Heterocyclization of 2-chloro-1-cyano-1-diethoxyphosphoryl-2-trifluoromethylethylene and 2-chloro-2-chlorodifluoromethyl-1-cyano-1-diethoxyphosphorylethylene

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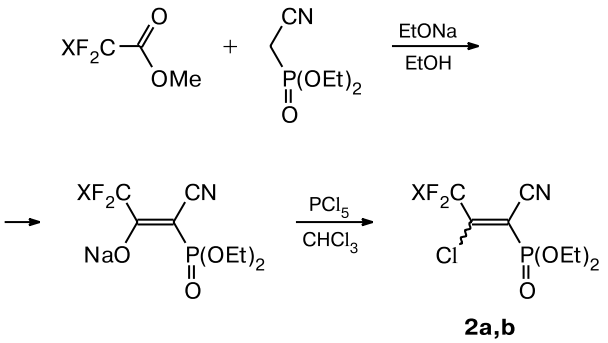
The reactions of 2-chloro-1-cyano-1-diethoxyphosphoryl-2-trifluoromethylethylene (**2a**) and 2-chloro-2-chlorodifluoromethyl-1-cyano-1-diethoxyphosphorylethylene (**2b**) with arylamines, arylhydrazines, amidines, 2-aminopyridines, and 5-aminopyrazoles were studied. Alkenes **2a,b** can serve as precursors of aminopyrazoles, pyrimidines, pyrido[1,2-*a*]pyrimidines, and pyrazolo[1,5-*a*]pyrimidines modified with the fluoroalkyl and diethoxyphosphoryl groups. Intermediates of some heterocyclization reactions were detected by NMR spectroscopy. The structures of the compounds were confirmed by X-ray diffraction analysis.

Key words: 2-chloro-1,1-dicyano-2-trifluoromethylethylene, 2-chloro-1-cyano-1-diethoxyphosphoryl-2-trifluoromethylethylene, 2-chloro-2-chlorodifluoromethyl-1-cyano-1-diethoxyphosphorylethylene, aminopyrazoles, pyrimidines, pyrido[1,2-*a*]pyrimidines, pyrazolo[1,5-*a*]pyrimidines, heterocyclization, X-ray diffraction analysis.

2-Chloro-1,1-dicyano-2-trifluoromethylethylene (**1**) serves as a convenient precursor of trifluoromethyl-substituted derivatives of pyrazole,[1a,b] quinoline,[1b] pyrimidine,[1c] coumarin,[1d] and pyrido[1,2-*a*]pyrimidine.[1e] In the present study, we examined the possibility of using 2-chloro-1-cyano-1-diethoxyphosphoryl-2-trifluoromethylethylene (**2a**) and 2-chloro-2-chlorodifluoromethyl-1-cyano-1-diethoxyphosphorylethylene (**2b**) as precursors of heterocyclic compounds modified with both the fluoroalkyl and diethoxyphosphoryl groups. In our opinion, this problem is of interest in the context of research on biological activities of fluorine-containing heterocycles[2] and a search for new biologically active phosphonates.[3] Only alkene **2a** has been described in the literature.[4] However, we found no data on the reactivity of **2a**.

Scheme 1



2a,b

X = F (**a**), Cl (**b**)

Results and Discussion

2-Chloro-2-chlorodifluoromethyl-1-cyano-1-diethoxyphosphorylethylene (**2b**) was prepared analogously to trifluoromethyl-substituted alkene **2a** by condensation of methyl chlorodifluoroacetate with diethoxyphosphorylacetonitrile followed by the replacement of the hydroxy group of the enolate that formed by the chlorine atom under the action of phosphorus pentachloride (Scheme 1).

Like alkene **2a**, its chlorodifluoromethyl analog **2b** was prepared as a mixture of *Z*,*E* isomers in a ratio *E* : *Z* = 5 : 1 (for **2a**, *E* : *Z* = 4.8 : 1). The assignment of the geometric isomers was made based on the ^{19}F NMR spectrum. The signal for the fluorine atom in the *E* isomer appears as a doublet with the spin-spin coupling constant $^4J_{F,P}$ = 2.0 Hz, whereas the signal for this atom in the *Z* isomer appears as a singlet.

Compounds **2a** and **2b**, like 2-chloro-1,1-dicyano-2-trifluoromethylethylene (**1**), react with arylamines already at room temperature to form 2-arylamino-1-cyano-1-diethoxyphosphoryl-2-polyfluoroalkylethylenes **3a—g** and **4a—g** in high yields (Scheme 2, Table 1). High reactivity of vinyl chlorides **2a** and **2b** is, evidently, explained by a two-step scheme of the reaction with amines involving the addition of amine to highly electrophilic acrylonitrile

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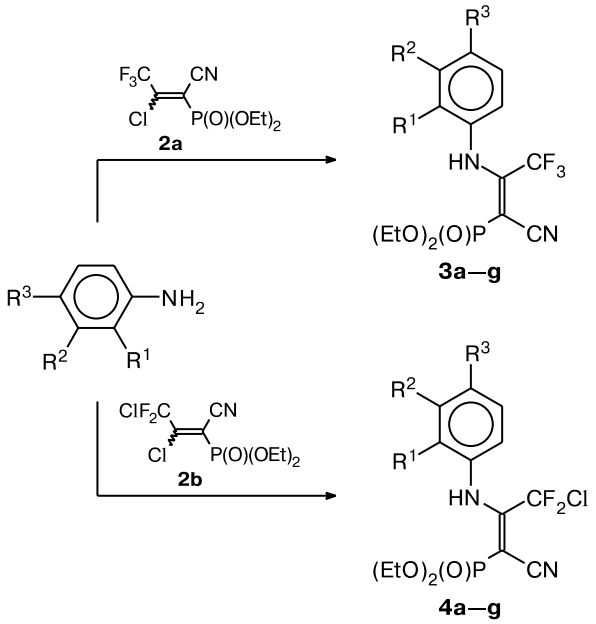
derivatives **2a** and **2b** followed by elimination of hydrogen chloride to form enamines **3** and **4**, respectively.

Scheme 2



Unlike alkenes **2a** and **2b** existing as mixtures of two stereoisomers (readily interconvertable), enamines **3** and **4** derived from these compounds exist exclusively as the *Z* isomer, which is, apparently, thermodynamically more stable due to intramolecular hydrogen bonding. The formation of the *Z* isomers and the presence of a hydrogen bond were confirmed by the results of X-ray diffraction analysis of compound **3b** and NMR spectroscopic studies. The ^{19}F NMR spectra of compounds **3** and **4** have a singlet with a width at half height of 1 Hz. It is known[4] that the *cis* arrangement of the trifluoromethyl and phosphonate groups is characterized by $^4J_{F,P} = 2.0$ Hz. Consequently, the trifluoromethyl and phosphonate groups in compounds **3** and **4** are in the *trans* arrangement.

Table 1. Physicochemical characteristics of compounds **3a—g** and **4a—g**

Compound	R^1	R^2	R^3	Yield (%)	M.p. /°C
3a	H	H	H	71	61
3b	H	H	OMe	74.5	62
3c	H	H	OPh	61.5	76.5
3d	—(CH=CH—)$_2$		H	83.5	118
3e	Cl	Cl	H	84	99
3f	H	H	Me	70	74
3g	H	H	Cl	79	76
4a	H	H	H	77.5	75
4b	H	H	OMe	78.6	77
4c	H	H	OPh	81	96
4d	—(CH=CH—)$_2$		H	79	140.5
4e	Cl	Cl	H	75	115.5
4f	H	H	Me	42	75
4g	H	H	Cl	79	96

The overall view of molecule **3b** is shown in Fig. 1. The central nitrogen atom, N(2), has a planar configuration (the sum of the bond angles is 360(3)°). According to the structural formula, this atom can be involved in conjugation with both the phenyl fragment and the C(6)=C(7) double bond. Analysis of the molecular geometry demonstrates that the N(2) atom is involved in conjugation only with the double bond, because the N(2)—C(7) bond length is 1.337(4) Å, whereas the N(2)—C(10) bond length is 1.446(4) Å. The angle between the planes of the valence bonds about the N(2) and C(7) atoms is 8(2)°, whereas the angle between the plane of the benzene ring and the plane of the bonds about the N(2) atom is 82(1)°.

The benzene ring is almost perpendicular to the plane of the conjugated system involving the N(2), C(7), and C(6) atoms. The angle between the mean plane passing through the N(2), C(6), C(7), C(8), C(9), and P(1) atoms and the plane of the benzene ring is 89.6(1)°. This orientation is determined by the presence of forced nonbonded contacts with the trifluoromethyl group (C(15)...F(2), 2.949(4) Å; C(11)...F(3), 3.076(4) Å), whose lengths are

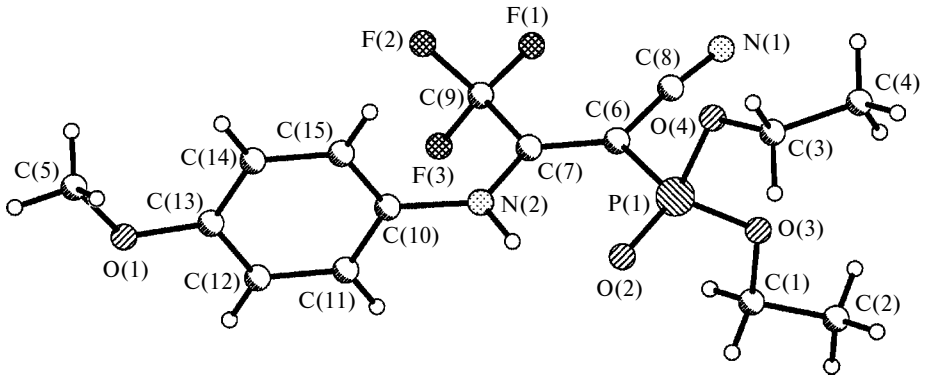


Fig. 1. Overall view of molecule **3b**.

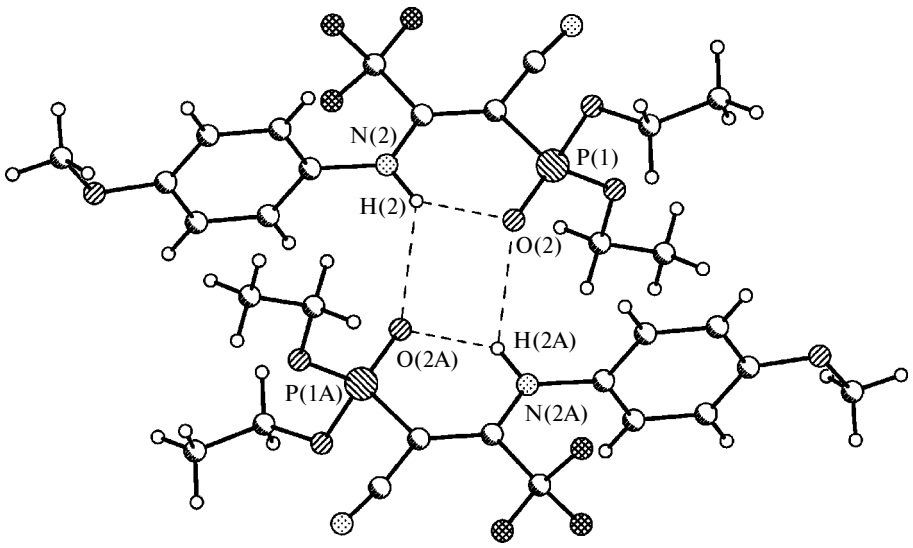


Fig. 2. Hydrogen bond network in the structure of **3b**.

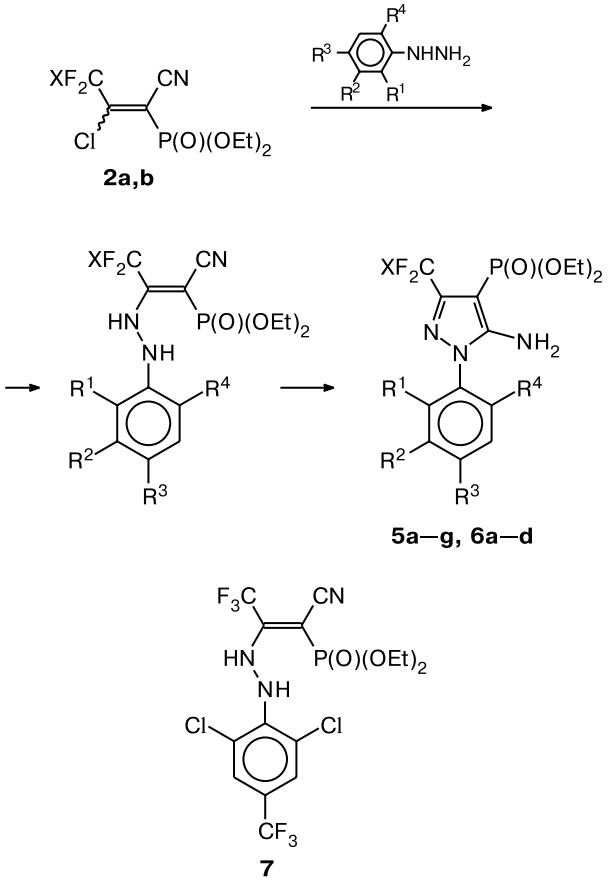
smaller than the sum of the van der Waals radii of these atoms (3.17 Å).[5] This orientation of the trifluoromethyl group gives rise to the intramolecular F(1)...C(8) contact (2.516(4) Å), which prevents the trifluoromethyl group from being rotated in spite of the fact that this group is generally disordered. An analogous effect is observed, for example, in the 7-amino-2-(4-chlorophenyl)-6-diethoxyphosphoryl-5-trifluoromethylpyrazolo[1,5-*a*]pyrimidine molecule (see below), in which the trifluoromethyl group is also not disordered due to the presence of intramolecular contacts, and has also been noted in the earlier research.[6]

It should be noted that there is the intramolecular N(2)—H(2)...O(2) hydrogen bond (N...O, 2.762(4) Å; H...O, 2.01(4) Å; N—H...O, 145(4)°) in molecule **3b**. These atoms are also involved in the weaker intermolecular N(2)—H(2)...O(2) hydrogen bond ($-x+1, -y, -z+2$) (N...O, 3.091(4) Å; H...O, 2.48(4) Å; N—H...O, 128(4)°; see Fig. 2). In the crystal packing, the H(15A) atom (at the C(15) atom of the benzene ring) forms a shortened contact with the O(1) atom of the methoxy group (C...O, 3.423(4) Å; H...O, 2.54 Å; C—H...O, 158°).

Like 2-chloro-1,1-dicyano-2-trifluoromethylethylene (**1**), compounds **2a** and **2b** react with arylhydrazines to give 5-aminopyrazole derivatives **5a—g** and **6a—d** (Scheme 3, Table 2).

The conditions of this reaction are more drastic than those of the reaction with alkene **1**. For the reaction of alkene **2a** with 2,6-dichloro-4-trifluoromethylphenylhydrazine to be brought to completion, prolonged refluxing (16—20 h) in carbon tetrachloride is required, whereas the reaction of dicyanoethylene **1** with 2,6-dichloro-4-trifluoromethylphenylhydrazine is completed at room temperature in several hours. The chlorine atom is rapidly replaced with the primary amino group of arylhydrazines

Scheme 3



to give products, which are slowly transformed into 5-amino-1-aryl-4-diethoxyphosphoryl-3-polyfluoroalkyl-

Table 2. Physicochemical characteristics of compounds **5a—g** and **6a—d**

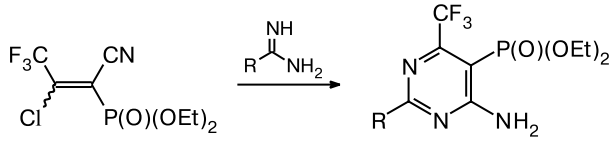
Compound	R^1	R^2	R^3	R^4	Yield (%)	M.p. /°C
5a	H	H	H	H	44	*
5b	H	H	Cl	H	76	*
5c	H	Cl	H	H	63	*
5d	Cl	H	H	H	71	*
5e	H	H	CF_3	H	56	*
5f	Cl	H	CF_3	Cl	55	139.5
5g	H	H	NO_2	H	67	130.5
6a	H	H	H	H	62	*
6b	H	H	Cl	H	41	*
6c	H	H	CF_3	H	37	*
6d	Cl	H	CF_3	Cl	35	*

* The amorphous compound.

pyrazoles (**5** and **6**). In the case of the 2,6-dichloro-4-trifluoromethylphenylhydrazine derivative, the formation of intermediate enamine **7** (see Scheme 3) was detected by NMR monitoring (see the Experimental section). Cyclization to 5-aminopyrazole derivatives **5** and **6** is, apparently, hindered due to intramolecular hydrogen bonding between the oxygen atom of the diethoxyphosphoryl group and the hydrogen atom of the amino group of the intermediate enamine. This assumption can be made based on the above-mentioned data for the *Z* isomers of stable enamines **3** and **4**.

We also studied the reactions of cyanoethylene **2a** with amidines and amidine-containing heterocycles. The reactions of **2a** with acetamidine and benzamidine at 20 °C afforded 4-amino-5-diethoxyphosphoryl-6-trifluoromethylpyrimidines **8a—b**, which were isolated in moderate (20—40%) yields (Scheme 4). In the ^{1}H NMR spectra of these pyrimidines, the signal for the NH_2 group appears as two singlets at δ_H 8.81 and 5.67 for **8a** and at δ_H 8.72 and 6.21 for **8b**. Consequently, there is an intramolecular hydrogen bond between the hydrogen atom of the amino group and the oxygen atom of the diethoxyphosphoryl group in compounds **8a,b**, like that observed in enamines **3** and **4**.

Scheme 4



2a **8a,b**

R = Me, (**8a**), Ph (**8b**)

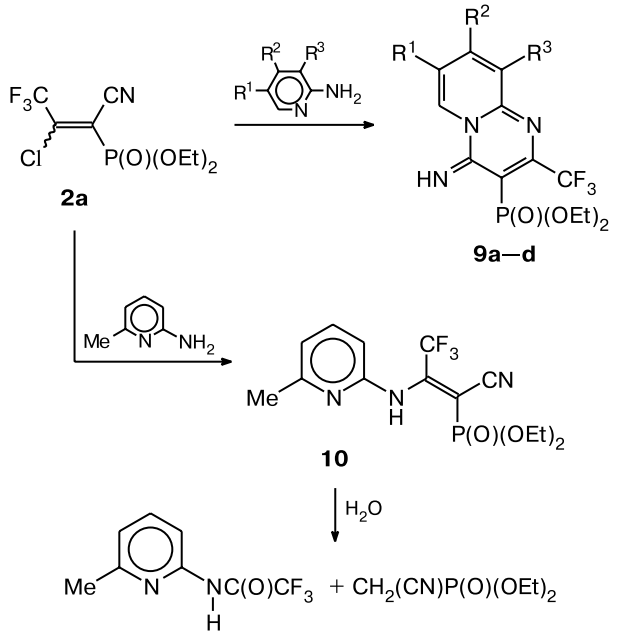
Earlier,[1e] we have demonstrated that the reaction of 2-chloro-1,1-dicyano-2-trifluoromethylethylene (**1**) with

Table 3. Physicochemical characteristics of compounds **9a—d**

Compound	R^1	R^2	R^3	Yield (%)	M.p. /°C
9a	H	H	H	40	89
9b	H	H	Me	22	75
9c	Me	H	H	74	81
9d	H	Me	H	53.5	67

2-aminopyridines proceeds at the exocyclic nitrogen atom of the amidine system and is accompanied by intramolecular cyclization of the nitrile group at the endocyclic nitrogen atom. 2-Chloro-1-cyano-1-diethoxyphosphoryl-2-trifluoromethylethylene (**2a**) reacts analogously to give substituted pyrido[1,2-*a*]pyrimidines **9a—d** in 20—75% yields (Scheme 5, Table 3). The reaction of sterically hindered 2-amino-6-methylpyridine with alkene **2a** stops at enamine **10** and is not accompanied by intramolecular cyclization. The structure of compound **10** was confirmed by ^{1}H NMR spectroscopy as well as by the fact that its IR spectrum shows an absorption band at 2200 cm^{-1} characteristic of the nitrile group. Enamine **10** is slowly hydrolyzed in air to give 6-methyl-2-trifluoroacetylaminopyridine and diethoxyphosphorylacetonitrile.

Scheme 5

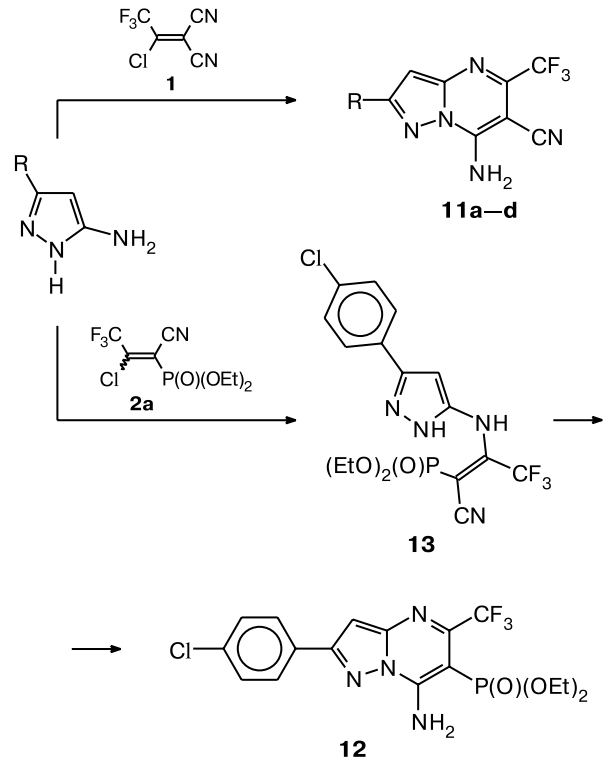


2a **9a—d** **10**

The reactions of 5-amino-1*H*-pyrazoles with polyfluoroalkyl-substituted dicyanochloroethylenes have not been studied earlier. First, we examined the reaction with 2-chloro-1,1-dicyano-2-trifluoromethylethylene (**1**). At room temperature, this reaction afforded pyrazo-

lo[1,5-*a*]pyrimidine derivatives **11a—d**. The structures of compounds **11** were determined by ^{1}H and ^{13}C NMR spectroscopy (the assignment of the signals in the ^{13}C NMR spectra was made based on the data published in the literature[7]). The reaction of 5-amino-3-(4-chlorophenyl)pyrazole with alkene **2a** proceeds analogously, although much more slowly, to give pyrazolo[1,5-*a*]pyrimidine **12**. Intermediate enamine **13** (Scheme 6) was detected by NMR monitoring (see the Experimental section).

Scheme 6



R = H (**a**), Me (**b**), 4-$OMeC_6H_4$ (**c**), 4-ClC_6H_4 (**d**)

The unit cell of compound **12** (Fig. 3) contains two crystallographically independent molecules (**A** and **B**), which are characterized by virtually identical geometry. The molecules differ only in the dihedral angle between the benzene ring and the plane of the bicyclic fragment (7.5(1)° for **A** and −11.0(1)° for **B**) and the orientation of the ethyl group at the O(3) atom. The conjugation of the amino group with the bicyclic fragment leads to shortening of the C(3)—N(4) bond to 1.326(3) Å (1.330(3) Å in **B**), which corresponds to the standard value (1.34 Å) for the $C(sp^2)—N(sp^2)$ bond length,[8] and elongation of the C(1)—C(3) bond to 1.424(3) Å (1.430(3) Å in **B**) compared to the average value (1.38 Å) based on the data retrieved from the Cambridge Structural Database (CSD)[9] (335 pyrimidine fragments). In both independent molecules, there is an intramolecular hydrogen bond between the amino group and the O(1) atom. The parameters of this bond are as follows: N...O, 2.712(2) Å; H...O, 2.02(3) Å; N—H...O, 138(2)° for **A**; and N...O, 2.732(2) Å; H...O, 1.97(3) Å; N—H...O, 143(2)° for **B**. In both molecules, the trifluoromethyl group, like that in the structure of **3b**, is ordered. This fact is attributable to the steric effect. The distances from the F(1) and F(3) atoms to the O(2) atom (2.760(2) and 2.728(2) Å in molecule **A** and 2.727(2) and 2.787(2) Å in molecule **B**, respectively) are smaller than the sum of the van der Walls radii of these atoms (2.99 Å).[5]

In the crystal structure of **12**, the hydrogen atoms of the amino group, which are not involved in intramolecular hydrogen bonding, form the N(4)—H(4B)...O(1′) and N(4′)—H(4B′)...O(1) ($x + 1$, y, z) hydrogen bonds with the O(1) atom of another independent molecule (Fig. 4) (N...O, 2.879(2) Å; H...O, 2.07(2) Å; N—H...O, 156(2)° for **A**; and N...O, 2.858(2) Å; H...O, 2.07(3) Å; N—H...O, 159(3)° for **B**).

We also attempted to prepare 4-aminoquinoline derivatives **14** starting from 2-arylamino-1-cyano-1-diethoxyphosphoryl-2-trifluoromethylethylenes **3** (Scheme 7). It is known that heating of 2-arylamino-1,1-

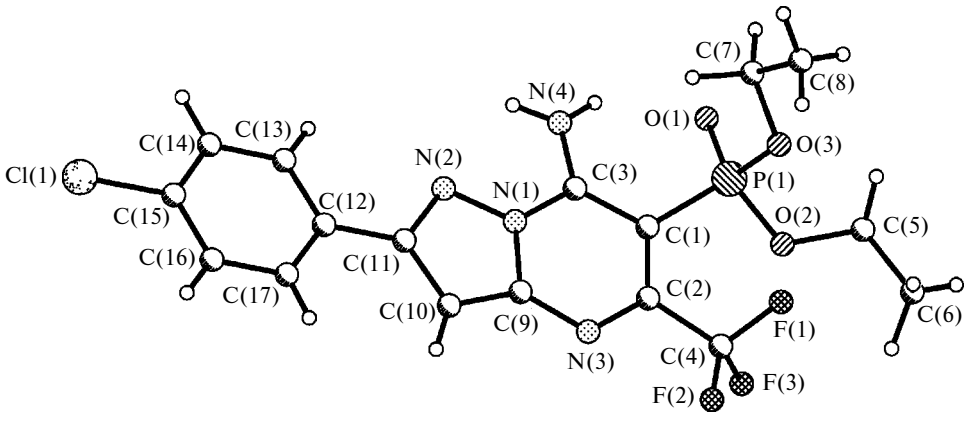


Fig. 3. Overall view of molecule **12**.

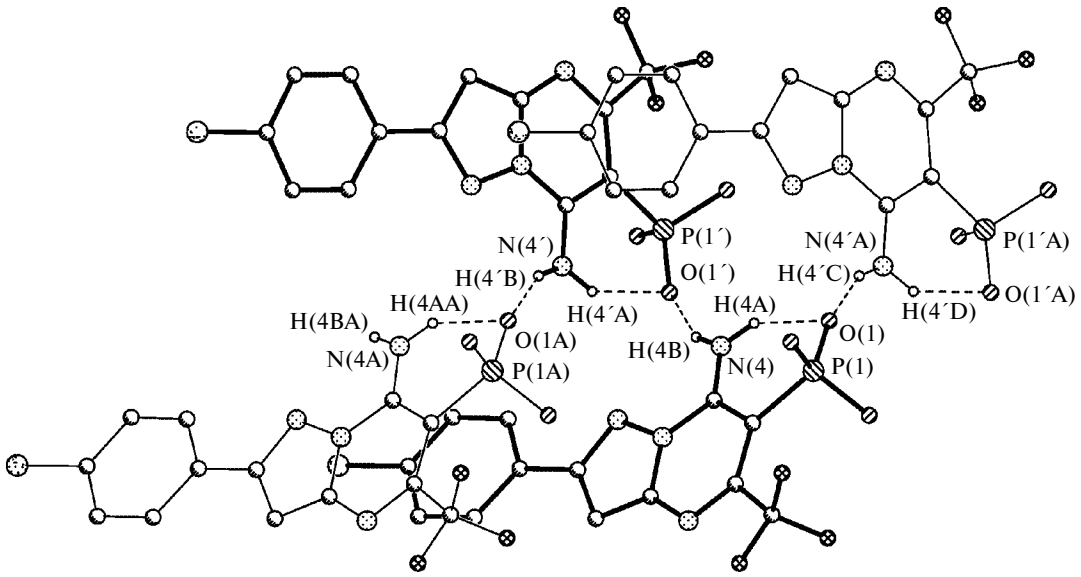
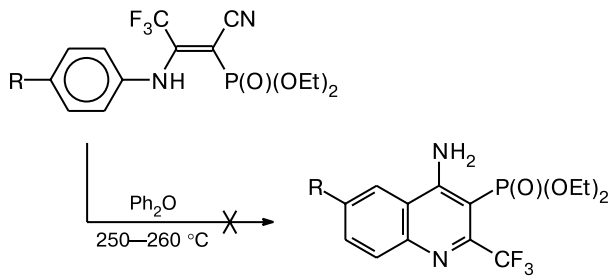


Fig. 4. Hydrogen bond network in the structure of **12**. Symmetrically related molecules generated from two independent molecules by the translation along the *a* axis are indicated by thin lines.

dicyano-2-trifluoromethylethylenes in diphenyl ether gave rise to 4-amino-3-cyano-2-trifluoromethylquinoline derivatives.[1b] An attempt to apply this procedure to the synthesis of 3-diethoxyphosphoryl-substituted 4-amino-2-polyfluoroalkylquinolines **14** was unsuccessful. We also failed to prepare the target compounds in the presence of polyphosphoric acid esters.

Scheme 7



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To summarize, we demonstrated that cyanoethylenes **2a** and **2b** containing the diethoxyphosphoryl group, like 2-chloro-1,1-dicyano-2-trifluoromethylethylene (**1**), serve as promising precursors of trifluoromethyl- or chlorodifluoromethyl-substituted nitrogen-containing heterocycles. The replacement of one cyano group in the starting alkenes with the diethoxyphosphoryl group leads to an increase in the reaction time of heterocyclization with various amino compounds and sometimes hinders this heterocyclization.

Experimental

The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AMX-400 spectrometer operating at 400.13, 100.61, and 160.62 MHz, respectively. The ^{19}F NMR spectra were measured on a Bruker WP-200SY spectrometer (188.31 MHz).

The ^{1}H and ^{13}C chemical shifts were determined relative to the residual signal of the deuterated solvent and recalculated with respect to $SiMe_4$. For the spectra measured with the use of CCl_4 as the solvent, the chemical shifts were determined relative to the residual signal of D_2O as the external standard (4.52 ppm). The ^{19}F and ^{31}P chemical shifts were determined relative to CF_3COOH and 85% H_3PO_4, respectively, as the external standard. The IR spectra (ν/cm^{-1}) were measured on a UR-20 spectrometer.

The crystals of compounds **3b** and **12** were studied by X-ray diffraction analysis. X-ray diffraction data for crystals of **3b** and **12** were collected on a SMART CCD 1000 diffractometer at 110 K. The structures were solved by direct methods and refined by the full-matrix least-squares method. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms in the structure of **12** were revealed from the difference electron density map and refined isotropically. The coordinates of the hydrogen atoms in the structure of **3b** (except for the hydrogen atom of the amino group, which was located from the difference electron density map) were calculated geometrically and refined using the riding model. The main parameters of the structure refinement are given in Table 4. All calculations were carried out using the SHELXTL PLUS program package.[10]

2-Chloro-1,1-dicyano-2-trifluoromethylethylene (1) was synthesized according to a procedure described earlier.[1a]

2-Chloro-1-cyano-1-diethoxyphosphoryl-2-trifluoromethylethylene (2a)[4] was prepared as a mixture of *Z*,*E* isomers (*E* : *Z* = 4.8 : 1 was established by ^{19}F and ^{31}P NMR spectroscopy). The yield was 37%, b.p. 85—90 °C (1 Torr). ^{19}F NMR

Table 4. Crystallographic characteristics and details of X-ray diffraction study and refinement of the structures of **3b** and **12**

Parameter	**3b**	**12**
Molecular formula	$C_{15}H_{18}F_3N_2O_4P$	$C_{17}H_{17}ClF_3N_4O_3P$
Molecular weight	378.28	448.77
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	8.021(3)	6.745(2)
b/Å	19.932(7)	12.730(3)
c/Å	11.361(5)	22.771(6)
α/deg	90	77.259(5)
β/deg	100.47(1)	88.392(5)
γ/deg	90	86.487(6)
V/Å^3	1786(1)	1903.2(8)
Z	4	4
μ(Mo-Kα)/cm^{-1}	2.05	3.41
d_{calc}/g cm^{-3}	1.407	1.566
$2\theta_{max}$/deg	52	60
Number of reflections	15767	22838
Number of independent reflections	3517	11019
R_{int}	0.0383	0.0343
Number of reflections with $I \geq 2\sigma(I)$	2040	7428
Number of parameters	242	655
R [$F^2 \geq 2\sigma(F^2)$]	0.0668	0.1321
wR (F^2), all data	0.1502	0.0509

(without a solvent), δ: *E* isomer: 14.83 (d, 3 F, CF_3, $^4J_{F,P}$ = 1.9 Hz); *Z* isomer: 11.70 (s, 3 F, CF_3). ^{31}P NMR (without a solvent), δ: *E* isomer: 2.57 (br.s, 1 P, $P(O)(OEt)_2$); *Z* isomer: 4.36 (s, 1 P, $P(O)(OEt)_2$).

2-Chloro-2-chlorodifluoromethyl-1-cyano-1-diethoxyphosphorylethylene (2b) was prepared analogously to **2a** as a mixture of *Z*,*E* isomers (*E* : *Z* = 5.0 : 1 was established by ^{19}F and ^{31}P NMR spectroscopy). The yield was 30%, b.p. 100—103 °C (1 Torr). ^{19}F NMR ($CDCl_3$), δ: *E* isomer: 25.59 (d, 3 F, CF_3, $^4J_{F,P}$ = 2.0 Hz); *Z* isomer: 21.96 (s, 3 F, CF_3). ^{31}P NMR ($CDCl_3$), δ: *E* isomer: −1.25 (br.s, 1 P, $P(O)(OEt)_2$); *Z* isomer: 0.66 (s, 1 P, $P(O)(OEt)_2$). ^{31}P NMR ($CDCl_3$), δ: a mixture of *Z*,*E* isomers: 1.43 (m, 6 H, $OCH_2C\underline{H}_3$); 4.32 (m, 4 H, $OC\underline{H}_2CH_3$).

Reaction of alkenes 2a and 2b with arylamines. A solution of 2-chloro-1-cyano-1-diethoxyphosphoryl-2-trifluoromethylethylene (**2a**) or 2-chloro-2-chlorodifluoromethyl-1-cyano-1-diethoxyphosphorylethylene (**2b**) (1.5 mmol) in diethyl ether (5 mL) was added dropwise with stirring to a solution of the corresponding arylamine (3 mmol) in diethyl ether (10 mL) at 20 °C. The reaction mixture was stirred at 20 °C for 3 h. The precipitate that formed was filtered off and washed with diethyl ether. The solvent was removed *in vacuo* and the residue was washed with water and light petroleum. The product was dried on a filter. These reactions afforded compounds **3a—g** and **4a—g** (see Tables 1 and 5)

Reaction of alkenes 2a and 2b with arylhydrazines. A solution of 2-chloro-1-cyano-1-diethoxyphosphoryl-2-trifluoromethylethylene (**2a**) or 2-chloro-2-chlorodifluoromethyl-1-cyano-1-diethoxyphosphorylethylene (**2b**) (1 mmol) in CCl_4 (3 mL) was added dropwise with stirring to a solution of the corresponding arylhydrazine (2 mmol) in CCl_4 (8 mL) at 20 °C. The reaction mixture was refluxed for 4—16 h. The precipitate that formed was filtered off and washed with diethyl ether. The solvent was removed *in vacuo*. The product was isolated by preparative TLC on silica gel using a 2 : 1 ethyl acetate—light petroleum mixture as the eluent. These reactions afforded compounds **5a—g** and **6a—e** (see Tables 2 and 6).

1-Cyano-2-[*N*′-(2,6-dichloro-4-trifluoromethylphenyl)hydrazino]-1-diethoxyphosphoryl-2-trifluoromethylethylene (7). The product was detected by ^{1}H, ^{19}F, and ^{31}P NMR spectroscopy. ^{19}F NMR ($CDCl_3$), δ: 9.77 (s, 3 F, CF_3); 15.10 (s, 3 F, $ArCF_3$). ^{31}P NMR ($CDCl_3$), δ: 13.00 (m, 1 P, $P(O)(OEt)_2$). ^{1}H NMR ($CDCl_3$), δ: 1.34 (t, 6 H, $OCH_2C\underline{H}_3$, *J* = 7.2 Hz); 4.23 (m, 4 H, $OC\underline{H}_2CH_3$); 7.53 and 10.19 (both s, 1 H each, NH—NH); 7.60 (s, 2 H, Ar).

Reaction of 2-chloro-1-cyano-1-diethoxyphosphoryl-2-trifluoromethylethylene (2a) with amidines. A solution of 2-chloro-1-cyano-1-diethoxyphosphoryl-2-trifluoromethylethylene (**2a**) (0.95 mmol) in acetonitrile (2 mL) was added dropwise with stirring to a solution of the corresponding amidine (1.8 mmol) in acetonitrile (3 mL) at 0—10 °C. The reaction mixture was stirred at 20 °C for 3 h. The solvent was removed *in vacuo* and the residue was washed with water. The product was isolated by preparative TLC on silica gel using a 2 : 1 ethyl acetate—light petroleum mixture as the eluent. These reactions afforded compounds **8a—b**.

4-Amino-5-diethoxyphosphoryl-2-phenyl-6-trifluoromethylpyrimidine (8a). The yield was 42%, m.p. 51 °C. Found (%): C, 47.87; H, 4.55; N, 11.30. $C_{15}H_{17}F_3N_3OP$. Calculated (%): C, 48.01; H, 4.57; N, 11.20. ^{19}F NMR (CCl_4), δ: 12.72 (s, 3 F, CF_3). ^{31}P NMR (CCl_4), δ: 18.47 (s, 1 P, $P(O)(OEt)_2$). ^{1}H NMR (CCl_4), δ: 1.21 (t, 6 H, $OCH_2C\underline{H}_3$, *J* = 7.2 Hz); 3.95 and 4.02 (both m, 2 H each, $OC\underline{H}_2CH_3$); 5.67 and 8.81 (both br.s, 1 H each, NH_2); 7.23—8.25 (m, 9 H, Ar).

4-Amino-5-diethoxyphosphoryl-2-methyl-6-trifluoromethylpyrimidine (8b). The yield was 20%, m.p. 75 °C. Found (%): C, 38.99; H, 4.85; N, 13.42. $C_{10}H_{15}F_3N_3OP$. Calculated (%): C, 38.85; H, 4.83; N, 13.42. ^{19}F NMR (CCl_4), δ: 12.77 (s, 3 F, CF_3). ^{31}P NMR (CCl_4), δ: 18.14 (s, 1 P, $P(O)(OEt)_2$). ^{1}H NMR (CCl_4), δ: 1.18 (t, 6 H, $OCH_2C\underline{H}_3$, *J* = 7.2 Hz); 2.31 (s, 3 H, Me); 3.91 and 3.96 (both m, 2 H each, $OC\underline{H}_2CH_3$); 6.21 and 8.72 (both br.s, 1 H each, NH_2).

Reaction of 2-chloro-1-cyano-1-diethoxyphosphoryl-2-trifluoromethylethylene (2a) with 2-aminopyridines. A solution of compound **2a** (0.68 mmol) in acetonitrile (1.5 mL) was added dropwise with stirring to a solution of the corresponding 2-aminopyridine (1.36 mmol) in acetonitrile (4 mL) at 0—10 °C. The reaction mixture was stirred at 20 °C for 2—3 h. The precipitate that formed was filtered off and washed with acetonitrile. The solvent was removed *in vacuo*. The product was isolated by preparative TLC on silica gel using a 2 : 1 ethyl acetate—light petroleum mixture as the eluent. These reactions afforded compounds **9a—d** (see Tables 3 and 7).

1-Cyano-1-diethoxyphosphoryl-2-[2-(6-methylpyridyl)]-2-trifluoromethylethylene (10). A solution of 2-chloro-1-cyano-1-diethoxyphosphoryl-2-trifluoromethylethylene (**2a**) (0.3 g, 1.03 mmol) in acetonitrile (1.5 mL) was added dropwise with stirring to a solution of 2-amino-6-methylpyridine (0.21 g, 1.94 mmol) in acetonitrile (4 mL) at 0—10 °C. The reaction mixture was stirred at 20 °C for 3 h. The precipitate that formed

Table 5. ^{1}H, ^{19}F, and ^{31}P NMR spectra ($CDCl_3$, δ, *J*/Hz) and results of elemental analysis for compounds **3a—g** and **4a—g**

Compound	^{1}H NMR	δ_F (s, CF_2X)	δ_P (s, $P(O)(OEt)_2$)	Found / Calculated (%)			Molecular formula
				C	H	N	
3a	1.45 (t, 6 H, $OCH_2C\underline{H}_3$, *J* = 7.2); 4.27 (m, 4 H, $OC\underline{H}_2CH_3$); 7.14 (d, 2 H, Ar, *J* = 7.5); 7.30—7.40 (m, 3 H, Ar); 10.71 (br.s, 1 H, NH)	18.61	16.03	48.30 48.28	4.63 4.63	7.98 8.04	$C_{14}H_{16}F_3N_2O_3P$
3b	1.45 (t, 6 H, $OCH_2C\underline{H}_3$, *J* = 7.2); 3.82 (s, 3 H, OMe); 4.26 (m, 4 H, $OC\underline{H}_2CH_3$); 6.87, 7.06 (both d, 2 H each, Ar, *J* = 8.7); 10.60 (br.s, 1 H, NH)	18.43	16.40	47.90 47.63	4.95 4.80	7.59 7.41	$C_{15}H_{18}F_3N_2O_4P$
3c	1.45 (t, 6 H, $OCH_2C\underline{H}_3$, *J* = 7.2); 4.27 (m, 4 H, $OC\underline{H}_2CH_3$); $OC\underline{H}_2CH_3$); 6.96—7.40 (m, 9 H, Ar); 10.65 (br.s, 1 H, NH)	18.33	16.11	54.39 54.55	4.48 4.58	6.49 6.36	$C_{20}H_{20}F_3N_2O_4P$
3d	1.50 (t, 6 H, $OCH_2C\underline{H}_3$, *J* = 7.2); 4.34 (m, 4 H, $OC\underline{H}_2CH_3$); 7.27—7.92 (m, 7 H, Ar); 10.95 (br.s, 1 H, NH)	17.90	16.21	53.80 54.28	4.55 4.55	6.97 7.03	$C_{18}H_{18}F_3N_2O_3P$
3e	1.46 (t, 6 H, $OCH_2C\underline{H}_3$, *J* = 7.2); 4.29 (m, 4 H, $OC\underline{H}_2CH_3$); 7.14 (d, 1 H, Ar, *J* = 7.79); 7.23 (t, 1 H, Ar, *J* = 7.8); 7.45 (d, 1 H, Ar, *J* = 7.8); 10.67 (br.s, 1 H, NH)	17.03	14.94	40.29 40.31	3.34 3.38	6.72 6.72	$C_{14}H_{14}Cl_2F_3N_2O_3P$
3f	1.45 (t, 6 H, $OCH_2C\underline{H}_3$, *J* = 7.2); 2.36 (s, 3 H, Me); 4.26 (m, 4 H, $OC\underline{H}_2CH_3$); 7.01, 7.16 (both d, 2 H each, Ar, *J* = 8.1); 10.64 (br.s, 1 H, NH)	18.54	16.16	50.13 49.73	4.98 5.01	7.93 7.73	$C_{15}H_{18}F_3N_2O_3P$
3g*	1.62 (t, 6 H, $OCH_2C\underline{H}_3$, *J* = 7.2); 4.38 (m, 4 H, $OC\underline{H}_2CH_3$); 7.47, 7.22 (both d, 2 H each, Ar, *J* = 8.7); 10.77 (br.s, 1 H, NH)	18.81	17.81	44.08 43.94	4.40 3.95	7.64 7.32	$C_{14}H_{15}ClF_3N_2O_3P$
4a	1.46 (t, 6 H, $OCH_2C\underline{H}_3$, *J* = 7.2); 4.27 (m, 4 H, $OC\underline{H}_2CH_3$); 7.20 (d, 2 H, Ar, *J* = 7.8); 7.30—7.40 (m, 3 H, Ar); 10.70 (br.s, 1 H, NH)	28.23	16.62	46.00 4.11	4.40 4.42	7.64 7.68	$C_{14}H_{16}ClF_2N_2O_3P$
4b	1.46 (t, 6 H, $OCH_2C\underline{H}_3$, *J* = 7.2); 3.82 (s, 3 H, OMe); 4.27 (m, 4 H, $OC\underline{H}_2CH_3$); 6.87, 7.11 (both d, 2 H each, Ar, *J* = 8.7); 10.58 (br.s, 1 H, NH)	28.07	16.95	45.35 45.64	4.66 4.60	7.10 7.10	$C_{15}H_{18}ClF_2N_2O_4P$
4c	1.46 (t, 6 H, $OCH_2C\underline{H}_3$, *J* = 7.2); 4.27 (m, 4 H, $OC\underline{H}_2CH_3$); 6.97—7.39 (m, 9 H, Ar); 10.64 (br.s, 1H, NH)	28.16	16.54	53.21 52.59	4.55 4.41	6.05 6.13	$C_{20}H_{20}ClF_2N_2O_4P$
4d	1.46 (t, 6 H, $OCH_2C\underline{H}_3$, *J* = 7.2); 4.28 (m, 4 H, $OC\underline{H}_2CH_3$); 7.31—7.87 (m, 7 H, Ar); 10.85 (br.s, 1 H, NH)	27.42	16.76	52.10 52.12	4.37 4.37	6.68 6.75	$C_{18}H_{18}ClF_2N_2O_3P$
4e	1.47 (t, 6 H, $OCH_2C\underline{H}_3$, *J* = 7.2); 4.29 (m, 4 H, $OC\underline{H}_2CH_3$); 7.21—7.48 (m, 3 H, Ar); 10.66 (br.s, 1 H, NH)	27.01	15.52	38.69 38.78	3.15 3.25	6.38 6.46	$C_{14}H_{14}Cl_3F_2N_2O_3P$
4f	1.45 (t, 6 H, $OCH_2C\underline{H}_3$, *J* = 7.2); 2.37 (s, 3 H, Me); 4.27 (m, 4 H, $OC\underline{H}_2CH_3$); 7.08, 7.17 (both d, 2 H each, Ar, *J* = 8.1); 10.64 (br.s, 1 H, NH)	28.17	16.88	47.77 47.57	4.80 4.79	7.50 7.40	$C_{15}H_{18}ClF_2N_2O_3P$
4g	1.39 (t, 6 H, $OCH_2C\underline{H}_3$, *J* = 7.2); 4.21 (m, 4 H, $OC\underline{H}_2CH_3$); 7.07, 7.28 (both d, 2 H each, Ar, *J* = 8.7); 10.58 (br.s, 1 H, NH)	28.25	16.14	42.13 42.13	3.80 3.79	7.05 7.02	$C_{14}H_{15}Cl_2F_2N_2O_3P$

* The spectrum was recorded in CCl_4.

was filtered off and washed with acetonitrile. The solvent was removed *in vacuo* and the residue was washed with water and light petroleum. The product was isolated by preparative TLC on silica gel using a 2 : 1 ethyl acetate—light petroleum mixture as the eluent. The yield of compound **10** was 0.27 g (77%). Found (%): C, 46.31; H, 4.72; N, 11.59. $C_{14}H_{17}F_3N_3OP$. Calculated (%): C, 46.29; H, 4.72; N, 11.57. ^{19}F NMR ($CDCl_3$), δ: 17.74 (s, 3 F, CF_3). ^{31}P NMR ($CDCl_3$), δ: 14.36 (s, 1 P, $P(O)(OEt)_2$). ^{1}H NMR ($CDCl_3$), δ: 1.43 (t, 6 H, $OCH_2C\underline{H}_3$, *J* = 7.2 Hz); 2.48 (s, 3 H, Me); 4.24 (m, 4 H, $OC\underline{H}_2CH_3$); 6.83 and 6.99 (both d, 1 H each, H(3), H(5), *J* = 7.8 Hz); 7.58 (t, 1 H, H(4), *J* = 7.8 Hz), 10.64 (br.s, 1 H, NH). IR, ν/cm^{-1}: 2900 (NH, broad), 2200 (CN).

In air, compound **10** underwent slow hydrolysis to give 6-methyl-2-trifluoroacetylaminopyridine (^{19}F NMR ($CDCl_3$), δ: 1.92 (s, 3 F, CF_3); ^{1}H NMR ($CDCl_3$), δ: 2.49 (s, 3 H, Me); 6.45—7.59

Table 6. ^{1}H, ^{19}F, and ^{31}P NMR spectra ($CDCl_3$, δ, J/Hz) and results of elemental analysis for compounds **5a—g** and **6a—d**

Compound	^{1}H NMR	^{19}F NMR (s, CF_2X)	^{31}P NMR (s, $P(O)(OEt)_2$)	Found / Calculated (%)					Molecular formula
				C	H	N	F	Cl	
5a	1.36 (t, 6 H, $OCH_2C\underline{H}_3$, J = 7.2); 4.10, 4.17 (both m, 2 H each, $OC\underline{H}_2CH_3$); 5.50 (br.s, 2 H, NH_2); 7.44—7.57 (m, 5 H, Ar)	14.96	12.40	46.10 46.29	4.76 4.72	11.50 11.57	—	—	$C_{14}H_{17}F_3N_3O_3P$
5b*	1.18 (t, 6 H, $OCH_2C\underline{H}_3$, J = 7.2); 3.84, 3.90 (both m, 2 H each, $OC\underline{H}_2CH_3$); 5.41 (br.s, 2 H, NH_2); 7.31, 7.41 (both d, 2 H each, Ar, J = 8.7)	15.39	14.23	42.19 42.28	4.18 4.05	10.49 10.57	13.86 14.33	9.43 8.91	$C_{14}H_{16}ClF_3N_3O_3P$
5c*	1.18 (t, 6 H, $OCH_2C\underline{H}_3$, J = 7.2); 3.82, 3.86 (both m, 2 H each, $OC\underline{H}_2CH_3$); 5.42 (br.s, 2 H, NH_2); 7.19—7.49 (m, 4 H, Ar)	15.38	14.11	42.54 42.28	4.20 4.05	10.61 10.57	13.99 14.33	9.35 8.91	$C_{14}H_{16}ClF_3N_3O_3P$
5d*	1.18 (t, 6 H, $OCH_2C\underline{H}_3$, J = 7.2); 3.86, 3.91 (both m, 2 H each, $OC\underline{H}_2CH_3$); 5.18 (br.s, 2 H, NH_2); 7.24—7.40 (m, 4 H, Ar)	15.42	14.40	42.32 42.28	4.14 4.05	10.49 10.57	14.03 14.33	9.71 8.91	$C_{14}H_{16}ClF_3N_3O_3P$
5e*	1.20 (t, 6 H, $OCH_2C\underline{H}_3$, J = 7.2); 4.20, 4.27 (both m, 2 H each, $OC\underline{H}_2CH_3$); 5.59 (br.s, 2 H, NH_2); 7.96 (s, 4 H, Ar)	15.40, 15.23	14.14	41.76 41.78	3.68 3.74	9.74 9.74	25.71 26.43	—	$C_{15}H_{16}F_6N_3O_3P$
5f	1.36 (t, 6 H, $OCH_2C\underline{H}_3$, J = 7.2); 4.09, 4.16 (both m, 2 H each, $OC\underline{H}_2CH_3$); 5.30 (br.s, 2 H, NH_2); 7.79 (s, 2 H, Ar)	14.76, 14.45	11.61	35.25 36.02	2.71 2.82	8.11 8.40	20.82 22.79	11.53 14.18	$C_{15}H_{14}Cl_2F_6N_3O_3P$
5g**	1.19 (t, 6 H, $OCH_2C\underline{H}_3$, J = 7.2); 4.02, 4.11 (both m, 2 H each, $OC\underline{H}_2CH_3$); 5.30 (br.s, 2 H, NH_2); 7.00, 7.72 (both d, 2 H each, Ar, J = 8.4)	13.07	9.25	41.11 41.19	3.84 3.95	13.71 13.72	12.82 13.96	—	$C_{14}H_{16}F_3N_4O_5P$
6a	1.42 (t, 6 H, $OCH_2C\underline{H}_3$, J = 7.2); 4.14, 4.23 (both m, 2 H each, $OC\underline{H}_2CH_3$); 5.59 (br.s, 2 H, NH_2); 7.50—7.62 (m, 5 H, Ar)	29.56		44.02 44.28	4.44 4.51	11.14 11.07	—	—	$C_{14}H_{17}ClF_2N_3O_3P$
6b	1.42 (t, 6 H, $OCH_2C\underline{H}_3$, J = 7.2); 4.14, 4.23 (both m, 2 H each, $OC\underline{H}_2CH_3$); 5.59 (br.s, 2 H, NH_2); 7.58 (s, 4 H, Ar)	29.35	9.88	40.53 40.60	3.97 3.89	10.06 10.15	—	—	$C_{14}H_{16}Cl_2F_2N_3O_3P$
6c	1.38 (t, 6 H, $OCH_2C\underline{H}_3$, J = 7.2); 4.12, 4.20 (both m, 2 H each, $OC\underline{H}_2CH_3$); 5.61 (br.s, 2 H, NH_2); 7.75, 7.81 (both d, 2 H each, Ar, J = 8.44)	15.02 (s, 3 F, CF_3); 29.15 (s, 2 F, CF_2Cl)	9.60	40.40 40.24	3.56 3.60	9.46 9.39	—	—	$C_{15}H_{16}ClF_5N_3O_3P$
6d	1.43 (t, 6 H, $OCH_2C\underline{H}_3$, J = 7.2); 4.15, 4.23 (both m, 2 H each, $OC\underline{H}_2CH_3$); 5.44 (br.s, 2 H, NH_2); 7.85 (s, 2 H, Ar)	14.42 (s, 3 F, CF_3); 29.01 (s, 2 F, CF_2Cl)	9.50	34.74 34.87	2.74 2.73	8.19 8.13	—	—	$C_{15}H_{14}Cl_3F_5N_3O_3P$

* The spectrum was recorded in CCl_4.

** The spectrum was recorded in C_6D_6.

Table 7. ^{1}H, ^{19}F, and ^{31}P NMR spectra ($CDCl_3$, δ, *J*/Hz) and results of elemental analysis for compounds **9a—d**

Compound	^{1}H NMR	δ_F	δ_P	Found / Calculated (%) C	H	N	Molecular formula
9a	1.37 (t, 6 H, $OCH_2C\underline{H}_3$, *J* = 7.2); 2.55 (s, 3 H, Me); 4.17, 4.23 (both m, 2 H each, $OC\underline{H}_2CH_3$); 7.23 (d, 1 H, Ar, *J* = 8.9); 7.89 (dd, 1 H, Ar, *J* = 6.0, 8.9); 7.58, 9.54 (both d, 1 H each, Ar, *J* = 6.0); 10.01 (br.s, 1 H, NH)	13.10	13.86	44.60 / 44.71	4.38 / 4.33	12.00 / 12.03	$C_{13}H_{15}F_3N_3O_3P$
9b	1.37 (t, 6 H, $OC\underline{H}_2CH_3$, *J* = 7.2); 2.55 (s, 3 H, Me); 4.17, 4.23 (both m, 2 H each, $OC\underline{H}_2CH_3$); 7.14 (t, 1 H, Ar, *J* = 6.8); 7.71, 9.36 (both d, 1 H each, Ar, *J* = 6.8); 9.91 (br.s, 1 H, NH)	13.12	14.23	46.12 / 46.29	4.72 / 4.72	11.45 / 11.57	$C_{14}H_{17}F_3N_3O_3P$
9c	1.36 (t, 6 H, $OCH_2C\underline{H}_3$, *J* = 7.2); 2.45 (s, 3 H, Me); 4.15, 4.22 (both m, 2 H each, $OC\underline{H}_2CH_3$); 7.72, 7.75 (both d, 1 H each, Ar, *J* = 9.1); 9.32 (s, 1 H, Ar); 9.87 (br.s, 1 H, NH)	13.12	14.32	46.17 / 46.29	4.76 / 4.72	11.51 / 11.57	$C_{14}H_{17}F_3N_3O_3P$
9d	1.36 (t, 6 H, $OCH_2C\underline{H}_3$, *J* = 7.2); 2.50 (s, 3 H, Me); 4.15, 4.23 (both m, 2 H each, $OC\underline{H}_2CH_3$); 7.37 (br.s, 1 H, Ar); 7.04, 9.37 (both d, 1 H each, Ar, *J* = 7.2); 9.87 (s, 1 H, NH)	13.06	14.16	46.20 / 46.29	4.70 / 4.72	11.64 / 11.57	$C_{14}H_{17}F_3N_3O_3P$

(m, 3 H, Ar); 15.39 (br.s, 1 H, NH)) and diethoxyphosphorylacetonitrile. The structure of the latter was confirmed by ^{1}H and ^{31}P NMR spectroscopy in a special experiment with the addition of an authentic sample.

Reaction of 2-chloro-1,1-dicyano-2-trifluoromethylethylene (1) with 5-amino-1*H*-pyrazoles. *A*. A solution of compound **1** (1.6 mmol) in dichloromethane or chloroform (5 mL) was added dropwise with stirring to a solution of the corresponding aminopyrazole (3.2 mmol) in dichloromethane or chloroform (20—30 mL) at 20 °C. The reaction mixture was stirred at 20 °C for 2—3 h. The precipitate that formed was filtered off and washed with water and light petroleum. The product was dried in a desiccator over P_2O_5. These reactions afforded compounds **11a—c**.

7-Amino-6-cyano-5-trifluoromethylpyrazolo[1,5-*a*]pyrimidine (11a). The yield was 68%, sublim.t. 195 °C. Found (%): C, 42.36; H, 1.78; F, 24.97; N, 30.83. $C_8H_4F_3N_5$. Calculated (%): C, 42.30; H, 1.77; F, 25.09; N, 11.20. ^{19}F NMR (DMSO-d_6), δ: 9.75 (s, 3 F, CF_3). ^{1}H NMR (DMSO-d_6), δ: 6.86 (s, 1 H, H(3)); 8.38 (s, 1H, H(2)); 9.40 (s, 2 H, NH_2). ^{13}C NMR (DMSO-d_6), δ: 70.5 (s, C(6)); 101.4 (s, C(3)); 114.2 (s, CN); 121.5 (q, CF_3, $^{1}J_{C,F}$ = 276 Hz); 147.0 (q, C(5), $^{2}J_{C,F}$ = 34 Hz); 147.1 (s, C(7)); 148.1 (s, C(2)); 152.6 (s, C(3a)).

7-Amino-6-cyano-2-methyl-5-trifluoromethylpyrazolo[1,5-*a*]pyrimidine (11b). The yield was 53%, sublim.t. 200 °C. Found (%): C, 44.67; H, 2.51; F, 23.60; N, 29.04. $C_9H_6F_3N_5$. Calculated (%): C, 44.82; H, 2.51; F, 23.63; N, 29.04. ^{19}F NMR (DMSO-d_6), δ: 9.78 (s, 3 F, CF_3). ^{1}H NMR (DMSO-d_6), δ: 2.45 (s, 3 H, Me); 6.64 (s, 1 H, H(3)); 9.16 (s, 2 H, NH_2).

7-Amino-6-cyano-2-(4-methoxyphenyl)-5-trifluoromethylpyrazolo[1,5-*a*]pyrimidine (11c). The yield was 89%, sublim.t. 235 °C. Found (%): C, 54.07; H, 3.02; F, 16.75; N, 21.01. $C_{15}H_{10}F_3N_5O$. Calculated (%): C, 54.06; H, 3.02; F, 17.10; N, 21.01. ^{19}F NMR (DMSO-d_6), δ: 9.79 (s, 3 F, CF_3),). ^{1}H NMR (DMSO-d_6), δ: 3.83 (s, 3 H, OMe); 7.07 and 8.04 (both d, 2 H each, Ar, *J* = 8.7 Hz); 7.24 (s, 1 H, H(3)); 9.17 (s, 2 H, NH_2).

***B*.** A solution of 2-chloro-1,1-dicyano-2-trifluoromethylethylene (**1**) (0.25 g, 1.3 mmol) in acetonitrile (5 mL) was added dropwise with stirring to a solution of 5-amino-3-(4-methoxyphenyl)-1*H*-pyrazole (0.24 g, 1.3 mmol) and triethylamine (0.13 g, 1.3 mmol) in acetonitrile (15 mL) at 20 °C. The reaction mixture was stirred at 20 °C for 2 h. The precipitate that formed was filtered off and washed with water and light petroleum. The product was dried in a desiccator over P_2O_5 to prepare 0.28 g of **7-amino-2-(4-chlorophenyl)-6-cyano-5-trifluoromethylpyrazolo[1,5-*a*]pyrimidine (11d).** The mother acetonitrile liquor was concentrated to 1/3 of the initial volume and poured into water. The precipitate that formed was filtered off and washed with light petroleum. The product was dried in a desiccator over P_2O_5, which gave additionally 0.10 g of compound **11d**. The total yield was 0.38 g (86%), sublim.t. 225 °C. Found (%): C, 49.90; H, 2.05; F, 16.85; N, 20.74. $C_{14}H_7F_3N_5$. Calculated (%): C, 49.80; H, 2.09; F, 16.88; N, 20.74. ^{19}F NMR (DMSO-d_6), δ: 9.77 (s, 3 F, CF_3). ^{1}H NMR (DMSO-d_6), δ: 7.37 (s, 1 H, H(3)); 7.59 and 8.13 (both d, 2 H each, Ar, *J* = 8.8 Hz); 9.25 (s, 2 H, NH_2).

7-Amino-2-(4-chlorophenyl)-6-diethoxyphosphoryl-5-trifluoromethylpyrazolo[1,5-*a*]pyrimidine (12). A solution of 2-chloro-1-cyano-1-diethoxyphosphoryl-2-trifluoromethylethylene (**2a**) (0.23 g, 0.79 mmol) in acetonitrile (5 mL) was added dropwise with stirring to a solution of 5-amino-3-(4-chlorophenyl)-1*H*-pyrazole (0.15 g, 0.79 mmol) and triethylamine (0.08 g, 0.79 mmol) in acetonitrile (10 mL) at 20 °C. The reaction mixture was stirred at 20 °C for 7 days. The solvent was removed *in vacuo* and the residue was washed with water and light petroleum. Compound **12** containing a small amount of an impurity (TLC data) was obtained in a yield of 0.22 g (63%). Additional purification by preparative TLC on silica gel (ethyl acetate—light petroleum, 2 : 1, as the eluent) afforded compound **12** in a yield of 0.19 g. The total yield was 55%, m.p. 128.5 °C. Found (%): C, 45.40; H, 3.66; N, 12.62. $C_{18}H_{21}ClF_3N_4O_3P$. Calculated (%): C, 46.51; H, 4.55; N, 12.05. ^{19}F NMR (DMSO-d_6), δ: 14.95 (s, 3 F, CF_3). ^{31}P NMR (DMSO-d_6), δ: 19.53 (s, 1 P, $P(O)(OEt)_2$). ^{1}H NMR (DMSO-d_6), δ: 1.26 (t, 6 H, $OCH_2C\underline{H}_3$, *J* = 7.2 Hz); 4.10 (m, 4 H, $OC\underline{H}_2CH_3$); 7.33 (s, 1 H, H(3)); 7.59 and 8.13 (both d, 2 H each, Ar, *J* = 7.8 Hz); 8.78 and 9.54 (both s, 1 H each,

NH_2). ^{13}C NMR (DMSO-d_6), δ: 21.0 (d, $OCH_2\underline{C}H_3$, $^3J_{C,P}$ = 7 Hz); 66.2 (d, $O\underline{C}H_2CH_3$, $^2J_{C,P}$ = 4 Hz); 85.5 (d, C(6), $^1J_{C,P}$ = 192 Hz); 101.4 (s, C(3)); 125.8 (q, CF_3, $^1J_{C,F}$ = 276 Hz); 134.1 and 133.3 (both s, CH, Ar); 139.5 and 135.7 (both s, C, Ar); 151.6 (s, C(2)); 157.3 (d, C(7), $^2J_{C,P}$ = 16 Hz); 160.4 (s, C(3a)).

2-[3-(4-Chlorophenyl)-1-cyano-1*H*-pyrazol-5-ylamino]-1-diethoxyphosphoryl-2-trifluoromethylethylene (13). The product was detected by ^{19}F and ^{31}P NMR spectroscopy. ^{19}F NMR (CD_3CN), δ: 21.45 (s, 3 F, CF_3). ^{31}P NMR (CD_3CN), δ: 21.49 (s, 1 P, $P(O)(OEt)_2$).

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