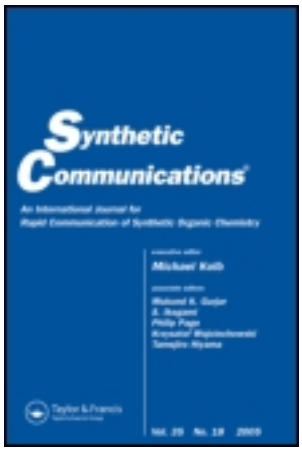

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Novel Mercaptopurine and Thioguanine Analogues: The Reaction of Dimethyl N-Cyanodithioiminocarbonate with Oxo- and Amino-diazoles

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Novel Mercaptopurine and Thioguanine Analogues: The Reaction of Dimethyl *N*-Cyanodithioiminocarbonate with Oxo- and Amino-diazoles

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ABSTRACT

A novel and efficient method for the synthesis of a new variety of methylsulfanyl derivatives of azoloazines and azoloazoles by the reaction of dimethyl *N*-cyanodithioiminocarbonate with diazoles containing oxo- and amino functions. The synthetic potential of the method is demonstrated.

Key Words: Mercaptopurine; Thioguanine; 4-Aminoantipyrine; Diazoles; Dimethyl *N*-cyanodithioiminocarbonate; Azoloazines; Azoloazoles.

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During the course of our studies directed toward exploring the synthetic potential of ketene dithioacetals for synthesizing new classes of novel antimetabolites,[1,2] we have recently reported different successful approaches for synthesis of purine analogues by the reaction of ketene dithioacetals with active methylene functions.[3,4] In an extension of this work, the present paper describes a novel and convenient method for the synthesis of fused imidazoles and pyrazoles carrying a methylsulfanyl group. Derivatives of these ring systems are interesting because they are sulfanylpurine analogues and as such may have useful properties as antimetabolites in purine biochemical reactions.

Thus, it has been found that reaction of cyanamide **I** with carbon disulfide in the presence of KOH followed by the alkylation with methyl iodide gives the dimethyl *N*-cyanodithioiminocarbonate **2**. Reaction of compound **2** with 2-thioxohydantoin derivatives **3a,b** in refluxing ethanol containing a catalytic amount of piperidine gives the corresponding 5-amino-7-(methylthio)-3-thioxo-imidazo[1,5-c]imidazol-1-ones **5**. The structures of **5** were established and confirmed on the basis of their elemental analysis and spectral data (MS, IR, ^{1}H NMR, and ^{13}C NMR). The formation of **5** from the reaction of **2** and thioxohydantoins **3** is assumed to proceed via the intermediacy of acyclic Michael adducts, which cyclize via CH_3SH elimination and addition to the cyano group to yield the final stable diazapentalene analogues **5**. The course of the reaction between **2** and **3** prompted us to investigate this reaction between 2-thioxohydantoin ketene dithioacetals **6** and cyanamide **1** under the same conditions. The products obtained were shown to be the same as those obtained from the reaction of **2** with **3** by their melting points and spectral data to give the imidazo[1,5-c]imidazoles **5**. The 2-thioxohydantoin ketene dithioacetals **6a,b** were prepared by the reaction of 2-thioxohydantoin derivatives **3a,b** with carbon disulfide in the presence of sodium ethoxide followed by treatment with methyl iodide (Sch. 1). The behavior of dithioacetals **2** towards pyrazolones was also investigated. Thus, it has been found that compound **2** react with 3-aryl-5-oxopyrazole **7** in refluxing ethanol containing catalytic amounts of piperidine to yield the corresponding 4-(methylthio)pyrazolo[4,3-e][1,3]oxazin-6-imine derivatives **9** in good yields. The structure of compounds **9** was established on the basis of their elemental analysis and spectral data (IR, ^{1}H NMR, and MS). The formation of **9** from the reaction of **2** and **7** is assumed to proceed via the initial Michael addition of the active methylene in **7** to the double bond of **2** to yield the intermediate **8**. This Michael adduct then cyclizes via CH_3SH elimination followed by cyclization to the cyano group to give the stable product **9**. Compounds **9** could also be prepared by the reaction of pyrazolone ketene ditlnoacetals **10** with cyanamide in refluxing ethanol containing catalytic amounts of piperidine (Sch. 2). The reaction of dimethyl **N**-cyanodithioiminocarbonate **2** with 4-amino-2,3-dimethyl-l-phenylpyrazolin-5-one **11** in refluxing ethanol containing piperidine afforded the

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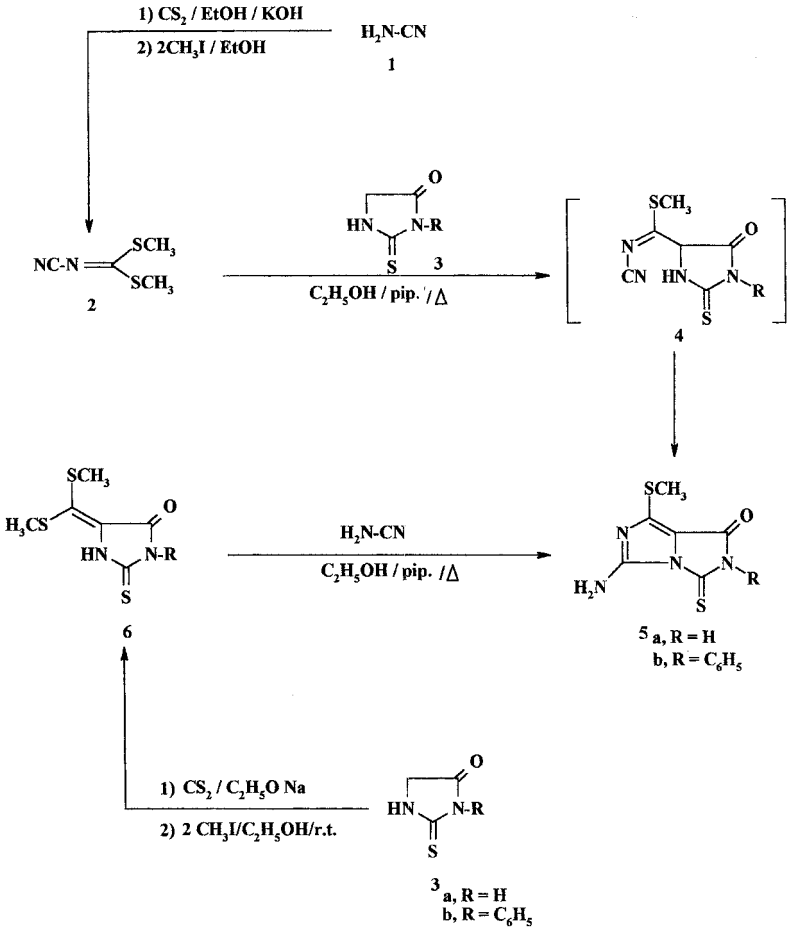

Scheme 1.

corresponding pyrazolone ketene *N*,*S*-acetal derivative **12**. The structure of **12** was established on the basis of its elemental analysis and spectral data (IR, ^{1}H NMR, ^{13}C NMR, and MS). Attempted cyclization of the compounds **12** in boiling ethanolic hydrochloric acid resulted in the formation of a colorless product, two possible isomeric structures, **13** and **14**, for which were considered according to the molecular weight (by mass spectra) (Sch. 3). The ^{1}H NMR spectrum revealed an imine function (D_2O exchangeable) and three different methyl protons indicating that the methyl group at C-3 was not involved in the cyclization. The pyrazolo[4,3-d]pyrimidine structure **14** was

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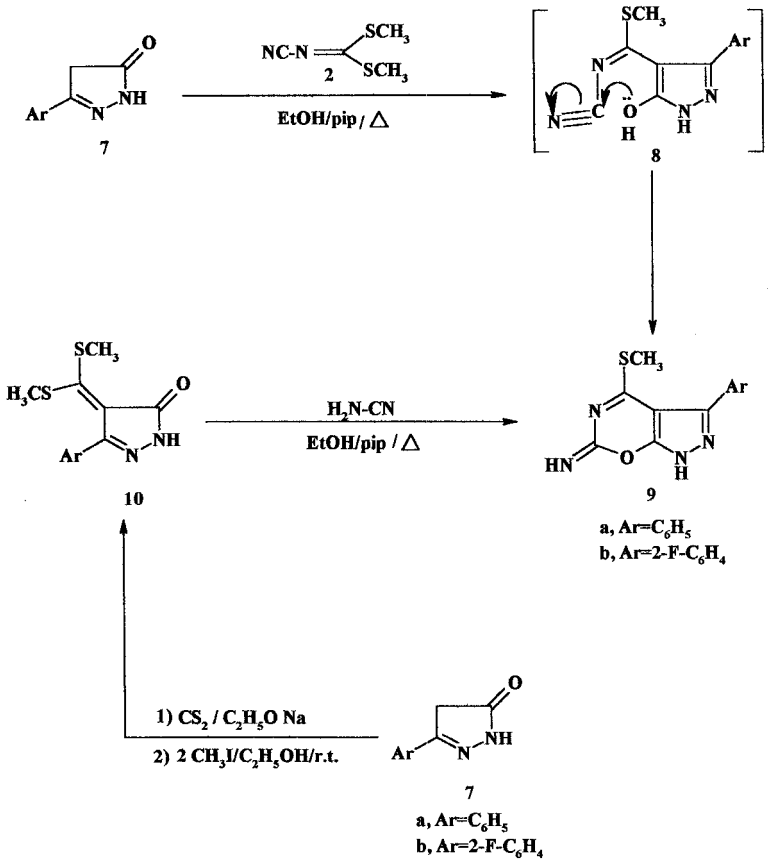
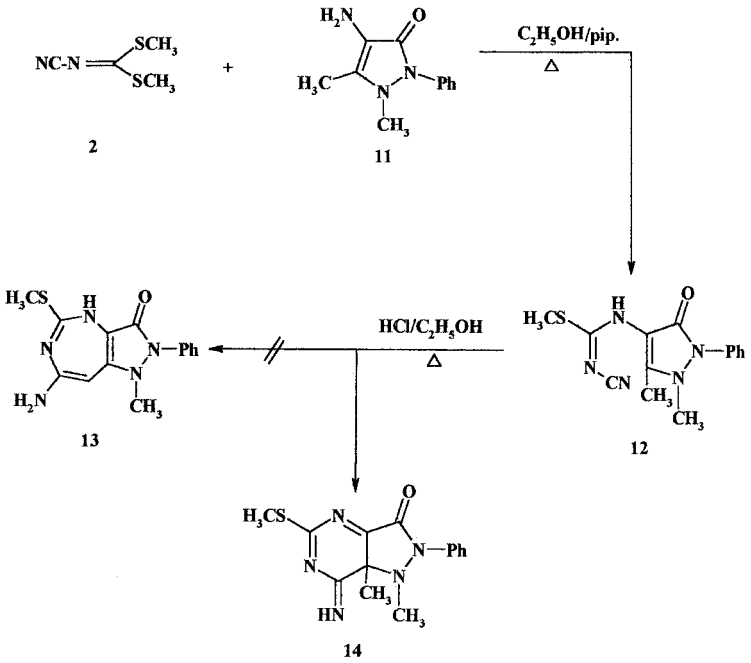


Scheme 2.

therefore suggested for the reaction product and not the pyrazolo[4,3-d]diazapine structure **13**. As far as we know this is the first intramolecular cyclization reaction of this type to be reported for pyrazolone ketene *S*,*N*-acetals. In order to investigate further the scope of reactions of compound **2** with oxo- and amino-diazoles, we studied the reaction of dimethyl *N*-cyanodithioiminocarbonate **2** with aminopyrazoles, thus, it has been found that reaction of dimethyl *N*-cyanodithioiminocarbonate **2** with 5-aminopyrazoles **15** in refluxing ethanol containing catalytic amounts of piperidine gave the corresponding 4-(methylthio)pyrazolo[1,5-a][1,3,5]-triazin-2-amines **18a–f** in good yield. The structure of compounds **18** were established and confirmed on the basis of their elemental analysis and spectral data (IR, ^{1}H

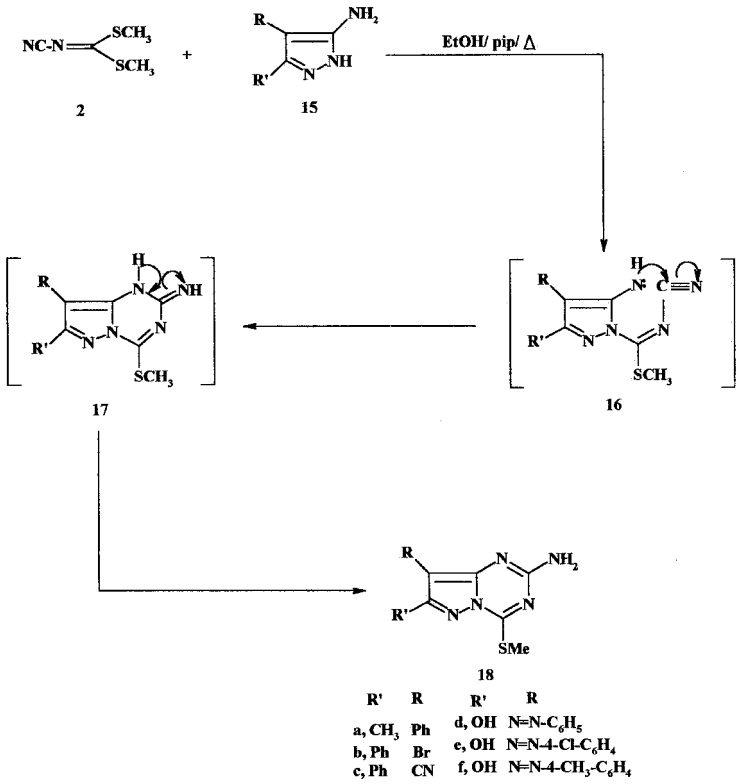


Scheme 3.

NMR, ^{13}C NMR, and MS). The formation of **18** from the reaction of **2** and **15** is assumed to proceed via the intermediate **16**, which cyclized to yield the end products 18 (Sch. 4). Although, one may argue that the reaction of **2** with 5-aminopyrazoles **15** may involve the exocyclic pyrazole nitrogen leading to the other possible 4-amino regioisomers. However, it is known that the endocyclic ring nitrogen is the most nucleophilic center in the molecule and in basic medium will initially add to the unsaturated bouble bond of **2**.[5] In summary, we have achieved a regiospecific synthesis of intersting mercaptopurine and thioguanine analogues by the reaction of dimethyl *N*-cyanodithioiminocarbonate with diazoles containing amino- and oxo-functions.

EXPERIMENTAL

All melting points are uncorrected on a Gallenkamp melting point apparatus. The IR spectra were recorded (KBr disk) on a Perkin Elmer 11650 FT-IR instrument. The ^{1}H NMR spectra were measured on a Varian 400 MHz



Scheme 4.

spectrometer for solutions in $(CD_3)_2$ SO using $Si(CH_3)_4$ as an internal standard. Mass spectra were recorded on a Varian MAT 112 spectrometer.

5-Amino-7-(methylthio)-3-thioxo-2,3-dihydro-1*H*-imidazo [1,5-c]imidazol-1-ones (5a,b)

Method (a): General Procedure

A mixture of imidazolidines **3a,b** (0.01 mol) and dimethyl *N*-cyano-dithioiminocarbonate **2** (0.01 mol, 1.48 g) was boiled under reflux in ethanol (30 mL) containing a catalytic amount of piperidine for 4 hr. The product precipitated was collected and recrystallized from the appropriate solvent.

Method (b): General Procedure

Imidazolidine ketene dithioacetals **6a,b** (0.01 mol) and 3 drops of piperidine were added to a stirred suspension of cyanamide **1** (0.01 mol, 0.4 g) in ethanol (50 mL). The mixture was refluxed for 5 hr and then allowed to cool. The solid precipitate was isolated by suction and recrystallized from the appropriate solvent.

5a: Yellow; m.p. 268–270°C; from DMF; yield, 80%; ν_{max}/cm^{-1} (KBr) 3400–3300 (NH, NE_2); 1710 (CO); ^{1}H NMR (DMSO) δ: 2.60 (s, 3H, SCH_3); 8.55 (s, br, 2H, NH_2), 10.96 (s, br, 1H, NH); $m/z = 214$; calcd. for $C_6H_6N_4OS_2$ (214): C, 33.64; H, 2.80; N, 26.17%; found: C, 33.4; H, 2.5; N, 26.0%. **5b**: Yellow; m.p. 288–290°C, from ethanol–DMF; yield, 70%; ν_{max}/cm^{-1} (KBr) 3450–3300 (NH_2); 1700 (CO); ^{1}H NMR (DMSO) δ: 2.50 (s, 3H, SCH_3); 7.19–7.89 (m, 5H, C_6H_5); 8.90 (s, br, 2H, NH_2); ^{13}C NMR: 19.31 (SCH_3); 126.00–130.00 (phenyl-C); 133.50 (C-8); 138.22 (C-7), 145.62 (C-5); 155.61 (C-3); 170.54 (C-1); m/z 290; calcd. for $C_{12}H_{10}N_4OS_2$ (290): C, 49.66%; H, 3.45%; N, 19.31%; found: C, 49.5%; H, 3.3%; N, 19.0%.

5-[Bis(methylthio)methylene]-2-thioxoirnidazolidin-4-ones (6a,b)

General Procedure

A mixture of 2-thioxohydantoin derivatives **3a,b** (0.01 mol) and sodium ethoxide (0.02 mol, 1.36 g) in ethanol (30 mL) was boiled under reflux for 15 min. The solution was cooled and carbon disulphide (0.01 mol, 0.76 g) was added followed by addition of methyl iodide (0.02 mol, 2.82 g). The solution was stirred for 10 min at room temperature. The formed solid product was filtered off and recrystallized from ethanol.

6a: Yellow; m.p. 248°C; from ethanol; yield, 77%; ν_{max}/cm^{-1} (KBr) 3417–3134 (NH), 1714 (CO); ^{1}H NMR (DMSO) δ: 2.40 (s, 3H, SCH_3); 2.45 (s, 3H, SCH_3); 11.76 (s, 1H, NH); 12.16 (s, 1H, NH); ^{13}C NMR: 17.31 (SCH_3); 17.77 (SCH_3); 128.89 (C-6); 130.02 (C-5); 161.06 (C-2); 174.72 (C-4); $m/z = 220$; calcd. for $C_6H_8N_2OS_3$: C, 32.72%; H, 3.63%; N, 12.72% found: C, 32.5; H, 3.7%; N, 12.7% **6b**: Orange; m.p. 202°C; from ethanol; yield, 85%; ν_{max}/cm^{-1} (KBr) 3155, 3124 (NH), 1720 (CO); ^{1}H NMR (DMSO) δ: 2.05 (s, 3H, SCH_3); 2.51 (s, 3H, SCH_3); 7.32–7.52 (m, 5H, C_6H_5); 12.24 (s, 1H, NH); ^{13}C NMR: 17.36 (SCH_3); 17.97 (SCH_3); 127.37-128.88 (Phenyl-C); 131.99 (C-6); 133.48 (C-5); 159.12 (C-2); 174.31 (C-4); $m/z = 296$; calcd. for $C_{12}H_{12}N_2OS_3$: C, 48.64%; H, 4.05%; N, 9.46%; found: C, 48.8%; H, 3.9%; N, 9.5%.

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3-Aryl-4-(methylthio)pyrazolo [4,3-e][1,3]oxazin-6(1*H*)-imine (9a,b)

Method (a): General Procedure

A suspension of dimethyl *N*-cyanodithioiminocarbonate **2** (0.01 mol, 1.46 g) in ethanol (30 mL) was refluxed with 3-aryl-5-oxopyrazole **7a,b** (0.01 mol) and 3 drops of piperidine for 3 hr, the reaction mixture was left to cool to room temperature and the crystals separated on cooling were filtered off and crystallized from the appropriate solvent.

Method (b): General Procedure

Pyrazolin-5-one ketene dithioacetals **10a,b** (0.01 mol) and 3 drops of piperidine were added to a stirred suspension of cyanamide **1** (0.01 mol, 0.4 g) in ethanol (50 mL). The mixture was refluxed for 5 hr and then allowed to cool. The solid precipitate was isolated by suction and recrystallized from the appropriate solvent.

9a: Yellow, m.p. 188°C (from EtOH), yield (85%). IR (KBr) ν_{max}/cm^{-1} 3440–3360 (NH). ^{1}H NMIR (DMSO) δ: 2.71 (s, 3H, SCH_3), 7.08 (s, br, 1H imine NH). 7.15–7.94 (m, 5H, C_6H_5), 10.07 (s, br, IH, NH); M^+ 258, $C_{12}H_{10}N_4OS$. Calcd: C, 55.81%; H, 3.88%; N, 21.72%. Found: C, 55.6%; H, 3.5%; N, 21.5%. **9b**: Yellow, m.p. 231°C (from DMF), yield (70%). IR (KBr) ν_{max}/cm^{-1} 3400, 3250 (NH). ^{1}H NMR (DMSO) δ: 2.45 (s, 3H, SCH_3), 7.00 (s, br, 1H, imine NH). 7.20–7.99 (m, 411, C_6H_4), 9.89 (s, br, 1H, NH). ^{13}C NMR (DMSO): 17.00 (SCH_3), 120.09–129.22 (phenyl carbons), 143.77 (C-8), 145.00 (C-3), 148.11 (C-4), 156.67 (C-7), 167.00 (C-6). $C_{12}H_9FN_4OS$. Calcd: C, 52.17%; H, 3.26%; N, 20.29%. Found: C, 52.0%; H, 3.3%; N, 20.2%.

5-Aryl-4[bis(methylthio)methylene]-2,4-dihydro-3*H*-pyrazol-3-ones (10a,b)

General Procedure

A mixture of pyrazolin derivatives **7a,b** (0.01 mol) and sodium ethoxide (0.02 mol, 1.36 g) in ethanol (30 mL) was boiled under reflux for 15 min. The solution was cooled and carbon disulphide (0.01 mol, 0.76 g) was added, followed by addition of methyl iodide (0.02 mol, 2.82 g). The solution was stirred for 10 min at room temperature. The formed solid product was filtered off and recrystallized from the appropriate solvent. **10a**: Yellow; m.p. 150°C; from methanol; yield, 70%; ν_{max}/cm^{-1} (KBr); 3480–3670 (NH), 1690 (CO);

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^{1}H NMR (DMSO) δ: 2.55 (s, 3H, SCH_3); 2.62 (s, 3H, SCH_3); 7.11–7.82 (m, 5H, C_6H_5); 11.00 (s, 1H, NH); ^{13}C NMR: 16.00 (SCH_3); 18.43 (SCH_3); 120.56–129.00 (phenyl-C), 130.48 (C-6); 138.00 (C-4); 158.68 (C-5); 177.00 (C-3); $m/z = 264$; calcd. for $C_{12}H_{12}N_2OS_2$: C, 54.55%; H, 4.55%; N, 10.61%. found: C, 54.3%; H, 4.5%; N, 10.3% **10b**: Buff; m.p. 189°C; from ethanol; yield, 70%; ν_{max}/cm^{-1} (KBr) 3380, 3200 (NH), 1700 (CO); ^{1}H NMR (DMSO) δ: 2.44 (s, 3H, SCH_3); 2.58 (s, 3H, SCH_3); 7.05–7.78 (m, 4H, C_6H_4); 12.00 (s, 1H, NH); ^{13}C NMR: 17.00 (SCH_3); 19.12 (SCH_3); 120.11–129.34 (Phenyl-C); 132.78 (C-6); 137.00 (C-4); 157.00 (C-5); 170.00 (C-3); calcd. for $C_{12}H_{11}FN_2OS_2$: C, 51.06%; H, 3.90%; N, 9.93%. Found: C, 51.0%; H, 3.9%; N, 9.5%.

Methyl *N*-cyano-*N*-(1,5-dimethyl-3-oxo-2-phenyl-2,3-Dihydro-1*H*-pyrazol-4-yl)imidothiocarbamate (12)

General Procedure

A mixture of ketene dithioacetal **2** (0.01 mol, 1.46 g) and 4-amino-antipyrine **11** (0.01 mol, 2.03 g) was refluxed in ethanol containing piperidine (3 drops) for 30 min. The formed solid product was collected and recrystallized from ethanol. Yellow crystals, (from ethanol), m.p. 220°C (yield 85%); ν_{max}/cm^{-1} (KBr) 3440, 3380 (NH), 2220 (CN), 1680 cm^{-1} (CO); ^{1}H NMR (DMSO) δ: 2.28 (s, 3H, CH_3), 2.48 (s, 3H, SCH_3), 2.99 (s, 3H, N–CH_3), 7.12–7.90 (m, 5H, C_6H_5), 9.22 (s, 1H, NH); ^{13}C NMR: 11.99 (CH_3), 16.50 (SCH_3), 32.12 (N–CH_3), 109.00 (CN), 121.00–128.32 (phenyl-C), 131.60 (C-5), 148.78 (C-4), 163.00 (C-6), 175.73 (C-3); m/z 301; calcd. for $C_{14}H_{15}N_5OS$: C, 55.5%, H, 4.6%, N, 23.2%. Found: C, 55.81%, H, 4.98%, N, 23.26%.

7-Imino-1,7a-dimethyl-5-(methylthio)-2-phenyl-1,2,7,7a-tetrahydro-3*H*-pyrazolo[4,3-d]pyrimidin-3-one (14)

General Procedure

A solution of each of **12** (0.01 mol, 3.01 g) in ethanol (30 mL) was treated with concentrated hydrochloric acid (1 mL). The reaction mixture was heated under reflux for 30 min and then evaporated under reduced pressure. The resulting solid product was collected by filtration and recrystallized from ethanol. Colorless crystals, (from ethanol), m.p. 260–62°C (yield 50%); ν_{max}/cm^{-1} (KBr) 3400, 3430 (NH), 1700 (CO); ^{1}H NMR (DMSO) δ: 2.26 (s, 3H, CH_3), 2.40 (s, 3H, SCH_3), 2.95 (s, 3H, N–CH_3), 5.13 (s, 1H, =NH),

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7.08–7.59 (m, 5H, C_6H_5); $m/z = 301$; ^{13}NMR: 17.00 (CH_3), 19.13 (SCH_3), 31.67 (N–CH_3), 109.00 (C-7a), 121.22–129.00 (Phenyl-C), 145.17 (C-4a), 157,56 (C-5), 163.98 (C-7), 175.88 (C-3); calcd. for $C_{14}H_{15}N_5OS$: C, 55.81%, H, 4.98%, N, 23.26%. Found: C, 55.6%; H, 4.7%; N, 23.2%.

4-(Methylthio)pyrazolo[1,5-a][1,3,5]triazin-2-amine (18a–f)

General Procedure

A suspension of dimethyl *N*-cyanodithioiminocarbonate **2** (0.01 mol, 1.46 g) in ethanol (30 mL) was refluxed with 5-aminopyrazoles **15a–f** (0.01 mol) and 3 drops of piperidine for 3 hr, the reaction mixture was left to cool to room temperature. The crystals separated on cooling were filtered off, and recrystallized from the appropriate solvent. **18a**: Yellow, m.p. 277–79°C, (from EtOH), yield (80%). IR (KBr) ν_{max}/cm^{-1} 3400, 3300 (NH_2). ^{1}H NMR (DMSO) δ: 2.28 (s, 3H, CH_3), 2.55 (s, 3H, SCH_3), 7.10–7.92 (m, 5H, C_6H_5), 8.10 (s, 2H, NH_2). ^{13}C NMR (DMSO): 13.00 (CH_3), 17.32 (SCH_3), 113.55 (C-9), 120.45–129.84 (Phenyl-C), 147.22 (C-8), 154.97 (C-7), 156.73 (C-4), 160.99 (C-2). ($m/z = 271$); calcd. for $C_{13}H_{13}N_5S$: C, 57.56%; H, 4.80%, N, 25.83%; found: C, 57.5%; H, 4.6%; N, 25.5%. **18b**: Yellow, m.p. 207–09°C (from DMF), yield (80%). IR (KBr) ν_{max}/cm^{-1} 3480, 3300 (NH_2). ^{1}H NMR (DMSO) δ: 2.55 (s, 3H, SCH_3), 7.11–7.92 (m, 5H, C_6H_5), 8.50 (s, br, 2H, NH_2). ^{13}C NMR (DMSO): 18.00 (SCH_3), 115.00 (C-9), 121.67–130.45 (Phenyl-C), 146.00 (C-8), 153.11 (C-7), 158.56 (C-4), 163.28 (C-2). Calcd. for $C_{12}H_{10}BrN_5S$: C, 42.86%; H, 2.98%; N, 20.83%. Found: C, 42.8%; H, 3.0%; N, 21.0%. **18c**: Brown, m.p. > 300°C (from EtOH), yield (80%). IR (KBr) ν_{max}/cm^{-1} 3400 (NH_2). $C_{13}H_{10}N_6S$, calcd: C, 55.32%; H, 3.55%; N, 29.79%; found: C, 55.0%; H, 3.5%; N, 29.5%. **18d**: Yellow, m.p. > 278–280°C (from DMF), yield (70%). IR (KBr) ν_{max}/cm^{-1} 3420 (NH, NH_2); 1685 (CO). ^{1}H NMR (DMSO) δ: 2.58 (s, 3H, SCH_3), 7.19–7.65 (m, 4H, C_6H_5), 8.21 (s, 2H, NH_2), 9.28 (s, 1H, NH). ^{13}C NMR (DMSO): 14.54 (SCH_3), 121.00 (C-9), 122.78–130.14 (Phenyl-C), 150.00 (C-8), 157.61 (C-4), 158.15 (C-2), 171.12 (C-7). ($m/z = 301$); calcd. for $C_{12}H_{11}N_7SO$: C, 47.84%; H, 3.65%; N, 32.56%; found: C, 47.6%; H, 3.5%; N, 32.5%. **18e**: Yellow, m.p. > 300°C (from DMF), yield (70%). IR (KBr) ν_{max}/cm^{-1} 3480, 3400 (NH, NH_2), 1690 (CO). ^{1}H NMR (DMSO) δ: 2.50 (s, 3H, SCH_3), 7.18–7.90 (m, 4H, C_6H_4), 8.50 (s, br, 2H, NH_2), 9.40 (s, br, 1H, NH). ^{13}C NMR (DMSO): 13.00 (SCH_3), 117.00 (C-9), 123.78–128.00 (Phenyl-C), 150.28 (C-8), 155.00 (C-4), 158.00 (C-2), 172.37 (C-7). Calcd. for $C_{12}H_{10}ClN_7OS$: C, 42.92%; H, 2.98%; N, 29.21%. Found: C, 42.6%; H, 3.2%; N, 29.0%. **18f**: Orange, m.p. 288–90°C (from DMF), yield (90%). IR (KBr) ν_{max}/cm^{-1} 3400, 3360 (NH, NH_2); 1690

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(CO). ^{1}H NMR (DMSO) δ: 2.60 (s, 3H, SCH_3), 7.10–7.90 (m, 4H, C_6H_4), 8.20 (s, br, 2H, NH_2), 9.49 (s, br, 1H, NH). ^{13}C NMR (DMSO): 15.00 (SCH_3), 117.00 (C-9), 125.29–129.99 (Phenyl-C), 145.78 (C-8), 157.73 (C-4), 160.17 (C-2), 169.95 (C-7). Calcd. for $C_{13}H_{13}N_7SO$: C, 49.52%; H, 4.13%; N, 31.11%. Found: C, 49.2%; H, 4.4%; N, 31.2%.

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