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DIBORANE AND INORGANIC FLUORIDES AS A REDUCING AGENT FOR POLYFLUORINATED OLEFINS

Richard L. Johnson* and Donald J. Burton
Department of Chemistry, University of Iowa
Iowa City, Iowa

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Although the utility of the hydroboration reaction has been examined in some detail,(1) little attention has been devoted to the use of this elegant reaction with halogen-containing olefins. In general, systems containing a halogen atom beta to the boron of the intermediate organoborane undergo elimination with the formation of a boron-halogen bond.(2-7) Systems containing a halogen atom gamma to the boron atom undergo ring closure with base to form cyclopropanes.(2,4,8,9) Halogens further along the carbon chain have little effect on the hydroboration reaction or the stability of the intermediate organoborane.(3,8,9)

Polyhalogenated systems have received even less attention. Stone and co-workers(10,11) have studied several reactions of polyfluorinated ethylenes and reported that a complex mixture of products was obtained. These workers reported that violent reactions occurred when the reactions were carried out at elevated temperatures. Somewhat milder reactions gave similar products when carried out at room temperature for extended periods of time. Since these reactions were carried out in the gas phase, it is difficult to compare this system to a normal solution hydroboration reaction.

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Our interest in the reduction of polyfluorinated olefins led us to investigate the hydroboration of several alicyclic fluorinated olefins. In contrast to the gas phase work of Stone, these olefins did not react with diborane in diglyme at 0°C. (cf. Table I). Apparently, the presence of halogen substituents on the ring deactivated the olefinic bond enough to prevent hydroboration under these conditions. One implication of this inertness of the halogenated double bond to hydroboration is that it should be possible to utilize selective hydroboration to achieve transformations of dienes of the type, CF_2=CF-CH_2-CH=CH_2, to yield trifluoro-vinyl functional derivatives. This possibility is currently under investigation.(12)

In contrast to the inertness of these alicyclic polyhalogeanted olefins to diborane, it was found, however, that in the presence of inorganic fluorides such as sodium fluoride and potassium fluoride, diborane brought about rapid reduction of the olefin with replacement of the vinylic substituents by hydrogen. The results of these experiments are summarized in Table I. In the case where the vinylic substituents were different, vinylic fluorine was selectively replaced.

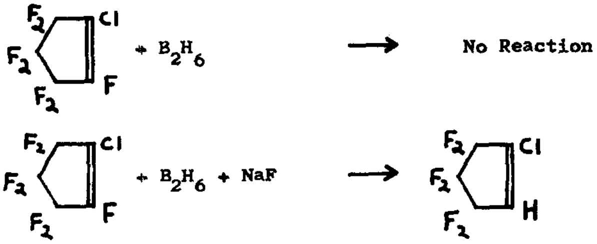

Table I

$\overline{CF_2CF_2CF_2CX=CY}$	X	Y	BH_3 mMoles	MX mMoles	$\overline{CF_2CF_2CF_2CX=CY}$	$\overline{CF_2CF_2CF_2CX=CH}$
50	Cl	Cl	50	---	50	---
50	Cl	Cl	50	150(NaF)	10	33
50	Cl	Cl	50	150(KF)	4	39
50	Cl	F	50	---	47	---
50	Cl	F	16.6	150(NaF)	15	23
50	Cl	F	25	150(KF)	6	36[a]
50	F	F	50	---	47	---
50	F	F	50	150(NaF)	0	22[b]
50	Cl	Cl	50	150(NaCl)	49	---
50	Cl	F	50	150(NaCl)	46	---[c]

a. Six mmoles of 1,2-dihydrohexafluorocyclopentene also obtained.

b. Twelve mmoles of 1,2-dihydrohexafluorocyclopentene also obtained.

c. Trace of material having the same G.L.C. retention time as 1-hydro-2-chlorohexafluorocyclopentene was obtained.

A typical procedure is as follows: Diborane (25 mmoles) was generated externally from sodium borohydride and borontrifluoride-etherate according to the method of Brown.(13) The diborane (diluted with nitrogen) was bubbled into a slurry of 12.25 g. (0.050 moles) of 1,2-dichlorohexafluorocyclopentene and 6.30 g. (0.150 moles) of anhydrous sodium fluoride in 50 ml. dry diglyme at 0° over a period of 1-2 hours. The excess hydride was then cautiously hydrolyzed by the addition of water and the organic layer separated. G. L. C. Analysis on dinonylphthalate indicated 10 mmoles of 1,2-dichlorohexafluorocyclopentene and 33 mmoles of 1-hydro-2-chlorohexafluorocyclopentene. Each material was separated by preparative gas chromatography and the infrared spectrum of the separated compounds was identical in all respects to authentic samples of 1,2-dichlorohexafluorocyclopentene and 1-hydro-2-chlorohexafluorocyclopentene, respectively. The aqueous layer was treated with silver nitrate to precipitate the chloride ion. After filtration and drying to constant weight, 37 mmoles of silver chloride were obtained.

The reduction reaction in this case probably occurs through the formation of $(BH_3F)^-$ which then functions as the reducing agent.

$$B_2H_6 + 2NaF \longrightarrow 2NaBH_3F$$

Muetterties and co-workers(14) have reported the preparation of KBH_3F from diborane and potassium fluoride, but no reactions or properties of this material were given. The products from the reduction reaction are similar to those obtained from the sodium borohydride reduction of polyhalogenated olefins(15) suggesting that the $(BH_3F)^-$ ion is an intermediate in the borohydride reduction of perfluoroolefins.

Similar reductions with inorganic chloride (NaCl) failed to yield any reduction of the olefin. Either the $(BH_3Cl)^-$ ion was not formed, or, if it were formed, it does not act as a reducing agent. No preparation of any MBH_3Cl (M=metal) compounds have been reported; hence, no definite conclusions can be made concerning the stability of this system. Our work with sodium borohydride, however, leads us to believe that if this substituted borohydride ion is formed, it is probably of limited stability. However, additional work is required before any definite conclusions can be made.

Work is continuing in this area, and complete details concerning these reactions will be published in due course.

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