

**Reactions with 6-amino-5-cyano-3-methyl-1,4-diphenyl-1H,4H-pyrano[2,3-c]-pyrazole- A novel synthesis of 4-arylidene-3-methyl-1-phenyl-2-pyrazolin-5-one derivatives**

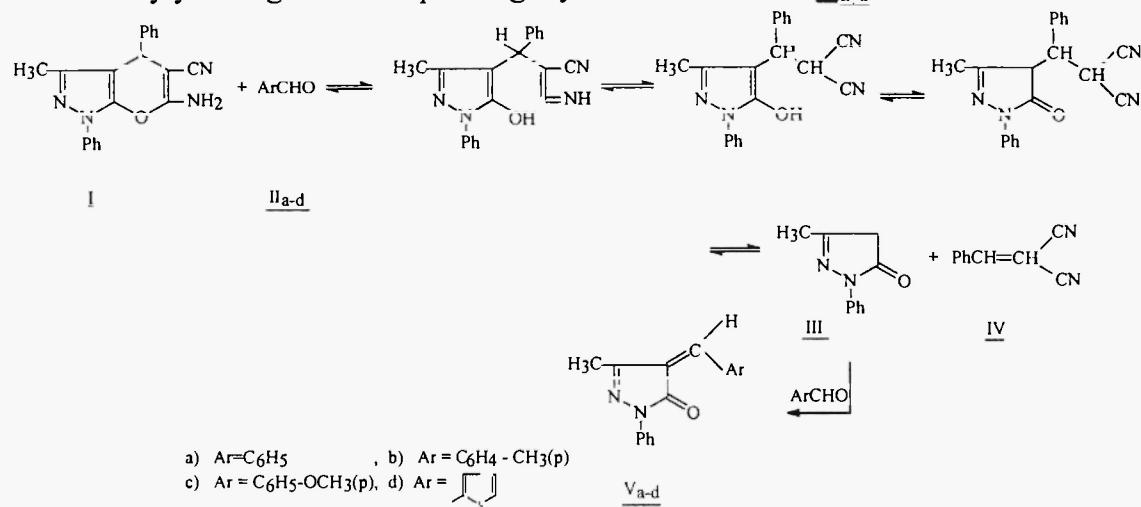
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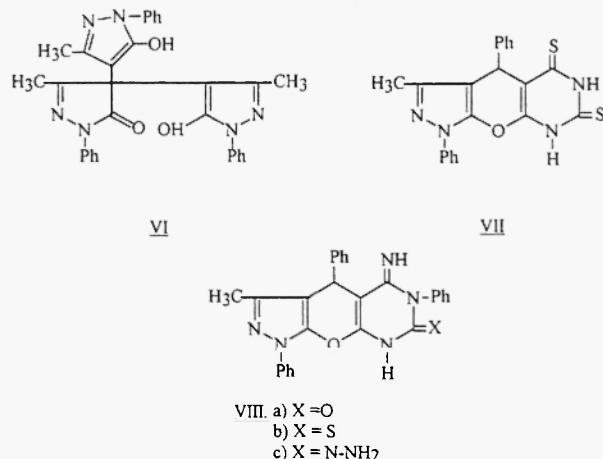
**Abstract:** Treating of 6-amino-5-cyano-3-methyl-1,4-diphenyl-1H,4H-pyrano[2,3-c]pyrazole with aromatic aldehyde yielding the corresponding 4-arylidene-3-methyl-1-phenyl-2-pyrazolin-5-ones, with formamide gives trispyrazolone derivative. Other reactions were discussed.

In previous papers<sup>(1-4)</sup> we used 6-amino-5-cyano-3-methyl-1,4-diphenyl-1H,4H-pyrano[2,3-c]pyrazole **I** in preparation of many heterocyclic compounds. We found that **I** behaved abnormal behavior towards amines and hydrazines<sup>(2)</sup>, this attracted our attention to study the reactivity of **I** towards other reagents. Thus treating of **I** with aromatic aldehydes **IIa-d** gave a deeply coloured products, identified as 4-arylidene-3-methyl-1-phenyl-2-pyrazolin-5-ones **V<sub>a-d</sub>** on the basis of spectral, elemental analysis beside m.p. and m.m.p. with authentic samples<sup>(5,6)</sup>. The reaction mechanism can be represented as shown in the following scheme in which pyrazolopyran ring is cleaved<sup>(2)</sup> to benzylidenemalononitrile **IV** and 3-methyl-1-phenyl-2-pyrazolin-5-one **III** which further reacted with aromatic aldehyde in the normal way yielding the corresponding arylidene derivatives **V<sub>a-d</sub>**.



Benzylidenemalononitrile **IV** was isolated from the mother liquor. Using formamide with **I** we obtained trispyrazolone derivative **VI** which was identified by spectral, elemental analysis as well as m.p. and mixed m.p. with an authentic sample<sup>(7)</sup>.

Treating of **I** with carbon disulphide in DMF and in the presence of sodium methoxide yielded in the formation of **VII**<sup>(8)</sup>, while heating of **I** with phenyl isocyanate and/or phenyl isothiocyanate gave **VIII<sub>a,b</sub>** respectively. Treating of **VIII<sub>b</sub>** with hydrazine hydrate gave the corresponding hydrazide **VIII<sub>c</sub>**.



## Experimental

All melting points are uncorrected. IR spectra were recorded on a Shimadzu-408 spectrometer using KBr pellet.  $^1\text{H-NMR}$  spectra on a Varian XL-100 spectrometer using TMS as internal standard. Mass spectra were obtained by mass spectrum unit at Cairo University. Microanalysis were carried out at Microanalysis Unit at Assiut University.

## Reactions of 6-amino-5-cyano-3-methyl-1,4-diphenyl-1H,4H-pyrano[2,3-c]pyrazole with aromatic aldehydes: General procedure

A mixture of **I** and aldehyde **II<sub>a-d</sub>** (0.001 mol) in ethanol (20 ml) was heated under reflux for 10-12 h. The solvent was removed under reduced pressure, the solid formed is extracted with petroleum ether (60-80) to give deeply red crystals, identified as arylidene derivatives **V<sub>a-d</sub>** (c.f. Table). The residue is crystallized several times with ethanol to give colourless needleless, m.p. 77°C, identified as benzylidene-malononitrile **IV**.

## Preparation of 3,3',3''-trimethyl-1,1',1''-triphenyl-[4,4',4''-ter-2-pyrazoline]-5,5',5''-trione VI

To a solution of **I** (0.001 mol) in ethanol (20 ml), formamide (10 ml) was added, the reaction mixture was refluxed for 5 h., and then poured into 100 ml ice cold water. The solid formed was collected and crystallized from ethanol to give colourless needle; m.p. 200°C (lit.<sup>(7)</sup>, 199°C.), m.m.p. with an authentic sample 200°C.

Table . Physical properties of compounds prepared.

| Comp.          | M.P. <sup>o</sup> C              | Yield % | Molecular formula   | MS            | IR ν(cm <sup>-1</sup> )                        | <sup>1</sup> H-NMR (CDCl <sub>3</sub> )   |   |       | Calcd/ Found |       |       |
|----------------|----------------------------------|---------|---|---------------|--|---|---|-------|--------------|-------|-------|
|                |                                  |         |   |               |  | C   | H | N     | C            | H     | N     |
| V <sub>1</sub> | 105<br>lit. <sup>(5)</sup> 105-6 | 52      | C <sub>17</sub> H <sub>4</sub> N <sub>2</sub> O<br>(262.3)              | 262<br>(77.6) | 1700(C=O)                                      | -   | - | -     | 77.86        | 5.38  | 10.68 |
| V <sub>2</sub> | 112<br>lit <sup>(5)</sup> 111-12 | 42      | C <sub>18</sub> H <sub>6</sub> N <sub>2</sub> O<br>(276.3)              | -             | 1690(C=O)                                      | 1.9(s,3H,CH <sub>3</sub> 2.2(s,3H,CH <sub>3</sub> ),<br>5.2(s,1H,CH),7.2-7.8(m,9H,Ar-H).      | - | 77.69 | 5.27         | 10.80 |       |
| V <sub>3</sub> | 127<br>lit <sup>(5)</sup> 127    | 65      | C <sub>18</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub><br>(292.3) | 292<br>(100)  | 1690(C=O)                                      | 1.95(s,3H,CH <sub>3</sub> ), 3.7(s,3H,OCH <sub>3</sub> ),<br>5.4(s,1H,CH), 7.0-7.9(m,9H,Ar-H) | - | 78.23 | 5.84         | 10.14 |       |
| V <sub>4</sub> | 118<br>lit <sup>(6)</sup> 127-28 | 83      | C <sub>15</sub> H <sub>2</sub> N <sub>2</sub> O <sub>3</sub><br>(268.3) | 268<br>(79)   | 1710(C=O)                                      | -   | - | 78.08 | 5.92         | 10.07 |       |
| V <sub>5</sub> | 200<br>lit <sup>(7)</sup> 199    | 73      | C <sub>10</sub> H <sub>6</sub> N <sub>6</sub> O <sub>2</sub><br>(518.6) | 518<br>(82)   | 3370(OH),<br>1715(C=O)                         | -   | - | 77.21 | 4.41         | 10.37 |       |
| V <sub>6</sub> | 115                              | 49      | C <sub>2</sub> H <sub>6</sub> N <sub>4</sub> OS <sub>2</sub><br>(404.4) | 404<br>(8.7)  | 3130(NH),<br>1190(C=S)                         | 2.0(s,3H,CH <sub>3</sub> ), 5.1(s,1H of ·pyran),<br>6.45(s,2H,2NH) 7.15-7.7(m,10H,Ar-H)       | - | 69.48 | 5.05         | 16.20 |       |
| V <sub>7</sub> | 228                              | 64      | C <sub>2</sub> H <sub>2</sub> N <sub>5</sub> O <sub>2</sub><br>(447.5)  | 447           | 3280(NH),<br>1700(C=O)                         | -   | - | 69.41 | 5.92         | 16.12 |       |
| V <sub>8</sub> | 137                              | 53      | C <sub>17</sub> H <sub>11</sub> N <sub>2</sub> OS<br>(463.5)            | -             | 3320(NH),<br>1195(C=S)                         | 1.95(s,3H,CH <sub>3</sub> ), 5.1(s,1H, of pyran),<br>6.9-7.8(m,15H,Ar-H), 8.2(s,2H,2NH).      | - | 72.47 | 4.73         | 15.65 |       |
| V <sub>9</sub> | 150                              | 70      | C <sub>27</sub> H <sub>21</sub> N <sub>2</sub> O<br>(461.4)             | 461           | 3400, 3310<br>(NH <sub>2</sub> ),<br>3200(NH). | -   | - | 72.50 | 4.82         | 15.56 |       |

**Reaction of I with carbon disulphide**

To a solution of I (0.001 mol) in DMF (20 ml), carbon disulphide (5 ml) and sodium methoxide (0.2 gm) were added, the mixture was refluxed for 15 h., and then poured into ice cold water. A solution of sodium hydroxide (1M, 10 ml) was added to it and left overnight. The solution was filtered and acidified with dilute acetic acid to give a yellow precipitate. It was collected, washed with dilute acetic acid, dried and crystallized from ethanol to give yellow powder (VII) (c.f. Table).

**Formation of (VIII<sub>a,b</sub>)**

A mixture of I (0.001 mol) and phenyl isocyanate or phenyl isothiocyanate (0.001 mol) in pyridine (20 ml) was refluxed for 8 h., the reaction mixture was then cooled and poured into ice cooled water. The resulting solid was filtered, washed several times with water, dried and crystallized from ethanol to give yellowish crystals (c.f. Table).

**Reaction of VIII<sub>b</sub> with hydrazine hydrate**

To a solution of VIII<sub>b</sub> (0.001 mol) in 30 ml of ethanol, 5 ml of hydrazine hydrate was added. The reaction mixture was heated under reflux for 5 h.. After cooling, the yellowish precipitate formed is collected and crystallized from ethanol to give yellowish powder (VIII<sub>c</sub>); m.p. 150°C.

**References**

- (1) M.I. Younes, S.A.M. Metwally, A.H. Atta, *Synthesis* 8, 704 (1990).
- (2) M.I. Younes, A.H. Atta, S.A.M. Metwally, *J. of Chinese Chem. Soc.* 37, 617, (1990).
- (3) M.I. Younes, A.H. Atta, S.A. Metwally, *Bull. Of Assiut*, 19, 45 (1990).
- (4) M.E. Abd Elmonem, M.I. Younes, S.A. Metwally, A.H. Atta, *Collec. Czech. Chem. Commun.* 56, 1977 (1991).
- (5) G. Desimoni, A. Gamba, P.P. Righetti, G. Tacconi, *Gazz. Chim. Ital.* 102, 491 (1972).
- (6) G.W. Sawdey, M.K. Ruoff, P.W. Vittum, *J. Amm. Chem. Soc.* 72, 4947 (1950).
- (7) M.F. Aly, M.I. Younes, A.H. Atta, S.A. Metwally, *Heterocyclic Comm.* 3, 231 (1997).
- (8) A.O. Abdelhamid, C. Parkanyi, A.S. Shawali, M.A. Abdalla, *J. Heterocyclic Chem.* 21, 1049 (1984).

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