The reaction of 3-substituted oxetanes with nitric acid in dichloromethane

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The reactions of 3-phenyloxetane 1, 3-(4-nitrophenyl)oxetane 5 and 3,3-pentamethyleneoxetane 7 with nitric acid in dichloromethane or trichloromethane under anhydrous conditions have been investigated. Quantitative conversion to 2-substituted propane-1,3-diol dinitrates occurs. Compound 1 reacts initially by a mixture of *ortho*- and *para*-aromatic nitration and oxetane ring-opening. Aromatic nitrations of 1 and 1,4-dichlorobenzene, the former reacting through its majority hydrogen-bonded complexed form, are approximately sixth order in nitric acid and proceed at a comparable rate. The oxetane ring-opening reactions are approximately second order in nitric acid except in the case of 3-(2-nitrophenyl)oxetane 3, where there is evidence of intramolecular catalysis by the nitro group.

Introduction

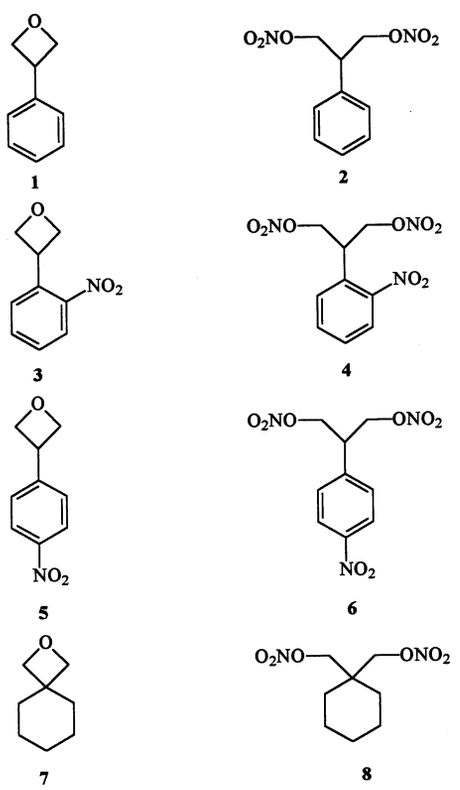
Oxiranes[1] and 3-substituted oxetanes[2] react with dinitrogen pentoxide in dichloromethane to give the corresponding dinitrates in good yield. These and related reactions are of considerable interest as new synthesis routes for energetic materials.[3] We have sought to investigate their mechanism,[4–6] including in our studies the reactions of the same substrates with nitric acid because of its likely presence in solutions of dinitrogen pentoxide. We report here on the reaction of some 3-substituted oxetanes with nitric acid. These reactions, which do not appear to have been studied previously, are relatively slow, permitting independent study of the initial equilibrium extent of hydrogen-bonded complex formation between several oxetanes and nitric acid.[7] The slow conversion of the hydrogen-bonded complexes of the oxetanes **1**, **3**, **5** and **7** into the corresponding dinitrates **2**, **4**, **6** and **8**, a reaction accompanied in the case of 3-phenyloxetane **1** by aromatic nitration, is the subject of this paper.

Results

The reaction of the oxetanes in dichloromethane required high concentrations of nitric acid; there was no detectable reaction of **1** in 0.15 mol dm^{-3} nitric acid after 20 h at room temperature. In preliminary studies, using 2–8 mol dm^{-3} nitric acid, three products were recognised and identified as **4**, **5** and **6** (Scheme 1). It was noted that **5** was slowly converted to **6** and that the **4**:**6** ratio decreased with time in a particular run.

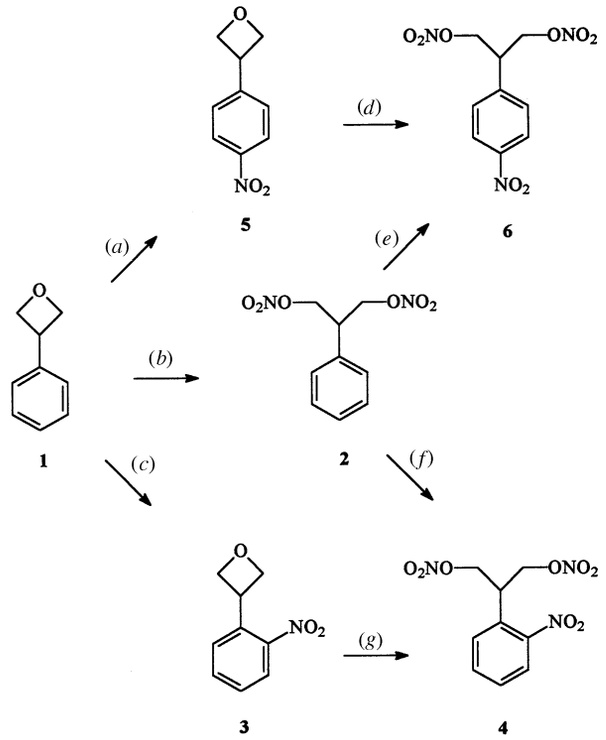
It seemed likely that some or all of the reactions shown in Scheme 1 were operating. At this stage neither **2** nor **3** had been identified as intermediates, but traces of an unidentified compound were present in the initial stages when the nitric acid concentration was 2 mol dm^{-3}.

Further studies revealed that this compound peaked at 18% when the nitric acid concentration was 1 mol dm^{-3}, and it was the major product after three days when the nitric acid concentration was reduced further to 0.5 mol dm^{-3}. The latter conditions were used to isolate and characterise this compound as 2-phenylpropane-1,3-diol dinitrate **2**, thus confirming that path (*b*) was important. The aromatic nitration of this compound in 1 and 2 mol dm^{-3} nitric acid was investigated independently and it was found under both conditions to give both **4** and **6**, in a molar ratio of 1:3. This means that, in the nitration of **1**, the early formation of **4** without **6** (Tables 1–3) cannot be explained unless path (*c*) is also involved. The results also require, rather surprisingly, that the ring opening of **3** to give **4** is much quicker than the ring opening of **5** to give **6**, making **3** a rather transient intermediate. It has not been possible to confirm its presence with certainty. Signals have been observed in the aromatic region of the ^{1}H NMR spectra which may be assigned to *ortho*-substitution of an aromatic ring and are more than can be accounted for by the amount of **4** present. It seems likely therefore that **3** is indeed formed as an intermediate but in amounts too small to quantify.



1 **2** **3** **4** **5** **6** **7** **8**

Further insight was obtained by a least squares fitting procedure (see Appendix). The mechanism of Scheme 1 was assumed, with all steps pseudo-first order, nitric acid being in considerable excess. The data of Tables 1–3 were used to obtain values for the rate constants (Table 4). These values are approximate, and relate to a temperature of 22–25 °C because they were not originally planned for kinetics and were conducted at room temperature, without thermostatic control. Satisfactory fits of the data for all observed intermediates and products were obtained for the runs with 1 and 2 mol dm^{-3}



Scheme 1

Table 1 Percentages at times, *t*, of reactant, intermediates and products of reaction of 3-phenyloxetane **1** (0.04 mol dm^{-3}) with nitric acid (0.5 mol dm^{-3}) in dichloromethane, 22–25 °C

t/h	**1**	**3** + **5**[a]	**4**	**6**	**2**[b]
0.5	99	1			
2	96	2	0	0	2
24	47	5	<1	<1	26 (22)
48	22	11	2	<1	46 (20)
72	17	11	1	<1	50 (21)

[a] Of these, **3** is a very minor component; see text. [b] Figures in parentheses represent the yield of the unknown product believed to be the mononitrate corresponding to the dinitrate **2**.

Table 2 Percentages at times, *t*, of reactant, intermediates and products of reaction of 3-phenyloxetane **1** (0.04 mol dm^{-3}) with nitric acid (1.0 mol dm^{-3}) in dichloromethane, 22–25 °C

t/h	**1**	**3** + **5**[a]	**4**	**6**	**2**
0.5	72	20	4	0	3
2	45	34	8	2	11
24	0	42	16	38	2
48	0	18	16	66	0
72	0	8	15	79	0

[a] Of these, **3** is a very minor component; see text.

nitric acid (Figs. 1 and 2). The run at 0.5 mol dm^{-3} nitric acid (Table 1) gave an additional unknown product, the NMR of which was consistent with it being the mononitrate ester corresponding to the dinitrate **2**. On this assumption the yields of this and **2** were aggregated for the purpose of the fitting, which gives information only on reactions *a–c* (Table 4).

For comparison with the aromatic nitrations, the kinetics of the reaction of 1,4-dichlorobenzene were studied (Table 5), and for comparison with the oxetane ring openings, the reactions of 3-(4-nitrophenyl)oxetane and 3,3-pentamethyleneoxetane were investigated (Table 6).

There was no evidence of ^{15}N CIDNP (chemically induced dynamic nuclear polarisation) effects in these reactions (see Experimental section) and therefore no reason to suppose that radical mechanisms, important in the reactions of substituted styrenes under similar conditions,[6] were involved here.

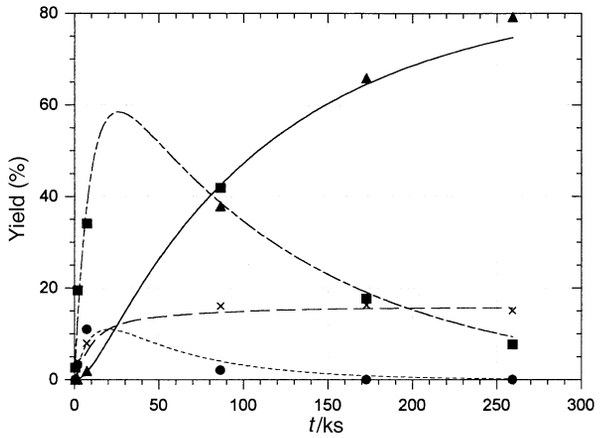


Fig. 1 Observed (points) and calculated (curves) percentages of **3** + **5** (squares, dash-dot line) **2** (circles, dotted line) **4** (crosses, dashed line) and **6** (triangles, full line) in the reaction of **1** with 1.0 mol dm^{-3} nitric acid in dichloromethane at 22–25 °C

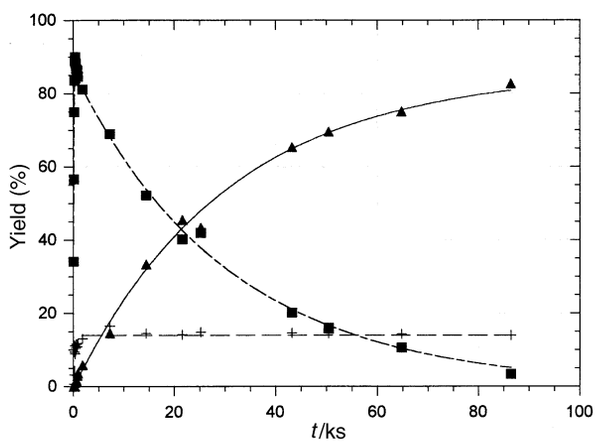


Fig. 2 Observed (points) and calculated (curves) percentages of **3** + **5** (squares, dash-dot line) **4** (crosses, dashed line) and **6** (triangles, full line) in the reaction of **1** with 2.0 mol dm^{-3} nitric acid in dichloromethane at 22–25 °C

Table 3 Percentages at times, *t*, of reactant, intermediates and products of reaction of 3-phenyloxetane, **1** (0.04 mol dm^{-3}) with nitric acid (2.0 mol dm^{-3}) in dichloromethane, 22–25 °C

t/min	**1**	**3** + **5**[a]	**4**	**6**	**2**
1.0	66	34	0	0	<1
2.0	42	57	1	0	<1
3.0	22	75	3	0	<1
4.0	7	84	9	0	<1
5.0	0	89	11	0	<1
6.0	0	90	9	1	<1
8.0	0	88	11	1	<1
10.0	0	87	11	2	<1
13.0	0	86	11	3	<1
15.0	0	85	12	4	<1
t/h					
0.5	0	81	13	6	<1
2.0	0	69	17	15	<1
4.0	0	52	15	33	0
6.0	0	40	14	46	0
8.0	0	42	15	43	0
12	0	20	15	65	0
14	0	16	15	70	0
38	0	11	14	75	0
24	0	3	14	83	0

[a] Of these, **3** is a very minor component; see text.

Discussion

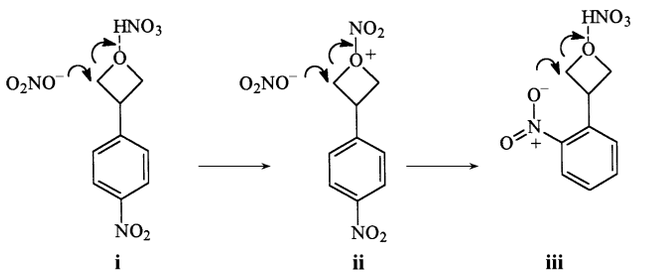
Aromatic nitration

First-order rate constants for aromatic nitration, as represented by $k_a + k_c$ and $k_e + k_f$ (the suffixes relating to the steps in Scheme 1) increase very rapidly with the concentration of nitric acid; the formal reaction order in nitric acid is >6. This appears to be typical for nitronium ion nitrations under the conditions.[6] The kinetics of nitration of 1,4-dichlorobenzene, investigated using [$^2H_2$]dichloromethane as solvent to permit direct monitoring by ^{1}H NMR, show an entirely similar dependence upon the concentration of nitric acid (Table 5). This indicates that aromatic nitration of **1** occurs, not through the minority free base form (the concentration of which would dwindle with increasing concentration of nitric acid and lead to a lower observed reaction order) but through the majority species, *i.e.* the hydrogen-bonded complex of **1** with nitric acid.[7] This complexation perhaps accounts for the surprisingly low reactivity (**1** is almost as unreactive as *p*-dichlorobenzene towards aromatic nitration). The rather strongly *para*-directing influence (86% *para*-nitration) of the (complexed) oxetane ring may reflect steric hindrance to *ortho* attack. There was no evidence of *meta*-nitration of either **1** or **2** but it is possible that this occurred to a small extent and was not detected.

The oxetane ring-opening reaction

First-order rate constants for oxetane ring-opening, as represented by k_b and k_d (k_g is considered separately below) increase with the nitric acid concentration much less rapidly than those for aromatic nitration (Table 4). This is why the initial reaction of **1** changes from 15% aromatic nitration, 85% oxetane ring-opening in 0.5 mol dm^{-3} nitric acid to nearly 100% aromatic nitration in 2 mol dm^{-3} nitric acid (Table 4). For comparison we studied independently by ^{1}H NMR the kinetics of ring-openings of **5** to give **6** [step (*d*)] and of **7** to give **8**. These were clean, quantitative and apparently single step reactions exhibiting good pseudo-first-order kinetics. The solvent used for these studies was [^{2}H]trichloromethane rather than the more expensive [$^2H_2$]dichloromethane but it is unlikely that the change of solvent has a profound effect.

The results (Table 6) confirm the formal approximately second order dependence on the concentration of nitric acid and add support to the conclusions drawn from the study of the more complicated reaction of **1** (Scheme 1 and Appendix). Oxetanes **1**, **5** and **7** all react at comparable rates and the effect of substituents at the 3-position is relatively small. It seems likely that the reaction occurs by nucleophilic attack of nitrate ion at the 2-position of the complexed oxetane, with an S_N2 type transition state as in Scheme 2 **i** and **ii**. It is not clear



Scheme 2

whether the attack is on the hydrogen bonded complex, **i** giving initially the mononitrate which is subsequently converted to the dinitrate, or on the nitronium ion complex **ii**,[7] giving the dinitrate directly. If the identification of the unknown compound in the reaction of **1** with 0.5 mol dm^{-3} nitric acid as the mononitrate ester is correct, then the former is more likely, with the mononitrate–dinitrate equilibrium (which on the evidence of the ready exchange of ^{15}N label between nitrate function and nitric acid, see Experimental section, is established on a shorter timescale than the present reactions) swinging towards the dinitrate as the concentration of nitric acid increases.

The reaction of **3** [step (*g*) in Scheme 1], in sharp contrast, has a rate constant which is of lower order in the nitric acid concentration and is much faster (*ca.* 200 times faster in 1 mol dm^{-3} nitric acid, compare k_d and k_g in Table 4). This difference between 3-(*ortho*-nitrophenyl)- and 3-(*para*-nitrophenyl)-oxetanes is too large to be a simple steric or polar effect and indicates that the *ortho*-nitro compound enjoys a special mechanism. A tentative suggestion is illustrated in Scheme 2 **iii** in which there is intramolecular nucleophilic catalysis in the ring opening. (This would produce an intermediate which would then give the product dinitrate after rapid ring-opening by nitrate.)

Table 4 First-order rate constants for the steps in Scheme 1, k_a for step (*a*) *etc*., calculated as described in the Appendix to fit the data of Tables 1–3

[HNO_3]/mol dm^{-3}	0.5	1.0	2.0
$k_a/10^{-5}$ s^{-1}	0.15	7.7	720
$k_b/10^{-5}$ s^{-1}	0.67	1.7	—[b]
$k_c/10^{-5}$ s^{-1}	0.025	1.25	120
$k_d/10^{-5}$ s^{-1}	—[b]	0.82	3.3
$k_e/10^{-5}$ s^{-1}	—[a]	1.3	—[b]
$k_f/10^{-5}$ s^{-1}	—[a]	0.45	—[b]
$k_g/10^{-5}$ s^{-1}	—[a]	180	340
$f[=(k_a + k_c)/(k_a + k_b + k_c)]$	0.15	0.84	1.0

[a] Extent of reaction too small to obtain reliable value. [b] Fraction of reaction by step (*b*) insignificant, precluding determination of this quantity.

Table 5 Observed first-order rate constants[a] k for nitration of 1,4 dichlorobenzene in [$^2H_2$]dichloromethane at 30.0 °C

[HNO_3]/mol dm^{-3}	1.0	1.5	2.0
$k/10^{-5}$ s^{-1}	1.8	23	170, 200

[a] ±5%.

Conclusions

Treatment of 3-substituted oxetanes with nitric acid (≥1 mol dm^{-3}) in dichloromethane or trichloromethane gives high yields of 2-substituted propane-1,3-diol dinitrates. 3-Phenyloxetane reacts, initially, predominately by oxetane ring-opening at low concentrations and by aromatic nitration at high concentrations of nitric acid, and the orders in nitric acid for the ring-opening and aromatic nitrations are approximately

Table 6 Observed first-order rate constants[a] k for oxetane ring-openings **5** ⟶ **6** and **7** ⟶ **8** with nitric acid in [^{2}H]trichloromethane at 30.0 °C

5 ⟶ **6**								
[HNO_3]/mol dm^{-3}	1.5		3.0			4.5		6.0
$k/10^{-5}$ s^{-1}	9.0		34			97		186
7 ⟶ **8**								
[HNO_3]/mol dm^{-3}		2.4	3.0	3.6	4.2	4.8	5.4	6.0
$k/10^{-5}$ s^{-1}		34	48	75	120	160	200	260

[a] ±5%. Mean of two or three determinations.

2 and 6, respectively. Aromatic nitration is by a normal nitronium ion reaction of the complexed substrate which is comparable in reactivity to 1,4-dichlorobenzene. Ring opening involves S_N2 reaction of the complexed substrate with nitrate ion. A special mechanism operates in the ring-opening reaction of **3**.

Appendix

The rate constants in Table 4 were derived as follows.

The mechanism of Scheme 1 leads to analytical expressions for the concentrations of **1**–**6**. These are more conveniently expressed with the following symbol changes, in which k_1 is the global rate constant ($k_a + k_b + k_c$) for loss of **1**, k_3 is the global rate constant ($k_e + k_f$) for aromatic nitration of **2**, and k_d and k_g retain their significance; f is the fraction, $(k_a + k_c)/k_1$, of **1** undergoing aromatic nitration, g is the fraction of this, $k_a/(k_a + k_c)$, which occurs at the *para* position, and h is the fraction, $k_e/(k_e + k_f)$, of aromatic nitration of **3** which occurs at the *para* position. Thus in Scheme 1, $k_a = fgk_1$, $k_b = (1 - f)k_1$, $k_c = f(1 - g)k_1$, $k_e = hk_3$, $k_f = (1 - h)k_3$. The concentrations, expressed as percentages, p**1**, *etc.*, of **1**–**6** are then the following functions of time, t:

$$\mathrm{p}\mathbf{1} = 100\ \mathrm{e}^{-k_1 t}$$

$$\mathrm{p}\mathbf{2} = 100(1 - f)[k_1/(k_3 - k_1)](\mathrm{e}^{-k_1 t} - \mathrm{e}^{-k_3 t})$$

$$\mathrm{p}\mathbf{3} = 100f(1 - g)[k_1/(k_g - k_1)](\mathrm{e}^{-k_1 t} - \mathrm{e}^{-k_g t})$$

$$\mathrm{p}\mathbf{5} = 100fg[k_1/(k_d - k_1)](\mathrm{e}^{-k_1 t} - \mathrm{e}^{-k_d t})$$

$$\mathrm{p}\mathbf{6} = \{fg + (1 - f)h\}(100 - \mathrm{p}\mathbf{1}) - \mathrm{p}\mathbf{5} - h\mathrm{p}\mathbf{2}$$

$$\mathrm{p}\mathbf{4} = 100 - \mathrm{p}\mathbf{1} - \mathrm{p}\mathbf{2} - \mathrm{p}\mathbf{3} - \mathrm{p}\mathbf{5} - \mathrm{p}\mathbf{6}$$

Values for the unknown parameters amongst k_1, k_3, k_g, k_d, f and g, were then found by least-squares fitting[8] of calculated with observed (Tables 1–3) concentrations. The value of h was established as 0.75 from independent study of the *ortho*:*para* isomer proportions in the nitration of **2**. For the run in 2 mol dm^{-3} HNO_3, f was unity [no significant contribution from path (*b*) and k_3 therefore not required]. This run was used to obtain a best fitting value of g, 0.86, which was then used at the other two nitric acid concentration runs also, to reduce the number of fitting parameters. In the run with 0.5 mol dm^{-3} nitric acid, the concentration of the unknown compound, believed to be the mononitrate corresponding to **2**, was added to that of **2** for the purposes of the fitting procedure.

Experimental

Apparatus

All ^{1}H and ^{13}C NMR spectra were recorded on either a 250 MHz Bruker spectrometer or a 300 MHz Bruker spectrometer. CIDNP (chemically induced dynamic nuclear polarisation) experiments and ^{15}N NMR spectra were recorded on a 400 MHz Hitachi spectrometer. IR spectra were recorded using a Perkin-Elmer 881 IR spectrophotometer. Mass spectra were obtained using a Kratos Profile.

Materials

1,1-Bis(hydroxymethyl)cyclohexane and 3,3-pentamethyleneoxetane were kindly provided by Dr John Dormer. [$^2H_2$]Dichloromethane was refluxed over calcium hydride and then distilled immediately before use. [^{2}H]Trichloromethane, dichloromethane and tetrahydrofuran were dried by distillation in silanized glassware over calcium hydride immediately before use.

3-Phenyloxetane,[7] 3-(*p*-nitrophenyl)oxetane,[7] ^{15}N enriched anhydrous nitric acid and [^{15}N]nitrobenzene[10] were prepared as described.

Lack of reaction of 3-phenyloxetane with a dilute solution of anhydrous nitric acid in dichloromethane

To a solution of 3-phenyloxetane in dry dichloromethane (0.15 mol dm^{-3}, 1.0 cm^3) at room temp. was added a solution of anhydrous nitric acid (0.15 mol dm^{-3}; 9.0 cm^3) in dichloromethane also at room temp. The reaction was left to stand for 20 h after which the reaction mixture was quenched in an excess of ice-cold aqueous sodium hydrogen carbonate solution. The organic layer was separated and dried over anhydrous magnesium sulfate. After filtration the solvent was evaporated to leave a yellow oil which was shown by ^{1}H NMR to be unreacted starting material only.

Reaction between 3-phenyloxetane and 2.0 mol dm^{-3} anhydrous nitric acid in dichloromethane

To 3-phenyloxetane (0.050 g, 0.37 mmol) was added a solution of anhydrous nitric acid (2.0 mol dm^{-3}, 5 cm^3), in dry dichloromethane such that the solution rapidly turned golden yellow. The reaction mixture was left to stand at room temp. for 20 h. The solution was then quenched in an excess of ice-cold sodium hydrogen carbonate and the organic layer separated. The aqueous layer was extracted with dichloromethane (2 × 20 cm^3) and the combined extracts dried over anhydrous magnesium sulfate for 24 h. After filtration an orange–brown oil (0.085 g, 81%) was obtained.

Two components were recognised by NMR, and separated and purified by column chromatography over flash silica in order to allow identification and characterisation of the products as **4** (*ca.* 25%) and **6** (*ca.* 75%).

4 2-(*o*-Nitrophenyl)propane-1,3-diol dinitrate: ν_{max}/cm^{-1} (oil) 2924 (m, CH_2 stretch), 1629 (vs, asym. NO_2 str. O–NO_2), 1528 (vs, aromatic asym. C–NO_2 str.), 1350 (vs, sym. C–NO_2 str.), 1283 (vs, sym. NO_2, str., O–NO_2), 856 (s, 2 adjacent aromatic C–H), 731 (s, 4 adjacent aromatic C–H/NO_2 wagging); δ_H(300 MHz; $CDCl_3$) 4.15 (1 H, p, J 6.02, C-2 methine), 4.76–4.92 (4 H, m, methylenes), 7.46–7.57 (2 H, m, aromatic *ortho*-substituted), 7.63–7.68 (1 H, m, aromatic *ortho*-substituted), 7.94–8.00 (1 H, dd, aromatic *ortho*-substituted); δ_C(75.5 MHz; $CDCl_3$) 36.449 (C-2 methine), 71.154 (C-1 and C-3 methylenes), 125.520, 129.138, 129.439, 133.557 (aromatic C–H), *ca.* 138 (*ipso*-aromatic C), *ca.* 148 (aromatic C–NO_2).

6 2(*p*-Nitrophenyl)propane-1,3-diol dinitrate: ν_{max}/cm^{-1} (oil) 2960, 2908, 2858 (m, CH_2 stretch), 1638 (vs, asym. NO_2 stretch, O–NO_2), 1606 (m, Ar–H str.), 1522 (vs, aromatic asym. C–NO_2 str.), 1440 (m, C–H def.), 1276 (vs, sym. NO_2 str., O=NO_2), 855 (s, 2 adjacent aromatic C–H), 754 (m, *ortho*-substituted aromatic), 734 (ms, 4 adjacent aromatic C–H)/NO_2 wagging); δ_H(300 MHz; $CDCl_3$) 3.63 (1 H, m, C-2 methine), 4.78 (4 H, dd, C-1 and C-3 methylenes), 7.47 (2 H, dt, aromatic *para*-substituted), 8.25 (2 H, dt, aromatic *para*-substituted); δ_C(75.5 MHz; $CDCl_3$) 41.547 (C-2 methine), 71.314 (C-1 and C-3 methylenes), 124.410, 128.990 (aromatic C–H), 142.711 (aromatic *ipso*-C), 148.001 (aromatic C–NO_2).

General procedure for the product studies of the reaction of 3-phenyloxetane with various concentrations of anhydrous nitric acid in dichloromethane as reported in Tables 1–3

To a solution of 3-phenyloxetane in dry dichloromethane (1.0 cm^3, 0.08 mol dm^{-3}, 0.08 mmol) was added a combination of dichloromethane and anhydrous nitric acid in dichloromethane such that the solution was 0.04 mol dm^{-3} in substrate and either 0.50, 1.0 or 2.0 mol dm^{-3} in nitric acid. The solution was left for a known time at room temp. (*ca.* 22–25 °C) and then neutralised in an excess of ice-cold aqueous sodium hydrogen carbonate solution. The organic layer was separated and the product extracted further (3 × 20 cm^3 dichloromethane). After drying over magnesium sulfate the solvent was evaporated to yield a mixture of products which was analysed by ^{1}H NMR

spectroscopy. By this method yields were determined with an accuracy of ±2%.

Reaction of 3,3-pentamethyleneoxetane with anhydrous nitric acid in dichloromethane

To a solution of 3,3-pentamethylene oxetane (0.050 g, 0.396 mmol) in dry dichloromethane was added a solution of nitric acid (2.0 mol dm^{-3}, 5.0 cm^3, 10 mmol) in dry dichloromethane. The reaction was allowed to stand at room temp. for 20 h then quenched in an excess of aqueous sodium hydrogen carbonate solution. The dichloromethane layer was separated and the aqueous layer extracted further by dichloromethane (2 × 20 cm^3). The combined extracts were dried over anhydrous magnesium sulfate for 24 h. After filtration the solvent was removed to give a pale-yellow oil (0.058 g, 0.248 mmol) identified as the dinitrate product in 63% yield: δ_H(300 MHz; $CDCl_3$), 1.51 (10 H, s, cyclohexane ring, methylenes), 4.40 (4 H, s, methylenes adjacent to nitrate functional groups), δ_C(75.5 MHz; $CDCl_3$), 20.85, 25.45, 29.84 (cyclohexane ring methylenes), 37.23 (cyclohexane carbon), 74.40 (methylenes adjacent to nitrate functions).

Reaction of 2-phenylpropane-1,3-diol with anhydrous nitric acid in dichloromethane

To 2-phenylpropane-1,3-diol (0.045 g, 0.3 mmol) in a 5 ml graduated flask was added a solution of anhydrous nitric acid in dry dichloromethane (2.0 mol dm^{-3}, 5.0 cm^3, 10 mmol), the solution turning yellow on mixing. The reaction mixture was left to stand at room temp. for 20 h. The solution was quenched by mixing with an excess of ice-cold aqueous sodium hydrogen carbonate solution. The organic layer was separated and the aqueous layer further extracted by dichloromethane (2 × 20 cm^3). The combined organic aliquots were then dried over magnesium sulfate for 24 h. After filtration the solvent was evaporated to give a yellow oil (0.065 g, 76.5%). NMR revealed that this consisted of **6** (*ca.* 40%) and **4** (*ca.* 60%).

Reaction of 1,1-bis(hydroxymethyl)cyclohexane with anhydrous nitric acid in dichloromethane

To 1,1-bis(hydroxymethyl)cyclohexane (0.053 g, 0.37 mmol) in dichloromethane was added a solution of anhydrous nitric acid (2.0 mol dm^{-3}, 5.0 cm^3) in dry dichloromethane. The reaction was allowed to stand for 20 h then quenched in an excess of ice-cold aqueous sodium hydrogen carbonate solution. The dichloromethane layer was separated and the aqueous layer extracted further by dichloromethane (2 × 20 cm^3). The combined organic extracts were then dried over anhydrous magnesium sulfate for 24 h. After filtration the solvent was evaporated to give a pale-yellow oil (0.060 g, 0.26 mmol) identified as 2,2-pentamethylenepropane-1,3-diol dinitrate **8**, in 70% yield: δ_H(300 MHz; $CDCl_3$), 1.51 (10 H, s, cyclohexane ring methylenes), 4.40 (4 H, s, methylenes adjacent to nitrate functional groups), δ_C(75.5 MHz; $CDCl_3$), 20.85, 25.45, 29.84 (cyclohexane ring methylenes), 37.23 (cyclohexane carbon), 74.40 (methylenes adjacent to nitrate functions).

Preparation of 2-phenylpropane-1,3-diol dinitrate, 2

To 3-phenyloxetane (0.153 g, 1.14 mmol) in dry dichloromethane (22.8 cm^3) at room temp. was added a solution of anhydrous nitric acid in dry dichloromethane (2.5 mol dm^{-3}, 5.7 cm^3). The solution was allowed to stand at room temp. for 72 h after which it was neutralised using an excess of ice-cold aqueous sodium hydrogen carbonate solution. The organic layer was separated and the product extracted further (3 × 50 cm^3 dichloromethane). The combined extracts were dried over calcium sulfate for 4 h. After filtration the solvent was evaporated to yield a yellow–brown oil. ^{1}H NMR spectroscopy showed this to be a mixture of products, the desired **2** being the predominant compound in *ca.* 50% yield. Column chromatography over flash silica allowed purification of the components, the first of which was 2-phenylpropane-1,3-diol dinitrate, **2**: clear colourless oil (0.081 g, 30.0%) (Found: C, 44.63; H, 4.16; N, 11.57. $C_9H_{10}N_2O_6$ requires C, 44.61; H, 4.21; N, 11.41%); (R_f = 0.90, 100% CH_2Cl_2); ν_{max}/cm^{-1} (oil) 3036, 2965, 2903 (mw, CH_2 str.), 1640 (vs, O–NO_2 str.), 1275 (vs, O–NO_2 asymm. str), 1072 (mw, C–O str.), 756, 701 (s, 5 adjacent aromatic C–H, mono-substituted aromatic); δ_H(300 MHz; $CDCl_3$) 3.49 [1 H, q, *J* 6.54, C–H methine (2-phenylpropane-1,3-diol dinitrate)], 4.74 (4 H, d, *J* 6.55, C-1/C-3 methylenes), 7.2–7.45 (5 H, m, aromatic monosubstituted); δ_C(75.5 MHz; $CDCl_3$) 41.598 (C-2 methine), 72.323 (C-1/C-3 methylenes), 127.796, 128.524, 129.302 (aromatic C–H), 135.436 (*ipso* C); m^+/z (Reqd. 242.053 886, actual 242.053 21, deviation 2.7 ppm).

The next two fractions contained, in addition to **2** and **4**, an unknown compound, δ_H(300 MHz; $CDCl_3$) 3.35 (1 H, br m, methine), 3.70 (2 H, br m, methylene), 4.65 (2 H, br m, methylene), 7.1–7.35 (m, unsubstituted aromatic).

This is thought to be the mononitrate ester of 2-phenylpropane-1,3-diol.

Nitration of 2-phenylpropane-1,3-diol dinitrate, 2, in dichloromethane

To a solution of **2** in dry dichloromethane (0.60 cm^3) at room temp. was added a solution of anhydrous nitric acid in dry dichloromethane (0.40 cm^3, 5.0 mol dm^{-3}) also at room temp., the reaction mixture instantly pale yellow. After 5 min the reaction mixture was quenched in an excess of ice-cold aqueous sodium hydrogen carbonate. The organic layer was separated and the product extracted further (2 × 5 cm^3). The combined organic aliquots were dried over magnesium sulfate for 12 h. After filtration the solvent was evaporated to yield a pale-yellow oil (0.0074 g) identified by ^{1}H NMR spectroscopy as a mixture of **4** (26%) and **6** (74%) only.

Search for ^{15}N CIDNP effects

A solution of the substrate in dry [^{2}H]trichloromethane (0.20 mol dm^{-3}, 250 mm^3) was added to a 5 mm NMR tube. To this was added a reference solution of ^{15}N enriched nitrobenzene in [^{2}H]trichloromethane (2.50 mol dm^{-3}, 20 mm^3). A solution of 10% ^{15}N enriched nitric acid in dry [^{2}H]trichloromethane (8.7 mol dm^{-3}, 230 mm^3) was then added to the reaction mixture. The tube was shaken and inserted into the NMR spectrometer. Data collection was started approximately 100 s after mixing. Data collections consisted of eight scans with a time interval between consecutive data collections of 2 min.

No ^{15}N CIDNP effects were seen for any of the substrates studied [3-phenyloxetane, 3-(4-nitrophenyl)oxetane and 2-phenylpropane-1,3-diol dinitrate]. In the case of the last-mentioned substrate it was noteworthy that the aromatic nitro groups and the nitrate groups in the product showed the same degree of isotopic enrichment; ready exchange of the nitrate groups with nitric acid had occurred.

A ^{1}H NMR kinetic study of the nitric acid nitration of 3-substituted oxetanes in [^{2}H]trichloromethane at 30 °C

3,3-Pentamethyleneoxetane. To a solution of 3,3-pentamethyleneoxetane in [^{2}H]trichloromethane (250 mm^3, 0.203 mol dm^{-3}) in a 5 mm NMR tube was added a known volume of dry [^{2}H]trichloromethane and anhydrous nitric acid in [^{2}H]trichloromethane (12.0 mol dm^{-3}) such that the reaction could be studied over an acidity range of 2.4 to 6.0 mol dm^{-3}. The NMR tube was shaken and inserted into the NMR spectrometer which was maintained at a temperature of 30 °C. The time between addition of the nitric acid to the substrate solution and the midpoint of the data collection for the first NMR spectrum was noted. Spectra of six scans each were collected consecutively, without a time delay such that the time

period between the mid-point of each data collection was 34.5 ± 0.5 s.

3-(4-Nitrophenyl)oxetane. To a solution of 3-(4-nitrophenyl)oxetane in [^{2}H]trichloromethane (250 mm^3, 0.20 mol dm^{-3}) in a 5 mm NMR tube was added a known volume of dry [^{2}H]trichloromethane and anhydrous nitric acid in [^{2}H]trichloromethane (12.0 mol dm^{-3}) such that the reaction could be studied over an acidity range of 1.5 to 6.0 mol dm^{-3}. The NMR tube was shaken and inserted into the NMR spectrometer which was maintained at a temperature of 30 °C. The time between addition of the nitric acid to the substrate solution and the midpoint of the data collection for the first NMR spectrum was noted. Spectra of six scans each were collected consecutively, without a time delay such that the time period between the mid-point of each data collection was 34.5 ± 0.5 s.

A kinetic study by ^{1}H NMR spectroscopy of the nitric acid nitration of 1,4-dichlorobenzene in [$^2H_2$]dichloromethane

A known volume of [$^2H_2$]dichloromethane was added to a solution of 1,4-dichlorobenzene (0.050 mol dm^{-3}) and 1,4-dinitrobenzene reference (0.050 mol dm^{-3}) in [$^2H_2$]dichloromethane (100 mm^3) in a NMR tube such that when anhydrous nitric acid in [$^2H_2$]dichloromethane (10.0 mol dm^{-3}) was added the total volume was 500 mm^3. The sample was inserted into a NMR spectrometer maintained at 30 °C and data collection started as soon as possible. Each data set consisted of six scans. The time between each data collection was 33 s.

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References

1 P. Golding, R. W. Millar, N. C. Paul and D. H. Richards, *Tetrahedron*, 1993, **49**, 7037.
2 P. Golding, R. W. Millar, N. C. Paul and D. H. Richards, *Tetrahedron*, 1993, **49**, 7051.
3 R. W. Millar, M. E. Colclough, P. Golding, P. J. Honey, N. C. Paul, A. J. Sanderson and M. J. Stewart, *Phil. Trans. R. Soc. Lond. A*, 1992, **339**, 305.
4 J. Dormer and R. B. Moodie, *J. Chem. Soc., Perkin Trans. 2*, 1994, 1195.
5 R. J. Lewis and R. B. Moodie, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1315.
6 R. J. Lewis and R. B. Moodie, *J. Chem. Soc., Perkin Trans. 2*, 1996, in press.
7 K. A. Hylands and R. B. Moodie, *J. Chem. Soc., Perkin Trans. 2*, 1996, 2073.
8 SCIENTIST package, MicroMath Scientific Sofware.
9 P. Picard, D. Leclerq, J. P. Bats and J. Moulines, *Synthesis*, 1980, **81**, 550.
10 J. F. Johnston, J. H. Ridd and J. P. B. Sandall, *J. Chem. Soc., Perkin Trans. 2*, 1991, 623.

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