Preliminary Note

Reduction of polyhalofluoroalkanes with formate to hydrogen-bearing alternatives initiated by carbon dioxide anionic radical

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Abstract

Reduction of polyhalofluoroalkanes with formate in the presence of a catalytic amount of persulfate is described. Such a reagent possesses good selectivity in the reduction of carbon–chlorine bonds. A chain mechanism including carbon dioxide anionic radicals and polyhalofluoroalkyl radicals is proposed.

There is renewed interest worldwide in the synthesis of hydrochloro-fluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) as alternatives for chlorofluorocarbons (CFCs) since HCFCs are less depletive and HFCs not ozone-depleting in comparison to CFCs. The phasing out of CFCs in the near future provides an urgent need for fluorine scientists to seek new methods for making HCFCs and HFCs [1].

The reaction of formate with persulfate results in the generation of the carbon dioxide anionic radical. Although the chemical properties of this anionic radical have been investigated [2–4], only a few reports have appeared in the literature concerning the use of formate and persulfate in organic synthesis [5–7]. We wish to report in this paper the conversion of poly-halofluoroalkanes to hydrogen-bearing alternatives by reduction of car-bon–halogen bonds with formate.

In a typical experiment, a mixture of polyhalofluoroalkane (50.0 mmol), ammonium formate (60–80 mmol) and a catalytic amount of ammonium persulfate (5–15 mmol) in 50 ml DMF was stirred at 30–40 °C for 1–5 h. The extent of reduction was monitored by gas chromatography or ^{19}F NMR spectroscopy. Additional formate and persulfate were introduced when nec-essary. The product was characterized by MS, ^{1}H and ^{19}F NMR spectroscopy. The spectra conformed to those documented in the literature [8–11]. The results are summarized in Table 1.

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TABLE 1

Reduction of polyhalofluoroalkanes with formate initiated by $CO_2^{\cdot-}$

Substrate	Molar ratio of persulfate:formate relative to substrate	Product	Conversion[a] (%)	Yield[b] (%)
$ClCF_2CFCl_2$	0.25:1.5	$ClCF_2CHClF$	100	80
$ClCF_2CFCl_2$	0.30:2.6	CHF_2CHClF	100	60
CHF_2CHClF	0.50:2.0	no reaction		
CF_3CCl_3	0.25:1.5	CF_3CHCl_2	100	82
CF_3CCl_3	0.25:2.5	CF_3CH_2Cl	100	77
$CF_3CFClCF_2Cl$	0.30:1.6	CF_3CHFCF_2Cl	90	74[a]
$CF_3CFClCF_2Cl$	0.30:2.8	$CF_3CHFCHF_2$	100	58[a]
CF_2Cl_2	0.30:1.8	$CHClF_2$	100	
$CHClF_2$	0.50:2.0	no reaction		
CF_3CFBr_2	0.30:2.8	CF_3CH_2F	100	87
CF_3CBr_2Cl	0.30:2.8	CF_3CH_2Cl	100	65
$CF_2BrCFBrCl$	0.30:2.8	CHF_2CHClF	100	63
CF_2Br_2	0.30:2.8	CH_2F_2	100	90
CF_2BrCl	0.30:2.0	$CHClF_2$	100	
$CF_3(CF_2)_5I$	0.30:2.0	$CF_3(CF_2)_5H$	40	78
$Cl(CF_2)_6I$	0.30:2.0	$Cl(CF_2)_6H$	30	85
$Cl(CF_2)_6H$	0.20:1.4	$H(CF_2)_6H$	100	88

[a]Determined by ^{19}F NMR spectroscopy.
[b]Isolated yield.

Although zinc is a favorite reagent for the reductive cleavage of carbon–halogen bonds, elimination of vicinal halogens (chlorine, bromine or iodine) occurs with this reagent [12]. No such dehalogenated product was detected in our experiments.
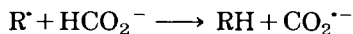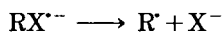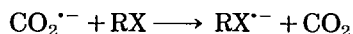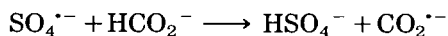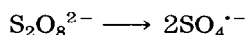
As shown in Table 1, such a hydrodechlorination process possesses good selectivity. For example, $ClCF_2CFCl_2$ was converted to $ClCF_2CHClF$ in DMF at 30 °C in 80% yield with 1.5 equiv. of formate and 0.25 equiv. of persulfate. When another equivalent of formate was added to the reaction mixture, CHF_2CHClF was produced in 60% overall yield. However, conversion of $-CHClF$ to $-CH_2F$ with formate and persulfate was unsuccessful. CH_3CFHCF_2Cl and $CF_3CHFCHF_2$ were obtained successively from $CF_3CFClCF_2Cl$ showing that the secondary chlorine atom was reduced preferentially to the primary one.

Although CF_3CH_2F and CH_2F_2 may be conveniently obtained from CF_3CFBr_2 and CF_2Br_2 respectively, selective hydrodebromination with such a reagent was unsuccessful. A mixture of CF_3CH_2Cl and $CF_3CHBrCl$ was formed from CF_3CBr_2Cl even in the presence of less than one equivalent of formate. Obviously the cleavage of carbon–bromine bonds is much easier than that of carbon–chlorine bonds.

With such a reagent, the reduction of carbon–iodine bonds occurred only in low conversion. A careful study showed that the iodide ion derived

from the reduction of the carbon–iodine bond was responsible for such a result. For example, the complete conversion of $ClCF_2CFCl_2$ to $ClCF_2CHClF$ failed in the presence of either iodine or iodide. It is obvious that I^- or I_2 adversely affects the redox system.

In such a redox system the carbon dioxide anionic radical is formed [2–4]. A chain mechanism for such reductions is proposed (Scheme 1). A catalytic amount of persulfate is necessary in the reduction while formate must be present in stoichiometric amounts. The resultant reaction mixture was quite acidic. Evolution of carbon dioxide was detected during the reaction.

$$S_2O_8{}^{2-} \longrightarrow 2SO_4{}^{\cdot-}$$

$$SO_4{}^{\cdot-} + HCO_2{}^- \longrightarrow HSO_4{}^- + CO_2{}^{\cdot-}$$

$$CO_2{}^{\cdot-} + RX \longrightarrow RX^{\cdot-} + CO_2$$

$$RX^{\cdot-} \longrightarrow R^{\cdot} + X^-$$

$$R^{\cdot} + HCO_2{}^- \longrightarrow RH + CO_2{}^{\cdot-}$$

Scheme 1.

References

1 P. S. Zurer, *Chem. Eng. News*, 67 (30) (1989) 7.
2 J. R. Harbour and M. L. Hair, *Can. J. Chem.*, 57 (1979) 1150.
3 H. D. Connor and R. D. Marson, *J. Biol. Chem.*, 261 (1986) 4542.
4 E. G. Janzen, *Free Rad. Res. Commun.*, 4 (1988) 359.
5 C. M. Hu and F. L. Qing, *Tetrahedron Lett.*, 31 (1990) 1307.
6 C. M. Hu, F. L. Qing and H. G. Zhang, *J. Fluorine Chem.*, 49 (1990) 275.
7 C. M. Hu, Y. L. Qiu and F. L. Qing, *J. Fluorine Chem.*, 51 (1991) 295.
8 F. G. Weigert, *J. Fluorine Chem.*, 46 (1990) 375.
9 J. W. Emsley, J. Feeney and L. H. Sutcliffe, *Prog. Nucl. Magn. Reson. Spectrosc.*, 7 (1971) 133, 166.
10 C. H. Dungan and J. R. Van Wazer, *Compilation of Reported F-19 NMR Chemical Shifts*, Wiley, New York, 1970.
11 V. Wray, *Annu. Rep. NMR Spectrosc.*, 14 (1983) 9.
12 M. Hudlicky, *Chemistry of Organofluorine Compounds*, 2nd Edn., Ellis Horwood, Chichester, England, 1976.