bined with 2 mol of ethanethiol, then with 1 mol of methanol. Similarly, 3 mol of ethanethiol was used to obtain triethyl phosphorotrithioite.[23] However, attempts to make *S*-ethyl-*O,O*-dimethyl phosphorothioite were unsuccessful. Combining phosphorus trichloride with first 2 mol of methanol, then 1 mol of ethanethiol, or in the reverse order, yielded fractions distilling over a wide temperature range (30–81°, 0.02–8.0 mm). The lower boiling fractions consisted primarily of dimethyl phosphonate; higher boiling fractions contained *S*-ethyl-*O,O*-dimethyl phosphorothioate and *S*-ethyl-*O,O*-dimethyl phosphorodithioate. Treating freshly prepared ethyl phosphorodichloridothioite[24] with methanol led to similar results. Diethyl phosphonothionate was prepared by the reaction of distilled commercial diethyl phosphorochloridite with hydrogen sulfide in the presence of pyridine.[25] *S,S*-Diethyl-*O*-methyl phosphorodithioate resulted from air oxidation of the corresponding phosphite. Triethyl phosphorotrithiolate occurred as a high-boiling fraction in the distillation of the corresponding phosphite. Since it was found that sulfur does not add to this phosphite, triethyl phosphorotetrathioate was prepared by reaction of the sodium salt of ethanethiol with thiophosphoryl chloride.[26] Contrary to a statement in the reference, vacuum distillation of the product did not degrade it to triethyl phosphorotrithioite. Preparations of sodium phosphorotrithioate, sodium phosphorotetrathioate, and tri-*tert*-butyl phosphorotetrathioate were referred to earlier.[18,19] Extended refluxing of 2-methyl-2-propanethiol with phosphorus trichloride produced, not tri-*tert*-butyl phosphorotrithioite as has been indicated,[27] but pure tri-*tert*-butyl phosphorotrithiolate (as indicated by its ^{31}P NMR spectrum, particularly the chemical shift). Commercially available fluorosulfuric acid was twice distilled before use in the preparation of solutions.

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Nucleophilic Displacements on Halogen Atoms. V. Reactions of α-Halo Sulfones with Sterically Hindered Nucleophiles

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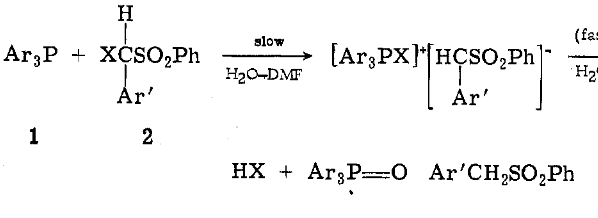
The rates of reaction of α-bromo- and α-iodo-*m*-cyanobenzyl phenyl sulfones (**3**) with a number of sterically hindered phosphines in aqueous DMF are reported. The variation in rates for tris(*o*-tolyl)phosphine (**4**) and tris(*o*-anisyl)phosphine (**5**) with **3a** is best explained in terms of a steric rather than special electronic effect. The reactions of **3** with *cis*-bis(diphenylphosphino)ethene (**8**) and bis(diphenylphosphino)ethane (**11**) exhibit no unusual characteristics.

The reductions of α-halobenzyl phenyl sulfones by triarylphosphines has been shown to involve nucleophilic attack on the halogen atom (eq 1).[1–3] Hydrolysis of the charged complex yields the phosphine oxide, the reduced sulfone, and a hydrohalic acid.

In these reports it was observed that, contrary to the normal SN2 reaction at carbon atoms, the reactivity decreased in the order α-Br > α-I ≫ α-Cl. The anomalous behavior of the α-iodobenzyl phenyl sulfones was rationalized in terms of the relative strengths of the bonds formed and broken upon entering the transition state.



$$\mathrm{Ar_3P} + \mathrm{X}\overset{\mathrm{H}}{\underset{\mathrm{Ar'}}{\mathrm{C}}}\mathrm{SO_2Ph} \xrightarrow[\mathrm{H_2O\text{-}DMF}]{\text{slow}} [\mathrm{Ar_3PX}]^+\left[\mathrm{H}\underset{\mathrm{Ar'}}{\mathrm{C}}\mathrm{SO_2Ph}\right]^- \xrightarrow[\mathrm{H_2O}]{\text{(fast)}} \mathrm{HX} + \mathrm{Ar_3P{=}O} \quad \mathrm{Ar'CH_2SO_2Ph} \qquad (1)$$

1 **2**

It has been demonstrated that this reaction is strongly dependent upon the electron-withdrawing ability of the parent sulfone.[2] ρ values, determined from the variation of

Table I
Rate Constants for the Reactions of 3a and 3b with Phosphines 4–12 in 90% Aqueous DMF

Sulfone	Phosphine[a]	Temp, °C	$10^3 k_2$, $M^{-1} \cdot \sec^{-1}$
3a	4	50.00	0.462 ± 0.018
		61.20	0.905 ± 0.012
		75.00	2.10 ± 0.06
		84.00	3.10 ± 0.08
3a	5	0.00	252 ± 7
		10.00	402 ± 5
		20.00	715 ± 9
		25.00	923 ± 2
3a	6	25.40	66.9 ± 0.4
		37.5	145 ± 5
		50.3	303 ± 8
		58.0	393 ± 6
3a	7	0.00	119 ± 10
		10.00	184 ± 7
		20.00	355 ± 6
		24.30	451 ± 5
3a	8	50.00	0.669 ± 0.004
		66.00	1.72 ± 0.09
		75.00	2.80 ± 0.20
3a	9	20.00	6.31 ± 0.07
		50.00	33.3 ± 0.7
		74.60	109 ± 10
		83.60	148 ± 12
3a	10	20.00	23.2 ± 0.5
		35.00	41.2 ± 0.5
		50.00	69.3 ± 0.9
		67.00	136 ± 8
3a	11	25.60	131 ± 2
		35.00	247 ± 3
		43.60	424 ± 10
		45.00	550 ± 10
3a	12	5.70	760 ± 30
		10.00	1040 ± 30
		14.80	1330 ± 10
		20.00	1820 ± 35
3b	5	10.00	32.8 ± 0.1
		20.00	64.1 ± 0.1
		35.00	219 ± 4
3b	6	43.30	11.2 ± 1.2
		50.00	17.8 ± 1.0
		58.50	30.8 ± 1.3
		60.50	36.0 ± 1.2
3b	7	0.00	6.66 ± 0.14
		20.00	29.1 ± 0.1
		35.00	94.3 ± 0.1
		52.50	318 ± 0.07
3b	8	20.00	0.0966 ± 0.005
		58.55	0.750 ± 0.022
		65.90	1.02 ± 0.20
		71.70	1.30 ± 0.02
3b	9	25.00	0.301 ± 0.01
		47.97	1.63 ± 0.05
		58.55	2.93 ± 0.18
		71.70	6.57 ± 0.26
3b	10	20.00	2.35 ± 0.18
		50.00	11.2 ± 1.0
		67.00	25.7 ± 1.8
3b	11	25.60	7.74 ± 0.20
		35.00	12.0 ± 0.1
		50.00	30.6 ± 0.4
		73.00	128 ± 10
3b	12	14.80	43.6 ± 0.7
		19.10	59.5 ± 1.2
		28.00	130 ± 1.5

[a] Rate of reaction of **3b** with **4** was too slow to measure accurately owing to decomposition of **3b** at high temperatures (>90°).

reaction rates with changes in the substituents on the benzyl group in the sulfones **2**, are $(\mathrm{Cl})\rho = +2.33$, $(\mathrm{Br})\rho = +5.97$, and $(\mathrm{I})\rho = +6.29$. These data indicate a carbanionic transition state with respect to sulfone.

We have also shown,[3] by varying the substituents on the triarylphosphine, that the reaction is quite sensitive to changes in the nucleophile. These ρ values, determined from the changes in the phosphine, are $(\mathrm{Cl})\rho = -1.84$, $(\mathrm{Br})\rho = -3.03$, and $(\mathrm{I})\rho = -3.30$. These data indicate that a large degree of positive charge is present on the phosphorus atom during the transition state and that the phosphorus–halogen bond formation process is very near completion.

We have examined the rates of reaction of various hindered phosphine nucleophiles with α-halo-m-cyanobenzyl phenyl sulfone (**3**) in search of evidence for the steric requirement for the S_N2 displacement by phosphines on halogen atoms. Two types of substituted tertiary phosphines were used in this study: ortho-substituted triarylphosphines (**4** and **5**) (rates for the para-substituted isomers **6** and **7** also are reported for comparison) and substituted vinyldiphenylphosphines (**8–10**) (rates for the ethyldiphenylphosphines **11** and **12** also are reported for comparison). The rate data for the reactions of **4–12** with **3a** and **3b** in 90% aqueous DMF (eq 2) are reported in Tables I and II.

$$m\text{-}\mathrm{CNC_6H_4CHXSO_2Ph} + \mathrm{R_3P} \xrightarrow{\mathrm{H_2O{-}DMF}}$$

3a, X = Br **4–12**
b, X = I

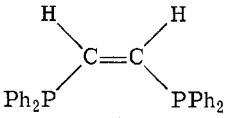
$$m\text{-}\mathrm{CNC_6H_4CH_2SO_2Ph} + \mathrm{R_3P{=}O} + \mathrm{HX} \qquad (2)$$

$(o\text{-}\mathrm{CH_3C_6H_4})_3\mathrm{P}$ **4**

$(o\text{-}\mathrm{CH_3OC_6H_4})_3\mathrm{P}$ **5**

$(p\text{-}\mathrm{CH_3C_6H_4})_3\mathrm{P}$ **6**

$(p\text{-}\mathrm{CH_3OC_6H_4})\mathrm{P}$ **7**



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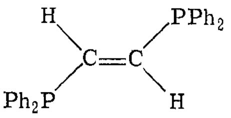

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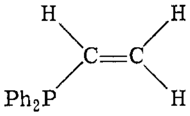

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$\mathrm{Ph_2PCH_2CH_2PPH_2}$ **11**

$\mathrm{Ph_2PCH_2CH_3}$ **12**

The most striking feature of Table II is the large difference in rates between **4** (ortho)/**6** (para) when compared with the methoxy compounds **5** (ortho)/**7** (para). An ortho methyl substituent greatly reduces the rate of reaction when compared to the p-methyl compound $[(k_p/k_o)_{\mathrm{CH_3}} = 810$ for the reactions of **6** and **4** with **3a**], whereas for the reactions of the methoxyarylphosphines **5** and **7** the k_p/k_o ratio is reversed, i.e., $(k_p/k_o)_{\mathrm{OCH_3}} = 0.5$. The ratio $k_{o\text{-}\mathrm{OCH_3}}/k_{o\text{-}\mathrm{CH_3}}$ for the reactions of **5** and **4** with the α-bromo sulfone **3a** is greater than 10^4. These data may be compared with those rates measured for reactions 3–5.

$$\mathrm{XC_6H_4NH_2} + \mathrm{PhCOCl} \longrightarrow \mathrm{XC_6H_4NHCOPh} \quad \frac{k_{o\text{-}\mathrm{OCH_3}}}{k_{o\text{-}\mathrm{CH_3}}} = 3.2$$ (3)[4]

$$\mathrm{XC_6H_4N(CH_3)_2} + \mathrm{CH_3I} \longrightarrow \mathrm{XC_6H_4\overset{+}{N}(CH_3)_3I^-} \quad \frac{k_{o\text{-}\mathrm{OCH_3}}}{k_{o\text{-}\mathrm{CH_3}}} = 60$$ (4)[5]

$$\mathrm{(XC_6H_4)_3P} + \mathrm{PhCH_2Cl} \longrightarrow \mathrm{(XC_6H_4)_3\overset{+}{P}CH_2Ph\,Cl^-} \quad \frac{k_{o\text{-}\mathrm{OCH_3}}}{k_{o\text{-}\mathrm{CH_3}}} = 610 \qquad (5)$$

Table II
Rate Constants and Activation Parameters for the Reaction of α-Halo Sulfones 3 with Phosphines 4–12 in 90% Aqueous DMF at 25° [a]

Sulfone	Phosphine	k_2, M^{-1} sec^{-1}	$\Delta H^\ddagger$	$\Delta S^\ddagger$
3a	**4**	8.70×10^{-5}	12.2	−36
3a	**5**	9.06×10^{-1}	9.0	−33
3a	**6**	6.74×10^{-2}	11.7	-29_4
3a	**7**	4.53×10^{-1}	8.5	-32_5
3a	**8**	1.26×10^{-4}	12.2	−35
3a	**9**	8.55×10^{-3}	9.8	−35
3a	**10**	2.79×10^{-2}	6.8	−42
3a	**11**	1.23×10^{-1}	11.1	−25
3a	**12**	2.41	9.3	-26_6
3b	**5**	1.02×10^{-1}	12.6	−25
3b	**6**	2.82×10^{-3}	13.5	−25
3b	**7**	4.69×10^{-2}	12.4	−23
3b	**8**	9.59×10^{-5}	10.8	−39
3b	**9**	3.05×10^{-4}	12.8	-31_6
3b	**10**	3.11×10^{-3}	9.5	−38
3b	**11**	6.67×10^{-3}	11.7	-29_6
3b	**12**	1.01×10^{-1}	13.8	−27

[a] The k_2 at 25° for the reaction of **3a** with triphenylphosphine is 2.07×10^{-3} M^{-1} sec^{-1}; the k_2 at 25° for the reaction of **3b** with triphenylphosphine is 7.76×10^{-5} M^{-1} sec^{-1}.[2]

The data for eq 5 have been explained in terms of a through space $(2p\text{–}3d)_\pi$ overlap of the *o*-anisyl groups with the incipient phosphonium cation in the transition state.[6] Indeed, if $k_{o\text{-OCH}_3}/k_{o\text{-CH}_3}$ is a measure of such interaction, we are observing an even stronger interaction during the reaction of **5** with the bromo sulfone **3a**.[7] However, this interpretation loses force when one compares the $(k_o/k_p)_{\text{OCH}_3}$ ratios for reactions 2–5; these ratios vary from 0.3 to 4.[11] The $(k_p/k_o)_{\text{CH}_3}$ ratios for reactions 3–5 are 11, 61, and 80, respectively. The small variation in $(k_o/k_p)_{\text{OCH}_3}$ for reactions 2–5 seems inconsistent with a special electronic effect on an *o*-methoxy group, i.e., if $(2p\text{–}3d)_\pi$ overlap is important,[10] then it seems most unlikely that this effect through bonds (viz., *p*-OCH$_3$) would parallel the effect through space (viz., *o*-OCH$_3$) for a series of such divergent reactions as 2–5.

Charton[12] maintains that the differences in the behavior of ortho substituents (other than H or very large groups such as *tert*-butyl) in the reactions of ortho-substituted arenes are due principally to electronic rather than steric factors, although some reactions do appear to be strongly influenced by the size of the ortho groups.[13] Steric influences likely may be involved for reactions 2 and 5. Certainly, in going from reaction 3 to reaction 5, the steric requirements are increasing in the transition states;[14] however, the steric requirements for a displacement reaction on a univalent bromine atom are not easy to assess relative to reactions at a tetrahedral carbon atom.[15] The transition state for reaction 2 lies very far toward bond making and bond breaking as shown by the large Hammett ρ values.[2,3] This means that the P–Br bond is nearly formed in the transition state, and the geometry of the activated complex is close to that of a halotriarylphosphonium cation in which the Ar–P–Ar bond angle is ca. 110°.[18] At first glance, this would seem to result in a reduction of back strain, since the Ar–P–Ar bond angle in tris(*o*-tolyl)phosphine is only 102.5°.[19] However, from crystal structure work and NMR studies in solution, there is known to be significantly more crowding in tris(*o*-tolyl)phosphine selenide (Ar–P–Ar bond angles of 107°) than in either the corresponding phosphine or phosphine oxide.[19] This crowding appears to be due to an unfavorable steric interaction between the *o*-methyl groups and the large selenium atom. Since bromine and selenium atoms are nearly the same size, one might expect a similar unfavorable effect in the transition state for reaction 2 in the case of tris(*o*-tolyl)phosphine. This effect would be greatly diminished for tris(*o*-anisyl)phosphine, since the methoxy group is effectively considerably smaller than a methyl group.[20]

The reactions of the vinyldiphenylphosphines with the α-bromo sulfone **3a** and the α-iodo sulfone **3b** show expected behavior with no special effect noted for those phosphines **8** and **11** in which a second phosphino group could have assisted in the transition state.[23] The difference in reactivity between *cis*-**8** and *trans*-**9** is probably steric in origin whereas the difference in reactivity of **9**, **10**, **11**, and **12** is electronic.

Experimental Section

Kinetic measurements were taken in 90% DMF–H$_2$O. Distilled deionized water was used. Reagent grade dimethylformamide was twice distilled from P$_2$O$_5$ and stored under nitrogen. Separate solutions of phosphine and sulfone were placed in a constant-temperature bath and allowed to equilibrate for 30 min. The solutions were mixed in a Freas conductivity cell which was thermostated in the same constant-temperature bath. Conductance readings were taken at various intervals with a Barnstead conductivity bridge, Model PM-70CB. The rate constants were obtained by plotting log $(C_\infty - C_t)$ vs. time, where C is the conductance reading in mhos. The second-order rate constants were obtained by dividing the pseudo-first-order rate constants by the concentrations of the phosphine. The phosphine concentrations were 0.10–0.20 *M* and the sulfone concentration was 0.0010 *M*.

All the phosphines used in this study have been prepared previously. The observed physical and spectral data agreed well with those reported in the literature. Triarylphosphines[25] were prepared from an excess of the appropriate aryl Grignard reagent with phosphorus trichloride and recrystallized from ethanol under nitrogen. *cis*- and *trans*-1,2-bis(diphenylphosphino)ethene and 1,2-bis(diphenylphosphino)ethane were prepared from the appropriate alkyl chloride and lithium diphenylphosphide according to the method of Aguiar.[26] The remaining alkyldiphenylphosphines were prepared via Grignard reaction with diphenylchlorophosphine.[27]

The preparation of the α-halobenzyl phenyl sulfones **3a** and **3b** have been described previously.[2] The reactions of **3a** and **3b** with phosphines **4–12** give the reduced sulfone, *m*-cyanobenzyl phenyl sulfone, in >90% yield.

Acknowledgment. Support from the University of Maryland Computer Science Center is gratefully acknowledged.

Registry No.—**3a**, 41037-82-5; **3b**, 41037-87-0; **4**, 6163-58-2; **5**, 4731-65-1; **6**, 1038-95-5; **7**, 855-38-9; **8**, 983-80-2; **9**, 983-81-3; **10**, 2155-96-6; **11**, 1663-45-2; **12**, 607-01-2.

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Ion Radicals. XXXIII. Reactions of 10-Methyl- and 10-Phenylphenothiazine Cation Radicals with Ammonia and Amines. Preparation and Reactions of 5-(*N*-Alkyl)sulfilimines and 5-(*N,N*-Dialkylamino)sulfonium Salts[1]

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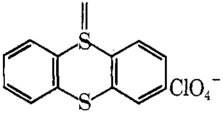
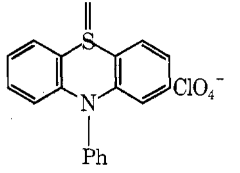
10-Phenyl- (7) and 10-methylphenothiazine cation radical perchlorate (8) reacted readily with primary alkyl amines in acetonitrile solution to form N-protonated *N*-alkylsulfilimine perchlorates, and the parent heterocycle was also formed. Reaction of 7 and 8 with dialkylamines gave *N,N*-dialkylsulfilimine perchlorates. Tertiary amines led to reduction of the cation radicals; with ammonia, dimeric products were formed. 5-(*tert*-Butylimino)-5,5-dihydro-10-methylphenothiazine perchlorate with perchloric acid gave 10-methylphenothiazine cation radical; with HCl, formation of the cation radical was followed by reduction and chlorination.

Although *N*-arylsulfilimines have been known since 1968,[4-10] *N*-alkylsulfilimines were unknown until very recently. Franz and Martin reported in 1973 that the reaction of diphenyl(1,1,1,3,3,3-hexafluoro-2-phenyl-2-propoxy)sulfurane [**1**, $R_F = C(CF_3)_2Ph$] with primary amides gave *N*-aryl- and *N*-alkylidiphenylsulfilimines (**2**, eq 1).[8] Subsequently, Shine and Kim[11] reported that the cation radicals of thianthrene and 10-phenylphenothiazine reacted with *tert*-butylamine to give the perchlorates **3** and **4**, respectively, which were easily deprotonated to give the corresponding *N*-*tert*-butylsulfilimines. Also, dimethylamine reacted with thianthrene cation radical perchlorate to give **5**. At that time the curious reaction was also discovered in which not only ammonia but also methyl-, ethyl-, propyl-, and cyclohexylamine reacted with thianthrene cation radical perchlorate to give the dimeric product **6a**. It appeared at that time, therefore, that the preparation of *N*-alkylsulfilimines by reaction of organosulfur cation radicals with alkylamines would not be a viable reaction. We now show that this is not so. Most recently, Franz and Martin have reported that sulfuranes such as **1** react with primary aryl- and alkylamines to give *N*-aryl- and *N*-alkylsulfilimines (**2**).[12]

$$\underset{\mathbf{1}}{Ph_2S(OR_F)_2} + PhCONHR \longrightarrow \underset{\mathbf{2}}{Ph_2S{=}NR} + PhCO_2R_F + R_FOH \quad (1)$$



3



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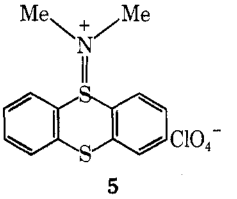
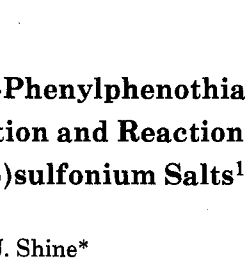


5



6a, X = S
b, X = *N*-Ph
c, X = *N*-Me

Results and Discussion

Preparation of Sulfilimines. We have found that, in contrast with thianthrene cation radical perchlorate, 10-phenyl- (**7**) and 10-methylphenothiazine cation radical perchlorate (**8**) react with a variety of simple primary alkylamines to give *N*-alkylsulfilimines. Reaction with dialkylamines gives products corresponding with **5**, i.e., *N,N*-dialkylaminosulfonium salts, while reaction with tertiary amines causes reduction to the parent compounds. Reaction with primary and secondary amines was carried out in acetonitrile solution and was rapid. Not only was the sulfilimine-