REACTIONS OF N-POLYFLUOROPHENYLCARBONIMIDOYL DICHLORIDES WITH PRIMARY AND SECONDARY AMINES. KINETICS AND MECHANISM. SYNTHESIS OF POLYFLUORINATED CARBODIIMIDES, CHLOROFORMAMIDINES, GUANIDINES AND BENZIMIDAZOLES*

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SUMMARY

The reactions of N-polyfluorophenylcarbonimidoyl dichlorides with primary and secondary aliphatic and aromatic amines have been studied. With primary aliphatic amines, the reactions led to carbodiimides or guanidines, depending on the amount of amine. The carbodiimides obtained reacted with amines to form guanidines. The reactions with primary aromatic amines produced only triarylguanidines. N-Pentafluorophenylcarbonimidoyl dichloride (I) reacted with tetrafluoro-o-phenylene diamine to give 2-pentafluoroanilino-4,5,6,7-tetrafluorobenzimidazole. Polyfluorinated benzimidazole derivatives were also produced by the thermolysis of polyfluorinated triarylguanidines. Heating of N^1,N^2,N^3-tris(pentafluorophenyl)guanidine with K_2CO_3 in dimethylformamide led to 1,2,3,4,7,8,9,10-octafluoro-5-pentafluorophenyl-5H-benzimidazo[1,2-a]benzimidazole. N-Polyfluorophenylcarbonimidoyl dichlorides reacted with various secondary amines already at room temperature giving N-polyfluorophenylchloroformamidines in high yields. Elevated temperature and prolonged reaction time led to formation of N-polyfluorophenylguanidines. Kinetics and mechanism of the reactions of N-polyfluorophenylcarbonimidoyl dichlorides with primary and secondary amines in acetonitrile at 25°C have been studied. The reactions have been found to proceed by a bimolecular

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nucleophilic addition-elimination mechanism via a tetrahedral intermediate. Possible reasons of formation of different products in the above transformations are discussed in terms of this mechanism.

INTRODUCTION

N-Polyfluorophenylcarbonimidoyl dichlorides, which became available quite recently [1,2], are potentially very reactive compounds owing to the presence of the $-N=CCl_2$ group in their molecule, but their chemical properties have been little studied. For the non-fluorinated analogues of such compounds, very typical reactions are those with the nucleophilic agents, in particular with amines, leading to a large variety of the derivatives, including heterocyclic compounds [3,4]. It was also interesting to study the reactions with amines to examine the reactivity distinctions of compounds with the N=C group from those with the C=O and activated C=C groups. In view of all this, we have studied the reactions of N-polyfluorophenylcarbonimidoyl dichlorides with various amines. This work discusses the products, kinetics and mechanism of interaction of N-polyfluorophenylcarbonimidoyl dichlorides with primary and secondary aliphatic and aromatic amines.

RESULTS AND DISCUSSION

The aliphatic primary amines are known to react with N-arylcarbonimidoyl dichlorides forming N^1-alkyl-N^2-arylcarbodiimides [5] or guanidines [3], whereas with aromatic amines they led only to N^1,N^2,N^3- triarylguanidines [5]. N^1,N^2-Diarylcarbodiimides may only be obtained if, instead of amines, their less basic hydrochlorides are used [5,6].

Treatment of N-pentafluorophenylcarbonimidoyl dichloride (I) with a two- or three-fold mole excess of n-butyl- or t-butylamine in ether or acetonitrile at 20°C led to the respective N-pentafluorophenylcarbodiimides (II) and (III) in more than 70 % yields (see Scheme 1). When the amount of amine was raised to four moles, the reaction products were guanidines (IV) and (V). It should be noted that to achieve a high yield of guanidine (V), the reaction should be carried out under heating. An attempt to isolate carbodiimide (II) from the reaction mixture by silica gel column chromatography afforded N^1-butyl-N^2-pentafluorophenylurea (VI). The latter was also formed in the hydrolysis of carbodiimide (II) by the concentrated hydrochloric acid in dioxan. Individual carbodiimides may be isolated from the reaction mixtures by vacuum distillation.

Carbonimidoyl dichloride (I) vigorously reacted with aniline excess at 20°C in the absence of solvent giving N^1,N^3-diphenyl-N^2-pentafluorophenylguanidine (VII). The same guanidine is the sole reaction product, apart from the unchanged starting compound, if the reaction proceeds in non-polar solvents (ether, carbon tetrachloride) or with a lack of amine and with the use of bases as the hydrogen chloride scavenger (KF or K_2CO_3). By analogy with the reaction in the non-fluorinated series [5,6], the reaction of compound (I) with aniline hydrochloride in o-dichlorobenzene gave N^1-phenyl-N^2-pentafluorophenylcarbodiimide (VIII).

The reaction of carbonimidoyl dichloride (I) with low-basic pentafluoroaniline requires more rigid conditions than with aniline. In boiling acetonitrile and in the presence of KF used as the hydrogen chloride scavenger it gave guanidine (IX) in yields of up to 70 %. Again variation of conditions led to no other products except guanidine (IX).

Heating of the equimolar amounts of compound (I) with tetrafluoro-o-phenylene diamine in sulpholane at 140°C in the presence of the two-fold mole excess of KF afforded 2-pentafluoroanilino-4,5,6,7-tetrafluorobenzimidazole (X) in a 32 % yields. This transformation is similar to the one in the non-fluorinated series [7] except for the more rigid reaction conditions required because of the lower basicity of tetrafluoro-o-phenylene diamine.

Polyfluorinated benzimidazole derivatives were quite unexpectedly obtained in an endeavour to carry out the thermolytic transformation of guanidines to carbodiimides known in the non-fluorinated series [5]. The thermolysis of polyfluorinated guanidines (VII) and (IX) was found to proceed via the intramolecular cyclisation with elimination of hydrogen fluoride and formation of polyfluorinated benzimidazole derivatives (XI) and (XII). The transformation of guanidine (IX) in this case proceeds at a higher temperature and with a lower yield of the benzimidazole derivative, which may be due to the lower nucleophilicity of the $-NHC_6F_5$ group as compared with $-NHC_6H_5$.

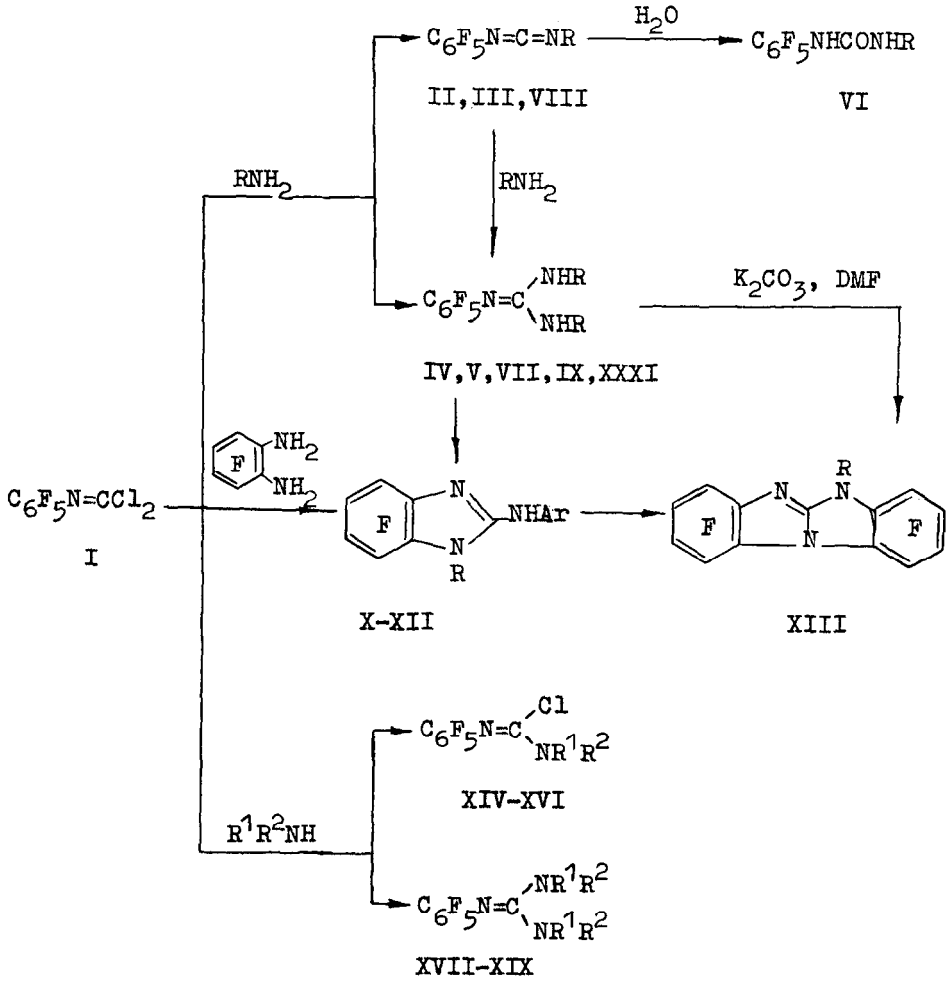
An attempt to transform guanidine (IX) to the benzimidazole derivative (XII) in conditions of intramolecular cyclisation of polyfluoroaromatic compounds [8], that is by heating with K_2CO_3 in dimethylformamide, led to its deeper transformation to 1,2,3,4,7,8,9,10-octafluoro-5-pentafluorophenyl-5H-benzimidazo[1,2-a]benzimidazole (XIII) via the intramolecular cyclisation in the intermediate imidazole (XII), as confirmed by a separate experiment. Analytical and spectral characteristics of compound (XIII) do not deny the suggested structure. It should be noted that in the non-fluorinated series the heterocyclic system of 5H-benzimidazo[1,2-a]benzimidazole was obtained by the thermolysis or photolysis of benzotriazolyl derivatives [9,10].

The reaction of N-arylcarbonimidoyl dichlorides with secondary amines are also known to proceed with removal of one or two chlorine atoms, but unlike the reactions with primary amines, the stages here may be separated to obtain, as a consequence of slower substitution of the second chlorine, N-arylchloroformamidines [11,12] or N-arylguanidines [13,14] respectively.

In the case of N-polyfluoroarylcarbonimidoyl dichlorides, the reactions with various secondary amines have been found by us to proceed in a similar way (see Scheme 1). Thus carbonimidoyl dichloride (I) reacted with diethylamine, N-methylaniline and dibenzylamine in acetonitrile or ether at room temperature to give chloroformamidines (XIV-XVI) in nearly quantitative yields. Synthesis of the respective guanidines (XVII-XIX), the products of substitution of two chlorine atoms by the amine residue, requires much more rigid conditions - elevated temperature and prolonged reaction time. In the case of sterically strained amines, sulfolane is used as a solvent instead of acetonitrile.

The structures of compounds obtained in this work have been established both from the analytical and spectral characteristics, and the transformations specific to such classes of compounds. Carbodiimide (VIII) could not be isolated because of its low stability in the analytically pure form, but its spectral characteristics, molecular weight and conversion to guanidine (VII) in the reaction with aniline unambiguously confirm its structure. It should be noted that the ^{19}F NMR spectrum of guanidine (IX) in acetonitrile recorded in normal conditions contains three broadened fluorine signals, which may result from the tautomeric transformations typical for such compounds [15]. Indeed, when the temperature is lowered and the rate of such transformations drops, the spectrum becomes more resolved. Thus at $-50^{\circ}C$ it shows two broadened multiplet signals at 19.0 and 13.8 ppm with the intensity ratio 2:1, a triplet and multiplet at 7.3 and 5.8 ppm with the intensity ratio 1:1 and a complex multiplet at -1.1:2.5 ppm of the rest seven fluorine atoms. Attempts to obtain a more resolved spectrum failed, as the further decrease of temperature led to freezing of the solution.

Thus we have found that the reactions of N-pentafluorophenylcarbonimidoyl dichloride (I) with primary aliphatic and aromatic amines proceed with elimination of two chlorines to form, in the case of aliphatic amines, non-symmetric carbodiimides or (with a large excess of amine) guanidines, whereas with aromatic amines, irrespective of the amount of amine, the reaction products are N^1,N^2,N^3-triarylguanidines. These results differ from those obtained in the reactions of compound (I) with secondary amines, where at first one chlorine is substituted by the amine residue to form



R = n-C_4H_9 (II, IV, VI); t-C_4H_9 (III, V); C_6H_5 (VII, VIII); C_6F_5 (IX, XIII); R = H, Ar = C_6F_5 (X); R = Ar = C_6H_5 (XI); R = Ar = C_6F_5 (XII); R = n-C_4H_9 and C_6H_5 (XXXI); R^1 = R^2 = C_2H_5 (XIV, XVII); R^1 = CH_3, R^2 = C_6H_5 (XV, XVIII); R^1 = R^2 = $CH_2C_6H_5$ (XVI, XIX).

Scheme 1

chloroformamidines, which further react with amine excess very slowly, so that synthesis of guanidines from them requires more rigid reaction conditions. It was of interest to find out the reason of such routes of the reactions and formation of different products in the above transformations. For that purpose, this work studies kinetics and mechanism of the reactions of N-pentafluorophenylcarbonimidoyl dichloride with various primary and secondary amines. It should be noted that literature reports practically no quantitative data on the reactions of N-arylcarbonimidoyl dichlorides with such amines.

We shall consider first the results of the kinetic studies of N-polyfluoroarylcarbonimidoyl dichlorides with secondary amines, as in this case it is possible to single out the stage of removal of the first chlorine atom.

Kinetics and mechanism of the reactions of N-arylcarbonimidoyl dichlorides with secondary amines have been studied very little.

Thus on the basis of the kinetic data on interaction of N-phenylcarbonimidoyl dichloride with morpholine in dioxan-water at 25°C, it was concluded [16] that substitution of the first chlorine atom by the morpholine residue follows the bimolecular mechanism but the subsequent reaction is complicated by the hydrolysis of the morpholine derivative formed. In more detail the kinetics of the reactions of N-arylcarbonimidoyl dichlorides with various secondary amines has been studied in acetone-water [13]. The rate of the reaction of N-phenylcarbonimidoyl dichloride with diethylamine was shown in [13] to be defined by the first-order equation in the amine, the slow stage being the amine attack on the carbonimidoyl dichloride. The reaction products were N^1,N^1,N^3,N^3-tetraethyl-N^2-phenylguanidine and N^1,N^1-diethyl-N^2-phenylurea. The authors did not succeed in separating the stages of the first and second chlorine substitution, and the presence of water in the system again complicated the general picture. Therefore it was of interest to study the mechanism of interaction of N-polyfluoroarylcarbonimidoyl dichlorides with secondary amines in aprotic media, like it has been done for the aminolysis of imidoyl chlorides [17,18]. In this case, disappearance of the reaction pathway arising from the presence in the reaction mixture of the second nucleophile, water, simplifies the process, which provides a more unambiguous mechanistic conclusion.

We have studied the kinetics of interaction of N-polyfluorophenylcarbonimidoyl dichlorides (I,XX-XXIV) with secondary amines (XXV) in acetonitrile giving chloroformamidines (XXVI) at 25°C (eqn. 2).

$$4\text{-}XC_6F_4N{=}CCl_2 + 2HNR^1R^2 \longrightarrow 4\text{-}XC_6F_5N{=}C(Cl)\text{-}NR^1R^2 + R^1R^2\overset{+}{N}H_2.Cl^- \qquad (2)$$

I,XX-XXIV XXV XXVI

X=F(I), CH_3(XX), CN(XXI), Br(XXII), CF_3(XXIII), NO_2(XXIV);

$R^1{=}R^2{=}CH_3$, C_2H_5, i-C_3H_7, i-C_4H_9, $CH_2C_6H_5$;

$R^1{+}R^2{=}$ $-(CH_2)_5-$, $-(CH_2)_6-$, $-C_2H_4-O-C_2H_4-$;

$R^1{=}CH_3$, $R^2{=}C_6H_5$, 4-$C_6H_4CH_3$, 4-$C_6H_4OCH_3$.

Chloroformamidines (XXVI) react with an amine excess very slowly: at X=F, $R^1{=}R^2{=}C_2H_5$ or $CH_2C_6H_5$ there are no signs of the reaction with piperidine (b=1 mol.l^{-1}) during half an hour; for the reaction of the dichloride (I, X=F) at the same concentration, the half- conversion period calculated from the second-order rate constants k (see Table 1) is $1.61.10^{-4}$ sec.

The rate of reaction (2) was controlled conductometrically by a change in the conductivity of the reaction mixture due to the evolution of the amine hydrochloride. The reaction was carried out in conditions of [XXV] >> [I,XX-XXIV]~$(1\text{-}100).10^{-7}$ mol.l^{-1}. The observed pseudo-first-order rate constants (k^1) remain unchanged in the process (see an example in Table 2) and show a linear dependence on the amine concentration (see Table 3). The second-order rate constants k determined from this dependence for the reactions of dichlorides (I,XX-XXIV) with dibenzylamine and of N-pentafluorophenylcarbonimidoyl dichloride (I) with various amines are represented in Tables 4,5,1.

Introduction of the acceptor (as compared with fluorine) substituent to the phenyl ring of a substrate leads to the increased reaction rate, of the donor substituent - to the decreased reaction rate (see Table 4).

The observed substituent effect is well defined by the Hammett equation:

$$\lg k = -(5.40 \pm 0.05).10^{-1} + (2.11 \pm 0.09)\sigma \qquad (3)$$

n 6; r 0.996; s 0.074

The positive sign of ρ and second order of the reaction suggest that it does not involve the preionisation stage, proceeding entirely as the bimolecular substitution, by the nucleophilic addition-elimination mechanism (route A) or by the synchronous mechanism with a transition state (XXVII) (route B) (Scheme 4).

TABLE 1

Rate constants for the reaction of N-pentafluorophenylcarbonimidoyl dichloride with secondary aliphatic amines, acetonitrile, 25°C

No	Amine	Concentration range of amine, mol . l^{-1}	k $l \cdot mol^{-1} \cdot s^{-1}$	$\Sigma\sigma$	$-E_N$	n[a]
1	Dimethylamine	$(2.07 \div 21.1) \cdot 10^{-6}$	13100 ± 460	0.49	0.47	4
2	Diethylamine	$(1.87 \div 70.0) \cdot 10^{-5}$	114 ± 5	0.29	1.98	7
3	Diisopropylamine	$(3.27 \div 26.2) \cdot 10^{-2}$	0.141 ± 0.011	0.11	3.90	8
4	Diisobutylamine	$(1.23 \div 44.1) \cdot 10^{-2}$	4.92 ± 0.04	0.24	2.47	10
5	Piperidine	$(2.42 \div 81.1) \cdot 10^{-6}$	4300 ± 140	0.35	0.79	5
6	Hexamethyleneimine	$(9.68 \div 133) \cdot 10^{-6}$	4540 ± 280	0.29	1.10	6
7	Dibenzylamine	$(1.65 \div 35.9) \cdot 10^{-6}$	0.378 ± 0.018	0.92	1.50	5
8	Morpholine	$(3.44 \div 93.4) \cdot 10^{-5}$	411 ± 2	1.16 0.62 [21]	0.79	5

[a] n - number of points.

TABLE 2

Kinetic data for the reaction of N-pentafluorophenylcarbonimidoyl dichloride with dibenzylamine (DBA), acetonitrile, 25°C (C_{DBA} = 8.31 . 10^{-2} mol . l^{-1})

Time, s	Yield, %	k^I . 10^2, s^{-1}
1.2	7.1	3.05
2.4	13.6	3.05
3.6	20.3	3.15
4.8	26.4	3.19
6.0	31.4	3.14
7.2	36.4	3.14
8.4	40.6	3.10
9.6	45.0	3.11

TABLE 3

The observed pseudo-first-order rate constants k^I for the reaction of N-pentafluorophenylcarbonimidoyl dichloride with dibenzylamine (DBA), acetonitrile, 25°C

No	C_{DBA} . 10^2, mol . l^{-1}	k^I . 10^3, s^{-1}
1	1.65	6.57 ± 0.15
2	3.92	15.9 ± 0.3
3	8.31	31.2 ± 0.5
4	19.1	81.6 ± 4.0
5	35.9	134 ± 3

$k^I = (1.8 \pm 3.3) \cdot 10^{-3} + (0.378 \pm 0.018) \cdot C_{DBA}$

s 0.005; r 0.997

TABLE 4

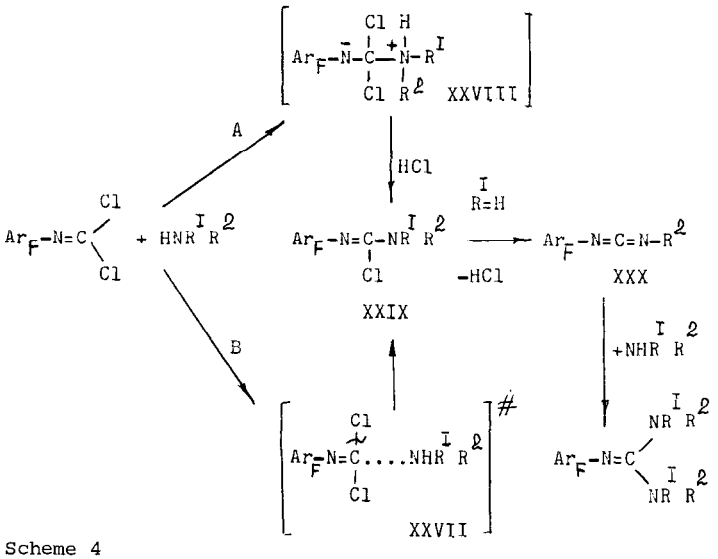
Rate constants for the reaction of dibenzylamine (DBA) with para-substituted carbonimidoyl dichlorides 4-X-C_6F_4-N=CCl_2 , acetonitrile, 25°C

X	Concentration range of DBA, mol . l^{-1}	k . 10 l . mol^{-1} . s^{-1}	n
CH_3	(4.60 ÷ 230) . 10^{-3}	1.38 ± 0.09	7
F	(1.65 ÷ 35.9) . 10^{-2}	3.78 ± 0.18	5
Br	(4.60 ÷ 34.6) . 10^{-3}	8.00 ± 0.91	4
CF_3	(1.36 ÷ 34.6) . 10^{-3}	37.5 ± 1.0	5
CN	(1.58 ÷ 174) . 10^{-4}	93.7 ± 2.5	7
NO_2	(1.36 ÷ 34.6) . 10^{-3}	109 ± 6	5

TABLE 5

Rate constants for the reaction of N-pentafluorophenylcarbonimidoyl dichloride with substituted N-methylaniline (4-R-$C_6H_4NHCH_3$), acetonitrile, 25°C

R	Concentration range of amine, mol . l^{-1}	k . 10^3 l . mol^{-1} . s^{-1}	n
CH_3O	0.113 ÷ 1.21	30.4 ± 1.9	5
CH_3	0.304 ÷ 1.36	6.01 ± 0.10	3
H	0.340 ÷ 2.54	1.12 ± 0.01	4



Scheme 4

The inductive effect of the amine R^1 and R^2 substituents ($\Sigma\sigma^*$) and the amine steric hindrance effect (E_N) may be defined by the modified Taft equation (5) (the Bogatkov-Popov-Litvinenko equation [19]), where

$$\lg k = \lg k_0 + \rho^*\Sigma\sigma + \delta E_N \qquad (5)$$

ρ^* and δ represent the sensitivity of the given reaction series to the respective effect. For the above reaction with the first seven amines of Table 1 the equation is as follows:

$$\lg k = (7.23 \pm 0.41) - (5.04 \pm 0.59)\Sigma\sigma^* + (1.98 \pm 0.13)E_N \qquad (6)$$

n 7; R 0.991; S 0.33

The point for morpholine strongly deviates from the general dependence when the $\Sigma\sigma^*$ value equal to 1.16 is used (the sum of the σ^* values for radicals H and $-C_2H_4OC_2H_4-$). Such (frequently occurring) behaviour of morpholine was explained [20] by the formation of the intramolecular hydrogen bond N-H..O, which led to the increased nucleophilicity of this amine. When

the $\Sigma\sigma^*$ value of 0.62 is used, as has been suggested in view of the above circumstance [21], the point for morpholine fits in the general dependence.

For the amines with the same steric environment of the reaction centre - N-methylanilines (Table 5), the phenyl substituent effect on the reaction rate is given by the Hammett eqn (7):

$$\lg k = -(2.29 \pm 0.13) - (5.20 \pm 0.72)\sigma \qquad (7)$$

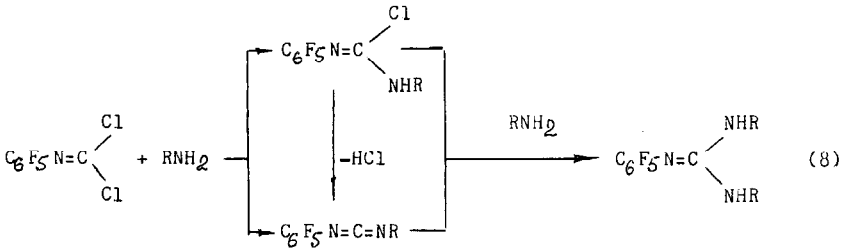
n 3, r 0.991, s 0.14;

This equation shows a high negative ρ value (as the correlation involves only three points, this value of ρ should be regarded as tentative), which coincides in the range of experimental error with the Taft ρ^* value from equation (6). Such a high sensitivity of the reaction to the electronic effects of the structure of nucleophile is generally observed in stepwise processes (for example, substitution in the aromatic ring [22]). This makes route A (the addition-elimination mechanism) preferable over route B (the synchronous mechanism) (Scheme 4). It should be noted that in literature the synchronous mechanism of nucleophilic substitution at the C=N bond is not discussed as a rule, in all the cases the stepwise mechanisms were suggested [23,24].

As there are no data on the leaving group effect, it is difficult to make a definite conclusion about which of the stages - formation of the tetrahedral intermediate (XXVIII) or its breakdown - is rate determining, only suggestions may be made. For the methanolysis of arylbenzimidates $Ar^1C(OAr^2)=NC_6H_4R$ with variable substituent in the N-phenyl ring, whose slow step is formation of the tetrahedral intermediate, the value of 1.98 has been found [25]; for the arylaminolysis of N-benzenesulphonylbenzimidoyl chlorides $Ar^1C(Cl)=NSO_2C_6H_4R$ (the slow stage is breakdown of the tetrahedral intermediate) this value is 0.3 [17]. This leads us to suggest that in the reaction studied by us the rate-determining step is also the attack of amine on dichloride (I), and breakdown of (XXVIII) is fast. This conclusion coincides with the one made in [13]. Non-catalysis by the second molecule of amine, suggesting the proton transfer at the fast stage, does not contradict this suggestion.

As mentioned above, the products of the reaction of carbonimidoyl dichloride (I) with primary amines are carbodiimides and guanidines.

Possible routes of formation of these compounds are represented in Scheme 8.



Scheme 8

The Scheme shows that, irrespective of the nature of primary amine, guanidines may be formed via the intermediate carbodiimides. In this connection it was necessary to find out whether carbodiimides are really the intermediate products in the transformations of compound (I) to guanidines.

Kinetics of the reaction of N-pentafluorophenylcarbonimidoyl dichloride (I) with primary amines was studied in acetonitrile at 25°C in conditions of a large excess of nucleophile, where, irrespective of the nature of amine, the final products of the reaction are guanidines and hydrogen chloride (bound by the amine excess to hydrochloride). The reaction rate was also controlled conductometrically, by a change in the conductivity of the reaction mixture due to the evolution of hydrogen chloride, in the concentration conditions of $[RNH_2] >> [I] \sim (1:5).10^{-6}$ mol.l^{-1}. It should be realised that if substitution of two geminal chlorines proceeded stepwise and with small rate differences between the successive steps, the dependence of hydrogen chloride concentration on the reaction time might have been rather complex (examples of such substitution at the C=C bond are well known [26]). However for the reaction under study, the conductivity changes exponentially; the observed pseudo-first-order rate constant k^1 remains unchanged in the process and linearly depends on the amine concentration, the line passing the origin of coordinates (Tables 6 and 7 give the examples for the reaction with t-butylamine). The calculation of the second-order rate constant k has taken into account that the rate of consumption of the starting imidoyl dichloride (I) (taken for the reaction rate) is twice as low as the rate of accumulation of the conducting species (one carbonimidoyl dichloride (I) molecule generates two HCl molecules).

Such simple kinetic regularities allow us to make some important conclusions. The first order in the substrate implies that either the rate of the second chlorine substitution (elimination of the second HCl molecule) is higher than

TABLE 6

The reaction of N-pentafluorophenylcarbonimidoyl dichloride with t-butylamine , acetonitrile, 25°C. $\left[(CH_3)_3C\text{-}NH_2\right]$ = 5.10 . 10^{-2} M.

Time, s	Yield, %	k^I . 10^3, s^{-1}
6	3.71	6.30
12	7.25	6.27
18	10.8	6.37
24	14.2	6.36
30	17.6	6.47
36	20.2	6.25
42	23.1	6.24

k^I_{av} = (6.32 ± 0.08) . 10^{-3}, s^{-1}

TABLE 7

The observed pseudo-first-order rate constant k^I of the reaction of N-pentafluorophenylcarbonimidoyl dichloride with t-butylamine at different concentrations of nucleophile, acetonitrile, 25°C.

$\left[(CH_3)_3C\text{-}NH_2\right]$, M.	k^I, s^{-1}
1.24 . 10^{-2}	(2.21 ± 0.15) . 10^{-3}
4.82 . 10^{-2}	(5.35 ± 0.11) . 10^{-3}
5.10 . 10^{-2}	(6.32 ± 0.08) . 10^{-3}
6.41 . 10^{-2}	(7.89 ± 0.32) . 10^{-3}
1.40 . 10^{-1}	(1.55 ± 0.04) . 10^{-2}
4.48 . 10^{-1}	(5.83 ± 0.08) . 10^{-2}
5.83 . 10^{-1}	(6.84 ± 0.13) . 10^{-2}

k^I = (4.11 ± 113) . 10^{-5} + (0.122 ± 0.004) . $\left[(CH_3)_3C\text{-}NH_2\right]$

n 7; r 0.997; s 2.2 . 10^{-3}

k = (6.10 ± 0.20) . 10^{-2} M^{-1} . s^{-1}

that of the first chlorine substitution, or both HCl molecules appear after the rate determining step. Elimination of two HCl molecules at a time or their formation together with carbodiimide in one elementary step seem to be unlikely. Though formation of guanidine requires at least two amine molecules, the reaction may not be trimolecular - this is denied by the first order in the nucleophile. If initially only one amine molecule participates in the reaction, it should undoubtedly proceed stepwise with the intermediate formation of, e.g., chloroformamidine of the general formula (XXIX) and carbodiimide (XXX) (Scheme 4).

Formation of carbodiimide as the intermediate product in the reaction carried out in excess aliphatic amine is easy to prove. The UV spectrum of the reaction mixture of N-pentafluorophenylcarbonimidoyl dichloride (I) with t-butylamine (in large excess) in acetonitrile contains a new absorption band with a maximum at 254 nm, distinct from the absorption bands of the starting dichloride (216 and 270 nm) and amine. The optic density at this wavelength rapidly increases, then slowly decreases. In the same wavelength range there is an absorption maximum (λ_{max}= 254 nm, ε_{254}= 13100) of the authentic N^1-t-butyl-N^2-pentafluorophenylcarbodiimide (III). Some time after having reached the maximal value, the optic density decrease (λ_{max}= 254 nm) for the reaction mixture of compound (I) with an excess of t-butylamine obeys the law of the first-order rate. The optic density of a mixture of authentic carbodiimide (III) with t-butylamine decreases in the same manner. Kinetics of these processes in acetonitrile at 25°C has been studied in the concentration conditions of [t-BuNH$_2$] >> [substrate]$\sim 5.10^{-4}$ mol.l^{-1}. Table 8 represents the observed pseudo-first-order rate constants for these processes at different concentrations of nucleophile. Obviously, the reactivity towards t-butylamine is the same both for the intermediate product of the reaction of carbonimidoyl dichloride (I) with t-butylamine and for the authentic carbodiimide (III). The data obtained unequivocally indicate participation of carbodiimides as the intermediate products in the reaction of carbonimidoyl dichloride (I) with aliphatic primary amines.

The structure effect of primary aliphatic amines (the first 10 ones in Table 9) on the rate of their reaction with compound (I) is adequately defined by the modified Taft equation (9):

$$\lg k = (8.26 \pm 1.17) - (5.46 \pm 1.02)\Sigma\sigma^* + (3.26 \pm 0.38)\cdot E_N \qquad (9)$$

n 10; R 0.956; S 0.525

A high ρ value is also obtained in processing the data for anilines (nucleophiles with the same steric environment of the reaction centre) according to the Hammett equation:

$$\lg k = -(2.84 \pm 0.14) - (4.68 \pm 0.76)\sigma \qquad (10)$$

n 3, r 0.987; s 0.146

In its parameters, equation (9) is very close to the corresponding equation (6) specifying the reactivity of secondary aliphatic amines (see p.11). The combined treatment of the data for the primary and secondary aliphatic amines gave the following equation:

TABLE 8

The observed pseudo-first-order rate constants k^I of the reaction of t-butylamine with N^1-t-butyl-N^2-pentafluorophenylcarbodiimide (k_a^I) and the intermediate product of the reaction of N-pentafluorophenylcarbonimidoyl dichloride with t-butylamine (k_b^I) at different concentrations of amine, acetonitrile, 25°C

Concentration of t-butylamine, M.	$k_a^I \cdot 10^3$, s^{-1}	$k_b^I \cdot 10^3$, s^{-1}
$9.59 \cdot 10^{-2}$	1.43 ± 0.03	1.39 ± 0.09
$2.40 \cdot 10^{-1}$	3.82 ± 0.07	3.58 ± 0.20
$4.79 \cdot 10^{-1}$	6.79 ± 0.26	6.86 ± 0.10
$7.19 \cdot 10^{-1}$	9.67 ± 0.14	10.4 ± 0.3
$9.59 \cdot 10^{-1}$	14.1 ± 0.0	13.9 ± 0.5

$$k_a^I = (9.1 \pm 40.1) \cdot 10^{-5} + (1.42 \pm 0.07) \cdot 10^{-2} \cdot \left[(CH_3)_3C\text{-}NH_2\right]$$

n 5; r 0.997; s $4.7 \cdot 10^{-4}$

$$k_b^I = (5.8 \pm 69.1) \cdot 10^{-6} + (1.45 \pm 0.02) \cdot 10^{-2} \cdot \left[(CH_3)_3C\text{-}NH_2\right]$$

n 5; r 0.999; s $8.2 \cdot 10^{-5}$

TABLE 9

Second-order rate constants k for the consumption of N-pentafluorophenylcarbonimidoyl dichloride in the reactions with primary aliphatic and aromatic amines, acetonitrile, 25°C.

No	Amine	Concentration range of amine, M.	k, $M^{-1} \cdot s^{-1}$	$\Sigma\sigma$	$-E_N$	n[a]
1	Methylamine	$(7.95 \div 175) \cdot 10^{-6}$	224 ± 10	0.98	0.07	7
2	Ethylamine	$(7.88 \div 69.1) \cdot 10^{-6}$	205 ± 5	0.88	0.36	4
3	i-Propylamine	$(1.71 \div 56.0) \cdot 10^{-4}$	11.6 ± 0.3	0.79	0.93	5
4	n-Butylamine	$(1.79 \div 69.0) \cdot 10^{-5}$	153 ± 4	0.85	0.40	7
5	i-Butylamine	$(7.18 \div 296) \cdot 10^{-6}$	214 ± 4	0.86	0.35	10
6	t-Butylamine	$(1.24 \div 44.8) \cdot 10^{-2}$	$(6.10 \pm 0.20) \cdot 10^{-2}$	0.68	1.74	7
7	t-Octylamine	$(2.21 \div 86.0) \cdot 10^{-1}$	$(1.35 \pm 0.08) \cdot 10^{-2}$	0.68	1.91	6
8	Allylamine	$(1.63 \div 27.9) \cdot 10^{-4}$	49.2 ± 0.9	1.14	0.20	5
9	Benzylamine	$(6.69 \div 95.9) \cdot 10^{-5}$	32.6 ± 1.7	1.20	0.38	4
10	Ammonia	$(4.36 \div 139) \cdot 10^{-1}$	0.315 ± 0.01	1.47	0.00	6
11	Deuteroammonia	$(3.83 \div 122) \cdot 10^{-1}$	0.478 ± 0.006			6
12	Aniline	$0.52 \div 3.24$	$(1.61 \pm 0.10) \cdot 10^{-3}$			5
13	4-Toluidine	$(7.72 \div 236) \cdot 10^{-2}$	$(6.92 \pm 0.03) \cdot 10^{-3}$			6
14	4-Anisidine	$(6.93 \div 96.2) \cdot 10^{-2}$	$(3.16 \pm 0.02) \cdot 10^{-2}$			4

[a] n - number of points.

$$\lg k = (7.64 \pm 0.74) - (5.31 \pm 0.69)\Sigma\sigma^* + (2.28 \pm 0.25)E_N \quad (11)$$

n 17; R 0.927; S 0.717

If we discard the most strongly deviating points for t-octylamine (Δ =-1.55), t-butylamine (Δ =-1.28) and benzylamine (Δ =1.11), the correlation coefficients are considerably improved:

$$\lg k = (7.35 \pm 0.34) - (5.09 \pm 0.33)\Sigma\sigma^* + (2.03 \pm 0.12)E_N \quad (12)$$

n 14; R 0.983; S 0.315

The correlation parameters (the $\lg k_o$, ρ^* and δ values of the intercept) in this case remain practically unchanged. They coincide within the error with the corresponding values for the series of primary and secondary amines. This suggests a common mechanism of the reaction of primary and secondary amines with polyfluorinated carbonimidoyl dichlorides. We think this mechanism (see Scheme 4) to involve the amine attack on the carbonimidoyl dichloride (a slow step) giving the tetrahedral intermediate (XXVIII) (route A), which rapidly loses one HCl molecule to form chloroformamidine (XXIX). In the case of secondary amines, the reaction practically ends at this stage. In the case of primary amines, chloroformamidine (XXIX) also quickly (quicker than the nucleophilic attack on the carbonimidoyl dichloride occurs) loses one HCl molecule to form carbodiimide (XXX). Carbodiimide (XXX) in the case of primary aliphatic amines is rather slowly transformed to guanidine and may therefore be recorded and isolated. It should be noted that, e.g., carbodiimide (III) (R = $-C(CH_3)_3$) reacts with t-butylamine only 4 times as slowly as compound (I) (cf. the data of Tables 7 and 8). Evidently, upon substitution of the alkyl substituent by the more electron-attracting aryl one, the electrophilic nature of carbodiimide (XXX) will increase, and it will react with amine more rapidly than the starting carbonimidoyl dichloride. Possibly due to this, the attempts to isolate the intermediate carbodiimide in the reactions with primary arylamines usually fail. This does not contradict the known data on the reactivity of aromatic and aliphatic carbodiimides with nucleophiles [27], and is confirmed by the transformations of carbodiimides (II) and (VIII) with butylamine and aniline to the respective guanidines (IV), (VII) and (XXXI).

In the synchronous displacement (alternative to the stepwise mechanism) involving a transition state (XXVII) (route B), formation of the "new" C-N bond, and cleavage of the "old" C-Cl and N-H bonds occur in one (naturally, rate-determining) step. Substitution of hydrogen by deuterium in the amino group of nucleophile would be expected to lead to a decreased reaction rate.

In reality the case is just the opposite: on passing from ammonia to deuteroammonia the reaction rate increases (see Table 9). In terms of the stepwise mechanism (route A), this may be easily explained: the slow stage of the reaction is the amine attack on carbonimidoyl dichloride (I), cleavage of the N-H bond occurs after this stage.

EXPERIMENTAL

The IR spectra of the CCl_4 and $CHCl_3$ solutions of the compounds (layer thickness 0.4 mm) were recorded on the UR-20 spectrophotometer. The ^{19}F and ^{1}H NMR spectra of the CCl_4 and $CHCl_3$ solutions of the compounds were recorded on a Varian A56/60A spectrometer at 56.4 and 60 MHz, with hexafluorobenzene and hexamethyldisiloxane respectively as internal standards. Molecular weights were determined by the vapour-phase osmometry and mass-spectrometrically on a high-resolution Finnigan MAT 8200 GC/MC chromatomass-spectrometer.

Synthesis of carbonimidoyl dichlorides has been described earlier [1,2].

Experimental conditions for the reactions of carbonimidoyl dichloride (I) with amines and the constants of the products are given in Table 10. The spectral data for the newly synthesized compounds are represented in Table 11, the elemental analyses data and molecular weights - in Table 12.

The conductometric procedure of rate measurements is described in [18]. Spectrophotometric measurements were carried out on the СФ-26 spectrophotometer with thermostatted cell holder.

For the kinetic measurements the aromatic amines were purified by repeated distillations in vacuum (the last distillation run before the kinetic measurements). Liquid aliphatic amines were purified by recrystallisation of their hydrochlorides from isopropyl alcohol, then, after decomposing the hydrochlorides with an alkali - by repeated distillations over sodium. Ethylamine was obtained by treatment of an aqueous solution of hydrochloride with an alkali, and dried by passing through a column with solid alkali. Methylamine was prepared by oxidation of acetamide with an alkaline solution of bromine, and passed over solid alkali. Ammonia was obtained from the purest grade ammonia chloride by treatment with aqueous alkali, and dried with solid potassium hydroxide. Due to the necessity to use rather large concentrations of ammonia (see Table 9), the time of its passing through acetonitrile may be significant, and the procedure may involve blowing off part of the solvent. Therefore the concentration of ammonia solutions was checked by titrating an aqueous HCl solution (indicator - methyl red). The same refers to deuteroammonia (commercial grade reagent, the weight content of the main

TABLE 10

Interaction of pentafluorophenylcarbonimidoyl dichloride (I) with amines

(I), g	Amine, g	Solvent, ml	Reaction temperature, °C	Reaction time, h	Product	Method of isolation, yield, g (%)	B.p.°C (mm Hg) or m.p.°C
0.39	$n\text{-}C_4H_9NH_2$ 0.33	Acetonitrile 10	20	5	II	A, 0.29 (74)	102-103 (10)
0.39	$t\text{-}C_4H_9NH_2$ 0.33	Acetonitrile 7	20	5	III	A, 0.28 (72)	84-85 (5)
0.66	$n\text{-}C_4H_9NH_2$ 0.73	Acetonitrile 5	20	2	IV	B/100°C (5 mm), 0.76 (91)	76-77
0.33	$t\text{-}C_4H_9NH_2$ 0.37	Acetonitrile 7	80	5	V	B/100°C (6 mm), 0.36 (86)[a]	84-85
0.88	$C_6H_5NH_2$ 0.78	-	20	20 min	VII	C (aq ethanol) 0.75 (60)[a]	159-160
1.32[b]	$C_6F_5NH_2$ 1.70	Acetonitrile 5	80	20	IX	B/100°C (38 mm), 1.84 (66)	200-201
0.27[c]	$o\text{-}(NH_2)_2C_6H_4$ 0.18	Sulpholane 1	145	5	X	B/200°C (12 mm), 0.12 (32)[a]	244-245

1.32	$(C_2H_5)_2NH$ 1.46	Ether 10	20	15 min	XIV	A, 1.34 (90)	138-139 (10)
2.00	$C_6H_5NHCH_3$ 3.20	Acetonitrile 20	20	3	XV	B/80°C (5 mm) 2.3 (91)	76-77
0.79	$(C_6H_5CH_2)_2NH$ 1.20	Acetonitrile 10	20	2	XVI	C, 1.2 (92)	97-98
1.32	$(C_2H_5)_2NH$ 2.19	Acetonitrile 10	80	9	XVII	A, 0.76 (45)	139-140 (6)
1.00	$C_6H_5NHCH_3$ 1.62	Sulpholane 5	120	8	XVIII	C, 1.2 (80)	104-105
0.40	$(C_6H_5CH_2)_2NH$ 1.80	Sulpholane 6	145	16	XIX	C, 0.7 (79)	132-133

a The reaction product was treated with aqueous ammonia, washed with water and dried over P_2O_5.

b In the presence of 1.16 g of KF.

c In the presence of 0.14 g of KF.

substance 99.6 %, enrichment 99.6 %). Dimethylamine was isolated from aqueous solution by treatment with an alkali, then - passed through the solid potassium hydroxide column. Other aliphatic amines were purified by boiling over metallic sodium during many hours, with subsequent distillation. N-Methylaniline was purified by three distillations in vacuum. N-Methyltoluidine and p-anisidine were obtained by the known method [28], via the potassium salts of the acetyl derivatives of the respective primary amines, and purified by distillation in vacuum.

Acetonitrile was purified by the known method - by two distillations over P_2O_5 and calcined potassium carbonate.

Interaction of N-pentafluorophenylcarbonimidoyl dichloride (I) with amines

To a solution of compound (I) in a absolute solvent was added slowly, with stirring, a solution of amine in the same solvent, and the reaction mixture was kept at the appropriate temperature. After having been cooled, the amine hydrochloride residue was filtered off, the solvent distilled off from the filtrate and the residue distilled in vacuum (method A), sublimed in vacuum (method B), or recrystallised from hexane (method C).

N^1-Butyl-N^2-pentafluorophenylurea (VI) (nc)

(a) The reaction mixture (0.5 g) obtained in the reaction of compound (I) with butylamine and containing, according to the ^{19}F NMR data, carbonimidoyl dichloride (I) and carbodiimide (II) in the ratio 1:4, was separated on a 125-135μ silica gel column, eluent - hexane (300 ml) and chloroform (200 ml) to give urea (VI) (0.29 g, 77 %). M.p. 148-149.5°C (sublimation at 145°C (6 mm)).

(b) A solution of carbodiimide (II) (0.27 g) in dioxan (0.5 ml) and concentrated HCl (2 ml) was stirred during 1.5 h at 55°C, cooled and extracted with ether. The ether extract was dried over $CaCl_2$, and the solvents were distilled off. The residue (0.3 g) was identic, by the ^{19}F NMR spectrum, to the product obtained by method (a).

N^1-Phenyl-N^2-pentafluorophenylcarbodiimide (VIII) (nc)

A mixture of aniline hydrochloride (0.49 g), o-dichlorobenzene (5 ml) and compound (I) (1 g) was heated with stirring for 6 h at 180°C. Separation of

the reaction mixture by TLC on silica gel LSL 5/40 μ (eluent - hexane: benzene, 3:1 v/v) gave a mixture of carbodiimide (VIII) and o-dichlorobenzene (1.14 g). Analysis: Found: M^+ 284.0038. $C_{13}H_5F_5N_2$ requires M^+ 284.0041. IR spectrum (o-dichlorobenzene), ν, cm^{-1}:2160 (N=C=N), 1520 (C_6F_5), 1040 (C-F). ^{19}F NMR spectrum (o-dichlorobenzene), δ, ppm:13.3 ($2F_o$), 1.2 (F_p), -0.9 ($2F_m$). An attempt to isolate o-dichlorobenzene by vaccum distillation gave a complex mixture of unidentified compounds, which does not contain carbodiimide (VIII).

Interaction of carbodiimide (VIII) with aniline

Aniline (0.65 g) was added with stirring to a solution of carbodiimide (VIII) obtained in o-dichlorobenzene according to the procedure described above, and the mixture was kept for 16 h at 20°C. Guanidine (VII) hydrochloride (0.3 g) was filtered off, and treated with aqueous ammonia to give guanidine (VII).

Interaction of carbodiimide (II) with amines

(a) Butylamine (0.11 g) was added with stirring to a solution of compound (II) (0.2 g) in absolute ether (2 ml). After being kept for 18 h at 20°C the reaction mixture was shown by ^{19}F NMR to contain only guanidine (IV).

(b) Aniline (0.07 g) was added with stirring to a solution of compound (II) (0.2 g) in absolute ether. After being kept for 14 h at 20°C the mixture was distilled to remove ether, and the residue recrystallised from hexane to give N^1-butyl-N^3-phenyl-N^2-pentafluorophenylguanidine (XXXI) (nc) (0.15 g, 56 %), m.p. 120-121°C.

1-Phenyl-2-anilino-4,5,6,7-tetrafluorobenzimidazole (XI) (nc)

Guanidine (VII) (0.2 g) was heated for 6 h at 170°C in a sealed evacuated tube. Recrystallisation from chloroform and sublimation at 200°C (5 mm) gave compound (XI) (0.14 g, 74 %), m.p. 232.5-234°C.

1-Pentafluorophenyl-2-pentafluoroanilino-4,5,6,7-tetrafluorobenzimidazole (XII) (nc)

Guanidine (IX) (1.24 g) was heated for 27 h at 200°C in a sealed evacuated tube. The reaction mixture was separated on a silica gel (140-315 μ) column, eluent - benzene, to yield compound (XII) (0.44 g, 37 %), m.p. 184-185°C (benzene).

1,2,3,4,7,8,9,10-Octafluoro-5-pentafluorophenyl-5H-benzimidazo[1,2-a] benzimidazole (XIII) (nc)

(a) To a suspension of calcined K_2CO_3 (0.12 g) in absolute dimethylformamide (7 ml) was added with stirring a solution of guanidine (IX) (0.9 g) in dimethylformamide (2 ml). The reaction mixture was heated for 7 h at 140°C. After it has been cooled, the precipitate was filtered off, the filtrate distilled to remove the solvent, and the residue passed through a silica gel layer (eluent - benzene). Benzene was distilled off, and the solid residue (0.75 g) sublimated at 160°C (7 mm) to give compound (XIII) (0.54 g, 64 %), m.p. 143-145°C.

(b) To a suspension of calcined K_2CO_3 (0.04 g) in absolute dimethylformamide (3 ml) was added with stirring a solution of compound (XII) (0.3 g) in dimethylformamide (1 ml), and the mixture was heated for 2 h at 140°C. Treatments of the reaction mixture according to method (a) gave compound (XIII) (0.25 g).

Preparation of N-pentafluorophenylchloroformamidines (XIV-XVI) and N-pentafluorophenylguanidines (XVII-XIX) (nc)

These compounds were obtained by the slow addition of a solution of amine in an absolute solvent to a solution of N-pentafluorophenylcarbonimidoyl dichloride (I) in the same solvent and stirring the mixture at the appropriate temperature. Further treatment and methods of isolating the products are similar to those described for the reactions with primary amines. In the case of guanidines (XVIII) and (XIX), the cooled reaction mixture was diluted with water, and extracted with ether. The ether solution was washed with water, dried with $CaCl_2$, and the ether was distilled off. The residue was dissolved in hexane, the hexane solution was passed through the silica gel layer, hexane was partially distilled off, and the guanidine precipitate filtered off.

TABLE 11

Spectral data for the new compounds

Compound	^{1}H NMR spectrum, δ, ppm	^{19}F NMR spectrum, δ, ppm	IR spectrum, ν, cm^{-1}			
			C_6F_5	N=C	NH	Other bands
II[a]	1.0 m, 1.6 m, 3.5 m (n-Bu)	12.4 ($2F_o$), -1.4 ($2F_m$,F_p)	1520 1550	-	-	1000, 2880, 2940, 2970
III[b]	1.4 s (t-Bu)	12.6 ($2F_o$), -1.8 ($2F_m$,F_p)	1530	-	-	970, 1000, 2980
IV	1.0 m, 1.4 m, 3.1 m (n-Bu) 3.9 br. (2NH)	10.1 ($2F_o$), -2.8 ($2F_m$), -5.8 (F_p)	1510	1620	3450 3470	1000, 2880, 2940, 2970
V	1.3 s (t-Bu), 3.7 br. (2NH)	9.9 ($2F_o$), -3.4 ($2F_m$), -7.6 (F_p)[c]	1510	1620	3420 3480	990, 2880, 2930
VI	1.0 m, 1.4 m, 3.2 m (n-Bu) 6.1 s (NH), 7.5 s (NH)[d]	16.7 ($2F_o$), 1.6 (F_p), -2.0 ($2F_m$)[e]	1505	-	3280 3330	995, 1650 (C=O), 2940, 2960
VII[f]	6.9 m (2NH), 7.2 m ($2C_6H_5$)	10.8 ($2F_o$), -3.4 ($2F_m$), -6.7 (F_p)	1510	1650	3430	1000, 1600, 3050
IX[cg]	7.0 s (2NH)	15.4; 1.2 ; -1.6	1520	1650 1670	3410	1000, 1020
X[f]	8.2 br. (2NH)	17.1 ($2F_o$), 4.4 (F_p, 2F) -0.4 ($2F_m$), -6.2 (2F)	1490 1530 1550[h]	1600	3430	1020
XI[e]	6.7-7.5 ($2C_6H_5$, NH)	4.4 (F), 1.1 (F), -6.5(2F)	1490	1610	3430	1000, 3060

(continued overleaf)

TABLE 11 (cont.)

			1560			
			1580			
XII[e]	7.2 s (NH)	19.7 (2F), 14.4 (2F),	1500	1690	3400	1000, 1300
		12.2 (F), 6.7 (F), 2.0(2F)	1520			
		-0.9 (2F), -3.2 (4F)	1540			
XIII[e]	-	19.5 (2F), 13.1 (F),	1490	1680	-	1000, 1060
		9.6 (2F), 7.5 (F), 2.7	1550			
		(3F), 0.5 (2F), -0.4 (F),	1600			
		-3.0 (F)				
XIV	1.3 t, 3.6 qu ($2C_2H_5$)	9.4 ($2F_o$), -3.2 ($2F_m$, F_p)	1510	1650	-	1000, 2940, 2980
XV	3.5 s (CH_3), 7.8 s (C_6H_5)	9.9 ($2F_o$), -2.3 ($2F_m$, F_p)	1510	1650	-	1000, 1600, 2930
XVI	4.8 s, 7.3 s ($2CH_2C_6H_5$)	10.5 ($2F_o$), -2.1 ($2F_m$, F_p)	1510	1640	-	1000, 2930, 3030
XVII	1.1 t, 3.1 qu ($4C_2H_5$)	7.6 ($2F_o$), -3.9 ($2F_m$),	1510	1590	-	1000, 2880,
		-8.2 (F_p)				2930, 2980
XVIII	3.1 s,($2CH_3$), 7.0 m ($2C_6H_5$)	7.8 ($2F_o$), -3.7 ($2F_m$),	1500	1580	-	1000, 2950,
		-6.0 (F_p)				1610, 3040
XIX	4.2 s, 7.2 s ($4CH_2C_6H_5$)	9.0 ($2F_o$), -3.0 ($2F_m$),	1500	1580	-	1000, 2875,
		-6.9 (F_p)				2925, 3030
XXXI	0.9 m, 1.5 m, 3.4 m (n-Bu)	10.1 ($2F_o$), -3.9 ($2F_m$),	1520	1630	3420	1000, 1600,
	5.6 br (NH), 7.2 br	-8.0 (F_p)[f]			3440	2880, 2940,
	(C_6H_5, NH)[d]					2870

[a] In the IR spectrum the absorption band of the N=C=N grouping at 2170 cm^{-1}.
[b] In the IR spectrum the absorption band of the N=C=N grouping at 2160 cm^{-1}.
[c] In CH_3CN.
[d] In d-acetone.
[e] In THF.
[f] In acetone.
[g] The signals in the ^{19}F NMR spectrum recorded at ambient temperature.
[h] KBr pellets.

TABLE 12

The elemental analyses data and molecular weights of the new compounds

Compound	Found %						Composition	Calculated %					M.w.
	C	H	Cl	F	N	M.w.		C	H	Cl	F	N	(^{35}Cl)
II	50.15	3.39	-	35.88	10.65	268	$C_{11}H_9F_5N_2$	50.00	3.41	-	35.98	10.61	264
III	50.10	3.58	-	36.11	10.65	264	$C_{11}H_9F_5N_2$	50.00	3.41	-	35.98	10.61	264
IV	53.26	5.95	-	27.86	12.45	325	$C_{15}H_{20}F_5N_3$	53.41	5.93	-	28.19	12.46	337
V	53.73	6.03	-	28.33	12.68	337	$C_{15}H_{20}F_5N_3$	53.41	5.93	-	28.19	12.46	337
VI	47.01	3.66	-	33.80	9.95	280	$C_{11}H_{11}F_5N_2O$	46.81	3.90	-	33.69	9.93	282
VII	60.48	3.43	-	25.28	10.99	378	$C_{19}H_{12}F_5N_3$	68.48	3.18	-	25.20	11.14	377
IX	40.87	0.39	-	51.09	7.58	557	$C_{19}H_2F_{15}N_3$	40.93	0.36	-	51.16	7.54	557
X	42.57	0.78	-	46.00	11.16	371	$C_{13}H_2F_9N_3$	42.00	0.54	-	46.10	11.30	371
XI	63.77	3.05	-	21.79	11.81	357	$C_{19}H_{11}F_4N_3$	63.87	3.08	-	21.29	11.76	357
XII	42.59	0.26	-	49.52	7.38	537	$C_{19}HF_{14}N_3$	42.46	0.19	-	49.53	7.82	537
XIII	44.06	-	-	47.79	7.83	517	$C_{19}F_{13}N_3$	44.10	-	-	47.78	8.12	517
XIV	43.92	3.20	12.04	31.73	9.38	310	$C_{11}H_{10}ClF_5N_2$	43.93	3.33	11.81	31.61	9.32	300.5
XV	50.05	2.35	10.67	29.02	8.47	334	$C_{14}H_8ClF_5N_2$	50.22	2.39	10.61	28.40	8.37	334
XVI	59.65	3.30	8.45	22.25	6.45	424	$C_{21}H_{14}ClF_5N_2$	59.36	3.30	8.36	22.38	6.60	424
XVII	53.34	5.93	-	28.15	12.68	332	$C_{15}H_{20}F_5N_3$	53.41	5.93	-	28.19	12.46	337
XVIII	62.30	3.98	-	23.69	10.30	405	$C_{21}H_{16}F_5N_3$	62.22	3.95	-	23.46	10.37	405
XIX	71.26	4.76	-	16.53	6.98	585	$C_{35}H_{28}F_5N_3$	71.79	4.79	-	16.24	7.18	585
XXXI	57.39	4.52	-	26.75	11.63	357	$C_{17}H_{16}F_5N_3$	57.14	4.48	-	26.61	11.76	357

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