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Aminoazoles in Heterocycles Synthesis: II.* Trifluoromethyl-containing Diketones in the Synthesis of Pyrazolo[1,5-a]pyrimidines

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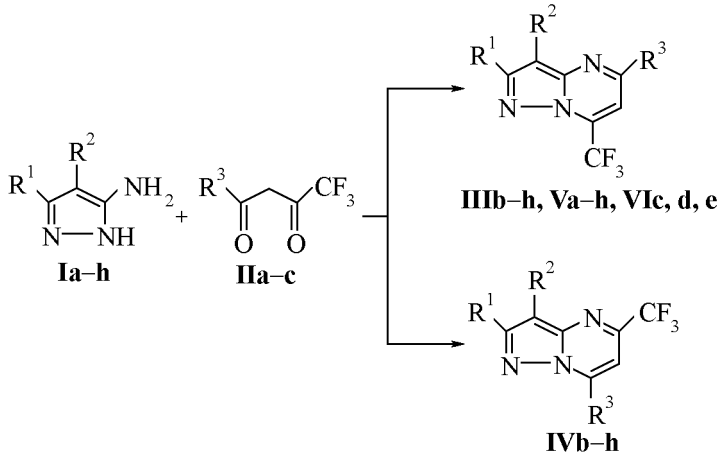
Abstract—A regioselective synthesis was carried out of 7-trifluoromethylpyrazolo[1,5-a]pyrimidines by reaction of 3(5)aminopyrazoles with 1,3-diketones containing CF_3 group. The characteristic chemical shifts were established for C^5 and C^7 atoms of the pyrimidine ring and of substituents thereof in the ^1H, ^{13}C, and ^{19}F NMR spectra of pyrazolo[1,5-a]pyrimidines.

3(5)-Aminopyrazoles are widely applied to preparation of various polycyclic nitrogen-containing heterocycles [2–5]. However the rules governing the reactions between 3(5)-aminopyrazoles and nonsymmetrical dielectrophiles yielding regioisomers of pyrazolo[1,5-a]pyrimidines [3–9} are poorly studied, and definite proofs of the regiostructure of compounds obtained are seldom given. Note that the unambiguous proof of the regiostructure of the heterocycles formed is not an easy task. Just in a few works was independently obtained every regioisomer of pyrazolo[1,5-a]pyrimidines [1, 6, 10], and in [1, 10] were reported unambiguous proofs of their structure based on ^1H and ^{13}C NMR spectra.

In the present study we investigated reactions of substituted 3(5)-aminopyrazoles **Ia–h** with trifluoromethyl-containing 1,3-diketones **IIa–c**. The structure of pyrazolo[1,5-a]pyrimidines obtained was determined from the ^1H, ^{19}F, and ^{13}C NMR spectra.

The reaction of 3(5)aminopyrazoles **Ib–h** with 1,1,1-trifluoropentane-2,4-dione (**IIc**) in ethanol gave rise to two isomeric pyrazolopyrimidines, **IIIb–h**, and **IVb–h** (Tables 1, 2).

Scheme.



I, III–VI, R^1 = XC_6H_4, R^2 = H: X = 4-*t*-Bu (**a**), 4-Me (**b**), H (**c**), 4-Br (**d**), 4-Cl (**e**), 3-Br (**f**); R^2 = Ph, R^1 = H (**g**), Me (**h**); R^3 = Me (**IIIb–h, IVb–h**), Ph (**Va–h**), *t*-Bu (**VIc, d, f**). **II**, R^3 = Me (**a**), Ph (**b**), *t*-Bu (**c**).

Compounds	IIIb/IVb	IIIc/IVc	IIId/IVd	IIIe/IVe	IIIf/IVf	IIIg/IVg	IIIh/IVh
Isomers ratio, %	75/25	70/30	79/21	85/15	69/31	97/3	92/8

* For communication I see [1].

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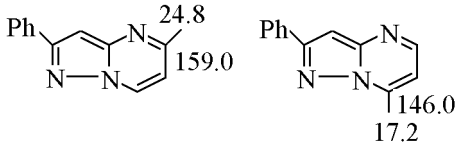
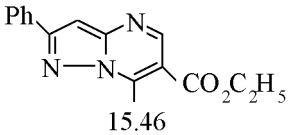
Boiling in acetic acid and fusion of the reagents provides only pyrazolopyrimidines **IIIb–h**.

The determination of the regiostructure of pyrazolpyrimidines **IIIb–h** and **IVb–h** is based on comparison of the chemical shifts of protons and carbons belonging to pyrimidine ring and methyl groups in the ^1H and ^{13}C NMR spectra with the corresponding characteristic chemical shifts observed previously in the NMR spectra of model 2-phenylpyrazolo[1,5-a]-pyrimidines: 5-methyl- (**VII**) [10], 7-methyl- (**VIII**) [10], 7-methyl-6-ethoxycarbonyl- (**IX**) [1], 5,7-dimethyl- (**X**) [1, 10]: C^5CH_3 (δ ~2.6–2.7 ppm, δ_C ~24 and ~158 ppm), C^7CH_3 (δ ~2.8–2.9 ppm, δ_C ~17 and ~147 ppm).



VII

VIII

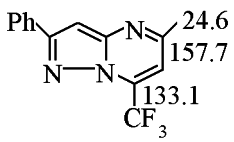


IX

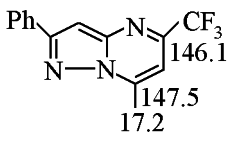
The comparison of the chemical shifts in the ^1H and ^{13}C NMR spectra of the model compounds **VII–X** (Table 3) and of pyrazolopyrimidines **IIIb–h** and **IVb–h** (Tables 1, 2) shows that the proton signals in the 2.64–2.70 ppm region and carbon signals at ~25 and ~158 ppm correspond to C^5CH_3 group of pyrazolopyrimidines **IIIb–h**, and the resonances at 2.89–2.91 and ~17.2, ~147.5 ppm belong to C^7CH_3 group of pyrazolopyrimidines **IVb–h**.

The above analysis of the characteristics of ^1H and ^{13}C NMR spectra from the isomeric pyrazolopyrimidines **IIIb–h**, **IVb–h** showed that the reaction of aminopyrazoles **Ib–h** with 1,1,1-trifluoropentane-2,4-dione affords in ethanol predominantly and in acetic acid and at fusion solely **IIIb–h** isomers with trifluoromethyl group located in *7* position.

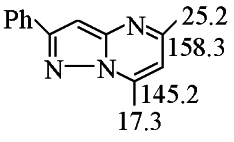
The assignment of carbon signal from CF_3 group and from C^5 and C^7 atoms at the CF_3 group of pyrazolopyrimidines **IIIb–h, IVc**, (Table 1, 2) is easy since they appear as characteristic quartets with the coupling constants J(C–F) ~280 Hz and J(C–CF_3) ~37 Hz respectively. The comparison of the ^{13}C NMR spectra of compounds **IIIb–h, IVc** with that of a model compound 5,7-dimethyl-2-phenylpyrazolo[1,5-a]pyrimidine (**XI**) revealed that introduction of the trifluoromethyl group in positions *5* and *7* respectively changed $\delta\underline{C}^{5(7)}CF_3$ by 10–12 ppm, whereas the effect on the chemical shift of $\underline{C}^{7(5)}CF_3$ from the pyrimidine ring was small. Besides the chemical shifts of the carbon atoms of the isomeric pyrazolopyrimidines **IIIb–h, IVc** are well consistent with those of the model symmetrical 5,7-bis(trifluoromethyl)-2-phenylpyrazolo[1,5-a]pyrimidine (**XI**), δ_C, ppm: 145.5 q ($\underline{C}^5CF_3$, J_{CF} 37.0 Hz), 135.1 q ($\underline{C}^7CF_3$, J_{CF} 38.5 Hz) (Table 3).



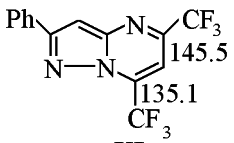
IIIc



IVc



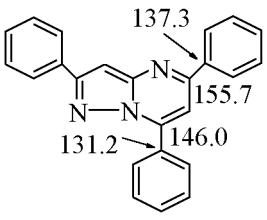
X



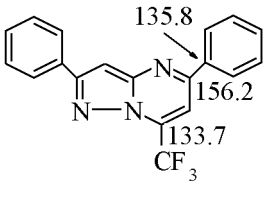
XI

Thus the observed signals of C^5 and C^7 atoms from pyrimidine ring at CF_3 group in pyrazolopyrimidines **IIIb–h, IVc, XI** in the ^{13}C NMR spectra appear as characteristic quartets with considerably different chemical shifts: $\underline{C}^5CF_3$–δ_C ~147 ppm, $\underline{C}^7CF_3$–δ_C ~134 ppm.

The cyclocondensation of substituted aminopyrazoles **Ia–h** with 4-phenyl-1,1,1-trifluorobutane-2,4-dione by boiling in acetic acid ot by fusion also gives rise to a single isomer of pyrazolopyrimidines. The regiostructure of compounds **Va–h** obtained was proved by ^{13}C NMR spectra with the use of the previously assigned characteristic signals of the *ipso*-atoms in the phenyl ring ($C^5\underline{C}^{ipso}$, δ_C ~136 ppm, $C^7\underline{C}^{ipso}$, δ_C ~131 ppm) [1, 10], and also by comparison of the chemical shifts of C^5 and C^7 atoms with those of the characteristic signals $\underline{C}^7CF_3$, $\underline{C}^5CF_3$ (Table 2). The presence of the characteristic quartet $\underline{C}CF_3$ at δ ~134 ppm and of signal C^{ipso} of the phenyl group at δ_C 136 ppm permits an unambiguous assignment of the compounds obtained to the 7-trifluoromethyl-5-phenyl-containing isomers **Va–h**.



XII



Vc

Table 1. Yields, melting points, ^{1}H NMR spectra, and elemental analyses of pyrazolopyrimidines **III**– **VI, XI**

Compd. no.	Yield, %[a]	mp, °C	^{1}H NMR, δ, ppm ($CDCl_3$)	Found, %		Formula	Calculated, %	
				C	H		C	H
IIIb	82	167.5	2.42 s (3H, CH_3C^6H4), 2.67 s (3H, C5CH_3), 6.97 s (C^3H), 6.98 s (C^6H), 7.27–7.94 m (4H, C_6H_4)	61.90	4.21	$C_{15}H_{12}F_3N_3$	62.02	4.15
IIIc	84	179.5–180	2.64 s (C^5CH_3), 6.97 s (2H, C^3H, C^6H), 7.48–8.05 m (5H, Ph)	60.59	3.77	$C_{14}H_{10}F_3N_3$	60.65	3.63
IIId	83	188–189	2.69 s (3H, C^5CH_3), 6.95 s (1H, C^3H), 7.01 s (1H, C^6H), 7.57–7.90 m (4H, C_6H_4)	47.00	2.60	$C_{14}H_9BrF_3N_3$	47.21	2.55
IIIe	85	184.5–185	2.68 s (3H, C^5CH_3), 6.94 s (1H, C^3H), 7.01 s (1H, C^6H), 7.42–7.96 m (4H, C^6H_4)	53.90	2.99	$C_{14}H_9C_1F_3N_3$	53.95	2.91
IIIf	86	159–160	2.68 s (3H, C^5CH_3), 6.97 s (1H, C^3H), 7.05 s (1H, C^6H), 7.34–8.16 m (4H, C^6H4)	47.25	2.60	$C_{14}H_9BrF_3N_3$	47.21	2.55
IIIg[b]	83	116	2.75 s (3H, C^5CH_3), 7.07 s (1H, C^6H), 7.25–8.10 m (5H, Ph), 8.51 s (1H, C^3H)	60.45	3.75	$C_{14}H_{10}F_3N_3$	60.65	3.63
IIIh[b]	84	126–127	2.67 s (6H, C^2CH_3, C^5CH_3), 7.00 s (1H, C^6H), 7.36–7.71 m (5H, Ph)	62.10	4.20	$C_{15}H_{12}F_3N_3$	62.02	4.15
IVc	[c]	[c]	2.89 s (3H, C7CH_3), 6.95 s (1H, C^3H), 7.14 s (1H, C^6H), 7.50–7.98 m (5H, Ph)	60.53	3.71	$C_{14}H_{10}F_3N_3$	60.65	3.63
Va	83	137.5	1.40 s (9H, $3CH_3$), 7.14 s (1H, C^3H), 7.57 s (1H, C^6H), 7.49–8.18 m (9H, Ar)	69.72	5.22	$C_{23}H_{20}F_3N_3$	69.86	5.10
Vb	85	165–166	2.44 s (3H, CH_3), 7.13 s (1H, C^3H), 7.57 s (1H, C^6H), 7.25–8.19 m (9H, Ar)	67.78	4.15	$C_{20}H_{14}F_3N_3$	67.98	3.99
Vc	87	150	7.10 s (1H, C^3H), 7.62 s (1H, C^6H), 7.56–8.18 m (10H, Ar)	67.50	3.71	$C_{19}H_{12}F_3N_3$	67.26	3.56
Vd	88	176–178	7.10 s (1H, C^3H), 7.62 s (1H, C^6H), 7.54–8.14 m (9H, Ar)	54.42	2.77	$C_{19}H_{11}BrF_3N_3$	54.57	2.65
Ve	87	154.5–156.5	7.11 s (1H, C^3H), 7.61 s (1H, C^6H), 7.37–8.20 m (9H, Ar)	60.95	3.10	$C_{19}H_{11}ClF_3N_3$	61.06	2.97
Vf	87	169–170	7.10 s (1H, C^3H), 7.62 s (1H, C^6H), 7.32–8.20 m (9H, Ar)	54.39	2.85	$C_{19}H_{11}BrF_3N_3$	54.57	2.65
Vg[b]	85	201–202	7.62 s (1H, C^6H), 8.55 s (1H, C^2H), 7.30–8.29 m (10H, Ar)	67.28	3.62	$C_{19}H_{12}F_3N_3$	67.26	3.56
Vh[b]	85	133–135	2.72 s (3H, *C_2CH3), 7.60 s (1H, C^6*H), 7.30–8.29 m (10H, Ar)	67.83	4.15	C20Hi4F3N3	67.98	3.99
VIc	78	94.5–96	1.45 (9H, *t*-Bu), 7.03 s (1H, C^3H), 7.23 s (1H, C^6H), 7.49–8.05 m (5H, Ph)	63.52	5.09	$C_{17}H_{16}F_3N_3$	63.94	5.05
VId	79	93	1.46 (9H, *t*-Bu), 7.03 s (1H, C^3H), 7.23 s (1H, C^6H), 7.54–7.96 m (4H, Ar)	51.20	3.85	$C_{17}H_{15}BrF_3N_3$	51.26	3.80
VIh	81	115.5–117.5	1.45 s (9H, *t*-Bu), 2.74 s (3H, C^2CH_3), 7.21 s (1H, C^6H), 7.30–7.89 m (5H, Ph)	64.80	5.50	$C_{18}H_{13}F_3N_3$	64.86	5.44
XI	75	128–129	7.36 s (1H, C^3H), 7.45 s (1H, C^6H),7.47–8.09 m (5H, Ph)	50.25	2.43	$C_{14}H_7F_6N_3$	50.77	2.11

[a] Yields of compounds **IIIb**–**h** (procedure b) and **Va**–**h** (procedure c) were not optimized.

[b] Compounds **IIIg, IIIh, Vh, Vg** contain a phenyl group in position 4.

[c] Compounds **IVb**–**h** were identified in mixtures with compounds **IIIb**–**h**. Chemical shifts in ^{1}H NMR spectra of compounds **Vb, IVd**–**h**, δ, ppm, (**IVb**): 2.44 s (3H, $CH_3C_6H_4$), 2.94 s (3H, C7CH_3), 7.00 s (1H, C^3H), 7.15 s (1H, C^6H), 7.30–8.10 m (4H, Ar); (IVd): 2.92 s (3H, C7CH_3), 7.02 s (1H, C^3H), 7.13 s (1H, C^6H), 7.50–7.90 m (4H, Ar); (**IVf**): 2.94 s (3H, C^7CH_3), 7.03 s (1H, C^3H), 7.14 s (1H, C^6H), 7.40–8.00 m (4H, Ar); (**IVe**): 2.95 s (3H, C^7CH_3), 7.04 s (1H, C^3H), 7.16 s (1H, C^6H), 7.30–8.26 m (4H, Ar); (**IVa**–**c**): 2 .90 s (3H, C^7CH_3), 7.07 s (1H, C^3H), 7.22–8.14 m (5H, Ar), 8.60 s (1H, CH); (**IVh**): 2.74 s (3H, C^2CH_3), 2 .90 s (3H, C7CH_3), 7.00 s (1H, C^3H), 7.30–7.80 m (5H, Ar).

Table 2. ^{13}C NMR Spectra (δC, ppm) pirazolo[1,5-a]pirimidines (**III**–**VI**) in $CDCl_3$

Compd.no.	R^1	R^3	R^4	C^2	C^3	C^{3a}	C^5	c^{6a}	c^76^b	Ar	5-R	γ-R^c
IIIb	4-$CH_3C_6H_4$	CH_3	CF_3	157.73	93.85	150.91	158.28	106.91	133.87	21.76, 127.08, 129.87, 139.77	25.28	119.92
IIIc	Ph	CH_3	CF_3	156.9	93.4	150.1	157.7	106.4	133.08	126.4, 128.4, 129.0, 131.9	24.6	119.15
IIIc[d]	Ph	CH_3	CF_3	155.9	93.6	150.1	159.4	108.4	131.75	126.4, 129.0, 129.5, 131.9	24.53	119.50
IIId	4-BrC_6H_4	CH_3	CF_3	156.39	94.09	150.94	158.69	107.36	133.88	123.92, 128.64, 131.60, 132.32	25.34	119.82
IIIe	4-ClC_6H_4	CH_3	CF_3	156.36	94.09	150.94	158.66	107.32	133.88	128.37, 129.36, 131.16, 135.63	25.32	119.82
IIIf	3-BrCgH4	CH_3	CF_3	155.99	94.37	150.89	158.76	107.52	133.94	123.34, 125.76, 130.02, 130.69, 132.59, 134.75	25.35	119.81
IIIg	H[e]	CH_3	CF_3	143.28	110.69	145.03	157.96	106.93	133.37	126.23, 126.43, 128.44, 130.86	24.64	119.27
IIIh	Me[e]	CH_3	CF_3	154.29	110.35	147.12	158.37	106.87	133.47	127.18, 128.95, 129.52, 131.98	25.43, 14.71	119.97
IVc[e]	Ph	CF_3	CH_3	157.00	95.01	148.00	146.04	102.69	147.54	126.36, 128.40, 129.06, 131.94	120.48 q [*J* (5-CF_3) 277.8 Hz]	17.21
Va	4-$(CH_3)3C C_6H_4$	C_6H_5	CF_3	158.25	95.09	151.21	155.50	103.63	134.45	126.18, 127.01, 129.87, 153.07	C^{ipso} 127.59, 129.52, 131.34, 136.61	120.07
Vb	4-$CH_3C_6H_4$	C_6H_5	CF_3	158.15	95.00	151.20	155.50	103.63	134.85	21.81, 127.11, 127.60 129.92, 139.87	C^{ipso} 127.60, 129.50, 131.33, 136.80	120.10
Vc	Ph	C_6H_5	CF_3	156.16	94.46	150.48	155.09	103.32	133.71	123.28, 127.91, 130.77, 1131.62	C^{ipso} 126.86, 128.81, 131.62, 135.82	119.21
Vd	4-BrC_6H_4	C_6H_5	CF_3	156.91	95.20	151.23	155.83	104.10	134.50	28.65, 124.03, 132.04 132.37	C^{ipso} 127/62, 129.55, 131.51, 136.58	118.97

Table 2. (Contd.)

Compd.no.	R^1	R^3	R^4	C^2	C^3	C^{3a}	C^5	c^{6a}	$c^7 6^b$	Ar	5-R	γ-R^c
Vd	4-ClC_6H_4	C_6H_5	CF_3	156.88	95.22	151.23	155.82	104.05	134.49	128.41, 129.43, 131.12 135.75	C^{ipso} 127.62, 129.55, 131.52, 136.60	118.87
Ve	3-BrC_6H_4	C_6H_5	CF_3	156.47	95.49	151.17	155.87	104.21	134.54	123.38, 125.76, 130.04 130.72, 132.66, 134.70	C^{ipso} 127.63, 129.55, 131.53, 136.54	118.91
Va[c]	H[e]	C_6H_5	CF_3	144.41	112.57	145.97	155.44	104.02	134.85	127.01, 127.25, 129.84 131.66	C^{ipso} 127.70, 129.55, 131.58, 136.46	118.97
Vh	Me[e]	C_6H_5	CF_3	154.76	111.36	147.29	155.17	103.29	134.19	14.95 (C_2CH_3), 127.13, 128.02, 128.95, 132.09	C^{ipso} 127.61, 129.47, 131.34, 136.66	120.14
VIc	Ph	$C(CH_3)_3$	CF_3	157.59	94.56	150.57	168.83	103.68	134.08	127.16, 129.19, 129.60, 132.86	29.77, 38.95	120.10
VId	4-BrC_6H_4	$C(CH_3)_3$	CF_3	156.38	94.52	150.59	169.10	103.96	134.08	123.82, 128.64, 131.83, 132.35	29.76, 39.00	120.01
VIh	Me[d]	$C(CH_3)_3$	CF_3	154.13	110.16	146.57	168.58	103.38	133.65	126.82, 128.82, 129.20, 132.34	29.77, 39.07	120.15

[a] Quartet, coupling constants for compounds **IIIa**–**h** J_{CF} 2.8 Hz, for compounds **Va**–**h** J_{CF} 3.3 Hz.
[b] Quartet, coupling constants J_{CF} 37–38.5 Hz.
[c] Quartet, coupling constants J_{CF} 274.8 Hz.
[d] Solvent DMSO-d_6.
[e] R^2 = Ph.
[f] ^{13}C NMR spectra of compounds **IVb, d**–**h** were not registered because of low content of the isomer in the reaction mixture.

Table 3. ^{13}C NMR spectra (δC, ppm) of model pyrazolo[l,5-a]pyrimidines (**VII**–**XI**) in $CDCl_3$

Compd.no.	R^1	R^3	R^4	C^2	C^3	C^{3a}	C^5	c^{6a}	$c^7 6^b$	Ar	5-R	γ-R^c
VII [10]	C_6H_5	H	CH_3	155.68	93.65	149.98	148.57	107.40	146.03	126.60, 128.75, 128.89, 133.05		17.24
VIII [10]	C_6H_5	CH_3	H	156.05	92.22	149.05	158.68	108.39	133.84	126.13, 128.43, 128.59, 132.49		24.45
IX	C_6H_5	H	CH_3	151.68	95.21	150.12	158.06	110.75	150.27	127.09, 129.20, 129.73, 132.76		15.46
X	H	CH_3	CH_3	155.55	92.51	149.66	158.30	108.29	145.17	126.51, 128.70, 128.73, 133.22	24.60	17.04
XI	C_6H_5	CF_3	CF_3	159.19	96.76	149.31	145.48 q (J_{cp} 37.0)	101.76 q.q (J_{cp} < 2)	135.09 q (J_{cp} 38.5)	126.94, 128.91, 130.07, 131.12	120.10 q (J_{cp} 275.4)	118.93 q (J_{cp} 275.4)

Even a bulky *tert*-butyl group does not hamper the regioselectivity of the cyclocondensation of aminopyrazoles **Ic, d, f** with 5,5-dimethyl-1,1,1-trifluoromethylhexane-2,4-dione, and as a result of the reaction arise substituted 5-*tert*-butyl-7-trifluoromethylpyrazolo[1,5-a]pyrimidines **VIc, d, f,** δ ($\underline{C}^7CF_3$) 133.4 ppm (Table 2).

The analysis of ^{19}F NMR spectra of pyrazolopyrimidines **IIIc, IVc, Vc, VIc, XI** showed that the chemical shifts of fluorine atoms from the groups $C^5C\underline{F}_3$ and $C^7C\underline{F}_3$ are quite similar and are not characteristic ($\delta_F C^7CF_3$ –65.64 **IIIc**, –65.50 **Vc**, –65.54 ppm **VIc**, δ_F C^5CF_3 –65.02 **IVc**, δ_F $C^5C\underline{F}_3$ and $C^7C\underline{F}_3$ of model compound **XI** –65.03 and –65.82 ppm respectively).

The analysis of data from Tables 2, 3 revealed the characteristic chemical shifts of the regioisomeric pyrazolopyrimidines, especially those in the ^{13}C NMR spectra, that permit unambiguous assignment of isomer structure.

δ, ppm		δ, ppm	
$\underline{C}^5CH_3$	~158.5	$\underline{C}^7CH_3$	147.5
$\underline{C}^5CF_3$	146.0	$\underline{C}^7CF_3$	~133.5
$C^5\underline{C}H_3$	~25.0	$C^7\underline{C}H_3$	17.2
$\underline{C}^5C^{ipso}$(Ph)	155.7	$\underline{C}^7C^{ipso}$(Ph)	146.0
$C^5\underline{C}^{ipso}$(Ph)	~136.5	$C^7\underline{C}^{ipso}$(Ph)	~131.0

Note that since the nitrogen atom in the $-C^5(R)=N-$ group is more electronegative than the nitrogen from the $=C^7(R)-N<$ group of the pyrazolo[1,5-a]pyrimidines then the C^5 atom is less shielded than C^7 and therefore the former has a larger chemical shift in the ^{13}C NMR spectra. Consequently the carbon atoms of the methyl and trifluoromethyl groups and also ipso-atoms of the phenyl groups attached to C^5 atom (in compounds **IIIb–h, Va–h**) are located more downfield than the signals of the same groups linked to C^7 atom {compound **IVc**, model compounds (Table 3), and data from [1, 10]} (Table 1). It is not correct to extend this statement to the protons of the methyl group and fluorine atoms of the trifluoromethyl group of the pyrazolo[1,5-a]-pyrimidines. This invalid assumption in [8, 9] led to erroneous conclusions on regiostructure of trifluoromethyl-containing pyrazolopyrimidines synthesized in that study.

Thus significant alterations in the structure of the trifluoromethyl-containing 1,3-diketone **IIa–c** [R^3 = Me, Ph, *t*-Bu, R^4 = CF_3] and aminopyrazole **Ia–h** (the presence of a bulky phenyl group in *3* or *4* position) did not affect the regioisomeric structure of the reaction product. Aminopyrazoles **Ia–h** react with 1,3-diketones **IIa–c** in acetic acid or at fusion giving rise to a single isomer in virtually quantitative yield. This pyrazolo[1,5-a] pyrimidine contains the trifluoromethyl group in *7* position.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were registered on spectrometers Bruker AM-500, Bruker DPX300, Bruker WP-200 (500, 300, 200 and 125.74, 75.47, 50.3 MHz respectively), ^{19}F NMR spectra on spectrometer Bruker AM-500 (470.6 MHz, hexafluorobutadiene reference). $CDCl_3$ and DMSO-d_6 were used as solvents.

3(5)-Aminopyrazoles **Ia–h** were prepared according to procedures from [11, 12], compound **IX** as in [13]. The preparation procedure for fluoro-containing 1,3-diketones **IIa–c** was taken from [14].

Pyrazolo[1,5-a]pyrimidines. (a) Equimolar amounts of compounds **I** and **II** dissolved in ethanol were mixed at 18–20°C, and then heated at reflux for 2–4 h. The ethanol was distilled off at reduced pressure, and the compounds obtained were recrystallized from ethanol.

(b) Equimolar amounts of compounds **I** and **II** dissolved in acetic acid were mixed at 18–20°C, and then heated at reflux for 2–4 h. The acetic acid was distilled off at reduced pressure, and the compounds obtained were recrystallized from ethanol.

(c) Equimolar amounts of compounds **I** and **II** were mixed and heated at 160°C till the end of the reaction (TLC monitoring). The products were recrystallized from ethanol.

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