

Perfluoroalkyl Derivatives of Sulphur. Part XII.¹ The Reaction of Heptafluoro-1-iodopropane with Ethyl Methyl Sulphide, Methyl Trifluoromethyl Sulphide, and Methanethiol

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The photochemical reaction of heptafluoro-1-iodopropane with ethyl methyl sulphide gives heptafluoro-*n*-propyl methyl sulphide (7%), ethyl heptafluoro-*n*-propyl sulphide (21%), 1*H*-heptafluoropropane (58%), 1,1,1,2,2,3,3-heptafluoropentane (6%), dimethyl sulphide, diethyl sulphide, and minor products. Methyl trifluoromethyl sulphide gives trifluoroiodomethane, heptafluoro-*n*-propyl methyl sulphide (51%), perfluoro-*n*-hexane (20%), and 1*H*-heptafluoropropane (24%); with methanethiol the major products are 1*H*-heptafluoropropane (85%) and heptafluoro-*n*-propyl methyl sulphide (14%).

IN a continuation of the study of the reaction of polyfluoroiodoalkanes with dialkyl sulphides² and dialkyl disulphides¹ the photochemical reactions of heptafluoro-1-iodopropane with ethyl methyl sulphide and methyl trifluoromethyl sulphide have been investigated. The photochemical reaction of the iodoalkane with methanethiol has also been studied. The results of the present reactions are compared in the Table with that obtained

Reaction of heptafluoro-1-iodopropane with various sulphides

Sulphide	Irradiation period (days)	Extent of re-action (%)	Products [yield (%)]			
			C ₃ F ₇ H	C ₃ F ₇ SMe	C ₃ F ₇ SEt	C ₆ F ₁₄
Me ₂ S	28	100	46	50		Trace
MeSEt	49	95	58	7	21	Trace
CF ₃ SMe	35	43	24	51		20
MeSH	9	98	85	14		

Yields are based on the amount of iodoalkane consumed during the reaction.

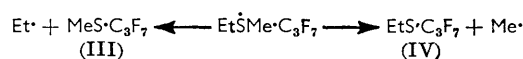
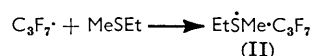
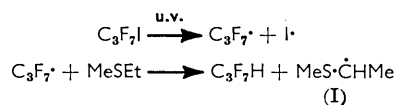
from the reaction of the iodoalkane with dimethyl sulphide.

The photochemical reaction of the iodoalkane with

¹ Part XI, R. N. Haszeldine, R. B. Rigby, and A. E. Tipping, *J.C.S. Perkin I*, 1972, 159.

methyl ethyl sulphide gives, in addition to the products shown in the Table, 1,1,1,2,2,3,3-heptafluoropentane (6%), and the following products derived only from methyl ethyl sulphide (yields based on the amount of sulphide consumed during the reaction): dimethyl sulphide (5%), diethyl sulphide (28%), ethane (4%), trimethylsulphonium iodide (16%), smaller amounts of methane, ethylene, and iodoethane, unidentified high-boiling material, and black tar; methyl ethyl sulphide (30%) was recovered unchanged.

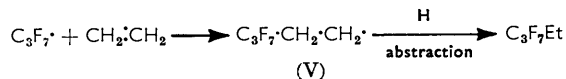
To account for the major fluorine-containing products, a mechanism is proposed similar to that postulated for the reaction of polyfluoromonoiodoalkanes with dimethyl sulphide.²



² R. N. Haszeldine, B. Higginbottom, R. B. Rigby, and A. E. Tipping, *J.C.S. Perkin I*, 1972, 155.

A higher yield of 1*H*-heptafluoropropane was obtained than in the corresponding reaction with dimethyl sulphide, which is consistent with the larger number of hydrogen atoms and the presence of secondary carbon-hydrogen bonds in methyl ethyl sulphide. Hydrogen abstraction would be expected to occur mainly at the secondary carbon-hydrogen bonds since the secondary radical (I) is stabilised both by the lone pairs on the adjacent sulphur atom and by the adjacent methyl group.

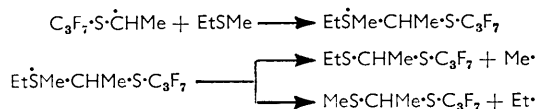
Decomposition of radical (I) ($\text{MeS}\cdot\dot{\text{C}}\text{H}\cdot\text{CH}_3 \rightarrow \text{MeS}\cdot + \text{CH}_2\cdot\text{CH}_3$) accounts for the ethylene observed in the reaction, and reaction of heptafluoro-*n*-propyl radicals with ethylene or decomposition of the radical (II)



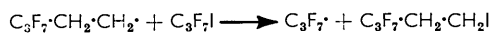
($\rightarrow \text{MeS}\cdot + \text{C}_3\text{F}_7\text{Et}$) is the probable source of the heptafluoropentane.

Since observation of the products (III) and (IV) indicates that both ethyl and methyl radicals are formed by decomposition of the expanded radical (II), it is possible that some heptafluoropentane is formed by the free-radical combination process $\text{C}_3\text{F}_7\cdot + \text{Et}\cdot \rightarrow \text{C}_3\text{F}_7\text{Et}$, although 1,1,1,2,2,3,3-heptafluorobutane would also have been expected to be formed by a combination of heptafluoro-*n*-propyl and methyl radicals.

Further reactions of radicals (I) and (V) are possible: these include radical displacement reactions on methyl ethyl sulphide, *e.g.*



[*cf.* reaction of radical $\text{MeS}\cdot\text{CH}_2\cdot$ with dimethyl sulphide to give bis(methylthio)methane²], and iodine abstraction, *e.g.*



However, such products would be high-boiling, and it is possible that they were present in the high-boiling product which was not characterised.

The formation of the ethyl sulphide (IV) in much higher yield than the sulphide (III) indicates that the major decomposition of the intermediate radical (II) is by loss of a methyl radical.

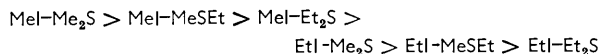
The alkyl radicals $\text{R}\cdot$ (where $\text{R} = \text{Me}$ or Et) formed by decomposition of the radical (II) may abstract iodine or hydrogen, or react with the reactant sulphide to form dimethyl sulphide or diethyl sulphide.



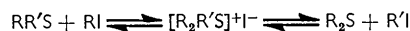
² E. E. Reid, 'Organic Chemistry of Bivalent Sulphur,' Chemical Publishing Co., Inc., New York, 1960, vol. 2, p. 67.

⁴ F. E. Ray and I. Levine, *J. Org. Chem.*, 1937, 2, 267.

The only compound required by the above scheme which was not detected in the products was iodomethane. However, it is reported³ that the reactivity of iodoalkanes with dialkyl sulphides, to form the corresponding trialkylsulphonium iodides, is in the order:



It is thus evident that any iodomethane and dimethyl disulphide formed in the present reaction will react faster than any other combination of iodoalkane and dialkyl sulphide. Trialkylsulphonium iodides are also known to be in equilibrium with the parent sulphides,⁴ and



so it is possible that trialkylsulphonium iodides other than the trimethyl compound were formed during the reaction, particularly in the early stages when the concentration of dimethyl sulphide was low. In the presence of iodomethane conversion of these into the observed trimethylsulphonium iodide is to be expected on the basis that this sulphonium iodide is the most stable of all the trialkylsulphonium iodides which could be formed in the reaction.

The observation that heptafluoro-1-iodopropane reacts faster with dimethyl sulphide than with methylethyl sulphide is possibly due to an increased steric factor in the latter case.

The above explanations are probably an oversimplification, since methyl ethyl sulphide is expected to dissociate on photolysis in a similar way to dimethyl sulphide,⁵ and the iodoalkanes (iodoethane and iodomethane) formed in the reaction are also known to dissociate on irradiation.⁶

The reaction of heptafluoro-1-iodopropane with methyl trifluoromethyl sulphide gave, in addition to the products shown in the Table, trifluoroiodomethane (75% based on the iodine available from the $\text{C}_3\text{H}_7\text{I}$ consumed during the reaction), and traces of trifluoromethane, perfluoro-*n*-butane, and tar. The results show that this reaction differed from the corresponding dimethyl sulphide reaction in that (i) attack on methyl trifluoromethyl sulphide was slower, (ii) hydrogen abstraction occurred to a lesser extent, (iii) the yield of the perfluoroalkyl radical dimerisation product, perfluoro-*n*-hexane, was greater, and (iv) the only sulphide formed was methyl heptafluoro-*n*-propyl sulphide.

The first two observations may be explained by the $-I$ effect of the trifluoromethyl group, which withdraws electron density from the adjacent sulphur atom and thus makes attack by the heptafluoro-*n*-propyl radical on the sulphur atom more difficult. This does not lead to an increase in hydrogen abstraction by the $\text{C}_3\text{F}_7\cdot$ radical, partly because of the presence of fewer hydrogen atoms in the sulphide than in dimethyl sulphide, and partly because stabilisation of the radical $\text{CF}_3\cdot\text{S}\cdot\text{CH}_2\cdot$

⁵ W. A. Pryor, 'Mechanisms of Sulphur Reactions,' McGraw-Hill Book Co. Inc., New York, 1962, p. 42; L. Horner and J. Dorges, *Tetrahedron Letters*, 1963, 757.

⁶ S. Hacopian and T. Iredale, *Nature*, 1950, 166, 156.

unchanged methyl trifluoromethyl sulphide (0.861 g, 7.41 mmol, 75% recovered), and an unidentified component (0.03 g), and (iv) a mixture (1.256 g) which was separated by g.l.c. (8 m column at 40°) into its four components, identified as perfluoro-n-hexane (0.080 g, 0.23 mmol, 20%), methyl heptafluoro-n-propyl sulphide (0.254 g, 1.17 mmol, 51%), unchanged iodoalkane (0.920 g, 3.11 mmol, 57% recovered), and an unidentified component (trace). A small amount of tar remained in the reaction tube.

(c) *With methanethiol.* The iodoalkane (6.76 g, 22.8 mmol) and methanethiol (1.10 g, 22.9 mmol), sealed in a silica tube (100 ml) and irradiated at a distance of 10 cm from the lamp (9 days), gave (i) a gas which did not con-

dense at -196° (0.008 g, 1.9 mmol; *M*, 4) and which showed no i.r. absorption in the range 2.5–15 μm and was presumed to be mainly hydrogen, (ii) 1*H*-heptafluoropropane (3.24 g, 19.0 mmol, 85%) (Found: *M*, 171. Calc. for C_3HF_7 : *M*, 170), (iii) a mixture (0.82 g) shown by g.l.c. (8 m column at 20°) to consist of unchanged iodoalkane (0.11 g, 0.37 mmol, 2% recovered) and methyl heptafluoro-n-propyl sulphide (0.71 g, 3.28 mmol, 14%), (iv) a higher-boiling liquid fraction (0.12 g), and (v) an acetone-soluble black tar (*ca.* 3.5 g).

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