Reactions of pentafluoroaniline with aromatic trihalomethyl derivatives in the presence of $AlCl_3$

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The reactions of pentafluoroaniline with aromatic CX_3-derivatives (X = F, Cl) in the presence of $AlCl_3$ were studied. It was shown that compounds with a CF_3 group can be used in reactions with polyfluoroaromatic amines instead of CCl_3-derivatives for the synthesis of imidoyl chlorides. In the case of compounds with several CX_3 groups, the formation of the imidoyl chloride moiety predominantly involves one of the CX_3 groups under the conditions studied. The introduction of a second CX_3 group can be carried out only under more drastic conditions.

Key words: pentafluoroaniline, aromatic trihalomethyl derivatives; aluminum trichloride; imidoyl chloride moiety.

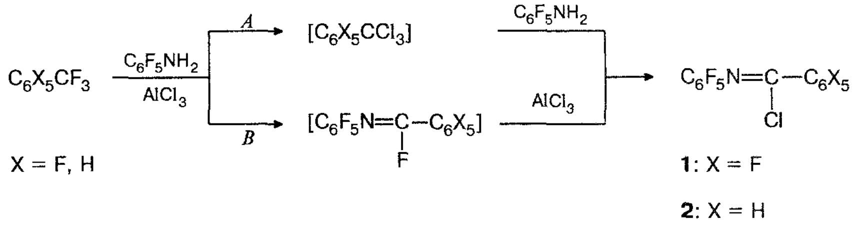
Polyfluoroaromatic amines react with CCl_4 and compounds containing a trifluoromethyl group at the aromatic or olefinic carbon atoms in the presence of $AlCl_3$ to give imidoyl chloride derivatives of various types.[1,2] It was of interest to study the possibilities of the trihalomethyl components in these transformations by using trifluoromethyl derivatives instead of compounds containing the CCl_3 group. These CF_3-derivatives are often more accessible and are used as starting reagents for the syntheses of compounds containing CCl_3 groups by reactions in the presence of $AlCl_3$ (*cf.* Ref. 3). In this work, we studied the reactions of pentafluoroaniline with aromatic trifluoromethyl derivatives. Furthermore, to simultaneously involve several CX_3 groups in the reaction, we studied reactions of pentafluoroaniline and $AlCl_3$ with bis-trihalomethyl derivatives containing chlorine or fluorine atoms in the CX_3 group.

Results and Discussion

As shown previously,[1] the reactions of pentafluoroaniline with pentafluorobenzotrichloride or benzotrichloride in the presence of $AlCl_3$ (mole ratio of the reagents 1 : 2 : 3) result in the corresponding benzimidoyl chlorides. We found that when the CCl_3-derivatives are replaced by octafluorotoluene or benzotrifluoride, the above reactions result in the same benzimidoyl chlorides in yields similar to those obtained in the case of the corresponding CCl_3-derivatives.

Compounds **1** and **2** can form either *via* intermediate benzotrichlorides through the replacement of the fluorine atoms in the CF_3 group by chlorine atoms during treatment with $AlCl_3$ (partway *A*), or by replacement of the fluorine atoms in the imidoyl fluorides, which are formed initially, by chlorine atoms (partway *B*). Both pathways are quite realistic (Scheme 1). The possibility of the formation of CCl_3-derivatives during the reaction is confirmed by the results in Refs. 3—5 that imply that the transformation of compounds such as $ArCF_3$ into $ArCCl_3$ when treated with $AlCl_3$ occurs sufficiently readily. On the other hand, we found that the authentic *N*-(pentafluorophenyl)pentafluorobenzimidoyl fluoride transforms into the corresponding imidoyl chloride **1** when treated with $AlCl_3$ under these reaction condi-

Scheme 1



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tions. Also, one should not rule out the possibility that products of the incomplete replacement of the fluorine atoms of the CF_3 group by chlorine atoms participate in the reaction, since in this case the reaction would probably result in compounds **1** and **2**.

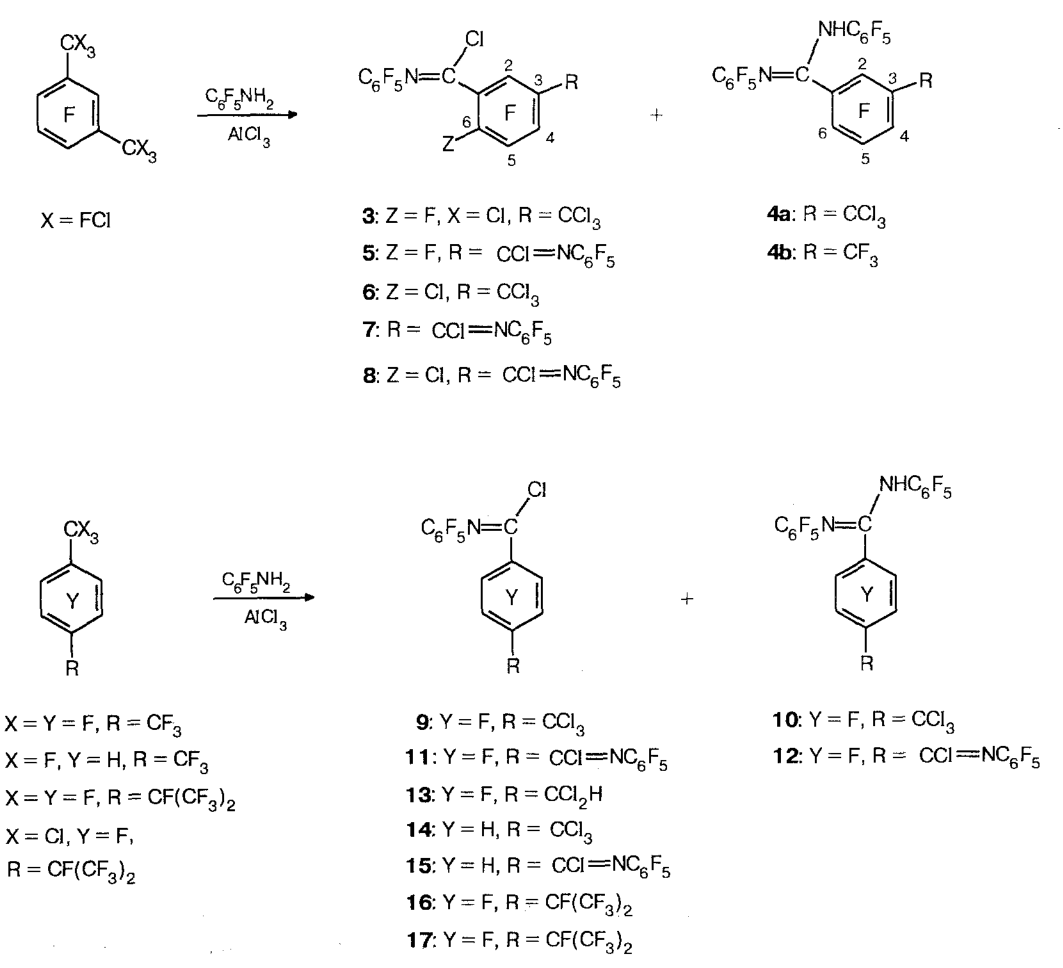
To test the possibility of utilizing aromatic derivatives with several CX_3 groups in this reaction, we used the reactions of pentafluoroaniline with *m*- and *p*-perfluoroxylenes, 1,4-bis(trifluoromethyl)benzene, perfluoro-*p*-cymene, as well as with 1,3-bis(trichloromethyl)tetrafluorobenzene and 4-(trichloromethyl)undecafluoroisopropylbenzene.

Perfluoro-*m*-xylene reacts with pentafluoroaniline and $AlCl_3$ (mole ratio of the reagents 1 : 1 : 3) at room temperature to give *N*-(pentafluorophenyl)-2,4,5,6-tetrafluoro-3-trichlorophenylbenzimidoyl chloride (**3**). The same product is formed from 1,3-bis(trichloromethyl)tetrafluorobenzene and an available isomer mixture of *m*- and *p*-perfluoroxylenes containing 75 % of the *meta* isomer and 25 % of the *para* isomer. We used this mixture based on the known data[5] on the reactivity of perfluoroxylenes in reactions with $AlCl_3$. According to these data, perfluoro-*m*-xylene reacts with $AlCl_3$ at 20—40 °C, whereas the *para* isomer undergoes this reaction to a noticeable extent only at 80 °C. Thus, we can involve in the reaction only the more reactive *meta* isomer from a mixture of *meta*, *para* isomers by varying the reaction conditions.

Amidines of type **4** are minor reaction products. Increasing the reaction temperature to 60 °C results in an increase in the content of imidoyl chloride **3** in the reaction mixture and in the appearance of traces of a bis-imidoyl derivative (**5**).

To involve both CF_3 groups of perfluoro-*m*-xylene in the formation of the imidoyl moieties, we used double the amount of pentafluoroaniline and $AlCl_3$ that had been used in the previous experiment (molar ratio of the reagents 1 : 2 : 6, respectively). In this case (below 60 °C), imidoyl chloride **3** is again the main reaction product, although a small amount of bis-imidoyl derivative **5**, identified by ^{19}F NMR and MS data, is also formed. Of the compounds formed, we could also identify a product of the replacement of one fluorine atom in imidoyl chloride **3** by chlorine. Based on the ^{19}F NMR

Scheme 2



X = FCl

3: Z = F, X = Cl, R = CCl_3
5: Z = F, R = $CCl{=}NC_6F_5$
6: Z = Cl, R = CCl_3
7: R = $CCl{=}NC_6F_5$
8: Z = Cl, R = $CCl{=}NC_6F_5$

4a: R = CCl_3
4b: R = CF_3

X = Y = F, R = CF_3
X = F, Y = H, R = CF_3
X = Y = F, R = $CF(CF_3)_2$
X = Cl, Y = F,
R = $CF(CF_3)_2$

9: Y = F, R = CCl_3
11: Y = F, R = $CCl{=}NC_6F_5$
13: Y = F, R = CCl_2H
14: Y = H, R = CCl_3
15: Y = H, R = $CCl{=}NC_6F_5$
16: Y = F, R = $CF(CF_3)_2$
17: Y = F, R = $CF(CF_3)_2$

10: Y = F, R = CCl_3
12: Y = F, R = $CCl{=}NC_6F_5$

and MS data, we assigned the structure of *N*-(pentafluorophenyl)-(6-chloro-3-trichloromethyl-2,4,5-trifluorobenz)imidoyl chloride (**6**) to this product. The amidine fraction contains mainly amidine **4a** and, presumably, amidiniimidoyl chloride **7**, which we could not isolate in the pure state. Its structure was deduced based on the NMR and MS spectra of a mixture of this compound with amidine **4a**. At 80 °C, the amidine fraction contains approximately equal amounts of amidine **4a** and amidinoimidoyl chloride **7**. The bis-imidoyl derivative **5** and a product of the replacement of one fluorine atom in **5** by chlorine (**8**) predominate among the reaction products. Compound **8** could not be isolated in the pure state; however, the NMR and mass-spectral data do not contradict the suggested structure (Scheme 2).

The less reactive perfluoro-*p*-xylene reacts with pentafluoroaniline and $AlCl_3$ to a noticeable extent at 80 °C. Irrespective of the amount of the starting pentafluoroaniline, the formation of the imidoyl chloride moiety mainly involves one CF_3 group, while the other one is mostly transformed to a trichloromethyl group. When excess pentafluoroaniline is present, the CF_3 group is also transformed to the imidoyl chloride moiety, although the degree of conversion is not high. The above temperature conditions and an excess of pentafluoroaniline lead to the formation of an amidine derivative. As a result, the main reaction products include imidoyl chloride **9** and amidine **10**; the content of these compounds in the reaction mixture varies from 6 : 1 to 2 : 1 (^{19}F NMR data) when the molar ratio of the reagents changes from 1 : 1 : 3 to 1 : 2 : 6. In the latter case, bis-imidoyl chloride **11** and a small amount of *p*-amidinoimidoyl chloride **12**, identified based on the ^{19}F NMR and MS data for its mixture with amidine **10**, are also formed. In some experiments, we identified yet another compound containing a hydrogen atom and differing from the imidoyl chloride **9** by one chlorine atom (MS data). We assume this compound to be *N*-pentafluorophenyl-4-dichloromethyltetrafluorobenz)imidoyl chloride (**13**).

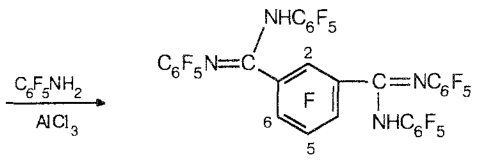
The reaction of pentafluoroaniline with 1,4-bis(trifluoromethyl)benzene mostly affords imidoyl chloride **14** along with minor products, such as a *p*-bis-imidoyl derivative (**15**, a mixture with compound **14**) (according to the ^{19}F NMR and MS data) and amidine-type compounds (^{19}F NMR and GLC data), whose content in the reaction mixture does not exceed 3 % (GLC data).

We also studied the reactions of pentafluoroaniline and $AlCl_3$ with perfluoro-*p*-cymene and 4-(trichloromethyl)undecafluoroisopropylbenzene. It is well known that the reactivity of perfluoro-*p*-cymene in reactions with $AlCl_3$ is comparable to that of perfluoro-*p*-xylene. The reactions involve only the *p*-trifluoromethyl group, while the heptafluoroisopropyl moiety remains unchanged.[5] Indeed, the reactions of perfluoro-*p*-cymene and 4-(trichloromethyl)undecafluoroisopropylbenzene with pentafluoroaniline and $AlCl_3$, like those of perfluoro-*p*-xylene, occur at 80 °C and result in a mixture of imidoyl chloride **16** and amidine **17**. An increase in the amount of $AlCl_3$ to five mols increases the content of imidoyl chloride **16** in the reaction mixtures.

Thus, the results presented in this work indicate that compounds containing one or two CF_3 groups can be used instead of the corresponding CCl_3-derivatives in reactions with polyfluoroaromatic amines for the synthesis of polyfluoroaromatic imidoyl chloride derivatives. More drastic conditions are required to involve both CX_3 groups in the formation of an imidoyl chloride moiety. The formation of amidine derivatives along with imidoyl chlorides is probably related to the ability of the imidoyl chloride moiety to undergo subsequent reactions with $AlCl_3$ and the base. In fact, an excess of pentafluoroaniline favors the formation of amidines. For example, the reaction of perfluoro-*m*-xylene with pentafluoroaniline and $AlCl_3$ (molar ratio of the reactants 1 : 3 : 3) affords amidine **4b** as the main product. No transformation of the CF_3 group into the trichloromethyl group is observed in this case, which may be due to the deficiency of free $AlCl_3$. Furthermore, imidoyl chloride **3** reacts with pentafluoroaniline and $AlCl_3$ at 80 °C to give (as judged by the spectral data) 2,4,5,6-tetrafluoro-1,3-bis[*N,N'*-di(pentafluorophenyl)amidino]benzene (**18**), which we could not obtain in an analytically pure form (Scheme 3).

Scheme 3

3



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Experimental

IR spectra of solutions of the compounds in $CHCl_3$ were recorded on a Specord M-80 spectrometer. ^{19}F and ^1H NMR spectra were obtained on a WP-200SY spectrometer (the chemical shifts were measured relative to hexafluorobenzene and Me_4Si as internal standards). The molecular masses were determined on a GC/MC Finnigan MAT-8200 high-resolution mass spectrometer. GLC analyses were carried out on an LKhM-7A chromatograph equipped with a catharometer and a 4000×4 mm column. The temperature was varied linearly by the internal normalization method. QF-1 or SE-30 on Chromosorb W were used as the fixed phase. Helium was used as the carrier gas. The column temperature was 50—250 °C, and that of the detector was 250 °C.

Reactions of pentafluoroaniline with trihalomethyl derivatives in the presence of $AlCl_3$. A trihalomethyl derivative and a solution of pentafluoroaniline in a solvent were successively added to a vigorously stirred suspension of freshly-sublimed $AlCl_3$ in the same solvent. The reaction conditions are indicated in Table 1. When the reaction was completed, the

Table 1. Reaction of pentafluoroaniline with aromatic trihalomethyl derivatives in the presence of $AlCl_3$

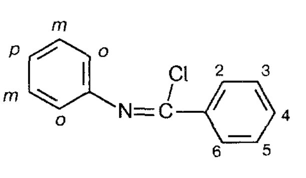
Pentafluoro-aniline /g(mmol)	$ArCX_3$ /g(mmol)	$AlCl_3$ /g(mmol)	Solvent /mL	Reaction temperature /°C	Reaction time /h	Reaction products		
						Com-pound	Yield (%)	M.p./°C [Subl.p./°C (*p*/Torr)]
2(11)	Octafluorotoluene 2.71 (11)	4.4 (33)	$CHCl_3$ 10	60	10	**1**	75	32—33 (*cf.* Ref. 6)
0.5(2.74)	Benzotrifluoride 0.4 (2.74)	1.1 (8.2)	$CHCl_3$ 7	60	10	**2**	50	76—73 (*cf.* Ref. 1)
0.64(3.5)	A mixture of perfluoro-*m*- and *p*-xylenes 1.0 (3.5)	1.4 (10.5)	$CHCl_3$ 10	20	10	**3** **4a**, **4b**	8 [b]	[a]
0.64(3.5)	A mixture of perfluoro-*m*- and *p*-xylenes 1.0 (3.5)	1.4 (10.5)	$CHCl_3$ 15	40	24	**3** **4a**	20 6[c]	
0.64(3.5)	A mixture of perfluoro-*m*- and *p*-xylenes 1.0 (3.5)	1.4 (10.5)	$CHCl_3$ 15	60	24	**3**	25 [d]	
1.28(7.0)	A mixture of perfluoro-*m*- and *p*-xylenes 1.0 (3.5)	2.8 (21.0)	$CHCl_3$ 15	40	24	**3** **5**	24 5[c] [e]	
1.28(7.0)	A mixture of perfluoro-*m*- and *p*-xylenes 1.0 (3.5)	2.8 (21.0)	$CHCl_3$ 15	60	24	**3**, **5**, **6**, **9** **4a** **7**[j]	[f] 6	 177—180
1.28(7.0)	A mixture of perfluoro-*m*- and *p*-xylenes 1.0 (3.5)	2.8 (21.0)	C_6F_6 15	80	24	**3**, **5**, **6**, **8**, **9** **4a**, **7**	[h] [i]	
0.13(0.7)	Perfluoro-*m*-xylene 0.2 (0.7)	0.28 (2.1)	$CHCl_3$ 5	40	10	**3**	18[c]	
1.78(9.7)	A mixture of perfluoro-*m*- and *p*-xylenes 1.0 (3.5)	1.4 (10.5)	$CHCl_3$ 15	40	24	**4b**	24	126—128 [130(20)]
1.83(10)	1,3-Bis(trichloromethyl)-2,4,5,6-tetrafluorobenzene 3.84 (10)	4.0 (30)	$CHCl_3$ 21	20	24	**3**	21	
0.39(2.1)	Perfluoro-*p*-xylene 0.6 (2.1)	0.84 (6.3)	C_6F_6 10	80	45	**9** **10** **13**[j]	30 5	[a] 169.5—172
1.28(7.0)	Perfluoro-*p*-xylene 1.0 (3.5)	2.8 (21.0)	C_6F_6 8	80	45	**9** **11** **10**, **12**	30 11 [k]	 142—145

Table 1. *Continued.*

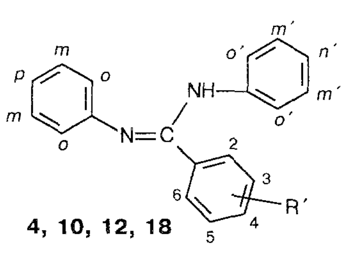
Pentafluoro-aniline /g(mmol)	$ArCX_3$ /g(mmol)	$AlCl_3$ /g(mmol)	Solvent /mL	Reaction temperature /°C	Reaction time /h	Reaction products		
						Com-pound	Yield (%)	M.p./°C [Subl.p./°C (*p*/Torr)]
0.43(2.3)	1,4-Bis(trifluoro-methyl)benzene 0.5 (2.3)	0.94 (7)	C_6F_6 8	80	40	**14** **15**	20 6[l]	125—128
0.18(1.04)	Perfluoro-*p*-cymene 0.4 (1.04)	0.42 (3.12)	C_6F_6 6	80	20	**16** **17**	31[c] [m]	 109—111
0.18(1.04)	Perfluoro-*p*-cymene 0.4 (1.04)	0.7 (5.2)	C_6F_6 6	80	20	**16** **17**	53[c] 19[c]	
0.63(3.3)	4-Trichloromethyl-undecafluoroiso-propylbenzene 1.5 (3.3)	2.2 (16.5)	C_6F_6 24	80	45	**16** **17**	39 6[c]	[a]

Notes. [a] A light yellow liquid. [b] 0.16 g of a mixture of **4a** with **4b** in the ratio 1 : 3.5 (according to ^{19}F NMR data). [c] Content in the reaction mixture, % (according to GLC data). [d] 0.06 g of a dark brown precipitate obtained by treating the reaction mixture with hexane before column chromatography. The precipitate contains compounds **3b**, **4a**, and **5** in the ratio 1.3 : 1.3 : 1 along with other minor products (according to ^{19}F NMR data). [e] 0.16 g of a strongly resinified precipitate obtained by treatment of the reaction mixture with hexane before column chromatography. The precipitate contains pentafluoroaniline and a compound incorporating an imidoyl chloride moiety (according to ^{19}F NMR data). [f] Chromatographic separation of the reaction mixture (0.7 g) gave the following fractions: 0.49 g of a mixture of compounds **3**, **6**, and **9** in the ratio 10 : 1 : 2 (^{19}F NMR data); 0.12 g of a mixture of compounds **5**, **9**, and 1,4-bis(trichloromethyl)tetrafluorobenzene in the ratio 2 : 1 : 1 (^{19}F NMR data); 0.1 g of a mixture of compounds **3**, **5**, **6**, **9**, and 1,4-bis(trichloromethyl)tetrafluorobenzene in the ratio 4 : 14 : 1 : 10 : 2 (^{19}F NMR data). Repeated column chromatography did not afford the individual compounds. [g] Repeated separation of the amidine fraction (0.46 g) on a column gave amidine **4a** and 0.13 g of a mixture of compounds **4a** and **7** in the ratio 1 : 2.7 (^{19}F NMR data). [h] Column chromatography of the reaction mixture (0.75 g) gave 0.08 g of a fraction containing compounds **3**, **6**, and **9** (1 : 1.1 : 2) (^{19}F NMR data); 0.34 g of a fraction containing compounds **3**, **6**, and **9** in the ratio 1 : 2 : 8; 0.22 g of a fraction containing compounds **5** and **8** in the ratio 1 : 2, and 0.06 g of a mixture of compounds **5** and **6** (2 : 1). No individual compounds could be isolated. [i] 0.7 g of the amidine fraction containing (^{19}F NMR data) approximately equal amounts of compounds **7** and **4a**. [j] An experiment starting from 0.6 g of perfluoro-*p*-xylene, 0.39 g of pentafluoroaniline, and 0.84 g of $AlCl_3$ (80 °C, 45 h) followed by column chromatography on silica gel (hexane as the eluent) gave 0.1 g of a product, containing 90 % of compound **13** (GLC data). [k] 0.37 g of a mixture of compounds **10** and **12** in the ratio 2 : 1 (^{19}F NMR). [l] Yield (%) according to GLC. [m] 0.05 g of a pure product obtained from three combined experiments.

Table 2. Molecular masses and spectral properties of nesly obtained compounds



3, 5—8, 9, 11, 13—17



4, 10, 12, 18

Com-pound	Found, Calculated (mol. mass)	Molecular formula	^{19}F NMR, δ (solvent) ^1H NMR, δ (solvent)	IR, ν/cm^{-1}
3	492.8642 492.8641	$C_{14}Cl_4F_9N$	54.55 (F_2), 42.77 (F_4), 34.04 (F_6), 13.04 ($2F_o$) 4.08 (F_p), 2.25 (F_5), 0.28 ($2F_m$) ($CDCl_3$)	985 s, 1000 s, 1135 s, 1160 med, 1490—1512 s, 1637 med, 1680 s
5	603.9103 603.9214	$C_{20}Cl_2F_{14}N_2$	47.19 (F_2), 36.06 (F_4, F_6), 2.03 (F_5), 13.09 ($4F_o$), 4.14 ($2F_p$), 0.29 ($2F_m$) ($CDCl_3$)	

Table 2. *Continued.*

Compound	Found, Calculated (mol. mass)	Molecular formula	^{19}F NMR, δ (solvent) ^{1}H NMR, δ (solvent)	IR, ν/cm^{-1}
6	508.8347 508.8346	$C_{14}Cl_5F_8N$	53.91 (F_2), 41.08 (F_4), 25.05 (F_5), 13.19 ($2F_o$), 4.34 (F_p), 0.30 ($2\ F_m$) ($CDCl_3$)	
7	751 751	$C_{26}HClF_{19}N_3$	49.04 (F_2), 37.20 (F_4), 34.93 (F_6), 19.21 ($2F'_o$), 13.18 ($2F''_o$), 10.53 ($2F_o$), 5.71 (F'_p), 4.21 (F''_p), 2.41 (F_5), 0.66 ($2F''_m$), −0.42 ($2F'_m$), −1.26 (F_p, $2F_m$); ^{1}H NMR: 9.59 (NH) (acetone-d_6)	
8	619.8935 619.8919	$C_{20}Cl_3F_{13}N_2$	46.70 (F_2), 34.55 (F_4), 24.88 (F_5), 13.09 ($4F_o$), 4.14 ($2F_p$), 0.29 ($4F_m$), ($CDCl_3$)	
9	492.8645 492.8641	$C_{14}Cl_4F_9N$	30.33 (F_3, F_5), 23.89 (F_2, F_6), 13.40 ($2F_o$), 4.52 (F_p), 0.53($2F_m$) ($CDCl_3$)	1015 s, 1100 s, 1475 s, 1520 s, 1655 w, 1657 med
11	603.9217 603.9214	$C_{20}Cl_2F_{14}N_2$	24.31 (F_2, F_3, F_5, F_6) 13.29 ($4F_o$), 4.28 ($2F_p$) 0.02($4F_m$) ($CDCl_3$)	975 s, 1000 s, 1325 med, 1488 s, 1512 s, 1625 s
13	458.9020 458.9031	$C_{14}HCl_3F_9N$	23.50 (F_2, F_3, F_5, F_6) 13.14 ($2F_o$), 4.18 (F_p) 0.27 ($2F_m$); ^{1}H NMR: 6.98(CH) ($CDCl_3$)	975 s, 1000 s, 1325 med, 1485—1512 s, 1650 med, 1675 s, 2925 med
14	420.9010 420.9018	$C_{14}H_4Cl_4F_5N$	12.20 ($2F_o$), 2.18 (F_p) −0.51 ($2F_m$) ($CDCl_3$) ^{1}H NMR: 8.25 (2H arom), 8.05 (2H arom) ($CDCl_3$)	975—990 s, 1190 med, 1400 med, 1510 s, 1650 s, 2950 w
15	531.9604 531.9592	$C_{20}H_4Cl_2F_{10}N_2$	13.18 ($4F_o$), 3.11 ($2F_p$) 0.28 ($4\ F_m$) ($CDCl_3$) ^{1}H NMR: 8.30 (4H arom) ($CDCl_3$)	
16	544.9452 544.9463	$C_{16}ClF_{16}N$	86.60 ($2CF_3$), 30.27, 27.40, 25.45 и 24.14 (F_2, F_6, F_3, F_5) 13.30 ($2F_o$), 4.61 (F_p), 0.48 ($2F_m$), −15.85 м (CF) ($CDCl_3$)	965 s, 975 s, 1000 s, 1200—1260 s, 1300 s, 1490 s, 1515 s, 1655 med, 1685 med
17	691.9775 691.9804	$C_{22}HF_{21}N_2$	88.56 ($2CF_3$), 29.86 27.66, 26.64 (1 : 2 : 1) (F_2, F_6, F_3, F_5), 19.19 ($2F'_o$), 10.52 ($2F_o$), 6.20 (F'_p), −0.16 ($2F'_m$), −1.20 (F_p, $2F_m$), −14.57(CF) (acetone-d_6); ^{1}H NMR: 9.48(NH) (acetone-d_6)	975 s, 1000 s, 1045 med, 1270 med, 1300 s, 1330 med, 1515 s, 1645 med, 1670 med, 3420 med
4a	639.9286 639.8981	$C_{20}HCl_3F_{14}N_2$	58.12 (F_2), 40.73 (F_4), 35.36 (F_6), 19.17 ($2F'_o$) 10.44 ($2F_o$), 5.68 (F'_p), 2.82 (F_5), −0.30 ($2F'_m$) −1.16 (F_p, $2F_m$) (acetone-d_6); ^{1}H NMR: 9.62(NH) (acetone-d_6)	990 s, 1030 med, 1130 s, 1155 med, 1330 med., 1455 med, 1505 s, 1640 s, 1665 s, 3421 med
4b	591.9981 591.9868	$C_{20}HF_{17}N_2$	107.52 (CF_3), 48.57 (F_2), 38.33 и 34.96 (F_4 и F_6), 19.16 ($2F'_o$) 10.34 ($2F_o$), 5.93 (F'_p), 2.71 (F_5), −0.20 ($2F'_m$) −1.06 (F_p, $2F_m$) (acetone-d_6) ^{1}H NMR: 9.63(NH) (acetone-d_6)	945 med, 1000 s, 1165 s, 1200 med, 1230 w, 1270 med, 1355 med, 1515 s, 1655 med, 1670 med, 3435 med
10	639.8975 639.8982	$C_{20}HCl_3F_{14}N_2$	30.65 (F_3, F_5), 25.75 (F_2, F_6), 19.17 ($2F'_o$), 10.47 ($2F_o$), 6.06 (F'_p), −0.21 ($2F'_m$), −1.05 (F_p, $2F_m$) (acetone-d_6); ^{1}H NMR: 9.44(NH) (acetone-d_6)	1000 s, 1015 s, 1315 med, 1330 med, 1490—1535 s, 1650 s, 1670 s, 3420 med
12	751 751	$C_{26}HClF_{19}N_3$	26.11 и 24.46 (F_3, F_5 и F_2, F_6), 19.21 ($2F'_o$), 13.33 ($2F''_o$), 10.48 ($2F_o$), 5.95 (F'_p), 4.50 (F''_p), 0.75 (F''_m), −0.26 ($2F'_m$), −1.10 (F_p, $2F_m$) (acetone-d_6); ^{1}H NMR: 9.49(NH) (acetone-d_6)	
18	898 898	$C_{32}H_2F_{24}N_4$	50.25 (F_2), 36.54 (F_4, F_6), 2.93 (F_5), 19.14 ($4F'_o$), 10.52, 9.64 ($4F_o$), 6.12 ($2F'_p$), −0.17 ($4F'_m$), −0.81, −1.34 ($2F_p$, $4F_m$) (acetone-d_6); ^{1}H NMR: 9.43(NH) (acetone-d_6)	990 s, 1030 s, 1515 s, 1650—1665 s, 2965 med, 3225 br, 3412 med

reaction mixture was poured into cold water and extracted with ether. The organic layer was dried with $CaCl_2$, and the solvents were distilled off. The residue thus obtained was analyzed by GLC and ^{19}F NMR. The reaction products were isolated by chromatography on a column with 140—315 μ silica gel (hexane, then CCl_4, $CHCl_3$, and acetone as eluents). To purify the products, they were sublimed *in vacuo*, repeatedly chromatographed on silica gel, or recrystallized. The strongly resinified amidine fractions were dissolved in CCl_4, and boiled with activated carbon; the carbon was filtered off, and the solution was passed through a layer of silica gel. The solvents were stripped by distillation, and the residue was recrystallized from petroleum ether (b.p. 70—100 °C) with an admixture of CCl_4. It should be noted that the reaction mixtures, along with nitrogen-containing products (imidoyl chlorides and amidines), also contained unreacted pentafluoroaniline as well as mono- and bis-trichloromethyl derivatives, which either were introduced as substrates or formed under the reaction conditions from the starting CF_3-derivatives due to the replacement of fluorine atoms by chlorine atoms in one or two CF_3 groups.

The analytical and spectral characteristics of the newly obtained compounds are presented in Table 2.

Synthesis of *N*-(pentafluorophenyl)pentafluorobenzimidoyl chloride (1). *N*-(pentafluorophenyl)pentafluorobenzimidoyl fluoride (0.3 g, 0.8 mmol) (for the synthesis of this compound, *cf.* Ref. 6) was added to a suspension of freshly-sublimed $AlCl_3$ (0.32 g, 2.4 mmol) in dry $CHCl_3$ (5 mL). The mixture was stirred for 10 h at 60 °C. Work-up as indicated above afforded 0.55 g of a residue which contained only imidoyl chloride **1** (^{19}F NMR data).

Synthesis of *N,N',N'',N'''*-tetrakis(pentafluorophenyl)-2,4,5,6-tetrafluoroisophthal-bis-amidine (18). Imidoyl chloride **3** (0.37 g, 0.7 mmol) and pentafluoroaniline (0.41 g, 2.2 mmol) were added to a suspension of freshly-sublimed $AlCl_3$ (0.3 g, 2.2 mmol). The reaction mixture was heated at 80 °C for 32 h with stirring, treated with water, and extracted with ether. The solvents were distilled off to give 0.56 g of a residue, which was treated with hexane. The hexane was decanted to give 0.23 g of a dark solid product, which was purified as indicated above for amidines. This afforded a sample of compound **18** with m.p. 89—91 °C, which was again chromatographed and recrystallized from a petroleum ether (b.p. 70—100 °C)/CCl_4 mixture.

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