Preparation of Dialkylamino-Substituted Benzenes and Naphthalenes by Nucleophilic Replacement of Fluorine in the Corresponding Perfluoroaromatic Compounds

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The reactions between hexafluorobenzene (HFB) and octafluoronaphthalene (OFN) with secondary aliphatic amines (pyrrolidine, dimethylamine and piperidine) and lithium amides (pyrrolidide, dimethylamide and piperidide) have been investigated both experimentally and (in part) theoretically. With amines HFB, depending on the selected conditions, gives either di-substituted products or a complex mixture of di-, tri- and tetrasubstituted compounds. Under similar conditions OFN produces almost exclusively the 2,3,6,7-tetrasubstituted compound. Interaction of HFB with the more nucleophilic lithium amides results in the replacement of four fluorines giving 1,2,4,5-tetrasubstituted difluorobenzenes, while OFN under similar conditions with lithium pyrrolidide produces an inseparable mixture of 1,2,4,5,6,8-hexa- and 1,2,3,4,5,6,8-hepta-substituted derivatives. With lithium dimethylamide, it is possible to substitute six (in dioxane) or seven (in THF) fluorines in OFN. Lithium piperidide in all employed solvents reacts with OFN to give only the 1,2,4,5,6,8-hexasubstituted derivative. Theoretical calculations indicate that with lithium dimethylamide the third fluorine is substituted at position 1, whereas with dimethylamine it is position 3. The basicities of selected hexa- and heptakis(dialkylamino)naphthalenes have been measured; they are all stronger bases than 1,8-bis(dimethylamino)naphthalene, although by less than expected.