

Electrophilic Aromatic Substitution. Part 30.¹ The Kinetics and Products of the Solvolyses in Aqueous Sulphuric Acids of 5-Chloro-2-methyl-2-nitrocyclohexa-3,5-dienyl Acetate: the Occurrence of $A_{AC}2$ and $A_{AL}1$ Solvolyses, and of an Acid-catalysed Elimination of Nitrous Acid, and the Relationship of the $A_{AL}1$ Solvolysis to the Nitration of 4-Chlorotoluene

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Good first-order kinetics of solvolysis of the above-named diene in water and in 6.5–43.6% H_2SO_4 at 25 °C, and in water and in 15.2–58.8% H_2SO_4 at 5 °C have been observed. The yields of 4-chlorotoluene, 5-chloro-2-methylphenyl acetate, 5-chloro-2-methylphenol, 4-chloro-2-nitrotoluene, 4-chloro-3-nitrotoluene, and 4-methyl-2-nitrophenol produced in water and in 21.5–92.4% H_2SO_4 at 25 °C in the presence of sulphanilic acid or hydrazinium sulphate, and additionally of 2- and 4-nitroanisole when anisole was also added, have been measured. The solvolysis proceeds by an acid-catalysed elimination of nitrous acid (confirming a tentative conclusion in another case¹), which competes with $A_{AC}2$ and $A_{AL}1$ ester solvolyses. With increasing acidity the solvolyses become dominant, the $A_{AL}1$ reaction increasingly so. The small yield of 4-chloro-3-nitrotoluene comes from a thermal reaction of the diene unrelated to the elimination and solvolyses. The $A_{AL}1$ reaction generates the *ipso*-Wheland intermediate (W_i^{Mc}) that is also formed in the nitration of 4-chlorotoluene. The intermediate reacts by return to 4-chlorotoluene and nitronium ion (which can be captured by anisole), by 1,2- and 1,4-nucleophilic capture by water (giving 5-chloro-2-methylphenol and 4-methyl-2-nitrophenol, respectively), and by 1,2-rearrangement to 4-chloro-2-nitrotoluene. The first of these reactions never accounts for more than about 12% of the W_i^{Mc} and competition between capture and rearrangement moves strongly in favour of the latter with increasing acidity. Re-examination of the nitration of 4-chlorotoluene has revealed products arising from 1,2- and 1,4-capture of W_i^{Mc} , previously overlooked. An improved assessment of positional reactivities shows 59% of primary attack by nitronium ion to occur at C-Me in 63% H_2SO_4 .

The results of nitrating 4-chlorotoluene in 63–85% H_2SO_4 have been discussed² in terms of the partial mechanism shown in Scheme 1. The yields of the chloronitrotoluenes fall off at low acidities because of nucleophilic capture by water of the W_i 's, (1) and (2). Because it could not be assumed that at the lowest acidity studied (63% H_2SO_4) capture was complete, and because nitrodechlorination did not occur, the results allowed positional reactivities to be evaluated only in the form represented in (3).

Recently Fischer *et al.*³ were able to isolate the 1,2-adduct (4) from the nitration of 4-chlorotoluene in acetic anhydride. This work, indicating $\geq 72\%$ of attack at C(1) (from n.m.r. spectroscopy of the reaction mixture, 'based on the initial amount of aromatic compound'), shows this *ipso*-position to be more reactive than might be concluded from the earlier work and that, unless a considerable medium effect exists, nucleophilic capture of (1) by water in 63% H_2SO_4 is far from complete.

Acid solvolyses, generating, from nitro-acetates by $A_{AL}1$ fission, W_i 's that are intermediates in nitrations, have earlier been used to elucidate the fates of these intermediates.^{1,4–8} We hoped by studying the acid solvolysis of (4) further to elucidate the processes occurring in the nitration of 4-chlorotoluene. Additionally, the retarding effect of the chlorine atom in (4) allowed us to examine not only the products but also the kinetics of the solvolyses. This has hitherto been possible in sulphuric acid in only one instance.¹ Furthermore, the nitro-acetates previously examined have all been 1,4-adducts. The behaviour of the 1,2-adduct (4) was therefore of extra interest.

Experimental

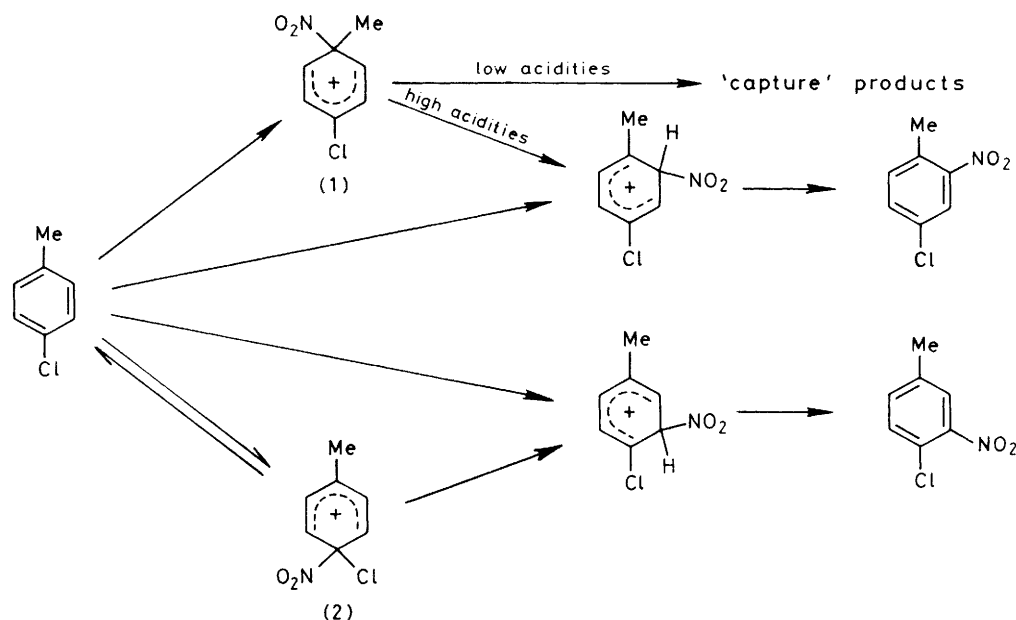
Materials.—Comments on the common reagents used in this work will be found in our earlier papers.¹ 4-Chlorotoluene

(b.p. 160 °C), 4-chloro-3-nitrotoluene (b.p. 140 °C, 16 mmHg) anisole (b.p. 154 °C), phenol (b.p. 182 °C), and 2-nitroanisole (b.p. 150 °C, 5 mmHg) were purified by distillation. 4-Chloro-2-nitrotoluene, m.p. 37–38 °C, and 4-nitroanisole, m.p. 54 °C, were crystallised from ethanol.

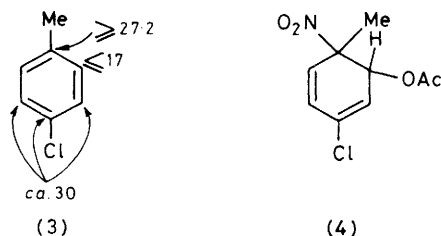
5-Chloro-2-methylphenol.—2-Amino-4-chlorotoluene (50 g) in water (200 ml) and sulphuric acid (60 ml, 98%) was diazotised at 0 °C with sodium nitrite (28 g dissolved in a minimum of water). The solution was added dropwise to a boiling solution of copper sulphate (30 g) in water (500 ml) and sulphuric acid (50 ml, 98%). The mixture was steam-distilled and the distillate was extracted with dichloromethane. Drying ($MgSO_4$) and concentration of the extract gave the phenol (36.5 g). Recrystallisation from ethanol gave needles, m.p. 73–73.5 °C. The acetate (m.p. 26–26.5 °C after vacuum sublimation) was prepared in the usual way.

5-Chloro-2-methyl-2-nitrocyclohexa-3,5-dienyl acetate.—We are obliged to Professor A. Fischer for unpublished details of his preparation of this compound. In this method 4-chlorotoluene is nitrated with a reagent prepared from nitric acid, acetic anhydride, and trifluoroacetic anhydride. The only minor variation that we introduced was to work up the reaction mixture using aqueous ammonia instead of sodium hydrogencarbonate. In this way 4-chlorotoluene (9.5 g) gave the pure diene (2 g, m.p. 49.5–50.0 °C), after crystallisation from ether–pentane. The 1H and ^{13}C n.m.r. spectra of this specimen agreed entirely with those reported.³

In another experiment a solution of 4-chlorotoluene (0.13 g) in hexadeuterio-acetic anhydride (0.48 g) and one prepared by adding nitric acid (0.41 g) to hexadeuterio-acetic anhydride (0.50 g) at 0 °C and keeping for 30 min were cooled to –15 °C and mixed. The reaction was followed at –15 °C by 1H n.m.r.



Scheme 1.



spectroscopy (100 MHz). The spectrum of the final reaction solution showed three signals due to methyl groups in dienes in the approximate ratios of 3 : 2 : 1, with δ 1.78, 1.93, and 1.88, respectively. The major peak was due to the methyl group of [(4), acetyl methyl deuteriated]. Integration of total methyl signals suggested an aggregated diene content of *ca.* 60%.

Thermolyses of (4).—(a) Direct injection of the diene in acetonitrile on to a g.c. column (for conditions see Table 1) gave 4-chlorotoluene, 5-chloro-2-methylphenyl acetate, and 4-chloro-3-nitrotoluene in the area ratios 64 : 1 : 35.

(b) A fresh solution of the diene in acetonitrile, kept at 25 °C for 15 h gave on g.c. 4-chlorotoluene and 4-chloro-3-nitrotoluene in the area ratio 70 : 30, and a trace of 5-chloro-2-methylphenyl acetate. A similar solution boiled for 15 h gave 4-chlorotoluene, the acetate, and 4-chloro-3-nitrotoluene in the area ratios 1 : 79 : 20.

Solvolyses of (4).—The diene was kept as stock solutions in acetonitrile at –40 °C. Under these conditions the diene was stable for about 1 week.

Kinetic methods were generally similar to those described earlier.¹ Details are given in Table 2.

Products formed from reactions in water and up to 66% H_2SO_4 , whether or not an aromatic trap was present, were obtained by quenching runs after ten half-lives of diene rearrangement. Reactions at acidities $\geq 66\%$ H_2SO_4 were kept for 8–10 half-lives of nitration of the aromatic trap. Where this rate of nitration or solvolysis was such that ten half-lives would be less than 2 min the runs were quenched after exactly 2 min (the shortest practicable reaction time). In all cases runs

Table 1. G.c. conditions for products and standard ^a

Compound	<i>R_t</i> /s	Response factor ^b
Anisole-phenol	<300	
4-Chlorotoluene	310	1.135
2-Chloro-5-methylphenol	410	Not calibrated
2,3-Dimethylbenzonitrile ^c	620	
5-Chloro-2-methylphenol	690	<i>d</i>
4-Methyl-2-nitrophenol	690	<i>d</i>
5-Chloro-2-methylphenyl acetate	750	0.741
2-Chloro-5-methylphenyl acetate	795	Not calibrated
4-Chloro-2-nitrotoluene	840	0.744
4-Chloro-3-nitrotoluene	1 030	0.666
2-Nitroanisole	1 080	0.534
4-Nitroanisole	1 230	0.446

^a Pye 104 instrument with flame-ionization detector and Datalab 308 integrator. Column: 50 m SP2250 capillary, helium flow rate 5 ml min⁻¹, make-up gas flow rate (nitrogen), 25 ml min⁻¹, split ratio 2 : 1, column temperature 190 °C. ^b (Area ratio/mol ratio), both for (compound/ref. standard). ^c Ref. standard. ^d Response factor varied with area ratio. A graph of response factor *versus* area ratio was constructed. These compounds showed identical response factors within experimental error.

lasting more than 30 min were performed by injecting aliquots of the stock solution of the diene into acids contained in thermostatted volumetric flasks. With runs shorter than 30 min the diene solution was injected into acid violently agitated (Vibromixer) in a pleated flask. All reactions were worked up by quenching in iced water and extracting with methylene chloride, and proceeding as described subsequently.⁷ Results are given in Tables 3 and 4, and Figures 1 and 2. The extent to which compounds could be recovered by the extraction process was checked (Table 5). 4-Methyl-2-nitrophenol can be recovered quantitatively.⁹

Two of the products of solvolysis, 4-methyl-2-nitrophenol and 5-chloro-2-methylphenol could not be separated under the g.c. conditions used (Table 1). Their separate yields were

Table 2. Rate coefficients for the solvolyses of 5-chloro-2-methyl-2-nitrocyclohexa-3,5-dienyl acetate in aqueous sulphuric acids

Temperature (°C)	H ₂ SO ₄ (%)	10 ² [Nitrous trap]/M	10 ⁴ k ₁ /s ⁻¹
25.0 ± 0.1 ^a	H ₂ O	4.22	6.3
	6.5	4.66	8.4
	15.2	4.27	12.3
	15.2 ^b	ca. 1	10.9
	21.0 ^b	ca. 1	17.3
	21.5	4.10	17.0
	28.8 ^b	ca. 1	30
	31.6	4.12	36
	33.2 ^b	ca. 1	39
	36.2 ^b	ca. 1	48
	37.1	4.66	63
	43.6	4.19	149
	43.6	4.19	150
	43.6	4.19	154
5.0 ± 0.1 ^c	15.2	4.27	0.725
	21.5	4.10	1.18
	31.6	4.12	2.1
	37.1	4.60	3.8
	43.6	4.19	10.5
	43.6	4.19	11.4
	47.9	4.15	24
	52.4	4.01	61
	47.0	4.30	76
	58.8	4.98	101

^a Measurements at $\lambda = 260$ nm (absorbance decrease) with urea as the nitrous trap, unless otherwise indicated. [Substrate] = 5.2×10^{-5} M. ^b Measurements at $\lambda = 300$ nm (absorbance increase) with sulphanilic acid as the nitrous trap. [Substrate] ca. 10^{-4} M, except in 15.2% H₂SO₄ when [Ar] ca. 5×10^{-5} M. ^c Measurements at $\lambda = 260$ nm with urea as the nitrous trap. In 15.2%, 21.5%, and >22% H₂SO₄ the substrate concentrations were 1×10^{-5} , 1.5×10^{-5} , and 3×10^{-5} M, respectively.

determined by g.c.m.s. using the peak $m/z = 153$ due to 4-methyl-2-nitrophenol and the peaks $m/z = 142$ and 144 due to 5-chloro-2-methylphenol [V.G. Micromass 16F instrument fitted with an SP 2250 SCOT capillary column (50 m) and S.G.E. splitless injection system]. The system was calibrated using mixtures of the two compounds in known molar ratios to give the relationship between mixture composition and peak-height ratios.

Nitration of 4-Chlorotoluene.—The products of nitration in 63.1% H₂SO₄ were determined as previously described.² Details of g.c. methods are in Table 1, and results are in Table 11. G.c. showed a broad peak with retention time of 2000 s (SP 2250, 50 m capillary column, at 220 °C; other conditions as in Table 1). A peak with the same characteristics was obtained from the product obtained by nitrating 5-chloro-2-methylphenol in 63.1% H₂SO₄ for ten half-lives and working up the reaction as usual.

The rate coefficient of nitration of 5-chloro-2-methylphenol in 63.1% H₂SO₄ was determined in the usual way (measurements at $\lambda = 310$ cm; [Ar] = 3×10^{-4} mol l⁻¹; [HNO₃] = 7.066×10^{-2} mol l⁻¹).

Results

Solvolysis of (4) gave good first-order kinetics which could be measured for solutions in water and up to 43.6% H₂SO₄ at 25.0 °C, and to higher acidities at lower temperatures. With urea as the nitrous trap the disappearance of diene was followed, but with sulphanilic acid as the trap it was necessary to use a higher wavelength and to follow the appearance of pro-

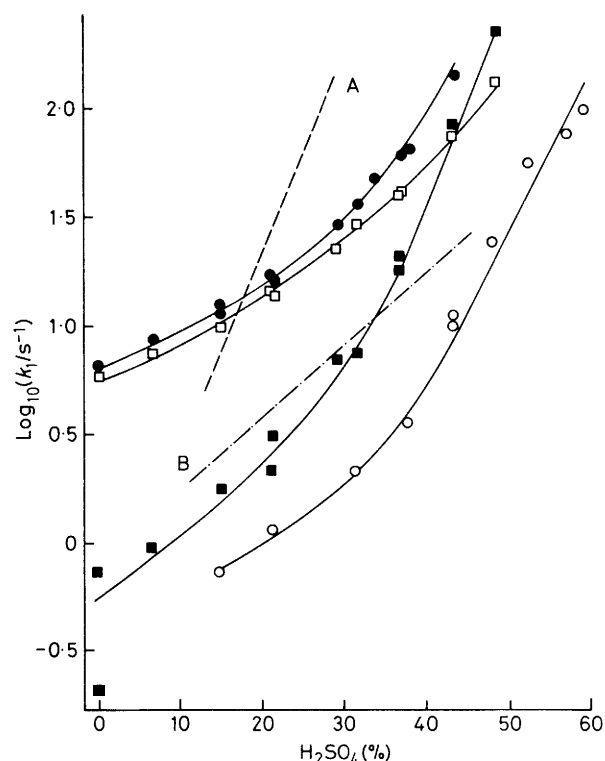


Figure 1. The acidity dependence of the first-order rate coefficients for solvolysis of, and for nitrous acid elimination from (4). ● Log₁₀ k₁ for the reaction of (4) at 25.0 ± 0.1 °C (Table 2); ○ log₁₀ k₁ for the reaction of (4) at 5.0 ± 0.1 °C (Table 2); A, hydrolysis of t-butyl acetate; B, hydrolysis of ethyl acetate; □ log₁₀ k_E for the elimination of nitrous acid from (4) (Table 9); and ■ log₁₀ k_S for ester solvolysis of (4) (Table 9)

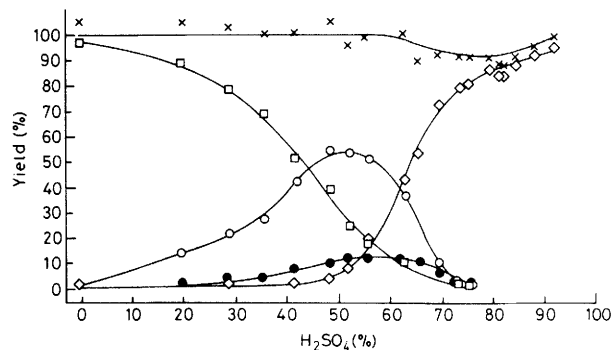


Figure 2. Yields of products from the reactions of (4) in sulphuric acid at 25.0 ± 0.1 °C in the presence of sulphanilic acid. ◆ 4-chloro-2-nitrotoluene; ◇ 'excess' 5-chloro-2-methylphenol; ○ 4-methyl-2-nitrophenol; □ corrected 5-chloro-2-methylphenyl acetate (5b) (see text); and × aggregate yield

ducts (Table 2). These two sources of rate coefficients gave concordant results (Figure 1).

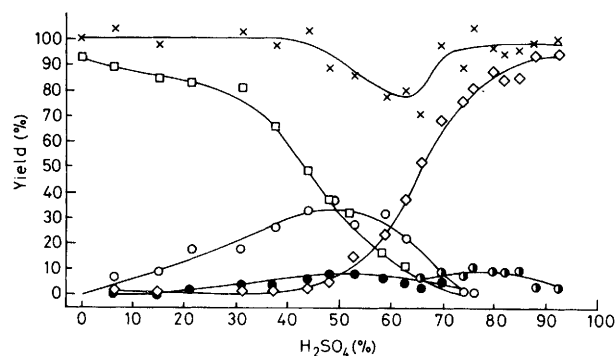
The products of solvolyses were determined in a range of media from water up to 92.4% H₂SO₄ in the presence of nitrous traps, and over a similar range of acidities with the additional presence of either anisole or phenol as a nitronium trap. In the first circumstance the isolated products were 4-chlorotoluene, 5-chloro-2-methylphenol, 5-chloro-2-methylphenyl acetate, 4-methyl-2-nitrophenol, 4-chloro-2- and 4-chloro-3-nitrotoluene (Table 3 and Figure 2). In ≥ 66% H₂SO₄

Table 3. Products of solvolysing 5-chloro-2-methyl-2-nitrocyclohexa-3,5-dienyl acetate in aqueous sulphuric acids at 25.0 ± 0.1 °C, in the presence of sulphanilic acid or hydrazinium sulphate

H ₂ SO ₄ (%)	10 ⁵ [Diene]/M	Reaction time (min)	10 ³	10 ³	Products (%) ^a								Total ^c
			[Hydrazinium sulphate]/M	[Sulphanilic acid]/M	(10)	6(α)	6(β)	5(α)	5(β)	(9)	(8)	(11)	
H ₂ O	1.0	180	5.7		0.2			97.0	97.0	2.8		6.4	106.4
21.5	4.0	66	4.8		0.5	46.8	12.8	54.4	88.4		1.8	2.2	105.7
28.8	10.0	30		11.3	0.7	42.3	20.8	56.3	78.3	1.6	3.7		104.6
37.1	4.0	19		10.0	2.5	47.3	25.9	47.7	69.1		3.5		101.0
43.6	4.0	8		10.0	0.1	51.7	41.5	40.1	50.3	1.6	7.1		100.6
47.9	4.0	4		10.0	0.1	58.2	52.7	34.0	39.5	4.1	9.8		106.2
52.4	4.0	2		10.0	0.2	53.9	51.6	22.2	24.6	8.5	10.7		95.2
57.0	4.0	2		10.0	0.7	50.8	48.7	15.3	17.4	20.0	11.9		98.7
63.4	4.0	2			2.5	31.3	29.5	8.3	10.1	41.4	12.4		95.9
63.4	4.0	2		1.0	0.9	34.1	32.1	9.3	11.3	41.4	9.9		95.6
63.4	4.0	2		9.9		37.4	35.4	9.1	11.1	43.9	10.3		100.7
63.4	4.0	2		50	1.4	36.9	34.7	9.9	12.1	43.6	12.8		104.6
66.0	10.0	1 335		20	3.0	20.0	<i>b</i>		<i>b</i>	53.1	10.6		86.7
70.0	10.0	24		19.5	3.1	8.7	<i>b</i>	1.3	<i>b</i>	73.3	5.3		91.7
70.0	10.0	24	5.2		0.9	7.5	<i>b</i>		<i>b</i>	73.4	4.6		86.4
74.3	10.0	2		19.8	3.3	2.9	1.7	2.8	4.0	79.2	2.4		90.6
74.3	10.0	2	5.0		1.8	0.2	0	1.7	2.4	82.4	0.3		86.4
75.9	10.0	2		19.9	3.3	2.0	0.8	2.1	3.3	80.5	2.6		90.5
75.9	10.0	2	5.6		0.9			1.3	2.2	84.8			87.0
79.7	10.0	2		19.8	1.4					87.3		1.6	90.3
79.7	10.0	2	4.8		1.1					89.8			90.9
81.8	10.0	2		19.5	1.8					84.3		1.7	87.8
82.5	10.0	2		10.6	1.3					83.5		1.5	86.3
84.8	10.0	2		19.5	0.6					88.2		2.7	91.5
84.8	10.0	2	5.0		0.3					94.3		2.6	97.2
88.4	10.0	2		20	0.1					92.6		2.8	95.5
92.4	10.0	2		20.5	0.1					90.3		3.2	93.6
92.4	10.0	2	5.2		0.3					94.3		3.5	98.1

^a Values \pm 4%: (10), 4-chlorotoluene; (6α) observed yield of 5-chloro-2-methylphenol; (6β) calculated yield of the 5-chloro-2-methylphenol which was not formed by hydrolysis of the acetate (see text); (5α) observed yield of 5-chloro-2-methylphenyl acetate; (5β) calculated yield of 5-chloro-2-methylphenyl acetate (see text); (9) 4-chloro-2-nitrotoluene; (8) 4-methyl-2-nitrophenol; and (11) 4-chloro-3-nitrotoluene.

^b Because of the long reaction time and the consequent near complete hydrolysis of 5-chloro-2-methylphenyl acetate the calculated yield of the phenol could not be obtained. ^c Given by (10) + (6α) + (5α) + (9) + (8) + (11).

**Figure 3.** Yields of products from the reactions of (4) in sulphuric acid at 25.0 ± 0.1 °C in the presence of sulphanilic acid and anisole. Symbols as for Figure 2. ● 2- and 4-Nitroaniline

solvolysis is fast and experiments in which anisole was present were run for ten half-lives of its nitration; 2- and 4-nitroaniline were then also formed in addition to the products already mentioned (Table 4 and Figure 3).

To check the validity of results for the recovery of 5-chloro-2-methylphenol from solutions in sulphuric acid (Table 5) we determined rate constants for the sulphonation of the phenol at several acidities (Table 6). Rate constants for the acid hydrolysis of 5-chloro-2-methylphenyl acetate were also needed, and are reported in Table 7. The related figures for

the recovery of the acetate by extraction from acid after known times are compared with the calculated quantities in Table 8.

Thermolysis of the diene was noteworthy for producing 4-chloro-3-nitrotoluene, in addition to the products of eliminating nitrous acid and acetyl nitrate.

Discussion

It is convenient to discuss our results in relation to the mechanisms which we believe to be operating in the reactions of the diene (4) in water and aqueous sulphuric acid (Scheme 2). Previous studies of such reactions of nitroacetates have revealed the parallel occurrence of an $A_{AL}1$ solvolysis and an elimination of nitrous acid. Work on 2-cyano-3,4-dimethyl-4-nitrocyclohexa-2,5-dienyl acetate (for which rate measurements could only be made down to 61.8% H₂SO₄ at 25.9 °C) showed the elimination of nitrous acid to be acid catalysed.¹ If we treat the initial product of nitrous acid elimination (5) as a member of the $A \rightarrow B \rightarrow C$ set, (4) \rightarrow (5) \rightarrow (6), we can partition the overall rate coefficient between the elimination reaction, E_{HNO_2} , and acid-catalysed solvolysis. Tables 3 and 4 contain the information so obtained expressed as the yields (5β) of acetate (5) corrected (Appendix) for hydrolysis to the phenol (6). In Table 9 we give some values for the fraction of the diene that reacts by the E_{HNO_2} process and by ester solvolysis, and rate coefficients for these processes derived by combining these fractions with the overall rate coefficients (Table 2). Several points emerge from this analy-

Table 4. Products of solvolysing 5-chloro-2-methyl-2-nitrocyclohexa-3,5-dienyl acetate in aqueous sulphuric acids at 25.0 ± 0.1 °C, in the presence of both a nitronium and a nitrous trap

H ₂ SO ₄ (%)	10 ⁵ [Diene]/M	Reaction time (min)	10 ²	10 ⁴ [Ni-	Product (%) ^a										Total ^j	
			[Nitrous trap]/M	tronium trap]/M	(10)	6(α)	6(β)	5(α)	5(β)	(9)	(8)	(11)	(12)	(13)		
H ₂ O	1.0	180	5.0 ^b	1.0 ^e	0.4				93.3	93.3			7.5			101.2
6.5	1.0	140	5.0 ^b	1.0 ^e	0.6	24.1 ^h	7.4	72.3	89.0	0.9	0.3	6.2				104.4
15.2	1.0	100	1.0 ^c	1.0 ^e	0.6	39.4 ^h	8.4	53.6	84.7	0.5	0.3	4.0				98.4
21.5	4.0	66	1.0 ^c	1.0 ^e	0.6	49.9	18.2	50.8	82.6		0.6	4.3				106.2
31.6	4.0	34	1.0 ^c	1.0 ^e	0.5	45.9	15.9	51.8	81.8	1.2	2.3	1.8				103.5
37.1	4.0	19	1.0 ^c	1.0 ^e	0.7	45.3	25.1	45.0	65.2	0.2	3.3	2.1				97.3
43.6	4.0	8	1.0 ^c	5.0 ^e	0.9	40.7	31.3	37.2	46.7	1.9	6.6	1.2				88.5
43.6	4.0	8	1.0 ^c	5.0 ^e		44.6	34.9	38.2	47.9	1.5	6.0	6.2				96.5
43.6	4.0	8	1.0 ^c	50 ^f	<i>g</i>	56.9	47.9	37.5	47.0	1.7	6.9					103.0
43.6	4.0	8	1.0 ^c	99 ^f	<i>g</i>	49.8	40.4	37.0	46.4		5.6					92.4
47.9	4.0	4	1.0 ^c	5.0 ^e	0.4	42.3	37.2	31.6	36.7	4.5	7.5	2.3				88.6
52.8	4.0	2	1.0 ^c	5.0 ^e	0.4	30.8	27.4	30.6	33.8	15.4	6.8	1.7				85.7
58.8	4.0	2	4.1 ^b	5.0 ^e		32.3	30.2	13.9	16.0	24.0	6.0	1.7				77.9
63.1	4.0	2	4.1 ^b	5.0 ^e	0.4	25.6	23.6	9.3	11.3	38.3	4.1	2.3				80.0
63.1	4.0	2	3.8 ^d	5.0 ^e	0.9	29.1	26.7	11.0	13.4	39.4	6.8					87.2
66.0	10.0	1 335	2.0 ^c	5.0 ^e	1.9	10.1	<i>i</i>		<i>i</i>	51.2	2.5	0.9	2.8	2.1		69.6
70.0	10.0	24	1.9 ^c	20 ^e		13.6	<i>i</i>	2.0	<i>i</i>	68.3	5.2	1.2	3.9	3.6		97.8
70.0	10.0	24	0.52 ^d	20 ^e	1.5	15.3	<i>i</i>	1.8	<i>i</i>	67.0	6.2	0.3	3.1	2.1		95.8
74.3	10.0	2	2.0 ^c	20 ^e	1.0	1.2	0.8	1.8	2.6	75.8	1.0	0.8	2.9	2.9		86.4
74.3	10.0	2	0.50 ^d	20 ^e	1.3	7.3	5.7	3.8	5.4	76.3	5.2	0.1	3.4	2.6		98.7
75.9	10.0	2	2.0 ^c	20 ^e	1.8	4.8	2.6	3.6	5.8	80.4	3.2	2.3	7.8	3.7		105.8
75.9	10.0	2	0.56 ^d	20 ^e	0.9	1.9	0.9	1.7	2.7	82.7	2.1	0.1	3.4	2.7		94.6
79.7	10.0	2	2.0 ^c	20 ^e	2.4					87.3		1.1	4.4	3.9		96.7
79.7	10.0	2	0.48 ^d	20 ^e	1.5					89.3		0.1	4.2	3.3		96.9
81.8	10.0	2	2.0 ^c	20 ^e	3.4					83.7		1.1	4.3	4.7		93.8
84.8	10.0	2	2.0 ^c	20 ^e	6.0					84.8		1.2	4.6	4.2		94.8
84.8	10.0	2	0.50 ^d	20 ^e	3.1					91.0			4.4	3.3		98.7
88.4	10.0	2	2.0 ^c	20 ^e						93.5		3.7	1.0			98.2
92.4	10.0	2	2.0 ^c	20 ^e	2.2					92.3		3.6		3.4		99.3
92.4	10.0	2	0.52 ^d	20 ^e	1.5					92.4		2.7	0.6	1.0		96.7

^a Values $\pm 4\%$: (10) (6α), 6(β), (5α), (5β), (9), (8), and (11) as in Table 3; (12) 2-nitroanisole; and (13) 4-nitroanisole. ^b Urea. ^c Sulphanilic acid. ^d Hydrazinium sulphate. ^e Anisole. ^f Phenol. ^g The g.c. peak due to 4-chlorotoluene would have been obscured by that due to the nitronium trap. ^h Corrected for incomplete extraction. ⁱ Because of the long reaction time and the consequent near complete hydrolysis of 5-chloro-2-methylphenyl acetate the calculated yield of the phenol could not be obtained. ^j In $<66\%$ H₂SO₄ taken as [(10) + (6α) + (5α) + (9) + (8) + (11)]. In $\geq 66\%$ H₂SO₄ taken as [(6α) + (5α) + (9) + (8) + (11) + (12) + (13)].

sis. First, the partitioning of (4) between ester solvolysis and E_{HNO_2} reactions moves in favour of the former with increasing acidity despite the fact that the E_{HNO_2} reaction is acid-catalysed (Table 9 and Figure 1). This last feature of the E_{HNO_2} reaction supports the earlier conclusion¹ that E_{HNO_2} is not a simple $E1$ reaction. Second, it is clear that the ester solvolysis changes its character with increasing acidity. We ascribe this to a shift from an $A_{\text{AC}2}$ process at low acidities to an $A_{\text{AL}1}$ process at high acidities. This is borne out by the values of $d(\log k)/d(\% \text{H}_2\text{SO}_4)$ which are compared in Figure 1 and Table 10 with those for ethyl acetate¹⁰ and *t*-butyl acetate,¹¹ esters which are hydrolysed by the $A_{\text{AC}2}$ and $A_{\text{AL}1}$ mechanisms, respectively. There were indications of a similar situation in the case of 2-cyano-3,4-dimethyl-4-nitrocyclohexa-2,5-dienyl acetate,¹ but the point could not be established because good kinetics were not observed at low acidities. Thus, (4) reacts by three mechanisms, all acid-catalysed: the E_{HNO_2} , $A_{\text{AC}2}$, and $A_{\text{AL}1}$ mechanisms.

Further consideration of the products of these reactions as they vary with acidity reveals more about their inter-relationships. It is possible to calculate (Appendix) the amount of 5-chloro-2-methylphenol which should be present in the reaction solution after a known time as a consequence of the hydrolysis of 5-chloro-2-methylphenyl acetate formed by the E_{HNO_2} process. The observed yield (6α) of the phenol is given in Tables 3 and 4 and is found to be greater than this calculated amount. The excess of (6β), the difference between the

observed yield and that calculated to have been formed by the E_{HNO_2} process, must therefore come from another reaction or reactions. At lower acidities some phenol must come from the $A_{\text{AC}2}$ process (Scheme 2) which we have identified (see above). However, at acidities above 30% H₂SO₄ the $A_{\text{AC}2}$ process diminishes in importance (Figure 1) and the amount of excess of phenol might be expected to diminish. This does not happen; rather, the amount of excess of phenol continues to increase, reaching a maximum in about 50% H₂SO₄ (Tables 3 and 4, Figures 2 and 3). We believe this to happen because of 1,2-nucleophilic capture by water of the W_1^{Me} (1) formed in the $A_{\text{AL}1}$ process.

Formation from (1) of 5-chloro-2-methylphenol would require capture to occur adjacent to the *ipso*-position, in the same way that (4) is formed by the capture of (1) by acetate.³ 1,2-Capture of (1) competes with 1,4-capture, as is shown by the formation of 4-methyl-2-nitrophenol (8); this must occur *via* the dienone (7).^{9,12} The observed yield of 4-methyl-2-nitrophenol measures the amount of dienone formed, and therefore the extent of 1,4-capture, despite the fact that product runs were made for only ten half-lives of reaction of the diene (4). This is a shorter time than is needed for complete rearrangement of the dienone (7) but it is known that the dienone is converted completely into 4-methyl-2-nitrophenol (8) during the extraction process.

As we have seen, with increasing acidity the relative importance of the two ester solvolyses together increases over

Table 5. Recovery of aromatics, by extraction with dichloromethane from solutions in aqueous sulphuric acids ^a at 25.0 ± 0.1 °C after dilution

Compound	H ₂ SO ₄ (%)	Recovery (%)	Compound	H ₂ SO ₄ (%)	Recovery (%)
4-Chlorotoluene ^b	6.5	75.6	4-Chloro-3-nitrotoluene ^e	6.5	103.5
	21.5	68.1		21.5	100.3
	31.6	64.0		31.6	103.1
	43.6	59.6		43.6	91.8
	52.8	58.6		52.8	103.0
	63.1	81.2		63.1	98.9
	66.0	72.0		66.0	92.8
	70.0	67.2		70.0	106.3
	74.3	76.6		74.3	100.3
	75.9	65.3		75.9	104.6
	81.8	82.1		81.8	96.1
	92.4	71.0		92.4	103.4
5-Chloro-2-methylphenol ^c	6.5	83.1	2-Nitroanisole ^f	6.5	98.5
	21.5	95.8		21.5	99.4
	31.6	105.2		31.6	105.6
	43.6	102.8		43.6	100.9
	52.8	97.7		52.8	99.2
	63.1	98.2		63.1	96.8
	66.0	93.0		66.0	90.7
	70.0	104.1		70.0	106.0
	74.3	97.8		74.3	94.0
	75.9	104.7		75.9	104.0
	81.8	92.8		81.8	92.2
	92.4	17.2		92.4	98.0
4-Chloro-2-nitrotoluene ^d	6.5	102.7	4-Nitroanisole ^g	6.5	96.1
	21.5	97.9		21.5	97.1
	31.6	99.9		31.6	106.4
	43.6	95.7		43.6	98.5
	52.8	101.7		52.8	95.1
	63.1	95.7		63.1	90.8
	66.0	94.6		66.0	100.0
	70.0	102.0		70.0	104.4
	74.3	100.9		74.3	96.9
	75.9	101.5		75.9	104.2
	81.8	95.1		81.8	101.9
	92.4	101.9		92.4	97.2

^a Solutions were kept for the same time as solvolyses carried out at corresponding acidities. [Ar] *ca.* 5 × 10⁻⁶M at the lowest acidity and [Ar] *ca.* 1 × 10⁻⁴M at the highest acidity. ^b The volatility of 4-chlorotoluene causes losses during concentration of the extract. Average recovery = 69.8% (S.D. = 7.5%). ^c The yield from 92.4% H₂SO₄ is not corrected for sulphonation. Average recovery over 31–82% H₂SO₄ = 100.4% (S.D. = 4.5%). ^d Average recovery = 99.1% (S.D. = 3.0%). ^e Average recovery = 101.0% (S.D. = 4.5%). ^f Average recovery = 98.8% (S.D. = 6.5%). ^g Average recovery = 99.0% (S.D. = 4.3%).

Table 6. Rate constants for the sulphonation of 5-chloro-2-methylphenol ^a in aqueous sulphuric acids at 25.0 ± 0.1 °C

H ₂ SO ₄ (%)	10 ⁵ k ₁ /s ⁻¹
76.8	1.25
78.8	2.1
80.1	6.2
82.5	13.7
84.8	52
86.7	96

^a [Ar] = 9.2 × 10⁻⁵M. Measurements at λ = 235 nm.

Table 7. Rate constants for the hydrolysis of 5-chloro-2-methylphenyl acetate ^a in aqueous sulphuric acids at 25.0 ± 0.1 °C

H ₂ SO ₄ (%)	10 ⁴ k' ₁ /s ⁻¹
6.5	0.29
15.2	0.90
21.5	1.45
31.6	2.6
36.2	3.5
41.0	4.6
45.3	5.6
50.2	7.7
52.8	9.5
56.7	12.2
58.9	12.1
61.8	14.7
65.5	17.4
70.4	20
74.3	29
76.8	51
78.8 ^b	75
80.6 ^b	185

^a For the first four acidities [Ar] *ca.* 4–5 × 10⁻⁵M. Above 32% H₂SO₄ [Ar] *ca.* 1.6 × 10⁻⁴M. Measurements at λ = 274 nm.

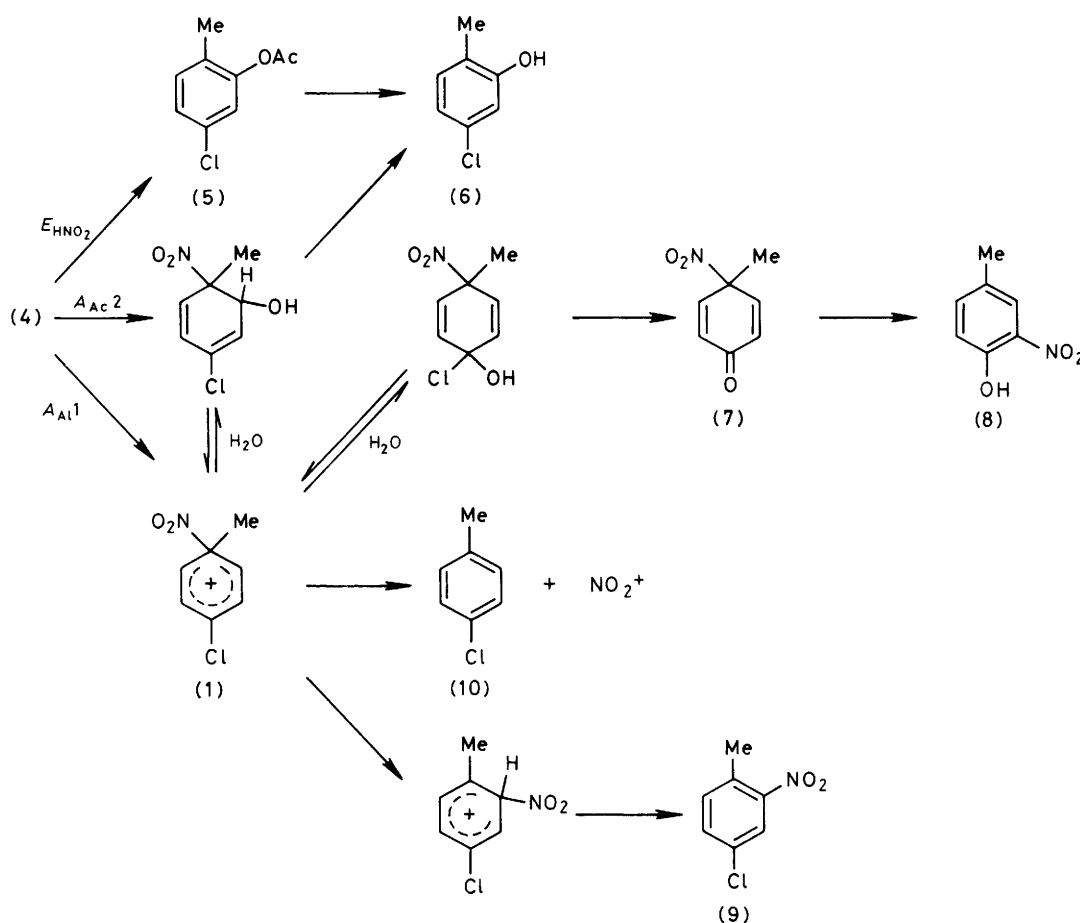
^b Measurements at λ = 266 nm (isosbestic point for phenol sulphonation). [Ar] *ca.* 5 × 10⁻³M.

that of the *E*_{HNO₂} reaction, and also the importance of the *A*_{AL1} reaction increases relative to that of the *A*_{AC2} reaction. In Scheme 2 we represent (1), the product of *A*_{AL1} reaction, as reacting in four ways: by two processes of nucleophilic capture by water, as already mentioned, by regression to 4-chlorotoluene and nitronium ion, and by 1,2-rearrangement to 4-chloro-2-nitrotoluene (9). The yield of 5-chloro-2-methylphenol (6) reaches a maximum in about 50% H₂SO₄, and that of 4-methyl-2-nitrophenol (8) in about 60% H₂SO₄. The difference cannot be taken to indicate a medium-dependence in the competition between 1,2- and 1,4-capture because even above 30% H₂SO₄ the *A*_{AC2} process will contribute to the

Table 8. Recovery of 5-chloro-2-methylphenyl acetate ^a by extraction with dichloromethane after reaction in aqueous sulphuric acids at 25.0 ± 0.1 °C

H ₂ SO ₄ (%)	Reaction time (min)	Recovery of acetate (%)	Recovery of phenol (%)	Total recovery (%)	Calculated acetate ^b recovery (%)
31.6	30	65.8	38.8	104.6	62.3
37.1	15	77.7	33.1	100.8	71.6
43.6	8	80.2	23.7	103.9	76.8
47.9	4	87.2	18.6	105.8	84.4
52.8	2	93.7	12.6	106.3	89.4
58.8	2	90.3	15.9	106.2	85.7
63.1	2	84.5	16.5	101.9	82.3

^a [Ar] = 4.108 × 10⁻⁵ M. ^b Based on [Ar]_t = [Ar]₀exp(-k₁t). Interpolated k₁ values used (see Table 7).

**Scheme 2.**

yield of 5-chloro-2-methylphenol. The diminution in yields of the two phenols at higher acidities is due to the reduction in overall nucleophilic capture as a consequence of the declining activity of water, and the relative increase in the importance of the other reactions of (1).

The fates of regression and 1,2-migration represented in Scheme 2 require closer scrutiny. They are part of the fuller scheme of behaviour of W_t^{Me} (1) shown in Scheme 3. By one route (1) reverts to the encounter pair which is an intermediate in the nitration of 4-chlorotoluene; this may recreate (1), and the other possible Wheland intermediates, the process which we have named extranuclear rearrangement,¹ or 'leak' to give its components, 4-chlorotoluene (10) and nitronium ion. In the other direction intramolecular ¹ 1,2-

rearrangement of (1) leads to 4-chloro-2-nitrotoluene (9). In the absence of measures to prevent it the regression to 4-chlorotoluene and nitronium would lead to re-nitration, *i.e.* to intermolecular ¹ rearrangement of (1). The extent to which the encounter pair formed from an aromatic molecule and nitronium ion leaks depends on the closeness of the rate constant for nitration of the aromatic to that for diffusion-controlled nitration (for which there is no leakage).⁹ In the range 63–74% H_2SO_4 the magnitude of the rate coefficient for the nitration of 4-chlorotoluene varies from about a fortieth to about a tenth of that of the rate-coefficient for an encounter-controlled nitration.² Consequently, even at the higher acidities about 90% of the encounter-pair leaks, and extra-nuclear rearrangement can be neglected. When solvolysis is effected in

Table 9. Partitioning of 5-chloro-2-methyl-2-nitrocyclohexa-3,5-dienyl acetate between the E_{HNO_2} reaction and ester solvolyses and the corresponding partitioned rate coefficients at $25.0 \pm 0.1^\circ\text{C}$

H_2SO_4 (%)	$10^4 k_1/\text{s}^{-1}$ ^a	E_{HNO_2} (%)	$10^4 k_E/\text{s}^{-1}$ ^b	Ester solvolysis (%) ^c	$10^4 k_S/\text{s}^{-1}$ ^d
H_2O	6.3	93.3	5.9	6.7	0.42
H_2O	6.3	97.0	6.1	3.0	0.19
6.5	8.4	89.0	7.5	11.0	0.92
15.2	12.2	84.7	9.9	15.3	1.8
21.5	17.4	82.6	14.4	17.4	3.0
21.5	17.4	88.4	15.4	11.6	2.0
28.8	28.2	78.3	22.1	21.7	6.1
31.6	34.6	81.8	28.3	18.2	6.2
37.1	61.6	65.2	40	34.8	21
37.1	61.6	69.1	42	30.9	19
43.6	148	46.7	69	53.3	79
43.6	148	50.3	74	49.7	88
47.9	(355 \pm 40) ^e	39.5	140	60.5	210

^a Interpolated values of the rate coefficient for diene solvolysis. Partitioning calculated from product yields in $<44\%$ H_2SO_4 in the presence of both a nitrous trap and of a nitrous and a nitronium trap. ^b $k_E = k_1 E_{\text{HNO}_2}/100$. ^c $(100 - E_{\text{HNO}_2})$. ^d $k_S = k_1(100 - E_{\text{HNO}_2})/100$. ^e In $>44\%$ H_2SO_4 , only product runs in the presence of sulphanilic acid used. k_1 extrapolated from results for 5°C .

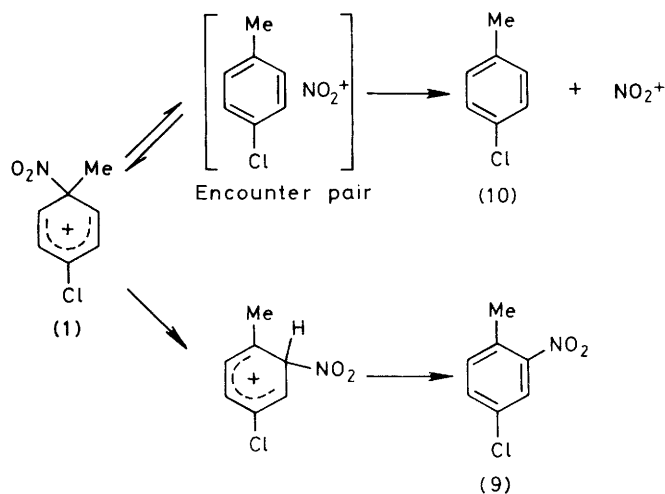
Table 10. Acid catalysis of the ester solvolysis of 5-chloro-2-methyl-2-nitrocyclohexa-3,5-dienyl acetate (4) and other esters at $25.0 \pm 0.1^\circ\text{C}$

H_2SO_4 (%)	$10^2 \text{d}(\log k_S)/\text{d}(\% \text{H}_2\text{SO}_4)$ ^a		
	(4)	Ethyl acetate ^b	t-Butyl acetate ^b
0–20	3.2		
13–43		3.5	
35–50	9.7		
12–26			9.3

^a k_S is the rate coefficient obtained by partitioning the rate coefficient for solvolysis of diene (4) between elimination and solvolysis (see Table 9). ^b See Figure 1, and refs. 10 and 11.

the presence of anisole or phenol, efficient nitronium traps, intermolecular rearrangement will be suppressed, and then the yield of 4-chloro-2-nitrotoluene is a measure of the degree to which (1) undergoes 1,2-intramolecular rearrangement. Further, the yield of nitroanisoles measures the extent to which the $A_{\text{AL}}1$ reaction leads to regression (Scheme 2). That the nitroanisoles arise by nitronium ion nitration of anisole is borne out by two facts; the ratio of 2- to 4-nitroanisole is appropriate for this reaction,¹³ and the change of nitrous trap from sulphanilic acid to hydrazinium sulphate is without effect on the results (Table 4). Even in the absence of a nitronium trap, because of the low concentrations of 4-chlorotoluene and nitronium ion produced, re-nitration of the 4-chlorotoluene should be very slow. Thus, much of the 4-chlorotoluene should, even in these conditions, be isolable as such.

As can be seen from Tables 3 and 4, 4-chlorotoluene (10) is a product over the whole range of reaction conditions. We comment on the formation of 4-chlorotoluene at very low acidities, where $A_{\text{AL}}1$ solvolysis is not important, below. Unfortunately, the volatility of 4-chlorotoluene (see Experimental section) prevents the attachment of quantitative significance to the isolated yields. However, we may conclude qualitatively that the regression represented in Scheme 2 does indeed occur



Scheme 3.

(though it is much less important than in the case of 2,3-dimethylbenzonitrile¹).

The aggregate yields of nitroanisoles from experiments in the range 66–85% H_2SO_4 (where nitration proceeds at a practicable rate) are, within experimental error, more or less constant, suggesting that in this range the extent of regression does not change significantly. Surprisingly, in the presence of anisole the excess yield of 5-chloro-2-methylphenol and the yield of 4-methyl-2-nitrophenol above 30% H_2SO_4 , where the $A_{\text{AL}}1$ reaction becomes important, are markedly lower than when anisole is absent (Figures 2 and 3). Furthermore, the aggregate yield of products drops correspondingly (Figure 3). This suggests that anisole is reacting not only with nitronium ion, but also with the precursor of the excess of 5-chloro-2-methylphenol and the 4-methyl-2-nitrophenol, *i.e.* with W_1^{Me} (1). The ability of W_1^{Me} 's to react as electrophiles and to effect substitution into reactive aromatics is well established.¹⁴ Unfortunately, we were unable to isolate the product to account for the loss of yield. Above 85% H_2SO_4 the aggregate yield of nitro-anisoles drops; this phenomenon accompanying the nitration of anisole at high acidities has been observed before and has not been explained.¹³

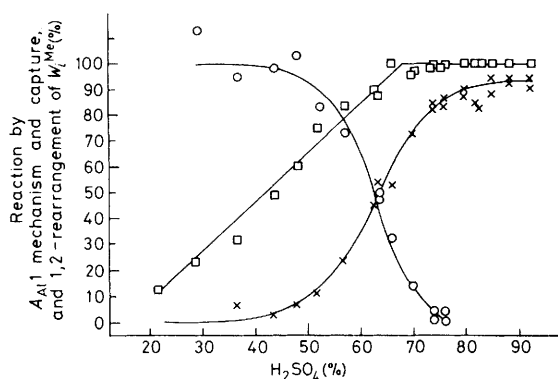
The yield of 4-chloro-2-nitrotoluene, the product of intramolecular 1,2-rearrangement of (1), is not influenced by the presence of anisole. The yield increases with acidity as would be expected since the rearrangement must become increasingly more important relative to nucleophilic capture. The implication is, that in the conditions used the *bulk* reactivity of water in capturing W_1^{Me} is similar to the *bulk* reactivity of anisole at the concentrations used.

We noted above that some 4-chlorotoluene was formed from (4) even at the lowest acidities, and in water. It is also the case that some 4-chloro-3-nitrotoluene is formed, a compound not accounted for by our reaction scheme. We believe 4-chloro-3-nitrotoluene, and to some extent 4-chlorotoluene to be artefacts arising from the thermal decomposition of (4) (see Experimental section). 4-Chloro-3-nitrotoluene would arise by a 1,3-migration not involving (1), just as 2,3-dimethyl-5-nitrobenzonitrile is formed in a thermal rearrangement of 2-cyano-3,4-dimethyl-4-nitrocyclohexa-2,5-dienyl acetate.¹ Such reactions have been regarded as sigmatropic rearrangements.¹⁵ No 4-chloro-3-nitrotoluene was formed in our experiments when quite fresh stock solutions of (4) were used, except in water and 6% H_2SO_4 . Under these last conditions the thermal reaction evidently competes successfully with the other reactions of (4).

Table 11. Products of nitration of 4-chlorotoluene in 63.1% H₂SO₄ at 25.0 ± 0.1 °C^a

[HNO ₃]/M	Time (min)	Extent of reaction (%) ^b	Product (%)				Total yield (%)
			(8)	(9)	(11)	5-Chloro-2-methylphenol	
0.2039	230	100	9.3	39.1	31.0	0.0	79.4
0.2003	20	37.6	ca. 5 ^c	14.0	11.4	ca. 1 ^{c,d}	31.4

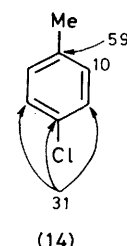
^a [Ar] = 8.228 × 10⁻⁵ M. Products are identified by the numbers used in Schemes and in Tables 3 and 4. ^b Calculated using $k_{2\text{ obs.}} = 1.96 \times 10^{-3}$ l mol⁻¹ s⁻¹ for 4-chlorotoluene. ^c Aggregate yields of nitrophenol and chlorophenol = 6.0%. G.c.m.s. gave an approximate molar ratio of 5:1. Precise values were not obtained because the figures obtained were outside the calibrated range used in other experiments (Tables 3 and 4). ^d Calculated amount of 5-chloro-2-methylphenol based on $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ ($k_1 = 1.96 \times 10^{-3}$; $k_2 = 1.89 \times 10^{-2}$ l mol⁻¹ s⁻¹) is ca. 1.4%.

**Figure 4.** The behaviour of (4) and of (1) in sulphuric acid at 25.0 ± 0.1 °C. □ Proportion % of (4) reacting by the A_{AL}1 mechanism; ○ proportion % of (1) captured by water; × proportion % of (1) rearranging to 4-chloro-2-nitrotoluene

In Figure 4 we illustrate the ways in which W_i^{Me} (1) is partitioned between combined 1,2- and 1,4-capture by water, and 1,2-rearrangement to 4-chloro-2-nitrotoluene. Even at the highest acidities the intermediate is not wholly converted into this product. We attribute the deficiency to regression, as discussed above; as expected, this reaction accounts for only a few parts percentage of the W_i^{Me} (1).

In the nitration of 4-chlorotoluene² the lowest acidity at which yields of products (4-chloro-2- and 4-chloro-3-nitrotoluene) were measured was 63.0% H₂SO₄. In view of the conclusions drawn above about the behaviour of W_i^{Me} (1) the products from the nitration of 4-chlorotoluene in 63.1% H₂SO₄ were re-examined. As expected, 4-methyl-2-nitrophenol was found (Table 11). Under these conditions, 4-chloro-2-methylphenol formed by 1,2-capture of W_i^{Me} (1) would be rapidly nitrated [$k_{2\text{ obs.}} = 1.89 \times 10^{-2}$ l mol⁻¹ s⁻¹ in 63.1% H₂SO₄ at 25.0 ± 0.1 °C. For 4-chlorotoluene interpolation from previous results² gave $k_{2\text{ obs.}} = 1.96 \times 10^{-3}$ l mol⁻¹ s⁻¹ under these conditions]. Gas chromatography of the nitration products showed a peak with the same retention time as that of material obtained by nitrating 5-chloro-2-methylphenol, but quantitative analysis was not possible (see Experimental section). If the deficiency of yield [(100–79.4)%] (Table 11) from the nitration of 4-chlorotoluene run to completion is attributed to 1,2-capture, the experiment gives a ratio of products for 1,4- to 1,2-capture of 9.3 : 20.6 = 0.45. This is roughly comparable to the value obtained from the solvolysis of (4). [Table 3, average value of (10)/(6β) = 0.35.]

In 63.1% H₂SO₄ the yield of 4-chloro-2-nitrotoluene was 39.1% (Table 11), whilst its maximum yield (in 79.2% H₂SO₄) was 64.2%. The difference, 25.1%, measures roughly the degree



to which the yield is reduced by capture of (1) by water. Figure 4 shows that in 63.0% H₂SO₄ (1) is about equally partitioned between capture and 1,2-rearrangement, so the extent of *ipso*-attack at C–Me in the nitration of 4-chlorotoluene is indicated to be roughly 50%. This value is considerably larger than the minimum value of 27% suggested earlier [see (3)],² and more comparable to the result of Fischer *et al.* for nitration in acetic anhydride, mentioned at the beginning of this paper.

The results permit the evaluation of positional reactivities as shown in (14) by the method outlined earlier,¹ which takes account of regression of the W_i^{Me} (1) to 4-chlorotoluene and nitronium ion during nitration.

The proposed scheme for the nitration of 4-chlorotoluene² includes not only *ipso*-attack at C–Me but also at C–Cl; explicit evidence for the latter is lacking, but its occurrence is made likely by the loss in yield of 4-chloro-3-nitrotoluene at low acidities, and by analogy. The present observation (see Experimental section) in the n.m.r. spectra of reaction solutions prepared from 4-chlorotoluene, nitric acid, and hexadeuterio-acetic anhydride, of signals from dienes other than (4) may be due to this form of *ipso*-attack, or to 1,4-capture by acetate of (1). If 1,4-capture does occur in acetic anhydride, as it does in aqueous media (see above), 4-methylphenyl acetate or 4-methylphenol might be expected amongst the products of work-up; we have not sought them. Our results show that in the nitration of 4-chlorotoluene the C–Me position is the most reactive one, and that total *ipso*-attack may account for most of the primary reaction.

Appendix

From Scheme 2, $(5\beta)_{t=t} = [(5) \text{ observed}]_{t=t} + [(6) \text{ formed from } (5)]_{t=t}$. Similarly $(6\beta)_{t=t} = [(6) \text{ observed}]_{t=t} - [(6) \text{ formed from } (5)]_{t=t}$. The last quantity is given by $[(6) \text{ formed from } (5)]_{t=t} = xZ[(4)]_{t=0}$, where x is the fraction of (4) reacting by the E_{HNO_2} pathway, and $Z = 1 + [k_1 \exp(-k_1 t) - k_1' \exp(-k_1' t)] / (k_1' - k_1)$. In the last expression k_1 is the rate coefficient for the diene reaction (Table 2), and k_1' that for the hydrolysis of (5) (Table 7).

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