and other epoxides yield vicinal dinitrates on treatment with N_2O_5 (dinitrogen pentoxide) in chlorinated solvents under mild conditions, the driving force for the reaction being the release of ring strain in the heterocycle[3]. With optimised technique, yields in excess of 97% were attainable provided certain conditions were met, namely: i) the N_2O_5 should be 100% pure, and, in particular, free from nitric acid (feasible if the N_2O_5 is prepared by ozonation of N_2O_4[4]), and ii) the epoxide should be added to the N_2O_5 solution and not *vice versa*, to suppress undesired cationic polymerisation reactions.

The object of the present study is to investigate the extension of this ring-opening reaction to other oxygen heterocycles possessing ring strain. The substrates under study comprise strained-ring cyclic ethers which are higher homologues of epoxides, namely the oxetanes (II). The behaviour of cyclic ethers with ring size larger than four, namely tetrahydrofuran (THF) and oxepane in the monohetero series, and the cyclic formals dioxolane, 1,3-dioxepane and 1,3-dioxane in the dihetero series, has already been described[5] and, in general, did not give rise to dinitrates in useful yield. The oxetanes are the next higher homologues of the epoxides, and therefore might be expected to resemble them most closely in their reactivities[6]; however, only a few oxetanes are available commercially, eg unsubstituted, 3-alkyl- and 3-hydroxyalkyloxetanes, and as it was necessary to examine a range of substituted oxetanes in order to establish the generality of the reaction, the synthesis of a number of compounds possessing this ring system was also undertaken (see experimental).

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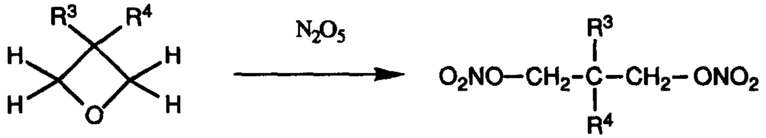
RESULTS AND DISCUSSION

Ten oxetanes were reacted with N_2O_5 in chlorinated solvents under various conditions summarised in Table 1. To facilitate discussion of the results, these oxetanes are subdivided into two main classes: i) those possessing purely alkyl substituents (including the parent compound, **IIa**), and ii) those bearing functional substituents. Description of results in class i) is further subdivided according to behaviour, thus: a) oxetanes unsubstituted at the 2- (4-) position, i.e. those likely to yield solely primary nitrate esters upon reaction with N_2O_5, and b) oxetanes bearing a 2-substituent (i.e. yielding mixed primary/ secondary nitrate esters). Attention is then turned to the behaviour of functional oxetanes, where the effects of hydroxyl, alkenyl and epoxy (oxiranyl) substituents upon the ring cleavage are assessed, and finally the results of a semi-quantitative study of the competitive reactions of two selected oxetanes *versus* an epoxide are described.

Alkyl Oxetanes Unsubstituted on the 2-Position

Three compounds unsubstituted at the 2-position were studied: oxetane (parent compound, **IIa**), 3,3-dimethyloxetane (**IIb**) and 3,3-(pentamethylene)oxetane (**IIc**) - see Eqn 1. Each substrate gave the corresponding 1,3-dinitrate (**Ia-c**), formed by addition of N_2O_5 across the C_1-heteroatom bond, in isolated yields of 73-88% (Table 1). These oxetanes thus behave analogously to the epoxides, albeit giving somewhat lower yields of 1,3-dinitrates; the epoxides gave the corresponding 1,2-dinitrates in 90 to >97% yield by the ring-opening nitration reaction discussed earlier[3]. The purity of the dinitrate products was measured by quantitative GC against authentic standards, prepared by mixed-acid nitration of the corresponding diols, and in each case the products were found to be contaminated by small to moderate amounts (*ca* 5 - 30%) of oligomeric by-products, also evident from the ^1H nmr spectra. Oxetane (**IIa**) gave the lowest proportion and 3,3-dimethyloxetane (**IIb**) the highest of these by-products.



IIa	$R^3 = R^4 = H$	**Ia**
IIb	$R^3 = R^4 = CH_3$	**Ib**
IIc	$R^3, R^4 = -(CH_2)_5-$	**Ic**

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2-Substituted Alkyloxetanes

Two such compounds, **IId** and **IIe**, were reacted with *ca* 33% excess N_2O_5 and each gave the corresponding 1,3-dinitrate, **Id** and **Ie** respectively (Eqn 2), but only as a minor component of the product mixture: net yields (from hplc) were 21 and 16-19% respectively. Additionally, the product mixture from **IId** (and, to a lesser extent, that from **IIe**) was found to contain a high proportion of material soluble in the aqueous base used to wash the reaction product. Examination of this mixture by i.r. and ^1H nmr indicated the presence of carboxylate-containing species (ν_{max} 1777 & 1723 cm^{-1}; δ 11.3 ppm), presumably resulting from oxidative side-reactions. Although the exact chemical constitution of these by-products was not rigorously established, it

Table 1: Reactions of Oxetanes with N_2O_5

Entry	Oxetane	Mol N_2O_5: substrate	Solvent	Temp. °C	Reaction time (hr)	Products	
						Dinitrate Yield (%)	Notes
1	**IIa**	1.33:1	$CHCl_3$	5 to 10	0.75	88	-
2	**IIb**	1.33:1	$CHCl_3$	10 to 15	3	73	+ oligomers
3	**IIc**	1.33:1	$CHCl_3$	10 to 15	"	86	+ oligomers
4	**IId**	1.41:1	$CDCl_3$	-5 to +5	1.5	21[1]	+ oxidation products
5a	**IIe** - i)	1.06:1	$CHCl_3$/MeCN	-10 to +2	16	19[1]	minor component of complex mixture
5b	- ii)	1.3:1	$CHCl_3$	-10 to 0	3	17[1]	ditto
6a	**IIf** - i)	2.46:1	$CDCl_3$	-10 to 0	0.5	62[2]	principally mono-nitrate
6b	- ii)	4:1	$CHCl_3$	-10 to +15	28	88[3]	-
7	**IIg**	1.6:1	"	-10 to 0	1	76[2]	mononitrate only
8	**IIh**	1.1:1	$CDCl_3$	-10 to 0	16	<5[4]	mainly nitro-nitrate
9	**IIi**	1.04:1	$CDCl_3$	-10 to +4	20	- [5]	complex mixture
10	**IIj**	1.0:1	$CDCl_3$	-10 to 0	3	22	mainly polymer

Key

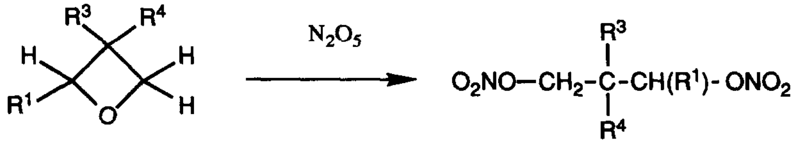
[1] Yields measured chromatographically *vs* standards - refer to pure compounds.

[2] Yield of mononitrate (VIII). Trinitrate (If) also present in 25% yield - oxetane (IIf) only (see text).

[3] Trinitrate (MTN, If).

[4] Principal product from reaction of N_2O_5 with ring double bond (see text).

[5] Gave products resulting from opening of both rings together with oxidation (see text).



IId $R^1 = Pr^n$ $R^3 = Et$ $R^4 = H$ **Id**

IIe $R^1 = Me$ $R^3 = R^4 = Et$ **Ie**

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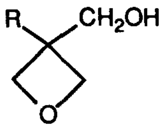
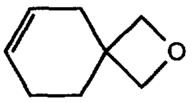
is likely that they are formed by N_2O_5 oxidation at the 2-position of the oxetane ring. Therefore the N_2O_5-oxetane reaction does not appear to be an effective means of preparing 1,3-dinitrates in which one of the nitrate ester groups is secondary.

Functional Oxetanes

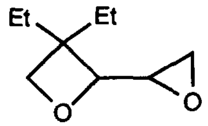
Five oxetanes bearing other functional groups were studied: two 3-(hydroxymethyl)-oxetanes (**IIf** & **IIg**), one alkenyloxetane (**IIh**), one epoxy-oxetane (**IIi**) and one spiro-bioxetane (**IIj**). The behaviour of each with N_2O_5 is now described.



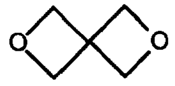
IIf R = CH_3-
IIg R = $ClCH_2$-



IIh

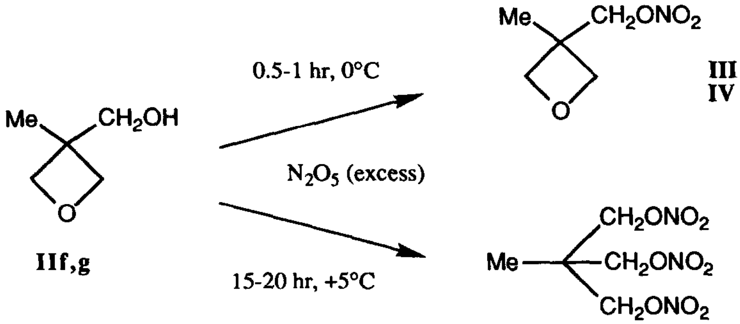


IIi



IIj

The first of these compounds, 3-(hydroxymethyl)-3-methyloxetane (**IIf**), was interesting in that it yielded two different products, one partially nitrated (**III**) and the other fully nitrated (**If**), depending on the nitration conditions (Eqn 3). Thus, brief reaction of **IIf** with sufficient N_2O_5 to produce the trinitrate **If** (metriol trinitrate, MTN) nevertheless yielded predominantly the nitratomethyloxetane (**III**), together with a little MTN. Closer investigation of the reaction, employing monitoring by hplc, indicated that **III** was an intermediate in the formation of MTN, and was not completely consumed until a reaction time of 15-20 hr had elapsed (at 5°C).



IIf,g

III R = CH_3
IV R = $ClCH_2$-

If

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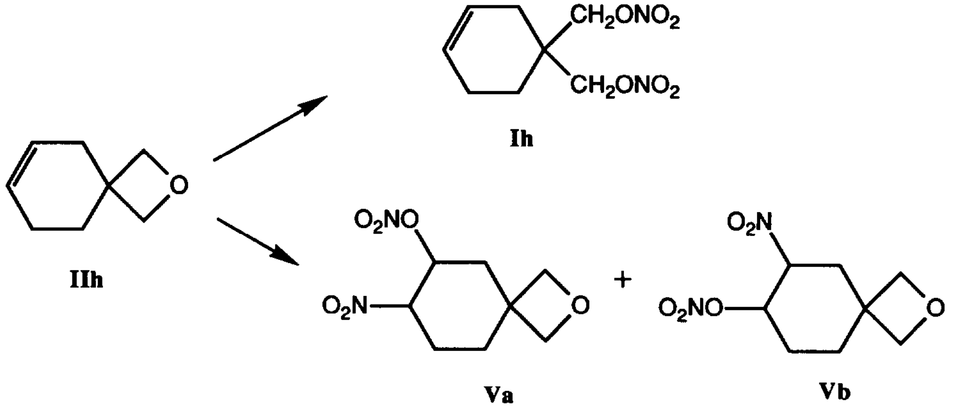
The sluggish reaction of this oxetane with N_2O_5 is surprising and evidently arises from increased steric effects of the bulky nitratomethyl ring substituent which hinders the ring-opening reaction[7].

Evidence supporting this assumption was obtained from the reaction of the second 3-(hydroxymethyl)-oxetane, 3-(chloromethyl)-3-(hydroxymethyl)oxetane, **IIg**, with excess N_2O_5. Under slightly more forcing conditions this substrate nevertheless gave the pure nitratomethyloxetane (IV) with no trace of ring-opened products (Eqn 3). Clearly here the bulky chloro substituent suppresses ring opening completely, a result not altogether unexpected considering the facile formation of this oxetane from the bischlorohydrin of pentaerythritol[8]. Further work on 3-(hydroxymethyl)-3-methyloxetane (IIf), detailed elsewhere[9], has indicated that the reaction conditions can be optimised to produce solely the mononitrate (III), and that compounds of this type can be polymerised to form polyethers with pendant energetic groups[10]. Polymers possessing such structural features form the basis of a new generation of materials for use as binders in explosive and propellant compositions[11].

The reactions of 3,3-((3',4'-bisdehydro)pentamethylene)oxetane (IIh) and 2-oxiranyl-3,3-diethyloxetane (IIi) were investigated only in a preliminary manner, each with one mol of N_2O_5, in order to establish the primary site of attack of the oxide of nitrogen. It was hoped that **IIh** would yield the corresponding dinitrate (Ih), whilst **IIi** would react on the epoxide function to yield a new 2-(1',2'-dinitratoethyl)oxetane (Ii). As will be seen, neither of these expectations was realised.

When **IIh** was treated with N_2O_5 (1 mol) reaction took place slowly and hplc examination showed that it was incomplete after 3 hr. The major product, isolated after 20 hr, was a mixture of the nitro-nitrates (**Va** & **Vb**), formed by addition of N_2O_5 across the double bond (Eqn 4). These nitro-nitrates were identified from the i.r. spectrum (ν_{max} 1549 (C-NO_2) and 1640 (O-NO_2) cm^{-1}), but in common with other compounds of this type they decomposed on standing[12]. Furthermore, other by-products were detected by hplc but were not identified. It is apparent, therefore, that the oxetane ring in this compound is less reactive than the double bond, presumably resulting from the geminal 3,3-disubstitution on the four-membered ring, and that this route is not suitable for the preparation of 1,3-dinitrates in this molecular environment.



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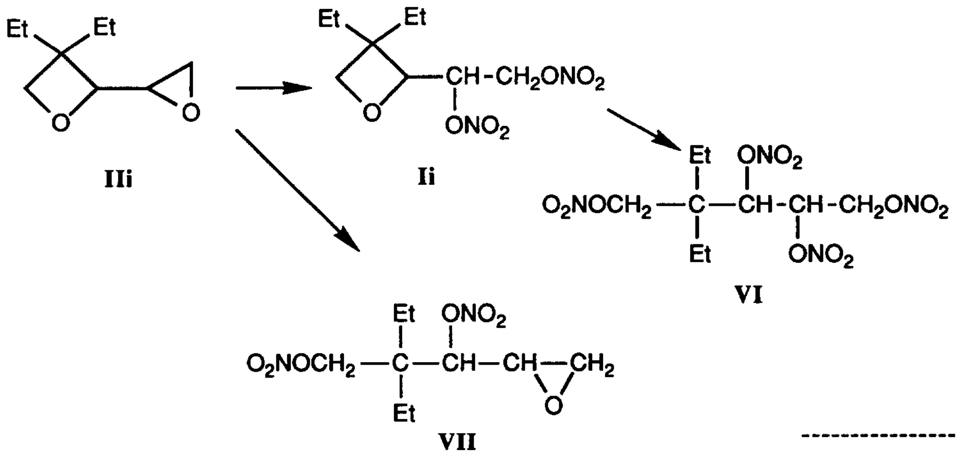
It was hoped that reaction of **IIi** with 1 mol of N_2O_5 would yield the dinitrate (Ii) by opening of the epoxide ring, which should be more labile than the oxetane ring, and that **Ii** could be further nitrated, possibly in a one-pot reaction, to the tetranitrate (VI; Eqn 5). In fact, a mixture was obtained which, from its hplc,



IIi Ii VI VII

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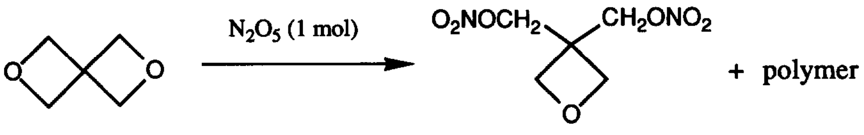
contained some unchanged **IIi** together with several unidentified components. It was evident from the ^1H nmr and i.r. spectra of the product mixture that much of the epoxide function was unchanged (peaks at δ 2.65-3.30 ppm and ν_{max} 977 cm^{-1} still present), whilst the oxetane group absorption in the i.r. at 864 cm^{-1}, surprisingly, was diminished in intensity compared with the starting material, both suggesting that the oxetane ring was attacked more rapidly than the epoxide ring, resulting in preferential formation of dinitrate (**VII**). Absorptions were also present in the carbonyl region of the i.r. spectrum of the product mixture, suggesting that oxidation of this substrate had taken place, in keeping with the behaviour already noted with other 2-substituted oxetanes. Therefore, apart from the anomalously high reactivity of this oxetane ring, which may be the result of some type of neighbouring-group participation by the epoxy function, the reaction is of little interest and would be unlikely to give a useful yield of the tetranitrate (**VI**) upon reaction with excess N_2O_5. For these reasons further study was discontinued.

Finally, the spirobioxetane (**IIj**) was found to give a low yield of 3,3-bis-(nitratomethyl)oxetane (**Ij**) upon reaction with 1 mol N_2O_5 (Eqn 6), but the major products from the reaction were oligomeric, in parallel with the behaviour found with polyepoxides[3]. Hence the reaction does not constitute a useful preparation of the dinitrate (**Ij**) and was not studied further.



IIj Ij

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Competitive Reactions of Oxetanes vs *Epoxides*

Two oxetanes were selected to represent the class: a reactive member (the parent compound, **IIa**) and a less reactive member (3,3-(pentamethylene)oxetane, **IIc**), and each was reacted with N_2O_5 in the presence of an equimolar amount of pent-2-ene oxide (**VIII**), a representative epoxide which was easy to handle. Since the amount of N_2O_5 present was sufficient to react completely with only one of the oxygen heterocycles, the distribution of dinitrate products therefore reflected the relative reactivities of these species in a semi-quantitative way (assuming that the rate of reaction is not entirely diffusion controlled, a reasonable assumption in view of the results quoted below).

The results are presented in Table 2, where it is seen that the reactivity of the parent oxetane (**IIa**) appeared to be comparable to that of pent-2-ene oxide (**VIII**), while the 3,3-disubstituted oxetane (**IIc**) was much less reactive, accounting for only *ca* 20% of the product mixture. These results suggest that the oxetane ring, when unsubstituted, is of the same order of reactivity as a substituted epoxide ring (which is of course, in turn, less reactive than ethylene oxide (**IX**)), i.e. the reactivity sequence is as shown below. However, when geminal substituents are introduced on the 3-position of the oxetane ring, it is stabilised and consequently the N_2O_5 reacts preferentially with the epoxide, in agreement with reactivity patterns noted earlier in this paper and elsewhere[7]. These results should also correlate with the CRSEs of these molecules (in parentheses), but incomplete data do not permit a thorough comparison of this type; nevertheless, a useful pattern of reactivities has been established from these experiments.

Table 2: Competitive Reactions of Oxetanes vs Epoxides

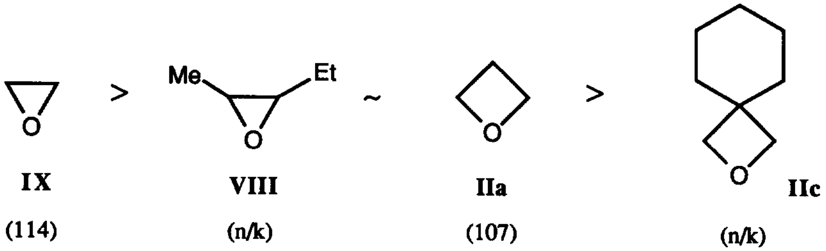
Run no	O-Heterocycles	Products (%)	
		1,3-Dinitrate[1]	1,2-Dinitrate[2]
1	Oxetane (**IIa**) + Pent-2-ene oxide (**VIII**)	50	50
2	3,3-(Pentamethylene)-oxetane (**IIc**)+ Pent-2-ene oxide (**VIII**)	20	80

Key

[1] Run 1: propane-1,3-diol dinitrate (**Ia**)

Run 2: 2,2-(pentamethylene)propane-1,3-diol dinitrate (**Ic**)

[2] Pentane-2,3-diol dinitrate (both runs)



IX (114)

VIII (n/k)

IIa (107)

IIc (n/k)

Conclusions

When unsubstituted on the 2-position, the alkyloxetanes reacted relatively cleanly to give 1,3-dinitrates in up to 88% yield (see Table 1), and addition of N_2O_5 with cleavage of the C-O bond was the predominant reaction, as with the epoxides[3]. Some of the alkyloxetanes also gave small amounts of oligomeric by-products, although there was no clear correlation of this behaviour with the structure of the oxetane. 2-Substituted oxetanes, on the other hand, yielded the expected 1,3-dinitrates only as minor components (maximum yield 21%) of complex reaction mixtures, in which products resulting from oxidative cleavage of the C-O bond, for instance carboxylic acids, were present in large amounts. Turning to the functional oxetanes, hydroxymethyloxetanes reacted preferentially with N_2O_5 by substitution of the hydroxyl hydrogen giving a mononitrato-oxetane, only giving ring-opened polynitrates under forcing conditions, whilst oxetanes bearing other types of functional group (epoxy, spiro-oxetane, alkenyl) did not give clean reactions. Presumably in these cases differences in behaviour from the epoxy analogues[3] result from the lower ring strain of the oxetanes, so that the reactions are not driven in a particular direction. Finally, the alkyloxetanes were shown, from competitive reaction studies (Table 2), to be less reactive than their epoxide counterparts towards ring opening. This is expected on account of their lower ring strain energies. It is hoped to present more detailed studies of N_2O_5-oxetane mechanisms in future publications.

EXPERIMENTAL

1. Materials and apparatus

All materials were used as received unless otherwise stated. Oxetane (**IIa**), 3,3- dimethyloxetane (**IIb**), 3-methyl-3-(hydroxymethyl)oxetane [3-methyl-3-oxetanemethanol] (**IIf**) and 3-chloromethyl-3-(hydroxymethyl)-oxetane [3-chloromethyl-3-oxetanemethanol] (**IIg**) were supplied by Aldrich (reagent or ABC grade respectively). 2-Oxiranyl-3,3-diethyloxetane (**IIi**) was kindly supplied by Drs A. O. Fitton, J. Hill and D. Jane, Salford University. Other oxetanes were prepared from the corresponding 1,3-diols as follows (yields and b.pts. in parentheses):- i) by ring closure of monotosylates using n-butyl-lithium according to the method of Picard *et al*[13] - 3,3-(pentamethylene)oxetane (**IIc**) (57%, 59.5-60.5°C/ 30 mbar [lit.[13] 69-70°C/ 20 Torr]), 2-propyl-3-ethyloxetane (**IId**) (33%, 70.5-72°C/ 100 mbar), 2-methyl-3,3-diethyloxetane (**IIe**) (32%, 48-49°C/ 45 mbar) and 3,3-((3',4'-bisdehydro)-pentamethylene)-oxetane (**IIh**) (45%, 59.5-60°C/ 15 mbar); ii) by thermolysis of an O,O-bis(tributylstannyl) derivative[14] - 2,6-dioxaspiro[3.3]heptane (**IIj**) (32%, m.pt. 86-87°C). The preparation of 1,3-diols is detailed later.

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[15], and N_2O_5 by ozonation of N_2O_4[4]; both of 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.

Gc and hplc separations and melting point determinations were carried out using the apparatus described earlier[3]; chromatographic conditions are given individually for each compound.

CAUTION: Many of the products described herein are explosives; all reactions utilising N_2O_5 were therefore carried out in armoured cupboards.

2. Reactions of Oxetanes with N_2O_5

General method. 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 N_2O_5 (25 to 50 ml solution in dichloromethane) was added with magnetic stirring. When the solution was at the stated temperature (Table 1) 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., ^{1}H nmr), and by comparison of gc (oxetanes **IIa-c**) or hplc (oxetanes **IId-f**, **IIh-j**) 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 (with oxetanes **IIg-j**) products were characterised solely by their spectra (i.r. and ^{1}H nmr). The following oxetanes were thus reacted with N_2O_5:-

2.1 *Oxetane* (**IIa**): **IIa** (0.90 g, 15.5 mmol) and N_2O_5 (2.16 g, *ca* 20 mmol) gave *propane-1,3-diol dinitrate* (**Ia**) as a colourless oil (2.26 g, 88%), δ ($CDCl_3$) 2.22 (qn,2), 4.65 (t,4) ppm; ν_{max} 1633 ($-NO_2$ asymm.), 1281 ($-NO_2$ symm.), 866 ($-ONO_2$) cm^{-1}, identified by comparison with an authentic sample (gc, 140°C). This material had >95% purity (^{1}H nmr).

2.2 *3,3-Dimethyloxetane* (**IIb**): **IIb** (1.29 g, 15 mmol) and N_2O_5 (2.16 g, 20 mmol) gave *2,2-dimethylpropane-1,3-diol dinitrate* (**Ib**) as a colourless oil (2.12 g, 73%), δ ($CDCl_3$) 1.10 (s,6), 4.28 (s,4) ppm; ν_{max} 1636 ($-NO_2$ asymm.), 1278 ($-NO_2$ symm.), 866 ($-ONO_2$) cm^{-1}. Comparison of the gc (145°C) with that of an authentic sample indicated the presence of impurities of longer retention time (presumably oligomeric) in addition to the dinitrate; the purity of the latter was estimated to be *ca* 70% by comparison with an authentic sample.

2.3 *3,3-(Pentamethylene)oxetane* (**IIc**): **IIc** (1.26 g, 10 mmol) and N_2O_5 (1.44 g, 13.3 mmol) gave *2,2-(pentamethylene)-propane-1,3-diol dinitrate* (**Ic**, 2.01 g, 86%), δ ($CDCl_3$) 1.53 (brs,10), 4.43 (s,4) ppm; ν_{max} 1635 ($-NO_2$ asymm.), 1278 ($-NO_2$ symm.), 866 ($-ONO_2$) cm^{-1}. Comparison of its gc (160°C) with authentic material indicated that it was *ca* 75% pure, with oligomeric material accounting for the rest of the product.

2.4 *2-Propyl-3-ethyloxetane* (**IId**): **IId** (0.50 g, 3.90 mmol) and N_2O_5 (0.60 g, 5.5 mmol) gave impure *2-ethylhexane-1,3-diol dinitrate* (**Id**) as a pale yellow oil (0.41 g), δ ($CDCl_3$) 0.8-1.75 (m,12), 1.8-2.2(m,1), 4.46 (d,2), 5.20 (qr,1) ppm; ν_{max} 1647, 1631 ($-NO_2$ asymm.), 1281 ($-NO_2$ symm.), 872, 865 ($-ONO_2$) cm^{-1}. The product was judged to be impure by comparison of the i.r. and ^{1}H nmr spectra with those of an authentic sample: additional moderate to weak absorptions at 1777, 1723, 1554 and 1170 cm^{-1} were present in the i.r., while the ^{1}H nmr spectrum showed a weak downfield singlet (δ 11.3 ppm) assigned to carboxylate proton. These observations were consistent with contamination of the nitrate ester by small amounts of carboxylic compounds arising from oxidative side-reactions. The purity was assessed quantitatively by hplc *vs* an authentic sample using di-(n-butyl) phthalate as an internal standard (conditions: RP18, $MeCN-H_2O$ 73:27, 210 nm; RRF dinitrate:phthalate = 0.504). The purity was found to be 46.5%, and the true yield of dinitrate (**Id**) was therefore 0.191 g (21%).

2.5 *2-Methyl-3,3-diethyloxetane* (**IIe**): **IIe** (0.064 g, 0.5 mmol) and N_2O_5 (0.057 g, 0.53 mmol) gave an oil (0.098 g) which turned brown on standing in air for several weeks. Quantitative hplc using di-(n-butyl) phthalate as internal standard (conditions as in Section 2.4; RRF dinitrate: phthalate = 0.448) indicated that the oil contained 17% of *2,2-diethylbutane-1,3-diol dinitrate* (**Ie**), δ ($CDCl_3$) 0.90 (t,6), 1.4 (m,5), 4.41 (s,2), 5.14 (qr,1) ppm; ν_{max} 1632 (-NO_2 asymm.), 1277 (-NO_2 symm.), 854 (-ONO_2) cm^{-1}. The yield was thus 15.5%. Repetition of the experiment using RDX as an internal standard (during the nitration step) indicated a yield of **Ie** of 19%.

2.6 *3-Methyl-3-(hydroxymethyl)oxetane* (**IIf**):

i) Under mild conditions: **IIf** (1.22 g, 12 mmol) and N_2O_5 (3.18 g, 29.5 mmol) gave a colourless mobile oil (1.84 g), hplc examination of which (RP18, MeCN-H_2O 60:40) showed that it was a two component mixture, the minor component comprising MTN (**If**), identified by comparison with an authentic sample, but the major component did not correspond to any hitherto known material. Further spectroscopic investigation of the mixture indicated the following: the ^1H nmr, run in $CDCl_3$, showed two upfield singlets, assigned as ring methyl belonging to MTN and the unknown, whilst the midfield region (δ 4-5 ppm) was complex and no positive assignment could be made. The i.r. spectrum of the mixture showed strong nitrate ester bands (ν_{max} 1646/1287/ 866 cm^{-1}) as expected, but in addition an absorption at 983 cm^{-1}, the region characteristic for oxetane ring breathing, was also present. When the ^1H nmr spectrum was rerun in D_6-benzene, shifts were observed at the precise values reported[17] for the nitrato-methyloxetane (**III**), thus confirming the identity of the unknown component. The yields, calculated from the nmr integration, were as follows: MTN (**If**)- 25%, 3-methyl-3-nitratomethyloxetane (**III**) - 62%.

ii) Under forcing conditions (with a greater excess of N_2O_5): Monitoring by hplc (RP8, MeCN-H_2O 65:35) showed that reaction to form MTN (**If**) was complete after *ca* 15 hr. After 28 hr the mixture was worked up in the usual manner to give MTN (**If**) (88%) which had i.r. and ^1H nmr spectra identical to authentic material (δ ($CDCl_3$) 1.20 (s,3), 4.50 (s,6) ppm; ν_{max} 1659, 1646, 1627 (-NO_2 asymm.), 1277 (-NO_2 symm.), 860 (-ONO_2) cm^{-1}; no contaminants were detected in this instance.

2.7 *3-Chloromethyl-3-(hydroxymethyl)oxetane* (**IIg**): **IIg** (0.26 g, 1.9 mmol) and N_2O_5 (0.32 g, 3 mmol) gave a pale yellow oil which was identified as *3-chloromethyl-3-nitratomethyloxetane* (**IV**, 76%), (δ ($CDCl_3$) 3.87 (s,2), 4.52 (s,4), 4.82 (s,2) ppm; ν_{max} 1639 (-NO_2 asymm.), 1278 (-NO_2 symm.), 867 (-ONO_2) cm^{-1}. No trinitrate was detected.

2.8 *3,3-((3',4'-Bisdehydro)-pentamethylene)oxetane* (**IIh**): **IIh** (2.73 g, 22 mmol) and N_2O_5 (2.50 g, 24 mmol) gave a pale yellow oil, 3.85 g (75%), which showed oxetane ring signals in the ^1H nmr and i.r. at δ 4.65 ppm and ν_{max} 849 cm^{-1} resp. The i.r. spectrum also showed strong absorptions at 1549 and 1640/1277/773 cm^{-1}, indicative of C-nitro and nitrate ester functionalities respectively. Moreover, the ^1H nmr showed a multiplet at δ 6.05 ppm, attributable to a secondary nitrate ester substituent. All of these data point to the identity of the major reaction product as being the vicinal nitro-nitrate isomers (**Va** & **Vb**), formed from N_2O_5 attack on the ring double bond, although the hplc trace indicated the presence of smaller amounts of other unidentified components as well. Precise quantitation was not possible owing to the lack of a suitable route for the preparation of an authentic sample of the nitro-nitrate (**Va,b**), which in any case appeared to be thermally/ chemically unstable, discolouring on standing in a stoppered flask over several weeks.

2.9 *2-Oxiranyl-3,3-diethyloxetane* (**IIi**)[18]: (**IIi**) (0.975 g, 6.25 mmol) was treated with N_2O_5 (0.70 g, 6.5 mmol) by the general method. A ^1H nmr spectrum of the mixture was taken 20 min. after mixing the reactants, and the diminution of the signals at δ 4.27 ppm (oxetane ring) as well as at δ 2.6-3.3 (epoxide ring) suggested that cleavage of both heterocyclic rings was taking place. The nmr spectrum did not change appreciably after a further period of 2.5 hr; after this time a trial sample was withdrawn and worked up in the usual manner prior to examination by i.r., whilst the bulk of the reaction mixture was kept overnight at 0 to 5°C. This i.r. spectrum confirmed the finding in the nmr spectrum, with the epoxide and oxetane peaks at 863 and 976 cm^{-1} respectively both diminishing in intensity, the latter somewhat more than the former, surprisingly. Workup of the main reaction mixture yielded an oil, 0.94 g, which on examination by hplc (RP2, MeCN-H_2O 70:30, 205 nm) was found to be a multi-component mixture comprising unchanged starting material and unidentified components, presumably partially nitrated or oxidised derivatives. It was not treated further.

2.10 *2,6-Dioxaspiro[3.3]heptane* (**IIj**): Treatment of **IIj** (2.40 g, 24 mmol) with N_2O_5 (2.77 g, 24 mmol) gave, after removal of a white solid (A) by filtration, a pale yellow oil (1.1 g) which crystallised slowly. It was identified as *3,3-bis(nitratomethyl)-oxetane* (**Ij**) as follows:- from its nmr and i.r. spectra: δ ($CDCl_3$) 4.65-4.8 (m) ppm; ν_{max} 1649, 1628 (-NO_2 asymm.), 1281 (-NO_2 symm.), 992 (oxetane) & 865 (-ONO_2) cm^{-1}, and by comparison (hplc, RP18) with an authentic sample[19]. The white solid (A), 2.70 g, which had m.pt. >220°C, was insoluble in all common solvents and was presumed to be polymeric.

3. Competitive Reactions of Oxetanes vs Epoxides (Semi-quantitative)

a) *General method*: Firstly, a hplc method for the separation of the expected nitrate ester products was developed, and the relative response factor (RRF) of each nitrate ester *vis-a-vis* its partner was measured. Then a mixture of the two heterocycles with mol ratio close to 1:1 was added to a solution of N_2O_5 in $CHCl_3$ containing sufficient N_2O_5 to react with only one of the substrates. After a reaction period of 30 min. at -5 to 0°C, the mixture was examined by hplc, then worked up in the usual manner and analysed by ^1H nmr if necessary.

b) *Oxetane* (**IIa**) vs *pent-2-ene oxide* (**VIII**): Hplc conditions: RP8 MeCN-H_2O 55:45. RRF propane-1,3-diol dinitrate : pentane-2,3-diol dinitrate = 1. The chromatograms showed approximately equal peak areas for propane-1,3-diol dinitrate and pentane-2,3-diol dinitrate, suggesting approximately equal reactivity for each heterocycle.

c) *3,3-(Pentamethylene)oxetane* (**IIc**) vs *pent-2-ene oxide* (**VIII**): Hplc conditions: RP18 MeCN-H_2O 77.5:22.5. RRF 2,2-(pentamethylene)propane-1,3-diol dinitrate : pentane-2,3-diol dinitrate = 1. The chromatograms showed the ratio of peak areas for 2,2-(pentamethylene)propane-1,3-diol dinitrate : pentane-2,3-diol dinitrate was *ca* 1:4. The oxetane therefore appears to be much less reactive than the epoxide in this instance.

4. Preparation of Authentic Dinitrates

These were prepared by nitration of diols either in nitric-sulphuric acid mixtures by the procedure reported earlier[3] (dinitrates **Ia**, **Ib**, **Id** and **Ie**; 2,2-diethylbutane-1,3-diol dinitrate showed a tendency to crystallise <25°C, therefore in this case workup was carried out above this temperature), or in 99% nitric acid as described below (2,2-(pentamethylene)propane-1,3-diol dinitrate, **Ic**) [CAUTION: these procedures involve the generation of explosive materials and appropriate precautions should be taken]. Authentic MTN (**If**) was an archive sample.

Diols unobtainable commercially were prepared as follows:- i) by aldol reaction (condensation of cyclohexanecarboxaldehyde with formalin[20]) - 2,2-(pentamethylene)-propane-1,3-diol (**IIc**) (72%, m.pt. 94-96°C [lit.[20] 97-97.5°C]); or ii) by reduction ($LiAlH_4$/ ether) of the corresponding β-ketoester (Fluka Chemicals Ltd) - 2,2-diethyl-butane-1,3-diol (**IIe**)(47%, b.pt. 106-108.5°C/ 7 mbar) from ethyl 2,2-diethylacetoacetate.

Solid diol (**IIc**) (4g) was added in small portions over 15 min. with vigorous stirring to 99% HNO_3 (10 ml) at -10 to -5°C. The mixture was stirred for 30 min. at -5±3 °C then poured into iced water (200 ml) and stirred vigorously for several min. The aq. layer was then decanted and the resulting product (**Ic**, oil) was washed with, successively, water (200 ml) and saturated $NaHCO_3$ soln. (200 ml) prior to drying over $MgSO_4$.

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