Photochemical Phenylation of Chlorobenzenes

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Summary Ultraviolet irradiation of benzene solutions of substituted chlorobenzenes results in formation of biphenyls, often in high yield.

PHOTOCHEMICAL reactions of aromatic halogen compounds include principally reduction (A), nucleophilic substitution (B), and arylation (C). Recent reviews[1] state that chlorobenzenes are photochemically unreactive and attribute this to the C–Cl bond strength being greater than that of C–Br or C–I. Notwithstanding, both reaction types (A) and (B) have recently been reported[2] to occur with chlorobenzenes, and there are isolated examples of inter-[3] and intra-molecular arylation[4] of such compounds.

We have found that replacement of halogen by a phenyl substituent occurs for a variety of chlorobenzenes on u.v. irradiation in benzene. Our results parallel those of Matsuura and Omura[5] on aromatic bromides and of Wolf and Kharasch[6] on iodides, while offering possible advantages for synthetic work. For example, 57% of starting chlorobenzene (6×10^{-3}M in benzene) disappeared in 24 hr. photolysis (Hanovia 15 w low-pressure mercury arc lamp), and 43% of biphenyl was formed (75·5% based on chlorobenzene decomposed). In a separate experiment at lower conversion the ratio of HCl : biphenyl was found to be 1·04 : 1.

These substituted chlorobenzenes which we have found to decompose at a useful rate on irradiation in benzene (>50% in 24 hr.) are listed below. The corresponding biphenyls formed account for 20—81% of the loss of starting compounds; they were characterised by mass spectra, in some cases by g.l.c. comparison with authentic samples, or isolated by chromatography on alumina. Alternative products arising from reductive dechlorination were detected in only those few cases indicated, when they were always of minor importance (except from 2-chlorobiphenyl). In the case of 4-chloroaniline the solution became turbid from separation of hydrochlorides, but this complication could be conveniently averted by irradiating the benzene solution in contact with a stirred lower phase of aqueous alkali.

Chlorobenzene substituent: H, 2-Me, 2-OH, 2-OMe,[a] 2-CN, 2-Cl,[b] 2-Ph,[c] 3-Me, 3-OH,[d] 3-CF$_3$, 4-Me, 4-OH,[a] 4-OMe,[a] 4-CN,[d] 4-NH$_2$,[d] 4-COMe,[d] 4-CO$_2$Et, 4-CH$_2$·CH$_2$·Ph,[a] 4-CH$_2$·CH$_2$·C$_6$H$_4$Cl-*p*.[e]

[a] Smaller amounts of reduced products also detected. [b] 2-Chlorobiphenyl accompanied by secondary photolysis products. [c] Biphenyl : *o*-terphenyl formed *ca.* 4·1 : 1. [d] Only *ca.* 20% conversion in 24 hr. [e] Only one chlorine atom replaced.

The photostability of 4-chlorobiphenyl in benzene solution has already been observed.[7] However, we find that 2-chlorobiphenyl is readily converted into a mixture of biphenyl and *o*-terphenyl; hydrogen chloride is again produced, but no chlorine is detected. Direct irradiation (3130 Å) of 1-*o*-chlorophenylnaphthalene in benzene similarly results in dechlorination, phenylation, and intramolecular cyclisation.[4]

This first survey clearly shows that the reaction has some generality for the formation of substituted biphenyls from chlorobenzenes. Nevertheless we have examined several aromatic chloro-compounds for which conversion is either extremely slow ($<$ 2% in 24 hr.) or undetectable by g.l.c. analysis. These include 2- and 4-chloronitrobenzenes, 3- and 4-chlorobiphenyls, 1-chloronaphthalene, 2-chloropyridine, 2-chloroquinoline, and 4-chloro-4′-phenylbibenzyl (I)†, for all of which the energies of the benzene-sensitised triplet states ($\leqslant$ 65 kcal./mole) are apparently insufficient to induce cleavage of the C–Cl bond.

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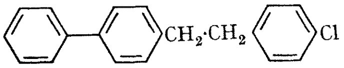
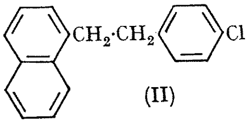
† New compounds had satisfactory elemental composition and n.m.r. and mass spectra.

To explain why 4,4′-dichlorobibenzyl suffers replacement of only one chlorine atom by a phenyl group and why the product (I) is photostable in the same conditions, we suppose that in the latter compound the sensitised excitation is quenched intramolecularly in the biphenyl group, thereby protecting the C–Cl bond. Such intramolecular energy transfer between insulated chromophores has been observed where luminescence is the criterion of sensitisation, and is known to be very efficient.[8] This explanation is consistent with our observation that 1-α-naphthyl-2-*p*-chlorophenylethane (II)† is also completely unchanged on irradiation under the same conditions.



(I)



(II)

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