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Studies on polyhaloalkanes. V. A new reduction system: zinc/hydrazine hydrate

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Abstract

Using zinc/hydrazine hydrate as a new reduction system, polyfluoroalkyl halides such as $Cl(CF_2)_nH$ (**1a–c**, $n=4, 6, 8$), $Cl(CF_2)_nI$ (**1e–g**, $n=4, 6, 8$) and $R(CF_2)_nCl$ ($n=4, 6$, **1h, i**) have been converted to the corresponding reduction products $H(CF_2)_nH$ (**2a–g**, $n=4, 6, 8$) and $R(CF_2)_nH$ ($n=4, 6$, **2h, i**) in high yield. Reduction of the CF_2Cl group was faster than that of the CHI in the reaction of **1m**.

Keywords: Polyhaloalkanes; Reduction; Zinc/hydrazine hydrate system; NMR spectroscopy; Mass spectrometry

1. Introduction

Zinc and hydrazine are useful reductants in organic synthesis, for example, zinc(Hg) in the Clemmensen reaction [1], zinc/hydrochloric acid in the hydrogenation of the carbon–halogen bond and hydrazine in the Wolff–Kishner reaction converting carbonyl groups into methylene [2]. Hydrazine is also used in catalytic hydrogenation as a hydrogen source [3]. Here we wish to report the application of zinc/hydrazine hydrate in the reduction of polyfluoroalkyl chlorides (R_FCl) and iodides.

2. Results and discussion

The carbon–chlorine bond may be cleaved to give the hydrogenation product with lithium aluminium hydride [4], dialkylaminolithium [5] and nickel in situ [6]. We have found that treatment of polyfluoroalkyl chloride with an excess of zinc and hydrazine hydrate in DMF at 70–80 °C for 2 h gives the corresponding hydrogenation product in high yield. Polyfluoroalkyl iodides were also reduced (Scheme 1). The reaction results are listed in Table 1.

$$\underset{(1)}{Cl(CF_2)_nH} \xrightarrow[\text{DMF, 80 °C}]{Zn/N_2H_4\cdot H_2O} \underset{(2)}{H(CF_2)_nH}$$

(**a**): $n=4$; (**b**): $n=6$; (**c**): $n=8$

$$\underset{(1)}{Cl(CF_2)_nI} \xrightarrow[\text{DMF, 80 °C}]{Zn/N_2H_4\cdot H_2O} \underset{(2)}{H(CF_2)_nH}$$

(**e**): $n=4$; (**f**): $n=6$; (**g**): $n=8$

$$\underset{(1)}{Cl(CF_2)_nR} \xrightarrow[\text{DMF, 80 °C}]{Zn/N_2H_4\cdot H_2O} \underset{(2)}{R(CF_2)_nH}$$

(**h**): $n=4$, $R=C_6H_{13}$; (**i**): $n=6$, $R=C_8H_{17}$

Scheme 1. The reduction of polyfluoroalkyl halides.

The presence of zinc and hydrazine hydrate appears to be essential for the reaction. For example, in the absence of hydrazine hydrate, $Cl(CF_2)_6H$ was the only product from the reaction of **1f** with zinc On the other hand, without zinc the product was again $Cl(CF_2)_6H$ but in lower conversion. Hence, the reaction may involve a new species formed in the

Table 1
Reduction of polyfluoroaklyl halides by zinc/hydrazine hydrate

R_FX	Temp. (°C)	Time (h)	Product	Yield (%)
1a	70	2	**2a**	94
1b	70	2	**2b**	95
1c	70	2	**2c**	90
1e	70	2	**2e**	90
1f	80	2	**2f**	92
1g	80	2	**2g**	90
1h	80	2	**2h**	92
1i	80	2	**2i**	92

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Table 2
Reduction of **1f** by zinc and hydrazine hydrate

Entry No.	Reductant	Product	Conversion (%) [a]
1	$Zn/N_2H_4 \cdot H_2O$	**2b**	100
2	Zinc	**1b**	100
3	$N_2H_4 \cdot H_2O$	**1b**	30

[a] The extent of conversion was determined by ^{19}F NMR spectroscopy.

reaction of zinc and hydrazine hydrate. Further results are listed in Table 2.

We have also found that the reduction of RCF_2Cl is faster than that of RCHI. Thus reaction of **1m** gave two products **2m** and **2m′** indicating that during the complete conversion of $-CF_2Cl$ into $-CF_2H$, the –CHI bond was only partially reduced. On extending the reaction time (3 h) reduction of the –CHI bond was complete and **2m** was the sole product.

$$\underset{(\mathbf{1m})}{CH_3(CH_2)_3CHICH_2(CF_2)_4Cl} \xrightarrow[\text{DMF, 80 °C, 2 h}]{Zn/N_2H_4 \cdot H_2O}$$

$$\underset{(\mathbf{2m'})\quad 38.1^{a}}{CH_3(CH_2)_3CHICH_2CF_2(CF_2)_3H} + \underset{(\mathbf{2m})\quad 36.5^{a}}{CH_3(CH_2)_5CF_2(CF_2)_3H}$$

$\mathbf{2m'}/\mathbf{2m} = 1{:}1^{a}$

[a] Ratio was estimated by ^{19}F NMR spectroscopy. Chemical shifts in ppm.

The reduction of polyfluoroalkyl halides by zinc/hydrazine hydrate provides a very simple and efficient alternative method for the preparation of hydropolyfluoroalkanes which can be transformed into a series of useful compounds [7].

3. Experimental details

All boiling points were uncorrected. ^{19}F NMR spectra were performed using an EM-360L spectrometer with TFA as external standard. Mass spectral data were recorded on a Finnigan 4021 spectrometer. The compounds $Cl(CF_2)_nH$ ($n = 4, 6, 8$) were obtained from the reaction of $Cl(CF_2)_nI$ with aqueous sodium hydroxide solution. The compounds **1h** and **1i** were prepared from reduction with zinc in alcoholic solution of the addition products of the corresponding polyfluoroalkyl iodides with olefins initiated by sodium dithionite in aqueous acetonitrile solution.

3.1. Typical procedure

A mixture of **1e** (0.9 g, 2.5 mmol), zinc (0.3 g, 5 mmol), hydrazine hydrate (1 ml, 20 mmol) and DMF (10 ml) was stirred at 70 °C for 2 h. The precipitate was filtered off. The filtrate was poured into water and the aqueous layer extracted with ether (3×20 ml). The combined organic layer was washed with saturated aqueous sodium chloride solution and dried over magnesium sulfate. After removal of ether, **2e** (0.45 g, 90%) was obtained by distillation [6]; b.p. 40 °C. ^{19}F NMR δ: 60.5 (d, 4F, $J_{H-F} = 54$ Hz, HCF_2); 52.6 (4F, HCF_2CF_2) ppm.

Other products showed the following characteristics: Compound **2b**: b.p. 84–85 °C. ^{19}F NMR δ: 60.5 (d, 4F, $J_{H-F} = 54$ Hz); 51.3 (4F); 45.4 (4F) ppm. Compound **2c**: b.p. 137 °C. ^{19}F NMR δ: 61.0 (d, 4F, $J_{H-F} = 53$ Hz); 52.7 (4F); 46.5 (4F); 45.0 (4F) ppm. Compound **2h**: b.p. 89 °C/31 mmHg. ^{19}F NMR δ: 60.6 (d, 2F, $J_{H-F} = 54$ Hz); 52.5 (2F); 48.0 (2F); 36.5 (2F) ppm. MS m/z: 286 (M^+); 285 ($M^+ - 1$); 284 ($M^+ - 2$); 57. Compound **2i**: b.p. 56–58 °C/20 mmHg. ^{19}F NMR δ: 60.0 (d, 2F, $J_{H-F} = 54$ Hz); 52.2 (2F); 46.0 (2F); 44.6 (8F); 36.0 (2F) ppm.

All known products were characterized by comparing their boiling points, ^{19}F NMR spectra and MS data with those of corresponding authentic compounds [6].

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