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Nucleophilic Displacements on Halogen Atoms. 8.[1] Reactions of α-Halo Sulfones with Triarylphosphines, Alkyldiphenylphosphines, and Phosphites

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A series of α-halo sulfones, m-(CN)$C_6H_4CHXSO_2Ph$, **1a** (where X = Cl, Br, and I), was treated with a set of substituted triarylphosphines (**2**) in aqueous DMF to give the reduced sulfone m-(CN)$C_6H_4CH_2SO_2Ph$ (**5a**) and the triarylphosphine oxides. Variation of the rates of reaction of **1a** with **2** correlated with normal Hammett σ constants for the substituents in **2** to yield (Cl)$\rho = -1.84$; (Br)$\rho = -3.03$; (I)$\rho = -3.30$. A similar study for the reactions of **1a** (X = Br) with alkyldiphenylphosphines showed a good correlation between Taft σ^* constants and log k_2 to give a $\rho = -4.21$. However, the rates of reaction of **1a** (X = Br) with trialkyl phosphites showed no correlation with Taft σ^* constants, and the triaryl phosphites contrary to expectation reacted more readily than trialkyl phosphites. The reactions of **1a** (X = Br and I) with optically active phosphine **6** gave the phosphine oxide **7** with inversion of configuration. Triphenylarsine and triphenylstibine were shown to be poor nucleophiles in these dehalogenation reactions.

Nucleophilic displacement reactions have occupied a central position in the studies of organic reaction mechanisms for over half a century.[2] Although the organic chemist has been concerned principally with nucleophilic substitutions at carbon atoms,[3] it is clear that many electrophilic sites such as oxygen,[4] nitrogen,[5] silicon,[6] sulfur,[7] phosphorus,[8] arsenic,[9] and many other inorganic elements[10] are open to nucleophilic attack if an appropriate leaving group is present. We have been examining nucleophilic displacement reactions on halogen atoms in α-halo sulfones with tertiary phosphines[11] and arenesulfinates as nucleophiles.[1]

The reactions of α-halobenzyl phenyl sulfones (1) with triphenylphosphine (TPP) in 90% aqueous dimethylformamide (DMF) (eq 1) are characterized by the following: (1) reduced sulfones **5** are produced quantitatively with no side reactions observed; (2) kinetics are second order, first order each in sulfone **1** and TPP; (3) large positive ρ values (ca. +6 for **1**, X = Br and I) were found; (4) the intermediate ions **3** and **4** are formed slowly and irreversibly, and their hydrolysis by protic solvent is very rapid; (5) for **1** (X = Cl, Br, and I), $k_{Br} > k_I \gg k_{Cl}$.[11a] These results and others obtained in a study of steric effects in the reactions of **1** with ortho-substituted triarylphosphines[11b] led us to maintain that a high degree of carbon–halogen bond breakage had occurred in the transition state. These results have encouraged us to examine more carefully the role of the phosphine nucleophile in these reactions. In particular, we now report the results of a study in which the variation in the phosphorus nucleophiles, tertiary phosphines and phosphites, has yielded detailed information on the mechanism of reaction 1 from the standpoint of the nucleophile.

$$\underset{1}{ArCHXSO_2Ph} + \underset{2}{Ar_3'P} \longrightarrow \underset{3}{[ArCHSO_2Ph]^-}\ \underset{4}{Ar_3'\overset{+}{P}X} \xrightarrow[DMF]{H_2O} \underset{5}{ArCH_2SO_2Ph} + Ar_3'PO + HX \qquad (1)$$

Results and Discussion

A series of meta- and para-substituted triarylphosphines were prepared and allowed to react with the α-halo-m-cyanobenzyl phenyl sulfones [**1a**, Ar = m-(CN)C_6H_4] in 90% aqueous DMF (eq 2). The reactions were monitored by conductance readings (see Experimental Section) as a function of the formation of hydrohalic acid from the neutral starting materials. The rate data are reported in Tables I–IV. The data in Table IV can be compared with similar activation parameter data gathered from other SN2 reactions (Table V).

$$\underset{\mathbf{1a}\ (X = Cl, Br, I)}{m\text{-}(CN)C_6H_4CHXSO_2Ph} + \underset{2}{Ar_3'P} \xrightarrow[DMF]{H_2O} \underset{\mathbf{5a}}{m\text{-}(CN)C_6H_4CH_2SO_2Ph} + Ar_3'PO + HX \qquad (2)$$

Tertiary phosphines have been shown to be effective nonbasic nucleophiles of wide utility.[12] They are classed as soft nucleophiles[12,13] and owe their high nucleophilicity in large part to their polarizability. The collection of data in Table V is an attempt, albeit of limited success, to correlate the various enthalpies and entropies of activation associated with the nucleophilicity of TPP with the nature of the electrophilic centers. This problem is complicated by (1) inherent difficulties in interpreting relatively small differences in the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values,[14] (2) relatively large errors in $\Delta S^{\ddagger}$ values,[15] and (3) use of different solvents for the reactions reported in Table V. In general, $\Delta S^{\ddagger}$ appears to be more negative for

Table I. Second-Order Rate Constants for the Reactions of α-Chloro-*m*-cyanobenzyl Phenyl Sulfone with Triarylphosphines, $(Y\text{-}C_6H_4)_3P$, in 90% Aqueous DMF

Y	Temp, °C (±0.1°)	$10^4 k_2$, $M^{-1} s^{-1}$
p-CH_3	50.0	2.17 ± 0.10
	61.4	4.74 ± 0.09
	73.0	10.2 ± 0.5
	97.2	44.8 ± 0.8
p-OCH_3	50.0	6.09 ± 0.10
	60.0	10.5 ± 0.6
	71.1	23.1 ± 0.9
	83.6	43.9 ± 0.1
m-CH_3	50.0	1.19 ± 0.07
	60.7	4.20 ± 0.12
	79.5	12.6 ± 1.4
	90.9	21.0 ± 0.8
p-C_6H_5	69.2	1.01 ± 0.03
	79.5	2.23 ± 0.03
	90.9	4.04 ± 0.15
	97.2	7.93 ± 0.09
H	80.6	3.10 ± 0.06
	90.8	6.33 ± 0.16
	100.1	11.6 ± 0.2

displacements by TPP on the harder electrophilic sites (carbon and nitrogen) than the $\Delta S^{\ddagger}$ values observed with the softer electrophilic centers (peroxide oxygen, sulfur, selenium, and halogen atoms). However, an analysis of the difference in the activation parameters for the reactions of the α-bromo and α-iodo sulfones **1a** with TPP (Table IV) points out a clear and significant difference between these two α-halo sulfone systems; the $\Delta H^{\ddagger}$'s for the α-bromo sulfones are ca. 4 kcal/mol less than the $\Delta H^{\ddagger}$'s for the α-iodo sulfones, but $\Delta S^{\ddagger}$'s for the α-bromo sulfones are ca. 8 eu more negative than the $\Delta S^{\ddagger}$'s for the α-iodo sulfones. Note that if the only difference in reactivity between the bromides and iodides was reflected in the $\Delta H^{\ddagger}$'s, the bromides would be ca. 10^3 times more reactive than the iodides instead of only ca. 20 as shown experimentally. These data support the contention[11] that the increased reactivity of the bromides over the iodides in these reductions is due to the enhanced bond strength of the phosphorus–bromine bond (cf. the phosphorus–iodine bond) that is forming in the transition state. The less negative value for the $\Delta S^{\ddagger}$'s associated with the iodo sulfones can be attributed to the lower ordering of polar solvent molecules about the more bulky iodophosphonium cation 4 (X = I) in the transition state.

Hammett plots of log *k* (Table IV) vs. $\Sigma\sigma$ give linear correlations with the following results: $(Cl)\rho = -1.84$ ($r = 0.993$); $(Br)\rho = -3.03$ ($r = 0.996$); $(I)\sigma = -3.30$ ($r = 0.990$). As in the case for the reactions of substituted 1 with TPP,[11a] $(I)\rho \gtrsim (Br)\rho \gg (Cl)\rho$, but in the present study the ρ values are negative since electron-donating groups on the phosphines increase reaction rates. These ρ values are compared with some previously determined ρ values from the literature in Table VI.

Since in the reactions of 1 with TPP the rate data correlated with σ^- constants significantly better than with normal σ constants,[11a] it was of interest to see whether the reaction rates of **1a** with substituted triarylphosphines (eq 2) would correlate better with σ^+ or σ constants. The correlation of reaction rates (Table IV) with σ^+ constants gave poorer correlation coefficients ($r < 0.93$) than those observed using normal Hammett σ values (vide supra). In addition, we could find no report in the literature of a study similar to those reported in Table VI where the nucleophilicity or basicity of substituted arylphosphines showed a better correlation with σ^+ than normal σ constants.[20]

Table II. Second-Order Rate Constants for the Reactions of α-Bromo-*m*-cyanobenzyl Phenyl Sulfone with Triarylphosphines, $(Y\text{-}C_6H_4)_3P$, in 90% Aqueous DMF

Y	Temp, °C (±0.1°)	$10^2 k_2$, $M^{-1} s^{-1}$
p-CH_3	25.4	6.69 ± 0.04
	37.5	14.5 ± 0.4
	50.3	30.3 ± 0.4
	58.0	39.3 ± 0.5
p-OCH_3	0.0	11.9 ± 0.7
	10.0	18.4 ± 0.7
	20.0	35.5 ± 0.5
	24.3	45.1 ± 0.5
p-Cl	65.5	0.0295 ± 0.0006
	73.0	0.0473 ± 0.0010
	85.0	0.0981 ± 0.0005
	93.5	0.158 ± 0.007
m-CH_3	20.0	1.05 ± 0.05
	30.8	2.24 ± 0.11
	42.8	4.94 ± 0.07
	50.0	7.60 ± 0.07
p-C_6H_5	20.0	0.119 ± 0.001
	30.8	0.269 ± 0.002
	42.8	0.617 ± 0.004
	50.0	1.00 ± 0.03
H	40.1	0.615 ± 0.028
	50.1	1.14 ± 0.07
	60.3	2.24 ± 0.04

Table III. Second-Order Rate Constants for the Reactions of α-Bromo-*m*-cyanobenzyl Phenyl Sulfone with Triarylphosphines, $(Y\text{-}C_6H_4)_3P$, in Aqueous DMF

Y	Temp, °C (±0.01°)	$10^2 k_2$, $M^{-1} s^{-1}$
p-CH_3	43.3	1.08 ± 0.06
	50.0	1.75 ± 0.08
	58.5	3.14 ± 0.07
	60.5	3.60 ± 0.07
p-OCH_3	0.0	0.662 ± 0.011
	20.0	2.91 ± 0.02
	35.0	9.44 ± 0.01
	52.5	32.8 ± 1.0
p-$C(CH_3)_3$	0.0	0.0942 ± 0.0005
	20.0	0.523 ± 0.003
	42.2	3.19 ± 0.06
m-CH_3	42.8	0.237 ± 0.012
	58.8	0.810 ± 0.005
	69.2	1.71 ± 0.12
	77.9	3.10 ± 0.02
p-C_6H_5	42.8	0.0375 ± 0.0021
	58.8	0.139 ± 0.003
	77.9	0.595 ± 0.004
H	40.1	0.0350 ± 0.0006
	50.2	0.0930 ± 0.0001
	60.3	0.216 ± 0.001

In general it is comparatively rare to find a case involving third-row elements where the Hammett correlations show a better fit with the exalted σ values (σ^+ or σ^-) than with normal σ values. This is not unexpected since delocalization effects are much more prominent between members of the second-row elements than with any other combination of bonding between members of the other row elements.[24] However, in another related study, the reductions of α-bromo- and α-iodo-*p*-cyanobenzyl phenyl sulfones by substituted sodium arenesulfinates showed Hammett correlations with σ^+ constants with a significantly better fit ($r > 0.998$) than those correlations observed with normal σ values ($r < 0.8$).[1,25] It is

Table IV. Rate Constants and Activation Parameters for the Reactions of α-Halo-*m*-cyanobenzyl Phenyl Sulfones, *m*-(CN)$C_6H_4CHXSO_2Ph$, with Triarylphosphines, $(Y\text{-}C_6H_4)_3P$, in 90% Aqueous DMF at 25 °C

X	Y	$10^4 k_2$, $M^{-1} s^{-1}$	$\Delta H^{\ddagger}$, kcal/mol	$-\Delta S^{\ddagger}$, eu	$(Y\text{-}C_6H_4)_3P$ registry no.
Cl[a]	*p*-OCH_3	1.06 ± 0.07	13.9 ± 0.8	33 ± 2	855-38-9
	p-CH_3	0.273 ± 0.006	16.0 ± 0.6	30 ± 2	1038-95-5
	m-CH_3	0.113 ± 0.008	17.4 ± 1.2	25 ± 3	6224-63-1
	H	0.0275 ± 0.0008	17.2 ± 0.4	26 ± 1	603-35-0
	p-C_6H_5	0.0203 ± 0.0009	18.2 ± 0.8	27 ± 2	13885-05-7
Br[b]	*p*-OCH_3	4570 ± 60	8.5 ± 0.6	33 ± 2	
	p-CH_3	683 ± 4	11.7 ± 0.3	30 ± 1	
	m-CH_3	147 ± 7	13.0 ± 0.6	27 ± 2	
	H	20.7 ± 1.6	12.7 ± 0.8	28 ± 3	
	p-C_6H_5	18.0 ± 0.3	13.7 ± 0.2	28 ± 1	
	p-Cl	0.148 ± 0.007	15.2 ± 0.7	33 ± 2	1159-54-2
I[c]	*p*-OCH_3	406 ± 5	12.0 ± 0.2	23 ± 1	
	p-CH_3	26.1 ± 0.7	15.0 ± 1.6	25 ± 4	
	p-$C(CH_3)_3$	73.7 ± 0.5	13.8 ± 0.2	25 ± 1	29949-79-9
	m-CH_3	5.06 ± 0.08	16.5 ± 0.9	21 ± 2	
	H	0.776 ± 0.004	18.5 ± 0.2	17 ± 1	
	p-C_6H_5	0.688 ± 0.009	18.0 ± 0.4	21 ± 1	

[a] Registry no., 41037-76-7. [b] Registry no., 41037-82-5. [c] Registry no., 41037-87-0.

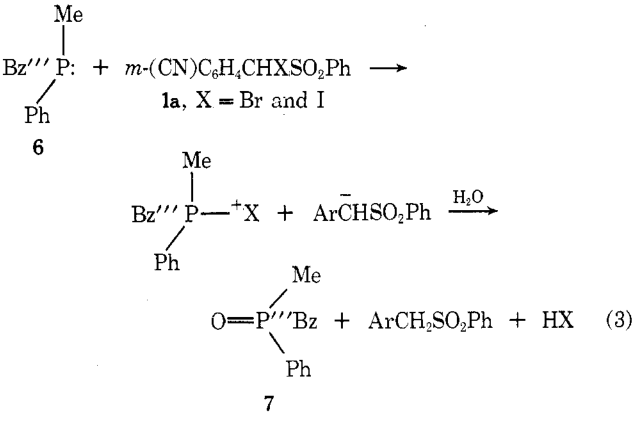
Table V. Activation Parameters for Selected Biomolecular Nucleophilic Substitution Reactions in Various Solvents at 25 °C

	Reactants	Solvent	Electrophilic site	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Ref
1.	$Ph_3P + EtI$	Me_2CO	C	14.2	−33	*a*
2.	$Ph_3P + PhCH_2Cl$	$CHCl_3$	C	12.6	−34	*b*
3.	$Ph_3P + PhCH_2Br$	$CHCl_3$	C	11.3	−39	*b*
4.	$(EtO)_3P + EtI$	MeCN	C	20.4	−19	*c*
5.	(*i*-PrO)$_3$P + EtI	MeCN	C	15.9	−31	*c*
6.	$Ph_3P + NH_2OSO_3^-$	$H_2O\text{–}Me_2SO$	N	11.1	−31	*d*
7.	$Ph_3P + PhN_3$	C_6H_6	N	9.6	−33	*e*
8.	Ph_3P + *t*-BuOOH	EtOH	O	10.2	−24	*f*
9.	$Ph_3P + S_8$	C_6H_6	S	14.5	−19	*g*
10.	Ph_3P + PhSSPh	C_6H_6	S	10.3	−40	*h*
11.	$Ph_3P + PhS(CH_3)NTs$	DMF	S	26.0	− 9	*i*
12.	$Ph_3 + Ph_3CNCSe$	c-C_6H_{12}	Se	8.6	−28	*j*
13.	Ph_3P + *m*-(CN)$C_6H_4CHClSO_2Ph$	H_2O–DMF	Cl	17.2	−26	*k*
14.	Ph_3P + *m*-(CN)$C_6H_4CHBrSO_2Ph$	H_2O–DMF	Br	12.7	−28	*k*
15.	Ph_3P + *m*(CN)$C_6H_4CHISO_2Ph$	H_2O–DMF	I	18.5	−17	*k*

[a] W. A. Henderson, Jr., and S. A. Buckler, *J. Am. Chem. Soc.*, **82**, 5794 (1960). [b] W. E. McEwen, W. I. Shiau, Y. I. Yeh, D. N. Schultz, R. U. Pagilagan, J. B. Levy, C. Symmes, G. O. Nelson, and I. Granoth, *J. Am. Chem. Soc.*, **97**, 1787 (1975). [c] G. Aksnes and D. Aksnes, *Acta Chem. Scand.*, **19**, 898 (1965). [d] B. A. Sudbury and J. H. Krueger, *Inorg. Chem.*, **13**, 1736 (1974). [e] J. E. Leffler and R. D. Temple, *J. Am. Chem. Soc.*, **89**, 5235 (1967). [f] Reference 4b. [g] Data calculated from rate constants given at two temperatures by P. D. Bartlett and G. Meguerian, *J. Am. Chem. Soc.*, **78**, 3710 (1956). [h] F. Feher and D. Kurz, *Z. Naturforsch., B*, **23**, 1030 (1968). [i] T. Aida, N. Furukawa, and S. Oae, *Chem. Lett.*, 805 (1973). [j] L. J. Stangeland, T. Austad, and J. Songstad, *Acta Chem. Scand.*, **27**, 3919 (1973). [k] This work.

not clear why these two systems, reactions of **1** with substituted triarylphosphines vs. substituted arenesulfinates, exhibit different characteristics vis-à-vis their reactivity as a function of different σ constants.[27]

The data presented in Table VI make it clear that the rates of reaction of **1a** with **2** (eq 2) are quite sensitive to the substituents on **2**, particularly for the bromide and iodide ($\rho \sim -3$). These ρ values for reaction 2 are the largest (most negative) ρ values reported for the reactions of tertiary phosphines with the exception of the reactions of triarylphosphines with tetracyanoethylene and 7,7,8,8-tetracyanoquinodimethane where ρ was found to be −3.4 and −3.2, respectively (correlation was with normal σ constants).[28] These latter reactions were shown to involve phosphonium radical cations as reaction intermediates and suggested to us the possibility that similar intermediates might be involved in our reactions.[29] To test for the intermediacy of a radical cation in reaction 2, we allowed optically active (*R*)-(+)-benzylmethylphenylphosphine (**6**) to react with **1a** (X = Br and I) in aqueous acetonitrile to give



6

7

(3)

Table VI. ρ Values for Selected Reactions of Substituted Phosphines

Reaction	ρ	Ref
1. pK_b of Ar_3P	−1.11	*a*
2. pK_b of $ArPEt_2$	−2.24	*b*
3. pK_b of R_3P	−2.67[c]	*d*
4. $Ar_3P + PhCH_2Br$	−1.06	*e*
5. $ArPEt_2 + EtI$	−1.11	*f*
6. $R_3P + EtI$	−0.77[c]	*g*
7. $Ar_3P + PhCOCH_2Br$	−1.22	*h*
8. $Ar_3P + PhN_3$	−1.07	*i*
9. Ar_3P + **1a** (X = Cl)	−1.84	*j*
10. Ar_3P + **1a** (X = Br)	−3.03	*j*
11. Ar_3P + **1a** (X = I)	−3.30	*j*

[a] H. Goetz and A. Sidhu, *Justus Liebigs Ann. Chem.*, **682**, 71 (1963). [b] This value was derived from a least-squares plot of pK_b vs. σ (*r* = 0.997). The original paper [H. Goetz and S. Domin, *ibid.*, **704**, 1 (1967)] gives ρ = −3.08 which was derived from a plot of pK_b vs. (σ + Σσ*) where Σσ* apparently includes the Taft constants for both the ethyl and aryl groups. [c] Determined by use of Taft σ* constants. [d] W. A. Henderson, Jr., and C. A. Streuli, *J. Am. Chem. Soc.*, **82**, 5791 (1960). [e] Reference *b*, Table V. [f] W. C. Davies and W. P. G. Lewis, *J. Chem. Soc.*, 1599 (1934). [g] Reference *a*, Table V. [h] I. J. Borowitz, *Phosphorus*, **2**, 91 (1972). [i] Reference *e*, Table V. [j] This work.

Table VII. Rate Constants for the Reactions of α-Bromo-*m*-cyanobenzyl Phenyl Sulfone with Alkyldiphenylphosphines, $RPPh_2$, in 90% Aqueous DMF at 25 °C

Registry no.	R	$10^2 k_2$, $M^{-1} s^{-1}$	σ*
607-01-2	CH_2CH_3	241 ± 12	−0.100
1486-28-8	CH_3	79.4 ± 0.6	0.000
7650-91-1	$CH_2C_6H_5$	12.5 ± 0.5	0.215
2155-96-6	$CH{=}CH_2$	2.79 ± 0.08	0.400
	C_6H_5	0.207 ± 0.016	0.600

Table VIII. Second-Order Rate Constants for the Reactions of α-Bromo-*m*-cyanobenzyl Phenyl Sulfone with Phosphites, $(RO)_3P$, in 90% Aqueous DMF

Registry no.	R	Temp, °C, (±0.1°)	$10^4 k_2$, $M^{-1} s^{-1}$
121-45-9	CH_3	50.0	0.568 ± 0.014
		75.0	3.36 ± 0.20
		97.2	12.6 ± 1.1
122-52-1	CH_2CH_3	50.0	0.405 ± 0.010
		75.0	2.53 ± 0.26
		97.2	9.93 ± 0.08
116-17-6	$CH(CH_3)_2$	50.0	1.17 ± 0.11
		75.0	5.94 ± 0.17
		97.2	21.3 ± 0.6
102-85-2	$(CH_2)_3CH_3$	50.0	0.167 ± 0.019
		75.0	1.96 ± 0.12
		97.2	9.10 ± 0.33
101-02-0	C_6H_5	50.0	3.02 ± 0.11
		66.0	7.48 ± 0.13
		76.0	17.4 ± 1.6
5679-61-8	*p*-ClC_6H_4	50.0	2.83 ± 0.10
		66.0	7.76 ± 0.16
		76.0	20.8 ± 3.7
19909-81-0	*p*-CH_3O-C_6H_4	50.0	3.51 ± 0.10
		66.0	9.05 ± 0.15
		76.0	20.8 ± 1.1

the phosphine oxide **7** whose stereochemistry would be indicative of the reaction pathway followed, viz., inversion of stereochemistry would result if the mechanism is as shown in eq 3,[30] but racemic **7** would result if a radical cation $Ar_3P^{\cdot+}$ were the intermediate.[31] The optical purities of the oxide **7** from the reactions of **1a** (X = Br and X = I, respectively) with **6** were 94% (6% of the enantiomer of **7** present) and 88% (12% of the enantiomer of **7** present), respectively, which confirms the suggested reaction mechanism and excludes the intermediacy of a phosphonium radical cation. The small loss of optical activity in these reactions is due to racemization of **7** by the hydrohalic acid produced.[32]

Since others have shown that the nucleophilicity of alkylphosphines toward carbon atoms could be correlated well with Taft σ* constants,[33] we thought it appropriate to make similar measurements in our system. Table VII gives the rate data for the reactions of α-bromo-*m*-cyanobenzyl phenyl sulfone (**1a**, X = Br) with a series of alkyldiphenylphosphines. A plot of log *k* vs. σ* gives a straight line whose slope (ρ) = −4.21 (*r* = 0.996). Again, the large negative value of ρ is indicative of a high degree of positive charge associated with the phosphorus atom in the activated complex.

We briefly examined the reactions of the bromo sulfone **1a** with triphenylarsine and triphenylstibine in aqueous DMF. Both of these nucleophiles proved to be very unreactive toward **1a** (X = Br) which is in contrast to their behavior toward peroxides. In the reactions of *tert*-butyl hydroperoxide with Ph_3M (M = P, As, and Sb) in ethanol, the order of reactivity is P ≥ Sb > As.[34] The bromo sulfone **1a** reacted with TPP >10^3 times as readily as either Ph_3As or Ph_3Sb, whose rates were too slow to measure.[35]

The general order of nucleophilicity for tertiary phosphorus(III) compounds is $R_3P > Ar_3P > (RO)_3P > (ArO)_3P$.[12,38] In reactions involving nucleophilic attack on halogen atoms, phosphines are significantly more reactive than phosphites.[39] Tables VIII and IX give the rate data associated with the reactions of **1a** (X = Br) with various trialkyl- and triarylphosphites (eq 4), and indeed the bromide **1a** reacts considerably faster with the triarylphosphines (Table IV) than with the phosphites.[40]

$$\underset{\mathbf{1a}}{m\text{-(CN)C}_6\text{H}_4\text{CHBrSO}_2\text{Ph}} + (\text{RO})_3\text{P} \xrightarrow[\text{DMF}]{\text{H}_2\text{O}} m\text{-(CN)C}_6\text{H}_4\text{CH}_2\text{SO}_2\text{Ph} + (\text{RO})_3\text{PO} + \text{HBr} \qquad (4)$$

The observed order of reactivity for $(RO)_3P$ is R = Ar > *i*-Pr > Me > Et > *n*-Bu (Table IX). This order of reactivity for the trialkyl phosphites parallels that observed in the reactions of trialkyl phosphites with α-bromo-α-cyano esters, a reaction which also involves nucleophilic attack on a bromine atom.[41] However, the higher reactivity of the triaryl phosphites over the trialkyl phosphites in reaction 4 is unprecedented for nucleophilic reactions of phosphites.[42] A plot of log *k* vs. Taft σ* constants for data in Table IX gives a very poor fit with the points for the triaryl phosphites falling considerably above the line. That the increased reactivity of the triaryl phosphites is not due to some through-space electronic effect of the aryl rings can be seen from the slight change in reactivity observed when the aryl ring of the phosphites is changed from a *p*-anisyl group to the *p*-chlorophenyl group.

We feel that the order of reactivity observed for reaction 4 strongly reflects the steric requirements of the phosphites.[42] Recently, Charton[43] has shown that the Taft σ* constants which have been correlated with the rates of hydrolysis of esters do not reflect differences in electrical effects but rather involve predominantly steric factors. Our data strongly support this view; the increased reactivity of the triaryl phosphites may be due to the relief of back strain in going from the triaryl phosphite to the triaryloxybromophosphonium cation intermediate.[44] The reason why a similar effect is not observed for

Table IX. Rate Constants and Activation Parameters for the Reactions of α-Bromo-*m*-cyanobenzyl Phenyl Sulfone with Phosphites, $(RO)_3P$, in 90% Aqueous DMF at 25 °C

R	Taft σ^*	$10^6 k_2$, $M^{-1} s^{-1}$	$\Delta H^{\ddagger}$, kcal/mol	$-\Delta S^{\ddagger}$, eu
CH_3	0.000	7.38 ± 0.15	14.9 ± 0.5	32 ± 1.5
CH_2CH_3	−0.100	4.87 ± 0.15	16.5 ± 0.5	31 ± 1.5
$CH(CH_3)_2$	−0.190	16.9 ± 1.1	14.0 ± 0.5	33 ± 1.6
$(CH_2)_3CH_3$	−0.130	1.20 ± 0.22	19.6 ± 0.9	20 ± 2
C_6H_5	0.600	41.1 ± 1.4	14.1 ± 0.7	31 ± 2
p-ClC_6H_4		29.2 ± 2.1	16.2 ± 1.4	25 ± 4
p-$CH_3OC_6H_4$		46.9 ± 1.2	14.4 ± 0.5	30 ± 1.5

the Arbuzov reaction[45,46] or the Staudinger reaction[47] is that little phosphorus–carbon (or in the Staudinger reaction, little phosphorus–nitrogen) bond formation is occurring in the transition state, and, therefore, relief of back strain in these reactions is relatively unimportant. However, for reactions involving nucleophilic attack by phosphorus nucleophiles on halogen atoms,[48] the transition states are very late, and nearly complete phosphorus–halogen bond formation has occurred in the activated complexes.[49]

It is clear from this and earlier work[11] that in reactions involving nucleophilic displacement by phosphorus(III) nucleophiles on halogen atoms in α-halo sulfones (particularly with bromides and iodides) bond breaking–bond making is very extensive in the transition state, whereas the reactions of phosphorus nucleophiles with carbon centers are characterized by a more nearly central type transition state.

Experimental Section

Kinetic measurements were performed in a manner described previously.[11a,b] The syntheses of the α-halo sulfones were reported earlier.[11a] 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[50] were prepared from an excess of the appropriate aryl Grignard reagent with phosphorus trichloride and recrystallized from ethanol under nitrogen. The alkyldiphenylphosphines[51] were prepared in a similar manner except that diphenylchlorophosphine (Aldrich) was used as the starting material. The phosphites, with the exception of tris(*p*-anisyl) phosphite (vide infra), are commercially available. Each was distilled under vacuum and stored under nitrogen prior to use.

Phosphorus NMR spectra were taken on a Varian Associates XL-100 spectrometer with 85% phosphoric acid as external standard. Optical rotation measurements were performed on a Schmidt and Haensch Polarimeter Model 11095 with use of the D line of sodium. Elemental analyses were performed by Dr. Franz Kasler, Department of Chemistry, University of Maryland.

The reactions of triphenylarsine and triphenylstibine (Aldrich) with α-bromo- and α-iodo-*m*-cyanobenzyl phenyl sulfone (**1a**) at 50 °C were monitored in the same manner as the reactions of **1a** with TPP.[11b] For the reaction of triphenylarsine, no change in the conductance of the solution was observed after 10 h. The solution containing **1a** (X = Br and X = I) and triphenylstibine did show a slow change in conductance; however, this change occurred in the absence of **1a** and therefore could not be ascribed to a reaction between triphenylstibine and **1a**.

Tris(*p*-anisyl) Phosphite.[52] A mixture of 10.0 ml (0.115 mol) of phosphorus trichloride, 43.5 g (0.341 mol) of *p*-methoxyphenol (Aldrich), and 35 ml of pyridine in 200 ml of ether was allowed to stir at ambient temperature under nitrogen for 5 h. The solution was filtered and the filtrate evaporated under reduced pressure. The residue was subjected to column chromatography on 1 kg of neutral alumina (activity I) packed in hexane. Elution with dichloromethane/hexane (1:3) gave an oil which was distilled, bp 235 °C (0.2 mm), to give 36.0 g (90%) of product, ^{31}P NMR δ −125 ppm, $n^{20}D$ 1.5835.

Anal. Calcd for $C_{21}H_{21}O_6P$: C, 63.00; H, 5.28; P, 7.75. Found: C, 63.01; H, 5.23; P, 7.59.

Reaction of (*R*)-(+)-Benzylmethylphenylphosphine (6) with α-Bromo- and α-Iodo-*m*-cyanobenzyl Phenyl Sulfones (1a). One gram (3.0 mmol) of α-Br-**1a** was dissolved in 50 ml of 90% aqueous acetonitrile. To this solution was added 0.600 g (2.8 mmol) of **6**[53] ($\alpha^{20}D$ 80° in benzene) in 5 ml of 90% aqueous acetonitrile. This solution was heated at 50 °C under nitrogen for 0.5 h and evaporated under reduced pressure to give an oil. The oil was subjected to column chromatography on neutral alumina (75 g, activity I). Elution with acetone/dichloromethane (1:9) gave the reduced sulfone **5a** (629 mg, 88%, mp 157–159 °C) followed by 400 mg (62%) of the phosphine oxide **7**, mp 122–126 °C, $\alpha^{20}D$ +45° (benzene) (lit.[53] $\alpha^{20}D$ +51°). The reaction of the iodo sulfone **1a** (X = I) with **6** was carried out in the same fashion to give **7** (70%), $\alpha^{20}D$ +38° (benzene).

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Registry No.—**6**, 25140-53-8; phosphorus trichloride, 7719-12-2; *p*-methoxyphenol, 150-76-5.

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$$RX + Ar_3P \longrightarrow R{\cdot}X^{-} + Ar_3P{\cdot}^{+} \xrightarrow[-HX]{H_2O} R\cdot + Ar_3\dot{P}OH \longrightarrow$$

$$R{:}^{-} + Ar_3\overset{+}{P}OH \longrightarrow RH + Ar_3PO$$

with the reactions of TPP with **1** and (2) why R· and $Ar_3P{\cdot}^{+}$ (or $Ar_3\dot{P}OH$) would not combine and lead to stable and isolable quaternary phosphonium salt (not observed). No evidence through use of free-radical initiators or inhibitors could be obtained for a free-radical chain reaction.

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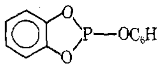

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2-Thenyl Group as Terminus *and* Migrating Moiety in the Stevens and Sommelet Rearrangements of a Quaternary Ammonium Ion[1]

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The presence of two thenyl groups as substituents on nitrogen in the ammonium salt **9** gave base-initiated rearrangements producing high yields of amines **13** and **14**. The absence of other rearrangement products and the relatively good linear fit of all log (**13**/**14**) values vs. $1/T$ which is independent of concentrations, base, or solvent system was taken as indicative of a common ylide precursor **16** but subsequently different reaction routes in the Stevens and the Sommelet rearrangement processes. Synthesis of a variety of compounds, including others which might be anticipated in such a reaction, ensured adequate knowledge of separation and spectroscopic characteristics to allow clear distinction of structures.

Much research has been done in recent years to broaden the scope and to unveil the mechanistic features of the Stevens and the Sommelet rearrangements of quaternary ammonium ions.[2] However, few papers[3–5] have appeared concerning heterobenzyl quaternaries, which, like the benzyl analogues, are potentially apt to yield both types of migration.

We have recently shown[5] that a 1,2-methyl shift to the α position of a 2-thenyl moiety may be induced by base to yield **2**. In this reaction, hints that the 2-thenyl group may also function as a migrating radical came from traces of rearranged amines **3** and **4** wherein the heterobenzyl moiety has undergone Sommelet and Stevens shifts, respectively.[4,5] Since a previous report[3] stated that no rearranged product could be detected from 2-thenyltrimethylammonium ion, which is in sharp contrast to our 2-thenyldimethylanilinum (**1**) results,[4,5] we felt that it was important to determine whether 2-thenyl