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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.

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 additivities (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.

Keywords: Dehalogenation; Hexafluorobenzene; Octafluoronaphthalene; Pentafluoropyridine

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 chlorofluorocarbons $C_6Cl_nF_{12-n}$ 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)).

$$\underset{\mathbf{1}}{C_6Cl_6F_6}\xrightarrow[500\,^{\circ}\mathrm{C,flow\ \ quartz\ \ reactor}]{\mathrm{Fe}}C_6F_6+C_6ClF_5+C_6Cl_2F_4 \tag{1}$$

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).

$$\underset{\mathbf{2}}{C_5Cl_4F_5N}\xrightarrow[500\,^{\circ}\mathrm{C}]{\mathrm{Fe}}C_5F_5N+2\text{-}C_5ClF_4N+3\text{-}C_5ClF_4N \tag{2}$$

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**.

$$\underset{\mathbf{3}}{C_{10}Cl_8F_8}\xrightarrow[350\,^{\circ}\mathrm{C}]{\mathrm{Fe}}C_{10}F_8+C_{10}ClF_7+C_{10}Cl_2F_6 \tag{3}$$

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 dopped with freshly precipitated copper (Zn/Cu), and zinc dust activated with complex ($NiCl_2\cdot6H_2O$ + 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)).

$$\underset{\mathbf{1}}{C_6Cl_6F_6}\xrightarrow[80-100\,^{\circ}\mathrm{C}]{\mathrm{Zn}}C_6F_6+C_6ClF_5+C_6Cl_2F_4 \tag{4}$$

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 $NiCl_2\cdot6H_2O$ with bpy or $NiCl_2\cdot6H_2O$ 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 ($NiCl_2\cdot6H_2O$ + 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 ($NiCl_2\cdot6H_2O$ + phen) was employed (Table 1, entry 5). When reaction of **1** with Zn and complex ($NiCl_2\cdot6H_2O$ + 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 ($NiCl_2\cdot6H_2O$ + bpy), 4 h.
[e] Zinc was activated with complex ($NiCl_2\cdot6H_2O$ + phen), 4 h.

Table 2
Dehalogenation of $C_5Cl_4F_5N$ (**2**) with zinc (80 °C, 5 h)

Entry	Solvent	Yield (%) based on **2**[a]
1	Sulfolane[b]	C_5F_5N (30), 2-C_5ClF_4N (8), 3-C_5ClF_4N (38)
2	Sulfolane[c]	C_5F_5N (38), 2-C_5ClF_4N (8), 3-C_5ClF_4N (34)
3	Diglyme[c]	C_5F_5N (29), 2-C_5ClF_4N (9), 3-C_5ClF_4N (33)
4	DMA[d]	C_5F_5N (34), 2-C_5ClF_4N (10), 3-C_5ClF_4N (36)

[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.

fluoropyridines in overall yield 80% although the yield of C_5F_5N was only 18%. The use of zinc activated with $SOCl_2$ in sulfolane **2** effected a higher yield of pentafluoropyridine (30%), while dichlorotrifluoropyridines were not found among products (Eq. (5)) (Table 2, entry 1).

$$\underset{\mathbf{2}}{C_5Cl_4F_5N} \xrightarrow[80\,^{\circ}C,4-5\,h]{Zn} C_5F_5N + 2\text{-}C_5ClF_4N + 3\text{-}C_5ClF_4N \quad (5)$$

Dehalogenation of **2** with zinc dust dopped with freshly precipitated copper in sulfolane (Table 2, entry 2), in diglyme (Table 2, entry 3) as well as with zinc and complex ($NiCl_2 \cdot 6H_2O$ + 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 independed of the method used to activate zinc. Thus, reaction of **3** with zinc activated with $SOCl_2$ 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 ($NiCl_2 \cdot 6H_2O$ + 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)).

$$\underset{\mathbf{3}}{C_{10}Cl_8F_8} \xrightarrow[80\,^{\circ}4-5\,h]{Zn} C_{10}F_8 + 1\text{-}C_{10}ClF_7 + 2\text{-}C_{10}ClF_7 + C_{10}Cl_2F_6 \quad (6)$$

Table 3
Dehalogenation of $C_{10}Cl_8F_8$ (**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), $C_{10}Cl_2F_6$ (33)
2	Sulfolane[c]	$C_{10}F_8$ (6), 1-$C_{10}ClF_7$ (9), 2-$C_{10}ClF_7$ (19), $C_{10}Cl_2F_6$ (37)
3	Diglyme[c]	$C_{10}F_8$ (7), 1-$C_{10}ClF_7$ (10), 2-$C_{10}ClF_7$ (19), $C_{10}Cl_2F_6$ (34)
4	DMA[d]	$C_{10}F_8$ (7), 1-$C_{10}ClF_7$ (9), 2-$C_{10}ClF_7$ (18), $C_{10}Cl_2F_6$ (35)

[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), 6 h.

2.2.2. Dehalogenation with $P(NEt_2)_3$

The dehalogenations with zinc proceed under heterogeous 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], CF_2BrCF_2Br [20] and 1,1,2-tribromopentafluorocyclobutane [19] to the corresponding polyfluoroalkenes. Dehalofluorination did not occur in any case.

However, the reaction of $C_6Cl_6F_6$ with $P(NEt_2)_3$ (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 ^{19}F NMR spectrum of the final reaction mixture (in diglyme) contained a signal assigned to $P(NEt_2)_3FCl$ ($\delta = -79.3$ ppm, d, $^1J_{FP} = 955$ Hz) beside resonances due to polyfluorobenzenes.

$$C_6Cl_6F_6 \xrightarrow[HMPA,20\,^{\circ}C,1\,h]{P(NEt_2)_3} \underset{18\%}{C_6F_6} + \underset{32\%}{C_6ClF_5} + \underset{14\%}{C_6Cl_2F_4} + \underset{7\%}{C_6F_5H} \quad (7)$$

Dehaloganation of $C_{10}Cl_8F_8$ with $P(NEt_2)_3$ in dichloromethane proceeded in a similar way to form octafluoronaphthalene (16%), chloroheptafluoronaphthalenes (42%), dichlorohexafluoronaphthalenes (24%) and trichloropentafluoronaphthalenes (15%) (Eq. (8)).

$$C_{10}Cl_8F_8 \xrightarrow[CH_2Cl_2,20\,^{\circ}C,1\,h]{P(NEt_2)_3} C_{10}F_8 + C_{10}ClF_7 + C_{10}Cl_2F_6 + C_{10}Cl_3F_5 \quad (8)$$

The picture obtained of dehalogenation of hexachlorohexafluorocyclohexanes (**1**), tetrachloropentafluoro-1-azacyclohexenes $C_5Cl_4F_5N$ (**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 $–CF_2–CCl_2–$ 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 additivities 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 $P(NEt_2)_3$ gave a somewhat different molar ratio of perhalogenated arenes derived from **1** and **3**. Unlike the metal used, $P(NEt_2)_3$ 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), $NiCl_2{\cdot}6H_2O$ (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 $C_6Cl_2F_4$, C_5ClF_4N, $C_5Cl_2F_3N$, $C_{10}ClF_7$, $C_{10}Cl_2F_6$ and $C_{10}Cl_3F_5$, 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 sequentally 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 $C_6Cl_2F_4$ in 30–32, 40–42 and 4–6% yield, respectively (GLC).

*3.1.2. Dehalogenation of tetrachloropentafluoro-1-azacyclohexenes $C_5Cl_4F_5N$ (**2**)*

Vapour-phase dehalogenation of **2** (1.6 g, 5 mmol) at 500 °C gave C_5F_5N, 2–C_5ClF_4N and 3–C_5ClF_4N in 40–43, 11–12 and 43–45% yield, respectively (GLC). Identification of 2-C_5ClF_4N and 3-C_5ClF_4N 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 $C_{10}F_8$, $C_{10}ClF_7$ and $C_{10}Cl_2F_6$ 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 $C_6Cl_6F_6$ (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 $C_6Cl_2F_4$ (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 $C_5Cl_4F_5N$ (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 C_5F_5N (18%), 2-C_5ClF_4N (11%), 3-C_5ClF_4N (27%), 4-C_5ClF_4N (4%), 2,4-$C_5Cl_2F_3N$ (2%), and 2,5-$C_5Cl_2F_3N$ (18%) was detected by ^{19}F NMR spectroscopy [23] (yields were determined using a quantitative internal reference $C_6H_5CF_3$).

*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 $C_6Cl_6F_6$, $C_{10}Cl_8F_8$ and $C_5Cl_4F_5N$, 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, $C_6Cl_6F_6$ (**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). $C_5Cl_4F_5N$ (**2**) (Table 2, entry 1) and $C_{10}Cl_8F_8$ (**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 $CuSO_4$*

Zinc dust ($n \times 15$ mmol; $n = 6$, 8 and 4 for $C_6Cl_6F_6$, $C_{10}Cl_8F_8$ and $C_5Cl_4F_5N$, 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 $CuSO_4$ ($n \times 1.5$ 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 ($NiCl_2 \cdot 6H_2O$ + bpy)*

$NiCl_2 \cdot 6H_2O$ (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 $C_6Cl_6F_6$, $C_{10}Cl_8F_8$ and $C_5Cl_4F_5N$, 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 ^{19}F NMR spectroscopy (Tables 1–3).

*3.2.6. Dehalogenation of **1** with zinc activated with complex ($NiCl_2 \cdot 6H_2O$ + 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 $P(NEt_2)_3$ (18.5 g, 75 mmol) in HMPA (20 mL) was added dropwise into a stirred solution of $C_6Cl_6F_6$ (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 $MgSO_4$ to give 1.65 g a mixture of C_6F_6, C_6ClF_5, $C_6Cl_2F_4$ and C_6F_5H (yields 18, 32, 14 and 7%, respectively) (^{19}F NMR, quantitative internal reference $C_6H_5CF_3$).

3.2.7.2. In diglyme. Solution of $P(NEt_2)_3$ (17.0 g, 68 mmol) in diglyme (20 mL) was added dropwise into a stirred solution of $C_6Cl_6F_6$ (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 ^{19}F NMR showed the presence of C_6F_6, C_6ClF_5, and C_6F_5H (yields 14, 56, and 15%, respectively) beside $P(NEt_2)_3ClF$ (ca. 30% yield) (quantitative internal reference $C_6H_5CF_3$).

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

$P(NEt_2)_3$ (2.3 g, 9.3 mmol) was added dropwise into a stirred solution of $C_{10}Cl_8F_8$ (1.0 g, 1.8 mmol) in CH_2Cl_2 (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 H_2SO_4 (3 mL), water and dried with $CaCl_2$. Solvent was distilled off and 0.6 g of a mixture of $C_{10}F_8$ (16%), $C_{10}ClF_7$ (13 and 29%), $C_{10}Cl_2F_6$ (7 and 17%) and $C_{10}Cl_3F_5$ (4, 5 and 6%) was obtained (yields of isomers were determined by GC–MS).

References

[1] J. Kvíčala, O. Paleta, Dehalogenation, in: B. Baasner, H. Hagemann, J. C. Tatlow (Eds), Houben–Weyl Methods of Organic Chemistry. Organo-Fluorine Compounds, fourth ed., vol. E10b, part 2, Thieme, Stuttgart, 2000, pp. 125–162.

[2] J.A. Marcella, A.G. Gilicinska, A.M. Coughlin, G.P. Pez, J. Org. Chem. 57 (1992) 2856–2860.

[3] G.C. Saunders, Angew. Chem. 108 (1996) 2783–2785.

[4] K. Sung, R.J. Lagow, J. Chem. Soc. Perkin Trans. 2 (1998) 637–638.

[5] J.L. Kipling, T.G. Richmond, J. Am. Chem. Soc. 118 (1996) 1805–1806.

[6] J. Burdeniuc, B. Jedlicka, R.H. Crabtree, Chem. Ber. 130 (1997) 145–154.

[7] G. Sandford, Tetrahedron 59 (2003) 437–454.

[8] P. Johncock, R.H. Mobbs, W.K.R. Musgrave, Ind. Eng. Chem. 1 (1962) 267–271.

[9] R.D. Chambers, J. Heyes, W.K.R. Musgrave, Tetrahedron 19 (1963) 891–900.

[10] G.M. Brooke, R.D. Chambers, J. Heyes, W.K.R. Musgrave, J. Chem. Soc. (1964) 729–733.

[11] L.A. Bigelow, J.H. Pearson, J. Am. Chem. Soc. 56 (1934) 2773–2774.

[12] V. Grakauskas, J. Org. Chem. 34 (1969) 2835–2839.

[13] V.V. Bardin, S.G. Bardina, J. Fluorine Chem. 125 (2004) 1411–1414.

[14] D.V. Trukhin, N.Yu. Adonin, V.F. Starichenko, Zh. Org. Khim. 38 (2002) 942–943;
D.V. Trukhin, N.Yu. Adonin, V.F. Starichenko, Russ. J. Org. Chem. 38 (2002) 900–901. English Translation.

[15] D.V. Trukhin, N.Yu. Adonin, V.F. Starichenko, Zh. Org. Khim. 36 (2000) 143–144;
D.V. Trukhin, N.Yu. Adonin, V.F. Starichenko, Russ. J. Org. Chem. 36 (2000) 132–133. English Translation.

[16] D.V. Trukhin, N.Yu. Adonin, V.F. Starichenko, Zh. Org. Khim. 36 (2000) 1261–2162;
D.V. Trukhin, N.Yu. Adonin, V.F. Starichenko, Russ. J. Org. Chem. 36 (2000) 1227–1228. English Translation.

[17] N.Yu. Adonin, V.F. Starichenko, J. Fluorine Chem. 101 (2000) 65–67.

[18] N.Yu. Adonin, V.F. Starichenko, Mendeleev Commun. (2000) 60–61.

[19] V. Montanari, D. DesMarteau, J. Org. Chem. 57 (1992) 5018–5019.

[20] V.V. Bardin, Synth. Commun. 23 (1993) 1409–1413.

[21] V.V. Bardin, L.S. Pressman, V.F. Cherstkov, Synth. Commun. 25 (1995) 2425–2433.

[22] C. Stuebe, H.P. Lankelma, J. Am. Chem. Soc. 78 (1956) 976–977.

[23] S. Berger, S. Braun, H.-O. Kalinowski, NMR-Spektroskopie von Nichtmetallen. Bd 4. ^{19}F-NMR-Spektroskopie. Thieme, Stuttgart, 1994, S. 50.