

Preliminary Note

Catalytic hydrogen-transfer reduction of polyhalofluoroalkanes using sodium hypophosphite

Chang-Ming Hu* and Ming-Hu Tu

Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai 200032 (China)

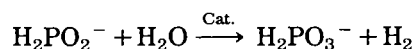
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Abstract

The catalytic hydrogen-transfer reduction of polyhalofluoroalkanes using sodium hypophosphite in the presence of a platinum or palladium catalyst is described. A selective reduction of carbon-bromine bonds could be performed under mild conditions.

In a previous paper, we have described a method for the selective reduction of carbon–chlorine bonds using ammonium formate in the presence of a catalytic amount of ammonium persulfate under mild conditions [1]. However, such a reducing agent is rather strong and consequently the selective reduction of carbon–bromine bonds in polyhalofluoroalkanes failed.

Sodium hypophosphite is known to be an effective reagent for the transfer hydrogenolysis of certain functional groups in the presence of an appropriate catalyst [2–5].



Boyer and coworkers have reported that benzylic chloride and phenyl chloride are cleanly reduced to the corresponding hydrocarbons and carbon tetrachloride to chloroform using sodium hypophosphite in the presence of a catalytic amount of palladium on carbon [2]. However, reduction of polyhalofluoroalkanes with such a reagent has not been tested. Herein we wish to report the reduction of polyhalofluoroalkanes using sodium hypophosphite in the presence of a catalytic amount of platinum or palladium on carbon.

In a typical experiment, 50 mmol of substrate was dissolved in *ca.* 30 ml glacial acetic acid, followed by sodium hypophosphite (*ca.* 55–150 mmol), sodium acetate (*ca.* 55–150 mmol) and a catalytic amount of 5% platinum on carbon (*ca.* 10 mg). The mixture was stirred at 30–65 °C. The extent

*Author to whom correspondence should be addressed.

of the reduction was monitored by gas chromatography or ^{19}F NMR spectroscopy. Additional sodium hypophosphite and sodium acetate were introduced when necessary. The reduction ended within 2–10 h. The solution was diluted with ice water (30 ml) and the separated organic layer was dried, fractionally distilled and carefully redistilled if necessary. The products were characterized by MS, ^{19}F and ^1H NMR spectroscopy. The spectra conformed to those documented in the literature [1, 6–9]. Table 1 summarizes the reduction of polyhalofluoroalkanes using sodium hypophosphite in the presence of a catalytic amount of platinum on carbon.

It is obvious that a selective hydrodebromination of several polyhalofluoroalkanes is possible. Thus CF_3CHBrX ($\text{X}=\text{Br}, \text{Cl}$) can be conveniently prepared from $\text{CF}_3\text{CBr}_2\text{X}$ ($\text{X}=\text{Br}, \text{Cl}$) in high yield. On adding another equivalent of sodium hypophosphite and sodium acetate to the reaction mixture, $\text{CF}_3\text{CH}_2\text{X}$ ($\text{X}=\text{Br}, \text{Cl}$) was formed from CF_3CHBrX ($\text{X}=\text{Br}, \text{Cl}$) in good yield; $-\text{CBrX}-$ ($\text{X}=\text{Br}, \text{F}$) can also be reduced to $-\text{CHX}-$, but the reduction of $-\text{CBr}_2-$ is easier. Although conversion of $-\text{CFBrX}$ ($\text{X}=\text{Br}, \text{Cl}$) to $-\text{CHF}_2$ is possible, conversion of $-\text{CF}_2\text{Br}$ in polyhalofluoroalkanes to $-\text{CHF}_2$ failed even at higher temperature with excess of sodium hypophosphite and sodium acetate. When attached to a carboxylic group, $-\text{CF}_2\text{Br}$ can be partly reduced in this manner.

Other polyhalofluoroalkanes such as CF_3CCl_3 and $\text{CF}_3(\text{CF}_2)_5\text{I}$ can also be reduced.

In the absence of sodium acetate, polyhalofluoroalkanes can also be reduced to hydrogen-bearing alternatives, but much longer reaction times

TABLE 1

Reduction of polyhalofluoroalkanes using sodium hypophosphite/Pt

Substrate	Molar ratio of $\text{NaH}_2\text{PO}_2/\text{CH}_3\text{COONa}$ relative to substrate	Temp. ($^\circ\text{C}$)/ time (h)	Product	Yield ^a (%)
CF_3CBr_3	1.1:1.1	30/2	CF_3CHBr_2	88
CF_3CBr_3	1.2:2.2	40/6	$\text{CF}_3\text{CH}_2\text{Br}$	90 ^b
$\text{CF}_3\text{CBr}_2\text{Cl}$	1.1:1.1	30/3	CF_3CHBrCl	86
$\text{CF}_3\text{CBr}_2\text{Cl}$	2.2:2.2	40/6	$\text{CF}_3\text{CH}_2\text{Cl}$	95 ^b
CF_3CFBr_2	1.1:1.1	40/6	CF_3CHBrF	86 ^b
$\text{CF}_2\text{BrCFBrCl}$	1.1:1.1	40/6	$\text{CF}_2\text{BrCHClF}$	76
$\text{CF}_3\text{CBr}_2\text{CF}_2\text{CF}_2\text{Br}$	1.1:1.1	40/3	$\text{CF}_3\text{CHBrCF}_2\text{CF}_2\text{Br}$	85
$\text{CF}_3\text{CFBrCF}_2\text{CF}_2\text{Br}$	1.3:1.3	60/8	$\text{CF}_3\text{CHF}_2\text{CF}_2\text{CF}_2\text{Br}$	71 ^c
$\text{CF}_3(\text{CF}_2)_3\text{Br}$	1.5:1.5	65/10	no reaction	—
BrCF_2COOH	1.5:1.5	60/10	HCF_2COOH	70 ^{b,d}
CF_3CCl_3	1.1:1.1	40/4	CF_3CHCl_2	92 ^b
$\text{CF}_3(\text{CF}_2)_5\text{I}$	1.1:1.1	40/6	$\text{CF}_3(\text{CF}_2)_5\text{H}$	81

^aIsolated yield unless otherwise mentioned.

^bEstimated by ^{19}F NMR spectroscopy.

^c80% conversion.

^d60% conversion.

were needed. In addition, palladium on carbon was also an effective catalyst, but a longer reaction time was required.

Compared with the reduction method using ammonium formate and ammonium persulfate [1], the present method possesses less reactivity but better selectivity for the reduction of carbon–bromine bonds in polyhalo-fluoroalkanes.

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