stirred suspension of 2.0 g (52.63 mmol) of lithium aluminum hydride in 50 mL of dry ether was added a solution of 3.2 g (9.79 mmol) of 1-*n*-hexyl-1-mesyloxymethyl-5-methoxybenzocyclobutene (**30**) under nitrogen and this was heated under reflux for 2 h. The workup as above gave 1.5 g (66.08%) of a pale yellow oil: NMR (CCl_4) δ 0.88 [3 H, br t, $(CH_2)_5CH_3$], 1.10–1.87 (10 H, m, 5 CH_2), 1.50 (3 H, s, C_1 CH_3), 2.79 (2 H, br, $ArCH_2$), 3.69 (3 H, s, OCH_3), 6.50 (1 H, d, J = 2 Hz, C_6 H), 6.58 (1 H, dd, J = 7 and 2 Hz, C_4 H), 6.85 (1 H, d, J = 7 Hz, C_3 H).

Thermolysis of 1-*n*-Hexyl-5-methoxy-1-methylbenzocyclobutene (31). A solution of 1.0 g (4.31 mmol) of 1-*n*-hexyl-5-methoxy-1-methylbenzocyclobutene (**31**) in 50 mL of dry toluene was heated in a sealed tube for 12 h at 220 °C. The evaporation of the solvent gave 0.95 g (95.0%) of a pale yellow oil, which was chromatographed on 50 g of silicic acid using *n*-hexane as eluent. The first eluate gave 420 mg (42.0%) of 2-(5′-methoxy-2′-methylphenyl)octene-1 (**32**) as a colorless oil: NMR (CCl_4) δ 0.87 [3 H, br t, $(CH_2)_5CH_3$], 1.07–1.60 (10 H, m, 5 CH_2), 2.17 (3 H, s, $ArCH_3$), 3.69 (3 H, s, OCH_3), 4.79 (1 H, m, C=CH), 5.07 (1 H, m, C=CH), 6.46 (1 H, d, J = 2 Hz, $C_{6'}$ H), 6.58 (1 H, dd, J = 8 and 2 Hz, $C_{4'}$ H), 6.94 (1 H, d, J = 8 Hz, $C_{3'}$ H).

Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.53; H, 10.16.

The second eluate gave 410 mg (41%) of 2-(5′-methoxy-2′-methylphenyl)octene-2 (**33**) as a colorless oil: NMR (CCl_4) δ 0.93 [3 H, br t, $(CH_2)_4CH_3$], 1.17–1.63 (8 H, m, 4 CH_2), 1.88 (3 H, s, olefinic CH_3), 2.15 (3 H, s, aromatic CH_3), 3.69 (3 H, s, OCH_3), 5.23 (1 H, br t, J = 7 Hz, C=CH), 6.49 (1 H, d, J = 2 Hz, $C_{6'}$ H), 6.58 (1 H, dd, J = 9 and 2 Hz, $C_{4'}$ H), 6.93 (1 H, d, J = 9 Hz, $C_{3'}$ H).

2-(5′-Methoxy-2′-methylphenyl)octane (34). A. From the Styrene 24 and 25. A suspension of 53 mg (0.23 mmol) of a mixture of **24** and **25** and 3 mg of platinum oxide in 5 mL of ethanol was shaken in hydrogen atmosphere for 24 h. After removal of the catalyst, the ethanol was evaporated off to give an oil, which was chromatographed on 5 g of silica gel using benzene as eluent to afford 51 mg (94.6%) of **34** as a colorless oil: NMR δ (CCl_4) 2.21 (3 H, s, $ArCH_3$) 2.88 (1 H, sextet, ArCH–), 3.67 (3 H, s, OCH_3), 6.43 (1 H, dd, J = 3 and 8 Hz, $C_{4'}$ H), 6.58 (1 H, d, J = 3 Hz, $C_{6'}$ H), 6.87 (1 H, d, J = 8 Hz, $C_{3'}$ H).

B. From the Styrene 33. A suspension of 268 mg (1.155 mmol) of **33** and 10 mg of platinum oxide in 30 mL of ethanol was treated in the same way as above to give 254 mg (94.1%) of **34** as a colorless oil, whose physical data were identical with those of the sample obtained by method A.

Acknowledgment. We thank Mrs. C. Koyanagi, Miss K. Mushiake, Mrs. R. Kobayashi, Miss R. Suenaga, Miss E. Nagaoka, Miss M. Tanno, and Mr. K. Kawamura, Pharmaceutical Institute, Tohoku University, for microanalyses and spectral measurements. We also thank the Mitsubishi Foundation for the financial help.

Registry No.—**4,** 1199-31-1; **5,** 62562-24-7; **6a,** 62562-25-8; **6b,** 62562-26-9; **7a,** 62587-54-6; **8a,** 62562-27-0; **8b,** 62562-28-1; **9,** 62562-29-2; **10,** 62562-30-5; **11,** 62562-31-6; **12a,** 62562-32-7; **13,** 62562-33-8; **15,** 62562-34-9; **16,** 62562-35-0; **17,** 62562-36-1; **18,** 62562-37-2; **19,** 62562-38-3; **20,** 62562-39-4; **21,** 62562-40-7; **22,** 62587-47-7; **23,** 62562-41-8; **24a,** 62562-42-9; **24b,** 62562-43-0; **25,** 62562-44-1; **26,** 62562-45-2; **27,** 62562-46-3; **28,** 62562-47-4; **29,** 62562-48-5; **30,** 62562-49-6; **31,** 62562-50-9; **32,** 62562-51-0; **33,** 62562-52-1; **34,** 62562-53-2; methyl iodide, 74-88-4; benzocyclobutene, 694-87-1; maleic anhydride, 108-31-6; 1-bromo-6-chlorohexane, 6294-17-3; *p*-toluenesulfonyl chloride, 98-59-9; methanesulfonyl chloride, 124-63-0; hexyl bromide, 111-25-1.

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Nucleophilic Displacements on Halogen Atoms. 9.[1] Reactions of Triarylphosphines with Halomethylpyridyl Phenyl Sulfones

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The rates of reactions of halomethylpyridyl phenyl sulfones with triphenylphosphine have been used to determine σ^- values for the heterocyclic ring in 2-, 3- and 4-substituted pyridine derivatives, e.g., pyridines, pyridine *N*-oxides, and *N*-methylpyridinium salts.

The reactions of α-halo sulfones with tertiary phosphorus compounds (e.g., alkyl and aryl phosphines and phosphites) have been studied extensively.[1-3] These reactions occur by S_N2 displacement by the nucleophile on the halogen atom to give α-sulfonyl carbanions which are subsequently protonated by solvent to give the reduced sulfone (eq 1). The rates of these reactions were shown to be very sensitive to changes in structure in both the α-halo sulfones and in the nucleophiles.[1-4] In particular, the Hammett ρ values associated with the reactions of α-bromobenzyl and α-iodobenzyl phenyl sulfones with both triphenylphosphine[1] and sodium benzenesulfinate[4] in aqueous dimethylformamide (DMF) are

Table I. σ^- Values for the Nitrogen Moiety within the Pyridine Ring Derived from Reactions of Chloropyridine Compounds with Methoxide Ion[6]

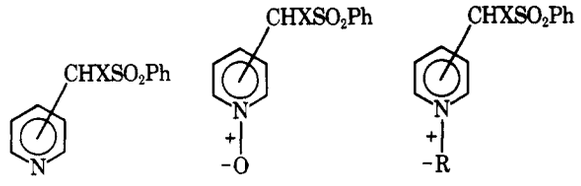
Position	N:	$^+NO^-$	$^+NCH_3$
2	1.00	1.50	2.49
3	0.60	1.23	1.15
4	1.17	1.67	2.16

quite large (ca. +6).

$$\underset{1}{ArCHXSO_2Ph} + Ar'_3P \xrightarrow{slow} \underset{2}{[ArCHSO_2Ph]^-[Ar'_3PX]^+}$$

$$\xrightarrow[H_2O]{fast} ArCH_2SO_2Ph + Ar'_3PO + HX \quad (1)$$

It is clear from these and additional data[1-4] that the transition state for step 1 in the above reaction lies very close to carbanion 2. Previously, we used this reaction to measure the interaction of various groups in the benzyl ring with the carbanionic center in 2, thus determining σ^- values for these groups (p-COOH, p-COOEt, and p-SO_2CH_3).[5] Herein, we report the reactions of various pyridine analogues of 1 with triarylphosphines; these reactions have been used as a probe for the interaction of an α-picolyl carbanion with the pyridine ring system. A particularly attractive feature of the pyridine system is that the electronic nature of the nitrogen atom in the ring can be altered dramatically by oxidation or alkylation, viz., 3–5.



3 4 5

The rates of reaction of methoxide ion with various chloropyridine derivatives (an aromatic nucleophilic displacement reaction) have shown a strong dependence upon the position of the chlorine atom in the ring and the electronic state of the nitrogen atom.[6] From these data, σ^- constants for N:, $^+NO^-$, and $^+NCH_3$ at various positions in the ring were determined. The σ^- values found are shown in Table I.

A number of groups have assigned normal σ constants to these pyridine derivatives based on the reactions of various picolyl derivatives,[7] but few measurements have been made which would lead to σ^- values based on exocyclic reactions for all three pyridine systems (N:, N^+O^-, and N^+R).[8]

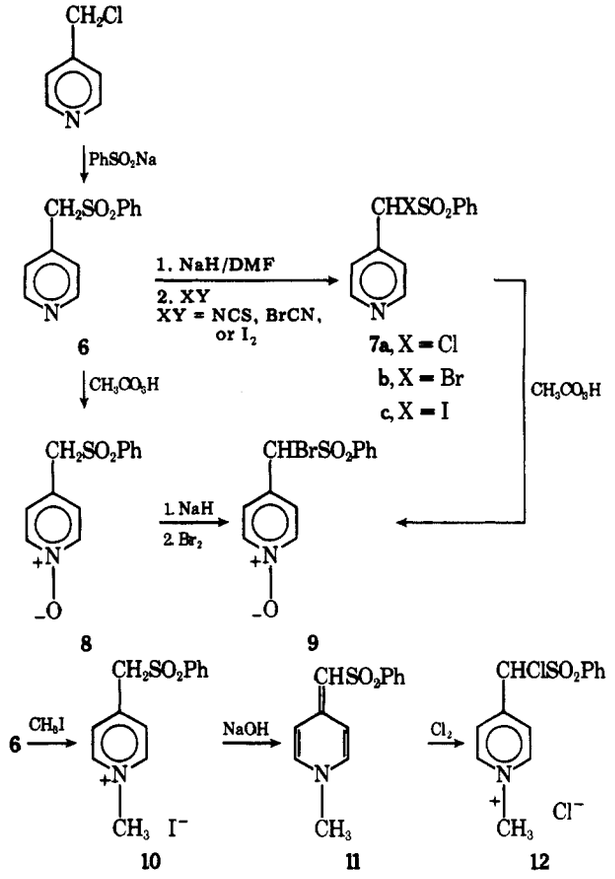
Results and Discussion

The syntheses of the various halomethylpyridyl phenyl sulfones used in this study are shown in Scheme I.

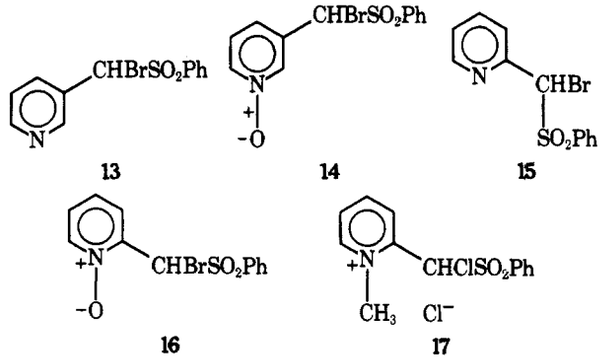
Compounds **7a–c** were synthesized in order to determine their relative reactivity toward triphenylphosphine. Since previous studies[1-4] had established that the normal order of reactivity for the α-halo sulfones is Br > I ≫ Cl, it was of importance to establish whether this trend also is operative in the picolyl system. The data in Table II show this to be the case, giving us confidence that the halomethylpyridyl phenyl sulfones react with triphenylphosphine (TPP) in a manner very similar to the reactions of α-halobenzyl phenyl sulfones with TPP.[1,2]

For the purposes of determining σ^- constants, the reactions of the α-bromo sulfones with TPP were chosen since the rates of these reactions showed somewhat higher correlation coefficients in the Hammett $\sigma\rho$ plots than the correlation coefficients derived from similar plots with α-chloro and α-iodo sulfones.[2]

Scheme I. Syntheses of 4-Halomethylpyridyl Phenyl Sulfones



The 2- and 3-bromomethylpyridyl phenyl sulfones and the corresponding N-oxides (13–16) were made in a manner similar to that shown for the 4-bromomethylpyridyl phenyl sulfones in Scheme I. Preliminary results with 2- and 4-bromomethylpyridinium methobromide phenyl sulfones showed these compounds to be too reactive to study by our techniques, and so the corresponding chloro sulfones (12 and 17) were studied.



Compounds 7, 9, and 12 were shown to react smoothly with TPP and 90% aqueous DMF to give the corresponding reduced sulfones in quantitative yields (eq 2). The rates of re-

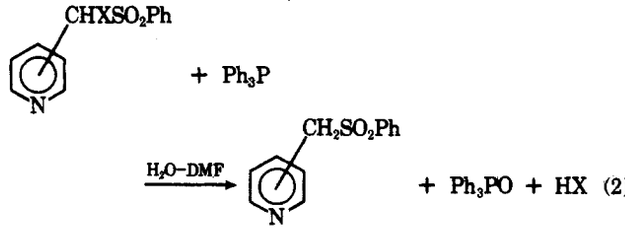


Table II. Kinetic Data and Arrhenius Parameters for the Reactions of 2-, 3-, and 4-Halomethylpyridyl Phenyl Sulfones ($YC_5H_4CHXSO_2Ph$) with Triphenylphosphine in 90% DMF–H_2O

Registry no.	Y	(X)	Temp, °C	k_2, M^{-1} s^{-1}	Data at 25 °C
62586-50-9	2-N:	(Br)	20.0	$4.36 \pm 0.01 \times 10^{-3}$	$6.59 \pm 0.02 \times 10^{-3}$ M^{-1} s^{-1}
			35.2	$1.48 \pm 0.02 \times 10^{-2}$	$\Delta H^{\ddagger} = 13.4 \pm 0.2$ kcal/mol
			45.4	$2.92 \pm 0.02 \times 10^{-2}$	$\Delta S^{\ddagger} = -24 \pm 1$ eu
62586-51-0	3-N:	(Br)	40.1	$1.15 \pm 0.13 \times 10^{-3}$	$3.44 \pm 0.19 \times 10^{-4}$
			50.0	$2.79 \pm 0.29 \times 10^{-3}$	$\Delta H^{\ddagger} = 14.8 \pm 1.5$
			60.0	$5.01 \pm 0.15 \times 10^{-3}$	$\Delta S^{\ddagger} = -33 \pm 5$
62586-52-1	4-N:	(Br)	9.3	$1.93 \pm 0.04 \times 10^{-1}$	$5.08 \pm 0.04 \times 10^{-1}$
			15.0	$2.93 \pm 0.04 \times 10^{-1}$	$\Delta H^{\ddagger} = 9.5 \pm 0.5$
			20.0	$3.65 \pm 0.08 \times 10^{-1}$	$\Delta S^{\ddagger} = -28 \pm 2$
			25.0	$4.92 \pm 0.01 \times 10^{-1}$	
62586-53-2	4-N:	(Cl)	50.0	$1.78 \pm 0.01 \times 10^{-4}$	$2.21 \pm 0.08 \times 10^{-5}$
			74.9	$1.21 \pm 0.10 \times 10^{-3}$	$\Delta H^{\ddagger} = 15.6 \pm 0.4$
			97.3	$4.46 \pm 0.09 \times 10^{-3}$	$\Delta S^{\ddagger} = -26 \pm 1$
62586-54-3	4-N:	(I)	25.0	$1.68 \pm 0.11 \times 10^{-1}$	$1.68 \pm 0.11 \times 10^{-1}$
62586-55-4	$2\text{-}^{+}NCH_3$ Cl^-	(Cl)	9.3	$2.51 \pm 0.01 \times 10^{-1}$	$8.43 \pm 0.06 \times 10^{-1}$
			18.3	$5.11 \pm 0.07 \times 10^{-1}$	$\Delta H^{\ddagger} = 9.1 \pm 0.9$
			25.0	$8.43 \pm 0.15 \times 10^{-1}$	$\Delta S^{\ddagger} = -28 \pm 3$
62586-56-5	$4\text{-}NCH_3$ Cl^-	(Cl)	25.0	$2.90 \pm 0.02 \times 10^{-2}$	$2.90 \pm 0.04 \times 10^{-2}$
			40.0	$1.18 \pm 0.07 \times 10^{-1}$	$\Delta H^{\ddagger} = 9.5 \pm 0.8$
			50.0	$2.95 \pm 0.02 \times 10^{-1}$	$\Delta S^{\ddagger} = -29 \pm 3$

Table III. Kinetic Data and Arrhenius Parameters for the Reactions of 2-, 3-, and 4-Bromomethylpyridyl Phenyl Sulfone *N*-Oxides with Tris(*p*-chlorophenyl)phosphine (TCP) in 90% DMF–H_2O

Registry no.	Position[a]	Temp, °C	k_2, M^{-1} s^{-1}	Data at 25 °C
62586-57-6	2	5.1	$9.24 \pm 0.12 \times 10^{-1}$	3.93 ± 0.07 M^{-1} s^{-1}
		9.3	1.26 ± 0.08	
		15.6	2.04 ± 0.04	$\Delta H^{\ddagger} = 11.5 \pm 1.1$ kcal/mol
		20.0	2.78 ± 0.03	$\Delta S^{\ddagger} = -17 \pm 4$ eu
62586-58-7	3	9.3	$2.63 \pm 0.03 \times 10^{-2}$	$8.56 \pm 0.03 \times 10^{-2}$
		15.6	$4.36 \pm 0.03 \times 10^{-2}$	
		20.0	$5.97 \pm 0.05 \times 10^{-2}$	$\Delta H^{\ddagger} = 11.9 \pm 0.3$
		25.0	$8.52 \pm 0.02 \times 10^{-2}$	$\Delta S^{\ddagger} = -23 \pm 1$
62586-59-8	4	9.3	$1.41 \pm 0.01 \times 10^{-1}$	$3.58 \pm 0.06 \times 10^{-1}$
		15.6	$2.08 \pm 0.05 \times 10^{-1}$	
		20.0	$2.78 \pm 0.11 \times 10^{-1}$	$\Delta H^{\ddagger} = 9.3 \pm 0.9$
		25.0	$3.56 \pm 0.06 \times 10^{-1}$	$\Delta S^{\ddagger} = -29 \pm 3$

[a] Position of heterocyclic nitrogen oxide with respect to α-halo sulfone substituent.

Table IV. Rate Constants for the Reactions of 4-Bromomethylpyridyl Phenyl Sulfone with Triarylphosphines, $(YC_6H_4)_3P$, in 90% DMF–H_2O at 25 °C

Registry no.	Y	k_2, M^{-1} s^{-1}	Σσ
6224-63-1	*m*-CH_3	$2.46 \pm 0.16 \times 10^{0}$	−0.207
603-35-0	H	$5.08 \pm 0.04 \times 10^{-1}$	0.000
29949-84-0	*m*-OCH_3	$1.15 \pm 0.02 \times 10^{-1}$	0.345
	p-Cl	$2.39 \pm 0.01 \times 10^{-3}$	0.681

action of **7**, **12**, **13**, **15**, and **17** with TPP in 90% aqueous DMF were determined and the rate data are given in Table II. However, the reaction rates of the pyridine *N*-oxides **9** and **16** with TPP were too fast to measure accurately, and so rate measurements with the pyridine *N*-oxides **9**, **14**, and **16** were determined for their reactions with the less reactive nucleophile, tris(*p*-chlorophenyl)phosphine (TCP) (Table III). Since the Hammett ρ value for the reactions of substituted triarylphosphines with α-bromo-*m*-cyanobenzyl phenyl sulfone has been determined (ρ = −3.03),[1] one can use this datum to determine k_{TPP} from k_{TCP} by use of the formula $\log k_{TCP} = \Sigma\sigma(\rho) + \log k_{TPP}$. The use of this expression assumes that the ρ values for reactions 1 and 2 are the same. This in fact must be the case if the Hammett correlation is to be valid.[10] If one can obtain substituent constants (σ) for a group in one reaction and use it in other reactions, it should be reasonable therefore to transfer reaction constants (ρ) and apply them to different substituents in the same reaction series.[11]

The validity of this approach was further reinforced by determining the Hammett ρ value for the reaction of **7b** with substituted triarylphosphines (Table IV): ρ = −3.12. This value agrees well with that reported earlier for the reaction of substituted arylphosphines with α-bromo-*m*-cyanobenzyl phenyl sulfone (ρ = 3.03).[1]

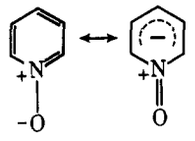
Table V summarizes data derived from Tables II and III and lists σ^- constants calculated from the formula $\log k_x = \sigma^-\rho + \log k_0$. The ρ values for X = Cl, Br, and I are +2.23, +5.97, and +6.29, respectively;[2] $\log k_0$ values are the rate constants for the reactions of the unsubstituted α-halobenzyl phenyl sulfones (**1**, Ar = Ph) with TPP at 25 °C in 90% aqueous DMF.[2]

The σ^- values calculated from our data (Table V) may be contrasted with normal σ constants reported earlier. The average values for σ constants for the 2-, 3-, and 4-substituted pyridines are 0.71, 0.65, and 0.94, respectively.[12] In the pyri-

Table V. Rates of Reaction for the Reductions of Halomethylpyridyl Phenyl Sulfones, $YC_5H_4CHXSO_2Ph$, with Triphenylphosphine in 90% DMF–Water at 25 °C

Set	Y	X	k_2, M^{-1} s^{-1}	σ^-
1	4-N:	Cl	2.21×10^{-5}	1.18
	4-N:	Br	5.08×10^{-1}	0.94
	4-N:	I	1.68×10^{-1}	0.90
2	2-N:	Br	6.59×10^{-3}	0.62
	3-N:	Br	3.44×10^{-3}	0.42
	4-N:	Br	5.08×10^{-1}	0.94
3	2-NO	Br	4.55×10^{2}	1.44
	3-NO	Br	9.91×10^{0}	1.17
	4-NO	Br	4.15×10^{1}	1.27
4	$2\text{-}NCH_3$	Cl	8.43×10^{-1}	3.25
	$4\text{-}NCH_3$	Cl	2.90×10^{-2}	2.59

dinium ion system, these values increase markedly to 3.11, 2.10, and 2.57 for the 2-, 3-, and 4-substituted pyridinium ions.[12] In general, the pyridine *N*-oxide system is intermediate between the above. However, great variance has been observed in the reactivities of various pyridine *N*-oxides,[13] and the σ values for the pyridine *N*-oxides appear to be strongly solvent dependent.[14] Polar (and protic) solvents tend to coordinate the oxygen atom and reduce the tendency to donate electron density into the ring. This produces large values for σ and large differences between the reactivity of the 3 position and the 2 and 4 positions. However, in less polar (and aprotic) solvents, the ring receives maximum back-donation from the oxygen atom; hence low σ values result. This also leads to closer similarity in reaction rates for the 2-, 3- and 4-substituted pyridine *N*-oxides.



Experimental Section

Kinetic measurements were performed in a manner described previously.[2,3] All the phosphines used in this study have been prepared previously.[1] The syntheses of 2-, 3-, and 4-methylpyridyl phenyl sulfones and their methiodides were carried out as described by others.[15]

NMR spectra were taken on a Varian Associates XL-100 spectrometer in deuteriochloroform with Me_4Si as an internal standard (δ 0). Elemental analyses were performed by Dr. Franz Kasler, Department of Chemistry, University of Maryland.

Preparation of 3-Methylpyridyl *N*-Oxide Phenyl Sulfone. One gram of 3-methylpyridyl phenyl sulfone in 60 mL of glacial acetic acid was warmed until a clear solution was obtained. Cold 30% hydrogen peroxide (10.0 mL) was added and the temperature was maintained at 100 °C for 12 h. The reaction mixture was distilled under reduced pressure. After ca. 80% of the original volume had distilled, 50 mL of distilled water was added and the distillation continued. The product separated out of the solution near the end of the distillation. The paste was dissolved in 100 mL of methanol and evaporated three times to remove water. The resulting oil was dissolved in 100 mL of acetone, dried over $MgSO_4$, filtered, and evaporated. The oil was then subjected to column chromatography on neutral alumina with methanol in acetone as the eluent to yield the pure product (0.92 g) in an 82% yield (Table VI).

Preparation of 4-Bromomethylpyridyl Phenyl Sulfone. 4-Methylpyridyl phenyl sulfone (1.20 g) was dissolved in 30 mL of dry DMF. To this solution was added 240 mg of NaH (in an oil dispersion, 50%) in a flask fitted with a condenser and a magnetic stirrer. A positive nitrogen pressure was maintained during the reaction. A yellow solution resulted, and this was heated to 50 °C for 10 min. The solution was cooled and added by syringe to a solution of cyanogen bromide (480 mg in 30 mL of DMF). The dark brown solution was allowed to stand for 15 min and then added to 100 mL of water. Three methylene chloride extractions (30 mL each) were combined and washed with 20% sodium thiosulfate solution and once with water. The organic layer was dried ($MgSO_4$), filtered, and evaporated to an oil which was then dissolved in 50 mL of ether. The ether solution was washed with 50 mL of water, dried ($MgSO_4$), filtered and evaporated to dryness. Chromatography of the material on neutral alumina (methanol/acetone eluent) yielded pure product in 30% yield (Table VI).

Table VI. Physical Data for Substituted Halomethylpyridyl Phenyl Sulfones, $YC_5H_4CHXSO_2Ph$[a,b]

X	Y	Mp, °C	NMR, δ
Br	2-N:	105–106	6.83 (s, 1 H) 7.30–8.10 (m, 8 H) 8.38–8.60 (m, 1 H)
Br	3-N:	146–148	5.99 (s, 1 H) 7.30–8.20 (m, 8 H) 9.36 (d, 1 H)
Br	4-N:	124–125	7.00 (s, 1 H) 7.44 (d, 2 H) 7.65–7.94 (m, 5 H) 8.65 (m, 2 H)
Cl	4-N:	132–133	6.97 (s, 1 H) 7.50 (d, 2 H) 7.70–7.95 (m, 5 H)
I	4-N:	170–173	7.05 (s, 1 H) 7.25–8.10 (m, 7 H) 8.55–9.10 (m, 2 H)
Br	2-NO	128–129	7.20 (s, 1 H) 7.35–8.30 (m, 9 H)
Br	3-NO	132–134	7.02 (s, 1 H) 7.25 (m, 2 H) 7.45–7.90 (m, 5 H) 8.25 (d, 2 H)
Br	4-NO	190–192	7.00 (s, 1 H) 7.38 (d, 2 H) 7.60–7.90 (m, 5 H) 8.25 (d, 2 H)
Cl	$2\text{-}NCH_3$ (Cl^-)	207–210	4.64 (s, 3 H) 7.70–9.0 (m, 9 H) 9.30–9.55 (m, 1 H)
Cl	$4\text{-}NCH_3$ (Cl^-)	210–215	4.05 (s, 3 H) 7.30–7.95 (m, 8 H) 8.60 (d, 2 H)
H[c]	2-NO	153–155	5.12 (s, 2 H) 7.25–7.95 (m, 8 H) 8.15–8.35 (m, 1 H)
H[d]	3-NO	186–187	4.85 (s, 2 H) 7.05–7.55 (m, 2 H) 7.65–7.90 (m, 5 H) 8.00–8.30 (m, 2 H)
H[e]	4-NO	195–196	4.88 (s, 2 H) 7.20 (d, 2 H) 7.60–7.90 (m, 5 H) 8.20 (d, 2 H)

[a] Satisfactory combustion analytical data for C, H, N (±0.3%) were reported for all new compounds. Ed. [b] All compounds were recrystallized from ethanol. [c] Registry no., 62586-60-1. [d] Registry no., 62586-61-2. [e] Registry no., 62586-62-3.

Preparation of 4-Iodomethylpyridyl Phenyl Sulfone. The 4-methylpyridylphenylsulfonyl carbanion (see above) was added to a solution of 1.0 g of iodine in 15 mL of DMF. The product was isolated in a manner analogous to the α-bromo compound described above (yield 25%, see Table VI).

Preparation of 4-Chloromethylpyridyl Phenyl Sulfone. A cold solution of the base-generated carbanion of the 4-methylpyridyl phenyl sulfone (see above) was added to a solution of 0.5 g of *N*-chlorosuccinimide in 20 mL of DMF. The workup of the reaction mixture was the same as that used in the case of the α-bromo sulfone (yield of 40%, see Table VI).

Preparation of 4-Bromomethylpyridyl *N*-Oxide Phenyl Sulfone. One gram of α-bromomethylpyridyl phenyl sulfone was dissolved in 100 mL of glacial acid. Hydrogen peroxide (10.0 mL of a 30% solution) was added and the solution was heated to reflux for 12 h. The isolation of the product was similar to that of the unhalogenated

compound (vide infra). Chromatography on silica gel (methanol/acetone eluent) gave the pure product in 85% yield from the α-halo sulfone and a 34% yield overall from the parent sulfone (Table VI).

Preparation of 4-Chloromethylpyridyl Phenyl Sulfone Methochloride (12). A solution of 5.0 g of 4-methylpyridyl phenyl sulfone methiodide in 25 mL of hot ethanol was treated with 10 mL of 0.5 N NaOH. The dehydrohalogenated sulfone (anhydro base)[15] was filtered, washed with water, and dissolved in chloroform. Chlorine gas was passed through the solution, instantaneously forming the solid product. The solid was filtered and recrystallized from ethanol. Note: the anhydro base must be in large excess since the α,α-dichloride is readily formed in the presence of excess chlorine. The 2-chloro isomer 17 was prepared in a similar manner (Table VI).

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Registry No.—Tris(*p*-chlorophenyl)phosphine, 1159-54-2; 3-methylpyridyl phenyl sulfone, 1620-51-5; 4-methylpyridyl phenyl sulfone, 1620-52-6; 4-methylpyridyl phenyl sulfone methiodide, 62586-63-4.

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Nucleophilic Displacements on β-(Perfluoroalkyl)ethyl Iodides. Synthesis of Acrylates Containing Heteroatoms

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Replacement of iodine in $R_FCH_2CH_2I$ by nucleophilic reagents predominates over the usual elimination to olefin $R_FCH{=}CH_2$ when the reagent is strongly nucleophilic but only weakly basic. Such reagents as RS^-, NCS^-, and N_3^- react very well in displacements. In difunctional reagents $HX(CH_2)_nYH$, where X and Y are different, sulfur is more reactive than nitrogen, which is more reactive than oxygen. The products $R_F(CH_2)_2X(CH_2)_nYH$ were transformed into polymerizable acrylates and methacrylates.

The readily available compounds $R_FCH_2CH_2I$ (1) are attractive intermediates for the preparation of polymerizable monomers bearing a perfluoralkyl "tail". However, when they are treated with sodium hydroxide to make the alcohols $R_FCH_2CH_2OH$, the olefins $R_FCH{=}CH_2$ are formed nearly quantitatively. Methoxide ion behaves similarly. Even the weakly basic methacrylate ion gives a substantial amount of olefin along with the desired methacrylate ester.[1] Such facile elimination is common among alkyl halides bearing an electron-attracting (acid-strengthening) group on the β-carbon atom.

The present work was aimed at preparing polymerizable compounds from the iodides 1 without serious yield loss from elimination. Normally second-row elements are "softer" (more polarizable) than first-row elements, and tend to have greater affinity for "soft" carbon than for the "hard" proton. Thus sulfur and phosphorus nucleophiles (Nu) should give less elimination than oxygen and nitrogen nucleophiles.[2] The sulfur nucleophiles hydrosulfide (HS^-), thiocyanate (NCS^-), and thiourea [$HN{=}C(NH_2)SH$] reacted smoothly with 1 to yield the respective mercaptan, thiocyanate, and thiuronium salt. Very little elimination occurred. Azide ion is also strongly nucleophilic but weakly basic, and the organic azide was readily prepared with little elimination. Phosphorus nucleophiles were not examined.

$$\underset{1}{F(CF_2)_nCH_2CH_2I} + Nu^- \rightarrow \underset{2}{F(CF_2)_nCH_2CH_2Nu} + I^- \quad (1)$$

Nucleophiles carrying a second group capable of being later converted to a polymerizable derivative were then examined. These included 1,4-butanedithiol, 2-hydroxyethanethiol, 2-aminoethanethiol, and mercaptosuccinic acid. High yields of displacement products 3 were obtained, with negligible elimination. 2-Hydroxyethylamine was alkylated successfully by the corresponding tosylate, although elimination was more prominent with this stronger base. The less reactive group was not alkylated unless excess 1 was used.

$$1 + HX(CH_2)_mYH \rightarrow \underset{3}{F(CF_2)_nCH_2CH_2X(CH_2)_mYH} \quad (2)$$

The functional groups YH were converted to acrylate, thioacrylate, or acrylamide by reaction with methacryloyl chloride or methyl methacrylate, or by direct esterification with acrylic acid. These monomers were readily polymerized or copolymerized in solution, in bulk, or in emulsion.