9. G. Wanag and A. Veinbergs, Chem. Ber., 75, 725 (1942).
10. R. Silverstein, G. Bassler, and T. Morill, Spectroscopic Identification of Organic Compounds, Wiley (1974).
11. V. Wray, J. Chem. Soc., Perkin II, No. 9, 855 (1978).
12. A. V. Stetsenko and V. Ya. Demchenko, Vestn. Kievsk. Gos. Univ., No. 12, 69 (1971).
13. É. B. Lifshits, Dokl. Akad. Nauk SSSR, 179, 596 (1968).
14. V. I. Troitskaya, V. I. Rudyk, É. B. Lifshits, and L. M. Yagupol'skii, Zh. Org. Khim., 9, 1051 (1973).
15. A. Albert and E. Serjeant, Ionization Constants of Acids and Bases, Wiley (1962).
16. I. L. Knunyants and G. G. Yakobson (editors), Syntheses of Organic Fluorine Compounds [in Russian], Khimiya, Moscow (1973), pp. 190, 193, 198, 201.
17. É. B. Lifshits, N. S. Spasokukotskii, L. M. Yagupol'skii, E. S. Kozlova, D. Ya. Naroditskaya, and I. I. Levkoev, Zh. Obshch. Khim., 38, 2025 (1968).

SYNTHESIS OF FLUORINE-CONTAINING TETRASUBSTITUTED PYRIMIDINES FROM 1-CYANO-2-CHLORO-2-TRIFLUOROMETHYLETHYLENES

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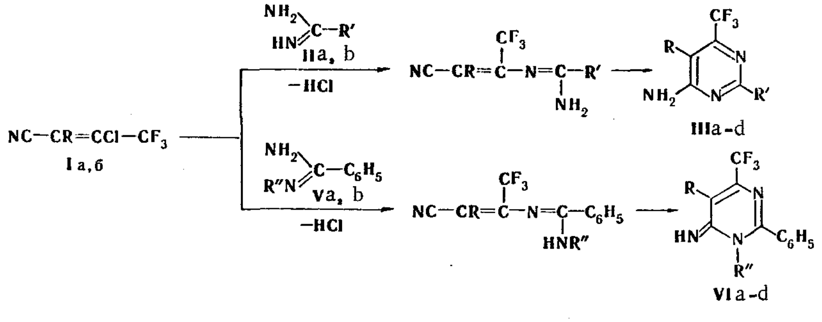
The condensation of 1,1-dicyano- and 1-trifluoromethylthio-1-cyano-2-chloro-2-trifluoromethylethylenes with amidines of trifluoro- or trichloroacetic acid gave 2,4-bis(trifluoromethyl)(or 2-trichloromethyl-4-trifluoromethyl)-5-cyano(or 5-trifluoromethylthio)-6-aminopyrimidines. The corresponding substituted 1-methyl(or 1-phenyl)-6(1H)-pyrimidineimines were synthesized by condensation of the same ethylenes with N-methyl(or N-phenyl)benzamidines.

We have previously shown that 2-trifluoromethyl-substituted 1-cyano-2-chloroethylenes, which are extremely reactive compounds, can be used for the synthesis of diverse heterocyclic compounds [1, 2]. In the present paper we describe a method for the preparation of fluorine-containing polyfunctional derivatives of pyrimidine. The method consists in the reaction of 2-trifluoromethyl-1-cyano-2-chloroethylenes (Ia, b) with acid amidines IIa, b. The initial products are evidently those formed by replacement of the chlorine atom in I, which subsequently undergo cyclization to 4-trifluoromethyl-6-aminopyrimidines (IIIa-d).



Ia, IIIa, b, VIa, b R=CN; Ib, IIIc,d, VIc,d R=SCF$_3$; IIa, IIIa, c, R′=CCl$_3$; IIb, IIIb,d R′=CF$_3$; Va, VIa, c R″=CH$_3$; Va, VIb,d R″=C$_6$H$_5$

We used this method to obtain pyrimidines that contain various substituents (see Table 1), which can be used to obtain a large number of other pyrimidine derivatives. From 1,1-dicyano-2-chloroethylene and trifluoroacetamidine by a similar method we synthesized 2-trifluoromethyl-5-cyano-4-aminopyrimidine (IV), which was previously obtained by condensation of the same trifluoroacetamidine with ethoxymethylenemalonodinitrile [3].

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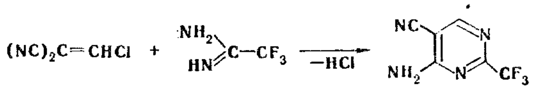
TABLE 1. Pyrimidine Derivatives IIIa-d and VIa-d

Compound	mp, °C	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H	N		C	H	N	
IIIa	183—185	27,5	0,5	18,1	$C_7H_2Cl_3F_3N_4$	27,5	0,7	18,3	58
IIIb	168—169	32,7	0,8	21,6	$C_7H_2F_6N_4$	32,8	0,8	21,9	62
IIIc	121—122	22,2	0,7	11,1	$C_7H_2Cl_3F_6N_3S$	22,1	0,5	11,0	66
IIId	68—69	24,9	0,6	12,7	$C_7H_2F_9N_3S$	25,4	0,6	12,7	57
VIa	219	56,3	3,3	20,0	$C_{13}H_9F_3N_4$	56,1	3,2	20,1	93
VIb	235—236	63,2	3,3	16,7	$C_{18}H_{11}F_3N_4$	63,5	3,2	16,5	75
VIc	116—117	44,4	2,4	11,6	$C_{13}H_9F_6N_3S$	44,2	2,6	11,9	73
VId	132—133	52,4	2,7	10,1	$C_{18}H_{11}F_6N_3S$	52,1	2,7	10,1	79

TABLE 2. IR Spectra of Pyrimidine Derivatives IIIa-d and VIa-d

Compound	Vibrational frequencies, cm^{-1}			
	ν_{C-F}	$\nu_{C\equiv N}$	$\nu_{C=N}$	$\nu_{NH_2, NH}$
IIIa	1160, 1197, 1125	2250		1642, 3216, 3331
IIIb	1160—1250	2250		1633, 3205, 3365
IIIc	1180, 1278			1633, 3220, 3325
IIId	1150, 1175, 1230			1633, 3205, 3365
VIa	1142, 1170, 1200, 1240	2230	1593	3340
VIb	1145, 1175, 1195, 1245	2235	1600	3305
VIc	1150, 1160, 1210, 1220		1600	3340
VId	1150, 1160, 1198, 1235		1600	3350



IV

The structure of IIIa-d is confirmed by the IR spectra, which contain bands of asymmetrical and symmetrical vibrations of N—H bonds of an amino group at 3325-3380 and 3205-3250 cm^{-1}, respectively, bands of deformation vibrations of an amino group at 1630-1650 cm^{-1}, and absorption bands that are characteristic for trifluoromethyl groups at 1150-1280 cm^{-1} (Table 2).

Compounds VIa-d, which contain imino groups, are formed in the reaction of Ia, b with N-methyl- or N-phenyl-substituted benzamidines Va, b.

The IR spectra of VI contain bands of vibrations of C=N bonds at 1590-1600 cm^{-1} and of N—H bonds at ∿3340 cm^{-1}.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer.

General Method for the Preparation of IIIa-d and VIa-d. A 5-mmole sample of Ia or Ib was added dropwise with stirring to a solution of 0.01 mole of amidine IIa, b or Va, b in 15 ml of diethyl ether, and the mixture was stirred for 1 h. The precipitated amidine hydrochloride was removed by filtration, the ether was removed from the filtrate by distillation, and the solid reaction product was washed with water and dried. Compounds IIIb, VIa, and VIb were purified by sublimation. The yields, melting points, and results of analysis are given in Table 1. The absorption bands of the IR spectra of IIIa-d and VIa-d are presented in Table 2. Compound IV, with mp 246°C (mp 245-246°C [3]), was similarly obtained in 79% yield.

LITERATURE CITED

1. V. I. Krokhtyak and A. Ya. Il'chenko, Zh. Org. Khim., 16, 1694 (1980).
2. V. I. Krokhtyak, A. Ya. Il'chenko, and L. M. Yagupol'skii, Zh. Org. Khim., 17, 268 (1981).
3. J. A. Barone, E. Peters, and H. Tieckelmann, J. Org. Chem., 24, 198 (1959).