# Reactions of 1-(2-benzothiazolyl)-4-(dicyanomethylene)-3-methyl-2-pyrazolin-5-one towards Amines

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**ABSTRACT:** The reaction of 1-(2-Benzothiazolyl)-4-(dicyanomethylene)-3-methyl-2-pyrazolin-5-one (1) with amines has been investigated. Primary and secondary amines react with (1) to yield 4-substituted(aminocyanomethylene)pyrazolone derivatives (4a-j) and (6a, b) respectively. o-substituted arylamines afford 4-azolylidene pyrazolone derivatives (8a, b) Tertiary amines (9a, b) adds to the dicyano derivative (1) by stirring in acetic acid solution and in exclusion of light to give adducts (10a, b) The latter products gave the condensation products (11a, b) by heating in DMF.

***Key words :*** 2-pyrazolin-5-one derivatives.

## INTRODUCTION

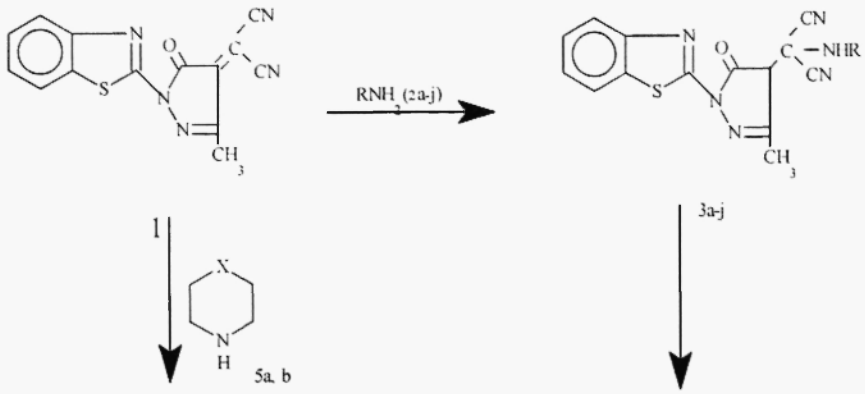
Since the last few years we are interested in the reactions of pyrazolones.[1-4]. Owing to the vitial importance of pyrazolone derivatives due to their wide applications for industerial uses [5-7] and medicial fields[7-10], I aim to synthesis some heterocyclic compounds starting with 1-(2-benzothiazolyl)-4-(dicyanomethylene)-3-methyl-2-pyrazolin-5-one (1)[4] hoping that such new compounds will have certain biological effects or other applied uses.

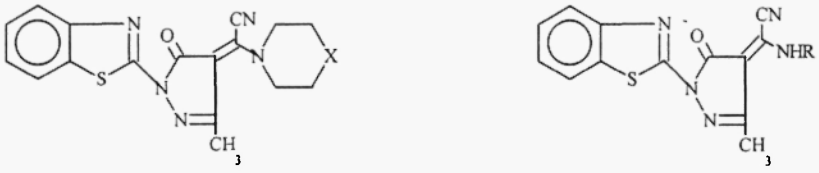
## RESULTS AND DISCUSSION

I found that compound (1) condenses with primary amines (2a-j) by attack at C-$\alpha$ of the dicyanomethylene moiety[11-13] to afford (3) which loses hydrogen cyanide yielding 4-alkyl- or aryl-(aminocyanomethylene)-3-methyl-2-pyrazolin-5-one derivatives (4a-j). In the same manner secondary amines (5a,b) reacts with 1 to give the corresponding products (6a, b). Structures of (4a-j) and (6a, b) were confirmed by spectral and elemental analyses.

o-Phenylenediamine and o-aminophenol (7a, b) reacts with the dicyano derivative (1) to give 4-azolylidene pyrazolones (8a, b) through elemination of two molecules of hydrogen cyanide.

N,N-Dimethylaniline and N,N-diethylaniline as tertiary amines adds to the dicyano derivative (1) in acetic acid soultion and in exclusion of light to give the disubstituted malononitriles (10a, b). These colourless adducts (10a, b) are unstable when heated in DMF, hydrogen cyanide is eleminated and deeply coloured arylcyanomethylene pyrazolone derivatives (11a, b) are formed[14].

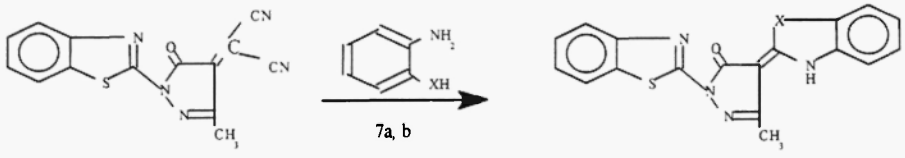


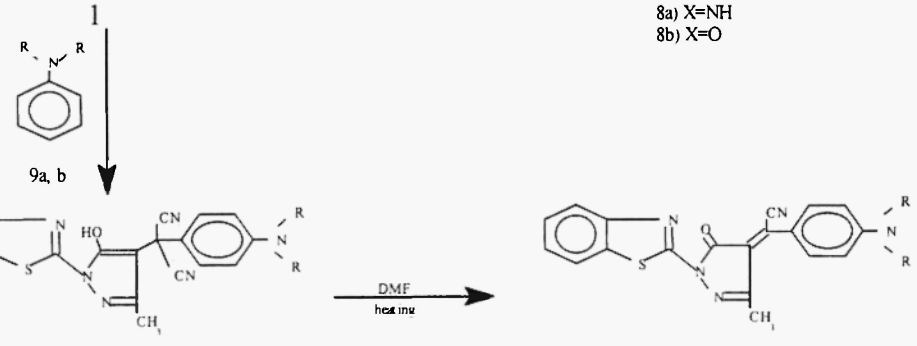
4a-j

6a) X=$CH_2$
6b) X=O

| | R | | R |
|---|---|---|---|
| 4a | $CH_3$ | f | $C_6H_4OH(4)$ |
| b | $C_2H_5$ | g | Cyclohexyl |
| c | $C_6H_5$ | h | benzyl |
| d | $C_6H_4CH_3$-(4) | i | $NH_2$ |
| e | $C_6H_4OCH_3$-(4) | j | NHph |




8a) X=NH
8b) X=O




10a, b

11a, b

9-11 : a) R=Me
b) R=Et

## EXPERIMENTAL

All melting points are uncorrected. Infrared spectra were recorded with a Shimadzo 408 Infrared spectrometer using KBr discs. $^1$H NMR spectra were measured with a Varian XL-100 spectrometer; Chemical Shifts are reported in ppm; initial standard was tetramethylsilane (δ scale). Mass spectra were obtained at Cairo University. Microanalyses were carried out at microanalysis unit at Assiut University.

**1-(2-benzothiazolyl)-4-(dicyanomethylene)-3-methyl-2-pyrazolin-5-one(1)** was prepared according to ref[4].

**Reactions of 1-(2-benzothiazolyl)-4-(dicyanomethylene)-3-methyl-2-pyrazolin 5-one (1) with primary, secondary amines and o-substituted arylamines : General Method :** A mixture of an equimolar amount of the dicyano derivative (1) and primary, secondary amine or o-substituted arylamine (2, 5 or 7) (1 m mol) in absolute ethanol (30 ml) was stirred for 1/2-2h. The precipitated product was collected and crystallized from the proper solvent. The results are listed as the following :

(4a) : Yield 71%, pale yellow crystals, m.p. 272 °C; (ethanol). - IR : ν = 3250 cm$^{-1}$ (NH); 1650 (CO). - MS : m/z (%) = 297 (14.6) [M$^+$], 282 (28.3) [M$^+$-CH$_3$], Found C, 56.42; H, 3.81; N, 23.62; S, 10.70, $C_{14}H_{11}N_5OS$ (297.3), requires C 56.55 H 3.73 N 23.55 S 10.78.

(4b) : Yield 61%, pale yellow crystals, m.p. 275 °C (ethanol). - IR : ν = 3200 cm$^{-1}$ (NH); 1680 (CO). -$^1$H NMR (DMSO) : δ = 1.2 (t, 3H, CH$_3$), 2.1 (s, 3H, CH$_3$), 3.4 (q, 2H, CH$_2$), 7.2-8.0 (m, 4H, aromatic H), Found C 57.81 H 4.11 N 22.52 S 10.28., $C_{15}H_{13}N_5OS$ (311.4), requires C 57.86 H 4.21 N 22.49 S 10.30.

(4c) : Yield 67%, orange crystals, m.p. 222 °C (ethanol) - IR : ν 3400 cm$^{-1}$ (NH) 1670 (CO). -MS : m/z (%) = 359 (91.4) [M$^+$], 267 (13.6) [M$^+$-(HN-C$_6$H$_5$)], Found C 63.52 H 3.60 N 19.38, $C_{19}H_{13}N_5OS$ (359.4), requires C 63.50 H 3.65 N 19.49.

(4d) : Yield 69%, orange crystals, m.p. 219 °C (benzene) IR : ν 1670 cm$^{-1}$ (CO). - $^1$H NMR ($CDCl_3$) : δ = 2.2 (s, 3H, CH$_3$), 2.4 (s, 3H, CH$_3$), 7.2-8.1 (m, 8H, aromatic H), 12.0 (s, 1H, NH)., Found C 64.42 H 4.11 N 18.67., $C_{20}H_{15}N_5OS$ (373.4), requires C 64.33 H 4.05 N 18.75.

(4e) : Yield 82%, orange crystals, m.p. 210 °C (ethanol). - IR : ν 1650 cm$^{-1}$ $^1$H NMR ($CDCl_3$) : δ = 2.6 (s, 3H, CH$_3$), 3.85 (s, 3H, OCH$_3$), 7.0 - 8.1 (m, 8H, aromatic H), 11.9 (s, 1H, NH). - MS : m/z (%) = 389 (56.6) [M$^+$], 374(11) [M$^+$-CH3], 358(1.2) [M$^+$-OCH$_3$], Found C 61.62 H 3.92 N 17.82 S 8.09, $C_{20}H_{15}N_5O_2S$ (389.4), requires C 61.68 H 3.88 N 17.98 S 8.23.

(4f) : Yield 83%, red crystals, m.p. 296 °C (ethanol). - IR : ν 3400 cm$^{-1}$ (NH); 1670 (CO). - $^1$H NMR (DMSO) : δ = 2.4 (s, 3H, CH$_3$), 6.8 - 8.2 (m, 9H, 8 aromatic H + NH), 10.0 (s, 1H, OH). - MS : m/z (%) = 375 (70.5) [M$^+$], 358 (3.1) [M$^+$-OH], 367(13.6) [M$^+$-HNC$_6$H$_4$OH(4)], Found C 60.71 H 3.53 N 18.55 S 8.42, $C_{19}H_{13}N_5O_2S$ (375.4), requires C 60.79 H 3.49 N 18.66 S 8.54.

(4g) : Yield 81%, cream crystals, m.p. 224 °C (ethanol) IR : ν 1660 cm$^{-1}$ (CO). - $^1$H NMR ($CDCl_3$) : δ = 1.2 - 2.5 (m, 10 H, cyclohexyl H), 2.5 (s, 3H, CH$_3$), 7.4 - 8.2 (m, 4H, aromatic H), 10.6 (s, 1H, NH), Found C 62.52 H 5.17 N 19.07, $C_{19}H_{19}N_5OS$ (365.5), requires C 62.45 H 5.24 N 19.16.

(4h) : Yield 89%, yellow crystals, m.p. 225 °C (ethanol). IR : ν 3200 cm$^{-1}$ (NH); 1775 (CO) - $^1$H NMR ($CDCl_3$) : δ = 2.5 (s, 3H, CH$_3$), 4.8 (s, 2H, CH$_2$), 7.2 - 8.1 (m, 9H, aromatic H), 10.4 (s, 1H, NH), Found C 64.39 H 4.09 N 18.81 S 8.65. $C_{20}H_{15}N_5OS$ (373.4), requires C 64.33 H 4.05 N 18.75 S 8.59.

(4i) : Yield 71%, brownish yellow crystals, m.p. 189 °C (ethanol). - IR :ν = 3350, 3250 $cm^{-1}$ ($NH_2$), 2200 (CN). - MS : m/z (%) = 298 (100) [$M^+$], 282(13) [$M^+$-$NH_2$], Found C 52.51 H 3.29 N 28.07, $C_{13}H_{10}N_6OS$ (298.3), requires C 52.34 H 3.38 N 28.17.

(4j) : Yield 67%, cream crystals, m.p. 168 °C (ethanol). - IR : ν = 3400 $cm^{-1}$ (NH), 2210 (CN). - $^1$H-NMR ($CDCl_3$) : δ = 2.4 (s, 3H, $CH_3$), 7.05 - 7.95 (m, 11H, 9 aromatic H + 2 NH), Found C 60.91 H 3.67 N 22.36., $C_{19}H_{14}N_6OS$ (374.4), requires C 60.95 H 3.77 N 22.45.

(6a) : Yield 61%, cream crystals, m.p. 215 °C (methanol). - IR : ν 2220 $cm^{-1}$ (CN), 1680 (CO). - MS : m/z (%) = 351 (62.4) [$M^+$], Found C 61.41 H 4.73 N 19.81, $C_{18}H_{17}N_5OS$ (351.4), requires C 61.52 H 4.88 N 19.93.

(6b) : Yield 57%, cream crystals, m.p. 197 °C (ethanol) IR : ν 1680 $cm^{-1}$ (CO). - $^1$H NMR ($CDCl_3$) : δ = 2.5 (s, 3H, $CH_3$), 3.95 (s, 8H, 4 $CH_2$ of morpholine), 7.2 - 8.0 (m, 4H, aromatic H), Found C 57.82 H 4.22 N 19.71, $C_{17}H_{15}N_5O_2S$ (353.4), requires C 57.78 H 4.28 N 19.82.

(8a) : Yield 71%, reddish crystals, m.p. 322 °C (ethanol) IR : ν 1640 (CO). - $^1$H NMR (DMSO) : δ = 2.4 (s, 3H, $CH_3$), 7.3 - 8 (m, 8H, aromatic H). - MS : m/z (%) 347 (100). [$M^+$], Found C 62.26 H 3.71 N 20.02 S 9.18, $C_{18}H_{13}N_5OS$ (347.4),requires C 62.23 H 3.77 N 20.16 S 9.23.

(8b) : Yield 79%, orange crystals, m.p. 220 °C (ethanol) IR : ν 3100 $cm^{-1}$ (NH), 1660 (CO). - MS : m/z (%) 348 (100) [$M^+$], Found C 62.15 H 3.39 N 16.12 S 9.11, $C_{18}H_{12}N_4O_2S$ (348.4), requires C 62.06 H 3.47 N 16.08 S 9.20.

**Preparation of adducts (10a,b)-General Method :** N,N-dialkyl aniline (9a, b) (10 m mol) was added slowly to a solution of 10 m mol of 1-(2-benzothiazolyl)-4-(dicyanomethylene)-3-methyl-2-pyrazolin-5-one (1) in acetic acid (15 ml) with magnetic stirrer at room temperature with the exclusion of light. Stirring was continued 2h. The precipitated product by dilution was collected, washed with water, purified by dissolving in acetic acid and reprecipitated by addition of water. The products were colourless powders, they were dried at room temperature in vacue and in the dark. $^1$H NMR and mass spectra could not be recorded due to the instability of the products.

**2-[1-(2-Benzothiazolyl)-5-hydroxy-3-methyl-1H-pyrazol-4-yl]-N,N-dimethylanilin-4-yl)-malononitrile** (10a) : Yield, 89%,colourless powder, m.p. 163 -165 °C. IR : ν =3450 $cm^{-1}$(OH), Found C 63.71 H 4.31 N 20.17 S 7.59, $C_{22}H_{18}N_6OS$ (414.5), requires C 63.75 H 4.38 N 20.28 S 7.74.

**2-[1-(2-Benzothiazolyl)-5-hydroxy-3-methyl-1H-pyrazol-4-yl]-N,N-diethylanilin-4-yl)-malononitrile** (10b) : Yield 86%, colourless powder, m.p. 174 - 176 °C. IR : ν = 3400 $cm^{-1}$ (OH). Found C 65.07 H 5.09 N 19.12 S 7.13, $C_{24}H_{22}N_6OS$ (442.5), requires C 65.14 H 5.01 N 18.99 S 7.25.

**Preparation of the condensation products (11a, b) :** A solution of (10a, b) in DMF (1.5 gm in 10 ml) was heated at 100 °C for 1/2 h. After cooling the precipitated product by dilution with water was collected and crystallized from dilute DMF as deep violet crystals.

(11a) : Yield 92%, m.p. 158 °C. - IR : ν = 1670 $cm^{-1}$ (C=O, pyrazolone). $^1$H NMR (DMSO) : δ = 2.5 (s, 3H, $CH_3$), 3.4 (s, 6H, N($CH_3$)), 7.0 - 8.2 (m, 8H, aromatic H). - MS : m/z (%) = 387 (75.9%) [$M^+$], 372(17.7) [$M^+$-$CH_3$], 343(8.1) [$M^+$-N($CH_3$)$_2$], Found C 65.21 H 4.37 N 18.13, $C_{21}H_{17}N_5OS$ (387.5), requires C 65.10 H 4.42 N 18.07.

(11b) : Yield 90%, m.p. 165 °C. IR : ν 1680 $cm^{-1}$ (C=O, pyrazolone). - $^1H$ NMR (DMSO) : δ = 1.1 (t, 6H, 2 $\underline{CH_3}$ $CH_2$), 2.5 (s, 3H, $CH_3$); 3.4 (q, 4H, 2 $\underline{CH_2}$ $CH_3$), 6.8 - 8.2 (m, 8H, aromatic H). - MS : m/z (%); 415 (44.8) [$M^+$], 400(100) [$M^+$-$CH_3$], 386(1.6) [$M^+$-$C_2H_5$], 434(3.5) [$M^+$-$N(C_2H_5)_2$], Found C 66.39 H 5.12 N 16.79, $C_{23}H_{21}N_5OS$ (415.5), requires C 66.48 H 5.09 N 16.85.

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**REFERENCES**

1) M.I.Younes, S.A. Metwally, A.H. Atta, *synthesis* 704(1990).

2) M.I.Younes, A.H.Atta, S.A. Metwally, *J. of the Chinese Chem. Soc.* **37**, 617(1990).

3) M.E. Abd Elmonem, M.I. Younes, S.A. Metwally, A.H. Atta, Collec *Czech. Chem. Commun.* **56**, 1977(1991).

4) A.H. Atta, R.F.Fandy, M.I. Younes, S.A.Metwally, *Bull. J. of Assiut*, **25** , 35 (1996)

5) C. Prakash, G.S. Saharia, H.R. Sharma, *J. Indian Chem. Soc.* **54**, 381(1977).

6) G. Tacconi, G. Marinoni, P.P. Righetti, G. Desimoni, *J. Prakt. Chem.* **322**, 674(1980).

7) A.I. Koraiem, *J. Prakt. Chem.* **326,** 695-, 811- (1984).

8) A. Nayak, A.S. Mittra, *J. Indian Chem. Soc.* **57**, 643(1980).

9) A.M. Ismaiel, M.Y. Yousif, M.A. Metwally, M. El-Kerdawy, *Indian J. Chem.* **25 B** (12), 1238(1986).

10) F.A. Adam, M.T. El-Haty, A.I. Koraiem, A.H. Amrallah, *J. Indian Chem. Soc.* **66**, 157(1989).

11) H. Junek, H. Aigner, H. Fisher-Colbrie, *Monatsh. Chem.* **103** 639. (1972)

12) H. Junek, H. Fisher-Colbrie, H. Sterk, *Chem. Ber.* **110** , 2276. (1977)

13) S.A.M. Metwally, G.M. El Naggar, M.I. Younis, T.I. El-Emary, M.H. Elnagdi, *Liebigs Ann. Chem.*, 1037 (1989) .

14) R. Dworczak, W.M.F. Fabian, H. Sterk, C. Kratky, H. Junek, *Liebigs Ann. Chem.*, 7. (1992).

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