Electrophilic Aromatic Substitution. Part 24.[1] The Nitration of Isopropylbenzene, 2- and 4-Isopropyltoluene, 1-Chloro-4-isopropylbenzene, 4-Isopropylanisole, and 2-Bromotoluene: Nitrodeisopropylation

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The kinetics and products of nitration in aqueous sulphuric acid of the title compounds have been studied. 4-Isopropyl-phenol and -anisole are nitrated at or near the encounter rate. In 65—79% H_2SO_4 2-isopropyltoluene suffers *ca.* 25% *ipso*-attack; the only fate of $W_i^{Pr^i}$ (*ipso*-Wheland intermediate) is nitrodeisopropylation. From 4-isopropyltoluene $W_i^{Pr^i}$ is also nitrodeisopropylated, but some 1,2-nitro-migration may occur. From the same compound W_i^{Me} may be captured by water, rearrange, or give 4-methylacetophenone; a mechanism is proposed for the formation of the last compound. Nitrodeisopropylation occurs without the assistance of water. With 4-isopropylanisole, demethoxylation and nitrodeisopropylation are consequences of the formation of $W_i^{Pr^i}$. The results are consistent with increasing attack at C-4 with increasing acidity, loss of isopropyl without assistance from water, and decomposition of the unobserved intermediate, 4-isopropyl-4-nitrocyclohexa-2,5-dienone, by two processes. One, acid-catalysed process gives 4-nitrophenol and possibly 4-isopropyl-2-nitrophenol. The other, probably radical, process gives 4-isopropyl-2-nitrophenol. In contrast to 4-bromotoluene, 2-bromotoluene is not nitrodebrominated.

ipso-SUBSTITUTION is not an uncommon reaction, but not many examples of it have been studied quantitatively. We recently described such a study of nitrodebromination,[2] and now report on some nitrodeisopropylations.

The nitration of isopropylbenzene (cumene) has often been reported. Under a variety of conditions [3,4] 2-, 3-, and 4-nitro-isomers are formed. Yields were not always given but the proportions obtained [4] (24.1% of 2-, 7.7% of 3-, and 68.2% of 4-nitro-isopropylbenzene; relative rate by competition, 16.6) using nitric acid and acetic anhydride in nitromethane are representative of results obtained with this reagent and with mixed acid. However, mixed acid in sulpholan and acetic acid,[5] and methyl nitrate with boron trifluoride in nitromethane,[6] gave high proportions of 2-nitration.

Thus, nitrodeisopropylation does not occur with isopropylbenzene, but it occurs readily,[3d,7] but not invariably,[8] if an activating group is in the 4-position with respect to the isopropyl group. The case of 4-isopropyltoluene (*p*-cymene) has been extensively studied. From nitrations in sulphuric acid, 4-isopropyl-2-nitrotoluene, 4-nitrotoluene, and 4-methylacetophenone were obtained. The yield of 4-isopropyl-2-nitrotoluene increased, and that of 4-methylacetophenone decreased with increasing acidity.[9] Other results are in Table 1. Nitration in concentrated sulphuric acid gave essentially the same results as when the nitronium salt was used, but with acetyl nitrate–acetic anhydride the yield of 4-isopropyl-2-nitrotoluene was halved, the material appearing as 1-isopropyl-4-methyl-4-nitrocyclohexa-2,5-dienyl acetate (I) [10] [at lower temperature some 2-(4-tolyl)propan-2-ol was formed with higher yields of the adduct [11]].

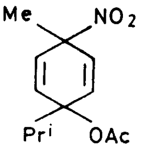
TABLE 1

The nitration of 2- and 4-isopropyltoluene

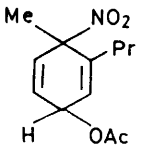
Substrate	Reagent	Products (%) 2-Nitro	3-Nitro	4-Nitro	5-Nitro	6-Nitro	Nitrotoluene	Adducts	Ref.
2-Isopropyltoluene	$AcONO_2$–Ac_2O		3			15		22 [a]	12
	$NO_2^+BF_4^-$–sulpholan		0.6	25	11	22	41 [b]		3d
4-Isopropyltoluene	$AcONO_2$–Ac_2O, 0 °C	41	8				10 [c]	41 [d]	10, 12
	$AcONO_2$–Ac_2O, −15 °C	26	5				12	57 [d]	11
	H_2SO_4–HNO_3	82	7				11		10, 12
	$NO_2^+BF_4^-$–sulpholan	85	5				10		3d

[a] (II) + (III). [b] 2-Nitrotoluene. [c] 4-Nitrotoluene. [d] (I).

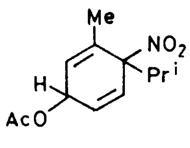
In the nitration of 2-isopropyltoluene nucleophilic capture of $W_i^{Pr^i}$ (*ipso*-Wheland intermediate) can forestall nitrodeisopropylation (Table 1). Solvolysis of the mixture of (II) and (III) [12] gave no 3-nitro-2-isopropyltoluene, so that the small yield of this compound formed in nitration must arise by direct nitrodeprotonation at C-3.



(I)



(II)



(III)

With mixed acid 1-chloro-4-isopropylbenzene gave

73% of 1-chloro-4-isopropyl-3-nitrobenzene.[13] The result has no quantitative significance because the starting material was probably a mixture of 2- and 4-isopropyl-1-chlorobenzene. Nitration of 4-isopropylanisole in acetic anhydride gave 4-isopropyl-2-nitroanisole (81%) and 4-isopropyl-2-nitrophenol (10%).[14] No care was taken to avoid nitration *via* nitrosation.

We now report the kinetics of nitration, in aqueous sulphuric acid, of the title compounds, and also the yields of the products formed in these reactions. 2-Bromotoluene was included for comparison with 2-isopropyltoluene.

EXPERIMENTAL

^{1}H N.m.r. spectra (100 MHz; CDCl$_3$) were recorded on a JEOL MH100 instrument. Preparative g.l.c. was carried out with a Pye 105 and analytical g.l.c. with a Pye 104 instrument. H.p.l.c. analyses were carried out using a Waters Associates model 6000A pump and Cecil 272 detector at ambient temperature. The products of nitration of isopropylanisole were separated on a 25 cm × $\frac{1}{4}$ in Merkosorb S160 column using a 13% ethyl acetate in cyclohexane solvent mixture at 2 ml min^{-1}. The nitro-compounds then had the following retention times: 4-isopropyl-2-nitrophenol, 150 s; 4-isopropyl-2-nitroanisole, 224 s; *p*-nitrophenol, 760 s; *p*-nitroanisole, 260 s; and 2-methyl-3-nitrophenol (reference standard), 510 s. They were detected at 300 nm.

Materials.—Sulphuric acid, urea, and sulphanilic acid were AnalaR reagents. Sulphuric acid concentrations were determined by density measurements. Pure nitric acid was prepared and stored as described in earlier Parts.

Isopropylbenzene, b.p. 153, 40 °C at 18 mmHg, and 4-isopropyltoluene, b.p. 177 °C, were obtained by twice distilling technical grade materials. 4-Hydroxyacetophenone, 4-methylacetophenone, 3-methyl-6-nitrophenol, 1-chloro-4-nitrobenzene, 2-nitrophenol, 2- and 4-nitrotoluene, 4-nitro-*o*-xylene, nitro-*p*-xylene, 1,4-di-isopropylbenzene, and 4-isopropylphenol were commercial products. 4-Nitroanisole, m.p. 52 °C (from EtOH), and 4-chloro-3-nitroanisole, m.p. 45 °C (from MeOH), were crystallised from the indicated solvent.

Nitroisopropylbenzenes.—Isopropylbenzene was nitrated by the method of Hansch and Helmkamp.[15] The three isomers were separated by g.l.c. (15 ft column of 15% SE30 on Chromosorb W, nitrogen flow rate 80 ml min^{-1}, column temperature 150 °C): ^{1}H n.m.r. spectra, 2-nitro-compound, δ 8.12 (1 H, d), 7.50 (3 H, m), 3.2 (1 H, m), and 1.32 (6 H, d); 4-nitro-compound, δ 8.00 (2 H, d), 7.24 (2 H, d), 2.96 (1 H, sept), and 1.26 (6 H, d). The mass spectrum of the 2-nitro-compound showed no M or $M - 15$ peak, but gave an $M - 17$ ($M -$ OH) peak, as expected: *m/e*, 2-nitro-compound, 148(66%), 130(26), 120(40), 115(25), and 107(41); 3-nitro-compound, 165(29%), 150(87), 120(10), and 104(100); 4-nitro-compound, 165(37%), 150(105), 120(28), and 104(34).

4-*Isopropylnitrotoluenes*.—Fuming nitric acid (3 ml) in chloroform (10 ml) was added to 4-isopropyltoluene (10 ml) in chloroform (100 ml) and the solution was shaken vigorously. After 1 h the solution was washed with water and after drying (MgSO$_4$) the chloroform was removed. The nitro-compounds were separated by g.l.c. (15 ft column of 15% Apiezon on Chromasorb W; nitrogen flow rate 100 ml min^{-1}; column temperature 150 °C). The ratio of the 2- to the 3-nitro-compound was *ca.* 12 : 1: ^{1}H n.m.r. spectra, 2-nitro-compound, δ 7.80 (1 H, d), 7.32 (1 H, dd), 7.25 (1 H, d), 2.92 (1 H, sept), 2.58 (3 H, s), and 1.3 (6 H, d); 3-nitro-compound, δ 7.5 (1 H, s), 7.4 (1 H, s), 7.2 (1 H, s), 3.4 (1 H, sept), 2.32 (3 H, s), and 1.20 (6 H, d).

2-*Isopropyltoluene*.—Ethyl *o*-toluate was treated with methylmagnesium iodide,[16] the product was dehydrated,[16, 17] and the styrene was hydrogenated.[17] Distillation gave 2-isopropyltoluene, b.p. 60 °C at 14 mmHg, n_D^{20} 1.500 0 (lit.,[17] b.p. 57.3 °C at 10 mmHg, n_D^{20} 1.500 6); δ 7.3 (4 H, m), 3.2 (1 H, sept), 2.36 (3 H, s), and 1.24 (6 H, d).

2-*Isopropyl*-4-*nitrotoluene*.—This was prepared by the method of Desseigne.[18] Distillation gave an oil, b.p. 139 °C at 14 mmHg (lit.,[18] 144—145 °C at 15 mmHg); δ 7.90 (1 H, d), 8.6 (1 H, dd), 8.8 (1 H, d), 3.19 (1 H, sept), 2.43 (3 H, s), and 1.27 (6 H, d).

1-*Chloro*-4-*isopropylbenzene*.—The Friedel–Crafts isopropylation of chlorobenzene [13] gave a mixture of the 2- and 4-isomers. The 4-isomer, b.p. 197 °C at atmospheric pressure and 74 °C at 15 mmHg (lit., 197—198 °C at 746 mmHg [19] and 74 °C at 10 mmHg [20]); δ 7.08 (2 H, d), 7.24 (2 H, d), 2.8 (1 H, sept), and 1.20 (6 H, d), was obtained from 4-isopropylaniline by diazotisation followed by a Sandmeyer reaction.[19]

4-*Isopropylnitrochlorobenzenes*.— 4-Isopropylchlorobenzene (5 g) in acetic acid (10 ml) was added in one go, with stirring, to nitric acid (5 g) in 89% H$_2$SO$_4$ (500 ml). After being stirred for 10 min the mixture was quenched in iced water and the products were recovered with dichloromethane. The residue after removal of this solvent was chromatographed on alumina in light petroleum (b.p. 40—60 °C), the separation being monitored by g.l.c. The 3-nitro-isomer was eluted first. 1-Chloro-4-isopropyl-2-nitrobenzene had δ 7.70 (1 H, d), 7.40 (2 H, dd), 2.94 (1 H, sept), and 1.20 (6 H, d); *m/e* 201(10%), 199(31), 186(38). 184(114), 140(12), and 138(36); n_D^{20} 1.531 2. 1-Chloro-4-isopropyl-3-nitrobenzene had δ 7.66 (1 H, d), 7.42 (2 H, dd), 3.32 (1 H, sept), and 1.22 (6 H, d); *m/e* 184(13%), 182(39), 166(5), 164(15), 153(10), and 139(12).

4-*Isopropyl*-2-*nitroanisole*.—Nitric acid (3 ml) in chloroform (25 ml) was added with stirring to 4-isopropylphenol (10 g) in chloroform (100 ml). The solution was stirred for 1 h and quenched in iced water (500 ml). Steam-distillation gave a yellow oil. Column chromatography [neutral alumina; 1 : 1 chloroform–light petroleum (b.p. 40—60 °C)] and distillation gave 4-isopropyl-2-nitrophenol (10 g), b.p. 130—131 °C at 14 mmHg, n_D^{20} 1.561 0 (lit., b.p. 131—133 °C at 19 mmHg,[21, 22] n_D^{20} 1.553 3 [21]); δ 10.2 (1 H, s), 7.72 (1 H, d), 7.28 (1 H, dd), 6.88 (1 H, d), 2.80 (1 H, sept), and 1.22 (6 H, d).

4-Isopropylanisole, b.p. 214 °C, and 2-nitro-4-isopropylanisole, b.p. 176 °C at 14 mmHg, were prepared from the phenols by methylation with dimethyl sulphate.

2-*Bromonitrotoluenes*.—2-Bromotoluene, b.p. 61 °C at 15 mmHg, and 2-bromo-4-nitrotoluene, m.p. 76 °C [from light petroleum (b.p. 40—60 °C)], *m/e* 217(55%). 215(56), 187(30), 185(31), 171(37), and 169(42), were commercial specimens. 2-Bromo-3-, m.p. 42 °C (from ethanol) (lit.,[23] 41—42 °C), *m/e* 217(28%), 215(30), 187(19), 185(18). 171(14), and 169(16); 2-bromo-5-, m.p. 75 °C [from light petroleum (b.p. 40—60 °C)] (lit.,[23] 75—76 °C), *m/e* 217(118%), 215(112), 187(58), 185(55), 171(80), 169(85), 160(20), 158(19); and 2-bromo-6-nitrotoluene, m.p. 42 °C (from ethanol) (lit.,[23] 42 °C), *m/e* 217(26%). 215(28), 200(116), 198(120), 187(28), and 185(27), were obtained from the amines by Sandmeyer's reaction using the method described for the 3-nitro-compound.[24]

Solubilities.—A solution of aromatic compound was preprepared in acetic acid (10 ml) such that 10 μl of it, syringed into 2.5 ml of sulphuric acid, gave a concentration of *ca.* 2×10^{-5} mol dm^{-3}. Portions of this solution were syringed into a u.v. cell containing a sulphuric acid solution (2.5 ml) and the absorbance was recorded. A saturated solution was prepared by shaking the aromatic compound (1 ml) with aqueous sulphuric acid (10 ml) for 30 min. The mixture was centrifuged and the absorbance of the acid layer (diluted with sulphuric acid if necessary) was measured. The concentration was determined from the plot of concentration *versus* absorbance.

The maximum solubilities of isopropylbenzene, 2-isopropyl-, and 4-isopropyl-toluene in 67.0, 69.0, and 66.4% H_2SO_4 respectively, were 3.0×10^{-3}, 8.64×10^{-4}, and 1.02×10^{-3} mol dm^{-3}. That of 2-bromotoluene in 69% H_2SO_4 was 1.2×10^{-3} mol dm^{-3}.

Kinetic Measurements.—A stock solution of the aromatic compound (0.05 g) in acetic acid (10 ml) was prepared and a volume of this (typically 10 μl) was syringed into sulphuric acid (3 ml) containing nitric acid and sulphanilic acid or urea (10^{-2} mol dm^{-3}) in a u.v. cell maintained at 25 °C. The nitric acid was present in at least a 10-fold excess. The change of absorbance with time at a selected wavelength was measured.

Product Analyses.—These were carried out essentially by the methods already described.[25,26]

A temperature programme was used for the g.l.c. analysis of the product from 4-isopropyltoluene. This allowed the estimation of unchanged 4-isopropyltoluene. To make the estimation more accurate a reference standard (1,4-di-isopropylbenzene) was used which was eluted close to 4-isopropyltoluene. 4-Nitro-*o*-xylene was also used since it was eluted in a time closer to those required for the other products. In runs where unchanged starting material remained the product yields were corrected for this.

Isopropylbenzene and 4-isopropyltoluene and their nitro-derivatives, 4-nitrotoluene, 4-methylacetophenone, 4-isopropyl-2-nitrophenol, 4-isopropyl-2-nitroanisole, and 4-nitroanisole were stable in, and, except for 2-nitroisopropylbenzene, quantitatively recoverable from, aqueous acids after periods comparable with the length of the nitration experiments. 1-Isopropyl-2-nitrobenzene was regularly recovered only to the extent of 95%. Only 44% of 1-chloro-4-isopropylbenzene could be recovered from 62.0% H_2SO_4 (with no nitric acid) after 24 h in the dark; 94% was recovered from 63.0% H_2SO_4 after 3 h in the dark.

RESULTS

Kinetics.—Second-order rate coefficients for nitration are given in Table 2 and Figure 1.

Good first-order kinetics were observed with isopropylbenzene, 2-isopropyltoluene, 1-chloro-4-isopropylbenzene, 4-isopropylanisole, 4-isopropylphenol, and 2-bromotoluene, but with 4-isopropyltoluene an ' infinity ' reading could not be obtained for nitration in sulphuric acid. Rate constants were estimated in this case by assuming a value for the ' infinity ' reading and using this in a computer-assisted, least-squares analysis. 4-Isopropyltoluene gave good first-order kinetics when nitrated in trifluoroacetic acid.

4-Isopropylphenol seems to be very slightly more reactive than mesitylene. That nitrosation was not involved was tested by varying the concentration of sulphanilic acid threefold for nitration in 60.3% sulphuric acid; the rate coefficient was unchanged.

Products.—G.l.c. information is given in Table 3 and product yields in Table 4 and Figure 2.

The aggregate yield of products from isopropylbenzene was *ca.* 90% over the range 60—75% H_2SO_4. The cause of the deficiency has not been identified; *ipso*-attack and capture, giving phenolic products might have been suspected to account for the result at the lower acidities, but would not account for its persistence at high acidities. The deficiency is not accounted for by the non-quantitative extraction of 1-isopropyl-2-nitrobenzene (see Experimental section), and no phenolic products were detected by washing with alkali and re-analysing. Nitrobenzene, acetophenone, 2-nitroacetophenone, and 2-nitrophenol were not formed. The deficit in yield occurred also with nitration in trifluoroacetic acid.

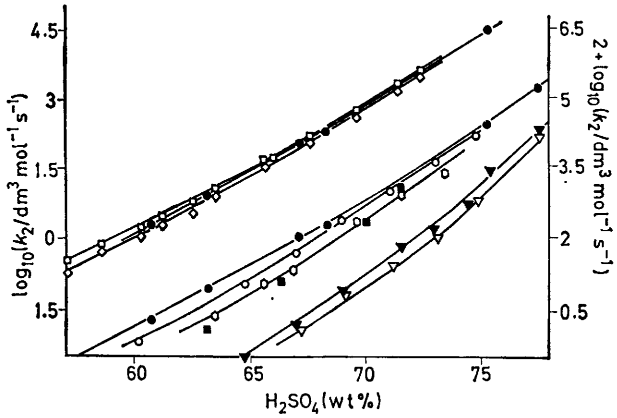


FIGURE 1 Rate profiles for nitration in sulphuric acid at 25 °C. Plots of H_2SO_4 (wt. %) *versus* $\log_{10} k_{2.obs.}$ for nitration of mesitylene (●), isopropylbenzene (⬡), 2-isopropyltoluene (○), 4-isopropyltoluene (■), 4-isopropylchlorobenzene (▼) and 2-bromotoluene (▽). Plots of H_2SO_4 (wt. %) *versus* ($2 + \log_{10} k_{2.obs.}$) for nitration of mesitylene (●), 4-isopropylanisole (◇) and 4-isopropylphenol (□)

Five products were obtained from 2-isopropyltoluene, their aggregate yield being quantitative in >65% H_2SO_4. The products were readily identified with the help of g.l.c.–m.s. Comparisons amongst a number of compounds used in this work, and results in the literature lead to the following generalisation: compounds with an isopropyl group give M and $M - 15$ peaks, the intensity of the latter being greater than that of the former; compounds with a methyl group give a molecular ion peak; compounds with nitro

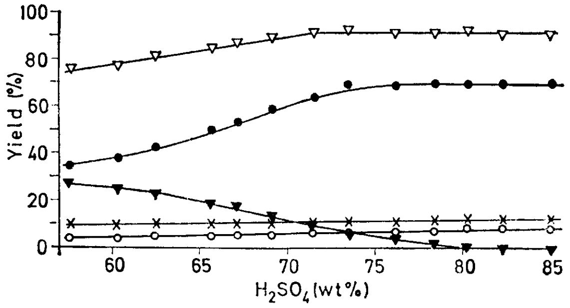


FIGURE 2 Nitration of 4-isopropyltoluene. Yields of isomers plotted against the weight percentage of sulphuric acid. ▽, mass balance; ●, 4-isopropyl-2-nitrotoluene; ○, 4-isopropyl-3-nitrotoluene; ×, 4-nitrotoluene; ▼, 4-methylacetophenone

TABLE 2

Second-order rate coefficients for nitration in sulphuric acid at 25.0 ± 0.1 °C

	H_2SO_4[b] (%)	$10^2[HNO_3]$/mol dm^3	$k_{2,obs}$/dm^3 mol^{-1} s^{-1}
Isopropylbenzene [a,c,d]	63.5	16.2	2.2×10^{-2}
	65.6	16.1	11.2×10^{-2}
	66.9	4.2	0.23
	69.7	5.6×10^{-1}	2.4
	71.6	1.52×10^{-1}	9.7
	73.5	8.8×10^{-2}	26
2-Isopropyltoluene [c,e,f]	60.2	19.6	6.0×10^{-3}
	64.8	23.0	1.17×10^{-1}
	67.0	1.50	5.0×10^{-1}
	69.0	7.8×10^{-1}	2.4
	71.1	2.9×10^{-1}	11.2
	73.1	8.7×10^{-2}	50
	74.8	4.3×10^{-2}	178
4-Isopropyltoluene [c,f,o]	63.2 [g]	2.2	1.57×10^{-2}
	66.4	5.1	1.30×10^{-1}
	70.0	2.5×10^{-1}	2.4
	70.0	2.5×10^{-1}	2.4
	71.6	2.1×10^{-1}	13.0
	71.6	2.3×10^{-1}	10.5
1-Chloro-4-isopropylbenzene [a,c,h]	64.8	15.1	3.2×10^{-3}
	67.0	10.2	16.6×10^{-3}
	69.1	3.4	8.4×10^{-2}
	71.6	1.03×10^{-1}	69×10^{-2}
	73.0	3.4×10^{-1}	1.51
	74.5	1.97×10^{-1}	6.4
	75.5 [i]	1.09×10^{-2}	30
	77.6 [i]	1.09×10^{-2}	260
4-Isopropylanisole [a,j,k]	57.1	21	1.90×10^{-3}
	58.6	21	5.4×10^{-3}
	60.3	21	1.20×10^{-2}
	61.2	20	2.0×10^{-2}
	62.5	20	3.7×10^{-2}
	63.5	21	8.3×10^{-2}
	65.6	5.2	3.8×10^{-1}
	67.6	1.2	1.30
	69.6	4.0×10^{-1}	4.6
	71.4	1.1×10^{-1}	15.9
	72.4 [f,l]	8.2×10^{-2}	33
4-Isopropylphenol [a,j,k]	57.1	21	3.6×10^{-3}
	58.6	21	8.4×10^{-3}
	60.3	22	1.80×10^{-2}
	60.3 [m]	21	1.80×10^{-2}
	60.3 [n]	21	1.70×10^{-2}
	61.2	20	3.0×10^{-2}
	62.5	20	6.1×10^{-2}
	63.5	21	1.30×10^{-1}
	65.6	5.2	5.2×10^{-1}
	66.0	2.1	5.8×10^{-1}
	67.6	1.2	1.70
	69.6	4.0×10^{-1}	6.3
	71.4	1.1×10^{-1}	22
	72,4 [f,l]	8.2×10^{-2}	45
2-Bromotoluene [a,c,f]	64.8	20.9	2.4×10^{-3}
	67.1	21.8	1.00×10^{-2}
	69.0	4.7	6.2×10^{-2}
	71.1	2.4	2.2×10^{-1}
	73.1	0.34	8.4×10^{-1}
	74.8	6.6×10^{-2}	5.2
	77.6 [p]	1.42×10^{-2}	167

[a] [ArH] = *ca.* 1 × 10^{-4} mol dm^{-3} except when otherwise mentioned. [b] ±0.1%. [c] [Urea] = *ca.* 3 × 10^{-2} mol dm^{-3}. [d] Measurements at 250 nm. [e] [ArH] = *ca.* 4 × 10^{-5} mol dm^{-3}. [f] Measurements at 300 nm. [g] Calculated by g.l.c. analysis of product yields from reactions left for given times. See Table 4. [h] Measurements at 275 nm. [i] [ArH] = *ca.* 1.5 × 10^{-5} mol dm^{-3}. [j] Measurements at 325 nm. [k] [Sulphanilic acid] = 10^{-2} mol dm^{-3}. [l] [ArH] = 7 × 10^{-5} mol dm^{-3}. [m] [Sulphanilic acid] = 3 × 10^{-2} mol dm^{-3}. [n] [Sulphanilic acid] = 6 × 10^{-2} mol dm^{-3}. [o] [ArH] = *ca.* 2 × 10^{-4} mol dm^{-3}. [p] [ArH] = 2.02 × 10^{-5} mol dm^{-3}.

Table 3

G.l.c. conditions

Substrate	Products and related substances	Column (t/°C) [a]	R_t/s
Isopropylbenzene	Isopropylbenzene	15% Silicone SE-30 (150) [b]	170
	Nitrobenzene		330
	2-Nitrophenol		370
	Acetophenone		340
	4-Nitrotoluene [c]		475
	1-Isopropyl-2-nitrobenzene		600
	1-Isopropyl-3-nitrobenzene		850
	1-Isopropyl-4-nitrobenzene		970
	2-Nitroacetophenone		930
2-Isopropyltoluene	2-Isopropyltoluene	15% Silicone SE-30 (150) [b]	310
	2-Methylacetophenone		450
	2-Nitrotoluene		510
	Nitro-*p*-xylene [c]		840
	2-Isopropyl-3-nitrotoluene		1 445
	2-Isopropyl-4-nitrotoluene		2 245
	2-Isopropyl-5-nitrotoluene		2 450
	2-Isopropyl-6-nitrotoluene		1 725
4-Isopropyltoluene	4-Isopropyltoluene	5% Polyethylene glycol [d]	259
	1,4-Di-isopropylbenzene [c]		333
	4-Methylacetophenone		679
	4-Nitrotoluene		805
	3-Methyl-6-nitrophenol		860
	4-Isopropyl-3-nitrotoluene		930
	4-Isopropyl-2-nitrotoluene		1 085
	4-Nitro-*o*-xylene [c]		1 267
	2,4-Dinitrotoluene		>4 000
	4-Methylacetophenone	10% OV-17 (175) [e]	520
	4-Nitrotoluene		610
	4-Isopropyl-3-nitrotoluene		1 044
	4-Isopropyl-2-nitrotoluene		1 216
1-Chloro-4-isopropylbenzene	1-Chloro-4-isopropylbenzene	15% Silicone SE-30 (175) [b]	240
	1-Chloro-4-nitrobenzene		350
	4-Chloroacetophenone		450
	Nitro-*p*-xylene [c]		400
	1-Chloro-4-isopropyl-3-nitrobenzene		680
	1-Chloro-4-isopropyl-2-nitrobenzene		960
4-Isopropylanisole	4-Isopropyl-2-nitrophenol	1% Polyethylene glycol (138) [f]	227
	4,6-Di-isopropyl-2-nitrophenol		320
	4-Methoxyacetophenone		370
	4-Nitroanisole		497
	4-Chloro-3-nitroanisole [c]		799
	4-Isopropyl-2-nitroanisole		955
	4-Hydroxyacetophenone		1 330
2-Bromotoluene	2-Bromotoluene		400
	2-Bromo-6-nitrotoluene	15% Silicone SE-30 (125) [g]	1 865
	2-Bromo-3-nitrotoluene		2 305
	2-Bromo-5-nitrotoluene		2 382
	2-Bromo-4-nitrotoluene		2 482
	2-Bromotoluene	10% Polypropylene glycol adipate (150) [h]	110
	1,4-Dimethyl-2-nitrobenzene		590
	2-Bromo-6-nitrotoluene		1 290
	2-Bromo-4-nitrotoluene		1 770
	2-Bromo-5-nitrotoluene		1 770
	2-Bromo-3-nitrotoluene		2 200
	2-Bromotoluene	15% Silicone SE-30 (170) [b]	200
	1,4-Dimethyl-2-nitrobenzene [c]		470
	2-Bromo-6-nitrotoluene		760
	2-Bromo-3-nitrotoluene		935
	2-Bromo-5-nitrotoluene		935
	2-Bromo-4-nitrotoluene		980

[a] All on Chromasorb W-AW, DCMS. [b] 9 ft column, nitrogen flow rate 40 ml min^{-1}. [c] Reference standard. [d] Temperature programmed, 2 min at 80 °C, rising to 148 °C at 20 °C min^{-1}. Pair of matched columns. 6 ft column, nitrogen flow rate 40 ml min^{-1}. [e] 8 ft column, helium flow rate 30 ml min^{-1}. [f] 6 ft column, nitrogen flow rate 40 ml min^{-1}. [g] 9 ft column, helium flow rate 30 ml min^{-1}. [h] 9 ft column, nitrogen flow rate 100 ml min^{-1}.

adjacent to methyl gave the $M - 17$ peak but the M peak did not totally disappear: compounds with nitro adjacent to isopropyl gave the $M - 17$ peak and no M or $M - 15$ peaks. 3- and 6-Nitro-2-isopropyltoluene were thus easily identified. 4- and 5-Nitro-2-isopropyltoluene were differentiated by use of a synthetic sample of the former.

Nitration of 4-isopropyltoluene in either sulphuric or trifluoroacetic acid gave four products (Table 4), readily identified by g.l.c.–m.s. 4-Isopropyltoluene in sulphuric acid was neither oxidised to 4-methylacetophenone nor deisopropylated in the absence of nitric acid. The deficit in aggregate yield at lower acidities was probably due to the formation of phenolic 'capture products', but washing of the product with alkali and re-analysing by g.l.c. showed that phenols were not distorting the apparent yield of the four identified products. The deficit in aggregate yield persisting at higher acidities has not been accounted for.

The change of yield with time of each of the products for nitration in 63.2% H_2SO_4 was followed (Table 4). Results for 4-methylacetophenone, 4-isopropyl-2-nitrotoluene, and the aggregate yield are shown in Figure 3. The ratios of product yields were independent of time and the results permitted the calculation of a second-order rate coefficient in good agreement with that for nitration obtained by

TABLE 4

Yields of products from the nitration of isopropylbenzene and its derivatives at 25.0 ± 0.1 °C

		Yields (%)					
		x-Nitro-isopropylbenzene					Mass
Compound	H_2SO_4 (%)	x = 2 [c]	x = 3 [c]	x = 4 [c]			balance (%)
Isopropylbenzene [a,b]	60.3 [d]	26.0	7.9	66.1			88.7
	64.6	23.6	7.9	68.5			87.5
	66.4	25.5	7.5	67.0			84.2
	71.6	24.3	7.1	68.6			90.9
	74.5	25.9	6.6	67.5			94.8
	TFA [e]	19.0	2.8	78.2			90.0
			x-Nitro-2-isopropyltoluene				
		2-Nitrotoluene	x = 3	x = 4	x = 5	x = 6	
2-Isopropyltoluene [a,f]	60.2 [g]	21.8	3.4	25.2	31.9	11.9	94.2
	62.0 [g]	21.6	3.7	25.0	32.3	12.4	95
	64.8	22.9	3.6	26.0	33.4	12.3	98.2
	67.1	23.0	3.8	27.1	35.3	12.8	102
	70.9	21.4	3.8	26.7	35.4	12.4	99.7
	72.5	20.2	3.7	27.9	34.5	12.3	98.6
	75.3 [h]	19.5	3.8	27.8	37.6	12.7	101
		4-Methylacetophenone	4-Nitrotoluene	x-Nitro-4-isopropyltoluene			
				x = 2	x = 3		
4-Isopropyltoluene [a]	57.6	27.8	9.9	34.5	4.2		76.3
	60.3	25.1	9.9	37.7	4.2		76.9
	62.5	23.2	10.3	42.8	5.4		81.7
	65.6	18.7	10.7	50.0	5.7		85.1
	67.2	17.8	10.5	53.5	5.6		87.4
	69.2	13.9	10.7	59.0	6.0		89.6
	71.4	9.9	11.2	64.2	6.5		91.8
	73.5	5.5	11.0	69.5	6.7		92.7
	76.2	3.8	11.8	69.0	7.4		92.0
	78.5	2.4	11.8	70.1	7.6		91.9
	80.3	1.1	13.0	69.8	9.0		92.9
	82.3	<0.1	12.8	70.1	8.9		91.2
	85.2	<0.1	12.6	70.4	8.9		91.9
	TFA [i]	1.3	12.5	66.7	4.4		84.9
	63.2 [j]	3.59	1.88	6.03	0.93		12.43
		4.83	2.14	8.37	0.94		16.28
		5.17	2.33	9.95	1.01		18.46
		6.86	3.18	12.8	1.40		24.25
		8.42	3.67	16.67	1.62		30.38
		10.87	5.27	20.90	2.31		39.35
		12.18	5.19	23.36	2.39		43.12
		12.79	5.78	23.42	2.89		44.88
		13.08	5.57	25.28	2.48		46.41
		1-Chloro-4-nitrobenzene	x-Nitro-4-isopropylchlorobenzene				
			x = 2	x = 3			
1-Chloro-4-isopropylbenzene [b]	60.2	19.8 [k]	64.7	9.3			93.8
	62.0	19.8 [k]	67.8	9.1			96.7
	63.0	19.8 [k]	65.6	8.8			94.2
	64.8	19.8	68.2	10.4			98.4
	67.0	19.5	70.4	9.5			99.4
	68.4	19.4	70.1	12.5			102
	69.1	19.9	70.1	11.4			101
	71.4	20.0	71.2	10.9			102
	73.1	20.1	71.3	10.7			102
	74.5	19.3	70.5	10.7			100.5
	75.1	19.4	71.8	10.6			102

TABLE 4 (*Continued*)

		4-Nitroanisole	4-Nitrophenol	4-Isopropyl-2-nitroanisole	4-Isopropyl-2-nitrophenol	
4-Isopropylanisole [l,m]	56.1	1.6	3.2	77.7	15.9	98.4
	57.6	2.8		74.8	(1.7)	(79.3)
	58.1	2.6	3.7	76.7	16.1	99.1
	60.3	5.5		75.1	(2.2)	(82.8)
	59.6	4.0	4.2	76.7	12.2	97.1
	61.2	7.0		75.5	(1.5)	(84.0)
	62.2	8.6	4.3	74.7	11.6	99.3
	63.5	8.4		76.2	(1.5)	(86.1)
	65.4	11.6		75.2	(1.8)	(88.7)
	67.2	13.8		71.4	(1.6)	(86.8)
	69.2	16.5		72.6	(1.6)	(90.6)
	71.9	18.1		68.0	(1.9)	(88.0)
	74.5	20.0		66.0	(1.9)	(87.9)
	77.3	21.7		64.5	(1.3)	(87.5)
	80.8	26.3		62.3	(5.5)	(94.1)
	82.3	28.7		58.4	(2.4)	(89.5)
	85.0	27.4		43.7	(2.2)	(73.3)
		2-Bromo-x-nitrotoluene				
		$x = 3$	$x = 4$	$x = 5$	$x = 6$	
2-Bromotoluene [a,n]	63.1 [o]	12.9	17.2	23.8	11.8	65.7
	66.2 [p]	15.3	18.0	29.1	18.7	81.1
	69.1	16.4	18.2	29.1	20.8	84.5
	72.6	18.7	18.4	27.8	24.3	89.2
	76.7	19.4	18.8	33.6	27.3	99.1
	78.9 [h]	20.0	19.3	32.2	27.4	98.9
	83.1 [h]	20.9	18.6	32.7	27.0	99.2

[a] [Urea] = *ca.* 3×10^{-2} mol dm^{-3}. [b] [ArH] = *ca.* 1×10^{-4} mol dm^{-3}. [Reference] = *ca.* 3×10^{-5} mol dm^{-3}. [c] Yields normalised for 100% mass balance. [d] Reaction time 9 h. Carried out in dark. [e] Aqueous trifluoroacetic acid. $[H_2O]$ = 1.0 mol dm^{-3}. k_2 = 0.83 dm^3 mol^{-1} s^{-1}. [f] [ArH] = *ca.* 2×10^{-4} mol dm^{-3}. [Reference] = *ca.* 5×10^{-5} mol dm^{-3}, except where otherwise mentioned. [g] Reaction time 2 h. Carried out in dark. [h] Equimolar amounts, pleated flask, 5 min. [i] Aqueous trifluoroacetic acid. $[H_2O]$ = 1.0 mol dm^{-3}. k_2 2.9 dm^3 mol^{-1} s^{-1}. [j] Measurements at differing times (440, 825, 900, 1 320, 1 840, 2 770, 3 600, 4 800, 6 000 s). Yields in 10^{-6} mol. [ArH] = 2×10^{-4} mol dm^{-3}. $[HNO_3]$ = 2.2×10^{-2} mol dm^{-3}. [k] The yield of 1-chloro-4-nitrobenzene from these experiments was assumed to be the same as the average yield in the other experiments. The yields of the other products were adjusted proportionately. See text. [l] Results which include yields of 4-nitrophenol were obtained by h.p.l.c. The others were obtained by g.l.c., and because of the difficulty in estimating 4-isopropyl-2-nitrophenol by this method (see text) the yields of this compound in these instances, and the corresponding aggregate yields, are given in parentheses. [m] [Sulphanilic acid] = *ca.* 10^{-2} mol dm^{-3}. [n] [ArH] = *ca.* 2×10^{-4} mol dm^{-3}. [Reference] = *ca.* 2×10^{-5} mol dm^{-3}. [o] Reaction time 20 h. Carried out in dark. [p] Reaction time 3.3 h. Carried out in dark.

kinetic methods. Further, rate coefficients calculated from the changing yields of 4-methylacetophenone and 4-isopropyl-2-nitrotoluene were the same.

Three products were identified from the nitration of 1-chloro-4-isopropylbenzene (Table 4). 4-Chloroacetophenone was not formed. In the range 65—75% H_2SO_4 aggregate yields were quantitative. At lower acidities, when reaction times are longer aggregate yields declined, and the deficit increased with the time of reaction. Some reactions were allowed to run for only one half-life of nitration and yields were calculated by taking into account the unchanged starting material. Similar product ratios were obtained from runs at one acidity kept for different times. The deficit was therefore largely due to the reaction of 1-chloro-4-isopropylbenzene with sulphuric acid (see Experimental section). The yield of 1-chloro-4-nitrobenzene in 65—75% H_2SO_4 was effectively constant, and product yields at acidities <65% H_2SO_4 were therefore calculated assuming an average 19.8% formation of 1-chloro-4-nitrobenzene.

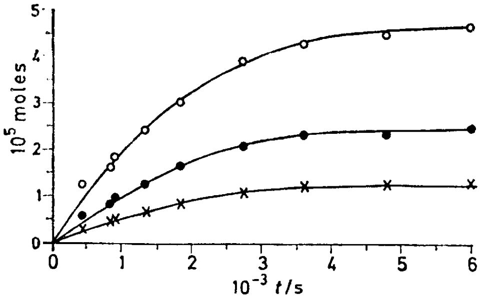


FIGURE 3 Variation in yield of 4-isopropyl-2-nitrotoluene (●), 4-methylacetophenone (×), and mass balance (○) from the nitration of 4-isopropyltoluene in 53.2% H_2SO_4 with time. [ArH] = 2×10^{-4} mol dm^{-3}

Results for 4-isopropylanisole based on g.l.c. analyses of products led to the prediction that observed deficiencies in aggregate yields were due to the formation of 4-nitrophenol, a compound which would not be detected by this method of analysis. The subsequent search for 4-nitrophenol using h.p.l.c. confirmed the prediction of its formation, but also revealed an inadequacy in the g.l.c. analyses for 4-isopropyl-2-nitrophenol which was formed in larger amounts than the latter method indicated. The cause of this failure is unknown, but its detection showed that the aggregate yields of the four products (Table 4) were quantitative. The two methods were in satisfactory agreement as regards the yields of 4-isopropyl-2-nitroanisole and 4-nitroanisole.

From 2-bromotoluene the four possible nitro-compounds were obtained and identified by g.l.c. Yields were quantitative above 77% H_2SO_4 but decreased below this.

DISCUSSION

4-Isopropylphenol is nitrated at the encounter rate (Figure 1), and 4-isopropylanisole slightly below that limit. Isopropylbenzene and 4-isopropyltoluene are very similar to toluene in reactivity. It is noteworthy that 4-isopropyltoluene, unlike *p*-xylene, does not react at the encounter rate. 1-Chloro-4-isopropylbenzene is somewhat less reactive than is 4-chlorotoluene.

In aqueous trifluoroacetic acid ($[H_2O]$ 1.0 mol dm^{-3}) the second-order rate coefficients for *p*-xylene,[26] 4-isopropyltoluene, toluene,[26] isopropylbenzene, and benzene [26] are 5.3, 2.9, 1.5, 0.83, and 0.050 dm^3 mol^{-1} s^{-1}, respectively. Isopropylbenzene is slightly less reactive than toluene, and again 4-isopropyltoluene falls behind the limit reached by *p*-xylene.

Isopropylbenzene.—The proportions of the three nitro-derivatives found in the present work from nitration in sulphuric acid are very similar to those reported earlier,[4] and also to those from nitration in acetic anhydride.[4] The last fact, and the insensitivity of the isomer proportions to changes in the acidity of the medium indicate that *ipso*-attack is of little consequence.

2-*Isopropyltoluene.*—Nitration of this compound in acetic anhydride shows that $W_i^{Pr^i}$, as well as giving 2-nitrotoluene by nitrodeisopropylation, can, like the accompanying W_i^{Me}, be captured by acetate.[12]

In 65—79% H_2SO_4 the quantitative aggregate yield of products shows that there is no nucleophilic capture by water of either W_i^{Me} or $W_i^{Pr^i}$. The apparent drop in aggregate yield in <65% H_2SO_4 may indicate the onset of capture, but the changes in yields of 2-nitrotoluene and 6-nitro-2-isopropyltoluene are not big enough to be significant. The constant yield of 2-nitrotoluene suggests that water is not necessary for the removal of the isopropyl cation. The fall in yield of 5-nitro-2-isopropyltoluene probably is significant, but cannot be related to *ipso*-attack. The yields of 2-nitrotoluene and 3- and 6-nitro-2-isopropyltoluene are very similar to those reported by Hahn,[12] and suggest that the proportion of *ipso*-attack ($W_i^{Me} + W_i^{Pr^i}$) is *ca.* 25%,* and that the yield of the 3-nitro-compound (3.7%) indicates the degree of direct nitration at C-3 (since $W_i^{Pr^i}$ does not give the 3-nitro compound [12]). In the absence of capture the proportion of *ipso*-attack cannot be dissected into its components.

4-*Isopropyltoluene.*—In the range 57.6—85.2% H_2SO_4 the yield of 4-nitrotoluene increased from 9 to 13%. This is probably a ' medium effect '.[27] The change with acidity is in the sense opposite to what would be expected if nitrodeisopropylation required the assistance of water. To a first approximation the fraction of *ipso*-attack at C–Pr^i which leads to nitrodeisopropylation is independent of acidity.

What that fraction is concluded to be depends on the significance which is ascribed to the yield of 4-isopropyl-3-nitrotoluene. This is doubled in the region 58—85% H_2SO_4, a result which could be ascribed to decreasing capture by water of $W_i^{Pr^i}$. However, the yield and the change in it are absolutely small and if the possibility of there being a medium effect is admitted this, and the fact that in nitration in acetic anhydride no capture occurs,[10,12] suggests that $W_i^{Pr^i}$ undergoes only nitrodeisopropylation, or this combined with an undetermined, but probably small degree of 1,2-nitro-migration.

The marked increase (*ca.* 36%), with increasing acidity, in the yield of 4-isopropyl-2-nitrotoluene is largely compensated for by the decrease (*ca.* 28%) in the yield of 4-methylacetophenone. The latter is probably formed from W_i^{Me} (see below), so it appears that with increasing acidity W_i^{Me} is diverted to rearrangement to the nitro-compound from formation of the ketone and also of phenols by capture. The extent of such capture would be *ca.* 8%, which does not wholly account for the loss in aggregate yield (16% in the range 58—85% H_2SO_4). The results are compared with those for nitration in acetic anhydride in Table 5.

TABLE 5

Nitration of 4-isopropyltoluene

Medium	Direct attack at C-2	Direct attack at C-3	*ipso*-Attack at C–Pr^i	*ipso*-Attack at C–Me
Acetic anhydride	$\leqslant$20.5 [10,12]	$\leqslant$4 [10,12]	$\geqslant$10 [10,12]	$\geqslant$41 [10,12]
	$\leqslant$13 [11]	$\leqslant$5 [11]	$\geqslant$12 [11]	$\geqslant$57 [11]
Aqueous sulphuric acid	$\leqslant$17	$\leqslant$2	$\geqslant$11	$\geqslant$36 [a]

[a] From the maximum yield of 4-methylacetophenone plus the estimated minimum loss by capture, or from the difference between the maximum and minimum yields of 4-isopropyl-2-nitrobenzene.

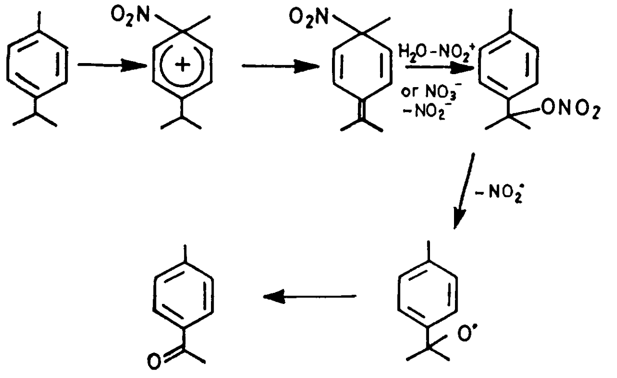
The inequalities arise because for neither medium is it certain that in the appropriate case capture has totally suppressed rearrangement, or that the latter is not occurring alongside *ipso*-substitution. The non-quantitative aggregate yield from nitration in aqueous sulphuric acid also introduces uncertainty. Some workers (but not others [10–12]) using nitronium salts have observed the formation of di-isopropyltoluene in quantitative yield. The undetected formation of this compound could account for some of the deficiency in aggregate yield.

A satisfactory explanation of the formation of 4-methylacetophenone has not hitherto been given. It is not formed during nitrations in acetic anhydride [10,11] but arose (59%) during the decomposition of the 1-isopropyl-4-methyl-4-nitrocyclohexa-2,5-dienyl acetates so obtained in acetic acid containing sulphuric acid. It was suggested that the ketone was formed by *ipso*-attack of acetylium ion on 4-isopropyltoluene. Our kinetic results clearly link the production of the ketone to the nitration process, and we suggest that the likely reactions are as in Scheme 1. A reaction analogous to the last step, involving breakage of a carbon–carbon bond is observed in the free radical oxidation of dimethylphenylcarbinol.[28] The yield of 4-methylacetophenone is acidity-dependent, a feature in which our results confirm earlier ones.[9] The significance of the dependence is not obvious since processes probably having conflicting requirements are involved.

The proposed mechanism of nitration is shown in

---

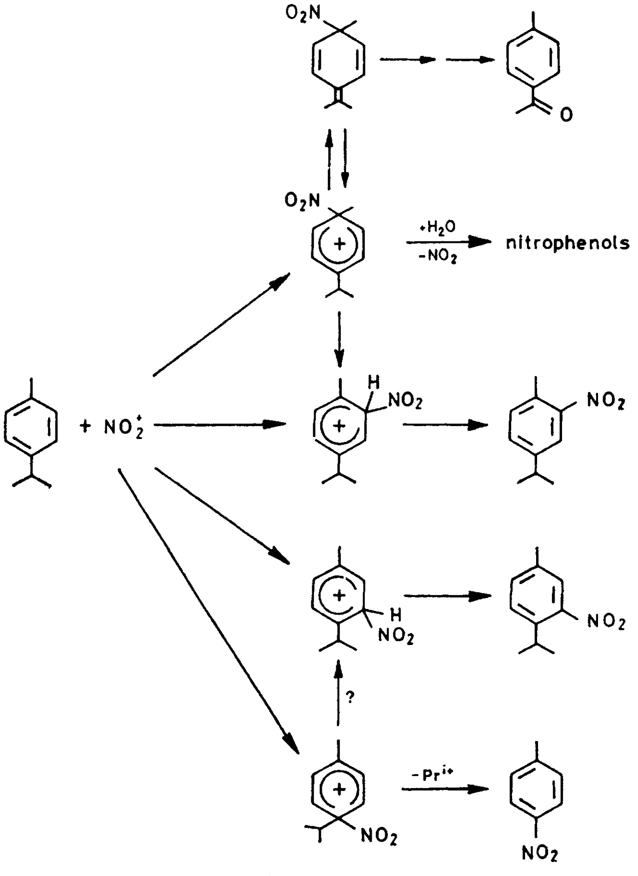
* If x is the percentage of 2-nitrotoluene formed from W_i^{Me}, and y the percentage formed from $W_i^{Pr^i}$, and z the percentage of 2-isopropyl-6-nitrotoluene formed from W_i^{Me}, then our results show $x + y = 22\%$ and Hahn's [12] $x/z = 7.7$. Therefore $z < 22/7.7$ and $x + y + z \approx 25\%$.



SCHEME 1

Scheme 2. Present results and those of earlier workers (Tables 1 and 5) agree in providing the order of positional reactivities C-1 > C-2 > C-4 > C-3.

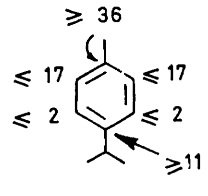
The Behaviour of Isopropyltoluenes compared with that of Bromotoluenes.—The pairs of compounds, 4-isopropyl- and 4-bromo-toluene, and 2-isopropyl- and 2-bromotoluene show interesting similarities and differences. Results obtained for 4-isopropyltoluene (Table 5), and early results for 4-bromotoluene [2] allow the construction of diagrams (IV) and (V) showing *very approximately* the percentage of direct attack at each nuclear position, *i.e.* the relative positional reactivities. Various factors already mentioned make the results only approximate.



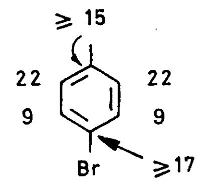
SCHEME 2

Nevertheless, the generally similar patterns of reactivity are obvious. In each case W_i^{Me} can either rearrange by 1,2-migration of the nitro-group or be captured by water, but in 4-isopropyltoluene the additional reaction of isopropyl-group modification may occur. $W_i^{Pr^i}$ reacts predominantly (if not exclusively [10]) by loss of isopropyl (unassisted by water), but W_i^{Br} can rearrange or lose the bromo-substituent (assisted by water).[2]

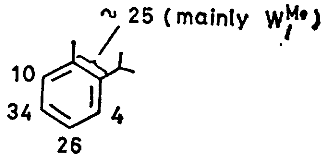
A similar comparison between 2-isopropyltoluene and 2-bromotoluene is made in (VI) and (VII). As regards the bromo-compound it is found again, as with 1,2-dibromobenzene and 2-bromo-1,3-xylene,[2] that an *ortho*-substituent prevents nitrodebromination. Here, $W_i^{Pr^i}$ is the minor *ipso*-intermediate [12] (W_i^{Me} : $W_i^{Pr^i}$ = 87 : 13). The rearrangement of W_i^{Me} in this case goes preferentially towards C-2 rather than C-6 [12] (in the ratio of *ca.* 77 : 10), and the $W_i^{Pr^i}$ loses its isopropyl group. The proportions of the two *ipso*-intermediates contributing to the total (≥21%) from 2-bromotoluene cannot be separated, but they appear to be partitioned between C-6 and -3 more evenly (the yield of the 6-nitro compound increases from 12 to 27% with increasing acidity, and that of the 3-nitro compound from 13 to 21%).



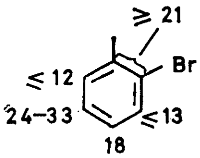
(IV)



(V)



(VI)

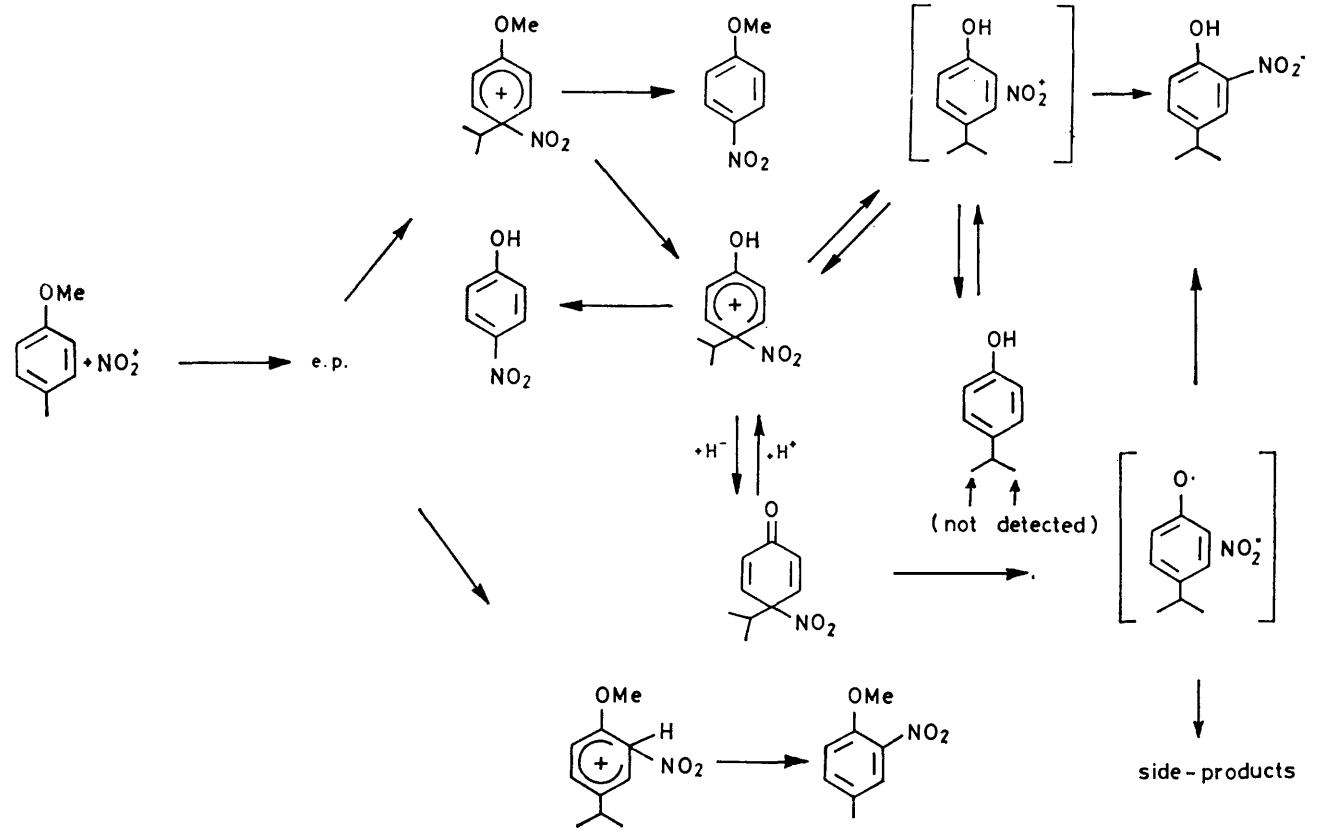


(VII)

1-*Chloro-4-isopropylbenzene.*—Over the acidity range studied the yields of the three products were effectively constant. $W_i^{Pr^i}$ is formed in amounts ≥20%, the inequality arising because the possibility of some rearrangement to give 1-chloro-4-isopropyl-3-nitrobenzene cannot be excluded. Again nitrodeisopropylation does not need assistance from water. In the absence of capture or nitrodechlorination the extent of formation of W_i^{Cl} cannot be determined, nor can the yield of 1-chloro-4-isopropyl-2-nitrobenzene be divided between direct attack and formation by rearrangement of W_i^{Cl}. This difficulty commonly occurs with chloro-substituents; [2] it might have been circumvented in the present case if 4-chloroacetophenone had been among the products. The fact that it is not is surprising, but does not warrant the conclusion that W_i^{Cl} was not formed.

4-*Isopropylanisole.*—Yields of 4-isopropyl-2-nitrophenol obtained by g.l.c. and given in parentheses in

Table 4 are probably unreliable and are not further discussed. The remaining results are accounted for by Scheme 3, analogous to that for 4-methylanisole,[29] but with the added complication of deisopropylation. In Scheme 3 wherever a species may be partitioned between two reactions that which is expected to be favoured by high acidities is shown as the upper one of the alternatives. Thus, the initial nitration is expected to favour the 4-position with increasing acidity, as with other anisoles;[29] deisopropylation does not need water, whereas conversion of $W_i^{\mathrm{Pr}^i}$ into the cyclohexadienone does; and finally, loss of isopropyl from the cyclohexadienone would be expected to be acid-catalysed, whereas isomerisation to 4-isopropyl-2-nitrophenol may occur by both acid-catalysed and uncatalysed processes.[30] [The cyclohexadienone was not detected spectroscopically in this case, in contrast to that of 4-methylanisole.[31] Experiments made with 4-isopropylphenol under conditions where the initial nitration was very rapid showed that, assuming the degree of *ipso*-attack to be *ca.* 30% (see the case of 4-isopropylanisole, Table 4), the rate coefficient for decomposition of the dienone in 73.8% H_2SO_4 was $\geqslant 3 \times 10^{-2}$ s^{-1} (for the 4-methyl compound $k = 7.9 \times 10^{-3}$ s^{-1}). Nitration of 4-isopropylphenol in 63.2% H_2SO_4 followed very good first-order kinetics ($k_{2\mathrm{obs}} = 9.67 \times 10^{-2}$ dm^3 mol^{-1} s^{-1}), showing that the rate coefficient for decomposition of the dienone was $>2.03 \times 10^{-2}$ s^{-1}.] These trends are discernible in the results, though the short acidity range over which the ratio of the yields of the phenols has been measured makes the evidence for the effect of acidity on this ratio less than convincing.



SCHEME 3

The decrease in aggregate yields at acidities >80% H_2SO_4 is not explained by Scheme 3, but is characteristic of some anisoles.[29] The formation of 4-isopropylphenol shown in Scheme 3 was not detected because product studies were always made using an excess of nitric acid. In the similar case of 4-methylanisole the production of *p*-cresol has been demonstrated in reactions where 4-methylanisole was in excess over nitric acid.[31] In Scheme 3 no account is taken of the possibility that the cyclohexadienones might decompose by loss of isopropyl radical.

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