Benzylic Chlorination by Sulphuryl Chloride: Suppression of Chlorine Atom Chains

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Summary Suppression of chlorine-atom chains by trace amounts of trichloroethylene has been achieved in the chlorination of *p*-xylene, and of benzaldehyde in competition with cyclohexane, by sulphuryl chloride in CCl_4 solution.

BENZYLIC chlorination by sulphuryl chloride in dilute CCl_4 solution has recently been found[1] to exhibit different selectivity to those found for photo-chlorination[2] under similar conditions. We now report the first study of sulphuryl chloride chlorination in which chlorine-atom chains are believed to be completely suppressed.

Walling and McGuinness[3] have demonstrated that chlorine-atom chains may compete with alkoxy-radical chains in the reaction of hypochlorites with alkylbenzenes, and in the decomposition of benzyl-dimethylcarbinyl hypochlorite. These chlorine chains are, however, eliminated by traces of olefins, *e.g.* trichloroethylene, which act as chlorine atom traps, and greatly suppressed in mixed aliphatic–benzylic systems where chains propagate largely through alkyl radicals.

The light-initiated chlorination of *p*-xylene and of benzaldehyde relative to cyclohexane by sulphuryl chloride, in a number of solvents, has been measured[1] in presence of 2 mole % of trichloroethylene (relative to SO_2Cl_2) (Table). The reactivity values for *p*-xylene in benzene remain constant at 0·65 for varying substrate concentration, with or without trichloroethylene. This can be attributed[4,5] to the benzene-complexed chlorine atoms as the hydrogen-abstracting species.

TABLE

Reactivities (per *hydrogen atom*)[a] *of* p-*xylene and benzaldehyde relative to cyclohexane at* 40°

Substrate	Concn. M[b] Solvent	0·4	0·8	1·2	1·6	2·0	2·4	2·8
$K_{p\text{-xylene}}$	C_6H_6	0·64	0·66	—	0·66	—	0·66	—
$K_{p\text{-xylene}}$	C_6H_6 + 2% C_2HCl_3	0·64	0·66	—	0·68	—	0·64	—
$K_{p\text{-xylene}}$	CCl_4	1·04	1·02	0·86	0·70	0·58	0·48	0·48
$K_{p\text{-xylene}}$	CCl_4 + 2% C_2HCl_3	1·06	1·06	1·02	1·06	—	1·02	—
K_{PhCHO}	CCl_4	8·04	8·16	8·16	8·75	—	8·40	—
K_{PhCHO}	CCl_4 + 2% C_2HCl_3	—	8·04	8·16	8·28	8·28	—	—
Concn. M of $PhBu^t$ in CCl_4		0	0·4	0·8	1·2	1·6	2·0	
K_{PhCHO} at 1·6 M each of PhCHO + C_6H_{12}		8·75	14·4	17·0	18·7	19·7	20·7	—

[a] Average of triplicate experiments, with mean deviation of $\leqslant \pm 3\%$.

[b] Concn. of each substrate, cyclohexane and sulphuryl chloride, and reaction time adjusted for 20—30% consumption of organic substrates.

In contrast, the value in CCl_4 solution varies with concentration of *p*-xylene, being approximately 1·0 up to 0·8 M, and drops linearly with increasing concentration to 0·50 at

2·2 M but flattens out to 0·48 at higher concentration. This variation is understandable as *p*-xylene is a stronger electron-donor than benzene,[4] and, as the concentration increases hydrogen-abstraction by the strongly π-complexed chlorine atom predominates, and is quite complete at concentrations of 2·4 M. However, in the presence of trichloroethylene the reactivity values remain constant at 1·04 up to 2·4 M *p*-xylene in CCl_4. Thus, it appears that the olefin acts as an efficient chlorine-atom trap and completely suppresses complexing by *p*-xylene. The results here suggest that chlorine-atom chains can be largely suppressed, allowing hydrogen-abstraction by the chlorosulphinyl radicals to predominate, as in the cases reported[1] for dilute solution in CCl_4.

Benzaldehyde, a weaker electron-donating solvent than benzene, in contrast to *p*-xylene, shows no concentration effect on its reactivity even in the absence of trichloroethylene, *i.e.* substantially constant at 8·2 per hydrogen atom. However, on addition of t-butylbenzene, a strongly electron-donating solvent,[4] the values increase substantially to about 20 for 2·0 M–hydrocarbon. This clearly indicates participation of π-complexed chlorine-atom chains.

The present results support our earlier findings[1,6] that in dilute CCl_4 solution the polar effects shown in the chlorination of ring-substituted toluenes, ethylbenzenes, and benzaldehydes by sulphuryl chloride can be attributed to the chlorosulphinyl radical as the principal hydrogen-abstracting species.

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