Journal of Fluorine Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Short Communication

The hydrogenation of fluorinated ethylenes with sodium borohydride in protic media

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(Received December 1st, 1970)

Complex metal hydrides have been shown to be excellent nucleophilic reagents for the introduction of hydrogen into polyfluorinated compounds[1]. In olefinic systems, two major pathways have been demonstrated, either displacement of vinylic halogen or allylic attack with displacement of halogen[2].

We wish to report a third, and novel, pathway for these reactions with sodium borohydride. When fluorinated ethylenes are treated with $NaBH_4$ in diglyme with added water, ethanol, or t-butyl alcohol, the major product is not due to displacement of vinylic halogen but to the addition of the elements of H_2 to the fluorinated olefin.

$$CF_2{=}CXY + NaBH_4 \xrightarrow[0°C]{H_2O} CF_2HCHXY\ (X = F, Cl, Br;\ Y = Cl, Br)$$

Significantly, this reduction of the fluoro-olefin occurred without hydrogenolysis of the carbon–halogen bond. Catalytic hydrogenation reactions of similar olefins leads to products with resultant hydrogenation of carbon–halogen bonds[1]. Consequently, this facile, novel, reaction affords a convenient unambiguous hydrogenation of these olefinic systems.

The results of the ethylenes investigated are summarized in Table 1.

Compounds in which allylic displacement can occur also give hydrogenation of the double bond, although in these cases a significant amount of the allylic displacement product is also formed, as shown below for $CF_3CH{=}CClCF_3$.

$$\begin{aligned} &CF_3CH{=}CClCF_3 + NaBH_4 \xrightarrow{H_2O} \\ &CF_3CH_2CHClCF_3\ (51\%) + CF_2{=}CClCH_2CF_3\ (41\%) \\ &\qquad + CFH{=}CClCH_2CF_3\ (\sim 2\%) \end{aligned}$$

When the vinylic halogen is iodine, only hydrogenolysis of the halogen occurs.

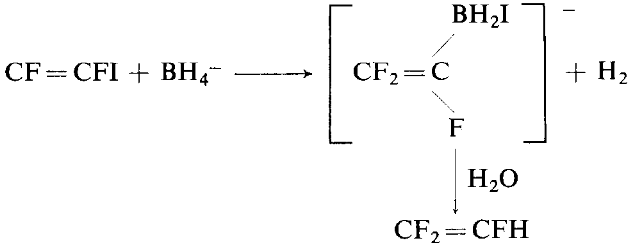
$$CF_2{=}CFI + NaBH_4 + H_2O \longrightarrow CF_2{=}CFH\ (73\%)$$

This reaction may proceed through an intermediate boron complex, similar to that observed by Burton and Mettille for the $LiAlH_4$ reduction of alicyclic fluoro-olefins which contained vinylic iodine[3].

TABLE 1

Reactants (mmoles)				Products (mmoles)			
X,Y	$CF_2=CXY$	BH_4^-	H_2O	$CF_2=CXY$	CF_2HCHXY	$CF_2=CFH$	CF_2HCH_2X
F, Cl	20	20	100	0.8	17.1	1.2	—
F, Br	20	20	100	—	18.7	0.6	—
Cl, Cl	20	20	100	0.9	17.8	—	1.3
F,I	10.5	10.5	50	2.9	—	7.7*	—

* 8.2 mmoles AgI found.



A typical preparative reaction procedure is described below for bromotrifluoroethylene.

In a four-necked flask were placed 40.2 g (0.25 mole) of bromotrifluoroethylene, 22.5 g (1.25 moles) of water and 100 ml of dry diglyme. To the stirred solution at 0–5° was added, drop-wise, 250 ml (0.25 mole) of 1.00 *M* sodium borohydride in diglyme. The hydride addition required 5.5 h. Hydrogen was evolved during the hydride addition and a white precipitate was formed. The reaction mixture was stirred an additional hour, and was hydrolyzed cautiously by the addition of 20 ml of 3 *M* nitric acid *via* a syringe. Hydrogen evolved vigorously during the acid hydrolysis. The volatile material was removed under reduced pressure (63° at 81 mm for 2 h). The volatile product separated into two layers. The lower organic layer was separated, dried over anhydrous calcium sulfate and distilled to yield 16.4 g of material boiling up to 42°. This distillate was dried over 4A molecular sieves and re-distilled to give 15.1 g (37.5%) of 1-bromo-1,2,2-trifluoroethane, b.p. 40–41° (744 mm), n_D^{20} 1.3555. Reported for 1-bromo-1,2,2-trifluoroethane[1]: b.p. 40–41° (735 mm), n_D^{20} 1.36175.

Further work on the synthetic scope of this novel hydrogenation reaction and the mechanism of this process is underway and will be reported in future publications.

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