Electrophilic Aromatic Substitution. Part 37.[1] Products of Aromatic Nitrations of some Chloronitrobenzenes and Substituted Benzoic Acids in Solutions of Dinitrogen Pentaoxide and of Nitronium Salts in Nitric Acid

Roy B. Moodie,* Andrew J. Sanderson‡ and Richard Willmer
Department of Chemistry, University of Exeter, EX4 4QD, UK

Yields of aromatic products of nitration in nitric acid solutions containing dinitrogen pentaoxide or nitronium salt have been determined. Evidence for the intrusion of a mechanism other than the normal nitronium ion one comes from comparison of products in the two media and from the observation of ^{15}N NMR CIDNP effects. The additional mechanism operative with some substrates in concentrated solutions of dinitrogen pentaoxide is postulated to be one in which reversible addition of the NO_3 radical is followed by combination with NO_2. Dienes produced in this way can give aromatic nitroproducts by elimination of nitric acid. Nitrodecarboxylation of substituted benzoic acids occurs by a radical process.

We reported previously[1] on the kinetics of nitration of several substrates in the title media. The comparison of the rate constants in the two media at the same concentration of nitronium ion gave evidence for the predominance of the normal nitronium ion mechanism, though clear evidence for the intrusion of an additional mechanism in dinitrogen pentaoxide solutions was obtained in one case. We now report product studies which confirm this, show that it occurs with several substrates, and indicate the nature of the additional mechanism.

The following aromatic substrates were chosen for investigation, in part because they were of convenient reactivity and not easily oxidised, and in part to give evidence about the nature of the additional mechanism; 1,2-dichloro-4-nitrobenzene, 1,2,4-trichloro-5-nitrobenzene, 2-nitrobenzoic acid, 3-nitrobenzoic acid, 2-chloro-3-nitrobenzoic acid, 4-chloro-3-nitrobenzoic acid, 2-chloro-5-nitrobenzoic acid, benzene-1,3-dicarboxylic acid, 4-methyl-3-nitrobenzoic acid and 2-methyl-5-nitrobenzoic acid.

Results and Discussion

1,2,4-*Trichloro-*5-*nitrobenzene*.—This was nitrated in mixtures of nitronium trifluoromethanesulphonate and dinitrogen pentaoxide in nitric acid; yields of the expected nitroproduct are given in Table 1 and are seen to decrease as the proportion of dinitrogen pentaoxide increases. This is accompanied by an increase in the first-order rate constant as previously reported[1] and an increase in the yield of the unstable non-aromatic products previously[2] identified as a diastereoisomeric pair of 3,5,6-trichloro-2,4-dinitrocyclohexa-2,5-dienyl nitrates, (**1**). In order to confirm this identification, and also to gain information on the mechanism of formation of these unstable products, the progress of the reaction was monitored by ^{15}N NMR spectroscopy under three sets of conditions: ^{15}N labelled substrate in N_2O_5/NHO_3 of normal isotopic abundance, normal substrate in ^{15}N enriched N_2O_5/HNO_3, and labelled substrate in ^{15}N enriched N_2O_5/NHO_3. The three experiments, spectra from the last of which are shown in Fig. 1, gave results in accord with the assignments labelled *b–i* in Fig. 1 and Scheme 1. Spectra recorded with and without proton decoupling show that the signals from the nitro and nitrato groups, *f,g* and *d,e* respectively show coupling to protons; in the latter pair the doublet structure is sufficiently well resolved to give a measured $^3J_{N,H}$ coupling constant of 4.7 Hz.

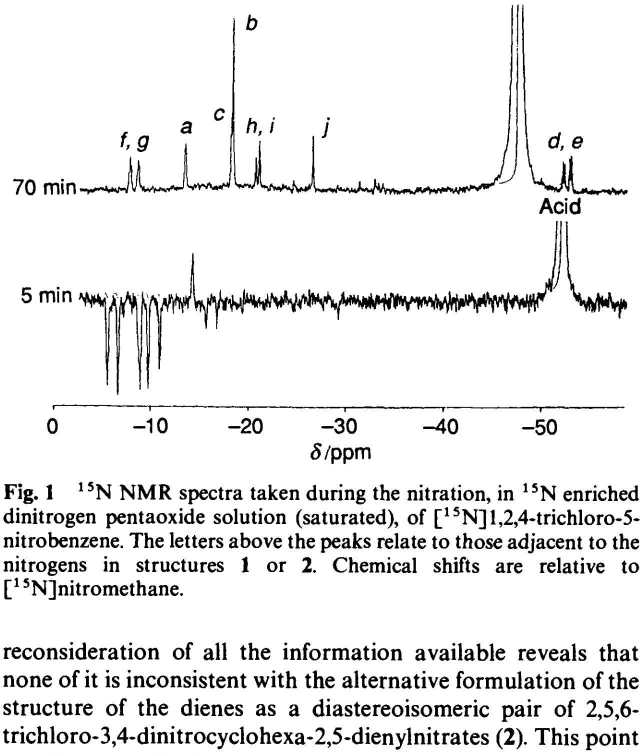


Fig. 1 ^{15}N NMR spectra taken during the nitration, in ^{15}N enriched dinitrogen pentaoxide solution (saturated), of [^{15}N]1,2,4-trichloro-5-nitrobenzene. The letters above the peaks relate to those adjacent to the nitrogens in structures **1** or **2**. Chemical shifts are relative to [^{15}N]nitromethane.

The formation of the dienes is confirmed. However, reconsideration of all the information available reveals that none of it is inconsistent with the alternative formulation of the structure of the dienes as a diastereoisomeric pair of 2,5,6-trichloro-3,4-dinitrocyclohexa-2,5-dienylnitrates (**2**). This point remains unresolved.

The use of labelled substrate has made it possible to measure the chemical shifts of the nitrogens in the 2-nitro groups in the diastereoisomeric dienes, *h* and *i*. These show that the previous tentative assignment of peaks to these groups[2] from an experiment with unlabelled substrate was incorrect, as was the suggestion that these arose from nitrodenitration accompanying diene formation. It is now clear that there is no nitrodenitration and that the mechanism previously proposed for diene formation is wrong. The larger of the two peaks previously so assigned appears again in the present spectrum (peak *j*) and is due to an unidentified impurity or diene decomposition product.

Consideration of the correct mechanism for formation of the dienes is aided by the observation of emission peaks in the ^{15}N NMR spectra during the early stages of reaction (Fig. 1). Two of

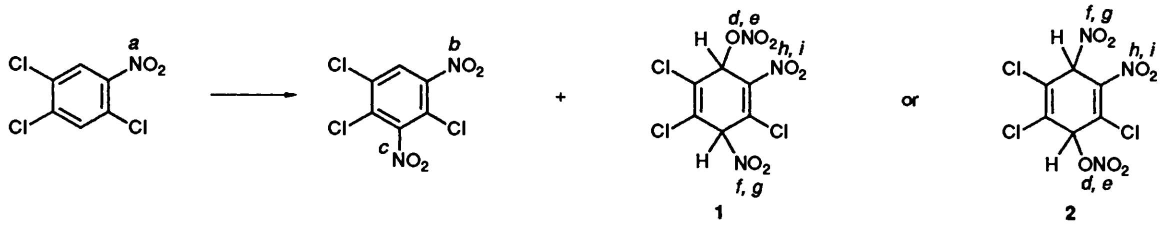
---

‡ *Present address:* RARDE Powdermill Lane, Waltham Abbey, Essex EN9 1AX, UK.

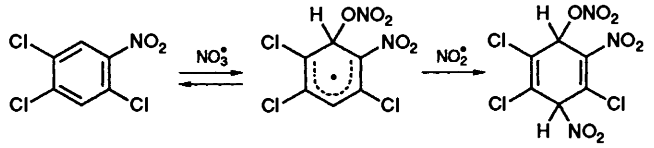
Table 1 Yields[a] of 1,2,4-trichloro-3,5-dinitrobenzene from nitration of 1,2,4-trichloro-5-nitrobenzene in nitric acid containing mixtures of dinitrogen pentaoxide and nitronium trifluoromethanesulphonate at 30 °C

P^b/mol dm^{-3}	S^b/mol dm^{-3}	Yield (%)
5.0	0	69
5.1	0	58
4.2	0.9	66
3.4	1.7	70
2.5	2.6	80
1.7	3.4	86
0	5.1	96

[a] By ^{1}H NMR spectroscopy. [b] In these solutions $P + S = 5.1$ mol dm^{-3}. P and S are the stoichiometric concentrations of dinitrogen pentaoxide and nitronium trifluoromethanesulphonate respectively.



Scheme 1



Scheme 2

Table 2 Yields of 1,2-dichloro-3,5-dinitrobenzene (A) and 1,2-dichloro-4,5-dinitrobenzene (B) from the nitration of 1,2-dichloro-4-nitrobenzene at 25 °C

Conditions	Yield[a] (%) A	B	A + B
92.0% H_2SO_4, $[HNO_3] = 1$ mol dm^{-3}	35	54	89
Duplicate experiment	37	53	90
HNO_3, $[N_2O_5] = 5.5$ mol dm^{-3}	32	50	82
Duplicate experiment	30	50	80

[a] Measured by GC Pye-Unicam 104 with fid detector, 7 ft (1 ft ≈ 30.5 cm) glass column with 10% Dexil on Chromosorb WHP, N_2 40 cm^3 min^{-1}, $T = 205$ °C, reference standard 1,3-dinitrobenzene. Retention times: reference standard, 243 s; A 411 s; B 451 s.

these, labelled *f* and *g*, finally appear as absorption peaks, the rest disappear completely. The decomposition of the N_2O_5 which occurs causes the solvent peak to shift downfield as reaction progresses, revealing the nitrate peaks *d* and *e* only towards the end of the reaction. The fact that *f* and *g* appear first in emission suggests that the product is formed by the combination of two independently formed radicals, one of which is NO_2. We now suggest that the dienes are formed as in Scheme 2 (or an analogous scheme if **2** is the correct formulation for the dienes) by reversible addition of nitrate radical to substrate followed by combination of the adduct radical with NO_2.

The ^{15}N nuclear polarisation occurs in the nitrogen dioxide in the final radical combination (Scheme 2). If the reasonable assumption is made that the *g*-value of the aromatic radical with which it combines is greater than that of NO_2 ($g = 2.000$) then application of Kaptein's rules[3] leads to the expectation of an emission signal, as observed. Neither the kinetics nor the product mix of the reaction are affected by addition of NO_2, and this is understandable if the second step of Scheme 2 is rate determining because an increase in the concentration of NO_2 will result in a decrease in the concentration of NO_3 [see eqn. (1)] and thus of the adduct radical, so that there is no net effect.

$$NO_2{}^+ + NO_3{}^- \rightleftharpoons N_2O_5 \rightleftharpoons NO_2 + NO_3 \quad (1)$$

The other emission peaks (Fig. 1) suggest that other less stable dienes are formed by a similar pathway, perhaps because adduct radical formation is non-regiospecific and/or because combination with NO_2 can occur 1,2 as well as 1,4.

1,2-*Dichloro-4-nitrobenzene*.—This was nitrated in ^{15}N-enriched N_2O_5/HNO_3 and the progress of the reaction monitored by ^{15}N NMR spectroscopy. Again emission peaks were seen in the early stages of reaction (Fig. 2). This suggests that a similar mechanism operates with this substrate but the dienes are less stable, all disappearing during the progress of the reaction. A new feature in this case is that one of the aromatic product peaks, that due to 1,2-dichloro-3,5-dinitrobenzene, appears first in emission. This means that this product is formed in part by a radical pathway, most probably by elimination of nitric acid from a diene precursor, the nuclear polarisation of which is carried over into the product (Scheme 3). It was expected that the yield of this isomer would be relatively lower when nitration was effected in sulphuric acid because of the absence of the covalent N_2O_5, which by homolysis gives the NO_3 radical [eqn. (1)]. Accordingly products of the reaction of 1,2-dichloro-4-nitrobenzene were reinvestigated using GC and the results are shown in Table 2. Yields are not quantitative as was previously stated on the basis of ^{1}H NMR work.[2] Surprisingly, relative yields of the two products in the two media were almost the same. The medium effect on the isomer proportions formed by normal nitronium ion nitration cannot be ascertained, but this result suggests strongly that most of the 1,2-dichloro-3,5-dinitrobenzene is formed by the normal nitronium ion mechanism and the CIDNP signal arises from the small fraction formed by the radical pathway. The smaller overall yield when nitration is effected in N_2O_5/HNO_3 indicates that the bulk of the dienes decompose to non-aromatic products.

In another experiment nitration of 1,2-dichloro-4-nitrobenzene was effected with a saturated solution of nitronium trifluoromethanesulphonate. No emission peaks were seen, and the ratio of the two aromatic product peaks was no different from that observed when N_2O_5 was used, reinforcing the view that the radical pathway in Scheme 3 is a very minor one.

Substituted Benzoic Acids.—Kinetics of nitration have been reported on previously.[1] We now report additionally that 2-chloro-5-nitrobenzoic acid is closely similar in reactivity to 3-nitrobenzoic acid and that benzene-1,3-dicarboxylic acid, 4-methyl-3-nitrobenzoic acid and 2-methyl-5-nitrobenzoic acid

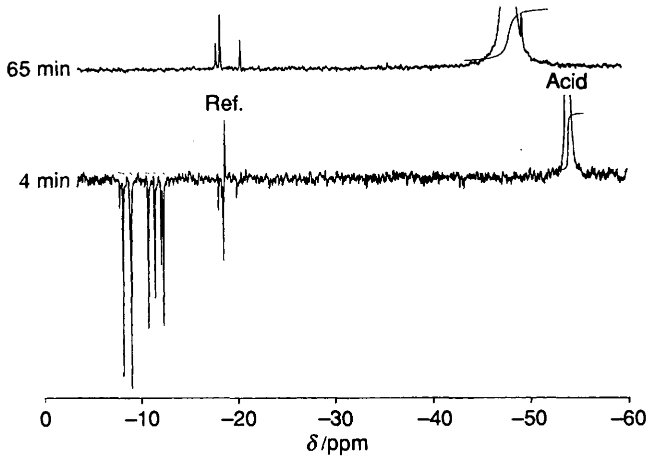
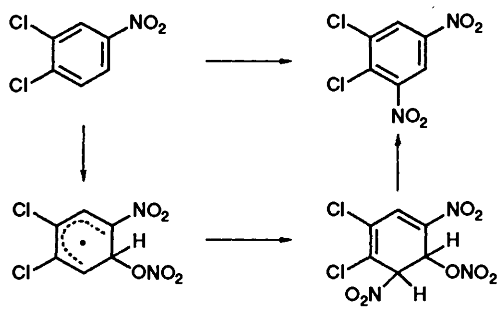
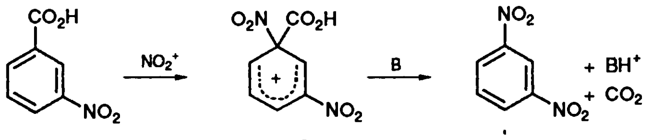


Fig. 2 ^{15}N NMR spectra taken during the nitration, in ^{15}N enriched dinitrogen pentaoxide (saturated), of unlabelled 1,2-dichloro-4-nitrobenzene. The added reference standard is 1,2,4-trichloro-3,5-dinitrobenzene (marked 'Ref.'). Chemical shifts are relative to [^{15}N]nitromethane.



Scheme 3



Scheme 4

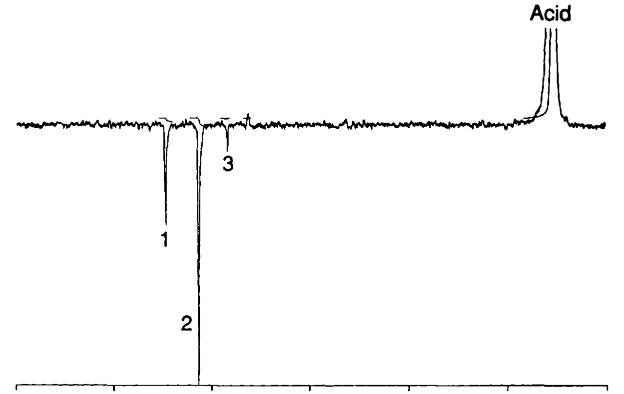


Fig. 3 ^{15}N NMR spectrum taken in the early stages of the nitration, in enriched dinitrogen pentaoxide solution (saturated), of unlabelled 3-nitrobenzoic acid. Later work with labelled material showed that peak 1 corresponded to the absorption signal for labelled 1,3-dinitrobenzene, while peak 2 coincided with that for 3,5-dinitrobenzoic acid. Peak 3 has not been assigned. Chemical shifts are relative to [^{15}N]nitromethane.

Table 3 GC Data for analysis of products from nitration of substituted benzoic acids following methyl esterification of the product mix

Component of product mix	Response factor[a]	t_r/s
2-Nitrobenzoic acid[b]		
Methyl 2-nitrobenzoate	1.115	132
Methyl 2,3-dinitrobenzoate	0.985	563
Methyl 2,4-dinitrobenzoate	1.080	374
Methyl 2,5-dinitrobenzoate	0.914	380
Methyl 2,6-dinitrobenzoate	0.998	465
1,2-Dinitrobenzene	1.011	217
1,3-Dinitrobenzene (ref.)	1	165
3-Nitro-, 2-methyl-5-nitro- and 4-methyl-3-nitro-benzoic acids[b]		
Methyl 3-nitrobenzoate	1.269	125
Methyl 3,5-dinitrobenzoate	0.868	357
1,3-Dinitrobenzene	1.032	162
Methyl 2-methyl-3,5-dinitrobenzoate	1.033	411
Methyl 4-methyl-3,5-dinitrobenzoate	d	415
1-Chloro-2,4-dinitrobenzene (ref.)	1	216
Benzene-1,3-dicarboxylic acid[c] (isophthalic acid)		
Dimethyl 5-nitroisophthalate	1.406	363
1-Chloro-2,4-dinitrobenzene (ref.)	1	259
2-Chloro-3-nitrobenzoic acid[e]		
Methyl 2-chloro-3,5-dinitrobenzoate	0.855	326
1,4-Dinitrobenzene (ref.)	1	60
2-Chloro-5-nitro- and 4-chloro-3-nitrobenzoic acids[f]		
Methyl 2-chloro-5-nitrobenzoate	1.120	310
Methyl 2-chloro-3,5-dinitrobenzoate	0.855	660
Methyl 4-chloro-3-nitrobenzoate	1.180	308
Methyl 4-chloro-3,5-dinitrobenzoate	0.905	664
1-Chloro-2,4-dinitrobenzene	1.026	253
1,4-Dinitrobenzene (ref.)	1	165

[a] Response factor defined as before[2]. [b] Conditions: 3% OV225 on Chromasorb W 100–120 mesh, T = 225 °C, N_2 flow rate 45 cm^3 min^{-1}, glass column 9 ft long with 4 mm bore. [c] Conditions: same but with 40 cm^3 min^{-1} flow rate. [d] Not measured. Assumed to be unity in yield calculations. [e] Conditions: 3% OV225 on Chromasorb W 100–120 mesh, T = 180 °C, N_2 flow rate 40 cm^3 min^{-1}, glass column 5 ft long with 4 mm bore. [f] Conditions: 5% OV1 on WHP 100–120 mesh, T = 180 °C, N_2 flow rate 45 cm^3 min^{-1}, glass column 7 ft long with 4 mm bore.

though they react inconveniently quickly for kinetic study, are very approximately 400, 150 and 800 times, respectively, more reactive. Evidence that the benzoic acid derivatives are not substantially protonated or converted to the benzoyl nitrate under the conditions was given previously.[1]

Products were determined by GC after methyl esterification of substituted benzoic acids; conditions are given in Table 3. Overall yields, which are based on reacted aromatic at the time of analysis, and yields of individual products, which are expressed as percentages of the determined products, are in Table 4.

3-Nitrobenzoic acid gives, along with the expected 3,5-dinitrobenzoic acid, some 1,3-dinitrobenzene which is the formal product of nitrodecarboxylation. We were concerned to determine whether this was formed by a nitronium ion mechanism as in Scheme 4. Our results (Table 4 and Fig. 3) indicate that it is not formed in this way for the following reasons.

(*a*) No such product was formed when nitration was affected with nitronium trifluoromethanesulphonate rather than N_2O_5.

(*b*) The relative yield of 1,3-dinitrobenzene increases with the concentration of N_2O_5. A related observation is that the relative yield of 1,3-dinitrobenzene decreases with long reaction times presumably because of the diminishing concentration of N_2O_5 due to decomposition.

These results rule out the mechanism of Scheme 4 with the first step rate-determining. They could be explained if the

Table 4 Yields[a] for reactions in solutions of dinitrogen pentaoxide of concentration *P* (or of nitronium trifluoromethanesulphonate of concentration *S*) in nitric acid.

(*a*) Substrate: 2-nitrobenzoic acid[b]

	P/mol dm^{-3}					S/mol dm^{-3}
Product	0[c]	3.5[c,d]	4.0	4.9	5.2	2.5
1,2-Dinitrobenzene	*f,g*	1.5	0.6	1.0	1.0	*f*
2,3-Dinitrobenzoic acid	4	7	4	5	5	5
2,4-Dinitrobenzoic acid[e] 2,5-Dinitrobenzoic acid[e]	69	65	69	65	68	64
2,6-Dinitrobenzoic acid	27	26	26	29	26	31
Overall yield	—	—	100	100	100	—

(*b*) Substrate: 3-nitrobenzoic acid[b]

	P/mol dm^{-3}								S/mol dm^{-3}
Product	1.5	2.5	4.0	4.2[h]	5.2[d]	5.2	5.2[c,d]	5.2[c]	4.4
1,3-Dinitrobenzene	0	6	10	5	19	10	15	13	0
3,5-Dinitrobenzoic acid	100	94	90	95	81	90	85	87	100
Overall yield	100	100	95	95	—	95	87	89	100

(*c*) Substrate: isophthalic acid

	P/mol dm^{-3}		
Product	2.5	3.5	5.2
5-Nitroisophthalic acid	100	100	100
Overall yield	96	100	—

(*d*) Substrate: 2-chloro-3-nitrobenzoic acid[c,k]

	P/mol dm^{-3}
Product	5.2
2-Chloro-3,5-dinitrobenzoic acid	100
Overall yield	97

(*e*) Substrate: 2-chloro-5-nitrobenzoic acid[b]

	P/mol dm^{-3}	
Product	3.5	5.2
1-Chloro-2,4-dinitrobenzene	*f*	0.5
2-Chloro-3,5-dinitrobenzoic acid	100	99.5
Overall yield	—	100

(*f*) Substrate: 4-chloro-3-nitrobenzoic acid[b]

	P/mol dm^{-3}		S/mol dm^{-3}	
Product	3.5[c,d]	5.2	2.5	4.4
1-Chloro-2,4-dinitrobenzene	4	2.5	1	1.5
4-Chloro-3,5-dinitrobenzoic acid	96	97.5	99	98.5
Overall yield	—	86	—	—

[a] Overall yields based on the reacted aromatic at the time of analysis. Yields of individual components are expressed as percentages of the mix of determined products. [b] Reaction time *ca.* two half-lives and $T = 25$ °C unless otherwise stated. [c] $T = 36$ °C. [d] Reaction time 0.5 $t_{\frac{1}{2}}$. [e] The peaks for methyl 2,4-dinitrobenzoate and methyl 2,5-dinitrobenzoate were incompletely resolved but the two products were clearly formed in approximately equal amounts. The mean of the response factors was used in the calculation of the stated combined yields of these two products. [f] Trace amount evident. [g] It was shown in a separate experiment that this was not formed from 2,3-dinitrobenzoic acid under the conditions. [h] Reaction time seven half-lives. [j] $T = 0$ °C. [k] Reaction time ten half-lives.

second step were rate-determining and required a base synchronously to abstract the proton, since nitrate ion (the concentration of which is closely similar to the stoichiometric concentration of N_2O_5) may be sufficiently basic for this purpose. However this possibility also can be discounted for the following reasons:

(*c*) The effect of a 4-chloro substituent which should enhance the reactivity of the position *ipso* to the CO_2H substituent relative to the 5-position gives much less nitrodecarboxylation.

(*d*) Benzene-1,3-dicarboxylic acid would be expected also to give the product of nitrodecarboxylation but in fact gave only the expected nitroproduct quantitatively. This substrate was also nitrated in sulphuric acid (85–95%) and again gave a quantitative yield of the 5-nitro derivative.

(*e*) The reaction of ^{15}N-labelled 3-nitrobenzoic acid in ^{15}N-enriched N_2O_5/HNO_3 shows two emission peaks in the ^{15}N NMR spectrum in the early stages of the reaction; these eventually become the absorption peaks due to the two products, 3,5-dinitrobenzoic acid and 1,3-dinitrobenzene. The enhancement of the emission for the latter is much greater than for the former.

These results taken together show that nitrodecarboxylation requires the presence of N_2O_5 and that it is a radical process. (The very small amount of nitrodecarboxylation of 4-chloro-3-nitrobenzoic acid even in nitronium trifluoromethanesulphonate solutions suggests that the mechanism of Scheme 4 may operate in particularly favourable circumstances and this point will be investigated further.)

The radical nitrodecarboxylation process possibly starts with cyclohexadiene formation analogous to Scheme 2, followed by the elimination of the elements of both nitric acid and carbon dioxide, with carry-over of the nuclear polarisation. If this is correct the elimination must be particularly facile because no peaks which could be attributed to cyclohexadienes were seen in the ^{15}N NMR spectrum during the nitration of 3-nitrobenzoic acid (Fig. 3). Emission peaks in the correct region of the ^{15}N NMR spectrum were evident in the early stages of the nitration of 2-nitrobenzoic acid (Fig. 4), a substrate which

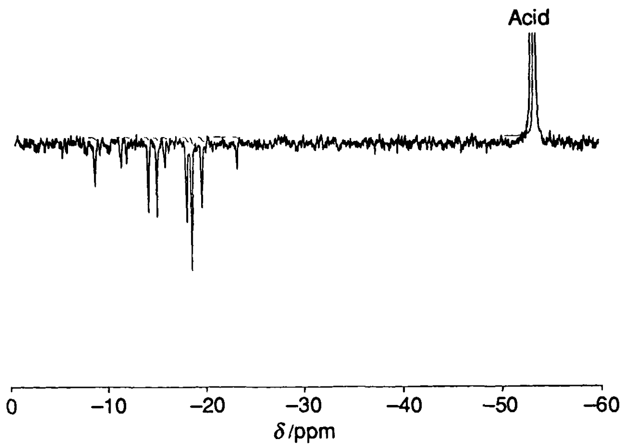


Fig. 4 ^{15}N NMR spectrum taken in the early stages of the nitration, in enriched dinitrogen pentaoxide solution (saturated), of unlabelled 2-nitrobenzoic acid, showing emission signals in the diene region. Chemical shifts are relative to [^{15}N]nitromethane.

also gave a small amount of the nitrodecarboxylation product (Table 4).

It is noteworthy that 3,5-dinitrobenzoic acid also gives an emission peak in the ^{15}N NMR spectrum (Fig. 3) and therefore is, in small part, formed by a radical process, as with 1,2-dichloro-3,5-dinitrobenzene formation discussed above.

Neither of the methylnitrobenzoic acids gave any 2,4-dinitrotoluene, the expected product of nitrodecarboxylation.

Conclusions

Reactions of aromatic compounds with concentrated solutions of N_2O_5 in nitric acid, though predominantly nitration by the normal nitronium ion mechanism, can have a radical component that in some cases at least involves addition first of NO_3 and then of NO_2 to give cyclohexadienes. These are unstable and in some cases there can be elimination from them to give aromatic nitro products. It seems likely that the radical mechanism is less sensitive to deactivation by electron-withdrawing substituents than is the normal nitronium ion mechanism. The radical process therefore becomes more likely the more deactivated the substrate is to electrophilic attack.

Experimental

Materials.—These were as described.[1,2] In addition, the following were obtained and purified: 2-methyl-5-nitrobenzoic acid (m.p. 175–177 °C, aq. EtOH), 4-methyl-3-nitrobenzoic acid (m.p. 188–190 °C, H_2O), 2-chloro-5-nitrobenzoic acid (m.p. 165–166 °C, H_2O) and 1,2-dichloro-4-nitrobenzene (m.p. 40–41 °C, MeOH).

Samples of the nitro- and dinitro-benzoates were prepared by the addition, to the relevant acid, of diazomethane. Diazomethane was prepared, as a solution in AR diethyl ether, by a standard preparation[4] and the diazomethane was added to a solution of the acid in AR diethyl ether at *ca.* 0 °C. The purity of the esters was checked by NMR spectroscopy and m.p. tests. The acids were all purchased, with the exception of 2,3-dinitrobenzoic acid (prepared by the oxidation of 2,3-dinitrotoluene by a method analogous to that described for 2,4-dinitrobenzoic acid[5]), 2,5-dinitrobenzoic acid[6] and 1,2-dichloro-3,5-dinitrobenzene,[7] which were prepared as described in the literature. [^{15}N]3-Nitrobenzoic acid was prepared by the addition of 100% [^{15}N]nitric acid (4 g) to benzoic acid (0.3 g). The nitric acid was removed under reduced pressure, and the resulting mixture of 2-nitrobenzoic acid and 3-nitrobenzoic acid used without further purification.

[^{15}N]1,2,4-*Trichloro-5-nitrobenzene.*—2,4,5-Trichloroaniline (8 g), prepared as described,[8] was dissolved in fluoroboric acid (20 cm^3) by warming the acid to 80 °C and stirring for 1 h. This solution was then cooled to 0 °C and nitrosylsulphuric acid (1 equivalent) was slowly added. This was stirred for 4 h at 0 °C, allowed to rise to ambient temperature, and then poured onto crushed ice (100 cm^3). Filtration gave solid 2,4,5-trichlorobenzenediazonium tetrafluoroborate which was washed with water and then ether (yield 65%). To a stirred mixture of [^{15}N]sodium nitrite (0.3 g) and copper-bronze (0.06 g) in water (5 cm^3), was added dropwise a suspension of 2,4,5-trichlorobenzenediazonium tetrafluoroborate (1.2 g) in water (5 cm^3). After this addition, the reaction was left for 10 min and then filtered. The residue was washed with water, 5% sodium hydroxide solution and water again, before being taken up in acetone and filtered. The acetone was removed and the product distilled under reduced pressure (yield 0.3 g, m.p. 55–57 °C).

Products by GC Analysis.—Benzoic acids. The reactions of the substrates were carried out as follows: known amounts of substrate and reference standard were placed in a round-bottomed flask, to which was added a roughly measured volume of nitrating medium. The flask was stoppered and placed in a constant temperature bath. GC analysis was carried out on solutions obtained in one of the following ways.

(a) *Reactions in solutions of dinitrogen pentaoxide.* After a certain length of time the nitrating medium was removed under reduced pressure. The solid residue was then treated with diazomethane in the manner described above.

(b) *Reactions in solutions of nitronium trifluoromethanesulphonate.* The reaction was quenched by adding some or all of the reaction mixture to chilled water so that a dilution of at least twenty five times was effected. The quenched reaction mixture was extracted with AR diethyl ether and treated with diazomethane.

In all experiments, the ether was removed under reduced pressure and the methylated residues dissolved in AR acetone, the resulting solutions being the ones used for analysis.

Chloronitrobenzenes. A solution of dinitrogen pentaoxide in nitric acid was added to a known amount of substrate. After an appropriate time, the reaction was quenched and a known amount of reference added. The aromatics were then extracted with dichloromethane which was then washed with water, dried and concentrated down for analysis.

Products by ^1H NMR *Spectroscopy.*—A method similar to that used previously[1] for kinetic studies was employed.

Products by ^{15}N NMR *Spectroscopy.*—The substrate to be studied (*ca.* 200 mg) was placed in an NMR tube (8 mm internal diameter). The tube was slotted into a 10 mm tube containing D_2O for the deuterium lock and was held in place by a polythene ring. Enriched nitrating medium (*ca.* 3 cm^3) was added. The assembly was then placed in the probe of a Bruker FT 250 MHz spectrometer and spectra were taken when desired. The number of pulses was maximised bearing in mind the rate of the reaction being studied.

Acknowledgements

We thank Dr. P. Golding for helpful discussions and the Ministry of Defence for maintenance grants (to A. J. S. and R. W.).

We thank A. Gregory for some of the work pertaining to isophthalic acid.

References

1 Part 36, R. B. Moodie, A. J. Sanderson and R. Willmer, *J. Chem. Soc., Perkin Trans. 2*, 1990, 833.

2 R. B. Moodie and R. J. Stephens, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1059.

3 R. Kaptein, *J. Chem. Soc., Chem Commun.*, 1971, 732; P. Helsby, J. H. Ridd and J. P. B. Sandall, *J. Chem. Soc., Chem Commun.*, 1981, 827.

4 A. Vogel, *Textbook of Practical Organic Chemistry*, 4th edn., Longman, London, 1978, p. 289.

5 J. F. J. Dippy, B. D. Hawkins and B. V. Smith, *J. Chem. Soc.*, 1964, 154.

6 *Organic Synthesis*, Coll. Vol. 3, 1955, 334.

7 A. F. Holleman, *Recl. Trav. Chim., Phys-Bas*, 1920, **39**, 449.

8 H. M. Colquhon, J. Holten, D. J. Thompson and M. V. Twigg, *New Pathways for Organic Synthesis*, Plenum, New York, 1984, p. 315.

Paper 0/04706F
Received 19th October 1990
Accepted 2nd January 1991