Reactions with other sodium thiolates were carried out under the same experimental conditions described above for the Me_2CHSNa.

Sulfones were obtained by oxidation with H_2O_2 in acetic acid; the solution was warmed on a water bath for 2 h and then poured into ice. The solid was filtered and crystallized from ethanol. The IR spectra of the sulfones presented the characteristic absorptions at 1320–1300 and 1150 cm^{-1}. Physical and NMR data of the products obtained are reported in Table III.

The NMR spectra of the sulfones were particularly useful to confirm the assigned structures. It was in fact observed that when two RSO_2 groups are in the ortho position, the protons linked to the α carbon in R are considerably deshielded; for instance, while the septet of the isopropyl groups in the sulfone of **8c** is found at δ 3.3, that of the sulfone 4 resonates at δ 4.3.

Acknowledgments. Financial support from the CNR,

(23) Th. Zincke and W. Frohneberg, *Chem. Ber.*, **42**, 2721 (1909).
(24) G. M. Bennett and F. S. Statham, *J. Chem. Soc.*, 1684 (1931).
(25) W. A. Baldwin and R. Robinson, *J. Chem. Soc.*, 1445 (1932).

Nucleophilic Aromatic Substitution Reactions of Unactivated Aryl Halides with Thiolate Ions in Hexamethylphosphoramide
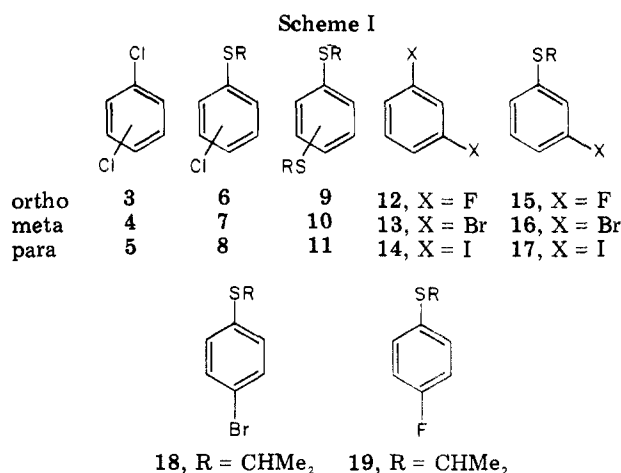
Pietro Cogolli, Filippo Maiolo, Lorenzo Testaferri, Marco Tingoli, and Marcello Tiecco*

Istituto di Chimica Organica, Facoltà di Farmacia, Università di Perugia, 06100 Perugia, Italy

A simple, high-yields method for the synthesis of aryl thioethers via nucleophilic displacement of unactivated aryl halides by the sodium salts of thiols in hexamethylphosphoramide (HMPA) is reported. The reactions are proceeding by the bimolecular displacement mechanism S_NAr. Competitive experiments showed that the four halogenobenzenes presented comparable reactivities toward isopropanethiol anions; the relative halogen mobility was I > F > Br > Cl. The effect of some substituents on the reactivity of chlorobenzene has also been measured.

In a previous paper,[1] we discussed the nucleophilic displacement of aromatic nitro groups, which were activated by an ortho or para alkyl thioether function, by sodium thiolates; the best results were obtained when these alkylthiodenitration reactions were carried out in hexamethylphosphoramide. It has been observed recently that unactivated aryl halides react with sodium methoxide in HMPA to afford methyl aryl ethers in good yields,[2] and we report in this paper that several aryl halides easily give alkylthiodehalogenation reactions when treated with sodium alkanethiolates in HMPA. Few examples of nucleophilic substitutions of unactivated aryl halides are reported in the literature. Reactions can be performed with aryl thiolates in refluxing quinoline or DMF, but yields are generally low with simple halogenobenzenes;[3] successful substitutions were obtained with PhSNa and aryl dihalides in dimethylacetamide at 170–5 °C[4] and with butyl mercaptide and bromo- or fluoronaphthalene in Me$_2$SO at 80 °C.[5] Because of the simple procedure and

Scheme I

ortho	3	6	9	12, X = F	15, X = F
meta	4	7	10	13, X = Br	16, X = Br
para	5	8	11	14, X = I	17, X = I

18, R = CHMe$_2$ **19**, R = CHMe$_2$

of the high yields obtained, the results described in this paper represent an improvement of the previously reported methods. Kinetic experiments were also carried out to clarify the mechanism of these alkylthiodehalogenation

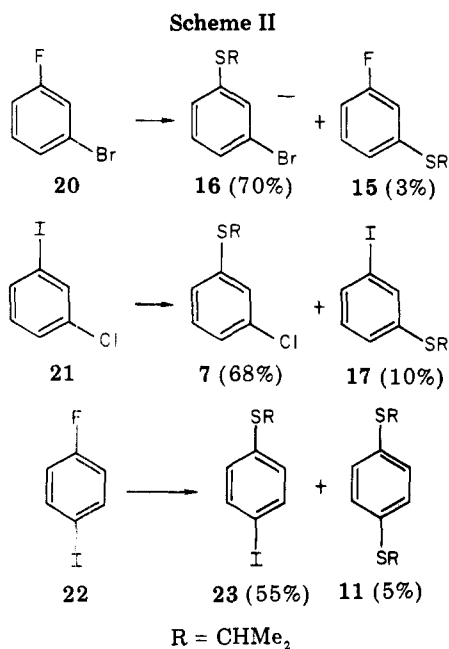(1) P. Cogolli, L. Testaferri, M. Tingoli, and M. Tiecco, *J. Org. Chem.*, accompanying paper.
(2) J. E. Shaw, D. C. Kunerth, and S. B. Swanson, *J. Org. Chem.*, **41**, 732 (1976).
(3) J. H. Uhlenbrock, *Recl. Trav. Chim. Pays-Bas*, **80**, 1057 (1961).
(4) J. R. Campbell, *J. Org. Chem.*, **29**, 1830 (1964).
(5) J. S. Bradshaw, J. A. South, and R. H. Hales, *J. Org. Chem.*, **37**, 2381 (1972).

Scheme II

R = CHMe$_2$

Scheme III

$$RSNa + 8 \rightarrow p\text{-}RSC_6H_4SCHMe_2 + NaCl$$
26, R = Me
27, R = Et
28, R = Me$_3$C
29, R = Ph

reactions and to measure the effect of activation of some substituents.

Results

The four halogenobenzenes **1** smoothly react with Me$_2$CHSNa in HMPA at 80 °C to afford the substitution product, phenyl isopropyl sulfide (**2**), in good yields:

$$C_6H_5X + Me_2CHSNa \rightarrow C_6H_5SCHMe_2 + NaX$$
**1**, X = F,   **2**
Cl, Br, I
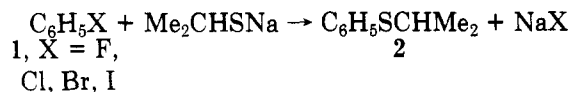
The *o*- (**3**), *m*- (**4**), and *p*-dichlorobenzenes (**5**) give the products of mono substitution **6**, **7**, and **8** or those of disubstitution **9**, **10**, and **11**, respectively, depending on the amount of the Me$_2$CHSNa used and on the reaction time (Table II); compounds **9**, **10**, and **11** can obviously be obtained also starting from **6**–**8**. The reaction occurs more easily with the para isomers **5** and **8** than with the meta, **4** and **7** or the ortho **3** and **6** (Scheme I).

Similarly, *m*-difluoro– (**12**), *m*-dibromo– (**13**), and *m*-diiodobenzene (**14**) react with 1 mol of Me$_2$CHSNa to afford, almost exclusively, the products of mono substitution **15**, **16**, **17**, respectively. Under the same conditions, *p*-dibromobenzene gives *p*-bromophenyl isopropyl sulfide (**18**) together with small amounts of **11**. On the contrary, *p*-difluorobenzene, even at low conversions, affords directly **11**, indicating that the intermediate *p*-fluorophenyl isopropyl sulfide (**19**) is considerably more reactive than the starting *p*-difluorobenzene.

In order to have an indication of the relative rate of substitution of the various halogens, *m*-fluorobromobenzene (**20**), *m*-chloroiodobenzene (**21**), and *p*-fluoroiodobenzene (**22**) were treated with 1 molar equiv of Me$_2$CHSNa (Scheme II). A mixture of *m*-bromo- (**16**) and *m*-fluorophenyl isopropyl sulfide (**15**) in the ratio 70:3 was obtained from **20**; **21** gave **7** and **17** in the ratio 68:10. From **22**, *p*-iodophenyl isopropyl sulfide (**23**) was obtained together with small amounts of **11**; the formation of compound **19**, deriving from the displacement of iodine, could not be evidenced by GLC even in the early stages of the reaction.

Thus, from these results it emerges that fluorine is displaced much more easily than bromine or iodine and that iodine is substituted faster than chlorine.
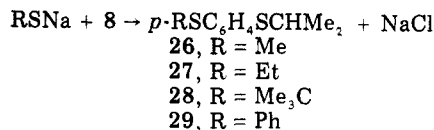
Finally, *p*-chlorotoluene (**24**) and *p*-chloroanisole (**25**) were also investigated. The reaction of **24** required longer reaction times and gave low yields of the desired substitution product, *p*-MeC$_6$H$_4$SCHMe$_2$. With a *p*-methoxy group, the displacement of chlorine was suppressed and, interestingly, the reaction took a different course; the product obtained in this case was in fact the *p*-chlorophenol deriving from the nucleophilic attack of the thiolate anion at the carbon atom of the methoxy group. Similarly, anisole afforded phenol in 68% yields.

This clean cleavage of aryl methyl ethers by Me$_2$CHSNa in HMPA to afford phenols is noteworthy, and it has already been observed to occur also with ethanethiol anions in DMF.[6]

In order to explore the field of application of the reactions described in this paper, several sodium thiolates were allowed to react with chlorobenzene; under the experimental conditions employed for the reaction of Me$_2$CHSNa, only EtSNa gave C$_6$H$_5$SEt in good yields, while MeSNa, Me$_3$CSNa, and PhSNa did not afford appreciable quantities of the desired substitution product. On the contrary, when the more reactive *p*-chlorophenyl isopropyl sulfide (**8**) was used as substrate, good yields of bis sulfides were obtained with all the thiolates, with the exception of the PhSNa, which required longer reaction times and gave the substitution product **29** in only 31% yields (Scheme III). This lower reactivity of PhSNa with respect to the sodium alkanethiolates was already observed in the case of the nitro displacement reactions.[1]

Some competitive experiments were then carried out to determine the relative reactivities of the four halogenobenzenes and other aryl halides and thus to have information about the mechanism by which these reactions are proceeding. For this purpose, an equimolecular mixture of fluorobenzene and *o*-chlorophenyl isopropyl sulfide (**6**) was allowed to compete for a small quantity of Me$_2$CHSNa; the ratio of the formed products, phenyl isopropyl sulfide (**2**) and *o*-bis(isopropylthio)benzene (**9**), is assumed to give the reactivity of fluorobenzene relative to **6**. Similar experiments were performed with the other halogenobenzenes, as well as with other substituted chlorobenzenes. The values of the so obtained relative rates k_{ArX}/k_6 are reported in Table I. For comparison, some competitive experiments were also carried out using a less reactive reference compound, *p*-chlorotoluene, and the new set of relative rates, $k_{ArX}/k_{MeC_6H_4Cl}$, is also reported in Table I. From these data, the values of the reactivity of the various halides in respect to chlorobenzene, $k_{ArX}/k_{C_6H_5Cl}$, can be calculated, and the results obtained from the two sets of experiments are in satisfactory agreement. Also included in Table I are the values of some experiments performed in the presence of azobenzene.

Discussion

The results of competitive experiments collected in Table I indicate that the four unsubstituted halogenobenzenes do not present substantial differences in reactivity toward the isopropanethiol anion in HMPA; the observed halogen mobility sequence is I > F > Br > Cl.

(6) G. I. Feutrill and R. N. Mirrington, *Tetrahedron Lett.*, 1327 (1970).

Table I. Relative Rates of Isopropylthiodehalogenation

	$\dfrac{k_{ArX}}{k_6}$ [a]	$\dfrac{k_{ArX}}{k_{MeC_6H_4Cl}}$ [b]	$\dfrac{k_{ArX}}{k_{C_6H_5Cl}}$ [c]
C_6H_5F	1.2	76.8	9.23 (8.93)
C_6H_5Cl	0.13	8.6	1 (1)
C_6H_5Br	1.00	68.0	7.69 (7.91)
C_6H_5I	1.85[d]	115.9	14.23 (13.48)
o-ClC$_6$H$_4$SCHMe$_2$	1		7.69
m-ClC$_6$H$_4$SCHMe$_2$	2.05		15.77
p-ClC$_6$H$_4$SCHMe$_2$	14.2		109.23
p-ClC$_6$H$_4$Me		1	(0.12)

[a] Experimental values obtained using *o*-chlorophenyl isopropyl sulfide (6) as reference substrate. [b] Experimental values obtained using *p*-chlorotoluene as reference substrate. Owing to the larger differences in reactivity between the halogenobenzenes and *p*-chlorotoluene, these values are considered to be less accurate than the k_{ArX}/k_6. [c] Rates relative to chlorobenzene calculated from the k_{ArX}/k_6 values. The same relative rates calculated from $k_{ArX}/k_{MeC_6H_4Cl}$ are reported in parentheses. [d] In the presence of azobenzene, the relative rate was 1.75

In principle, these reactions can proceed either through the S$_{RN}$1 or the S$_N$Ar mechanism. However, the successful substitution reactions obtained with fluorobenzene, *p*-difluorobenzene, and the aryl fluorides 12, 20, and 22 indicate that, at least in these cases which involve the displacement of fluorine, the S$_{RN}$1 mechanism[7] does not operate; aryl fluorides in fact do not generally react in S$_{RN}$1 reactions.[8,9] The results of the competitive experiments carried out in the presence of azobenzene seem to exclude that this mechanism can be important even in the case of iodobenzene. Azobenzene is a good electron acceptor,[10] and it would interfere with the electron transfer from the Me$_2$CHS anion to the aryl halides; thus, different values of relative rates or even inhibition of the substitution process should be observed. On the contrary, the reactivity of iodobenzene relative to *o*-chlorophenyl isopropyl sulfide (6) remained practically unchanged when the reactions were performed in the presence of azobenzene. Moreover, the fact that *m*-dibromobenzene (13) and *m*-chloroiodobenzene (21) react with 1 molar equiv of Me$_2$CHSNa to form almost exclusively the monosubstitution products, 16 and 7 plus 17, respectively, is an argument against the S$_{RN}$1 mechanism; in fact, if this mechanism were operating, one should expect to find the bis-substituted compound, *m*-bis(isopropylthio)benzene, 10, as the major reaction product as it has been observed to occur in the photostimulated reactions of 13 and 21 with thiophenoxide ions.[9] Finally, it can be observed that the S$_{RN}$1 mechanism implies the intermediate formation of the radical anion of the substitution products. The radical anions of aryl alkyl sulfides are known to give fragmentation into alkyl radicals and thiophenoxide ions;[11] on the contrary, in all the examples investigated in the present work the isopropyl group is retained in the substitution products.

The results obtained are best explained assuming that the reactions proceed by the classical S$_N$Ar mechanism;[12] in activated systems, the addition step is generally rate determining and fluorine is displaced considerably faster

than chlorine, bromine, and iodine.[13] Such a sequence is not respected in the present case, and this can be explained tentatively assuming that, with the isopropanethiol anion and unactivated halogenobenzenes in HMPA, the rate of the substitution process is determined by the rates of both the addition and the elimination steps which contribute to a different extent depending on the nature of the halogen atom suffering the displacement. In the case of the *m*-fluorobromobenzene (20) and the *p*-fluoroiodobenzene (22), the substitution of fluorine is instead greatly favored in respect to the substitution of bromine or iodine (Scheme II). This high selectivity cannot be anticipated from the values of the relative rates of the four halogenobenzenes nor can it be explained simply on the basis of the electronic mutual effect of the two halogen atoms; the high preference for fluorine displacement seems rather to suggest that in compounds 20 and 22 the formation of the intermediate complex becomes rate controlling.

In agreement with the proposed S$_N$Ar mechanism, the substitution of chlorine is inhibited by a *p*-methoxy group and retarded by a *p*-methyl substituent. In the previous work[1] on alkylthiodenitration, it was observed that the alkylthio group activates the displacement of the nitro group by alkanethiol anions. This activation effect has now been confirmed and measured in the alkylthiodehalogenation reactions; from the data of competitive reactions collected in Table I it can be observed that the *p*-chlorophenyl isopropyl sulfide (8) reacts about 100 times faster than chlorobenzene; low activation is also observed from the meta and ortho positions. Weak activation by a *p*-methylthio group has been observed previously in the methoxydechlorination of 1-chloro-2-nitro-4-methylthiobenzene when compared with *o*-chloronitrobenzene.[14] Finally the results reported in this paper indicate that the method employed represents a useful synthetic procedure for the preparation of mono and bis alkylthiobenzenes; in the latter case, two different alkylthio substituents can be introduced in two steps starting from a dihalogenobenzene. These reactions can be used as an alternative of the alkylthiodenitration processes[1,15] with the advantage of avoiding the undesirable products deriving from the reduction of the nitro group which sometimes form in these reactions. The success of the nucleophilic displacement reactions in unactivated or scarcely activated aryl halides, described in this paper, is very likely due to the use of HMPA, a solvent which greatly enhances the reactivity of the nucleophile by specific solvation of the cation.

Experimental Section[16]

Commercial HMPA was used without further purification for all the syntheses described in this work; in the case of the competitive experiments, HMPA was purified by distillation from sodium under reduced pressure. Sodium thiolates were prepared by adding thiols to a solution of sodium ethoxide in ethanol; the solid residue obtained after evaporation of the solvent was washed with ether, filtered, and dried under vacuum.

General Procedure. The solutions of the aryl halides (0.01 mol) and Me$_2$CHSNa in HMPA (50 mL) were stirred under nitrogen, at 80 °C; the amounts of Me$_2$CHSNa and the reaction

(7) J. K. Kim and J. F. Bunnett, *J. Am. Chem. Soc.*, 92, 7463, 7464 (1970).
(8) J. F. Bunnett and R. P. Traber, *J. Org. Chem.*, 43, 1867 (1978); F. Ciminale, G. Bruno, L. Testaferri, M. Tiecco, and G. Martelli, *ibid.*, 43, 4509 (1978).
(9) J. F. Bunnett and X. Creary, *J. Org. Chem.*, 39, 3611 (1974).
(10) J. A. Zoltewicz and T. M. Oestreich, *J. Am. Chem. Soc.*, 95, 6863 (1973).
(11) J. F. Bunnett and X. Creary, *J. Org. Chem.*, 40, 3740 (1975).
(12) J. F. Bunnett, *Q. Rev., Chem. Soc.*, 12, 1 (1958).

(13) J. Miller, "Aromatic Nucleophilic Substitution", Elsevier, New York, 1968, pp 140–156.
(14) J. Miller, *Aust. J. Chem.*, 9, 61 (1956).
(15) J. R. Beck and J. A. Yanher, *J. Org. Chem.*, 43, 2048 (1978).
(16) NMR spectra were recorded, in CDCl$_3$ solutions, on a 60 MHz Jeol C60HL instrument; IR spectra were recorded, in CH$_2$Cl$_2$ solutions, on a Beckman Acculab TM5 spectrometer; and GLC analyses were performed on a Hewlett-Packard 5830A chromatograph with a 20 in. 10% UCW 982 column.

Table II. Reactions of Halogenobenzenes with Sodium Thiolates in HMPA at 80 °C

substrate	R in RSNa	molar equiv of RSNa	react time, h	products[a]	% yields[b]
C₆H₅F	Me₂CH	3	2	C₆H₅SCHMe₂	71
C₆H₅Cl	Me₂CH	3	2	C₆H₅SCHMe₂	57
C₆H₅Br	Me₂CH	3	2	C₆H₅SCHMe₂	71
C₆H₅I	Me₂CH	3	4	C₆H₅SCHMe₂	81
C₆H₅Cl	Et	3	40	C₆H₅SEt	52
p-C₆H₄Cl₂	Me₂CH	1	0.5	p-ClC₆H₄SCHMe₂ and p-C₆H₄(SCHMe₂)₂[c]	72 / 7
m-C₆H₄Cl₂	Me₂CH	1	0.5	m-ClC₆H₄SCHMe₂ and m-C₆H₄(SCHMe₂)₂	60 / 5
o-C₆H₄Cl₂	Me₂CH	1	0.5	o-ClC₆H₄SCHMe₂	92
p-C₆H₄Cl₂	Me₂CH	3	4	p-C₆H₄(SCHMe₂)₂	96
m-C₆H₄Cl₂	Me₂CH	3	36	m-C₆H₄(SCHMe₂)₂	56
o-C₆H₄Cl₂	Me₂CH	3	36	o-C₆H₄(SCHMe₂)₂ and o-ClC₆H₄SCHMe₂	68 / 11
p-ClC₆H₄SCHMe₂	Me₂CH	1.5	6	p-C₆H₄(SCHMe₂)₂	94
m-ClC₆H₄SCHMe₂	Me₂CH	1.5	22	m-C₆H₄(SCHMe₂)₂	77
o-ClC₆H₄SCHMe₂	Me₂CH	1.5	30	o-C₆H₄(SCHMe₂)₂[c]	83
p-C₆H₄F₂	Me₂CH	1	4	p-C₆H₄(SCHMe₂)₂[d,e]	44
m-C₆H₄F₂	Me₂CH	1	2	m-FC₆H₄SCHMe₂ and m-C₆H₄(SCHMe₂)₂[c]	48 / 8
p-C₆H₄Br₂	Me₂CH	1	2.5	p-BrC₆H₄SCHMe₂ and p-C₆H₄(SCHMe₂)₂[c]	55 / 15
m-C₆H₄Br₂	Me₂CH	1	1	m-BrC₆H₄SCHMe₂	61
m-C₆H₄I₂	Me₂CH	1	1	m-IC₆H₄SCHMe₂ and m-C₆H₄(SCHMe₂)₂[c]	85 / 3
m-C₆H₄FBr	Me₂CH	1	1	m-BrC₆H₄SCHMe₂ and m-FC₆H₄SCHMe₂	70 / 3
m-C₆H₄ClI	Me₂CH	1	2	m-ClC₆H₄SCHMe₂ and m-IC₆H₄SCHMe₂[c]	68 / 10
p-C₆H₄FI	Me₂CH	1	1	p-IC₆H₄SCHMe₂ and p-C₆H₄(SCHMe₂)₂[d,f]	55 / 5
p-MeC₆H₄Cl	Me₂CH	3	45	p-MeC₆H₄SCHMe₂	35
p-MeOC₆H₄Cl	Me₂CH	2	25	p-ClC₆H₄OH	22
C₆H₅OMe	Me₂CH	1.2	30	C₆H₅OH	68
p-ClC₆H₄SCHMe₂	Me	1.5	1.5	p-MeSC₆H₄SCHMe₂	60
p-ClC₆H₄SCHMe₂	Et	1.5	1.5	p-EtSC₆H₄SCHMe₂	95
p-ClC₆H₄SCHMe₂	Me₃C	1.5	7	p-Me₃CSC₆H₄SCHMe₂	95
p-ClC₆H₄SCHMe₂	Ph	1.5	44	p-PhSC₆H₄SCHMe₂	31

[a] Satisfactory analytical data (±0.4% for C,H) were obtained for all new compounds. [b] Based on isolated products after column chromatography and calculated on the amount of the aryl halide employed. [c] Some unreacted starting compounds was also recovered. [d] The progress of the reaction was monitored by GLC; no p-FC₆H₄SCHMe₂ could be evidenced at any time. [e] Unreacted p-C₆H₄F₂ (50%) was recovered. [f] Unreacted p-C₆H₄FI (30%) was recovered.

times are reported in Table II. The progress of the reactions was monitored by TLC or GLC. The colorless reaction mixtures were poured into a saturated sodium chloride solution and extracted with ether. The organic layer was washed with water and dried, and the solvent was evaporated. The residue was chromatographed on silica gel using a mixture of light petroleum (bp 40–60 °C) and ethyl ether (98:2) as eluant. The products were purified by distillation.

Sulfones were obtained in 80–90% yields by oxidation of the sulfides with H₂O₂ in acetic acid solution and were purified by distillation or by crystallization from ethanol. Their IR spectra presented the characteristic absorptions at 1320–1300 and 1150 cm⁻¹.

The following compounds were obtained under the conditions and with the yields reported in Table II.

Phenyl isopropyl sulfide (2): bp 92–4 °C (16 mm) (lit.[17] bp 92–4 °C (16 mm)); NMR δ 7.25–7.0 (m, 5 H), 3.3 (spt, 1 H), 1.25 (d, 6 H, J = 7 Hz).

Phenyl ethyl sulfide: bp 128–9 °C (18 mm) (lit.[18] bp 123 °C (12 mm)); NMR δ 7.25–7.0 (m, 5 H), 2.85 (q, 2 H), 1.25 (t, 3 H, J = 7 Hz).

o-Chlorophenyl isopropyl sulfide (6): bp 113–4 °C (18 mm) (lit.[19] bp 130 °C (22 mm)); NMR δ 7.45–6.75 (m, 4 H), 3.4 (spt,

1 H), 1.3 (d, 6 H, J = 7 Hz). Sulfone: bp 187–8 °C (1 mm); NMR δ 8.15–7.8 (m, 1 H), 7.6–7.2 (m, 3 H), 3.75 (spt, 1 H), 1.3 (d, 6 H, J = 7 Hz).

m-Chlorophenyl isopropyl sulfide (7): bp 53–4 °C (1 mm) (lit.[20] bp 71–2 °C (4 mm)); NMR δ 7.25 (m, 1 H), 7.05 (m, 3 H), 3.3 (spt, 1 H), 1.25 (d, 6 H, J = 7 Hz). Sulfone: bp 105–7 °C (1 mm); NMR δ 7.9–7.3 (m, 4 H), 3.2 (spt, 1 H), 1.3 (d, 6 H, J = 7 Hz).

p-Chlorophenyl isopropyl sulfide (8): bp 117–8 °C (18 mm) (lit.[21] bp 132 °C (50 mm)); NMR δ 7.25 (s, 4 H), 3.3 (spt, 1 H), 1.25 (d, 6 H, J = 7 Hz). Sulfone: mp 88–9 °C (lit.[22] mp 89 °C); NMR δ 8.0 (s, 4 H), 3.3 (spt, 1 H), 1.35 (d, 6 H, J = 7 Hz).

o-Bis(isopropylthio)benzene (9): bp 164–5 °C (18 mm); NMR δ 7.3–7.15 (AA'BB', 4 H), 3.45 (spt, 2 H), 1.3 (d, 12 H, J = 7 Hz). Sulfone: mp 153–4 °C; NMR δ 8.4–7.8 (AA'BB', 4 H), 4.3 (spt, 2 H), 1.3 (d, 12 H, J = 7 Hz).

m-Bis(isopropylthio)benzene (10): bp 102–3 °C (0.5 mm) (lit.[23] bp 102–3 °C (0.62 mm)); NMR δ 7.35 (m, 1 H), 7.15 (m, 3 H), 3.3 (spt, 2 H), 1.25 (d, 12 H, J = 7 Hz). Sulfone: mp 99–101 °C; NMR δ 8.4–7.6 (m, 4 H), 3.3 (spt, 2 H), 1.35 (d, 12 H, J = 7 Hz).

p-Bis(isopropylthio)benzene (11): bp 167–9 °C (18 mm);

(17) H. Böhme and H. J. Gran, *Justus Liebigs Ann. Chem.*, **577**, 68 (1952).

(18) H. Britzinger and H. Ellwanger, *Chem. Ber.*, **87**, 314 (1954).

(19) K. Tanaka, J. Hagami, and A. Kaji, *Bull. Chem. Soc. Jpn.*, **44**, 2815 (1971).

(20) D. Landini and A. Maia, *J. Chem. Soc., Perkin Trans. 2*, **218** (1975).

(21) G. Borgogno, S. Colonna, and R. Fornasier, *Synthesis*, **529** (1975).

(22) G. Maccagnani and F. Taddei, *Boll. Sci. Fac. Chim. Ind. Bologna*, **23**, 381 (1965).

(23) A. M. Kuliev and S. M. Aliev, *Azerb. Khim. Zh.*, **82** (1968); *Chem. Abstr.*, **70**, 19718g (1969).

NMR δ 7.22 (s, 4 H), 3.3 (spt, 2 H), 1.25 (d, 12 H, *J* = 7 Hz). Sulfone: mp 163–4 °C; NMR δ 8.1 (s, 4 H), 3.3 (spt, 2 H), 1.35 (d, 12 H, *J* = 7 Hz).

m-Fluorophenyl isopropyl sulfide (15): bp 86–7 °C (18 mm); NMR δ 7.35–6.6 (m, 4 H), 3.35 (spt, 1 H), 1.3 (d, 6 H, *J* = 7 Hz). Sulfone: bp 159–60 °C (18 mm); NMR δ 7.8–7.2 (m, 4 H), 3.3 (spt, 1 H), 1.3 (d, 6 H, *J* = 7 Hz).

m-Bromophenyl isopropyl sulfide (16): bp 129–31 °C (18 mm); NMR δ 7.4 (m, 1 H), 7.35–6.75 (m, 3 H), 3.25 (spt, 1 H), 1.25 (d, 6 H, *J* = 7 Hz). Sulfone: bp 134–5 °C (0.1 mm); NMR δ 8.0–7.25 (m, 4 H), 3.2 (spt, 1 H), 1.3 (d, 6 H, *J* = 7 Hz).

p-Bromophenyl isopropyl sulfide (18): bp 125–6 °C (18 mm) (lit.[24] bp 120 °C (11 mm)). NMR δ 7.4–7.05 (AA'BB', 4 H), 3.25 (spt, 1 H), 1.25 (d, 6 H; *J* = 7 Hz). Sulfone: mp 63–4 °C (lit.[25] bp 66–7 °C); NMR δ 7.6 (s, 4 H), 3.15 (spt, 1 H), 1.25 (d, 6 H, *J* = 7 Hz).

m-Iodophenyl isopropyl sulfide (17): bp 114–5 °C (1 mm); NMR δ 7.7–6.7 (m, 4 H), 3.3 (spt, 1 H), 1.25 (d, 6 H, *J* = 7 Hz). Sulfone: NMR δ 8.2–7.1 (m, 4 H), 3.2 (spt, 1 H), 1.3 (d, 6 H, *J* = 7 Hz).

p-Iodophenyl isopropyl sulfide (23): bp 145–6 °C (18 mm); NMR δ 7.5–7.3 (m, 2 H), 7.0–6.8 (m, 2 H, AA'BB'), 3.25 (spt, 1 H), 1.2 (d, 6 H, *J* = 7 Hz). Sulfone: mp 68–9 °C; NMR δ 7.9–7.4 (AA'BB', 4 H), 3.15 (spt, 1 H), 1.3 (d, 6 H, *J* = 7 Hz).

p-Tolyl isopropyl sulfide: bp 125–6 °C (18 mm) (lit.[26] bp 110 °C (14 mm)); NMR δ 7.4–6.9 (AA'BB', 4 H), 3.25 (spt, 1 H), 2.25 (s, 3 H), 1.25 (d, 6 H, *J* = 7 Hz). Sulfone: mp 81–2 °C (lit.[27] mp 80 °C); NMR δ 7.9–7.2 (AA'BB', 4 H), 3.2 (spt, 1 H), 2.4 (s, 3 H), 1.3 (d, 6 H, *J* = 7 Hz).

p-(Isopropylthio)phenyl methyl sulfide (26): bp 122–3 °C (1 mm); NMR δ 7.4–7.0 (AA'BB', 4 H), 3.3 (spt, 1 H), 2.4 (s, 3 H), 1.25 (d, 6 H, *J* = 7 Hz). Sulfone: mp 139–40 °C; NMR δ 8.1 (s, 4 H), 3.3 (spt, 1 H), 3.15 (s, 3 H), 1.3 (d, 6 H, *J* = 7 Hz).

p-(Isopropylthio)phenyl ethyl sulfide (27): bp 97–8 °C (1 mm); NMR δ 7.2 (s, 4 H), 3.3 (spt, 1 H, *J* = 7 Hz), 2.9 (q, 2 H, *J* = 7 Hz), 1.25 (t, 3 H), 1.25 (d, 6 H). Sulfone: mp 117–9 °C; NMR δ 8.05 (s, 4 H), 3.3 (spt, 1 H), 3.2 (q, 2 H), 1.3 (d, 6 H, *J* = 7 Hz), 1.25 (t, 3 H, *J* = 7 Hz).

p-(Isopropylthio)phenyl tert-butyl sulfide (28): bp 134–5 °C (1 mm); mp 23–5 °C; NMR δ 7.5–7.1 (AA'BB', 4 H), 3.3 (spt, 1 H, *J* = 7 Hz), 1.3 (d, 6 H), 1.2 (s, 9 H). Sulfone: mp 235–6 °C; NMR δ 7.55 (s, 4 H), 3.3 (spt, 1 H; *J* = 7 Hz), 1.35 (s, 9 H), 1.3 (d, 6 H).

p-(Isopropylthio)phenyl phenyl sulfide (29): bp 135–6 °C (1 mm); NMR δ 7.2 (m, 9 H), 3.3 (spt, 1 H), 1.3 (d, 6 H, *J* = 7 Hz). Sulfone: mp 129–30 °C; NMR δ 8.2–7.8 (AA'BB', 4 H), 7.7 (m, 2 H), 7.5 (m, 3 H), 3.2 (spt, 1 H), 1.25 (d, 6 H, *J* = 7 Hz).

p-Fluorophenyl Isopropyl Sulfide (19). This compound was prepared from p-fluorothiophenol and 2-iodopropane fol-

lowing the procedure[22] reported for the synthesis of p-chlorophenyl isopropyl sulfide: yields 75%; bp 81–2 °C (18 mm) (lit.[28] bp 110 °C (23 mm)); NMR δ 7.4–6.7 (m, 4 H), 3.2 (spt, 1 H), 1.2 (d, 6 H, *J* = 7 Hz). Sulfone: mp 86–8 °C; NMR δ 7.8 (m, 2 H), 7.2 (m, 2 H), 3.2 (spt, 1 H), 1.25 (d, 6 H, *J* = 7 Hz).

Competitive Experiments. Solutions of the aryl halide (1.25 mmol), o-chlorophenyl isopropyl sulfide (1.25 mmol), and Me$_2$CHSNa (0.2 mmol) in HMPA (4 mL) were put in sealed tubes and heated at 80 °C for 6 h. The reaction mixture was worked up according to the general procedure described above, and the organic layer was directly analyzed by GLC. Pure substitution products were used to determine the relative detector response. Relative rates were calculated according to the following expression which refers to the halogenobenzenes: $k_{ArX}/k_6 = [2][6]_0/[9][ArX]_0$. Three independent experiments were performed with each substrate. The averaged values of the relative rates are reported in Table I; these values can be considered accurate to ±5%.

Reactions in which p-chlorotoluene was used as reference substrate were carried out under the same conditions.

In the case of iodobenzene, the relative rate was also determined from experiments effected in the presence of azobenzene (0.2 mmol).

(24) H. S. Holt and E. E. Reid, *J. Am. Chem. Soc.*, **46**, 2329 (1924).
(25) E. Koenigs and A. Wylezich, *J. Prakt. Chem.*, **132**, 24 (1931).
(26) K. Auwers and F. Arndt, *Chem. Ber.*, **42**, 2706 (1909).
(27) J. Troeger and R. Uhde, *J. Prakt. Chem.*, **59**, 320 (1899).

(28) N. Sharghi and I. Lalezari, *J. Chem. Eng. Data*, 8, 276 (1963); *Chem. Abstr.*, **59**, 567g (1963).