ELSEVIER

Journal of Fluorine Chemistry 91 (1998) 21–23

JOURNAL OF FLUORINE CHEMISTRY

Reductive defluorination of perfluoroarenes by zinc in aqueous ammonia

Sergey S. Laev, Vitalii D. Shteingarts *

N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division of Russian Academy of Sciences, Lavrentiev ave. 9, Novosibirsk 630090, Russian Federation

Received 5 November 1997; accepted 12 March 1998

Abstract

A very simple reductive system such as zinc in aqueous ammonia has been shown to be applicable for hydrodefluorination of some perfluoroarenes (hexafluorobenzene, octafluorotoluene, octafluoronaphthalene and decafluorobiphenyl) under mild conditions. In all cases an ammonia concentration effect has been observed. Moreover, for octafluoronaphthalene, the presence of NH_4Cl is of importance and for decafluorobiphenyl this factor and the addition of an organic solvent to the aqueous ammonia are significant.

Keywords: Reductive defluorination; Zinc; Aqueous ammonia; Perfluoroarenes; Hexafluorobenzene; Octafluorotoluene; Octafluoronaphthalene; Decafluorobiphenyl

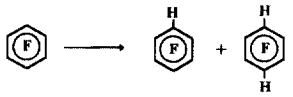
1. Introduction

The reductive defluorination of perfluoroarenes is a potentially promising approach to partially fluorinated arenes which are valuable starting compounds for synthesis but significantly less accessible than perfluoroarenes. We have found that aqueous ammonia is a good medium allowing the highly selective reductive defluorination of polyfluoroarene functional derivatives by zinc at room temperature [1]. In this communication we report this very simple reductive system to be applicable for the hydrodefluorination of simple perfluoroarenes such as hexafluorobenzene (**1**), octafluorotoluene (**2**), octafluoronaphthalene (**3**) and decafluorobiphenyl (**4**) under mild conditions. The influence of various factors (ammonia concentration, presence of NH_4Cl[1] or organic solvent) has been revealed.

2. Results and discussion

The results of the reduction of hexafluorobenzene (**1**) by zinc in aqueous ammonia are represented in Table 1. With 20% aqueous ammonia (exp. 1) the reaction gave pentafluorobenzene (**5**) in low conversion. The use of 30% aqueous ammonia (exp. 2) considerably increased conversion of **1**, and even a small amount of defluorination product **5**, 1,2,4,5-tetrafluorobenzene (**6**) was observed. Addition of NH_4Cl to aqueous ammonia (exp. 3) brought about greater conversion of **1**, but this effect was of little importance as compared with ammonia concentration effect.

Table 1
Reaction of hexafluorobenzene (**1**) with zinc



1 **5** **6**

N exp.	Time, h	**1**:Zn:NH_4Cl, mol ratio	Ammonia concentration, %	Product distribution, mol%		
				1	**5**	**6**
1	24	1:5:0	20	76	24	< 1
2	24	1:5:0	30	33	64	3
3	24	1:5:2	30	25	71	4

Analogously, for octafluorotoluene (**2**) the content of defluorination product (Table 2) α,α,α,2,3,5,6-heptafluorotoluene (**7**) rose with ammonia concentration (exp. 1, 3) and remained practically invariant upon the addition of NH_4Cl (exp. 3, 4). The reduction of **2** with zinc in aqueous ammonia is more rapid than of **1**, and compound **7** can be obtained with high yield (~85%) from this reaction (exp. 2).

* Corresponding author. Fax: +7-383-234-4752.

[1] Simultaneously and independently, an electrolyte effect was observed in hydrodehalogenation of polyfluoroarenes by the action of Zn(Cu) in water or DMF–H_2O on heating [2].

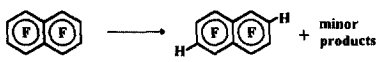
0022-1139/98/$ - see front matter
PII S0022-1139(98)00194-8

Table 2
Reaction of octafluorotoluene (**2**) with zinc

2 **7**

N exp.	Time, h	**2**:Zn:NH_4Cl, mol ratio	Ammonia concentration, %	Product distribution, mol%	
				2	**7**
1	15	1:4.6:0	20	31	69
2	39	1:4.6:0	20	2	98
3	15	1:4.6:0	30	11	89
4	15	1:4.6:1.8	30	9	91

Table 3
Reaction of octafluoronapthalene (**3**) with zinc



3 **8**

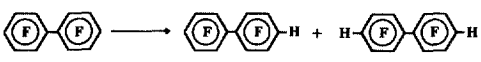
N exp.	Time, h	**3**:Zn:NH_4Cl, mol ratio	Ammonia concentration, %	Product distribution, mol%[a]	
				3	**8**
1	20	1:12:0	20	64	30
2	20	1:12:0	30	32	56
3	20	1:12:6	30	<1	91
4	15	1:12:6	0	97	<1

[a]The remainder of the mixture consists of unidentified defluorination compounds. Product distribution for exp. 2, 4 was estimated only by ^{19}F NMR data, for exp. 1, 3 by ^{19}F NMR and GLC data which were in agreement.

The reduction defluorination of octafluoronaphthalene (**3**) (Table 3) gave mainly the product of removal of two fluorine atoms, 1,2,4,5,6,8-hexafluoronaphthalene (**8**) (this structure was assigned by ^{19}F NMR spectroscopy)—the formation of which is in accordance with the reduction of **3** by $(C_5H_5)_2$-$ZrCl_2$–Mg–$HgCl_2$ in THF [3]. Just as for **1** and **2**, for compound **3** the amount of the main defluorination product increased with ammonia concentration (exp. 1, 2). The presence of NH_4Cl was also significant (exp. 2, 3) leading to practically complete conversion of **3** and high content of **8** in the product mixture (exp. 3). However, the reduction of **3** by zinc in an aqueous solution of NH_4Cl at room temperature did not occur (exp. 4), confirming the importance of ammonia for this reaction.

The reduction of decafluorobiphenyl (**4**) by zinc in aqueous ammonia (Table 4) was more complicated as compared with **1**, **2** and **3**. Thus, this compound was not reduced at all by zinc in 20% aqueous ammonia (exp. 1). The formation of defluorination products 2,2′,3,3′,4,5,5′,6,6′-nonafluorobiphenyl (**9**) and 2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl (**10**) occurred upon addition of organic cosolvents such as diethyl ether (~4% conversion for 22 h), THF (exp. 2) or acetone (~45% conversion for 20 h), to aqueous ammonia with acetone to be the most efficient one. Upon the reduction by zinc in the presence of THF (exp. 2) or acetone, in addition to **9** and **10**, unidentified products were also observed. These products may contain amino groups as indicated by the upfield shifts of ^{19}F NMR signals and IR data and are probably formed by nucleophilic substitution of fluorine. However, in the absence of zinc this process was not occurred (exp. 3). The content of hydrodefluorination products increased with ammonia concentration (exp. 2, 4, 5), but the content of unidentified products in the case of THF was very high (exp. 5). The addition of NH_4Cl to 30% aqueous ammonia caused the defluorination reaction of **4** by zinc in the absence of

Table 4
Reaction of decafluorobiphenyl (**4**) with zinc



4 **9** **10**

N exp.	Time, h	**4**:Zn:NH_4Cl, mol ratio	Ammonia concentration, %	Organic cosolvent	Product distribution, mol%[a]		
					4	**9**	**10**
1	22	1:13.3:0	20	–	100	0	0
2	10	1:13.3:0	20	THF	90	3	<2
3	22	1:0:0	20	acetone	100	0	0
4	22	1:13.3:0	30	Et_2O	83	9	7
5	22	1:13.3:0	30	THF	30	15	10
6	10	1:13.3:6.7	30	–	88	6	5
7	20	1:13.3:6.7	30	Et_2O	40	48	11
8	22	1:13.3:6.7	30	THF	<1	5	68
9	22	1:13.3:6.7	30	acetone	16	7	9

[a]The remainder of the mixture for exp. 2, 5, 8 and 9 consists of unidentified compounds. Product distribution for exp. 1–3, 5 was estimated only by ^{19}F NMR data, for exp. 4, 6–9 by ^{19}F NMR and GLC data which were in agreement.

organic solvent but conversion was low (exp. 6) and was favourable for the reduction of **4** in the presence of Et_2O or THF (exp. 7, 8) but led to a very complicated mixture of unidentified products besides **9** and **10** in the presence of acetone (exp. 9). By the reaction of **4** with zinc in 30% aqueous ammonia in the presence of NH_4Cl and THF (exp. 8) compound **10** can be obtained.

Thus, for all perfluoroarenes under study the defluorination rate rose with ammonia concentration in aqueous solution. Perhaps, the higher the ammonia concentration the higher the activation of the zinc surface thus increasing the reduction rate, but another reasons are also possible. For the reduction of compounds **3** and **4** the presence of NH_4Cl is of importance, but for **1** and **2** this factor is insignificant. Therefore, an influence of NH_4Cl is not related to the active zinc surface, as it is not displayed for all substrates. It is possible that addition of this compound alters the redox potential of the substrate, but the present experimental data do not confirm this. Finally, the effect of organic solvent upon the reaction of **4** with zinc seems certainly caused by the very low solubility of this compound in aqueous solution. Thus, compound **4** is more reactive in the presence of water-miscible solvents such as acetone or THF as compared to Et_2O.

3. Experimental details

Melting points were determined in sealed capillaries and boiling points were measured during distillation, both are uncorrected. ^1H and ^{19}F NMR spectra were recorded in CD_3COCD_3 using a Bruker WP-200 SY spectrometer at 200.1 and 188.3 MHz, respectively. Chemical shifts are reported with respect to TMS and $CFCl_3$. IR spectra were obtained with a Specord M80 spectrometer. GLC analysis was performed on a HP 5890 instrument using the HP G1800A GCD system (capillary GC column 0.26 mm/30 m, 0.25 μm film HP-5 phase).

3.1. Reaction of hexafluorobenzene (1) with zinc

Compound **1** (5.2 g, 28 mmol), zinc powder (9.1 g, 140 mmol) and (in exp. 3, Table 1) NH_4Cl (3.0 g, 56 mmol) in aqueous ammonia (45 ml) were stirred at room temperature for 24 h. The mixture was diluted with water and gradually heated to 100°C. An organic mixture was collected in a Dean–Stark trap, separated from water, dried (yield ~50–60%) and analyzed by ^{19}F NMR.

3.2. Reaction of octafluorotoluene (2) with zinc

Compound **2** (5.9 g, 25 mmol), zinc powder (7.5 g, 115 mmol) and (in exp. 4, Table 2) NH_4Cl (2.4 g, 45 mmol) in aqueous ammonia (40 ml) were stirred at room temperature. After standard work-up (vide supra), an organic mixture (yield ~80–85%) was analyzed by ^{19}F NMR. Compound **7** (4.7 g) has been isolated from exp. 3, yield 86%, b.p. 110.5–111.5°C (lit. 111–112°C [4]). ^1H, ^{19}F NMR spectra were identical to those of an authentic specimen.

3.3. Reaction of octafluoronaphthalene (3) with zinc

Compound **3** (0.90 g, 3.3 mmol), zinc powder (2.6 g, 40 mmol) and (in exp. 3 and 4, Table 3) NH_4Cl (1.07 g, 20 mmol) in aqueous ammonia (25 ml) were stirred at room temperature. Unreacted zinc was separated and washed with water. The aqueous solution was extracted with diethyl ether (3×25 ml). The combined ether extract was dried over $MgSO_4$. The solvent was removed by distillation to give a mixture (yield ~65–75%) which was analyzed by ^{19}F NMR and GLC. A crude product (0.55 g) from exp. 3 was crystallized from ethanol to afford 0.35 g of **8** (yield 45%). ^{19}F NMR, δ: 117.3 (*F*-4,8; J=64 Hz), 136.4 (*F*-2,6), 149.4 (*F*-1,5; J=64 Hz). Anal. calc. for $C_{10}H_2F_6$: C, 50.87; H, 0.85; F, 48.28. Found: C, 50.64; H, 0.78; F, 48.11%.

3.4. Reaction of decafluorobiphenyl (4) with zinc

Compound **4** (1.00 g, 3 mmol), zinc powder (2.6 g, 40 mmol) (except exp. 3, Table 4) and (in exp. 6–9, Table 4) NH_4Cl (1.07 g, 20 mmol) in aqueous ammonia (25 ml) with addition of organic solvent (8 ml) (in exp. 2–5 and 7–9, Table 4) were stirred at room temperature. The isolation described above for **3** was used. An organic mixture (yield ~80–90%) was analyzed by ^{19}F NMR and GLC. A crude product (0.79 g) from exp. 8 was crystallized from ethanol to afford 0.25 g of solid containing 95% of **10** (yield 27%), m.p. 80.5–82.5°C (lit. 82–83.5°C [5]). The IR spectrum was in accordance with literature IR data [5].

Acknowledgements

This work was supported by the Russian Foundation of Basic Research under Grant 96-03-32984a.

References

[1] S.S. Laev, V.D. Shteingarts, Tetrahedron Lett. 38 (1997) 3765.
[2] V.I. Krasnov, V.E. Platonov, 15th Int. Symp. Fluorine Chemistry, Program and Abstracts, Vancouver, August 1997, IL-29.
[3] J.L. Kiplinger, T.G.J. Richmond, J. Chem. Soc., Chem. Commun. (1996) 1115.
[4] C. Tamborski, E.J. Soloski, J. Org. Chem. 31 (1966) 746.
[5] G.G. Yakobson, V.D. Shteingarts, A.I. Miroshnikov, N.N. Vorozhtsov, Dokl. Akad. Nauk SSSR 159 (1964) 1109.