Novel Synthesis of Mercaptopurine and Pentaaza-as-Indacene Analogues: Reaction of [Bis(methylthio)methylene]malononitrile and Ethyl 2-Cyano-3,3-bis(methylthio)acrylate with 5-Aminopyrazoles

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A novel synthesis of 7-methylthiopyrazolo[1,5-*a*]pyrimidines via reaction of [bis(methylthio)methylene]-malononitrile and ethyl 2-cyano-3,3-bis(methylthio)acrylate with 5-aminopyrazoles is reported and the synthetic potential of the method is demonstrated.

Many analogues of purine bases and nucleosides have been synthesised and investigated.[1,2] Four of these have clinical importance. 6-Mercaptopurine (6-MP) and 6-thioguanine (6-TG) are valuable antileukemic agents. Allopurinol (or zyloprim), a hypoxanthine analogue that inhibits the synthesis of uric acid, is used to prevent hyperuricemia during chemotherapy and on the treatment of gout. Azathioprine (or imuran), a 6-mercaptopurine derivative, used primarily as an immunosuppressive agent. As a part of our program directed for development of new simple and efficient procedures for the synthesis of purine analogues and other antimetabolites,[3—5] we have recently reported different successful approaches for synthesis of pyrazolopyrimidines.[6] Derivatives of this ring system are interesting because they are purine analogues and as such they have useful properties as antimetabolites in purine biochemical reactions. We report in this paper a new, one-pot synthesis of 7-methylthiopyrazolo[1,5-*a*]-pyrimidines and dipyrazolo[1,5-*a*:4′,3′-*e*]pyrimidines by the reaction of ketene dithioacetals with 5-aminopyrazoles. Moreover, the results of our work aimed to define the scope and limitation of our procedures for the synthesis of mercaptopurine analogues and their important condensed derivatives is also reported. Thus, it has been found that both [bis(methylthio)methylene]-malononitrile **2a** and ethyl 2-cyano-3,3-bis(methylthio)-acrylate **2b** reacted with 5-aminopyrazoles **3a**—**k** in refluxing ethanol containing catalytic amounts of piperidine to give the corresponding 7-(methylthio)pyrazolo[1,5-*a*]pyrimidines **5a**—**v** in good yields (Scheme 1). The structures of **5** were established and confirmed for the reaction products on the basis of their elemental analysis and spectral data (MS, IR, and ^{1}H NMR). The analytical data for **5k** revealed a molecular formula $C_{15}H_{14}N_8SO$ (M^+ 354), ^{1}H NMR spectroscopy was used to confirm this structure for the product. Thus, ^{1}H NMR revealed a band at $\delta=2.94$ assignable to SCH_3 group, a multiplet at $\delta=7.10$—7.22 assigned for aromatic protons and two broad singlets at $\delta=6.98$ and 7.79 assignable for two amino groups. The formation of **5** from the reaction of **2** with **3** is assumed to proceed via intermediacy of **4**, which cyclized to yield the final 5-amino derivatives **5**. Although one may argue that the reaction of **2** with 5-aminopyrazoles **3** may lead to the other possible 7-amino regioisomers. However, analogues for both last two possible isomers were previously synthesized and reoprted to have different NMR chemical shifts for the amino function.[7] Chemical shifts for amino groups in **5** were in agreement with those of 5-amino analogues.[7] Compounds **5** bearing latent functional substituent were found useful for the synthesis of fused derivatives. Thus, it has been found that compounds **5** reacted with aromatic amines in refluxing ethanol containing catalytic amounts of piperidine to afford the corresponding 7-anilino derivatives **6**. The each structure of compounds **6** was established on the basis of elemental analysis and spectral data. Thus, the mass spectrum of **6a** was compatible with the molecular formula $C_{19}H_{15}N_9$ (M^+ 369), and ^{1}H NMR spectrum contained a broad band at $\delta=10.04$ assignable to NH group, a multiplet at $\delta=7.21$—7.50 assigned to the aromatic protons and two broad singlets at $\delta=6.95$ and 7.70 assignable for two NH_2 groups. When compounds **5** were subjected to the reaction with hydrazine, the hydrazino derivatives could not be isolated, but cyclize to the dipyrazolo[1,5-*a*:4′,3′-*e*]pyrimidine derivatives **7**. The structure of compounds **7** was established on the basis of elemental analysis and spectral data. Thus, the IR spectrum of **7a** revealed the absence of a CN band, the mass spectrum was compatible with the molecular formula $C_{13}H_{12}N_{10}$ (M^+ 308), and ^{1}H NMR spectrum contained a broad band at $\delta=6.61$ assignable to two amino functions, a multiplet at $\delta=7.32$—7.59 assigned to the aromatic protons and two broad singlets at $\delta=7.71$ and 8.74 assignable for an NH_2 and NH groups, respectively.

In summary, we have achieved a regiospecific synthesis of interesting mercaptopurine and pentaaza-as-indacene analogues by the reaction of ketene dithioacetals with 5-aminopyrazoles. The compounds obtained seem promising for further chemical transformations and for biological evaluation studies.

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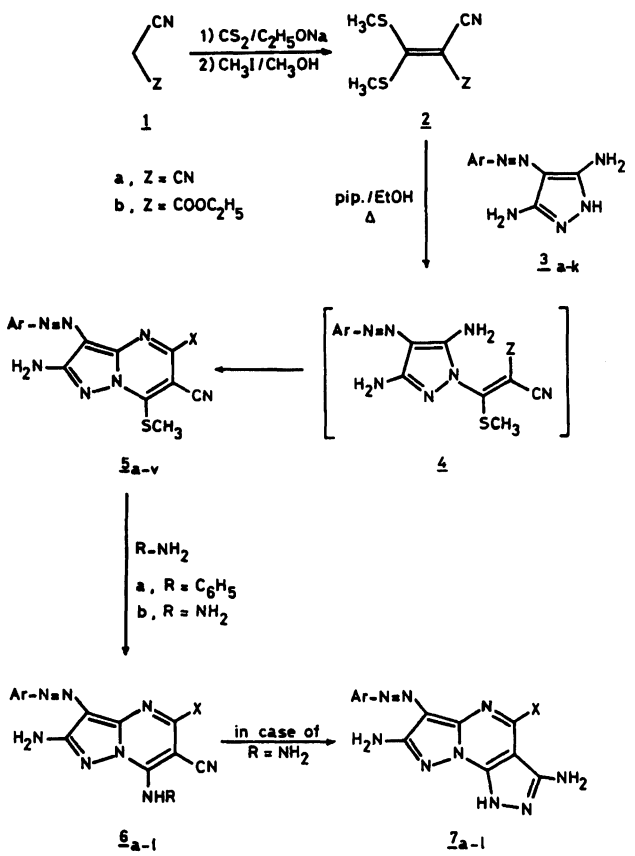

3	Ar
a,	C_6H_5
b,	C_6H_4-4-Br
c,	C_6H_4-2-Cl
d,	C_6H_4-3-Cl
e,	C_6H_4-4-Cl
f,	C_6H_4-2-CH_3
g,	C_6H_4-3-CH_3
h,	C_6H_4-4-CH_3
i,	C_6H_4-2-OCH_3
j,	C_6H_4-3-OCH_3
k,	C_6H_4-4-OCH_3

5	Ar	X		Ar	X
a,	C_6H_5	NH_2	l,	C_6H_5	OH
b,	C_6H_4-4-Br	NH_2	m,	C_6H_4-4-Br	OH
c,	C_6H_4-2-Cl	NH_2	n,	C_6H_4-2-Cl	OH
d,	C_6H_4-3-Cl	NH_2	o,	C_6H_4-3-Cl	OH
e,	C_6H_4-4-Cl	NH_2	p,	C_6H_4-4-Cl	OH
f,	C_6H_4-2-CH_3	NH_2	q,	C_6H_4-2-CH_3	OH
g,	C_6H_4-3-CH_3	NH_2	r,	C_6H_4-3-CH_3	OH
h,	C_6H_4-4-CH_3	NH_2	s,	C_6H_4-4-CH_3	OH
i,	C_6H_4-2-OCH_3	NH_2	t,	C_6H_4-2-OCH_3	OH
j,	C_6H_4-3-OCH_3	NH_2	u,	C_6H_4-3-OCH_3	OH
k,	C_6H_4-4-OCH_3	NH_2	v,	C_6H_4-4-OCH_3	OH

6	R	Ar	X
a,	C_6H_5	C_6H_5	NH_2
b,	C_6H_5	C_6H_4-2-Cl	NH_2
c,	C_6H_5	C_6H_4-4-Cl	NH_2
d,	C_6H_5	C_6H_4-3-CH_3	NH_2
e,	C_6H_5	C_6H_4-4-CH_3	NH_2
f,	C_6H_5	C_6H_4-4-OCH_3	NH_2
g,	C_6H_5	C_6H_5	OH
h,	C_6H_5	C_6H_4-2-Cl	OH
i,	C_6H_5	C_6H_4-4-Cl	OH
j,	C_6H_5	C_6H_4-3-CH_3	OH
k,	C_6H_5	C_6H_4-4-CH_3	OH
l,	C_6H_5	C_6H_4-4-OCH_3	OH

7	Ar	X
a,	C_6H_5	NH_2
b,	C_6H_4-2-Cl	NH_2
c,	C_6H_4-4-Cl	NH_2
d,	C_6H_4-3-CH_3	NH_2
e,	C_6H_4-4-CH_3	NH_2
f,	C_6H_4-4-OCH_3	NH_2
g,	C_6H_5	OH
h,	C_6H_4-2-Cl	OH
i,	C_6H_4-4-Cl	OH
j,	C_6H_4-3-CH_3	OH
k,	C_6H_4-4-CH_3	OH
l,	C_6H_4-4-OCH_3	OH

Scheme 1.

Experimental

IR spectra were recorded for KBr discs on a Pye Unicam SP-1000 or a Shimadzu IR 200 spectrophotometer. ^{1}H NMR spectra were run on Wilmad 270 mHz or Bruker 300 MHz spectrometers with dimethyl sulfoxide as solvent and tetramethylsilane as internal reference. Mass spectra were recorded on an AEI MS 30 mass spectrometer, at 70 eV, in Virginia polytechinic Institute and State University, USA. Analytical data were provided by the Microanalytical Data Centre at Cairo University, Egypt.

7-(Methylthio)pyrazolo[1,5-*a*]pyrimidine-6-carbonitriles 5a—v. A suspension of **2** (0.01 mol) in ethanol (30 ml) was refluxed with 5-aminopyrazoles **3** (0.01 mol) and three drops of piperidine for 4 h, the mixture was left to cool to room temperature. The crystals separating on cooling were fitlered off and crystallized from the appropriate solvent.

5a (90% yield): Mp>300°C; IR (KBr) 3469, 3424, 3284 (NH_2), and 2207 cm^{-1} (CN); ^{1}H NMR (DMSO) δ=2.92 (3H, s, SCH_3), 7.18 (2H, broad s, NH_2), 7.33—7.52 (5H, m, C_6H_5), and 7.75 (2H, broad s, NH_2). Found: C, 51.8; H, 3.7; N, 34.2%; M$^+$, 324. Calcd for $C_{14}H_{12}N_8S$: C, 51.5; H, 3.4; N, 33.9%; M, 324.

5b (75% yield): Mp>300°C; IR (KBr) 3458, 3400 (NH_2), and 2220 cm^{-1} (CN); ^{1}H NMR (DMSO) δ=2.84 (3H, s, SCH_3), 7.09 (2H, broad s, NH_2), 7.28—7.49 (4H, s, C_6H_4), and 7.67 (2H, broad s, NH_2). Found: C, 42.0; H, 2.9; N, 27.5%. Calcd for $C_{14}H_{11}BrN_8S$: C, 41.7; H, 2.7; N, 27.8%.

5c (90% yield): Mp>300°C, IR (KBr) 3480, 3395, 3275 (NH_2), and 2210 cm^{-1} (CN); ^{1}H NMR (DMSO) δ=2.88 (3H, s, SCH_3), 7.22 (2H, broad s, NH_2), 7.26—7.57 (4H, m, C_6H_4), and (2H, broad s, NH_2). Found: C, 46.5; H, 3.4; N, 31.5%; M$^+$, 358. Calcd for $C_{14}H_{11}ClN_8S$: C, 46.8; H, 3.1; N, 31.2%; M, 358.

5d (80% yield): Mp 305 °C; IR (KBr) 3520, 3460, 3400 (NH_2), and 2215 cm^{-1} (CN); ^{1}H NMR (DMSO) δ=6.90 (2H, broad s, NH_2), 7.21—7.50 (4H, m, C_6H_4), and 7.66 (2H, broad s, NH_2). Found: C, 46.5; H, 3.5; N, 31.5%; M$^+$, 358. Calcd for $C_{14}H_{11}ClN_8S$: C, 46.8; H, 3.1; N, 31.2%; M, 358.

5e (80% yield): Mp>300°C; IR (KBr) 3475, 3415 (NH_2), and 2210 cm^{-1} (CN). Found: C, 46.4; H, 2.9; N, 31.3%; M$^+$, 358. Calcd for $C_{14}H_{11}ClN_8S$: C, 46.8; H, 3.1; N, 31.2%; M, 358.

5f (80% yield): Mp>300°C; IR (KBr) 3480, 3420 (NH_2), and 2208 cm^{-1} (CN); ^{1}H NMR (DMSO) δ=2.62 (3H, s, CH_3), 2.88 (3H, s, SCH_3), 7.12 (2H, broad s, NH_2), 7.31—7.53 (4H, m, C_6H_4), and 7.58 (2H, broad s, NH_2). Found: C, 53.4; H, 4.3; N, 32.8%; M$^+$, 338. Calcd for $C_{15}H_{14}N_8S$: C, 53.3, H, 4.1; N, 33.1%; M, 338.

5g (75% yield): Mp>300°C; IR (KBr) 3470, 3380, 3285 (NH_2), and 2210 cm^{-1} (CN). Found: C, 53.6; H, 4.4; N,

33.4%. Calcd for $C_{15}H_{14}N_8S$: C, 53.3; H, 4.1; N, 33.1%.

5h (85% yield) Mp>300°C; IR (KBr) 3450, 3410, 3380 (NH_2), 2222 cm^{-1} (CN). Found: C, 53.5; H, 4.1; N, 33.3%; M^+, 338. Calcd for $C_{15}H_{14}N_8S$: C, 53.3; H, 4.1; N, 33.1%; M, 338.

5i (70% yield): Mp 297 °C; IR (KBr) 3500, 3430 cm^{-1} (NH_2); ^1H NMR (DMSo) δ=3.05 (3H, s, SCH_3), 4.15 (3H, s, OCH_3), 7.15 (2H, broad s, NH_2), 7.22—7.65 (4H, m, C_6H_4), and 8.00 (2H, broad s, NH_2). Found: C, 51.0; H, 4.1; N, 31.3%; M^+, 354. Calcd for $C_{15}H_{14}N_8SO$: C, 50.8; H, 4.0, N, 31.6%; M, 354.

5j (80% yield): Mp 295 °C; IR (KBr) 3390, 3350 (NH_2), and 2210 cm^{-1} (CN). Found: C, 50.5; H, 3.8; N, 31.2%. Calcd for $C_{15}H_{14}N_8SO$: C, 50.8; H, 4.0; N, 31.6%.

5k (85% yield): Mp>300°C; IR (KBr) 3469, 3424, 3284 (NH_2), and 2202 (CN); ^1H NMR (DMSO) δ=2.94 (3H, s, SCH_3), 3.88 (3H, s, OCH_3), 6.98 (2H, broad s, NH_2), 7.10—7.72 (4H, m, C_6H_5), and 7.79 (2H, broad s, NH_2). Found: C, 50.8; H, 4.0; N, 31.6%. Calcd for $C_{15}H_{14}N_8SO$: C, 50.8; H, 4.0; N, 31.6%.

5l (75% yield): Mp>300°C; IR (KBr) 3496, 3425, 3274 (NH_2, NH), 2213 (CN), and 1669 (CO); ^1H NMR (DMSO) δ=2.75 (3H, s, SCH_3), 4.10 (1H, broad s, OH), 7.33—7.71 (5H, m, C_6H_5), and 7.79 (2H, broad s, NH_2). Found: C, 51.2; H, 3.2; N, 29.9%; M^+, 325. Calcd for $C_{14}H_{11}N_7SO$: C, 51.7; H, 3.4; N, 30.2%.; M, 325.

5m (80% yield): Mp 310 °C IR (KBr) 3580, 3500, 3470 (NH_2, NH), 2215 (CN), and 1680 (CO). Found: C, 42.0; H, 2.7; N, 24.0%. Calcd for $C_{14}H_{10}BrN_7SO$: C, 41.6; H, 2.5; N, 24.3%.

5n (59% yield): Mp>300°C; IR (KBr) 3540, 3480, 3400 (NH_2, NH), 2220 (CN), and 1660 cm^{-1} (CO); ^1H NMR (DMSO) δ=2.82 (3H, s, SCH_3), 4.05 (1H, broad s, OH), 7.40—7.78 (4H, m, C_6H_4), and 7.85 (2H, broad s, NH_2). Found: C, 46.5; H, 2.6; N, 27.0%; M^+, 359. Calcd for $C_{14}H_{10}ClN_7SO$: C, 46.7; H, 2.8; N, 27.3%; M, 359.

5o (82% yield): Mp 190 °C; IR (KBr) 3420—3320 (NH_2, NH), 2220 (CN), and 1710 cm^{-1} (CO). Found: C, 47.0; H, 3.0; N, 27.1%. M^+, 359. Calcd for $C_{14}H_{10}ClN_7SO$: C, 46.7; H, 2.8; N, 27.3%; M, 359.

5p (70% yield): Mp>300°C; IR (KBr) 3540, 3450 (NH_2, NH), 2210 (CN), and 1665 cm^{-1} (CO). Found: C, 46.9; H, 3.0; N, 27.1%. Calcd for $C_{14}H_{10}ClN_7SO$: C, 46.7; H, 2.8; N, 27.3%.

5q (80% yield): Mp>300°C; IR (KBr) 3500, 3380 (NH_2, NH), 2210 (CN), and 1675 cm^{-1} (CO). Found: C, 53.4; H, 4.0; N, 30.1%. Calcd for $C_{15}H_{13}N_7SO$: C, 53.1; H, 3.8; N, 28.9%.

5r (70 yield): Mp>300°C; IR (KBr) 3561, 3491 (NH_2, NH), 2213 (CN), and 1684 cm^{-1} (CO). Found: C, 52.8; H, 3.5; N, 28.6%. Calcd for $C_{15}H_{13}N_7SO$: C, 53.1; H, 3.8; N, 28.9%.

5s (72% yield): Mp>300°C; IR (KBr) 3565, 3403, 3276 (NH_2, NH), 2213 (CN), and 1699 cm^{-1} (CO); ^1H NMR (DMSO) δ=2.58 (3H, s, CH_3), 2.81 (3H, s, SCH_3), 4.0 (1H, broad s, OH), 6.99—7.39 (4H, m, C_6H_4), and 7.48 (2H, broad s, NH_2). Found: C, 53.4, H, 3.6; N, 28.7%. Calcd for $C_{15}H_{13}N_7SO$: C, 53.1; H, 3.8; N, 28.9%.

5t (64% yield): Mp>300°C; IR (KBr) 3520—3380 (NH_2, NH), 2220 (CN), and 1660 cm^{-1} (CO). Found: C, 51.0; H, 4.0; N, 27.8%; M^+, 355. Calcd for $C_{15}H_{13}N_7SO_2$: C, 50.7; H, 3.7; N, 27.6%; M, 355.

5u (69% yield): Mp>300°C; IR (KBr) 3450—3320 (NH_2, NH), 2207 (CN), and 1670 cm^{-1} (CO). Found: C, 51.0; H, 3.8; N, 27.8%. Calcd for $C_{15}H_{13}N_7SO_2$: C, 50.7; H, 3.7; N, 27.6%.

5v (72% yield): IR (KBr) 3565, 3394, 3273 (NH_2, NH), 2213 (CN), and 1686 cm^{-1} (CO); ^1H NMR (DMSO) δ=2.73 (3H, s, SCH_3), 3.75 (1H, broad s, OH), 3.95 (3H, s, OCH_3), and 6.85—7.51 (6H, m, C_6H_4 and NH_2). Found: C, 50.5; H, 3.4, N, 27.5%. Calcd for $C_{15}H_{13}N_7SO_2$: C, 50.7; H, 3.7; N, 27.6%.

7-Anilinopyrazolo[1,5-*a*]pyrimidine-6-carbonitriles 6a—1. A mixture of **5** (0.01 mol) and aniline (0.01 mol) were heated at 150 °C (bath temperature) for 30 min, the resulting solid product was triturated with water, filtered off and crystallized from the appropriate solvent.

6a (78% yield): Mp>300°C; IR (KBr) 3481, 3302 (NH_2, NH), and 2201 cm^{-1} (CN); ^1H NMR (DMSO) δ=6.95 (2H, broad s, NH_2), 7.21—7.50 (10H, m, $2C_6H_5$), 7.70 (2H, broad s, NH_2), and 10.04 (1H, broad s, NH). Found: C, 61.6; H, 3.9; N, 34.0%; M^+, 369. Calcd for $C_{19}H_{15}N_9$: C, 61.8; H, 4.1; N, 34.1%.; M, 369.

6b (75% yield): Mp>300°C; IR (KBr) 3565, 3291 (NH_2, NH), and 2202 cm^{-1} (CN); ^1H NMR (DMSO) δ=7.00 (2H, broad s, NH_2), 7.18—7.44 (9H, m, C_6H_5 and C_6H_4), 7.61 (2H, broad s, NH_2), and 10.0 (1H, broad s, NH). Found: C, 56.6; H, 3.5; N, 31.3%. Calcd for $C_{19}H_{14}ClN_9$: C, 56.5; H, 3.5; N, 31.2%.

6c (58% yield): Mp>300°C; IR (KBr) 3510—3420 (NH_2, NH), and 2220 cm^{-1} (CN). Found: C, 56.5; H, 3.5; N; 30.9%; M^+, 403. Calcd for $C_{20}H_{14}ClN_9$: C, 56.5; H, 3.3; N, 31.3%; M, 403.

6d (60% yield); Mp>300°C; IR (KBr) 3390, 3300 (NH_2, NH), and 2210 cm^{-1} (CN). Found: C, 42.4; H, 4.1; N, 32.7%. Calcd for $C_{20}H_{17}N_9$: C, 62.7; H, 4.4; N, 32.9%.

6e (55% yield): Mp>300°C; IR (KBr) 3450, 3400 (NH_2, NH), and 2215 cm^{-1} (CN). Found: C, 62.3; H, 4.4; N, 32.7%. Calcd for $C_{20}H_{17}N_9$: C, 62.6; H, 4.4; N, 32.9%.

6f (80% yield): Mp>300°C; IR (KBr) 3565, 3486, 3367 (NH_2, NH), and 2201 cm^{-1} (CN). Found: C, 60.5; H, 4.4; N, 31.5%; M^+, 399. Calcd for $C_{20}H_{17}N_9O$: C, 60.2; H, 4.3; N, 31.6%; M 399.

6g (86% yield): Mp > 300°C; IR (KBr) 3500, 3390 (NH_2, NH), and 2220 (CN), and 1680 cm^{-1} (CO); ^1H NMR (DMSO) δ=4.12 (1H, broad s, OH), 7.22—7.57 (12H, m, $2C_6H_5$ and NH_2), and (1H, broad s, NH). Found: C, 61.4; H, 3.6; N, 30.0%. Calcd for $C_{19}H_{14}N_8O$: C, 61.6; H, 3.8; N, 30.3%.

6h (75% yield): Mp>300°C; IR (KBr) 3410, 3370 (NH_2, NH), 2205 (CN), and 1666 cm^{-1} (CO). Found: C, 56.6; H, 3.5; N, 27.6%. Calcd for $C_{19}H_{13}ClN_8O$: C, 56.4; H, 3.2; N, 27.7%.

6i (68% yield): Mp>300°C; IR (KBr) 3520, 3460, 3300 (NH_2, NH), 2220 (CN), and 1670 cm^{-1} (CO). Found: C, 56.1; H, 2.9; N, 27.5%. Calcd for $C_{19}H_{13}ClN_8O$: C, 56.4; H, 3.2; N, 27.7%.

6j (73% yield): Mp>300°C; IR (KBr) 3450, 3400 (NH_2, NH), 2210 (CN), and 1690 cm^{-1} (CO). Found: C, 62.8; H, 4.0; N, 29.1%. Calcd for $C_{20}H_{16}N_8O$: C, 62.5; H, 4.2; N, 29.2%.

6k (87% yield): Mp>300°C; IR (KBr) 3565—3334 (NH_2, NH), 2202 (CN), 1662 cm^{-1} (CO). Found: C, 62.3; 4.6; N, 29.2%. Calcd for $C_{20}H_{16}N_8O$: 62.5; H, 4.2; N, 29.2%.

6l (83% yield): Mp>300°C; IR (KBr) 3540—3390 (NH_2, NH), 2210 (CN), and 1690 cm^{-1} (CO). Found: C, 59.7; H, 3.8; N, 27.8%. Calcd for $C_{20}H_{16}N_8O_2$: C, 60.0; H, 4.0; N, 28.0%.

1*H*-Dipyrazolo[1,5-*a*:4′,3′-*e*]pyrimidines 7a—l. A solution of **5** (0.01 mol) and hydrazine (0.01 mol) in ethanol (30 ml) and a few drops of triethylamine was refluxed for 5 h, cooled, the precipitate was filtered off and crystallized from the appropriate solvent.

7a (80% yield): Mp>300°C; IR (KBr) 3480, and 3390 cm^{-1} (NH_2, NH); ^{1}H NMR (DMSO) δ=6.61 (4H, broad s, $2NH_2$), 7.32—7.59 (5H, m, C_6H_5), 7.71 (2H, broad s, NH_2), and 8.74 (1H, broad s, NH). Found: C, 50.4; H, 3.7; N, 45.6%; M^+, 308. Calcd for $C_{13}H_{12}N_{10}$: C, 50.6; H, 3.9; N, 45.5%; M, 308.

7b (70% yield): Mp>300°C; IR (KBr) 3412, and 3329 cm^{-1} (NH_2, NH). Found: C, 45.7; H, 3.4; N, 41.0%. Calcd for $C_{13}H_{11}ClN_{10}$: C, 45.5; H, 3.2; N, 40.9%.

7c (62% yield): Mp>300°C; IR (KBr) 3530, and 3440 (NH_2, NH). Found: C, 45.2; H, 3.0; N, 41.2%. Calcd for $C_{13}H_{11}ClN_{10}$: C, 45.5; H, 3.2; N, 40.9%.

7d (70% yield): Mp>300°C; IR (KBr) 3589, 3465, and 3329 cm^{-1} (NH_2, NH); ^{1}H NMR (DMSO) δ=2.61 (3H, s, CH_3), 6.63 (4H, broad s, $2NH_2$), 7.17—7.49 (4H, m, C_6H_4), 7.58 (2H, broad s, NH_2), and 8.50 (1H, broad s, NH). Found: C, 51.9; H, 4.3; N, 43.1%. Calcd for $C_{14}H_{15}N_{10}$: C, 52.0; H, 4.6; N, 43.3%.

7e (76% yield): Mp>300°C; IR (KBr) 3327 (NH_2, NH); ^{1}H NMR (DMSO) δ=2.34 (3H, s, CH_3), 6.56 (4H, broad s, $2NH_2$), 7.23—7.26 (2H, m, phenyl protons), 7.36 (2H, broad s, NH_2), 7.54—7.57 (2H, m, phenyl protons), and 8.44 (1H, broad s, NH). Found: C, 42.2; H, 4.5; N, 43.5%. Calcd for $C_{14}H_{15}N_{10}$: C, 52.0; H, 4.6; N, 43.3%.

7f (83% yield): Mp>300°C; IR (KBr) 3577, 3408, and 3314 cm^{-1} (NH_2, NH); ^{1}H NMR (DMSO) δ=3.81 (3H, s, OCH_3), 6.36 (2H, broad s, NH_2), 6.48 (2H, broad s, NH_2), 6.92 (2H, m, phenyl protons), 7.38 (2H, broad s, NH_2), 7.61 (2H, m, phenyl protons),a nd 8.44 (1H, broad s, NH). Found: C, 50.0; H, 41.6%; M^+, 338. Calcd for $C_{14}H_{14}N_{10}O$: C, 49.7; H, 4.1; N, 41.4%; M, 338.

7g (63% yield): Mp>300°C; IR (KBr) IR (KBr) 3550, 3440, and 3380 cm^{-1} (NH_2, NH). Found: C, 51.3; H, 3.8; N, 41.0%. Calcd for $C_{13}H_{11}N_9O$: C, 50.5; H, 3.6; N, 40.8%.

7h (66% yield): Mp>300°C; IR (KBr) 3470 and 3400 cm^{-1} (NH_2, NH). Found: C, 44.5; H, 3.2; N, 37.0%. Calcd for $C_{13}H_{10}ClN_9O$: C, 45.4; H, 2.9; N, 36.7%.

7i (75% yield): Mp>300°C; IR (KBr) 3460 and 3400 cm^{-1} (NH_2, NH). Found: C, 45.6; H, 3.1; N, 36.4%. Calcd for $C_{13}H_{10}ClN_9O$: C, 45.4; H, 2.9; N, 36.7%.

7j (72% yield): Mp 195 °C; IR (KBr) 3540 and 3460 cm^{-1} (NH_2, NH). Found: C, 52.2; H, 4.2; N, 38.9%. Calcd for $C_{14}H_{13}N_9O$: C, 52.0; H, 4.0; N, 39.0%.

7k (69% yield): Mp 190 °C IR (KBr) 3500, 3450, and 3390 cm^{-1} (NH_2, NH). Found: C, 51.7; H, 3.8; N, 39.3%. Calcd for $C_{14}H_{13}N_9O$: C, 52.0; H, 4.0; N, 39.30%.

7l (62% yield): Mp>300°C; IR (KBr) 3480, 3455, and 3400 cm^{-1} (NH_2, NH). Found: C, 49.5; H, 3.6; N, 36.9%. Calcd for $C_{14}H_{13}N_9O$: C, 49.6; H, 3.8; N, 37.2%.

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