Nucleophilic Displacement in Polyhalogenoaromatic Compounds. Part 11.[1] Kinetics of Protiodeiodination of Iodoarenes in Dimethyl Sulphoxide–Methanol

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The rates of methoxide-ion induced protiodeiodination of a number of polychloroiodobenzenes and their derivatives have been measured in dimethyl sulphoxide–methanol (9:1 v/v; 323.2 K). The true reagent under these conditions appears to be the dimethyl sulphoxide anion, and the rates of reaction in some cases appear to approach that expected of a diffusion controlled process. This corresponds to a major decrease in the efficacy of further activating substituents in the aromatic system, although deactivating groups such as *p*-OMe still show large effects. Chlorine promotes protiodeiodination in the order of efficiency *o*-Cl > *m*-Cl > *p*-Cl; the trifluoromethyl group activates displacement in the order *o*-CF_3 > *p*-CF_3 > *m*-CF_3, although with much less difference between isomeric sites. *o*-Nitro-groups promote protiodeiodination whereas the *p*-nitro-group encourages methoxydeiodination. No evidence of methoxydeiodination was found in attack of the polychloroiodobenzenes, although the rates of methoxydechlorination of the corresponding polychlorobenzenes suggest that in some cases this might occur. Evidence rejecting the possible $S_{RN}1$ mechanism and supporting nucleophilic attack by a carbanionic species upon iodine is presented.

Protiodeiodination of polyhalogenoiodobenzenes has been studied kinetically in mixtures of butanone and methanol in the presence of sodium methoxide.[2] Similar reduction of polybromofluorobenzenes,[3] of polybromobenzenes,[4,5] and of 1,3-dichloro-2-bromobenzene [6] have been reported, and the interchange of bromine or of iodine between sites in some polyhalogenobenzenes in solutions of amide ion in liquid ammonia has been studied in detail.[7] More recently, a radical mechanism by which iodine is lost from iodobenzene and some monosubstituted derivatives has been proposed, following the observations (i) that the reaction was catalysed by light and by dissolving metals, and showed other properties associated with free-radical processes, and (ii) that the formation of iodide ion showed unusual kinetics.[8-10] As the reaction conditions in some cases resembled our own quite closely, we began a re-investigation of the base-catalysed protiodeiodination process to determine which of the possible mechanisms proposed by Bunnett and his colleagues might apply to these reactions in solutions of dimethyl sulphoxide (DMSO)–methanol and of butanone–methanol. We sought to do this by three general methods: (i) by changing the solvent and the carbanionic species present, to show the generality of the process; (ii) by suitably diverting the displaced halogen, to show the intermediacy of the alkyl halides proposed; and (iii) by showing the nucleophilic nature of the displacement through studies of the effects of substituents.

Table 1. Second-order rate constants for protiodeiodination of derivatives (1)—(21) of iodobenzene (NaOMe; DMSO–methanol, 9 : 1 v/v; 323.2 K)

Substituents	10^4k_2/l mol^{-1} s^{-1}
2-Chloro- (1)	0.006
2,3-Dichloro- (2)	30
2,4-Dichloro- (3)	9
2,5-Dichloro- (4)	37
2,6-Dichloro- (5)	1 600
2,3,4-Trichloro- (6)	340
2,4,5-Trichloro- (7)	900 [a]
2,4,6-Trichloro- (8)	3 200
2,3,4,5-Tetrachloro- (9)	2 500
2,3,4,6-Tetrachloro- (10)	4 700
2,3,5,6-Tetrachloro- (11)	12 000
2,3,4,5,6-Pentachloro- (12)	15 000
2-Trifluoromethyl- (13)	1.4
3-Trifluoromethyl- (14)	0.06
4-Trifluoromethyl- (15)	0.20
4-Bromo-2-trifluoromethyl- (16)	57
2-Nitro- (17)	2 100
2,6-Dichloro-4-bromo- (18)	2 300
2,6-Dichloro-4-iodo- (19)	2 100
2,3,5,6-Tetrachloro-4-methoxy- (20)	0.10
2,3,4,5,6-Pentabromo- (21)	18 000

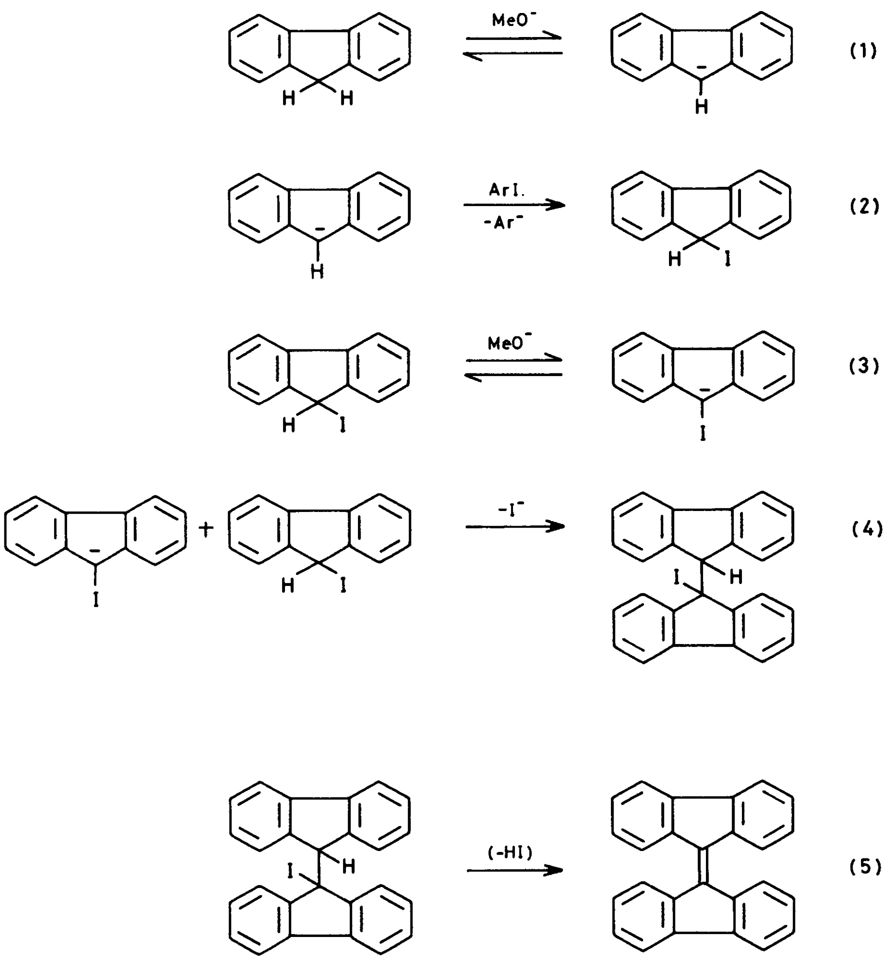
[a] 10^4k_2 *ca.* 650 in the presence of fluorene; see Table 3.

Discussion

Protiodeiodination. Mechanism.—No intermediate has yet been isolated linking the aryl iodide reagent and the iodide ion product, nor has any organic product of the proposed alkyl halide intermediate been identified. 3,5-Dimethylanisole and 3,5-dimethylphenoxide ion in DMSO–methanol were not iodinated by pentachloroiodobenzene, which also did not attack dimedone or diethyl malonate in methanolic sodium methoxide. However, the addition of fluorene (Table 1) to solutions of sodium methoxide in DMSO–methanol (9 : 1 v/v), although it lowered the observed rate constant for attack of 2,4,5-trichloroiodobenzene at 323.2 K, caused the simultaneous formation of 9,9′-bifluorenylidene in 50—60% yield. This olefin is not formed in the absence of iodoarene, and so does not arise from oxidative coupling involving oxygen or the solvent.

Scheme 1 suggests a plausible route for its formation, based upon the known [11,12] reactions of 9-halogenofluorenes. Indeed, treatment of 9-bromofluorene with sodium methoxide under these conditions is a rapid route to this olefin. 9-Iodofluorene, whose presence was demonstrated in this way, arose from the iodination of fluorene anion [equation (2)], and we believe that the isolation of 9,9′-bifluorenylidene confirms the mechanism by which fluorene anion removes iodine from the aryl iodide and hence, by extension, confirms the general mechanism proposed.

Our reaction conditions are very similar to some in which Bunnett and his colleagues have demonstrated the $S_{RN}1$ mechanism. This mechanism does not operate under our conditions on the following evidence.



Scheme 1. Mechanism of formation of 9,9′-bifluorenylidene

(i) Aryl iodides (ArI) produce the corresponding hydrocarbon (ArH); in the $S_{RN}1$ mechanism, nucleophiles derived from ketones or sulphoxides become incorporated to give the arylated analogues. Correspondingly, fluorene anion produces bifluorenylidene under our reaction conditions, but 9-aryl- and 9,9-diaryl-fluorenes under $S_{RN}1$ conditions.[8-10]

(ii) The kinetics of formation of iodide ion in butanone–methanol or in DMSO–methanol ($d[I^-]/dt = k_2[ArI][MeO^-]$) are different from those found under $S_{RN}1$ mechanism conditions ($d[I^-]/dt = k_e[ArI]/[X^-]$, where $[X^-]$ parallels $[I^-]$, but X^- is not I^-).[10]

(iii) Nitrobenzene has a powerful effect upon the rate of the $S_{RN}1$ process;[8] it has no effect upon the rate of loss of iodide ion from pentachloroiodobenzene in butanone–methanol under our conditions. Correspondingly, neither light nor benzoyl peroxide initiated or accelerated the reaction of *o*-chloroiodobenzene with sodium methoxide in DMSO–methanol under our kinetic conditions

(iv) In benzene-rich (70% v/v) mixtures, aryl iodides decomposing under the influence of sodium methoxide in either butanone–methanol or DMSO–methanol gave no biaryls (mass spectrometry).

(v) Finally, the rate of formation of iodide ion by the $S_{RN}1$ mechanism from the attack of iodobenzene by pinacolone enolate anion in the presence of potassium t-butoxide is unaltered by added benzenediazonium borofluoride or phenylazotriphenylmethane, and remains at a value (k_e 7×10^{-7} s^{-1}) similar to that found by Bunnett and Scamehorn[10] until the addition of methanol (0.4M), which stops the reaction immediately. It is evidently this solvent which determines whether deiodination proceeds by a nucleophilic attack upon halogen, or by the radical mechanism.

Protiodeiodination Rates.—The rate coefficients reported in Table 1 show that chlorine accelerates the process, and that this acceleration increases in the order *p*-Cl < *m*-Cl < *o*-Cl, since iodide ion formation decelerates in the order (5) > (2), (4) > (3). Comparisons of these rate constants with that of *o*-chloroiodobenzene (k_2 6×10^{-7} l mol^{-1} s^{-1} at 323.2 K) provides the substituent rate constants $f_{o\text{-Cl}}$ 2.5×10^5, $f_{m\text{-Cl}}$ 5×10^3, and $f_{p\text{-Cl}}$ 1.5×10^3. However, these values fall markedly throughout the series of polychloroiodobenzenes; thus, $f_{o\text{-Cl}}$ becomes 3.5×10^2 [comparing (8) and (3)] and finally 6 [comparing (12) with (9)]. The simplest explanation of such a large decrease in sensitivity to substituent effect is a change in the rate-determining step, presumably from equation (7) to (9) in Scheme 2, However, in reactions in which pentachloroiodobenzene was treated with a deficiency of sodium methoxide we were unable to detect the formation of $I\cdot CH_2\cdot SO\cdot Me$ by mass spectrometry, nor could we produce a discontinuity in the kinetic plot on adding a further quantity of base after the original amount had been consumed. This explanation must therefore be rejected.

Because the true reagent is not methoxide ion, but apparently the dimethyl sulphoxide anion, the true rate constants are much greater than those shown in Table 1, and the attack

$$\mathrm{MeO^- + CH_3{\cdot}SO{\cdot}CH_3 \rightleftharpoons MeOH + CH_3{\cdot}SO{\cdot}CH_2^-} \quad (6)$$

$$\mathrm{ArI + CH_3{\cdot}SO{\cdot}CH_3 \longrightarrow Ar^- + CH_3{\cdot}SO{\cdot}CH_2I} \quad (7)$$

$$\mathrm{Ar^- + MeOH \rightleftharpoons ArH + MeO^-} \quad (8)$$

$$\mathrm{MeO^- + CH_3{\cdot}SO{\cdot}CH_2I \longrightarrow I^- + Products} \quad (9)$$

Scheme 2. Base-catalysed protiodeiodination of iodoarenes

of aryl iodide by dimethyl sulphoxide anion may become encounter-controlled. Thus, $d[I^-]/dt = k_2[ArI][MeO^-] = k_{true}[ArI][Me{\cdot}SO{\cdot}CH_2^-]$, *i.e.* $k_2 = k_{true}[DMSO]/K[MeOH]$, where $K = K_{MeOH}/K_{DMSO}$, the ratio of the acid dissociation constants of the two solvents. Evaluating K in the DMSO–methanol mixture is difficult. The recent work of Bordwell and his colleagues [13] shows acidity constants for the two solvents [pK_a 29.4 (MeOH) and 35.1 (DMSO)] which provides a value of $10^{5.7}$ for K, making k_{true} *ca.* $10^5 k_2$. This value of K requires further correction, partly because the present solvent contains 10% v/v methanol, and partly because no account has been taken of ion-pairing effects.[14] Because of this uncertainty, experimental (k_2) rate constants are therefore reported.

The largest rate constant for protiodeiodination in Table 1 is that of pentachloroiodobenzene (k_2 1.6 l mol^{-1} s^{-1}, corresponding to k_{true} *ca.* 2×10^5 l mol^{-1} s^{-1}). A theoretical maximum may be calculated for the rate of an encounter-controlled process in DMSO; [15] this corresponds to k_{true} *ca.* 3×10^9 l mol^{-1} s^{-1}. Although an encounter-controlled reaction between dimethyl sulphoxide anion and the more reactive aryl iodides seems unlikely therefore, the following observations are consistent with its occurrence.

(i) A *p*-chloro substituent in (11) (Table 1) raises the rate coefficient by a factor of 1.25, whereas the corresponding factor is 15 in the butanone–methanol mixture studied earlier.[2] The equilibrium concentration of butanone anion in such a system, however, is much greater than that of the DMSO anion, so that encounter-control is less likely in the ketone-rich system. In DMSO–methanol, however, a *p*-methoxy-group in (11) lowers the observed rate constant by a factor of *ca.* 10^5; the lack of sensitivity towards substituent effects applies only when further activation of the system is attempted. Comparison of the two substituents, *p*-chloro and *p*-methoxy, is particularly apt since their substituent constants ($\sigma_{p\text{-Cl}}$ +0.24; $\sigma_{p\text{-OMe}}$ −0.27) [16] are similar in magnitude but opposite in direction.

(ii) The observed rate of reaction of pentabromoiodobenzene with sodium methoxide in DMSO–methanol is sensibly the same as that of the pentachloro-analogue, although in butanone–methanol bromine is a better activating substituent than chlorine.[2] Such behaviour is expected when a rate-limiting step has been reached in which electronic effects play no part.

(iii) The rate of protiodeiodination of 2,6-dichloroiodobenzene is only little affected by the introduction of *p*-halogeno-substituents; neither chlorine, bromine, nor iodine triple the rate constant (Table 1). Here the rate limit appears to be somewhat less (k_2 *ca.* 0.4 l mol^{-1} s^{-1}) than that found in the pentachlorobenzene system.

Attempts to measure substituent effects in the present solvent systems have been frustrated by such self-limiting behaviour. The nitro-substituent shows a further peculiarity of behaviour. The *o*-nitro-group, as in (17), promotes protiodeiodination completely, but the *p*-nitro-group causes methoxydeiodination to the exclusion of any replacement by hydrogen. This may be interpreted in terms of a particularly appropriate geometry linking the sodium alkoxide, through the adjacent nitro-group, with the reaction site.

$$[\mathrm{ArI \cdots DMSO \cdots MeO^-}]$$

(I)

An alternative to encounter-control, as an explanation of the change of substituent effect with total reactivity of the aryl iodide, is a change in the nature of the transition state of the reaction. The kinetic form is consistent with either a bimolecular transition state, involving the dimethyl sulphoxide anion attacking the aryl iodide, or with a termolecular transition state involving a molecule each of DMSO, aryl iodide, and methoxide ion. The least reactive aryl iodides may lose iodine only to dimethyl sulphoxide anion, whose high reactivity outweighs its low equilibrium concentration. The more reactive substrates, however, may lose halogen through a transition state such as (I) in which the dimethyl sulphoxide anion is never completely formed. The difference in the two processes lies in the timing of proton-loss and subsequent iodination of the DMSO molecule, and in a sequence in which two processes occur at very nearly the same time the effects of aryl substituents in the aryl iodide may well be less marked than those in which the fully formed carbanion is the reagent.

Methoxydechlorination of Polychlorobenzenes.—Methoxydehalogenation and protiodehalogenation may occur simultaneously, as we have noted in the case of the polyfluorobromobenzenes.[3] We therefore checked the course of reaction of each polychloroiodobenzene with methoxide ion in our solvent mixture, using differential argentiometric titration to distinguish chloride from iodide ions, ^{1}H n.m.r. and g.l.c. to identify aryl methyl ethers in the reaction products. An independent check was attempted by a study of the rates of methoxydechlorination of some polychlorobenzenes under the same experimental conditions. The kinetic measurements (Table 2) suggested that the chlorine substituent effects upon the rate of methoxydechlorination are approximately described by the substituent rate factors $f_{o\text{-Cl}}$ 35, $f_{m\text{-Cl}}$ 47, and $f_{p\text{-Cl}}$ 12. These values parallel those found in the methoxydefluorination of a number of polyfluoropolychlorobenzenes in methanol at 323.2 K, but with a somewhat smaller (ρ 4.5) reaction constant. Table 2 also shows that methoxydechlorination shows influences between adjacent substituents similar to those found in the corresponding reactions of polyfluoronitrobenzenes [17] and in electric dipole moment studies of polychloroarenes,[18] and which diminish the observed substituent effect, possibly through self-cancelling interactions. Thus, 1,2,3,4- and 1,2,3,5-tetrachlorobenzene differ in their rates of displacement of chlorine from C-1 by a factor of 10, although each site formally is activated by the combined influences of an *o*-chloro, an *m*-chloro, and a *p*-chloro-substituent.

In this present solvent system, however, iodine substituents manifestly have a much smaller effect than those found in methanol.[19] Thus, the rate of methoxydechlorination of pentachlorobenzene at 323.2 K (k_2 0.14 l mol^{-1} s^{-1}) is of the same order as the rate of protiodeiodination of 2,3,4,5-tetrachloroiodobenzene (k_2 0.25 l mol^{-1} s^{-1}) and that of 2,3,4,6-tetrachloroiodobenzene (k_2 0.47 l mol^{-1} s^{-1}) under the same conditions; yet protiodeiodination is the only process observed in the reactions of either aryl iodide.

Experimental

AnalaR dimethyl sulphoxide was fractionally distilled under reduced pressure; middle fractions were then purified

Table 2. Second-order rate coefficients for methoxydechlorination of polychlorobenzene derivatives (NaOMe; DMSO–methanol, 9 : 1 v/v; 323.2 K) [a]

Substrate	Site attacked	[ArCl]$_0$/M	[NaOMe]$_0$/M	k_2/l mol^{-1} s^{-1}
1,2,3-Trichlorobenzene	C-1	0.0114	0.058	$2.3 \pm 0.2 \times 10^{-5}$
	C-2			$2.3 \pm 0.2 \times 10^{-5}$
	C-1	0.012	0.115	$2.5 \pm 0.2 \times 10^{-5}$
	C-2			$2.5 \pm 0.2 \times 10^{-5}$
1,3,5-Trichlorobenzene	C-1	0.009	0.046	$9.4 \pm 0.3 \times 10^{-5}$
	C-1	0.010	0.058	$9.4 \pm 0.1 \times 10^{-5}$
	C-1	0.013	0.029	$8.7 \pm 0.3 \times 10^{-5}$
1,2,3,4-Tetrachlorobenzene	C-1	0.009	0.029	$7.1 \pm 0.7 \times 10^{-5}$
	C-2			$1.29 \pm 0.10 \times 10^{-3}$
	C-1	0.009	0.058	$7.0 \pm 0.8 \times 10^{-5}$
	C-2			$1.20 \pm 0.10 \times 10^{-3}$
1,2,3,5-Tetrachlorobenzene	C-1	0.010	0.017	$3.0 \pm 0.1 \times 10^{-3}$
	C-2			$3.0 \pm 0.1 \times 10^{-4}$
	C-1	0.014	0.017	$3.0 \pm 0.2 \times 10^{-3}$
	C-2			$3.0 \pm 0.2 \times 10^{-4}$
	C-1	0.020	0.058	$3.1 \pm 0.2 \times 10^{-3}$
	C-2			$3.1 \pm 0.2 \times 10^{-4}$
1,2,4,5-Tetrachlorobenzene	C-1	0.008	0.0288	$6.0 \pm 0.2 \times 10^{-4}$
	C-1	0.009	0.058	$6.2 \pm 0.3 \times 10^{-4}$
	C-1	0.014	0.017	$6.1 \pm 0.4 \times 10^{-4}$
1,2,3,4,5-Pentachlorobenzene	C-1	0.007	0.012	$3.0 \pm 0.3 \times 10^{-2}$
	C-2			$7.3 \pm 0.6 \times 10^{-2}$
	C-1	0.009	0.012	$3.3 \pm 0.1 \times 10^{-2}$
	C-2			$7.9 \pm 0.3 \times 10^{-2}$
Hexachlorobenzene	C-1	0.003	0.006	0.36 ± 0.04
	C-1	0.007	0.007	0.36 ± 0.03

[a] Rates of attack reported at individual sites, using g.l.c. analysis of reaction products and the experimentally obtained rate coefficient of attack of the polychlorobenzene.

to m.p. 18.5—18.6° by fractional freezing (lit.,[20] 18.55°). Methanol, b.p. 64.6° at 760 mmHg (lit.,[21] 64.4—64.7° at 760 mmHg), was purified by previously reported methods. Concentrated solutions (2M) of sodium methoxide were made by dissolving the cleaned metal in purified methanol, and decanting the solution from small amounts of precipitated solid. Stock solutions of the solvent mixture, or of sodium methoxide in such a mixture, were made by weighing a suitable quantity of purified DMSO and adding to it, by pipette, a volume of methanol or of methanolic sodium methoxide which corresponded to one-ninth of the volume of the DMSO, calculated from the reported density (d_4^{20} 1.100 g cm^{-3}). The sodium methoxide content of such solutions was estimated by titration.

The polyhalogenoiodoarenes were made from the corresponding amines by two general synthetic methods.

(i) Purified commercial samples of aromatic amines (0.50 mol) in hydrochloric acid (6M, 1.5 mol) were diazotised at 0—5° by the slow addition of aqueous sodium nitrite (6M, 0.52 mol) and the resulting solution was then slowly added to aqueous potassium iodide (5M, 0.5 mol). When no more gas was evolved on warming, the crude product was washed with aqueous sodium hydroxide, with sodium metabisulphite, and with water before steam distillation after which liquid aryl iodides were fractionally distilled and solids were chromatographed in light petroleum (b.p. 60—80°) on alumina, followed by recrystallisation.

In this way were prepared 2-chloroiodobenzene, b.p. 96° at 9 mmHg (lit.,[22] 110° at 16 mmHg); 65% yield; 98% pure by g.l.c.; 2,3-dichloroiodobenzene, m.p. 35—36° (lit.,[23] 35—36°); 50%; 99%; 2,4-dichloroiodobenzene, b.p. 130° at 55 mmHg (lit.,[24] 259—261° at 760 mmHg); 74%; 97%; 2,5-dichloroiodobenzene, m.p. 21° (lit.,[25] 21°); 65%; 100%; 2,6-dichloroiodobenzene, m.p. 68—68.5° (lit.,[26] 68°); 68%; 100%; 3,4-dichloroiodobenzene, m.p. 30.5° (lit.,[26] 30—31°); 59%; 98%; 3,5-dichloroiodobenzene, m.p. 54° (lit.,[26] 54°); 60%; 97%; *o*-iodobenzotrifluoride, b.p. 199° at 762 mmHg (lit.,[27] 197.5—198° at 750 mmHg); 58%; 98%; *m*-iodobenzotrifluoride, b.p. 74° at 18 mmHg (lit.,[28] 82—82.5° at 25 mmHg); 52%; 97%; *p*-iodobenzotrifluoride, b.p. 190° at 759 mmHg (lit.,[27] 185.5—186° at 745 mmHg); 56%; 98%.

Using sulphuric acid (18M, 250 cm^3)—acetic acid (100 cm^3) in place of hydrochloric acid, and solid sodium nitrite instead of the concentrated aqueous solution, the following aryl iodides, were obtained: 2,3,4-trichloro-iodobenzene, m.p. 66° (lit.,[2] 66—66.5°); 59% yield; 99% pure by g.l.c.; 2,4,5-trichloroiodobenzene, m.p. 106.5—107.0° (lit.,[29] 107°); 64%; 100%; 1,3,5-trichloro-2-iodobenzene, m.p. 53—54° (lit.,[30] 54°); 67%; 100%; 2,3,4,5-tetrachloroiodobenzene, m.p. 84.5° (lit.,[31] 89—90°); 56%; 98%; 1,3,4,5-tetrachloro-2-iodobenzene, m.p. 71.4—71.8° (lit.,[29] 78.5°); 49%; 100%; 1,2,4,5-tetrachloro-3-iodobenzene, m.p. 88.5—89.5° (lit.,[32] 88—90°); 61%; 97%; pentachloroiodobenzene, m.p. 207° (lit.,[29] 208.5°); 65%; 99%; 1,3-dichloro-2-iodo-5-nitrobenzene m.p. 152—153° (lit.,[33] 153°); 60%; 99%; 1,3-dichloro-2-iodo-5-bromobenzene, m.p. 69.8—70.5° (lit.,[2] 67.5—68.2°); 68%; 100%; 1,3-dichloro-2,5-di-iodobenzene, m.p. 79—80° (lit.,[2] 79.2—80.4°); 55%; 99%; 2,4-dinitroiodobenzene, m.p. 89° lit.,[34] 88.5—90°); 72%; 100%; pentabromoiodobenzene, m.p. 312—313° (lit.,[35] 315—316°).

2-Trifluoromethyl-4-nitro-iodobenzene, m.p. 80° (lit.,[36] 82°); 48% yield, was obtained by Petit and Tatlow's method; 2-trifluoromethyl-4-bromoiodobenzene, m.p. 77° (lit.,[37] 77—78°); 52% yield, was made by reported methods. 2,3,5,6-Tetrachloro-4-iodophenol, m.p. 70° (lit.,[38] 72°); 54% yield, prepared by the successive monochlorination of *p*-iodophenol derivatives, gave 2,3,5,6-tetrachloro-4-iodoanisole, m.p. 164°; *m*/*e* 380 (75%), 382 (100), 384 (50), and 386 (11).

Kinetic studies were performed by quenching known volumes of reacting solutions in an excess of dilute aqueous

Table 3. Experimental second-order rate constants for protiodeiodination (DMSO–methanol, 9 : 1 v/v, 323.2 K)

Iodoarene	$[\mathrm{ArI}]_0$/M	$[\mathrm{NaOMe}]_0$/M	k_2/l mol^{-1} s^{-1}
o-Chloroiodobenzene	0.072	0.230	$6.6 \pm 0.3 \times 10^{-7}$
	0.215	0.288	$6.6 \pm 0.4 \times 10^{-7}$
	0.226	0.576	$6.2 \pm 1.5 \times 10^{-7}$
2,3-Dichloroiodobenzene	0.0126	0.0288	$3.4 \pm 0.2 \times 10^{-3}$
	0.0128	0.0144	$3.2 \pm 0.1 \times 10^{-3}$
	0.010	0.0144	$2.8 \pm 0.3 \times 10^{-3}$
2,4-Dichloroiodobenzene	0.021	0.072	$8.8 \pm 0.3 \times 10^{-4}$
	0.027	0.0288	$8.9 \pm 0.5 \times 10^{-4}$
	0.029	0.0288	$9.3 \pm 0.5 \times 10^{-4}$
2,5-Dichloroiodobenzene	0.010	0.0576	$3.6 \pm 0.1 \times 10^{-3}$
	0.0128	0.0144	$3.6 \pm 0.1 \times 10^{-3}$
	0.0126	0.0144	$3.8 \pm 0.1 \times 10^{-3}$
2,6-Dichloroiodobenzene	0.0080	0.0288	0.15 ± 0.01
	0.0124	0.0144	0.14 ± 0.01
	0.0141	0.0144	0.18 ± 0.01
2,3,4-Trichloroiodobenzene	0.010	0.0115	$3.4 \pm 0.2 \times 10^{-2}$
	0.011	0.0576	$3.3 \pm 0.1 \times 10^{-2}$
	0.017	0.0173	$3.4 \pm 0.2 \times 10^{-2}$
2,4,5-Trichloroiodobenzene	0.0078	0.0288	$9.0 \pm 0.4 \times 10^{-2}$
	0.0098	0.0115	$9.5 \pm 0.6 \times 10^{-2}$
	0.0134	0.0144	$8.8 \pm 0.4 \times 10^{-2}$
	0.0090 [a]	0.0115	$6.2 \pm 0.3 \times 10^{-2}$
	0.0115 [b]	0.0110	$6.8 \pm 0.6 \times 10^{-2}$
2,4,6-Trichloroiodobenzene	0.0050	0.0028	0.32 ± 0.1
	0.010	0.0144	0.30 ± 0.01
	0.011	0.023	0.35 ± 0.02
2,3,4,5-Tetrachloroiodobenzene	0.0085	0.0058	0.25 ± 0.01
	0.0090	0.0155	0.25 ± 0.01
	0.0100	0.0115	0.25 ± 0.01
2,3,4,6-Tetrachloroiodobenzene	0.0040	0.0058	0.47 ± 0.02
	0.0040	0.0115	0.45 ± 0.02
	0.0060	0.0288	0.49 ± 0.03
2,3,5,6-Tetrachloroiodobenzene	0.0078	0.0115	1.2 ± 0.2
	0.0078	0.0110	0.9 ± 0.2
	0.0050	0.0100	1.4 ± 0.2
2,3,4,5,6-Pentachloroiodobenzene	0.0035	0.0036	1.6 ± 0.1
	0.0050	0.0050	1.5 ± 0.1
	0.0077	0.0036	1.5 ± 0.2
o-Trifluoromethyliodobenzene	0.011	0.0115	$1.43 \pm 0.06 \times 10^{-4}$
	0.018	0.0288	$1.48 \pm 0.08 \times 10^{-4}$
	0.020	0.0576	$1.40 \pm 0.07 \times 10^{-4}$
m-Trifluoromethyliodobenzene	0.011	0.115	$6.2 \pm 0.3 \times 10^{-6}$
	0.018	0.115	$6.1 \pm 0.2 \times 10^{-6}$
	0.053	0.056	$5.8 \pm 0.6 \times 10^{-6}$
p-Trifluoromethyliodobenzene	0.010	0.0173	$2.0 \pm 0.2 \times 10^{-5}$
	0.012	0.115	$2.3 \pm 0.3 \times 10^{-5}$
	0.012	0.288	$1.6 \pm 0.3 \times 10^{-3}$
2-Trifluoromethyl-4-bromoiodobenzene	0.0057	0.0057	$5.8 \pm 0.4 \times 10^{-3}$
	0.0064	0.0173	$5.9 \pm 0.3 \times 10^{-3}$
	0.0105	0.0576	$5.5 \pm 0.3 \times 10^{-3}$
o-Nitroiodobenzene	0.0073	0.0115	0.21 ± 0.02
	0.0115	0.0115	0.20 ± 0.01
2,6-Dichloro-4-bromoiodobenzene	0.008	0.008	0.22 ± 0.01
	0.008	0.016	0.23 ± 0.01
2,6-Dichloro-1,4-di-iodobenzene	0.0122	0.0159	0.21 ± 0.01
	0.0142	0.0148	0.22 ± 0.02
2,3,5,6-Tetrachloro-4-iodoanisole	0.005	0.0576	$1.01 \pm 0.08 \times 10^{-5}$
	0.008	0.0115	$0.96 \pm 0.06 \times 10^{-5}$
Pentabromoiodobenzene	0.0036	0.008	1.95 ± 0.3
	0.0036	0.007	1.84 ± 0.4

[a] $[\mathrm{Fluorene}]_0$ 0.017M. [b] $[\mathrm{Fluorene}]_0$ 0.011M.

nitric acid and estimating iodide ion argentimetrically. A potentiometric method demonstrated the endpoint and also indicated chloride ion when this was also present. Second-order rate equations were applied, since the stability of the derived rate constant upon doubling the initial concentration of either the aryl iodide or the sodium methoxide demonstrated the general application of the rate equation $k_2[\mathrm{ArI}][\mathrm{MeO}^-] = \mathrm{d}[\mathrm{I}^-]/\mathrm{d}t$.

G.l.c. studies used a Pye 204 instrument and an OV-1 stationary phase. Mass spectrometry was carried out with a VG-Micromass 12B machine. ^{1}H N.m.r. spectra were measured using a Perkin-Elmer R12B machine at 60 MHz, or a JEOL FX909 instrument at 90 MHz.

The measurement of rates of methoxydechlorination of polychlorobenzenes was made by similar methods to that of the rates of protiodeiodination. The polychlorobenzenes were commercial samples, purified by recrystallisation to constant m.p. Their physical constants were in good agreement with those quoted in the literature.

Rate constants at individual points in the kinetic plot agreed to within 5%; in most cases ($k_2 > 10^{-5}$ l mol^{-1} s^{-1}) individual kinetic studies agreed to within ±10%.

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