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Selective hydrodechlorination of fluorinated arylamines

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Abstract

Chlorine-containing polyfluorinated anilines and *meta*-phenylenediamines undergo selective hydrodechlorination easily upon reduction by zinc in aqueous ammonia. A new approach is thus provided to synthetically valuable, partially fluorinated arylamines based on utilizing polyfluorochloroarenes, which are available as intermediates of perfluoroarene production from perchloroarenes. When chlorine atoms are present in positions both *ortho* and *para* to the amino group, *para* chlorine is initially eliminated. Based on this reaction, a one-pot synthesis of partially fluorinated 4-aminopyridines from 3,5-dichlorotrifluoro- and 3-chlorotetrafluoropyridine has been realized.
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Keywords: Reductive hydrodechlorination; Zinc; Aqueous ammonia; Polyfluorinated arylamines; Aminopyridines

1. Introduction

Polyfluorochloroarenes and polyfluorochloropyridines containing two or three chlorine atoms are accessible, primarily as isomer mixtures, as intermediates in the synthesis of hexafluorobenzene from hexachlorobenzene [1] and pentafluoropyridine from pentachloropyridine [2], respectively. Nevertheless, they have not found application as starting materials in fine organic synthesis. Their application, is especially important for developing new synthetic approaches to the functional derivatives of partially fluorinated arenes, particularly arylamines, valuable intermediates for the synthesis of biologically active substances [3–5], because current synthesis, based on consecutive introduction of several fluorine atoms into the aromatic ring, are cumbersome and inefficient.

A promising approach is the reverse strategy, namely, moving from accessible perfluoro- and perfluorochloroarenes toward less fluorinated compounds through selective dehalogenation, which in the series of polyfluoroarenes was mainly developed for compounds containing no functional groups. Thus, selective hydrodechlorination of polyfluorochloroarenes can be achieved with dihydrogen on a catalyst [6], copper upon heating in water [7], the Zn–Cu couple [8] or Zn–$NiCl_2$–bipyridyl complex [9] in aqueous DMF, or zinc in aqueous ammonia [10]. Two or three chlorine atoms can be sequentially removed from tetrafluorodichloro- or trifluorotrichlorobenzenes via reduction by metals [8,10]. One of the few types of functionalized polyhaloarenes involved in such transformations are amines. Perfluorochloro-4-aminopyridines [4,5] and polychloroanilines [11] were hydrodechlorinated by dihydrogen on a Pd catalyst. Ammonolysis of perfluorochlorobenzenes by aqueous ammonia in a steel autoclave, leading to polyfluorochloroanilines and polyphenylenediamines, also gave hydrodechlorination products as by-products [12,13].

We have developed a general approach to partially fluorinated arylamines based on the sequence of noncatalytic or catalytic ammonolysis of perfluorochlorobenzenes and hydrodechlorination of the resulting perfluorochloroanilines and polyphenylenediamines. Of particular interest are amines with an unsubstituted *ortho* position relative to the amino group for the preparation of polyfluorobenzoheterocycles. Procedures for the first stage of this scheme have already been described [12,13]; the present work examines hydrodechlorination of polyfluorochloroarylamines with a simple reducing system, previously applied to selective hydrodehalogenation of polyfluoroarenes, zinc in aqueous ammonia [10,14,15]. Using this system, *N*-acetyl derivatives

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Table 1
Reactions of compounds **1–3**, **7**, **13**, **14**, **18** with Zn in aqueous ammonia

Entry	Starting compound	Quantity (g)	Time (h)	Molar ratio			Yield of mixture (g)	Product distribution (wt.%, GLC)
				Substrate	Zn	NH_4Cl		
1	**1**[a]	0.3	17	1	10	–	0.27	**4** (65); **5** (20); **6** (3.5)
2	**7**[b]	0.3	48	1	4	–	0.26	**9** (61); **10** (3)
3	**7**[c]	0.2	24	1	10	10	0.10	**10** (80); **12** (10)
4	**13**[d]	3.6	18	1	10	–	2.41	**15** (70); **16** (8)
5	**18**	0.3	144	1	10	–	0.26	**19** (91)

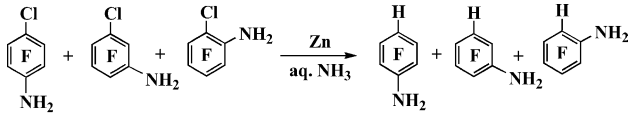
[a] An isomer mixture was used: 63% *para*-isomer **1**, 5% *meta*-isomer **2**, and 21% *ortho*-isomer **3**, (wt.%, GLC).
[b] The starting material, containing 83% amine **7** and 9% amine **8** (wt.%, GLC), was used, and obtained from ammonolysis of 1,2,4,6-tetrafluoro-3,5-dichlorobenzene [13], together with 5% aqueous ammonia.
[c] A mixture containing 83% amine **7** and 9% amine **8** (wt.%, GLC) was used, together with 30% aqueous ammonia.
[d] A 6:1 mixture of amines **13** and **14** was used, together with 30% aqueous ammonia.

of perfluoroanilines smoothly undergo selective hydrodefluorination at positions *ortho* to the acetoamido group [15].

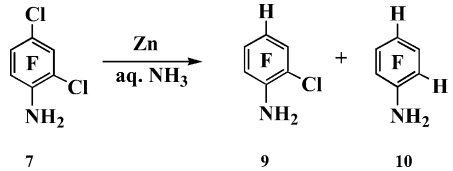
2. Results and discussion

The starting materials, reaction conditions, product ratios, and yields are reported in Table 1. Reduction of a mixture of tetrafluorochloroanilines **1–3** (the product of noncatalytic ammonolysis of pentafluorochlorobenzene [12]) resulted in a mixture of previously reported tetrafluoroanilines **4–6** in a ratio close to that of the starting mixture of **1–3** (Scheme 1, entry 1, Table 1).

Seeking to perform monodechlorination of 3,5,6-trifluoro-2,4-dichloroaniline **7** (the starting material used was the 9:1 mixture of **7** and 3,4,5-trifluoro-2,6-dichloroaniline **8** [13]), we took into account that the extent of polyfluoroarene hydrodefluorination by zinc in aqueous ammonia decreases with ammonia concentration and substrate to zinc ratio [10]. The reaction conducted with 5% aqueous ammonia and 1:4 substrate to zinc ratio mainly gave 3,5,6-trifluoro-2-chloroaniline **9** with a minor admixture of 2,3,5-trifluoroaniline **10** (Scheme 2, entry 2, Table 1).



Scheme 1.



Scheme 2.

Chlorine removal from the position *para* to the amino group is preferred and stepwise exchange of two chlorine atoms by hydrogen in **7** can occur with hydrodechlorination of **9**. Isomer **8**, which is present in the starting material, formed 3,4,5-trifluoro-2-chloroaniline **11**.

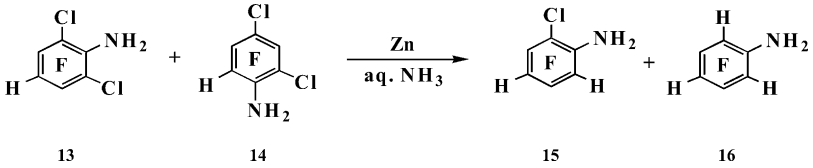
Polyfluoroarene reduction with zinc in aqueous ammonia can be promoted by ammonium and zinc salts [10,14,15]. To obtain amine **10**, reduction of **7** was carried out and an 8:1 mixture of **10** and 3,4,5-trifluoroaniline **12** (formed from **11**) was obtained (entry 3, Table 1).

Preferential *para*-chlorine substitution by hydrogen, found in the case of the reduction of **7** (see above), would afford 3,5-difluoro-2-chloroaniline **15** via the reduction of a mixture of 3,5-difluoro-2,6-dichloroaniline **13** and 3,5-difluoro-2,4-dichloroaniline **14** (the product of noncatalytic ammonolysis of 1,3,5-trifluoro-2,6-dichlorobenzene [13]). Indeed, **15** with a small admixture of 3,5-difluoroaniline **16** was obtained from the mixture of **13** and **14** with zinc in aqueous ammonia (Scheme 3, entry 4, Table 1).

Although the above reactions provide mixtures of amines, in some cases the latter are believed to be usable as starting materials for further synthesis without separation. This has been demonstrated by synthesis of unknown 5,7-difluoro-8-chloroquinoline **17** (Scheme 4) from **15** with an admixture of **16** via Skraup cyclization in 90% yield.

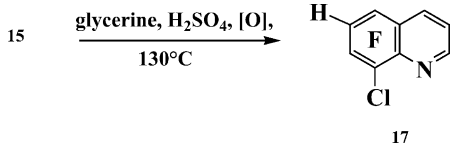
Similarly to the hydrodehalogenation of monoamines, from 2,5,6-trifluoro-4-chloro-1,3-phenylenediamine **18**, we obtained 2,5,6-trifluoro-1,3-phenylenediamine **19** in 85% yield (Scheme 5, entry 5, Table 1). Thus, a compound with two amino groups can also be reduced by zinc in aqueous ammonia, but the rate of its hydrodechlorination is appreciably lower compared with the reaction of anilines mentioned above.

We anticipated that with active substrates, subjected to mild ammonolysis under conditions compatible with those for polyfluorochloroarylamine hydrodechlorination (Table 1), aminodefluorination and subsequent hydrodechlorination of the initially formed amine could be performed as a one-pot process. Perfluorochloropyridines were thought to be suitable substrates for this process, since their



13 14 15 16

Scheme 3.



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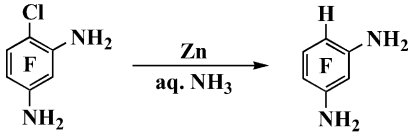
Scheme 4.



18 19

Scheme 5.

electron deficiency favors both nucleophilic substitution and the removal of halogen. The feasibility of a one-pot process of this kind is demonstrated for 3,5-dichloropyridine **20** and 3-chlorotetrafluoropyridine **21**.

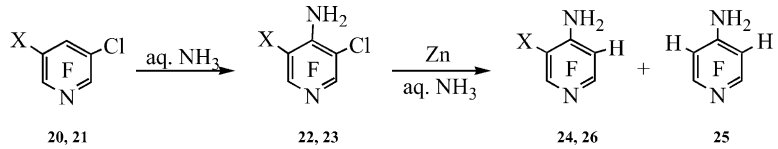
3,5-Dichloro-2,6-difluoro-**22** and 3-chloro-2,5,6-trifluoro-4-aminopyridine **23** are formed when **20** and **21** are treated with aqueous ammonia [5,16] (Scheme 6). To ascertain that dechlorination of **22** and **23** under the conditions used in this study is feasible, we treated **22** with zinc in aqueous ammonia and obtained a 2:1 mixture of 2,6-difluoro-3-chloro-4-aminopyridine **24** and 2,6-difluoro-4-aminopyridine **25**.

To prepare **24** directly from **20** we took into account that the rate of polyfluoroarene hydrodehalogenation decreases with ammonia concentration [10,14]. Therefore, after stirring **20** with 30% aqueous ammonia and subsequent treatment with zinc in 15% ammonia at room temperature **24** was obtained in 75% yield (entry 1, Table 2). Seeking to obtain **25**, we considered that the presence of ammonium and zinc chlorides promotes polyfluoroarene defluorination [10,14,15]. Indeed, after stirring with aqueous ammonia and then with zinc in the presence of these salts **20** gave a mixture containing 70% of **25** (entry 2, Table 2) (*cf.* [17]). To transform **21** to 2,3,6-trifluoro-4-aminopyridine **26** in a one-pot process, after ammonolysis had been completed, we added only zinc to the resulting **23** to obtain **26** as the major product (entry 3, Table 2).

To perform analogous synthesis of **24** and **25** from **20** and of **26** from **21** without separating the ammonolysis and hydrodechlorination stages, **20** was treated with zinc and aqueous ammonia. The reaction, however, yielded mixtures (entries 5–7, Table 2). In the presence of ammonium chloride or zinc chloride, the product ratio changed slightly, if at all (entries 8 and 9, Table 2). However, the presence of both salts markedly increased the extent of transformation and the 89% content of **25** among the reaction products was achieved (entries 10 and 11, Table 2). The interaction of **21** with zinc in aqueous ammonia for 24 h gave **26** in 70% isolated yield (entry 4, Table 2).

For aminopyridines **22** and **23** reductive hydrodechlorination of polyfluorochloro-4-aminopyridines by zinc in aqueous ammonia has been demonstrated and a one-pot synthesis of partially fluorinated 4-aminopyridines carried out. Previously, aminopyridines **24–26** were prepared from the same starting materials in two steps, by varying the sequence of catalytic reduction and amination. Thus, pyridines **20** and **21** were hydrodechlorinated on palladium to form 2,4,6-trifluoropyridine (75%) and 2,4,5,6-tetrafluoropyridine (80%), respectively [18], which gave with ammonia in aqueous dioxane a 2:1 mixture of **25** and 2,4-difluoro-6-aminopyridine in the former case and a 4:1 mixture of **26** and 2,4,5-trifluoro-6-aminopyridine in the latter [17]. Initial ammonolysis of **20** and **21** [5,16] and subsequent hydrodechlorination of **22** and **23** on palladium furnished a mixture of **24** and **25** isolated by chromatography in 57% and 33% yields, respectively, in the first case, and **26** (96% yield) in the latter [5]. **25** also formed upon catalytic hydrodechlorination of **22** in 90% yield [4].

Thus, polyfluorochloroamines, like polyfluorochloroarenes having no amino group [10], are hydrodechlorinated by zinc in aqueous ammonia. This is a fundamental difference between the reaction under study and hydrodefluorination of perfluoroarenes, which occurs in the same reductive



20, 21 22, 23 24, 26 25

X = Cl (**20**, **22**, **24**); F (**21**, **23**, **26**) (only from **20**)

Scheme 6.

Table 2
One-pot reactions of compounds **20** and **21** with Zn in aqueous ammonia

Entry	Starting compound	Quantity (g mmol)	Type of procedure	Time (h)	Molar ratio				Yield of mixture (g)	Product distribution (wt.%, GLC)[a]
					Substrate	Zn	$ZnCl_2$	NH_4Cl		
1[b]	**20**	1.0 (0.005)	A[c]	70	1	10	–	–	0.74	**22** (1); **24** (88); **25** (5)
2[b]	**20**	1.0 (0.005)	A	90	1	10	10	6	0.6	**24** (23); **25** (70)
3[d]	**21**	1.3 (0.007)	A	24	1	10	–	–	1.0	**23** (3); **26** (86)
4	**21**	0.3 (0.0016)	B[e]	24	1	10	–	–	0.2	**23** (1); **26** (89)
5	**20**	0.3 (0.0015)	B	8	1	10	–	–	0.2	**22** (12) **24** (73); **25** (5)
6	**20**	0.3 (0.0015)	B	12	1	10	–	–	0.2	**24** (72); **25** (18)
7	**20**	0.3 (0.0015)	B	24	1	10	–	–	0.2	**24** (51); **25** (26)
8	**20**	0.3 (0.0015)	B	24	1	10	10	–	0.2	**24** (63); **25** (20)
9	**20**	0.3 (0.0015)	B	24	1	10	–	6	0.2	**24** (61); **25** (24)
10	**20**	0.3 (0.0015)	B	24	1	10	10	6	0.2	**24** (40); **25** (45)
11[f]	**20**	0.3 (0.0015)	B	140	1	10	10	6	0.2	**24** (1); **25** (89)

[a] In all experiments, some unidentified components were present in the mixture of products (4–9%).
[b] Initial aminodefluoronation for 5 h, then water was added.
[c] Procedure A—initial aminodefluoronation, then addition of zinc and salts.
[d] Initial aminodefluoronation was for 24 h.
[e] Procedure B—all components charged at the start.
[f] Ammonia concentration was 34% ($\rho = 0.88$ G mL^{-1}).

system [10,14] but is hindered by incorporation of an amino group, so that additional modification, such as *N*-acetylation is necessary [15] obviously to diminish the electron-donor effect of the substituent.

It is believed that accepting an electron by the substrate is the rate-limiting stage of the reactions under study, since decay of the resulting radical anion is known to be a rather rapid process [19–22]. If an electron was accepted by the π*-LUMO in both cases, one could hardly expect any significant difference in the influence of the amino group on the efficient reaction rates of hydrodefluorination and -dechlorination. Hence, this difference is suggested to be caused by the difference in the character of the MOs accepting an electron. For example, from hexafluorobenzene a pseudo-π* type radical anion is formed [23] while chloropentafluorobenzene produces a pseudo-σ* type radical anion with the MO of the odd electron which is essentially the σ*-MO of the C–Cl bond [24]. Since pentafluoroaniline, unlike hexafluorobenzene, is not reduced by zinc in aqueous ammonia at ambient temperature [15], substitution of the amino group for fluorine obviously increases the energy of π*-MOs, so that the electron affinity of pentafluoroaniline is insufficient for the reduction to be realized. The same substitution in polyfluorochlorobenzenes should change the π*-MO energy in a similar way, but it likely exerts a substantially smaller effect on energy of the σ*-MO of the C-Cl bond, so that during the reduction of polyfluorochloroarylamines an electron enters MO mainly located on the C–Cl bond with practically synchronous fragmentation on it.

3. Experimental

^{19}F and ^{1}H NMR spectra were recorded on Bruker WP-200 and Bruker AM-400 instruments for 20% solutions in acetone-d_6 or $CDCl_3$ using C_6F_6 and $CHCl_3$ as internal standards, respectively. The product mixtures were analyzed by GLC on a Hewlett-Packard HP-5890 chromatograph equipped with a thermal conductivity detector; injector temperature 240 °C, detector temperature 280 °C, temperature programming from 40 to 280 °C at a rate of 10° min^{-1}; capillary column 15 000 mm × 0.53 mm, stationary phase 1.5 mm × 10^{-3} mm HP-5 [diphenyl (5%)-methylpolysiloxane]; carrier gas helium, 5 mL min^{-1}. The components were quantitated using the internal normalization technique.

The products were identified by GCMS on a Hewlett-Packard G1081A instrument consisting of an HP-5890 Series II gas chromatograph and an HP-5971 mass-selective detector (IE, 70 eV) with an HP5 capillary column: (30 000 × 0.25) mm × 0.25 μm. The He flow (1 mL min^{-1}) was used as carrier gas. The following temperature regime program was applied: 2 min at 50 °C, 50 to 280 °C at a rate of 10° min^{-1}, 5 min at 280 °C. Evaporator temperature was 280 °C. Ion source temperature was 173 °C. The scanning velocity was 1.2 scan s^{-1} in the mass interval 30–650 amu. The molecular weights were determined on a Finnigan MAT-8200 high-resolution mass spectrometer.

Pyridines **20** and **21** were obtained from the chemical pilot factory at the N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry. Pyridine **22** was obtained from pyridine **20** according to [5]. 30% Aqueous ammonia (0.888) G mL^{-1} was prepared by saturation of commercial aqueous ammonia with gaseous ammonia. Mixtures of products were separated by column chromatography on silica gel (40/100 μm).

Analyses of product mixtures were performed by GLC, GC–MS and NMR. The ^{19}F NMR spectral data of **4** and **5** agree with the literature data [25], and those of **6** are identical with the data of the authentic specimen [26]. The ^{19}F NMR spectral data of compounds are consistent

with the literature data: **9** [13].**11** [27], **10**, **12** [28], **15** and **16** [28,29], **19** [12].

4. General procedure

A glass reaction vessel was charged with the substrate, zinc, aqueous ammonia and, when necessary, zinc and ammonium chlorides. After stirring under conditions specified in Tables 1 and 2, the reaction mixture was extracted with CH_2Cl_2 (3 × 30 mL), the extract was dried with $MgSO_4$, the solvent was evaporated and the solid residue was analyzed by NMR, GLC and GC–MS.

4.1. 3,5-difluoro-2-chloroaniline *15*

3,5-difluoro-2-chloroaniline 15 (Entry 4, Table 1) (37% yield) was isolated by chromatography (silica gel, methylene chloride:benzene = 1:1)

4.2. 2,6-Difluoro-3-chloro-4-aminopyridine *24*

2,6-Difluoro-3-chloro-4-aminopyridine 24 (Entry 1, Table 2) was obtained in 75% yield by recrystallization of the crude product from petroleum ether (40–70 °C), mp 75–76 °C (84–85 °C [5]). NMR (solution in $CDCl_3$), δ/ppm: ^{19}F (C_6F_6 int.) 89.0, 88.8; ^1H ($CHCl_3$ int., δ: 7.24) 6.10 (C-H), 4.52 (NH_2). HRMS *m/z*: 163.99537 (M^+), calculated for $C_5H_3ClF_2N_2$ 163.99528.

4.3. 2,6-Difluoro-4-aminopyridine *25*

2,6-Difluoro-4-aminopyridine 25 (Entry 11, Table 2) was obtained in 80% yield after removal of volatile components from the crude product by sublimation at 40 °C/5 torr, mp 127.5–129 °C (125–127 °C [4]; 126–128 °C [5]).

4.4. 2,3,6-Trifluoro-4-aminopyridine *26*

2,3,6-Trifluoro-4-aminopyridine 26 (Entry 4, Table 2) was obtained in 70% yield by sublimation at 70 °C/5 torr, mp 98–99 °C (94–96 °C[5]). NMR (solution in $CDCl_3$), δ/ppm: ^{19}F (C_6F_6 int.) 87.2; 69.5; −10.7; ^1H ($CHCl_3$ int.) 6.10 (C–H), 4.90 (NH_2).

4.5. 5,7-Difluoro-8-chloroquinoline *17*

5,7-Difluoro-8-chloroquinoline 17 was obtained analogously to the procedures [30–32] from the mixture of **15** and **16**. The reaction mixture was subjected to steam distillation, the condensate was extracted by methylene chloride, the extract was dried over $MgSO_4$ and the solvent was evaporated in vacuum. After volatile components were removed from the crude product, the quinoline **17** was obtained by sublimation at 50 °C/5 torr in 70% yield, mp 143–145 °C. NMR (solution in acetone-d_6), δ/ppm: ^{19}F (C_6F_6 int.) 43.0 (dd, 1F, J = 9 Hz, J = 6 Hz, F-5) 55.8 (dd, 1F, J = 9 Hz, J = 6 Hz, F-7) (the signals were assigned according to the interpretation of 5,7-difluoroquinoline spectrum [31]); ^1H ($CHCl_3$ int., δ: 7.24) 7.55 (t, 2H, J = 9 Hz, H-6), 7.72 (dd, 1H, J = 9 Hz, J = 4 Hz, H-3); 8.55 (dd, 1H, J = 9 Hz, J = 2 Hz, H-4); 9.11 (dd, 1H, J = 4 Hz, J = 1.5 Hz, H-2). Found, %: C 54.30, H 2.25, N 6.91, Cl 17.75, F 19.19. Calculated, %: C 54.14, H 2.00, N 7.02, Cl 17.79, F 19.05. Found, *m/z*: M^+ 199.00029, calculated for $C_9H_4ClF_2N$ 199.0003.

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