The nitration of styrenes by nitric acid in dichloromethane

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Kinetics and products of reaction of 4-R-styrenes (R = Me, H, Cl, CF_3, NO_2) with nitric acid in dichloromethane are reported. Reaction occurs in the alkene group and aromatic nitration is insignificant. With increasingly electron-withdrawing substituents the reaction changes from one which is third order in nitric acid and gives rise to the 1-arylethyl nitrate, to one which is of higher order in nitric acid and gives rise to the 2-nitro-1-arylethyl nitrate (β-nitro-nitrate). Both reactions proceed through transition states with carbocation character, by initial β-addition of H^+ and NO_2^+ respectively. The β-nitro-nitrate is formed in part also by a radical pathway, as are other minor products.

Introduction

In a previous paper[1] we reported on the kinetics and mechanism of reaction of some substituted styrenes with dinitrogen pentaoxide. We report here on a parallel investigation of the reactions of the same substrates with nitric acid.

There have been several reviews which include reference to the reactions of nitric acid with alkenes.[2–4] The predominant product is reported to be the nitroalkene. However the reaction is complex and products can include those of oxidative double bond cleavage, or addition. Styrene and substituted styrenes are reported to react with nitric acid to give the corresponding β-nitrostyrenes,[5] and with nitric acid/acetic anhydride mixtures to give β-nitroacetates and β-nitronitrates, as well as β-nitrostyrene.[6–8]

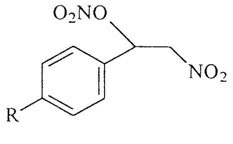
In this paper we report on the reaction of several ring-substituted styrenes with anhydrous nitric acid in dichloromethane.

Results

The number and relative yields of the products of reaction of the substituted styrenes with anhydrous nitric acid in dichloromethane varied markedly with the substituent and the reaction conditions. In the previous paper we identified compounds **1**–**4** as the major products of reaction with dinitrogen pentaoxide. In the present studies compounds **1**–**3** were again evident, though **2** and **3** were never more than minor constituents of the product mix, and compound **4** was not detected. A major product, not seen in the N_2O_5 reactions, was the 1-arylethyl nitrate **5** identified from its MS, ^{1}H NMR and IR spectra and (in the case R = H) by comparison with an authentic sample produced from the reaction of 1-phenylethanol with nitric acid.

Styrene and 4-methylstyrene

Nitration of styrene with an excess of anhydrous nitric acid in dichloromethane gave almost quantitatively 1-phenylethyl nitrate **5** (R = H). At room temperature and with $[HNO_3] = 0.2$ mol dm^{-3} (10-fold excess) this was formed rapidly and in 98% yield. The remaining 2% consisted of two compounds, 1-phenyl-2-nitroethyl nitrate **1** (R = H) and 1-(4-nitrophenyl)ethyl nitrate **5** (R = NO_2). The proportion of this latter compound slowly increased with time and it was clearly formed by subsequent aromatic ring nitration of **5** (R = H) in a reaction which was not further investigated. Nitration of 4-methylstyrene gave **5** (R = CH_3) quantitatively, and no other products were detected.



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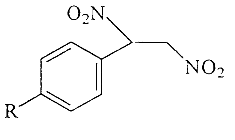

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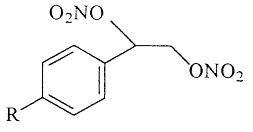

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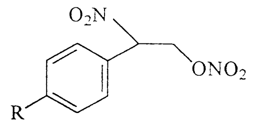

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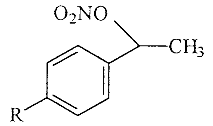

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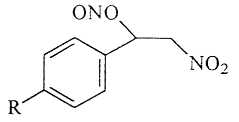

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Kinetics of the reaction of these two substrates with nitric acid were investigated by ^{1}H NMR spectroscopy, using deuteriated dichloromethane as solvent. Integrals of signals for the α-protons of **5** and of the β-protons of the substrate were compared with the integral of the signal from internal trichloromethane standard. With excess nitric acid, substrate depletion and product formation followed a first-order kinetic form and were monitored for two to three half-lives. Observed first-order rate constants are presented in Table 1. The reaction is steeply dependent on the nitric acid concentration and the nearest integral value of the order in nitric acid is three, making the reaction fourth-order overall. Mean values of the fourth-order rate constants for nitric acid addition to styrene and 4-methylstyrene are 0.0334 and 0.423 dm^9 mol^{-3} s^{-1} respectively.

4-Trifluoromethylstyrene and 4-nitrostyrene

The 1-arylethyl nitrates **5** were not formed. The reactions gave instead quantitative yields of the β-nitro-nitrates **1**. No other products were detected.

Kinetics were investigated as described above. With excess nitric acid, substrate depletion and product formation followed a first-order kinetic form and reactions were monitored for two to three half-lives. Observed first-order rate constants are presented in Table 2. The reactions are even more steeply dependent on the nitric acid concentration than those of styrene and 4-methylstyrene reported above. Log–log plots gave orders in

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Table 1 Observed first-order rate constants, k, for reaction of 4-R styrenes (R = H, Me) (concentration 0.02 mol dm^{-3}) with nitric acid to form **5** (R = H, Me) at 30 °C in [$^2H_2$]dichloromethane. Water was absent except where indicated

R = H		R = Me	
[HNO_3]/mol dm^{-3}	k/10^{-3} s^{-1}	[HNO_3]/mol dm^{-3}	k/10^{-3} s^{-1}
0.500	4.3	0.219	4.4
0.500	4.6	0.219	5.1
0.365	1.5	0.183	1.6
0.365	1.5	0.183	1.6
0.210	0.30	0.138	1.2
0.210	0.27	0.138	1.1
0.105		0.102	0.68
0.351[a]	1.2[a]		
0.351[b]	1.4[b]		
0.351[c]	1.3[c]		
0.351[d]	1.4[d]		

[a] [H_2O] = 0.018 mol dm^{-3}. [b] [H_2O] = 0.035 mol dm^{-3}. [c] [H_2O] = 0.053 mol dm^{-3}. [d] [H_2O] = 0.070 mol dm^{-3}.

Table 2 Observed first-order rate constants, k, for reaction of 4-R styrenes (R = CF_3, NO_2) (concentration 0.02 mol dm^{-3}) with nitric acid to form **1** (R = CF_3, NO_2) at 30 °C in [$^2H_2$]dichloromethane. Water was absent except where indicated

R = CF_3		R = NO_2	
[HNO_3]/mol dm^{-3}	k/10^{-3} s^{-1}	[HNO_3]/mol dm^{-3}	k/10^{-3} s^{-1}
0.60	0.21	0.75	0.17
0.60	0.26	0.75	0.18
0.75	2.6	1.01	0.46
0.91	3.9	1.01	0.51
0.91	3.0	1.01	0.51
1.01	6.1	1.25	2.2
1.01	7.1	1.25	2.3
		1.52	3.3
		1.25[a]	0.85[a]
		1.25[b]	0.64[b]

[a] [H_2O] = 0.062 mol dm^{-3}. [b] [H_2O] = 0.125 mol dm^{-3}.

nitric acid of 6.1 and 4.6 for 4-trifluoromethylstyrene and 4-nitrostyrene, respectively, but in view of the high and different ranges of concentrations of nitric acid used these figures probably contain unknown contributions from solvent effects and cannot be interpreted or compared with certainty. From the results with [HNO_3] = 1.01 mol dm^{-3} it appears that the reactivity of 4-trifluoromethylstyrene exceeds that of 4-nitrostyrene by a factor of about 13.

For both these substrates reducing the reaction temperature had no effect on the product composition but at elevated reaction temperatures small amounts of **2** and **3** were detectable.

4-Chlorostyrene

The polar effect of the substituent in this case is intermediate between the two contrasting pairs above and the product composition was therefore of particular interest. Compounds **1** and **5** were normally the major products. Low temperatures, low concentrations of nitric acid, the absence of water, and the presence of added nitrate salt, all favour **5** over **1**. Compounds **2** and **3** were also present in the product mixture from this particular substituted styrene, in proportions which varied with the conditions. (Two other unidentified products were sometimes observed but their combined yields never exceeded 2% and they are not considered further.) Yields of **1**, **2**, **3** and **5** under a variety of circumstances are in Table 3. Addition of nitrous acid scavengers (hydrogen peroxide, urea and sulfamic acid) had no significant effect, but ozone (which reacts with NO_2 to give N_2O_5) modestly enhanced the yield of **5** at the expense of **1** and **2**, whereas deliberate addition of NO_2 had the opposite effect.

Table 3 Product composition, given as percentages of the product mix, from the nitration of 3-chlorostyrene (0.1 mol dm^{-3}) by nitric acid in dichloromethane at various temperatures, concentrations of nitric acid and concentrations of other additives, A

T/ °C	[HNO_3]/mol dm^{-3}	[A]/mol dm^{-3}	**1**	**2**	**3**	**5**
+40	2.0	0	43	19	8	30
+20	2.0	0	37	15	7	41
0	2.0	0	33	11	8	48
−20	2.0	0	27	7	9	57
−60	2.0	0	5	0	0	95
+20	1.5	0	33	13	7	47
+20	1.0	0	30	9	5	56
+20	0.5	0	22	6	5	61
+20	2.0	0.04[a]	36	17	6	40
+20	2.0	0.2[a]	40	19	8	33
+20	2.0	0.4[a]	45	19	7	29
+20	2.0	0.2[b]	4	17	7	71
+20	2.0	0.22[c]	54	46	0	0
+20	2.0	0.02[c]	44	14	0	42
+20	2.0	0.1[d]	39	16	7	38
+20	2.0	0.1[e]	41	15	8	36
+20	2.0	0.1[f]	37	20	5	38
+20	2.0	*g*	32	11	8	49

[a] A = H_2O. [b] A = tetrabutylammonium nitrate. [c] A = NO_2. [d] A = H_2O_2. [e] A = Urea. [f] A = sulfamic acid. [g] A = O_3, the concentration of which was not determined. Ozonised oxygen was passed through the solution for 10 min prior to the addition of the substrate.

Table 4 Observed[a] percentages of reactant and products at time intervals in the reaction of 4-chlorostyrene **S** (0.1 mol dm^{-3}) with nitric acid (1.0 mol dm^{-3}) at 30 °C in [$^2H_2$]dichloromethane

t/s	**S**	**1**	**2**	**3**	**5**	**6**[b]
0	100	0	0	0	0	0
59	79	2	0	0	16	3
128	54	4	2	1	32	6
289	18	12	6	4	55	8
335	9	13	8	5	58	8
404	0	16	9	5	66	4
473	0	20	9	5	66	0

[a] By ^1H NMR spectroscopy, comparing the integrals of the signals for the α-protons to that for the internal trichloromethane reference. [b] An intermediate, believed to be 1-(4-chlorophenyl)-2-nitroethyl nitrite, see text.

An attempt was made to measure a rate constant for this reaction but it was found not to have a simple kinetic form. An intermediate was detectable, the NMR spectrum of which was consistent with the structure **6**. Concentrations as a function of time under typical conditions are presented in Table 4.

Search for CIDNP effects using ^{15}N NMR and ^{15}N-labelled nitric acid

The reactions of 4-nitrostyrene and 4-chlorostyrene with anhydrous ^{15}N-labelled nitric acid in deuteriated dichloromethane were investigated by ^{15}N NMR spectroscopy. In the case of 4-nitrostyrene initial spectra showed an enhanced emission at $\delta = -2.67$ and an enhanced absorption at $\delta = -9.20$ attributable to the α and β nitro groups, respectively, of **2** (R = NO_2). Accumulation of the ^{15}N NMR spectrum at the end of the reaction showed that these two signals were present and also signals at $\delta = -8.95$ and at $\delta = -52.68$, corresponding to the nitro and nitrato groups, respectively, of **1** (R = NO_2). The presence of **2**, about 20% of the product, was unexpected because with unlabelled nitric acid only **1** had been formed. We attribute this to the presence of a greater than usual concentration of adventitious NO_2 in the labelled acid, a consequence of slight changes in the method of preparation of the anhydrous acid. (Usually the first 10% of the distillate from the sulfuric acid–nitric acid mix is discarded, but this procedure was not followed with the labelled nitric acid because of the expensive nature of the material.) The important point is that no CIDNP signals were observed for the main product, **1**. In the case of 4-chlorostyrene CIDNP signals attributable to both **1** and **2** were observed. Also, the enhanced absorption at $\delta = -1.27$, not present in the final spectrum, may be due to the nitro group of the intermediate, 1-(4-chlorophenyl)-2-nitroethyl nitrite (see Discussion). Several other, weak, CIDNP signals were seen, not present in the final spectrum (see Experimental) and possibly linked to minor products arising from the rather lower purity of the labelled acid as described above.

Discussion

The main feature of these results is the rather abrupt change in major product from **5** to **1** as the substituent becomes more electron withdrawing. The mechanisms of the reactions leading to **5** and **1** are now discussed, from which emerge possible reasons for the change in the nature of the reaction with the substituent. This is followed by consideration of the minor products, **2** and **3**, observed in the case of 4-chlorostyrene.

The reaction leading to the formation of the 1-arylethyl nitrate 5

A comparison of the kinetics of reactions of styrene and 4-methylstyrene, both of which lead almost exclusively to **5**, suggest that in the transition state there is a considerable development of positive charge on the α-carbon. The reaction of 4-chlorostyrene is more complex, with several products, but the rate of formation of **5** is in accord with this conclusion (Table 4). The simplest explanation for the substituent effect, and the fact that the reaction is third-order in the concentration of nitric acid, is that there is rate-determining protonation of the β-carbon to give a carbocation. The fact that added nitrate salt in the case of 4-chlorostyrene enhances the relative yield of **5** (Table 3) suggests that protonation is not by protonated nitric acid formed along with nitrate ion in a pre-equilibrium, but by nitric acid, with two more nitric acid molecules needed to solvate the incipient nitrate ion in this non-polar medium. The carbocation then reacts with nitrate ion to give the product:

$$\mathrm{RC_6H_4CH{=}CH_2 + HNO_3(HNO_3)_2 \longrightarrow RC_6H_4CH^+CH_3 + NO_3^-(HNO_2)_2}$$

$$\mathrm{RC_6H_4CH^+CH_3 + NO_3^- \longrightarrow \underset{\textbf{5}}{RC_6H_4CH(ONO_2)CH_3}}$$

The reaction leading to the formation of the β-nitro-nitrates 1

A comparison of the kinetics of reactions of 4-trifluoromethylstyrene and 4-nitrostyrene, both of which lead almost exclusively to **1**, suggest that in this reaction also there is in the transition state considerable development of positive charge on the α-carbon. The simplest explanation for the substituent effect is that there is rate-determining attack of the nitronium ion at the β-carbon, to give a nitrocarbocation. The nitrocarbocation then reacts with nitrate ion to give the product:

$$\mathrm{RC_6H_4CH{=}CH_2 + NO_2^+ \longrightarrow RC_6H_4CH^+CH_2NO_2}$$

$$\mathrm{RC_6H_4CH^+CH_2NO_2 + NO_3^- \longrightarrow \underset{\textbf{1}}{RC_6H_4CH(ONO_2)CH_2NO_2}}$$

The diminished relative yield of **1** from 4-chlorostyrene when nitrate ion is present is then seen as arising from its effect on the nitronium ion concentration [eqn. (1)]. The high orders of this reaction in nitric acid (formally 6.1 and 4.6 for 4-trifluoromethylstyrene and 4-nitrostyrene, respectively, but at concentrations of nitric acid at which medium effects may become significant), may be because in the pre-equilibrium formation of the nitronium ion according to eqn. (1) further molecules of nitric acid are required to solvate the nitronium and nitrate ions.

$$\mathrm{2HNO_3 = NO_2^+ + NO_3^- + H_2O} \qquad (1)$$

The high order of the reaction in nitric acid is a possible reason why the reaction leading to **1** takes over from that leading to **5** with the styrenes bearing the more electron-withdrawing substituents, because higher concentrations of nitric acid are used in order to effect reaction at a reasonable rate with the deactivated substrates. An additional reason may be that, with increasingly reactive substrates, the rate of the reaction with the nitronium ion does not increase because the limit of diffusion-controlled reaction has been reached (a phenomenon well documented in aromatic nitrations[9]) allowing the reaction leading to **5** to become predominant.

Further evidence of an ionic rather than a radical pathway comes from the absence of CIDNP signals attributable to the product **1** from 4-nitrostyrene. However, the fact that the formation of **1** was not completely eliminated by nitrate addition, and that in the case of 4-chlorostyrene CIDNP signals attributable to **1** were seen (see above), suggests that there is an additional mechanism for the formation of **1**. This is discussed further below.

The reactions leading to the formation of the dinitro and dinitrato products, 2 and 3, and contributing to the formation of 1

Products **2** and **3** following reaction of the substituted styrene at or near room temperature, were only observed with 4-chlorostyrene, the substrate intermediate in reactivity between those producing only **5** and those producing only **1**. (At elevated temperatures small amounts of these products were also observed with 4-trifluoromethylstyrene and 4-nitrostyrene.) The dinitro compound **2** is probably formed as described in the previous publication,[1] *i.e.* by sequential addition of two NO_2 radicals. The signs of the CIDNP signals (see above and ref. 1) are in accord with this conclusion. The second NO_2 radical, combining with the first formed β-nitro radical in the step inducing the nuclear polarisation, can do so through nitrogen or through oxygen, as argued previously.[1] Combination through nitrogen leads directly to **2**, and combination through oxygen gives rise to the β-nitroethyl nitrite **6** which is oxidised to the β-nitroethyl nitrate **1** rapidly enough for the CIDNP to persist into the product. The intermediate **6** is sufficiently long lived to be observed during the progress of the reaction and it is clear from the way in which the relative concentrations vary with time that its further reaction does indeed lead to **1** (Table 4). We have demonstrated using isoamyl nitrite as a model compound that the oxidation of an alkyl nitrite to an alkyl nitrate would occur under these conditions (see Experimental section). Thus, the reaction which leads to **2** also leads, *via* **6**, to **1**, and provides the additional route to the latter which the results require. The failure of added water to suppress the formation of **1**, which would not accord with the ionic mechanism above in view of the pre-equilibrium (1), indicates that in the case of 4-chlorostyrene the radical route to **1** predominates. Deliberate addition of NO_2 to the reaction mixture enhances the yields of **1** and **2** relative to **3** and **5**. The fact that **2** is formed, howbeit in relatively low yield (Table 3), even in the absence of added NO_2, now requires comment. Addition of nitrous acid traps like urea, sulfamic acid and hydrogen peroxide had no significant effect, and the presence of ozone (which reacts with NO_2 to form N_2O_5) caused only a small decrease, in the relative yield of **2** (Table 3). Its relative yield is enhanced by high temperatures and it is possible that NO_2 is formed by homolysis of nitric acid.

The formation of the dinitrate **3**, which was formed from 4-chlorostyrene and in low relative yields (7 ± 2%) under a variety of conditions, is more difficult to explain. The only other styrenes to give any of product **3** were 4-trifluoromethyl and 4-nitrostyrene and these only in trace amounts at elevated temperatures. As we previously reported the dinitrate **3** was a much more significant product from the reactions of 4-trifluoromethyl and 4-nitrostyrene with dinitrogen pentaoxide,[1] and a mechanism was proposed which started with β-addition of the nitrate radical formed by homolysis of dinitrogen pentaoxide. However, the concentration of nitrate radicals formed from nitric acid must be extremely small, and in any case this intermediate radical would have been expected to give rise to **4**, as well as **3**,[1] but **4** was not detected in this study. It is not clear why, with nitric acid, 4-chlorostyrene gives rise to small but significant amounts of **3**.

Experimental

Materials

Nitrogen dioxide, isoamyl nitrite, styrene, 4-chlorostyrene, 4-methylstyrene and 4-(trifluoromethyl)styrene were used without further purification.

Anhydrous nitric acid was prepared by bulb-to-bulb high vacuum distillation of a 60:40 mixture of sulfuric acid and fuming nitric acid. The first 10% of distillate was discarded to prevent contamination with nitrous acid. The anhydrous acid was stored at −60 °C. Dichloromethane was dried by distillation from calcium hydride. Deuteriated dichloromethane and deuteriated chloroform were dried by distillation from phosphorous pentaoxide in silanised glassware.

4-Nitrostyrene,[1] 1,2-dinitrato-4-(chlorophenyl)ethane[10] and 4-chlorostyrene oxide[10] were prepared as described.

1-Phenylethyl nitrate, 1-(4-methylphenyl)nitrate and 1-(4-chlorophenyl)nitrate were prepared as described in the quenching method below.

In each case a material with identical NMR spectrum was prepared by the reaction of the substituted 1-phenylethanol with dinitrogen pentaoxide.

1-Phenylethyl nitrate δ_H(250 MHz; $CDCl_3$), 7.3 (5 H, m, aromatic), 5.9 (1 H, q, CH) and 1.6 (3 H, d, CH_3). *m/z* M^+ 167.05931. $C_8H_9NO_3$ requires 167.058 24. ν/cm^{-1}: 2991 (CH str, arom.) and 1631 (O–NO_2 str).

1-(4-Methylphenyl)ethyl nitrate δ_H(250 MHz; $CDCl_3$), 7.3 (2 H, d, aromatic), 7.2 (2 H, d, aromatic), 5.45 (1 H, q, CH), 2.4 (3 H, s, CH) and 1.65 (3 H, d, CH_3).

1-(4-Chlorophenyl)ethyl nitrate δ_H(250 MHz; $CDCl_3$), 7.3 (4 H, m, aromatic), 5.9 (1 H, q, CH) and 1.6 (3 H, d, CH_3). *m/z* M^+ 201.6193. $C_8H_8NO_3Cl$ requires 201.6094. ν/cm^{-1}: 2934 (CH str, arom.) and 1631 (O–NO_2 str).

The reaction of isoamyl nitrite with nitric acid

This was carried out as described in the quenching method below, with isoamyl nitrite in place of the substituted styrene. The product was isoamyl nitrate, δ_H(250 MHz; $CDCl_3$), 4.51 (2 H, t, CH_2), 1.73 (1 H, sept., CH), 1.62 (2 H, q, CH_2) and 0.95 (6 H, d, $2CH_3$). *m/z* M^+ 133.1242 $C_5H_{11}NO_3$ requires 133.0739.

The reactions of styrenes with anhydrous nitrous acid

The quenching method. Nitric acid (and in some cases an additive such as water, tetrabutylammonium nitrate, nitrous acid scavenger or nitrogen dioxide) was dissolved in dry dichloromethane (5 cm^3). The substituted styrene (0.001 mol) was dissolved in dry dichloromethane (4 cm^3). Both solutions were brought to the required temperature in a thermostatic bath then mixed and brought to 10 cm^3 by the addition of dichloromethane. After an appropriate time interval the solution was added to cold saturated aqueous sodium hydrogencarbonate. The organic layer was separated and dried ($MgSO_4$) and the solvent was removed under reduced pressure. The reaction products were analysed by one or more of the following: NMR, HPLC, IR and mass spectrometry.

The ^1H NMR method. Nitric acid (0.06–1.0 g) was weighed out in a dry glove box and dry CD_2Cl_2 was added to make 5 cm^3 of solution. This was stored at −60 °C until required. A solution of the substituted styrene was prepared similarly. Prior to the reaction both solutions were brought to the required temperature. A measured volume (0.25 cm^3) of each solution was then transferred to an NMR tube. Spectra were recorded on a 250 MHz Bruker spectrometer.

^{15}N-labelled nitric acid CIDNP studies with 4-chlorostyrene and 4-nitrostyrene

Anhydrous ^{15}N-labelled nitric acid (0.50 g, 0.008 mol) was dissolved in dry deuteriated dichloromethane (3 cm^3) in a dry glove box and placed in a 10 mm NMR tube. At the start of the experiment a solution of the 4-substituted styrene (5×10^{-4} mol) in dry deuteriated dichloromethane (2 cm^3) was added and the ^{15}N NMR spectra recorded on a Bruker 400 MHz spectrometer at frequent intervals. All ^{15}N chemical shifts are relative to external nitromethane.

The following enhanced emissions (ee) and enhanced absorptions (ea) were observed: 4-chlorostyrene: $\delta_{^{15}N}$(400 MHz; $CDCl_3$) 16.49, −1.27 (ea, medium), (ee, weak) 16.23, (ee, weak) 2.03, (ee, weak), 0.77 (ee, v. strong), −1.27 (ea, medium), −4.55 (ee, weak), −7.12 (ea, medium) and −7.12 (ea, medium). 4-Nitrostyrene: $\delta_{^{15}N}$(400 MHz; $CDCl_3$) −2.28 (ee, v. strong) and −9.29 (ea, v. weak).

The reactions were then worked up as described in the quenched method above and the mixtures analysed by ^1H and ^{15}N NMR spectroscopy.

4-Chlorostyrene. $\delta_{^{15}N}$(400 MHz; CD_2Cl_2), 0.77 (α-nitro of dinitro, d), −7.12 (β-nitro of β-nitronitrate, dd), −7.89 (β-nitro of dinitro, dd), −11.95 (aromatic, s), −13.53 (aromatic, s), −43.63 (α-nitrate of mononitrate, d), −45.84 (α-nitrate of dinitrate, d), −47.32 (β-nitrate of dinitrate, t) and −51.18 (α-nitrate of β-nitronitrate, d). δ_H(300 MHz, CD_2Cl_2) 7.5 (aromatic, m), 6.58 (α-H of β-nitronitrate, dd), 6.22 (α-H of dinitro, dd), 6.15 (α-H of dinitrate, t), 5.93 (α-H of mononitrate, q), 5.55 (β-H of dinitro, dd), 4.78 (β-H of nitronitrate, dd), 4.73 (β-H of dinitro, dd), 4.75 (β-H of dinitrate, d), 4.6 (β-H of β-nitronitrate, dd) and 1.70 (β-H of mononitrate, d). HPLC revealed three products in addition to the four expected ones, however these were not detectable in the ^1H NMR spectroscopy. They probably account for the unassigned peaks in the CIDNP studies.

4-Nitrostyrene. $\delta_{^{15}N}$(400 MHz; CD_2Cl_2) −2.67 (α-nitro of dinitro, d), −8.59 (β-nitro of β-nitronitrate, dd), −9.29 (β-nitro of dinitro, dd) and −52.68 (α-nitrate of β-nitronitrate, d). δ_H(300 MHz, CD_2Cl_2) 8.39 (aromatic, d), 7.70 (aromatic, d), 6.70 (α-H of β-nitronitrate, dd), 6.38 (α-H of dinitro, dd), 5.60 (β-H of dinitro, dd), 4.80 (β-H of -nitronitrate, dd), 4.75 (β-H of dinitro, dd) and 4.6 (β-H of β-nitronitrate, dd).

(In the case of 4-chlorostyrene, the experiment was repeated but ozonised oxygen was bubbled through the nitric acid solution for 10 min prior to the reaction. The CIDNP effects were unchanged, but the ^1H NMR spectroscopy of the final products revealed some changes in the product ratios.)

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References

1 R. J. Lewis and R. B. Moodie, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1315.

2 G. A. Olah, R. Malhotra and S. C. Narang, *Nitration: Methods and Mechanisms*, VCH, New York, 1989.

3 A. V. Topchiev, *The Nitration of Hydrocarbons and other Compounds*, Akad Nauk SSSR, Moscow, English Edition, Pergamon, 1959.

4 V. V. Perekalin, E. S. Lipina, V. N. Berestovitskaya and D. A. Efremov, *Nitroalkenes: Conjugated Nitro Compounds*, Wiley, New York, 1994.

5 S. W. Tinsley, *J. Org. Chem.*, 1961, **26**, 4723; F. van der Lee, *Recl. Trav. Chim, Pays-Bas*, 1928, **47**, 920.

6 F. G. Bordwell and E. W. Garbisch, *J. Org. Chem.*, 1963, **28**, 1765.

7 F. G. Bordwell and E. W. Garbish, *J. Org. Chem.*, 1962, **27**, 2322, 3049.

8 F. G. Bordwell and E. W. Garbisch, *J. Am. Chem. Soc.*, 1960, **82**, 3588.

9 R. B. Moodie, K. Schofield and G. D. Tobin, *J. Chem. Soc.*, *Perkin Trans. 2*, 1977, 1688.

10 J. Dormer and R. B. Moodie, *J. Chem. Soc.*, *Perkin Trans. 2*, 1994, 1195.

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