

724. *Perfluoroalkyl Grignard and Grignard-type Reagents.*
Part III. Heptafluoro-n-propylzinc iodide.*

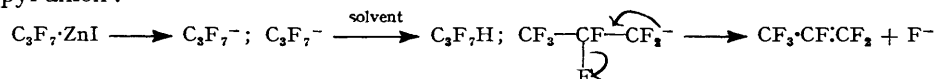
By R. N. HASZELDINE and E. G. WALASCHEWSKI.

Reaction of heptafluoroiodopropane with zinc in a solvent such as dioxan, diethyl ether, dibutyl ether, or tetrahydropyran (Lewis bases) yields heptafluoropropylzinc iodide (50—60%). The product from reaction in dioxan may be isolated as $C_3F_7 \cdot ZnI \cdot C_4H_8O_2$, and this can be converted into unsolvated heptafluoropropylzinc iodide. Heptafluoropropane, hexafluoropropene, and perfluoro-*n*-hexane are by-products, and the yield of the last compound increases with increase in reaction temperature. Heptafluoropropylzinc iodide is less reactive than heptafluoropropylmagnesium iodide. Some of its reactions are recorded.

THE preparation and reactions of heptafluoropropylmagnesium iodide have been described in Parts I (*J.*, 1952, 3423) and II *; the Grignard reagent is reactive, and unstable at temperatures much above 0°. The preparation of a Grignard-type reagent, heptafluoropropylzinc iodide, is now described (for a preliminary note see *Nature*, 1951, 168, 1028; also work by Miller, Amer. Chem. Soc. Meeting, Atlantic City, 1952).

Zinc fails to react with heptafluoroiodopropane in the absence of a solvent at temperatures up to 250°; at higher temperatures increasing amounts of perfluoro-*n*-hexane are formed, doubtless by combination of heptafluoropropyl radicals, and the formation of bisheptafluoropropylzinc cannot be detected. Reaction does not occur in perfluoromethylcyclohexane, perfluoro-*n*-butyl ether, or perfluorotributylamine solution, and a basic solvent (in the Lewis sense) is necessary; ethyl ether, butyl ether, dioxan, or tetrahydropyran have been found suitable. As shown in another series (Haszeldine, *J.*, 1953, 2622) a neutral-molecule base, B, combines with a fluoroalkyl iodide, RI, to give a molecular compound of the type (RI)B in which there is transfer of an electron from B to RI with formation of a weak covalent bond between the odd electron of B⁺ and (RI)⁻. It is suggested that the carbon-iodine bond in such a complex approaches more to that in, say, ethyl iodide in character, *i.e.*, it will undergo much more readily reactions which involve heterolytic fission of the bond, notably the formation of organometallic compounds. It was shown in Part I that the yield of heptafluoropropylmagnesium iodide increased with increase in basicity of the solvent.

As observed for the formation of heptafluoropropylmagnesium iodide, the yield of heptafluoropropylzinc iodide is markedly dependent on the reaction temperature, with a maximum (50—60%) at *ca.* 0°. Reaction of concentrated solutions of heptafluoroiodopropane with zinc gives low yields, and an iodide-solvent ratio of at least 1 : 5 should be employed. The by-products are heptafluoropropane, hexafluoropropene, and perfluoro-*n*-hexane. The first two probably arise by reaction or decomposition of the heptafluoropropyl anion :



The yield of perfluoro-*n*-hexane increases rapidly with increase in reaction temperature. In Part I (*loc. cit.*) the formation of this compound was visualised as a bimolecular reaction of heptafluoroiodopropane with heptafluoropropylmagnesium iodide, but now that molecular compound formation has been established for the perfluoroiodoalkanes, it seems probable that the valency structure of the carbon-iodine bond of heptafluoroiodopropane is sufficiently changed in solution to enable a Wurtz-type reaction to proceed without, necessarily, formation of the fluoroalkylzinc iodide as intermediate.

The presence of heptafluoropropylzinc iodide is shown by the liberation of heptafluoropropane when aqueous reagents are added. To prove that the heptafluoropropane

* Part II, Haszeldine, *J.*, 1953, 1748.

was not produced by the reduction of heptafluoroiodopropane in solution or as a complex, heptafluoropropylzinc iodide itself has been isolated. The solvated organometallic compound (one mol. of dioxan) is converted into the pure heptafluoropropylzinc iodide by fractional molecular sublimation; handling losses are high, and the organometallic compound should normally be used in solution. There is no indication of an equilibrium, $2C_3F_7 \cdot ZnI \rightleftharpoons (C_3F_7)_2Zn + ZnI_2$.

When unsolvated heptafluoropropylzinc iodide is heated, hexafluoropropene is formed; this reaction is similar to the formation of hexafluoropropene by pyrolysis of sodium heptafluorobutyrate (*J.*, 1952, 4259), and the heptafluoropropyl anion is probably the intermediate in each case. Aqueous sodium hydroxide converts the fluoroalkylzinc iodide quantitatively into heptafluoropropane. Water reacts similarly when hot, but much more slowly at room temperature, revealing a difference from heptafluoropropylmagnesium iodide. Chlorine converts the zinc compound into 1-chloroheptafluoropropane, whereas anhydrous hydrogen chloride gives heptafluoropropane. The reactions prove that the constitution of the organometallic compound is $C_3F_7 \cdot ZnI$.

The decreased reactivity of the zinc relative to the magnesium compound is also shown by its failure to react with carbon dioxide, although it yielded 3 : 3 : 4 : 4 : 5 : 5 : 5-heptafluoropentane-2-one when treated with acetyl chloride. These isolated results indicate that the fluoroalkylzinc iodides cannot undergo addition to a carbonyl group, *i.e.*, if the yields can be improved the zinc compounds may be of value for the preparation of fluoro-ketones.

In the series $R \cdot MgI$, $R \cdot ZnI$, $R \cdot HgI$, there is thus a much sharper change in reactivity from the magnesium compound to the zinc compound when $R =$ perfluoroalkyl than when $R =$ alkyl. The fluoroalkyl Grignard reagents appear to be less stable and more reactive (at least at low temperature) than the corresponding unsubstituted compounds, whereas the fluoroalkylzinc compounds resemble more the mercury compounds, which are less reactive towards functional groups.

EXPERIMENTAL

Heptafluoro-1-iodopropane, prepared from silver heptafluorobutyrate and iodine (Haszeldine, *J.*, 1951, 584; 1952, 4259), was dried over phosphoric oxide and stored in a vacuum. Reactions were carried out in conventional Grignard apparatus or in sealed tubes; moisture was excluded.

Reaction of Heptafluoroiodopropane with Zinc.—(a) *In dioxan.* Heptafluoroiodopropane (3.1 g.) and freshly prepared zinc powder (2.0 g.) were shaken with anhydrous dioxan (15 ml.) at 70° for 24 hr. The volatile products were 1*H*-heptafluoropropane (5%), b. p. -16° (Found: *M*, 170. Calc. for C_3HF_7 : *M*, 170), and hexafluoropropene (2%), identified spectroscopically. Haszeldine (*J.*, 1952, 3423) reports b. p. -14° for heptafluoropropane. The unchanged heptafluoroiodopropane and solvent were pumped off and then distilled, to give unchanged heptafluoroiodopropane (*ca.* 20%) and perfluoro-*n*-hexane (15%), b. p. 54–57°. The pale yellow solid which remained after removal of the solvent contained heptafluoropropylzinc iodide (30%), estimated by reaction with hydrochloric acid or aqueous sodium hydroxide as described below.

The effect of temperature on the yields (%) is shown in the following Table:

Temp.	10°	30°	55°	82°	100°
C_3F_7H	0	5	4	7	10
C_2F_6	0	6	~3	10	13
C_8F_{14}	~3	11	21	33	45
C_3F_7ZnI	46	48	34	27	14

Hexafluoropropene and heptafluoropropane were separated by bromination or chlorination (*cf.* *J.*, 1952, 3423).

Heptafluoroiodopropane (8.0 g.), zinc (0.5 g.), and dioxan (3 ml.) reacted vigorously and exothermically after being left for 30 min. at 20°. After 12 hr., analysis of the brown solid product obtained by removal of the solvent, etc., *in vacuo* showed that it was mainly zinc iodide with <10% of heptafluoropropylzinc iodide.

(b) *In ethers.* Zinc (2.5 g.) and diethyl ether (35 ml.) were stirred at -10° , and heptafluoroiodopropane (5.0 g.), dissolved in diethyl ether (10 ml.), was added dropwise (1 hr.). The pale

brown mixture was stirred for 4 hr., then filtered, and the solvent and the unchanged heptafluoriodopropane were removed *in vacuo*. The amount of unchanged heptafluoriodopropane (38%) was calculated from the ultra-violet spectrum of the ethereal solution. The slightly coloured solid which remained was treated with an excess of aqueous sodium hydroxide, and from the heptafluoropropane evolved (see below) the yield of heptafluoropropylzinc iodide was calculated to be 53%. With a reaction time of 24 hr., the yields at -30° , 0° , 35° , and 70° (sealed tube) were 11, 56, 39, and 21%.

Similar yields were obtained by use of dibutyl ether as solvent.

(c) *In tetrahydropyran*. The experimental details of (b) were followed, with tetrahydropyran (25 ml. total) instead of diethyl ether. The yields of heptafluoropropylzinc iodide, heptafluoropropane, hexafluoropropene, and perfluorohexane at 0° , 20° , and 80° were 55, 0, 0, 5; 49, ~1, 5, 10; and 31, 8, 7, 19%.

(d) *No solvent*. Heptafluoriodopropane (4.8 g.) and zinc (2.6 g.) were heated in a Carius tube at 165° (48 hr.), 190° (48 hr.), and 235° (48 hr.). Examination of the products at each stage revealed only small amounts of products with b. p. greater than that of heptafluoriodopropane, and these did not contain zinc.

Heptafluoriodopropane (6.0 g.) and zinc (2.6 g.), heated to 310° for 40 hr., gave unchanged iodide (4%) (Found: *M*, 296. Calc. for C_3F_7I : *M*, 296), perfluoro-*n*-hexane (*ca.* 60%), b. p. $55-58^{\circ}$ (Found: *M*, 337. Calc. for C_6F_{14} : *M*, 338), and an unidentified fraction (0.7 g.), b. p. $>58^{\circ}$ (Found: *M*, 492), which did not contain zinc. The solid reaction products failed to liberate heptafluoropropane when treated with aqueous sodium hydroxide.

Isolation and Reactions of Heptafluoropropylzinc Iodide.—The experiment with dioxan at 30° [(a) above] was repeated. After reaction the solution was filtered and the solvent, etc., were removed at 20° *in vacuo*. The pale yellow residual solid was hygroscopic. It was dissolved in the minimum quantity of anhydrous dioxan and filtered, and light petroleum (b. p. $40-60^{\circ}$) was added dropwise until crystals appeared on cooling. These were filtered off at 5° in a dried atmosphere and transferred to a vacuum-desiccator (yield: 0.4 g., 11%). Samples were decomposed for analysis by fusion with sodium, by treatment with 15% aqueous sodium hydroxide, or by pyrolysis in oxygen over silver vanadate. The solid is *heptafluoropropylzinc iodide* containing one mol. of dioxan of solvation [Found: C, 18.1; H, 1.4; C_3F_7 (as C_3HF_7), 37.9; I, 28.8; Zn, 14.8. $C_7H_8O_2IF_7Zn$ requires C, 18.7; H, 1.8; C_3F_7 , 37.6; I, 28.3; Zn, 14.5%].

Another sample of the solid was heated in a semimicro-sublimation apparatus at 10^{-4} mm. Dioxan was evolved at *ca.* 50° , and at *ca.* $60-75^{\circ}$ a colourless microcrystalline solid sublimed. Fractions of this were taken, since zinc iodide tends to contaminate the product. A middle fraction was *heptafluoro-n-propylzinc iodide* [Found: C, 10.0; I, 35.5; C_3F_7 (as C_3HF_7), 46.2. C_3IF_7Zn requires C, 10.0; I, 35.2; C_3F_7 , 46.8%]. At higher temperatures decomposition to volatile products, zinc iodide, and zinc fluoride occurred.

Unsolvated heptafluoropropylzinc iodide showed the following reactions:

A sample (0.19 g.) in a small platinum crucible was heated in a sealed Pyrex tube to $180-200^{\circ}/760$ mm. for 12 hr., to give hexafluoropropene (58%) (Found: *M*, 150. Calc. for C_3F_6 : *M*, 150), identified by its infra-red spectrum, and a solid residue which contained zinc iodide and fluoride.

A sample (0.103 g.) heated at 100° with 15% aqueous sodium hydroxide (12 hr.) gave heptafluoropropane (99.5%) (Found: *M*, 170. Calc. for C_3HF_7 : *M*, 170), identified spectroscopically.

A sample (0.094 g.) heated at 100° with water for 24 hr. gave heptafluoropropane (96.2%).

Anhydrous hydrogen chloride (100% excess) and heptafluoropropylzinc iodide (0.085 g.) were heated stepwise to 150° during 48 hr., to give heptafluoropropane (93%), identified spectroscopically.

The last reaction was repeated with chlorine and heptafluoropropylzinc iodide (0.089 g.); it gave 1-chloroheptafluoropropane (89%), b. p. -1° (isoteniscope) (Found: *M*, 203. Calc. for C_3ClF_7 : *M*, 204.5). Haszeldine (*J.*, 1952, 4259) reports b. p. -1° .

Heptafluoropropylzinc iodide (1.3 g.), sealed in a Pyrex tube with acetyl chloride (30% excess) and heated stepwise to 130° (10 hr.), gave 3 : 3 : 4 : 4 : 5 : 5 : 5-heptafluoropentan-2-one (18%), b. p. 60° (isoteniscope) (Found: C, 28.4%; *M*, 210. Calc. for $C_5H_3OF_7$: C, 28.3%; *M*, 212). Haszeldine (*J.*, 1953, 1748) reports b. p. $58-59^{\circ}$. The formation of the tertiary alcohol could not be detected.

The following reactions were carried out with solutions of heptafluoropropylzinc iodide or with the solvated solid:

The solvated solid (0.2 g.), dissolved in ethanol (5 ml.) and heated to 120° for 5 hr., gave heptafluoropropane (71%), identified spectroscopically.

A solution of heptafluoropropylzinc iodide (0.2 g.) in dioxan (10 ml.) was shaken with an excess of carbon dioxide in a sealed tube (10 hr.) and then heated stepwise to 60° (8 hr.). Examination of the products after reaction with dilute sulphuric acid failed to reveal the presence of heptafluorobutyric acid (cf. *J.*, 1952, 3423).

Solutions of heptafluoropropylzinc iodide in ethyl ether, butyl ether, dioxan, or tetrahydropyran gave heptafluoropropane almost quantitatively when treated with 15% sodium hydroxide or 7*N*-sulphuric acid at 100° for 12 hr. Reaction with water was slow at 20°: after 2, 8, and 20 hr. the decomposition was 15, 63, and 81% respectively.

The authors thank the Minnesota Mining and Manufacturing Company for a gift of heptafluorobutyric acid, used in the later stages of this work. One of the authors (E. G. W.) thanks the British Council for the award of a British Council Scholarship for Germany, during the tenure of which this work was carried out.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

[Received, July 27th, 1953]
