Selective mono- and diamination of polyfluorinated benzenes and pyridines with liquid ammonia*

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Amination of pentafluoropyridine, 2,3,5,6-tetrafluoropyridine, 4-chlorotetrafluoropyridine, 3,5-dichlorotrifluoropyridine, octafluorotoluene, α,α,α,2,3,5,6-heptafluorotoluene, decafluoro-*m*-xylene, decafluorobiphenyl, hexafluorobenzene, and pentafluorobenzene with liquid ammonia was investigated. Bis-aminodefluorination temperatures for the majority of substrates were shown to exceed significantly the corresponding temperatures of monoaminodefluorination. The optimal conditions for selective preparation of mono- and diaminopolyfluoro(het)arenes were elucidated. An efficient method for isolation of particular polyfluorophenylenediamines from product mixtures formed in nonselective reactions of pentafluorobenzene and hexafluorobenzene with aqueous ammonia based on complexation with a crown ether is proposed.

Key words: organofluorine compounds, ammonia, aminodefluorination, polyfluorodiaminopyridines, polyfluorophenylenediamines, nucleophilic substitution.

N. N. Vorozhtsov´s school made a considerable contribution to the chemistry of polyfluoroaromatic compounds: methods for the synthesis[1] and functionalization[2,3a] of base polyfluoroarenes were developed. Currently many polyfluoroarene derivatives are demanded for high-tech processes and materials. In particular, diamino- and dihydroxy(poly)fluoroarenes serve as structural blocks in the synthesis of polyimides used in fiber-optic and thin-film light guides, nanofilters, and membranes, dielectric coatings, liquid crystalline displays, optical diodes, laser media, *etc*.[4] Polyfluorinated amines of the benzene and pyridine series are used in the synthesis of biologically active compounds.[5]

It is known[6] that aminodehalogenation of arenes in aqueous ammonia, which is usually carried out in steel autoclaves at high temperatures (up to 250 °C), is often accompanied by competing transformations of arenes such as hydroxy- and/or hydrodehalogenation involving water and the autoclave material. The version of the method of polyfluoroarene amination developed in this study implies the use of liquid ammonia as both the reagent and the reaction medium. The possibility of aminodefluorination of some polyfluoroarenes with enhanced electrophilicity in liquid ammonia has been demonstrated previously.[7] The efficiency of liquid ammonia as a medium for aromatic nucleophilic substitution has been described in a review.[8] Note that the temperatures suitable for the work with liquid ammonia are limited by the range from −70 to 120 °C (m.p. −78 °C, critical point 133 °C).[9] It follows from analysis of published data that arene aminodehalogenation in liquid ammonia has a higher rate than that in aqueous ammonia; therefore, the processes are carried out at relatively low temperatures and the side reactions are minimized.

The purpose of this study was to elucidate the conditions for mono- and diamination of polyfluorinated benzene and pyridine derivatives in liquid ammonia, which are optimal as regards the selectivity and product yield, to develop simple and practically feasible techniques for separation of mixtures of amino compounds, and to synthesize new high-purity polyfluoroaromatic diamines demanded in high-tech applications.

Results and Discussion

The first group of substrates comprises pentafluoropyridine (**1a**), 3,5-dichlorotrifluoropyridine (**2a**), 4-chlorotetrafluoropyridine (**3a**), and 2,3,5,6-tetrafluoropyridine (**4a**). According to known data,[7] in liquid NH_3 at

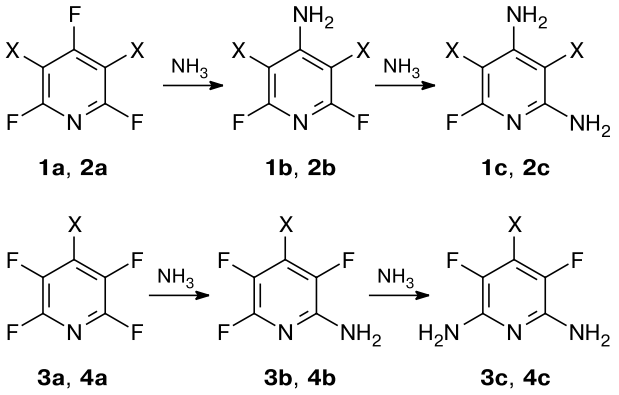
* Dedicated to the memory of Academician N. N. Vorozhtsov on the occasion of his 100th anniversary.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2163—2170, November, 2007.

–33 °C, compound **1a** is converted into 4-aminotetrafluoropyridine (**1b**). The amination of pyridines **2a**—**4a** in aqueous NH_3 or its mixture with THF at 60—100 °C results in 4-amino-3,5-dichloro-2,6-difluoropyridine (**2b**),[10] 2-amino-4-chloro-3,5,6-trifluoropyridine (**3b**),[11] and 2-amino-3,5,6-trifluoropyridine (**4b**),[11,12] respectively. According to published data,[13] two amino groups are introduced into pyridine **1a** in aqueous NH_3 at 130 °C. Note that the publications cited[10—13] present, most often, the yields of crude products (~75—90%) and describe methods for their purification but do not indicate the yields or purities of the final products. Diamination of pyridines **2a**—**4a** or their diamino derivatives have not been reported.

We found that both mono- and diamination of compounds **1a**—**4a** can be performed in liquid NH_3 (Scheme 1). The reaction conditions, the amounts of reactants, and the product yields are presented in Table 1. The introduction of an amino group in pyridine **2a**, as in pyridine **1a** (see Ref. 7), is possible at –33 °C (see Scheme 1 and Table 1). The monoamination of pyri-

Scheme 1



X = F (**1a**—**c**), Cl (**2a**—**c**, **3a**—**c**), H (**4a**—**c**)

Table 1. Reactions of polyfluoroarenes **1a**—**10a** with NH_3

Polyfluoroarene	Amounts of reactants		Reaction conditions		Reaction product		
	Substrate/g	Liquid NH_3/mL	*T*/°C	*t*[a]/h	(Di)aminopolyfluoro(het)arene	Yield of the crude product/g (purity (%))[b]	Yield of the purified product (%)
1a	8.0	50	100	15	**1c**	7.1 (>95)	81
2a	1.0	120[c]	–33	8	**2b**	0.95 (>95)	80
2a	10.0	50	60	10	**2c**	9.0 (>95)	65
3a	1.0	25	10—15	3	**3b**	0.95 (>95)	80
3a	1.0	25	110—120	10	**3c**	0.7 (>95)	60
4a	3.0	30	60	5	**4b**	2.4 (93)	78
4a	3.0	30	120	35	**4c**	2.9 (60)[d]	48
5a	100.0	300	120	48	**5c**	90.0 (>95)	80
6a	5.0	50	60	15	**6b**	4.3 (>95)	76
7a[e]	30.5	350[f]	30—40	5	**7b**	26.2 (>95)	—
7b[g]	26.2	35	60—70	6	**7c**	25.3 (>95)	56
8a	3.0	30	10—15	3	**8b**	2.8 (93)	80
8a	400.0	350[c]	70	2	**8b**	395 (88)	78
8a	5.0	30	50	6	**8c**	4.8 (>95)	80
9a	63.0	250	100	15	**9b**	60.0 (>95)	87
9a[h]	6.5	35[f]	200	6	**9c**,	5.0[i]	43
					9d		8
10a	50.0	300	100	10	**10b**	46.0 (>95)	89
10a	150.0	700[f]	220	8	**10b**,	135.0[j]	49
					10c		22

[a] Reaction time.
[b] According to ^{19}F NMR data.
[c] Dioxane was used as the co-solvent: for compound **2a**, 10 mL; for compound **8a**, 2.5 L.
[d] The crude product contains 36% of amine **4b** (GLC data).
[e] In a mixture containing *o*- (1%), *m*- (61%), *p*-decafluoroxylenes (18%), and decafluoroethylbenzene (12%) (^{19}F NMR data).
[f] Aqueous ammonia (d = 0.9 g mL^{-1}).
[g] The crude product was used for the preparation of diamine **7c** without purification.
[h] Compound **9a** was aminated by a known procedure.[3e]
[i] Composition of the crude product: diamine **9c** (84%), diamine **9d** (14%) (GLC data).
[j] Composition of the crude product: amine **10b** (72%), diamine **10c** (26%) (GLC data).

dine **3a** proceeds efficiently at 10—15 °C, whereas pyridine **2a** gives at this temperature not only monoamine **2b** but also up to 10—15% of 2,4-diamino-3,5-dichloro-6-fluoropyridine (**2c**). The least reactive pyridine **4a** reacts with liquid NH_3 at 60 °C to give monoamine **4b**. The yields of crude reaction products, monoamines **2b**—**4b**, are 80—95%, *i.e.*, they are comparable with those for reactions in aqueous NH_3. In our opinion, an important fact is that purification of crude products obtained in liquid NH_3 to ~99% purity can be easily performed by sublimation and/or a single crystallization.

Diamination of pyridines **1a**—**4a** requires higher temperature (60—120 °C) and longer reaction time. In the case of pyridines **1a**—**3a**, the reaction is selective, the purity of the crude product being, most often, >95%. 2,4-Diamino-3,5,6-trifluoropyridine (**1c**), diamine **2c**, and 2,6-diamino-4-chloro-3,5-difluoropyridine (**3c**) were obtained in 60—80% yield after recrystallization. Pyridine **4a** (120 °C, reaction time 35 h) is converted into monoamine **4b** and 2,6-diamino-3,5-difluoropyridine (**4c**) in ~1 : 2 ratio, the latter product being isolated from the mixture by crystallization.

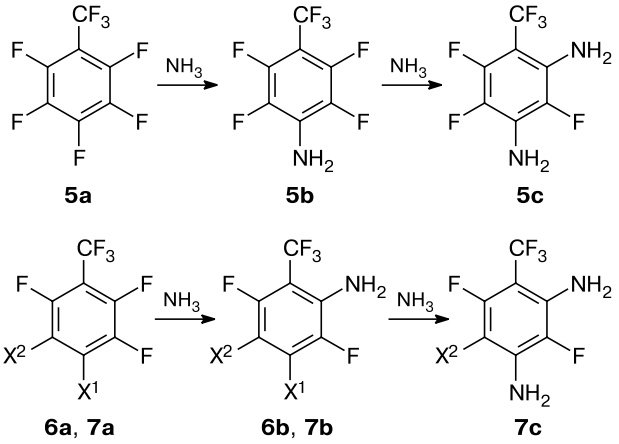
The relative reactivity of the substrates (see Table 1, *cf.* preparation conditions of monoamines **1b**,[7] **2b**—**4b** and diamines **1c**—**4c**) and the direction of mono- and bis-aminodefluorination are determined by the set of known[14,15] effects of substituents. The replacement of F atoms in the β-position by Cl atoms on going from pyridine **1a** to **2a** somewhat retards γ-aminodefluorination due to elimination of the activating effect of two F atoms in the *ortho*-position with respect to the reaction center. α-Aminodefluorination is also facilitated for pyridine **2a** owing to the absence of deactivating effect of the *para*-F atom. According to the available data,[10] nucleophilic displacement of the F atom in the γ-position of pyridine **2a** is often accompanied by the formation of some α-substituted and α,γ-disubstituted products. Nevertheless, selective mono- and diamination of pyridine **2a** is possible in liquid NH_3. The replacement of the F atom in the most reactive γ-position of pyridine **1a** by Cl or H atoms on going to pyridines **3a** and **4a** results in a change in the reaction center (γ- to α-) and substantially retards aminodefluorination due to the deactivating effect of the *para*-F atom.

The second group of substrates comprises polyfluorinated benzenes containing electron-withdrawing CF_3 or C_6F_5 groups: octafluorotoluene (**5a**), α,α,α,2,3,5,6-heptafluorotoluene (**6a**), decafluoro-*m*-xylene (**7a**), and decafluorobiphenyl (**8a**).

According to published data,[7] compound **5a** is aminodefluorinated in liquid NH_3 at −33 °C to give 2,3,5,6-tetrafluoro-4-trifluoromethylaniline (**5b**). The synthesis of 2,5,6-trifluoro-4-trifluoromethyl-1,3-phenylenediamine (**5c**) by treatment of compound **5a** with a liquid NH_3—H_2O mixture (9 : 1 v/v) at 150 °C was reported.[16] To our knowledge, these reaction conditions do not rule out hydrolysis of the trifluoromethyl group, which is probably responsible for the relatively low (48%) yield of the target compound. No spectroscopic or physical characteristics of compound **5c** were reported in the study cited,[16] except for the boiling point, although this compound was not described previously.

In this study we found that compound **5a** is bis-aminodefluorinated almost completely in liquid NH_3 at ~120 °C (Scheme 2, Table 1). The diamine **5c** thus formed was isolated with >99% purity and characterized by spectroscopy.

Scheme 2



X^1 = H, X^2 = F (**6a**,**b**); X^1 = F, X^2 = CF_3 (**7a**—**c**)

The amination of polyfluorotoluene **6a** has not been studied previously. We found that this compound is aminodefluorinated in liquid NH_3 at 60 °C to give 3,4,6-trifluoro-2-trifluoromethylaniline (**6b**) (see Scheme 2 and Table 1). More drastic amination conditions of heptafluorotoluene **6a** compared to octafluorotoluene **5a** are obviously caused by the same factors as for pyridines **4a** and **1a**. Diamination of compound **6a** in liquid NH_3 does not proceed to a noticeable extent up to 120 °C.

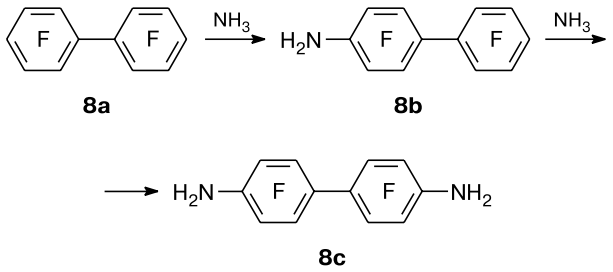
Perfluoroxylenes are most reactive toward nucleophiles; therefore, polysubstituted products are formed together with the major product.[17] Thus amination of *o*- and *p*-perfluoroxylenes with NH_3 in aqueous alcohol at 150 °C affords monoamino derivative in a moderate yield (~40—50%), which is caused, in particular, by complexity of product isolation (preparative GLC) from multicomponent mixtures. No data on amination of perfluoroxylene **7a** were found, although one paper[18] presents the ^{19}F NMR spectrum of 3,5,6-trifluoro-2,4-bis(trifluoromethyl)aniline (**7b**). Diamination of perfluoroxylenes or their diamino derivatives have not been reported.

In this study we implemented the consecutive preparation of monoamine **7b** and 2,5-difluoro-4,6-bis(tri-

fluoromethyl)-1,3-phenylenediamine (**7c**) where a mixture of perfluorinated isomeric xylenes and ethylbenzene served as the starting material.* The first stage carried out under mild conditions (aqueous NH_3, 30—35 °C) is aminaton of the most reactive component of the perfluoroarene mixture, *viz.*, perfluoroxylene **7a**, and then the unreacted perfluorinated xylenes and ethylbenzene are distilled off. The distillation residue, which is aniline **7b** according to ^{19}F NMR spectroscopy, is treated with liquid NH_3 at 60—70 °C. Double crystallization of the crude product gave diamine **7c** in a pure state in 56% yields with respect to the content of perfluoroxylene **7a** in the starting mixture (see Scheme 2 and Table 1).

Direct amination of perfluorobiphenyl **8a** with introduction of one amino group is hardly practicable due to its high reactivity toward nucleophiles. In aqueous NH_3 at 130 °C (see Ref. 19) or in liquid NH_3 at 100 °C (see Ref. 16) and even at 50 °C (Scheme 3, Table 1), this compound is diaminated, resulting in 4,4′-diaminooctafluorobiphenyl (**8c**) in 70—80% yield. The amination of compound **8a** with NH_3 in aqueous alcohol at 120 °C afforded 4-aminononafluorobiphenyl (**8b**) (97% purity) in 40% yield,[16] the reaction being arrested apparently at an incomplete conversion of the reactant. The traditional route to compound **8b** includes the reaction of nitropentafluorobenzene with pentafluorophenyllithium[20] or pentafluorophenylmagnesium bromide[21] and the subsequent reduction of 4-nitrononafluorobiphenyl.

Scheme 3

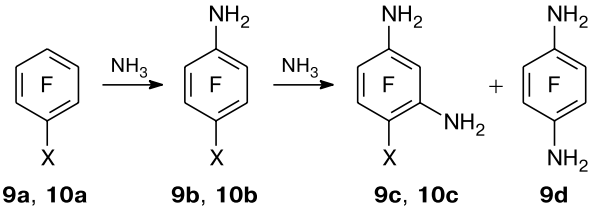


In this study we proposed two ways for monoamination of compound **8a** (see Scheme 3 and Table 1): in liquid NH_3 at 10—15 °C and in a liquid NH_3—dioxane mixture at 70 °C. The content of amine **8b** in crude products is ~90—93%; in the former case, the other component is diamine **8c**, while in the latter case, this is the starting biphenyl **8a**. In both cases, pure amine **8b** (98% purity) was isolated by crystallization in ~80% yield.

Hexafluorobenzene (**9a**) and pentafluorobenzene (**10a**) are least reactive toward aminodefluorination. It is known[3c,d] that monoamination of these substrates proceeds in aqueous NH_3 at 150—160 °C to give pentafluoroaniline (**9b**) and 2,3,5,6-tetrafluoroaniline (**10b**) in 70—75% isolated yields. According to known data,[22] amine **9b** was also prepared by treatment of compound **9a** with sodium amide in liquid NH_3 at −70 °C, but under these conditions bis(pentafluorophenyl)amine is also formed.[23]

We found that monoamination of polyfluorobenzenes **9a** and **10a** takes place in liquid NH_3 at 100 °C (Scheme 4, Table 1) to give anilines **9b** and **10b**, respectively, in high yields (87—89%) with ≥99% purity after a single distillation.

Scheme 4



X = F (**9a**—**c**), H (**10a**—**c**)

Compound **9a** is bis-aminodefluorinated[3e] in aqueous NH_3 at 200 °C to give isomers, tetrafluoro-*m*-phenylenediamine (**9c**) and tetrafluoro-*p*-phenylenediamine (**9d**) in ~85 : 15 ratio, and a minor amount of tetrafluoro-*o*-phenylenediamine. Diamine **9c** is isolated from this mixture by preparative GLC.[3e] The individual compounds **9c**,**d** can be prepared by alternative routes. Diamine **9c** is obtained (yield ~20%) from aminoiminocyclohexene (formed on treatment of decafluorocyclohexene with NH_3) by electrochemical defluorination on a mercury cathode[24] or by the action of H_2/Raney nickel.[25] The synthesis of diamine **9d** in the highest known yield (~25%) is based on catalytic ammonolysis of chloropentafluorobenzene in aqueous NH_3 in the presence of copper(I) salts.[6]

Direct diamination of compound **10a** to give 2,4,5-trifluoro-1,3-phenylenediamine (**10c**) has not been described. The preparation of **10c** by hydrodechlorination of 2,4-diamino-1-chloro-3,5,6-trifluorobenzene by treatment with Zn^0 in aqueous NH_3 was documented.[26] According to a publication,[6] compound **10c** is also formed in a mixture with other products upon the reaction of chloropentafluorobenzene with aqueous NH_3 in a steel autoclave at 200 °C.

In this study we found that diamination of benzenes **9a** and **10a** with liquid ammonia does not occur to a noticeable extent below 120 °C, while in aqueous NH_3 at ~220 °C, the conversion of pentafluorobenzene **10a** into diamine **10c** equals ~25% after 8 h. An increase in the process duration results in resinification of the reaction mixture.

* Fraction of hexafluorobenzene trifluoromethylation products obtained by analogy with the known method.[3b]

While considering extension of the scope of direct amination to be of prime importance, we developed an efficient procedure for the isolation of pure diamines from product mixtures formed in nonselective reactions of polyfluoroarenes **9a** and **10a** with aqueous ammonia. The procedure we propose is based on complexation of 18-crown-6 (host) with arylamines (guest)[27,28] and on the balance of the relative complexation abilities of polyfluorophenylenediamines, on the one hand, and the different solubilities of the complexes in organic liquids, on the other hand.

It was found that polyfluorophenylenediamines **9c**,**d** and **10c** form complexes with 18-crown-6. The complexes have limited solubility in ethers (*e.g.*, in methyl *tert*-butyl ether) and, hence, they can be obtained (precipitated) by mixing of solutions of the components. The complexes obtained in this way melt within narrow temperature ranges (1—2 °C) differing from the melting points of the precursors (diamines and the crown ether). The ratio of the integral intensities of the ^{1}H NMR signals for the NH_2 groups of diamines and for the CH_2 groups of the crown ether in solutions suggests that the component stoichiometry in the complex is close to 1 : 1. It was found that in a deficiency of the host, the complexes precipitate selectively with respect to the guest. For example, the addition of a solution of 18-crown-6 (1 mol. equiv.) to a solution of an artificial mixture of diamines **9c**,**d** and **10c** (1 mol. equiv. each) results in precipitation of mainly the complex of diamine **9d** (~80%, ^{19}F NMR data) together with complexes of diamines **9c** and **10c** (~10% each). Mixing of a solution of 18-crown-6 (1 mol. equiv.) with a solution of diamines **9c** and **10c** (1 mol. equiv. each) gives rise to a precipitate containing complexes of these compounds in 1 : 1.7 ratio, respectively. The complexes decompose quantitatively into the initial components on treatment with water; hydrophilic 18-crown-6 passes to the aqueous phase and can be recovered in a yield of at least ~98%.

On the basis of the observed trends, conditions for isolation of polyfluorophenylenediamines from product mixtures obtained upon amination of **9a** and **10a** in aqueous NH_3 were selected: **9c** (purity 97%, yield 66% relative to the content in the mixture), **9d** (purity 99%, yield 67%), and **10c** (purity 99%, yield 94%). In view of the efficiency of the described technique and the simplicity of experimental procedures and also the possibility of crown ether recovery and repeated complexation of the unseparated arene mixture, this method is of practical value.

To conclude, direct amination of a number of polyfluoro(het)arenes including pyridines, benzenes, toluenes, *m*-xylene, and biphenyl with liquid ammonia was studied. It was found that for most substrates bis-aminodefluorination takes place at much higher temperatures than monoaminodefluorination. Taking this into account, the optimal conditions for the selective preparation of new and known mono- and diamines in high yields and with high purity were found. For nonselective reactions of pentafluoro- and hexafluorobenzenes with aqueous ammonia, an effective method for isolation of individual polyfluoro-1,3- and -1,4-phenylenediamines from mixtures was developed, which opens up prospects for the use of direct amination in the synthesis of compounds of this type.

Experimental

^{1}H and ^{19}F NMR spectra were recorded on a Bruker AC-200 instrument using residual proton signals of the deuterated solvent and C_6F_6, respectively, as the internal standard. IR spectra were measured on a Vector-22 Bruker instrument for KBr pellets. UV spectra were recorded on an HP 8453 FT IR spectrometer for solutions of samples in EtOH. The mass spectra (EI, 70 eV) and exact molecular ion masses were measured on a Finnigan MAT-8200 instrument. The GLC-MS identification of components was carried out using an HP G1081A complex comprising an HP 5890 chromatograph, series II, and an HP 5971 mass selective detector. The ionization energy was 70 eV. A 30 m × 0.25 mm × 0.25 μm HP5 column (5%, biphenylsiloxane; 95%, dimethylsiloxane) and helium as the carrier gas (1 mL min^{-1}) were used. Column temperature programming mode: 2 min at 50 °C, heating at a rate of 10 °C min^{-1}, 5 min at 280 °C; temperature of the injector 280 °C; temperature of the ion source 173 °C. The data were collected at a rate of 1.2 scans s^{-1} in the region of 30—650 amu. The composition of product mixtures was established by GLC (internal normalization) on an HP 5890 instrument (katharometer as the detector); a 30 m × 0.22 mm × 2.6 μm quartz capillary column (HP5 stationary phase); helium as the carrier gas, 1 mL min^{-1}. Column temperature programming mode: 2 min at 90 °C, heating at 10 °C min^{-1} from 90 to 330 °C, maintenance at 330 °C; injector temperature 300 °C, detector temperature 320 °C. The melting points were determined on a Temp-2 instrument in an automated mode.

The following commercial chemicals were used: liquid ammonia, 28% aqueous ammonia (d = 0.9 g mL^{-1}), rectified methyl *tert*-butyl ether (MTBE) (99%). Sulfolane and dioxane were purified by a known procedure.[29] Potassium fluoride and calcium chloride were calcined immediately prior to use for 4 h at 400 °C and for 1 h at 300 °C, respectively. The fluoroplastic-4 (Teflon) chips were washed with acetone and dried for 30 min at 110—120 °C. The following compounds were prepared by published procedures: dicyclohexano-18-crown-6 (a mixture of stereoisomers),[30] 18-crown-6,[31] and α,α,α,2,3,5,6-heptafluorotoluene (**6a**).[32] Pentachloropyridine, chloropentafluorobenzene, pentafluoropyridine (**1a**), octafluorotoluene (**5a**), decafluorobiphenyl (**8a**), hexafluorobenzene (**9a**), and pentafluorobenzene (**10a**) were produced at the Pilot Chemical Plant of the Novosibirsk Institute of Organic Chemistry (Siberian Branch, Russian Academy of Sciences) by the process documents based on published procedures.[3a]

3,5-Dichlorotrifluoropyridine (2a) (*cf.* Ref. 33). A mixture of pentachloropyridine (40 g, 0.16 mol) and KF (41.6 g, 0.72 mol) in anhydrous sulfolane (100 mL) was vigorously stirred for 20 h at 145—150 °C. Using a Vigreux column (20 cm) and a condenser devoid of water cooling, the crude product was redistilled

off (26.5 g), b.p. 42—65 °C (15—20 Torr); then the product was distilled to collect the fraction with b.p. 46—51 °C (15—20 Torr). This gave pyridine **2a** (24.0 g, 73%), purity 98%, with physical parameters (d_4^{20}, n_D^{20}) identical to those reported in the literature.

4-Chlorotetrafluoropyridine (3a) (*cf.* Refs 15, 34). A mixture of pyridine **1a** (20 g, 0.12 mol), freshly calcined powdered $CaCl_2$ (20 g, 0.18 mol), and dicyclohexano-18-crown-6 (30 g, 0.08 mol) in anhydrous sulfolane (50 mL) was refluxed for 5 h with vigorous stirring. Then a fraction (19.2 g) with b.p. 100—135 °C was distilled off from the reaction mixture and fractionated on a column (25 TP) where the fraction with b.p. 122 °C was collected. This gave pyridine **3a** (16.4 g, 75%), purity 99% with physical parameters identical to those reported in the literature.

2,3,5,6-Tetrafluoropyridine (4a) (*cf.* Ref. 35). Zinc dust (50 g, 0.76 mol) and pentafluoropyridine (**1a**) (115.5 g, 0.68 mol) were added successively in portions to a vigorously stirred solution of NaOH (45 g, 1.13 mol) in water (350 mL), the temperature being maintained below 20 °C. The mixture was kept for 10 h under these conditions. Then azeotropic mixture was distilled off until organic phase was no longer formed in the distillate. The organic layer was separated from the aqueous layer and dried over $MgSO_4$ to give pyridine **4a** (65 g, 63%), purity 99%, b.p. 100—101 °C, the physical parameters were identical to those reported in the literature.

Pentafluorobenzene (10a) (*cf.* Ref. 3f). Zinc dust (20 g, 0.31 mol) and pentafluorochlorobenzene (42.9 g, 0.24 mol) were added successively to a vigorously stirred solution of NaOH (11 g, 0.28 mol) in water (350 mL). The mixture was refluxed for 10 h with continuous stirring. Then azeotropic mixture was distilled off until organic phase was no longer formed in the distillate. The organic layer was separated from the aqueous layer and dried over anhydrous $CaCl_2$ to give a mixture of polyfluoroarenes (36.5 g), which was fractionated on a column (25 TP) to collect the fraction with b.p. 84—86 °C to give compound **10a** (25.8 g, 65%), purity 99%, with physical parameters identical to those reported in the literature.

A mixture of perfluorinated xylenes and ethylbenzene (*cf.* Ref. 3b). Hexafluorobenzene **9a** (220 g, 1.18 mol) and Teflon (fluoroplastic-4) chips (100 g) were placed in a 2-L steel autoclave. The autoclave was sealed, heated to 540 °C with stirring of the reaction mixture by the rotation, and maintained under these conditions for 8 h. A metallic downflow condenser was connected to the autoclave valve and the mixture of volatile (below 500 °C) compounds was distilled off into a receiving vessel under a water bed, while the flowrate of the vapor mixture to the condenser was controlled using the valve. The organic layer (200 g) was separated and dried over $MgSO_4$. The organic mixture was fractionated on a column (25 TP) to give a fraction (40 g, 12%) with b.p. 122—128 °C. According to GLC-MS data, this was a mixture of perfluorinated *m*- (**7a**), *p*-, and *o*-xylenes and ethylbenzene in 61 : 18 : 1 : 12 ratio, respectively.

Amination of polyfluoro(het)arenes with liquid NH_3 (general procedure). Polyfluoro(het)arene was placed into a steel autoclave with a volume ~1.5 times greater than the total volume of the reactants. The required amount of liquid NH_3 was added through a measuring funnel with back pressure and the autoclave was sealed. The reaction mixture was stirred by rotation of the autoclave, heated to a specified temperature, and kept for a specified period of time. After completion of the reaction, the autoclave was cooled and gaseous NH_3 was slowly vented through the pressure release valve. The reaction mixture was extracted 2 or 3 times with CH_2Cl_2, the combined extract was dried over $MgSO_4$, and the extractant was evaporated to give the crude product, which was then purified. The reactant amounts, the reaction conditions, and product yields are presented in Table 1.

2,4-Diamino-3,5,6-trifluoropyridine (1c) was purified by crystallization from a benzene—hexane mixture (1 : 1 v/v), purity 99%, m.p. 114—116 °C (*cf.* Ref. 13: m.p. 111—112 °C).

4-Amino-3,5-dichloro-2,6-difluoropyridine (2b) was purified by crystallization from CCl_4, purity 99%, m.p. 113—114 °C (*cf.* Ref. 10: m.p. 112—113 °C).

2,4-Diamino-3,5-dichloro-6-fluoropyridine (2c) was purified by crystallization from CH_2Cl_2, purity 99%, m.p. 137—139 °C. UV, λ_{max}/nm (logε): 219 (1.3), 283 (0.1). IR, ν/cm^{-1}: 3458, 3357, 3295, 3185 (NH_2). ^{1}H NMR ($CDCl_3$), δ: 4.89, 5.14 (both br.s of equal intensity, C(4)NH_2, C(2)NH_2). ^{19}F NMR ($CDCl_3$), δ: 85.8 (s, F(6)). MS, *m/z* (I_{rel} (%)): 199 $[M]^+$ (10), 197 $[M]^+$ (63), 195 $[M]^+$ (100), 175 $[M - HF]^+$ (15), 168 $[M - HCN]^+$ (17). High-resolution MS, found: *m/z* 194.9764 $[M]^+$. $C_5H_4Cl_2FN_3$. Calculated: M = 194.9766.

2-Amino-4-chloro-3,5,6-trifluoropyridine (3b) was purified by sublimation, purity 99%, m.p. 123.5—125 °C (from CCl_4) (*cf.* Ref. 15: m.p. 117—117.5 °C). GLC-MS, *m/z*: 182 $[M]^+$.

2,6-Diamino-4-chloro-3,5-difluoropyridine (3c) was purified by crystallization from CCl_4, purity 99%, m.p. 145—146 °C (from CCl_4). UV, λ_{max}/nm (logε): 229 (0.7), 324 (0.9). IR, ν/cm^{-1}: 3446, 3357, 3301, 3171 (NH_2). ^{1}H NMR ($CDCl_3$), δ: 4.28 (br.s, C(2)NH_2, C(6)NH_2). ^{19}F NMR ($CDCl_3$), δ: 6.6 (s, F(3), F(5)). MS, *m/z* (I_{rel} (%)): 181 $[M]^+$ (32), 179 $[M]^+$ (100), 152 $[M - HCN]^+$ (55), 117 $[M - HCN - Cl]^+$ (18), 97 $[M - Cl - F - CNH_2]^+$ (19), 43 $[C_2F]^+$ (34). High-resolution MS, found: *m/z* 179.0065 $[M]^+$. $C_5H_4ClF_2N_3$. Calculated: M = 179.0062.

2-Amino-3,5,6-trifluoropyridine (4b) was purified by sublimation, purity 99%, m.p. 98—99 °C (*cf.* Ref. 11: m.p. 96—97 °C).

2,6-Diamino-3,5-difluoropyridine (4c) was purified by crystallization from CCl_4, purity 99%, m.p. 157—159 °C (from CCl_4). UV, λ_{max}/nm (logε): 227 (0.5), 324 (0.6). IR, ν/cm^{-1}: 3438, 3396, 3329, 3203 (NH_2); 3090 (C arom.—H). ^{1}H NMR ($(CD_3)_2CO$), δ: 5.08 (br.s, 4 H, C(2)NH_2, C(6)NH_2); 7.14 (t, 1 H, H(4), J = 10.0 Hz). ^{19}F NMR ($(CD_3)_2CO$), δ: 10.3 (d, 2 F, F(3), F(5), J = 10.0 Hz). MS, *m/z* (I_{rel} (%)): 145 $[M]^+$ (100), 118 $[M - HCN]^+$ (41), 117 $[M - CNH_2]^+$ (15). High-resolution MS, found: *m/z* 145.0451 $[M]^+$. $C_5H_5F_2N_3$. Calculated: M = 145.0452.

2,5,6-Trifluoro-4-trifluoromethyl-1,3-phenylenediamine (5c) was purified by crystallization from pentane, purity 99%, m.p. 31.5—32.5 °C. UV, λ_{max}/nm (logε): 214 (0.9), 235 (0.3), 291 (0.1). IR, ν/cm^{-1}: 3534, 3441, 3333, 3212 (NH_2). ^{1}H NMR ($CDCl_3$), δ: 4.08, 4.16 (both br.s of equal intensity, C(1)NH_2, C(3)NH_2). ^{19}F NMR ($CDCl_3$), δ: −9.2 (dd, 1 F, F(6), J = 20.0 Hz, J = 3.5 Hz); 1.5 (dd, 1 F, F(2), J = 10.0 Hz, J = 3.5 Hz); 15.9 (m, 1 F, F(5)); 107.4 (d, 3 F, CF_3, J = 23.0 Hz). MS, *m/z* (I_{rel} (%)): 230 $[M]^+$ (100), 211 $[M - F]^+$ (35), 210 $[M - HF]^+$ (89), 183 $[M - F - CNH_2]^+$ (30), 145 $[M - F - CNH_2 - F_2]^+$ (63). High-resolution MS, found: *m/z* 230.0294 $[M]^+$. $C_7H_4F_6N_2$. Calculated: M = 230.0279.

3,4,6-Trifluoro-2-trifluoromethylaniline (6b) was purified by fractional distillation, purity 98%, b.p. 128—132 °C. UV, λ_{max}/nm (logε): 228 (1.8), 309 (1.2). IR, ν/cm^{-1}: 3542, 3440 (NH_2); 3083 (C arom.—H). ^{1}H NMR ($(CD_3)_2CO$), δ: 5.08 (br.s, 2 H, NH_2); 6.24—6.45 (m, 1 H, H(5)). ^{19}F NMR ($(CD_3)_2CO$),

δ: 11.2 (ddd, 1 F, F(4), J = 21.0 Hz, J = 9.5 Hz, J = 1.5 Hz); 17.3 (m, 1 F, F(3)); 28.6 (ddd, 1 F, F(6), J = 9.5 Hz, J = 9.0 Hz, J = 1.5 Hz); 107.0 (d, 3 F, CF_3, J = 23.0 Hz). MS, m/z (I_{rel} (%)): 215 $[M]^+$ (82), 196 $[M - F]^+$ (43), 195 $[M - HF]^+$ (100), 168 $[M - F - CNH_2]^+$ (82), 130 $[M - F - CNH_2 - F_2]^+$ (29). High-resolution MS, found: m/z 215.0169 $[M]^+$. $C_7H_3F_6N$. Calculated: M = 215.0170.

4-Amininonafluorobiphenyl (8b) was purified by crystallization from $CHCl_3$, purity 98%, m.p. 143—144 °C (*cf.* Ref. 22: m.p. 144.5—145 °C).

4,4′-Diaminooctafluorobiphenyl (8c) was purified by crystallization from benzene, purity 98%, m.p. 179—181 °C (*cf.* Ref. 3g: m.p. 174—175.5 °C; *cf.* Ref. 21: m.p. 181—181.5 °C).

Pentafluoroaniline (9b) was purified by distillation, purity 99%, m.p. 34.5—35.5 °C (from hexane) (*cf.* Ref. 3c: m.p. 33—34 °C).

2,3,5,6-Tetrafluoroaniline (10b) was purified by distillation, purity 99%, m.p. 31—32 °C (from hexane) (*cf.* Ref. 3d: m.p. 31—32 °C).

4,6-Bis(trifluoromethyl)-2,5-difluoro-1,3-phenylenediamine (7c). A mixture of perfluoroxylene isomers and ethylbenzene obtained by above-described procedure (50.0 g, content of xylene **7a**, 30.5 g (0.11 mol)) and aqueous NH_3 (350 mL) were charged in a 500-mL autoclave. The autoclave was sealed, heated with stirring to 30—35 °C, and kept for 5 h under these conditions. After completion of the reaction, the reaction mixture was taken off from the autoclave and separated into organic and aqueous layers. The aqueous layer was extracted with CH_2Cl_2 (4×100 mL), and the extract was combined with the organic layer and dried over $MgSO_4$. The extractant and the unreacted perfluoroxylenes and ethylbenzene were distilled off to b.p. 128 °C to leave a residue (26.2 g) representing amine **7b** (>95%, ^{19}F NMR data). The residue was aminated in liquid ammonia by the general procedure (see above). The conditions and reactant amounts are presented in Table 1. The reaction gave diamine **7c,** which was purified by double crystallization from hexane, purity 99%, m.p. 67—68 °C. UV, λ_{max}/nm (log ε): 227 (2.9), 248 (1.1), 290 (0.2). IR, ν/cm^{-1}: 3558, 3450 (NH_2). ^{1}H NMR ($CDCl_3$), δ: 4.63 (br.s, C(1)NH_2, C(3)NH_2). ^{19}F NMR ($CDCl_3$), δ: −0.5 (d, 1 F, F(2), J = 11.0 Hz); 43.6 (sept, 1 F, F(5), J = 25.0 Hz, J = 11.0 Hz); 107.5 (d, 3 F, CF_3, J = 25.0 Hz). MS, m/z (I_{rel} (%)): 280 $[M]^+$ (100), 261 $[M - F]^+$ (47), 260 $[M - HF]^+$ (68), 240 $[M - 2\,HF]^+$ (73), 232 $[M - HF - CNH_2]^+$ (22), 213 $[M - F - HF - CNH_2]^+$ (40). High-resolution MS, found: m/z 280.0229 $[M]^+$. $C_8H_4F_8N_2$. Calculated: M = 280.0247.

Complex of diamine 9c and 18-crown-6. A solution of 18-crown-6 (0.55 g, 2.0 mmol) in MTBE (3 mL) was added to a solution of phenylenediamine **9c** (0.35 g, 1.9 mmol) in MTBE (5 mL) and the mixture was kept for 1 h at ~20 °C. The precipitate was filtered off, washed with a small amount of MTBE, and dried in air to a constant weight. The yield of the complex was 0.6 g (70%, **9c** : 18-crown-6 = 1 : 1), m.p. 89.5—90.5 °C (from CCl_4). ^{1}H NMR ($CDCl_3$), δ: 3.62 (br.s, 24 H, CH_2); 3.79 (br.s, 4 H, NH_2). ^{19}F NMR ($CDCl_3$), δ: −9.9 (m, 2 F, F(4), F(6)); −6.4 (m, 1 F, F(5)); 1.8 (m, 1 F, F(2)).

Complex of diamine 9d and 18-crown-6. A solution of 18-crown-6 (0.3 g, 1.1 mmol) in MTBE (1 mL) was added to a solution of phenylenediamine **9d** (0.2 g, 0.8 mmol) in MTBE (1 mL), and the mixture was kept for 1 h at ~20 °C. The precipitate was filtered off, washed with a small amount of MTBE, and dried in air to a constant weight. The yield of the complex was 0.45 g (91%, **9d** : 18-crown-6 = 1 : 1), m.p. 131—132 °C (from CCl_4). ^{1}H NMR ($CDCl_3$), δ: 3.59 (br.s, 4 H, NH_2); 3.66 (br.s, 24 H, CH_2). ^{19}F NMR ($CDCl_3$), δ: 0.8 (s, F(2), F(3), F(5), F(6)).

Complex of diamine 10c and 18-crown-6. A solution of 18-crown-6 (0.5 g, 1.9 mmol) in MTBE (1 mL) was added to a solution of phenylenediamine **10c** (0.3 g, 1.85 mmol) in MTBE (1 mL), and the mixture was kept for 1 h at ~20 °C. The precipitate was filtered off, washed with a small amount of MTBE, and dried in air to a constant weight. The yield of the complex was 0.6 g (76%, **10c** : 18-crown-6 = 1 : 1), m.p. 94—95 °C (from CCl_4). ^{1}H NMR ($CDCl_3$), δ: 3.62 (br.s, 24 H, CH_2); 3.86, 4.00 (both br.s, 2 H each, NH_2); 5.84—5.98 (m, 1 H, H(4)). ^{19}F NMR ($CDCl_3$), δ: −8.7 (m, 1 F, F(4)); 2.2 (m, 1 F, F(2)); 17.3 (m, 1 F, F(5)).

2,3,5,6-Tetrafluoroaniline (10b) and **2,4,5-trifluoro-1,3-phenylenediamine (10c)**. Pentafluorobenzene **10a** (150.0 g, 0.9 mol) and aqueous NH_3 (350 mL) were placed in a 1.5-L autoclave. The autoclave was sealed and heated with stirring to 220—230 °C and the mixture was kept for 8 h under these conditions. After completion of the reaction and cooling of the autoclave, the reaction mixture was taken off and separated into the organic and aqueous layers. The aqueous layer was extracted with CH_2Cl_2 (6×50 mL), the extract was combined with the organic layer and dried over $MgSO_4$, and the extractant was distilled off to give crude product (135.0 g) comprising aniline **10b** and phenylenediamine **10c** in ~3 : 1 ratio (GLC data). Aniline **10b** was distilled off as the fraction with b.p. 146—147 °C (82 g); crystallization of this fraction from petroleum ether gave aniline **10b** (71.4 g, 49% in relation to pentafluorobenzene **10a**), m.p. 31—32 °C. The heavy residue was distilled *in vacuo* to collect a fraction (35.6 g) with b.p. 90—100 °C (2 Torr) comprising, according to GLC, aniline **10b** and phenylenediamine **10c** in 5 : 95 ratio. This was used to isolate phenylenediamine **10c**.

A solution of 18-crown-6 (60.0 g, 0.23 mol) in MTBE (60 mL) was added to a solution of the obtained mixture of aniline **10b** and phenylenediamine **10c** (35.0 g, 0.19 mol) in MTBE (60 mL) and the mixture was kept for 2 h at ~20 °C. The precipitate was filtered off, washed with MTBE, and dried in air to a constant weight to give complex of diamine **10c** with 18-crown-6 (84.2 g). The complex was mixed with water (200 mL) by shaking occasionally over a period of 15 min. Diamine **10c** was extracted with MTBE (3×50 mL), the combined extract was washed with a small amount of water and dried over $MgSO_4$, and the extractant was distilled off to give phenylenediamine **10c** (31.5 g, 22% in relation to pentafluorobenzene **10a**), purity 99%, m.p. 71—72 °C (*cf.* Ref. 6: m.p. 68—68.5 °C).

Recovery of 18-crown-6. Aqueous solutions were combined and extracted with CH_2Cl_2 (6×50 mL), the extract was dried over $MgSO_4$, and the solvent was distilled off to give 18-crown-6 (58.8 g, 98%), purity 98%.

Tetrafluoro-*m*-phenylenediamine (9c) and **tetrafluoro-*p*-phenylenediamine (9d)**. A solution of 18-crown-6 (1.5 g, 6 mmol) in MTBE (10 mL) was added to a solution of a mixture of compounds **9c** and **9d** (5.0 g, 30 mmol, ~85 : 15, respectively) prepared by a reported procedure[3e] in MTBE (20 mL) and the mixture was kept for 2 h at ~20 °C. The precipitated complexes of phenylenediamines **9c** and **9d** with 18-crown-6 (2.1 g) were filtered off and washed on the filter with a small amount of MTBE. The filtrate was concentrated to half of the initial

volume and a solution of 18-crown-6 (1.0 g, 4 mmol) in MTBE (6 mL) was added. The precipitate (1.4 g) was filtered off and combined with the precipitate obtained previously. The filtrate was washed with water (4×15 mL), the organic layer was separated and dried over anhydrous $MgSO_4$, and MTBE was distilled off. From the filtrate, phenylenediamine **9c** was isolated (2.9 g, 66% in relation to the content in the initial mixture), purity 97%, m.p. 132—134 °C (*cf.* Ref. 24: m.p. 127—128 °C; *cf.* Ref. 3e: m.p. 132—132.5 °C).

The combined precipitates of the complexes (3.5 g) were shaken with a mixture of MTBE (30 mL) and water (30 mL). The organic layer was washed with water (4×15 mL) and dried over $MgSO_4$, and MTBE was distilled off to give a mixture of diamines **9c** and **9d** (1.4 g, 8 mmol) in 3 : 7 ratio. A solution of 18-crown-6 (0.7 g, 3.5 mmol) in MTBE (3 mL) was added to a solution of this mixture in MTBE (5 mL) to give the complex of individual phenylenediamine **9d** and 18-crown-6 (1.3 g), which was decomposed as described above to give phenylenediamine **9d** (0.5 g, 67% in relation to the content in the initial mixture), purity 99%, m.p. 145—146 °C (*cf.* Ref. 6: m.p. 142—144 °C).

The authors are grateful to the staff of the Novosibirsk Center STN International for the assistance in the search through electronic databases.

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Received February 9, 2007;
in revised form June 1, 2007