Highly Selective Aromatic Chlorination. Part 4.[1] The Chlorination of Aromatic Hydrocarbons with *N*-Chloroamines in Acidic Solution

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Benzene, toluene, some polymethylbenzenes, and naphthalene have been treated with *N*-chlorotrialkylammonium salts and *N*-chlorodialkylamines in trifluoroacetic acid at room temperature. With benzene, toluene, and 1,3,5-trimethylbenzene the major products arise from aromatic chlorination whereas with the other polymethylbenzenes side-chain reactions predominate. By controlling the acidity of the reaction and the nature of the *N*-chloroamine, the chlorination of toluene can be made to give preferentially 2- or 4-chlorination. However, the selectivities are not as great as reported previously with electron-rich aromatic compounds with a π-donor substituent. The products from the reaction of naphthalene are very dependent on the structure of the *N*-chlorinated amine. The bulky *N*-chlorotrialkylammonium salts selectively chlorinate the 1-position, but in low yield, whereas the less hindered *N*-chloropiperidine gives good yields of 1-(1-piperidino)-naphthalene. The results from these studies are discussed in terms of arenium-ion and electron-transfer mechanisms.

Electron-rich aromatic compounds with a π-donor (+*M*) substituent are efficiently monochlorinated by *N*-chloroamines in acidic solution. Furthermore, the reactions normally show a very high selectivity for the position *para* to the substituent.[1,2] Extensive product[2] and kinetic studies[1] have shown that for most aromatic substrates and *N*-chloroamines the reaction proceeds by an arenium-ion mechanism in which the active chlorinating species is the *N*-chloroammonium ion (Scheme 1 for anisole). The selectivity for 4-substitution arises from a preferred arrangement of the reactants in a donor–acceptor complex formed prior to chlorine transfer. For some aromatic compounds with low oxidation potentials an alternative electron-transfer chain reaction may compete with the arenium -ion mechanism (Scheme 2 for for 1,4-dimethoxybenzene).

Selective chlorination in the absence of a π-donor substituent is also a commercially attractive goal, since compounds such as 4-chlorotoluene, free from the 2-isomer, are valuable industrial intermediates. Some of the results from the many studies on the chlorination of toluene illustrate that the product distribution is influenced by the reaction conditions and the chlorinating agent employed (Table 1). For the majority of these chlorinations the ratio of yields of 2- to 4-chlorotoluene lies between 0.5 and 2.0, although a very recent report shows that selectivity for 4-chlorination can be greatly improved using t-butyl hypochlorite in the presence of a zeolite (faujasite X).[8]

We report here our work on the selectivity and mechanism of chlorination of some aromatic hydrocarbons with *N*-chlorotrialkylammonium salts and *N*-chlorodialkylamines.

Results

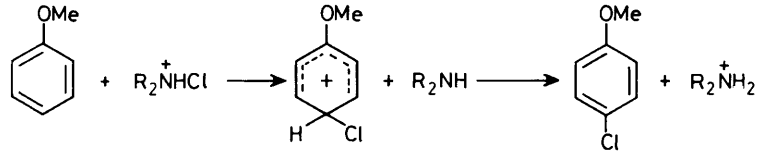
Benzene reacted very slowly with *N*-chlorotriethylammonium salts in trifluoroacetic acid (TFA). ^{1}H N.m.r. analysis showed that reactions in the dark or in diffuse laboratory light occur at similar rates and that even after 3 weeks at 26 °C reaction was not complete. The yield of chlorobenzene based on the chlorinating agent was typically 25%.

Toluene, as expected, reacted more quickly than benzene with the *N*-chlorotriethylammonium ion in TFA. In the dark at 26 °C chlorination was complete in 10 days, whilst in diffuse light it took 7 days. Both nuclear and side-chain chlorination occurred giving a combined yield of *ca.* 30%. Although the distribution of ring-substituted products was unaffected by light, the relative proportion of side-chain to ring chlorination was reduced by carrying out the reactions in the dark (Table 2). *N*-Chloromorpholine, *N*-chloro-*N*-methylbenzylamine, and *N*-chlorotriethylammonium ions give very similar distributions of chlorotoluenes, however, their rates of reaction are markedly different. The proportion of side-chain attack is less for the two more reactive *N*-chloroamines (Table 2).

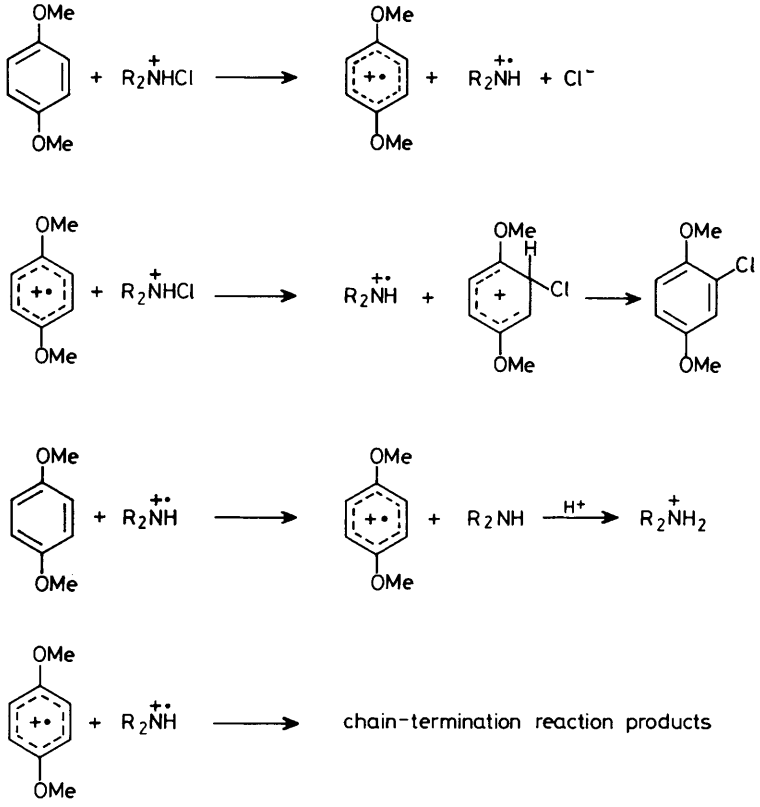
When the chlorinations with *N*-chloromorpholine were carried out in aqueous sulphuric acid there was negligible side-chain attack, although the rate and selectivity of nuclear chlorination showed a strong dependence on the acidity of the medium. Concentrated acid increases the rate and selectivity for 4-chlorination (Table 3). In 100% sulphuric acid sulphonation is a competing side reaction and to keep this to a minimum the reactions had to be carried out at a lower temperature.

1,3- and 1,4-dimethyl-, 1,3,5-trimethyl-, 1,2,4,5-tetramethyl- and hexamethyl-benzene were chlorinated with *N*-chloropiperidine in TFA. ^{1}H N.m.r. spectroscopy showed that the reactions of 1,3- and 1,4-dimethylbenzene were complete within a few hours, whilst those of the other polymethylbenzenes were over within a few minutes. In none of the ^{1}H n.m.r. spectra of these reaction mixtures was there any evidence of the paramagnetic line broadening observed previously with the reactions of some dimethoxybenzenes.

Of the polymethylbenzenes only 1,3,5-trimethylbenzene selectively gave one product. This compound was quantitatively converted into 2,4,6-trimethylchlorobenzene. The chlorination of the other substrates gave complex mixtures of which the monochlorinated products were only minor components (Table 4). For hexamethylbenzene, ^{1}H n.m.r. and mass spectroscopy show that the major product was pentamethylbenzyl trifluoroacetate (**1**) with lesser amounts of the benzyl alcohol (**2**) and a ditrifluoroacetate, possibly (**3**) (Scheme 3). Interestingly pentamethylbenzyl chloride reacted with TFA to give a mixture with an almost identical ^{1}H n.m.r. spectrum to that from the reaction of hexamethylbenzene with *N*-chloropiperidine and on work-up gave (**1**). With the dimethyl- and tetramethyl-benzenes *N*-chloropiperidine gave predominantly chlorinated and unchlorinated dimers and trimers. The chlorination of



Scheme 1.



Scheme 2.

Table 1. Product distributions and yields for the chlorination of toluene.

Reagent/Conditions	Yield %	Chlorotoluene product distribution (%) 2	3	4	Ref.
Cl_2/CH_3NO_2	—	34	—	66	3
Cl_2/HOAc	80	59.8	0.5	39.7	4
Cl_2/TFA	—	67	—	33	5
$ClOCOCH_3$/HOAc	—	62	2	36	6
Bu^{t}OCl/Silica	100	65	—	35	7
Bu^{t}OCl/H^+/Na^+ faujasite X	100	9	—	91	8
$FeCl_3$/50–60 °C	58	13	—	87	9
Trichlorocyanuric acid/$FeCl_3$	45	21	—	79	10
Anodic chlorination/LiCl/CH_3CN	—	34	—	66	11

tetramethylbenzene gives a deep red solution and a fine precipitate, the same changes occur on dissolving 2,4,5-trimethylbenzyl chloride in TFA.

Naphthalene was chlorinated with *N*-chlorotriethyl- and *N*-chlorotrimethyl-ammonium and *N*-chloropiperidine in TFA. All three reactions were readily monitored by ^1H n.m.r. spectroscopy which showed that during the early stages of each the substrate's absorptions were broadened. Within a period of hours the broad absorptions were replaced by well resolved signals of the products. Product studies, however, revealed a marked difference in behaviour between the *N*-chlorotrialkylammonium ions and *N*-chloropiperidine. An equimolar mixture of the latter with naphthalene reacted to give 1-(1-piperidino)naphthalene in high yield with small amounts of 1- and 2-chloronaphthalene and a chlorinated piperidinonaphthalene (Table 5). By contrast, with the *N*-chlorotrialkylammonium ions there was no evidence of amination and instead naphthalene was selectively 1-chlorinated. However, a major part of the reacted naphthalene remained unaccounted for. A further difference between the two types of chlorinating agent was the formation of *N,N*-dialkyliminium ions in the reaction of the *N*-chlorotrialkylammonium salts (Table 5). This formation of the iminium salts was observed by ^1H n.m.r. spectroscopy. The presence of naphthalene was shown to be essential for the production of the iminium ions since they were not formed by the thermal decomposition of the *N*-chlorotrialkylammonium salts in the absence of the aromatic substrate.

An e.s.r. study of the naphthalene–*N*-chlorotriethylammonium salt system in TFA showed a broad signal (*g*-value 2.0036), which increased in intensity during the first 2 h of reaction, and a second minor signal. The latter was assigned to the triethylaminium radical by comparison with a spectrum of this radical cation[9] generated by photolysis of this chloroammonium ion in TFA.

Table 2. The yields and product distributions from the chlorination of toluene with *N*-chlorinated amines in TFA.

Chlorinating agent	Time	Yield[a] (%)	Yield of benzyl chloride[a] (%)	Chlorotoluene distribution (%)[b] 2-	4-
N-Chlorotriethylammonium ion	7 days	28–30	6	62	38
N-Chlorotriethylammonium ion	10 days[c]	28–30	2	62	38
N-Chloro-*N*-methylbenzylamine	24 h	24	trace	66	34
N-Chloromorpholine	1 h	100	trace	61	39

[a] Yield of monochlorinated products based on *N*-chlorinated amine. [b] Product distribution measured by g.c. following work-up of reaction. [c] Reaction carried out in the dark.

Table 3. Influence of acidity on the yield and selectivity of chlorination of toluene by *N*-chloromorpholine in aqueous sulphuric acid.[a]

H_2SO_4 v/v (%)	Yield (%)[b]	Chlorotoluene product distribution (%)[c] 2-	4-
50	7	66	34
60	24	51	49
80	82	35	65
90	82	26	74
100[d]	—	27	73

[a] Reactions carried out for 1 h at 25 °C. [b] Yields based on *N*-chloromorpholine. [c] Product distribution measured by g.c. following work-up of reaction. [d] Reaction carried out at 5 °C.

Discussion

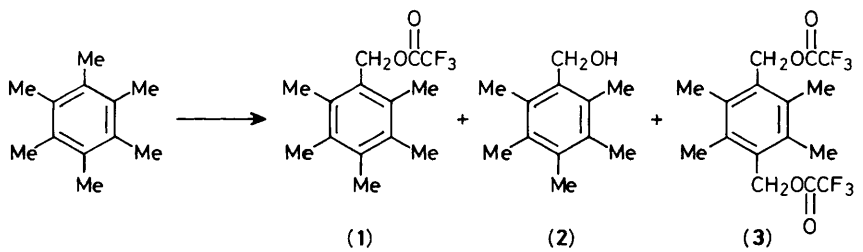
We have shown how aromatic compounds with strong electron-donating substituents can be selectively chlorinated by *N*-chloroamines in TFA. We have now extended this study to include benzene and some methylbenzenes which are less reactive towards electrophiles than the substrates studied earlier. Although no kinetic studies have been carried out, the reactions have been monitored by ^1H n.m.r. spectroscopy which showed that the rate of reaction increases with increased electron-withdrawal in the *N*-chlorinated amine (Table 2) and with increased methylation of the substrate. These trends were expected and confirm our previous conclusions that the reactions have the general characteristics of an electrophilic substitution.[1]

At first sight, the similarity of the product distributions from the chlorination of toluene by chlorine (Table 1) and by *N*-chlorinated amines (Table 2) in TFA would suggest that in both systems chlorine is the active species. However, there is strong evidence that with the *N*-chloroamine systems it is the *N*-chloroammonium ion that is the chlorinating agent.[1,2] The most significant difference between this study with toluene and our earlier investigations is the selectivity of the chlorination. Thus the 4- to 2-chlorotoluene product ratios are typically 0.6 (Table 2), whereas for anisole, a typical substrate with a π-donor substituent, the equivalent 4- to 2- ratio of chloroanisoles is 99.[2a] We have attributed the high selectivity in the latter reactions to the formation of an ordered charge-transfer complex (**4**) between the reactants that leads to preferred 4-chlorination.[1] Presumably the methyl group of toluene being very much less electron releasing than methoxy does not favour the strong orientation of reactants necessary for selective reaction.

Interestingly the selectivity of the toluene chlorinations with *N*-chloromorpholine can be altered to give predominantly 4-chlorotoluene by increasing the acidity of the solvent. In TFA and in 50% aqueous sulphuric acid, which have comparable acidities,[13] the relative yields of 4- to 2-chlorination are 0.64 and 0.52, respectively, whereas in 90% sulphuric acid this ratio becomes 2.85. Increasing the acidity to 100% sulphuric acid has no further effect on the chlorotoluene product distribution,

Table 4. Products from the reaction of *N*-chloropiperidine with polymethylbenzenes in TFA at room temperature.

Substrate	Reaction time	Main product(s)	Minor product(s)
1,3-Dimethylbenzene	2 h	Dimer, trimer chlorinated dimer and trimer	Methylbenzyl chloride and dimethylchlorobenzene
1,4-Dimethylbenzene	4 h		
1,3,5-Trimethylbenzene	10 min	2,4,6-trimethylchlorobenzene	—
1,2,4,5-Tetramethylbenzene	10 min	Dimer and chlorinated dimer	2,3,5,6-Tetramethylchlorobenzene
Hexamethylbenzene	—	Pentamethylbenzyl trifluoroacetate	Pentamethylbenzyl alcohol and a di(hydroxymethyl)tetramethylbenzene ditrifluoroacetate

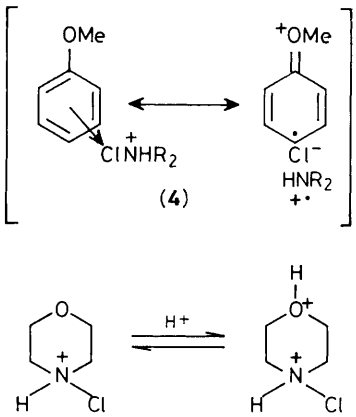


Scheme 3.

Table 5. Products from the reaction of naphthalene with equimolar amounts of *N*-chlorinated amines in TFA at room temperature.

Chlorinating agent	Unchanged naphthalene (%)	Chloronaphthalenes			Aminated naphthalene (%)[a]	Dialkyliminium ion
		Yield (%)[a]	Distribution (%)[b] 1-	2-		
N-Chloropiperidine	Trace	2	95	5	91	—
N-Chlorotriethylammonium ion	50	19	98	2	—	+[c]
N-Chlorotrimethylammonium ion	Trace	45[d]	99	1	—	+[c]

[a] Yield based on *N*-chlorinated amine. [b] Product distribution measured by g.c. following work-up reaction. [c] Detected by ^{1}H n.m.r. analysis of reaction mixture. [d] 10% of a dichloronaphthalene also formed.



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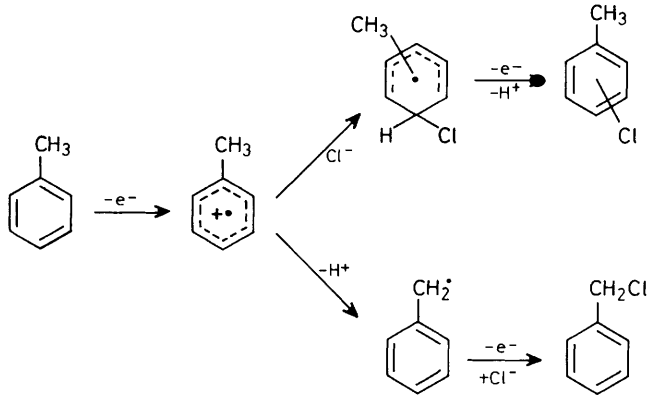
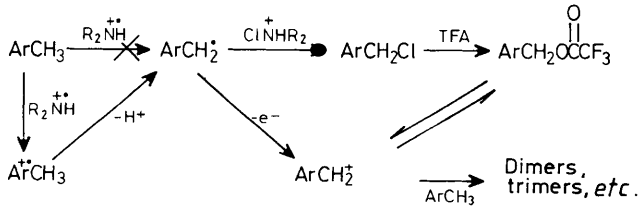


Scheme 5.



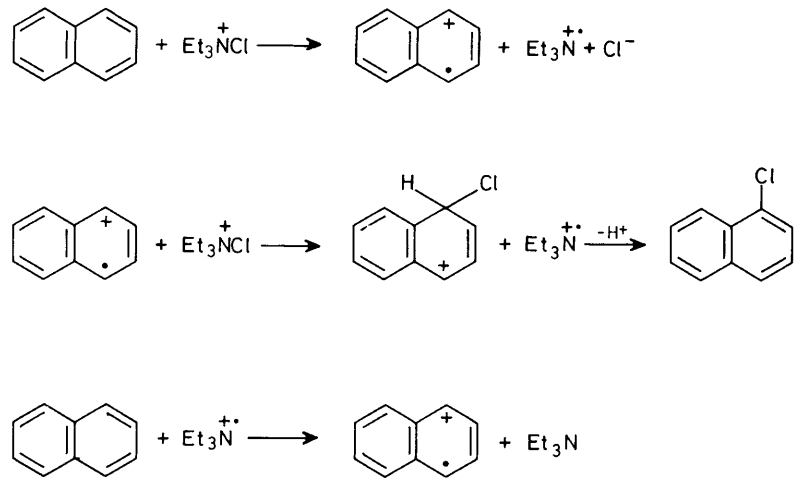
Scheme 6.

although it introduces complications from competing aromatic sulphonation. In a recent report[14] Minisci and his co-workers quote product distributions from the chlorination of toluene with a range of *N*-chloroamines in 98% sulphuric acid. Interestingly, the unsubstituted *N*-chlorodialkylamines give 4- to 2-chlorotoluene ratios (*ca.* 0.67) similar to those we have observed in TFA, whereas for heteroatom-substituted *N*-chloroamines, such as morpholine and piperazine, the ratio is *ca.* 2.0. The results from these two studies show that increased acidity increases the selectivity of the reaction of the heteroatom-substituted but not the unsubstituted *N*-chloroamines. A possible explanation is that in strong acids the heteroatom can be protonated to give a dicationic chlorinating agent that is more selective for the 4-position of toluene (Scheme 4). This effect, of increased positive charge on the chlorinating agent leading to an increased preference for 4-chlorination, resembles the greater reactivity and selectivity for 4-chlorination of anisole and of phenol shown by protonated *N*-chloroamines over the unprotonated species.[2]

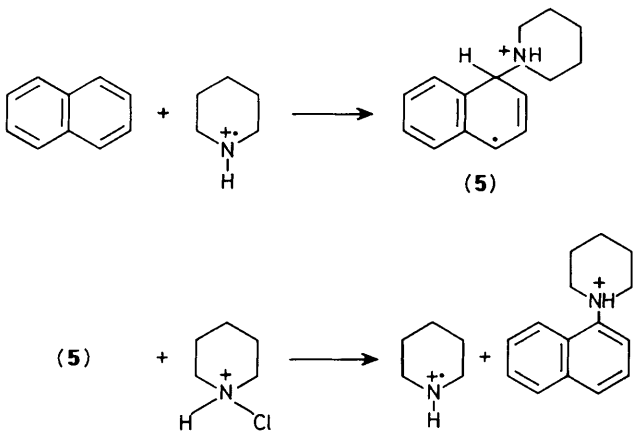
Many of the reagents that bring about aromatic chlorination are also capable of side-chain reaction with arylalkanes.[15] In general, nuclear chlorination is an ionic reaction that is favoured by polar conditions and by factors that inhibit the formation of radicals that could abstract hydrogen atoms from the saturated C–H bonds. However, with reactions initiated by electron transfer both nuclear and side-chain attack can occur *via* a common intermediate, the aromatic radical cation (Scheme 5).[16] In this study toluene gives little or no side-chain chlorination. The small yields of benzyl chlorides found in some of the slower reactions arise from a minor competitive radical chlorination initiated by the photo- or thermal-decomposition of either the *N*-chloroamine[17] or traces of chlorine. With the polymethylbenzenes, however, side-chain reaction is a major pathway, suggesting that there is a change with these more electron-rich aromatics from an arenium-ion mechanism to one involving an initial electron transfer. Reaction on the side-chain would then arise by deprotonation of the aromatic radical cation rather than by hydrogen-atom abstraction from the aromatic substrate by aminium radicals[18] (Scheme 6). The similarity of the products obtained from the reactions of hexamethylbenzene and 1,2,4,5-tetramethylbenzene with *N*-chloropiperidine in TFA to those from the corresponding benzyl chlorides (pentamethylbenzyl chloride and 2,4,5-trimethylbenzyl chloride respectively) with TFA can also be explained by Scheme 6. Side-chain chlorination of the polymethylbenzene leads to the benzyl chloride which is solvolysed to the trifluoroacetate and on further reaction gives the benzyl cation and hydrocarbon dimers and trimers.

It is noteworthy that with 1,3,5-trimethylbenzene nuclear chlorination is the dominant reaction whereas with the other polymethylbenzenes this is only a minor reaction. The marked difference in regioselectivity of 1,3,5-trimethyl- and 1,2,4,5-tetramethylbenzene in electron-transfer reactions has been observed previously[19] and has been attributed to the relatively facile loss of a proton from the tetramethylaromatic radical cation.[19b]

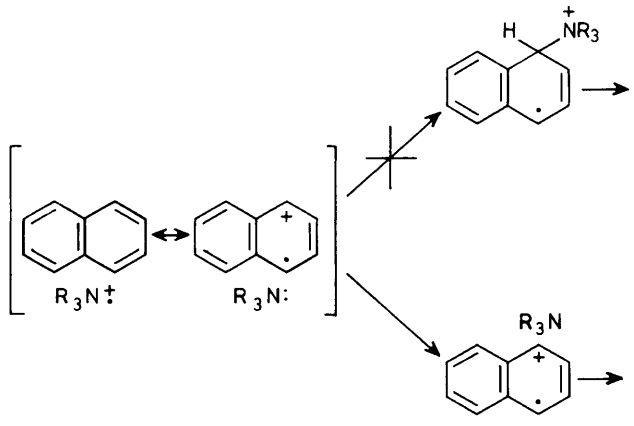
The broadening of the ^{1}H n.m.r. signals from naphthalene in the early stages of its reactions with *N*-chloroammonium ions is another example of the paramagnetic broadening noted previously in the reactions of dimethoxybenzenes.[1,2b] This, coupled with the characteristic e.s.r. spectrum of the



Scheme 7.



Scheme 8.



Scheme 9.

triethylaminium radical, together with a second broad signal in the reaction of naphthalene with *N*-chlorotriethylammonium ion, and the formation of dialkyliminium ions and poor accountability of naphthalene in its reactions with *N*-chlorotrialkylammonium salts, suggest that the reactions proceed by an electron-transfer chain reaction (Scheme 7). Rapid one-electron exchange between naphthalene and its radical cation would account for the paramagnetic broadening of the ^{1}H n.m.r. spectra and the broad signal in the e.s.r. spectrum.[20] The iminium ion arises from the competitive decomposition of the trialkylaminium radicals, as described previously.[2b] Oxidative polymerisation of the naphthalene radical cations[16d] would account for the poor recovery of the naphthalene.

The reaction of naphthalene with *N*-chloropiperidine, although it only leads to low yields of chloronaphthalenes, confirms the conclusion above that naphthalene reacts with *N*-chloroammonium ions by an electron-transfer mechanism. However, with this *N*-chloroamine, following the initial electron transfer, chain amination competes effectively with the chlorination so that the predominant product is the piperidinonaphthalene (Scheme 8).

Although there are no previous reports of the reaction of naphthalene with *N*-chloropiperidine, this chloroamine has been used to aminate other aromatic compounds.[21] Furthermore, Bock and Kompa[22] have shown that with *N*-chlorodimethylamine in sulphuric acid, naphthalene gives a 21% yield of *N*,*N*-dimethylaminonaphthalenes with a product distribution of 97% of the 1- and 3% of the 2-isomer. The same product distribution but higher overall yield was obtained when the reaction was performed with redox catalysis.[23]

The marked difference in the behaviour of the *N*-chlorotrialkylammonium salts and *N*-chloropiperidine is readily explained by the strong influence of steric effects on the reactions of aminium radicals. Minisci[24] has shown that less hindered dialkylaminium radicals, such as the piperidinium radical, rapidly aminate aromatic compounds but that more bulky analogues react relatively slowly. The transition states for these processes bear a strong resemblance to a charge-transfer complex. For the hindered trialkylaminium radicals steric effects in the transition state inhibit aromatic amination and favour electron transfer and subsequent chlorination (Scheme 9).

In conclusion, benzene and toluene are chlorinated by *N*-chlorinated amines in acidic solution by an arenium-ion mechanism. With *N*-chloromorpholine the selectivity of the chlorination of toluene is sensitive to the acidity of the reaction medium and shows the greatest preference for 4-chlorination in the most acidic solutions. However, even the most favourable conditions do not show the high selectivity for 4-chlorination observed with electron-rich aromatics with a π-donor substituent. By contrast the polymethylbenzenes and naphthalene appear to react by an electron-transfer mechanism. With the former substrates (except 1,3,5-trimethylbenzene) the aromatic

radical cations give a mixture of products from ring and side-chain attack. With naphthalene the product distribution is sensitive to steric effects in the *N*-chlorinated amine.

Experimental

Materials.—All the materials were commercial reagent grade unless otherwise stated. *N*-Chloroamines and *N*-chloroammonium salts were prepared as described previously.[2a]

Instrumentation.—^{1}H N.m.r. and e.s.r. spectroscopic and gas chromatographic procedures have been reported.[2a] The following phases were coated on 80–120 mesh Celite or 100–120 mesh Gas Chrome Q (Phase Separations Ltd.) for g.c. analysis: 20% w/w Polyox 600 000 (Union Carbide Ltd.) (products from benzene); 10% w/w, 4,4′-azodiphenetole (Supelco, Inc.) (products from toluene); 2.5% w/w SE30 (products from polymethylbenzenes); 5% w/w Bentone 34 (F. W. Berk and Co. Ltd.) and 10% w/w SE30 (chloronaphthalenes) and 1% w/w OV-1 (Phase Separations Ltd.) (piperidinonaphthalenes). H.p.l.c was carried out with a Du Pont 830 chromatograph coupled to a Du Pont 837 variable-wavelength u.v. detector. Analysis for quaternary ammonium salts was by reversed-phase ion-pair chromatography on an ODS pellicular column (Du Pont; 1 m × 4 mm) using 50% aqueous methanol containing 0.1 mol dm^{-3} sodium lauryl sulphate. Mass spectra were recorded with an AEI MS 3076 spectrometer operating at 70 eV. For combined g.c.–m.s. the instrument was coupled to a Pye 104 gas chromatograph.

Chlorination Procedures.—(*a*) *Reactions in TFA.* The experiments were carried out and worked up as described previously,[2a] except as described below. The methods were modified for sparingly soluble substrates (1,2,4,5-tetramethylbenzene, hexamethylbenzene, and naphthalene) to use a solution of the aromatic hydrocarbon in TFA, which was added to the acidic solution of *N*-chloroamine. In the analytical search for naphthyl quaternary ammonium salts, the aqueous and organic solutions, following the work-up, were analysed by reversed phase h.p.l.c.

(*b*) *Reactions in aqueous sulphuric acid.* The *N*-chloromorpholine (115 mg) was added to toluene (87 mg) in aqueous acid (10 cm^3) and the mixture was vigorously shaken. After 1 h the solution was diluted with water and carefully neutralised with aqueous NaOH. Any unchanged *N*-chloroamine was quenched with KI and liberated iodine was removed with sodium thiosulphate. The organic products were extracted into diethyl ether and analysed by g.c.

Reactions of Polymethylbenzyl Chlorides with TFA.—The polymethylbenzyl chloride (0.1 g) was added to TFA (2 cm^3) and the mixture was stirred for a short time. Any solid unchanged starting material was removed by filtration and the solution was poured into cooled water (25 cm^3) before the organic material was extracted into diethyl ether.

The products from reactions were identified by ^{1}H n.m.r. spectroscopy of reaction mixtures, and isolated materials, by comparison of retention times with those of authentic materials, by m.s. and combined g.c.–m.s. When authentic materials were unavailable the structures were assigned using data from the methods above and by comparison with data in the literature. Ring and side-chain halogenated compounds were distinguished by the method of McLafferty.[25] For ring chlorides M − Cl:M is < 2.5 and for benzyl chlorides M − Cl:M is > 3, where M refers to the mass of the parent ion and M − Cl to that of the ion formed by loss of a chlorine.

The Products from the Reactions of N-*Chloropiperidine with*—(*a*) 1,3-*Dimethylbenzene.* 4-Chloro-1,3-dimethylbenzene had *m*/*z* 142 (14%), 140 (M^+, 43), 125 (10), 105 (100), 103 (13), 77 (18), and 51 (19); M − Cl:M = 2.32. The spectroscopic data are in good agreement with literature values.[25]

The dimeric and trimeric products had principle ions *m*/*z* 210 and 314, respectively. Their monochlorinated derivatives had ions *m*/*z* 244, 246 and 348, 350.

(*b*) 1,4-*Dimethylbenzene.* Chlorine-free polymeric material had principle ions at 210, 314, 418, and 522.

(*c*) 1,3,5-*Trimethylbenzene.* 2,4,6-Trimethylchlorobenzene had δ(TFA) 2.3 (s, 3 H), 2.4 (s, 6 H) and 6.9 (s, 2 H); *m*/*z* 156 (19%), 154 (M^+, 58), 139 (15), 119 (100), and 91 (15). These spectroscopic data are in good agreement with literature values.[19a,25]

(*d*) 1,2,4,5-*Tetramethylbenzene.* The monomeric product (probably 3-chloro-1,2,4,5-tetramethylbenzene) had *m*/*z* 170 (18%), 168 (M^+, 54), 153 (24), 133 (100), 117 (12), 115 (14), 91 (14), and 51 (93), M − Cl:M = 1.85. The dimeric and chlorinated dimeric materials had principle ions *m*/*z* 266, and 300 and 302, respectively.

(*e*) *Hexamethylbenzene.* The product mixture containing predominantly pentamethylbenzyl trifluoroacetate with probable minor components pentamethylbenzyl alcohol and a bis(hydroxymethyl)tetramethylbenzene ditrifluoroacetate had δ($CDCl_s$) 2.23 (s), 2.28 (s), and 5.50 (s); *m*/*z* of mass ions 274, 178, and 386, respectively.

(*f*) *Naphthalene.* The reaction mixture was worked up and the product was isolated from the reaction mixture by column chromatography on silica gel using hexane followed by propan-2-ol–hexane (1:20) and identified as 1-piperidinonaphthalene, δ($CDCl_3$) 1.58–2.44 (m, 6 H), 3.36–4.00 (m, 4 H), 7.44–7.88 (m, 4 H), 7.88–8.16 (m, 2 H), and 8.30–8.52 (m, 1 H); *m*/*z* 212 (M^+ + 1, 13%), 211 (M^+, 94), 210 (100), 155 (21), 154 (35), 141 (16), 128 (22), and 127 (35), accurate M^+, 211.1356 $C_{15}H_{17}N$ requires 211.1361. G.c.–m.s. of the reaction mixture showed the presence of a small amount of a chlorinated piperidinonaphthalene.

Reaction of Pentamethylbenzyl Chloride with TFA.—A mixture containing predominantly pentamethylbenzyl trifluoroacetate with a trace of hexamethylbenzene, had δ($CDCl_3$) 2.23 (s), 2.28 (s), and 5.48 (s) and *m*/*z* 274 (M^+, 35%), 162 (43), 161 (97), 160 (100), 147 (56), 145 (17), 131 (11), 129 (9), 119 (9), 115 (10), 105 (12), 91 (17), and 77 (10). (In good agreement with literature values.[26])

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