Some Reactions of 3-Methyl-5-oxo-1-phenyl-Δ^2-pyrazoline-4-thiocarbohydrazide[1]

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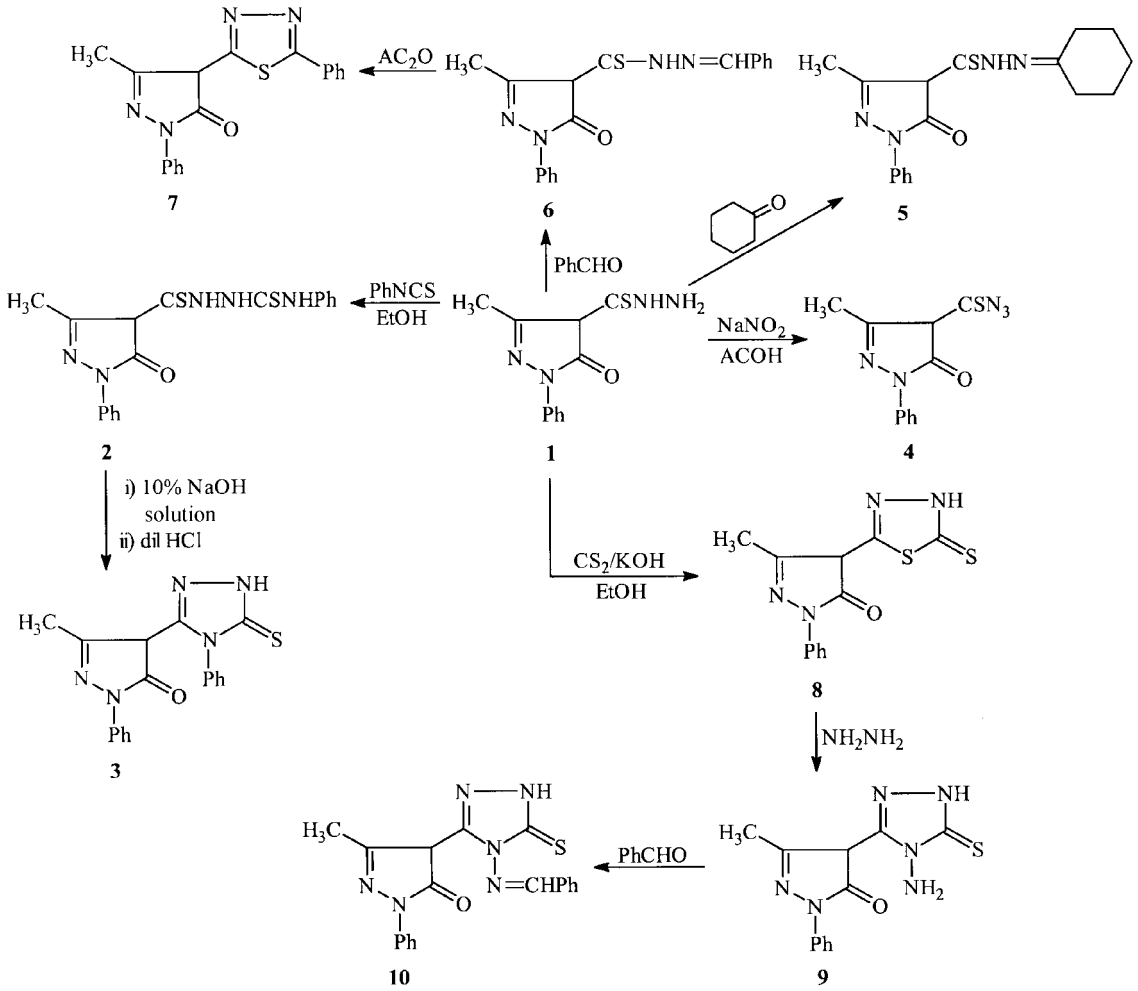
The reactions of 3-methyl-1-phenyl-5-oxo-Δ^2-pyrazoline-4-thiocarbohydrazide towards phenyl isothiocyanate, sodium nitrite, cyclohexanone, aromatic aldehydes, and carbon disulphide has been studied. The Vilsmeier-Haack reaction has been applied on 4-substituted pyrazolone derivatives.

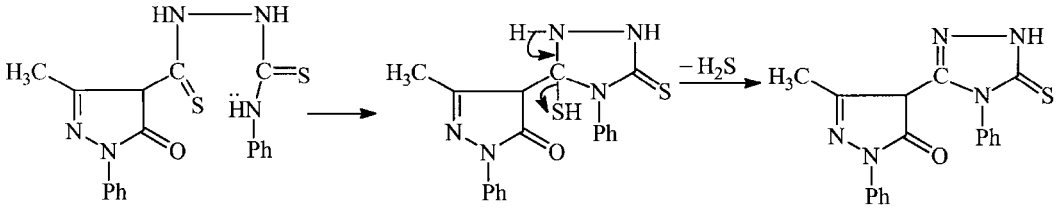
Keywords : 4-Thiocarbohydrazide, 1,3,4-Thiadiazole, 1,3,4-Triazole, Vilsmeier reaction.

There is continuing interest in the chemistry of pyrazolone derivatives[2-10] which mainly arises from the large variety of industrial and biological activities observed.[2,9,11,12] Pyrazolone compounds were recommended in the synthesis of cyanine dyes, which have been used as photosensitizers, filter dyes and electron acceptors.[13] Also, it is of interest to note that 5-thiopyrazolones possess antifungal activity against the rice blast pathogen P. oryzae.[11,12] In this investigation we aimed at the synthesis of 4-substituted-5-pyrazolone derivatives and applied the Vilsmeier-Haack reaction to 4-substituted derivatives to introduce different heterocyclic systems at the 3-position hoping to get improved biologicil activities.

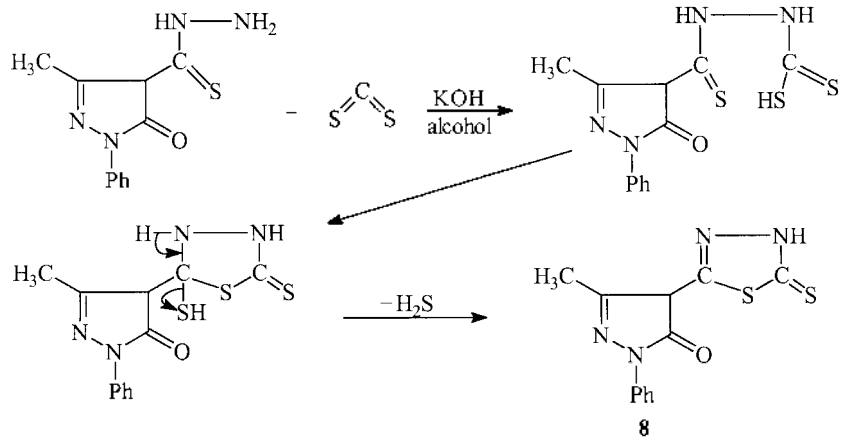
Thus, Heating of 3-methyl-5-oxo-1-phenyl-Δ^2-pyrazoline-4-thiocarbohydrazide[14] (**1**) with phenyl isothiocyanate[15] in absolute ethanol afforded N^1-(4,5-dihydro-3-methyl-5-oxo-1-phenylpyrazol-4-yl)thiocarbonyl-N^4-phenylthiosemicarbazide (**2**). Hydrolysis of **2** with 10% sodium hydroxide solution followed by acidification with dilute hydrochloric



Scheme 1



Scheme 2



Scheme 3

acid gave 4-(4,5-dihydro-1-phenyl-5-thioxo-1,3,4-triazol-2-yl)-3-methyl-1-phenyl-Δ^2-pyrazolin-5-one (**3**). as shown in Scheme 1. The mechanism of this reaction probably proceeded as represented in Scheme 2.

Treatment of **1** with sodium nitrite[16] in acetic acid yielded 4-azidothiocarbonyl-3-methyl-1-phenyl-Δ^2-pyrazolin-5-one (**4**). Compound **1** underwent facile condensation reaction with cyclohexanone/aromatic aldehydes *e.g.* benzaldehyde in absolute ethanol giving the corresponding N^1-cyclohexylidine-3,4-dihydro-3-methyl-5-oxo-1-phenylpyrazol-4-thiocarbohydzide (**5**) and N^1-benzylidine-3,4-dihydro-3-methyl-1-phenylpyrazol-4-thiocarbohydrazide (**6**) respectively. Compound **6** could be cyclized to 3-methyl-1-phenyl-4-(5-phenyl-1,3,4-thiadiazol-2-yl)-Δ^2-pyrazolin-5-one (**7**) on refluxing with acetic anhydride.

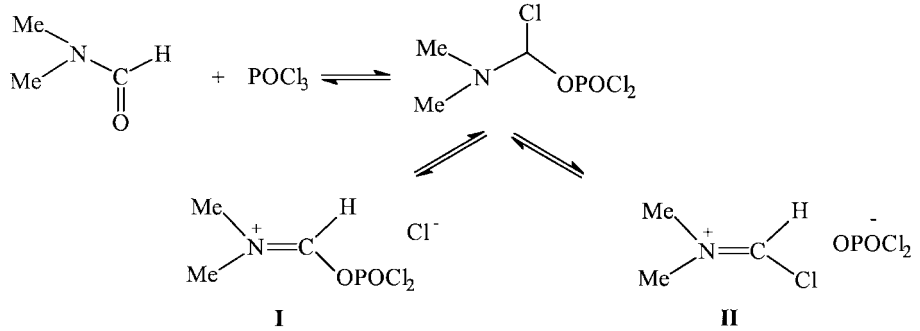
Compound **1** was also subjected to the reaction with carbon disulphide.[17] It was found that **1** reacted with CS_2 in KOH to give 4-(4,5-dihydro-5-thioxo-1,3,4-thiadiazol-2-yl)-3-methyl-1-phenyl-Δ^2-pyrazolin-5-one (**8**).

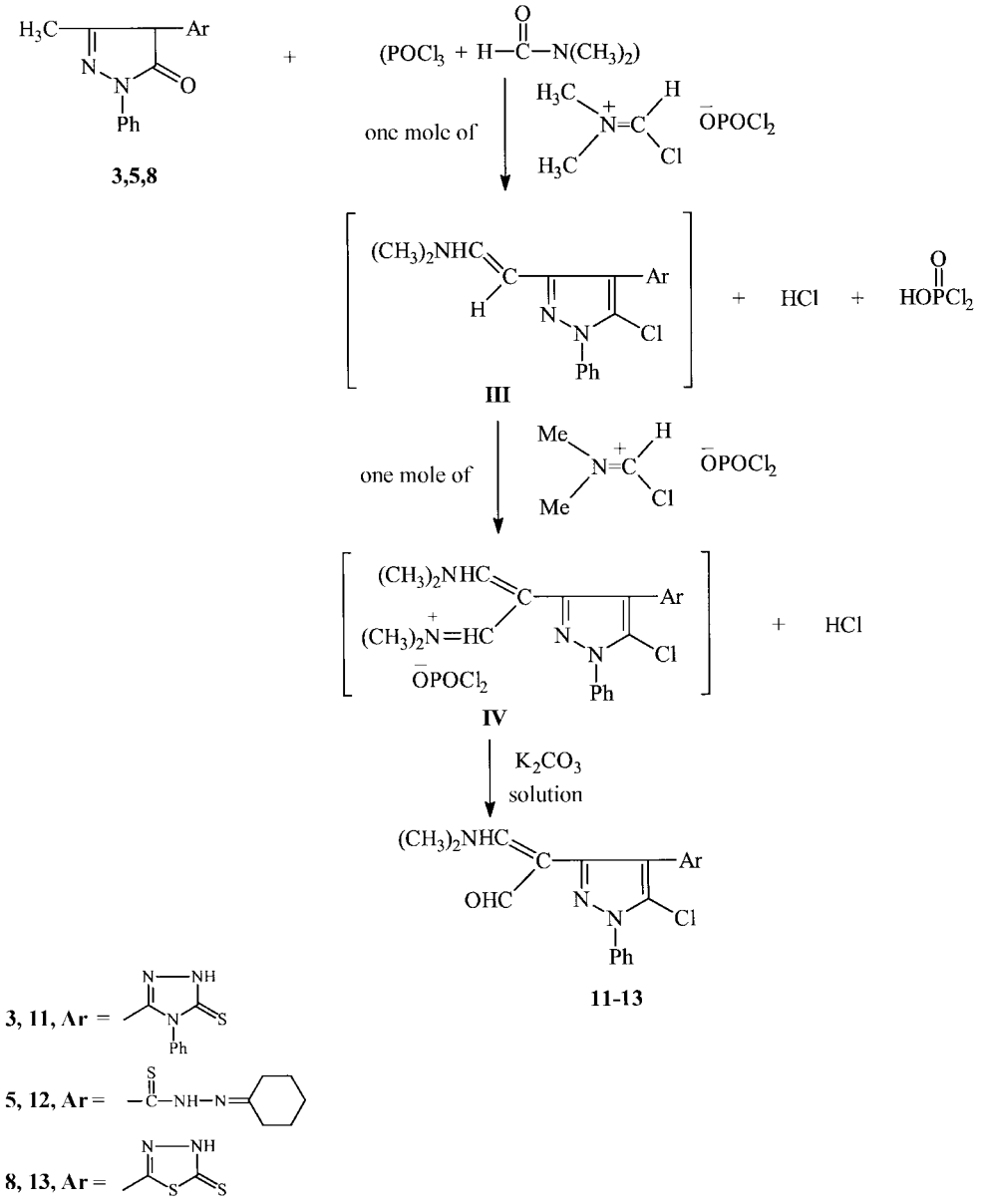
The reaction of 1 with CS_2 may be explained as shown in Scheme 3.

Compound **8** was reacted with hydrazine hydrate to give 4-(1-amino-4,5-dihydro-5-thioxo-1,3,4-triazol-2-yl)-3-methyl-1-phenyl-Δ^2-pyrazolin-5-one (**9**). Compound **9** was condensed with benzaldehyde at the amino group to give the benzylidene amino derivative **10**, as shown in Scheme 1.

The Vilsmeier reaction on **3**, **5** and **8** was performed under the usual conditions.[18] and the expected dimethyl aminoacrolein derivatives **11**. **12** and **13** respectively were obtained in a good yields after treatment of the reaction mixture with potassium carbonate solution. the reaction course may be proceeded as in Scheme 4.

It has to be pointed out that the 5-oxo positions in **3**, **5** and **8** were chlorinated by the action of $POCl_3$ under the experimental conditions. The mechanism of this reaction may be explained as follows: The Vilsmeir reagent made from DMF





Scheme 4

and phosphoryl chloride, is an equilibrium mixture of iminium salts I and II.[19]

Two moles of the mixture of I and II were used in the reaction with the methyl group of the pyrazole **3**, **5** and **8**.

It is well known that the hydrogen of methyl group in our moiety posseses a partially positive charge due to the hyperconjugation character and hence the methyl carbon is readily attacked by a strong and reactive electrophile.

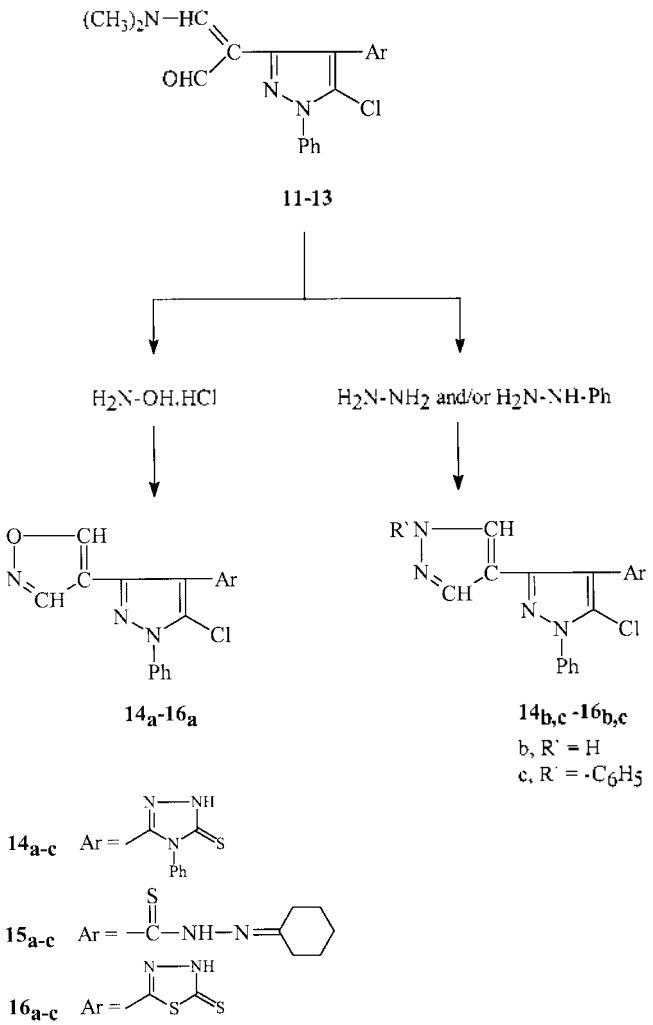
In the first step, one mole of the reagent reacts with the methyl group of compounds **3**, **5** and **8** to yield the N-dimethylamino formylidine methyl compound (III) together with one mole of HCl and one mole of $HOPOCl_2$. In the second step, the other mole of reagent reacts with the N-dimethylamino formylidine methyl compound (III) to give one mole of HCl together with an iminium salt IV which is usually hydrolyzed by alkaline solution to dimethylamino acrolein.

Dimethyl aminoacrolein derivatives **11**, **12** and/or **13** reacted with hydroxylamine, hydrazine and phenylhydrazine in ethanol to give the corresponding 4-isoxazolyl, 4-pyrazolyl and 1-phenyl-4-pyrazolyl derivatives **14**, **15** and **16**, Scheme 5.

The structure of new compounds is confirmed by elemental analysis (Tables 1 & 2) and spectral data (IR, ^{1}H-NMR and MS).

Experimental Section

General. Melting points were uncorrected. ^{1}H-NMR spectra were recorded on a 90 MHz Varian NMR spectrophotometer in a suitable deutrated solvent, using TMS as internal standard (chemical shifts in δ, ppm). Mass spectra were recorded on a JEOL-JMS 600 spectrometer and IR



Scheme 5

spectra in KBr on a Pye-Unicam infrared spectrophotometer (υ_{max} in cm^{-1}).

N^1-(4,5-Dihydro-3-methyl-5-oxo-1-phenylpyrazol-4-yl)-thiocarbonyl-N^4-phenylthiosemicarbazide (2): A mixture of **1** (2.5 g, 0.01 mol) and phenyl isothiocyanate (1.26 mL, 0.01 mol) in 30 mL ethanol was heated under reflux for 1 h. on cooling, the precipitated solid was collected, washed with ethanol, dried and recrystallized from dioxane in 79% yield. The IR (KBr): υ 3350, 3250 (NH), 1690 (C=O), 1605 (C=N) and 1500 (C=S); ^{1}H-NMR (DMSO-d_6): δ 2.49 (s, 3H, CH_3-Ar), 2.64 (s, 2H, two NHCS-), 6.82-7.76 (m, 11H, arom-H) and 10.22 (s, 1H, NHPh).

4-(4,5-Dihydro-1-phenyl-5-thioxo-1,3,4-triazol-2-yl)-3-methyl-1-phenyl-Δ^2-pyrazolin-5-one (3): Compound **2** (1 g) was refluxed in aqueous sodium hydroxide solution (15 mL, 10%) for 1 h. The cold reaction mixture was acidified with dilute HCl (5%). The precipitated product was collected, washed with water, dried and recrystallized from ethanol, yield 0.6 g (66%), m.p 313-315 °C. The IR spectra: (KBr): υ 3200 (NH), 1600 (C=O), 1580 (C=N) and 1500 (C=S); ^{1}H-NMR spectra (DMSO-d_6): δ 2.00 (s, 3H, CH_3-Ar), 7.19-7.75 (m, 11H, arom-H) and 14.08 (s, 1H, NH); MS: m/z (%) 349 [M^-] (84.3), 348 (100), 333 (2.3), 317 (2), 275 (2.4), 228 (1.4), 215 (19.8), 198 (3.4), 156 (4), 138 (2.1), 117 (6.2), 109 (2.9), 105 (8.6), 91 (6.3), 77 (36.4), 65 (3.4), 43 (4.8), 30 (5.3), 26 (24.5), 16 (17.3).

4-Azidothiocarbonyl-3-methyl-1-phenyl-Δ^2-pyrazolin-5-one (4): To a cold suspension of compound **2** (2.5 g, 0.01 mol) in acetic acid (30 mL), a cold solution of sodium nitrite (2 g, 0.03 mol) in water (10 mL) was added dropwise with stirring. Stirring was continued for 1 h at room temperature. The solid product thus formed was filtered, washed with water, dried and recrystallized from ethanol, the IR spectra (KBr): υ 2200 (N_3), 1610 (C=O) and 1505 (C=S); ^{1}H-NMR spectra (DMSO-d_6): δ 2.30 (s, 3H, CH_3-Ar) and 7.26-7.75 (m, 6H, arom-H); MS: m/z (%) 259 [M^-] (50.1), 257 (66), 255 (96.3), 233 (11), 232 (63.5), 223 (28.4), 216 (75.7), 215 (65.8), 214 (44.5), 200 (56), 198 (86.1), 193 (47.7), 191 (78.8), 174 (23.5), 170 (34.7), 161 (62.5), 159 (86.2), 155 (11.9), 154 (24), 148 (9.7), 132 (73.9), 130 (64.5), 127 (86.6), 119 (10.9), 114 (7.4), 107 (12.4), 105 (27.7), 103 (45.9), 99 (9), 96 (67.9), 91 (88), 79 (12.9), 78 (45.8), 77 (79.8), 67 (27.8), 66 (59.1), 64 (100), 52 (15.1), 51 (53.4), 44 (41.9), 42 (19.6), 39 (27.9), 32 (30), 28 (18), 18 (58.3), 17 (25), 16 (9.2), 15 (3.8).

N^1-Cyclohexylidine-3,4-dihydro-3-methyl-5-oxo-1-phenylpyrazol-4-thiocarbohydrazide (5). A mixture of compound **2** (2.5 g, 0.01 mol) and cyclohexanone (1 mL, 0.01 mol) was heated under reflux for 1 h in 30 mL ethanol, a white precipitate was formed on hot, it was filtered off and recrystallized from ethanol. The IR spectra (KBr): υ 2220 (NH), 1605 (C=O), 1595 (C=N) and 1520 (C=S); ^{1}H-NMR spectra (DMSO-d_6): δ 1.55 (s, 6H, H_b of cyclohexane), 2.02 (s, 4H, H_a of cyclohexane), 2.30 (s, 3H, CH_3-Ar), 6.50 (s, 1H, NH) and 7.05-8.00 (m, 6H, arom-H); MS: m/z (%) 328 [M^-] (100), 299 (5.9), 285 (58.6), 272 (17.8), 232 (2.3), 217 (11.9), 199 (13.3), 157 (1.0), 136 (1.9), 131 (4.1), 129 (22.7), 105 (58), 103 (3.1), 96 (10.0), 91 (12.3), 77 (30.4), 69 (9.1), 55 (7.6), 43 (3.7), 41 (17.1), 39 (6.1), 18 (2.6).

N^1-Benzylidine-3,4-dihydro-3-methyl-5-oxo-1-phenylpyrazole-4-thiocarbohydrazide (6). A mixture of compound **1** (1.3 g, 0.005 mol) and benzaldehyde (0.6 mL, 0.005 mol) in ethanol (30 mL) was refluxed for 1 h. On cooling, the precipitated product was collected and recrystallized from ethanol. The IR spectra (KBr): υ 3320 (NH), 1610 (C=O) and 1595 (C=N); ^{1}H-NMR spectra (DMSO-d_6): δ 2.49 (s, 3H, CH_3-Ar), 2.66 (s, 1H, NH) and 6.47-8.69 (m, 12H, arom-H); MS: m/z (%) 336 [M^+] (57.2), 335 (22.6), 334 (100), 307 (3.2), 271 (4.7), 247 (24.6), 232 (5.1), 216 (34.2), 207 (79), 200 (15.1), 180 (4.2), 160 (2.9), 138 (3.5), 130 (9.2), 119 (3.5), 103 (8.3), 91 (5.8), 77 (5.8), 42 (2.4), 16 (4.4).

3-Methyl-1-phenyl-4-(5-phenyl-1,3,4-thiadiazol-2-yl)-Δ^2-pyrazolin-5-one (7). Compound **6** (1 g) was refluxed in acetic anhydride for 2 h. On cooling and dilution with water, an oily compound solidified. The solid product was collected and recrystallized from aqueous ethanol. The IR spectra (KBr): υ 1680 (C=O), 1600 (C=N); ^{1}H-NMR spectra (DMSO-d_6): δ 2.46 (s, 1H, CH_3-Ar) and 7.26-7.78 (m, 11H, arom-H);

Table 1. Physical Data and Elemental Analysis of Compounds (2-10)

No	m.p. °C	Yield (%)	M. Wt.	Elemental Analysis Calcd/ Found.			
				C	H	N	S
2	195-197	79	$C_{18}H_{17}N_3OS_2$	56.39	4.43	18.27	16.71
			(383)	56.10	4.36	18.15	16.54
3	313-315	66	$C_{18}H_{15}N_3OS$	61.89	4.29	20.05	9.16
			(349)	61.64	4.52	19.77	9.35
4	112-114	77	$C_{11}H_9N_5OS$	50.96	3.47	27.02	11.89
			(259)	51.17	3.64	27.10	12.15
5	185	78	$C_{17}H_{20}N_4OS$	62.19	6.09	17.07	9.75
			(328)	62.35	5.93	17.12	9.47
6	115-117	68	$C_{18}H_{16}N_4OS$	64.28	4.76	16.66	9.52
			(336)	64.46	4.57	16.83	9.72
7	167	75	$C_{18}H_{14}N_4OS$	64.67	4.19	16.76	9.58
			(334)	64.45	4.13	16.68	9.34
8	245	41	$C_{12}H_{10}N_4OS_2$	49.65	3.44	19.31	22.06
			(290)	49.47	3.27	19.56	22.13
9	250	87	$C_{12}H_{12}N_6OS$	50.00	4.16	29.16	11.11
			(288)	50.17	4.32	29.21	11.32
10	265	65	$C_{19}H_{16}N_6OS$	60.63	4.25	22.34	8.51
			(376)	60.42	4.42	22.55	8.43

MS: m/z (%) 335 (46.4), 333.7 [M⁻] (100), 277 (0.9), 258 (7.2), 242 (1.1), 218 (4.7), 217 (27.5), 201 (13.4), 171 (1.1), 145 (1.1), 126 (1.7), 121 (6.6), 109 (1.3), 104 (8.7), 97 (1.5), 85 (1.3), 77 (17.2), 71 (2.0), 60 (1.0), 45 (22.9), 43 (14.9), 31 (37.8), 27 (7.2), 18 (92.8), 17 (19.3), 15 (2.1).

4-(4,5-Dihydro-5-thioxo-1,3,4-thiadiazol-2-yl)-3-methyl-1-phenyl-Δ²-pyrazolin-5-one (8). A mixture of compound **1** (2.48 g, 0.01 mol) and potassiumxanthate (1.6 g, 0.01 mol) and absolute ethanol (30 mL) was heated under reflux for 2 h. The reaction mixture was cooled, filtered and the filtrate was acidified with dilute acetic acid, the product formed was collected and recrystallized from ethanol. The IR spectra (KBr): υ 3400 (NH), 1602 (C=O), 1590 (C=N) and 1500 (C=S); ^{1}H-NMR spectra (DMSO-d_6): δ 2.45 (s, 3H, CH_3), 6.98-7.87 (m, 5H, arom-H); MS: m/z (%) 290 [M⁻] (5.7), 289 (100), 257 (7.7), 247 (1.6), 230 (2.9), 216 (7.3), 198 (17.7), 197 (10.1), 157 (4.1), 145 (4.4), 125 (3.5), 118 (2.2), 103 (5.3), 91 (19.9), 83 (2.1), 78 (6.4), 77 (31), 64 (5.9), 59 (3.6), 52 (1.4), 39 (3.7), 18 (8.8).

4-(1-Amino-4,5-dihydro-5-thioxo-1,3,4-thiadiazol-2-yl)-3-methyl-1-phenyl-Δ²-pyrazolin-5-one (9). A mixture of compound **8** (1 g, 0.003 mol) and hydrazinehydrate (0.7 mL, 80%) in 20 mL absolute ethanol was heated under reflux for 2 h, filtered while hot and the filtrate was concentrated and cooled. The solid precipitate was filtered off and recrystallized from aqueous ethanol (1 : 1). The IR spectra (KBr): υ 3400, 3200 (NH_2, NH), 1590 (C=N) and 1500 (C=S); ^{1}H-NMR spectra (DMSO-d_6): δ 2.23 (s, 3H, CH_3), 4.30 (s, 1H, NH), 4.50 (s, 2H, NH_2) and 7.15-7.80 (m, 6H, arom-H); MS: m/z (%) 289 [M⁺] (100), 258 (6.4), 231 (6.9), 217 (26.9), 199 (40.2), 173 (1.0), 157 (18.7), 145 (12.2), 130 (3.5), 118 (6.3), 103 (12.1), 91 (40.7), 83 (8.8), 77 (95.8), 66 (18.1), 59 (12.5), 51 (25.1), 45 (6), 39 (15.4), 28 (5.5), 15 (2).

4-(4-Benzylideneamino-4,5-dihydro-5-thioxo-1,3,4-triazol-2-yl)-3-methyl-1-phenyl-Δ²-pyrazolin-5-one (10). A mixture of compound **9** (1 g, 0.0034 mol) and benzaldehyde (0.36 g, 0.0034 mol) in absolute ethanol (20 mL) was refluxed for 3 h. The solvent was evaporated and the residue was recrystallized from ethanol to give schiffs base 10. The IR spectra (KBr): υ 3400 (NH), 1602 (C=O), 1590 (C=N) and 1500 (C=S); ^{1}H-NMR spectra (DMSO-d_6): δ 2.49 (s, 3H, CH_3), 4.33 (s, 1H, NH), 5.00 (s, 1H, CH=N) and 7.20-7.85 (m, 11H, arom-H).

3-(α-Dimethylaminomethylene-a-formylmethyl)-5-chloro-1-phenyl-4-substituted-Δ²-pyrazoline (11), (12) and (13). To dimethyl formamide (5 mL), cooled to 0 °C, phosphorous oxychloride was added (2.75 mL, 0.0285 mol) and the mixture left to stand for 15 min. To this mixture, the pyrazolone **3**, **5** and **8** (0.0057 mol) in dimethyl formamide (10 mL) was added with stirring, the reaction mixture was heated at 70-80 °C for 8 h. The cooled reaction mixture was poured into ice cold water (10 mL) and basified with K_2CO_3 solution to pH 9. The solid that separated was filtered, washed with water and crystallized from a proper solvent to give compounds **11**, **12** and **13** respectively. The physical and chemical data are listed in Table 2.

11. The IR (KBr): υ 3400 (NH), 1660 (C=O), 1595 (C=N), 1520 (C=S), 750 (C-Cl); ^{1}H-NMR spectra (DMSO-d_6): δ 2.9 (s, 1H, NH), 3.30 (s, 6H, $N(CH_3)_2$), 6.9-7.69 [m, 11H (10H of arom-H), 1H (C=CH)], 9.4 (s, 1H, CHO); MS: m/z (%) 451.5 (13.7), 450 [M⁺] (24.3), 367 (4.7), 334 (1.8), 325 (1.6), 283 (1.7), 263 (3.5), 250 (1.1), 227 (1.1), 218 (3.1), 200 (1.2), 185 (1.7),170 (1.6), 148 (6.4), 129 (4.8), 123 (2.2), 111 (3.5), 97 (5.8), 91 (6.3), 77 (3.4), 71 (7.2), 69 (9.2), 57 (12), 44 (53.5), 28 (30.6), 18 (100), 17 (20.6), 15 (3.5).

12. The IR spectra, υ 3400 (NH), 1675 (C=O), 1585 (C=N), 1520 (C=S), 750 (C-Cl). ^{1}H-NMR spectra (DMSO-d_6): δ 1.83 (s, 6H, H_b of cyclohexane), 2.50 (s, 4H, Ha of cyclohexane), 3.4 (s, 6H, $N(CH_3)_2$), 3.5 (s, 1H, NH), 7.26-8.29 [(m, 7H (arom-H: H of C=CH)], 8.4 (s, 1H, CHO); MS: m/z (%) 429.5 [M⁻] (14.5), 394 (2.4), 367 (1.7), 325 (1.5), 304 (1.9), 259 (5.3), 258 (100), 217 (19), 202 (4.4), 199 (29.7), 187 (10.4), 171 (1.0), 139 (10.3), 132 (1.2), 125 (13.3), 91 (2.8), 81 (4.4), 77 (1.7), 59 (2.0), 45 (7.1), 35 (1.2), 28 (7.9).

13. The IR spectra, υ 3400 (NH), 1660 (C=O), 1600 (C=C), 1500 (C=S), 750 (C-Cl); ^{1}H-NMR spectra (DMSO-d_6): δ 2.79 (s, 1H, NH), 3.32 (s, 6H, $N(CH_3)_2$), 7.47-7.93 [m, 5H (arom-H, H (C=CH)], 8.17 (s, 1H, CHO); MS: m/z (%): 391.5 [M⁺] (77), 367 (1.6), 283 (18), 278 (2.9), 263 (5.5), 255 (2.1), 237 (1.0), 220 (3.1), 218 (7.8), 204 (1.7), 181 (1.7), 164 (1.1), 155 (1.7), 148 (12.5), 139 (1.1), 129 (2.3), 115 (1.9), 98 (25), 97 (3.4), 87 (2.9), 83 (4.2), 78 (1.6), 73 (11.3), 64 (9.2), 57 (9.7), 45 (39.7), 44 (100), 41 (10.3), 36 (13.8), 29 (11.7), 28 (43.9), 18 (95.5), 17 (20.7), 15 (9.7).

3-(4-Isoxazolyl or pyrazolyl)-5-chloro-1-phenyl-4-substituted-Δ²-pyrazoline (14), (15) and (16). To a solution of acrolein derivatives (**11**, **12** and **13**) in ethanol (20 mL) was added an equimolar quantity of hydroxylaminehydrochloride.

Table 2. Physical Data and Elemental Analyses of Compounds (11-16)

No	m.p. °C	Solvent of crystalization	Yield (%)	M. Wt.	Elemental Analysis Calcd/Found.				
					C	H	N	S	Cl
11	225	Ethanol	85	$C_{22}H_{19}N_6OSCl$	58.64	4.21	18.64	7.10	7.88
				(450.5)	58.32	4.23	18.37	6.82	7.53
12	185	Ethanol	82	$C_{21}H_{24}N_5OSCl$	58.67	5.58	16.29	7.45	8.26
				(429.5)	58.25	5.87	16.44	7.15	8.52
13	342	D.M.F.	96	$C_{16}H_{14}N_6OS_2Cl$	49.04	3.57	17.87	16.34	9.06
				(391.5)	49.27	3.47	17.55	16.19	8.83
14_a	202	Ethanol	73	$C_{20}H_{13}N_6OSCl$	57.07	3.09	19.97	7.60	8.44
				(420.5)	56.93	3.12	20.13	7.67	8.53
14_b	185	$CHCl_3$/pet. ether (40-60°)	77	$C_{20}H_{14}N_7SCl$	57.21	3.33	23.36	7.62	8.46
				(419.5)	57.39	3.54	23.12	7.42	8.43
14_c	195	$CHCl_3$/pet. ether (40-60°)	69	$C_{26}H_{18}N_7SCl$	62.96	3.63	19.77	6.45	7.16
				(495.5)	62.72	3.45	19.48	6.37	7.28
15_a	165	Ethanol	63	$C_{19}H_{18}N_5OSCl$	57.07	4.50	17.52	8.01	8.88
				(399.5)	57.27	4.24	17.72	8.22	9.18
15_b	190-191	$CHCl_3$/pet. ether (40-60°)	65	$C_{19}H_{19}N_6SCl$	57.21	4.76	21.07	8.03	8.90
				(398.5)	57.52	4.58	21.22	7.84	8.62
15_c	152	Ethanol	72	$C_{25}H_{23}N_6SCl$	63.22	4.84	17.70	6.74	7.48
				(474.5)	63.46	5.12	17.47	6.87	7.31
16_a	225	$CHCl_3$/pet. ether (40-60°)	75	$C_{14}H_8N_5OS_2Cl$	46.47	2.21	19.36	17.76	9.82
				(361.5)	46.65	2.32	19.55	17.58	9.64
16_b	185	$CHCl_3$/pet. ether (40-60°)	77	$C_{14}H_9N_6S_2Cl$	46.60	2.48	23.30	15.75	9.84
				(360.5)	46.85	2.69	23.48	15.52	10.13
16_c	210	$CHCl_3$/pet. ether (40-60°)	66	$C_{20}H_{13}N_6S_2Cl$	54.90	2.97	19.24	14.66	8.13
				(436.5)	54.73	3.13	19.37	14.80	7.85

hydrazinehydrate or phenylhydrazine respectively. The reaction mixture was refluxed for 2 h, cooled, concentrated and added on the crushed ice. The precipitated coloured solid was filtered, washed throughly with water and crystallized from the proper solvent. The physical and chemical data are quoted in Table 2.

14_a. The IR spectra (KBr): υ 3250 (NH), 1590 (C=N), 1520 (C=S), 750 (C-Cl); ^{1}H-NMR spectra (DMSO-d_6): δ 2.84 (s, 1H, NH), 7.13-8.21 (m, 12H, arom-H); MS: m/z (%) 420 [M^-] (78), 386 (1.6), 380 (77), 366 (66.9), 362 (51.3), 350 (3.6), 316 (15), 307 (2.4), 290 (11.9), 270 (2.5), 256 (3.5), 243 (1.8), 230 (9.8), 222 (2.4), 211 (3.4), 191 (3.1), 177 (3.4), 155 (5.7), 149 (22.5), 135 (32.7), 119 (30.2), 69 (26.5), 57 (31.6), 51 (18.2), 45 (100), 36 (13.5), 28 (34), 18 (83.4), 14 (5.8).

14_b. The IR spectra (KBr): υ 3400, 3200 (NH), 1590 (C=N), 1510 (C=S), 750 (C-Cl); ^{1}H-NMR spectra (DMSO-d_6): δ 2.85 (s, 1H, NH), 2.68 (s, 1H, NH), 6.99-8.17 (m, 12H, arom-H); MS: m/z (%) 420 [M^-] (11.4), 404 (1.6), 380 (3.1), 366 (75.4), 362 (15.9), 352 (11.7), 350 (32.9), 345 (1.1), 331 (10), 321 (2.8), 307 (2.0), 290 (12.8), 273 (3.5), 262 (2.8), 234 (3.5), 218 (9.6), 211 (2.1), 186 (5.5), 179 (3.4), 150 (3.5), 129 (6.2), 118 (18.8), 105 (6.1), 93 (32.6), 91 (25.4), 83 (5.4), 77 (48.3), 65 (10.9), 51 (13.9), 45 (25.3), 44 (49.2), 36 (9.4), 28 (72), 18 (100), 14 (45).

14_c. The IR spectra (KBr): υ 3250 (NH), 1595 (C=N), 1520 (C=S), 750 (C-Cl); ^{1}H-NMR spectra (DMSO-d_6): δ 3.00 (s, 1H, NH), 6.75-8.22 (m, 17H, arom-H); MS: m/z (%) 495 [M^+] (2.2), 460 (1.2), 419 (1.1), 388 (1.1), 366 (29.1), 350 (74.6), 332 (10.8), 321 (2.4), 316 (20.8), 307 (2.3), 285 (3.4), 268 (8.4), 242 (3.7), 222 (3.7), 218 (15.6), 200 (3.7), 184 (11.1), 168 (7.1), 160 (24.6), 150 (7.3), 132 (21.4), 119 (32.5), 109 (9.4), 93 (100), 91 (54.4), 83 (7.1), 78 (17.9), 77 (91.7), 65 (33.2), 57 (11.5), 51 (26.8), 44 (30.2), 36 (19.2), 28 (25.4), 18 (99.5), 15 (4.1).

15_a. The IR spectra: υ 3300 (NH), 1585 (C=N), 1500 (C=S), 750 (C-Cl); ^{1}H-NMR spectra ($CDCl_3$): δ 1.52 (s, 6H, H_b of cyclohexane), 2.24 (s, 4H, H_a of cyclohexane), 2.69 (s, 1H, NH), 7.00-8.20 (m, 7H, arom-H); MS: m/z (%): 399.5 [M^-] (2.7), 363 (1.8), 327 (6.5), 298 (1.1), 284 (13.1), 271 (10.7), 257 (100), 216 (13.6), 201 (4.1), 199 (24.6), 198 (18.1), 185 (2.8), 171 (3.0), 149 (3.2), 138 (6.1), 129 (11.7), 125 (88.3), 118 (4.3), 163 (4.7), 96 (5.1), 91 (45.1), 85 (4.4), 83 (12.4), 77 (73), 67 (11.4), 64 (14.4), 38 (6.2), 28 (24.5), 18 (19.7).

15_b. The IR spectra: υ 3400, 3200 (NH), 1600 (C=N), 1510 (C=S), 750 (C-Cl); ^{1}H-NMR spectra (DMSO-d_6): δ 1.59 (s, 6H, H_b of cyclohexane), 2.20 (s, 4H, H_a of cyclohexane), 2.78 (s, 1H, NH), 3.5 (s, 1H, NH of pyrazoline), 7.00-8.82 (m, 9H, arom-H).

15_c. The IR spectra: υ 3400 (NH), 1585 (C=N), 1510 (C=S), 750 (C-Cl); ^{1}H-NMR spectra ($CDCl_3$): δ 1.56 (s, 6H, H_b of cyclohexane), 2.20 (s, 4H, H_a of cyclohexane), 2.6 (s, 1H, NH), 7.00-8.11 (m, 12H, arom-H).

16_a. The IR spectra: υ 3200 (NH), 1620 (C=C), 1590 (C=N), 1520 (C=S), 750 (C-Cl); ^{1}H-NMR spectra (DMSO-

d_6): δ 2.70 (s, 1H, NH), 7.38-8.16 (m, 7H, arom-H); MS: m/z (%) 361.5 [M^+] (100), 340 (2), 327 (1.7), 289 (5.4),255 (8.9), 235 (3), 217 (1.9), 215 (18.1), 198 (42.1), 197 (22), 192 (1.8), 174 (8.3), 157 (2.8), 150 (15.2), 144 (4), 136 (10.5), 129 (3.5), 118 (38.6), 105 (8.2), 97 (6.5), 91 (30), 81 (15.3), 77 (42.4), 73 (37.6), 69 (27.8), 65 (11), 57 (11.3), 45 (100), 93 (22.5), 41 (11.5), 27 (15), 18 (2.0), 15 (5.9).

16$_b$. The IR spectra: υ 3400, 3200 (NH), 1520 (C=S), 750 (C-Cl); ^{1}H-NMR spectra (DMSO-d_6): δ 2.54 (s, 1H, NH), 2.66 (s, 1H, NH), 7.36-8.18 (m, 7H, arom-H); MS: m/z (%) 340.5 [M^+] (1.8), 306.7 (1.9), 297 (1.6), 278 (1.7), 261 (2.4), 255 (18.8), 250 (2.2), 236 (7.5), 228 (2.4), 213 (5.4), 203 (1.6), 199 (13.1), 192 (3), 183 (4), 167 (6.4), 157 (4.2), 149 (15.1), 137 (6), 132 (3.4), 123 (7.1), 115 (7.3), 105 (5.4), 95 (11.4), 91 (9), 83 (19.9), 77 (8.8), 73 (25.4), 69 (28.7), 67 (8.7), 61(6.1), 60 (26.4), 57 (35.4), 55 (26.9), 51 (3.3), 45 (100), 43 (46.1), 41 (20), 39 (4.5), 36 (3.1), 32 (9.2), 28 (46.4), 27 (13.3), 18 (99.6), 17 (22.1), 15 (5.3).

16$_c$. The IR spectra: υ 3400 (NH), 1600 (C=C), 1520 (C=S), 750 (C-Cl); ^{1}H-NMR spectra (DMSO-d_6): δ 2.37 (s, 1H, NH), 7.35-7.99 (m, 12H, arom-H).

References And Notes

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