

Reactions of *N*-(Perfluorophenyl)carbonimidoyl Dichloride with Aromatic Acids and Their Derivatives in the Presence of AlCl₃. Formation of 2-(Perfluorophenyl)isoindoline-1,3-dione and its Derivatives

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Abstract—Reactions of *N*-(perfluorophenyl)carbonimidoyl dichloride with benzoic acid, benzoyl chloride, ethyl benzoate, and also with phthalic acid, phthaloyl dichloride, and phthalic anhydride in the presence of AlCl₃ at 170°C afford 2-(perfluorophenyl)isoindoline-1,3-dione. With benzoic acid and benzoyl chloride form also 2-(perfluorophenyl)-3-[(perfluorophenyl)imino]isoindolin-1-one. In reactions with compounds of the benzene series arise also derivatives of arylimidoyl chlorides and amide type compounds containing a CONHC₆F₅ moiety.

We formerly demonstrated that polyfluoroaromatic compounds containing an imidoyl chloride moiety in the presence of AlCl₃ acted as efficient electrophilic reagents capable of reacting with various aromatic compounds. Reactions with benzene and alkyl benzenes gave rise to imidoyl chlorides and azomethines [1], and with fluorinated benzenes depending on the number of fluorine atoms in the benzene ring the process afforded imidoyl chlorides, azomethines, or polyfluorinated derivatives of 1,2,3,4-tetrahydroquinazoline-2,4-dione [2]. The reaction with aromatic amines occurred at the amino group nitrogen affording the corresponding guanidines [3]. The reaction at the multiple carbon–nitrogen bond in the aromatic imidoyl chlorides or nitriles furnished 5- or 6-membered heterocyclic derivatives [4].

We report here on the study of reactions between *N*-(perfluorophenyl)carbonimidoyl dichloride (**I**) and some aromatic acids and their derivatives in the presence of AlCl₃.

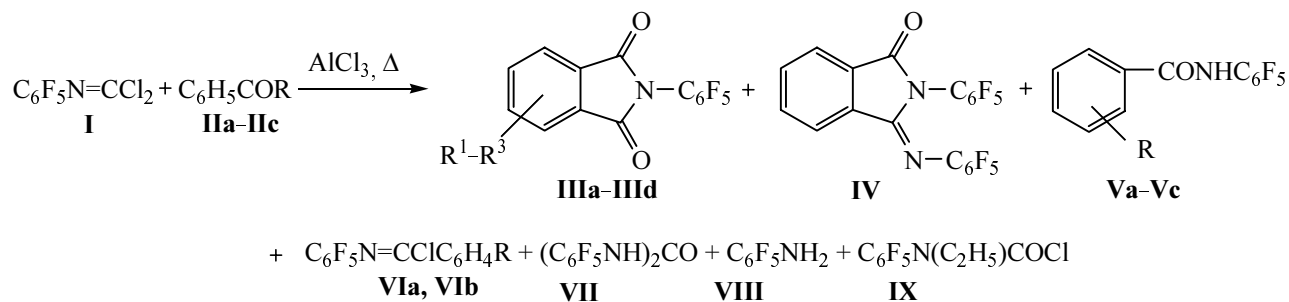
The reactions of equimolar amounts of dichloride **I** and benzoic acid (**IIa**) and also its derivatives, benzoyl chloride (**IIb**) and ethyl benzoate (**IIc**), in the presence of 2.5-molar amount of AlCl₃ at 130 and 170°C occurred with a considerable tarring and resulted in complex mixtures of products the majority of which were identified with the use of ¹⁹F NMR and IR spectroscopy, and also

of GC-MS analysis. According to these data the final mixtures contained unreacted initial compound **I**, 2-(perfluorophenyl)isoindoline-1,3-dione (**IIIa**), 2-(perfluorophenyl)-3-[(perfluorophenyl)imino]isoindolin-1-one (**IV**), compounds of amide type with a moiety CONHC₆F₅ **V**, imidoyl chloride derivatives C₆F₅N=C₆H₄R **VI**, decafluorodiphenylurea (**VII**), pentafluoroaniline (**VIII**), and unidentified compounds present in small amounts (Scheme 1). In reaction with ethyl benzoate (**IIc**) the reaction mixture obtained at 130°C contained also a considerable amount of compound presumably having structure of ethyl(perfluorophenyl)-carbamoyl chloride (**IX**). A specific feature of reaction with ester **IIc** consisted in formation of isomeric ethyl derivatives **IIIb–IIIc** where the number of the ethyl groups in the benzene ring grew with growing temperature from one to three.

The qualitative composition of the final reaction mixtures obtained with compounds **IIa–IIc** was not affected by increased reaction temperature and prolonged heating, but the conversion of substrate **I** grew and the relative quantity of the reaction products changed. Therewith the amounts of cyclic compounds **III** and **IV** and amides **V** increased.

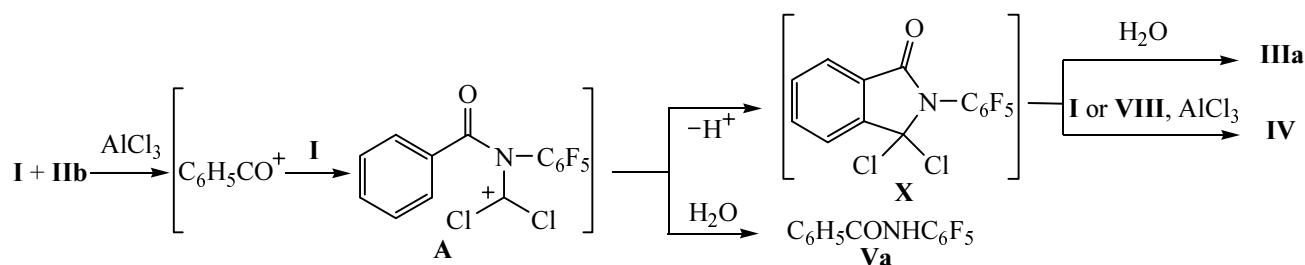
Heterocyclic compounds **IIIa** and **IV** are the main products of the reaction between dichloride **I** and benzoyl

Scheme 1.



II, R = OH (a), Cl (b), OEt (c); III, R¹ = R² = R³ = H (a); R¹ = R² = H, R³ = Et (b); R¹ = H, R² = R³ = Et (c); R¹ = R² = R³ = Et (d); V, R = H (a), CONHC₆F₅ (b), COOH (c); VI, R = H (a), COCl (b).

Scheme 2.



chloride **IIb**. With an enhanced molar amount of compound **I** and AlCl₃ [ratio equal to (I):(IIb): AlCl₃ = 2:1:5] at 170°C the relative formation of compound **IV** somewhat grew, but under these conditions the product **IIIa** still prevailed in the reaction mixture that also contained a large quantity of unreacted initial dichloride **I**.

In contrast to the reaction with acyl chloride **IIb** dichloride **I** with acid **IIa** in the presence of AlCl₃ afforded in the temperature range studied mainly amide derivatives **V** as the main reaction mixture components. At 130°C formed predominantly amide **Va**, and at 170°C alongside this compound the reaction mixture contained diamides **Vb** with prevailing content of one of the isomers. Initial compound **I** is virtually lacking in the final mixtures, and compounds **IIIa**, **IV** and **VI–VIII** are present as minor components.

The reaction of dichloride **I** with ester **IIc** alongside compounds **III** and **IX** also gave rise to a large quantity of amide derivatives **V**, but here at 130°C amide **Va** is a minor component of the mixture, and in reaction at 170°C it was not detected even by GC-MS method. Compound **IV** also was not identified in this reaction.

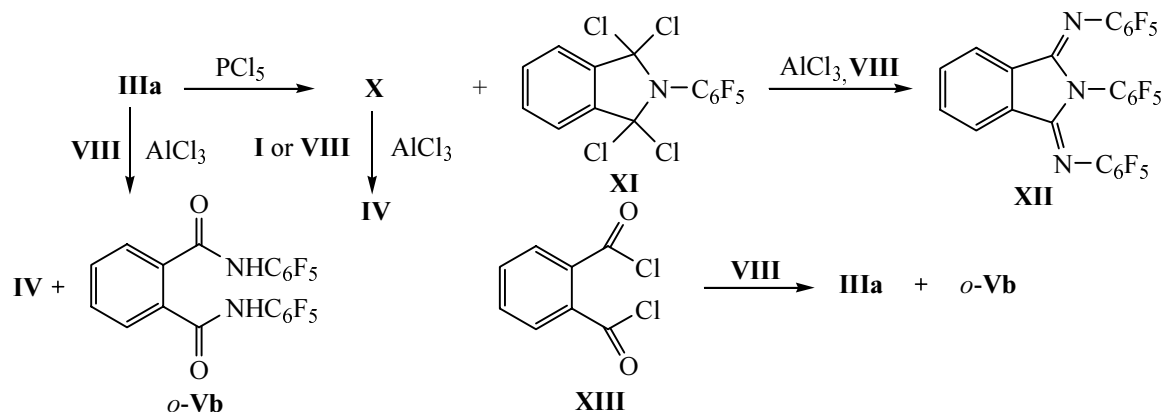
At the first glance the formation in reactions under study of compounds **IIIa** and **IV** containing a phthalimide fragment seems unexpected. However it can be understood assuming that in the course of the reaction a

benzoyl cation is intermediately formed and taking into consideration the already mentioned [3, 4] capability of imidoyl chloride moiety to react with electrophiles at the nitrogen

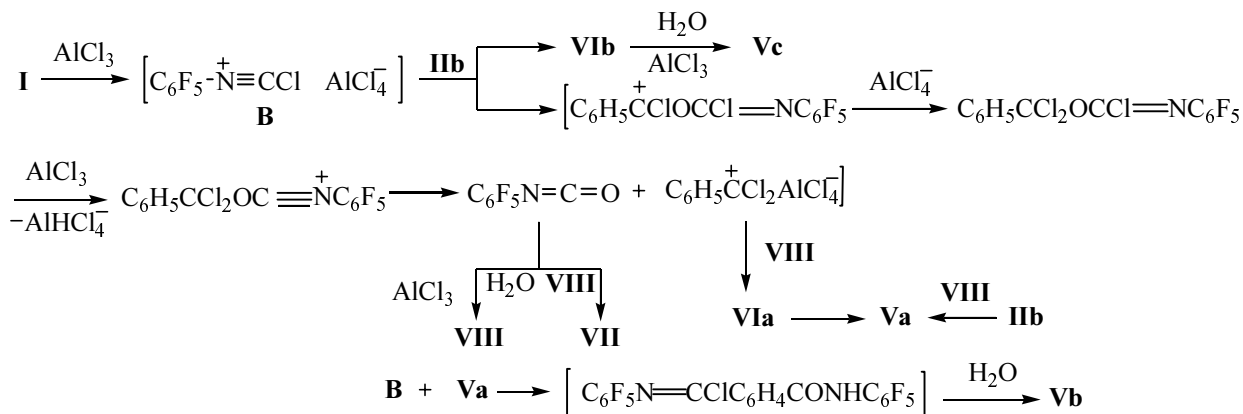
Possible patterns of compounds **IIIa** and **IV** formation in reaction of acyl chloride **IIa** involving an intermediate **A** are presented in Scheme 2.

This scheme is corroborated by transformation into reaction products **IIIa** and **IV** of independently synthesized 3,3-dichloro-2-(perfluorophenyl)isoindolin-1-one (**X**). The synthesis of substituted isoindolin-1-one **X** was performed by heating cyclic compound **IIIa** with PCl₅ (Scheme 3). This reaction provided also 1,1,3,3-tetrachloro-2-(perfluorophenyl)isoindoline (**XI**), and the ratio **X**:**XI** depended on the amount of PCl₅ used. Both compounds are very prone to hydrolysis, especially the tetrachloro derivative **XI**, and they are converted into dione **IIIa** even during column chromatography on silica gel, and therefore preparation of these compounds in a pure state has been a difficult task. Compound **X** by reaction with initial dichloride **I** or polyfluorinated aniline **VIII** is converted into (imino)isoindolin-1-one **IV**, and tetrachloroisoindoline **XI** is transformed into 1,3-bis-[(perfluorophenyl)imino]-2-(pentafluorophenyl)isoindoline (**XII**). The possibility of (imino)isoindolin-1-one **IV** formation from isoindoline-1,3-dione **IIIa** was checked

Scheme 3.



Scheme 4.



by a special experiment of heating the latter with pentafluoroaniline **VIII** in the presence of AlCl_3 , but the conversion of compound **IIIa** into substance **IV** was small, and besides a significant amount *N,N'*-bis-(perfluorophenyl)phthalamide (*o*-**Vb**) was obtained. Inasmuch as the latter compound was not detected in notable quantities in the products of reaction between dichloride **I** and acyl chloride **IIb** the contribution of isoindoline-1,3-dionea **IIIa** conversion into (imino)-isoindolin-1-one **IV** under the action of pentafluoroaniline **VIII** in the presence of AlCl_3 was minimal. The structure of phthalimide *o*-**Vb** was confirmed by an independent synthesis from phthaloyl dichloride (**XIII**) by treating with pentafluoroaniline **VIII**. The reaction occurred already at room temperature and afforded a mixture of products *o*-**Vb** and **IIIa**. On adding *N,N*-dimethylaniline as base the only reaction product formed was dione **IIIa**. Probably amide *o*-**Vb** transformed into dione **IIIa**. In any case in the analysis of individual compound *o*-**Vb** by GC-MS procedure only isoindoline-1,3-dione **IIIa** and pentafluoroaniline **VIII** were detected.

The presumable paths of amides **V** formation in reactions of dichloride **I** with acyl chloride **IIb** are shown on Schemes 2 and 4. The formation of imidoyl chloride derivatives in this reaction may be due to participation of a cationoid intermediate **B** of nitrilium type that reacts with compound **IIb** along Scheme 4. We formerly already pointed out the ability of polyfluoroaromatic compounds containing an imidoyl chloride moiety to act in the presence of AlCl_3 as active electrophiles of this type [1–4]. The stage of imidoyl chloride **VIa** formation presented on Scheme 4 involving the α,α -dichlorobenzyl cation is analogous to the process we have suggested before for the formation of this compound from benzotrichloride, aniline **VIII**, and AlCl_3 [5]. Scheme 4 provides also an understanding of appearance in the system of pentafluoroaniline **VIII** and urea **VII** involving perfluorophenyl isocyanate; however, these compounds may arise from a side reaction: a hydrolysis of initial dichloride **I** effected by traces of moisture that we have observed previously [4].

The reaction products of processes involving acid **IIa** and ester **IIc** apparently arise along pathways similar to those shown on Schemes 2 and 4. Therewith in reaction of acid **IIa** the intermediate formation of a benzoyl cation requires water liberation that may facilitate the hydrolysis of initial dichloride **I** and accumulation of aniline **VIII** in the system. Its reaction with the benzoyl cation should furnish amide **Va**. This reaction pattern probably accounts for the larger amount of amide **Va** in reaction products of acid **IIa** compared to those obtained from its chloride **IIb**.

Heterocyclic compounds **IIIb–III d** with the ethyl groups attached to the benzene ring form in reaction of dichloride **I** and ester **IIc** in the presence of AlCl_3 apparently from dione **IIIa** by Friedel–Crafts reaction. The ethylation of initial dichloride **I** at the nitrogen atom with subsequent hydrolysis may be responsible for compound **IX** formation.

The structure of reaction products obtained from dichloride **I** and acid **IIa** or its derivatives **IIb**, **IIc** was derived mainly from their analysis and spectral characteristics. Compound **IIIa** was synthesized earlier by other methods [6, 7]. Its ^{19}F NMR spectrum [7] was identical to that registered by us. However the characteristics given in [6] were unlike those obtained in the present study. We reproduced the synthesis described in [6] and obtained a sample of isoindoline-1,3-dione **IIIa** completely identical to our product.

The structure of ethyl derivatives **IIIb–III d** that were not isolated in an individual state was assigned to them based on the data of GC-MS analysis, the elemental analyses and molecular weights deduced from the high resolution mass spectra, and on the composition of fragment ions in the mass spectra (formation of a fragment ion $[\text{M}-\text{CH}_3]^+$ characteristic of compounds with an ethyl group attached to a benzene ring), on the appearance of ethyl group proton signals at ~ 1 and ~ 2.8 ppm in the ^1H NMR spectra, and close values of fluorine chemical shifts in the ^{19}F NMR spectra of these compounds and substance **IIIa**.

Amide derivatives **V** were identified mainly using their ^{19}F NMR spectra with characteristic position of signals from *ortho*-fluorine in the region 17.5–18.5, from *para*-fluorine in the region 4.2–4.9, and from *meta*-fluorine in the region 0.4–1.2 ppm. The close values of the fluorine chemical shifts in the amide derivatives of different structure (cf., e.g., our data for amide **Va**, for *o*-isomer **Vb**, and published data for *o*-isomer **Vc** [7] and *m*-isomer **Vb** [8, 9]) and also the ability of some among

the amides to suffer transformations in the course of GC-MS analysis complicated the individual identification of these compounds when obtained in a mixture.

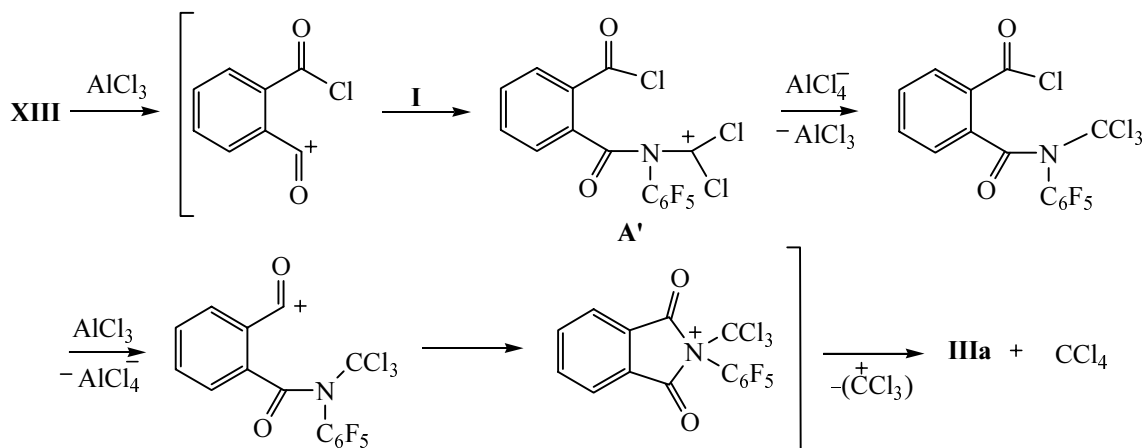
Imidoyl chlorides **VI** were identified in the reaction mixtures without separation using the data of GC-MS analysis and fluorine chemical shifts in the ^{19}F NMR spectra. The chemical shifts were close in values to those for the previously described [10] imidoyl chloride derivative **VIa** and other polyfluoroaromatic imidoyl chloride derivatives [11].

The spectral characteristics of compound **IX** which was detected but not isolated were similar to those of the previously described *N*-methyl analog [10] and thus they confirm the assumed structure.

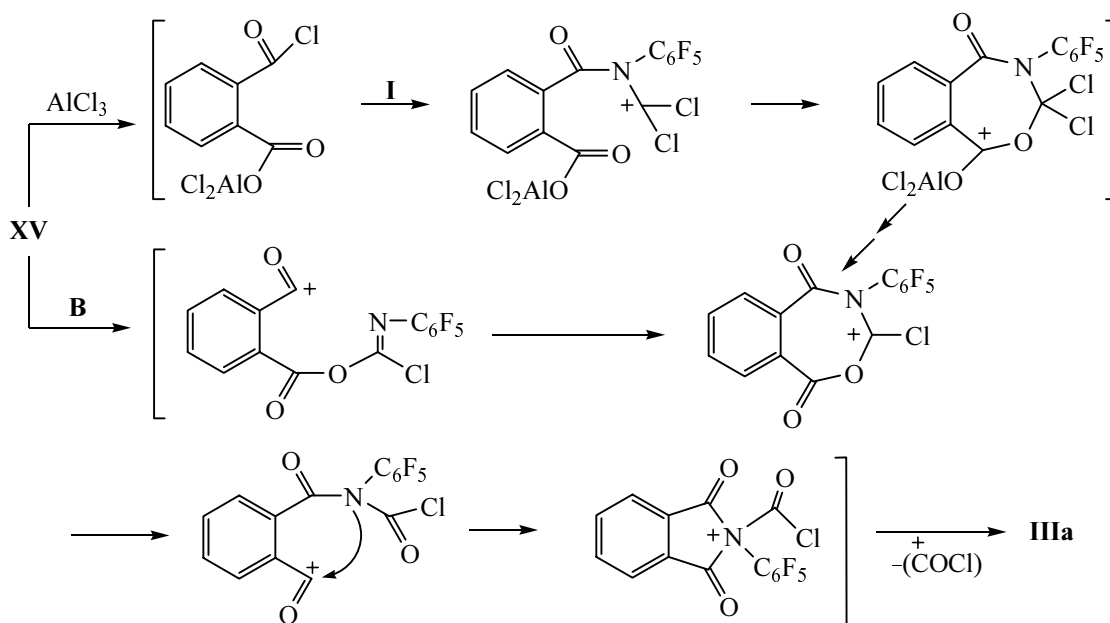
The formation of heterocyclic compounds in reaction of dichloride **I** with compounds **IIa–IIc** promoted the extension of the range of aromatic acids to be brought into reaction with it in the presence of AlCl_3 . In this connection it was interesting to study the behavior in this reaction of aromatic dicarboxylic acids and their derivatives since in this case it was expectable to obtain tricyclic systems containing two phthalimide fragments. Taking into account the experience obtained in this study we investigated the reaction of dichloride **I** with phthalic acid (**XIV**), phthaloyl dichloride (**XIII**), and phthalic anhydride (**XV**). It proved however that in all cases formed predominantly compound **IIIa** in a high yield. In the reaction mixture obtained from phthaloyl dichloride (**XIII**) among the reaction products was identified also a small amount of cyclic dichloride **X**, and in the case of acid **XIV** formed a little urea **VII**.

The formation of compound **IIIa** in these reactions can be understood by assuming (as in the case of benzoic acid **IIa** and its derivatives **IIb**, **IIc**) that in the processes take part cationoid intermediates of **A** or **B** type arising from initial carbonyl compounds **XIII–XV** and dichloride **I** under the action of AlCl_3 . One of the reaction routes involving the ionization of a carbonyl compound is shown on Scheme 5 by an example of phthaloyl dichloride (**XIII**). In the scheme reaction of dichloride **I** is assumed to occur with a cationoid intermediate of benzoyl type formed from phthaloyl dichloride (**XIII**) which at high temperature and in the presence of AlCl_3 can exist either in cyclic or open form [12]. The resulting cationoid intermediate **A'**, similar to intermediate **A**, is involved into a sequence of transformations leading finally to dione **IIIa** and CCl_4 . The latter was detected in the reaction products by GLC and GC-MS methods. Thus this scheme of compound **IIIa** formation seems quite likely. No CCl_4 was found in

Scheme 5.



Scheme 6.



the reaction products of acid **XIV** and anhydride **XV**, therefore these compounds presumably are converted in compound **IIIa** by another route. One possible pathway for anhydride **XV** is presented in Scheme 6.

For acid **XIV** similar schemes presumably exist involving seven-membered cationoid intermediates. On the other hand if the reaction with acid **XIV** would proceed as with benzoic acid **IIa** and at least one carboxy group of compound **XIV** would be converted into amide moiety CONHC_6F_5 then an *ortho*-isomer *o-Vc* would arise that is known [7] to undergo cyclization at heating into dione **IIIa**.

EXPERIMENTAL

^{19}F and ^1H NMR spectra were registered on a spectrometer Bruker WP-200SY (at 188.3 and 200 MHz respectively) using as internal standards hexafluorobenzene (-162.9 ppm from CCl_3F) and HMDS (0.04 ppm from TMS). ^{13}C NMR spectrum was measured on a spectrometer Bruker AM-400 (100.6 MHz), internal reference CDCl_3 (76.9 ppm from TMS). IR spectra were recorded on a spectrophotometer Specord M-80 from samples pelletized with KBr.

Analysis of the reaction mixtures by GC-MS method was carried out on a Hewlett-Packard G 1081A instrument

including a gas chromatograph HP 5890 (of II series) coupled with a mass-selective detector HP 5971 (nominal ionizing energy 70 eV); capillary column HP-5MS (5% of diphenyl- and 95% of dimethylsilicone), 30 m × 0.25 mm; carrier gas helium, flow rate 1 ml/min, vaporizer temperature 280°C, ion source temperature 170°C, mass range 30–650. Molecular weight and elemental composition were determined on a high resolution mass spectrometer Finnigan MAT-8200 (nominal ionizing energy 70 eV). Column chromatography was performed on silica gel (140–315 mesh). The ratio of products in the reaction mixtures was evaluated by ¹⁹F NMR spectroscopy.

Initial dichloride **I** was prepared by procedure [10]. Compound **XIII** was obtained by method [12]. Freshly sublimed AlCl₃ was used in the reactions. Petroleum ether of bp 70–100°C was used as one of the solvents.

Reaction of *N*-(perfluorophenyl)carbonimidoyl dichloride (I) with benzoic acid (IIa) and its derivatives. A mixture of 0.26 g (1 mmol) of dichloride **I**, 1 mmol of the acid or its derivative, and 0.34 g (2.5 mmol) of AlCl₃ was heated in a sealed glass ampule at the appropriate bath temperature. On cooling the obtained reaction mixture that had suffered tarring was cautiously treated with cold water (30 ml), extracted with ethyl ether (50 ml), the extract was washed with water till neutral washings, and dried on CaCl₂. The solvent was partially removed on a rotary evaporator, and the solution obtained was analyzed by ¹⁹F NMR spectroscopy and GC-MS method. Then ethyl ether was completely evaporated, the residue was washed with 3–5 ml of petroleum ether to remove unreacted initial dichloride **I**, imidoyl chloride derivatives **VI**, and pentafluoroaniline **VIII**, the insoluble residue was filtered off and extracted with 8–10 ml of CCl₄. The insoluble part was again separated; it contained mainly amide substances **V** and urea **VII**. The solution in CCl₄ was evaporated to dryness, and from the residue compounds **III** and **IV** were separated by sublimation and by chromatography on a column packed with silica gel.

Reactions with acid (IIa). *a.* The heating at 130°C was continued for 9 h; on evaporating the solvent from the ether extract we obtained 0.3 g of solid residue containing compounds **I**, **IIIa**, **IV**, **Va**, **VI** (in particular **VIa**), **VII**, and **VIII** in a ratio ~24 : 1.5 : 1 : 53.5 : 6 : 10 : 4. (Here and hereinafter to simplify the evaluation of the products ratio we took into account for amides **V** only one group CONHC₆F₅).

***N*-(Perfluorophenyl)benzamide (Va).** ¹⁹F NMR spectrum (ethyl ether), δ, ppm: –1.2 m (2F_m), 4.2 t (1F_n, *J* 20 Hz), 17.8 m (2F_O).

b. The heating at 170°C was continued for 17 h; on evaporating the solvent from the ether extract we obtained 0.3 g of solid residue containing compounds **IIIa**, **IV–VII** in a ratio ~13 : 4 : 65 : 14 : 4. The residue was treated with 10 ml of CCl₄ to extract compounds **IIIa**, **IV**, and **VI**, and the residue insoluble in CCl₄ (0.19 g) was filtered off; it contained a mixture of amides **V** and urea **VII** in a ratio ~94:6. IR spectrum of the residue, ν, cm⁻¹: 994 (CF), 1524 (C₆F₅), 1651, 1676, 1699 (CO), 3071 (CH), 3261 (NH). Amides **V**, ¹⁹F NMR spectrum (acetone), δ, ppm: –1.1...–0.7 m (2F_m), 4.8–5.2 m (1F_n), 17.9–18.2 m (2F_O).

Reactions with benzoylchloride (IIb). *a.* The heating at 130°C was continued for 8 h; on evaporating the solvent from the ether extract we obtained 0.32 g of a mixture containing **I**, **IIIa**, **IV–VIII** in a ratio ~38 : 13 : 13 : 6 : 14 : 3 : 13. Amides **V** (2 compounds in a ratio ~1:2.3), ¹⁹F NMR spectrum (ethyl ether), δ, ppm: –1.4 m (2F_m), 4.3 t (1F_n, *J* 21 Hz), 4.9 t (1F_n, *J* 21 Hz), 17.7 m (2F_O). Imidoyl chlorides **VI** (2 compounds in a ratio ~1:6), ¹⁹F NMR spectrum (ethyl ether), δ, ppm: –0.6...–0.3 m (2F_m), 1.6 t (1F_n, *J* 21 Hz), 2.4 t (1F_n, *J* 21 Hz), 12.0–12.3 m (2F_O).

b. The heating at 170°C was continued for 18 h; on evaporating the solvent from the ether extract we obtained 0.32 g of a mixture containing **I**, **IIIa**, **IV–VIII** in a ratio ~19:24:9:24:3:7:14. From the solution in petroleum ether we obtained 0.07 g of a mixture of compounds **I**, **IIIa**, **IV**, **V**, and **VIII** in a ratio ~61 : 15 : 8 : 6 : 9. From solution in CCl₄ on evaporating the solvent we obtained 0.09 g of solid residue that was sublimed at 170°C (5 mm Hg.). The sublimed product combined from several runs (0.16 g) was subjected to chromatography on a column packed with silica gel, eluent CHCl₃. We obtained 0.03 g of compound **IIIa**, 0.05 g of compound **IV**, 0.02 g of a mixture of cyclic products **IIIa** and **IV** (in a ratio 5 : 95), and 0.02 g of a mixture of compounds **IIIa** and **IV** (in a ratio 98:2). Compounds **IIIa** and **IV** were additionally purified by sublimation at 170°C (5 mm Hg.) and recrystallization from a mixture petroleum ether–CCl₄, 10:1.

2-(Perfluorophenyl)isoindoline-1,3-dione (IIIa), mp 169.5–171°C (in a sealed capillary) (publ.: mp 128–130°C [7]). IR spectrum (CCl₄), ν, cm⁻¹: 1012 (CF), 1518 (C₆F₅), 1734, 1790 (CO), 3101 (CH). ¹H NMR spectrum, δ, ppm, in CCl₄: 7.81 m (2H), 7.96 m (2H); in acetone-*d*₆: 8.02 m (4H) (publ.: 7.50 m [6]). ¹⁹F, δ, ppm, in CCl₄: 0.6 m (2F_m), 10.1 t (1F_n, *J* 22 Hz), 18.9 m (2F_O); in acetone-*d*₆: 1.0, 10.8, 20.1 (publ.: 1.3, 7.9, 21.6 [6]); in

DMSO- d_6 1.3 m, 11.5 t (J 22 Hz), 19.5 m (publ.: 1.7, 11.9, 19.9 [7]). ^{13}C NMR spectrum (CDCl_3), δ , ppm: 106.9 (C^1 , J 14.5 Hz), 124.3 (2C, $\text{C}^{4,7}$), 131.5 (2C, $\text{C}^{3a,7a}$), 134.9 (2C, $\text{C}^{5,6}$), 137.9 (2C, $\text{C}^{2,6'}$, J_{CF} 253 Hz), 141.9 (C^4 , J_{CF} 258, J 13.8 Hz), 144.0 (2C, $\text{C}^{3,5'}$, J_{CF} 256 Hz), 164.7 (2C, $\text{C}^{1,3}$). Mass spectrum, m/z (I_{rel} , %): 313 (100) $[M]^+$, 294 (3.38) $[M-F]^+$, 269 (78.51) $[M-\text{CO}_2]^+$, 104 (47.53) $[\text{C}_6\text{H}_4\text{CO}]^+$, 76 (78.01) $[\text{C}_6\text{H}_4]^+$. Found, %: C 53.43; H 0.89; F 30.23; N 4.30. $[M]^+$ 313.01588. $\text{C}_{14}\text{H}_4\text{F}_5\text{NO}_2$. Calculated, %: C 53.67; H 1.28; F 30.35; N 4.47. M 313.01621.

2-(Perfluorophenyl)-3-[(perfluorophenyl)imino]-isoindolin-1-one (IV), mp 171–173°C (in a sealed capillary). IR spectrum, ν , cm^{-1} : 990, 1090 (CF), 1517 (C_6F_5), 1686 (C=N), 1769 (CO), 2851, 2920 (CH). ^1H NMR spectrum (CCl_4), δ , ppm: 7.43 d (H^d , J 7.7 Hz), 7.88 t (1H, J 7.7 Hz), 8.03 t (1H, J 7.7 Hz), 8.27 d (H^7 , J 7.7 Hz). ^{19}F NMR spectrum (CCl_4), δ , ppm: 0.0 m (2F, $\text{F}^{3,5}$), 0.6 m (2F $_m$), 1.1 t (1F 4 , J 21.5 Hz), 10.4 t (1F $_n$, J 21.5 Hz), 10.7 m (2F, $\text{F}^{2,6}$), 19.5 m (2F $_O$). Mass spectrum, m/z (I_{rel} , %): 478 (53.39) $[M]^+$, 459 (100.00) $[M-F]^+$, 431 (2.81) $[M-F-\text{CO}]^+$, 269 (14.96), 167 (3.67) $[\text{C}_6\text{F}_5]^+$, 117 (5.00) $[\text{C}_5\text{F}_3]^+$, 76 (40.76) $[\text{C}_6\text{H}_4]^+$. Found, %: C 49.68; H 1.14; F 39.92; N 5.75. $[M]^+$ 478.01645. $\text{C}_{20}\text{H}_4\text{F}_{10}\text{N}_2\text{O}$. Calculated, %: C 50.21; H 0.83; F 39.75; N 5.86. M 478.01638.

The residue insoluble in petroleum ether and CCl_4 (0.1 g) contained a mixture of amides **V** and urea **VII** in a ratio 73 : 21. Among amide derivatives **V** by means of GC-MS method only compound **Va** was identified. ^{19}F NMR spectrum of a mixture of amide derivatives **V** (ethyl ether), δ , ppm: -0.8...-0.4 m (2F $_m$), 4.3–4.9 m (main signal 4.3 t) (1F $_n$), 18.0 m (2F $_O$).

c. A mixture of 0.52 g (2 mmol) of dichloride **I**, 0.14 g (1 mmol) of acyl chloride **IIa**, and 0.68 g (5 mmol) of AlCl_3 was heated at 170°C for 21 h. After evaporating ether we obtained 0.5 g of reaction mixture, containing compounds **I**, **IIIa–VIII** in a ratio ~29 : 13 : 11 : 11 : 13 : 7 : 16.

Reactions with ethyl benzoate (IIIc). *a.* The heating at 130°C was continued for 9 h; on evaporating the solvent from the ether extract we obtained 0.34 g of reaction mixture containing compounds **I**, **III** (mostly **IIIb**), **V**, **VIII**, **IX** in a ratio ~35 : 7 : 24 : 6 : 28.

Ethyl(perfluorophenyl)carbamoyl chloride (IX). ^{19}F NMR spectrum (ethyl ether), δ , ppm: 1.2 m (2F $_m$), 10.2 t (1F $_n$, J 20 Hz), 17.9 m (2F $_O$) [methyl(perfluorophenyl)carbamoyl chloride [10]: 1.6 m (2F $_m$), 10.3 t (1F $_n$), 17.4 m (2F $_O$)].

b. The ether extract of the reaction mixture obtained at 170°C (17 h) was filtered from black soot-like precipitate (0.1 g), and on distilling off the ethyl ether we obtained 0.18 g of residue containing compounds **III**, **V**, **VII**, **VIII** in a ratio ~40 : 36 : 8 : 16. According to GC-MS data the mixture of diones **III** contained mainly two isomers **IIIb** and four isomers **IIIc**, and also trace amounts of compounds **IIIa** and **IIIc**. On evaporating the solvent from the extract in petroleum ether we obtained 0.02 g of a mixture of cyclic derivatives **III** and aniline **VIII** in a ratio 67 : 33. ^{19}F NMR spectrum of diones **III** mixture (CCl_4), δ , ppm: 0.2–0.6 m (2F $_m$), 9.5–9.9 m (1F $_n$), 18.9 m (2F $_O$).

Ethyl-2-(perfluorophenyl)isoindoline-1,3-diones (IIIb). Found: $[M]^+$ 341.04707. $\text{C}_{16}\text{H}_8\text{F}_5\text{NO}_2$. Calculated: M 341.04751.

Diethyl-2-(perfluorophenyl)isoindoline-1,3-diones (IIIc). Found: $[M]^+$ 369.07689. $\text{C}_{18}\text{H}_{12}\text{F}_5\text{NO}_2$. Calculated: M 369.07881.

Triethyl-2-(perfluorophenyl)isoindoline-1,3-dione (IIIc). Found: $[M]^+$ 397.11007. $\text{C}_{20}\text{H}_{16}\text{F}_5\text{NO}_2$. Calculated: M 397.11011.

From the extract in CCl_4 after removing the solvent we obtained 0.05 g of a solid mixture of compounds **IIIa–IIIc** (mainly **IIIb**, **IIIc**), amides **V**, and aniline **VIII** in a ratio ~61 : 23 : 16. The solid residue insoluble in petroleum ether and CCl_4 (0.07 g) was composed of a mixture of amide derivatives **V** and urea **VII** in a ratio ~63 : 37. Compounds of amide type **V**, IR spectrum, ν , cm^{-1} : 993 (CF), 1524 (C_6F_5), 1651, 1675, 1700 (CO), 2887 (CH), 3296, 3439 (NH). ^{19}F NMR spectrum (ethyl ether), δ , ppm: -1.7 \times -1.1 m (2F $_m$), 4.2–4.3 m (1F $_n$), 17.8–18.2 m (2F $_O$).

Reaction of *N*-(perfluorophenyl)carbonimidoyl dichloride (I) with phthalic acid (XIV), phthaloyl dichloride (XIII), and phthalic anhydride (XV). A mixture of 0.26 g (1 mmol) of dichloride **I**, 1 mmol of the carbonyl compound, and 0.34 g (2.5 mmol) of AlCl_3 was heated in a sealed glass ampule at 170°C for 10 h. The cooled reaction mixture was cautiously treated with 20 ml of cold water and worked up along procedure *a* or *b*.

a. The separated precipitate was filtered off, washed with water till neutral washings, and dried in air. We obtained 0.3 g of reaction product containing over 90% of dione **IIIa** that was purified by sublimation at 170°C (5 mm Hg), yield of compound **IIIa** 0.24 g (78%), mp 170–171°C (in a sealed capillary).

b. The reaction mixture was extracted with ethyl ether, the ether solution was washed with water till neutral

washings, dried with CaCl₂, and analyzed by ¹⁹F NMR and GC-MS methods. On removing the solvent on a rotary evaporator we obtained 0.3 g of residue that was purified as in procedure *a*. In the case of phthaloyl dichloride (**XIII**) the ether extract contained according to ¹⁹F NMR data compounds **IIIa** and **X** in a ratio ~ 94:6. Data of GC-MS analysis: ~70% of compound **IIIa**, ~19% of CCl₄, ~3% of cyclic dichloride **X**. Content of CCl₄ according to GLC data (internal normalization procedure) was 17%. The ether extract of the reaction mixture obtained from acid **XIV** contained compounds **IIIa** and **VII** in a ratio ~ 91 : 9.

Reaction of phthaloyl dichloride (XIII) with pentafluoroaniline VIII. *a*. A solution of 0.4 g (2 mmol) of phthaloyl dichloride (**XIII**) and 0.37 g (2 mmol) of aniline **VIII** in 3 ml of anhydrous benzene was maintained for 4 days at room temperature, the separated precipitate was filtered off (0.37 g). The precipitate containing a mixture of compounds **IIIa**, *o*-**Vb**, and **VIII** was extracted with 4 ml of CCl₄. Diamide *o*-**Vb** insoluble in CCl₄ (0.24 g, 48%) was filtered off and recrystallized from aqueous acetone (1:1) and from a mixture CHCl₃–acetone, 3 : 1.

***N,N'*-Bis(perfluorophenyl)phthalamide (*o*-**Vb**)**, mp 209–212°C. IR spectrum, ν , cm⁻¹: 1005 (CF), 1503, 1525 (C₆F₅), 1670, 1686 (CO), 2977, 3075 (CH), 3291 (NH). ¹H NMR spectrum (acetone-*d*₆), δ , ppm: 7.69 m (2H_{arom}), 7.83 m (2H_{arom}), 9.69 C (NH). ¹⁹F NMR spectrum (acetone-*d*₆), δ , ppm: -1.0 m (4F_m), 4.5 t (2F_n, *J* 21 Hz), 18.5 m (4F_O). Found, %: C 48.85; H 1.23; F 37.70; N 5.77. C₂₀H₆F₁₀N₂O₂. Calculated, %: C 48.38; H 1.21; F 38.31; N 5.64.

From the benzene filtrate after distilling off benzene we obtained 0.09 g of a mixture of compound **IIIa** and amide *o*-**Vb** in a ratio 41 : 59.

b. To a solution of 0.37 g (2 mmol) of aniline **VIII** in 3 ml of anhydrous benzene was added 0.24 g (2 mmol) of *N,N*-dimethylaniline, 0.4 g (2 mmol) of phthaloyl dichloride (**XIII**), and the mixture was left standing at room temperature for 24 h. Then the benzene was evaporated without heating on a rotary evaporator, the residue was ground with 20 ml of 5% HCl and extracted with ethyl ether. The ether solution was washed with water till neutral washings, dried over CaCl₂, and the solvent was distilled off. We obtained 0.4 g (63.5%) of compound **IIIa**.

c. To a solution of 0.37 g (2 mmol) of aniline **VIII** in 2 ml of anhydrous benzene was added 0.24 g (2 mmol) of *N,N*-dimethylaniline in 2 ml of anhydrous benzene,

0.4 g (2 mmol) of phthaloyl dichloride (**XIII**), and the solution was boiled for 6 h. Then the benzene was removed on a rotary evaporator, the residue was ground with 20 ml of 5% HCl, the precipitate was filtered off, washed with water till pH ~7, and dried in air. We obtained 0.58 g (92%) of compound **IIIa**.

Reactions of 2-(perfluorophenyl)isoindoline-1,3-dione (IIIa).

Reaction with *N*-(perfluorophenyl)carbonimidoyl dichloride (I). From 0.11 g (0.4 mmol) of dichloride **I**, 0.13 g (0.4 mmol) of compound **IIIa**, and 0.13 g (1 mmol) of AlCl₃ after heating at 170°C for 10 h and workup along procedure described above we obtained ether solution of the reaction mixture containing initial dione **IIIa** and urea **VII** in a ratio 78:32.

Reaction with pentafluoroaniline VIII. From 0.1 g (0.32 mmol) of compound **IIIa**, 0.06 g (0.32 mmol) of aniline **VIII**, and 0.11 g (0.8 mmol) of AlCl₃ after heating at 170°C for 18 h and workup along procedure described above we obtained ether solution of the reaction mixture containing compounds **IIIa**, **IV**, *o*-**Vb**, **VIII** in a ratio ~25 : 18 : 1.4 : 0.9. After distilling off the solvent 0.15 g of residue was isolated that was extracted in succession with 2 ml of petroleum ether and 1.5 ml of CCl₄. From the petroleum ether extract after removing the solvent we obtained 0.03 g of a mixture of compounds **IIIa**, **IV**, **VIII** in a ratio 21 : 26 : 53. From the solution in 1.5 ml CCl₄ after removing the solvent we obtained 0.05 g of a mixture of cyclic compounds **IIIa** and **IV** in a ratio 61:39. The residue insoluble in petroleum ether and CCl₄ (0.03 g) was diamide *o*-**Vb**.

Reaction with PCl₅. *a*. A mixture of 0.1 g (0.33 mmol) of dione **IIIa** and 0.21 g (1 mmol) of PCl₅ was heated for 10 h in a sealed glass ampule at the bath temperature 200°C. To a cooled reaction mixture was added 2 ml of anhydrous CCl₄ to obtain a solution containing compounds **IIIa**, **X**, **XI** in a ratio 3 : 32 : 65. This extract was washed with 5 ml of cold water, dried over CaCl₂, the solvent was removed to afford 0.09 g of a solid residue containing a mixture of initial dione **IIIa** and reaction products **X** and **XI** in a ratio 9 : 70 : 21.

b. From 0.1 g (0.33 mmol) dione **IIIa** and 0.34 g (1.6 mmol) of PCl₅ by procedure *a* we obtained a solution of the reaction mixture in CCl₄ that on removing a solvent gave 0.14 g of solid residue containing compounds **X** and **XI** in a ratio 4 : 96.

3,3-Dichloro-2-(perfluorophenyl)isoindolin-1-one (X). ¹H NMR spectrum (CCl₄), δ , ppm: 7.29 d (H⁴, *J* 7 Hz), 7.65 t (H⁶, *J* 7 Hz), 7.80 t (H⁵, *J* 7 Hz), 7.87 d

(H⁷, J 7 Hz). ¹⁹F NMR spectrum (CCl₄), δ, ppm: 1.0 m (2F_m), 12.3 t (1F_n, J 21.5 Hz), 23.3 m (2F_O). Mass spectrum, *m/z* (*I*_{rel}, %): 332 (100) [M – Cl]⁺, 313 (3.15) [M – Cl – F]⁺, 304 (2.98) [M – Cl – CO]⁺, 269 (9.42) [M – 2Cl – CO]⁺, 167 (8.30) [C₆F₅]⁺, 148 (14.33) [C₆F₄]⁺, 117 (10.86) [C₅F₃]⁺, 76 (13.49) [C₆H₄]⁺. Found: [M]⁺ 366.95906. C₁₄H₄Cl₂F₅NO. Calculated: M 366.95900.

1,1,3,3-Tetrachloro-2-(perfluorophenyl)isoindoline (XI). ¹H NMR spectrum (CCl₄), δ, ppm: 7.65 m (2H, H^{5,6}), 7.77 m (2H, H^{4,7}). ¹⁹F NMR spectrum (CCl₄), δ, ppm: 1.4 m (2F_m), 13.7 t.t (1F_n, J 22, J 5 Hz), 29.7 m (2F_O). Mass spectrum, *m/z* (*I*_{rel}, %): 386 (46.33) [M – Cl]⁺, 351 (53.38) [M – 2Cl]⁺, 316 (40.91) [M – 3Cl]⁺, 184 (14.56) [M – 2Cl – C₆F₅]⁺, 176 (15.96), 167 (15.07) [C₆F₅]⁺. Found: [M – Cl]⁺ 385.93294. C₁₄H₄Cl₃F₅N. Calculated: [M – Cl] 385.93294.

Reactions of cyclic chlorides X, XI. A mixture of chloride, reagent, and AlCl₃ was heated for 17 h in a sealed glass ampule at the bath temperature 170°C, to a cooled reaction mixture was added 10 ml of cold water, it was extracted with 20 ml of diethyl ether, the ether extract was dried with CaCl₂, and the solvent was distilled off on a rotary evaporator.

a. From 0.06 g of a mixture of cyclic dichloro derivative **X** and dione **IIIa** (89 : 11), 0.04 g (0.16 mmol) of carbonimidoyl dichloride **I**, and 0.05 g (0.4 mmol) of AlCl₃ we obtained 0.06 g of dark solid residue containing compounds **I**, **IIIa**, **IV**, **VII**, **VIII**, **X** in a ratio ~26 : 38 : 10 : 18 : 3 : 5.

b. From 0.09 g of a mixture of cyclic dichloro derivative **X** and dione **IIIa** (96 : 4), 0.05 g (0.25 mmol) of aniline **VIII**, and 0.08 g (0.62 mmol) of AlCl₃ we obtained 0.09 g of dark residue containing compounds **IIIa**, **IV**, **VIII** in a ratio 5 : 43 : 52. The residue was extracted with 1.5 ml of petroleum ether, and 0.04 g (36%) of compound **IV** was filtered off and purified by sublimation at 170°C (3 mm Hg) followed by recrystallization from petroleum ether.

c. From 0.19 g of a mixture of cyclic di- and tetrachloro derivatives **X** and **XI** (63 : 37), 0.1 g (0.6 mmol) of aniline **VIII**, and 0.24 g (1.8 mmol) of AlCl₃ we obtained 0.17 g of residue containing compounds **IIIa**, **IV**, **VIII** in a ratio 13 : 42 : 45. A mixture of this composition (0.26 g) was subjected to column chromatography on silica gel, eluent CHCl₃. We obtained 0.05 g of (imino)-isoindolin-1-one (**IV**), 0.05 g of a mixture of isoindoline derivatives **IIIa** and **IV**, 9 : 91, and 0.04 g of dione **IIIa**. Compound **IV** was purified by recrystallization from petroleum ether and by sublimation at 170°C (4 mm Hg).

d. From 0.14 g (0.33 mmol) of tetrachloro derivative **XI**, 0.30 g (1.6 mmol) of aniline **VIII**, and 0.28 g (2.1 mmol) of AlCl₃ we obtained 0.28 g of black residue that was extracted with 1.5 ml of petroleum ether, and 0.15 g (71.5%) of compound **XII** was filtered off and purified by column chromatography on silica gel, eluent CHCl₃. We obtained 0.12 g of bis(imino)isoindoline derivative **XII**, that was recrystallized from a mixture petroleum ether–CCl₄, 10 : 1.

1,3-Bis[(perfluorophenyl)imino]-2-(perfluorophenyl)isoindoline (XII), mp 245.5–247°C (in a sealed capillary). IR spectrum, ν, cm⁻¹: 990 (CF), 1501, 1516 (C₆F₅), 1684 (C=N). ¹H NMR spectrum (CCl₄), δ, ppm: 7.23 br.m (2H_{arom}), 7.58 br.m (2H_{arom}). ¹⁹F NMR spectrum (CCl₄), δ, ppm: 0 m (4F, 2F³, 2F⁵), 0.5–1.0 m (4F, 2F_m, 2F⁴), 10.7 t (1F_n, J 21.5 Hz), 10.9 m (4F, 2F², 2F⁶), 19.7 m (2F_O). Mass spectrum, *m/z* (*I*_{rel}, %): 643 (62.52) [M]⁺, 624 (100) [M – F]⁺, 476 (1.68) [M – C₆F₅]⁺, 438 (5.61), 321 (7.36), 295 (8.06), 167 (5.43) [C₆F₅]⁺, 117 (7.36) [C₅F₃]⁺, 76 (10.08) [C₆H₄]⁺. Found, %: C 48.66; H 0.57; F 43.75; N 6.36. C₂₆H₄F₁₅N₃. Calculated, %: C 48.52; H 0.62; F 44.32; N 6.53.

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