Synthesis of Some New Fluorine-Containing 5-Amino-1,3-disubstituted Pyrazoles and 1*H*-Pyrazolo[3,4-*b*]pyridines

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Nine new fluorine containing 5-amino-1,3-disubstituted pyrazoles have been synthesized and characterized by spectral studies. Condensation reactions of these 5-amino-1,3-disubstituted pyrazoles with fluorinated 1,3-diketones in the presence of glacial acetic acid have been studied and the structures of the resulting 1*H*-pyrazolo[3,4-*b*]pyridines have been confirmed by ir, pmr and ^{19}F nmr spectral studies.

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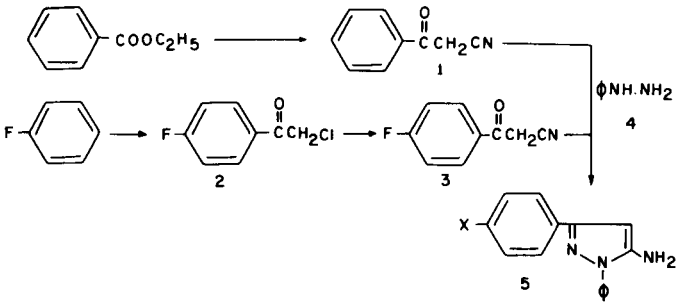
The pyrazolopyridine nucleus has aroused great interest in recent years due to a wide variety of biological activities associated with it. Antiinflammatory (1), antipyretic, analgesic (2), bactericidal (3), vasodilating, respiration stimulating, bronchodilating and hypotensive activities (4) of this system have been reported in the literature. The first synthesis of 1*H*-pyrazolo[3,4-*b*]pyridine nucleus was reported by Bülow (5). In our comprehensive program of developing new fluorinated heterocycles, we now report the synthesis and characterization of nine new fluorine-containing 5-amino-1,3-disubstituted pyrazoles and nineteen new fluorine containing 1*H*-pyrazolo[3,4-*b*]pyridines. The preparation of 5-amino-1,3-disubstituted pyrazoles is summarized in the following Scheme.

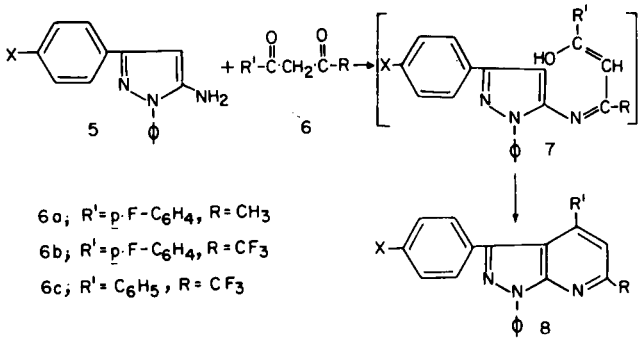


4a ; ϕ = p-Cl-C_6H_4
4b ; ϕ = p-Br-C_6H_4
4c ; ϕ = p-F-C_6H_4
4d ; ϕ = C_6F_5
4e ; ϕ = p-F-$C_6H_4SO_2$
4f ; ϕ = p-CH_3-$C_6H_4SO_2$

5a ; X=H, ϕ=p-Cl-C_6H_4
5b ; X=H, ϕ=p-Br-C_6H_4
5c ; X=H, ϕ=p-F-C_6H_4
5d ; X=F, ϕ=H
5e ; X=F, ϕ=C_6H_5
5f ; X=F, ϕ=C_6F_5
5g ; X=F, ϕ=p-Cl-C_6H_4
5h ; X=F, ϕ=p-Br-C_6H_4
5i ; X=F, ϕ=p-F-C_6H_4
5j ; X=F, ϕ=p-CH_3-$C_6H_4SO_2$
5k ; X=F, ϕ=p-F-$C_6H_4SO_2$
5l ; X=H, ϕ=H
5m, X=H ϕ=C_6H_5

Benzoylacetonitrile **1** was prepared by the condensation of ethyl benzoate with acetonitrile in presence of sodium ethoxide (6,7). 5-Fluorophenacyl chloride **2** was obtained by Friedel-Crafts reaction (8) of fluorobenzene with chloroacetyl chloride and the former gave 5-fluorobenzoylacetonitrile **3** by the nucleophilic replacement of chloride with sodium cyanide (9). Formation of compound **3** was confirmed by the appearance of a nitrile absorption peak at 2250 cm^{-1} in the ir spectra. Reactions of **1** and **3** with hydrazine or *p*-substituted arylhydrazines in absolute ethanol (10) gave the corresponding 5-amino-1,3-disubstituted pyrazoles (Table I). The pmr (deuteriochloroform) spectra of **5** exhibit a characteristic methine proton (=C*H*) resonance signal at δ 6.2, an amino proton resonance signal at δ 3.4 and aromatic proton signals at δ 7.0 to 7.9 ppm. Disappearance of the nitrile absorption peak in the ir spectra from the region of 2250 cm^{-1} and the appearance of a new broad band at 3440-3210 cm^{-1}, due to an amino group, provide firm support for the formation of compounds **5**.

Condensation of the appropriate 5-amino-1,3-disubstituted pyrazole with fluorinated 1,3-diketones (10) in presence of glacial acetic acid yielded the intermediates **7**, which were rapidly cyclised to give 1*H*-pyrazolo[3,4-*b*]-pyridines (**8**). Structures of these 1*H*-pyrazolo[3,4-*b*]-pyridines have been confirmed by ir, pmr and ^{19}F nmr spectral studies.



6a; R'=p-F-C_6H_4, R=CH_3
6b; R'=p-F-C_6H_4, R=CF_3
6c; R'=C_6H_5, R=CF_3

It is interesting to note that the reaction of 5-amino-3-phenylpyrazole or 5-amino-3-(4'-fluorophenyl)pyrazole with 1-(4'-fluorophenyl)-4,4,4-trifluorobutane-1,3-dione yields only one product. However, with 1-(4'-fluorophenyl)-butane-1,3-dione, two isomeric products, **9** and **10**, were obtained. These two isomers were separated by column chromatography on silica-gel, using different ratios of benzene ethyl acetate. Structures of these two isomers

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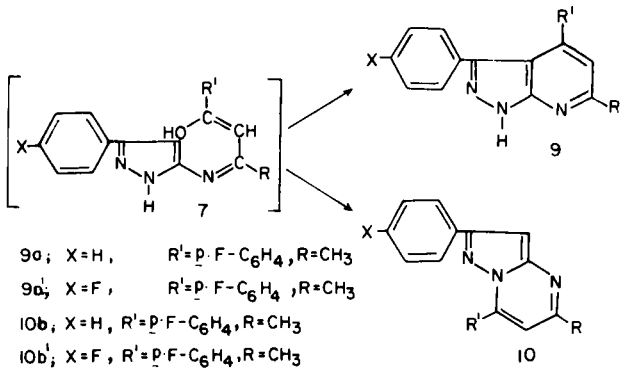
have been confirmed with the help of pmr and ir spectral studies. Isomer **9** is yellow in colour and can be formed if cyclization of the intermediate **7** takes place at position-4. The ir spectra of these compounds exhibit a characteristic =NH stretching mode at 3100 cm^{-1}. The pmr spectra also show a =NH resonance signal at δ 8.0 ppm, thus confirming their pyrazolo-pyridine nature. Isomer **10** is white in colour and can be formed on cyclization of the intermediate **7** at position-1. These isomers **10** are devoid of the =NH absorption peak in the ir spectra in the region of 3100 cm^{-1}. The pmr spectrum of **10b** (trifluoroacetic acid) shows a similar a_2, b_2 pattern for both fluorophenyl groups, suggesting a pyrazolo[1,5-*a*]pyrimidine structure.



EXPERIMENTAL

Melting points are uncorrected. Infrared spectra were recorded using a Perkin Elmer Model 337 spectrophotometer. Proton magnetic resonance spectra and fluorine magnetic resonance spectra were recorded on a Perkin Elmer Model RB-12 spectrometer using tetramethylsilane (TMS) and trifluoroacetic acid (TFA) as internal and external standards. The chemical shifts are reported in ten parts per million and hundred parts per million, respectively.

Benzoylacetonitrile (**1**).

Benzoylacetonitrile **1** was prepared by treating ethyl benzoate (150 g., 1 mole) with methyl cyanide (51 g., 1.25 mole) in the presence of sodium ethoxide (68 g., 1 mole). It was isolated in the usual manner (6,7) and was purified by recrystallization from ethanol, m.p. 80°.

4-Fluorophenacyl Chloride (**2**).

Compound **2** was prepared by the chloroacetylation of fluorobenzene (16 ml., 0.1 mole) with chloroacetyl chloride (19.8 ml., 0.1 mole) in the presence of anhydrous aluminium chloride (50 g.) in dry carbon disulfide. 4-Fluorophenacyl chloride was isolated and purified as mentioned earlier. It was crystallized from ethanol, m.p. 45°.

4-Fluorobenzoylacetonitrile (**3**).

To an ethanolic solution of 4-fluorophenacyl chloride (1.79 g., 0.01 mole), an aqueous solution of sodium cyanide (1.47 g., 0.03 mole) was added dropwise. The reaction mixture was kept as such for four hours, diluted with water (50 ml.) and again kept for an additional four hours. The solution was filtered and the filtrate made acidic with acetic acid. It was cooled and filtered, m.p. 80°, yield 56%.

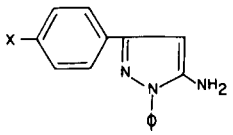
Anal. Calcd. for C_9H_6FNO: N, 8.58. Found: N, 8.42.

4-Fluorophenylhydrazine (**4c**).

4-Fluoroaniline (10 g., 0.1 mole) was diazotized with sodium nitrite in the usual manner (11) and the diazonium solution was filtered. This was added to a solution of sodium sulfite (36 g. in 70 ml. of water) and

Table I

5-Amino-1,3-Disubstituted Pyrazoles

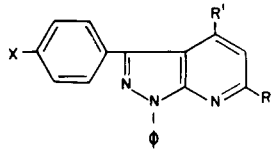


Compound No.	X	Φ	Yield %	M.p. °C	Recrystallization Solvent	Formula	Analysis % Calcd. N	Found N
5a	H	*p*-Cl-C_6H_4	80	148	Ethanol	$C_{15}H_{12}ClN_3$	15.58	15.32
5b	H	*p*-Br-C_6H_4	90	130	Ethanol	$C_{15}H_{12}BrN_3$	13.37	13.01
5c	H	*p*-F-C_6H_4	85	133	Methanol	$C_{15}H_{12}FN_3$	16.66	16.50
5d	F	H	80	130	Ethanol	$C_9H_8FN_3$	23.73	23.60
5e	F	C_6H_5	75	148	Ethanol	$C_{15}H_{12}FN_3$	16.60	16.49
5f	F	C_6F_5	85	135	Methanol	$C_{15}H_7F_6N_3$	12.24	12.01
5g	F	*p*-Cl-C_6H_4	75	135	Ethanol	$C_{15}H_{11}ClFN_3$	14.60	14.50
5h	F	*p*-Br-C_6H_4	78	139	Methanol	$C_{15}H_{11}BrFN_3$	12.65	12.60
5i	F	*p*-F-C_6H_4	80	145	Methanol	$C_{15}H_{11}F_2N_3$	15.50	15.00
5j	F	*p*-CH_3-$C_6H_4SO_2$	88	190	Ethanol	$C_{16}H_{14}FN_3SO_2$	12.68	12.51
5k	F	*p*-F-$C_6H_4SO_2$	78	170	Methanol	$C_{15}H_{11}F_2N_3SO_2$	12.52	12.21
5l (a)	H	H	60	124	Ethanol	$C_9H_9N_3$	—	—
5m (a)	H	C_6H_5	58	123	Methanol	$C_{15}H_{13}N_3$	—	—

(a)These compounds have been reported previously by Grandberg, *et al.* (17)

Table II

Analytical Data of 1*H*-Pyrazolo[3,4-*b*]pyridines

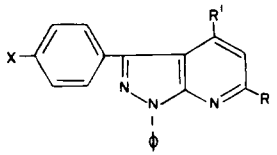


Compound No. (a)	X	φ	R′	R	Yield %	M.p. °C	Formula	Analysis Calcd C	H	F	N	Found C	H	F	N
1a (b)	C_6H_5	H	*p*-F-C_6H_4	CH_3	70	143	$C_{19}H_{14}FN_3$	75.25	4.62	6.27	13.86	74.98	4.43	6.01	13.45
1b	C_6H_5		*p*-F-C_6H_4	CH_3	25	171	$C_{19}H_{14}FN_3$	75.25	4.62	6.27	13.86	74.98	4.43	6.01	13.45
2	C_6H_5	H	*p*-F-C_6H_4	CF_3	80	194	$C_{19}H_{11}F_4N_3$	63.87	3.08	21.29	11.76	63.70	3.00	21.10	11.72
3	C_6H_5	*p*-Cl-C_6H_4	*p*-F-C_6H_4	CH_3	73	151	$C_{25}H_{17}ClFN_3$	72.56	4.11	4.59	10.16	72.45	4.10	4.40	10.01
4	C_6H_5	*p*-Cl-C_6H_4	*p*-F-C_6H_4	CF_3	78	170	$C_{25}H_{14}ClF_4N_3$	64.17	2.99	16.26	8.99	64.00	2.69	16.02	8.49
5	C_6H_5	*p*-Cl-C_6H_4	CF_3	CF_3	85	130	$C_{20}H_{10}ClF_6N_3$	54.36	2.26	25.82	9.51	54.10	2.16	25.43	9.60
6	C_6H_5	*p*-Br-C_6H_4	*p*-F-C_6H_4	CH_3	80	140	$C_{25}H_{17}BrFN_3$	65.50	3.71	4.15	9.17	65.31	3.42	4.01	9.00
7	C_6H_5	*p*-Br-C_6H_4	*p*-F-C_6H_4	CF_3	65	176	$C_{25}H_{14}BrF_4N_3$	58.58	2.77	14.83	8.20	58.28	2.53	14.30	8.01
8	C_6H_5	*p*-Br-C_6H_4	CF_3	CF_3	80	162	$C_{20}H_{10}BrF_6N_3$	49.38	2.06	23.45	8.85	49.31	2.10	23.21	8.45
9a (b)	*p*-F-C_6H_4	H	*p*-F-C_6H_4	CH_3	65	180	$C_{19}H_{13}F_2N_3$	71.02	4.04	11.83	13.08	71.04	4.08	11.45	12.98
9b	*p*-F-C_6H_4		*p*-F-C_6H_4	CH_3	30	210	$C_{19}H_{13}F_2N_3$	71.02	4.04	11.83	13.08	71.04	4.08	11.45	12.98
10	*p*-F-C_6H_4	H	*p*-F-C_6H_4	CF_3	50	183	$C_{19}H_{10}F_5N_3$	60.80	2.67	25.33	11.20	60.44	2.68	25.13	11.02
11	*p*-F-C_6H_4	H	CF_3	CF_3	75	158	$C_{14}H_6F_7N_3$	48.13	1.72	38.11	12.03	48.00	1.53	38.01	11.99
12	*p*-F-C_6H_4	*p*-Cl-C_6H_4	*p*-F-C_6H_4	CH_3	80	165	$C_{25}H_{16}ClF_2N_3$	69.52	3.70	8.80	9.73	69.42	3.51	8.70	9.61
13	*p*-F-C_6H_4	*p*-Cl-C_6H_4	CF_3	CF_3	83	166	$C_{20}H_9ClF_7N_3$	52.23	1.96	28.94	9.14	52.25	1.81	28.54	9.01
14	*p*-F-C_6H_4	*p*-F-$C_6H_4SO_2$	*p*-F-C_6H_4	CF_3	65	170	$C_{25}H_{13}F_6N_3SO_2$	56.29	2.44	21.39	7.88	56.19	2.31	21.31	7.77
15	*p*-F-C_6H_4	*p*-F-$C_6H_4SO_2$	CF_3	CF_3	68	158	$C_{20}H_9F_8N_3SO_2$	47.35	1.77	29.98	8.28	47.15	1.70	29.81	8.18
16	*p*-F-C_6H_4	*p*-$CH_3C_6H_4SO_2$	*p*-F-C_6H_4	CH_3	78	160	$C_{26}H_{19}F_2N_3SO_2$	65.69	4.00	8.00	8.83	65.58	3.99	8.02	8.71
17	*p*-F-C_6H_4	*p*-$CH_3C_6H_4SO_2$	*p*-F-C_6H_4	CF_3	70	150	$C_{26}H_{16}F_5N_3SO_2$	58.98	3.03	17.96	7.93	58.88	3.00	17.66	7.83
18	*p*-F-C_6H_4	*p*-$CH_3C_6H_4SO_2$	C_6H_5	CF_3	85	160	$C_{26}H_{17}F_4N_3SO_2$	61.05	3.32	14.88	8.22	61.00	3.31	14.63	8.01
19	*p*-F-C_6H_4	C_6F_5	CF_3	CF_3	88	175	$C_{20}H_5F_{12}N_3$	46.60	0.97	44.27	8.16	46.51	0.81	44.17	8.00

(a) **a** = Pyrazolo[3,4-*b*]pyridine derivatives; **b** = Pyrazolo[1,5-*a*]pyrimidine derivatives. (b) In these cases, two isomeric products were isolated and characterized.

Table III

Pmr and ^{19}F Nmr Data for the Pyrazolo[3,4-*b*]pyridine Derivatives



Compound No.	X	ϕ	R′	R	Chemical Shift, ppm (δ)							
					Pmr Spectral Data					^{19}F Nmr Spectral Data		
					NH	CH_3	Aromatic Protons	Solvent	Ar-F	CF_3	C_6F_5	Solvent
1a (a)	C_6H_5	H	*p*-F-C_6H_4	CH_3	7.9	2.5	6.9 to 7.8	TFA	36.4	—	—	Acetone
1b	C_6H_5	—	*p*-F-C_6H_5	CH_3	—	2.9	7.0 to 8.0	TFA	39.1	—	—	Acetone
2	C_6H_5	H	*p*-F-C_6H_4	CF_3	8.0	—	7.0 to 7.9	TFA	34.4	-6.8	—	DMSO
3	C_6H_5	*p*-Cl-C_6H_4	*p*-F-C_6H_4	CH_3	—	2.6	6.5 to 7.5	TFA	33.1	—	—	DMSO
4	C_6H_5	*p*-Cl-C_6H_4	*p*-F-C_6H_4	CF_3	—	—	7.0 to 7.9	DMSO	33.8	-7.4	—	DMSO
5	C_6H_5	*p*-Cl-C_6H_4	CF_3	CF_3	—	—	7.0 to 8.0	DMSO	—	-7.8 -13.9	—	Acetone
6	C_6H_5	*p*-Br-C_6H_4	*p*-F-C_6H_4	CH_3	—	2.5	6.9 to 7.9	TFA	33.8	—	—	Benzene
7	C_6H_5	*p*-Br-C_6H_4	*p*-F-C_6H_4	CF_3	—	—	6.5 to 7.6	TFA	35.6	-15.3	—	Acetone
8	C_6H_5	*p*-Br-C_6H_4	CF_3	CF_3	—	—	7.1 to 8.0	TFA	—	-8.2 -14.4	—	Acetone
9a (a)	*p*-F-C_6H_4	H	*p*-F-C_6H_4	CH_3	8.0	2.6	6.8 to 7.8	TFA	32.1 33.4	—	—	Acetone
9b	*p*-F-C_6H_4	—	*p*-F-C_6H_4	CH_3	—	2.8	7.1 to 8.1	TFA	33.1 35.4	—	—	Acetone
10	*p*-F-C_6H_4	H	*p*-F-C_6H_4	CF_3	7.9	—	7.0 to 8.1	DMSO	33.6 38.0	-7.4	—	DMSO
11	*p*-F-C_6H_4	H	CF_3	CF_3	8.2	—	6.9 to 7.8	TFA	33.4	-5.2 -5.9	—	Acetone
12	*p*-F-C_6H_4	*p*-Cl-C_6H_4	*p*-F-C_6H_4	CH_3	—	2.8	7.1 to 7.9	TFA	33.8 38.8	—	—	Acetone
13	*p*-F-C_6H_4	*p*-Cl-C_6H_4	CF_3	CF_3	—	—	7.2 to 8.1	TFA	39.2	-7.2 -14.6	—	Benzene
14	*p*-F-C_6H_4	*p*-F-$C_6H_4SO_2$	*p*-F-C_6H_4	CF_3	—	—	7.0 to 7.9	TFA	33.2 34.2 38.2	-8.4	—	Benzene
15	*p*-F-C_6H_4	*p*-F-$C_6H_4SO_2$	CF_3	CF_3	—	—	6.8 to 8.0	TFA	32.6 36.5	-6.2 -6.9	—	Acetone
16	*p*-F-C_6H_4	*p*-$CH_3C_6H_4SO_2$	*p*-F-C_6H_4	CH_3	—	2.6	7.1 to 8.0	TFA	32.4 38.6	—	—	Benzene
17	*p*-F-C_6H_4	*p*-$CH_3C_6H_4SO_2$	*p*-F-C_6H_4	CF_3	—	—	7.2 to 7.9	TFA	32.7 32.9	-8.2	—	Acetone
18	*p*-F-C_6H_4	*p*-$CH_3C_6H_4SO_2$	C_6H_5	CF_3	—	—	6.8 to 8.0	TFA	33.6	-9.2	—	Acetone
19	*p*-F-C_6H_4	C_6F_5	CF_3	CF_3	—	—	6.9 to 8.1	TFA	36.8	-8.4 -9.2	71 79 88	Acetone

(a) In these cases, two isomeric products were isolated and characterized.

potassium hydroxide (4 g.). The resultant bright orange solution was warmed at 60° for one hour and then filtered. The filtrate was acidified with hydrochloric acid (8 ml.) and again heated for six hours. On addition of hydrochloric acid (50 ml.), 4-fluorophenylhydrazine hydrochloride crystallized as tiny needles, m.p. 36°.

Sulphonyl Hydrazide (**4e,f**).

4-Fluorobenzenesulphonyl chloride or 4-toluenesulphonyl chloride (1 mole) was dissolved in ethanol (15 ml.) and added with stirring to hydrazine hydrate (80%, 2 mole), in ethanol (10 ml.) (12). The solid obtained was isolated in the usual way and recrystallized from hot water. Compound **4e** had m.p. 90° (lit. (13) m.p. 90-92°). Compound **4f** had m.p. 110° (14).

5-Amino-1,3-disubstituted Pyrazoles (**5a-k**).

Benzoylacetonitrile or 4-fluorobenzoylacetonitrile (0.92 mole) was dissolved in absolute ethanol (2000 ml.), and the appropriate phenylhydrazine (0.92 mole) was added to it. The reaction mixture was refluxed for six to eight hours and the excess solvent was removed under reduced pressure. The crude product was crystallized from ethanol, yields 70-90%. All of synthesized compounds, along with their analytical data, are given in Table I.

1-(4′-Fluorophenyl)-4,4,4-trifluorobutane-1,3-dione (**6b**).

These fluorinated-1,3-diketones were prepared by the procedure of Joshi, *et al.* (15), by treating the fluorinated aryl ketone (0.1 mole) with the appropriate ester (0.2 mole) in the presence of sodamide (7.8 g., 0.2 mole) in dry ether. The resultant sodium salt of the 1,3-diketone was dissolved in water and aqueous layer was acidified with hydrochloric acid (10%) yielding the corresponding 1,3-diketones. These 1,3-diketones were recrystallized from petroleum ether. Compound **6a** had m.p. 51°. Compound **6b** had m.p. 40° (lit. (16) m.p. 40-42°). Compound **6c** had m.p. 40°.

1-(4′-Chlorophenyl)-4,6-ditrifluoromethyl-3-(4′-fluorophenyl)pyrazolo-[3,4-*b*]pyridine (**13**).

5-Amino-1,3-disubstituted pyrazole (0.2 mole) was dissolved in glacial acetic acid (100 ml.) and fluorinated 1,3-diketone (0.2 mole) was added to it. The reaction mixture was heated to reflux for 10 to 12 hours on a sand bath. Excess of solvent was removed under reduced pressure and the compound recrystallized from ethanol. All synthesized compounds along with their analytical data are given in Table II and all spectral data are reported in Table III.

Reaction of **5d** and **5l** with **6a** resulted in a solid which gave two spots on tlc (benzene:ethyl acetate; 50:50). The solids were chromatographed on silica gel, eluting with benzene-ethyl acetate, yielded two isomeric products (**9** and **10**). The initial fraction (benzene:ethyl acetate; 75:25) yielded yellow solids which, after recrystallization from methanol, were identified as pyrazolo[3,4-*b*]pyridines (**9a** and **9a′**). The second fraction (benzene:ethyl acetate; 50:50) yielded white solid by-products, which were recrystallized from ethanol (55%) and were identified as pyrazolo[1,5-*a*]-pyrimidines (**10b** and **10b′**).

Acknowledgement.

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REFERENCES AND NOTES

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