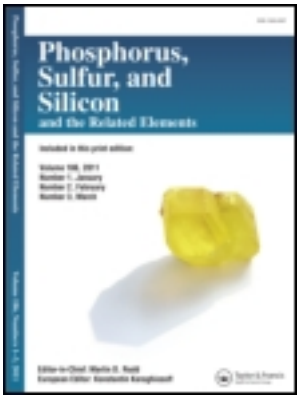

Phosphorus, Sulfur, and Silicon and the Related Elements

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SYNTHESIS OF NOVEL DERIVATIVES OF 4-METHYLTHIO-N-ARYL-2-PYRIDONE AND DEAZAPURINE ANALOGUES: THE REACTION OF KETENE DITHIOACETALS WITH SUBSTITUTED ACETANILIDES

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SYNTHESIS OF NOVEL DERIVATIVES OF 4-METHYLTHIO-N-ARYL-2-PYRIDONE AND DEAZAPURINE ANALOGUES: THE REACTION OF KETENE DITHIOACETALS WITH SUBSTITUTED ACETANILIDES

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A new one-pot synthesis of 4-methylthio-N-aryl-2-pyridones and their deazapurine analogues by the reaction of ketene dithioacetals with substituted acetanilides have been reported.

Keywords: 4-Methylthio-N-aryl-2-pyridones; ketene dithioacetals; substituted acetanilides

Ketene-*S,S*-acetals prepared by the reaction of nitriles or ketones with carbon disulphide in the presence of a base, followed by alkylation, have become a subject of current interest. Although several papers have appeared regarding their preparation, the synthetic utility of these intermediates have not been extensively explored. As a part of our program directed for development of new simple and efficient procedures for the synthesis of purine analogues and other antimetabolites,[1–3] we have recently reported different successful approaches for synthesis of methylthiopyrazolo[1,5-*a*]pyrimidines.[4,5] Derivatives of these ring systems are interesting because they are thioguanine and mercaptopurine analogues and as such they have useful properties as antimetabolites in purine biochemical reactions. We report in this part a new, one-pot synthesis of

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4-methylthio-*N*-aryl-2-pyridones and deazapurine analogues by the reaction of ketene dithioacetals with substituted acetanilides. Moreover, the results of our work aimed to define the scope and limitation of our procedures for the synthesis of pyridones and their important condensed derivatives are also reported. Thus, it has been found that [bis(methylthio)methylene]malononitrile **2a** reacted with cyano acetanilides **3** in a solution of sodium ethoxide to give the corresponding 4-methylthio-*N*-aryl-2-pyridones **5**. The structure of compounds **5** were established and confirmed for the reaction products on the basis of their elemental analysis and spectral data (MS, ^{1}H NMR and IR). The analytical data for **5a** revealed a molecular formula $C_{14}H_{10}N_4SO$ (M^+ 282). ^{1}H NMR spectroscopy was used to confirm this structure for the product. Thus, ^{1}H NMR revealed a band at $\delta = 2.79$ ppm assigned for SCH_3 group, a multiplet at $\delta = 7.30$–7.54 ppm assigned for aromatic protons and a broad band at $\delta = 7.59$ ppm assigned for an amino group. The ^{13}C NMR spectra were characterized by a signal at $\delta = 168.00$ ppm corresponding the carbonyl carbon atom. The formation of **5** from the reaction of **2a** with **3** is assumed to proceed via intermediacy of **4**, which were cyclized to yield the final 4-methylthio-2-pyridones **5**. In order to investigate the scope of this reaction further and in order to establish whether the reaction of ketene dithioacetals with substituted acetanildes could be extended to provide a general approach to N-substituted 4-methylthio-2-pyridones, we studied the reaction of ketene dithioacetals **2** with other functionalized acetanilides. Thus, **2a,b** reacts with aceto- and benzoylacetanilides **8a,b** in dioxane containing a catalytic amount of potassium hydroxide at room temperature to yield the 4-methylthio-2-pyridones **9**. The structure of **9** was established by mass spectroscopy and IR and ^{1}H NMR data. Compounds **5** and **9** bearing methylthio group and other latent functional substituents were found useful for the synthesis of fused derivatives. Thus, it has been found that compounds **5** reacted with aromatic amines in fusion to afford the corresponding 4-anilino derivative **6**. The structure of compounds **6** were established on the basis of elemental analysis and spectral data (MS, ^{1}H NMR and IR). Thus, the ^{1}H NMR spectrum of **6d** contained a broad band at $\delta = 13.45$ ppm assigned to NH group, a multiplet at $\delta = 6.93$–7.6 ppm assigned to the aromatic protons and a broad singlet at $\delta = 6.68$ ppm assignable for NH_2 group. When compounds **5** and **9** were subjected to the reaction with hydrazine, the hydrazino derivatives could not be isolated, but cyclized to the pyrazolo[4,3-*c*]pyridine derivatives **7**

and **11**, respectively. The structure of compounds **7** and **11** were established on the basis of elemental analysis and spectral data (MS, ^{1}H NMR and IR). Thus, the IR spectrum of **11e** revealed the absence of a CN band, and ^{1}H NMR spectrum contained a broad band at δ = 13.65 ppm assignable to NH group, a multiplet at δ = 7.30–7.62 ppm assigned to the aromatic protons and two broad singlets at δ = 6.64 and 8.12 ppm assignable for two NH_2 groups.

In summary, we have achieved a regiospecific synthesis of interesting methylthiopyridones and deazapurine analogues by the reaction of ketene dithioacetals with substituted acetanilides. The compounds obtained seemed promising for further chemical transformations and for biological evaluation studies.

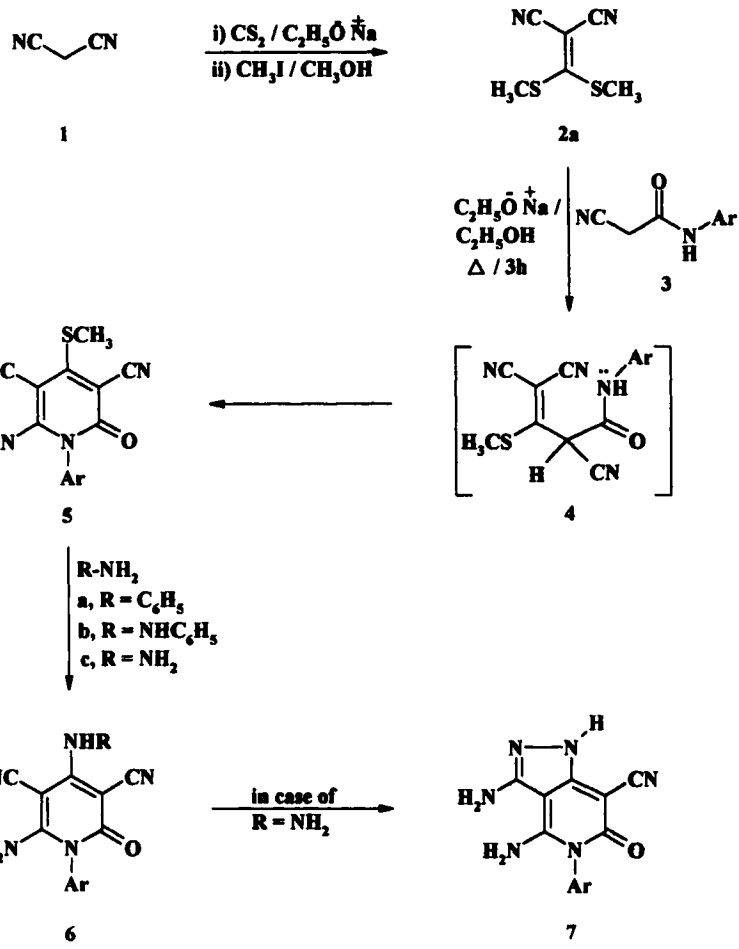
EXPERIMENTAL

All melting points are uncorrected. IR spectra were obtained (KBr disc) on a pye unicam instrument. ^{1}H NMR spectra were measured on a Varian 400 or Wilmed 270 MHz spectrometer for solutions $(CD_3)_2SO$ using $SiMe_4$ as internal standard. Mass spectra were recorded on a Varian MAT 112 spectrometer. Analytical data were obtained from the Microanalytical Data Center at Cairo University.

N-Aryl-3, 5-dicyano-4-methylthio-2-pyridones 5a-d

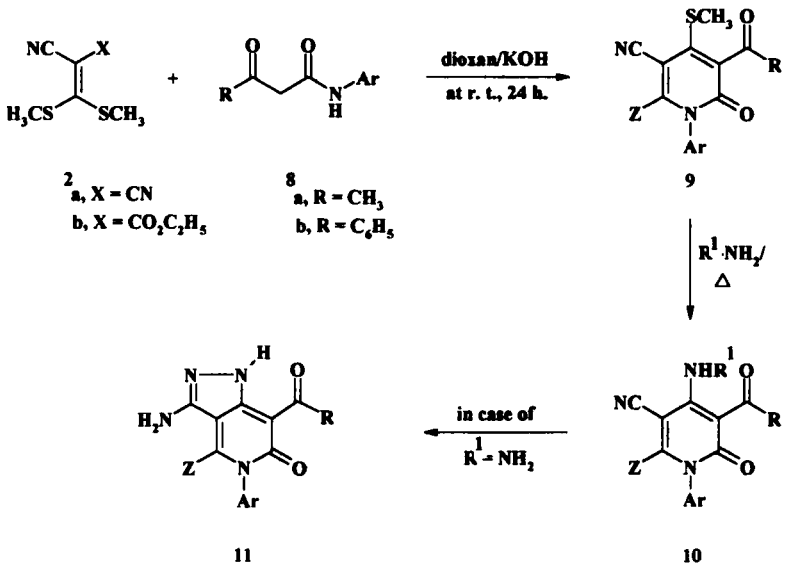
A mixture of [bis(methylthio)methylene]-malononitrile **2a** (0.01 mol) and substituted cyanoacetanilid derivatives **3** (0.01 mol) were dissolved in ethanol (30 ml) containing sodium ethoxide (0.01 mol). The mixture was refluxed for 3 h. Then allowed to cool to room temperature and acidified with cold diluted HCl. The resulting solid product was collected by filtration and crystallized from ethanol.

5a (85% yield): m.p. 290 °C; IR (KBr) 3404, 3312, 3211 (NH_2), 2206 (CN), and 1650 cm^{-1} (CO); ^{1}H NMR (DMSO) δ=2.79 (s, 3H, SCH_3), 7.3–7.54 (m, 5H, C_6H_5), and 7.59 (s, br, 2H, NH_2). ^{13}C NMR 21.11 (SCH_3), 113.25 (CN), 115.55 (CN), 123.75 (C-5), 126.99 (C-3), 130.00–139.34 (Ar-C), 150.27 (C-4), 155.29 (C-6), 168.00 (C-2). Found: C, 59.8; H, 3.8; N, 19.5%; M^+, 282. Calcd for $C_{14}H_{10}N_4SO$: C, 59.6; H, 3.6; N, 19.9%; M,



1 2a 3 4 5 6 7

6	Ar	R	6	Ar	R	3,5,7	Ar
a	C_6H_5	C_6H_5	e	C_6H_5	NHC_6H_5	a	C_6H_5
b	C_6H_4-4-Cl	C_6H_5	f	C_6H_4-4-Cl	NHC_6H_5	b	C_6H_4-4-Cl
c	C_6H_4-4-CH_3	C_6H_5	g	C_6H_4-4-CH_3	NHC_6H_5	c	C_6H_4-4-CH_3
d	C_6H_4-4-OCH_3	C_6H_5	h	C_6H_4-4-OCH_3	NHC_6H_5	d	C_6H_4-4-OCH_3



9,11	Ar	R	Z	10	Ar	R	Z	R^1
a	C_6H_5	CH_3	NH_2	a	C_6H_5	CH_3	NH_2	C_6H_5
b	C_6H_4-4-Cl	CH_3	NH_2	b	C_6H_4-4-Cl	CH_3	NH_2	C_6H_5
c	C_6H_4-4-CH_3	CH_3	NH_2	c	C_6H_5	C_6H_5	NH_2	C_6H_5
d	C_6H_4-4-OCH_3	CH_3	NH_2	d	C_6H_4-4-CH_3	C_6H_5	OH	C_6H_5
e	C_6H_5	C_6H_5	NH_2	e	C_6H_5	CH_3	NH_2	NHC_6H_5
f	C_6H_5	C_6H_5	OH	f	C_6H_4-4-Cl	CH_3	NH_2	NHC_6H_5
g	C_6H_4-4-Cl	C_6H_5	OH	g	C_6H_5	C_6H_5	NH_2	NHC_6H_5
h	C_6H_4-4-CH_3	C_6H_5	OH	h	C_6H_5	C_6H_5	OH	NHC_6H_5
				i	C_6H_4-4-CH_3	C_6H_5	OH	NHC_6H_5

282. **5b** (90% yield): m.p. 285 °C; IR (KBr) 3403, 3311, 3221 (NH_2), 2207 (CN), and 1648 cm^{-1} (CO); ^1H NMR (DMSO) δ=2.78 (s, 3H, SCH_3), 7.34–7.64 (m, 4H, C_6H_4), and 7.82(s, br, 2H, NH_2). Found: C, 53.4; H, 2.4; N, 17.9%; M^+, 316. Calcd for $C_{14}H_9ClN_4SO$: C, 53.1; H, 2.8; N, 17.7%; M, 316.5. **5c** (82% yield): m.p. 260 °C; IR (KBr) 3403, 3309, 3203 (NH_2), 2206 (CN), and 1648 cm^{-1} (CO); ^1H NMR (DMSO) δ=2.38 (s, 3H, CH_3), 2.78 (s, 3H, SCH_3), 7.16–7.38 (m, 4H, C_6H_4) and 7.58 (s, br, 2H, NH_2). Found: C, 62.5; H, 4.5; N, 18.9%; M^+, 296. Calcd for

$C_{15}H_{12}N_4SO$: C, 60.8; H, 4.1; N, 18.9%; M, 296. **5d** (88% yield): m.p. 255 °C; IR (KBr) 3405, 3314, 3218 (NH_2), 2205 (CN), and 1650 cm^{-1} (CO); ^1H NMR (DMSO) δ=2.78 (s, 3H, SCH_3), 3.82 (s, 3H, OCH_3), 7.07–7.26 (m, 4H, C_6H_4) and 7.77 (s, br, 2H, NH_2). Found: C, 57.9; H, 4.0; N, 17.7%; M^+, 312. Calcd for $C_{15}H_{12}N_4SO_2$: C, 57.7; H, 3.9; N, 17.9%; M, 312.

3-Acyl-N-aryl-5-cyano-4-methylthio-2-pyridones 9a-h

A mixture of [bis(methylthio)methylene]-malononitrile **2a** (0.01 mol) or ethyl-2-cyano-3,3-bis(methylthio)acrylate **2b** (0.01 mol), aceto- **8a** or benzoylacetanilide **8b** (0.01 mol) and potassium hydroxide (0.012 mol) in dry dioxan (50 ml), were stirred at room temperature for 24 h. Then diluted with cold water (100 ml), and acidified with HCl. The resulting solid product was collected by filtration and crystallized from ethanol. **9a** (86% yield): m.p. 283°C; IR (KBr) 3276, 3200 (NH_2), 2220 (CN), 1675 (CO), and 1648 cm^{-1} (CO). Found: C, 60.0; H, 4.7; N, 13.8%; M^+, 299. Calcd for $C_{15}H_{13}N_3SO_2$: C, 60.2; H, 4.3; N, 14.0%; M, 299. **9b** (80% yield): m.p. 264°C; IR (KBr) 3303, 3201 (NH_2), 2222 (CN), 1666 (CO), and 1643 cm^{-1} (CO); ^1H NMR (DMSO) δ=2.46 (s, 3H, CH_3), 2.73 (s, 3H, SCH_3), and 7.36–7.7 (m, 4H, C_6H_4). Found: C, 53.6; H, 3.1; N, 12.3%; M^+, 333. Calcd for $C_{15}H_{12}ClN_3SO_2$: C, 54.0; H, 3.6; N, 12.6%; M, 333.5. **9c** (73% yield): m.p. 270°C; IR (KBr) 3242 (NH_2), 2225 (CN), 1669 (CO), and 1633 cm^{-1} (CO). Found: C, 61.8; H, 4.5; N, 13.0%. Calcd for $C_{16}H_{15}N_3SO_2$: C, 61.3; H, 4.8; N, 13.4%; M, 313. **9d** (65% yield): m.p. 258°C; IR (KBr) 3411, 3224 (NH_2), 2222 (CN), 1672 (CO), and 1660 cm^{-1} (CO). Found: C, 58.3; H, 4.3; N, 13.0%; M^+, 329. Calcd for $C_{16}H_{15}N_3SO_3$: C, 58.4; H, 4.6; N, 12.8%; M, 329. **9e** (92% yield): m.p. 220 °C; IR (KBr) 3477, 3312, 3201 (NH_2), 2205 (CN), 1670 (CO), and 1649 cm^{-1} (CO); ^1H NMR (DMSO)δ=2.39 (s, 3H, SCH_3), 7.18 (s, br, 2H, NH_2), and 7.33–7.92 (m, 10H, $2C_6H_5$). Found: C, 66.1; H, 4.1; N, 11.9%; M^+, 361. Calcd for $C_{20}H_{15}N_3SO_2$:, 66.5; H, 4.2; N, 11.6%; M, 361. **9f** (89% yield): m.p. 155°C; IR (KBr) 3450–3272 (OH), 2223 (CN), 1708 (CO), and 1650 cm^{-1}(CO); ^1H NMR (DMSO) δ=2.37 (s, 3H, SCH_3), 7.17–7.32 (m, 10H, $2C_6H_5$), and 15.6 (s, br, 1H, OH). Found: C, 66.8; H, 3.6; N, 7.5%; M^+, 362. Calcd for $C_{20}H_{14}N_2SO_3$: C, 66.3; H, 3.9; N, 7.7%; M, 362. **9g** (90% yield): m.p. 217°C. Found: C, 60.3; H, 3.0; N, 7.5%. Calcd for $C_{20}H_{13}ClN_2SO_3$: C, 60.5; H, 3.3; N, 7.1%; M, 396.5. **9h** (84%

yield): m.p. 163 °C; IR (KBr) 3380 (OH), 2216 (CN), 1710 (CO), and 1658 cm^{-1} (CO). Found: C, 67.5; H, 4.5; N, 7.1%. Calcd for $C_{21}H_{16}N_2SO_3$: C, 67.0; H, 4.3; N, 7.4%; M, 376.

4-Anilino-2-pyridones 6a-d, 10a-d

A mixture of **5** or **9** (0.01 mol) and pure aniline (0.01 mol), were heated for 1 hour at 190 °C. The reaction mixture was diluted with ethanol, the resulting solid product was filtered off and crystallized from ethanol.

6a (65% yield): m.p. 273 °C; IR (KBr) 3645, 3422, 3315 (NH, NH_2), 2205 (CN), and 1650–1612 cm^{-1} (CO). Found: C, 69.3; H, 3.7; N, 21.9%. Calcd for $C_{19}H_{13}N_5O$: C, 69.7; H, 4.0; N, 21.4%; M, 327. **6b** (62% yield): m.p. >300°C; ^1H NMR (DMSO) δ=6.88 (s, br, 2H, NH_2), 7.23–7.77 (m, 9H, $C_6H_5$and C_6H_4), and 13.2 (s, br, 1H, NH). Found: C, 63.5; H, 3.5; N, 19.4%. Calcd for $C_{19}H_{12}ClN_5O$: C, 63.1; H, 3.3; N, 19.4%; M, 361.5. **6c** (54% yield): m.p. >300 °C Found: C, 70.0; H, 4.1; N, 20.8%. Calcd for $C_{20}H_{15}N_5O$: C, 70.4; H, 4.4; N, 20.5%; M, 341. **6d** (69% yield): m.p. 275 °C; IR (KBr) 3448, 3323, 3203 (NH, NH_2), 2206 (CN), and 1690–1650 cm^{-1} (CO); ^1H NMR (DMSO) δ=3.85 (s, 3H, OCH_3), 6.68 (s, br, 2H, NH_2), 6.93–7.6 (m, 9H, C_6H_5 and C_6H_4), and 13.45 (s, br, 1H, NH). Found: C, 67.0; H, 3.9; N, 19.9%. Calcd for $C_{20}H_{15}N_5O_2$: C, 67.2; H, 4.2; N, 19.6%; M, 357. **10a** (63% yield): m.p. 250 °C; IR (KBr) 3325–3018 (NH,NH_2), 2211 (CN), and 1645–1635 cm^{-1} (CO). Found: C, 70.1; H, 4.8; N, 16.0%. Calcd for $C_{20}H_{16}N_4O_2$: C, 69.8; H, 4.7; N, 16.2%; M, 344. **10b** (70% yield): m.p. 295°C; IR (KBr) 3343, 3182 (NH, NH_2), 2215 (CN), 1657 (CO), and 1635 cm^{-1} (CO). Found: C, 63.8; H, 4.2; N, 14.5%. Calcd for $C_{20}H_{15}ClN_4O_2$: C, 63.4; H, 4.0; N, 14.8%; M, 378.5. **10c** (66% yield): m.p. 180 °C; IR (KBr) 3464, 3317, 3212 (NH,NH_2), 2204 (CN), 1690 (CO), and 1650–1622 cm^{-1} (CO). Found: C, 73.6; H, 4.0; N, 14.1%. Calcd for $C_{25}H_{18}N_4O_2$: C, 73.9; H, 4.4; N, 13.8%; M, 406. **10d** (52% yield): m.p. >300 °C. Found: C, 74.5; H, 4.8; N, 10.1%. Calcd for $C_{26}H_{19}N_3O_3$: C, 74.1; H, 4.5; N, 10.0%; M, 421.

4-Phenylhydrazono-2-pyridones 6e-h, 10e-I

A mixture of **5** or **9** (0.01 mol) and phenylhydrazine (0.01 mol) were dissolved in ethanol (30 ml), a few drops of triethylamine were added. The

mixture was refluxed for 3 hours. The resulting precipitated solid was filtered off and recrystallized from ethanol.

6e (72% yield): m.p. >300 °C; IR (KBr) 3388, 3346, 3279 (NH, NH_2), 2195 (CN), and 1671 cm^{-1} (CO). Found: C, 66.9; H, 3.8; N, 24.1%. Calcd for $C_{19}H_{14}N_6O$: C, 66.7; H, 4.1; N, 24.6%; M, 342. **6f** (75% yield): m.p. >300 °C; IR (KBr) 3402, 3311, 3211 (NH, NH_2), 2208 (CN), and 1680–1660 cm^{-1} (CO). Found: C, 60.2; H, 3.2; N, 22.7%. Calcd for $C_{19}H_{13}ClN_6O$: C, 60.6; H, 3.5; N, 22.3%; M, 376.5. **6g** (70% yield): m.p. >300°C; IR (KBr) 3385, 3281 (NH, NH_2), 2192 (CN), and 1650–1623 cm^{-1} (CO). Found: C, 67.1; H, 4.2; N, 23.9%. Calcd for $C_{20}H_{16}N_6O$: C, 67.4; H, 4.5; N, 23.6%; M, 356. **6h** (79% yield) m.p. >300 °C; IR (KBr) 3405, 3318, 3222 (NH, NH_2), 2206 (CN), and 1650 cm^{-1} (CO). Found: C, 64.2; H, 4.0; N, 22.1%. Calcd for $C_{20}H_{16}N_6O_2$: C, 64.5; H, 4.3; N, 22.6%; M, 372. **10e** (82% yield): m.p. 150 °C. Found: C, 67.3; H, 5.0; N, 19.2%. Calcd. for $C_{20}H_{17}N_5O_2$: C, 66.9; H, 4.7; N, 19.5%; M, 359. **10f** (79% yield) m.p. >300°C. Found: C, 59.8; H, 3.9; N, 18.1%. Calcd for $C_{20}H_{16}ClN_5O_2$: C, 60.1; H, 4.1; N, 17.8%; M, 393.5. **10g** (85% yield): m.p. >300°C; IR (KBr) 3471, 3299, 3205 (NH, NH_2), 2211 (CN), 1685 (CO), and 1628 cm^{-1} (CO). Found: C, 71.6; H, 4.3; N, 16.9%. Calcd for $C_{25}H_{19}N_5O_2$: C, 71.3; H, 4.5; N, 16.6%; M, 421. **10h** (56% yield): m.p. 108 °C; IR (KBr) 3400–3201 (NH, NH_2), 2192 (CN), 1685 (CO), and 1650 cm^{-1} (CO). Found: C, 69.6; H, 4.5; N, 13.7%. Calcd for $C_{25}H_{18}N_4O_3$: C, 71.1; H, 4.3; N, 13.3%; M, 422. **10i** (68% yield): m.p. 252 °C; IR (KBr) 3420–3016 (OH, NH), 2214 (CN), I696 (CO), and 1676 cm^{-1} (CO). Found: C, 71.9; H, 4.8; N, 12.4%. Calcd for $C_{26}H_{20}N_4O_3$: C, 71.6; H, 4.6; N, 12.8%; M, 436.

Pyrazolo[4,3-c]pyridines 7a-d, 11a-h

A mixture of **5** or **9** (0.01 mol) and hydrazine (0.01 mol) was dissolved in ethanol (30 ml), a few drops of triethylamine were added. The mixture was refluxed for 3 hours. The resulting precipitated solid was filtered off and recrystallized from ethanol.

7a (62% yield): m.p. >300°C; IR (KBr) 3214 (NH,NH_2), 2198 (CN), and 1660 cm^{-1} (CO). Found: C, 58.9; H, 4.0; N, 31.2%. Calcd for $C_{13}H_{10}N_6O$: C, 58.7; H, 3.8; N, 31.6%; M, 266. **7b** (75% yield): m.p. >300°C; IR (KBr) 3401, 3328, 3230 (NH, NH_2), 2202 (CN), and 1644 cm^{-1} (CO). Found: C, 51.5; H, 2.8; N, 28.4%. Calcd for $C_{13}H_9ClN_6O$: C,

51.9; H, 3.0; N, 28.0%; M, 300.5. **7c** (64% yield): m.p. 253°C; IR (KBr) 3500–3211 (NH, NH_2), 2205 (CN), and 1690–1660 cm^{-1} (CO). Found: C, 59.6; H, 4.5; N, 30.4%. Calcd for $C_{14}H_{12}N_6O$: C, 60.0; H, 4.3; N, 30.0%; M, 280. **7d** (67% yield): m.p. >300 °C; IR (KBr) 3411, 3228 (NH, NH_2), 2197 (CN), and 1680 cm^{-1} (CN). Found: C, 56.5; H, 4.3; N, 28.1%. Calcd for $C_{14}H_{12}N_6O_2$: C, 56.8; H, 4.1; N, 28.4%; M, 296. **11a** (71% yield): m.p. >300 °C; IR (KBr) 3368 (NH, NH_2), 1668 (CO), and 1651 cm^{-1} (CO). Found: C, 59.0; H, 4.4; N, 25.0%. Calcd for $C_{14}H_{13}N_5O$: C, 59.4; H, 4.6; N, 24.7%; M, 283. **11b** (74% yield): m.p. >300 °C; IR (KBr) 3288 (NH, NH_2), and 1670–1632 cm^{-1} (CO). Found: C, 52.5; H, 4.0; N, 22.3%. Calcd for $C_{14}H_{12}ClN_5O_2$: C, 52.9; H, 3.8; N, 22.0%; M, 317.5. **11c** (77% yield): m.p. >300 °C; IR (KBr) 3278 (NH, NH_2), and 1690–1651 cm^{-1} (CO) Found: C, 60.9; H, 5.3; N, 23.4%. Calcd for $C_{15}H_{15}N_5O_2$: C, 60.6; H, 5.1; N, 23.6%; M, 297. **11d** (65% yield): m.p. >300°C. Found: C, 57.1; H, 4.9; N, 22.6%. Calcd for $C_{15}H_{15}N_5O_3$: C, 57.5; H, 4.8; N, 22.4%; M, 313. **11e** (76% yield): m.p. >300°C; IR (KBr) 3294, 3200 (NH, NH_2), 1684 (CO), and 1629 cm^{-1} (CO); ^1H NMR (DMSO) δ=6.64 (s, br, 2H, NH_2), 7.30–7.62 (m, 10H, $2C_6H_5$), 8.12 (s, br, 2H, NH_2), and 13.65 (s, br, 1H, NH). Found: C, 66.5; H, 4.7; N, 20.3%. Calcd for $C_{19}H_{15}N_5O_2$: C, 66.1; H, 4.3; N, 20.3%; M, 345. **11f** (66% yield): m.p. 195 °C; IR (KBr) 3309 (NH, NH_2), 1680 (CO), and 1665 cm^{-1} (CO); ^1H NMR (DMSO) δ=3.7 (s, br, 1H, OH), 7.07 (s, br, 2H, NH_2), 7.29–7.63 (m, 10H, $2C_6H_5$), and 11.0 (s, br, 1H, NH). Found: C, 65.4; H, 4.1; N, 16.0%. Calcd for $C_{19}H_{14}N_4O_3$: C, 65.9; H, 4.0; N, 16.2%; M, 346. **11g** (63% yield): m.p. >300 °C; IR (KBr) 3420–3127 (OH, NH, NH_2) and 1680–1653 cm^{-1} (CO). Found: C, 60.2; H, 3.5; N, 14.3%. Calcd for $C_{19}H_{13}ClN_4O_3$: C, 59.9; H, 3.4; N, 14.7%; M, 380.5. **11h** (60% yield): m.p. 210°C; IR (KBr) 3464–3057 (OH, NH, NH_2) and 1665–1645 cm^{-1} (CO). Found: C, 66.7; H, 4.6; N, 15.9%. Calcd for $C_{20}H_{16}N_4O_3$: C, 66.7; H, 4.4; N, 15.6%; M, 360.

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