

Nucleophilic Replacement in Decafluoroanthracene

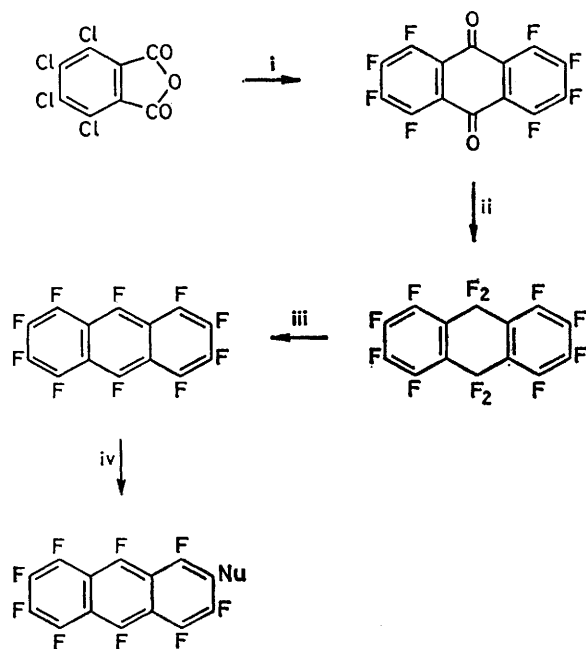
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Decafluoroanthracene undergoes replacement of the 2-fluorine when treated with sodium methoxide or with dimethylamine, and this is not in accord with the amplified I_{π} -repulsion theory which requires attack at the 9-position; there is now no theory which rationalizes the position of nucleophilic replacement in all polyfluoro-aromatic compounds.

Although decafluoroanthracene was first prepared¹ almost 20 years ago, its nucleophilic replacement reactions have never been described and it is the simplest perfluoro-poly-nuclear aromatic compound for which this is so. Treatment of the anthracene (prepared in 20–25% overall yield from tetrachlorophthalic anhydride by a modification of a method due to Russian workers²) with sodium methoxide (1 mol. equiv.) in methanol, or with dimethylamine in ether, gave crude products each of which contained only a single (according to ¹⁹F n.m.r.) mono-fluorine replacement product together with smaller amounts of di-fluorine replacement product and starting material.

The structures of the mono-replacement products (satisfactory elemental analyses have been obtained) were deduced from their ¹⁹F n.m.r. spectra. Decafluoroanthracene itself shows three ¹⁹F signals [(in p.p.m. upfield from CFCl₃): 144.1 (1,4,5,8-F); 153.8 (2,3,6,7-F); 122.5 (9,10-F); intensity ratios 4:4:2] with those from the (1,4,5,8) and (9,10) fluorine atoms showing a strong and typical^{3–5} *peri*-coupling (J ca. 75 Hz). In the nonafluoromonomethoxyanthracene there were peaks at 119.4 (2F, 9-, 10-F), 136.6 (1F, 1-F), 141.4–143.5 (3F, 4-, 5-, 8-F), 143.6 (1F, 3-F), and 150.9 (2F, 6-, 7-F); the down-field shift of about 5–7 p.p.m. for 1-F and 3-F is usual^{4–6} for the fluorine atoms *ortho* to a methoxy-group when this has replaced



Scheme 1. Reagents and conditions: i, KF, 300 °C, 3 h; ii, SF₄, HF, 360 °C, 24 h; iii, Zn, 280 °C, 3 h; iv, MeO⁻ or Me₂NH.

fluorine. Furthermore, the large *peri*-couplings were all still discernible although somewhat obscured; this shows that the 1,4,5,8,9, and 10 fluorine atoms were still present. The ¹⁹F n.m.r. spectrum of the dimethylaminononafluoroanthracene showed a similar pattern.

It is clear then that nucleophilic replacement in decafluoroanthracene takes place mainly or entirely in the 2-position (Scheme 1). This is not in accord with the amplified *I*_π-repulsion theory which predicts attack at the 9-position. This theory^{4,5,7} is based on the destabilization by a bonded fluorine of a negative charge on a carbon atom when that charge is

part of a π-system; the degree of destabilization is calculated from HOMO Hückel charge densities in Wheland intermediates. This procedure correctly gives the position of nucleophilic attack on perfluoro-naphthalene,⁷ -phenanthrene,⁷ -acenaphthylene,⁷ -pyrene,⁴ and -fluoroanthene;⁵ it does not do so for octafluorobiphenylene but strain provides an obvious reason why it does not here.⁷

As the decafluoroanthracene results outlined here cannot be reconciled with the amplified *I*_π-repulsion theory and since neither of the other theories^{8,9} in the literature can really be applied to perfluoropolynuclear aromatic compounds, there is now no all-embracing theory of nucleophilic attack on polyfluoro-aromatic compounds. (The original *I*_π theory¹⁰ correctly predicts 2-attack on decafluoroanthracene, but it is not satisfactory for some of the compounds just listed.)

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