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POLYFLUOROARYLCARBONIMIDOYL DICHLORIDES AND CHLORIDES. A NEW METHOD OF OBTAINING SUCH COMPOUNDS FROM POLYFLUOROAROMATIC AMINES AND COMPOUNDS OF THE CCl_3R TYPE IN THE PRESENCE OF $AlCl_3$ *

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SUMMARY

Reactions of some polyfluorinated amines of the benzene, diphenyl, naphthalene and pyridine series with CCl_4 in the presence of $AlCl_3$ have been investigated. A new method is proposed for producing polyfluoroarylcarbonimidoyl dichlorides $Ar_fN{=}CCl_2$. The reaction is shown to be sufficiently general and applicable in the series of polychlorinated anilines and low-base anilines of the hydrocarbon series as well. The possibility of involving other compounds of the type CCl_3R and other Lewis acids in the reaction has been studied. The factors influencing the course of the reaction and the mechanism of formation of polyfluoroarylcarbonimidoyl dichlorides are discussed.

INTRODUCTION

Polyfluoroarylcarbonimidoyl dichlorides and chlorides are among those polyfluorinated compounds which were first obtained recently and whose properties have been little investigated.

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* A part of this material was published earlier as a short communication [1] and reported at the 7-th European Symposium on Fluorine Chemistry [2] .

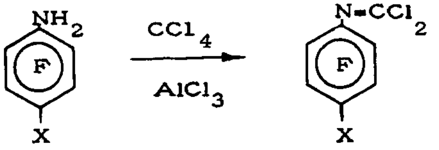
By analogy with non-fluorinated compounds [3,4,5] , one could expect the presence of a reactive imidoyl chloride grouping to condition their participation in various chemical transformations and, in particular, to allow their use as intermediates in the synthesis of heterocyclic systems and physiologically active compounds. However, the absence of convenient and simple methods of producing polyfluoroarylcarbonimidoyl dichlorides and chlorides has been a hindrance to systematic investigation of the properties of these compounds. Some traditional methods of synthesizing non-fluorinated analogues cannot be used in the case of polyfluorinated derivatives. For example, we did not succeed in converting trihaloacetyl derivatives of pentafluoroaniline into pentafluorophenyltrihaloacetimidoyl chlorides by interaction with PCl_5, only trichlorophosphazopentafluorophenyl having been formed in that case [6] . Polyfluorinated trihaloacetimidoyl chlorides were obtained only in the reactions of the corresponding trihaloacetyl derivatives of pentafluoroaniline with CCl_4 and triphenylphosphine [7]. An attempt to produce pentafluorophenylcarbonimidoyl dichloride from pentafluoroformanilide and a mixture of thionyl chloride and sulphuryl chloride [8] by analogy with the synthesis of non-fluorinated compounds of such type proved to be unsuccessful. It has been noted in the literature, that high-temperature thermolysis of N,4-dichloroperfluorocyclohexa-2,5-dienylidene amine gives, alongside of many other compounds, N-pentafluorophenylcarbonimidoyl fluorochloride, though in very small quantities [9] .

Recently we found a method for synthesizing polyfluoroarylcarbonimidoyl dichlorides and chlorides of the general formula $Ar_fN{=}CClR$ (R = Cl or Ar_f) by the copyrolysis of polyfluoroaromatic amines with chloroform or CCl_4 , and also with pentafluorobenzotrichloride, in a flow system at temperatures of 500-700° [10-12] . A number of polyfluoroarylcarbonimidoyl dichlorides and chlorides were synthesised by this method, but in some cases the yields were not high and side reactions took place, associated with the conversion of substituents in the initial amine. Therefore we have continued the elaboration of other methods of synthesizing polyfluoroarylcarbonimidoyl dichlorides and chlorides.

In the present paper we described a novel method of producing these compounds, in which, like in the above-cited thermolytic method [10-12] , the initial compounds are polyfluoroaromatic amines and compounds of the type CCl_3R, but the reaction is conducted at moderate temperatures (to 80°) in the presence of $AlCl_3$. In the elaboration of this method we proceeded from the data about an enhancement of the electrophilic properties of polychloromethanes in the presence of $AlCl_3$ [13] . We believed that the interaction of the compound CCl_3R thus activated with a polyfluoroaromatic amine could lead to the formation of a polychloroalkyl amine derivative, and further to a polyfluoroarylcarbonimidoyl dichloride or chloride. In such a case, however, one could not exclude a competing interaction of $AlCl_3$ with the polyfluoroaromatic amine. Yet, a lowered basicity of these amines gave grounds for hoping that interactions of such types would be hindered.

RESULTS AND DISCUSSION

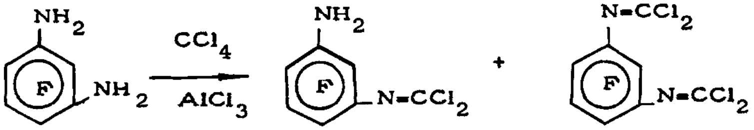
Heating of polyfluoroaromatic amines with CCl_4 and $AlCl_3$ at 40-80° (depending on the initial amine) gives polyfluoroarylcarbonimidoyl dichlorides with yields of 40-90%. In such a manner, penta- and tetrafluorophenylcarbonimidoyl dichlorides (IX-XVII) have been obtained from pentafluoroaniline (I) and p-X-tetrafluoroanilines (II-VIII) containing both electron-attracting and electron-donating substituents in the p-position to the amino group.



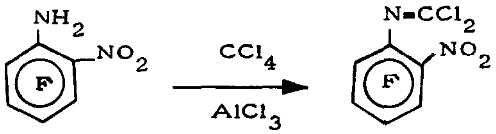
I-VIII IX-XVII

X = F (I, IX); Br (II, X); Cl (III, XI); NO_2 (IV, XII); CN (V, XIII); H (VI, XIV); CH_3 (VII, XV); NH_2 (VIII, XVI + XVII (X: $N=CCl_2$).

Meta- and ortho-derivatives of pentafluoroaniline also enter into similar reactions.



XVIII XIX XX

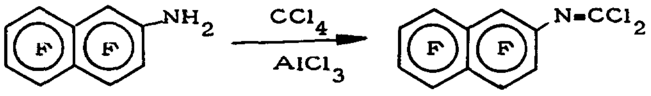

XXI XXII

The results of the experiments are presented in Table 1. For each amine, reaction conditions are indicated, under which the degree of amine conversion into carbonimidoyl dichloride was maximum and resinification of the reaction mass was minimum. The optimal molar amine-to-aluminium trichloride ratio was determined in experiments with aniline (I) and proved to be ~ 1:3. It should be noted that the reaction of amines with CCl_4 and $AlCl_3$ is heterogeneous, and therefore the effectiveness of stirring is an essential factor.

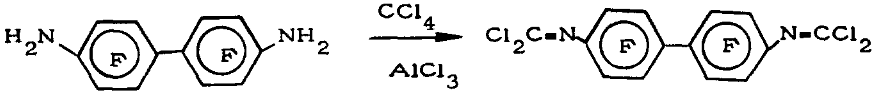
The constants, analytical and spectral characteristics of the newly synthesized arylcarbonimidoyl dichlorides are presented in Table 2.

It should be noted that the method of producing polyfluoroarylcarbonimidoyl dichlorides, proposed in the present paper, in a number of cases allows these compounds to be obtained in higher yields than the thermolytic one (for example, for carbonimidoyl dichloride (IX) the respective figures are 70% and 30% [11]) ; furthermore, with the present method, compounds can be produced which cannot be synthesized thermolytically. This applies, for instance, to carbonimidoyl dichlorides (X), (XV), (XIX), (XX) and (XXII). It is of interest that in the case of m- and p-tetrafluorophenylenediamines (XVIII) and (VIII) the reaction proceeds stepwise, so that mixtures of mono- and di-carbonimidoyl dichloride derivatives are formed with a predominance of the latter.

The proposed method of producing polyfluoroarylcarbonimidoyl dichlorides proved to be quite general. In the same way, polyfluorinated carbonimidoyl dichlorides of the naphthalene series (XXIV) and diphenyl series (XXVI) were obtained. The possibility of synthesizing polychlorinated arylcarbonimidoyl dichlorides (XXVIII) in such a manner was realised by the reaction of pentachloroaniline (XXVII) with CCl_4.



XXIII XXIV



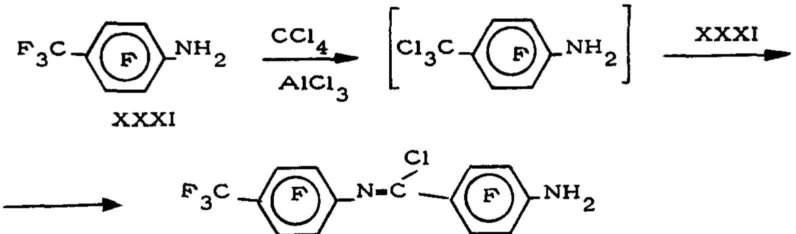
XXV XXVI

$$C_6Cl_5NH_2 \xrightarrow[AlCl_3]{CCl_4} C_6Cl_5N{=}CCl_2$$

XXVII XXVIII

Non-fluorinated aromatic amines in the interaction with CCl_4 in the presence of $AlCl_3$ also turned out to give corresponding arylcarbonimidoyl dichlorides provided that the basicity of the amines is low. Thus, p-nitroaniline (XXIX) reacts under these conditions, giving p-nitrophenylcarbonimidoyl dichloride (XXX) with the yield of 35%, whereas unsubstituted aniline undergoes transformation into high-melting compounds, probably, of a salt-like type [14] .

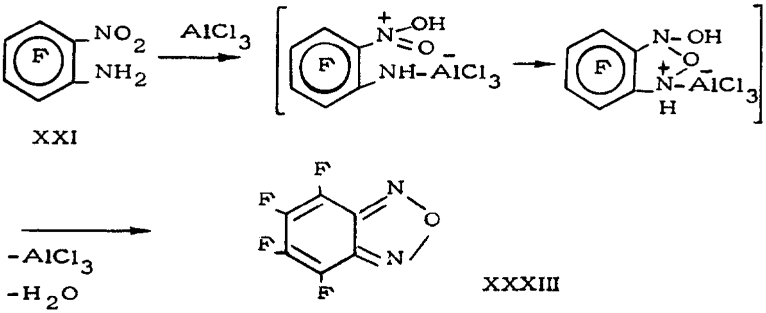
In a number of cases more complicated processes occur. Thus, heating of 4-trifluoromethyltetrafluoroaniline (XXXI) with CCl_4 and $AlCl_3$ at 70-80° leads, evidently, to polymeric products, while at room temperature, alonside of the unreacted initial amine, N-(p-trifluoromethyltetrafluorophenyl)-p-amino-tetrafluorobenzimidoyl chloride (XXXII) can be isolated. One of the possible pathways for the formation of this compound is presented in the scheme below:



XXXI

XXXII

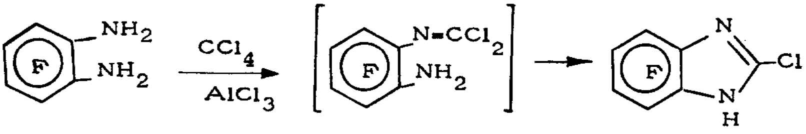
In the case of o-nitrotetrafluoroaniline (XXI) the final result depends on the conditions under which the reaction is conducted. The expected carbonimidoyl dichloride (XXII) is obtained, if the reaction is run at 40-50° (see Table 1). At 70-80° strong resinification of the reaction mass is observed; nevertheless, a small quantity of a compound can still be isolated from it, this compound, according to its analytical and spectral characteristics, being identifiable as 4,5,6,7-tetrafluorobenzofurazan (XXXIII). We are not aware of such a method of formation of benzofurazans in the non-fluorinated series. The formation of benzofurazan (XXXIII) possibly proceeds according to the scheme:



XXI

XXXIII

Heating of tetrafluoro-o-phenylenediamine (XXXIV) with CCl_4 and $AlCl_3$ gives 2-chloro-4,5,6,7-tetrafluorobenzimidazole (XXXVI).



XXXIV XXXV XXXVI

The formation of the latter can be explained by closure of the heterocyclic ring in the intermediate carbonimidoyl dichloride (XXXV) by analogy with the scheme of obtaining benzimidazole derivatives from the intermediately forming o-aminosubstituted arylcarbonimidoyl fluorides, suggested in [15].

4-Aminotetrafluoropyridine does not enter into reaction with CCl_4 and $AlCl_3$. Possibly, this is associated with the fact that $AlCl_3$ is coordinated with the nitrogen of the pyridine ring (see, e.g. [16]), thus inhibiting the conversion of the amine into the corresponding carbonimidoyl dichloride.

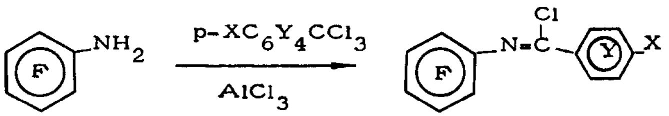
In the series of p-substituted tetrafluoroanilines most fully investigated by us, we tried to trace a relationship between the pK_a values of the initial amines [17] , the yield of arylcarbonimidoyl dichlorides (according to GLC), and the conditions under which the reaction was conducted (temperature and time). We did not succeed in revealing a clearcut correlation, though a sufficiently definite tendency is observed for the reactions to proceed under milder conditions and with better yields with lowering of the pK_a value of the anilines. It cannot be excluded, that the absence of clearcut regularities is associated with the heterogeneity of the reaction.

To elucidate the synthetic possibilities of the reaction studied by us more completely, it was of interest to consider the problem of extending the range of Lewis acids and chloromethanes involved in the reaction. In the system pentafluoroaniline (I) - CCl_4 such Lewis acids were investigated as $SnCl_4$, $GeCl_4$, $SbCl_5$, SbF_3, BF_3, $FeCl_3$, PCl_3. These compounds turned out not to be active, and only in the cases of $FeCl_3$, PCl_3 and $SbCl_5$ was the formation of 1 to 5% of carbonimidoyl dichloride (IX) noted, strong resinification taking place in the case of $SbCl_5$.

In the reaction with BF_3 a solid complex of aniline (I) with BF_3 was formed, and it did not react any further. The use of H_2SO_4 or HF instead of $AlCl_3$ did not give satisfactory results either, though it is known that species of the cationoid type are formed when compounds of class CCl_3R are acted upon by H_2SO_4 [18], and in the reaction of various phenols with CCl_4 and HF their trifluoromethyl ethers are formed [19]. In our case in the reaction with H_2SO_4 the content of imidoyl chloride (IX) in the reaction mixture was only 5% and in the reaction with HF this imidoyl chloride was not formed at all.

The specific character of action of $AlCl_3$ in the reaction studied by us, compared to other acid catalysts, so far cannot be accounted for, but this feature has been noted for other systems as well, for instance, in ionic addition of halomethanes to fluoroolefines [13] or in the interaction of p-cresol with CCl_4 [20].

In the reactions involving the aniline (I) and $AlCl_3$ we have investigated the use not only of CCl_4, but also of benzotrichloride (XXXVII), pentafluorobenzotrichloride (XXXVIII) and chloroform. Benzotrichloride (XXXVII) smoothly reacts with the aniline (I) in the presence of $AlCl_3$. Compound (XXXVIII) also proved to be sufficiently active and even at room temperature it gave imidoyl chloride (XL) with the yield of 35%. Increasing the reaction temperature leads to a higher yield of compound (XL), but there also takes place an exchange of the p-atom of fluorine in the initial benzotrichloride (XXXVIII) by chlorine, so that, alongside of the product (XL), imidoyl chloride (XLI) is formed. Such a course of the reaction is confirmed by experiments with authentic p-chlorotetrafluorobenzotrichloride (XLII), and also by other experiments which showed that under the reaction conditions the exchange of the fluorine atom by chlorine in imidoyl chloride (XL) does not occur.



I

X=Y=H XXXIX
X=Y=F XL
X=Cl, Y=F XLI

The reaction of pentafluoroaniline (I) with chloroform in the presence of $AlCl_3$ does not go.

The problem of the applicability of various solvents in the process studied was not specially investigated, but it was shown that sometimes hexafluorobenzene can be used as a solvent. Thus, for example, in the interaction of aniline (I) with benzotrichloride (XXXVIII) and $AlCl_3$ in hexafluorobenzene the yield of compound (XXXIX) grows from 35% to 50%. In the reaction of aniline (I) with CCl_4 and $AlCl_3$ carbon disulphide can be used as a solvent (see Table 1).

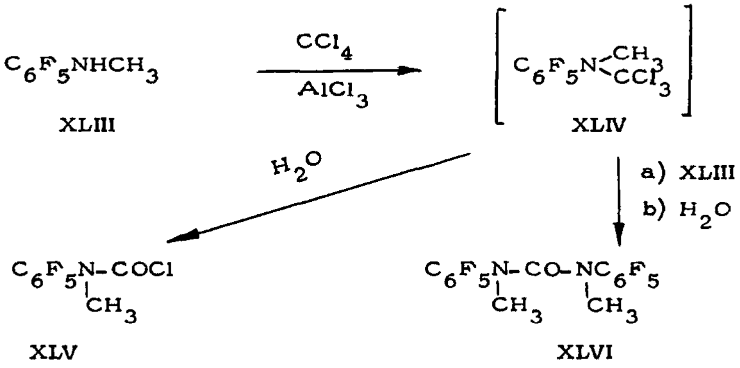
One of possible schemes for the formation of polyfluoroarylcarbonimidoyl dichlorides from aromatic amines and CCl_4 in the presence of $AlCl_3$ can be represented in the following manner:

$$Ar_fNH_2 + \left[\overset{+\delta}{C}Cl_3\cdots Cl\cdots \overset{-\delta}{Al}Cl_3\right] \longrightarrow \left[Ar_f\overset{+}{N}H_2CCl_3\right] \longrightarrow$$

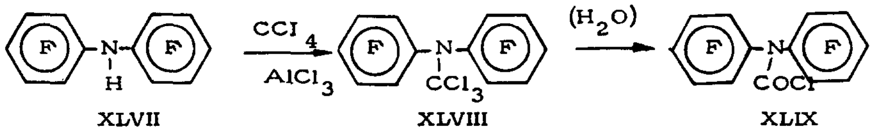
$$\xrightarrow{-H^+} Ar_fNHCCl_3 \xrightarrow{-HCl} Ar_fN{=}CCl_2$$

The complex of CCl_4 and aluminium chloride interacts with the amine, giving a trichloromethyl derivative of the amine as an intermediate, which undergoes a further transformation into an arylcarbonimidoyl dichloride.

Evidence in favour of the intermediate trichloromethylation of the initial amine could be furnished by isolation of its trichloromethyl derivative in the case when further transformation into a carbonimidoyl dichloride is impossible. To this end, we investigated the reaction of CCl_4 and $AlCl_3$ with N-methylpentafluoroaniline (XLIII). However, instead of the expected product of trichloromethylation (XLIV), we have isolated N-methyl-N-pentafluorocarbamic acid chloride (XLV) and bis(N-methyl-N-pentafluorophenyl)urea (XLVI). Evidently aniline (XLIV) is formed, but undergoes a further transformation, characteristic of the compounds of such type [21] .



In the case of decafluorodiphenylamine (XLVII) under rapid treatment of the reaction mixture, ^{19}F NMR spectra and mass spectrometry data indicated the formation of a compound which we have classified as a trichloromethyl derivative of amine (XLVIII); however, we have not succeeded in isolating this compound in its individual form, since in air it became transformed into N,N-bis(pentafluorophenyl)-carbamic acid chloride (XLIX).



The reaction of haloalkylation of amines in the presence of $AlCl_3$, found by us and described in this paper, is, so far as we are aware, the first example of such a reaction for aromatic amines. Its successful course in the series of polyhalogenated compounds is, possibly, associated with their lowered basicity and, as a result, with weakening of the competitive coordination of the nitrogen atom of the amine with the catalyst, which may interfere with the course of the main reaction. The results obtained in experiments with aniline and p-nitroaniline also lead to such a conclusion.

The method of obtaining polyfluorinated arylcarbonimidoyl chlorides, described in this paper, in combination with the thermolytic method of their synthesis, proposed by us earlier, have made these compounds sufficiently available to allow their properties to be investigated.

EXPERIMENTAL

^{19}F and ^{1}H NMR spectra were recorded on a 'Varian A56/60' spectrometer at the frequency of 56.4 and 60 MHz respectively for solutions in CCl_4. Internal standards were hexafluorobenzene and hexamethyldisiloxane. IR spectra were recorded on a 'UR-20' spectrophotometer for 5% solutions in CCl_4. UV spectra were recorded on a 'Specord' instrument for solutions in ethanol. GLC analysis was carried out on an 'LHM-7a' instrument with a katharometer and with linear programming of temperatures by the method of internal normalization. The length of the column was 4000mm, its diameter was 4 mm, the column temperature was 50-270°, and the detector temperature was 250°. The carrier gas was helium. The stationary phase was methylphenylsilicone 'SE-30' on Chromosorb W, silicon 'SKTFT-50' and 'SKTFV-803' on Celite. The stationary phase to solid carrier ratio was 15:100. Molecular weights were determined mass spectrometrically on an 'MS-902' instrument (resolution ~10000), the nominal energy of the electrons was 14 and 70 eV. Initial amines were prepared in accordance with the described procedures.

Interaction of aromatic amines with CCl_4 in the presence of $AlCl_3$

Pentafluorophenylcarbonimidoyl dichloride (IX)

To a vigorously stirred suspension of 8.8 g (0.066 mole) of freshly sublimed $AlCl_3$ in 15 ml of absolute CCl_4 a solution of 4 g (0.022 mole) of pentafluoroaniline (I) in 10 ml of CCl_4 was added with caution, and the reaction mixture was heated under vigorous stirring at 70-80° for 12 h. The reaction mass was then cooled down to room temperature, poured into ice, and extracted with ether. The ethereal layer was washed with water, dried over $MgSO_4$, the solvents were distilled off, the residue after the GLC analysis was distilled with steam, the distillate isolated and then distilled at 94°/40 mm. 4.0 g (69%) of imidoyl dichloride (IX) were obtained, the product being identical to that described in [10] .

The reactions with other amines were carried out by following a similar procedure (the reaction conditions are specified in Table 1). The molar ratio of $AlCl_3$ and amine was 3:1; in the case of tetrafluorophenylenediamines and octafluorobenzidine it was 6:1. Arylcarbonimidoyl dichlorides were isolated from the residue after distilling off the solvents by distillation in vacuum (method A), by sublimation (method B) or by thin-layer chromatography on silica gel, the eluent being hexane (method C). The yields of the isolated products were 30-70%. The results of experiments are presented in Table 1.

Interaction of aniline (I) with CCl_4 in the presence of other acid catalysts

The reaction of aniline (I) with CCl_4 in the presence of $SnCl_4$, $GeCl_4$, SbF_3, PCl_3, H_2SO_4 was carried out in the same manner as the above-described reaction with $AlCl_3$ at a temperature of 70-80° during 15-20 h. In all cases the recovery of the initial aniline (I) was ~ 95%. The formation or absence of imidoyl dichloride (IX) was inferred from the GLC data on the initial mixture and from the ^{19}F NMR spectra. In the reaction with $SbCl_5$ strong resinification of the reaction mass occurred even at room temperature, and initial aniline (I) could not be isolated. Passing of BF_3 into a solution of aniline (I) in CCl_4 at room temperature resulted in the formation of a solid precipitate of a complex of aniline (I) with BF_3, m.p. 80-81°, which could not be obtained in an analytically pure form. IR spectrum, ν, cm^{-1}: 1535; 1100; 3230; 3430. ^{19}F NMR spectrum, δ, ppm: -11.9 ($1F_p$); -2.84 ($2F_m$); 1.42 ($2F_o$); 11.7 ($3F$ BF_3). When the complex was treated with water, aniline (I) separated. Reactions with HF were carried out at room temperature and at 80° in an autoclave with various aniline (I)/HF ratios, but in all cases only the initial compound (I) was isolated.

N-(p-Trifluoromethyl-tetrafluorophenyl)-p-aminotetrafluorobenzimidoyl chloride (XXXII) (nc)

4 g (0.017 mole) of aniline (XXXI) and 6.8 g (0.051 mole) of $AlCl_3$ in 80 ml of absolute CCl_4 at room temperature during 14 h (after the decomposition of the reaction mixture and distilling off of the organic solvents) gave 3.48 g of an oily residue, which, according to the GLC data, contained 46.5% of the initial amine (XXXI) and 30% of imidoyl chloride (XXXII). At 0°, 0.5 g of imidoyl chloride (XXXII) crystallized out of the residue; this imidoyl chloride after washing with

TABLE 1

Interaction of aromatic amines with CCl_4 in the presence of $AlCl_3$

Nos.	Initial amine g		CCl_4	$AlCl_3$	Reaction temperature °C (time, h)	Weight of reaction mixture g	Products of reaction, % acc. to GLC[a)]				
							Arylcarbonimidoyl dichloride				Initial amine
							Compd No	Content in reaction mixture	Yield for reacted initial compd acc. to GLC	Method of isolation	
1[b)]	I	1	15	2.2	20 (20)	0.9	IX	26	31	C	58
2	I	4	25	8.7	70–80 (12)	4.3	IX	95	70	A	1
3	II	1.5	25	2.5	70–80 (10)	1.6	X	77	64	C	1.5
4	III	1.7	40	3.4	70–80 (31)	2.2	XI	75	90	A	4
5	IV	0.85	20	1.6	50–60 (8)	1.1	XII	91.5	88	A	0.6
6	V	2	40	4.2	70–80 (16)	2.2	XIII	89	69	B	-
7	VI	1.8	30	4.4	70–80 (15)	1.5	XIV	64	47	C	28
8	VII	2	40	4.0	70–80 (40)	2.5	XV	59.5	70	C	20
9	VIII	0.4	15	1.8	70–80 (24)	0.5	XVI	10	11	C[c)]	15
							XVII	58	47		

10	XVIII	2	40	8.9	70-80 (24)	2.5	XIX	21	18	C[c)]	3
							XX	66	45		
11	XXI	3	60	5.7	40-50 (8)	3.4	XXII	55	67	C[d)]	29
12	XXIII	2	40	3.0	60-70 (25)	1.3	XXIV	41	23	C	20
13	XXV	2	80	4.8	70-80 (40)	3.2	XXVI	26	56	C	32
14	XXVII	2	40	3.1	70-80 (40)	2.0	XXVIII	52	54	C	26.5
15	XXIX	1	20	1.9	70-80 (20)	0.67[e)]	XXX	82	35	B	-

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a) Only the main components of the obtained reaction mixtures are presented in the Table.

b) In a similar experiment, but with the addition of 12 ml of dry CS_2 , the content of imidoyl chloride (IX) in the reaction mixture was 19% (the yield 17.5%), that of the initial aniline was 62%.

c) The eluent was hexane/CCl_4 (3:1 by volume).

d) The eluent was hexane/benzene (15:1 by volume).

e) Upon pouring of the reaction mass into water, 0.52 g of a precipitate fell out, the precipitate being insoluble in organic solvents; the structure of the precipitate was not established.

petroleum ether (b.p. 70–100°) and sublimation at 80°/5 mm had m.p. of 80–81°. Analysis: Found: C, 37.92; H, 0.46; Cl, 8.15; F, 47.53; N, 6.16%. Mol. wt. 442. $C_{14}H_2ClF_{11}N_2$ requires C, 37.97; H, 0.45; Cl 8.02; F, 47.23; N, 6.3%. Mol. wt. 442 (^{35}Cl). IR spectrum, ν , cm^{-1} (KBr): 1150–1250, 1510 (C_6F_5), 1665 (N=C), 3350–3400 (NH_2). ^{19}F NMR spectrum, δ, ppm (acetone): 1.4 (2F), 14.4 (2F), 21.5 (4F), 108 (3F CF_3).

4,5,6,7-Tetrafluorobenzofurazan (XXXIII) (nc)

3 g (0.013 mole) of aniline (XXI) and 5.3 g (0.04 mole) of $AlCl_3$ in 60 ml of absolute CCl_4 at 70–80° during 4 h gave a strongly resinified reaction mixture, from which, after its decomposition and distillation with steam, 0.27 g of a product was obtained, which according to the GLC data, contained 92% of benzofurazan (XXXIII). Distillation at 100°/5 mm gave pure benzofurazan (XXXIII). Analysis: Found: Mol. wt. 192. $C_6F_4N_2O$ requires Mol. wt. 192. Elemental composition is calculated in conformity with [22] . IR spectrum, ν , cm^{-1}: 1050, 1400, 1520, 1570, 1650. UV spectrum, λ , nm (lg ε): 201.9 (4.11), 267.6 (3.30), 277.2 (3.38), 316.4 (3.38). The spectrum is similar to the UV spectrum of the non-fluorinated analogue [23] . ^{19}F NMR spectrum, δ , ppm: 14 (2F), 15.7 (2F).

2-Chloro-4,5,6,7-tetrafluorobenzimidazole (XXXVI) (nc)

0.6 g (0.003 mole) of o-phenylenediamine (XXXIV) and 2.7 g (0.02 mole) of $AlCl_3$ in 30 ml of absolute CCl_4 (70–80°, 15 h) after conventional treatment gave 1 g of a solid residue, from which by recrystalization from benzene and subsequent sublimation at 120°/5 mm 0.6 g of benzimidazole (XXXVI) was isolated, m.p. 198°. Analysis: Found: C, 36.93; H, 0.35; Cl, 16.32; F, 33.63; N, 12.07%. Mol. wt. 224. $C_7HClF_4N_2$ requires C, 37.4; H, 0.45; Cl, 15.81; F, 33.85; N, 12.47%. Mol. wt. 224 (^{35}Cl). IR spectrum, ν , cm^{-1} (KBr): 1025, 1430, 1490, 1560, 3450. UV spectrum, λ , nm (lg ε): 213 (4.68), 237,5 (4.08), 230 (4.11), 263 (3.81) (compare with the UV spectrum of 4,5,6,7-tetrafluorobenzimidazole [24]). ^{19}F NMR spectrum, δ , ppm [$(CD_3)_2CO$] : -3.4 (2F), 6.6 (2F). PMR spectrum, δ , ppm [$(CD_3)_2CO$] : 13.65 br. (NH).

N-(Pentafluorophenyl)-benzimidoyl chloride (XXXIX) (nc)

To a suspension of 2.2 g (0.016 mole) of $AlCl_3$ in 8 ml of hexafluorobenzene, 2.2 g (0.01 mole) of benzotrichloride (XXXVII) were added under stirring and a solution of 1 g (0.005 mole) of aniline (I) in 8 ml of hexafluorobenzene. After heating the mixture at 60° during 5 h and conventional treatment a residue was obtained, from which at 0° 0.8 g of imidoyl chloride (XXXIX) cristallized; the latter was filtered off, the filtrate distilled with steam, giving another 0.77 g of a solid product, which, according to the GLC data, contained 65.5% of imidoyl chloride (XXXIX). Sublimation of the latter at 110°/5 mm gave pure imidoyl chloride (XXXIX), m.p. 76-77°. Analysis: Found: C, 51.17; H, 1.59; Cl, 12.17; F, 30.46; N, 4.53%. $C_{13}H_5ClF_5N$ requires C, 51.06; H, 1.64; Cl, 11.62; F, 31.10; N, 4.58%. IR spectrum, ν, cm^{-1}: 675, 985-1000, 1515, 1655, 3070. ^{19}F NMR spectrum, δ, ppm: -0.71 ($2F_m$), 1.42 (F_p), 12.06 ($2F_o$). PMR spectrum, δ, ppm: 7.43-7.55, 8.12-8.27.

Interaction of aniline (I) with benzotrichloride (XXXVIII) in the presence of $AlCl_3$

(a) From 2 g (0.011 mole) of aniline (I), 6.5 g (0.023 mole) of compound (XXXVIII) and 4.4 g (0.032 mole) of $AlCl_3$ (25°, 3 h) 4.8 g of a residue were obtained, (which, according to the GLC data, contained 9% of unreacted aniline (I), 57% of compound (XXXVIII) and 25% of imidoyl chloride (XL)] which at 0° crystallizeed from the resulting mixture. In its characteristics it is identical to the product obtained earlier [12] . The yield for the reacted aniline (I) is 35%. After heating with $AlCl_3$ in CCl_4 at 70-80° for 5 h , compound (XL) was recovered unchanged in quantitative yield.

(b) In a similar experiment at 80° during 4 h, 4 g of a mixture were obtained, containing, according to the GLC data, 0.6% of aniline (I), 1% of compound (XLII), 52% of imidoyl chloride (XL) (yield 49%), 22% of benzotrichloride (XLII)* and 12% of imidoyl chloride (XLI).

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*) The product is identical to that obtained earlier [25] .

TABLE 2

Constants and spectral characteristics of newly synthesized polyfluoroarylcarbonimidoyl dichlorides [a] (nc)

Nos.	Compound	M.p. or b.p., °C/mm	Found composition [b] M.w. (^{35}Cl)	IR spectrum, ν, cm^{-1}			^{19}F NMR spectrum δ, ppm
				Ar_f	N=C	Other bands	
1	X	193–195/750 [c]	$C_7BrCl_2F_4N$ 325	1500	1660	1000 (C–F) 650 (C–Br)	14.2 (2F) 29.9 (2F)
2	XII	78/5	$C_7Cl_2F_4N_2O_2$ 290	1505	1640 1660	1350 (NO$_2$) 1560 (NO$_2$) 1010 (C–F)	15.8 (4F)
3	XV [d]	200–202/750 [c]	$C_8H_3Cl_2F_4N$ 259	1500	1660	2880 (CH$_3$) 2930 (CH$_3$)	11.0 (2F) 18.6 (2F)
4	XVII [e]	79–80	$C_8Cl_4F_4N_2$ 340	1510	1660	1005 (C–F)	13.1 (4F)
5	XIX		$C_7H_2Cl_2F_4N_2$ 260	1510	1665	1000 (C–F) 3410 (NH$_2$) 3500 (NH$_2$)	-3.6 (1F) -0.2 (1F) 3.9 (1F) 13.3 (1F)
6	XX	234/750 [c]	$C_8Cl_4F_4N_2$ 340	1500	1660	1000 (C–F)	-0.2 (1F) 16.7 (2F) 26.2 (1F)
7	XXII	240/750 [c]	$C_7Cl_2F_4N_2O_2$ 291	1500 1520	1670	1570 (NO$_2$) 1370 (NO$_2$) 1010 (C–F)	6.7 (1F) 15.0 (1F) 16.0 (1F) 17.7 (1F)

8	XXVI	145-147	$C_{14}Cl_4F_8N_2$ 488	1480 1500	1655	1000 (C-F)	13.6 (4F) 25.4 (4F)

a) Characteristics of the known arylcarbonimidoyl dichlorides are cited in the following references : X [10] , XIII, XI, XIV, XXIV [11] , XXVIII [4, p. 35] , XXX [4, p. 34] .

b) Elemental composition is calculated with the aid of a " Nairi C " computer from the exact values of the mass numbers of molecular ions, which were determined by using high-resolution mass spectrometry on a " MS-902 " instrument [22] .

c) B.p. is determined after Sivolobov.

d) PMR spectrum, δ, ppm : 2.3

e) p-Aminocarbonimidoyl dichloride (XVI) is identified in a mixture with compound (XVII) from the ^{19}F NMR spectrum (δ, ppm) : 0.4 (2F), 7.6 (2F).

(c) To a suspension of 6.6 g (4.94 mole) of $AlCl_3$ in 20 ml of C_6F_6 9.7 g (3.4 mole) of benzotrichloride (XXXVIII) and a solution of 3 g (1.64 mole) of aniline (I) in 10 ml of C_6F_6 were added. The mixture was kept for 4 h at room temperature, and this gave 6.4 g of a mixture, which, according to the GLC data, contained 15% of aniline (I), 24% of benzotrichloride (XXXVIII) and 35% of imidoyl chloride (XL) (yield 50%).

N-(Pentafluorophenyl)-p-chlorotetrafluorobenzimidoyl chloride (XLI) (nc)

From 1.5 g (0.82 mole) of aniline (I), 4.9 g (1.62 mole) of p-chlorotetrafluorobenzotrichloride (XLII) and 3.27 g (2.45 mole) of $AlCl_3$ in 15 ml of hexafluorobenzene (70-80°, 5 h) 4.45 g of a residue were obtained, from which imidoyl chloride (XLI) crystallized. 1.42 g of imidoyl chloride (XLI) were filtered off and purified by sublimation at 110°/5 mm. , m.p. 64°. Analysis: Found: C, 37.76; Cl 17.28; F, 40.52; N, 3.22%. $C_{13}Cl_2F_9N$ requires C, 37.86; Cl, 17.23; F 41.50; N, 3.40%. IR spectrum, ν , cm^{-1} : 1000, 1500, 1520, 1680 . ^{19}F MNR spectrum, δ , ppm : -0.89 (2F), 4.08 (1F), 13.65 (2F), 23.76 (4F). According to the GLC data the filtrate contained 40% of imidoyl chloride (XLI) and 40% of benzotrichloride (XLII).

Interaction of N-methylpentafluoroaniline (XLIII) with CCl_4 in the presence of $AlCl_3$

2 g (0.01 mole) of aniline (XLIII) and 4 g (0.03 mole) of $AlCl_3$ in 20 ml of absolute CCl_4 (70-80°, 10 h) gave 1.85 g of a residue, containing, according to the GLC data, 54% of the initial aniline (XLIII), 25% of N-methyl-N-pentafluorophenylcarbamic acid chloride (XLV) and 19% of bis(N-methyl-N-pentafluorophenyl)urea (XLVI). At 0°, from this mixture, urea (XLVI) crystallized, was filtered off and purified by sublimation at 90°/25 mm. M.p. 103-104°. Analysis: Found: C, 42.50; H, 1.56; F, 46.20; N, 6.50%. Mol. wt. 420. $C_{15}H_6F_{10}N_2O$ requires C, 42.80; H, 1.42; F, 45.20; N, 6.66%. Mol.wt. 420. IR spectrum, ν , cm^{-1}; 1500, 1740, 2450-3000. ^{19}F NMR spectrum, δ , ppm : -0.8 (4F), 6.6 (2F), 10.2 (4F). PMR spectrum, δ, ppm: 3.05 (CH_3). The filtrate was distilled at 90°/20 mm and gave a liquid, which, according to the GLC data, contained 50% of initial aniline (XLIII) and 40% of acid

chloride (XLV). A pure sample of acid chloride (XLV) was isolated by preparative GLC (220°, SKTFT-50 on Chromatron N, N_2). B.p. 195-196° (after Sivolobov). Analysis: Found: C, 37.15; H, 1.25; Cl, 13.73; F, 36.58; N, 5.38%. Mol. wt. 259. $C_8H_3ClF_5NO$ requires C, 36.90; H, 1.15; Cl, 13.68; F, 36,90; N, 5.39%. Mol.wt. 259 (^{35}Cl). IR spectrum, ν, cm^{-1} : 1510, 1760, 2950, 3000. ^{19}F NMR spectrum, δ, ppm: 1.6 ($2F_m$), 10.3 ($1F_p$), 17.4 ($2F_o$). PMR spectrum, δ, ppm: 3.25 (CH_3)(nc).

Interaction of decafluorodiphenylamine (XLVII) with CCl_4 in the presence of $AlCl_3$

From 1 g (0.003 mole) of amine (XLVII) and 1.15 g (0.009 mole) of $AlCl_3$ in 25 ml of absolute CCl_4 at 60-70° during 6 h, after rapid decomposition of the reaction mixture and distilling off of the solvents, 1.4 g of a residue were obtained; in the ^{19}F NMR spectrum of this residue signals were present at 1.6 ppm ($4F_m$), 11.8 ppm ($2F_p$), 27.3 ppm ($4F_o$), which were assigned by us to amine (XLVIII), and also signals of N,N-bis(pentafluorophenyl)carbamic acid chloride (XLIX). The ratio of the products was ~ 88% and 10%. In the mass spectrum of the sample, molecular ions of amine (XLVIII) and acid chloride (XLIX) were identified with the mass numbers 465 and 411 respectively. Sublimation of the residue at 110°/5 mm gave acid chloride (XLIX). M.p. 123-124° (in a sealed capillary). Analysis: Found: C, 38.40; Cl, 8.16; F, 45.84; N, 3.27%. Mol. wt. 411. $C_{13}ClF_{10}NO$ require C, 37.90; Cl, 8.63; F, 46.17; N, 3.40%. Mol. wt. 411 (^{35}Cl). IR spectrum, ν , cm^{-1} : 1530, 1785. ^{19}F NMR spectrum, δ, ppm: 1.8 ($4F_m$), 11.20 (F_p), 20.21 ($4F_o$) (nc)

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