Factors Governing the Direct Reaction Between Aromatic Cation Radicals and Chloride Ion

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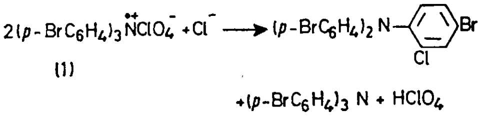
Summary Moderately stable aromatic cation radicals (generated by the peroxydisulphate ion) react directly with chloride ion to give quantitative yields of nuclear chlorinated hydrocarbons.

WE have recently shown that copper(II) chloride is a highly efficient scavenger of organic cation radicals, providing a novel chlorination procedure for aromatic molecules.[1] With aromatics whose cation radical is moderately stable (relative to that of benzene) chloride ion alone has now been found to be equally effective in the nuclear chlorination reaction, and this provides useful information as to the general reactivity of organic cation radicals.

It has been established that highly reactive cation radicals (produced by the reaction of substrate and SO$_4^{\cdot -}$ [1–3]) such as those from benzene and toluene, do not undergo nuclear chlorination when chloride ion alone is present, although in the case of toluene very efficient side-chain chlorination was observed. In contrast rapid nuclear chlorination has now been shown to occur when the ammoniumyl salt (**1**) was allowed to react with added chloride ion in acetonitrile solvent.[4] Similar observations of chloride ion reaction with stable cation radicals have previously been reported by Shine and co-workers.[5]

We now report experiments which help to resolve this apparent conflict. Cation radicals from toluene, *m*- and *p*-xylene, and mesitylene were generated by reactions with peroxydisulphate ion in the presence of standard amounts of hydrochloric acid and lithium chloride. In each case nuclear and/or side chain chlorination took place, with the ratio varying, depending on the stability of the intermediate radical cations (Table).



(1)

TABLE

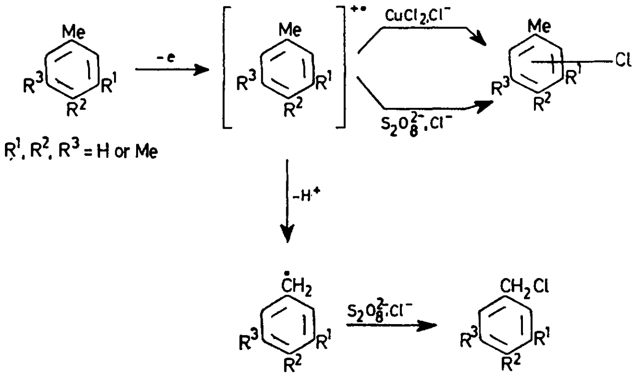
Reaction of sodium peroxydisulphate[a] with aromatic hydrocarbons in the presence of lithium chloride[b]

Substrate	Monochlorohydrocarbon products[c] Side chain %	Nuclear %
Toluene	100	0
p-Xylene	100	0
m-Xylene	90	10
Mesitylene	25	75

[a] $[Na_2S_2O_8]_0$ = 0·05M; solvent 4/1 v/v MeCN/H_2O. Reactions at 80° for 3·0 h in the presence of HCl, 0·2M. [b] [LiCl] = 0·3M. [c] G.l.c. analysis of ether extracted solutions; g.l.c.– m.s. used for further identification.

The experiments were then repeated in the presence of lithium chloride and a catalytic amount of copper(II) chloride. As expected, quantitative yields of the corresponding nuclear chlorinated hydrocarbon were obtained in each case. The two sets of results are summarised in the Scheme.

The stability of the cation radicals would be expected to increase in the order toluene < *m*-xylene < mesitylene and yields of nuclear chlorinated product increase from 0 to 75% in this sequence. In this respect the difference between *m*-xylene and *p*-xylene is particularly significant since the relative stabilization energies of initially formed cation radical, and substituted benzyl radical produced by deprotonation, will differ less for the *meta*-isomer.



SCHEME

Other aromatic derivatives whose cation radicals are stable, relative to that from benzene, are also nuclear chlorinated by the peroxydisulphate–chloride ion system. Thus monochlorinated derivatives were obtained from anisole (*para* + *meta* 75%, *ortho*- 25%), phenol (*para* + *meta* 50%, *ortho*-50%) and naphthalene (mixture of 1- and 2-) in essentially quantitative yields when the aromatic molecules were allowed to react with $Na_2S_2O_8$ and LiCl in water–acetonitrile solution. Isomer ratios are only approximate but identical product mixtures were obtained when the reactions were carried out in the presence of copper(II) chloride.

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