Heptafluoro-n-propyl Derivatives of Boron

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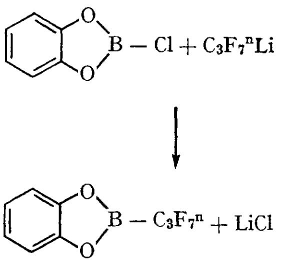
ALTHOUGH perfluorovinyl[1] and perfluoroaryl[2] compounds of boron are well known, no stable perfluoroalkyl derivatives of three-covalent boron have been reported. Trifluoromethylboron difluoride was obtained and found to be "enduringly metastable".[3] We now report the preparation of the first heptafluoro-n-propyl derivatives of boron by two different routes. They show unusual thermal stability for compounds containing a boron–perfluoroalkyl bond.

Heptafluoro-n-propyl derivatives of boron, (I) and (II), may be prepared in moderate yields (30%) by the reaction of 2-chloro-1,3,2-benzodioxaborole or bis(dimethylamino)halogenoboranes, respectively, with heptafluoro-n-propyl-lithium[4] at −50° in diethyl ether.



(I)

$$(Me_2N)_2BX + C_3F_7{}^nLi \longrightarrow (Me_2N)_2B - C_3F_7{}^n + LiX$$

(II)

[X = Cl, Br]

The bisdimethylamino-derivative (II) prepared in this manner contains tris(dimethylamino)borane as an impurity, which is difficult to separate. However (II) may also be obtained in moderate yield by the reaction of heptafluoro-1-iodopropane with the yellow solution obtained by shaking bis(dimethylamino)bromoborane with sodium amalgam in cyclohexane for several days in the dark. This solution is extremely sensitive to air and light, and is thought to contain the mercurial, $(Me_2N)_2B{\cdot}Hg{\cdot}B(NMe_2)_2$, since attempts to isolate it have resulted in decomposition to tetrakis(dimethylamino)diborane, tris(dimethylamino)borane, and mercury.[5]

Alkaline hydrolysis of heptafluoropropylboron derivatives gives 1*H*-heptafluoropropane in virtually quantitative yield. The mass spectrum of the bisdimethylamino-derivative (II) (b.p. 34—36°/10 mm.) shows the presence of the molecular ion at $[(Me_2N)_2B{\cdot}C_3F_7{}^n]^+$ at $m/e = 268$; there is also a peak at $m/e = 169$ ($C_3F_7{}^+$).

The ^{19}F n.m.r. spectrum of the benzodioxaborole (I) (b.p. 60—64°/0·2 mm.) shows the pattern normally found for heptafluoro-n-propyl derivatives.[6] Three absorptions occur at 81·0 (triplet), 127·7 (singlet), and 129·3 p.p.m.* (quartet), $J_{\alpha\gamma} =$ 9·2 c./sec. These may be assigned to the CF_3, β-CF_2, and α-CF_2 groups respectively. The spectrum of the bis(dimethylamino)-derivative (II) shows only two bands centred at 81·1 and 126·0 p.p.m. (with relative integrated intensities 5:2), $J_{\alpha\gamma} = 9{\cdot}7$ c./sec. The latter is a sharp singlet which may be assigned to the β-CF_2 group, while the former is a complex band probably arising from overlap of the α-CF_2 quartet with the CF_3 triplet.

The thermal decomposition of these compounds gives rise to 1*H*-heptafluoropropane. No hexafluoropropene can be detected. For example the benzodioxaborole (I), which can be recovered unchanged after 3 hr. at 120°, gives 1*H*-heptafluoropropane in 25% yield after 12 hr. at 172°. Thus internal nucleophilic attack on boron by fluorine in the side chain is apparently prevented by the presence of groups which are able to π-bond strongly with boron.

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* Relative to CCl_3F (0·0 p.p.m.) increasing to high field.

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