Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

THE HALOGEN–METAL EXCHANGE REACTION BETWEEN PERFLUORO-n-HEPTYL IODIDE AND n-BUTYLLITHIUM*

PETER JOHNCOCK
Royal Aircraft Establishment, Ministry of Technology, Farnborough, Hants. (Great Britain)

(Received July 7th, 1969)

SUMMARY

Perfluoro-n-heptyl iodide and 1–1.5 molar equivalents of n-butyllithium in diethyl ether or halide-free diethyl ether/pentane undergo 40–50% halogen–metal exchange below −90° and form a stable heterogeneous system. The stability of the perfluoro-n-heptyllithium present is attributed to its association with perfluoro-n-heptyl iodide. Such a mixture reacts only slowly with acetaldehyde below −90° to give a low yield of 1-(perfluoro-n-heptyl)ethanol. Halogen–metal exchange is complete in the presence of a sufficient excess of the fluoroalkyl iodide, in accord with the relative carbanion stabilities. In the presence of a large excess of n-butyllithium the system is considerably less stable and *trans*-1-n-butyltridecafluoro-1-heptene is a major product. The stable heterogeneous mixture becomes homogeneous above *ca* −90°, and in the presence of acetaldehyde the fluoroalkyllithium then undergoes a fast reaction to give a quantitative yield of the fluoroalcohol. Perfluoro-n-heptyllithium decomposes very rapidly even at −75°, but it can be utilised at this and higher temperatures by producing it in the presence of an appropriate substrate.

Perfluoro-n-propyl iodide and perfluoroisopropyl iodide also undergo 40–50% halogen–metal exchange when treated with an excess of n-butyllithium in ether below *ca.* −90°, indicating that the ability of perfluoroalkyllithiums to form stable heterogeneous systems is general.

Carboxylation of perfluoro-n-propyllithium, perfluoroisopropyllithium, and perfluoro-n-heptyllithium was effected.

INTRODUCTION

Perfluoroalkyllithium compounds are useful synthetic reagents[1,2,3]. They can be made directly from perfluoroalkyl iodides and lithium metal[2], and from monohydrofluorocarbons by hydrogen–metal exchange[4], but are best prepared from perfluoroalkyl iodides by halogen–metal exchange[1,3]. Because of the instability of perfluoroalkyllithium compounds, procedures involving the simultaneous additon of the alkyllithium and the substrate[1], or their alternating addition[3], to the perfluoro-

---

* British Crown Copyright, reproduced with the permission of the Controller, Her Britannic Majesty's Stationary Office. This paper was presented in part at the 3rd International Symposium on Fluorine Chemistry, Munich, September, 1965.

TABLE 1

THE REACTIONS OF PERFLUORO-n-HEPTYLLITHIUM/n-BUTYLLITHIUM WITH ACETALDEHYDE AT $-95°$[a]

Expt. no.	n-C_4H_9Li (mmole)	CH_3CHO (mmole)	Solvent	t (min)	Hydrolysis temp. (°C)	Products[b]				
						n-$C_7F_{15}I$ (mmole)	n-C_4H_9I (mmole)	n-$C_7F_{15}CH(OH)CH_3$ (mmole)	n-$C_4H_9CH(OH)CH_3$ (mmole)	n-$C_5F_{11}CF{=}CFC_4H_9$ (mmole)
1	10	23	Ether	3	0	3.3	4.1	4.1	3.9	Trace
2	10	23	Ether	30	0	3.3	4.2	4.2	2.8	Trace
3[c]	10	23	Ether	5	0	2.8	4.2	4.2	3.1	Trace
4	15	32	Ether	30	0	3.2	4.3	4.3	7.0	0.1
5	11	10.4	Ether	5	−95	3.6	3.7	0.8	5.3	Trace
6[d]	11	10.4	Ether	0	−95	1.3	8.3	6.4	1.7	Trace
7[e]	11	10.4	Ether		−95	2.4	6.9	3.6	4.3	0.1
8	5	14	Ether	5	0	4.7	2.9	2.7	< 0.01	None
9	5	14	Ether	30	0	4.2	3.3	2.9	< 0.01	None
10	5	14	Ether/pentane	30	0	4.7	2.9	2.7	< 0.01	None
11	10	23	Ether/pentane	3	0	4.2	4.3	4.0	2.1	0.1
12	10	23	Ether/pentane	30	0	4.0	4.5	4.2	1.7	0.3
13	11	5	Ether	5	−95	3.0	4.0	0.5	3.3	Trace
14	11	5	Ether/pentane	5	−95	3.6	4.2	1.5	1.2	Trace

[a] See *Experimental* for full procedure. Except where stated, n-C_4H_9Li in diethyl ether or pentane (*ca.* 1 *M*) was added to n-$C_7F_{15}I$ (10 mmole) in diethyl ether (*ca.* 170 ml) and, after *t* min, the CH_3CHO added. Reaction mixtures were either kept at $-95°$ for 5 min before warming to 0° and hydrolysis, or kept at $-95°$ for 40 min and hydrolysed at that temperature. [b] Analysed by GLC. Product from expt. 7 was resolved by preparative GLC and the compounds fully characterised (see *Experimental*). [c] n-$C_7F_{15}I$ added to n-C_4H_9Li. [d] n-C_4H_9Li added to n-$C_7F_{15}I$ and CH_3CHO. [e] n-C_4H_9Li and CH_3CHO added alternately to n-$C_7F_{15}I$.

alkyl iodide have been used. This paper is concerned with factors affecting the stability and synthetic application of perfluoroalkyllithium compounds, to which end a more detailed study of the halogen–metal exchange reaction between perfluoro-n-heptyl iodide and n-butyllithium has been made.

RESULTS AND DISCUSSION

The halogen–metal exchange reaction between perfluoro-n-heptyl iodide and n-butyllithium in diethyl ether in the presence of lithium bromide, and in halide-free diethyl ether/pentane, was investigated by treatment of the resultant mixtures with acetaldehyde. Acid hydrolysis gave reaction products in which the amounts of perfluoro-n-heptyl iodide, n-butyl iodide, 2-hexanol (I), and 1-(perfluoro-n-heptyl)-ethanol (II) present were determined by GLC analysis.

$$C_7F_{15}I + C_4H_9Li \rightleftarrows C_7F_{15}Li + C_4H_9I$$

$$\downarrow CH_3CHO$$

$$\underset{(I)}{C_4H_9CH(OH)CH_3} + \underset{(II)}{C_7F_{15}CH(OH)CH_3}$$

Perfluoro-n-heptyllithium was stable below *ca.* −90° providing that n-butyllithium was not present in too great an excess, but its stability decreased markedly above this temperature region. Decomposition in the presence of n-butyllithium afforded *trans*-1-n-butyltridecafluoro-1-heptene (III) as the major decomposition product. The results are given in Tables 1, 2, and 3.

$$C_7F_{15}Li + C_4H_9Li \rightarrow \underset{(III)}{C_5F_{11}CF{=}CFC_4H_9} + 2\ LiF$$

TABLE 2

EFFECT OF CONCENTRATION OF n-BUTYLLITHIUM ON STABILITY OF PERFLUORO-n-HEPTYLLITHIUM AT −95°C[a]

Expt. no.	n-$C_7F_{15}I$ (mmole)	n-C_4H_9Li (mmole)	Ether (ml)	*t* (min)	Products[b]			
					n-$C_7F_{15}I$ (mmole)	n-C_4H_9I (mmole)	n-$C_5F_{11}CF{=}CFC_4H_9$ (mmole)	n-$C_7F_{15}H$ (mmole)
15	10	15	210	30 (C_2H_5OH)	4.4	5.4	0.2	3.6
16	6	9	300	10 (H_2O)	2.4	3.5	0.2	2.8
17	10	34	220	30 (H_2O)	0.8	8.2	3.6	0.6
18	6	21	300	10 (H_2O)	0.2	4.9	3.1	0.2

[a] See *Experimental* for full procedure. n-C_4H_9Li in diethyl ether (*ca.* 1 *M*) added to n-$C_7F_{15}I$ in diethyl ether and, after *t* min, the mixture hydrolysed at −95°C. [b] Analysed by GLC. Products from expts. 15 and 17 resolved by GLC and characterised (see *Experimental*).

The stability of the fluoroalkyllithium was associated with the heterogeneity of the system and, for certain perfluoroalkyl iodide/butyllithium molar ratios, the halogen–metal exchange reaction had equilibrium constants of the order of one. A solution of perfluoro-n-heptyl iodide in diethyl ether (0.05 *M*) became opaque below *ca.* −90°. Treatment at −95° with a molar equivalent of n-butyllithium (prepared

TABLE 3

EFFECT OF TEMPERATURE ON STABILITY OF PERFLUORO-n-HEPTYLLITHIUM[a]

Expt. no.	Reaction temp. (°C)	Products[b]				
		$n\text{-}C_7F_{15}I$ (mmole)	$n\text{-}C_4H_9I$ (mmole)	$n\text{-}C_7F_{15}CH(OH)CH_3$ (mmole)	$n\text{-}C_4H_9CH(OH)CH_3$ (mmole)	$n\text{-}C_5F_{11}CF{=}CFC_4H_9$ (mmole)
19[c]	−75	0.1	9.0	7.7	0.8	0.7
20[d]	−75	1.1	8.2	1.5	< 0.005	1.6
21	−75	0.1	9.0	7.0	0.9	0.8
22	−30	0.7	8.3	6.4	1.0	1.2
23	0	1.7	7.2	3.9	0.9	2.0

[a] See *Experimental* for full procedure. Except where stated, 11 mmole of $n\text{-}C_4H_9Li$ (*ca.* 1 *M* ethereal solutio added to 10 mmole of $n\text{-}C_7F_{15}I$ and 10.4 mmole of CH_3CHO in *ca.* 180 ml of diethyl ether. [b] Analysed by GL Products from expt. 19 resolved by GLC and characterised (see *Experimental*). [c] $n\text{-}C_4H_9Li$ and CH_3CHO add alternately to $n\text{-}C_7F_{15}I$. [d] $n\text{-}C_4H_9Li$ added to $n\text{-}C_7F_{15}I$ over 30 sec and then, after 1 min, CH_3CHO added.

from n-butyl bromide and lithium in diethyl ether) effected a reduction in opacity; no tendency for layers to separate was observed but a marked turbidity remained. The mixture was stable at −95° : addition of an excess of acetaldehyde after 3 or 30 minutes, followed by warming to 0° before hydrolysis, afforded quantitative yields of the fluoroalcohol (II) based on the amount of n-butyl iodide (*ca.* 40%) formed (expts. 1 and 2). The reverse addition of perfluoro-n-heptyl iodide to n-butyllithium (expt. 3), or the use of a 50% molar excess of n-butyllithium (expt. 4), also effected about 40% halogen–metal exchange, and the stability of the mixtures was again demonstrated by reaction with acetaldehyde to give quantitative yields of (II). Allowing for the consumption of n-butyllithium by the presence of water in the solvent (< 0.01%), the rather low yields of 2-hexanol (50–65%) suggested that n-butyllithium was also taking part in aldol condensation reactions. Reaction between perfluoro-n-heptyllithium and acetaldehyde occurred slowly at −95° : thus, when the mixture was hydrolysed at that temperature after 40 minutes, the yield of (II) was only 22% (expt. 5); n-butyllithium must have remained in solution since (I) was formed in 72% yield. Breakdown of the stable heterogeneous system to release highly reactive perfluoro-n-heptyllithium was presumably associated with the formation of a clear solution above *ca.* −90°. When perfluoro-n-heptyllithium was prepared in the presence of acetaldehyde at −95°, the extent of halogen–metal exchange was high (82%) and (II) was formed in good yield (73%) (expt. 6). This demonstrated that halogen–metal exchange occurred considerably faster than the reaction between n-butyllithium and acetaldehyde, and that unless the presence of acetaldehyde was affecting the solubility characteristics of the mixture, formation of "stabilised" perfluoro-n-heptyllithium occurred more slowly than the reaction between perfluoro-n-heptyllithium and acetaldehyde. Perfluoro-n-heptyllithium showed a marked decrease in stability at −95° in the presence of a large excess of n-butyllithium, and this instability was not due to an absolute organometallic concentration effect (Table 2): an increase in the molar ratio of n-butyllithium to fluoroalkyl iodide from 1.5/1 (expts. 15 and 16) to 3.5/1 (expts. 17 and 18), led to greater exchange (to *ca.* 80%) and the formation of large amounts of the decomposition product, (III).

The ability of perfluoro-n-heptyl iodide and n-butyllithium in diethyl ether to form stable systems in which the extent of halogen–metal exchange was only *ca.* 40% was unexpected. The halogen–metal exchange equilibrium constants for various alkyl, alkenyl, and aryl systems in diethyl ether and diethyl ether/pentane are in accord with the relative carbanion stabilities[5], and thus exchange between perfluoro-n-heptyl iodide and n-butyllithium should be complete since the pK_a values for 1*H*-pentadecafluoroheptane and n-butane are 27 and *ca.* 40, respectively[4,6]. It was concluded that the stability of perfluoro-n-heptyllithium in diethyl ether at −95° is dependent on its association with perfluoro-n-heptyl iodide in a separate phase, in which state the reactivities of both compounds are considerably reduced. On addition of acetaldehyde, reaction with n-butyllithium goes to completion at −95°, and the main reaction with perfluoro-n-heptyllithium occurs above *ca.* −90°. The instability of the system in the presence of a large excess of n-butyllithium is attributed to slow additional halogen–metal exchange to the point where the perfluoro-n-heptyllithium is destabilised: formation of (III) can then occur, presumably according to the following reaction sequence which involves an established mode of decomposition[1,2].

$$C_7F_{15}Li \rightarrow C_5F_{11}CF{=}CF_2 + LiF \xrightarrow{C_4H_9Li} \underset{\text{(III)}}{C_5F_{11}CF{=}CFC_4H_9} + LiF$$

In accordance with this interpretation, halogen–metal exchange was, in fact, shown to be essentially complete in the presence of a 100% excess of the fluoroalkyl iodide: treatment of the iodide with 0.5 molar equivalents of n-butyllithium and then with acetaldehyde at −95°, followed by hydrolysis at 0° gave (II) (93%) and only a trace of (I) (expts. 8 and 9).

The extent to which diethyl ether is associated with the fluoroalkyllithium/fluoroalkyl iodide phase is not known. However, in view of the ability of lithium halide to stabilise organolithium reagents and to decrease their reactivity by the formation of mixed complexes[7], the exchange reaction was examined in halide-free diethyl ether containing *ca.* 10% pentane. Although the heterogeneity of the system was marked by the separation of white solid when n-butyllithium in pentane was added to perfluoro-n-heptyl iodide in diethyl ether at −95°, the behaviour of the system in terms of extent of exchange, stability of perfluoro-n-heptyllithium and yield of (II) obtained in homogeneous reaction with acetaldehyde (the white solid dissolved in the range −90° to −85°) was much the same as with diethyl ether as the only solvent, and in the presence of lithium bromide (*cf.* expts 10, 11, and 12 with 9, 1, and 2). However, there was a significant difference in reactivity at −95°: the reactions between perfluoro-n-heptyllithium and acetaldehyde in diethyl ether containing lithium bromide at −95° gave less (II) than was obtained in halide-free diethyl ether/pentane (*cf.* expts. 5 and 13 with 14). The lower reactivity of perfluoro-n-heptyllithium in the presence of lithium bromide could thus be due to the formation of a mixed complex. The yields of 2-hexanol obtained in diethyl ether/pentane were significantly lower than obtained in diethyl ether.

The effect of temperature on the stability of perfluoro-n-heptyllithium is shown in Table 3. It decomposed rapidly at −75° (expt. 20): addition of n-butyllithium to perfluoro-n-heptyl iodide in diethyl ether, followed after 1 minute by the addition of acetaldehyde, gave a low yield of (II) (18%) and a similar yield of decomposition product, (III). The effect of increasing temperature on stability was examined by the addition of n-butyllithium to the fluoroalkyl iodide and acetaldehyde in diethyl ether at the appropriate temperature, and the relative tendencies to form (II) and (III) determined (expts. 21–23): the yield of (II) was 74% at −75°, 64% at −30°, and 39% at 0°, and the amount of (III) formed correspondingly increased.

Carboxylation of perfluoro-n-heptyllithium, perfluoro-n-propyllithium, and perfluoroisopropyllithium (prepared from the iodides and a 50% molar excess of n-butyllithium) in diethyl ether at −90° to −100°, followed by warming to 0°, gave lithium perfluoro-n-octanoate (38%), lithium perfluoro-n-butyrate (54%), and lithium perfluoroisobutyrate (4%), respectively. The extent of halogen–metal exchange was about 50% in each case, and thus the ability of perfluoroalkyllithiums to form stable heterogeneous systems appears to be general. The behaviour of perfluoro-n-propyllithium at higher temperature was similar to that of perfluoro-n-heptyllithium: carboxylation at −75° afforded a much lower yield of the fluoroacid (10%), and the extent of exchange (85%) was considerably higher.

The marked instability of perfluoroalkyllithiums at even quite low temperatures will restrict their use in synthesis to reactions with highly reactive substrates such as carbonyl compounds and metal halides. When reaction occurs sufficiently fast that competing decomposition of the perfluoroalkyllithium is negligible, high yields of the desired products can be obtained. Thus, perfluoro-n-heptyllithium, prepared from perfluoro-n-heptyl iodide and n-butyllithium at −95°, reacts rapidly with acetaldehyde at *ca.* −90° to give a quantitative yield of 1-(perfluoro-n-heptyl)-ethanol (50% conversion based on fluoroalkyl iodide). The difficulty of controlling the vigour of the reaction will presumably restrict the procedure to small-scale experiments. However, it is possible that 100% conversion of iodide could be effected by using an inert organofluoro compound as cosolvent to associate with the perfluoroalkyllithium but this aspect was not investigated. For large-scale reactions, addition of the hydrocarbon organolithium compound to the perfluoroalkyl iodide and the substrate in diethyl ether above *ca.* −90° provides a simple experimental procedure, and can give yields comparable to those obtained using more tedious simultaneous or alternating procedures.

EXPERIMENTAL

Reactions were carried out under an atmosphere of oxygen-free nitrogen. Anhydrous grade diethyl ether and pentane (b.p. 34–36°) were distilled and stood over sodium wire. n-Butyllithium was prepared in diethyl ether (from n-butyl bromide and lithium) and in pentane (from n-butyl chloride and lithium) according to literature procedures, and solution strengths were determined before use[8]. n-Butyllithium in pentane (1.2 *M*) was found to contain only a small amount (0.35 g/l) of lithium chloride. Commercial perfluoro-n-heptyl iodide was used without further purification. Acetaldehyde was distilled and stored at 0°. Perfluoro-1-heptene and 1*H*-pentadecafluoroheptane were prepared by described procedures[9]. 2-Hexanol (b.p. 137°) was synthesised from acetaldehyde and n-butyllithium in diethyl ether. IR spectra were determined on a Perkin–Elmer 337 spectrometer.

trans-1-*n*-*Butyltridecafluoro*-1-*heptene*

n-Butyllithium (27.0 ml of 0.80 *M* ethereal solution, 0.022 mole) was added over

10 min to a stirred solution of perfluoro-1-heptene (7.0 g, 0.020 mole) in diethyl ether (200 ml) at −30°. After 30 min, the mixture was allowed to warm to room temperature. Most of the solvent was removed by distillation, and a fraction (6.0 g) collected when the residue was heated to 100° at 0.1 mm. GLC analysis (dinonyl phthalate at 86°) showed, besides a small diethyl ether peak, four peaks of approximate relative areas 1/2/16/2, the second and fourth being incompletely resolved from the main peak. Pure major component was isolated as a middle cut by GLC (8 ft. × 1 in. column containing 40% dinonyl phthalate on 52–60 AW Celite 545 at 90°) and was *trans*-1-n-butyltridecafluoro-1-heptene, b.p. 160.5°, n_D^{20} 1.329. (Found: C, 34.0; H, 2.5; F, 63.9. $C_{11}H_9F_{13}$ calcd.: C, 34.0; H, 2.3; F, 63.7%.) ν_{max} 1720 cm^{-1} (CF=CF[10]). The fluorine NMR spectrum showed doublets at 137 and 165 ppm (assignable[11] to =CF), and the coupling constant, *J* 140 Hz, was characteristic of the *trans* isomer[12]. The relative peak areas were in agreement with the structure. The mass spectrum showed a low intensity parent ion.

Reactions of perfluoro-n-heptyllithium/n-butyllithium mixtures with acetaldehyde in diethyl ether and diethyl ether/pentane

n-Butyllithium in diethyl ether or pentane (1–1.2 *M*), and acetaldehyde in diethyl ether (1 *M* or 10 *M*) were used. Reactions were carried out with stirring, and the following addition procedures were employed:

(1). n-Butyllithium was added over 1–2 min to the perfluoro-n-heptyl iodide in diethyl ether (or the iodide added to the n-butyllithium in diethyl ether) and, after the appropriate time, the acetaldehyde added rapidly.

(2). n-Butyllithium was added in 10 aliquots at 1 min intervals to the perfluoro-n-heptyl iodide and acetaldehyde in diethyl ether.

(3). Ten aliquots of n-butyllithium, each followed after 15–30 sec by an aliquot of acetaldehyde, were added to the fluoroalkyl iodide in diethyl ether at 1 min intervals.

Reactions performed at −95° were either kept at that temperature for 5 min and allowed to warm to 0° before hydrolysis or, kept at −95° for 40 min and hydrolysis effected at that temperature. Reactions done at −75° were allowed to warm to 0° before hydrolysis. At 0°, 50 ml of 4 *N* sulphuric acid were added. The ethereal layer and two 25 ml diethyl ether extracts were dried ($MgSO_4$) and fractionated through a column packed with glass helices to give, after removal of most of the solvent, a residue (6–10 g) in which the amounts of perfluoro-n-heptyl iodide, n-butyl iodide, 1-(perfluoro-n-heptyl)ethanol, 2-hexanol, and *trans*-1-n-butyltridecafluoro-1-heptene were determined by GLC (5 ft. × $\frac{1}{4}$ in. columns) using calibrated peak areas. Packings and column temperatures were: perfluoro-n-heptyl iodide (10% dinonyl phthalate on 52–60 AW Celite 545 at 77°); *trans*-1-n-butyltridecafluoro-1-heptene (10% diethyleneglycol succinate on 85–100 Embacel at 80°); n-butyl iodide, 1-(perfluoro-n-heptyl)ethanol, and 2-hexanol (diethyleneglycol succinate at 100°). Experimental details and results are given in Tables 1 and 3.

The reaction residue (10.0 g) obtained in expt. 7 was resolved by GLC [20 ft. × $\frac{3}{8}$ in. column containing 20% poly(*m*-phenylene ether) on Chromosorb W; temperature programmed from 100–190°). A total of 6.7 g (0.25 ml charges) gave 1*H*-pentadecafluoroheptane (0.32 g), 2-hexanol (0.21 g), and n-butyl iodide (0.64 g) (each characterised by its IR spectrum); and 1-(perfluoro-n-heptyl)ethanol (0.65 g), b.p.

170.5°, n_D^{20} 1.317. (Found: C, 26.1; H, 1.6; F, 68.7. $C_9H_5F_{15}O$ calcd.: C, 26.1; H, 1.2; F, 68.8%.) ν_{max} (liquid) 3380 (bonded hydroxyl), and ν_{max} (1% v/v in carbon tetrachloride) 3607 cm^{-1} (free hydroxyl). The mass spectrum showed a low intensity parent ion.

The fluoroalcohol (0.40 g), heated with 1-naphthyl isocyanate (0.30 g) and a drop of pyridine in ether, gave the crude urethane (0.33 g), m.p. 110–114° (from petroleum ether, b.p. 100–120°). Three recrystallisations gave an analytical sample, m.p. 115.5–116.5°. (Found: C, 41.5; H, 2.1; N, 2.8. $C_{10}H_{12}F_{15}NO_2$ calcd.: C, 41.2; H, 2.1; N, 2.4%.)

GLC similarly allowed the separation of n-butyl iodide (1.1 g, 60%), 1-(perfluoro-n-heptyl)ethanol (1.9 g, 50%), and a trace of 2-hexanol from the residue obtained in expt. 19.

Effect of the concentration of n-butyllithium on the stability of perfluoro-n-heptyllithium in diethyl ether at −95°

n-Butyllithium in diethyl ether (1–1.2 *M*) was added over 5 min to a stirred mixture of perfluoro-n-heptyl iodide in diethyl ether at −93° to −95° and, after the appropriate time, water (5 ml) was added. The mixture was kept at −95° for 5 min, the temperature allowed to rise to 0°, and 50 ml of 4 *N* sulphuric acid added. The procedure described above was then followed. Reaction residues were quantitatively analysed by GLC for 1*H*-pentadecafluoroheptane and perfluoro-n-heptyl iodide (dinonyl phthalate at 70°), and for *trans*-1-n-butyltridecafluoro-1-heptene (diethyleneglycol succinate at 72°). Experimental details and results are given in Table 2.

The reaction product obtained in expt. 15 was resolved by GLC (1 in. × 8 ft. column containing 40% dinonyl phthalate on 52–60 AW Celite 545 at 100°) to give 1*H*-pentadecafluoroheptane (1.0 g, 49%), perfluoro-n-heptyl iodide (1.4 g, 28%), and n-butyl iodide (0.87 g, 47%), which were characterised by their IR spectra. Similarly, in expt. 17, GLC (column temperature 87°) allowed the isolation of slightly impure *trans*-1-n-butyltridecafluoro-1-heptene (1.4 g), identified by its IR spectrum.

Carboxylation of perfluoroalkyllithiums

(*a*). *Perfluoro-n-heptyllithium.* n-Butyllithium (12.0 ml of 1.25 *M* ethereal solution, 0.015 mole) was added to a stirred solution of perfluoro-n-heptyl iodide 5.0 g, 0.010 mole) in diethyl ether (200 ml) at −90°. After 4 min, powdered carbon dioxide (9.0 g) was added, the mixture kept at −90° for 30 min, and then allowed to warm to room temperature. After hydrolysis with aqueous potassium hydroxide and continuous ether extraction, the aqueous solution was acidified (sulphuric acid) and again continuously extracted with diethyl ether. The two ether extracts were dried and concentrated in the usual way.

The concentrated solution from alkaline extraction was shown by GLC (dinonyl phthalate at 85°) to contain n-butyl iodide (0.90 g, 49%) and perfluoro-n-heptyl iodide (1.7 g, 34%). On allowing the solution to stand, there was deposited lithium perfluoro-n-octanoate (0.78 g, 38%), m.p. 160–190° (washed with petroleum ether), which was readily soluble in ether.

Acidification of an aqueous solution of the salt (0.2 g), followed by filtration and sublimation, afforded perfluoro-n-octanoic acid (0.18 g), m.p. 44–47°, identified by its IR spectrum. The salt (0.10 g) and *S*-benzylisothiouronium chloride (0.050 g) in water yielded the crude *S*-benzylisothiouronium derivative (0.12 g). This, recrystallised from aqueous ethanol, gave the pure compound (0.88 g), m.p. 195–196°, which was identical (IR spectrum and mixed m.p.) to an authentic sample.

The concentrated solution from acidic extraction was shown by GLC (20% Apiezon L on 52–60 AW Celite 545 at 208°) to contain n-pentanoic acid (0.94 g, 93%).

(*b*). *Perfluoro-n-propyllithium.* Addition of n-butyllithium (25 ml of 1.08 *M* ethereal solution, 0.027 mole) to perfluoro-n-propyl iodide (5.0 g, 0.017 mole) in diethyl ether (200 ml) at −90°, followed by carboxylation and work-up as in (*a*), gave a concentrated ether extract from alkaline solution which, by GLC, contained n-butyl iodide (1.7 g, 55%). Removal of volatiles at 80°C under vacuum gave ether-soluble lithium perfluoro-n-butyrate (1.1 g, 54%), m.p. 145–175°C, which readily yielded the *S*-benzylisothiouronium derivative, m.p. 191–193°, identical (IR spectrum and mixed m.p.) to an authentic sample.

Following the same procedure, carboxylation at −70° yielded n-butyl iodide (85%) and lithium perfluoro-n-butyrate (8%).

(*c*). *Perfluoroisopropyllithium.* Carboxylation of perfluoroisopropyllithium (from 5 g of perfluoroisopropyl iodide) in diethyl ether at −90°, following the procedure described in (*b*), gave n-butyl iodide (1.3 g, 42%) and lithium perfluoroisobutyrate (0.15 g, 4%), which decomposed without prior melting at *ca.* 180°. This salt yielded the *S*-benzylisothiouronium derivative, m.p. 148–149°. (Found: C, 38.3; H, 3.0; F, 35.2; S, 8.4. $C_{12}H_{11}F_7N_2O_2S$ calcd.: C, 37.9; H, 2.9; F, 35.0; S, 8.4%.)

Carboxylation at −100° afforded n-butyl iodide (51%) and lithium perfluoroisobutyrate (0.12 g, 3%).

ACKNOWLEDGEMENTS

The author thanks Dr. J. L. Cotter for the mass spectra, and Dr. I. J. Lawrenson (National Physical Laboratory, Teddington) for the NMR data.

REFERENCES

1 O. R. Pierce, E. T. McBee and G. F. Judd, *J. Amer. Chem. Soc.*, 76 (1954) 474; E. T. McBee, C. W. Roberts and S. G. Curtis, *J. Amer. Chem. Soc.*, 77 (1955) 6387; R. D. Chambers, W. K. R. Musgrave and J. Savory, *J. Chem. Soc.*, (1962) 1993.
2 J. A. Beel, H. C. Clark and D. Whyman, *J. Chem. Soc.*, (1962) 4423; H. C. Clark, J. T. Kwan and D. Whyman, *Can. J. Chem.*, 41 (1963) 2628.
3 P. Johncock, *J. Organometal. Chem.*, 6 (1966) 433.
4 S. Andreades, *J. Amer. Chem. Soc.*, 86 (1964) 2003.
5 D. E. Applequist and D. F. O'Brien, *J. Amer. Chem. Soc.*, 85 (1963) 743.
6 D. J. Cram, *Fundamentals of Carbanion Chemistry*, Academic Press, New York and London, 1965, p. 19, 69.
7 W. Glaze and R. West, *J. Amer. Chem. Soc.*, 82 (1960) 4437; R. Waack and M. A. Doran, *Chem. Ind. (London)*, (1964) 496; R. Waack, M. A. Doran and E. B. Baker, *Chem. Commun.*, (1967) 1291.
8 R. G. Jones, *Organic Reactions*, Vol. 6, Wiley, New York, 1951, p. 352; D. Bryce-Smith and E. E. Turner, *J. Chem. Soc.*, (1953) 861; C. W. Kamiensky and D. L. Esmay, *J. Org. Chem.*, 25 (1960) 115.
9 J. D. LaZerte, L. J. Hals, T. S. Reid and G. H. Smith, *J. Amer. Chem. Soc.*, 75 (1953) 4525.
10 L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen, London, 1958, p. 42.
11 S. K. Alley and R. L. Scott, *J. Chem. Eng. Data*, 8 (1963) 117.
12 H. M. McConnell, C. A. Reilly and A. D. McLean, *J. Chem. Phys.*, 24 (1956) 479.