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POLYCYCLIC FLUORO-AROMATIC COMPOUNDS. PART 11 [1]. HEXAFLUORO-1,2-NAPHTHALYNE

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SUMMARY

Heptafluoro-2-naphthyl-lithium decomposes to give hexafluoro-1,2-naphthalyne and not the 2,3-compound. This was demonstrated by capture of the aryne with furan and with heptafluoro-2-naphthyl-lithium; in this last reaction the ratio of attack at the 2-position of the naphthalyne to that at the 1 was 9:2.

INTRODUCTION

Although there is a vast literature on arynes, relatively little of it concerns naphthalynes. In particular, there are only a few reports on competition between 1,2- and 2,3-naphthalyne formation by, for example, treatment of a 2-halogenonaphthalene with base. Huisgen and co-workers [2] found that 2-fluoro- and 2-chloro-naphthalene gave 1,2- and 2,3-naphthalyne in about 4:1 ratio with phenyl-lithium, but that the chloro-compound, and the bromo and iodo, gave only 1,2-naphthalyne with lithium piperidide. The present paper reports the opposite type of competition in which there are two possible halides which may leave with one hydrogen (or lithium), instead of two hydrogens (or lithiums) with one halide: in 2-heptafluoronaphthyl-lithium the lithium may leave with either the 1- or the 3- fluorine.

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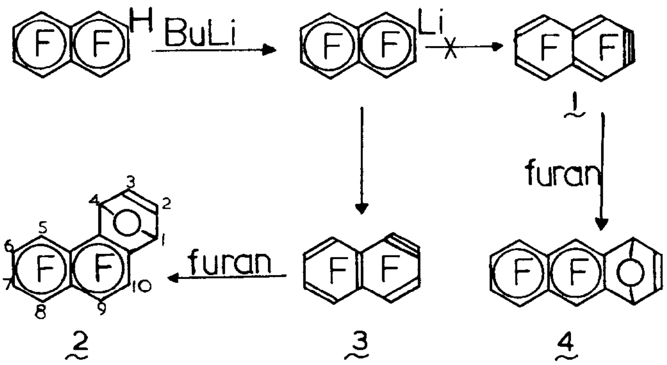
DISCUSSION

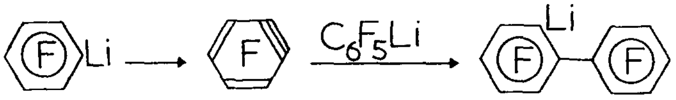
2H-Heptafluoronaphthalene is lithiated in the normal way at -75°C [1]; on warming to room temperature in the presence of furan, a Diels-Alder adduct formed (Scheme 1). The ^{19}F spectrum shows quite trivially - there are more than three signals - that the adduct is not 4 ; and further that it is 2. Thus, octafluoronaphthalene itself shows two ^{19}F nmr signals at 145.9 (α-F) and 155.0 (β-F) [3]: the adduct has signals for fluorines 6 and 7 (all ^{19}F chemical shifts are in ppm upfield from internal $CFCl_3$) at 158.6 and 159.4 and a broad signal at 147.6 for the three α-fluorines at 5, 8, and 9. Fluorine-10 resonates at 143.9, about 11 ppm downfield from the β-fluorine position in octafluoronaphthalene, and this, while being a little more upfield than we had expected, is only in accord here with replacement of a fluorine ortho to fluorine-10 by a carbon-linked group [4].



Scheme 1

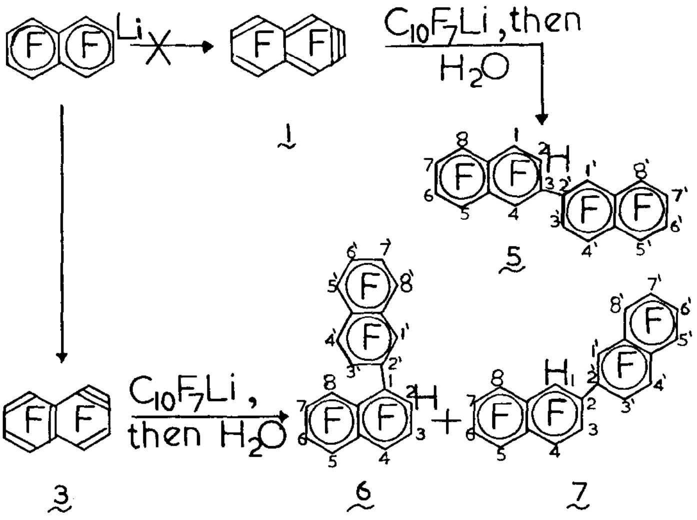
Further evidence that the lithio-compound decomposed to give the 1,2-aryne (3) came from an investigation of the products of its decomposition in the absence of Diels-Alder trapping agents.

When pentafluorophenyl-lithium is allowed to stand at room temperature the reactions in Scheme 2 - tetrafluorobenzyne formation followed by addition of pentafluorophenyl-lithium to it - occur [5].



Scheme 2

A similar reaction took place with heptafluoro-2-naphthyl-lithium, although here two arynes are possible with two possible directions of addition to one of them (Scheme 3).



Scheme 3

That the products were a mixture of 6 and 7 and not 5 followed from the ^{19}F and ^{2}H nmr spectra of the mixture. There were two signals, in intensity ratio 9:2, in the latter: the stronger ($\delta = 8.24$) was a doublet with J = 5.4 Hz, typical of J_{HF} - meta [6] and so, of the three possibilities, was consistent only with 7; the weaker ($\delta = 7.91$) was a doublet of doublets (J = 11.1 Hz - ortho HF; J = 7.8 Hz - meta HF) consistent with either 5 or 6 [Compare 2H- heptafluoronaphthalene which shows a doublet (6.0 Hz - meta HF) and a triplet (10.8 Hz - ortho HF)]. The ^{19}F spectra (see Table) were naturally more complex: the major component (7) showed signals for fluorines 4,5,6,7,8,4',5',6',7', and 8' in approximately the same positions as the corresponding α or β fluorines in octafluoronaphthalene, but the key signals for structural purposes are those due to fluorines 3, 1', and 3'. Most importantly, the signal at 118.3 was a doublet with a typical [7] peri-coupling; this can only be the α-fluorine 1' brought downfield from the α-fluorine of octafluoronaphthalene by about the expected [4] 25 ppm by the adjacent hexafluoronaphthyl-group. The 3 and 3' fluorines resonate at 137.2 and 139.1, each about 17 ppm downfield from the expected position owing to the adjacent polyfluoro-naphthyl-groups. Isomers 6 and 7 would both be expected to have ^{19}F spectra like this but the former is ruled out by the ^{1}H spectrum. Isomer 5 is completely ruled out because it would have three low-field (ca. 115-120 ppm) α-fluorine signals, not one; fluorines 4 and 1' would be brought downfield by polyfluoronaphthyl-groups, and 1 by H-2 which would have [4] a similar effect.

Some of the signals due to the minor component (6) were obscured by those of the major one (7): most significantly though, there was only one low field α-fluorine signal (119.6, d, J = 71 Hz - due to F 1'), again ruling out isomer 5 which would have three, and confirming 6.

The favoured direction of addition of hexafluoro-2-naphthyl-lithium to hexafluoro-1,2-naphthalyne (3) is as expected from work [8] on 1,2-naphthalyne itself where 2-attack by nucleophiles was again favoured over 1 by between 2 and 7 to 1, depending on the size of the nucleophile.

The present work has been reported briefly in a preliminary note [9].

EXPERIMENTAL

Reaction of hexafluoro-1,2-naphthalyne with furan

n-Butyl-lithium in hexane (1.6M, 2.4cm³), diluted with ether (20cm³), was added dropwise over 45 min to a stirred and cooled (-75°C) solution of 2H-heptafluoronaphthalene [10] (1.0g) in ether (30cm³), the whole experiment being conducted under nitrogen. After 2 hr at -75°C furan (30cm³) was added and the reaction mixture was kept at -75°C for 30 min and then allowed to warm to room temperature where it was maintained for 24 hr. Water (20cm³) was added and the ether layer was separated, dried ($MgSO_4$), and evaporated to leave a residue (0.84g) which was sublimed (40°C, 25 mmHg) to give 2H-heptafluoronaphthalene (0.2g, i.r.). The unsublimed material was passed down a column (9 in. x 1 in.) of silica gel with light petroleum (b.p. 60-80°C) as eluant to give a brown product (0.47g) which was purified by sublimation (106°C, 30 mmHg) to yield 1,4-epoxy-5,6,7,8,9,10-hexafluoro-1,4-dihydrophenanthrene (**2**) (nc) (0.32g), m.p. 120-121°C (Found: C, 55.8; H, 1.3; M^+, 302. $C_{14}H_4F_6O$ requires: C, 55.6; H, 1.3%; M, 302); λ_{max} (nm, in EtOH) 222.5 (ε, 38500), 312 (ε, 3580), and 335 (ε, 2240); ν_{max} 1667cm^{-1} (C=C).

Reaction of hexafluoro-1,2-naphthalyne with heptafluoro-2-naphthyl-lithium

2H-Heptafluoronaphthalene (2.0g) was lithiated as above at -75°C, the reaction mixture was then allowed to warm to room temperature and kept there, with stirring, for 21 hr. Hydrolysis with sulphuric acid (3M, 65cm³), followed by evaporation of the dried ether layer, left a residual oil (2.40g) which was purified by chromatography on a column (16in x 1in) of alumina using hexane as eluant to yield, after crystallization from light petroleum (b.p. 60-80°C), a mixture (82:18 by ^1H nmr) of 1H-tridecafluoro-2,2'-binaphthyl (**7**) and 2H-tridecafluoro-1,2'-binaphthyl (**6**) (0.48g), m.p. 142-143°C (Found: C, 49.4; H, 0.2; M^+, 488. $C_{20}HF_{13}$ requires C, 49.2; H, 0.2%; M, 488); λ_{max} (nm, in EtOH). 216 (ε, 41800), 230 (ε, 40300), 243 (ε, 40800), 280 (ε, 10700), and 330 (ε, 5830).

NMR Spectra

These were run on a Varian XL 100 at 100 MHz (^1H) and 94.1 MHz (^{19}F). Acetone -D_6 was used as solvent in all cases and ^{19}F chemical shifts are from internal $CFCl_3$. The spectral data for adduct **2** and for 2H-heptafluoronaphthalene are given in the text, and those for isomers **6** and **7** in the Table below.

	Fluorine Chemical Shifts [a]				
Compound	3,3'	4,5,8 4',5',8'	6,7	1'	Couplings (Hz)
7	137.2, 139.1	143-145.2, 146.2-147.7, 149.4	154.8, 156.2, 157.3	118.3	$J_{1'8'}$, 67[b]
6[c]	138.0	142.8,142.2, 145.8,150.4	153.9	119.6	$J_{1'8'}$, 71[b]

[a] See Scheme 3 for numbering. [b] Only visible in 1' signal - 8' signal is buried within rest of α-fluorines.

[c] Only those signals which are clearly visible are recorded - rest are obscured by strong signals from isomer **7**.

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