A NEW ENTRY TO PYRAZOLO[1,5-*a*]PYRIDO[3,4-e]PYRIMIDINE DERIVATIVES

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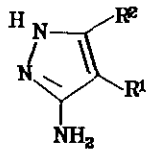
Abstract - Treatment of 3-aminopyrazoles (**1a-e**) with 3-ethoxymethylenpentane-2,4-dione afforded the new pyrazolo[1,5-*a*]pyrimidines (**2a-e**) which were then converted into the enamines (**3a-e**) by reaction with dimethylformamide dimethyl acetal; ring closure of these latter compounds led to pyrazolo[1,5-a]pyrido[3,4-e]pyrimidines (**5a-e**).

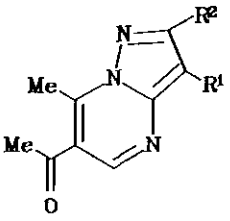
Following our interest into the chemistry of five-membered heterocyclic derivatives as building blocks for polycyclic compounds with potential biological or pharmacological activity,[1,2] we wish to report here a new synthesis of some pyrazolo[1,5-a]pyrimidine derivatives. These latter substances, readily available from 3-aminopyrazoles (**1a-e**), can be considered as good starting materials for the obtainment of the title compounds, otherwise synthesized starting from pyridine derivatives.[3]

Thus, refluxing of commercial **1a-c** or easily available compounds (**1d**[4] and **1e**[5]) with 3-ethoxymethylenpentane-2,4-dione[6] in EtOH for 1-2 h affords in good yields and regiospecifically[7] the pyrazolo[1,5-a]pyrimidines (**2a-e**) whose structures follow from spectroscopic evidence (see Table 1).

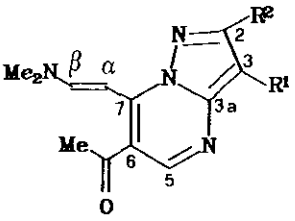
In particular the resonances of carbon atoms at positions 5 and 2 of compound (**2a**) were assigned on the basis of proton coupled spectra; the former appears as a doublet whereas the latter shows the structure of a doublet of doublets owing to the long-range coupling to H-3 ($^2J_{C2\text{-}H3}$ = 5.35 Hz). As regards the quaternary atoms C-7 and



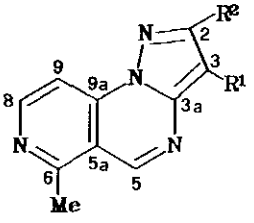
1a–e



2a–e



3a–e



5a–e

a) $R^1 = R^2 = H$

b) $R^1 = CO_2Et$, $R^2 = H$

c) $R^1 = CN$, $R^2 = H$

d) $R^1 = Ph$, $R^2 = H$

e) $R^1 = H$, $R^2 = Me$

C-3a, their resonances were still distinguished on the basis of the coupled spectra for compound (**2b**) and selective decoupling experiments for compound (**2a**). In fact, they appear in **2b** as a pseudo quintet (doublet of quartets, $^3J_{C7\text{-}H5} = {}^2J_{C7\text{-}Me} = 6.43$ Hz) and a doublet of doublets ($^3J_{C3a\text{-}H5} = 13.9$ Hz and $^3J_{C3a\text{-}H2} = 5.0$ Hz), respectively, whereas the situation is more complex in compound (**2a**); for this latter the distinction was achieved by irradiation of the methyl group at position 7 which converts the doublet of quartets in a simple doublet. For compound **2b** the distinction between C-2 and C-5 was then achieved by selective heteronuclear decouplings; in fact, irradiation of the signal at 9.04 ppm in the ^{1}H-nmr spectrum not only transforms the doublet at 151.77 ppm into a singlet but also reduces the signals of C-7 and C-3a to a simple quartet and a doublet, respectively, thus allowing us to confirm the protons assignment too. As regards compounds (**2c-e**), assignment of the above resonances was achieved by HETCOR spectra.

Owing to its electronic environment, the methyl group at position 7 of compounds (**2a-e**) is both acidic and reactive.[8,9] Hence, treatment of the above compounds with dimethylformamide dimethyl acetal in toluene, affords in good yields the (*E*)-enamines (**3a-e**), the trans geometry being ascertained by the coupling constant between the olefinic protons[10] (see Table 2).

Finally, refluxing compounds (**3a-e**) with ammonium acetate in acetic acid gave the pyrazolo[1,5-*a*]pyrido[3,4-*e*]pyrimidines (**5a-e**); the formation of the pyridine ring could be accounted for by an intramolecular nucleophile-

Table 1. ^{13}C-Nmr data for compounds **2a-e** and **3a-e**[a]

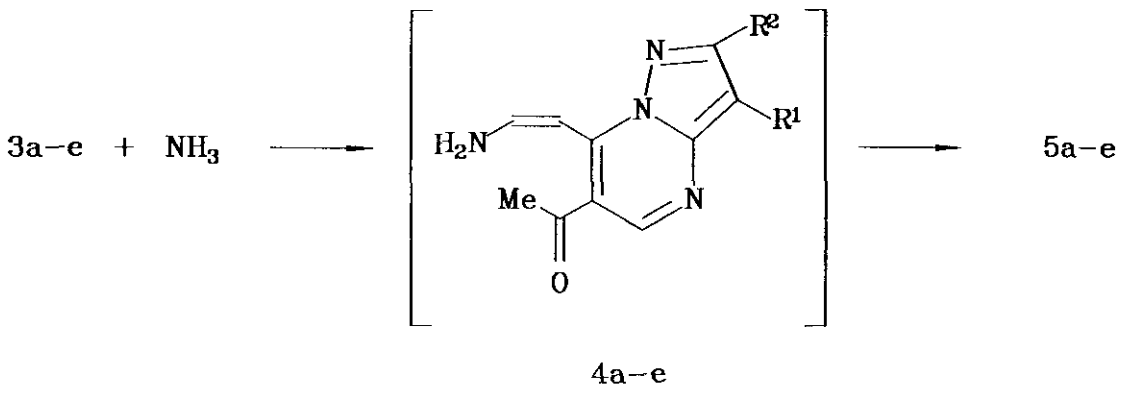
Compd	C-2	C-3	C-3a	C-5	C-6	C-7	7-Me	Others
2a	146.97	97.94	148.21	148.80	117.60	150.40	15.07	196.42(s, *C*OMe), 29.80(q, CO*Me*)
2b	148.87	103.875	147.375	151.77	119.20	151.35	15.13	196.00(s, *C*OMe), 161.96(s, CO_2Et), 60.475 (t, OCH_2), 29.75(q, CO*Me*), 14.30(q, Me)
2c[b]	148.64	84.30	150.06	152.24	120.28	151.98	15.38	195.76(s, *C*OMe), 112.16(s, CN) 30.08(q, CO*Me*)
2d[b]	144.66	111.33	143.97	148.74	117.55	150.60	15.01	196.16(s, *C*OMe), 131.05(s, C_{ipso}), 128.64(d, C_{ortho}), 126.56(d, C_{para}), 126.12(d, C_{meta}), 29.67(q, CO*Me*)
2e	157.50	97.30	148.72	148.66	116.61	149.70	14.98	196.21(s, *C*OMe), 29.53(q, CO*Me*) 14.71(q, 2-Me)
3a	145.02	96.01	149.48	151.30	109.93	146.79	-	196.87(s, *C*OMe), 158.39(d, C-β), 86.90(d, C-α), 45.82(q, NMe), 36.89 (q, NMe), 29.89(q, CO*Me*)
3b	147.19	101.73	148.96	153.97	111.30	146.88	-	196.71(s, *C*OMe), 162.83(s, CO_2Et), 159.07(d, C-β), 86.57(d, C-α), 60.11 (t, OCH_2), 46.07(q, NMe), 36.85(q, NMe), 29.79(q, CO*Me*),14.48(q, Me)
3c	146.58	81.80	151.91	154.17	111.75	147.01	-	196.58(s, *C*OMe), 159.47(d, C-β), 113.48(s, CN), 86.75(d, C-α), 46.47 (q, NMe), 37.17(q, NMe), 30.00(q, CO*Me*)
3d[b]	143.01	109.39	145.64	151.32	110.18	146.81	-	196.76(s, *C*OMe), 158.38(d, C-β), 132.24(s, C_{ipso}), 128.58(d, C_{ortho}), 126.22(d, C_{meta}), 125.88(d, C_{para}), 86.82(d, C-α), 45.84(q, NMe), 36.71 (q, NMe), 29.88(q, CO*Me*)
3e	155.36	95.99	150.10	151.185	109.67	146.24	-	196.72(s, *C*OMe), 158.14(d, C-β), 86.76(d, C-α), 45.75(q, NMe), 36.59(q, NMe), 29.78(q, CO*Me*), 14.80(q, 2-Me)

[a]Assignments made on the basis of proton coupled spectra and selective decoupling experiments.

[b]Assignments made on the basis of HETCOR spectra.

Table 2. ^{1}H-Nmr data for compounds **2a-e** and **3a-e**

Compd	*δ_H (CDCl$_3$, 300 MHz)*
2a	2.698(s, 3H, COMe), 3.155(s, 3H, 7-Me), 6.748(d, J_{H3-H2} = 2.25 Hz, 1H, H-3), 8.250(d, J_{H2-H3} = 2.25 Hz, 1H, H-2), and 8.843(s, 1H, H-5)
2b	1.168(t, J = 7.09 Hz, 3H, OCH_2*Me*), 2.680(s, 3H, COMe), 3.117(s, 3H, 7-Me), 4.386(q, J = 7.09 Hz, 2H,OCH_2), 8.600(s, 1H, H-2), and 9.045(s, 1H, H-5)
2c	2.753(s, 3H, COMe), 3.176(s, 3H, 7-Me), 8.488(s, 1H, H-2), and 9.064(s, 1H, H-5)
2d	2.606(s, 3H, COMe), 3.080(s, 3H, 7-Me), 7.229-7.437(m, 3H, ArH_3), 7.943-7.981(m, 2H, ArH_2), 8.476 (s, 1H, H-2), and 8.782(s, 1H, H-5)
2e	2.430(d, $^4J_{2Me-H3}$ = 0.5 Hz, 3H, 2-Me), 2.571(s, 3H, COMe), 2.989(s, 3H, 7-Me), 6.393(br q, $^4J_{H3-2Me}$ = 0.5 Hz, 1H, H-3), and 8.654(s, 1H, H-5)
3a	2.635(s, 3H, COMe), 3.069(s, 3H, NMe), 3.262(s, 3H, NMe), 6.499(d J_{H3-H2} = 2.25 Hz, 1H, H-3), 7.279 (d, $^3J_{trans}$ = 12.66 Hz, 1H, *CH*CHNMe$_2$), 8.060(d, J_{H2-H3} = 2.25 Hz, 1H, H-2), 8.714(s, 1H, H-5), and 9.730(d, $^3J_{trans}$ = 12.66 Hz, 1H, CHC*H*NMe$_2$)
3b	1.407(t, J = 7.12 Hz, 3H, OCH_2*Me*), 2.640(s, 3H, COMe), 3.100(s, 3H, NMe), 3.305(s, 3H, NMe), 4.423 (q, J = 7.12 Hz, 2H, OCH_2), 7.249(d, $^3J_{trans}$ = 12.58 Hz, 1H, *CH*CHNMe$_2$), 8.462(s, 1H, H-2), 8.917(s, 1H, H-5), and 9.666(d, $^3J_{trans}$ = 12.58 Hz, 1H, CHC*H*NMe$_2$)
3c	2.663(s, 3H, COMe), 3.141(s, 3H, NMe), 3.347(s, 3H, NMe), 7.297(d, $^3J_{trans}$ = 12.64 Hz, 1H, C*H*CHNMe$_2$), 8.260(s, 1H, H-2), 8.843(s, 1H, H-5), and 9.639(d, $^3J_{trans}$ = 12.64 Hz, 1H, CHC*H*NMe$_2$)
3d	2.660(s, 3H, COMe), 3.080(s, 3H, NMe), 3.266(s, 3H, NMe), 7.262-7.471(m, 4H, ArH_3 and C*H*CHNMe$_2$), 8.034-8.057(m, 2H, ArH_2), 8.385(s, 1H, H-2), 8.827(s, 1H, H-5), and 9.719(d, $^3J_{trans}$ = 12.65Hz, 1H, CHC*H*NMe$_2$)
3e	2.458(d , $^4J_{2Me-H3}$ = 0.5 Hz, 3H, 2-Me), 2.597(s, 3H, COMe), 3.030(s, 3H, NMe), 3.228(s, 3H, NMe), 6.271(br q, $^4J_{H3-2Me}$ = 0.5 Hz, 1H, H-3), 7.215(d, $^3J_{trans}$ = 12.68 Hz, 1H, *CH*CHNMe$_2$), 8.644(s, 1H, H-5), and 9.713(d, $^3J_{trans}$ = 12.68 Hz, 1H, CHC*H*NMe$_2$)



4a–e

electrophile cyclization of the intermediate enamine (**4**) as reported in Scheme 2.

The spectral data of compounds (**5a-e**) (Tables 3 and 4) agree well with the assigned structures. In particular, the distinction between C-5 and C-8 was based on the coupled spectra, the latter exhibiting the structure of a doublet of doublets owing to the coupling to H-9. Finally, the resonance of C-3 in compound (**5a**) was assigned on the basis of selective decoupling of H-3 whereas the distinction between C-2 and C-5 in **5d** was confirmed by the HETCOR spectrum.

Table 3. ^{13}C-Nmr data for compounds **5a-e**[a]

Compd	C-2	C-3	C-3a	C-5	C-5a	C-6	C-8	C-9	C-9a	6-Me	Others
5a	144.35	100.59	146.04	148.83	112.17	159.37	151.30	106.81	140.57	21.73	-
5b	146.41	106.55	145.33	152.22	112.66	160.04	152.015	107.17	140.39	21.79	161.96(s, CO), 60.59(t, OCH_2), 14.35(q,OCH_2*Me*)
5c	146.37	87.09	148.25	152.93	112.09	160.62	152.76	107.28	140.54	22.09	113.16(s, CN)
5d[b]	142.10	114.01	141.77	148.43	112.24	159.22	151.21	106.68	140.53	21.61	130.92(s, C_{ipso}), 128.60(d, C_{ortho}), 126.79(d, C_{para}), 126.37(d, C_{meta})
5e	154.42	100.06	146.44	148.46	111.70	159.11	150.91	106.38	139.90	21.56	14.45(q, 2-Me)

[a]Assignments made on proton coupled spectra . [b]Assignments made on the basis of HETCOR spectra.

Table 4. ^{1}H Nmr data for compounds **5a-e**

Compd	*δ_H(CDCl$_3$, 300 MHz)*
5a	3.045(s, 3H, 6-Me), 6.876(d, J_{H3-H2} = 2.15 Hz, 1H, H-3), 8.161(dd, J_{H9-H8} = 5.85 Hz, J_{H9-H5} = 0.80 Hz, 1H, H-9), 8.182(d, J_{H2-H3} = 2.15 Hz, 1H, H-2), 8.805(d, J_{H8-H9} = 5.85 Hz, 1H, H-8), and 9.163(d J_{H5-H9} = 0.80 Hz, 1H, H-5)
5b	1.450(t, J = 7.13 Hz, 3H, OCH$_2$*Me*), 3.084(s, 3H, 6-Me), 4.456(q, J = 7.13 Hz, 2H, OCH$_2$), 8.208 (dd, J_{H9-H8} = 5.84 Hz, J_{H9-H5} = 0.90 Hz, 1H, H-9), 8.592(s, 1H, H-2), 8.879(d, J_{H8-H9} = 5.84 Hz, 1H, H-8), and 9.444(d, J_{H5-H9} = 0.90 Hz, 1H, H-5)
5c	3.113(s, 3H, 6-Me), 8.211(dd, J_{H9-H8} = 5.86 Hz, J_{H9-H5} = 0.80 Hz, 1H, H-9), 8.430(s, 1H, H-2), 8.932(d, J_{H8-H9} = 5.86 Hz, 1H, H-8), and 9.412(d, J_{H5-H9} = 0.80 Hz, 1H, H-5)
5d	2.874(s, 3H, 6-Me), 7.222-7.415(m, 3H, ArH$_3$), 7.903-7.965(m, 2H, ArH$_2$), 7.937(d, J_{H9-H8} = 5.63 Hz, 1H, H-9), 8.281(s, 1H, H-2), 8.661(d, J_{H8-H9} = 5.63 Hz, 1H, H-8), and 8.958(s, 1H, H-5)
5e	2.417(d, $^4J_{2Me-H3}$ = 0.50 Hz, 3H, 2-Me), 2.835(s, 3H, 6-Me), 6.461(br q, $^4J_{H3-2Me}$ = 0.50 Hz, 1H, H-3), 7.825(d, J_{H9-H8} = 5.86 Hz, 1H, H-9), 8.546(d, J_{H8-H9} = 5.86 Hz, 1H, H-8), and 8.864(s, 1H, H-5)

Due to the good overall yields and to the availability of the starting material as well as to the possibility of further functionalization of the reaction products, we think that this pathway represents a new attractive approach to this class of compounds which are structurally related to a series of condensed heterocyclic systems exhibiting antipsychotic efficacy.[11]

EXPERIMENTAL

All melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. Infrared spectra were measured for nujol mulls with a Perkin-Elmer 283 spectrophotometer. ^{1}H- And ^{13}C-nmr spectra were recorded in CDCl$_3$ on a Varian VXR-300 instrument; chemical shifts are reported in ppm high frequency from tetramethylsilane as secondary reference standard and coupling constants in Hz. Silica gel plates (Merck F$_{254}$) were used for analytical tlc. Solvents were removed under reduced pressure.

Preparation of Compounds **2a-e**

a) 3-Aminopyrazole (**1a**) (10.6 g; 128 mmol) was added to a solution of 3-ethoxymethylenpentane-2,4-dione[6] (22 g; 141 mmol) in EtOH (200 ml) and the solution was refluxed for 2 h. Removal of the solvent left a brownish solid (20.2 g, 90%) mainly consisting (tlc and ^{1}H-nmr spectrum) of 6-acetyl-7-methylpyrazolo[1,5-*a*]pyrimidine (**2a**). An analytical sample (white crystals) melted at 81-82 °C (after two crystallizations from cyclohexane). Ir ν_{max}: 1690(CO) and 1605 cm^{-1}. Anal. Calcd for $C_9H_9N_3O$: C, 61.70; H, 5.18; N, 23.99. Found: C, 61.92; H, 5.17; N, 24.20.

b) Operating as above, compound (**1b**) (18.6 g; 120 mmol) and 3-ethoxymethylenpentane-2,4-dione[6] (20.6 g; 132 mmol) in EtOH (200 ml), afforded compound (**2b**) as white solid (18.6 g). Evaporation to dryness of the mother liquors gave a second crop (2.95 g, overall 73%) of ethyl 6-acetyl-7-methylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (**2b**), mp 167-168 °C (from EtOH). Ir ν_{max}: 1735(CO_2Et), 1690(CO), and 1610 cm^{-1}. Anal. Calcd for $C_{12}H_{13}N_3O_3$: C, 58.29; H, 5.30; N, 16.99. Found: C, 58.47; H, 5.35; N, 17.02.

c) Compound (**1c**) (7.73 g; 71.5 mmol) and 3-ethoxymethylenpentane-2,4-dione[6] (12.3 g; 79 mmol) were refluxed for 1 h in EtOH (100 ml) to give compound (**2c**) as a brownish solid (11.2 g). Evaporation to dryness of the mother liquors gave a second crop (1.1 g, overall 86%) of 6-acetyl-3-cyano-7-methylpyrazolo[1,5-*a*]pyrimidine (**2c**), mp 177-178 °C (from EtOH). Ir ν_{max}: 3120, 2240(CN), 1700(CO), and 1610 cm^{-1}. Anal. Calcd for $C_{10}H_8N_4O$: C, 60.00; H, 4.03; N, 27.99. Found: C, 59.82; H, 4.12; N, 28.06.

d) Operating under the same conditions, compound (**1d**)[4] (6.36 g; 40 mmol) and 3-ethoxymethylenpentane-2,4-dione[6] (6.87 g; 44 mmol) in EtOH (100 ml) afforded 6-acetyl-7-methyl-3-phenylpyrazolo[1,5-*a*]pyrimidine (**2d**) as a yellow solid (8.6 g); a second crop of the same material was then recovered from the mother liquors (1.05 g, overall 96%), mp 140-141 °C (from EtOH). Ir ν_{max}: 3120, 1690(CO), and 1600 cm^{-1}. Anal. Calcd for $C_{15}H_{13}N_3O$: C, 71.70; H, 5.21; N, 16.72. Found: C, 71.62; H, 5.33; N, 16.86.

e) 3-Amino-5-methylpyrazole (**1e**)[5] (4.86 g; 50 mmol) was added to a solution of 3-ethoxymethylenpentane-2,4-dione[6] (8.59 g; 55 mmol) in EtOH (60 ml) and the solution was refluxed for 1 h to give 6-acetyl-2,7-dimethylpyrazolo[1,5-*a*]pyrimidine (**2f**) as a yellowish solid (7.91g, 83%) which was filtered and dried. An analytical sample obtained by crystallization from EtOH melted at 144-145 °C. Ir ν_{max}: 3110, 1690(CO), and 1600 cm^{-1}. Anal. Calcd for $C_{10}H_{11}N_3O$: C, 63.48; H, 5.86; N, 22.21. Found: C, 63.61; H, 5.70; N, 22.13.

6-Acetyl-7-(2-dimethylaminovinyl)pyrazolo[1,5-*a*]pyrimidines **3a-e**

a) Compound (**2a**) (3.5 g; 20 mmol) in toluene (30 ml) containing dimethylformamide dimethyl acetal (4.0 ml; d = 0.897 g/l) was warmed under nitrogen at 90 °C for 1 h. Removal of the solvent left an orange solid which was recrystallized from ethyl acetate to afford the enamine (**3a**) as yellow needles (3.45 g, 75%), mp 152-153 °C. Anal. Calcd for $C_{12}H_{14}N_4O$: C, 62.59; H, 6.13; N, 24.33. Found: C, 62.34; H, 6.16; N, 24.53.

b) Operating under the same conditions, compound (**2b**) (9.9 g; 40 mmol) and dimethylformamide dimethyl acetal (8 ml) gave, after cooling, ethyl 6-acetyl-7-(2-dimethylaminovinyl)pyrazolo[1,5-*a*]pyrimidine-3-carboxylate (**3b**) as a yellow solid (10.5 g). Evaporation to dryness of the mother liquors afforded a second crop (0.78 g, overall 93%) of the same material (tlc, $CHCl_3$-MeOH 5:1 v/v as eluant), mp 147-148 °C (after two crystallizations from ethyl acetate). Anal. Calcd for $C_{15}H_{18}N_4O_3$: C, 59.59; H, 6.00; N, 18.53. Found: C, 59.39; H, 6.22; N, 18.71.

c) Compound (**2c**) (5 g; 25 mmol) in toluene (80 ml) containing dimethylformamide dimethyl acetal (5 ml) was refluxed under nitrogen for 2 h. Removal of the solvent left a yellow solid which was recrystallized from 2-methoxyethanol to give 6-acetyl-3-cyano-7-(2-dimethylaminovinyl)pyrazolo[1,5-*a*]pyrimidine (**3c**) (5.72 g, 90%), mp 245-246 °C. Anal. Calcd for $C_{13}H_{13}N_5O$: C, 61.17; H, 5.13; N, 27.43. Found: C, 61.30; H, 5.04; N, 27.20.

d) Compound (**2d**) (2.51 g; 10 mmol) in toluene (100 ml) containing dimethylformamide dimethyl acetal (2 ml) was maintained at reflux under nitrogen for 4 h. The orange solid obtained by filtration was recrystallized twice from EtOH to give 6-acetyl-7-(2-dimethylaminovinyl)-3-phenylpyrazolo[1,5-*a*]pyrimidine (**3d**) (2.2 g, 72%), mp 218-219 °C. Anal. Calcd for $C_{18}H_{18}N_4O$: C, 70.57; H, 5.92; N, 18.29. Found: C, 70.36; H, 6.08; N, 18.01.

e) Operating as above, compound (**2e**) (5.67 g; 30 mmol) in toluene (60 ml) containing dimethylformamide dimethyl acetal (10 ml) afforded 6-acetyl-7-(2-dimethylaminovinyl)-2-methylpyrazolo[1,5-*a*]pyrimidine (**3f**) (4.61 g, 63%), mp 194-195 °C (from EtOH). Anal. Calcd for $C_{13}H_{16}N_4O$: C, 63.92; H, 6.60; N, 22.93. Found: C, 63.83; H, 6.73; N, 22.81.

6-Methylpyrazolo[1,5-*a*]pyrido[3,4-*e*]pyrimidines **5a-e**

a) The enamine (**3a**) (2.3 g; 10 mmol) was refluxed in acetic acid (30 ml)-ammonium acetate (20 g) for 1 h. After cooling, the mixture was diluted with water (50 ml) and the yellow precipitate was filtered off, washed with water, and dried to yield compound (**5a**) (0.95 g, 52%), mp 168-169 °C (from *i*-PrOH). Ir ν_{max}: 3120 and 1600 cm^{-1}. Anal. Calcd for $C_{10}H_8N_4$: C, 65.21; H, 4.28; N, 30.42. Found: C, 64.93; H, 4.37; N, 30.24.

b) Operating as above, compound (**3b**) (1.1 g) afforded ethyl 6-methylpyrazolo[1,5-*a*]pyrido[3,4-*e*]pyrimidine-3-carboxylate (**5b**) (0.66 g, 72%), mp 212-213 °C (from EtOH). Ir ν_{max}: 3120, 1725, and 1610 cm^{-1}. Anal. Calcd for $C_{13}H_{12}N_4O_2$: C, 60.93; H, 4.72; N, 21.86. Found: C, 60.73; H, 4.81; N, 21.66.

c) Compound (**3c**) (2.55 g) was refluxed for 3 h in acetic acid (20 ml) containing ammonium acetate (20 g) to give 3-cyano-6-methylpyrazolo[1,5-*a*]pyrido[3,4-*e*]pyrimidine (**5c**) (0.9 g, 43%), mp 284-285 °C (from EtOH). Ir ν_{max}: 3120, 3100, 2240, and 1600 cm^{-1}. Anal. Calcd for $C_{11}H_7N_5$: C, 63.15; H, 3.37; N, 33.47. Found: C, 63.02; H, 3.51; N, 33.19.

d) Refluxing of the enamine (**3d**) (1.3 g) in acetic acid (20 ml)-ammonium acetate (8.6 g) for 5 h afforded 6-methyl-3-phenylpyrazolo[1,5-*a*]pyrido[3,4-*e*]pyrimidine (**5d**) as a pale yellow solid (0.75 g, 68%), mp 166-167 °C (from EtOH). Ir ν_{max}: 3110 and 1600 cm^{-1}. Anal. Calcd for $C_{16}H_{12}N_4$: C, 73.83; H, 4.65; N, 21.52. Found: C, 73.67; H, 4.85; N, 21.39.

e) Operating under the same conditions, the enamine (**3e**) (2 g; 8.2 mmol) gave 2,6-dimethylpyrazolo[1,5-*a*]pyrido[3,4-*e*]pyrimidine (**5e**) (0.9 g, 55%). An analytical sample obtained after two recrystallizations from EtOH melted at 164-165 °C. Ir ν_{max}: 3100 and 1605 cm^{-1}. Anal. Calcd for $C_{11}H_{10}N_4$: C, 66.66; H, 5.08; N, 28.26. Found: C, 66.52; H, 5.19; N, 28.06.

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