Synthesis of Methyl Polyfluoroalkyl Sulphides and Polyfluoroalkane-sulphonic Acids

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Summary Methyl polyfluoroalkyl sulphides, synthesised by two novel routes: (i) photochemical reaction of a polyfluoroiodoalkane with dimethyl sulphide or dimethyl disulphide and (ii) reaction of a polyfluoroiodoalkane with sodium methanethiolate in the presence of dimethyl disulphide, are useful precursors of polyfluoroalkane-sulphonic acids.

An investigation into solvent effects on the free-radical addition of trifluoroiodomethane to fluoro-olefins revealed that when dimethyl sulphide was the solvent, photochemically initiated replacement of methyl by trifluoromethyl occurred to give methyl trifluoromethyl sulphide.[1] The present communication shows that this exchange reaction (Method A) is capable of wide application and describes other new routes (Methods B and C) for the synthesis of methyl polyfluoroalkyl sulphides which are valuable precursors of the industrially important polyfluoroalkane-sulphonic acids.

Use of a dimethyl sulphide–polyfluoroiodoalkane ratio of *ca.* 4:1 and an irradiation period of 14—28 days, gives the methyl polyfluoroalkyl sulphide in 30–65% yield (see Table) and 78—100% conversion; this compound, the 1*H*-polyfluoroalkane (an undesirable by-product), and the other major products, the sulphonium iodide, $Me_3S^+I^-$ (83—92%), and bis(methylthio)methane (15—53%), can be explained by the free-radical Scheme.

$$R_fI \longrightarrow R_f\cdot + I\cdot$$

$$R_f\cdot + Me_2S \longrightarrow R_f\dot{S}Me_2 \longrightarrow R_fSMe + Me\cdot$$

$$R_f\cdot + Me_2S \longrightarrow R_fH + MeS{\cdot}CH_2\cdot$$

$$MeS{\cdot}CH_2\cdot + Me_2S \longrightarrow MeS{\cdot}CH_2{\cdot}\dot{S}Me_2 \longrightarrow (MeS)_2CH_2 + Me\cdot$$

$$Me\cdot + R_fI \longrightarrow MeI + R_f\cdot$$

$$MeI + Me_2S \longrightarrow Me_3S^+I^-$$

Scheme

Table

Reactant R_fI		Products (% yield)[a] R_fSMe			R_fH	
	A	B	C	A	B	C
CF_3I	63	92	85	33	5	10
$CF_3{\cdot}CF_2{\cdot}CF_2I$ ..	50	93	75	46	6	7
$(CF_3)_2CFI$	32	83	39	66	12	5
$CF_2Cl{\cdot}CF_2I$	45	82		52	14	
$(CF_3)_2CF(CF_2)_4I$ ..	46	80	84	45	17	7
n-$C_6F_{13}I$		76	88		15	4
n-$C_8F_{17}I$		73	86		10	3
$(CF_3)_2CF(CF_2)_6I$ ..		74	76		15	4

[a] 300 ml silica tubes; Hanovia S 500 medium-pressure u.v lamps at a distance of 10—15 cm; reaction temp. *ca.* 40 °C.

The use of dimethyl disulphide in place of dimethyl sulphide (Method B) results in much higher yields (75—95%) of the methyl polyfluoroalkyl sulphides with conversions of 92—100% from a disulphide–polyfluoroiodoalkane ratio between 2:1 and 8:1 (see Table).

$$R_f\cdot + MeS{\cdot}SMe \longrightarrow R_f\dot{S}Me{\cdot}SMe \longrightarrow R_fSMe + MeS\cdot$$

$$R_f\cdot + MeS{\cdot}SMe \longrightarrow R_fH + MeS{\cdot}S{\cdot}CH_2\cdot$$

$$MeS\cdot \text{ or } MeS{\cdot}S{\cdot}CH_2\cdot + R_fI \longrightarrow R_f\cdot\ (+Me_2S_2,\ MeS{\cdot}S{\cdot}CH_2I,\ \textit{etc.})$$

$$2MeS\cdot \longrightarrow MeS{\cdot}SMe$$

Method C, the reaction of the polyfluoroiodoalkane with sodium methanethiolate in the presence of dimethyl disulphide, is more convenient since it obviates the need for photochemical reaction.

$$R_fI + MeS^-Na^+ \xrightarrow{Me_2S_2} R_fSMe$$

A molar ratio of polyfluoroiodoalkane–methanethiolate–disulphide of *ca.* 1·0:1·2:5, in an aprotic solvent, preferably dimethyl sulphoxide, approximately equal in volume to that of the liquid reactants, a temperature of *ca.* 105°, and a reaction period of 20—40 h depending on the polyfluoroiodoalkane used (longer-chain polyfluoroiodoalkanes are less soluble in the solvent and require longer reaction time) give high yields (see Table) of the methyl polyfluoroalkyl sulphide. The relatively low yield from heptafluoro-2-iodopropane, in which chain branching occurs on the α-carbon, can be associated with the difference in reactivity of, and ease of olefin formation from, the carbanion derived from it compared with carbanions of type $-CF_2^-$; it is noteworthy that branching further along the fluorocarbon chain does not affect the yield.

$$R_fI + MeS^- \longrightarrow R_f^- + MeSI$$
$$R_f^- + MeSI \longrightarrow R_fSMe + I^-$$
$$R_f^- + MeS{\cdot}SMe \longrightarrow R_fSMe + MeS^-$$
$$R_f^- + MeS{\cdot}SMe \longrightarrow R_fH + MeS{\cdot}S{\cdot}CH_2^-$$

The methyl polyfluoroalkyl sulphides may be converted into the sulphones by hydrogen peroxide[2] or better by cold potassium permanganate in glacial acetic acid.[3] Aqueous hypochlorite converts the sulphones into the trichloromethyl polyfluoroalkyl sulphones, and potassium hydroxide in aqueous dioxan affords the salt of the polyfluoroalkanesulphonic acid in high yield. Oxidation of the methyl polyfluoroalkyl sulphones by neutral aqueous potassium permanganate under reflux also gives good yields of the sulphonic acids.

$$R_fSMe \longrightarrow R_fSO_2Me \xrightarrow{NaOCl} R_fSO_2{\cdot}CCl_3 \xrightarrow{OH^-} R_fSO_3^-$$

All new compounds gave satisfactory analytical and spectral data.

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[1] B. Higginbottom and R. N. Haszeldine, unpublished results.

[2] R. B. Ward, *J. Org. Chem.*, 1965, **30**, 3009; U.S.P. 3,346,606/1967.

[3] K. E. Rapp, R. L. Pruett, J. T. Barr, C. T. Bahner, J. D. Gibson,and R. H. Lafferty, *J. Amer. Chem. Soc.*, 1950, **72**, 3642.