An Intramolecular Nucleophilic Alkylation by a Stabilized Carbanion: Synthesis of 1,2,3,4,5,6,7,8-Octafluorofluorene and Related Compounds

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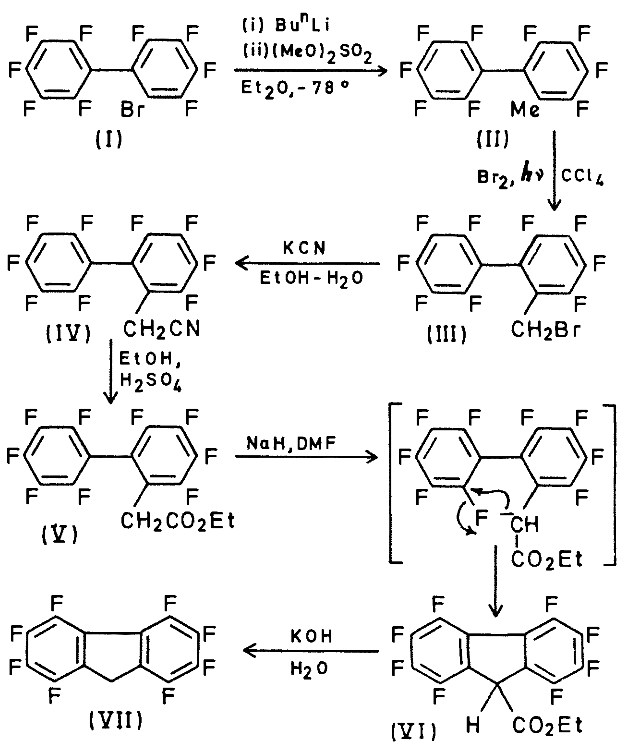
Summary The synthesis is reported of 1,2,3,4,5,6,7,8-octafluorofluorene and related compounds by means of an intramolecular nucleophilic cyclization carried out with a stabilised carbanion generated at a saturated carbon atom.

IN recent communications we discussed the effect of polyfluoroaryl substitution on the equilibrium acidities of hydrocarbons[1] and the synthesis of octafluorofluoren-9-one.[2] We now report a synthetic route to 1,2,3,4,5,6,7,8-octafluorofluorene and related compounds by means of an intramolecular nucleophilic alkylation. A number of such cyclizations involving nucleophilic displacement of aromatic fluoride ions by hetero-atoms[3] and unsaturated carbanions[4] has been reported. To our knowledge, the present work is the first example of a nucleophilic cyclization carried out with a stabilized carbanion generated at a saturated carbon atom.

2-Bromononafluorobiphenyl (I),[5] has been used to prepare the key ester intermediate (V) (see Scheme). Compound (V) can also be prepared less reliably by insertion into the carbon–copper bond[6] of 2-(pentafluorophenyl)tetrafluorophenylcopper, using ethyl diazoacetate. Treatment of (V) with an excess of sodium hydride in purified dimethylformamide at 80—90° gives the stabilized carbanion which cyclizes to (VI) in yields of 40—50%. 9-Ethoxycarbonyloctafluorofluorene (VI), m.p. 75—76·5°, was characterized by its ^{1}H n.m.r. spectrum [methine proton at δ 5·10 (CCl_4)], and elemental analysis. Cyclization failed when either (II) or (IV) were similarly treated with sodium hydride in dimethylformamide, although the corresponding carbanions appeared to be generated.

The cyclic ester (VI) is conveniently decarboxylated (60—70% yields) by refluxing in 5% aqueous KOH. The resulting compound (VII), m.p. 113—115° (sealed capillary), shows the methylene protons at δ 4·10 (CCl_4). A correct elemental analysis for (VII) was obtained. Compound (VII) was readily oxidised to octafluorofluoren-9-one[2] by sodium dichromate in acetic acid in yields of 63—74%.



SCHEME

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