

Intramolecular Homolytic Aromatic *Ips*o Substitution in Halogenobenzenes by Aryl Radicals

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Summary Aryl radicals (**1a,b**) afford dihalogenodibenzo-thiophens (**4a,b**) as a result of intramolecular homolytic aromatic *ipso* substitution; the yields increase with temperature and are greater when the displaced halogen is bromine rather than chlorine.

SEVERAL displacement reactions of a number of groups by nucleophilic carbon radicals reported recently appear to show that homolytic *ipso* substitution is a general process at least in heteroaromatic systems.¹ However, only a few examples have been reported of substitution by 'neutral' phenyl radicals at the *ipso* position of a substituted benzene ring.² We report here a preliminary investigation of the behaviour of aryl radicals in *ipso* aromatic substitution. We chose the *o*-(2,4,6-trihalogenophenyl)thiophenyl radicals (**1a,b**) for this study because they seemingly show only two kinds of reaction: attack on the solvent or intramolecular aromatic *ipso* substitution. The radicals (**1a,b**) were generated by aprotic diazotization³ of the parent amines (**2a,b**) with *n*-pentyl nitrite in substituted benzenes as solvents.

Reactions were carried out by careful addition of *n*-pentyl nitrite to refluxing solutions of the amines (**2a,b**) in benzene, chlorobenzene, or *o*-dichlorobenzene; vigorous gas evolution occurred during addition, all the reactions being complete after a few minutes. Column chromatography of the reaction mixtures afforded (**3a,b**) (**4a,b**), (**5a,b**), and (**6a,b**) (Scheme 1). None of these products have been

previously reported, and they were identified by spectral data and elemental analysis. The m.p.s. are reported in Table I.

TABLE I

Product ^a	M.p./°C	Product ^a	M.p./°C
(2a) ^b	76—77	(5b)	152—154
(2b) ^b	108—109	(6a)	120—121
(3a)	59—60	Ar=Ph (6b) ^c	169—171
(3b)	73—75	Ar=Ph (6a) ^c	—
(4a)	155—156	Ar=C ₆ H ₄ Cl (6b) ^c	—
(4b)	157—158	Ar=C ₆ H ₄ Cl (6a) ^c	—
(5a)	102—103	Ar=C ₆ H ₃ Cl ₂ (6b) ^c	—
		Ar=C ₆ H ₂ Cl ₂	—

^a All the products gave satisfactory mass spectral data. ^b Obtained by reduction with H₂-Pd from the corresponding nitro derivative, which, in turn, was prepared from 2,4,6-trihalogenobenzethiol and *o*-chloronitrobenzene in sodium methoxide. ^c The isomer products were not separated so their m.p.s. are not reported.

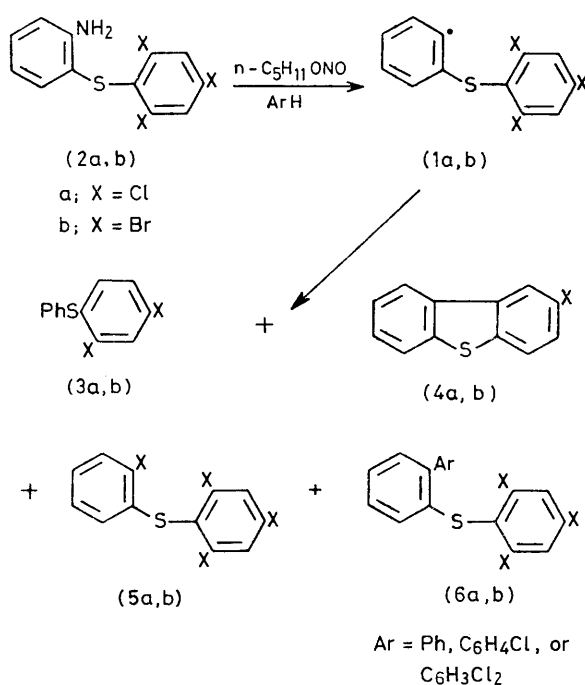
The formation of these products is most readily explained as follows: (**6**) is the expected aromatic substitution product from the solvent, while (**4**) is the result of intramolecular *ipso*-substitution (**3**) and (**5**) are, respectively, the hydrogen and halogen abstraction reaction products by the

TABLE 2. Relative yields of products from the reaction of amine (2) with pentyl nitrite in substituted benzenes

ArH	T/°C	X	(3) %	(4) %	(5) %	(6) %	Isolated yields/%
C ₆ H ₆	80	Cl	21.0	1.5	0.7	77	65
PhCl	130	Cl	15.0	6.0	1.5	77	60
<i>o</i> -C ₆ H ₄ Cl ₂	180	Cl	8.5	9.5	8.5	73	75
C ₆ H ₆	80	Br	25.0	4.0	Traces	71	58
PhCl	130	Br	8.5	13.0	3.5	75	55
<i>o</i> -C ₆ H ₄ Cl ₂	180	Br	2.0	24.5	6.0	66	66

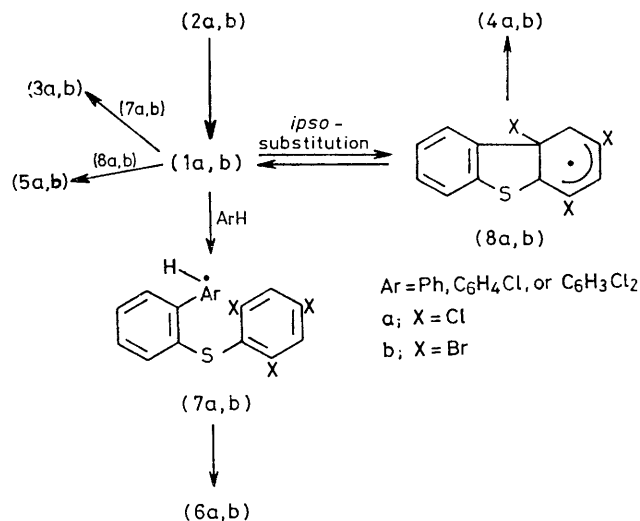
radical (2) from the radicals (7) and (8), as shown in Scheme 2.

As shown in Table 2, the yields of the *ipso*-substitution products (4a,b) and of the halogen abstraction products (5a,b) increase with temperature. These findings are



SCHEME 1

interesting, and might be ascribed to the reversibility of the first addition step of *ipso* substitution.



SCHEME 2

At low temperature it seems possible that the radicals (8a,b) give only kinetically controlled products, *i.e.* the initial radicals (1a,b). However, at higher temperatures, there is more possibility of halogen abstraction from (8a,b) by a carbon radical, affording (4a,b) and (5a,b). Also, bromine is more easily displaced than chlorine in agreement with the lower strength of the C-Br bond.

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