Substitution accompanying Addition in the Reactions of Chlorobenzene and Benzonitrile with Chlorine under Free Radical Conditions

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Reaction of liquid chlorobenzene or benzonitrile with chlorine under free radical conditions at 100—170° gives, apart from the well known products of additive chlorination, small amounts of dichlorobenzenes and chlorobenzonitriles, respectively. Relative rate and isomer patterns resemble those of the gas-phase, thermal chlorination, known to take place at *ca.* 300° and above in a flow system. In our opinion this substitution occurs *via* intermediate aryl radicals, arising through (endothermal) hydrogen abstraction by chlorine atoms.

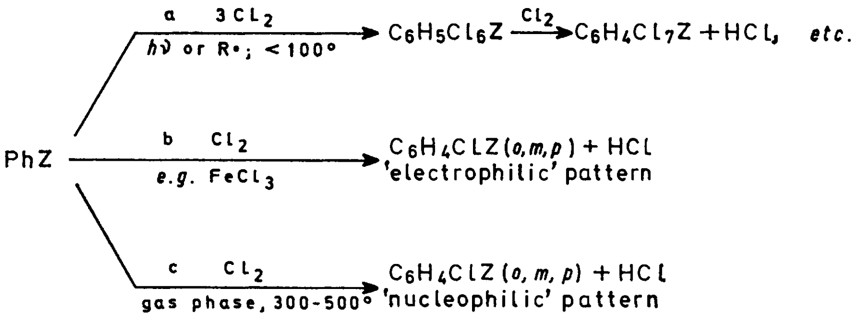
THE interaction of chlorine with benzene and its derivatives (*e.g.*, chlorobenzene, benzonitrile) at room temperature in the liquid phase, under the influence of light or free radical sources, has been intensively studied.[1] Hexachloro-adducts and their higher chlorinated analogues (cyclohexane derivatives; Scheme 1a) are produced.

This behaviour contrasts with that observed under ' Friedel–Crafts ' conditions (Scheme 1b); substitution occurs, giving *o*- and *p*-dichlorobenzene from chlorobenzene (<5% of *m*-isomer) and 70% *meta*-substitution in benzonitrile or benzotrifluoride (<5% of *p*-isomer).[2]

Yet other phenomena are observed when these arenes are allowed to react with chlorine in the vapour phase at 300—500 °C; the substitution ArH $\longrightarrow$ ArCl, albeit characterized by ' electrophilic ' substrate reactivities (benzene *ca.* 10-fold faster than benzonitrile; Scheme 1c), leads to peculiar ' nucleophilic ' *meta* : *para*-isomer ratios (*e.g.* $C_6H_5CN \longrightarrow ClC_6H_4CN$; *m* : 2*p* *ca.* 0·8).[3]

Recently [4] we have shown that reaction c can be made to occur at temperatures at least as low as 180° by adding $CCl_3SO_2CCl_3$ as initiator; interestingly, additive chlorination a is still unimportant under these conditions.

On the other hand, there is no clear-cut example of the substitution of type c possibly accompanying addition a occurring at even lower temperatures. We were interested in bridging this gap and wished to learn whether ' gas-phase ' substitution c would also proceed in the liquid phase. Therefore we have investigated the interaction of liquid chlorobenzene and benzonitrile with chlorine (80—180°) in the presence and absence of bistrichloromethyl sulphone (S) and benzoyl peroxide (B) respectively. Indeed, in addition to the expected type a products, dichlorobenzenes and chlorobenzonitriles were formed, their isomer distributions being comparable with those of vapour-phase reactions.



SCHEME 1

RESULTS AND DISCUSSION

In the dark and without catalysts boiling chlorobenzene is essentially inert towards chlorine. In daylight, however, the rate of reaction becomes higher, both additive chlorination and formation of a little *o*-, *m*-, and *p*-dichlorobenzene taking place. Addition of *ca.* 0·5 mole % of S led to a marked increase in rate. Further experiments (summarized in the Table) only refer to catalysed ' dark ' reactions. Our data show that, with added S, above 150° (using chlorobenzene–benzonitrile mixtures in these cases) the isomer distributions are varying but the *meta*-percentages remain large, thus indicating the occurrence of the ' gas-phase ' type c substitution (Scheme 1) even at *ca.* 130°.

In fact these distributions differ largely from those for Friedel–Crafts type b substitution. The latter mode of reaction appears to be involved when SO_2Cl_2 rather than $Cl_2 + S$ is employed (control run no. 7, Table). Very probably this (polar) chlorination occurs as a side reaction in our Cl_2–S chlorinations. In agreement with

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[1] *Cf.* M. L. Poutsma in ' Methods in Free-Radical Chemistry,' ed. E. S. Huyser, Marcel Dekker, New York, 1969, vol. 1, ch. 3.

[2] R. O. C. Norman and G. K. Radda, *J. Chem. Soc.*, 1961, 3610.

[3] (*a*) C. A. de Mey and E. C. Kooyman, *Rec. Trav. chim.*, 1971, **90**, 1337; (*b*) E. C. Kooyman, *J. Pure Appl. Chem.*, 1963, **7**, 193; (*c*) ' Advances in Free-Radical Chemistry,' ed. G. H. Williams, Logos Press, London, 1965, ch. 4.

[4] W. Dorrepaal and R. Louw, *Rec. Trav. chim.*, 1971, **90**, 700.

this interpretation, type c chlorination appears to be the only one when B is used as a catalyst (runs 8 and 9).

Reaction of chlorine with chlorobenzene and benzonitrile, catalysed by bistrichloromethyl sulphone (S) or benzoyl peroxide (B); formation of dichlorobenzenes and chlorobenzonitriles

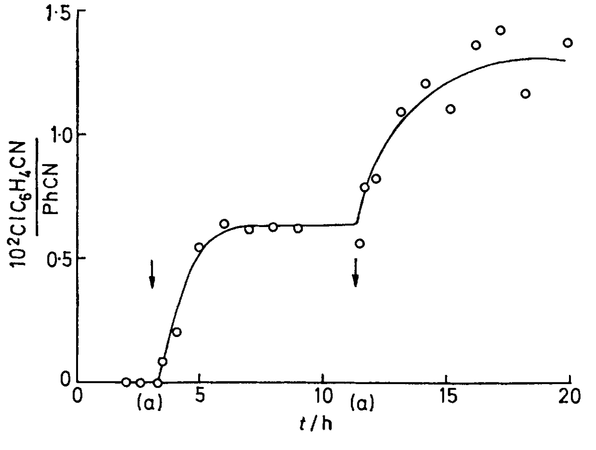
Chlorobenzene Run number	PhCl (mmol)	S or B (mmol)	Temp. (°C)	Reaction time (h)	$C_6H_4Cl_2$ formed †			
					mmol	*ortho* (%)	*meta* (%)	*para* (%)
1 [a]	4700	50 S	127	17	*	32	30	38
2 [b]	960	6·9 S	127	4	*ca.* 5	15	56	29
3 [c]	475	2·7 S	130	5	*ca.* 10	35	27	38
4 [c]	300	3·4 S	155	1·5	2·4	21	50	29
5 [d]	89	3·9 S	168	1·5	1·33	14	57	29
6 [e]	93	3·1 S	177	1·5	0·84	15	52	33
			ca. 175 [f]			9	67	24
			ca. 350 [g]			13	62	25
			ca. 500 [h]			18	60	22
7	1080	‡	130	3	*	16	6	78
8 [i]	1090	22 B	126	3	10	16	63	21
9 [k]	701	22 B	145	4	6	12	55	33

Benzonitrile Run number	PhCN (mmol)	S or B (mmol)	Temp. (°C)	Reaction time (h)	ClC_6H_4CN formed †			
					mmol	*ortho* (%)	*meta* (%)	*para* (%)
10 [l]	391	5·3 S	145	9	4	13	87	
4 [c]	500	3·4 S	155	1·5	0·60	11	49	40
5 [d]	500	3·9 S	168	1·5	1·35	11	49	40
6 [e]	759	3·1 S	177	1·5	1·06	11	51	38
			ca. 190 [f]			8	55	37
			ca. 340 [g]			13	54	33
			ca. 490 [m]			20	50·5	29·5
9	758	22 B	145 [k]	4	1·5	7	52	41
11	1198	17 B	150 [n]	1·5	*	7	53	40

* Not determined. † Determined by g.l.c. with the aid of standard mixtures of known composition. ‡ With SO_2Cl_2 as reagent (32·6 mmol), added over 2·5 h (no Cl_2 employed).

[a] S in chlorobenzene added over a 12 h period. [b] As *a*, over 3 h. [c] Competition experiment PhCl–PhCN; product contained C_2Cl_6 (0·30 mmol). [d] Competition experiment PhCl–PhCN; S in PhCl–PhCN added over 1 h; product contained C_2Cl_6 (0·68 mmol). [e] As *d*; C_2Cl_6 (0·80 mmol) produced. [f] S catalysed, gas-phase chlorination.[4,6]. [g] Thermal, vapour-phase chlorination.[6] [h] Chlorination with CCl_4.[6] [i] B in chlorobenzene added over 2·5 h. [k] Competition experiment; B in PhCl–PhCN added over 3 h. [l] S added in two portions, *cf.* Figure. [m] Chlorination with CCl_4 or C_2Cl_6.[6] [n] B in PhCN added over 1 h; at 100° rather than at 150° only traces of ClC_6H_4CN are produced.

Analogous observations have been made with benzonitrile. Without S or B there is no formation of chlorobenzonitrile; addition of S (Figure) is essential. The isomer pattern of the chlorobenzonitriles is identical with that of the gas-phase reactions. Here, the strongly deactivating cyano-group prevents type b substitution throughout.*



Chlorination of benzonitrile catalysed by $CCl_3SO_2CCl_3$ (S) at 150°. (a), 0·7 mol % S added

Type c chlorination is not very sensitive to substituent effects. This is illustrated by the results of our competitive runs; experiments 4—6 and 9 lead to values of 5 ± 1, very close to that observed for S catalysed chlorination in the vapour phase at *ca.* 200°, *ca.* 4.[4,6]

Our observations are consonant with a free radical mechanism for type c chlorination. Chlorine atoms, produced thermally or (photo)chemically, add to aromatic nuclei [Scheme 2, reaction (1), given for a monosubstituted benzene PhZ]. At moderate temperatures, in the liquid phase, step (3) leads to chlorine adducts, which may be converted (*via* hydrogen abstraction) into perchloroarenes.

Although hydrogen abstraction (2) is an endothermal process, it may detectably compete with addition (1)

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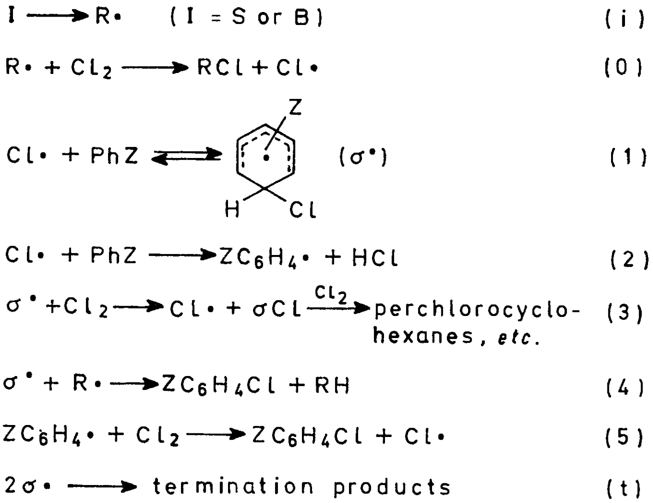
* Ref. 2 appears to be the only report on (direct) polar electrophilic chlorination of benzonitrile; attempted brominations—with *e.g.* $Br_2/FeBr_3$—were reported to be unsuccessful.[5] A recent paper (E. Baciocchi, F. Cacace, G. Ciranni, and G. Illuminati, *J. Amer. Chem. Soc.*, 1972, **94**, 7030) describes the uncatalysed reaction of benzonitrile with Cl_2 in aqueous acetic acid (dark, room temp.). After several months the degree of conversion was still <0·1%.

[5] J. W. Engelsma, Thesis, Leiden, 1960, p. 46.

[6] W. Dorrepaal and R. Louw, to be published; W. Dorrepaal, Thesis, Leiden, 1972.

and (3). For the reasonable estimates $\log k_1 = 13 - 4/2{\cdot}303RT$,* $\log k_2 = 13 - 8/2{\cdot}303RT$ † one obtains k_2/k_{-1} *ca.* 10^{-2} at 150°. As (1) is very probably a reversible reaction under our conditions ‡ this estimate must be considered a minimum value for the substitution : addition ratio.



SCHEME 2

Formation of ZC_6H_4Cl *via* $\sigma\cdot$ radicals, formed in (1), is considered unlikely. In fact, substituent effects on isomeric distributions (relative stabilities) of aryl ($ZC_6H_4\cdot$) and of $\sigma\cdot$ ($ZC_6H_5Cl\cdot$) radicals are expected to be different. Certainly with $Z = CN$ the conjugative power of Z with the π radical system of $\sigma\cdot$ would favour *ortho*- (and *para*-)addition of Cl• over *meta*-addition, as is well documented for other homolytic substitutions occurring *via* addition (methylation, phenylation).[10] Therefore, acceptance of route (1) and (4) rather than (2) and (5) would imply a fortuitous coincidence of isomer distributions ZC_6H_4Cl for these widely different modes of formation.

The stability of $\sigma\cdot$ increases, of course, at lower temperatures; perhaps, the somewhat higher percentage of *o*-dichlorobenzene at *ca.* 130° (runs 1 and 3) is due to a contribution *via* $\sigma\cdot$ type radicals [reaction (4)].

Formation of ZC_6H_4Cl *via* σCl [*cf.* reaction (3)] is considered very unlikely; the latter diene intermediates are able to react with Cl_2,[1,11] a process which will be much faster than elimination of HCl.§

At increasing temperatures (Cl•) : ($\sigma\cdot$) and the substitution–addition ratio will increase. In the vapour phase chlorination (300—500°) route (2) and (5) may be the predominant, if not the sole, reaction leading to products. Mechanistic and kinetic aspects of the latter system will be discussed in a forthcoming paper.[6]

EXPERIMENTAL

Chemicals.—Chlorobenzene (Baker) and benzonitrile (Merck) were redistilled before use; benzoyl peroxide (Lamers and Indemans) and tank chlorine (Loosco) were used as such. Bistrichloromethyl sulphone was described previously.[4] Dichlorobenzenes were commercially available, chlorobenzonitriles were prepared according to standard methods.

Dichlorobenzenes as products (experiment 1, Table) were isolated by distillation *in vacuo* on a spinning band column; a middle fraction (*ca.* 1 g) analysed for *o* : *m* : *p* *ca.* 2 : 3 : 5, together with chlorobenzene 4%) [g.l.c., Becker Multigraph F 410 (flame ionization detector); column; Benton SE, 2 m, 100°, 1 atm. N_2). The i.r. spectrum was almost identical with that of a synthetic mixture of this composition. Chlorobenzonitriles were analysed on a CA column (2 m, 120°, 1 atm. N_2).

Products of Additive Chlorination of Chlorobenzene.—In a separate run at 128°, chlorobenzene (120 g, 1·07 mol) and S (2·9 g, 9·7 mmol) reacted under a slow stream of chlorine over a period of 3 h. After flushing with nitrogen until colourless, chlorobenzene (and dichlorobenzene) were removed *in vacuo* (113·8 g). Of the semisolid residue (8·7 g) 7·3 g was chromatographed over neutral aluminium oxide, employing hexane and benzene as eluants, and gave various fractions (total 5 g). In order of elution these contained hexachlorobenzene (*ca.* 1 g), (i.r., m.p.), unchanged S (1·5 g), and hepta- and octa-chlorocyclohexanes (*ca.* 1 g), predominantly β-$C_6H_4Cl_8$ (i.r.).

[2/2017 *Received, 24th August*, 1972]

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* For $Cl\cdot + C_2H_4 \longrightarrow (C_2H_5Cl)\cdot$, $\log k = 13{\cdot}3 - 1{\cdot}5/2{\cdot}303RT$.[7] As arenes are employed as a solvent for free-radical chlorination of aliphatic compounds, the minimum value of E_1 should be several kcal mol^{-1} for uncomplexed chlorine atoms.[8a]

† With $D(Ph{-}H) = 109$ kcal mol^{-1} [6,9] $\Delta H_2 = +6$. Our estimate implies $E_{-2} = 2$ (exothermal abstraction); for the methyl analogue ($\cdot CH_3 + HCl \underset{a}{\overset{-a}{\rightleftharpoons}} CH_4 + Cl\cdot$), $\log k_a = 13 - 3{\cdot}8/2{\cdot}303RT$ [8b] and hence $\log k_{-a} = 13 - 3/2{\cdot}303RT$.

‡ (Photo)chlorination of liquid t-butylbenzene at *ca.* 30° involves both addition and (side chain) abstraction (*ca.* 1 : 1); at 80° only substitution is observed. *Cf.* also ref. 8*c*.

§ Molecular 1,2-elimination of HCl from σCl is expected to have an appreciable activation energy (perhaps, well over 30 kcal mol^{-1}), whereas elimination *via* H• abstraction by Cl• cannot compete with rapid reactions involving molecular chlorine under our conditions.

[7] J. A. Kerr, *Quart. Rev.*, 1968, **22**, 549..

[8] (*a*) Ref. 1, p. 131; (*b*) p. 86; (*c*) p. 133.

[9] G. A. Chamberlain and E. Whittle, *Trans. Faraday Soc.*, 1971, **67**, 2077.

[10] G. H. Williams, 'Homolytic Aromatic Substitution,' Pergamon, Oxford, 1960.

[11] K. Mislow and H. M. Hellman, *J. Amer. Chem. Soc.*, 1951, **73**, 244.