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Catalytic and Noncatalytic Ammonolysis of Polyfluorinated 1,3-Dichlorobenzenes*

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Abstract—Reactions of 1,3-dichlorotetrafluorobenzene and 1,3-dichloro-2,4,6-trifluorobenzene with aqueous ammonia in the presence and in the absence of copper(I) salt lead to fluorine replacement by amino group in the *para* and *ortho* positions with respect to the chlorine atom. Ammonolysis of the resulting chloropolyfluoroanilines in the absence of a catalyst involves replacement of fluorine atom in the *meta* position with respect to the amino group. In the presence of copper(I) salt, catalytic aminodechlorination occurs at the *para* and *ortho* positions with respect to the amino group introduced in the first stage.

Reactions of polyhalogenated arenes with ammonia and amines provide a general procedure for synthesizing polyfluorinated aromatic amines and diamines [1–4]. If a substrate contains other halogen atoms in addition to fluorine, replacement of the latter occurs [1, 2]. For example, ammonolysis of pentafluorohalobenzenes gives rise mainly to the corresponding 4-halotetrafluoroanilines [1, 2]. In the subsequent ammonolysis, the amino group in the primary substitution products (polyfluoroanilines) behaves as a *meta*-orienting group, leading to formation of the corresponding *meta*-phenylenediamines. Treatment of hexafluorobenzene or pentafluoroaniline with aqueous ammonia gives mainly tetrafluoro-1,3-phenylenediamine (~90%) [3], while from 4-chlorotetrafluoroaniline 4-chlorotrifluoro-1,3-phenylenediamine is obtained [4]. Thus polyfluorinated *para*- and *ortho*-phenylenediamines are almost inaccessible via the above reaction. This considerably narrows the scope of application of ammonolysis of polyfluoroarenes as a route to polyfluorophenylenediamines which are very promising reagents for fine organic synthesis. Therefore, it becomes important to study the synthetic potential of catalytic ammonolysis as applied to polyfluorohalobenzenes. It is known that in the ammonolysis of halofluorobenzenes in the presence of a catalyst "heavier" halogen atoms are more labile than fluorine [5]. Such a study is also important from the viewpoint of extending the scope of application of fairly readily accessible chloropolyfluorobenzenes which are concomitant products in the synthesis of hexafluorobenzene from hexachlorobenzene [6]. With chloropentafluorobenzene as an example [4] we previously showed that the first stage of the ammonolysis in the absence of a catalyst and in the presence of copper(I) chloride is replacement of fluorine atom. As a result, introduction of amino group into the *para* or *ortho* position with respect to chlorine change the ratio of rates of concurrent processes in the second stage of ammonolysis to the reverse, namely in favor of catalytic replacement of chlorine. Thus a new procedure for preparation of 2,3,5,6-tetrafluoro-1,4-phenylenediamine appears. With the above in mind, a question arises so as to whether the observed effect is general for the ammonolysis of polyfluorinated chlorobenzenes and how its application scope can be extended in order to obtain polyfluorinated phenylenediamines.

In the present work we studied the ammonolysis of 1,3-dichlorotetrafluorobenzene (**I**) and 1,3-dichloro-2,4,6-trifluorobenzene (**II**) in the absence of a catalyst and in the presence of copper(I) salt with the goal of comparing the results with those obtained previously while studying the ammonolysis of chloropentafluorobenzene [4]. In the first case, the substrate was

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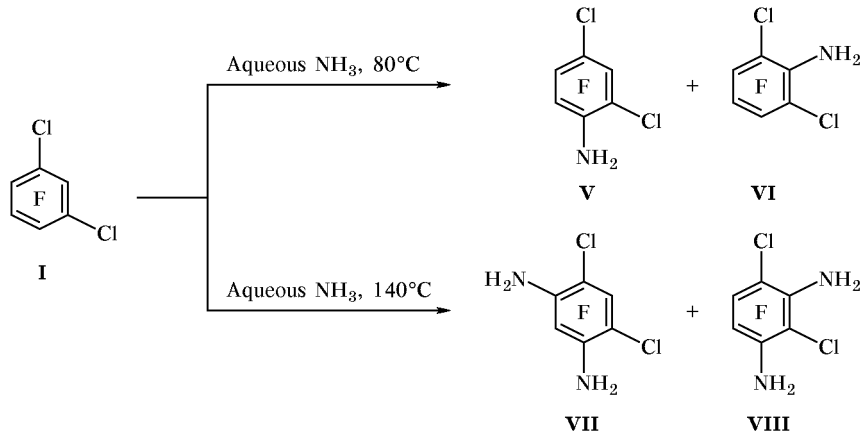
Scheme 1.



a mixture of isomers formed by reaction of hexachlorobenzene with potassium fluoride [6]; according to the GLC data, it contained 67% of compound **I**, 20% of 1,2-dichlorotetrafluorobenzene (**III**), and 10% of 1,4-dichlorotetrafluorobenzene (**IV**). The reaction mixtures and products isolated by column chromatography were analyzed by GLC, GC–MS, and ^{19}F and ^{1}H NMR. The experimental results are summarized in Table 1, and Table 2 contains the ^{19}F and ^{1}H NMR parameters of the products.

1,3-dichlorotetrafluorobenzene (**I**) reacted with aqueous ammonia at 80°C under pressure (reaction time 48 h) to give 2,4-dichloro-3,5,6-trifluoroaniline (**V**) with a small impurity of 2,6-dichloro-3,4,5-trifluoroaniline (**VI**) (ratio 12 : 1; Scheme 1; Table 1, run no. 1). Amine **V** was synthesized previously in 80% yield by the action of ammonia on difficultly accessible compound **I** in aqueous ethanol at 180°C [8]. In our case, the lower yield of **V** (50%) is fully compensated by the use as starting material of an accessible mixture of dichlorotetrafluorobenzenes. When the same reaction was carried out at 140°C (48 h), a 3 : 1 mixture of 4,6-dichloro-2,5-difluoro-1,3-phenylenediamine (**VII**) and 2,4-dichloro-5,6-difluoro-1,3-phenylenediamine (**VIII**) was obtained (Scheme 1; Table 1, run no. 2). Separation of this mixture by column chromatography gave a fraction containing previously unknown diamine **VII** with an impurity of isomer **VIII** (ratio 5 : 1); their elemental composition and molecular weight was determined by high-resolution mass spectrometry. The ^{19}F NMR chemical shifts of compounds **VII** and **VIII** are very consistent with those calculated by the additivity scheme using the corresponding increments [7] (Table 2). In all

Table 1. Noncatalytic and catalytic ammonolysis of 1,3-dichlorotetrafluorobenzene (**I**) and 1,3-dichloro-2,4,6-trifluorobenzene (**II**) (48 h, 60 ml of 30% aqueous ammonia)

Run no.	Substrate (3 g)	Temperature, °C	Molar ratio **I**(**II**) : CuCl	Product weight, g	Product composition (mol %, GLC data)
1[a]	**I**	80	–	2.9	**I** (6), **III** (9), **IV** (5), **V** (60), **VI** (5), **VII** (1), **XIX** (6)
2[a]	**I**	140	–	2.9	**I** (1), **V** (2), **VI** (5), **VII** (53), **VIII** (16), **XIX** (12), unidentified (6)
3[a]	**I**	80	1 : 1	2.9	**I** (6), **III** (10), **IV** (7), **V** (55), **VI** (5), **XIX** (6)
4[a]	**I**	140	1 : 1	1.9	**IX** (24), **X** (23), **XI** (8), **XII** (9)
5[b]	**II**	100	–	2.9	**XIII** (75), **XIV** (13), **XV** (4)
6[b]	**II**	150	–	2.6	**XIII** (10), **XV** (76)
7[b]	**II**	100	1 : 1	2.5	**XIII** (53), **XIV** (11), **XV** (4)
8[b]	**II**	150	1 : 1	1.0	**XVI** (46), **XVII** (18), **XVII** (9)

[a] A mixture containing 67% of **I**, 20% of its *ortho* isomer **III**, and 10% of *para* isomer **IV** was used (GLC).
[b] A mixture containing 90% of **II** was used (GLC).

Table 2. NMR spectra of polyfluorinated aromatic amines **V**–**XIX** (acetone-d_6, c = 20%)

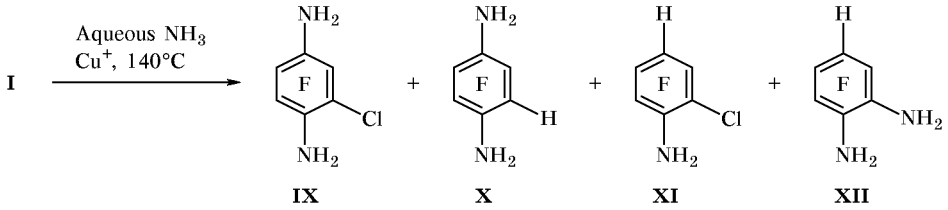
Comp. no.	^{19}F NMR spectrum, δ_F, ppm (J, Hz)		^{1}H NMR spectrum, δ, ppm (J, Hz)
	experimental	calculated[a]	
V	42.1 (3-F), 22.5 (5-F), 3.3 (6-F), (F–*o*-F 22, F–*p*-F 8, F–*m*-F ≤ 1)	3-F 43.8, 5-F 23.3, 6-F 1.2	5.81 (2H, NH_2)
VI	26.5 (3-F, 5-F), –10.5[b] (4-F), (F–*o*-F 22, F–*m*-F ≤ 1)	3-F, 5-F 23.3, 4-F 0.2	5.65 (2H, NH_2)
VII	6.5 (2-F), 40.3 (5-F), (F–*p*-F 9)	2-F 4.0, 5-F 40.2	5.12 (2H, NH_2)
VII[c]	4.5 (2-F), 40.0 (5-F), (F–*p*-F 9)	2-F 4.0, 5-F 40.2	4.00 (4H, $2NH_2$)
VIII	21.6 (5-F), –6.1 (6-F), (F–*o*-F 21)	5-F 21.0, 6-F –7.0	5.25 (2H, NH_2)
VIII[c]	21.2 (5-F), –6.6 (6-F), (F–*o*-F 21)	5-F 21.0, 6-F –7.0	4.25 (2H, NH_2)
IX	24.2 (2-F), 5.8 (5-F), 1.2 (6-F), (F–*o*-F 20, F–*m*-F 9, F–*p*-F 9)	3-F 23.1, 5-F 3.9, 6-F –1.1	4.43 (2H, NH_2), 4.68 (2H, NH_2)
X	–2.0 (2-F), 6.9 (3-F), 25.8 (5-F), (F–*p*-F 10, F–*o*-F 19, F–*m*-F 9, H–*p*-F 2, H–*o*-F 10, H–*m*-F 8)	2-F –3.2, 3-F 6.3, 5-F 25.8	6.86 m (H_{arom}), (H–*p*-F 2, H–*o*-F 10, H–*m*-F 8), 4.58 (2H, NH_2), 4.91 (2H, NH_2)
XI	45.0 (3-F), 25.0 (5-F), 1.2 (6-F), (F–*p*-F 10, F–*o*-F 19, F–*m*-F ≤ 1, H–*o*-F 10.5, H–*o*-F 9.5, H–*m*-F 7)	3-F 46.2, 5-F 27.0, 6-F –0.9	6.61 m (H_{arom}), (H–*o*-F 10.5, H–*o*-F 9.5, H–*m*-F 7), 5.65 (2H, NH_2)
XI[c]	44.0 (3-F), 24.6 (5-F), 0.2 (6-F), (F–*p*-F 11, F–*o*-F 20, F–*m*-F 3, H–*o*-F 8.5, H–*o*-F 10, H–*m*-F 6.5)	3-F 46.2, 5-F 27.0, 6-F –0.9	6.38 m (H_{arom}), (H–*o*-F 10, H–*o*-F 8.5, H–*m*-F 6.5), 4.37 (2H, NH_2)
XII	–2.1 (3-F), 14.2 (4-F), 24.6 (6-F), (F–*p*-F 11, F–*o*-F 22, F–*m*-F 2, H–*o*-F 10, H–*m*-F 7)	3-F –3.2, 4-F 14.8, 6-F 25.8	6.37 m (H_{arom}), (2H–*o*-F 10, H–*m*-F 7), 3.4 (2H, NH_2), 3.4 (2H, NH_2)
XIII[c]	46.2 (3-F), 49.0 (5-F), (H–*p*-F not determined; H–*o*-F 9)	3-F 49.9, 5-F 50.2	6.32 d (H_{arom}), (H–*o*-F 9, H–*p*-F not determined), 4.31 (2H, NH_2)
XIV[c]	48.8 (3-F, 5-F), (F–*m*-F ≤ 3, H–*o*-F 9)	3-F, 5-F 50.2	6.42 t (H_{arom}), (2H–*o*-F 9), 4.71 (2H, NH_2)
XV[c]	44.85 (5-F), (H–*o*-F 11)	5-F 51.7	6.03 d (H_{arom}), (H–*o*-F 11), 4.49 (2H, NH_2), 4.06 (2H, NH_2)
XVI	31.06 (3-F), 40.19 (5-F), (F–*m*-F ≤ 3, H–*o*-F 10)	3-F 32.2, 5-F 40.7	6.24 m (H_{arom}), 3.71 (2H, NH_2), 3.04 (2H, NH_2)
XVII	31.10 (2-F, 6-F), (F–*m*-F ≤ 3, H–*o*-F 10)	2-F, 6-F 32.2	6.17 d.d (H_{arom}), (H–*o*-F 10, H–*m*-H 2), 3.40 (2H, NH_2), 3.27 (2H, NH_2)
XVIII	46.53 (5-F), (2H–*o*-F 10)	5-F 49.3	5.91 t (H_{arom}), (2H–*o*-F 10, H–*m*-H 1), 4.05 (4H, $2NH_2$)
XIX	28.1 (2-F), 21.7 (5-F), –6.6 (6-F), (F–*p*-F 8, F–*o*-F 21, F–*m*-F 12)	2-F 25.4, 5-F 19.3, 6-F 6.2	5.59 (2H, NH_2)

[a] The increments for calculations by the additivity scheme were taken from [7].

[b] In some cases, the difference between the calculated and experimental chemical shifts of the fluorine atom in the *meta* position with respect to the amino group can be minimized using other increments (see [4]).

[c] The spectra were recorded in $CDCl_3$.

Scheme 2.



cases the reaction mixtures also contained amines formed by ammonolysis of isomers of **I**, which were present in the initial compound (see above; Table 1).

Comparison of the monoamine and diamine ratios **V**:**VI** and **VII**:**VIII** indicates that the most part of diamine **VIII** is formed from amine **V**. The ratios of amines **V** and **VI** and diamines **VII** and **VIII**, the first of which considerably exceeds the *para*:*ortho* ratio (3) in the ammonolysis of chloropentafluorobenzene [4], suggest that the rate of fluorine replacement by amino group in the *para* position with respect to the chlorine atom is generally higher than the rate of fluorine replacement in the *ortho* position. This conclusion is consistent with the compositions of products formed by reactions of a mixture of isomeric dichlorotetrafluorobenzenes with various amines in dimethylformamide [9].

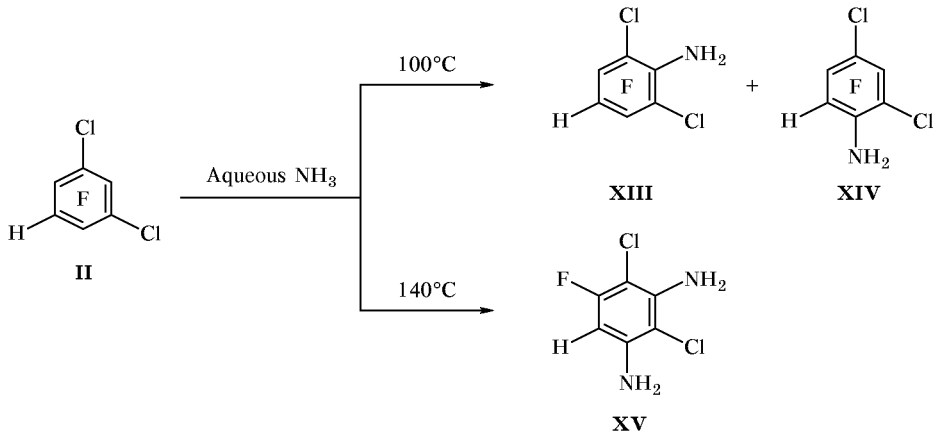
The reaction of **I** with aqueous ammonia in the presence of copper(I) chloride at 80°C (Table 1, run no. 3) gave a mixture of almost the same compounds as in the ammonolysis of **I** in the absence of a catalyst (Table 1; cf. runs nos. 1 and 3). These results indicate that copper(I) chloride does not affect the orientation of monoaminodehalogenation of **I**; an analogous pattern was observed in the ammonolysis of chloropentafluorobenzene [4]. However, when the reaction in the presence of CuCl was carried out at 140°C (Scheme 2; Table 1, run no. 4), a mixture of 2-chloro-3,5,6-trifluoro-1,4-phenylenediamine (**IX**), 2,3,5-trifluoro-1,4-phenylenediamine (**X**), 2-chloro-3,5,6-trifluoroaniline (**XI**), and previously described [10] 3,5,6-trifluoro-1,2-phenylenediamine (**XII**) at a ratio of 3:3:1:1 was obtained. By column chromatography we isolated diamine **IX** (yield 19%), amine **XI** (yield 12%), and a mixture of phenylenediamines **X** and **XII** (yield 60%).

As noted above, the calculated chemical shifts of fluorine nuclei in diamines **IX**, **X**, and **XII** agree well with those observed in the experimental ^{19}F NMR spectra but differ appreciably from those expected for isomeric compounds. The fine structure of signals in the ^{19}F and ^{1}H NMR spectra also corresponds to the assumed structures (Table 2). By contrast, it was impossible to choose between structure **XI** and isomeric 4-chloro-2,3,5-trifluoroaniline for the product with *m*/*z* 181 ($[M]^+$) present in the reaction mixture on the basis of ^{19}F NMR data. The calculated δ_F values (–0.9, 26.7, and 46.2 ppm for 4-chloro-2,3,5-trifluoroaniline; cf. δ_F values given in Table 2 for amine **XI**) are almost similar. However, the ^{1}H signal is split with two similar coupling constants which correspond to fluorine atoms in the *ortho* positions (Table 2); the respective couplings are observed for two fluorine atoms in the ^{19}F NMR spectrum. These data led us to choose structure **XI**.

Presumably, diamines **IX**, **X**, and **XII** are formed via replacement of the corresponding chlorine atoms in aniline **V**. This indicates a general character of the assistance by the amino group in the initially formed aniline to catalytic aminodechlorination in the *para* and *ortho* position (rather than to aminodefluorination in the subsequent amination), which was revealed by us while studying the ammonolysis of chloropentafluorobenzene [4]. Obviously, amine **XI** and diamines **X** and **XII** result from reduction of amines **V** and **IX** with copper(I) salt or material of reactor walls. Analogous processes, namely the formation of pentafluorobenzene in the reduction of chloropentafluorobenzene with copper in water at 300°C [11] and of 2,4,5-trifluoro-1,3-phenylenediamine in the reaction of the same substrate with aqueous ammonia in a steel high-pressure reactor at 200°C [4], have been reported. It remains unclear which process, reduction of **V** or its ammonolysis, occurs first.

The reaction of 1,3-dichloro-2,4,6-trifluorobenzene (**II**) with aqueous ammonia at 100°C gave 2,6-dicloro-3,5-difluoroaniline (**XIII**) with an admixture of 2,4-dichloro-3,5-difluoroaniline (**XIV**) (ratio 6:1; Scheme 3; Table 1, run no. 5). At 150°C, the products were 2,6-dichloro-5-fluoro-1,3-phenylenediamine (**XV**) and amine **XIII** at a ratio of 7:1 (Scheme 3; Table 1, run no. 6). In both cases, a fairly large fraction of the major product makes it possible to use the resulting mixtures in further syntheses without separation into particular isomers. Compound **XV** was isolated in 73% yield by column chromatography.

Scheme 3.



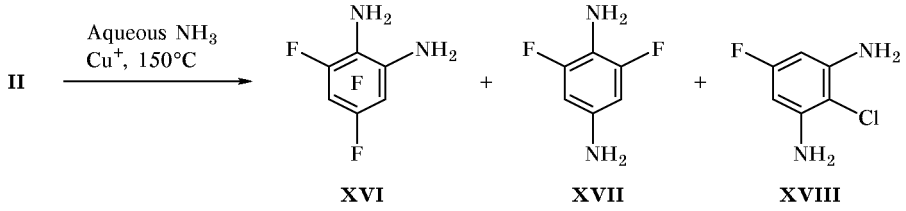
Compounds **XIII** [12, 13] and **XIV** [13] were previously synthesized via a series of transformations, starting from difficultly accessible 3,5-dichloro-2,4,6-trifluorobenzonitrile. Another known procedure for preparation of aniline **XIII** includes synthesis and subsequent reduction of the corresponding nitrobenzene [14]. However, no parameters of amines **XIII** and **XIV** were given in the above publications. Also, we have found no data on phenylenediamine **XV** which is likely to be formed from amine **XIII** and from **XIV**. The experimental ^{19}F NMR chemical shifts (Table 2) showed a better agreement with those calculated by the additivity scheme for isomeric 4,6-dichloro-5-fluoro-1,3-phenylenediamine than for compound **XV**. However, the former cannot be obtained from amine **XIII**.

The predominant formation of amine **XIII** via replacement by amino group of the fluorine atom in the *ortho* position with respect to both chlorine atoms contradicts the substitution patterns observed for compound **I** (see above) and chloropentafluorobenzene [4], where the *para*-fluorine atom with respect to chlorine is replaced preferentially. Presumably, in the ammonolysis of **II** we have the overall effect of five halogen atoms, which favors replacement of the middle of them [15].

The product mixture obtained in the reaction of **II** with aqueous ammonia in the presence of copper(I) chloride at 100°C (Table 1, run no. 7) is analogous to the mixture formed in the ammonolysis in the absence of catalyst, other conditions being equal (Table 1, cf. run nos. 5 and 7). When the reaction was carried out with copper(I) chloride under more severe conditions (Scheme 4; Table 1, run no. 8), strong tarring was observed, and the overall yield of ammonolysis products was as low as ~30%. The major products were those formed via aminodechlorination and hydrodechlorination: 3,5-difluoro-1,2-phenylenediamine (**XVI**), 2,6-difluoro-1,4-phenylenediamine (**XVII**), and 2-chloro-5-fluoro-1,3-phenylenediamine (**XVIII**) at a ratio of 5 : 2 : 1. All these were isolated by column chromatography in 23, 7, and 5% yield, respectively.

Diamine **XVI** can be obtained in four steps from *m*-difluorobenzene [16] with an overall yield of 30%, and diamine **XVII** is available from 1,3,5-trifluorobenzene [17] in six steps with an overall yield of 5–8%. We have found no published data on diamine **XVIII**. In the reaction shown in Scheme 4 diamine **XVI** may be formed from amine **XIII** or **XIV**, and diamine **XVII** may originate from amine **XIV** as a result of aminodechlorination and hydrodechlorination. Diamine **XVIII** is likely to arise from amine **XIII** or **XIV** via replacement by amino group of the fluorine atom in the *meta* position with respect to the existing amino group and subsequent hydrodechlorination.

Scheme 4.



Thus, as we found previously with chloropentafluorobenzene [4] as an example, the ammonolysis of 1,3-dichlorotetrafluorobenzene (**I**) and 1,3-dichloro-2,4,6-trifluorobenzene (**II**) under mild conditions in the presence and in the absence of copper(I) salt results in replacement of fluorine in the *para* and *ortho* positions with respect to the chlorine atom. The subsequent ammonolysis of the resulting aniline in the absence of catalyst involves fluorine replacement in the *meta* position with respect to the amino group and formation of dichloro-*m*-phenylenediamines. In the presence of copper(I) chloride, the main reaction pathway is not aminodefluorination but replacement of chlorine in the *para* and *ortho* positions with respect to the amino group (in the case of compound **I**). In the case of compound **II**, the presence of CuCl favors the latter process in the competition with aminodefluorination. These reactions illustrate the general character of the previously revealed effect [4] of amino group as a substituent ensuring the possibility for catalysis by copper(I) salt of *para*- and *orto*-aminodechlorination in chlorine-containing polyfluorinated aromatic substrate.

EXPERIMENTAL

The ^{1}H and ^{19}F NMR spectra were obtained on Bruker WP-200 and Bruker AM-400 instruments from 20% solutions in acetone-d_6 using, respectively, hexamethyldisiloxane and hexafluorobenzene as internal references. The product mixtures were analyzed by GLC on a Hewlett–Packard HP-5890 chromatograph equipped with a thermal conductivity detector; injector temperature 200°C, detector temperature 240°C, oven temperature programming from 40 to 240°C at a rate of 10 deg/min;, capillary column $15\,000 \times 0.53$ mm, stationary phase 1.5×10^{-3} mm HP-5 (methylphenylpolysiloxane containing 5% of methylphenyl groups); carrier gas helium, 5 ml/min. The components were quantitated using the internal normalization technique.

The products were identified by gas chromatography–mass spectrometry using a Hewlett–Packard G1081A instrument consisting of an HP-5890 Series II gas chromatograph and an HP-5971 mass-selective detector; energy of ionizing electrons 70 eV; oven temperature programming from 50°C (2 min) to 280°C at a rate of 10 deg/min (5 min at the final temperature); injector temperature 280°C; ion source temperature 173°C; HP-5 capillary column, 30 m × 0.25 mm × 0.25 μm (5% of diphenyl- and 95% of dimethylsiloxane); carrier gas helium, flow rate 1 ml/min. The data were acquired in the mass range from 30 to 650 amu at 1.2 scan/s. The molecular weights were determined on a Finnigan MAT-8200 high-resolution mass spectrometer.

Mixtures of products were separated by column chromatography on silica gel (40/100 μm).

As substrates we used a mixture containing 67% of compound **I**, 20% of **III**, and 10% of **IV** and compound **II** containing 90% of the main substance. These materials were obtained from the chemical pilot factory at the Novosibirsk Institute of Organic Chemistry (Siberian Division, Russian Academy of Sciences). 30% Aqueous ammonia (d = 0.893 g/cm^3) was prepared by saturation of commercial aqueous ammonia with gaseous ammonia.

Reactions of polyfluorinated aromatic substrates with aqueous ammonia (Table 1). A mixture of compound **I** or **II**, aqueous ammonia, and copper(I) halide (if required) was kept for 48 h at a specified temperature in a rotating steel high-pressure reactor. The mixture was cooled and extracted with diethyl ether, the extract was dried over $MgSO_4$, the solvent was evaporated, and the residue was analyzed and subjected to column chromatography.

Column chromatography of the residue (20 g) obtained in the reaction of compound **I** with aqueous ammonia at 80°C (run no. 1), eluent petroleum ether, bp 40–70°C, gave (in the order of elution): 4.3 g of a mixture consisting of compounds **I** (30%), **III** (41%), **IV** (23%), **V** (3%), and **VI** (3%); 7.4 g of 2,4-dichloro-3,5,6-trifluoroaniline (**V**, 90% of the main substance; yield 50%. Found, %: C 33.05, 33.22; H 0.80, 0.89; Cl 33.00, 33.10; F 26.00, 26.35; N 6.60. $C_6H_2Cl_2F_3N$. Calculated, %: C 33.30; H 0.92; Cl 32.87; F 26.38; N 6.48) with admixtures of amine **VI** and 3,4-dichloro-2,5,6-trifluoroaniline (**XIX**); 6 g of a mixture of amines **V** (81%), **VI** (2.5%), and **XIX** (16%); 1.25 g of a mixture of compounds **V** (43%), **VI** (~1%), **XIX** (21%), **VII** (21%), and **VIII** (7.7%).

Column chromatography of the residue (0.5 g) obtained in run no. 2 (eluent methylene chloride) gave (in the order of elution): 0.06 g of a mixture containing 49% of amine **XIX** and 8% of diamine **VII**; 0.32 g of a mixture containing 82% of 4,6-dichloro-2,5-difluoro-1,3-phenylenediamine (**VII**) and 15% of diamine **VIII** (mp 136–138°C. Found M^+: 211.97207. $C_6H_4Cl_2F_2N_2$. Calculated M: 211.97196); 0.6 g of a mixture containing 57% of diamine **VII** and 28% of an unidentified product.

From the residue (1.6 g) obtained in run no. 4, using benzene as eluent, we isolated (in the order of elution): 0.20 g of a mixture containing 70% of 2-chloro-3,5,6-trifluoroaniline (**XI**) (Found M^+: 180.98969. $C_6H_3ClF_3N$. Calculated M: 180.99061);

0.35 g of a mixture containing 70% of 2-chloro-3,5,6-trifluoro-1,4-phenylenediamine (**IX**) [sublimation of this mixture at 100°C (5 mm) gave a crystalline substance. Found M^+: 196.00137. $C_6H_4ClF_3N_2$. Calculated *M*: 196.00151]; 0.53 g of a mixture of isomeric diamines **X** (73%) and **XII** (14%); 0.35 g of a mixture containing 84% of 2,3,5-trifluoro-1,4-phenylenediamine (**X**) and 7% of its isomer **XII** (Found M^+: 162.04192. $C_6H_5F_3N_2$. Calculated *M*: 162.04048).

The residue (1 g) obtained in run no. 5 was recrystallized from petroleum ether (bp 40–70°C) to isolate 0.93 g of 2,6-dichloro-3,5-difluoroaniline (**XIII**) with its isomer **XIV** as an impurity. Found M^+: 196.96052. $C_6H_3Cl_2F_2N$. Calculated *M*: 196.96106.

Column chromatography of the residue (2.3 g) obtained in run no. 6 (with methylene chloride as eluent) gave 1.9 g (yield 73%) of 2,6-dichloro-5-fluoro-1,3-phenylenediamine (**XV**) containing 92% of the main substance. mp 115.5–117°C. Found M^+: 193.98235. $C_6H_5Cl_2FN_2$. Calculated *M*: 193.98138.

Column chromatography of the residue (0.8 g) obtained in run no. 8 (using petroleum ether as eluent, bp 40–70°C) gave (in the order of elution): 0.07 g of 3-chloro-5-fluoro-1,3-phenylenediamine (**XVIII**), mp 86–87°C. Found M^+: 160.02026. $C_6H_5ClF_2N_2$. Calculated *M*: 160.02035; 0.3 g of diamine **XVI**, mp 48–50°C (published data [16]: mp 48.5–49.5°C); 0.1 g of 2,6-difluoro-1,4-phenylenediamine (**XVII**), mp 84–86°C (published data [17]: mp 91–92°C). Found M^+: 144.05001. $C_6H_6F_2N_2$. Calculated *M*: 144.04990.

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