372. *Organometallic and Metalloid Compounds Made from Heptafluoro-2-iodopropane, and their Properties.*

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Hitherto unknown perfluoroisopropyl derivatives of magnesium, lithium, zinc, and sulphur have been prepared from heptafluoro-2-iodopropane. The magnesium and lithium compounds could not be hydrolysed to 2*H*-heptafluoropropane but reacted with carbonyl compounds to produce alcohols; the physical properties of these alcohols are compared with those of the corresponding perfluoro-n-propyl compounds. A perfluoroisopropylsilane, $(CF_3)_2CF{\cdot}SiMe_3$, was prepared by using the Grignard reagent, and was unchanged at 250°. The infrared spectra of perfluoroisopropyl compounds have been examined and are correlated.

THE addition of "iodine monofluoride" (a stoicheiometric mixture of iodine and iodine pentafluoride) to hexafluoropropene[1] has provided an easy route to the secondary fluoroalkyl iodide, heptafluoro-2-iodopropane. Heptafluoro-1-iodopropane is well known and has been used to prepare perfluoropropylmagnesium iodide directly;[2] perfluoropropylmagnesium bromide[3] and -lithium[4] have also been made by exchange methods. These appear to be the only perfluoroalkyl Grignard or lithium reagents which have proved of synthetic value; they undergo a variety of normal reactions. Using techniques developed by McBee and his co-workers[3,4] we have found that iodine exchange takes place between heptafluoro-2-iodopropane and phenylmagnesium bromide and butyl- or methyl-lithium at −78°, to yield the perfluoroisopropyl Grignard reagent $(CF_3)_2CF{\cdot}MgBr$ and lithium derivative $(CF_3)_2CFLi$, respectively; these reagents decompose at room temperature, yielding 70·5% and 74% of hexafluoropropene, respectively. Butyl iodide is obtained in 80% yield from the reaction with butyl-lithium and this indicates the extent to which exchange takes place. The corresponding reaction with heptafluoro-1-iodopropane and butyl-lithium resulted in 77% conversion[4] into hexafluoropropene when the mixture was warmed. Thus the change from a primary to a secondary perfluoroalkyl iodide has no significant effect on the extent of iodine exchange.

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[1] Chambers, Musgrave, and Savory, *Proc. Chem. Soc.*, 1961, 113; *J.*, 1961, 3776.

[2] Henne and Francis, *J. Amer. Chem. Soc.*, 1951, **73**, 3518; 1953, **75**, 992; Haszeldine, *J.*, 1952, 3423; 1953, 1748; Pierce and Levine, *J. Amer. Chem. Soc.*, 1953, **75**, 1254.

[3] Pierce, Meiners, and McBee, *J. Amer. Chem. Soc.*, 1953, **75**, 2516; McBee, Roberts, and Meiners, *ibid.*, 1957, **79**, 335.

[4] Pierce, McBee, and Judd, *J. Amer. Chem. Soc.*, 1954, **76**, 474.

Perfluoroisopropyl-lithium and -magnesium bromide yielded little or no heptafluoropropane with either 3N-sulphuric acid or ethanol under similar conditions to those in which Pierce *et al.*[4] obtained a 77% yield from perfluoro-n-propyl-lithium and 3N-sulphuric acid. This effect of chain-branching is surprising. If we consider hydrolysis or alcoholysis to involve the formation of a fluoro-carbon anion $(CF_3)_2{\cdot}CF^-$, then this anion has greater opportunity for resonance stabilisation of the type $CF_3{\cdot}^-CF{\cdot}CF_3 \longleftrightarrow CF_3{\cdot}CF{=}CF_2F^-$, etc., than the corresponding 1-heptafluoropropyl anion $CF_3{\cdot}CF_2{\cdot}CF^-$. On this basis it can be argued that the perfluoroisopropyl anion would be a weaker nucleophile than the normal isomer and so should eliminate a fluoride ion in preference to reacting with a proton.

Reaction of perfluoroisopropyl-lithium with acetone and propionaldehyde gave the alcohols $(CF_3)_2CF{\cdot}CMe_2{\cdot}OH$, and $(CF_3)_2CF{\cdot}CHEt{\cdot}OH$ in 13% and 53% yield, respectively. The reactions were carried out by the method of McBee and his co-workers:[4] heptafluoro-2-iodopropane in ether at −78° was treated simultaneously with methyl-lithium or phenylmagnesium bromide and the reactant. Table 1 shows boiling points of some of the alcohols prepared, for comparison with the straight-chain isomers. No uniform effect on b. p. is apparent for the replacement of a primary by a secondary perfluoroalkyl group.

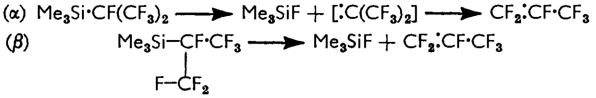
TABLE 1.

B. p.s of heptafluoropropyl alcohols.

	$R_F = (CF_3)_2CF$	$R_F = CF_3{\cdot}CF_2{\cdot}CF_2$		$R_F = (CF_3)_2CF$	$R_F = CF_3{\cdot}CF_2{\cdot}CF_2$
$Me{\cdot}CHR_F{\cdot}OH$	90°	101°[5]	$MeEtCR_F{\cdot}OH$	126°	—
$Et{\cdot}CHR_F{\cdot}OH$	109	115[4]	$Pr^n{\cdot}CHR_F{\cdot}OH$	128	128[5]
$Me_2CR_F{\cdot}OH$	109	107[4]			

An approximate pK_a value for $(CF_3)_2CF{\cdot}CHPr{\cdot}OH$ has been determined and gives $K = 0{\cdot}2 \times 10^{-12}$, whereas Haszeldine[5] found for $n\text{-}C_3F_7{\cdot}CHEt{\cdot}OH$ and $n\text{-}C_3F_7{\cdot}CHPr{\cdot}OH$ $K = 4 \times 10^{-12}$. As Haszeldine points out, these actual values have little significance since they were determined by using the Henderson equation and the approximation is not very accurate in that region. The comparison, however, confirms the fact that replacement of a fluorine atom by a trifluoromethyl group reduces the inductive effect of the fluoroalkyl group and hence the acidity of the alcohol. This reduction in acidity is, therefore, much more pronounced in passing from $CF_3{\cdot}CF_2$ to $(CF_3)_2CF$ than from CF_3 to $CF_3{\cdot}CF_2$.[5]

Reaction of perfluoroisopropyl-lithium with chlorotrimethylsilane at −50° gave a low yield (17·5%) of trimethylperfluoroisopropylsilane, b. p. 95°. Although there was insufficient of this compound on which to perform any searching tests, it was stable at 250° for 1½ hr. Haszeldine and his co-workers have shown that α- and β-fluorine atoms in fluoroalkyl-chlorosilanes[6] and -siloxanes,[7] when heated, undergo α- and β-elimination of fluorine; *e.g.*, $CHFCl{\cdot}CF_2{\cdot}SiCl_3$ decomposed at 250° and the major organic product was $CHF{:}CFCl$;[6] $[CHF_2{\cdot}CH_2{\cdot}SiO_{1{\cdot}5}]_n$ decomposed at 220°, yielding $CHF{:}CH_2$.[7] It seems, therefore, either that other groups attached to silicon have a marked effect on the thermal stability of fluoroalkyl-silicon compounds or that migration of fluorine to silicon is not as easy from a perfluoroalkyl group as from a fluoroalkyl or chlorofluoroalkyl group. If α- or β-elimination from $(CF_3)_2CF{\cdot}SiMe_3$ had been easy, then hexafluoropropene would have been produced:



$$(\alpha)\quad Me_3Si{\cdot}CF(CF_3)_2 \longrightarrow Me_3SiF + [{:}C(CF_3)_2] \longrightarrow CF_2{:}CF{\cdot}CF_3$$

$$(\beta)\quad Me_3Si{-}\underset{F-CF_2}{\underset{|}{C}}F{\cdot}CF_3 \longrightarrow Me_3SiF + CF_2{:}CF{\cdot}CF_3$$

Perfluoroisopropylzinc iodide can be formed easily by refluxing heptafluoro-2-iodopropane with zinc dust in dioxan but, like perfluoro-n-propylzinc iodide,[8] is too stable to

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[5] Haszeldine, *J.*, 1953, 1757.

[6] Haszeldine and Young, *Proc. Chem. Soc.*, 1959, 394.

[7] Haszeldine, Newlands, and Plumb, *Proc. Chem. Soc.*, 1960, 147.

[8] Miller, Bergmann, and Fainberg, *J. Amer. Chem. Soc.*, 1957, **79**, 4159.

be of much synthetic value; *e.g.*, reaction of perfluoroisopropylzinc iodide with benzoyl chloride gave none of the expected ketone, and 74% of the starting iodide could be accounted for after final hydrolysis.

With respect to homolysis the carbon–iodine bond in heptafluoro-2-iodopropane is even more labile than in heptafluoro-1-iodopropane. Consequently, heptafluoro-2-iodopropane reacts easily with mercury when irradiated with ultraviolet light, to give the coupled product perfluoro-(2,3-dimethylbutane),[1] $(CF_3)_2CF{\cdot}CF(CF_3)_2$, in 96·5% yield; and when a mixture of heptafluoro-2-iodopropane and chlorine was irradiated, ready replacement of iodine led to 2-chloroheptafluoropropane (98%). When the iodide was heated with sulphur in a sealed tube at 243°, the bisperfluoroisopropyl sulphide (11%), disulphide (34%), and trisulphide (17·5%) were produced; they were separated easily by vapour-phase chromatography. The disulphide was also prepared in low yield (22%) by the reaction of mercuric sulphide with heptafluoro-2-iodopropane in a quartz tube under the influence of ultraviolet radiation. The boiling points are compared in Table 2 with those of the corresponding isopropyl compounds and the perfluoro-n-propyl compounds. Hauptschein and Grosse,[9] using a reaction temperature of 250°, did not isolate any appreciable amount of the monosulphide, but Tiers,[10] using a temperature of 300°, isolated the monosulphide in 11% yield. As for many fluorocarbons, the boiling points of these fluoroalkyl compounds are lower than those of their alkyl analogues, but a surprising point is the similarity between the values for the perfluoroisopropyl mono- and di-sulphide; moreover, in vapour-phase chromatography the retention time (on tritolyl phosphate as stationary phase) for the disulphide was shorter than for the monosulphide. Steric interaction between the perfluoroisopropyl groups will be at a maximum in the monosulphide, tending to make the C–S–C skeleton more linear and, as a consequence, the mono- will be more symmetrical than the di-sulphide, with a consequent effect on the b. p. of the former.

TABLE 2.

B. p.s of perfluoro-n- and -iso-propyl sulphides.

	R = $CF_3{\cdot}CF_2{\cdot}CF_2$			
	(ref. 9)	(ref. 10)	$(CF_3)_2CF$	$(CH_3)_2CH$
R_2S	—	88°	116·9°	120·5°
R_2S_2	122°	123	119·0	174·5
R_2S_3	153	155·5	150·0	—

Very few conclusive spectral assignments of fluorocarbon groups have been possible because of the many interactions which occur. However, the infrared spectra of perfluoroisopropyl compounds can be divided into three regions: 1299—1126, 1009—892 and 759—713 cm.$^{-1}$ (see Table 3). The bands are strong unless otherwise indicated. Absorption in the region 1299—1126 cm.$^{-1}$ is undoubtedly associated with C–F stretching and the 759—713 cm.$^{-1}$ region can be assigned to CF_3–CF deformation; Bellamy and Branch [11] examined a large number of fluorocarbons and found that compounds containing either $CF_3{\cdot}CF$ or $CF_3\,CF_2$ absorbed in the region 745—730 cm.$^{-1}$, which they assigned to CF_3 deformation since the simple CF_3 derivatives did not absorb in this region. The remaining region 970—892 cm.$^{-1}$ in which absorption has consistently appeared for our compounds, we tentatively assign to C–F deformation. Because of the close similarity between the spectra of heptafluoro-2-iodopropane and our disulphide, it appears that a C–S stretching frequency either is too weak to be observed or is masked by C–CF_3 deformation. Extra bands appear in the spectrum of our trisulphide at and between 705 and 671 cm.$^{-1}$ which

[9] Hauptschein and Grosse, *J. Amer. Chem. Soc.*, 1951, **73**, 5461.

[10] Tiers, *J. Org. Chem.*, 1961, **26**, 3515.

[11] Bellamy and Branch, *Nature*, 1954, **173**, 633.

could be associated with C–S stretching; this vibration in alkyl–sulphur compounds normally appears in the region 700—600 cm.$^{-1}$.[12]

TABLE 3.

Infrared spectra (cm.$^{-1}$) of perfluoroisopropyl compounds.

Compound	C–F stretching	C–F def. (?)	C–CF_3 def.	
$(CF_3)_2CFI$	1290	961	755	
	1250	892	717	
	1188		713	
	1126			
$(CF_3)_2CFBr$	1292	963	756	
	1239	932	714	
	1190			
	1135			
$[(CF_3)_2CF]_2S$	1266	936	747	701
	1247			
	1217			
$[(CF_3)_2CF]_2S_2$	1295	966	749	
	1277	929	717	
	1248			
	1190			
	1145			
$[(CF_3)_2CF]_2S_3$	1297	970	759	705w
	1267	934	733	681w
	1250		719	676w
	1229			671w
	1190			
	1142			
$[(CF_3)_2CF]_2$	1299	1009	747	
	1227	980	722	
	1149	980	722	
		961		
		892		

EXPERIMENTAL

Infrared measurements were made with a Grubb–Parsons type G.S.2A spectrometer. Analytical-scale vapour-phase chromatography was carried out with a Griffin–George model MK. IIB apparatus, and preparative-scale separations with an apparatus constructed in the laboratory.[1, 13] Tritolyl phosphate was found to be an excellent stationary phase for separations involving fluorine-containing alcohols and sulphur compounds. Starting materials and apparatus were dried scrupulously before the preparation of Grignard reagents or lithium derivatives, and reactions were carried out under dry nitrogen.

Perfluoroisopropyl-lithium.—(*a*) *Preparation and decomposition.* Heptafluoro-2-iodopropane (15·0 g., 0·0506 mole) in dry pentane (50 ml.) and a 0·73N-solution (69·5 ml., 0·0506 mole) of butyl-lithium in pentane were added simultaneously during 30 min. to pentane (20 ml.) at −78°, contained in a 250-ml. flask fitted with a stirrer and two dropping funnels. The mixture was allowed to warm slowly to room temperature and then refluxed for 1 hr. Hexafluoropropene (5·6 g., 74%) (Found: *M*, 151. Calc. for C_3F_6: *M*, 150) was evolved, purified by fractionation *in vacuo*, and characterised by its infrared spectrum which was identical with that of an authentic sample. The remaining solution was shown by quantitative vapour-phase chromatography to contain butyl iodide (7·5 g., 80%).

(*b*) *Reaction with sulphuric acid.* Perfluoroisopropyl-lithium, prepared as above, was allowed to warm to −10°, treated with 3N-sulphuric acid (26 ml.), and very slowly raised to the b. p. Hexafluoropropene (5·0 g., 66%) was the only gaseous product. The same product in similar yield was obtained with diethyl ether as solvent; in this case the hexafluoropropene had to be isolated by preparative-scale vapour-phase chromatography.

(*c*) *Reaction with ethanol.* Reaction with ethanol was carried out as with sulphuric acid; hexafluoropropene (5·0 g., 66%) was formed in each reaction.

(*d*) *Reaction with acetone.* Heptafluoro-2-iodopropane (20 g., 0·0676 mole) in ether (20 ml.) at −78° was treated simultaneously with a solution of methyl-lithium (0·0676 mole) in ether (80 ml.) and of acetone (12 g., 0·207 mole) in ether (20 ml.), during 25 min. This mixture was then allowed to warm to room temperature at the rate of 20° per hr., and hexafluoropropene (1·5 g.) was evolved in the process. The mixture was treated with 2N-sulphuric acid (40 ml.); distillation of the ethereal portion, vacuum-distillation of the residue, and separation of the latter by preparative-scale vapour-phase chromatography (tritolyl phosphate, 150°) yielded 3,4,4,4-*tetrafluoro-2-methyl-3-trifluoromethylbutan-2-ol* (2·5 g., 13%) (Found: F, 57·5. $C_6H_7F_7O$

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[12] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1958, p. 353; Brandt, Emeléus, and Haszeldine, *J.*, 1952, 2549.

[13] Musgrave, *Chem. and Ind.*, 1961, 3779.

requires F, 58·3%), b. p. 109°/756 mm., n_D^{20} 1·33421, $\nu_{max.}$ 3472, 1389, 1355, 1290 (broad), 1250, 1208 (doublet), 1145, 1107, 1021, 999, 980, 956, 846, 755, and 725 cm.$^{-1}$.

(*e*) *Reaction with propionaldehyde.* Perfluoroisopropyl-lithium (0·07 mole) was treated with propionaldehyde (5·9 g., 0·102 mole) as above. 1,1,1,2-Tetrafluoro-2-trifluoromethylpentan-3-ol (9·0 g., 53%) was obtained, and identified by its infrared spectrum, which was identical with that of an authentic sample prepared by the reaction of propionaldehyde and perfluoroisopropylmagnesium bromide (see below). Hexafluoropropene (1·5 g.) was also formed and a fluorine analysis on the ether distillate showed that heptafluoro-2-iodopropane (9·5 g.) remained unchanged.

(*f*) *Reaction with chlorotrimethylsilane.* Butyl-lithium (0·10 mole) in ether (77 ml.) and chlorotrimethylsilane (10 g., 0·09 mole) in ether (10 ml.) were added simultaneously during 30 min. to a solution of heptafluoro-2-iodopropane (30 g., 0·10 mole) in ether (20 ml.) at −50°. The mixture was allowed to warm to room temperature during 3 hr. and then refluxed for 3 hr. During this process hexafluoropropene (7·5 g., 0·05 mole) was evolved. After an initial rapid distillation of the ether layer, the higher-boiling fractions were separated by preparative-scale vapour-phase chromatography (silicone elastomer, 134°), yielding butyl iodide (14·5 g., 78%) and *trimethylperfluoroisopropylsilane* (4·2 g., 17·5%) (Found: F, 54·0. $C_6H_9F_7Si$ requires F, 54·9%), b. p. 95°/763 mm., n_D^{20} 1·33837, $\nu_{max.}$ 2959, 2941 (doublet), 2882, 1745, 1385, 1370 (sh.), 1342 (sh.), 1242, 1212 (sh.), 1198, 1170, 1159 (doublet), 1098, 1005, 985, 956, and 735 cm.$^{-1}$. A sample of the silane was heated in an evacuated glass tube at 250° for 1½ hr. No hexafluoropropene was then detected. The infrared spectrum of the remaining silane was identical with that of the starting material and analytical vapour-phase chromatography indicated that no other volatile material had been formed.

Perfluoroisopropylmagnesium Bromide.—(*a*) *Preparation and decomposition.* Phenylmagnesium bromide (0·05 mole) in ether (50 ml.) was added to heptafluoro-2-iodopropane (15·0 g., 0·05 mole) in ether (15 ml.) at −78°. This mixture was eventually allowed to warm to room temperature, then refluxed for 1 hr., a fraction boiling up to 36° being distilled off; hexafluoropropene (5·3 g., 70·5%) was isolated by preparative-scale vapour-phase chromatography. Analysis of the ether solution for fluorine showed that heptafluoro-2-iodopropane (4·0 g.) remained unchanged.

(*b*) *Reaction with ethanol.* The cold mixture obtained by mixing heptafluoro-2-iodopropane (15·0 g., 0·05 mole) and phenylmagnesium bromide (0·05 mole) in ether at −78° was treated with a mixture of ethanol (5 g., 0·19 mole) and ether (30 ml.) during 25 min. The mixture was allowed to warm to room temperature at the rate of 20° per hour, then refluxed for 3 hr. Volatile material which collected in a cold trap was separated by preparative-scale vapour phase chromatography (tritolyl phosphate, 20°) into hexafluoropropene (6·0 g., 76%) and 2*H*-heptafluoropropane (1·0 g., 9%) (Found: *M*, 172. Calc. for C_3HF_7: *M*, 170); the infrared spectra of these two compounds were identical with those of authentic samples.

(*c*) *Reaction with sulphuric acid.* The exchange reaction was carried out at −60°, as described above, and then the mixture was allowed to warm to −30° before treatment with 3N-sulphuric acid (15 ml.). Further warming to room temperature followed by heating to the b. p. yielded hexafluoropropene (6·2 g., 82%) which was obtained pure on preparative-scale vapour-phase chromatography.

(*d*) *Reaction with acetone.* Phenylmagnesium bromide (0·05 mole) in ether (44·5 ml.) and acetone (9·0 g., 0·16 mole) in ether (10 ml.) were added simultaneously to heptafluoro-2-iodopropane (15 g., 0·05 mole) in ether (30 ml.) at −78° during 30 min. The mixture was allowed to warm to room temperature at the rate of 15° per hour and hexafluoropropene (1·0 g.) was evolved. Ice-cold 2N-sulphuric acid (20 ml.) was slowly added, the ether portion was separated and dried ($MgSO_4$) and the ether removed by distillation; this distillate was analysed for fluorine, which indicated that heptafluoro-2-iodopropane (1·1 g.) remained unchanged. The product, with iodobenzene, was separated from a black oily residue (4·0 g.) by distillation in a vacuum from a bath at 100°. Separation was achieved by preparative scale vapour-phase chromatography (tritolyl phosphate, 150°), giving iodobenzene (8·5 g., 82·5%), identified by its infrared spectrum, and 3,4,4,4-tetrafluoro-2-methyl-3-trifluoromethylbutan-2-ol (4·0 g., 35%) (Found: F, 57·8. Calc. for $C_6H_7F_7O$: F, 58·3%) which gave an infrared spectrum identical with the sample described above.

(*e*) *Reaction with propionaldehyde.* Perfluoroisopropylmagnesium iodide was treated with propionaldehyde (5·9 g 0·10 mole), the same quantities and conditions being used as above;

they gave 1,1,1,2-*tetrafluoro-2-trifluoromethylpentan*-3-*ol* (2 g., 17·5%) (Found: F, 58·1%; *M*, 227·1. $C_6H_7F_7O$ requires F, 58·3%; *M*, 228), b. p. 109°/758 mm., n_D^{20} 1·32875, iodobenzene (7·9 g., 77%), and a black oil (3·0 g.). The alcohol had $\nu_{max.}$ 3636, 3472, 2985, 1471, 1393, 1370, 1355 (triplet), 1250 (broad), 1136, 1101, 1063, 1046, 1031, 1020, 990 (sh.), 980, 970 (doublet), 934, 840 (sh.), 826, 757, 724, and 649 cm.$^{-1}$.

(*f*) *Reaction with ethyl methyl ketone.* Heptafluoro-2-iodopropane (20 g., 0·07 mole) in ether (20 ml.), phenylmagnesium bromide (0·07 mole) in ether (60 ml.), and ethyl methyl ketone (9·5 g., 0·135 mole) in ether (25 ml.) were mixed, as previously described, at −40° and then treated with 2N-sulphuric acid (20 ml.). Preparative-scale vapour-phase chromatography (silicone elastomer, 150°) afforded 2-*ethyl*-3,4,4,4-*tetrafluoro*-3-*trifluoromethylbutan*-2-*ol* (4 g., 24·5%) (Found: F, 54·3. $C_7H_9F_7O$ requires F, 55·0%), b. p. 126·5°, n_D^{25} 1·34996, iodobenzene (12 g., 87%), and unchanged heptafluoro-2-iodopropane (1·0 g.) from the ether layer. The alcohol had $\nu_{max.}$ 3623 (sh.), 3448, 2994, 2959 (sh.), 1307, 1266, 1220, 1170, 1143 (doublet), 1112, 1099 (doublet), 1053, 990, 966, 736, 729 (doublet), and 669 cm.$^{-1}$.

(*g*) *Reaction with acetaldehyde.* Acetaldehyde (5·8 g., 0·13 mole) was treated with perfluoroisopropylmagnesium iodide (from heptafluoro-2-iodopropane, 20 g., 0·07 mole) at −40° in the usual manner and the products were eventually isolated by preparative-scale vapour-phase chromatography (silicone elastomer, 90°), giving hexafluoropropene (2·0 g.) and 3,4,4,4-*tetrafluoro*-3-*trifluoromethylbutan*-2-*ol* (3·1 g., 22·7%) (Found: F, 61·5. $C_5H_5F_7O$ requires F, 62·2%), b. p. 90°, n_D^{25} 1·31722, $\nu_{max.}$ 3434 (broad), 1292, 1224, 1168, 1127, 1120 (doublet), 1099, 1081 (sh.), 1010, 996, 963, 947, 731, and 726 (doublet) cm.$^{-1}$.

(*h*) *Reaction with butyraldehyde.* Dry butyraldehyde (14·7 g., 0·20 mole) in ether (10 ml.) and phenylmagnesium bromide (0·10 mole) in ether (50 ml.) were added simultaneously during 30 min. to a stirred solution of heptafluoro-2-iodopropane (30 g., 0·10 mole) at −50°. The mixture was allowed to warm to room temperature during 1 hr., then refluxed for 15 min., cooled to −10°, and treated with 2N-sulphuric acid (40 ml.). The ether layer was separated and dried ($MgSO_4$), the ether distilled off through a Vigreux column, and the residue distilled in a vacuum. The various fractions were finally separated by preparative-scale vapour-phase chromatography, giving iodobenzene (16·9 g., 82%) and 1,1,1,2-*tetrafluoro*-2-*trifluoromethylhexan*-3-*ol* (9·0 g., 37%) (Found: F, 54·2. $C_7H_9F_7O$ requires F, 55·0%), b. p. 128·5°, n_D^{20} 1·34407, $\nu_{max.}$ 3425, 2967, 2941 (sh.), 2882, 1307, 1266 (sh.) 1220, 1167, 1147 (doublet), 1121, 1110 (doublet), 1068, 1038, 983, 954, 734, 725, 675, and 671 (sh.).

Perfluoroisopropylzinc Iodide.—Preparation. Zinc dust (6·6 g., 0·101 g.-atom), freshly purified dioxan (20 ml.), and 8 ml. of a solution of heptafluoro-2-iodopropane (15 g., 0·0506 mole) in dioxan (11 ml.) were heated to the b. p. Then the remainder of the iodide solution was slowly added, and the mixture was refluxed for a further 2 hr. During this time, a mixture of hexafluoropropene (1·9 g.) and 2*H*-heptafluoropropane (1·0 g.) was evolved; the two components were separated by preparative-scale vapour-phase chromatography (tritolyl phosphate, 20°).

Hydrolysis. The reaction mixture, prepared by the method above, was cooled to room temperature and then treated with 2N-sodium hydroxide (15 ml.). 2*H*-Heptafluoropropane (4·0 g., 46·5%) (Found: *M*, 171. Calc. for C_3HF_7: *M*, 170) was evolved when the mixture was refluxed for 2 hr.; its infrared spectrum was identical with that of authentic 2*H*-heptafluoropropane.

Reaction with benzoyl chloride. Perfluoroisopropylzinc iodide was prepared as described above, but on twice the scale. During this process, hexafluoropropene and heptafluoropropane were evolved, accounting for 32·8% of the original heptafluoro-2-iodopropane. Benzoyl chloride (37·5 g., 0·27 mole) in dioxan (20 ml.) was run into the mixture and the whole was refluxed for 2 hr. Final hydrolysis gave heptafluoropropane (6·5 g.), thus accounting for a total of 74% of the original heptafluoro-2-iodopropane. Distillation followed by separation of the various fractions by preparative-scale vapour-phase chromatography did not yield any of the desired ketone.

Free-radical Reactions of Heptafluoro-2-iodopropane.—(*a*) *Reaction with sulphur.* Heptafluoro-2-iodopropane (20 g., 0·07 mole) and sulphur (28 g.) were heated, under vacuum, in a sealed Pyrex tube (100 ml. capacity) at 243° for 13 hr. Volatile material was removed from the tube by vacuum-transfer and separated into four components by preparative-scale vapour-phase chromatography (tritolyl phosphate, 80°); these were, in sequence, heptafluoro-2-iodopropane (1·5 g.), *bisperfluoroisopropyl disulphide* (4·5 g., 34%) (Found: F, 65·7. $C_6F_{14}S_2$ requires F, 66·1%), b. p. 119°/773 mm., n_D^{20} 1·32614, *monosulphide* (1·3 g., 11%) (Found: F, 71·2. $C_6F_{14}S$ requires F, 71·7%), b. p. 116·9°/762 mm., and *trisulphide* (2·5 g., 17·5%) (Found: F, 61·4. $C_6F_{14}S_3$ requires F, 61·3%), b. p. 150·0°/764 mm., n_D^{20} 1·36092.

(*b*) *Reaction with chlorine.* A mixture of heptafluoro-2-iodopropane (11·2 g., 0·038 mole) and chlorine (8·6 g., 0·12 mole), sealed in a quartz Carius tube (70 ml. capacity), was irradiated at a distance of 24″ from a Hanovia model II ultraviolet lamp, for 4 days. Gaseous material was passed through 2N-sodium hydroxide and collected in a cold trap; this material was shown by analytical vapour-phase chromatography to be pure 2-chloroheptafluoropropane (6·0 g., 78%) (Found: *M*, 205. Calc. for C_3ClF_7: *M*, 204·5) (correct infrared spectrum).

(*c*) *Reaction with mercuric sulphide.* Heptafluoro-2-iodopropane (18 g., 0·061 mole) and mercuric sulphide (42 g.) were sealed in a quartz tube (70 ml. capacity) and irradiated with ultraviolet light while being shaken in a horizontal position for 216 hr. Volatile material (12·5 g.) was removed under a vacuum and separated by preparative-scale vapour-phase chromatography (silicone elastomer, 75°) into heptafluoro-2-iodopropane (4·6 g.) and perfluoroisopropyl disulphide (2·0 g., 22%); each product was identified by its infrared spectrum by comparison with an authentic sample.

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