Oxidation Reduction Reactions Involving Nitro Groups in Trifluoromethanesulfonic Acid. Part 2.[1] The Reactions of Chloromethylbenzenes with Aromatic Nitro Compounds

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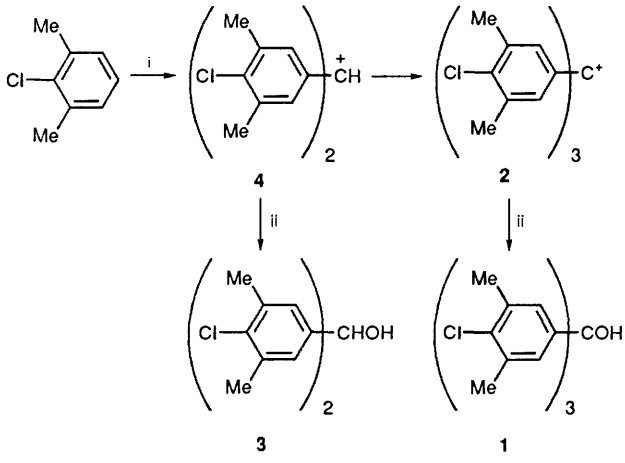
2-Chloro-1,3-dimethylbenzene reacts with 1,4-dinitrobenzene in trifluoromethanesulfonic acid (99%) at 70 °C to give, after quenching, a 45% yield of tris(4-chloro-3,5-dimethylphenyl)methanol. Some other chloro compounds and a range of aromatic nitro compounds react in a similar manner. From isotopic labelling (^{13}C, ^{2}H), kinetic studies, and substituent effects, the reaction appears to involve a rate-determining hydride transfer from the aromatic chloro compound to the protonated nitro compound followed by a series of benzylations, debenzylations and rebenzylations accompanied by further oxidation reactions and leading finally to the corresponding triarylmethyl cations.

The original aim of this work was to extend our studies of rearrangements in trifluoromethanesulfonic acid from nitroalkylbenzenes to chloroalkylbenzenes. Previous studies[2] have shown that 1,3-dimethyl-2-nitrobenzene and related compounds undergo an intramolecular 1,3-nitro group rearrangement on heating to *ca.* 70 °C in concentrated trifluoromethanesulfonic acid. Under similar conditions, the dimethylbenzenes undergo methyl migrations leading to an equilibrium mixture of the three dimethylbenzenes with 1,3-dimethylbenzene as the predominant isomer.[3] Some transalkylation also occurs, particularly with ethylbenzenes.[4] 2-Chloro-1,3-dimethylbenzene was therefore heated in concentrated trifluoromethanesulfonic acid to determine whether any migration of the chloro and methyl substituents occurred. In fact, a very different reaction was observed involving 1,4-dinitrobenzene, which had been added as a standard for the integrals of the aromatic methyl signals in the ^{1}H NMR spectra.



Scheme 1 *Reagents and conditions:* i, CF_3SO_3H, 70 °C, $C_6H_4(NO_2)_2$; ii, H_2O, CH_2Cl_2

Results

Products.—A solution of 2-chloro-1,3-dimethylbenzene (0.5 g) was heated to 70 °C in trifluoromethanesulfonic acid (8 cm^3, 99%) for 6 h in the presence of 1,4-dinitrobenzene (0.1 g). Earlier studies had shown 1,4-dinitrobenzene to be inert when heated in trifluoromethanesulfonic acid at this temperature. However, most unexpectedly, 2-chloro-1,3-dimethylbenzene and 1,4-dinitrobenzene were found to react together under these conditions to give, as the only major products after extraction, the triarylmethylalcohol **1** (Scheme 1) in a yield of 45%† and 1,4-diaminobenzene. This reaction appears to be dependent on the high acidity of trifluoromethanesulfonic acid for no reaction was observed when the same compounds were heated together in trifluoroacetic acid. In the absence of the 1,4-dinitrobenzene, 2-chloro-1,3-dimethylbenzene in trifluoromethanesulfonic acid undergoes a slower set of reactions that appear to involve some of the expected isomerisations; these have not yet been investigated in detail.

When the reaction was followed in a ^{1}H NMR spectrometer (Fig. 1), the progress could be studied from the disappearance of the methyl signal for the starting material and the appearance of the methyl signal for the triarylmethyl cation **2** (Scheme 1). The signals for the aromatic protons of the starting material are not present in the spectrum presumably because of rapid exchange with the protons of the medium. Sharp peaks are seen for the

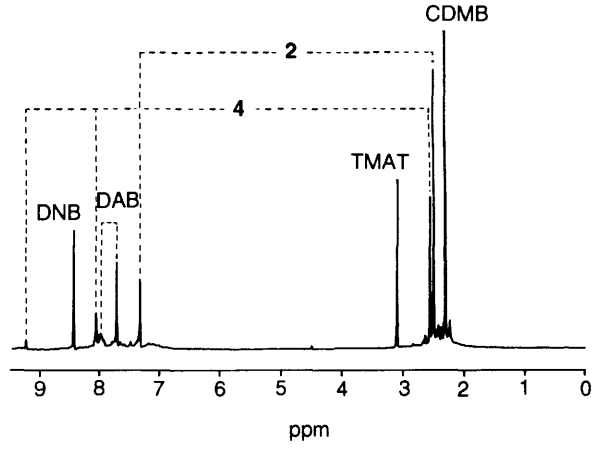


Fig. 1 Assignment of the signals in a ^{1}H NMR spectrum taken 2 h after the start of a reaction of 2-chloro-1,3-dimethylbenzene (CDMB, 0.468 mol dm^{-3}) with 1,4-dinitrobenzene (DNB, 0.119 mol dm^{-3}) in trifluoromethanesulfonic acid (99%) at 70 °C. The numbers **2** and **4** refer to the structures in Scheme 1; DAB = 1,4-diaminobenzene; TMAT = tetramethylammonium trifluoromethanesulfonate.

aromatic protons of 1,4-dinitrobenzene and for the aromatic protons of 1,4-diaminobenzene (present as the diconjugate acid) together with a broad signal for the N–H protons of the latter species. Tetramethylammonium trifluoromethanesulfonate has been used as an NMR standard[5] at δ 3.1. Surprisingly, in view of the complexity of the reaction, the spectra indicated the

† The calculation of this and subsequent yields is discussed later.

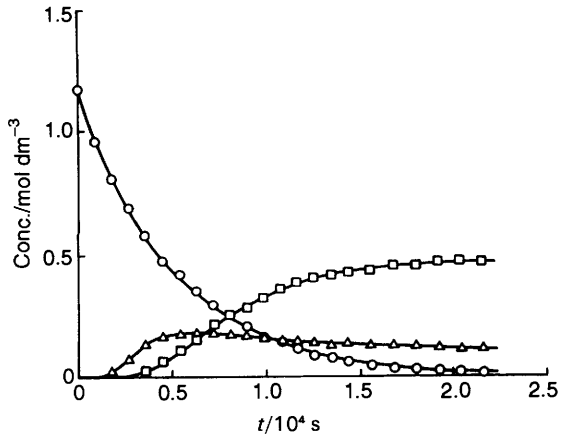
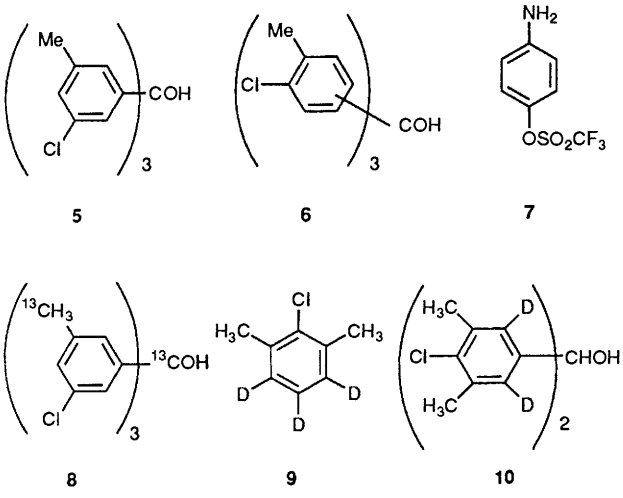


Fig. 2 Variation in the concentrations of 2-chloro-1,3-dimethylbenzene (CDMB), the diarylmethylcation **4**, and the triarylmethylcation **2** during a reaction of 2-chloro-1,3-dimethylbenzene (0.468 mol dm^{-3}) with 1,4-dinitrobenzene (0.119 mol dm^{-3}) in 99% trifluoromethanesulfonic acid at 70 °C. ○: [CDMB]/4; △: [**4**]; □: [**2**].

presence of only one intermediate present in significant concentration. When the reaction mixture was quenched and extracted after 35 min (a relatively early stage of the reaction), the diarylmethanol **3** was isolated. On dissolving in trifluoromethanesulfonic acid, the alcohol **3** gave rise to the additional ^{1}H NMR signals observed during the reaction and attributed to the intermediate. The intermediate is therefore the diarylmethyl cation **4**. The assignment of the signals is shown in Fig. 1. The plots in Fig. 2 show how the concentrations of the two arylmethyl cations vary with time.

The reaction has also been carried out using 3- and 2-chlorotoluene under the same conditions. With 3-chlorotoluene, the triarylmethanol **5** was isolated in a yield of 42%. With 2-chlorotoluene, a 43% overall yield of triarylmethanols was isolated but, from the ^{1}H and ^{13}C NMR spectra, this yield appeared to be a mixture of the four possible structures of type **6** with the –COH group either *para* to the methyl group or *para* to the chlorine atom. Attempts to separate this mixture by HPLC were unsuccessful. The related reactions of 1,4-dinitrobenzene with 1,3-dimethylbenzene and with toluene have also been tried over a range of conditions but yielded only complex decomposition products.



The reactions of 2-chloro-1,3-dimethyl benzene with a number of other nitro compounds in trifluoromethanesulfonic acid at 70 °C have been followed by ^{1}H NMR spectroscopy. There was no reaction with nitromethane. The reaction with

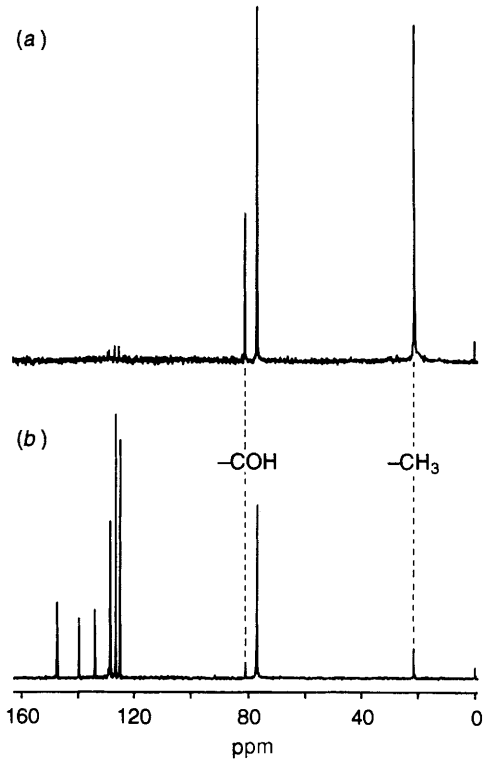


Fig. 3 ^{13}C NMR spectra of (*a*) the ^{13}C-labelled triarylmethanol **8** and (*b*) the corresponding unlabelled compound

1,3,5-trinitrobenzene is slightly slower than that with 1,4-dinitrobenzene, but appears to give a higher combined yield (76%) of the di- and tri-arylmethyl cations **2** and **4**. The reduction products of the nitro compound are more complex and 1,3,5-triaminobenzene is not formed. The reactions with nitrobenzene and with 4-nitroaniline occur more slowly and give lower yields of the triarylmethyl cations (*ca.* 30%). 4-Nitroaniline is reduced in the reaction to 1,4-diaminobenzene, but the nitrobenzene is reduced to 4-aminophenyltrifluoromethanesulfonate **7**; this was isolated from the reaction in a yield of 47% based on the nitrobenzene used. The formation of this compound can be understood as the Bamberger rearrangement of *N*-phenylhydroxylamine in trifluoromethanesulfonic acid and separate experiments[6] showed that the amine **7** could be isolated from the reaction of *N*-phenylhydroxylamine in trifluoromethanesulfonic acid in a yield of 78%.

Studies using Isotopic Tracers.—The most obvious question posed by this reaction is the source of the extra exocyclic carbon atom present in structures **1**–**6**. This was settled by synthesising 3-chloro-1-[^{13}C]methylbenzene and using this as the substrate in the reaction with 1,4-dinitrobenzene. Comparison of the ^{13}C NMR spectra of the product from this reaction with that from the reaction of unlabelled 3-chlorotoluene showed that the relative heights of the signals for the –CH_3 and –COH groups were the same in the two spectra (Fig. 3). The product from the labelled substrate is therefore the triarylmethanol **8** and the 'additional' carbon must be derived from one of the methyl groups of a fourth substrate molecule.

This information permits an estimate to be made of the stoichiometry of these reactions, which, for 2-chloro-1,3-dimethylbenzene, we believe to be approximately as shown in Scheme 2. This scheme implies that 2-chlorotoluene should be formed in the reaction, but this has not been detected possibly because, as outlined above, it can give rise to several products. The stoichiometry shown in Scheme 2 has been used to estimate

$$C_6H_4(NO_2)_2 + 8\ C_6H_3Me_2Cl + 8\ H^+$$

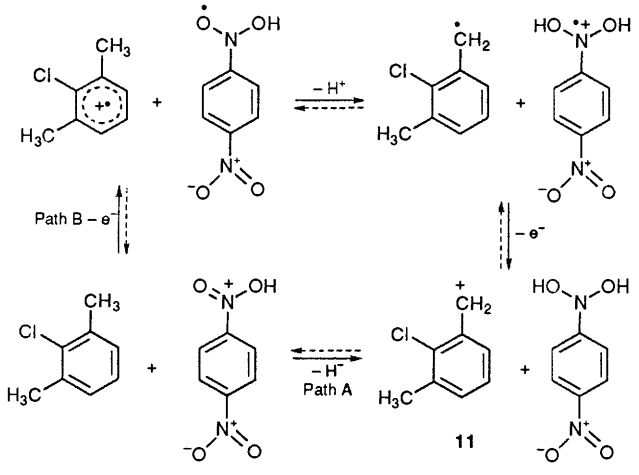
$$\downarrow$$

$$2\ (C_6H_2Me_2Cl)_3C^+ + C_6H_4(NH_3^+)_2 + 2\ C_6H_4MeCl + 4\ H_3O^+$$

Scheme 2

the yields quoted above. Since the yields are only *ca.* 40–50% based on this stoichiometry, it is clear that a number of other processes must be occurring.

The analogy with the apparent hydride transfer to the protonated nitro group in the conjugate acid of 1-ethyl-2-nitrobenzene[1] suggests that the initial stage of the reaction involves a hydride transfer from one of the methyl groups of the substrate to a protonated nitro group in the conjugate acid of 1,4-dinitrobenzene (Scheme 3, path A). To determine whether



Scheme 3 Symbols (*e.g.*, $-e^-$) by the arrows refer to the chloro-compound

or not this step is rate-determining, the reaction of 2-chloro-1,3-dimethylbenzene with 1,4-dinitrobenzene was carried out in deuteriotrifluoromethanesulfonic acid (99%).

The ^1H NMR spectra of the reaction mixture gave no indication of any deuterium exchange in the methyl groups but, to prove this, the products were isolated after 30 min and a ^2H NMR spectrum was run on the mixture of the remaining substrate and the diarylmethanol formed. There was no detectable ^2H NMR signal corresponding to the $-CH_2{}^2H$ group or to the $-C^2HOH$ group. The combined ^1H and ^2H NMR spectra indicate that the starting material and the product are deuteriated in the positions shown in structures **9** and **10**; the extent of the deuteriation at other positions must be less than 1–2%. This establishes that any hydride transfer must be irreversible for otherwise hydrogen isotope exchange at the OH protons of the reduced nitro compound would lead to the introduction of deuterium into the methyl groups.

Kinetics.—Several characteristics of these reactions make them a difficult subject for a detailed kinetic study. They are complex multistage processes involving a significant concentration of at least one intermediate and also generate water and basic species which must affect the rate of the reaction by reducing the acidity of the medium. Hence, although some kinetic runs were carried out on the overall reaction (*e.g.*, that shown in Fig. 2), these were not used to analyse the kinetic form.

Instead, attention was concentrated on the initial rate in the reaction of 2-chloro-1,3-dimethylbenzene with 1,4-dinitrobenzene and this was followed from the decrease in the integral of the methyl signal for the substrate measured relative to that

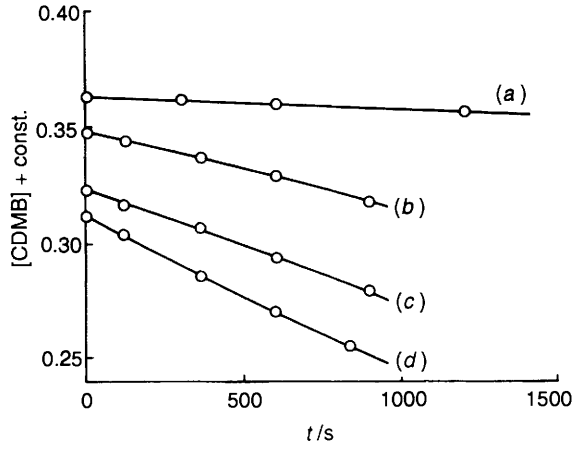


Fig. 4 Plots for determining initial rates in the reaction of 2-chloro-1,3-dimethylbenzene (CDMB, 0.308 ± 0.05 mol dm^{-3}) with 1,4-dinitrobenzene in trifluoromethanesulfonic acid (98.69%) at 70 °C. For clarity, plots (*a*), (*b*) and (*c*) have been moved vertically by 0.06, 0.04 and 0.02 units, respectively. Initial concentrations of 1,4-dinitrobenzene: run (*a*), 0.0; (*b*), 0.076; (*c*), 0.155; (*d*), 0.226 mol dm^{-3}.

for the tetramethylammonium ion as an NMR standard. Five or more points were taken to cover *ca.* 15% of the reaction as shown by the typical plots in Fig. 4. The plots were almost linear but were fitted to a quadratic and the slope determined at zero time. The results from a number of kinetic runs carried out to determine the kinetic form of the reaction are given in Table 1. The H_0 values in this Table are taken from the indicator measurements of Marziano[7] together with the value[8] of −10 for the pK_a of picramide.

The first three runs illustrate the background reaction of 2-chloro-1,3-dimethylbenzene in this solvent; the results accord with first-order kinetics and a rate coefficient of (1.66 ± 0.04) × 10^{-5} s^{-1}. The next four runs illustrate the effect of varying the concentrations of 1,4-dinitrobenzene and 2-chloro-1,3-dimethylbenzene. The rate coefficients in the final column have been calculated from eqn. (1) using the above

$$\text{Rate} = k_1[\text{chloro compound}] + k_2[\text{chloro compound}][\text{nitro compound}] \quad (1)$$

value for k_1; the agreement between the k_2 values indicates that this kinetic equation is obeyed to a reasonable approximation. The chemical species are written by name in this equation to show that the stoichiometric not the molecular concentrations are implied. The final group of runs show that the reaction rate decreases as expected with a decrease in the concentration of trifluoromethanesulfonic acid.

Evidence on how the structure of the nitro compound influences the initial reaction rate and the yields of the arylmethyl cations formed is given in Table 2 together with the pK_a values[9] of the protonated nitro compounds; there is no obvious correlation between the relative rates and the basicities of the nitro compounds.

Discussion

If we accept that the reaction occurs through the initial formation of the substituted benzyl cation **11** by either path A or path B in Scheme 3, the rest of the reaction can be understood by the sequence of benzylations, debenzylations and rebenzylations shown in Scheme 4. Some substitution may also occur *ortho* to the methyl groups but the reversibility of these benzylations should ensure that the most stable product predominates. Related sequences of reactions have been reported in the literature when benzylations have been carried out using

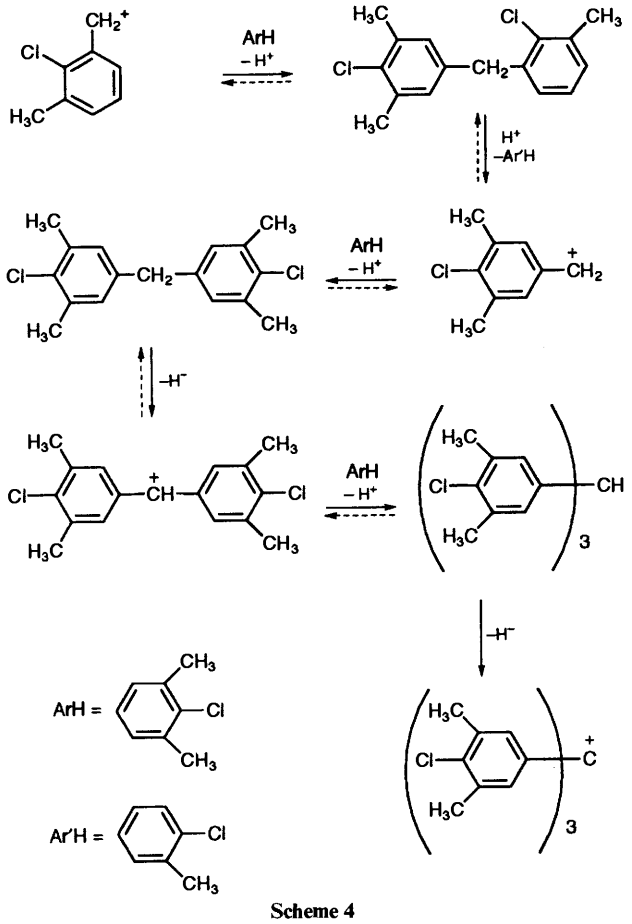
Table 1 Initial reaction rates (IR) and second-order rate coefficients [k_2, eqn. (1)] for the reaction of 2-chloro-1,3-dimethylbenzene (CDMB) with 1,4-dinitrobenzene (DNB) in trifluoromethanesulfonic acid (TA) at 70 °C

[CDMB]/mol dm^{-3}	[DNB]/mol dm^{-3}	TA (%)	$-H_0$	IR/10^{-5} mol dm^{-3} s^{-1}	k_2/10^{-4} mol^{-1} s^{-1} dm^3
0.155	—	98.69	11.90	0.264	—
0.235	—	98.69	11.90	0.383	—
0.303	—	98.69	11.90	0.501	—
0.308	0.076	98.69	11.90	2.81	9.82
0.303	0.155	98.69	11.90	4.89	9.34
0.312	0.226	98.69	11.90	7.52	9.93
0.219	0.239	98.69	11.90	5.64	10.1
0.299	0.226	98.29	11.74	3.42	6.56
0.305	0.229	97.77	11.55	2.09	4.66
0.302	0.226	97.32	11.41	1.74	3.95
0.300	0.225	96.61	11.21	1.05	2.02

Table 2 Initial reaction rates (IR) and second-order rate coefficients [k_2, eqn. (1)] for the reaction of 2-chloro-1,3-dimethylbenzene (0.306 ± 0.04 mol dm^{-3}) with a range of substituted nitrobenzenes (0.152 ± 0.03 mol dm^{-3}) in 98.69% trifluoromethanesulfonic acid at 70 °C. The combined yields of the arylmethyl cations **2** and **4**, as calculated from the ^{1}H NMR spectra at the end of the reaction, are also given

Substituents	pK_a	Yield (%)	IR/10^{-5} mol dm^{-3} s^{-1}	k_2/10^{-4} mol^{-1} s^{-1} dm^3	k_2^*/10^{-3} mol^{-1} s^{-1} dm^3
None	−12.14	35.7	1.23	1.60	0.438
4-Me	−11.35	22.6	1.32	1.75	0.224
4-Fl	−12.44	53.9	1.40	1.94	0.867
4-Cl	−12.70	62.5	1.27	1.60	1.17
4-NH_3^+	−13.91[a]	33.6	1.42	1.93	19.9
4-NO_2	−14.24[a]	62.8	5.07	9.72	214.0
3,5-$(NO_2)_2$	−16.04	75.8	2.39	3.98	5494.0

[a] Calculated by correlation analysis: see Experimental section.



Scheme 4

the stronger Friedel–Crafts catalysts. Thus, the aluminium chloride catalysed reaction of 1,4-dichloromethylbenzene with excess benzene was found to give mainly diphenylmethane instead of the expected 1,4-dibenzylbenzene.[10] A related sequence of reactions has been used to explain some of the side-products formed in the nitrous acid catalysed nitration of mesitylene.[11]

The main interest in this work comes therefore from the initial step, the formation of the substituted benzyl cation **11**, and, from the work in deuteriotrifluoromethanesulfonic acid described above, it is this initial step that is rate-determining. Since the concentration of the cation **11** never becomes sufficient to detect by ^{1}H NMR spectroscopy, this species must react rapidly with another molecule of the substrate and so the actual rate of formation of the cation **11** cannot be more than half the initial rate of disappearance of 2-chloro-1,3-dimethylbenzene. The following discussion is based on the experimental k_2 values on the assumption that the rate of formation of the initial benzyl cation is proportional to the rate of disappearance of the substrate over the range of conditions studied. The consistency of the results (see below) supports this assumption.

The variation of the k_2 values with the concentration of trifluoromethanesulfonic acid in Table 1 shows that the reaction is acid catalysed and the plot of log k_2 against the H_0 values for the medium (Table 2) is approximately linear with a slope of 0.94 ± 0.08. Since 1,4-dinitrobenzene is only slightly protonated over the range of conditions used, this result is consistent with reaction through the conjugate acid of the nitro compound.

Further evidence for reaction through the protonated nitro compounds comes from the values of the rate coefficient k_2^*, defined in terms of the molecular concentrations by eqn. (2). In

$$k_2[\text{chloro compound}][\text{nitro compound}] = k_2^*[\text{ArCl}][\text{ArNO}_2\text{H}^+] \quad (2)$$

using this equation, we have assumed that the molecular concentration of the chloro compound is equal to its stoichiometric concentration since the ^{1}H NMR chemical shift of the methyl groups of 2-chloro-1,3-dimethylbenzene remains at δ 2.3 over

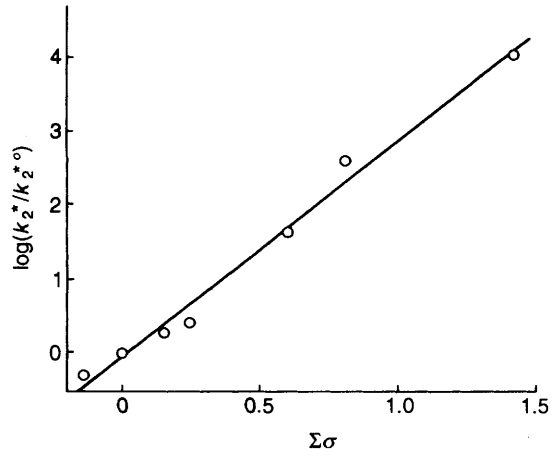


Fig. 5 Hammett plot of the molecular rate coefficients [eqn. (4)] for the reaction of 2-chloro-1,3-dimethylbenzene with the conjugate acids of the nitro-compounds listed in Table 2

the range 92–99% trifluoromethanesulfonic acid. In contrast, the corresponding chemical shift for mesitylene changes from δ 2.28 to 2.68 over this range of acidity. This accords with the range over which protonated mesitylene becomes the bulk component of the equilibrium.[12] The concentrations of the protonated nitro compounds are given by eqn. (3) and, from

$$K_a = [ArNO_2]h_0/[ArNO_2H^+] \quad (3)$$

this equation, the relationship between k_2^* and k_2 is given by eqn. (4). The values of k_2^* are included in Table 2 and are shown

$$k_2^* = k_2(K_a + h_0)/h_0 \quad (4)$$

as a conventional Hammett plot in Fig. 5 using the 'statistical' σ-values of Exner;[13] the slope is 2.93 ± 0.15 and the correlation coefficient is 0.994. For the conjugated acid of 1,3,5-trinitrobenzene, the substituent effects of the two unprotonated nitro groups are considered to be additive and so the substituent constant is taken as $2\sigma_m$.

The ρ-value obtained in Fig. 5 is near that for the acidity of substituted anilinium ions (2.77) and that reaction has also a formal change of one unit in the charge on the nitrogen atom attached to the aromatic ring. This analogy has led us to plot the values of (k_2^*/k_2^{*0}) against σ^-, but a slightly lower value of the correlation coefficient (0.983) is then obtained.

The linearity of the plot in Fig. 5 shows that the lack of any obvious pattern in the values of the stoichiometric rate coefficients (k_2) comes from the way in which the substituents modify both the concentration of the protonated nitro compound and its reactivity. For the nitro compounds used, the extent of protonation in 98.69% trifluoromethanesulfonic acid varies widely: from 78% for 4-nitrotoluene to 0.007% for 1,3,5-trinitrobenzene.

One remaining mechanistic problem concerns whether the transfer of H^- to the protonated nitro compound occurs as a one step process (Scheme 3, path A) or as a multistep process (Scheme 3, path B). For simplicity, only the chloro compound and the nitro compound are shown in these steps although, for the proton transfer on path B, the trifluoromethanesulfonate ion could also be involved.

On path B, the final step cannot be rate-determining since the reverse of the second step would then lead to hydrogen isotope exchange in the methyl groups and this is not observed. The second step of path B is also unlikely to be rate-determining since this would imply an equilibrium concentration of the radicals $ArCl^{\bullet+}$ and $ArNO_2H^{\bullet}$ in the solution. The reaction of 2-chloro-1,3-dimethylbenzene with 1,4-dinitrobenzene in trifluoromethanesulfonic acid (99%) at 70 °C was carried out in an EPR spectrometer in an attempt to detect these radicals but, although an EPR signal was observed in the first runs, this was not present when rigorously purified 2-chloro-1,3-dimethylbenzene was used. The purification of the substrate caused no change in the course of the reaction.

The distinction between paths A and B is therefore one between a rate-determining hydride transfer and a rate-determining electron transfer. The linearity of the plot in Fig. 5 points to the former since the substituent constants are defined with reference to a reaction at a side-chain, not to electron acceptance by the molecule as a whole.

One final problem concerns the lack of any reaction with nitromethane. This was unexpected, since the pK_a of protonated nitromethane (−11.7) (ref. 14) is within the range of acidity of the other protonated nitro compounds used (Table 2). The unreactivity of nitromethane can be understood if the reaction occurs through the formation of a charge transfer complex between the protonated nitrocompound and the aromatic substrate for nitromethane forms much weaker charge transfer complexes than the aromatic nitro compounds.[15] If the reaction indeed occurs through such a charge transfer complex, the distinction between the direct hydride ion transfer and the initial electron transfer becomes less significant because the successive stages of the electron transfer process (Scheme 3, path B) could all occur within the lifetime of the complex.

Experimental

Materials.—The aromatic chloro compounds, the nitro compounds, trifluoromethanesulfonic acid, and deuteriotrifluoromethanesulfonic acid (98% D) were bought from Aldrich. One sample of 2-chloro-1,3-dimethylbenzene was purified by HPLC using 2 × 25 × 1 cm Lichoprep 5–20 μm silica gel columns, refractive index detection, and elution with neat hexane. No difference could be detected in the reactivity of the purified and unpurified materials and so the purification stage was omitted in the main part of the work. Dichloromethane and diethyl ether were freshly distilled over sodium hydride.

3-Chloro-1-[^{13}C]methylbenzene was prepared by the reaction of [^{13}C]methyllithium with 3-chloro-1-iodobenzene. To a suspension of finely chopped lithium (0.2 g) in dry diethyl ether (20 cm^3) was added [^{13}C]iodomethane (2.0 g) in dry diethyl ether (40 cm^3). After this solution had been stirred for 1 h at room temperature, a solution of 3-chloro-1-iodobenzene (3.34 g) in dry diethyl ether (40 cm^3) was added and the stirring continued for 90 min. The reaction mixture was then quenched with water (30 cm^3) followed by the addition of a solution of sodium metabisulfite (2 mol dm^{-3}; 30 cm^3). This solution was extracted with diethyl ether and the extract dried over $CaCl_2$, the solvent was then removed under reduced pressure and the product purified by preparative GLC [column, 3.05 × (9.5 × 10^{-3}) m 7% Bentone 34 + 7% diisodecyl phthalate on Chromosorb W 85–100 mesh; injector temperature, 200 °C; oven temperature, 140 °C] giving 3-chloro-1-[^{13}C]methylbenzene (150 mg) with the expected ^{1}H and ^{13}C NMR spectra.

Products.—A Schlenk tube containing 2-chloro-1,3-dimethylbenzene (0.5 g) and 1,4-dinitrobenzene (0.1 g) in trifluoromethanesulfonic acid (99%; 8 cm^3) was swept out with dry argon and heated at 70 °C for 6 h. The solution was then extracted with dichloromethane, the extract was dried ($MgSO_4$), and the solvent was removed under reduced pressure leaving a dark brown gum (0.48 g). This was separated by HPLC using 2 × 25 cm × 1 cm Lichoprep 5-20 μm silica gel columns, refractive index detection, and elution with hexane:ethyl acetate (97:3). The major product was tris(4-chloro-3,5-dimethylphenyl)methanol (**1**) obtained as a pale

orange solid (179 mg). After two recrystallisations from methanol, the product was obtained as a white crystalline solid, m.p. 200–202 °C (Found: C, 66.8; H, 5.6; Cl, 23.7. $C_{25}H_{25}Cl_3O$ requires C, 67.0; H, 5.6; Cl, 23.8%); $\delta_H(CDCl_3)$ 6.95 (6 H, s), 2.62 (1 H, s) and 2.33 (18 H, s); $\delta_C(CDCl_3)$ 144.1, 135.8, 133.9, 127.8, 80.9 and 20.9.

The aqueous layer from the above reaction was basified (NaOH, 2 mol dm^{-3}) and extracted with dichloromethane (5 × 30 cm^3). The extracts were dried ($MgSO_4$) and the solvent was removed under reduced pressure to give crude 1,4-diaminobenzene as a purple solid (33 mg). After purification by adsorption on an alumina column and elution with dichloromethane–methanol (99:1), the product gave identical IR and ^1H NMR spectra to those from pure 1,4-diaminobenzene. When the original reaction was carried out using 2-chloro-1,3-dimethylbenzene (0.6 g) and nitrobenzene (0.25 g), the extraction from the aqueous layer yielded 4-aminophenyltrifluoromethanesulfonate **7** (0.23 g). The ^1H and ^{13}C NMR spectra of this material were identical to those of an authentic sample.[6]

The reaction of 2-chloro-1,3-dimethylbenzene with 1,4-dinitrobenzene in deuteriotrifluoromethanesulfonic acid was carried out as described above.

The isolation of the intermediate diarylmethanol **3** was carried out in the same way using 2-chloro-1,3-dimethylbenzene (2 g) and 1,4-dinitrobenzene (0.4 g) in trifluoromethanesulfonic acid (99%; 32 cm^3). The reaction was stopped after 35 min and, after product isolation, the unchanged starting material was removed by vacuum distillation. Purification of the remaining product by HPLC gave bis(4-chloro-3,5-dimethylphenyl)-methanol (**3**) as a pale orange solid (20 mg) (Found: C, 65.8; H, 6.0. $C_{17}H_{18}Cl_2O$ requires C, 66.0; H, 5.9%); $\delta_H(CDCl_3)$ 7.07 (4 H, s), 5.66 (1 H, s), 2.36 (12 H, s) and 2.11 (1 H, s); $\delta_C(CDCl_3)$ 141.3, 136.4, 133.9, 126.3, 75.2 and 20.8.

The reaction of 3-chlorotoluene (0.5 g) with dinitrobenzene (0.2 g) in trifluoromethanesulfonic acid (99%; 8 cm^3) was carried out in the same way to yield 166 mg of tris(3-chloro-5-methylphenyl)methanol (**5**); m.p. 184–185 °C (Found: C, 64.7; H, 4.8; Cl, 26.0. $C_{22}H_{19}Cl_3O$ requires C, 65.1; H, 4.7; Cl, 26.2%); $\delta_H(CDCl_3)$ 7.10 (3 H, s), 7.00 (3 H, s), 6.92 (3 H, s), 2.69 (1 H, s) and 2.28 (9 H, s); $\delta_C(CDCl_3)$ 147.5, 139.7, 133.9, 128.6, 126.6, 125.0, 81.0 and 21.4. The reaction with 3-chloro-1-[^{13}C]methylbenzene was carried out on one tenth of the above scale. The corresponding reaction of 2-chlorotoluene was studied in the way described for 3-chlorotoluene above.

Kinetics.—The kinetic studies were carried out by dissolving the required weight of the nitro compound and tetramethylammonium trifluoromethanesulfonate (0.0057 g) in trifluoromethanesulfonic acid of the required concentration and bringing the volume to 2 cm^3. Part of this solution (0.5 cm^3) was then added to the required amount of 2-chloro-1,3-dimethylbenzene in an NMR tube. The tube was then sealed and the reaction was followed from the integrals of the ^1H NMR signals using a Varian VXR-400 spectrometer. The calculations of the initial rates were based on the integral for the methyl signal of the substrate relative to that of tetramethylammonium trifluoromethanesulfonate. The replacement of the air above the solution by argon was found to have no effect on the reaction rate.

The calculation of the rate coefficients for the protonated nitro compounds eqn. (4) required an estimate of the pK_a values of two of the compounds used (Table 2). These were obtained from a Yukawa–Tsuno plot of the pK_a values of Gillespie and Peel[9] using the σ-values of Exner.[13] The plot gave $r = 0.62$, $\rho = 2.95$, with a correlation coefficient of 0.995. Further details are available elsewhere.[6]

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