



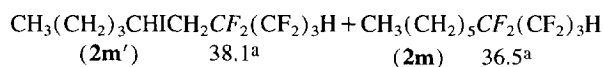
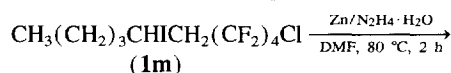
Table 2  
Reduction of **1f** by zinc and hydrazine hydrate

Entry No.	Reductant	Product	Conversion (%) <sup>a</sup>
1	Zn/N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O	<b>2b</b>	100
2	Zinc	<b>1b</b>	100
3	N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O	<b>1b</b>	30

<sup>a</sup> The extent of conversion was determined by <sup>19</sup>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<sub>2</sub>Cl is faster than that of RCHI. Thus reaction of **1m** gave two products **2m** and **2m'** indicating that during the complete conversion of –CF<sub>2</sub>Cl into –CF<sub>2</sub>H, 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.



**2m'**/**2m** = 1:1<sup>a</sup>

<sup>a</sup> Ratio was estimated by <sup>19</sup>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. <sup>19</sup>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<sub>2</sub>)<sub>n</sub>H (*n* = 4, 6, 8) were obtained from the reaction of Cl(CF<sub>2</sub>)<sub>n</sub>I 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. <sup>19</sup>F NMR δ: 60.5 (d, 4F, *J*<sub>H-F</sub> = 54 Hz, HCF<sub>2</sub>); 52.6 (4F, HCF<sub>2</sub>CF<sub>2</sub>) ppm.

Other products showed the following characteristics: Compound **2b**: b.p. 84–85 °C. <sup>19</sup>F NMR δ: 60.5 (d, 4F, *J*<sub>H-F</sub> = 54 Hz); 51.3 (4F); 45.4 (4F) ppm. Compound **2c**: b.p. 137 °C. <sup>19</sup>F NMR δ: 61.0 (d, 4F, *J*<sub>H-F</sub> = 53 Hz); 52.7 (4F); 46.5 (4F); 45.0 (4F) ppm. Compound **2h**: b.p. 89 °C/31 mmHg. <sup>19</sup>F NMR δ: 60.6 (d, 2F, *J*<sub>H-F</sub> = 54 Hz); 52.5 (2F); 48.0 (2F); 36.5 (2F) ppm. MS *m/z*: 286 (*M*<sup>+</sup>); 285 (*M*<sup>+</sup> – 1); 284 (*M*<sup>+</sup> – 2); 57. Compound **2i**: b.p. 56–58 °C/20 mmHg. <sup>19</sup>F NMR δ: 60.0 (d, 2F, *J*<sub>H-F</sub> = 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, <sup>19</sup>F NMR spectra and MS data with those of corresponding authentic compounds [6].

### References

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