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.

References and Notes

(1) Part 8: B. B. Jarvis and B. A. Marien, *J. Org. Chem.*, **41**, 2182 (1976).
(2) B. B. Jarvis and J. C. Saukaitis, *J. Am. Chem. Soc.*, **95**, 7708 (1973).
(3) B. B. Jarvis and B. A. Marien, *J. Org. Chem.*, **40**, 2587 (1975).
(4) B. B. Jarvis and W. P. Tong, *J. Org. Chem.*, **41**, 1557 (1976).
(5) B. B. Jarvis, R. L. Harper, Jr., and W. P. Tong, *J. Org. Chem.*, **40**, 3778 (1975).
(6) M. Liveris and J. Miller, *J. Chem. Soc.*, 3486 (1963).
(7) (a) R. A. Abramovitch and G. M. Singer in "Heterocyclic Compounds", Vol 14, Supplement, Part 1, R. A. Abramovitch, Ed., Wiley-Interscience, New York, N.Y., 1974, pp 117–119; (b) P. Tomasik and C. D. Johnson, *Adv. Heterocycl. Chem.*, **20**, 1 (1976).
(8) There are qualitative data available which suggest that carbanion-generating reactions, e.g. base-catalyzed H–D exchange of the α protons in picolines,[9] are most successful for positions 2 and 4 and least efficacious at position 3. Values for σ^- constants derived from the measurements of the second pK_as of amino- and dimethylaminopyridines and of the second pK_as of the corresponding *N*-oxides are ca. 2.1 and 4.0 for the β and γ positions, respectively.[7b]
(9) N. N. Zatsepina, I. F. Tupitsyn, and L. S. Efros, *Zh. Obshch. Khim.*, **33**, 2705 (1963).
(10) C. D. Johnson and K. Schofield, *J. Am. Chem. Soc.*, **95**, 270 (1973).
(11) O. Exner, *Collect. Czech. Chem. Commun.*, **39**, 515 (1974).
(12) J. H. Blanch, *J. Chem. Soc. B*, 937 (1966).
(13) Acidity measurements of methylpyridyl phenyl sulfones and the corresponding *N*-oxides in dimethyl sulfoxide solution show that the change in acidity, ΔpK_a, going from the pyridines to the pyridine *N*-oxides decreases as one proceeds from 2- to 3- to the 4-substituted compounds. In fact, 4-methylpyridyl phenyl sulfone differs only slightly in acidity from the corresponding 4-sulfone *N*-oxide (F. G. Bordwell, private communication). The change in σ^- values ($\Delta\sigma^-$) in going from the pyridines to the pyridine *N*-oxides parallels the above changes in ΔpK_a ($\Delta\sigma_2{}^- = 0.82$, $\Delta\sigma_3{}^- = 0.75$, $\Delta\sigma_4{}^- = 0.33$), although these changes do not appear to be as dramatic as in the case of the ΔpK_as.
(14) H. Shindo, *Pharm. Bull. Jpn.*, **4**, 460 (1956); *Chem. Abstr.*, **51**, 12661*b* (1957).
(15) S. Golding, A. R. Katritzky, and H. Z. Kucharska, *J. Chem. Soc.*, 3090 (1965).

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.

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

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.

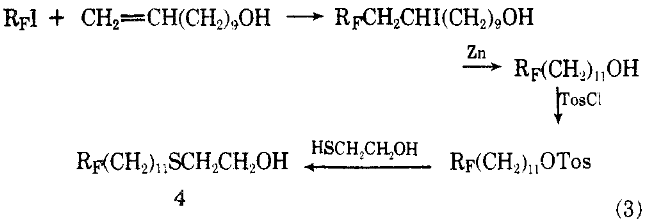
$$\mathbf{1} + HX(CH_2)_mYH \rightarrow \underset{\mathbf{3}}{F(CF_2)_nCH_2CH_2X(CH_2)_mYH} \tag{2}$$

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.

The sulfonic acid $R_FCH_2CH_2SO_3H$ was readily prepared by oxidation of the thiocyanate with nitric acid.[3]

Since the amine $R_FCH_2CH_2NH_2$ cannot be prepared by amination of 1 with ammonia because of supervening elimination, it was prepared instead by hydrogenation of the azide $R_FCH_2CH_2N_3$.

To study the effect of a longer intervening hydrocarbon segment, the alcohol 4 was prepared by the sequence in eq 3.



$$R_FI + CH_2{=}CH(CH_2)_9OH \longrightarrow R_FCH_2CHI(CH_2)_9OH \xrightarrow{Zn} R_F(CH_2)_{11}OH \xrightarrow{TosCl} R_F(CH_2)_{11}OTos \xrightarrow{HSCH_2CH_2OH} \underset{4}{R_F(CH_2)_{11}SCH_2CH_2OH} \qquad (3)$$

The compounds prepared in this work are described in the Experimental Section and in the accompanying tables.

Experimental Section

The starting β-(perfluoroalkyl)ethyl iodides (1) were prepared by addition of ethylene to the corresponding perfluoroalkyl iodides.[4] These in turn had been prepared by telomerization of tetrafluoroethylene with perfluoroethyl iodide,[5] followed by fractional distillation to separate the individual telomers. Purity of these compounds was assayed by GC on a DC-200 silicone oil column.

Mercaptans. A. Thiourea Route. The iodide 1, $n = 6$ (94.8 g, 0.2 mol), was added in 15 min to a boiling solution of 16.0 g (0.21 mol) of thiourea in 300 mL of absolute ethanol, and the mixture was refluxed for 2 h. The ethanol was removed (rotary evaporator), and the residue was treated with 16 g (0.4 mol) of sodium hydroxide in 150 mL of water. The mixture was kept overnight, then boiled for 15 min, diluted with water, acidified (Congo red) with sulfuric acid, and extracted with methylene chloride. The washed extracts were dried and distilled. The mercaptan cut was followed by a cut boiling at 94 °C (0.4 mm), $n^{25}{}_D$ 1.3338, which is considered to be the disulfide resulting from inadequate exclusion of air. The combined yields were nearly 0.2 mol.

B. Thiocyanate Route. A mixture of 239 g (0.50 mol) of iodide 1, $n = 6$, 65 g (0.80 mol) of sodium thiocyanate, 250 mL of anhydrous *tert*-butyl alcohol, and 1000 mL of dimethyl sulfoxide (distilled from calcium hydride) was held at 90 °C under nitrogen for 5 h. The cooled solution was diluted with 500 mL of water, and the nonaqueous layer was distilled. Perfluorohexylethene (15.8 g, 9%) was removed first, and the thiocyanate (184.7 g, 87%) was collected at 100–104 °C (10 Torr). Its infrared spectrum showed the sharp band at 4.63 μ which distinguished it from the isomeric isothiocyanate.

The thiocyanate (183.6 g, 0.43 mol) in 1 L of ether was reduced by adding 38 g (1.0 mol) of lithium aluminum hydride over 3 h under nitrogen. The excess hydride was then destroyed with ethyl acetate (80 mL), followed by 600 mL of 10% hydrochloric acid. The ether phase was dried with sodium sulfate and distilled through a 30-cm helix-packed column. The yield of mercaptan was 95.3 g (58%). Its infrared spectrum showed the expected mercaptan absorption at 3.95 μ, and its NMR spectrum was consistent with the assigned structure.

C. Hydrosulfide Route. The iodide 1, $n = 10$ (135.0 g, 0.20 mol), in 500 mL of *tert*-butyl alcohol and 22.0 g (0.20 mol) of technical sodium hydrosulfide trihydrate in 40 mL of water in an attached dropping funnel were degassed by evacuating and breaking the vacuum with nitrogen four times. While the nitrogen atmosphere was maintained, the flask was heated to 75 °C and held while the hydrosulfide solution was added dropwise in 2 h. After an additional 1.5 h at 75 °C, the mixture was cooled, treated with 200 mL of 20% hydrochloric acid, and extracted with trichlorotrifluoroethane (Freon 113). The solvent was stripped, and the residue was steam distilled. The distillate was extracted with trichlorotrifluoroethane and the extract was evaporated to leave the solid mercaptan. The same procedure was followed for the lower homologue $n = 6$, except that the product was vacuum distilled, yield 27%.

Oxidation of Thiocyanate to Sulfonic Acid. The thiocyanate, $n = 6$ (5.0 g, 12 mmol), was heated at 50 °C with 2 mL (32 mmol) of 15 N nitric acid for 27 h with no apparent effect. But when the temperature was raised to 80 °C, considerable foaming occurred. After 1.5 h at 80 °C, the mixture was cooled and neutralized with saturated sodium bicarbonate solution. The white solid was collected and washed with acetone, yield 3.33 g (65%) as monohydrate. Recrystallized from water, it melted at 238–239 °C.

Anal. Calcd for $C_8H_4F_{13}NaO_3S{\cdot}H_2O$: C, 20.4; H, 1.3. Found: C, 20.4; H, 1.1.

The sodium salt was converted to the free acid with concentrated hydrochloric acid and then to the *p*-toluidine salt which was recrystallized from water, mp 210–211 °C.

Anal. Calcd for $C_{15}H_{14}F_{13}NO_3S$: C, 33.7; H, 2.4; F, 46.2. Found: C, 33.6; H, 2.6; F, 46.2.

Such sulfonic acids may also be prepared by oxidation of mercaptans with chlorine water.[3]

β-(Perfluoroalkyl)ethyl β-Hydroxyethyl Sulfides. A mixture of 1.5 L of *tert*-butyl alcohol, 132 g (3.3 mol) of powdered sodium hydroxide, and 273 g (3.5 mol) of 2-mercaptoethanol was refluxed under nitrogen for 10 min. Then 1422 g (3.0 mol) of 1, $n = 6$, was added during 1 h with vigorous stirring at reflux. The mixture was refluxed for an additional 1 h, and about 900 mL of solvent was evaporated at 100 Torr. The precipitated sodium iodide (389 g) was removed, and the filtrate was further concentrated. The residue was drowned in water, and the insoluble liquid was washed and dried (1259 g), then distilled to yield 1041 g (82%) of sulfide alcohol. A little higher boiling material, bp 98–125 °C (0.7 Torr), $n^{25}{}_D$ 1.3914, could be the symmetrical ether or the dialkylation product. Only a trace of olefin was detected in the solvent removed. The main product showed no impurities by GC. In smaller scale experiments, yields were 93%.

The homologues were prepared from 1, $n = 8$ or 10, by the same procedure. The procedure was applied also to a mixture of 1, $n = 6$, 8, 10, 12, with similar results.

β-(Perfluorohexyl)ethyl 4-Mercaptobutyl Sulfide. A mixture of 150 mL of *tert*-butyl alcohol, 12 mL of water, and 8.4 g (0.21 mol) of sodium hydroxide was degassed by bubbling nitrogen through it for 45 min. Then 25.0 g (0.21 mol) of 1,4-butanedithiol was added, and the mixture was heated to 80 °C. The iodide 1, $n = 6$ (97.0 g, 0.205 mol), was added and the mixture was held at 80 °C for 2.5 h under nitrogen. The reaction mixture was drowned in water, and the insoluble material was dried with sodium sulfate. Distillation gave 45.6 g (98% based on iodide consumed). The -SH absorption was visible at 3.90 μ, and the NMR spectrum was consistent with the assigned structure.

β-(Perfluorohexyl)ethanethiosuccinic Acid. A mixture of 15.0 g (0.10 mol) of mercaptosuccinic acid, 200 mL of *tert*-butyl alcohol, and 8.0 g (0.2 mol) of sodium hydroxide in 8 mL of water was degassed, 47.4 g (0.10 mol) of iodide 1, $n = 6$, was added, and the mixture was held at 70 °C for 32 h. It was then acidified with hydrochloric acid. The cloudy liquid which separated was triturated with concentrated hydrochloric acid to induce crystallization. The product, 23.5 g, was recrystallized from benzene. Its infrared and NMR spectra are consistent with the assigned structure. Compounds of this type have been prepared by base-catalyzed addition of $R_F(CH_2)_nSH$ to maleic acid.[6]

β-(Perfluorohexyl)ethyl β-Aminoethyl Sulfide. A mixture of 100 mL of *tert*-butyl alcohol and 8.1 g (0.205 mol) of powdered sodium hydroxide was evacuated until the solvent boiled. The vacuum was broken with nitrogen, and 11.4 g (0.10 mol) of 2-mercaptoethylamine hydrochloride was added. The flask was again evacuated, then refluxed for 10 min under nitrogen. Then 47.4 g (0.10 mol) of iodide 1, $n = 6$, was added during 15 min. Reflux was continued for an additional 1 h. The mixture became dark brown and solid separated. It was drowned in water, and the oil which separated became a stiff gel when fresh water was added. This gel formation is characteristic of compounds containing an R_F group and another group capable of hydrogen bonding. Addition of ether broke the gel, and the dried solution was distilled.

The infrared spectrum of the product showed no -SH band, but strong absorption at 6.25 μ ($-NH_2$ deformation). The NMR spectrum unequivocally located two protons on nitrogen, none on sulfur.

β-(Perfluorohexyl)ethyl-β-hydroxyethylamine. Use of a Tosylate. β-(Perfluorohexyl)ethyl *p*-toluenesulfonate was prepared from the alcohol with tosyl chloride and pyridine. A solution of 37.0 g (0.6 mol) of 2-aminoethanol in 125 mL of *tert*-butyl alcohol at 80 °C was treated dropwise with a solution of 90.0 g (0.17 mol) of the tosylate in 130 mL of *tert*-butyl alcohol during 2.5 h. After an additional 4 h at 80 °C, the mixture was drowned in 1 L of dilute sodium bicarbonate solution. The nonaqueous phase was taken up in Freon 113, washed, and dried. Removal of the solvent left 40.1 g (58%) of the amino alcohol. It was converted to the hydrochloride, mp 171–173 °C (acetonitrile), for analysis.

ω-(Perfluorobutyl)undecyl β-Hydroxyethyl Sulfide. Perfluorobutyl iodide (137 g, 0.4 mol) was added to 43 g (0.226 mol) of un-

Table I. Properties of $F(CF_2)_nCH_2CH_2X$

Registry no.	n	X	Method	Yield, %	Bp (Torr) or mp,[a] °C	$n^{25}{}_D$	Formula	Anal., %							
								Calcd				Found			
								C	H	N[b] or S	F	C	H	N[b] or S	F
26650-09-9	6	SCN	B	87	100–104 (10)		$C_9H_4F_{13}NS$	26.6	1.0	7.9		26.3	1.0	7.9	
34451-26-8	6	SH	B	58[c]	110–113 (65)[c]										
34451-28-0	10	SH	C	48	63–64[a]		$C_{12}H_5F_{21}S$	24.8	0.9	5.3	68.8	24.5	0.8	5.2	69.0
62571-54-4	10	S[d]	C	87	103–105[a]		$C_{24}H_8F_{42}S$	25.6	0.7	2.8	70.0	25.4	0.7	3.3	68.8
36097-00-4	6	$S(CH_2)_2OH$		82–93	80–95 (0.5)	1.3683	$C_{10}H_9F_{13}OS$	28.3	2.1	7.5		28.1	2.0	7.1	
34360-26-4	8	$S(CH_2)_2OH$		96	74.5–75.0[a]		$C_{12}H_9F_{17}OS$	27.5	1.7	6.1	61.6	27.2	1.8	6.0	61.4
36097-05-9	10	$S(CH_2)_2OH$		88	109.5–110.5[a]		$C_{14}H_9F_{21}OS$	26.9	1.5	5.1		26.9	1.5	4.8	
36097-07-1	6	$S(CH_2)_4SH$		98[e]	150 (1)										
60280-04-8	6	$SCHCO_2H$ | CH_2CO_2H		47	133–134[a]		$C_{12}H_9F_{13}O_4S$	29.0	1.8		49.8	29.1	1.8		50.3
36097-08-2	6	$S(CH_2)_2NH_2$		71	63 (0.5)	1.3695	$C_{10}H_{10}F_{13}NS$	28.4	2.4	3.3[b]		28.3	2.4	3.7[b]	
36097-10-6	6	$NH(CH_2)_2OH$		58	171–173[a,f]		$C_{10}H_{11}ClF_{13}NO$[f]	27.0	2.5		55.6	27.8	2.5		55.4
62571-55-5	6	N_3		90[g,h]			$C_8H_4F_{13}N_3$	24.7	1.0	10.8[b]		24.5	1.0	11.1[b]	[h]

[a] Melting point. [b] Value given is % N. [c] By method A, bp 63–64 °C (20 mm); by method C, bp 84–85 °C (58 mm). [d] The sulfide $(R_FCH_2CH_2)_2S$. [e] Based on unrecovered iodide. [f] Amine hydrochloride. [g] Conversion. [h] The sample also contained 2.3% I, corresponding to 8.5% unchanged iodide in the azide.

Table II. Properties of Monomers $R_F(CH_2)_nX(CH_2)_mYCOC(R){=}CH_2$

Registry No.	R_F	n	X	m	Y	R	Method	Yield, %	Bp, °C (Torr)	Formula	Anal., %							
											Calcd				Found			
											C	H	F	S	C	H	F	S
58038-05-4	C_6F_{13}	2	[a]	[a]	S	CH_3	A[b]	20	101 (9)									
62601-24-5	$C_{10}F_{21}$	2	[a]	[a]	S	CH_3	A	28	Solid									
35180-63-3	C_4F_9	11	S	2	O	CH_3	A	64										
36097-01-5	C_6F_{13}	2	S	2	O	CH_3	B	89	90 (0.4)	$C_{14}H_{13}F_{13}O_2S$	34.2	2.7	50.2	6.5	34.2	3.1	50.1	6.1
36097-02-6	C_6F_{13}	2	S	2	O	H	C	19	79 (0.1)	$C_{13}H_{11}F_{13}O_2S$	32.6	2.3	51.7	6.7	32.6	2.3	51.9	6.6
45305-83-7	C_6F_{13}	2	S	4	S	CH_3	A	27	130 (0.5)									
36097-04-8	C_8F_{17}	2	S	2	O	CH_3	B	74	130 (0.3)	$C_{16}H_{13}F_{17}O_2S$	32.4	2.2	54.6	5.4	32.5	2.2	53.8	5.1
36097-06-0	$C_{10}F_{21}$	2	S	2	O	CH_3	B	92	55–56[c]	$C_{18}H_{13}F_{21}O_2S$	31.2	1.9		4.6	31.3	1.9		4.4
36097-11-7	C_6F_{13}	2	NH	2	O	CH_3	A	29										
36097-09-3	C_6F_{13}	2	S	2	NH	CH_3	A	57	120 (0.05)									

[a] The $-X(CH_2)_m-$ segment is not present. [b] For description of methods A, B, and C, see Experimental Section. [c] Melting point.

decylenyl alcohol by heating for 8 h at 85 °C under nitrogen in the presence of 0.5 g of azobisisobutyronitrile.[4] The unreacted iodide was removed at reduced pressure, and the iodine atom was reductively removed by adding the residue in 225 mL of 95% ethanol dropwise to a slurry of 60 g of zinc dust in 150 mL of ethanol and 30 mL of concentrated hydrochloric acid. The mixture was diluted with 400 mL of water and filtered to remove zinc. The organic layer was washed with water and vacuum dried. The crude product (87% overall yield) was converted to the tosylate with *p*-toluenesulfonyl chloride in pyridine. The tosylate, 20 g (0.037 mol), was refluxed with 1.5 g (0.0375 mol) of sodium hydroxide, 2.5 g (0.032 mol) of 2-mercaptoethanol, and 150 mL of moist *tert*-butyl alcohol for 3.5 h. The product was isolated by drowning in water, washing, and vacuum drying. The infrared and NMR spectra were consistent with the assigned structure.

β-(Perfluorohexyl)ethyl Azide. The iodide 1, $n = 6$, was refluxed with 1.1 mol of sodium azide in moist *tert*-butyl or isopropyl alcohol. Conversion was followed by the increasing infrared absorption at 4.7 μ. The best conversion was about 90%. The azide and unchanged iodide are difficult to separate by distillation through a small column. Our sample contained 8.5% of starting iodide, calculated from the analysis (2.3% I).

β-(Perfluorohexyl)ethylamine. Reduction of the azide by the method of Adams and Blomstrom[7] with alkaline dithionite in aqueous isopropyl alcohol was unsuccessful because of the azide's very low solubility. A solution of the azide in ethanol–hydrogen chloride failed to absorb hydrogen over platinum/carbon. However, hydrogenation proceeded to completion in acetic acid over Pt/C in 6 h at 60 psi hydrogen pressure. The product formed a stiff gel when the mixture was added to aqueous base. Benzene was added, and the benzene layer was azeotropically distilled to dry it; the solution foamed severely because of the surfactant properties of the amine. Adding dry hydrogen chloride to the benzene solution precipitated a very hygroscopic amine hydrochloride. The amine also formed a solid benzoyl derivative. The products were not further characterized.

Preparation of (Meth)acrylyl Derivatives. A. With Methacryloyl Chloride. The alcohol, thiol, or amine in anhydrous ether was treated dropwise with separate ethereal solutions of methacryloyl chloride and pyridine. The mixture was then refluxed for 0.5 h, washed with water, saturated sodium bicarbonate solution, and water, dried with potassium carbonate, and distilled. The monomers were identified by their analyses, spectra, and polymerization behavior.

B. Transesterification with Methyl Methacrylate. A mixture of 0.2 mol of alcohol, 0.5 mol of methyl methacrylate, and 0.3 g of 3,3′,5,5′-tetramethyldiphenoquinone (polymerization inhibitor) was refluxed under a fractionating column; 10.5 g of ester was removed, carrying with it any water as the azeotrope. Then 0.2 mL (0.67 mmol) of tetraisopropyl titanate was added. The methanol–methyl methacrylate azeotrope was distilled overhead. When the head temperature could no longer be held below 66 °C, transesterification was complete (about 15 min). From the weight and refractive index of the azeotrope, 6.3 g of methanol had been removed (theory 6.4 g). (When necessary, additional methyl methacrylate and titanate may be added and distillation continued to ensure completion.) The very rapid transesterification bespeaks assistance by the sulfur atom β to the hydroxyl. $R_FCH_2CH_2OH$ require several hours.

Two drops of water was added to hydrolyze the titanates, and the product was fractionally distilled. The higher homologues were yellow from codistilling quinone, but that did not interfere with polymerization because it was easily overridden by the initiator. Only negligible polymeric residue was formed in this esterification.

C. Fischer Esterification. A mixture of 100 mL of dry toluene, 0.6 mL of concentrated sulfuric acid, 14.4 g (0.20 mol) of acrylic acid, 0.3 g of tetramethyldiphenoquinone, 2 drops of nitrobenzene, and 84.8 g (0.20 mol) of $C_6F_{13}CH_2CH_2SCH_2CH_2OH$ was refluxed under a water separator. The theoretical amount of water (3.6 mL) was collected in 4 h. The mixture was taken up in 650 mL of ether and washed with 650 mL of 30% sodium chloride solution and 200 mL of saturated sodium bicarbonate solution. The product was distilled, but only 18.1 g (19%) of monomer was obtained because of extensive polymerization in the still pot.

Polymerization of (Meth)acrylates. Each monomer (Table I), 10.0 g, was dissolved in 11.4 mL of difluorotetrachloroethane (Freon 112) and 2.6 mL of Freon 113 containing 10 mg of azobisisobutyronitrile. The solution was purged with nitrogen and held at 75 °C under nitrogen for 12 h. Two additional 10-mg portions of initiator were added after 4 and 8 h. The polymer was precipitated with methanol and purified by two additional methanol precipitations from trichlorotrifluoroethane solution. The surface properties of these polymers have been reported elsewhere,[8] along with descriptions of procedures for bulk and emulsion polymerization of these monomers.

Registry No.—1($n = 6$), 2043-57-4; 1($n = 8$), 2043-53-0; 1($n = 10$), 2043-54-1; thiourea, 62-56-6; sodium thiocyanate, 540-72-7; sodium hydrosulfide, 16721-80-5; $C_6F_{13}(CH_2)_2SO_3H$ Na salt, 27619-94-9; $C_6F_{13}(CH_2)_2SO_3H$ $CH_3C_6H_4$-*p*-NH, 62571-56-6; 2-mercaptoethanol, 60-24-2; mercaptosuccinic acid, 70-49-5; 2-mercaptoethylamine HCl, 156-57-0; β-(perfluorohexyl)ethyl-*p*-toluenesulfonate, 51740-38-6; 2-aminoethanol, 141-43-5; β-(perfluorohexyl)ethyl-β-hydroxyethylamine, 62571-57-7; perfluorobutyl iodide, 423-39-2; sodium azide, 26628-22-8; methacryloyl chloride, 920-46-7; methyl methacrylate, 80-62-6.

References and Notes

(1) R. W. Fasick, U.S. Patent 3 239 557; C. S. Rondestvedt, Jr., *J. Org. Chem.*, in press.

(2) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, N.Y., 1963, p 250; C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, **75**, 141 (1953).

(3) British Patent 1 348 409; Belgian Patent 764 420; German Patents 2 059 257 and 2 013 103.

(4) N. O. Brace, U.S. Patents 3 016 406 and 3 145 222; *J. Org. Chem.*, **27**, 3027, 3033, 4491 (1962); **28**, 3093 (1963).

(5) C. S. Rondestvedt, Jr., U.S. Patent 3 377 390; R. E. Parsons, Jr., U.S. Patents 3 132 185 and 3 385 682.

(6) R. B. Hager, U.S. Patent 3 471 518; N. O. Brace, U.S. Patent 3 172 910; W. S. Freedman, U.S. Patent 3 088 849.

(7) R. Adams and D. C. Blomstrom, *J. Am. Chem. Soc.*, **75**, 3405 (1953).

(8) C. S. Rondestvedt, Jr., U.S. Patents 3 655 732; 3 773 826; 3 786 089; 3 808 251.