The Preparation of 1,2,3-Trifluorobenzene and of 2,3- and 2,6-Difluorophenyl Compounds

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PREVIOUS work has indicated that fluoro-,[1] 1,2,3,4-tetrafluoro-[2], 1,2,5,6-tetrafluoro-[2], and pentafluoro-benzene[2] can be lithiated by butyl-lithium.

We have found that both 1,2-difluoro-, and 1,3-difluoro-benzene (as well as 1,3-dichlorobenzene) in tetrahydrofuran : hexane or heptane (2 : 1—4 : 1) are readily lithiated by butyl-lithium. The resulting 2,3- (or 2,6-) difluorophenyl-lithium is stable below −50° and is an excellent intermediate for the preparation of many fluoroaromatic compounds.[3]

Carbonation of the aryl-lithiums gave 2,3- (m.p. 161·5–162·5) (74%) and 2,6-difluorobenzoic acids (m.p. 159–160°) (81%); the acids were converted by the Schmidt reaction into anilines in 77% and 86% yields. Diazotization of the weakly basic anilines in 42% fluoroboric acid furnished the crystalline diazonium borofluorides, each of which gave 1,2,3-trifluorobenzene in low yield on dry distillation. Analysis (C,H, and F), and n.m.r. (proton and fluorine) spectra verified the constitution of this, the last of the twelve possible fluoroaromatics to be characterised. Finger,[4] and Feast and Stephens[5] have reported preparations of this compound which has b.p. 94·5—95·5°.

1,2,3-Trifluorobenzene has also been obtained, again only in low yield, directly from both of the difluorophenyl-lithiums by reaction with perchloryl fluoride. This is apparently the first description of the reaction of perchloryl fluoride with an organometallic compound.

The preparation of 2,3-difluoro- and 2,6-difluorophenyl–lithium has provided a simple route to the corresponding benzaldehydes, arylcarbinols and acetophenones by standard procedures. 2,3-Difluoro- and 2,6-difluoro-phenol were obtained from the lithium derivatives in 65% and 40% yields by the method of Hawthorne.[6]

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[3] All compounds mentioned have been fully characterised.
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