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PRELIMINARY COMMUNICATION

AN INTRAMOLECULAR ADDITION TO A BENZYNE*: THE SYNTHESIS OF MONOSUBSTITUTED HEPTAFLUOROBIPHENYLENES

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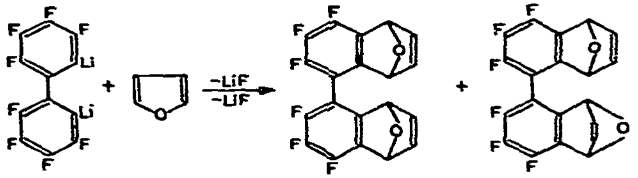
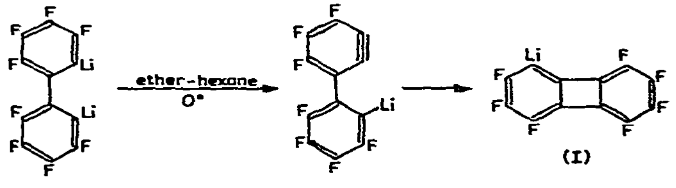
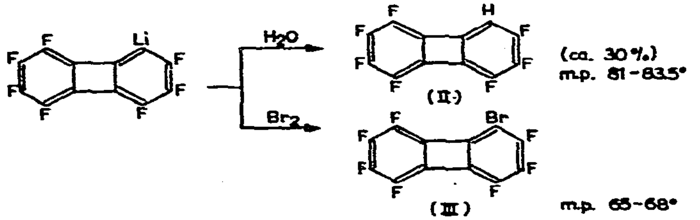
As a continuation of our studies[2] on the thermal decomposition of polyfluoroaryllithium reagents we allowed 2,2'-dilithiooctafluorobiphenyl[3] to decompose at room temperature in the presence of furan and obtained two isomeric difuran benzyne adducts:



However, if the 2,2'-dilithiooctafluorobiphenyl is held at 0° for 30 minutes in the absence of a trapping reagent, the loss of one mole of lithium fluoride appears to be followed by an intramolecular addition of the intact half of the molecule to the benzyne to give 1-lithioheptafluorobiphenylene:



which can be converted, via either hydrolysis or bromination, to the pale yellow compounds 1-hydro- or 1-bromo-heptafluorobiphenylene:



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* Part XVIII of a series; for Part XVII see ref. 1.

The reaction is a remarkably clean one in that if sufficient time is allowed for the total decomposition of 2,2'-dilithiooctafluorobiphenyl (*e.g.* about 30 minutes for 1.5 g quantities) the only impurities in the biphenylenes are polymeric species of much lower volatility. The biphenylenes (II) and (III) can thus be sublimed from the reaction mixtures in a state of high purity.

The proton NMR spectrum of (II) is centred at 6.53 ppm (*cf.* biphenylene[4]) whilst the ^{19}F NMR spectrum consists of the expected seven groups of lines. The mass spectrum of (II) shows (as the main points of interest) a parent ion at $m/e = 278$, an ion at $m/e = 277$, a doubly-charged parent ion at $m/e = 139$ and three metastable peaks corresponding to the loss of CF, CF_2 and CF_3 from the parent ion.

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