

Dehalogenative aromatization of perchlorofluoroalicyclic compounds $C_6Cl_6F_6$, $C_{10}Cl_8F_8$ and $C_5Cl_4F_5N$ in the vapour phase or in solution

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Dedicated to Professor Hermann-Josef Frohn on the occasion of his 60th birthday.

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Abstract

Dehalogenation of perhalogenated cyclohexanes $C_6Cl_6F_6$, 1-azacyclohexenes $C_5Cl_4F_5N$ and bicyclo[4.4.0]dec-1(6)-enes $C_{10}Cl_8F_8$ in the vapour phase over iron filings at 350–500 °C and in solution with Zn and additives (Cu, $NiCl_2 \cdot 6H_2O$ + bpy) at 80 °C (heterogeneous reaction) or with $P(NEt_2)_3$ at 20 °C (homogeneous reaction) was studied. In all cases, perfluoroarenes, chloroperfluoroarenes and dichloroperfluoroarenes (benzenes, naphthalenes and pyridines) were obtained in good overall yield.

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1. Introduction

Dehalogenation of perfluorinated alicyclic compounds were studied intensively as a route to perfluoroarenes. Initially these reactions were performed by passing of vapour of perfluorinated material over heated (200–500 °C) iron placed into a horizontal metal reactor [1]. During the last decade defluorinations of perfluorocycloalkanes in solution with the very strong reducing reagents Na–benzophenone [2–4], Al– $HgCl_2$ – Cp_2TiF_2 [3,5], Mg– $HgCl_2$ – Cp_2ZrCl_2 [5] and related reducing agents [6,7] were reported.

The easier removal of chlorine than fluorine from perchlorofluorocyclohexanes over heated iron was demonstrated previously [8,9]. However, preparations of perchlorofluorocyclohexanes by fluorine addition to perchloroarenes using elemental fluorine [10–12], chlorine trifluoride [9] or cobalt trifluoride [8] are difficult to control, and usually these resulted in a mixture of cyclohexanes $C_6Cl_nF_{12-n}$ with an average number of chlorine atoms, $n = 4–7$. To our knowledge, dehalogenation of perchlorofluorocyclohexanes $C_6Cl_nF_{12-n}$ with definite number of chlorine atoms, $n = 5, 6$ and 7 was described only in reference [9]. In other cases, a mixture of cyclic chloro-

fluorocarbons $C_6Cl_nF_{12-n}$ with various $n = 5–7$ was used for dehalogenation [8,10–12]. The related syntheses of polyfluorinated naphthalenes and pyridines from the corresponding perchlorofluorocycloalkanes and perchlorofluorocycloalkenes were not reported except of the defluorination of perfluorinated materials [1].

Recently we described a simple and convenient method of fluorine addition to perchloroarenes using vanadium pentafluoride [13]. Reaction of hexachlorobenzene with VF_5 (bp 48 °C) occurred at 20–50 °C in chlorofluorocarbons ($CFCl_3$, $C_2Cl_3F_3$) or without solvent and gave hexachlorohexafluorocyclohexanes $C_6Cl_6F_6$ (1) in a quantitative yield. Similarly, tetrachloropentafluoro-1-azacyclohexenes $C_5Cl_4F_5N$ (2) and octachlorooctafluorobicyclo[4.4.0]dec-1(6)-enes (3) were prepared from pentachloropyridine and octachloronaphthalene, respectively, using standard laboratory equipment. Herein dehalogenation of these compounds to polyfluoroarenes in either the vapour phase or in solution is reported.

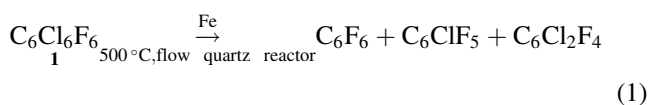
2. Results and discussion

2.1. Dehalogenation in the vapour phase

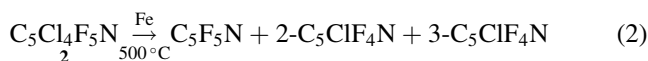
The previously reported dehalogenation of $C_6Cl_6F_6$ at 300 °C, by passing the vapour over iron gauze in a horizontal

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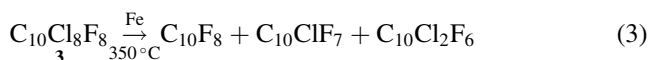
metal flow reactor gave C_6F_6 , C_6ClF_5 , $C_6Cl_2F_4$ and $C_6Cl_3F_3$ in 2, 39, 33 and 2% yield, respectively [9]. Brooke et al. studied the dehalogenation of $C_6Cl_6F_6$ (average composition) over iron gauze and over fine iron filings at 330–340 °C and obtained a better overall yield of C_6F_6 and C_6ClF_5 in the latter case [10]. Following this, we dehalogenated compounds **1–3** at higher temperature by passage of their vapours in a stream of nitrogen over fine iron filings packed in a vertical quartz tube. Dehalogenation of $C_6Cl_6F_6$ at 500 °C led to a quantitative conversion in hexafluorobenzene, chloropentafluorobenzene and dichlorotetrafluorobenzenes in 30–32, 40–42 and 4–6% yields, respectively (Eq. (1)).



Dehalogenation of $C_5Cl_4F_5N$ under the same conditions gave pentafluoropyridine in 40–43% yield, apart from 2-chlorotetrafluoropyridine (11–12%) and 3-chlorotetrafluoropyridine (43–45%) (Eq. (2)). The formation of 4- C_5ClF_4N and highly chlorinated polyfluoropyridines was not detected (^{19}F NMR).



Octafluoronaphthalene, 1-chloroheptafluoronaphthalene, 2-chloroheptafluoronaphthalene and dichlorohexafluoronaphthalenes (isomer mixture) were obtained by passing $C_{10}Cl_8F_8$ vapour over heated iron filings (Eq. (3)). In contrast to the dehalogenation of **1** and **2**, the yield of perfluorinated naphthalene did not exceed 9% with ca. 55% overall yield of polyfluoronaphthalenes based on quantitative conversion of **3**.



The yields of polyfluoroarenes were not optimized. However, the results obtained together with the recent availability of the starting materials **1–3** demonstrate the possibility of an alternative preparation of polyfluoroarenes from perchloroarenes.

2.2. Dehalogenation in solution

For a complete picture of the dehalogenation of **1**, **2** and **3** under the different conditions, their reactions in the liquid phase with zinc reagent or tris(diethylamino)phosphine were studied.

2.2.1. Dehalogenation with zinc dust

In many cases, the quality of zinc affects significantly on the result of dehalogenation [1]. We compared reaction of **1**, **2** and **3** with commercial zinc dust, zinc dust pre-treated with $SOCl_2$, zinc dust doped with freshly precipitated copper (Zn/Cu), and zinc dust activated with complex ($NiCl_2 \cdot 6H_2O$ + bpy).

Reaction of $C_6Cl_6F_6$ with zinc dust in refluxed dioxan gave hexafluorobenzene, chloropentafluorobenzene and dichlorotetrafluorobenzenes in 14, 32 and 10% yields, respectively. However, dehalogenation proceeded slowly and total conversion of **1** was achieved within 10 h (Eq. (4)).



Next, commercial zinc dust was treated with $SOCl_2$ in sulfolane at 20–25 °C for 30 min before **1** was added and the reaction mixture was stirred for 5 h at 80 °. This modification gave a better yields of both C_6F_6 and C_6ClF_5 (27 and 39%, respectively), while $C_6Cl_2F_4$ remained the minor component (Eq. (4)) (Table 1, entry 1). The activation of zinc by preliminary reaction with $CuSO_4$ (0.1 equivalent) (formation of zinc–copper couple, Zn/Cu) and subsequent reaction with **1** under the above conditions led to the slightly increased yield of hexafluorobenzene and chloropentafluorobenzene (Table 1, entry 2). Dehalogenation of **1** with Zn/Cu couple in diglyme gave a similar result (Table 1, entry 3).

Recently we described the reductive hydrodefluorination and hydrodechlorination of polyfluoroarenes and polychloroarenes with zinc catalyzed by complexes of $NiCl_2 \cdot 6H_2O$ with bpy or $NiCl_2 \cdot 6H_2O$ with phen in aqueous DMF [14–18]. It could be expected that the reaction of this system with hexachlorohexafluorocyclohexanes $C_6Cl_6F_6$ (**1**) will result in the related hydrodehalogenation. However, treatment of **1** with zinc and complex ($NiCl_2 \cdot 6H_2O$ + bpy) (5 mol%) in anhydrous dimethylacetamide (DMA) at 80 °C gave C_6F_6 , C_6ClF_5 and $C_6Cl_2F_4$ (Eq. (5)) (Table 1, entry 4). The same result was obtained when complex ($NiCl_2 \cdot 6H_2O$ + phen) was employed (Table 1, entry 5). When reaction of **1** with Zn and complex ($NiCl_2 \cdot 6H_2O$ + bpy) was performed in DMF, partial reduction of C_6ClF_5 in pentafluorobenzene took place (Table 1, entry 6). The formation of highly chlorinated benzenes $C_6Cl_nF_{6-n}$ ($n \geq 3$) as well as polychlorofluorocycloalkenes was not detected (^{19}F NMR, GLC).

Reaction of tetrachloropentafluoro-1-azacyclohexenes (**2**) with commercial zinc dust in refluxed THF was complete within 3 h and gave a mixture of pentafluoropyridine, 2-, 3- and 4-chlorotetrafluoropyridines, 2,4- and 2,5-dichlorotri-

Table 1
Dehalogenation of $C_6Cl_6F_6$ (**1**) with zinc (80 °C, 5 h)

Entry	Solvent	Yield (%) based on 1 ^a
1	Sulfolane ^b	C_6F_6 (27), C_6ClF_5 (39), $C_6Cl_2F_4$ (7)
2	Sulfolane ^c	C_6F_6 (35), C_6ClF_5 (42), $C_6Cl_2F_4$ (7)
3	Diglyme ^c	C_6F_6 (30), C_6ClF_5 (40), $C_6Cl_2F_4$ (5)
4	DMA ^d	C_6F_6 (34), C_6ClF_5 (44), $C_6Cl_2F_4$ (7)
5	DMA ^e	C_6F_6 (31), C_6ClF_5 (41), $C_6Cl_2F_4$ (10)
6	DMF ^d	C_6F_6 (30), C_6ClF_5 (34), $C_6Cl_2F_4$ (5), C_6F_5H (12)

^a Determined by GLC.

^b Zinc was activated with $SOCl_2$.

^c Zinc was activated with $CuSO_4$.

^d Zinc was activated with complex ($NiCl_2 \cdot 6H_2O$ + bpy), 4 h.

^e Zinc was activated with complex ($NiCl_2 \cdot 6H_2O$ + phen), 4 h.

Table 2
Dehalogenation of C₅Cl₄F₅N (**2**) with zinc (80 °C, 5 h)

Entry	Solvent	Yield (%) based on 2 ^a
1	Sulfolane ^b	C ₅ F ₅ N (30), 2-C ₅ ClF ₄ N (8), 3-C ₅ ClF ₄ N (38)
2	Sulfolane ^c	C ₅ F ₅ N (38), 2-C ₅ ClF ₄ N (8), 3-C ₅ ClF ₄ N (34)
3	Diglyme ^c	C ₅ F ₅ N (29), 2-C ₅ ClF ₄ N (9), 3-C ₅ ClF ₄ N (33)
4	DMA ^d	C ₅ F ₅ N (34), 2-C ₅ ClF ₄ N (10), 3-C ₅ ClF ₄ N (36)

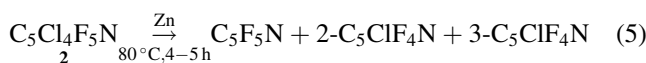
^a Determined by GLC.

^b Zinc was activated with SOCl₂.

^c Zinc was activated with CuSO₄.

^d Zinc was activated with complex (NiCl₂·6H₂O + bpy), 4 h.

fluoropyridines in overall yield 80% although the yield of C₅F₅N was only 18%. The use of zinc activated with SOCl₂ in sulfolane **2** effected a higher yield of pentafluoropyridine (30%), while dichlorotrifluoropyridines were not found among products (Eq. (5)) (Table 2, entry 1).



Dehalogenation of **2** with zinc dust doped with freshly precipitated copper in sulfolane (Table 2, entry 2), in diglyme (Table 2, entry 3) as well as with zinc and complex (NiCl₂·6H₂O + bpy) in DMA (Table 3, entry 4) gave the same polyfluoropyridines in similar yields (Eq. (5)).

Similarly to **1** and **2**, the results of dehalogenation of octachlorooctafluorobicyclo[4.4.0]dec-1(6)-enes (**3**) were practically independent of the method used to activate zinc. Thus, reaction of **3** with zinc activated with SOCl₂ in sulfolane (Table 3, entry 1), with freshly precipitated copper in sulfolane (Table 3, entry 2) or in diglyme (Table 3, entry 3) and with complex (NiCl₂·6H₂O + bpy) in DMA (Table 3, entry 4) led to the formation of octafluoronaphthalene (6–9%), 1-chloroheptafluoronaphthalene (9–10%), 2-chloroheptafluoronaphthalene (18–19%) and dichlorohexafluoronaphthalenes (isomer mixture) (33–37%) (Eq. (6)).

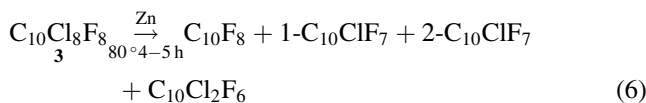


Table 3
Dehalogenation of C₁₀Cl₈F₈ (**3**) with zinc (80 °C, 8 h)

Entry	Solvent	Yield (%) based on 3 ^a
1	Sulfolane ^b	C ₁₀ F ₈ (9), 1-C ₁₀ ClF ₇ (10), 2-C ₁₀ ClF ₇ (19), C ₁₀ Cl ₂ F ₆ (33)
2	Sulfolane ^c	C ₁₀ F ₈ (6), 1-C ₁₀ ClF ₇ (9), 2-C ₁₀ ClF ₇ (19), C ₁₀ Cl ₂ F ₆ (37)
3	Diglyme ^c	C ₁₀ F ₈ (7), 1-C ₁₀ ClF ₇ (10), 2-C ₁₀ ClF ₇ (19), C ₁₀ Cl ₂ F ₆ (34)
4	DMA ^d	C ₁₀ F ₈ (7), 1-C ₁₀ ClF ₇ (9), 2-C ₁₀ ClF ₇ (18), C ₁₀ Cl ₂ F ₆ (35)

^a Determined by GLC.

^b Zinc was activated with SOCl₂.

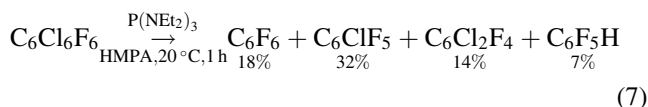
^c Zinc was activated with CuSO₄.

^d Zinc was activated with complex (NiCl₂·6H₂O + bpy), 6 h.

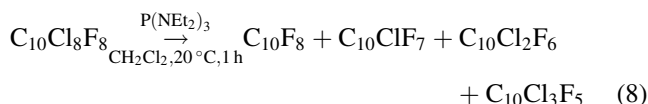
2.2.2. Dehalogenation with P(NEt₂)₃

The dehalogenations with zinc proceed under heterogeneous conditions, and the observed domination of chloro containing polyfluoroarenes could arise from the formation of zinc difluoride, which is insoluble in organic solvents. Trying to increase yield of perfluorinated arenes, we studied the reaction of **1** and **3** with tris(diethylamino)phosphine. Recently the latter was used successfully for dehalogenation of some aliphatic perhalofluoroalkanes R_FCFXCYZR'_F (X, Y, Z = Cl, Br, I) [19], CF₂BrCF₂Br [20] and 1,1,2-tribromopentafluorocyclobutane [19] to the corresponding polyfluoroalkenes. Dehalofluorination did not occur in any case.

However, the reaction of C₆Cl₆F₆ with P(NEt₂)₃ (5–6 equivalents) in polar aprotic solvents (HMPA or diglyme) gave hexafluorobenzene in lower yield than by dehalogenation with zinc; chloropentafluorobenzene and dichlorotetrafluorobenzene were major products besides pentafluorobenzene (Eq. (7)). The reaction pathway was not analysed but the ¹⁹F NMR spectrum of the final reaction mixture (in diglyme) contained a signal assigned to P(NEt₂)₃FCl (δ = –79.3 ppm, d, ¹J_{FP} = 955 Hz) beside resonances due to polyfluorobenzenes.



Dehalogenation of C₁₀Cl₈F₈ with P(NEt₂)₃ in dichloromethane proceeded in a similar way to form octafluoronaphthalene (16%), chloroheptafluoronaphthalenes (42%), dichlorohexafluoronaphthalenes (24%) and trichloropentafluoronaphthalenes (15%) (Eq. (8)).



The picture obtained of dehalogenation of hexachlorohexafluorocyclohexanes (**1**), tetrachloropentafluoro-1-azacyclohexenes C₅Cl₄F₅N (**2**) and octachlorooctafluorobicyclo[4.4.0]dec-1(6)-enes (**3**) either in the vapour phase over iron filings or in solutions with zinc or with tris(diethylamino)phosphine showed the facile conversion of these perhalogenated materials in perfluorinated and chlorofluorinated arenes. It should be noted that **1**, **2** and **3** are mixtures of *cis* and *trans* isomers with –CFCl–CFCl– fragments and, probably, of isomers with –CF₂–CCl₂– fragments [13]. Despite this circumstance, dehalogenation of **1–3** under significantly different conditions is characterised by a remarkable similarity. Thus, dehalogenation of **1** in the vapour phase over heated iron and in the liquid phase with zinc and additives gave closely related yields of hexafluorobenzene, chloropentafluorobenzene and dichlorotetrafluorobenzenes. A similar situation is observed for dehalogenation of **2** and **3** with iron and zinc. Dehalogenation with P(NEt₂)₃ gave a somewhat different molar ratio of

perhalogenated arenes derived from **1** and **3**. Unlike the metal used, $\text{P}(\text{NEt}_2)_3$ can react partially with intermediate cycloalkenes at the C–F and C–Cl bonds of olefinic moiety [21] to decrease yields of desirable polyfluoroarenes.

3. Experimental

^{19}F NMR spectra were measured on a BRUKER WP 200 SY spectrometer at 188.28 MHz in CDCl_3 . The chemical shifts are referenced to CCl_3F with C_6F_6 as secondary reference (-162.9 ppm). GC–MS analyses were performed on Hewlett Packard G1800A and Hewlett Packard GS6890 instruments. GLC analyses were performed on LKhM 72 chromatograph (25% SKTFT-50 on chromosorb W, gas-carrier He, 60 mL per min).

Organic solvents (DMF, DMA, THF, HMPA, sulfolane, diglyme, dioxan and dichloromethane) were purified by standard procedures. Zinc dust (purum), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (purum), 1,10-phenanthroline (phen) (purum for analysis) and 2,2'-bipyridyl (bpy) (Aldrich) were used as supplied. Tris(diethylamino)phosphine was prepared from PCl_3 and HNEt_2 in hexane [22] and distilled in vacuum. Thionyl chloride was freshly distilled before use. Preparation of **1**, **2** and **3** was described in reference [13]. If not specified otherwise, the compositions of isomer mixtures of $\text{C}_6\text{Cl}_2\text{F}_4$, $\text{C}_5\text{ClF}_4\text{N}$, $\text{C}_5\text{Cl}_2\text{F}_3\text{N}$, $\text{C}_{10}\text{ClF}_7$, $\text{C}_{10}\text{Cl}_2\text{F}_6$ and $\text{C}_{10}\text{Cl}_3\text{F}_5$, were not determined.

3.1. Dehalogenation of **1**, **2** and **3** in the vapour phase

A quartz tube (30 mm diameter, 750 mm length) equipped with an internal quartz pocket for a thermocouple, pressure equilized dropping funnel with nitrogen inlet on top and with two sequentially connected traps cooled with ice and liquid nitrogen, respectively, was charged with iron filings (0.2–1 mm size) and placed into a vertical cylindric electric furnace. The reactor was flushed with nitrogen (100–150 mL per min) at 400°C for 2 h and then at the working temperature for 20–30 min. Dehalogenation was performed by an addition of **1** (**2** or **3**) under a slight pressure of nitrogen (2–5 mL per min) (time of contact ~ 25 s). At the end, the reactor was flushed with nitrogen (10–15 mL per min) for 10–15 min. Products from both traps were combined, weighed and analysed by GLC.

3.1.1. Dehalogenation of hexachlorohexafluorocyclohexanes (**1**)

Vapour-phase dehalogenation of **1** (2.0 g, 5 mmol) at 500°C gave C_6F_6 , C_6ClF_5 and $\text{C}_6\text{Cl}_2\text{F}_4$ in 30–32, 40–42 and 4–6% yield, respectively (GLC).

3.1.2. Dehalogenation of tetrachloropentafluoro-1-azacyclohexenes $\text{C}_5\text{Cl}_4\text{F}_5\text{N}$ (**2**)

Vapour-phase dehalogenation of **2** (1.6 g, 5 mmol) at 500°C gave $\text{C}_5\text{F}_5\text{N}$, 2- $\text{C}_5\text{ClF}_4\text{N}$ and 3- $\text{C}_5\text{ClF}_4\text{N}$ in 40–

43, 11–12 and 43–45% yield, respectively (GLC). Identification of 2- $\text{C}_5\text{ClF}_4\text{N}$ and 3- $\text{C}_5\text{ClF}_4\text{N}$ and determination of their molar ratio was performed by the ^{19}F NMR spectroscopy [23].

3.1.3. Dehalogenation of octachlorooctafluorobicyclo[4.4.0]dec-1(6)-enes (**3**)

Vapour-phase dehalogenation of **3** (2.3 g, 4 mmol) at 350°C gave C_{10}F_8 , $\text{C}_{10}\text{ClF}_7$ and $\text{C}_{10}\text{Cl}_2\text{F}_6$ in 7–9, 39–40 and 46–48% yield, respectively (GLC).

3.2. Dehalogenation of **1**, **2** and **3** in solution

3.2.1. Dehalogenation of **1** with zinc dust

Zinc dust (80 g, 1.23 mol) and dioxan (150 mL) were charged into a 1 L three-necked flask equipped with stirrer, reflux condenser and dropping funnel and were heated to reflux. Then solution of $\text{C}_6\text{Cl}_6\text{F}_6$ (20 g, 50 mmol) in dioxan (20 mL) was added dropwise within 1 h. After 10 h, GLC monitoring showed the total consumption of **1**. The hot reaction mixture was filtered under a slight pressure of argon to prevent losses of volatile fluorinated benzenes and the filtrate was diluted with water (1 L). The organic phase was separated and dried with MgSO_4 to give a mixture of 6.5 g of C_6F_6 , C_6ClF_5 and $\text{C}_6\text{Cl}_2\text{F}_4$ (yields 14, 32 and 10%, respectively) (GLC).

3.2.2. Dehalogenation of **2** with zinc dust

Zinc dust (1.0 g, 15 mmol) and THF (5 mL) were heated to reflux with stirring. A solution of $\text{C}_5\text{Cl}_4\text{F}_5\text{N}$ (1.4 g, 4.5 mmol) in THF (1 mL) was added dropwise and the reaction mixture was stirred under reflux for 3 h. After cooling to 22 – 25°C , the formation of $\text{C}_5\text{F}_5\text{N}$ (18%), 2- $\text{C}_5\text{ClF}_4\text{N}$ (11%), 3- $\text{C}_5\text{ClF}_4\text{N}$ (27%), 4- $\text{C}_5\text{ClF}_4\text{N}$ (4%), 2,4- $\text{C}_5\text{Cl}_2\text{F}_3\text{N}$ (2%), and 2,5- $\text{C}_5\text{Cl}_2\text{F}_3\text{N}$ (18%) was detected by ^{19}F NMR spectroscopy [23] (yields were determined using a quantitative internal reference $\text{C}_6\text{H}_5\text{CF}_3$).

3.2.3. Dehalogenation of **1**, **2** and **3** with zinc activated with SOCl_2

Zinc dust ($n \times 15$ mmol; $n = 6, 8$ and 4 for $\text{C}_6\text{Cl}_6\text{F}_6$, $\text{C}_{10}\text{Cl}_8\text{F}_8$ and $\text{C}_5\text{Cl}_4\text{F}_5\text{N}$, respectively) and sulfolane (10 mL) were charged into a three-necked flask equipped with magnetic stirrer, reflux condenser, thermometer and dropping funnel. With vigorous stirring, thionyl chloride (0.1 mL) was added. After 30 min, $\text{C}_6\text{Cl}_6\text{F}_6$ (**1**) (10 mmol) was added and stirred at 80°C till consumption of **1** (^{19}F NMR). The reaction mixture was cooled to 20 – 25°C , filtered and diluted with water. Products were steam distilled, the organic phase was separated, dried with MgSO_4 and analysed by GLC (Table 1, entry 1). $\text{C}_5\text{Cl}_4\text{F}_5\text{N}$ (**2**) (Table 2, entry 1) and $\text{C}_{10}\text{Cl}_8\text{F}_8$ (**3**) (Table 3, entry 1) were dehalogenated in a similar way. In the latter case, after steam distillation polyfluoronaphthalenes were extracted with ether, the extract was dried and solvent was removed under reduced pressure.

3.2.4. Dehalogenation of **1**, **2** and **3** with zinc activated with CuSO₄

Zinc dust ($n \times 15$ mmol; $n = 6, 8$ and 4 for C₆Cl₆F₆, C₁₀Cl₈F₈ and C₅Cl₄F₅N, respectively) and sulfolane or diglyme (10 mL) were charged into a three-necked flask equipped with magnetic stirrer, reflux condenser, thermometer and dropping funnel. Under vigorous stirring, anhydrous CuSO₄ ($n \times 1.5$ mmol) was added. The further manipulations were performed as above (see 3.2.3) (Tables 1–3, entries 2 and 3).

3.2.5. Dehalogenation of **1**, **2** and **3** with zinc activated with complex (NiCl₂·6H₂O + bpy)

NiCl₂·6H₂O (120 mg, 0.5 mmol), 2,2'-bipyridyl (bpy) (78 mg, 0.5 mmol) and anhydrous DMF (or DMA) (10 mL) were charged into a three-necked flask equipped with magnetic stirrer, reflux condenser, thermometer and dropping funnel. Reaction mixture was stirred at 80 °C for 30–40 min until green solution was formed. Addition of zinc dust ($n \times 15$ mmol; $n = 6, 8$ and 4 for C₆Cl₆F₆, C₁₀Cl₈F₈ and C₅Cl₄F₅N, respectively) caused the deep coloration of solution after that substrate **1** (**2** or **3**) (10 mmol) was added in one portion. The further manipulations were performed as above (see 3.2.3). Composition of products was determined by GC–MS and ¹⁹F NMR spectroscopy (Tables 1–3).

3.2.6. Dehalogenation of **1** with zinc activated with complex (NiCl₂·6H₂O + phen)

Reaction was performed as mentioned above (3.2.5) using phen (0.5 mmol) instead of bpy (Table 1, entry 6).

3.2.7. Dehalogenation of **1** with tris(diethylamino)phosphine

3.2.7.1. In HMPA. Solution of P(NEt₂)₃ (18.5 g, 75 mmol) in HMPA (20 mL) was added dropwise into a stirred solution of C₆Cl₆F₆ (5.0 g, 12.5 mmol) in HMPA (20 mL) under cooling with cold water (5–10 °C). The formed solution was stirred at 20–25 °C for 1 h, diluted with water (40 mL), and products were steam distilled. The organic phase was separated and dried with MgSO₄ to give 1.65 g a mixture of C₆F₆, C₆ClF₅, C₆Cl₂F₄ and C₆F₅H (yields 18, 32, 14 and 7%, respectively) (¹⁹F NMR, quantitative internal reference C₆H₅CF₃).

3.2.7.2. In diglyme. Solution of P(NEt₂)₃ (17.0 g, 68 mmol) in diglyme (20 mL) was added dropwise into a stirred solution of C₆Cl₆F₆ (5.1 g, 12.7 mmol) in diglyme (30 mL) under cooling with cold water (5–10 °C). The formed solution was stirred at 20–25 °C for 1 h. The ¹⁹F NMR showed the presence of C₆F₆, C₆ClF₅, and C₆F₅H (yields 14, 56, and 15%, respectively) beside P(NEt₂)₃ClF (ca. 30% yield) (quantitative internal reference C₆H₅CF₃).

3.2.8. Dehalogenation of **3** with tris(diethylamino)phosphine

P(NEt₂)₃ (2.3 g, 9.3 mmol) was added dropwise into a stirred solution of C₁₀Cl₈F₈ (1.0 g, 1.8 mmol) in CH₂Cl₂ (10 mL) under cooling with cold water (5–10 °C). The formed solution was stirred at 20–25 °C for 1 h, washed with concentrated H₂SO₄ (3 mL), water and dried with CaCl₂. Solvent was distilled off and 0.6 g of a mixture of C₁₀F₈ (16%), C₁₀ClF₇ (13 and 29%), C₁₀Cl₂F₆ (7 and 17%) and C₁₀Cl₃F₅ (4, 5 and 6%) was obtained (yields of isomers were determined by GC–MS).

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