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Heterocyclization of Functionalized Heterocumulenes with C,N- and C,O-Binucleophiles: IV.* Reactions of 1-Chloroalkylheterocumulenes and *N*-(1-Chloroalkylidene)carbamates with 2-Benzimidazolylacetonitriles and Methyl 2-Benzimidazolylacetates

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Abstract—1-Chloroalkyl isocyanates and 1-chloroalkylcarbodiimides undergo regioselective cyclization with nitriles and esters of 2-benzimidazolylacetic acid to give derivatives of 1-oxo and 1-arylimino-1,2,3,5-tetrahydrobenzo[4,5]imidazo[1,2-*c*]pyrimidine respectively. The cyclocondensation of 1,1-dichloroalkyl isocyanates or *N*-(1-chloroalkylidene)carbamates with nitriles and esters of 2-benzimidazolylacetic acid afforded 1,5-dihydrobenzo[4,5]-imidazo[1,2-*c*]pyrimidin-1-one derivatives.

We formerly [2, 3] reported on a regioselective cyclization of 1-chloroalkylheterocumulenes and *N*-(1-chloroalkylidene)carbamates with derivatives of 2-pyridyl- and 2-benzothiazolylacetic acids that provided a new synthetic approach to trihalomethyl-containing 1*H*-pyrido-[1,2-*c*]pyrimidines and pyrimido[6,1-*b*][1,3]benzothiazoles. In this study aiming at preparation of virtually unknown [4] trihalomethyl-substituted benzimidazo[1,2-*c*]pyrimidines we investigated reactions of a series of trihalomethyl-substituted 1-chloroalkylheterocumulenes and their derivatives with 2-benzimidazolylacetonitriles and methyl 2-benzimidazolylacetates.

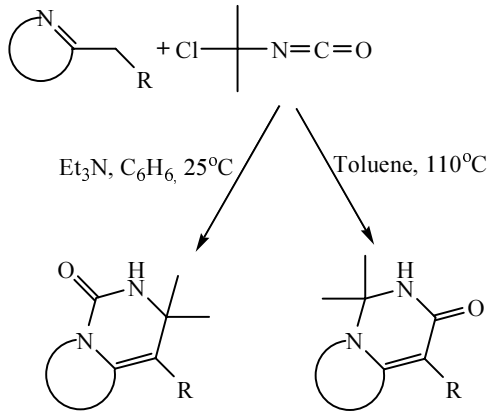
A thorough analysis of publications shows that nowadays the azoles reactions with heterocumulenes are extensively used for preparation of their fused derivatives [5]. In particular, the reaction of ethyl 2(1*H*)-benzothiazolylacetate with alkyl isocyanates gave rise to 2-alkyl-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*c*]-pyrimidine [6], whereas 2(1*H*)-benzimidazolylacetonitriles and ethyl 2(1*H*)-benzimidazolylacetate with ethoxycarbonyl or chlorosulfonyl isocyanates afforded their 4-cyano-(ethoxycarbonyl)-substituted analogs [7]. The first stage of these reaction proceeds like N-carbamoylation (for alkyl isocyanates) or C-carbamoylation (for ethoxycarbonyl and chlorosulfonyl isocyanates), and the fusion occurs involving the functional groups of the 2-substituted benzimidazoles or the corresponding isocyanates.

Basing on the previously found [2, 3] effect of reaction conditions of the 1-chloroalkyl isocyanates with the derivatives of 2-pyridyl- and 2-benzothiazolylacetic acids on the structure of the cyclocondensation products we presumed that the revealed relations would hold also for the 2-benzimidazolyl acid derivatives.

The detailed investigation of the reaction between 1-chloroalkyl isocyanates **Ia–c** and 2-benzimidazolylacetonitriles **IIa, b** or methyl 2-benzimidazolylacetates **IIc**, **d** demonstrated that the process carried out both in the presence of an organic base at room temperature or without base at heating resulted in a single type of compounds: 3-trifluoromethyl-1,2,3,5-tetrahydrobenzo-[4,5]imidazo-[1,2-*c*]pyrimidin-1-one derivatives (**IIIa–l**).

This result is obviously due to the enhanced basicity of the benzimidazole ring compared to those of benzothiazole and pyridine. Therefore the product of the primary N-carbomoylation (salt **A**) is more stable than its

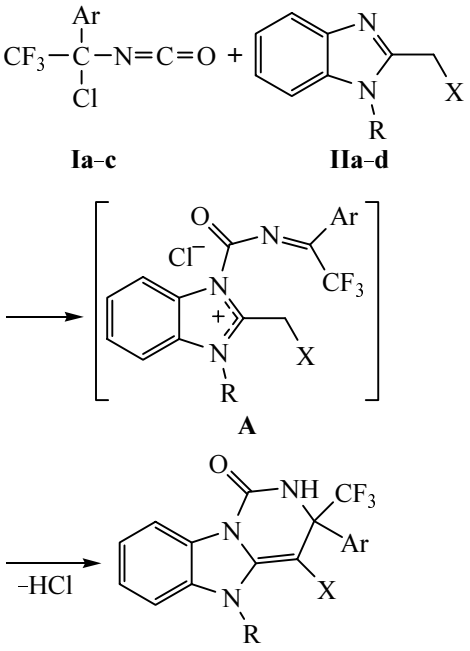
For communication III see [1].



pyridinium and benzothiazolium analogs and does not dissociate into the initial reagents at heating thus facilitating formation of C-carbomoylation products. The organic base effects the generation of a carbanion on the carbon of the methylene group thus ensuring the cyclization completion within 3 h at room temperature. The reaction without a base requires a prolonged heating (15–18 h) of the reagents in boiling toluene.

Compounds **IIIa–f, j–l** (Table 1) are high-melting colorless crystalline substances whose structure is consistent with their IR, ^{1}H, ^{19}F, ^{13}C NMR, and mass spectra. The assumed structure was reliably identified by the presence of the most downfield signal among those from the aromatic protons belonging to the H^9 doublet in the range 7.83–7.97 ppm. This downfield signal is due to the deshielding effect of the C=O group [2, 3]. In addition in the ^{13}C NMR spectrum of compound **IIIb** the signal from carbon atom of the C=O group is located at 146.93 ppm; in the spectrum of an 3-oxo isomer this signal should have appeared in the range 160–166 ppm [2, 3].

Compounds **IIIg–i** were not isolated in the analytically pure state. Their ^{1}H and ^{19}F NMR spectra showed that the substances separated from the reaction mixtures contained 85–90% of the main compound. The attempt



I, Ar = Ph (**a**), 4-$CH_3C_6H_4$ (**b**), 4-$CH_3OC_6H_4$ (**c**); **II**, X = CN, R = H (**a**), CH_3 (**b**); X = C(O)OCH_3, R = H (**c**), CH_3 (**d**); **III**, R = H, X = CN, Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 4-$CH_3OC_6H_4$ (**c**); R = CH_3, X = CN, Ar = Ph (d), 4-$CH_3C_6H_4$ (**e**), 4-$CH_3OC_6H_4$ (**f**); R = H, X = C(O)OCH_3, Ar = Ph (**g**), 4-$CH_3C_6H_4$ (**h**), 4-$CH_3OC_6H_4$ (**i**); R = CH_3, X = C(O)OCH_3, Ar = Ph (**j**), 4-$CH_3C_6H_4$ (**k**), 4-$CH_3OC_6H_4$ (**l**).

Table 1. Yields, physical constants, and elemental analyses of 3-aryl-1-oxo-3-trifluoromethyl-1,2,3,5-tetrahydrobenzo[4,5]imidazo-[1,2-*c*]pyrimidine-4-carbonitriles (or -4-methylcaroxylates) **IIIa–f, j–l**

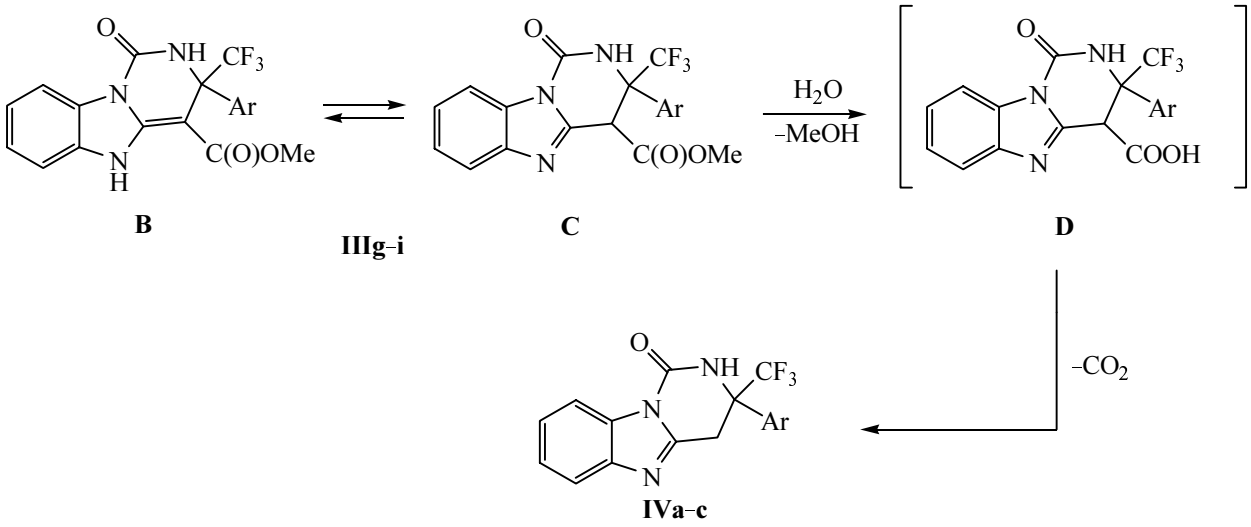
Compd. no.	Yield, %		mp, °C (solvent for crystallization)	Found, %			Formula	Calculated, %		
	a	*b*		C	H	F		C	H	F
IIIa	65	68	>250 (ethanol–dioxane, 1:1)	61.15	3.27	15.73	$C_{18}H_{11}F_3N_4O$	60.67	3.09	16.01
IIIb	63	60	>250 (ethanol–dioxane, 1:1)	62.03	3.37	15.18	$C_{19}H_{13}F_3N_4O$	61.62	3.51	15.40
IIIc	63	61	210–211 (ethanol–dioxane, 2:1)	59.46	3.30	15.03	$C_{19}H_{13}F_3N_4O_2$	59.06	3.36	14.76
IIId	86	85	227–228 (ethanol–dioxane, 5:1)	61.81	3.47	15.05	$C_{19}H_{13}F_3N_4O$	61.62	3.54	15.39
IIIe	80	85	225–226 (ethanol–dioxane, 5:1)	62.83	4.06	15.09	$C_{20}H_{15}F_3N_4O$	62.50	3.90	14.84
IIIf	74	80	206–207 (ethanol)	60.19	3.84	14.54	$C_{20}H_{15}F_3N_4O_2$	60.00	3.78	14.24
IIIj	77	72	208–209 (ethanol–dioxane, 8:1)	59.90	4.11	13.75	$C_{20}H_{16}F_3N_3O_3$	59.55	4.00	14.13
IIIk	64	60	191–192 (ethanol–dioxane, 8:1)	60.80	4.30	13.95	$C_{21}H_{18}F_3N_3O_3$	60.43	4.35	13.66
IIIl	42	43	209–210 (ethanol–dioxane, 9:1)	59.17	4.35	12.89	$C_{21}H_{18}F_3N_3O_4$	58.20	4.19	13.15

to recrystallize them from DMF for the compounds did not dissolve at heating in other solvents resulted in considerable worsening of their quality. To gain an understanding of this fact we heated compounds **IIIg–i** in boiling DMF for 2 h. As a result we isolated in 75–80% yields 3-aryl-3-trifluoromethyl-1,2,3,4-tetrahydrobenzo-[4,5]imidazo[1,2-*c*]-pyrimidin-1-ones **IVa–c**.

Apparently compounds **IIIg–i** at high temperature can be present as tautomer mixture of **B** and **C** forms. The trace amounts of water present in the DMF effect hydrolysis of the ester group in **C** form giving acid **D** that decarboxylates under the reaction conditions. Compounds **IIIj–l** are not subject to this tautomerism and do not suffer analogous transformations.

The protons of the CH_2 group in compounds **IVa–c** are diastereotopic and appear in the ^1H NMR spectra as doublets at 4.21–4.22 ppm with the coupling constants of 16.1–16.4 Hz. The change in the valence state of the C^4 atom in the tetrahydropyrimidine ring practically did not affect the resonance position of the CF_3 groups in the ^{19}F NMR spectrum (–76.0 ppm). The cyclic structure of compound **IVa** is reliably proved by its ^{13}C NMR spectrum [δ, ppm: 29.36 (C^4), 62.87 q (C^3, $^2J_{C,F}$ 28.8 Hz), 113.65, 119.21, 124.09, 124.38 (C^6–C^9), 126.54 q (CF_3, $^1J_{C,F}$ 285.7 Hz), 126.98, 128.83, 129.45, 142.36 (C_6H_5), 131.11 (C^{5a}), 134.69 (C^{9a}), 148.38 (C^{4a}), 148.76 (C^1)].

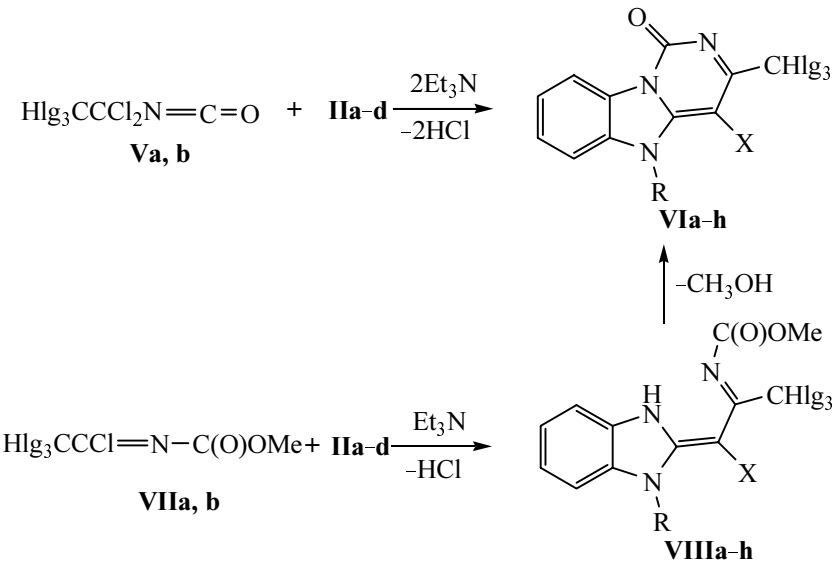
1,1-Dichloro-2,2,2-trihaloethyl isocyanates **Va, b** react with nitriles and acetates **IIa–d** along the scheme given above for 1-chloroalkyl isocyanates to furnish 3-trihalomethyl-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*c*]-pyrimidin-1-one derivatives **VIa–h** (procedure *a*). Sufficient yields of the target products were obtained by reaction carried out in benzene in the presence of a double excess of triethylamine. The heating in the absence of a base resulted in intractable mixtures of compounds.



IV, Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 4-$MeOC_6H_4$ (**c**).

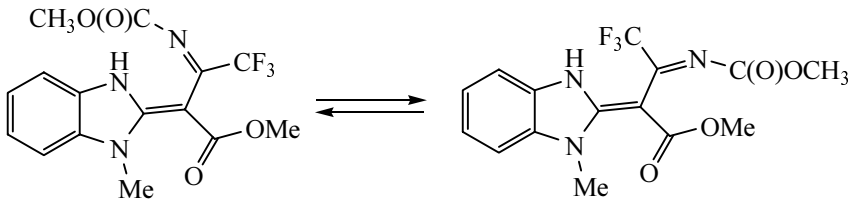
We also developed an alternative approach to the synthesis of compounds **VIa–h**: *N*-(1-chloroethylidene)carbamates **VIIa, b** [8] were applied as electrophilic components of cyclization. The latter are a certain blocked form of isocyanates **V** with a more pronounced electrophilic center on the imidoyl carbon atom, and they react with substarte **IIa–d** at the endocyclic methylene group. Therewith arise compounds of an 1-aza-1,3-diene structure **VIIIa–h** (compound **VIIIg** has been isolated and characterized).These substances undergo cyclization into 1,5-dihydro-benzo-[4,5]imidazo[1,2-*c*]pyrimidin-1-ones **VIa–h** by an attack of the nitrogen of the imidazole ring on the carbonyl carbon of the methoxycarbonyl group. Depending on the character of X, R, and Hlg substituents the reaction occurs either at room temperature or at boiling in dioxane.

^1H NMR spectrum of compound **VIIIg** is characterized by a double set of singlet proton signals from groups



V, VII, Hlg = F (**a**), Cl (**b**); **VI, VIII**, R = H, X = CN, Hlg = F (**a**), Cl (**b**); R = Me, X = CN, Hlg = F (**c**), Cl (**d**); R = H, X = C(O)OMe, Hlg = F (**e**), Cl (**f**); R = Me, X = C(O)OMe, Hlg = F (**g**), Cl (**h**).

attached to the double C=C bond NCH_3 (3.29 and 3.34 ppm) and $C(O)OCH_3$ (3.74 and 3.81 ppm), and the ^{19}F NMR spectrum contains two signals from CF_3 group (–64.84 and –65.26 ppm). We believe that under conditions of NMR spectra registering (solution in DMSO-d_6) exists an equilibrium between two *E,Z-s-cis*- and *E,Z-s-trans*-conformations present in a 2 : 1 ratio.



E,Z-s-cis-**VIIIg** *E,Z-s-trans*-**VIIIg**

The structure of compounds **VIa–h** (Table 2) is confirmed by IR, ^1H and ^{19}F NMR spectra. In particular, ^1H NMR spectra contain the doublet of proton H^9 at 8.46–8.63 ppm in keeping with the spectral data of the structural analogs [2, 3, 7].

It should be also pointed out that unlike 1,2,3,5-tetrahydro derivatives **IIIg–I** their 1,5-dihydro analogs **VIe, f** were more stable against hydrolysis and thus were isolated in a pure state, although at a reduced yield (procedure *b*).

1-Chloroalkylcarbodiimides **IXa–c** under mild conditions (benzene, 25°C) in the presence of *N*-ethyl-*N,N*-diisopropylamine underwent cyclocondensation with 2-benzimidazolylacetonitriles **IIa, b** and methyl 2-benzimidazolylacetate (**IId**) to afford 1,2,3,5-tetrahydrobenzo[4,5]-imidazo[1,2-*c*]pyrimidine 1-imino derivatives **Xa–e** (Table 3). A suggestion was published formerly [2] in a report on a similar reaction of 1-chloroalkylcarbodiimides with 2-cyanomethylpyridine that first formed products of C-carbodiimidoalkylation. We believe that in our case due to the enhanced basicity of the benzimidazole ring the primary *N*-carbamoylation is more feasible leading to salt-like intermediates (**E**) prone to further relatively easy ring closure.

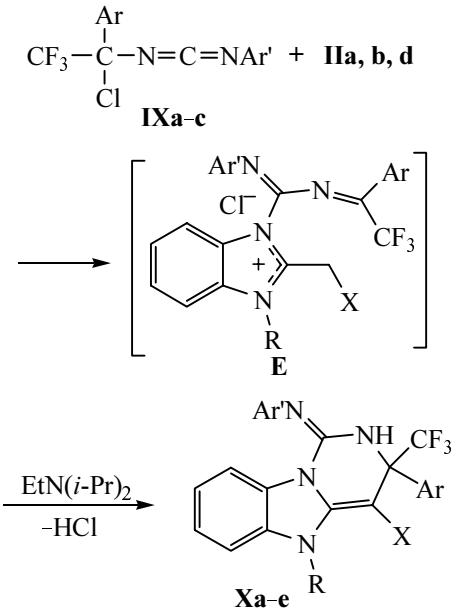
The character of NMR spectra of compounds **Xa–e** depends on the polarity of the solvent used. When the ^{13}C NMR spectrum of compound **Xc** is recorded in $CDCl_3$ the characteristic signal at 139.59 ppm convincingly evidences the presence of the exocyclic arylimino group in the position *1* of the tetrahydropyrimidine ring. In the ^1H

Table 2. Yields, physical constants, and elemental analyses of 1-oxo-3-trihalomethyl-1,5-dihydrobenzo[4,5]imidazo[1,2-*c*]pyrimidine-4-carbonitriles (or -4-methylcaroxylates) **VIa–h**

Compd. no.	Yield, %		mp, °C (solvent for crystallization)	Found, %			Formula	Calculated, %		
	a	*α*		C	H	N		C	H	N
VIa	40	67	>250 (DMF–dioxane, 1:5)	52.18	2.07	20.39	$C_{12}H_5F_3N_4O$	51.81	1.81	20.14
VIb	48	66	>250 (DMF–dioxane, 1:4)	44.28	1.46	17.18	$C_{12}H_5Cl_3N_4O$	43.97	1.53	17.09
VIc	72	68	>250 (DMF–dioxane, 1:3)	53.71	2.38	18.92	$C_{13}H_7F_3N_4O$	53.43	2.41	19.17
VId	54	45	>250 DMF–dioxane, 1:3)	45.93	2.17	16.67	$C_{13}H_7Cl_3N_4O$	45.68	2.05	16.40
VIe	38	35	>250 (DMF–dioxane, 1:2)	49.85	2.38	13.84	$C_{13}H_8F_3N_3O_3$	50.17	2.59	13.50
VIf	50	23	>250 (ethanol–dioxane, 1:4)	43.64	2.18	11.51	$C_{13}H_8Cl_3N_3O_3$	43.30	2.24	11.65
VIg	80	60	232–233 (dioxane)	52.04	3.29	13.17	$C_{14}H_{10}F_3N_3O_3$	51.70	3.10	12.92
VIh	77	57	>250 (DMF–dioxane, 1:4)	54.19	2.52	11.49	$C_{14}H_{10}Cl_3N_3O_3$	44.89	2.69	11.22

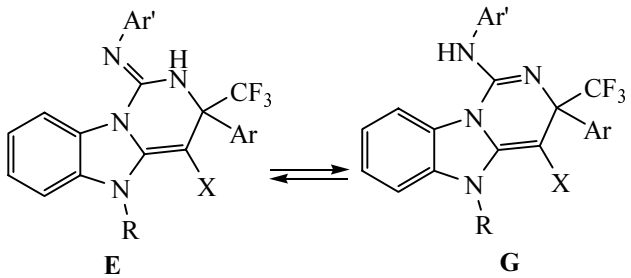
Table 3. Yields, physical constants, and elemental analyses of 3-aryl-1-(*N*-arylimino)-3-trifluoromethyl-1,2,3,5-tetrahydrobenzo[4,5]imidazo[1,2-*c*]pyrimidine-4- carbonitriles (or -4-methylcaroxylates) **Xa–e**

Compd. no.	Yield, %	mp, °C (ethanol)	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
Xa	80	217–218	67.14	4.30	15.35	$C_{25}H_{18}F_3N_5$	67.41	4.07	15.72
Xb	78	221–222	67.11	3.59	16.20	$C_{25}H_{18}F_3N_5$	66.82	3.74	16.23
Xc	71	206–207	68.28	4.59	15.03	$C_{26}H_{20}F_3N_5$	67.97	4.39	15.24
Xd	70	175–176	65.94	4.53	11.50	$C_{27}H_{23}F_3N_4O_2$	65.85	4.71	11.38
Xe	72	173–174	68.60	5.35	8.48	$C_{28}H_{25}F_3N_4O_2$	68.90	5.18	8.31



IX, Ar = Ar' = Ph (**a**); Ar = Ph, Ar' = 4-$CH_3C_6H_4$ (**b**); Ar = Ar' = 4-$CH_3C_6H_4$ (**c**); X, R = H, X = CN, Ar = Ph, Ar' = 4-$CH_3C_6H_4$ (**a**); R = CH_3, X = CN, Ar = Ar' = Ph (**b**); Ar = Ph, Ar' = 4-$CH_3C_6H_4$ (**c**); R = CH_3, X = C(O)OCH_3, Ar = Ph, Ar' = 4-$CH_3C_6H_4$ (**d**); Ar = Ar' = 4-$CH_3C_6H_4$ (**e**).

NMR spectra the doublets from H^9 proton appear in the region 8.34–8.48 ppm, and in the ^{19}F NMR spectra the singlets belonging to CF_3 group are located in the range –76.0...–77.4 ppm. The spectral pattern obtained at recording the ^1H NMR spectra of the mentioned compounds in DMSO-d_6 is complicated by appearance of additional signals of aromatic protons and substituents R and X. In the ^{19}F NMR spectra taken in DMSO-d_6 the signals from the CF_3 group of compounds **Xa–c** are observed as two signals of nearly identical intensity closely located at –74...–75 ppm, and in the spectra of compounds **Xd, e** two signals of different intensity are seen at –75 and –71 ppm. From these data we assumed that in the medium of high polarity a prototropic rearrangement became pos-



sible in the amidine fragment of the pyrimidene of ring compounds **Xa–e**.

The triad prototropic rearrangement of compounds **Xa–e** was studied by means of IR spectroscopy. The spectra were recorded from KBr pellets and solutions of compounds in CCl_4, CH_2Cl_2, CH_3CN, and $(CH_3)_2SO$. As most informative proved to be the absorption bands corresponding to stretching vibrations of C=N and C=C bonds and to bending vibrations of N–H bond (1580–1700 cm^{-1}), and also to the stretching vibrations of associated and free N–H groups (3100–3500 cm^{-1}). In the IR spectrum of compound **Xb** in the range of 1580–1700 cm^{-1} four bands were observed at 1597, 1611, 1630, and 1675 cm^{-1}, and only the intensity of the band at 1630 cm^{-1} depended on the character of solvent and gradually decreased in the series $CCl_4 > CH_2Cl_2 > CH_3CN > (CH_3)_2SO$. The first two narrow weak bands were assigned to the benzene rings vibrations, the band at 1675 cm^{-1} to vibrations of the C=C bond of the tetrahydropyrimidine ring [9], and the band at 1630 cm^{-1} to vibrations of C=N bond of the tautomer form **F**. In $(CH_3)_2SO$ a new wide band at 1598 cm^{-1} additionally appeared that we identified as belonging to the bending vibrations of the N–H bond in form **G**.

In the region of the stretching vibrations of the N–H bond a weak band was observed at 3378 cm^{-1} (KBr, CCl_4) and 3390 cm^{-1} (CH_2Cl_2). In CH_3CN and $(CH_3)_2SO$ this band did not appear, but in $(CH_3)_2SO$ a wide band at 3200 cm^{-1} was present evidencing the formation of form **G** associates [NH···O=S$(CH)_3$]. Similar pattern is also observed with compound **Xc** however without a band at 1611 cm^{-1} that should correspond to the region 1580–1700 cm^{-1}.

Compound **Xa** containing an N–H group in the imidazole ring could form involving the latter intermolecular associates with the exocyclic N-phenylimino group of **F** form that were revealed in the spectra recorded in CCl_4 and CH_2Cl_2 by a wide strong band at 3165 cm^{-1} and a narrow band at 3390 cm^{-1}. On decreasing the solution concentration the intensity of the band at 3165 cm^{-1} was reduced, and a new band appeared at 3445 cm^{-1}. The band at 3390 cm^{-1} also observed for compounds **Xa, b** remained therewith unchanged and thus it may be reliably assigned to the vibrations of the N–H bond in position *2* of **F** form. Consequently the band at 3445 cm^{-1} belonged to the stretching vibrations of the N–H bond in the imidazole ring. In $(CH_3)_2SO$ these bands are lacking, and only a wide band at 3450 cm^{-1} is observed.

IR spectra of compound **Xa** solutions in CCl_4, CH_2Cl_2, and CH_3CN in the region 1580–1700 cm^{-1} contain three bands: very weak at 1605 cm^{-1} (benzene ring vibrations) and two very strong bands at 1647 (C=N) and 1676 cm^{-1} (C=C) whose intensity almost does not depend on the solvent character indicating that the intermolecular associations prevent the occurrence of the prototropic shift in the triad N–C=N. The cleavage of the intermolecular associates in $(CH_3)_2SO$ solution results in formation of a certain amount of **G** tautomer as seen by the decrease in the intensity of the absorption band of the C=N bond in the IR spectrum and by the appearance of the band of the N–H bond bending vibrations at 1602 cm^{-1}.

EXPERIMENTAL

IR spectra were recorded on spectrophotometer UR-20 from samples prepared as KBr pellets. ^1H, ^{13}C, and ^{19}F spectra were registered on spectrometer Varian-Gemini (300, 75.0, 188.28 MHz respectively), internal references TMS (^1H, ^{13}C), CCl_3F (^{19}F).

1-Chloroalkyl isocyanates **Ia–c** were obtained by procedure [10], 1,1-dichloroalkyl isocyanates **Va, b** by method [11, 12], N-(1-chloroalkylidene)carbamates **VIIa, b** were synthesized as in [13], 1-chloroalkylcarbodiimides **IXa–c** as in [14].

3-Aryl-1-oxo-3-trifluoromethyl-1,2,3,5-tetrahydrobenzo[4,5]imidazo[1,2-*c*]pyrimidine-4-carbonitriles (or methyl 4-carboxylates) (IIIa–f, j–l) (Table 1). (a) To a dispersion of 0.0035 mol of benzimidazole **IIa–d** in 15 ml of benzene was added at stirring a solution of 0.0035 mol of 1-chloroalkyl isocyanate **Ia–c** in 5 ml of benzene, and 10 min later was added a solution of 0.354 g (0.0035 mol) of triethylamine in 3 ml of benzene. The reaction mixture was stirred for 3 h and then left standing for 24 h. The solid precipitate was filtered off, washed with water (3×20 ml), dried, and recrystallized.

(b) A mixture of 0.0035 mol of 1-chloroalkyl isocyanate **Ia–c** and 0.0035 mol of benzimidazole **IIa–d** in 20 ml of toluene was heated at reflux for 15–18 h. The reaction mixture was cooled, the separated precipitate was filtered off and recrystallized.

1-Oxo-3-phenyl-3-trifluoromethyl-1,2,3,5-tetrahydro[4,5]imidazo[1,2-*c*]pyrimidine-4-carbonitrile (IIIa). IR spectrum, cm^{-1}: 1710 (C=O), 2207 (C···N), 3240 (N–H). ^1H NMR spectrum (DMSO-d_6), ppm: 7.10–7.52 m (6H, H arom), 7.44–7.52 m (3H, H arom), 7.68 d (2H, H arom, *J* 8.0 Hz), 7.85 d (1H, H^9, *J* 7.9 Hz), 9.46 s (1H, CONH), 12.23 s (1H, NH). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –76.05.

3-(4-Methylphenyl)-1-oxo-3-trifluoromethyl-1,2,3,5-tetrahydro[4,5]imidazo[1,2-*c*]pyrimidine-4-carbonitrile (IIIb). IR spectrum, cm^{-1}: 1705 (C=O), 2212 (C≡N), 3250 (N–H). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.37 s (3H, CH_3), 7.06–7.21 m (3H, H arom), 7.68 d (2H, H arom, *J* 8.0 Hz), 7.52 d (2H, H arom, *J* 8.0 Hz), 7.84 d (1H, H^9, *J* 7.4 Hz), 9.32 s (1H, CONH), 12.08 s (1H, NH). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –76.25. Mass spectrum, *m/z* (I_{rel}, %): 370(48), $[M]^+$, 327(30) $[M - HNCO]^+$, 301(100) $[M - CF_3]^+$, 214(16), 183(50), 155(28), 117(15), 89(30).

3-(4-Methoxyphenyl)-1-oxo-3-trifluoromethyl-1,2,3,5-tetrahydro[4,5]imidazo[1,2-*c*]pyrimidine-4-carbonitrile (IIIc). IR spectrum, cm^{-1}: 1710 (C=O), 2210 (C≡N), 3245 (N–H). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.81 s (3H, OCH_3), 7.97 d (2H, H arom, *J* 7.8 Hz), 7.04–7.16 m (3H, H arom), 7.54 d (2H, H arom, *J* 7.8 Hz), 7.54 d (2H, H arom, *J* 7.8 Hz), 7.83 d (1H, H^9, *J* 7.3 Hz), 9.26 s (1H, CONH), 12.04 s (1H, NH). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –76.61.

5-Methyl-1-oxo-3-phenyl-3-trifluoromethyl-1,2,3,5-tetrahydro[4,5]imidazo[1,2-*c*]pyrimidine-4-carbonitrile (IIId). IR spectrum, cm^{-1}: 1718 (C=O), 2203 (C≡N), 3235 (N–H). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.73 s (3H, NCH_3), 7.13–7.49 m (6H, H arom), 7.65 d (2H, H arom, *J* 7.2 Hz), 7.93 d (1H, H^9, *J* 7.6 Hz), 9.45 s (1H, CONH). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –76.16. Mass spectrum, *m/z* (I_{rel}, %): 370(100) $[M]^+$, 327(20) $[M - HNCO]^+$, 301(100) $[M - CF_3]^+$.

5-Methyl-3-(4-methylphenyl)-1-oxo-3-trifluoromethyl-1,2,3,5-tetrahydro[4,5]imidazo[1,2-*c*]pyrimidine-4-carbonitrile (IIIe). IR spectrum, cm^{-1}: 1715 (C=O), 2205 (C≡N), 3245 (N–H). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.35 s (3H, CH_3), 3.71 s (3H, NCH_3), 7.19 t (1H, H arom, *J* 7.3 Hz), 7.26–7.37 m (4H, H arom), 7.55 d (2H, H arom, *J* 7.9 Hz), 7.93 d (1H, H^9, *J* 7.3 Hz), 9.47 s (1H, CONH). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 20.54 (CH_3), 30.37 (NCH_3), 50.46 (C^4), 64.91 q (C^3, $^2J_{C-F}$ 27.8 Hz), 108.71, 113.49, 122.69, 124.45 (C^6–C^9), 118.40 (C≡N), 127.90 q (CF_3, $^1J_{C-F}$ 290.4 Hz), 127.55, 127.41, 128.87, 138.25 (C_6H_4), 133.79 (C^{5a}), 133.80 (C^{9a}), 146.93 (C^1), 148.29 (C^{4a}). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –75.90.

5-Methyl-3-(4-methoxyphenyl)-1-oxo-3-trifluoromethyl-1,2,3,5-tetrahydro[4,5]imidazo[1,2-*c*]pyrimidine-4-carbonitrile (IIIf). IR spectrum, cm^{-1}: 1715 (C=O), 2210 (C≡N), 3255 (N–H). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.72 s (3H, NCH_3), 3.82 s (3H, OCH_3), 7.04 d (2H, H arom, *J* 8.7 Hz), 7.17–7.39 m (3H, H arom), 7.60 d (2H, H arom, *J* 8.7 Hz), 7.93 d (1H, H^9, *J* 7.2 Hz), 9.47 s (1H, CONH). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –76.15.

Methyl 5-methyl-1-oxo-3-phenyl-3-trifluoro-methyl-1,2,3,5-tetrahydro[4,5]imidazo[1,2-*c*]pyrimidine-4-carboxylate (IIIj). IR spectrum, cm^{-1}: 1710 (CONH), 1725 (COO), 3255 (N–H). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.04 s (3H, NCH_3), 3.35 s [3H, $C(O)OCH_3$], 7.20–7.57 m (8H, H arom), 7.97 d (1H, H^9, *J* 7.2 Hz), 9.19 s (1H, CONH). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –75.32.

Methyl-5-methyl-3-(4-methylphenyl)-1-oxo-3-trifluoromethyl-1,2,3,5-tetrahydro[4,5]imidazo[1,2-*c*]-pyrimidine-4-carboxylate (IIIk). IR spectrum, cm^{-1}: 1707 (CONH), 1725 (COO), 3250 (N–H). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.31 s (3H, CH_3), 3.07 s (3H, NCH_3), 3.31 s [3H, $C(O)OCH_3$], 7.18–7.42 m (7H, H arom), 7.95 d (1H, H^9, *J* 7.8 Hz), 9.12 s (1H, CONH). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –75.61. Mass spectrum, *m/z* (I_{rel}, %): 417(8) $[M]^+$, 374(8) $[M–HNCO]^+$, 348(100) $[M - CF_3]^+$.

Methyl-5-methyl-3-(4-methoxyphenyl)-1-oxo-3-trifluoromethyl-1,2,3,5-tetrahydro[4,5]imidazo[1,2-*c*]-pyrimidine-4-carboxylate (IIIl). IR spectrum, cm^{-1}: 1705 (CONH), 1720 (COO), 3250 (N–H). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.11 s (3H, NCH_3), 3.30 s [3H, $C(O)OCH_3$], 3.77 s (3H, OCH_3), 6.95 d (2H, H arom, *J* 8.0 Hz), 7.18–7.32 m (2H, H apom), 7.38 d (1H, H arom, *J* 7.3 Hz), 7.44 d (2H, H arom, *J* 8.0 Hz), 7.95 d (1H, H^9, *J* 7.3 Hz), 9.09 c (1H, CONH). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –75.11.

3-Aryl-3-trifluoromethyl-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*c*]pyrimidin-1-ones (IVa-c). Compounds **IIIg–i** obtained by procedure *a* from 0.0035 mol of benzimidazole **IIc** and 0.0035 mol of 1-chloroalkyl isocyanate **Ia–c** were isolated from the reaction mixture and afterwards boiled in 10 ml of DMF for 2 h. The reaction mixture was cooled and poured into 40 ml of water. The separated precipitate was filtered off, dried, and recrystallized.

3-Phenyl-3-trifluoromethyl-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*c*]pyrimidin-1-one (IVa). Yield 79%, mp 232–233°C (ethanol). IR spectrum, cm^{-1}: 1725 (C=O), 3220 (NH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.99 d (1H, CH_2, *J* 16.1 Hz), 4.21 d (1H, CH_2, *J* 16.1 Hz), 7.25–7.48 m (5H, H arom), 7.59 d (1H, H^6, *J* 7.7 Hz), 7.77 d (2H, H arom, *J* 7.7 Hz), 7.96 d (1H, H^9, *J* 7.7 Hz), 9.92 s (1H, NH). ^{19}F NMR spectrum (DMSO-

d_6), δ, ppm: –76.04. Found, %: C 61.99; H 3.53; F 16.91. $C_{17}H_{12}F_3N_3O$. Calculated, %: C 61.63; H 3.65; F 17.20.

3-(4-Methylphenyl)-3-trifluoromethyl-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*c*]pyrimidin-1-one (IVb). Yield 80%, mp 214–215°C (ethanol). IR spectrum, cm^{-1}: 1720 (C=O), 3235 (NH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.26 s (3H, CH_3), 3.98 d (1H, CH_2, *J* 16.4 Hz), 4.21 d (1H, CH_2, *J* 16.4 Hz), 7.24–7.38 m (4H, H arom), 7.59–7.68 m (3H, H arom), 7.97 d (1H, H^9, *J* 7.9 Hz), 9.91 s (1H, NH). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –76.22. Found, %: C 62.80; H 4.35; F 16.27. $C_{18}H_{14}F_3N_3O$. Calculated, %: C 62.61; H 4.09; F 16.27.

3-(4-Metoxiphenyl)-3-trifluoromethyl-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*c*]pyrimidin-1-one (IVb). Yield 75%, mp 188–189°C (2-propanol). IR spectrum, cm^{-1}: 1725 (C=O), 3240 (NH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.72 s (3H, OCH_3), 3.95 d (1H, CH_2, *J* 16.2 Hz), 4.22 d (1H, CH_2, *J* 16.2 Hz), 6.98 d (2H, H arom, *J* 8.5 Hz), 7.25–7.32 m (2H, H arom), 7.61 d (1H, H^6, *J* 7.1 Hz), 7.67 d (2H, H arom, *J* 8.5 Hz), 7.97 d (1H, H^9, *J* 7.1 Hz), 9.89 c (1H, NH). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –76.38. Found, %: C 60.08; H 4.04; F 15.51. $C_{18}H_{14}F_3N_3O_2$. Calculated, %: C 59.83; H 3.91; F 15.77.

1-Oxo-3-trihalomethyl-1,5-dihydrobenzo[4,5]-imidazo[1,2-*c*]pyrimidine-4-carbonitriles (or methyl 4-carboxylates) (VIa–h) (Table 2). (a) To a dispersion of 0.0027 mol of benzimidazole **IIa–d** in 20 ml of benzene was added dropwise at stirring a solution of 0.0027 mol of 1,1-dichloroalkyl isocyanate **Va–c** in 5 ml of benzene, and 10 min later was added a solution of 0.55 g (0.0054 mol) of triethylamine in 5 ml of benzene. The reaction mixture was stirred for 3 h and then left standing for 24 h. The solid precipitate was filtered off, washed with water (3×20 ml), and dried. The filtrate was evaporated, to the residue 5 ml of ethanol was added, and the mixture was heated. The solid reaction product thus obtained was combined with the first portion of the precipitate and recrystallized.

(b) To a dispersion of 0.0027 mol of benzimidazole **IIa–d** in 15 ml of dioxane was added at stirring a solution of 0.0027 mol of *N*-(1-chloroalkylidene)carbamate **VIIa, b** in 3 ml of dioxane, and 15 min later was added a solution of 0.273 g (0.0027 mol) of triethylamine in 3 ml of dioxane. In the synthesis of compounds **VIa, c, e** the reaction mixture was stirred for 2 h and then left standing for 24 h. The formed precipitate was filtered off, washed with water (3×15 ml), and recrystallized. In the case of compounds **VIb, d, f–h** the reaction mixture was stirred for 1 h, the triethylamine hydrochloride precipitate was filtered off, and the filtrate was boiled for 3 h. The reaction mixture was cooled, the separated precipitate was filtered off and recrystallized.

1-Oxo-3-trifluoromethyl-1,5-dihydrobenzo[4,5]-imidazo[1,2-*c*]pyrimidine-4-carbonitrile (VIa). IR spectrum, cm^{-1}: 1680 (C=O), 2240 (C≡N), 3120 (N–H). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 7.54 t (1H, H^7, *J* 7.5 Hz), 7.63 t (1H, H^8, *J* 7.5 Hz), 7.75 d (1H, H^6, *J* 7.5 Hz), 8.46 d (1H, H^9, *J* 7.5 Hz). The proton of the NH group was in exchange with the residual water contained in DMSO-d_6 and therefore was not observed. ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –66.58.

1-Oxo-3-trichloromethyl-1,5-dihydrobenzo[4,5]-imidazo[1,2-*c*]pyrimidine-4-carbonitrile (VIb). IR spectrum, cm^{-1}: 1670 (C=O), 2235 (C≡N), 3120 (N–H). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 7.49–7.70 m (3H, H arom), 8.49 d (1H, H^9, *J* 7.6 Hz). The proton of the NH group was in exchange with the residual water contained in DMSO-d_6 and therefore was not observed.

5-Methyl-1-oxo-3-trifluoromethyl-1,5-dihydrobenzo[4,5]imidazo[1,2-*c*]pyrimidine-4-carbonitrile (VIc). IR spectrum, cm^{-1}: 1685 (C=O), 2232 (C≡N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 4.22 s (3H, NCH_3), 7.65 t (1H, H^7, *J* 7.6 Hz), 7.77 t (1H, H^8, *J* 7.6 Hz), 8.03 d (1H, H^6, *J* 7.6 Hz), 8.60 d (1H, H^9, *J* 7.6 Hz). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –66.88.

5-Methyl-1-oxo-3-trichloromethyl-1,5-dihydrobenzo[4,5]imidazo[1,2-*c*]pyrimidine-4-carbonitrile (VId). IR spectrum, cm^{-1}: 1685 (C=O), 2235 (C≡N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 4.21 s (3H, NCH_3), 7.60 t (1H, H^7, *J* 7.1 Hz), 7.73 t (1H, H^8, *J* 7.1 Hz), 7.97 d (1H, H^6, *J* 7.8 Hz), 8.55 d (1H, H^9, *J* 7.5 Hz).

Methyl 1-oxo-3-trifluoromethyl-1,5-dihydrobenzo[4,5]imidazo[1,2-*c*]pyrimidine-4-carboxylate (VIe). IR spectrum, cm^{-1}: 1692 (CON), 1718 (COO), 3118 (N–H). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.93 s (3H, OCH_3), 7.53 t (1H, H^7, *J* 7.5 Hz), 7.63 t (1H, H^8, *J* 7.5 Hz), 7.81 d (1H, H^6, *J* 7.5 Hz), 8.51 d (1H, H^9, *J* 7.5 Hz). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –64.48.

Methyl 1-oxo-3-trichloromethyl-1,5-dihydrobenzo[4,5]imidazo[1,2-*c*]pyrimidine-4-carboxylate (VIf). IR spectrum, cm^{-1}: 1680 (CON), 1725 (COO), 3115 (N–H). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.93 s (3H, OCH_3), 7.50 t (1H, H^7, *J* 7.6 Hz), 7.59 t (1H, H^8,

J 7.6 Hz), 7.77 d (1H, H^6, *J* 7.6 Hz), 8.47 d (1H, H^9, *J* 7.6 Hz). The proton of the NH group was in exchange with the residual water contained in DMSO-d_6 and therefore was not observed.

Methyl 5-methyl-1-oxo-3-trifluoromethyl-1,5-dihydrobenzo[4,5]imidazo[1,2-*c*]pyrimidine-4-carboxylate (VIg). IR spectrum, cm^{-1}: 1675 (CON), 1720 (COO). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.80 s (3H, NCH_3), 3.97 c (3H, OCH_3), 7.58 t (1H, H^7, *J* 7.1 Hz), 7.97 t (1H, H^8, *J* 7.1 Hz), 7.96 d (1H, H^6, *J* 7.1 Hz), 8.63 d (1H, H^9, *J* 7.1 Hz). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –65.43.

Methyl 5-methyl-1-oxo-3-trichloromethyl-1,5-dihydrobenzo[4,5]imidazo[1,2-*c*]pyrimidine-4-carboxylate (VIh). IR spectrum, cm^{-1}: 1675 (CON), 1715 (COO). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.77 s (3H, NCH_3), 3.95 s (3H, OCH_3), 7.53 t (1H, H^7, *J* 7.3 Hz), 7.66 t (1H, H^8, *J* 7.3 Hz), 7.90 d (1H, H^6, *J* 7.3 Hz), 8.59 d (1H, H^9, *J* 7.3 HZ).

Methyl 4,4,4-trifluoro-3-[(methoxycarbonyl)-imino]-2-(1-methyl-2,3-dihydro-1*H*-benzo[*d*]-imidazol-2-ylidene)bytanoate (VIIIi). To a dispersion of 0.0027 mol of benzimidazole **IId** in 15 ml of dioxane was added at stirring a solution of 0.0027 mol of *N*-(1-chloroalkylidene)carbamate **VIIb** in 3 ml of dioxane and 15 min later was added a solution of 0.273 g (0.0027 mol) of triethylamine in 3 ml of dioxane. The reaction mixture was left standing for 24 h, the separated precipitate was filtered off, washed with water (2×20 ml), and dried. Yield 75%, mp 226–227°C (2-propanol). IR spectrum, cm^{-1}: 1743, 1720 (C=O), 3140 (NH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.29 , 3.43 s (3H, NCH_3), 3.69 s (3H, OCH_3), 3.74, 3.81 s (3H, OCH_3), 7.23–7.35 m (2H, H arom), 7.59–7.66 m (2H, H arom), 10.30 s (1H, NH). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –64.84 s, –5.26 s (3F, CF_3). Found, %: C 50.79; H 4.13; F 16.27. $C_{15}H_{14}F_3N_3O_4$. Calculated, %: C 50.42; H 3.95; F 15.95.

3-Aryl-1-(*N*-arylimino)-3-trifluoromethyl-1,2,3,5-tetrahydrobenzo[4,5]imidazo[1,2-*c*]pyrimidine-4-carbonitriles (or methyl 4-carboxylates) (Xa–e) (Table 3). To a dispersion of 0.0025 mol of benzimidazole **IIa, b, d** in 10 ml of benzene was added 0.323 g (0.0025 mol) of *N*-ethyl-*N,N*-diisopropylamine, and then at stirring was added a solution of 0.0025 mol of carbodiimide **IXa–c** in 10 ml of benzene. The reaction mixture was stirred for 3 h and then left standing for 24 h. The precipitate of *N*-ethyl-*N,N*-diisopropylamine hydrochloride was filtered off, the filtrate was evaporated, to the residue 8 ml of ethanol was added, and the mixture was heated to boiling. On cooling the separated precipitate was filtered off and recrystallized from ethanol.

1-[N-(4-Methylphenyl)imino]-3-phenyl-3-trifluoromethyl-1,2,3,5-tetrahydrobenzo[4,5]-imidazo[1,2-*c*]pyrimidine-4-carbonitrile (Xa). IR spectrum, cm^{-1}: 1665 (C=N), 3400 (N–H). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.30 s (3H, CH_3), 5.01 s (1H, NH), 6.87 d (2H, H arom, *J* 7.5 Hz), 7.01 d (1H, H^6, *J* 7.5 Hz), 7.09–7.16 m (4H, H arom), 7.40–7.48 (3H, H arom), 7.62 d (2H, H arom, *J* 6.6 Hz), 8.34 d (1H, H^9, *J* 7.5 Hz), 9.81 s (1H, NH). ^{19}F NMR spectrum, δ, ppm: –77.40 ($CDCl_3$); –75.02, –75.16 (DMSO-d_6). Mass spectrum, *m/z* (I_{rel}, %): 445(100) $[M]^+$, 376(58) $[M-CF_3]^+$, 314(18), 289(83), 272(30), 244(10), 220(23), 188(9), 155(10), 130(10), 115(11), 103(14), 80(51), 76(19), 65(28).

5-Methyl-3-phenyl-1-(*N*-phenylimino)-3-trifluoromethyl-1,2,3,5-tetrahydrobenzo[4,5]imidazo-[1,2-*c*]pyrimidine-4-carbonitrile (Xb). IR spectrum, cm^{-1}: 1660 (C=N), 3380 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.82 s (3H, NCH_3), 5.03 s (1H, NH), 6.96–7.52 m (11H, H arom), 7.62 d (2H, H arom, *J* 6.5 Hz), 8.47 d (1H, H^9, *J* 7.3 Hz). ^{19}F NMR spectrum, δ, ppm: –77.23 ($CDCl_3$); –74.15, –74.99 (DMSO-d_6).

5-Methyl-1-[N-(4-methylphenyl)imino]-3-phenyl-3-trifluoromethyl-1,2,3,5-tetrahydrobenzo[4,5]-imidazo[1,2-*c*]pyrimidine-4-carbonitrile (Xc). IR spectrum, cm^{-1}: 1665 (C=N), 3410 (N–H). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.30 s (3H, CH_3), 3.82 s (3H, NCH_3), 5.05 s (1H, NH), 6.86 d (2H, H arom, *J* 7.7 Hz), 7.04–7.37 m (5H, H arom), 7.38–7.44 (3H, H arom), 7.63 d (2H, H arom, *J* 7.7 Hz), 8.46 d (1H, H^9, *J* 7.7 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 20.79 (Me), 30.78 (NMe), 51.03 (C^4), 64.54 q (C^3,$^2J_{C-F}$ 29.0 Hz), 107.36, 116,03, 123.07, 124.35 (C^6, C^7, C^8, C^9), 119.12 (C≡N), 127.90 q (CF_3, $^1J_{C-F}$ 290.0 Hz), 121.43, 127.34, 128.45, 128.79, 129.30, 130.59, 133.36, 143.00 (C_6H_4, C_6H_5), 133.81 (C^{9a}), 136.38 (C^{5a}), 139.59 (C^1), 148.31 (C^{4a}). ^{19}F NMR spectrum, δ, ppm: –77.21 ($CDCl_3$); –74.08, –74.88 (DMSO-d_6). Mass spectrum, *m/z* (I_{rel}, %): 459(13) $[M]^+$, 390(100) $[M-CF_3]^+$, 328(25), 308(9), 258(10), 195(9), 132(10), 91(11), 77(12).

Methyl 1-methyl-1-[N-(4-methylphenyl)imino]-3-phenyl-3-trifluoromethyl-1,2,3,5-tetrahydrobenzo-[4,5]imidazo[1,2-*c*]pyrimidine-4-carboxylate (Xd). IR spectrum, cm^{-1}: 1710 (C=O), 1670 (C=N), 3420 (N–H). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.27 s (3H, CH_3), 3.05 s (3H, NCH_3), 3.43 s (3H, OCH_3), 4.96 s (1H, NH), 6.85 d (2H, H arom, *J* 7.8 Hz), 7.07–7.36 m (8H, H arom),

7.54 d (2H, H arom, *J* 7.8 Hz), 8.48 d (1H, H^9, *J* 7.5 Hz). ^{19}F NMR spectrum, δ, ppm: –76.95 ($CDCl_3$); –71.74, –74.94 (DMSO-d_6).

Methyl 5-methyl-3-(4-methylphenyl)-1-[N-(4-methylphenyl)imino]-3-trifluoromethyl-1,2,3,5-tetra-hydrobenzo[4,5]imidazo[1,2-*c*]pyrimidine-4-carboxylate (Xe). IR spectrum, cm^{-1}: 1705 (C=O), 1660 (C=N), 3400 (N–H). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.27 s (3H, CH_3), 2.31 s (3H, CH_3), 3.09 s (3H, NCH_3), 3.42 s (3H, OCH_3), 4.92 s (1H, NH), 6.83 d (2H, H arom, *J* 8.1 Hz), 7.04–7.28 m (7H, H arom), 7.42 d (2H, H arom, *J* 8.1 Hz), 8.48 d (1H, H^9, *J* 7.3 Hz). ^{19}F NMR spectrum, δ, ppm: –77.08 ($CDCl_3$); –71.45, –75.11 (DMSO-d_6).

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