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A general method for nearly reduction-free dehalogenations in a fluorinated biphasic system[☆]

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Abstract

We have studied the dehalogenations of halofluorinated alkanes and fluorinated ethers, both linear and cyclic, as well as halofluorinated alkanes containing an aromatic moiety, to their corresponding unsaturated species in a biphase fluorinated/hydrogenated solvent system.

The reactions in the biphase system lead to higher selectivities and better yields than those obtained performing the reaction in the traditional hydrogenated monophasic system. By this method, the concentrations of hydrogenated by-products of general formula R–CF_2H or RCFHR' are as low as 100 ppm.

This novel biphasic system provides therefore a useful synthetic route to materials and chemicals for electronics, optical polymers, plasma etching, etc. which require a very high purity of all compounds involved.

Keywords: Fluorous biphase system; Dehalogenations; Fluorinated olefins; Reduction

1. Introduction

Dehalogenation reactions, and specifically 1,2 eliminations, are a simple and efficient means for obtaining, generally, a multiple bond and particularly a carbon–carbon double bond, both hydrogenated and fluorinated, in high yields [1].

Fluorinated olefins are important molecules in free radical polymerization [2] and are also the starting material for a wide variety of reactions [3]. Perfluoroalkyl vinyl ethers represent a particularly important and versatile class of reactive olefins which is used to make fluoroelastomers, thermoprocessable fluoroplastics as well as new polymeric materials for electronic and optical applications [4,5]. (Per)fluoro cyclic olefins and perfluoro 1,3-butadiene are used *per se* as products for the critical etching of silicon wafers in the semiconductor industry [6].

Typically, 1,2 eliminations involving the diatomic elimination of chlorine, bromine or the elimination of bromine and fluorine, proceed smoothly and with high yields and selectivities in the presence of Zn powder, in protic or aprotic solvents such as dimethylformammide (DMF), isopropyl alcohol (IPA), acetonitrile, etc., at temperatures ranging from 70 to 100 °C [7–10]. With these solvents, and particulartly with alcohols, there's the risk of a carbon–halogen bond reduction.

The demanding applications of the materials made from the above-cited fluorinated monomers, require extremely high purity. It is therefore necessary that the final step of the monomer synthesis be free of side reactions generating impurities, such as hydrogenated by-products, arising from the elimination reaction. As a matter of fact, dehalogenations performed with Zn are potentially reducing systems and so can generate hydrogen containing side products, whose structure contains –CF_2H and/or –CFH– groups: the hydrogenated solvent can often act as the proton source. The concentrations of these hydrogenated by-products range between 600 and 10,000 ppm [6] and are too high for the applications outlined above. From a standard chemical point of view, these concentrations are very low (0.06–1 mol%) and therefore, make conventional separation techniques (distillation, chromatography) highly inefficient. More sophisticated techniques (preparatory HPLC, electrophoretic methods) are more efficient in terms of monomer recovery, but are not applicable and costly on an industrial scale.

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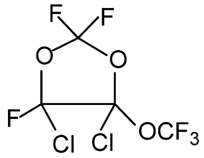
The elegant concept of fluorous biphase system (FBS) first published by Horváth and Rábai in 1994 [11] describes a means of performing classical organic reactions in a two-phase medium consisting of a hydrogenated and a fluorinated solvent. FBS has served since as the basis of a wide variety of applications in catalysis [12], synthetic chemistry [13], and "green chemistry" [14,15]. This gave us the idea of applying Horváth and Rábai's FBS concept to dehalogenation reactions in order to reduce the amount of hydrogenated solvent and hence of the undesired reduced products.

In this paper, we perform dehalogenations (especially dechlorinations) in a system formed of Zn, a fluorinated solvent and a stoichiometric amount of an aprotic hydrogenated solvent (mFBS) and show that concentrations of hydrogenated products in the range of 150–250 ppm and, in some cases, as low as 100 ppm can be obtained thereby improving the selectivity of the same Zn mediated reactions performed solely with a protic or an aprotic hydrogenated solvent.

2. Results and discussion

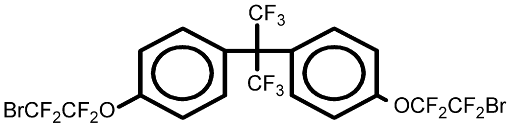
We have studied the dehalogenation of four classes of (per)fluorinated-dihalo-compounds:

- A linear alkane: 1,2,3,4-tetrachloro-1,1,2,3,4,4-hexafluorobutane, $ClCF_2CFClCFClCF_2Cl$ (**1**).
- A linear oxa-alkane: perfluoro-1,2-dichloro-3,5-dioxaheptane, $ClCF_2CFClOCF_2OCF_2CF_3$ (**2**).
- A cyclic oxa-alkane: 4,5-dichloro-2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxolane (**3**).



(3)

- An aromatic structure: 2,2-bis(4-(1-bromo-tetrafluoroethoxy)phenyl)-1,1,1,3,3,3-hexafluoropropane (**7**).



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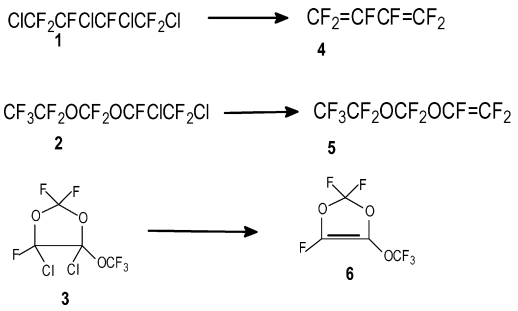
The dehalogenation reactions are reported in Scheme 1.

2.1. Mechanistic aspects

Spectroscopic analysis of the reaction mixture arising from the reaction of compounds **1** and **2** showed that only two general types of hydrogenated impurities were observed: the first one being a mono-chlorinated derivative having a primary (terminal) hydrogen, R–CFCl–CF_2**H** and the second being a mono-chlorinated molecule with a secondary hydrogen, R–CF**H**CF_2Cl. Non-chlorinated hydrogenated impurities having the general structure R–CF**H**CF_3 or R–CF_2CF_2**H** were, at least in our hands, not observed either because they do not form or because their concentration was below the detection limits of our instruments. Analysis of the dechlorination of compound **3** showed two distinct hydrogenated compounds identified and quantified by ^{1}H NMR as the mono-chlorinated fluoro-alkane derivative bearing the H atom on C4 and the remaining Cl atom on C5 (H–C4 species), and its isomer, the mono-chlorinated derivative bearing the H atom on C5 and the remaining Cl atom on C4 (H–C5). The H–C4/H–C5 molar ratio was 9/1.



Scheme 1.

Being quite different from compounds **1**–**3**, the debromofluorination of compound **7** will be dealt with later on separately.

The dehalogenation, could follow four different reaction mechanisms: E2, E1, E1cB and E1cB via "primary carbon metallation" (excluding, of course, compound **3**) [16–19].

Postulating that the observed hydrogenated impurities arise mainly from the proton transfer of an acidic H^+, coming from the hydrogenated solvent, onto the charged intermediate, the E2 mechanism can then be excluded since it follows a concerted pathway.

A plausible way to obtain a hydrogenated by-product via the E2 mechanism would be the addition of HF (very often present in fluorinated systems) *after* having formed the olefin since fluorinated olefins, in the presence of Lewis acids, can react with HF [20].

The E1 elimination mechanism can also be ruled out due to the formation of a carbocationic intermediate which is not stable enough in the reaction conditions.

The E1cB mechanism with secondary carbon metallation (preferred) and primary carbon metallation (minor) seems to be the favorite route for 1,2 elimination reactions. Fig. 1 shows that both E1cB reaction pathways could lead to the observed hydrogenated by-products.

2.2. Modified fluorous biphase system (mFBS)

For dehalogenations to occur with good efficiency, the Zn must be solvated by either a protic solvent (such as isopropyl alcohol) or a polar aprotic solvent (such as DMF). However, even if in trace amounts, the transfer of an "acidic" H^+ from the solvent to the organometallic carbanion, formed in the transition state (see Fig. 1), does occur [6], giving rise to the observed hydrogenated by-products HCF_2CFCl–R and $ClCF_2CFH$–R. By "trace amounts" we intend anywhere between 0.5 and 1 mol% (5000–10000 ppm).

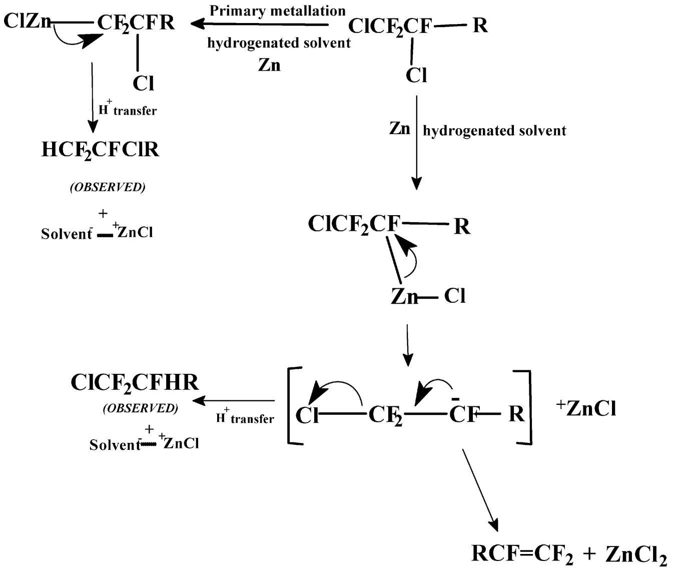


Fig. 1. General E1cB reaction mechanism for both the dechlorination reaction and the formation of hydrogenated impurities.

We therefore wanted to see if it was possible to keep the acidic proton transfer from the reaction's hydrogenated solvent to a minimum by using a fluorinated biphase system – *m*FBS [21,22]. In this system, the Zn is solvated by the *minimum* quantity of a protic or polar aprotic solvent (the "co-solvent"); the reaction medium is composed of a fluorinated solvent immiscible with the hydrogenated "co-solvent", but fully miscible with the fluorinated substrate. Vigorous stirring brings the heterogeneous system into contact and 1,2 elimination occurs at the solvent interface yielding the desired olefin as it is shown in the cartoon of Fig. 2. Since the two solvents employed are immiscible, and since the concentration of the hydrogenated "co-solvent" is low, the contact between the hydrogenated solvent and the substrate is kept to a minimum. This should avoid an excessive proton transfer by the hydrogenated "co-solvent" keeping the concentration of undesired hydrogenated by-products as low as possible.

There are three main differences between our *m*FBS and the classical FBS:

1. The hydrogenated phase and the fluorinated phase remain separate at the reaction temperature.
2. The concentration of the hydrogenated solvent ≅ concentra-concentration of Zn.

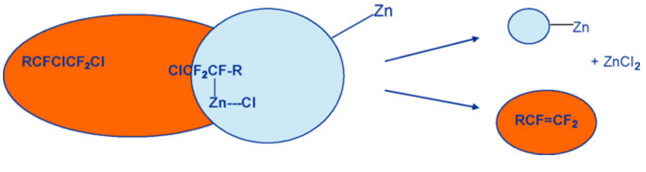


Fig. 2. Pictorial representation of *m*FBS: the fluorinated solvent is depicted in dark grey (red in web version) and the hydrogenated co-solvent is depicted is in light grey (blue in web version). The line connecting the Zn to the hydrogenated co-solvent represents solvation. The R–Zn–Cl intermediate is postulated to exist at the fluorinated-hydrogenated solvent interface.

3. The reaction occurs presumably at the interface of the hydrogenated and the fluorinated solvents thus minimizing H^+ contact with the substrate.

For simplicity, we will present in detail the results pertaining to the dechlorination of **3**. The optimized reaction parameters will then be applied to the other substrates and discussed.

The fluorinated solvents examined were perfluorohexane, C_6F_{14} (b.p. = 56 °C); Galden® D-80 (an aliphatic perfluoro *iso*-octane with b.p. = 80 °C); Galden® D-100 (an 80/20 mixture of perfluoro-2-butylfuran/perfluoro-2-propylpyran with b.p. = 100 °C); H-Galden® ZT-85 (a perfluoropolyether with formula $HCF_2O(CF_2O)_p(CF_2CF_2O)_qCF_2H$, mean MW = 500 g/mol with b.p. = 85 °C); Galden® HT-55, (a perfluoropolyether with formula $CF_3[(OCF(CF_3)CF_2)_n(OCF_2)_m]OCF_3$, with a mean MW = 350 g/mol and a b.p. = 55 °C); Galden® HT-100 (a perfluoropolyether with a mean MW = 660 and b.p. = 100 °C); Galden® HT-200 (a perfluoropolyether with MW = 1200 g/mol and b.p. = 200 °C).[1]

The hydrogenated solvents examined were dimethylformammide (DMF); dimethylacetammide (DMAC); isopropyl alcohol (IPA) and diglyme.

The reaction parameters studied were:

1. The type of fluorinated/hydrogenated binary solvent system and its ratio.
2. The concentration of the hydrogenated by-products as a function of:
   - Moles of zinc.
   - Molar quantity of the hydrogenated solvent remaining in the desired product.
   - Molar quantity of the fluorinated solvent remaining in the desired product.
3. Conversion as a function of:
   - Reaction temperature.
   - Moles of zinc.

2.2.1. *m*FBS solvent system

The choice of the solvents to have *m*FBS was studied as a function of **3** conversion and unsaturated product purity; fixed reaction conditions were: F-solvent/**3** = 2/1 (w/w), H-solvent/**3** = 2/1 (mol/mol), Zn/**3** = 1.5 (mol/mol). The criteria used for defining the optimal biphase system were:

1. High conversion.
2. Low residual concentration of both fluorinated and hydrogenated solvents in the olefin as it distilles out of the reaction medium during the dehalogenation.

Table 1a shows that the best fluorinated solvent is Galden® HT-200. Although the conversion was higher with Galden® HT-110, Galden® HT-200 was chosen since in the final dioxole **6** a markedly lower concentration of solvent was observed. The

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[1] Galden® PFPEs are a Solvay Solexis tradename.

Table 1a
Conversion of **3** and residual solvents in product **6** as a function of the fluorinated solvent

Solvent	T_{R} (°C)	Conversion 3 (%)	Yield 6 (%)	Residual F-solvent (mmol)	Residual DMAC (ppm)
D-80	80	49	31	7.03	3700
ZT-85	85	40	29	1.05	3600
HT-200	100	92	73	**0.18**	**2200**
D-100	100	83	71	0.88	3500
HT-110	100	98	90	2.01	3700

Hydrogenated solvent: DMAC.

Table 1b
Conversion of **3** and impurities in product **6** as a function of the hydrogenated solvent (fluorinated solvent: Galden® HT-200)

Solvent	TR(°C)	Conversion 3 (%)	Hydro-product (ppm)	Residual HT-200 (mmol)	Residual solvent (ppm)
DMAC	100	90	**152**	0.18	**2200**
IPA	80	25	6000	0.1	25900
DMF	100	62	900	0.09	1000
Diglyme	100	20	4100	0.11	3200

lower concentration of Galden® HT-200 vs. Galden® HT-110 in the dioxole is easily explained by the boiling point and vapour pressure difference (900 mmHg for Galden® HT 110 vs. 300 mmHg for Galden® HT 200, at 100 °C). The higher vapor phase concentration in the experiment with Galden® HT-110 also allowed more DMAC vapours to co-distill with **6**. DMAC, as well as the other polar aprotic hydrogenated solvents, can be removed by an aqueous work up. Then, a second distillation of the product can remove the fluorinated solvent. Of course, this work up becomes increasingly more tedious and longer as the concentrations of the impurities increase. Table 1b shows that, among the aprotic solvents studied, DMAC was by far the solvent that transferred fewer protons during the course of the 1,2 elimination. Therefore, the mFBS solvent system of choice is Galden® HT-200/DMAC.

We studied next the influence of the fluorinated solvent Galden® HT-200/**3** weight ratio (Table 1c) and the DMAC/**3** molar ratio at a fixed Galden® HT-200/**3** weight ratio (Table 1d). We observed that a fluorinated solvent alone is not able to solvate Zn sufficiently well to make it come into contact with the chlorinated reagent in order for 1,2 elimination to occur: no substrate conversion is observed. A 2-fold molar excess of DMAC/**3** was the minimal ratio necessary to adequately solvate the Zn giving a conversion >90% to the dioxole, **6**. Increasing further the DMAC/**3** molar ratio resulted in an increase of hydrogenated by-products. It can be noted that

Table 1c
Conversion of **3** and hydrogenated by-products as a function of Galden® HT-200 and DMAC

HT-200 (w/w)	DMAC (mol/mol)	Conversion 3 (%)	Hydro-products (ppm)
0	20	91	767
2	**2**	92	**152**
18	2	89	161
18	0	0	–

Fixed parameters: Zn/**3** = 1.5/1 mol/mol; reaction temperature = 100 °C.

Table 1d
Conversion of **3** and Hydrogenated by-products as a function of DMAC/**3** ratio

DMAC/3 (mol/mol)	Hydro-products (ppm)	Conversion 3 (%)
0	–	0
0.01	100	6
1	140	46
1.05	140	60
2	**152**	**92**
10	193	95
20	311	99

Fixed parameters: Zn/**3** = 1.5/1 mol/mol; Galden® HT-200/**3**: 2/1 w/w; reaction temperature: 100 °C.

Table 2
Conversion and hydrogenated products as a function of reaction temperature and Zn/**3** molar ratio

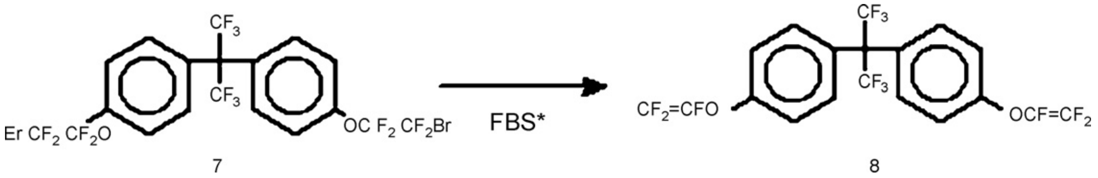
T (°C)	Zn/3 (mol/mol)	Conversion (%)	Hydro-products (ppm)
55	2	25	–
95	1	44	125
95	1.5	85	162
95	2	87	1300
110	2	98	–

Fixed parameters: fluorinated solvent: Galden® HT-110; hydrogenated solvent: DMAC; F-solvent/**3**: 18/1 w/w; DMAC/**3**: 5/1 mol/mol.

Table 3
Application of *m*FBS to different classes of substrates and compared to the dehalogenation in a hydrogenated solvent (DMF or IPA)

Reaction	Hydro-products Hydrogenated system (ppm)	Hydro-products mFBS (ppm)	Product yield (%)
1 → **4**	650	100	85
2 → **5**	900	230	89
3 → **6**	800	152	73

Fixed parameters: Zn/**Substrate**: 1.5/1 mol/mol; Galden® HT-200/**Substrate**: 2/1 w/w; reaction temperature: 75 °C for **1** → **4**; 90 °C for **2** → **5** and 100 °C for **3** → **6**.



Scheme 2. Debromofluorination of **7** to give the corresponding vinyl-ether **8** using *m*FBS (Galden® D-100/DMAC).

to achieve an almost complete conversion of **3** the DMAC/**3** molar ratio must be increased 10-fold (20/1), but this results in doubling the hydrogenated by-products which are not as easily removed by a conventional work up as the fluorinated and hydrogenated solvents and the unconverted **3** are. A higher purity of **3** is therefore obtained with a non-quantitative conversion and recycling the unconverted **3** after work up.

2.2.2. Conversion and concentration of hydrogenated by-products vs. temperature and Zn concentration

Having fixed the fluorinated and hydrogenated solvent (Galden® HT-110 and DMAC, respectively) the ratio between the F-solvent and **3** (18/1 w/w) and the H-solvent and **3** (5/1 mol/mol), we studied the effect of temperature (at constant Zn/**3** ratio, mol/mol) and the effect of Zn/**3** ratio, at constant temperature, on the conversion of **3** and on the amount of hydrogenated by-products. The results are summarized in Table 2. The best conditions found are: temperature = 95 °C and Zn/**3** ratio = 1.5. These data eliminate C_6F_{14} as a potential solvent due to its low boiling point. At a Zn/**3** ratio >1.5 we observed a drastic increase of the concentration of hydrogenated by-products.

A possible explanation for this observation is that as the Zn/**3** ratio increases, there is a greater contact between the hydrogenated solvent and the organic intermediate due to the coordination of the Zn to the hydrogenated solvent (solvation) as shown in Fig. 2; this increases the probability of proton transfer from the hydrogenated solvent to the substrate resulting in the observed increase of hydrogenated by-products.

To have the experimental proof that the trace amounts of reduced products come from the hydrogenated solvent the dehalogenation reaction was performed in standard, homogeneous non *m*FBS conditions, in dry, deuterated DMF. The absence of signals in the ^{1}H-suggest that the hydrogenated solvent (or co-solvent in the case of *m*FBS) is, actually, the major H^+ source, even if traces of water can be often present in the system. Studies are currently underway to try to isolate and fully characterize the postulated deuterated intermediates.

*2.2.3. Application of mFBS to substrates **1** and **2***

In order to verify the soundness of the *m*FBS 1,2 dechlorination with other substrates, the best conditions discussed in Sections 2.2.1 and 2.2.2 were applied to a linear alkane (substrate **1**) and to a linear ether (substrate **2**). The results, compared with those of the dehalogenation of **3** are shown in Table 3.

The *m*FBS reaction is shown to lower the hydrogenated by-products [21] respectively by >6-fold for the dechlorination of **1** to the etching gas Sifren 46® **4**, and by >4-fold for the dechlorination of **2** to the monomer for low T_g polymer applications perfluoro-3,5-dioxahept-1,2-ene **5** [23] with respect to the same reaction performed in standard dehalogenation conditions: Zn in a aprotic (or protic) hydrogenated solvent.

These results compare quite well with the >5-fold decrease in hydrogenated by-products for the dechlorination of **3** to the monomer for optical applications 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole **6** [5].

*2.3. mFBS for the debromofluorination of 2,2-bis(4-(1-bromo-pentafluoroethoxy)phenyl)-1,1,1,3,3,3-hexafluoropropane **7**: a special case*

Compound **7** is easily synthesized from readily available starting materials [7] and it is converted to the corresponding vinyl-ether **8** in high yield using the mFBS dehalogenation [22] (Scheme 2). Due to the high b.p. of **8**, the fluorinated solvent Galden®HT-200 was substituted with Galden® D-100

in order to isolate it easily by distillation at reduced pressure. This is because **8** readily undergoes 2 + 2 thermal cycloaddition already at 150 °C [24,25].

As it can be seen from Table 4, *m*FBS enabled both higher yield and selectivity (less dimer of **7** formation) with respect to the literature data [7]. The formation of the dimer of **7** involves an organometallic species $R–CF_2^{\delta-}$ $(ZnBr)^{\delta+}$. The $R–CF_2^{\delta-}$ then attacks another $R–CF_2Br$ yielding $ZnBr_2$ and the dimer of **7**. These reactions are typically run in polar, hydrogenated solvents such as CH_3CN or 1,4-dioxane etc. which stabilize and coordinate well to the organometallic intermediate. In *m*FBS such hydrogenated solvents are not present and this therefore can help to explain the decrease in dimer formation.

Summarizing, the best results obtained for 1,2 eliminations employing *m*FBS in terms of low concentration of hydrogenated by-products, high conversion and low residual solvents in the resulting olefin are:

- Fluorinated solvent: Galden®HT-200 or Galden®D-100 depending on the final products' boiling point; Galden®/reagent = 2/1 (w/w)
- Hydrogenated co-solvent: DMAC; DMAC/reagent = 2/1 (mol/mol)
- Zn/reagent = 1.5/1 (mol/mol)
- Reaction temperature = 100 °C.

Table 4
*m*FBS vs. hydrogenated solvent system (CH_3CN) for the debromofluorination of **7**

8 yield hydrogenated solvent (mol%)	79
8 yield *m*FBS (mol%)	**92**
Hydro-products hydrogenated solvent (ppm)	30,000
Hydro-products mFBS (ppm)	**8000**
Dimer hydrogenated solvent (mol%)	15
Dimer *m*FBS (mol%)	**7**

Fixed parameters: Zn/**7**: 1.5/1 mol/mol; Galden® D-100/**7**: 4/1 w/w; reaction temperature: 100°C.

3. Conclusions

A novel fluorinated by-phase system (*m*FBS) has been developed for 1,2 elimination reactions of halogenated substrates which involves the employment of both a fluorinated solvent and a stoichiometric amount of an aprotic hydrogenated co-solvent immiscible with the fluorinated solvent. With respect to the standard dehalogenation elimination reactions performed in Zn and either protic or aprotic solvents, the new *m*FBS allows to lower by as much as 7-fold the concentration of hydrogenated by-products, which are inevitably formed in competing side reactions during dehalogenations, presumably by limiting the contact of the hydrogenated co-solvent with the halogenated substrate. Deuterium labeling studies are underway to determine if the hydrogenated co-solvent is the H^+ source for the hydrogenated by-products. With respect to the standard 1,2 elimination reactions performed in hydrogenated (protic or aprotic) solvents, yields and reaction times with the newly developed *m*FBS remained the same or even improved.

4. Experimental

^{19}F and ^1H NMR spectra were recorded on a Varian mercury 200 MHz spectrometer using, respectively $CFCl_3$ and TMS as internal standard, chemical shifts are in ppm. Mass spectra were recorded on a Finnigan MAT SSQ700 chromatographer employing a methyl silicone CPSIL (Varian–Chrompack) column (50 m, int. diameter = 0.32 mm). Gas chromatographic analyses were performed on a Carlo Erba GC 8000 Top gas chromatographer using a silicone wide bore column 0.54 μm thick, and 25 m long.

GC–MS was used to both determine the empirical formula (MS) and to quantify (GC and quantitative MS) the hydrogenated by-products; NMR spectrometry (with added $CHCl_3$ and C_6F_6 of known concentration as internal standard) was used either to assign the correct structure to the by-products or to cross-check the concentration determined by GC–MS. By this means, the purity of the olefin obtained was assessed as a function of the calculated concentration (in ppm) of the hydrogenated products identified.

The starting substrates (**1**, **2**, **3** and **7**) were all synthesized according to literature procedures [5,7,23,24]. All of the hydrogenated solvents were thoroughly dried by distillation over P_2O_5 and stored over activated 4A molecular sieves and kept in a dry-box. The fluorinated solvents were distilled and stored over activated 4A molecular sieves.

The Zn employed throughout this work was purchased from Carlo Erba Reagenti S.p.A. and was furnished as an extra fine powder. Prior to its use, it was washed several times with commercial acetone, filtered and dried in a vacuum oven at 130 °C and 5 mm Hg for 4 h. It was then stored under an inert atmosphere.

4.1. Dehalogenation reactions employing mFBS—general example with 3

6.14 g (95.1 mmol) of finely powdered Zn, 10.9 g of DMAC (125,4 mmol) and 35 g of Galden®HT-200 were placed in a three-necked round bottom glass flask equipped with a condenser maintained at 25 °C with a circulating water bath, a distillation head, a round bottom collecting flask immersed in a dry-ice bath at −78 °C, a magnetic stir bar, a dripping funnel and a thermometer. The mixture is heated to 100 °C with vigorous stirring for 20 min. Then, 17.6 g (62.7 mmol) of **3** (b.p. = 78 °C) were added to the heterogeneous mixture in 20 min. Immediate refluxing and product collection was observed and the internal reaction temperature dropped to 55–60 °C. Once the 1,2 elimination reaction was over, the internal temperature rose back to 100 °C. At this point, the temperature of the circulating water bath was lowered to 0 °C and a slight (100 mm Hg) vacuum was applied in order to collect all of the resulting olefin 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (**6** b.p. 34 °C) and the hydrogenated by-products. Quantitative ^{19}F, ^1H NMR and GC–MS of the contents of the trap and the reaction flask enabled the identification and the quantification of all the reaction products.

4.2. Analyses of substrates, olefins and hydrogenated by-products

- $Cl{}^aCF_2{}^bCFClCFClCF_2Cl$ (**1**): ^{19}F NMR δ −62.3 (q, 4F, $–{}^aCF_2–$), −121.5 (d, 2F, $–{}^bCF–$).
- ${}^aCF_2{=}{}^bCFCF{=}CF_2$ (**4**) [26]: ^{19}F NMR δ −93.4 (q, 2F, ${}^aCF_2$), −107.1 (q, 2F, ${}^aCF_2$), −181.3 (q, 2F, ${}^bCF$).
- ${}^aCF_2{=}{}^bCF{}^cCFH{}^dCF_2Cl$: ^{19}F NMR δ −96.4 (q, 1F, ${}^aCF_2$), −105.2 (q, 1F, ${}^aCF_2$), −181.3 (q, 1F, ${}^bCF$), −182.4 (d, 1F ${}^cCFH$), −68 (q, 2F, ${}^dCF_2$) ^1H NMR δ 6.3 (m, 1H, ${}^cCFH$).
- $Cl{}^aCF_2{}^bCFClO{}^cCF_2O{}^dCF_2{}^eCF_3$ (**2**) [23]: ^{19}F NMR δ −47.2 (q, 2F, $O{}^cCF_2O$), −66.3 (q, 2F, ${}^aCF_2$), −73.6 (s, 1F, ${}^bCF$), −83.1 (s, 3F, ${}^eCF_3$), −852 (s, 2F, ${}^dCF_2$).
- ${}^aCF_2{=}{}^bCFO{}^cCF_2O{}^dCF_2{}^eCF_3$ (**5**): ^{19}F NMR δ −52.5 (s, 2F ${}^cCF_2$), −83.1 (s, 3F, ${}^eCF_3$), −86.3 (s, 2F, ${}^dCF_2$), −111.3 (q, 1F, ${}^aCF_2$), −119.5 (q, 1F, ${}^aCF_2$), −133.0 (q, 1F, ${}^bCF$).
- $Cl{}^aCF_2{}^bCFH\ O{}^cCF_2O{}^dCF_2{}^eCF_3$ ^{19}F NMR δ −66.3 (q, 2F, ${}^aCF_2$), −139.7 (d, 1H, ${}^bCFH$), −47.3 (q, 2F, $O{}^cCF_2O$), −83.1 (s, 3F, ${}^eCF_3$), −85.4 (s, 2F, ${}^dCF_2$) ^1H NMR δ 6,7 (m, 1H, ${}^bCFH$).
- $H{}^aCF_2{}^bCFClO{}^cCF_2O{}^dCF_2{}^eCF_3$: ^{19}F NMR δ −136.3 (d, 2F, $J_{HF} = 47$ Hz, $H{}^aCF_2$), −72.6 (s, 1F, ${}^bCF$), −47.2 (q, 2F, $O{}^cCF_2O$), −83.2 (s, 3F, ${}^eCF_3$), −85.4 (s, 2F, ${}^dCF_2$) ^1H NMR: δ 6,6 (m, 1H, $H{}^aCF_2$).
- $–O–{}^aCF_2–O{}^bCFCl{}^cCCl(O{}^dCF_3)$-4,5-dichloro-2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxolane (**3**) [27]: ^{19}F NMR δ −50.3 (s, 2F, ${}^aCF_2$), −56.1 (s, 1F anti, ${}^bCFCl$), −62.6 (s, 1F syn, ${}^bCFCl$), −57.5 (s, 3F ${}^dCF_3$).

- –O–$^{a}CF_2$–O$^{b}CF{=}^{c}C(O^{d}CF_3)$–2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (**6**): ^{19}F NMR δ −44.2 (s, 2F, $^{a}CF_2$), −58.4 (s, 3F, O$^{d}CF_3$), −145.5 (s, 1F, ^{b}CF).FT-IR: 1851 cm^{-1} (C=C st), 1395 cm^{-1}, 1304 cm^{-1}, 1275 cm^{-1}, 1239 cm^{-1}, 1189 cm^{-1}, 997 cm^{-1}, 945 cm^{-1}, 686 cm^{-1}, 457 cm^{-1}.MS (m/z): 31 (25%), 47 (37%), 69 (100%), 116 (14%), 210 (61%), 211 (0,7%).
- –O–$^{a}CF_2$–O$^{b}CFH^{c}CCl(O^{d}CF_3)$–5-chloro-2,2,4-trifluoro-4-hydro-5-trifluoromethoxy-1,3-dioxolane. ^{19}F NMR δ −50.3 (s, 2F, $^{a}CF_2$), −137.6 (d, 1H, –O^{b}CFH), −56.1 (s, 3F $^{d}CF_3$)^{1}H NMR δ 6.3 (m, 1H, ^{b}CFH)MS (m/z): 29 (75%), 69 (75%), 96 (60%), 132 (47%), 145 (100%), 161 (41%), 227 (0,95%).
- –O–$^{a}CF_2$–O$^{b}CFCl^{c}CH(O^{d}CF_3)$-4-chloro-2,2,4-trifluoro-5-hydro-5-trifluoromethoxy-1,3-dioxolane: ^{19}F NMR δ −50.3 (s, 2F, $^{a}CF_2$), −62.2 (s, 1F, ^{b}CFCl), −57.5 (s, 3F $^{d}CF_3$);^{1}H NMR δ 5.1 (m, 1H, ^{c}CH)
- 2,2-bis(4-(1-Bromo-tetrafluoroethoxy)phenyl)-1,1,13,3,3-hexafluoropropane:(**7**), $Br^{b}CF_2{}^{c}CF_2O–C_6H_4–C(^{a}CF_3)_2C_6H_4$-O$^{c}CF_2{}^{d}CF_2Br$ [7]: ^{19}F NMR δ −62.5 (s, 6F, $^{a}CF_3$), −68.3 (s, 4F, $^{b}CF_2$), −85.2 (s, 4F, $^{c}CF_2$).
- 2,2-bis(4-(Trifluoroethenoxy)phenyl)-1,1,13,3,3-hexafluoropropane:(**8**), $^{b}CF_2{=}^{c}CFO–C_6H_4–C(^{a}CF_3)_2C_6H_4–O^{c}CF{=}^{b}CF_2$ [7]: ^{19}F NMR δ −62.5 (s, 6F, $^{a}CF_3$), −119.3 (q, 2F, $^{b}CF_2$), −126.4 (q, 2F, $^{b}CF_2$), −134.7 (q, 2F, ^{c}CFO).
- 2,2-bis(4-(2-Hydrotetrafluoroethoxy)phenyl)-1,1,1,3,3,3-hexafluoropropane: $H^{b}CF_2{}^{c}CF_2O–C_6H_4–C(^{a}CF_3)_2C_6H_4–O^{c}CF_2{}^{d}CF_2H$ ^{19}F NMR δ −62.5 (s, 6F, $^{a}CF_3$), −88.3 (s, 4F, $–OCF_2CF_2H$), −137.4 (d, 4F, $J_{HF} = 47$ Hz, $^{d}CF_2H$). ^{1}H NMR δ 7.6 (m, 8H, pH), 6.6 (t, 4H, $–CF_2H$).
- Dimer of (**7**), $[Br^{b}CF_2{}^{c}CF_2O–C_6H_4–C(^{a}CF_3)_2C_6H_4–O^{d}CF_2{}^{e}CF_2]_2$: ^{19}F NMR δ −62.5 (s, 12F, $^{a}CF_3$), −68.3 (s, 4F, $^{b}CF_2$), −85.2 (s, 4F, $^{c}CF_2$), −88.4 (s, 4F, $^{d}CF_2$), −120.7 (s, 4 F, $^{e}CF_2$).

References

[1] D.S. Kemp, F. Vellaccio, Organic Chemistry, Worth Publishers, Inc., New York, NY, 1980, 165–195.

[2] G. Houghhem (Ed.), Fluoropolymers, Academic Plenum Publishers, N.Y., 1999.

[3] R.D. Chambers, Fluorine in Organic Chemistry, Blackwell Publishing Ltd, 2004 167–218.

[4] W. Navarrini, V. Tortelli, A. Russo, S. Corti, J. Fluorine Chem. 95 (1999) 27–39.

[5] W. Navarrini, V. Tortelli, P. Colaianna, J. Abusleme, US Patent 5,646,223, CA 122 (1997) 187563.

[6] M. Riva, Chem. Today 21 (2003) 310–311.

[7] D.W. Smith, D.A. Babb, Macromolecules 29 (1996) 852–860.

[8] J. Miki, H. Yoshimi, H. Aoyama European Patent 1,247,791; CA 135 (2000) 108913.

[9] T. Araki, T. Shimizu, T. Yamato, M. Kumegawa, Y. Yamamoto US Patent 5,670,593; CA 124 (1997) 177249.

[10] K. Takai, T. Kakiuchi, Y. Kataoka, K. Utimoto, J. Org. Chem. 59 (1994) 2668–2670.

[11] I.T. Horváth, J. Rábai, Science 266 (1994) 72–75.

[12] E.G. Hope, A.M. Stuart, J. Fluorine Chem. 100 (1999) 75–83, and references therein.

[13] M. Cavezzini, F. Montanari, J. Fluorine Chem. 94 (1999) 183–193, and references therein.

[14] S.J. Tavener, J.H. Clark, J. Fluorine Chem. 123 (2003) 31–36.

[15] D.P. Curran, Z. Lee, Green Chem. 3 (2001) G3.

[16] W.H. Saunders Jr., A.F. Cockeril, Mechanisms of Elimination Reactions, Wiley, New York, 1973.

[17] J.R. Gandler, Patai Supplement A: ‘‘The Chemistry of Double-bonded Functional Groups Part 1’’ vol. 2, Wiley, New York, 1989, 733–797.

[18] R.A. More O’Ferrall, Patai ‘‘The Chemistry of the Carbon–Halogen Bond Part 2’’, Wiley, New York, 1973, 609–675.

[19] H.F. Koch, Acc. Chem. Res. 17 (1984) 137–144.

[20] G.A. Olah, E.B. Baker, J.C. Evans, W.S. Tolgyesi, J.S. McIntyre, I.J. Bastien, J. Am. Chem. Soc. 86 (1964) 1360–1373.

[21] I. Wlassics, V. Tortelli, European Patent 1,719,750; US Patent Appl. 0,252,966 (2006); CA 145 (2006) 471990.

[22] I. Wlassics, V. Tortelli, European Patent 1,719,751; US Patent Appl. 0,252,968 (2006); CA 145 (2006) 471244.

[23] W. Navarrini, S. Corti, J. Fluorine Chem. 125 (2004) 189.

[24] I. Wlassics, J. Fluorine Chem. 125 (2004) 1519–1528.

[25] D.W. Smith, D.A. Babb, H.V. Shah, A. Hoeglund, R. Traiphol, D. Perahia, H.W. Bone, C. Langhoff, M. Radler, J. Fluorine Chem. 104 (2001) 109.

[26] S.L. Mannat, M.T. Bowers, J. Am. Chem. Soc. 91 (1969) 4381.

[27] W. Navarrini, L. Bragante, S. Fontana, V. Tortelli, A. Zedda, J. Fluorine Chem. 71 (1995) 111.