Photochemical Reactions of Chlorobenzene Derivatives in Benzene

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U.v. irradiation of a variety of substituted chlorobenzenes in benzene gives the corresponding biphenyls, accompanied in some cases by products of reductive dechlorination. *m*-Chlorofluorobenzene and *p*-bromochlorobenzene react with selective replacement of the heavier halogen. Isomer ratios have been measured for the photochemical phenylation of anisole with chloro-, bromo-, and iodo-benzenes. The excited singlet state of the chloro-compound is implicated in the mechanism of these reactions. Chloronitrobenzenes, which are photostable in benzene, are slowly reduced to nitrobenzene on irradiation in ethanol.

AROMATIC chloro-compounds have been described as photochemically unreactive,[1] in contrast to bromo- and iodo-compounds, by virtue of the greater strength of the carbon–chlorine bond. There are indeed numerous examples in the literature in which an aromatic chlorine substituent survives unchanged some other photochemical transformation in a substrate molecule,[2] and other reports contrasting the photostability of aromatic chloro-compounds with the reactions undergone by the corresponding bromo- and iodo-compounds on irradiation under the same conditions.[3] Most remarkable is the use of chlorobenzene as solvent for photochemical reactions of iodobenzene and its derivatives with organic phosphines.[4]

However, recent work has shown that all types of photochemical reaction known for bromo-aromatic compounds also occur with chlorobenzene derivatives. One such reaction is nucleophilic substitution, exemplified by the photolysis of *m*-chlorophenol in aqueous alkali [5] or alcoholic solvents,[6] and by the formation of *p*-cyanophenol from *p*-chlorophenol in aqueous potassium cyanide.[5] Photochemical amination of chlorobenzene derivatives has also been reported.[7,8]

In less nucleophilic media, or when the chlorine atom is less labile to photonucleophilic substitution, homolysis of the carbon–chlorine bond may occur, and products are obtained resulting from secondary reactions of aryl radicals. Reductive dechlorination, the result of

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hydrogen abstraction, occurs predominantly for chlorobenzene,[7] *o*- and *p*-chlorophenols, and chloroanisoles,[9] and for α-*o*-chlorophenylnaphthalene,[10] all photolysed in alcoholic solvents. Isolation of pinacol[9] from the photolysis of *p*-chloroanisole in propan-2-ol is evidence of a homolytic mechanism. Other workers have measured the quantum yield for formation of chloride ion from the photolysis of chloroanilines, chlorophenols, chlorobenzoic acids, *etc.* in alcoholic solvents under a variety of conditions,[11] but reported less explicitly the organic reaction products. When aromatic amines are irradiated in the presence of chlorobenzene derivatives, electron transfer apparently occurs from the excited amine molecule to the chloro-compound, inducing its dissociation into an aryl radical and a halide ion.[12]

Yet another type of photochemical reaction is arylation, whereby chlorobenzene is converted into biphenyl on irradiation in benzene.[13] Our preliminary work showed the generality of this phenylation reaction.[13a] Prior to this the only other examples known to us were the formation of isomeric chlorobiphenyls as intermediates in the photopolymerisation of chlorobenzene itself,[7] and the competition between intermolecular and intramolecular arylation of α-*o*-chlorophenylnaphthalene on irradiation in benzene.[10] We now describe further details of our photochemical studies involving chlorobenzenes.

Photolysis Products.—All the biphenyls encountered in this work are known compounds; authentic samples of those not commercially available were prepared for comparison purposes, some by a photochemical route. U.v. irradiation of the appropriately substituted chlorobenzenes in benzene gave 2-cyano-, 2-methoxy-, 3-fluoro-, 4-hydroxy-, and 4-methyl-biphenyls, and ethyl biphenyl-4-carboxylate, isolated in 5—13% yields after concentration and column chromatography of the photolysates. Difficulties of separation from unused starting material on a small scale and wasteful conversion into other unidentified products, as revealed by the incomplete product balances of other photolyses (Table 1), partly account for the low yields. For synthetic applications, photolysis of iodobenzenes, where available, is a preferable route, by which Wolf and Kharasch[14] isolated several biphenyls in 50—80% yield, although some *ortho*-substituted derivatives gave lower yields. We also obtained 4-methoxybiphenyl in 35% yield from the photolysis of *p*-iodoanisole in benzene.

Photochemical products from a number of substituted chlorobenzenes are given in Table 1. Some variation in conditions used for different experiments makes quantitative comparisons unreliable, but a spread of photochemical reactivity is apparent similar to that found for bromo-compounds by Matsuura and Omura.[15] α-Chloronaphthalene disappeared only slowly on irradiation, and *o*- and *p*-chloronitrobenzenes, 3- and 4-chlorobiphenyls, and *p*-chlorobenzophenone were photostable in benzene. Additionally, *o*- and *p*-chlorobenzaldehydes were consumed on irradiation but the products were not identified.

TABLE 1

Photolysis[a] of substituted chlorobenzenes in benzene

Substrate ArCl	t/h	Analysis of photolysate (% remaining or produced) ArCl	ArPh	ArH
Chlorobenzene	24	43	43	[b]
o-Chlorotoluene	26	13	14	[b]
m-Chlorotoluene	20	26	26	[b]
p-Chlorotoluene	24	27	48	[b]
2-Chloromesitylene	24	0	0	40
o-Chlorophenol	24	17	23	8
m-Chlorophenol	30	45	34[c]	8
p-Chlorophenol[d]	22	46	27	5
o-Chloroanisole	21	15	26	4
p-Chloroanisole	22	25	46	5
p-Chloroaniline[e]	26	77	9	0
m-Chlorobenzylidyne trifluoride	24	28	58[c]	0
o-Chlorobenzonitrile	24	59	15	0
p-Chlorobenzonitrile	22	67	24	0
Ethyl *p*-chlorobenzoate	24	42	48	0
p-Chloroacetophenone	20	76	5	0
m-Chlorofluorobenzene	24	5	63	[b]
p-Bromochlorobenzene	0·5	89	7[f]	0
	3	55	24[f]	Trace[g]
	24	7	49[f]	1[g]
α-Chloronaphthalene[d]	71	[b]	4	0

[a] Hanovia 15 W low-pressure mercury-arc lamp; solution stirred and exposed to the air (unless otherwise stated). [b] Not determined. [c] Authentic material not available for comparison. [d] Hanovia 100 W medium-pressure lamp; solution stirred by bubbling nitrogen. [e] Solution in contact with a gently stirred lower phase of aqueous sodium hydroxide (2M) during photolysis, which prevented turbidity due to the separation of *p*-chloroaniline hydrochloride. [f] 4-Chlorobiphenyl. [g] Biphenyl.

As well as biphenyls, reduction products from the starting chlorobenzenes were formed in several cases (phenols and anisoles). 2-Chloromesitylene gave only mesitylene and no phenylation product, a result attributable either to the availability of benzylic hydrogen atoms for abstraction, *e.g.* intramolecularly from the *o*-methyl groups, or to steric hindrance of the free-radical attack on solvent benzene; no other products resulting from coupling of benzylic radicals were detected. The use of benzene as solvent for these photolyses, and the presence in it of traces of toluene impurity, precluded the estimation of reduction products from chlorobenzene or the chlorotoluenes. This limitation is unfortunate, particularly in the case of *o*-chlorotoluene for which the occurrence of extensive reduction would parallel the

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behaviour of 2-chloromesitylene and explain the otherwise unsatisfactory product balance. Fluorobenzene, if formed from *m*-chlorofluorobenzene, could not be satisfactorily resolved from benzene by g.l.c., so it too was not detected. In all other cases in Table 1 the reduction product was either measured or shown to be absent.

Flash photolysis studies [16] of some dihalogenobenzenes in the gas phase indicate the formation of aryl radicals by loss of the heavier of two different halogen substituents, *i.e.* by dissociation of the weaker carbon–halogen bond. Products obtained photochemically from *p*-bromophenyl-*p*-chlorophenylmethane [17] in benzene are consistent with selective loss of bromine, and other workers have described [18] the stepwise replacement of iodine before bromine or chlorine, and of bromine before fluorine, in the photolysis of dihalogenobenzenes in trimethyl phosphite. Our studies have included two examples illustrating the same type of selectivity. *m*-Chlorofluorobenzene gave only 3-fluorobiphenyl, and *p*-bromochlorobenzene gave 4-chlorobiphenyl and traces of biphenyl, but neither 4-bromobiphenyl nor its secondary photolysis product,[3c] *p*-terphenyl. *o*-Dichlorobenzene was converted into 2-chlorobiphenyl and its secondary photolysis products,[13a] biphenyl and *o*-terphenyl (*cf.* *o*-di-iodobenzene [19]).

In view of the photo-isomerisation of 2-methylbiphenyls recently reported,[20] we have specifically checked the photostability of 2-cyano-, 2-hydroxy-, and 2-methoxy-biphenyls. We have also carefully analysed all photolysates for traces of isomers of the expected biphenyl product. We have confirmed the conversion of 2-methylbiphenyl on irradiation in benzene into 3- and/or 4-isomers (these were clearly separable from 2-methylbiphenyl but not from each other under a variety of g.l.c. conditions), but this isomerisation is slow compared with the formation of 2-methylbiphenyl from *o*-chlorotoluene. In no other case have we any indication of isomerisation of biphenyls, nor of formation of rearranged biphenyls by photolysis of substituted chlorobenzenes.

Mechanistic Considerations.—Isomer ratios of phenylated products formed on photolysis of iodobenzene in isopropylbenzene support a free-radical mechanism, although the observed product distribution is changed if diphenylmercury or tetraphenyl-lead replaces iodobenzene as the source of phenyl radicals.[21] From the unpublished results [22] of photochemical phenylation of other aromatic solvents using iodobenzene, it is claimed [1] that thermally equilibrated phenyl radicals are involved. We have measured proportions of isomeric methoxybiphenyls obtained on photolysis of chloro-, bromo-, and iodo-benzenes in anisole, and the competitive formation of methoxybiphenyls and biphenyl from chlorobenzene in anisole–benzene. There is some variation in product distribution from the different halogenobenzenes (Table 2), and only the results from bromobenzene are closely comparable to those from phenylation by radicals generated by thermal routes.[23,24] The phenyl radicals produced from chlorobenzene photolysis are apparently 'hotter', *i.e.* less selective, and those from iodobenzene more selective in their position of attack. In the cationic phenylation of anisole, *ortho*-substitution also predominates (56—76% of biaryl product depending on co-solvent),[25] but there is characteristically greater discrimination between attack at *meta*- and *para*-positions. An ionic mechanism has been discounted for photolysis of α-*o*-chlorophenylnaphthalene [10] for reasons which are equally relevant here.

TABLE 2

Phenylation of anisole by various methods

Reaction	Isomer distribution of methoxybiphenyls (%) 2-	3-	4-	Relative reactivity anisole : benzene
PhCl photolysis	56·0	20·4	23·6	2·3
PhBr photolysis	68·5, 71·1	15·8, 14·4	15·7, 14·5	
PhI photolysis	78·0, 78·3	9·4, 9·9	12·6, 11·8	
$(PhCO_2)_2$ thermolysis [c]	69·8	14·7	15·6	2·0 [a]
PhN(NO)Ac thermolysis [d]	69·3	18·1	12·6	1·7 [b]

[a] Values of 1·2 and 2·5 are given in ref. 23*b*. [b] A value of 2·0 is given in ref. 24*b*. [c] Ref. 23. [d] Ref. 24.

In photolyses of chlorobenzenes (typically *ca.* 10^{-2}M) in benzene with the low-pressure mercury-arc source (emitting principally at 254 nm), most of the incident light is absorbed by the solvent [$\lambda_{max.}$ 255 nm (ε 230)] [26] and only 0·1—1% directly by the substrate. Decompositions of the chloro-compounds may therefore be due to photo-sensitisation by benzene. Both singlet and triplet sensitation by benzene have been recorded,[27,28] although occurrence of the latter in the

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liquid phase has been uncertain.[27a] Singlet–singlet energy transfer to the substrate is competitive with other processes leading to deactivation of the benzene excited singlet, provided the latter has a mean lifetime in solution of *ca.* 10 ns or longer.[29] Chlorine substitution generally causes only a small bathochromic shift (*ca.* 10 nm) of the first absorption maximum (B band) of aromatic compounds.[26] From the limited data available,[30,31] it appears that chlorine substitution causes only a slight lowering of the energies of the first excited singlet and triplet levels above the ground electronic state of an aromatic molecule. In organic compounds containing iodine the heavy atom effect makes for a high intersystem crossing efficiency from excited singlet to excited triplet states (and, for example, the enhancement of phosphorescence at the expense of fluorescence[10,32]), but this effect is much less marked for chloro-compounds.

Some evidence can be adduced against the involvement of excited triplet states in these reactions (*cf.* ref. 10). The chlorophenols, *p*-chloroaniline, *o*- and *p*-chlorobenzonitriles, and *p*-chloroacetophenone are all fairly extensively photolysed (see Table 1). The energies of their first excited triplet states are not known with certainty, but they are probably close to, but no higher than, the values for the corresponding aromatic compounds without chlorine, *i.e.* in the range 74—82 kcal mol^{-1}.[28,30] It is doubtful whether this represents sufficient energy for homolytic dissociation of the aromatic carbon–chlorine bond, which requires 85·6 kcal mol^{-1} for chlorobenzene.[33] Baum and Pitts[3b] conjectured that loss of halogen atoms from bromo- and iodo-butyrophenones on photolysis in toluene occurred from vibrationally excited ground state molecules, but this seems unlikely in a condensed phase. All things considered, we believe the decompositions of chlorobenzenes most probably take place from the excited singlet states.

The photostability of *p*-chlorobenzophenone and the relatively slow photolysis of *p*-chloroacetophenone in benzene may be due to the high intersystem crossing efficiency of aromatic ketones forming the lowest excited triplet states (benzophenone 69 and acetophenone 74 kcal mol^{-1}),[28] which then have insufficient energy for reaction. Nevertheless, conversion into 4-acetylbiphenyl, even in low yield, contrasts with photochemical formation of the pinacol from *p*-chloroacetophenone in propan-2-ol,[2d] when no dechlorinated products were described, and also with the failure of *p*-chlorobutyrophenone to react on irradiation in toluene.[3b]

Wolf and Kharasch[14] noted incomplete photolysis of *p*-iodonitrobenzene in benzene even after prolonged irradiation, and Matsuura and Omura[15] obtained no nitrobiphenyl product from *m*- or *p*-bromonitrobenzene. The chloronitrobenzenes are also photostable in benzene, although they are slowly consumed giving small yields of nitrobenzene on irradiation in ethanol. α-Chloro- and α-bromo-naphthalenes are likewise reduced to naphthalene on photolysis in ethanol noticeably faster than they give α-phenylnaphthalene in similar conditions but in benzene. This difference is probably due to predominant absorption and inefficient sensitisation by benzene at the low concentrations of substrate employed, whereas in ethanol the halogen-containing compound itself absorbs the incident light (typically >90% through a path length of 1 cm).

EXPERIMENTAL

G.l.c. analyses were performed using a Pye Series 104 chromatograph, on 1·5 m × 4 mm columns containing either silicone SE 30 (20%) or diethylene glycol adipate (15%) on Celite. Mass spectra were recorded on an A.E.I. MS 12 low-resolution mass spectrometer operating at 70 eV, with a direct insertion probe and with facility for rapid scanning of g.l.c. peaks. Photolyses were carried out with immersion-type Hanovia mercury-arc lamps with quartz envelopes, the medium-pressure lamps (100 and 500 W rating) being water-cooled.

Substituted chlorobenzenes were either commercial samples or they were prepared by standard methods; in every case the purity was checked by g.l.c. 2-Chloromesitylene was prepared from 2,4,6-trimethylaniline (Emmanuel) as described[34] for *o*-chlorotoluene. The crude product in ether was extracted with aqueous sodium hydroxide, and the alkaline phase was acidified to give 2,4,6-trimethylphenol (37%), m.p. 71—73° (from light petroleum) (lit.,[35] 71·5—71·8°). The residual ethereal solution was fractionally distilled to give 2-chloromesitylene (19%) as an oil, b.p. 75—76° at 15 mmHg (lit.,[35] 103·6° at 25 mmHg), *m/e* 154 and 156 (M^+, 51 and 17%) and 119 ($M - Cl$, 100).

2- and 3-Methyl-, 2-hydroxy-, 4-amino-, and 4-chlorobiphenyls were commercial samples. 4-Cyanobiphenyl (7%) was prepared from 4-aminobiphenyl (Emmanuel) *via* a Sandmeyer reaction using cuprous cyanide solution;[36] it crystallised as needles, m.p. 85—86° [from aqueous ethanol (1 : 1 v/v)] (lit.,[37] 85—86°). 4-Acetylbiphenyl (45%) was prepared as described[38] from biphenyl and acetyl chloride; it crystallised as prisms, m.p. 118—120° (from ethanol) (lit.,[38] 120·5°).

Photolysis of Chlorobenzenes.—The results given in Table 1 were obtained by u.v. irradiation of 100—300 ml samples of solutions of substituted chlorobenzenes (*ca.* 0·1—0·3% w/v) in benzene (Fisons AnalaR grade) at ambient temperatures using a Hanovia 15 W low-pressure mercury-arc resonance lamp. The extent of reaction was monitored by g.l.c., and in most cases after irradiation the photolysate was concentrated for g.l.c. analysis.

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Products were identified by comparison of g.l.c. retention times, and in some cases mass spectra, with those of authentic compounds; quantitative measurements were made by calibrating the flame ionisation detector response with authentic samples of the products, and by using appropriate internal standards chosen from naphthalene, biphenyl, 4-bromobiphenyl, bibenzyl, and phenyl benzoate. 3-Hydroxybiphenyl [*m/e* 170 (M^+ 100%)] and 3-trifluoromethylbiphenyl [*m/e* 222 (M^+ 100%)] were identified by mass spectra recorded for g.l.c. peaks, in the absence of authentic materials for comparison.

α-Chloro- and α-bromo-naphthalene (*ca.* 0·1% w/v) in ethanol (Burroughs AnalaR grade) in 24 h irradiation (15 W low-pressure lamp) gave naphthalene (7 and 53% respectively); α-bromonaphthalene in benzene irradiated under the same conditions for 24 h gave α-phenylnaphthalene (7%) and naphthalene (2%). Similarly photolysis of *o*-, *m*-, and *p*-chloronitrobenzene in ethanol for 24 h (15 W low-pressure lamp) gave nitrobenzene (8, 8, and 3%, respectively).

Photochemical Preparation of Biphenyls.—The following biphenyls were prepared by irradiation (Hanovia 500 W medium-pressure lamp) of substituted chlorobenzenes (4·0—5·0 g) in benzene (950 ml) under nitrogen. After evaporation of the photolysate, the residue was chromatographed on alumina (Laporte type H) and the biaryl fraction was eluted with light petroleum (b.p. 40—60°) (except where otherwise stated), recovered, and recrystallised from a suitable solvent. The extent of photolysis and the chromatographic separation were monitored by g.l.c. analysis (silicone SE 30). In this way *o*-chloroanisole (photolysed 22 h) gave 2-methoxybiphenyl (8%), m.p. 25—27° (from light petroleum) (lit.,[39] 29°); *o*-chlorobenzonitrile (32 h) gave 2-cyanobiphenyl (13%), eluted with light petroleum–benzene, m.p. 37—39° (from aqueous ethanol) (lit.,[37, 40] 30—32°, 37°, 41°); *m*-chlorofluorobenzene (48 h) gave 3-fluorobiphenyl (12%), m.p. 25—26° (from light petroleum) (lit.,[41] 26—27°); *p*-chlorotoluene (24 h) gave 4-methylbiphenyl (9%), m.p. 46—47° (from light petroleum) (lit.,[42] 46°); *p*-chlorophenol (20 h with 100 W medium-pressure lamp) gave 4-hydroxybiphenyl (5%), eluted with ether, m.p. 161—613° (from aqueous ethanol) (lit.,[43] 163°); ethyl *p*-chlorobenzoate (34 h) gave ethyl biphenyl-4-carboxylate (6%), m.p. 42—44° (from light petroleum) (lit.,[44] 45°). In the same way irradiation of irradiation of *p*-iodoanisole (12 h) gave 4-methoxybiphenyl (35%), m.p. 87—89° (from ethanol) (lit.,[42] 89°).

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