856. *The Direct Synthesis and Stability of Perfluoro-n-propyl-lithium.*

By J. A. BEEL, H. C. CLARK, and D. WHYMAN.

Perfluoro-n-propyl-lithium is obtained best from heptafluoro-n-propyl iodide and lithium metal containing 2% of sodium. Diethyl ether is the best solvent for this reaction; in tetrahydrofuran or di-(2-ethoxyethyl) ether abstraction of hydrogen occurs to a greater extent.

PERFLUOROALKYL derivatives of many elements have been prepared recently,[1] but the synthetic methods used in most cases have been specific. By analogy with alkyl-metal compounds, perfluoroalkyl Grignard reagents and perfluoro-organolithium compounds may be expected to provide synthetic methods of general applicability. Perfluoro-n-propyl–lithium has been prepared at low temperatures in ethereal solution by halogen–metal interchange between alkyl-lithium compounds and heptafluoro-n-propyl iodide.[2,3] The formation of perfluoro-n-propyl-lithium was inferred from the formation of 1,1,1,2,2,3,3-heptafluoropropane when the reaction mixture was hydrolysed with concentrated sulphuric acid. Furthermore, experiments in which various carbonyl compounds were added to the reaction mixture gave the products expected for the addition of perfluoro-n-propyl-lithium across the carbonyl group.

McBee *et al.*[4] have observed that addition of ethyl heptafluorobutyrate to perfluoro-n-propyl-lithium in ether is accompanied by side reactions which include (i) decomposition of perfluoro-n-propyl-lithium to perfluoropropene and lithium fluoride, (ii) reactions of the alkyl-lithium to give products other than the perfluoro-lithium compound, (iii) reactions in which perfluoro-n-propyl-lithium abstracts hydrogen from the solvent, and (iv) the formation of large quantities of polymeric material.

If perfluoro-n-propyl-lithium is to be used as a synthetic reagent, these side reactions should be eliminated as far as possible. We have therefore attempted to synthesise this compound directly from lithium metal and heptafluoro-n-propyl iodide, and to study its behaviour in various solvents.

Preliminary experiments indicated that lithium metal does not react with heptafluoro-n-propyl iodide in pentane or diethyl ether at temperatures between —50° and 20°. Although the reactivity of lithium metal is enhanced by the presence of small quantities of sodium,[5] perfluoro-n-propyl-lithium did not react in pentane with lithium–sodium alloy

[1] Banks and Haszeldine, " Advances in Inorganic Chemistry and Radiochemistry," Vol. III, Academic Press Ind., New York, 1961.
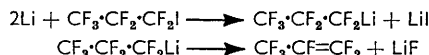[2] Pierce, McBee, and Judd, *J. Amer. Chem. Soc.*, 1954, **76**. 474.
[3] Emeléus, *J.*, 1954, 2979; Haszeldine, *Roy. Inst. Chem. Lectures*, 1956, No. 1.
[4] McBee, Roberts, and Curtis, *J. Amer. Chem. Soc.*, 1955, **77**, 6387.
[5] Beel, Koch, Tomasi, Hermansen, and Fleetwood, *J. Org. Chem.*, 1959, **24**, 2036; Stiles and Mayer, *J. Amer. Chem. Soc.*, 1959, **81**, 1497; Wright and Gutsell, *ibid.*, p. 5193; Kamienski and Esmay, *J. Org. Chem.*, 1960, **25**, 1807; West and Glaze, *ibid.*, 1961, **26**, 2096.

containing 2% of sodium; however, in diethyl ether an exothermic reaction proceeded steadily at $-74°$, the products including hexafluoropropene, a trace of **1,1,1,2,2,3,3-hepta-fluoropropane**, and involatile polymers. The following reactions therefore appear to have taken place:

$$2Li + CF_3 \cdot CF_2 \cdot CF_2I \longrightarrow CF_3 \cdot CF_2 \cdot CF_2Li + LiI$$
$$CF_3 \cdot CF_2 \cdot CF_2Li \longrightarrow CF_3 \cdot CF=CF_2 + LiF$$

The appearance of polymer and heptafluoropropane may be attributed to abstraction of hydrogen from the solvent by heptafluoro-n-propyl-lithium.

At $-40°$, solvent attack again occurred, as shown by the appearance of resinous material, and perfluoropropene but not heptafluoropropane was produced. Thus, decomposition of perfluoro-n-propyl-lithium and hydrogen-abstraction are competing reactions; the former is favoured by increase in temperature and at $-40°$ the latter is totally suppressed.

That perfluoro-n-propyl-lithium was formed in diethyl ether but not in pentane may be due to a stabilising solvation by ether or, at least in part, to formation of an insoluble film of lithium iodide on the surface of the alloy. In an attempt to find a solvent more effective in stabilising perfluoro-n-propyl-lithium and yet less susceptible to attack, reaction in tetrahydrofuran and in di-(2-ethoxyethyl) ether was studied.

An exothermic reaction occurred in tetrahydrofuran at $-40°$ but ceased when the alloy had become coated with a resinous deposit, and heptafluoropropane and perfluoropropene were formed in considerable quantity, in a $10:1$ molar ratio. Perfluoro-n-propyl-lithium is therefore formed in this system, and solvation by tetrahydrofuran reduces its decomposition to perfluoropropene more effectively than does diethyl ether. However, the large quantities of the heptafluoropropane indicate that the greater solvating power of tetrahydrofuran merely facilitates abstraction of hydrogen from the solvent.

Although the involatile residue did not crystallise, its infrared spectrum exhibited well-defined absorption bands at 3400 and 2900 cm.$^{-1}$, and strong absorption in the region 1100—1330 cm.$^{-1}$, characteristic of O–H, C–H, and C–F stretching modes, respectively. A strong band was not in evidence near 1080 cm.$^{-1}$, where the C–O bond in tetrahydrofuran gives rise to strong absorption.

With di-(2-ethoxyethyl) ether as solvent, a temperature of $15°$ was required for reaction at a reasonable rate, but again reaction ceased when the alloy became coated with resinous material. In spite of the higher temperature, perfluoropropene was not present among the reaction products, but the isolation of the heptafluoropropane in considerable quantity indicates that the perfluoro-n-propyl-lithium had been formed. Apparently, therefore, di-(2-ethoxyethyl) ether solvates perfluoro-n-propyl-lithium more strongly than either diethyl ether or tetrahydrofuran, but, while this prevents the lithium compound's decomposing to give perfluoropropene, abstraction of hydrogen from the solvent is facilitated. The infrared spectrum of the polymeric residue, from which di-(2-ethoxyethyl) ether could not be removed, was similar to that already described (absorption at 3400 and 1100—1330 cm.$^{-1}$).

The results show that with increasing solvation the instability of perfluoro-n-propyl-lithium with respect to perfluoropropene and lithium fluoride decreases with the solvents studied in the order: diethyl ether, tetrahydrofuran, di-(2-ethoxyethyl) ether. However, the ease of hydrogen abstraction increases in the same order, so that perfluoro-n-propyl-lithium is most readily available for reaction as a synthetic reagent when in diethyl ether.

To establish finally that perfluoro-n-propyl-lithium is formed by direct interaction of the lithium alloy and heptafluoro-n-propyl iodide in diethyl ether, benzaldehyde was included in such a system, and a product was obtained which, after hydrolysis, was identified as 2,2,3,3,4,4-heptafluoro-1-phenylbutan-1-ol. Benzaldehyde was chosen for this reaction merely to obtain a derivative which had been previously characterised,[2] not as a means of estimating the extent to which perfluoro-n-propyl-lithium is formed. Further experience has shown that benzaldehyde was, in fact, a poor choice for the latter

purpose. A perfluoropropylsilicon compound has since been prepared in good yield by a similar route. This synthesis, together with others, will be reported later.

EXPERIMENTAL

Except where otherwise stated, experiments were carried out in a conventional vacuum-system with magnetic stirring. Solvents were dried over sodium for 48 hr. before use. Compounds were identified by their infrared absorption spectra, and also for more volatile compounds by molecular-weight determinations by Regnault's method.

Reaction of Lithium–Sodium Alloy and Heptafluoro-n-propyl Iodide.—(a) *In diethyl ether.* Diethyl ether (20 ml.), followed by heptafluoro-n-propyl iodide (16·0 g.), was condensed on to lithium–sodium (0·33 g.) at −196°. The flask was then warmed to −74° and the mixture stirred vigorously. An exothermic reaction proceeded steadily at this temperature, and a brown colour soon appeared. Reaction ceased after 6 hr. Removal of the volatile material left a brown, resinous material covering unchanged alloy. The volatile material consisted of diethyl ether, heptafluoro-n-propyl iodide, perfluoropropene, and a small quantity of 1,1,1,2,2,3,3-heptafluoropropane.

A similar reaction at −40° was also arrested by the accumulation of resin around the alloy. The volatile materials in this case consisted only of diethyl ether, heptafluoro-n-propyl iodide, and perfluoropropene (2·82 g.).

(b) *In tetrahydrofuran.* Tetrahydrofuran (17·2 g.) and heptafluoro-n-propyl iodide (14·0 g.) were condensed on to the alloy (0·297 g.) at −196°. With vigorous stirring, an exothermic reaction commenced at −40° and proceeded steadily at this temperature until, after 6 hr., it was arrested by a brown resinous deposit on the alloy. The volatile products were perfluoropropene (0·142 g., 0·947 mmole), 1,1,1,2,2,3,3-heptafluoropropane (1·44 g., 8·45 mmoles), heptafluoro-n-propyl iodide, and tetrahydrofuran. The brown residue was insoluble in light petroleum, ethanol, and water but, although soluble in tetrahydrofuran, di-n-butyl ether, acetone, and carbon tetrachloride, it could not be obtained crystalline.

(c) *In di-(2-ethoxyethyl) ether.* Lithium–sodium alloy (0·304 g.) and di-(2-ethoxyethyl) ether (12·6 g.) were mixed under dry nitrogen. The mixture was frozen and the flask evacuated before heptafluoro-n-propyl iodide (18·0 g.) was condensed into it. An exothermic reaction commenced and proceeded steadily at 15° until arrested by formation of brown resin around the alloy. The volatile materials were 1,1,1,2,2,3,3-heptafluoropropane (0·979 g.) and heptafluoro-n-propyl iodide (8·98 g.). Owing to its low volatility, di-(2-ethoxyethyl) ether was not separated from the resin and unchanged alloy.

Reaction of Lithium–Sodium Alloy, Heptafluoro-n-propyl Iodide, and Benzaldehyde in Diethyl Ether.—Benzaldehyde (8·2 g.), lithium–sodium alloy (1·1 g.), and diethyl ether (30 ml.) were mixed under dry nitrogen. The mixture was cooled to −40° and stirred vigorously while a solution of heptafluoro-n-propyl iodide (28·5 g.) in diethyl ether (10 ml.) was added slowly. The reaction was kept at −40° for 48 hr., then allowed to warm to room temperature, 1,1,1,2,2,3,3-heptafluoropropane and perfluoropropene being evolved. The ethereal solution was then separated and, under an atmosphere of nitrogen, was shaken with 6N-sulphuric acid, separated, dried (Na_2SO_4), and distilled, yielding diethyl ether and a fraction of b. p. 65—80°/48 mm. whose infrared absorption indicated that it was a mixture of benzaldehyde and 2,2,3,3,4,4,4-heptafluoro-1-phenylbutan-1-ol. An unidentified resinous residue remained.

Benzaldehyde was removed from this mixture by refluxing it for 30 min. with an aqueous solution of Girard's reagent T (1 g. in 10 ml. of water), methanol (10 ml.), and aqueous 10% acetic acid (0·5 ml.). From an ether extract, a pale yellow liquid (0·86 g.) was obtained which gave infrared absorption bands expected for 2,2,3,3,4,4,4-heptafluoro-1-phenylbutan-1-ol, namely, at 3440m, br, (O–H stretching), at 1345s, 1225s, br, 1188s, br, and 1112s (perfluoro-n-propyl), and at 1498m, 1458m, 1065m, 808w, 800w, and 698m (Ph) cm.⁻¹. The phenylurethane had m. p. 93° (lit.,[2] 97°) (Found: C, 51·8; H, 3·4; F, 33·8. Calc. for $C_{17}H_{12}F_7NO_2$: C, 51·6; H, 3·1; F, 33·7%).

UNIVERSITY OF BRITISH COLUMBIA,
VANCOUVER 8, B.C., CANADA (H. C. C. and D. W.).
COLORADO STATE COLLEGE, GREELEY,
COLORADO, U.S.A. (J. A. B.). [*Received, March 19th, 1962.*]

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