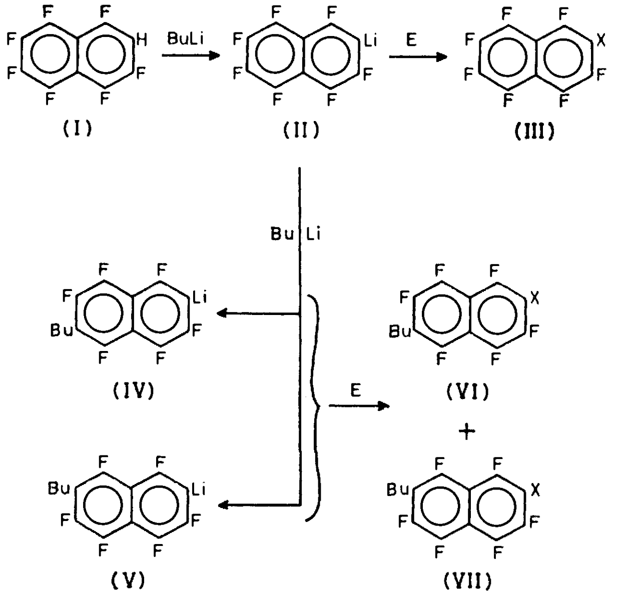
Polycyclic Fluoro-aromatic Compounds. Part 10.[1] Nucleophilic Replacement of Fluorine in Heptafluoro-2-naphthyl-lithium

By **James Burdon,* Harpal S. Gill, and Ian W. Parsons**, Chemistry Department, The University, P.O. Box 363, Birmingham B15 2TT

Heptafluoro-2-naphthyl-lithium, prepared from *2H*-heptafluoronaphthalene, reacts with an excess of butyl-lithium to give a 4 : 1 mixture of 6-butyl- and 7-butyl-hexafluoro-2-naphthyl-lithium. Carbonation, bromination, and hydrolysis of all the lithio-compounds gave the expected products.

In the literature there appear to be no examples of the attack of a nucleophile on an aryl-lithium to give replacement of, for example, a halogen, with the lithium entity remaining intact during the reaction. We now report such a case and this is shown in Scheme 1.



(a) X = CO_2H (E = CO_2, H^+) (b) X = Br (E = Br_2) (c) X = H (E = H_2O)

Scheme 1

The reaction of *2H*-heptafluoronaphthalene (I) [2] with a 2.5 molar ratio of butyl-lithium, followed by treatment with carbon dioxide, bromine, or water gave, in each case, a 4 : 1 mixture of the compounds (VI) and (VII). The obvious explanation for this is that the naphthalene (I) is first metallated to give lithio-compound (II), a process which has ample precedent generally [3] and in the polyfluoro-aromatic field,[4] and that (II) is then attacked by more butyl-lithium with replacement of the 6- and 7-fluorines to give a mixture (4 : 1) of the lithio-compounds (IV) and (V).

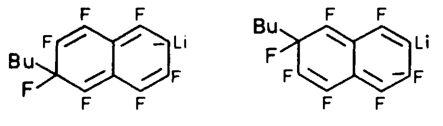
The structures of (VIa—c) and (VII a—c) were determined by n.m.r. spectroscopy (see Table), using an argument similar to that employed by other workers [5] who have studied polyfluoronaphthalenes. It has been observed [6] throughout the polyfluoro-aromatic field that replacement of a fluorine by another substituent brings about a downfield shift in a fluorine that is *ortho* to the replaced fluorine; also, there is always a characteristically large (55—82 Hz) coupling between *peri*-fluorines in polyfluoronaphthalenes.[5a,7] These two points lead to the conclusion that in (VI a—c) the two lowest field signals (F^1 and F^5) which show large *peri*-couplings should not be *peri*-coupled together, but should be *peri*-coupled to fluorines (F^8 and F^4) which are at higher field, in about the positions recorded for the corresponding nuclei in perfluoronaphthalene; decoupling studies showed this to be so. In (VII a—c) on the other hand, the two low field *peri*-coupled fluorines (F^1 and F^8) *are* *peri*-coupled together [F^4 and F^5 should also show *peri*-coupling, but in the three cases, (VIIa, b, c) they either had identical chemical shifts or were obscured under the stronger signals from (VI)]. Also, in (VI a—c) and (VII a—c), the fluorines which were *ortho* to the Bu and X substituents were shifted downfield from their positions in perfluoronaphthalene by amounts which were in accord with previous results.[6]

Evidence for the internal consistency of the structures of (VIa) and (VIIa) and (VIc) and (VIIc) was obtained by decarboxylation of the mixture (4 : 1) of acids (VIa) and (VIIa) when the same (4 : 1) mixture of hydro-compounds (VIc) and (VIIc) was produced as was obtained from direct treatment of lithio-compounds (IV) and (V) with water.

There is nothing peculiar about heptafluoro-2-naphthyl-lithium (II): treatment of *2H*-heptafluoronaphthalene with one molar proportion of butyl-lithium, followed by carbon dioxide or bromine gave the expected acid (IIIa) and bromo-compound (IIIb).

Whichever of the current models [8] of nucleophilic replacement in polyfluoro-aromatics is employed, it is necessary to argue that the resonance contributor (VIII) for attack at C-6 is slightly more stable than the corresponding one (IX) for attack at C-7 (Scheme 2); that is, a negative charge is slightly more stable when it is on a carbon bearing a lithium than when it is on a carbon bearing a fluorine.

This is at first sight surprising: one might expect (VIII) to be much less stable than (IX) because the negative charge is being placed on a carbon which is already bearing such a charge by virtue of being joined to lithium. This, however, supposes that lithio-compounds are largely ionic and this is not so; many of them are, after all, soluble in petroleum. It seems we must conclude that the amount of negative charge produced on C-2 by virtue of the adjacent lithium atom is relatively slight,



(VIII) (IX)

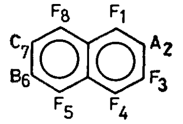
Scheme 2

and is not enough to outweigh the destabilizing effect of a fluorine on a negative charge in a π-system ($I\pi$-repulsion [8a]). That is, the situation $\bar{\mathrm{C}}(\delta^-)$-Li$(\delta^+)$ is more stable than $\dot{\mathrm{C}}$–$\ddot{\mathrm{F}}$.

EXPERIMENTAL

Heptafluoro-2-naphthyl-lithium (II).—2*H*-Heptafluoronaphthalene [2] (0.5 g) in dry ether (15 cm^3) was stirred at -75 °C, under N_2, while butyl-lithium in hexane (1.2 cm^3; 1.6 M), diluted with dry ether (10 cm^3), was added dropwise during 10 min. The reaction mixture was maintained at -75 °C for 2 h before the following reactions were carried out.

N.m.r. spectra [a] of polyfluoronaphthalenes



Compound [b] A	B	C		Chemical shifts [c] 1	2	3	4	5	6	7	8	Coupling constants [d]
CO_2H [e]	F	F	(IIIa)	117.4	10.5	138.3	146.7 [f]	149.5 [f]	152.7 [g]	156.2 [g]	144.1	$J_{1.8} = 72.2$; $J_{3.4} = J_{5.6} = J_{7.8} = 17$; $J_{4.5} = 58.7$; $J_{6.7} = 19.2$
H	F	F	(IIIc)	116.0	7.62	134.0	146.0 [f]	150.1 [f]	153.0 [g]	156.7 [g]	144.0	$J_{1.8} = 65$; $J_{3.4} = J_{5.6} = J_{7.8} = 17$; $J_{6.7} = 19$; $J_{4.5} = 58$; $J_{1.2} = J_{2.3} = 10.8$; $J_{2.4} = 6$
Br [e]	F	F	(IIIb)	111.6		129.7	147.0	147.0	154.6 [g]	155.6 [g]	145.0	$J_{1.8} = 65$; $J_{6.7} = 17$
CO_2H [e]	C_4H_9	F	(VIa)	118.3	9.96	140.4	148.6	123.7	*h*	140.4	148.6	$J_{1.8} = 65$; $J_{4.5} = 68$
CO_2H [e]	F	C_4H_9	(VIIa)	116.0	9.96	136.3	150.7	150.7	139.1	*h*	120.9	$J_{1.8} = 70$
H [i]	C_4H_9	F	(VIc)	118.1	7.06	137.1	149.6	124.2	*h*	141.4	149.6	$J_{1.8} = 60$; $J_{4.5} = 65$; $J_{1.2} = J_{2.3} = 10$; $J_{2.4} = 5.5$
H [i]	F	C_4H_9	(VIIc)	116.4	*k*	135.7	151.1	151.1	138.4	*h*	122.5	$J_{1.8} = 65$
Br [j]	C_4H_9	F	(VIb)	112.3		131.2	148.4	123.7	*h*	139.8	146.2	$J_{1.8} = 66.6$; $J_{4.5} = 68.9$
Br [j]	F	C_4H_9	(VIIb)	110.8		129.5	*k*	*k*	137.8	*h*	121.1	$J_{1.8} = 74.4$

[a] Run on a Varian XL 100 [at 94.1 MHz (^{19}F) and 100.1 MHz (^{1}H)] or on a Perkin-Elmer R12B [at 56.4 MHz (^{19}F) and 60 MHz (^{1}H)] at 34 °C. [b] See Scheme 1 for (IIIa), (IIIb) *etc.* [c] ^{19}F Shifts in p.p.m. upfield from internal $CFCl_3$; ^{1}H shifts on δ scale. [d] In Hz. Most peaks were more complex than the given couplings suggest; couplings given to the nearest whole number are only approximate because of this. [e] In $(CD_3)_2CO$. [f] Or *vice-versa*. [g] Or *vice-versa*. [h] Butyl group peaks [0.9—1.1 (3 H), 1.54—1.56 (2 H), and 2.84—2.89 (2 H)]. [i] In $CDCl_3$. [j] In CCl_4. [k] Peaks hidden by those of major isomers.

(a) *Carbonation.* Carbon dioxide was bubbled through the above solution of heptafluoro-2-naphthyl-lithium for 30 min at -75 °C and 4M HCl (30 cm^3) was added. The ether layer was separated, dried ($MgSO_4$), and evaporated to leave a solid (0.5 g) which was taken up in aqueous Na_2CO_3; the resulting solution was extracted with ether, acidified with HCl, and re-extracted with ether. Evaporation of these final extracts left a solid which was crystallized from aqueous MeOH to give heptafluoro-2-naphthoic acid (IIIa) (0.36 g), m.p. 182—183 °C (lit.,[9] 188—189 °C) (Found: C, 44.6; H, 0.4; F, 44.1. Calc. for $C_{11}HF_7O_2$: C, 44.3; H, 0.3; F, 44.6%).

(b) *Bromination.* Br_2 (1.5 g) in ether (10 cm^3) was added dropwise during 20 min at -75 °C to heptafluoro-2-naphthyllithium. After 1 h at -75 °C, the reaction mixture was allowed to warm to room temperature and kept there for a further hour before aqueous sodium thiosulphate was added. The ethereal layer was separated, dried ($MgSO_4$), and evaporated to leave a residue (0.6 g) which was separated by chromatography on alumina (25 cm × 2.5 cm), using light petroleum (b.p. 60—80 °C) as eluant, into (i) 2*H*-heptafluoronaphthalene (0.04 g), and (ii) a fraction (0.29 g) which was further purified by g.l.c. [Pye series 104 instrument; column 9.1 m × 8 mm; packed with silicone gum SE30 on Universal B (1 : 40); temp. 200 °C; N_2 carrier gas] to yield; (*a*) more 2*H*-heptafluoronaphthalene (0.01 g) and (*b*) 2-bromoheptafluoronaphthalene (IIIb) (0.24 g), m.p. 73—74 °C (lit.,[10] 68.5—69.5 °C) (Found: C, 35.9; top mass peak, 334. Calc. for $C_{10}BrF_7$: C, 36.1%; $M^{+\bullet}$, 334).

Reaction of 2H-*Heptafluoronaphthalene with an Excess of Butyl-lithium.*—2*H*-Heptafluoronaphthalene (0.5 g) was treated with an excess of butyl-lithium (3 cm^3; 1.6M) as in the previous experiment. The reaction mixture was maintained at -30 to -40 °C for 2 h before the following reactions were carried out.

(a) *Carbonation.* This was performed as in (a) above, but at -30 to -40 °C. The product (0.32 g), m.p. 145—149 °C, was a mixture (4 : 1 by ^{19}F n.m.r.) of 6-butylhexafluoro-2-naphthoic acid (VIa) and 7-butylhexafluoro-2-naphthoic acid (VIIa) (Found: C, 53.5; H, 2.9. Calc. for $C_{15}H_{10}F_6O_2$: C, 53.6; H, 3.0%).

(b) *Bromination.* This was carried out as in (b) above, but at -30 to -40 °C. The alumina separation gave: (i) a mixture (4 : 1 by n.m.r.) of 6- and 7-butyl-2*H*-hexafluoronapththalenes (VIc) and (VIIc); and (ii) a residue which was sublimed *in vacuo* to give a semisolid mixture (4 : 1 by n.m.r.) of 2-bromo-6-butylhexafluoronaphthalene (VIb) and 2-bromo-7-butylhexafluoronaphthalene (VIIb) (0.42 g) (Found: C, 45.9; H, 2.3. Calc. for $C_{14}H_9BrF_6$: C, 45.3; H, 2.4%).

(c) *Hydrolysis.* 2*H*-Heptafluoronaphthalene (2.0 g) was used in this experiment. Treatment of the mixed lithio-compounds (IV) and (V) at −60 °C with H_2O (75 cm^3) and then 2M H_2SO_4, followed by ether extraction, gave a residue (2.60 g) which was separated by g.l.c. [see (b) of previous experiment; temp. 250 °C] into: (i) 2*H*-heptafluoronaphthalene (0.47 g); and (ii) a mixture (4 : 1 by n.m.r.) of 6-butyl-2*H*-hexafluoronaphthalene (VIc) and 7-butyl-2*H*-hexafluoronaphthalene (VIIc) (1.54 g), b.p. 281—283 °C (Found: C, 57.8; H, 3.6. Calc. for $C_{14}H_{10}F_6$: C, 57.5; H, 3.4%).

Decarboxylation of Polyfluoronaphthoic Acids.—Heptafluoro-2 naphthoic acid (0.20 g) and dry (CaH_2) dimethylformamide (3 cm^3) were refluxed for 4 h. The reaction mixture was poured into water (20 cm^3) and 2*H* heptafluoronaphthalene (0.13 g), identified by i.r. spectroscopy, precipitated.

In a similar way, the 4 : 1 mixture ((0.15 g) of 6- and 7-butylhexafluoro-2-naphthoic acids gave a 4 : 1 mixture (0.08 g) (isolated by ether extraction) of 6- and 7-butyl-2*H*-hexafluoronaphthalenes.

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