658. *Perfluoroalkyl Grignard Reagents. Part I. The Preparation and Some Reactions of Heptafluoro-*n*-propylmagnesium Iodide.*

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The factors influencing the formation of heptafluoro-*n*-propylmagnesium iodide have been examined, and experimental directions are given for the preparation of this reagent in yields of 80% at low temperature, with high dilution in donor solvents, by using pure magnesium. Decomposition of the Grignard reagent yields heptafluoropropane, hexafluoropropene, traces of perfluoro-*n*-hexane and a hexafluoropropene polymer, and the mechanism of formation of these compounds is discussed; by-products from the solvent have been identified. The concept of loss of fluorine as fluoride from a fluoro-anion is discussed. The carbonation of heptafluoropropylmagnesium iodide gives heptafluorobutyric acid in yields of 75—80%. Formaldehyde, acetaldehyde, and acetone react with the Grignard reagent to give the expected primary, secondary, and tertiary alcohols, respectively.

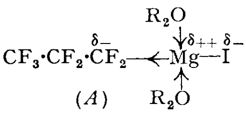
THIS series of communications describes the preparation and reactions of perfluoroalkyl and perfluoro*cyclo*alkyl Grignard reagents, derived from perfluoro-organic bromides and iodides. Summaries of the results have been given (*J.*, 1950, 2789; *Nature*, 1951, **167**, 139; **168**, 1028; 120th Meeting, Amer. Chem. Soc., September, 1951).

The preparation of Grignard reagents from fluorine compounds has been achieved only with compounds containing fluorine, hydrogen, and another halogen (McBee and Truchan, *J. Amer. Chem. Soc.*, 1948, **70**, 2910; Haszeldine, *J.*, 1951, 588, 2459, and unpublished), and attempts to prepare Grignard reagents from hydrogen-free polyhalogeno-compounds [*e.g.*, bromotrichloromethane and trichloroiodomethane (Simons, Sloat, and Meunier, *J. Amer. Chem. Soc.*, 1939, **61**, 435)] have hitherto been unsuccessful. Brice, Pearlson, and Simons (*ibid.*, 1946, **68**, 968) observed that a bromoheptafluoropropane reacted with magnesium in the presence of ether, and visualised the product as a Grignard reagent, since addition of water yielded a heptafluoropropane. This observation alone does not necessarily indicate Grignard formation, since it has been found that bromofluoro-compounds can be reduced to the hydrofluoro-compounds under similar conditions.

The conditions which have been found to affect the formation and reactions of perfluoroalkyl Grignard reagents are : (i) the magnesium used, (ii) the initiation of the reaction, (iii) the solvent, (iv) the dilution of the fluoro-iodide in the solvent, (v) the temperature, and (vi) the conditions for the reaction of the Grignard reagent with the second component. The main cause of instability in the transient Grignard reagents obtained in earlier experiments (Emeléus and Haszeldine, *J.*, 1949, 2953) has been traced to conditions (i) and (vi).

Perfluoroalkyl Grignard reagents are apparently much more sensitive to traces of impurities in the magnesium than are their hydrocarbon analogues, but smooth Grignard formation occurs when spectroscopically pure magnesium, or magnesium substantially free from traces of metals such as cobalt, iron, nickel, or manganese, is used. Suitable methods for the preparation of the magnesium and for the initiation of the reaction are described in the Experimental.

The solvent plays an important part in the formation of Grignard compounds. Little or no Grignard compound can be obtained from heptafluoroiodopropane and magnesium in perfluoromethyl*cyclo*hexane, diperfluoro-*n*-butyl ether, or benzene, and at higher temperatures the main products are magnesium iodide and fluoride, hexafluoropropene, and (in benzene) heptafluoropropane. These reaction media are poor solvents for the Grignard reagent and for magnesium iodide or fluoride formed on the surface of the magnesium, and thus tend to promote coating effects. Since the C–Mg bond in heptafluoropropylmagnesium iodide will be more ionic than in, say, propylmagnesium iodide, good donor solvents facilitate its formation and stabilisation, by formation of complexes, such as (*A*). Ethyl and *n*-butyl ether have therefore been used for much of



$$\mathrm{CF_3{\cdot}CF_2{\cdot}\overset{\delta-}{CF_2}\longleftarrow\underset{\underset{R_2O}{\uparrow}}{\overset{\overset{R_2O}{\downarrow}\;\delta++}{Mg}}\overset{\delta-}{-}I}$$

(*A*)

the work now recorded, but improved results can be obtained with tetrahydropyran and with *tert.*-amines; not only is the Grignard reagent produced in higher yield, but it is stable to a much higher temperature.

The use of concentrated solutions of the fluoroiodide causes appreciable side-reactions with the formation of heptafluoropropane, polymeric material, and products arising from the solvent. Thus, when acetaldehyde-free ethyl ether is used as solvent under such conditions, the pentanol (I), ethane, ethylene, and acetaldehyde are formed; decomposition of the Grignard reagent into a heptafluoropropyl radical is postulated to account for these products:

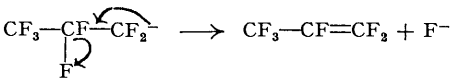
$$\begin{tikzcd}
C_3F_7\cdot + C_2H_5\cdot O\cdot C_2H_5 \arrow[r] & CH_3\cdot\dot{C}H\cdot O\cdot CH_2\cdot CH_3 + C_3F_7H & & & \\
CH_3\cdot\dot{C}H\cdot O\cdot CH_2\cdot CH_3 \arrow[r] & C_2H_5\cdot \arrow[d] & + & CH_3\cdot CHO \arrow[d, "C_3F_7MgI"] & \\
& C_2H_4 + C_2H_6 & & C_3F_7\cdot CH(OH)\cdot CH_3 & (I)
\end{tikzcd}$$

The Grignard reagent is much more stable in dilute solution.

One of the main differences between fluoroalkyl and normal Grignard reagents is the temperature-instability of the former, *i.e.*, they must be prepared and used at abnormally low temperatures (−50° to 0°); above 20° decomposition of the heptafluoropropylmagnesium iodide, mainly to heptafluoropropane, is rapid. Because of this instability during formation and storage, it has often been found convenient to have the second component (*e.g.*, carbon dioxide or a carbonyl compound) present throughout the reaction, so that it can combine with the organometallic derivative as soon as the latter is formed. Carbon dioxide reacts with heptafluoropropylmagnesium iodide to give heptafluorobutyric acid (thereby proving that a Grignard compound has been formed) at temperatures down to −80°, and this reaction provides a simple alternative to the oxidation route described earlier (Haszeldine, *J.*, 1950, 2789; *Nature*, 1950, **166**, 192) for the conversion of fluoroiodides into fluoro-acids.

The by-products from the interaction of magnesium and heptafluoroiodopropane in a solvent are heptafluoropropane, hexafluoropropene, traces of perfluoro-*n*-hexane, by-products from the solvent, a brown resinous polymer, and magnesium iodide and fluoride. It is suggested that the decomposition of the Grignard reagent during its formation or storage yields hexafluoropropene *via* the heptafluoropropyl anion:

$$CF_3\cdot CF_2\cdot CF_2\cdot MgI \longrightarrow CF_3\cdot CF_2\cdot CF_2^- + \overset{+}{M}gI$$



$$CF_3-CF(F)-CF_2^- \longrightarrow CF_3-CF{=}CF_2 + F^-$$

Decomposition of heptafluoropropylmagnesium iodide to a heptafluoropropyl *radical* would undoubtedly be followed by hydrogen-abstraction from the solvent to give heptafluoropropane (cf. Banus, Emeléus, and Haszeldine, *J.*, 1950, 3041); furthermore, the formation of hexafluoropropene from this radical by disproportionation would involve homolytic C–F fission and is therefore unlikely. The known reactivity of the heptafluoropropyl radical also excludes radical combination as the mechanism for the formation of perfluoro-*n*-hexane, so that the bimolecular reaction, $C_3F_7\cdot MgI + C_3F_7I \longrightarrow C_6F_{14} + MgI_2$, is presumably involved.

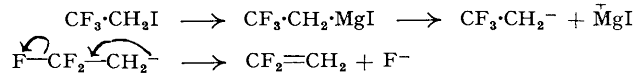
The polymer produced during Grignard formation yields hexafluoropropene on pyrolysis and is apparently derived from this olefin by anionic polymerisation:

$$C_3F_7\cdot MgI \longrightarrow C_3F_7^- + \overset{+}{M}gI \qquad C_3F_7^- + C_3F_6 \longrightarrow (CF_3\cdot CF\cdot CF_2\cdot C_3F_7)^- (MgI)^+ \xrightarrow{C_3F_6} \text{etc.}$$

The ready addition of alkoxide ion to hexafluoropropene indicates its susceptibility to anionic attack.

The mechanism proposed above for fluoride elimination from a fluoro-anion can be applied to the results obtained by Gilman and Jones (*J. Amer. Chem. Soc.*, 1943, **65**, 2037) and Henne (*ibid.*, 1938, **60**, 2275), that 1 : 1 : 1-trifluoro- and 1 : 1-difluoro-2-iodoethane underwent a ready reaction with magnesium in ether to give 1 : 1-difluoroethylene and vinyl fluoride, respectively, and equimolar amounts of magnesium iodide and fluoride.

These workers considered that the Grignard reagent had not been formed, but it now seems probable that Grignard formation had been effected but under unsuitable conditions, leading to decomposition :



$$CF_3{\cdot}CH_2I \longrightarrow CF_3{\cdot}CH_2{\cdot}MgI \longrightarrow CF_3{\cdot}CH_2^- + \overset{+}{M}gI$$

$$F{-}CF_2{-}CH_2^- \longrightarrow CF_2{=}CH_2 + F^-$$

and similarly

$$CHF_2{\cdot}CH_2{\cdot}MgI \longrightarrow F{-}CHF{-}CH_2^- \longrightarrow CHF{=}CH_2 + F^-$$

Application of the technique used for the perfluoroalkyl iodides has shown (*Nature*, 1951, **168**, 1028) that 1 : 1 : 1-trifluoro-2-iodoethane yields a Grignard reagent which is stable only at low temperatures and yields 1 : 1-difluoroethylene and small amounts of 1 : 1 : 1-trifluoroethane on decomposition. As might be expected on this basis, 3 : 3 : 3-trifluoropropylmagnesium iodide is perfectly stable at room temperature. The ready formation of perfluoro-olefins on heating the sodium salts of perfluoro-acids (*Nature, loc. cit.*) may also be due to similar fluoro-anion decomposition.

The reaction of the perfluoroalkyl Grignard reagents with carbonyl compounds proceeds normally. Thus heptafluoropropylmagnesium iodide reacts with formaldehyde, acetaldehyde, and acetone to give the expected alcohols, heptafluorobutanol, heptafluoropentan-2-ol, and heptafluoro-2-methylpentan-2-ol in satisfactory yield. More heptafluoropropane is formed by reduction than during the reaction with carbon dioxide under comparable conditions. It is clear, however, that with suitable development in experimental technique, the perfluoroalkyl Grignard reagents will prove of great value in synthetical fluorine chemistry.

EXPERIMENTAL

Heptafluoroiodopropane was used for the present study since its behvaiour is typical of fluoroiodides other than trifluoroiodomethane and pentafluoroiodoethane, and its boiling point enables conventional apparatus to be used. It was prepared by the method described in *J.*, 1949, 2856, and later by extension of the method of *J.*, 1951, 584, to heptafluorobutyric acid. The fluoroiodide (b. p. 39·5°, n_D^{17} 1·329, absorption spectrum in ethanol : $\lambda_{max.}$, 251 mμ; ε 230) was stored in a vacuum system. Sealed Pyrex 50—500 ml. tubes were used for the early experiments, the reactants and products being transferred *in vacuo*. Conventional Grignard apparatus was also used. Stringent precautions were taken to use anhydrous reactants and exclude moisture, oxygen, and carbon dioxide.

Conditions affecting Formation of Grignard Compounds.—The yield of Grignard reagent in the experiments outlined below (taken from over 300 carried out to determine optimum conditions) was determined (after removal of excess of magnesium, used in all experiments) (*a*) by hydrolysis with water, 5N-hydrochloric acid, or saturated ammonium chloride, or (*b*) by the carboxylation with carbon dioxide as solid or gas, or addition of the Grignard solution to a mixture of solid carbon dioxide and the solvent. Control experiments showed that the hydrolysis and carbonation techniques gave substantially the same result. Heptafluorobutyric acid was isolated as its sodium salt and converted into the amide (*J.*, 1950, 2789) for estimation ; a correction of 10—20%, determined from blank experiments, was applied to cover handling losses. In an alternative procedure the acid was estimated by conversion into silver heptafluorobutyrate.

(a) *Magnesium.* Spectroscopic examination of the magnesium used initially (Emeléus and Haszeldine, *loc. cit.*), which gave yields of *ca.* 70% of Grignard reagents from ethyl iodide or iodobenzene but only about 3% from heptafluoroiodopropane, revealed contamination by traces of cobalt and other metals. Spectroscopically pure magnesium has therefore been used for the results described below. 45—55% Yields of heptafluoropropylmagnesium iodide were obtained (in ethyl or *n*-butyl ether at −30° to 0°) by using magnesium shavings freshly cut from a magnesium rod, but better yields (55—60%, under comparable conditions) resulted if the magnesium rod was cut into fine shavings under anhydrous ether, with oxygen and air excluded. Care was taken to avoid contamination of the magnesium by grease, etc.

(b) *Initiation of reaction.* With magnesium, substantially free from oxide film, formation of Grignard compound was spontaneous; in other cases a crystal of iodine was added. For formation of Grignard compounds at low temperatures, and with greater conversion of the fluoroiodide, freshly powdered iodine (*ca.* 10% of the amount required to give magnesium iodide) was heated to 150° with the magnesium in absence of solvent. In an alternative procedure, a 15% excess of magnesium over that required for perfluoroalkyl Grignard formation was added to ether in a flask with a tap at the base. Methyl, ethyl, or phenyl bromide or iodide was added and formation of Grignard compound allowed until 10—15% of the magnesium had dissolved. The Grignard solution was drained off and the washed residual pitted magnesium used immediately for reaction with heptafluoroiodopropane. For experiments at temperatures below −50°, reaction was initiated at −10° to −20° and the temperature was then reduced to that required.

(c) *Solvents.* (i) A series of experiments, with perfluoromethyl*cyclo*hexane (10 ml.) as solvent, between heptafluoroiodopropane (2·0 g.) and magnesium (1·0 g.) in sealed tubes showed that little reaction occurred below 100°, above which increasing amounts of hexafluoropropene and magnesium iodide and fluoride were formed. The yield of olefin at 210° was 10%. Diperfluoro-*n*-butyl ether gave substantially the same results as fluorocarbons, and heptafluorobutyric acid could not be detected after prolonged reaction at 20° in an atmosphere of carbon dioxide. A 5% yield of the acid was obtained after reaction at 35° for 72 hours in benzene in a carbon dioxide atmosphere; at 150°, 60% of the fluoroiodide was recovered and hexafluoropropene (5%) and heptafluoropropane (10%) were isolated.

(ii) The results of typical experiments, in which alkyl ethers, tetrahydropyran, and alkylamines were used as solvents, are given in Table 1. The yields, obtained in experiments with heptafluoroiodopropane (5·0 g.) and magnesium (2·5 g.) in solvent (150 ml.) for 36 hours (carbon dioxide being always present), are based on the quantity of fluoroiodide taken and are the mean of two or three on this scale, the products being combined.

Separation of heptafluoroiodopropane from ethyl ether is difficult, and the fluoroiodide was often converted into heptafluoropropane by heating the ethereal concentrate with alcoholic potassium hydroxide.

TABLE 1. *Yield, %, of Grignard compound (and recovery, %, of starting material) at various temperatures.*

	−60°	−30°	0°	20°	40°			
Et_2O	58(8)	68(5)	59	50(~1)	33			
Bu_2O	62(11)	66(7)	61(8)	49(4)	27(0)			
$[CH_2]_5{>}O$	64(13)	72(7)	65(4)	57(~1)	48(0)			
	−60°	−40°	−20°	−10°	−5°	10°	20°	40°
NMe_3	—	41(13)	56(4)	—	51(6)	—	—	—
NEt_3	27(37)	45(21)	—	52(12)	—	55(2)	56(0)	52(0)

(d) *Dilution.* The effect of dilution is shown in Table 2 for butyl ether at 0°; similar data were obtained for experiments in ethyl ether.

TABLE 2.

Solvent, ml.	5	20	50	100	150
C_3F_7I recovered, %	17	11	12	10	13
By-products, % (C_3F_6, C_3F_7H, and C_6F_{14})	32	18	14	14	16
$C_3F_7{\cdot}MgI$ formed, %	6	15	32	43	59
Decomp., %, in 24 hrs. at −30°	60	31	—	12	14
,, ,, 72 hrs. at −30°	90	74	—	28	26

The marked effect of dilution on the stability of the Grignard reagent is also shown in the Table. Two parallel preparations of the Grignard reagent were made at −30° for each dilution, and the amount of residual Grignard reagent after the storage of one of them for the time shown was measured.

(e) *Temperature.* The data in Table 3, obtained by using magnesium (2·0 g.) and heptafluoroiodopropane (5.0 g.) in ether (150 ml.) for 24 hours (carbon dioxide being present throughout), show the effect of temperature. Similar results were obtained with butyl ether, tetrahydropyran, trimethylamine, and triethylamine.

TABLE 3.

Temp., ° c.	−80	−60	−40	−20	0	10	20	40
C_3F_7I recovered, %	23	9	10	12	7	9	3	0
C_3F_7MgI formed, %	37	55	59	64	58	44	41	27

Heptafluoropropylmagnesium iodide decomposes at a much slower rate at low temperatures: thus, in ethyl ether, the decomposition at −60°, −40°, −20°, 0°, 20°, and 40° after 24, 168, 168, 72, 72, and 36 hours was 2, 29, 38, 48, 75, and 61%, respectively. The decomposition at −40°, 0°, 20°, and 40° after 168, 72, 72, and 40 hours in tetrahydropyran as solvent was 29, 37, 44, and 39%, respectively, showing the increased thermal stability in this solvent.

(f) *Reaction with the second component.* The increase in yield obtained by having the compound for further reaction with the Grignard reagent (*e.g.*, carbon dioxide) present during Grignard formation is illustrated by the following: at −40°, −20°, 0°, and 20° the yields of heptafluorobutyric acid under a particular set of conditions, with carbon dioxide present during Grignard formation, were 57, 65, 56, and 43%, whereas in parallel experiments with carbon dioxide added after the Grignard reagent had been formed the yields were 50, 59, 46 and 23%, respectively.

By-products arising during Formation of Grignard Compounds.—The volatile by-products were 1 : 1 : 1 : 2 : 2 : 3 : 3-*heptafluoropropane* (Found: C, 21·2; H, 0·8%; *M*, 170. C_3HF_7 requires C, 21·2; H, 0·6%; *M*, 170), b. p. −14° (Brice, Pearlson, and Simons, *loc. cit.*, report b. p. −20° for 1 : 1 : 1 : 2 : 3 : 3 : 3-heptafluoropropane), and hexafluoropropene (Found: *M*, 150. Calc. for C_3F_6: *M*, 150), b. p. −28·5° (Henne and Waalkes, *J. Amer. Chem. Soc.*, 1946, **68**, 496, report b. p. −29°). These products were separated by treatment with a slight excess of bromine with exposure to ultra-violet light in a silica tube for 30 minutes, followed by distillation of the 1 : 2-dibromohexafluoropropane (Found: C, 11·5%; *M*, 308. Calc. for $C_3Br_2F_6$: C, 11·6%; *M*, 310), b. p. 71°, n_D^{20} 1·358. *Perfluoro*-n-*hexane* (Found: C, 21·3%; *M*, 337. C_6F_{14} requires C, 21·3%; *M*, 338), b. p. 56°, was isolated by distillation. Simons ("Fluorine Chemistry," Academic Press, 1950, p. 411) reports b. p. 55·1—56·1° for a perfluorohexane of unknown structure.

The amount of heptafluoropropane as by-product increased from 9% for reaction at −30° to 28% at 40°, while the amounts of hexafluoropropene and perfluorohexane formed were approximately constant at 5% and 2%, respectively. The remaining 15—20% of the product was magnesium iodide and fluoride, resinous polymer, and unidentified materials. The resin (*ca.* 5%) was washed with acid, base, alcohol, and ether, and then heated in a high vacuum. The white sublimate [Found: C, 24·0; H, 0; F, 75·7. Calc. for $(C_3F_6)_n$: C, 24·0; H, 0; F, 76·0%] (*ca.* 10% of the resin) had a similar appearance to a tetrafluoroethylene polymer, but gave hexafluoropropene on pyrolysis. The residue from the sublimation was heated in platinum at 700° in a high vacuum to give a 10% yield of hexafluoropropene, identified as the dibromide; other fluorine-containing pyrolysis products could not be identified on the scale used.

Side-reactions of the Grignard reagent with the solvent gave ethylene and ethane (1—4% yield when Grignard decomposition was at a maximum); experiments in ethyl ether gave 3 : 3 : 4 : 4 : 5 : 5 : 5-*heptafluoropentan*-2-*ol* (0·4%) (Found: C, 28·3; H, 2·6. $C_5H_5OF_7$ requires C, 28·0; H, 2·3%), b. p. 100—102°, n_D^{20} 1·315, shown to be identical with a specimen prepared as below.

Thermal Decomposition of Heptafluoropropylmagnesium Iodide.—A solution of the Grignard reagent was prepared at −20° in butyl ether (60% yield) and was freed from excess of magnesium and volatile by-products. The solution was then heated rapidly to reflux: there were obtained 76% of heptafluoropropane, 6% of hexafluoropropene, and the remainder was a resin and products involving the solvent.

Optimum Conditions for the Conversion of Heptafluoroiodopropane into Heptafluorobutyric Acid.—From the experiments summarised above, the optimum conditions for Grignard formation and its reaction with carbon dioxide are as follows. To spectroscopically pure magnesium shavings (10 g.; prepared under *n*-butyl ether, freed from dissolved oxygen) and *n*-butyl ether (600 ml.) were added two crystals of iodine. The mixture was stirred and cooled to −10°, a slow stream of carbon dioxide was passed into the flask, and a solution (5 ml.) of heptafluoroiodopropane (30·0 g.) in butyl ether (100 ml.) was added. The solution became cloudy after 5 minutes, and after 20 minutes it was a pale brown. The temperature was then lowered to −30°, and the rest of the fluoroiodide added during 2 hours, small pieces of solid carbon dioxide being added to the reaction mixture, which slowly became brown. Addition of carbon dioxide was continued for 8 hours and stirring for a further 20 hours, during which the temperature was allowed to rise to that of the room. The volatile products in the liquid-air traps were washed with sodium hydroxide solution, dried (P_2O_5), and fractionated *in vacuo* to give heptafluoropropane (7%) and hexafluoropropene (2%). The ethereal solution was decanted from the excess of magnesium and poured slowly into excess of 5N-hydrochloric acid. The ether layer was extracted with sodium hydroxide solution, and the aqueous layer was filtered and extracted with ethyl ether, and the ethereal extract concentrated in presence of 5N-sodium hydroxide. The combined aqueous alkaline extracts were neutralised (bromothymol-blue) and evaporated to dryness *in* *vacuo.* The sodium heptafluorobutyrate was extracted by methanol and converted into heptafluorobutyric acid (77%), b. p. 120·5—121°, n_D^{10} 1·297, identified by comparison with a genuine specimen prepared earlier (*J.*, 1950, 2789). After the above alkaline extraction, the butyl ether solution was washed with water, dried, and distilled to give heptafluoroiodopropane (5%) and perfluorohexane (0·5%). The resinous material obtained by filtration was freed from magnesium fluoride by treatment with concentrated acid. The combined inorganic fluoride residues were converted into fluorosilicic acid (F^- equivalent to *ca.* 3% of the heptafluoroiodopropane taken). The total weight balance was thus *ca.* 94%.

Reaction of Heptafluoropropylmagnesium Iodide with Formaldehyde, Acetaldehyde, and Acetone.—Formaldehyde (from trioxymethylene), acetaldehyde (from paraldehyde), and acetone were purified and thoroughly dried in a vacuum system. Heptafluoropropylmagnesium iodide was prepared from heptafluoroiodopropane (10·0 g.) and magnesium (3·2 g.) at −25° in *n*-butyl ether (150 ml.) during 8 hours, and into it was passed an excess of formaldehyde (2·0 g.) during 3 hours. After the mixture had been stirred for a further 8 hours, the temperature was allowed to rise overnight to that of the room, and the reaction mixture was then heated to 60° and the volatile by-products were removed. The reaction mixture was hydrolysed by pouring it on excess of acid, and the ethereal layer was separated, dried (P_2O_5), and distilled to give crude heptafluorobutanol, b. p. 95—105°, which, after being heated with phosphoric oxide at 80° for 3 hours, was redistilled to give 2 : 2 : 3 : 3 : 4 : 4 : 4-*heptafluorobutan*-1-*ol* (42%) (Found: C, 23·9; H, 1·3. $C_4H_3F_7O$ requires C, 24·0; H, 1·5%), b. p. 96·5°, n_D^{10} 1·299. Heptafluoropropane (17%), hexafluoropropene (4%), and unchanged heptafluoroiodopropane (24%) were also isolated.

In similar manner, acetaldehyde (3·0 g.) reacted with heptafluoropropylmagnesium iodide, to give heptafluoropropane (21%), hexafluoropropene (2%), unchanged heptafluoroiodopropane (8%), and 3 : 3 : 4 : 4 : 5 : 5 : 5-heptafluoropentan-2-ol (37%) (Found: C, 27·9; H, 2·1. Calc. for $C_5H_5OF_7$: C, 28·0; H, 2·3%), b. p. 101°. identical with that described above.

Acetone (4 ml.) was added dropwise to a Grignard solution prepared as above (58% yield of heptafluoropropylmagnesium iodide estimated from a parallel carbonation experiment), and gave a 32% yield of 3 : 3 : 4 : 4 : 5 : 5 : 5-*heptafluoro*-2-*methylpentan*-2-*ol* (Found: C, 31·8; H, 3·2. $C_6H_7OF_7$ requires C, 31·6; H, 3·1%), b. p. 106·5—107°, n_D^{25} 1·324. Heptafluoropropane (20%) and unchanged heptafluoroiodopropane (21%) were also isolated.

The yields of the alcohols, when formaldehyde, acetaldehyde, or acetone was added at intervals during Grignard formation under the above conditions, were 49%, 44% and 37%, respectively.

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