REACTIONS OF *N*-(PENTAFLUOROPHENYL)CARBONIMIDOYL DICHLORIDE WITH FLUORINATED BENZENES IN THE PRESENCE OF $AlCl_3$

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Dedicated to the memory of Professor Miloš Hudlický.

N-(Pentafluorophenyl)carbonimidoyl dichloride (**1**) reacts, in the presence of excess $AlCl_3$, with fluorinated benzenes containing 1–5 fluorine atoms in the molecule. With fluoro- and 1,3,5-trifluorobenzene the reaction gives the corresponding imidoyl chlorides and azomethines; at elevated temperatures, azomethines are formed in increased amounts. With 1,2,4,5-tetrafluorobenzene and pentafluorobenzene, intramolecular cyclization, leading to polyfluorinated 1,2,3,4-tetrahydroquinazoline-2,4-diones **9** is preferred. The side reactions are fluorine substitution with chlorine and formation of 1,3-bis(pentafluorophenyl)urea (**10**).

Keywords: Electrophilic aromatic substitutions; Friedel–Crafts reaction; $AlCl_3$; Fluorinated benzenes; Imidoyl chlorides; Azomethines; Intramolecular cyclization; 1,2,3,4-Tetrahydroquinazoline-2,4-diones.

Previously, polyfluoroaromatic compounds with an imidoyl chloride group were shown to be effective electrophilic reagents capable of interacting with aromatic compounds in the presence of $AlCl_3$ [1–3]. Thus reactions with aromatic amines occur at the amino nitrogen and lead to the corresponding guanidines[1]. Reaction with a nitrogen–carbon multiple bond in aromatic imidoyl chlorides or nitriles is a cycloaddition process giving five- and six-membered N-heterocyclic derivatives[2]. Reactions with benzene and alkylbenzenes yield azomethines[3]. In order to expand knowledge of the behaviour of aromatic compounds with polyfluorinated imidoyl chloride derivatives as electrophilic reagents, it seemed interesting to study the reactions of low-basicity fluorinated benzenes in order to find the new reg-

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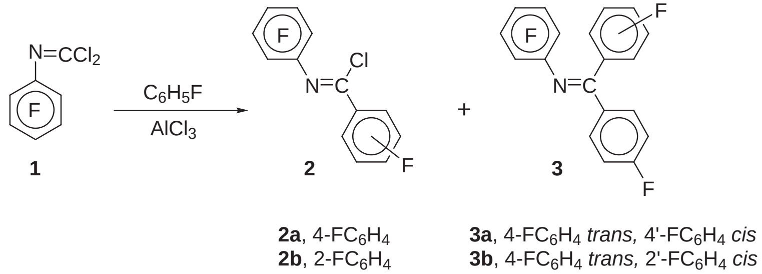
ularities and synthetic range. In the present paper, the results of investigation of the reactions of *N*-(pentafluorophenyl)carbonimidoyl dichloride (**1**) with fluorinated benzenes used as reagents and solvents and containing 1–5 fluorine atoms in the ring (fluorobenzene, 1,3,5-trifluorobenzene, 1,2,4,5-tetrafluorobenzene and pentafluorobenzene), occurring in the presence of $AlCl_3$ are considered.

Reactions with Fluorobenzene

Carbonimidoyl dichloride **1** reacted with fluorobenzene in the presence of a 2.5-fold molar excess of $AlCl_3$ at 20 °C, giving a mixture of isomeric imidoyl chlorides **2**. A considerable amount of the starting dichloride **1** was unchanged (the ratio of **1** : **2** is 1 : 1.3, ^{19}F NMR data). At 80 °C, the starting dichloride reacted completely, but the reaction mixture contained azomethines **3** along with imidoyl chlorides **2** (Scheme 1).



SCHEME 1

According to ^{19}F NMR data, at 80 °C (12 h) the ratio of **2** : **3** was 3.6 : 1. At 120 °C (17 h), the sole reaction products were azomethines **3**.

As indicated by GC/MS, imidoyl chlorides **2** were obtained as a mixture of three (**2a**–**2c**) or two (**2a**, **2b**) isomers containing mainly **2a**. In the reaction mixture obtained at 20 °C, isomer **2a** prevailed (≈40%), the amount of **2b** ranged from 1 to 3%, and the content of **2c** was less than 1%. In the ^{19}F and ^{1}H NMR spectra of the isomer mixture of **2a**–**2c**, the ^{19}F and ^{1}H signals of **2b** and **2c** virtually do not appear because of the low contents of these isomers in the mixture. The ^{19}F NMR spectrum of **2a** showed the signals of the fluorine atoms of the C_6F_5 group as well as the multiplet of the fluorine atom of the benzene ring bonded to the carbon atom of the N=C bond (C-benzene ring). The values of F-H spin-spin coupling constants observed for the latter signal suggest that the fluorine atom is in position 4. This is confirmed by ^{1}H NMR data. The ^{1}H NMR spectrum contains two equally intense signals, whose fine structure suggests that the aromatic hydrogens are in the 2,6 and 3,5 positions of the C-benzene ring. Thus the major isomer **2a** is 4-fluoro-*N*-(pentafluorophenyl)benzimidoyl chloride. It can be assumed that compound **2a** is in *Z* configuration since this is the most typical form of aromatic imidoyl chlorides[3,4]. Based on the data on the orientation of fluorobenzene (para > ortho > meta)[5] in electrophilic reactions, including Friedel–Crafts reactions[5,6], and mass-spectral data on fragmentation of compounds **2a**–**2c**, it was inferred that **2b** is an isomer with fluorine in position 2 and **2c** in position 3.

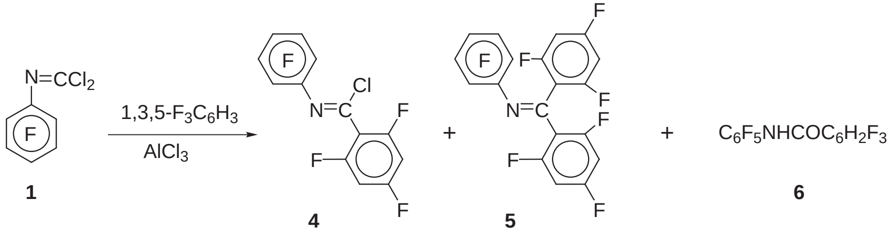
The mixture of azomethine products **3** consists of three isomers (**3a**–**3c**), among which **3a** always prevails. We were unable to isolate the individual isomers in analytically pure form, probably because of the similarity of their physical properties. The ^{19}F NMR spectrum of **3a** shows the signals of the C_6F_5 fluorine atoms as well as two equally intense signals of the C-benzene fluorine atoms, whose fine structure is similar to that of the fluorine signal of the fluorobenzene ring of **2a**. This gives us grounds to believe that these fluorine atoms occupy the same (4,4′) position in the two C-benzene rings. For one of these signals, the chemical shift is close to the corresponding value for the C-benzene fluorine atom of **2a**, and the signal might be assigned to the fluorine atom in position 4 of the C-benzene ring which is trans to the C_6F_5 group. Regretfully, the structure of **3a** cannot be unambiguously inferred from ^{1}H NMR data, since the ^{1}H signals of the two C-benzene rings partly overlap. The spectrum consists of two multiplets with the intensity ratio 2 : 6. The only assumption that can be made based on these data is that the two protons of the trans-benzene ring, like the protons in **2a**, correspond to the multiplet signal with intensity 2 (H-2,6) and that the signal of the other two protons virtually coincides with the signal of four protons of the cis-benzene ring. Nevertheless, based on the NMR data we ascribed to compound **3a** the structure of bis(4-fluorophenyl) ketone *N*-(pentafluorophenyl)imine, which was confirmed by X-ray structure analysis data.

In the ^{19}F NMR spectrum of isomer **3b**, the signals of the C_6F_5 fluorine atoms are downfield as compared with **3a**. One of the signals of the C-benzene fluorine atoms coincides in its chemical shift with the analogous signal in **3a**; therefore it may belong to the fluorine atom in position 4 of the trans-C-benzene ring. Poor resolution of the signal of the fluorine atom in the other C-benzene ring and lack of ^{1}H NMR data for pure isomer **3b** made it impossible to unambiguously establish the structure of azomethine **3b**. X-Ray structure analysis data, however, indicate that **3b** is (2-fluorophenyl) (4-fluorophenyl) ketone *N*-(pentafluorophenyl)imine. Note that

X-ray structure analysis was performed for a 1 : 1.1 mixture of **3b** and **3a** (^{19}F NMR) because the individual isomer **3b** was not isolated. The data obtained for both **3b** and **3a** confirm the above assumption about the trans-position of the *N*-(pentafluorobenzene) ring bonded to the nitrogen atom of the N=C bond and the C-benzene ring with a fluorine atom in position 4. The structure of the minor isomer **3c** was not elucidated.

Reactions with 1,3,5-Trifluorobenzene

The reaction of **1** with 1,3,5-trifluorobenzene in the presence of $AlCl_3$ at 50–60 °C (17 h) was insignificant; it left a large amount of unchanged starting dichloride **1** and led to imidoyl chloride **4** and azomethine **5**, the former being predominant. According to ^{19}F NMR data, the ratio of **1** : **4** and of **4** : **5** was 5 : 1. At elevated temperature (85 °C, 17 h), more imidoyl chloride **4** and azomethine **5** were formed (1 : 1, ^{19}F NMR), and the starting compound **1** was found only in trace amounts (Scheme 2).

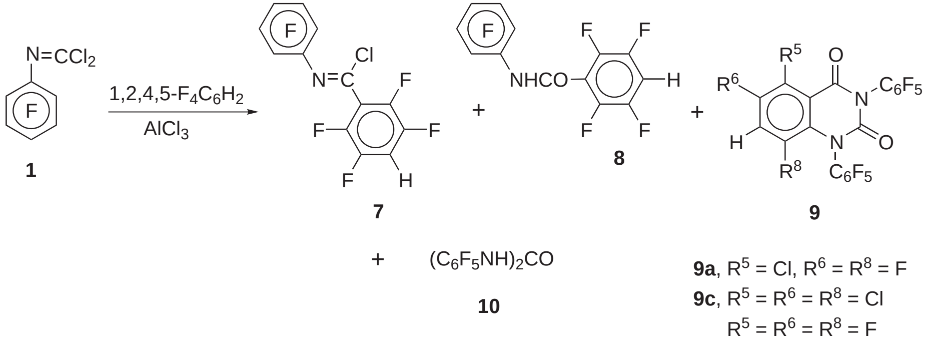


SCHEME 2

According to GC/MS data, the reaction mixture also contained a small amount of 2,4,6-trifluoro-*N*-(pentafluorophenyl)benzamide (**6**), which may be result of the hydrolysis of imidoyl chloride **4**. An attempt to obtain a predominant amount of imidoyl chloride **4** under the above conditions by taking 1,3,5-trifluorobenzene in an equimolar amount (but not in excess) also afforded a mixture of imidoyl chloride **4** and azomethine **5** along with a large amount of unchanged starting dichloride **1** (4 : 1 : 3.4, ^{19}F NMR). When the reaction was carried out with an excess of trifluorobenzene, as mentioned above, but at 120 °C (22 h), the major reaction product was azomethine **5** (the ratio of **4** : **5** is 1 : 3, ^{19}F NMR), and the content of amide **6** in the reaction mixture was but a few per cent. At 170 °C (18 h), only azomethine **5** is produced. The analytical and spectral data for compounds **4** and **5** completely agree with the structures of 2,4,6-trifluoro-*N*-(pentafluorophenyl)benzimidoyl chloride (**4**) and bis(2,4,6-trifluorophenyl) ketone *N*-(pentafluorophenyl)imine (**5**).

Reactions with 1,2,4,5-Tetrafluorobenzene

Heating **1** and $AlCl_3$ with 1,2,4,5-tetrafluorobenzene at 170 °C (31 h) led to a complex mixture of products. Approximately one third of the mixture was the starting tetrafluorobenzene; dichloride **1** was present in trace amounts (GC/MS). The other products identified by GC/MS were 2,3,5,6-tetrafluoro-*N*-(pentafluorophenyl)benzimidoyl chloride (**7**) (≈1%) and 2,3,5,6-tetrafluoro-*N*-(pentafluorophenyl)benzamide (**8**) (≈5%) (Scheme 3). The expected azomethine was absent. Another one third of the mixture was consisted of the halogen derivatives of 1,3-bis(pentafluorophenyl)-1,2,3,4-tetrahydroquinazoline-2,4-dione **9**, among which the major products were 5-chloro-6,8-difluoro-1,3-bis(pentafluorophenyl)-1,2,3,4-tetrahydroquinazoline-2,4-dione (**9a**) and the isomeric 7-chloro-6,8-difluoro-1,3-bis(pentafluorophenyl)-1,2,3,4-tetrahydroquinazoline-2,4-dione (**9b**). GC/MS data indicated that the reaction mixture contained trace amounts of 5,6,8-trifluoro-1,3-bis(pentafluorophenyl)-1,2,3,4-tetrahydroquinazoline-2,4-dione and derivatives of 1,2,3,4-tetrahydroquinazoline-2,4-diones with two hydrogen atoms in the molecule.



SCHEME 3

The reaction mixture also contained the products of fluorine exchange for chlorine in the starting tetrafluorobenzene and imidoyl chloride **7**. The ^{19}F NMR spectrum of the reaction mixture showed the signals of 1,3-bis(pentafluorophenyl)urea (**10**), decomposing under conditions of GC/MS analysis into pentafluoroaniline and pentafluorophenylisocyanate. The product ratio can be determined by ^{19}F NMR only roughly because many signals overlap: 0.5 : 1.1 : 0.6 : 0.1 : 1 for compounds **7**, **8**, **9a**, **9b**, and **10**. The previously unknown heterocyclic derivatives **9a**–**9c** were isolated from the reaction mixture and characterized. Their structure was determined by high-resolution mass spectrometry and also by ^{19}F and ^{1}H NMR and IR spectroscopy. The molecular weights of **9a**–**9c** as well as their elemental compositions and MS fragmentation are consistent with the suggested structures. The ^{19}F NMR spectrum of **9a** contains two sets of signals from two pentafluorobenzene rings and two equally intense signals from the fluorine atoms of the carbocycle ring. Both signals are doublets of doublets with spin-spin coupling constant *J*(F,F) = 5.2. This value of the constant rules out the ortho position of the fluorine atoms, indicating that they are probably in meta position to each other (*cf*. ref.[7]). The downfield signal was assigned to the fluorine atom in position 6, with hydrogen and chlorine occupying the ortho position; the upfield signal was attributed to the fluorine atom in position 8, with hydrogen atom in the ortho position. The second constant of the F-6 signal seems to be due to spin-spin coupling of this fluorine atom with the ortho proton in position 7. The second constant of the upfield F-8 signal may also be due to spin-spin coupling with the neighboring proton H-7. The ^{1}H NMR spectrum of **9a** shows one signal with a doublet of doublets structure, also agreeing with the arrangement of hydrogen and fluorine atoms suggested for **9a**.

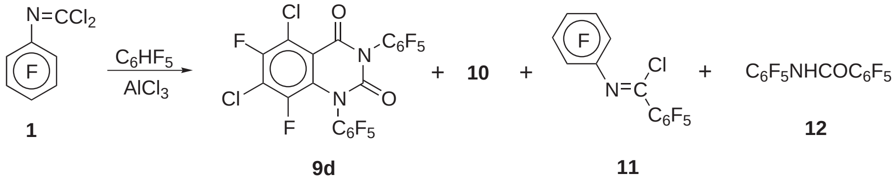
In the ^{19}F NMR spectrum of isomer **9b**, one can also observe two sets of signals from the two pentafluorophenyl groups and two equally intense downfield signals from the two fluorine atoms of the carbocycle ring of the heterocyclic system. The chemical shifts of these signals are close to those of the signals of F-6 and F-8 atoms of isomer **9a**, suggesting that in **9b** they also belong to F-6 and F-8. One signal is a downfield doublet of doublets, which may be assigned to the fluorine atom in position 6 [*J*(6,5) and *J*(6,8)]. The other is a broad singlet assigned to the fluorine atom in position 8. The ^{1}H NMR spectrum of **9b** supports this assignment. It contains a doublet of doublets with expected *J*(5,6) and *J*(5,8) constants. The downfield position of this signal compared with that of isomer **9a** seems to be a consequence of the effect of the neighboring carbonyl group, thus supporting the structure suggested for **9b**.

For the trichloro derivative **9c**, the ^{19}F NMR spectrum contains only the signals of the two pentafluorophenyl substituents, and the ^{1}H NMR spectrum shows a singlet for one proton.

MS fragmentation of heterocyclic derivatives of type **9** containing two hydrogen atoms does not permit an unambiguous structural conclusion.

Reactions with Pentafluorobenzene

Carbonimidoyl dichloride **1** does not react with pentafluorobenzene in the presence of excess $AlCl_3$ at 80 °C. At 150 °C (6 h), the unchanged starting compounds still make the bulk of the reaction mixture, but traces of the 1,3-bis(polyfluorophenyl) derivatives of 1,2,3,4-tetrahydroquinazoline-2,4-dione with different numbers of fluorine and chlorine atoms are already present. Moreover, minor (several per cent) quantities of pentafluoroaniline and 2,3,4,5,6-pentafluoro-*N*-(pentafluorophenyl)benzimidoyl chloride (**11**) were identified in the mixture. At 170 °C (31 h), the unchanged starting dichloride **1** is still found in the reaction mixture, but the major product under these conditions was 5,7-dichloro-6,8-difluoro-1,3-bis(pentafluorophenyl)-1,2,3,4-tetrahydroquinazoline-2,4-dione (**9d**) (Scheme 4).



SCHEME 4

Urea **10** was also formed in a considerable amount. The content of imidoyl chloride **11** (identified by GC/MS alone) changed insignificantly. Pentafluoroaniline was also present in the mixture along with 2,3,4,5,6-pentafluoro-*N*-(pentafluorophenyl)benzamide (**12**). The ratio of **1** : **9d** : **10** : **12** : pentafluoroaniline was 2.6 : 6.2 : 3.8 : 1.25 : 1 (^{19}F NMR). The mixture also contained the products of chlorine exchange for fluorine in the starting compounds and products as well as chlorination products (GC/MS). Even hexachlorobenzene was identified in the mixture though in trace amounts only.

The structure of compound **9d** was determined by elemental analysis and spectroscopy and confirmed by X-ray structure analysis.

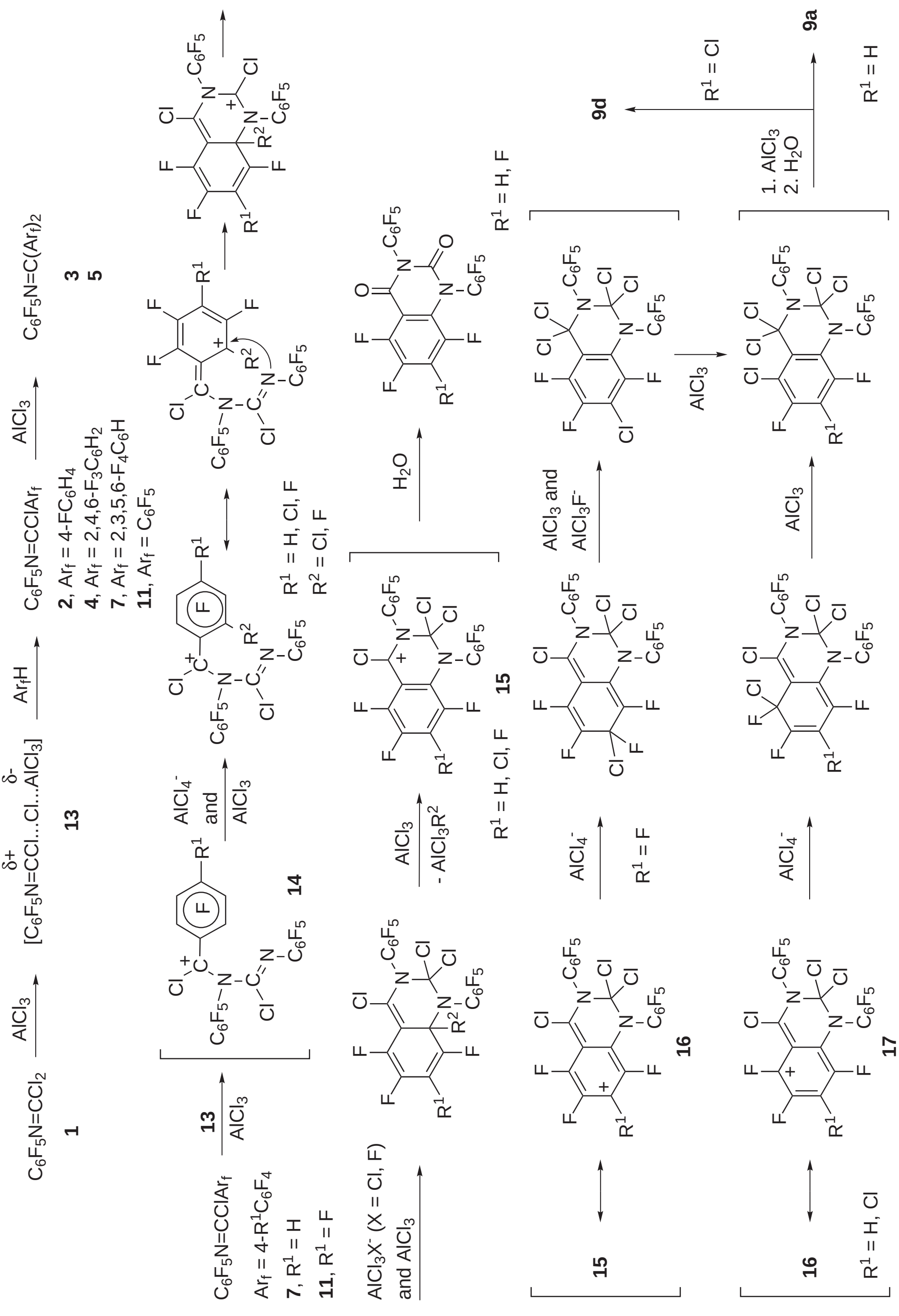
RESULTS AND DISCUSSION

The results of the present work indicate that the paths of the reactions of dichloride **1** with various fluorobenzenes in the presence of excess $AlCl_3$ depend on the number of fluorine atoms in the fluorobenzene molecule. When 1–3 fluorine atoms are present (reactions with fluorobenzene and 1,3,5-trifluorobenzene), the major products are imidoyl chlorides and azomethines resulting from alkenylations of fluorobenzenes (elevated reaction temperature promotes formation of azomethines). For fluorobenzenes with four or more fluorine atoms (1,2,4,5-tetrafluorobenzene and pentafluorobenzene) the dominant reaction is intramolecular cyclization leading to polyfluorinated derivatives of 1,2,3,4-tetrahydroquinazoline-2,4-dione. In this case, imidoyl chlorides are formed in small amounts, and azomethines are absent in the reaction mixture. A possible scheme of these transformations is presented below (Scheme 5).

Parts of this scheme are analogous to those which we published previously for reactions of **1** and $AlCl_3$ with alkylbenzenes[3] and for cyclizations with substrates containing a nitrogen–carbon multiple bond[2].

The electrophilic intermediate **13** formed in the reaction of carbonimidoyl dichloride **1** with $AlCl_3$ attacks fluorinated benzene, giving imidoyl chloride. The latter, in turn, is analogously converted by $AlCl_3$ into another electrophilic intermediate capable of reacting with a second fluorinated benzene molecule, forming azomethine. Fluorinated benzenes with up to 3 fluorine atoms seem to be sufficiently potent donors to react with the electrophilic intermediate generated from **1** under the action of $AlCl_3$. In polyfluorinated benzene, the electron-accepting ability of the aromatic ring increases, and their reactivity with electrophilic agents decreases[8]. Moreover, one can expect that ionisation of the C–Cl bond in imidoyl chlorides **7** and **11** also decreases to some extent because of increasing destabilization of the positive charge that appears on carbon under the action of $AlCl_3$. These factors are probably responsible for the fact that in the case of 1,2,4,5-tetrafluorobenzene and pentafluorobenzene intermediate **13** interacts with the nitrogen–carbon double bond of the imidoyl chloride with subsequent intramolecular cyclization to 1,2,3,4-tetrahydroquinazoline-2,4-diones **9**. It is noteworthy that intermediate **14** is a benzyl type carbocation in which the para- and ortho-fluorine atoms may be replaced by chlorine under the action of $AlCl_4^-$ (*cf.* ref.[9]) so that the cyclization step may involve an attack of the nucleophilic center on the positively charged carbon bonded to both the fluorine atom ($=C^+–F$) and the chlorine atom ($=C^+–Cl$). Possible paths to compounds **9a** and **9d** are schematically represented (Scheme 5) by including the contributions from resonance structures **16** and **17**.

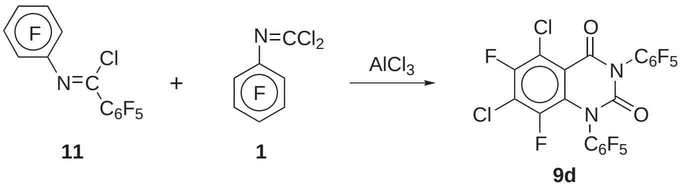
Isomer **9b** containing a hydrogen atom in position 5 is probably formed according to a scheme analogous to Scheme 5, but the reaction involves isomeric 1,2,3,4-tetrafluorobenzene. Indeed, analysis of the 1,2,4,5-tetrafluorobenzene used for the reaction indicated that the starting material contained about 97% of the compound and approximately 2% of


$C_6F_5N=CCl_2$
1
$AlCl_3$
δ+ δ-
$[C_6F_5N=CCl...Cl...AlCl_3]$
13
Ar_fH
$C_6F_5N=CClAr_f$
2, $Ar_f = 4\text{-}FC_6H_4$
4, $Ar_f = 2,4,6\text{-}F_3C_6H_2$
7, $Ar_f = 2,3,5,6\text{-}F_4C_6H$
11, $Ar_f = C_6F_5$
$AlCl_3$
$C_6F_5N=C(Ar_f)_2$
3
5
$C_6F_5N=CClAr_f$
$Ar_f = 4\text{-}R^1C_6F_4$
7, $R^1 = H$
11, $R^1 = F$
13
$AlCl_3$
14
$AlCl_4^-$ and $AlCl_3$
$R^1 = H, Cl, F$
$R^2 = Cl, F$
$AlCl_3X^-$ (X = Cl, F) and $AlCl_3$
$AlCl_3$
$- AlCl_3R^2$
$R^1 = H, Cl, F$
15
H_2O
$R^1 = H, F$
15
16
$AlCl_4^-$
$R^1 = F$
$AlCl_3$ and $AlCl_3F^-$
$AlCl_3$
9d
$R^1 = Cl$
16
$R^1 = H, Cl$
17
$AlCl_4^-$
$AlCl_3$
1. $AlCl_3$
2. H_2O
9a
$R^1 = H$

SCHEME 5

1,2,3,4-tetrafluorobenzene impurity, which led to compound **9b**. The formation of heterocyclic derivative **9b**, in turn, suggests that under the given conditions isomeric tetrafluorobenzenes may behave analogously to 1,2,4,5-tetrafluorobenzene.

Scheme 5 was supported by formation of heterocyclic compound **9d** as the major product in the reaction occurring on heating (in a separate run) of carbonimidoyl dichloride **1** with the authentic imidoyl chloride **11** in the presence of excess $AlCl_3$ (Scheme 6).



SCHEME 6

At elevated temperatures, side reactions are promoted. These are primarily processes of chlorine exchange for fluorine. These processes in substrates, leading to products which may be involved in the transformations, and analogous processes with the end products complicate the composition of the reaction mixtures and the general picture of transformations. Thus chlorine atoms may appear in compound **9a** as a result of the side reaction of chlorine exchange for fluorine in the initially formed 5,6,8-trifluoro-1,3-bis(pentafluorophenyl)-1,2,3.4-tetrahydroquinazoline-2,4-dione, identified in trace amounts in the reaction mixture obtained in the experiment with 1,2,4,5-tetrafluorobenzene. On the other hand, chlorine atoms may appear as a result of the reaction of **1** and $AlCl_3$ with the products of chlorine exchange for fluorine in the starting tetrafluorobenzene, which were also identified in the reaction mixture. The same holds for compound **9c**.

Other side reactions also occur in the presence of $AlCl_3$ at high temperatures. One of these processes leads to urea **10**. The reaction path leading to **10** is not quite apparent, but it seems to be the consequence of the transformations involving the products of hydrolysis of **1** by air moisture. One of these products, pentafluoroaniline, was recorded in reaction mixtures by ^{19}F NMR. For 1,2,4,5-tetrafluorobenzene and pentafluorobenzene possessing low reactivity, the contribution from the reactions with pentafluoroaniline is comparable with the contributions from other transformations and hence the content of urea **10** is reasonably high. The low reactivity of these fluorobenzenes and the high content of tar products lead to low yields of major products.

EXPERIMENTAL

^{19}F and ^{1}H NMR spectra were recorded on a Bruker WP-200-SY instrument with hexafluorobenzene (162.9 ppm from CCl_3F) and hexamethyldisiloxane (0.04 ppm from TMS) as internal standards and CCl_4 as a solvent. IR spectra were measured on a Specord M-80 instrument for 5% CCl_4 solutions. GC/MS analyses of the reaction mixtures were performed on a Hewlett–Packard G 1081A system which consisted of an HP 5890 (series II) gas chromatograph and an HP 5971 mass selective detector (EI 70 eV). Capillary column HP-5MS (5% diphenyl- and 95% dimethylpolysiloxane): 30 m × 0.25 mm × 0.25 μm. Carrier gas helium, 1 ml/min. Column temperature elevation mode: 50 °C for 2 min, 10 °C/min, 280 °C for 5 min; evaporator temperature 280 °C and ion source temperature 170 °C. The data were collected at a rate of 1.2 scan/s, mass region 30–650 amu. The GC/MS data are given without correction and hence they are approximate. Column chromatography was carried out on silica gel (140–315 mesh). The molecular weights and molecular formulae were determined mass-spectrometrically on a Finnigan-MAT-8200 high-resolution instrument (nominal ionizing electron energy 70 eV). Petroleum ether (b.p. 70–100 °C) was used as one of the solvents. Authentic imidoyl chloride **11** was prepared by a known procedure[10]. MS and IR data are given in Table I; NMR data of amides, imidoyl chlorides, and azomethines are listed in Table II; NMR data for 1,2,3,4-tetrahydroquinazoline-2,4-diones are presented in Table III.

Reactions of 1 with Fluorinated Benzenes in the Presence of $AlCl_3$

A mixture of compound **1**, freshly sublimated $AlCl_3$, and excess of fluorinated benzene was heated in a flask equipped with a stirrer and a reflux condenser with a calcium chloride tube or in a sealed glass ampoule at an appropriate bath temperature. The reaction mixture was cooled and then decomposed with cold water (100 ml), extracted with ether (100 ml), the extract was washed with water to neutral pH and dried over anhydrous $CaCl_2$. The solvent was distilled off till the precipitate started to settle, and the ether solution was analyzed by ^{19}F NMR and GC/MS.

Reactions with Fluorobenzene

The reactions of compound **1** (0.26 g, 1 mmol), $AlCl_3$ (0.34 g, 2.5 mmol) and fluorobenzene (1 g, 12.8 mmol) were carried out at room temperature (22.5 h) and at 80 °C (12 h) in a flask equipped with a stirrer and a reflux condenser with a calcium chloride tube. The reaction mixture obtained at 80 °C (19.5 h) from compound **1** (0.78 g, 3 mmol), freshly sublimated $AlCl_3$ (1.02 g, 7.5 mmol) and fluorobenzene (3 g, 38.4 mmol) contained compounds **2** and **3** in the ratio 2 : 1.5 (^{19}F NMR). According to ^{19}F NMR data, the ratio of **3a** and **3b** was 1 : 0.4. The mixture was combined with the reaction mixture obtained from the starting compound **1** (0.26 g, 1 mmol). After the ether was distilled off, silica gel column chromatography (CCl_4 as eluent) of the residue gave imidoyl chlorides **2** (0.75 g), which were purified by dissolving in heptane (5 ml) and passing through a silica gel layer. The solvent was distilled off and imidoyl chlorides **2** were isolated as yellow oil (0.66 g, 69%), which solidified. M.p. 40–43 °C. According to GC/MS data, the mixture contained about 97% of **2a** and about 3% of **2b**. For $C_{13}H_4ClF_6N$ calculated: 48.30% C, 1.24% H, 10.00% Cl, 4.33% N, 322.9936 M; found: 49.34% C, 1.55% H, 10.02% Cl, 4.00% N, 322.9934 M. The second fraction (0.18 g) was a mixture of isomeric azomethines **3**, which was purified by sublimation at 100 °C/1330 Pa

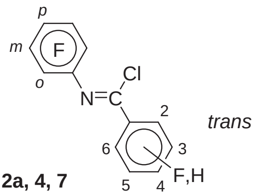
TABLE I
MS and IR data for imidoyl chlorides **2a**, **4**, **7**, azomethines **3a**, **3b**, **5**, amide **8** and 1,2,3,4-tetrahydroquinazoline-2,4-diones **9a**–**9d**

Comp.	MS, m/z, %	IR, ν, cm^{-1}
2a	$[M]^+$ 323 (22.96), $[M - Cl]^+$ 288 (100), $[M - Cl - F]^+$ 269 (1.35), $[C_6F_5]^+$ 167 (3.88), $[C_6H_4F]^+$ 95 (55.12)	977–994 s, 1159 m, 1240 s, 1510–1514 vs (C_6F_5), 1598 m, 1643–1659 s (C=N), 2858 w, 2931 w, 2963 w (C–H)
3a	$[M]^+$ 383 (80.15), $[M - F]^+$ 364 (10.77), $[M - C_6H_4F]^+$ 288 (77.68), $[M - C_6F_5N - H]^+$ 201 (100), $[C_6F_5]^+$ 167 (3.37), $[C_5F_3]^+$ 117 (6.82), $[C_6H_4F]^+$ 95 (72.28)	986–998 vs, 1155 m, 1240 s, 1308 m, 1504–1514 vs (C_6F_5), 1602 s, 1627 m (C=N), 3083 w (C–H)
3b	$[M]^+$ 383 (57.41), $[M - F]^+$ 364 (7.33), $[M - C_6H_4F]^+$ 288 (100), $[M - C_6F_5N - H]^+$ 201 (77.87), $[C_6F_5]^+$ 167 (7.13), $[C_6H_4F]^+$ 95 (80.35)	
4	$[M]^+$ 359 (15.55), $[M - Cl]^+$ 324 (100), $[M - Cl - C_6H_2F_3]^+$ 193 (1.93), $[C_6F_5]^+$ 167 (21.39), $[C_5F_3]^+$ 117 (24.91)	939 s, 1002 s, 1126 s (C–F), 1446 s, 1508–1515 vs (C_6F_5), 1597 s, 1639 vs (C=N), 3107 w (C–H)
5	$[M]^+$ 455 (50.62), $[M - F]^+$ 436 (11.02), $[M - C_6H_2F_3]^+$ 324 (100), $[M - NCC_6H_2F_3]^+$ 298 (8.04), $[C_6F_5]^+$ 167 (14.65), $[C_5F_3]^+$ 117 (14.69)	979 s, 1001 s, 1051 s, 1129 s, 1447 m, 1510–1517 vs (C_6F_5), 1600 m, 1678 s (C=N), 3108 w (C–H)
7	$[M]^+$ 377 (20.12), $[M - Cl]^+$ 342 (100), $[M - Cl - F]^+$ 323 (2.11), $[M - Cl - C_6F_4H]^+$ 193 (1.39), $[C_6F_5]^+$ 167 (25.63), $[C_5F_3]^+$ 117 (33.57)	1001 s (C–F), 1514 vs (C_6F_5), 1681 m (C=N)
8	$[M]^+$ 359 (11.13), $[M - C_6F_5NH]^+$ 177 (100), $[M - C_6F_5NHCO]^+$ 149 (35.32), $[C_5F_3]^+$ 117 (2.63)	
9a	$[M]^+$ 564 (12.60), $[M - F]^+$ 545 (0.52), $[M - C_6F_5NCO]^+$ 355 (100), $[M - C_6F_5NCO - CO]^+$ 327 (11.59), $[M - C_6F_5NCO - CO - F]^+$ 308 (35.90), $[M - C_6F_5NCO - CO - Cl]^+$ 292 (26.89), $[M - C_6F_5NCO - CO - CF_2]^+$ 277 (17.08), $[C_6F_5NCO]^+$ 209 (6.69), $[C_6F_5N]^+$ 181 (4.93)	
9b	$[M]^+$ 564 (48.62), $[M - F]^+$ 545 (1.57), $[M - C_6F_5NCO]^+$ 355 (100), $[M - C_6F_5NCO - CO]^+$ 327 (12.60), $[M - C_6F_5NCO - CO - F]^+$ 308 (17.18), $[M - C_6F_5NCO - CO - Cl]^+$ 292 (18.35), $[M - C_6F_5NCO - CO - CF_2]^+$ 277 (7.48), $[C_6F_5NCO]^+$ 209 (0.74), $[C_6F_5N]^+$ 181 (1.02)	
9c	$[M]^+$ 596 (41.85), $[M - C_6F_5NCO]^+$ 387 (100), $[M - C_6F_5NCO - Cl]^+$ 352 (22.97), $[M - C_6F_5NCO - Cl - CO]^+$ 324 (27.01), $[M - C_6F_5NCO - CO - 3Cl]^+$ 254 (10.84), $[C_6F_5NCO]^+$ 209 (4.13)	
9d	$[M]^+$ 598 (8.63), $[M - C_6F_5NCO]^+$ 389 (100), $[M - C_6F_5NCO - CO - F]^+$ 342 (17.16), $[M - C_6F_5NCO - CO - Cl]^+$ 326 (18.52), $[M - C_6F_5NCO - CO - 2Cl - F]^+$ 272 (6.16), $[C_6F_5NCO]^+$ 209 (5.70)	999 s (C–F), 1200 vs, 1523 vs (C_6F_5), 1711 vs (C=O), 1748 s (C=O) ($CHCl_3$)

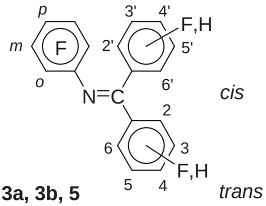
and recrystallization from petroleum ether. M.p. 74–76 °C; composition (GC/MS data): 52% of **3a**, 42% of **3b**, and 6% of **3c**. According to ^{19}F NMR data, the ratio of **3a** : **3b** was 1.1 : 1. For $C_{19}H_8F_7N$ calculated: 59.50% C, 2.09% H, 34.73% F, 3.66% N, 383.0545 M; found: 59.11% C, 2.11% H, 34.59% F, 3.57% N, 383.0535 M. The third fraction (0.13 g) was also a mixture of azomethines **3**, in which **3a** prevailed. It was purified by sublimation at 100 °C/1 330 Pa and recrystallization from petroleum ether. M.p. 104–112 °C; composition (GC/MS data): 95% of **3a**, 3% of **3b**, and 2% of **3c**. For $C_{19}H_8F_7N$ calculated: 59.50% C, 2.09% H, 34.73% F, 3.66% N, 383.0545 M; found: 59.86% C, 2.24% H, 34.62% F, 3.63% N, 383.0535 M. The total yield of azomethines **3** was 27%.

TABLE II

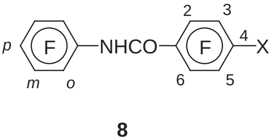
NMR data for imidoyl chlorides **2a**, **4**, **7**, azomethines **3a**, **3b**, **5** and amide **8**



2a, 4, 7



3a, 3b, 5



8

Comp.	^{1}H NMR δ, ppm (solvent)	^{19}F NMR, δ, ppm (integral intensity); *J*, Hz (solvent)					
		F_o	F_p	F_m	$F_{2,6}$ ($F_{2',6'}$)	$F_{3,5}$	F_4 ($F_{4'}$)
2a	8.20 m (H-2, H-6), 7.15 m (H-3, H-5)	11.70 m (2)	1.60 tt (1)	–0.78 m (2)			57.75 tt *J*(4,2)=*J*(4,6)=5 *J*(4,3)=*J*(4,5)=8.5
3a	7.75 m (H-2, H-6) 7.18–6.99 m, 6 H	10.07 m (2)	–0.81 tt (1)	–1.38 m (2)			55.70 tt (1) *J*(4,2)=*J*(4,6)=5.5 *J*(4,3)=*J*(4,5)=8.3 (53.11 tt (1)) *J*(4′,2′)=*J*(4′,6′)=5.5 *J*(4′,3′)=*J*(4′,5′)=8.3
3b	7.77 m (H-2, H-6) 7.08 m, 5 H 7.36 m, 1 H	10.67 m (2)	–0.68 m (1)	–1.66 m (2)	50.36 m (1) ($F_{2'}$)		55.70 m (1)
4	6.79 m (H-3, H-5)	12.46 m (2)	2.82 t (1)	–0.32 m (2)	54.97 m (2)		60.80 tt (1) *J*(4,3)=*J*(4,5)=8 *J*(4,2)=*J*(4,6)=8
5	6.74 m (H-3, H-5) trans 6.62 m (H-3′, H-5′) cis	11.02 m (2)	1.69 t (1)	–0.72 m (2)	54.20 bs (2) trans (52.90 m (2) cis)		60.01 tt (1) trans *J*(4,3)=*J*(4,5)=8 *J*(4,2)=*J*(4,6)=8 (59.44 tt (1) cis) *J*(4′,3′)=*J*(4′,5′)=8 *J*(4′,2′)=*J*(4′,6′)=8
7	7.05 m (H-4) (hexane)	13.11 m (2) (hexane)	3.48 t (1)	0.01 m (2)	22.74 m (2)	25.57 m (2)	
8	9.84 c (NH) 7.55 m (H-4) (ether)	18.40 m (2) (ether)	5.77 t (1)	–0.55 m (2)	21.57 m (2)	24.86 m (2)	

The experiment of compound 1 (0.26 g, 1 mmol) at 120 °C (17 h) was performed in a sealed glass ampoule. The reaction mixture was treated as described above, ether was distilled off and the solid residue was washed with a small amount of petroleum ether (0.5 ml). This gave 0.15 g (40%) of a mixture of azomethines **3**, which was purified by sublimation at 105 °C/1 330 Pa giving 0.12 g of a mixture containing 88% of **3a**, 9% of **3b**, and 3% of **3c**; m.p. 89–107 °C. According to ^{19}F NMR data, the mixture contained isomers **3a** and **3b** in the ratio 10 : 1.

Reactions with 1,3,5-Trifluorobenzene

Carbonimidoyl dichloride **1** (0.26 g, 1 mmol), freshly sublimated $AlCl_3$ (0.34 g, 2.5 mmol), and 1,3,5-trifluorobenzene (0.52 g, 4 mmol) were mixed in a flask with a reflux condenser and a calcium chloride tube at a bath temperature of 50–60 °C (17 h). The reaction mixture was treated as described above and analyzed by ^{19}F NMR and GC/MS.

The reaction at 85 °C (17 h) and with analogous batch of reagents was accomplished in a sealed glass ampoule. The residues of two runs after evaporation were combined and fractionated on a silica gel column (hexane). This gave 0.16 g of 2,4,6-trifluoro-*N*-(pentafluorophenyl)benzimidoyl chloride (**4**), solidifying on storage (98% purity). M.p. 30–33.5 °C. For $C_{13}H_2ClF_8N$ calculated: 358.9748 M; found: 358.9742 M. Using CCl_4 as eluent, 0.45 g (50%) of bis(2,4,6-trifluorophenyl) ketone *N*-(pentafluorophenyl)imine (**5**) with m.p. 91–94 °C was obtained. For $C_{19}H_4F_{11}N$ calculated: 50.11% C, 0.88% H, 45.93% F, 3.08% N, 455.0158 M; found: 50.65% C, 0.60% H, 46.29% F, 3.18% N, 455.0157 M.

The reactions at 120 °C (22 h) and 170 °C (20 h) with the above batches were also carried out in sealed ampoules. The reaction mixtures from 3 runs at 170 °C were combined, the solvent was distilled off and the residue was separated on a silica gel column (CCl_4) yielding 0.6 g (44%) of azomethine **5**, purified by recrystallization from petroleum ether. M.p. 94–95 °C.

TABLE III
NMR data for 1,2,3,4-tetrahydroquinazoline-2,4-diones **9**

Comp.	^{1}H NMR δ, ppm; *J*, Hz	^{19}F NMR, δ, ppm (integral intensity); *J*, Hz				
		F_o	F_p	F_m	F_6	F_8
9a	7.30 dd (H-7) *J*(7,6)=7.63 *J*(7,8)=12.20	17.66 m (2) 16.07 m (2)	12.02 t (1) 11.61 t (1)	1.08 m (4)	51.35 dd (1) *J*(6,7)=7.63 *J*(6,8)=5.22	39.52 dd (1) *J*(8,7)=12.20 *J*(8,6)=5.22
9b	7.96 dd (H-5) *J*(5,6)=7.32 *J*(5,8)=1.83	17.71 m (2) 16.36 m (2)	12.60 t (1) 11.77 t (1)	1.51 m (2) 1.09 m (2)	48.36 dd (1) *J*(6,5)=7.32 *J*(6,8)=1.60	39.20 bs (1)
9c	8.36 s (H-7)	17.84 m (4)	12.30 m (1) 11.82 m (1)	1.05 (4)		
9d		18.49 m (2) 17.26 m (2)	12.65 t (1) 11.75 t (1)	1.39 m (2) 0.97 m (2)	51.15 d (1) *J*(6,8)=2.03	39.80 bs (1)

Reactions with 1,2,4,5-Tetrafluorobenzene

Compound **1** (0.26 g, 1 mmol), $AlCl_3$ (0.34 g, 2.5 mmol), and 1,2,4,5-tetrafluorobenzene (1 g, 6.7 mmol) were heated in an ampoule (170 °C, 31 h). The residue after evaporation (0.45 g) was treated with a small amount of petroleum ether (1 ml), and the undissolved residue (0.12 g) containing amide **8**, compound **9a**, and urea **10** in the ratio 1 : 1 : 1 (^{19}F NMR) was filtered off. This residue was dissolved in CCl_4 (1.5 ml), and the undissolved part (0.05 g) containing amide **8**, compound **9a**, and urea **10** in the ratio 10 : 1 : 10 was filtered off. For amide **8**, $C_{13}H_2F_9NO$ calculated: 358.9993 M; found: 358.9990 M. The CCl_4 solution was evaporated to dryness and the solid residue (0.07 g) was sublimed at 160 °C/933 Pa and recrystallized from petroleum ether to give 5-chloro-6,8-difluoro-1,3-bis(pentafluorophenyl)-1,2,3,4-tetrahydroquinazoline-2,4-dione (**9a**), where the content of the major substance was about 91% (3% **9b** and other minor components, GC/MS). M.p. 185–190 °C, yield 12.5%. For $C_{20}H_1Cl_1F_{12}N_2O_2$ calculated: 563.9535 M; found: 563.9549 M. The petroleum ether filtrates obtained from two runs were combined, the solvent was distilled off, and the residue was fractionated on a silica gel column (CCl_4). Fraction 1 (0.25 g) contained the starting compounds, the products of chlorine exchange for fluorine in tetrafluorobenzene, imidoyl chloride **7**, and other minor components (GC/MS). Repeated silica gel chromatography of this fraction (hexane) gave imidoyl chloride **7** (0.03 g, 4%). For $C_{13}H_1Cl_1F_9N$ calculated: 376.9654 M; found: 376.9670 M. Fraction 2 (0.02 g) contained 80% of **9c**, 1% of **9a** and **9b**, along with a large amount of minor impurities (GC/MS). The yield of **9c** was 3%. For $C_{20}H_1Cl_3F_{10}N_2O_2$ calculated: 595.8944 M; found: 595.8937 M. Fraction 3 (0.04 g) was purified by sublimation at 160 °C/933 Pa and recrystallization from petroleum ether. It contained compound **9b** (about 86% purity, GC/MS) with an admixture of heterocyclic compounds **9** with two and three chlorine atoms, having close retention times. M.p. 176–181 °C. For **9b**, $C_{20}H_1Cl_1F_{12}N_2O_2$ calculated: 563.9535 M; found: 563.9549 M.

Reactions with Pentafluorobenzene

A mixture of compound **1** (0.26 g, 1 mmol), $AlCl_3$ (0.34 g, 2.5 mmol), and pentafluorobenzene (1 g, 5.9 mmol) was heated in an ampoule at 170 °C (31.5 h) gave, after evaporation, 0.29 g of a viscous solid residue. The residues from three experiments were combined (0.88 g), treated with CCl_4 (3 ml), and the undissolved solid (0.11 g) was filtered off to give a mixture of urea **10** and amide **12** in the ratio 1.5 : 1 (^{19}F NMR). The filtrate was chromatographed on a silica gel column (CCl_4). Fraction 1 (0.18 g) contained starting compound **1** (30%), imidoyl chloride **11** (17%), and the products of chlorine exchange for fluorine in pentafluorobenzene, including hexachlorobenzene (11%, GC/MS). The ratio of the starting compound **1** and imidoyl chloride **11** was 2 : 1 (^{19}F NMR). Fraction 2 (0.22 g) contained compound **9d**, which was purified by sublimation at 140 °C/1 330 Pa and recrystallization from petroleum ether. M.p. 145–147.5 °C, yield of **9d** 24%. For $C_{20}Cl_2F_{12}N_2O_2$ calculated: 40.07% C, 11.85% Cl, 38.06% F, 4.67% N, 597.9145 M; found: 39.71% C, 11.66% Cl, 38.11% F, 4.24% N, 597.9151 M.

Reaction of **1** with Imidoyl Chloride **11** in the Presence of $AlCl_3$

A mixture of compound **1** (0.26 g, 1 mmol), imidoyl chloride **11** (0.4 g, 1 mmol), and freshly sublimated $AlCl_3$ (0.34 g, 2.5 mmol) was heated in a sealed glass ampoule at 170 °C (31 h). The reaction mixture was cooled and decomposed with cold water (100 ml). The light-colored residue was filtered off, washed with water to neutral pH and dried on air. This residue was dissolved in ether (100 ml), the undissolved inorganic residue (0.05 g) was filtered off and the solution was analyzed by GC/MS and ^{19}F NMR. According to GC/MS data, the solution contained 80% of **9d** with an admixture of trace amounts of heterocyclic derivatives of type **9** containing different numbers of fluorine and chlorine atoms in the carbocyclic ring, products of chlorine exchange for fluorine in the starting imidoyl chloride **11**, and unidentified compounds (maximum 5%). The solvent was distilled off to give 0.45 g of the solid residue, from which compound **9d** was separated by recrystallization from petroleum ether. Yield 55%.

X-Ray Structure Analysis of Compounds **9d**, **3a** and **3b**

A Bruker P4 diffractometer (monochromatic MoKα radiation, θ/2θ scans, 2θ < 50°) was used to measure the unit cell dimensions and to collect data for compound **9d**. Crystallographic data for compound **9d**: $C_{20}Cl_2F_{12}N_2O_2$, M_w = 599.12, crystal class monoclinic, space group $P2_1/n$, a = 22.034(3) Å, b = 8.7048(8) Å, c = 22.655(3) Å, β = 107.672(9)°, V = 4 140.2(8) Å^3, Z = 8, d_{calc} = 1.922 g/cm^3, μ = 0.446 mm^{-1}, crystal size 0.30 mm × 0.42 mm × 0.46 mm. Absorption corrections by empirical method based on ψ-scans were applied (transmission 0.43–0.63). The structure was solved by direct methods (SHELXS97) and refined by a full matrix least-squares procedure (SHELXL97) using anisotropic thermal parameters. The final indexes are wR_2 = 0.1801, S = 1.015 for all 7 238 F^2 and R_1 = 0.0597 for 4 629 $F_o > 4\sigma$.

Crystal structure of the first molecule from two crystallographically independent ones is shown in Fig. 1. The quinazoline fragment is planar with root mean square (Rms) deviation 0.019 and 0.010 Å accordingly for two molecules. The angles between the quinazoline and

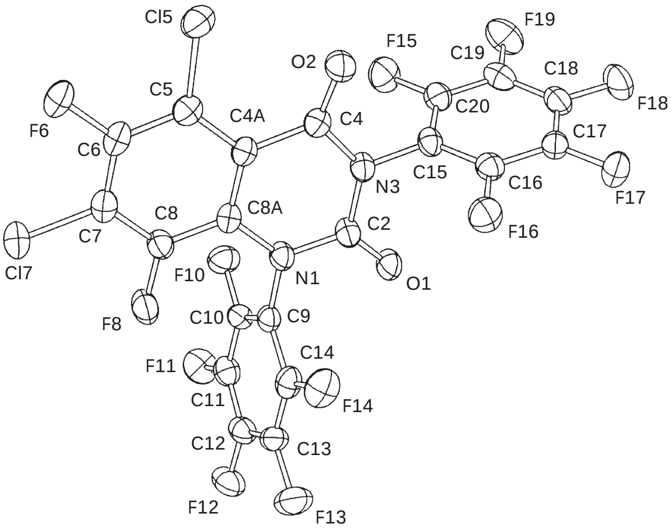


FIG. 1
ORTEP diagram of 5,7-dichloro-6,8-difluoro-1,3-bis(pentafluorophenyl)-1,2,3,4-tetrahydroquinazoline-2,4-dione (**9d**)

benzene planes are equal to 76.3(1) (69.4(1)°) for C15–C20 and 78.6(1) (88.2(1)°) for C9–C14. Bond lengths in the quinazoline moiety are almost the same as in 3-amino-6-bromo-1-methyl-1,2,3,4-tetrahydroquinazolin-2,4-dione[11]. It is necessary to note a strong intermolecular contacts (Cl5···Cl5′ 3.328(2) Å) and light shorted intermolecular contacts[12] (Cl5···F17 3.058(3), Cl7′···F10 3.163(3), Cl7′···F16 3.142(3), Cl7···O1′ 2.952(3), F12···F12′ 2.717(6) Å).

X-Ray structure analysis of the single crystal grown from a mixture of compounds **3a** and **3b** in petroleum ether was carried out on a Syntex $P2_1$ difractometer (CuKα radiation with graphite monochromator, θ/2θ scans, 2θ < 140°). Crystallographic data: $C_{19}H_8F_7N$, M_w = 383.26, crystal class monoclinic, space group $P2_1/c$, a = 9.326(1) Å, b = 17.703(2) Å, c = 10.539(1) Å, β = 110.888(10)°, V = 1 625.7(4) Å^3, Z = 4, d_{calc} = 1.566 g/cm^3, μ = 1.322 mm^{-1}, crystal size 0.10 mm × 0.20 mm × 0.50 mm. Absorption corrections by the integration method were applied (transmission 0.64–0.88). The structure was solved by direct methods (SHELXS97) and refined by a full-matrix least-squares procedure (SHELXL97) using anisotropic thermal parameters. The final indexes are wR_2 = 0.2290, S = 1.042 for all 3 076 F^2 and R_1 = 0.0685 for 1 712 $F_o > 4\sigma$.

Molecular structure of compounds **3a** and **3b** is shown in Fig. 2. In crystalline phase compounds **3a** and **3b** are mixed in the 3 : 2 ratio since the localization probabilities of fluorine atom in the benzene ring of C9–C14 are equal to 61.6(7) and 38.4(7)% for *para* (F12 atom)

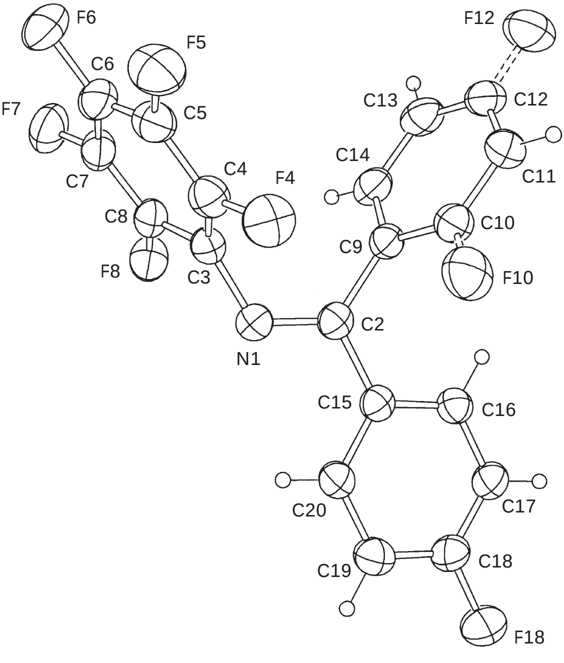


FIG. 2
ORTEP diagram of bis(4-fluorophenyl) ketone *N*-(pentafluorophenyl)imine (**3a**) and (2-fluorophenyl) (4-fluorophenyl) ketone *N*-(pentafluorophenyl)imine (**3b**) mixture (3 : 2)

and *ortho* (F10 atom) positions, respectively. The C3–N1=C2(C9)–C15 fragment is planar with Rms deviation 0.015 Å and its angles with benzene rings C15–C20, C9–C14 and C3–C8 planes are 15.9(2), 66.1(2) and 70.7(1)°, respectively. The conformation and geometry of compounds under investigation are almost the same as, for example, in 2-[anilino(phenyl)methyl] phenol[13]. CCDC 179891 (for **9d**) and CCDC 179892 (for **3a** + **3b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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