Hexafluoro-1,2-naphthalyne

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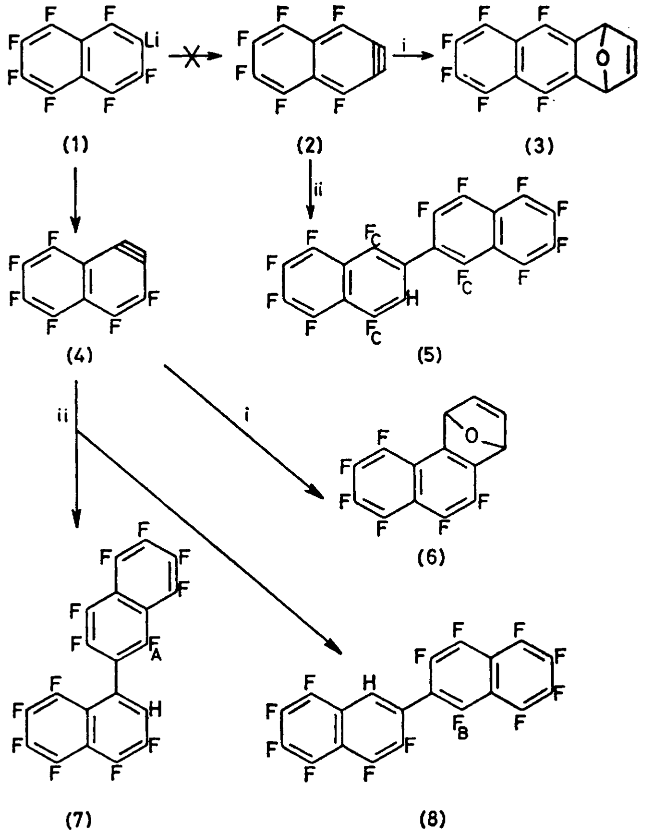
Summary 1,3,4,5,6,7,8-Heptafluoronaphthyl-lithium eliminates lithium fluoride to give only hexafluoro-1,2-naphthalyne, and not its 2,3-isomer, as shown by trapping with furan and by addition of undecomposed 1,3,4,5,6,7,8-heptafluoronaphthyl-lithium to give a characteristic mixture of tridecafluorobinaphthyls.



SCHEME. Reagents: i, excess of furan; ii, $C_{10}F_7Li$, H_2O.

AMONG the vast number of publications on arynes, relatively few refer to naphthalynes and to competition between 1,2- and 2,3-naphthalyne formation. We now report an example of such a competition where the outcome is determined by the relative stabilities of the two naphthalynes and by the C–F bond strengths at C-1 and C-3 of the parent naphthalene.

When 1,3,4,5,6,7,8-heptafluoronaphthyl-lithium (**1**) (prepared at −78 °C by treatment of 2*H*-heptafluoronaphthalene[1] with butyl-lithium) was allowed to warm to room temperature in the presence of a great excess of furan, a single non-polymeric product† was formed. The ^{19}F and ^{1}H n.m.r. spectra were clearly incompatible with the symmetrical Diels–Alder adduct (**3**) and the four fluorine signals‡ [143·9 (relative intensity 1) (β-F adjacent to oxygen-containing ring), 147·6 (3) (three overlapping signals, α-F), 158·6 (1) (β-F), and 159·4 (1) (β-F)] and two proton signals [6·34 (bridgehead) and 7·29 (olefinic), both complex multiplets] were consistent with structure (**6**).

Confirmation of 1,2-naphthalyne (**4**) formation was obtained by allowing the heptafluoronaphthyl-lithium (**1**) to warm up, in ether, without any added trapping agent, and then, after 24 h, adding water. The reactions that can occur are shown in the Scheme. Here the naphthalyne is captured by addition of its parent heptafluoronaphthyl-lithium across the triple bond of (**2**) or (**4**), the tridecafluorobinaphthyl (**5**), (**7**), or (**8**) being subsequently liberated by the added water. This type of reaction has been observed[2] with pentafluorophenyl-lithium: tetrafluorobenzyne formed and was captured by addition of pentafluorophenyl-lithium, the final product being a nonafluoro-2-halogenobiphenyl if halide salts were present, and 2*H*-nonafluorobiphenyl in the absence of halides, and after water had been added. In the present work, two non-polymeric products were formed in about a 4 : 1 ratio (determined from ^{1}H and ^{19}F

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† This compound, and the mixture of tridecafluorobinaphthyls, gave satisfactory elemental analyses and mass spectra.

‡ ^{19}F chemical shifts are in p.p.m. upfield from $CFCl_3$.

n.m.r. signal intensities). The ^{1}H signal of the major product was a doublet (J 5·4 Hz), indicating[3] no fluorines *ortho* to the proton and one *meta* [compare 2*H*-heptafluoronaphthalene which shows a doublet (6·0 Hz, *meta*-F) of triplets (10·8 Hz, two *ortho*-F)]; the major product must therefore be (**8**). The ^{19}F n.m.r. spectrum is consistent with this as it showed only one low-field signal at δ 118·3 with a large doublet coupling (67 Hz), typical[4] of *peri*-coupling in polyfluoronaphthalenes: this must be the α-fluorine F_B in (**8**) shifted downfield by the vicinal hexafluoronaphthyl ring from its position[5] (145·9) in octafluoronaphthalene by about the expected[6] 25 p.p.m. The major product cannot therefore be (**5**) which would show three low field signals [F_C in (**5**)]. The minor product was (**7**) [^{1}H n.m.r. spectrum a doublet (7·8 Hz, *meta*-F) of doublets (11·1 Hz, *ortho*-F)] as shown by the presence of only one low field α-fluorine signal [F_A; 119·6, d (J 71 Hz)] which again eliminates (**5**). These two products (**7**) and (**8**) are obviously formed by addition of the heptafluoronaphthyl-lithium (**1**) in the two possible ways across the 'triple' bond of hexafluoro-1,2-naphthalyne (**4**). There was no evidence for the presence of the adduct (**5**).

We therefore conclude that lithium fluoride elimination from the heptafluoronaphthyl-lithium (**1**) involves only an α-fluorine, giving the 1,2-naphthalyne (**4**), and that elimination by loss of the β-fluorine to give the 2,3-naphthalyne (**2**) does not occur (β-fluorine is usually lost in nucleophilic replacement reactions of polyfluoronaphthalenes).[1,4a,7]

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