

Full Paper

## Microwave Assisted Condensation Reactions of 2-Aryl Hydrazonopropanals with Nucleophilic Reagents and Dimethyl Acetylenedicarboxylate

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**Abstract:** The reaction of methyl ketones **1a-g** with dimethylformamide dimethylacetal (DMFDMA) afforded the enaminones **2a-g**, which were coupled with diazotized aromatic amines **3a,b** to give the corresponding aryl hydrazones **6a-h**. Condensation of compounds **6a-h** with some aromatic heterocyclic amines afforded iminoarylhydrazones **9a-m**. Enaminoazo compounds **12a,b** could be obtained from condensation of **6c** with secondary amines. The reaction of **6e,h** with benzotriazolylacetone yielded **14a,b**. Also, the reaction of **6a,b,d-f,h** with glycine and hippuric acid in acetic anhydride afforded pyridazinone derivatives **17a-f**. Synthesis of pyridazine carboxylic acid derivatives **22a,b** from the reaction of **6b,e** with dimethyl acetylenedicarboxylate (DMAD) in the presence of triphenylphosphine at room temperature is also reported. Most of these reactions were conducted under irradiation in a microwave oven in the absence of solvent in an attempt to improve the product yields and to reduce the reaction times.

**Keywords:** 2-Arylhydrazonopropanals, heterocyclic amines, active methylene, microwave irradiation.

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## Introduction

Over the last 100 years mankind has not paid much attention to the environmental impact of chemistry, but in the last decade this has changed radically and the need for “Green Chemistry” has become apparent. The utility of microwaves in heterocyclic synthesis is also receiving now considerable attention [1-4]. Enaminones has been recently extensively utilized as precursors for the synthesis of heteroaromatics [5-8]. We report herein on the synthesis of iminoarylhydrazono-propanone, azolopyrimidine and 3-oxaloalkanonitrile derivatives of potential interest as pharmaceuticals and photochromic dyes [9-13], starting from enaminones. It has been reported that methylalkyl ketones and methylaryl ketones condense readily with dimethylformamide dimethylacetal (DMFDMA) to yield enaminones, whose chemistry has recently attracted considerable interest [5,6,12-20]. The chemistry of 2-arylhydrazonopropanals has also received considerable interest in the last few years [21-25]. As part of an ongoing project in our laboratory aimed at exploring potential utility of microwave irradiation as a source of heat for producing polyfunctionally substituted heteroaromatics and because of our recent interest in making our synthetic approaches environmentally attractive, we have decided to investigate here the possibility of conducting our reactions in two ways:

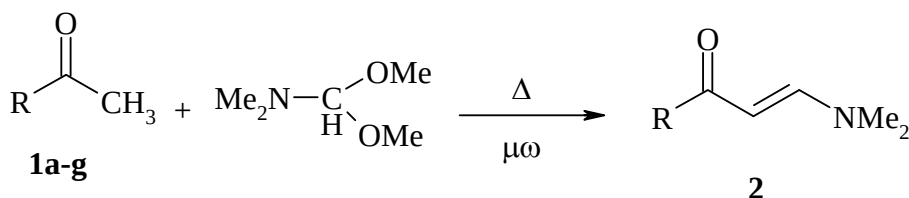
- (i) *Classical conventional heating methods with solvents ( $\Delta$ ).*
- (ii) *Microwave heating without solvent ( $\mu\omega$ ).*

The yield of products obtained with the microwave heating technique and the time taken to complete the reactions will be compared with those seen with conventional methods [8, 26].

## Results and Discussion

The enaminones required for this investigation were first synthesized *via* condensation of methyl aryl **1a** or heteroaryl ketones **1b-g** with DMFDMA in refluxing xylene. The desired compounds were obtained in low yield, consequently we have modified this synthetic approach by condensing the methyl ketones with slightly excess of DMFDMA in the absence of solvent [26] (Scheme 1). In this case the reaction products **2b-g** were obtained in almost quantitative yields yield on cooling in a much more economical synthesis.

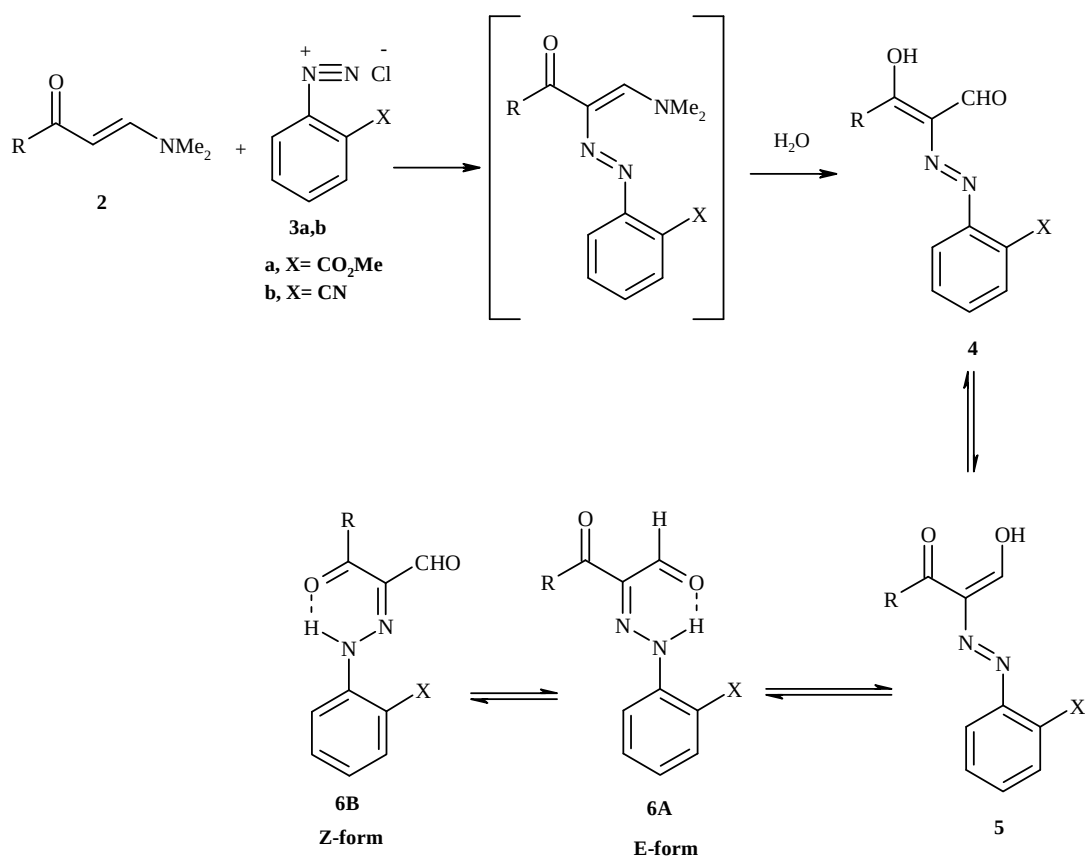
Scheme 1



| 2 | R               | 2 | R                                         |
|---|-----------------|---|-------------------------------------------|
| a | CH <sub>3</sub> | e | <i>o</i> -OHC <sub>6</sub> H <sub>4</sub> |
| b | 2-furyl         | f | <i>p</i> -OHC <sub>6</sub> H <sub>4</sub> |
| c | 2-pyrrolyl      | g | <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> |
| d | 2-pyridyl       |   |                                           |

Enaminones **2a-g** coupled with diazotized methyl anthranilate **3a** or diazotized anthranilonitrile **3b** in the presence of ethanolic sodium acetate to yield the corresponding aryl hydrazone coupling products **6 a-h** [17, 27] (Scheme 2).

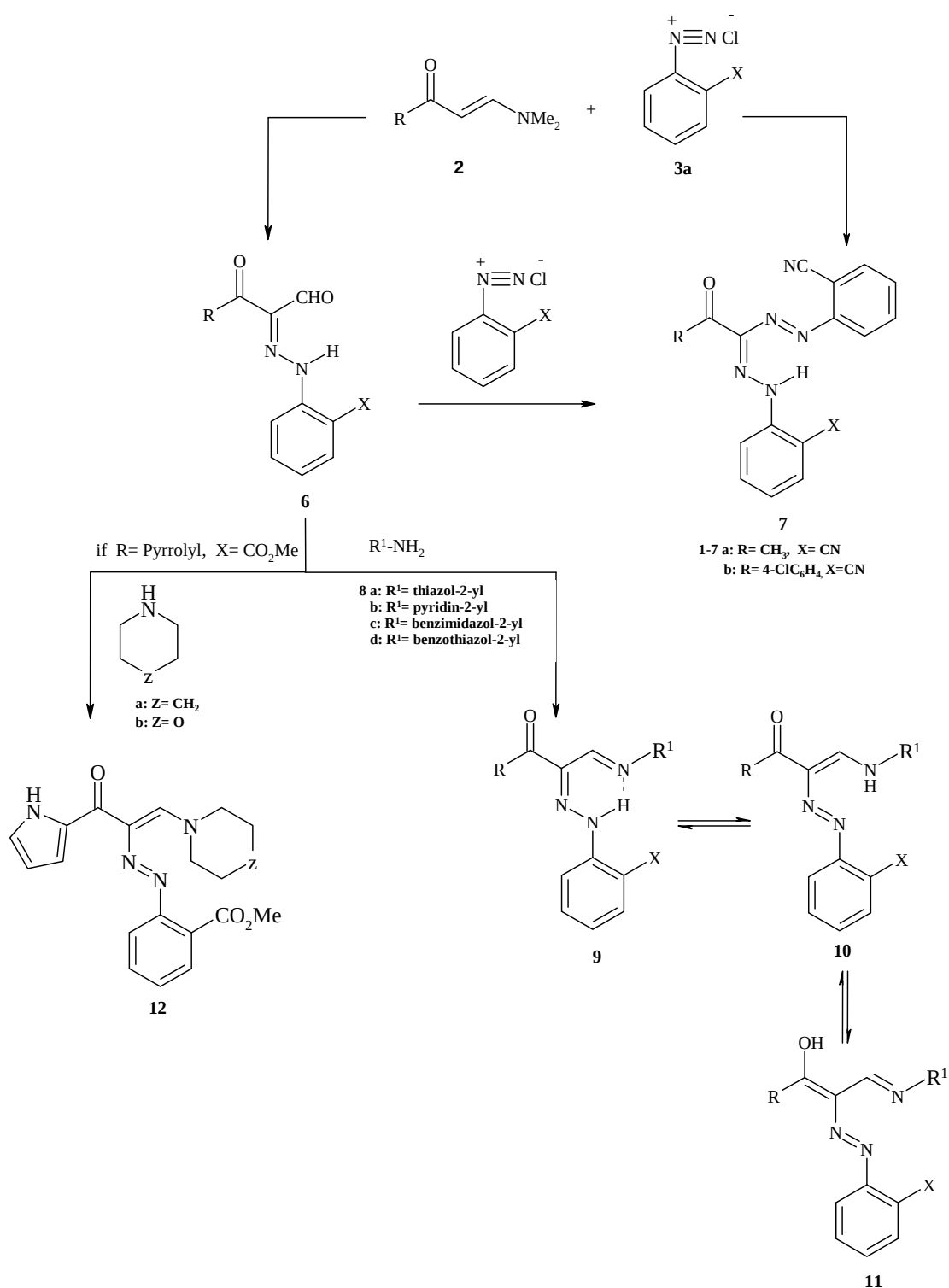
Scheme 2



| 6 | R                                 | X                        | 6 | R                                 | X  |
|---|-----------------------------------|--------------------------|---|-----------------------------------|----|
| a | $\text{CH}_3$                     | $\text{CO}_2\text{CH}_3$ | e | $\text{CH}_3$                     | CN |
| b | 2-furyl                           | $\text{CO}_2\text{CH}_3$ | f | 2-furyl                           | CN |
| c | 2-pyrrolyl                        | $\text{CO}_2\text{CH}_3$ | g | 2-pyrrolyl                        | CN |
| d | $\text{C}_6\text{H}_4\text{Cl-p}$ | $\text{CO}_2\text{CH}_3$ | h | $\text{C}_6\text{H}_4\text{Cl-p}$ | CN |

When *N,N*-dimethylamino-3-buten-2-one (**2a**) and 3-*N,N*-dimethylamino-1-(4-chloro phenyl)-2-propen-1-one (**2g**) were treated with excess diazotized anthranilonitrile **3b** the bisazo compounds **7a** and **7b** was formed in a Japp-Klingmann type reaction which proceed *via* intermediate formation of **6a,b** [28] (Scheme 3). The  $^1\text{H}$ -NMR of the resulting product **7a** showed a single absorption signal at  $\delta$  15.50 ppm, corresponding to the NH proton resonance. The  $^{13}\text{C}$ - NMR showed two absorption signals for the two CN groups at  $\delta$  117.05, 117.46 ppm.

Scheme 3.

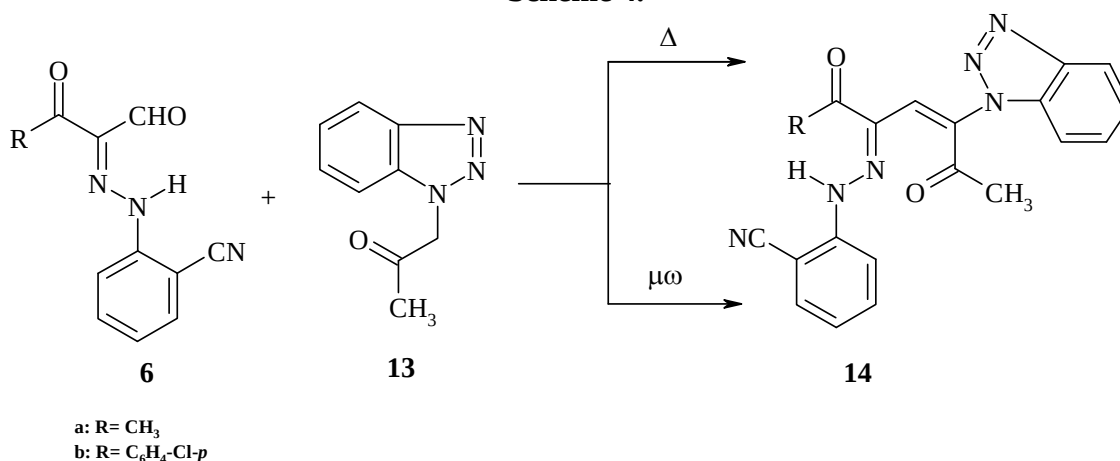


| 9 | R                                          | X                               | R <sup>1</sup> | 9 | R                                           | X                               | R <sup>1</sup>     |
|---|--------------------------------------------|---------------------------------|----------------|---|---------------------------------------------|---------------------------------|--------------------|
| a | CH <sub>3</sub>                            | CO <sub>2</sub> CH <sub>3</sub> | thiazol-2-yl   | h | 2-furyl                                     | CO <sub>2</sub> CH <sub>3</sub> | benzoimidazol-2-yl |
| b | 2-furyl                                    | CO <sub>2</sub> CH <sub>3</sub> | thiazol-2-yl   | i | 2-pyrrolyl                                  | CO <sub>2</sub> CH <sub>3</sub> | benzoimidazol-2-yl |
| c | 2-pyrrolyl                                 | CN                              | thiazol-2-yl   | j | C <sub>6</sub> H <sub>4</sub> -Cl- <i>p</i> | CO <sub>2</sub> CH <sub>3</sub> | benzoimidazol-2-yl |
| d | C <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> | CO <sub>2</sub> CH <sub>3</sub> | pyridine-2-yl  | k | 2-pyrrolyl                                  | CO <sub>2</sub> CH <sub>3</sub> | benzothiazol-2-yl  |
| e | CH <sub>3</sub>                            | CN                              | pyridine-2-yl  | l | CH <sub>3</sub>                             | CN                              | benzothiazol-2-yl  |
| f | 2-pyrrolyl                                 | CN                              | pyridine-2-yl  | m | C <sub>6</sub> H <sub>4</sub> -Cl- <i>p</i> | CN                              | benzothiazol-2-yl  |
| g | 2-furyl                                    | CN                              | pyridine-2-yl  |   |                                             |                                 |                    |

We also report herein on the reactivity of **6a-h** towards a variety of nitrogen and carbon nucleophiles in the absence of solvent under irradiation ( $\mu\omega$ ) in a domestic microwave oven. The yields of products obtained under the microwave heating technique  $\mu\omega$  and the time taken to complete the reactions are compared with those obtained by conventional heating ( $\Delta$ ) in Table 2 (see Experimental). Thus, **6a-h** were heated with a variety of heterocyclic amines such as 2-aminothiazole (**8a**), 2-aminopyridine (**8b**), 2-aminobenzimidazole (**8c**) and 2-amino- benzothiazole (**8d**) yielding the corresponding condensation products **9a-m**. Several tautomeric forms (cf. **10**, **11**), seemed possible for the iminoaryl hydrazone condensation products **9a-m**, whose structures were established based on spectral data. For example, the  $^1\text{H}$ -NMR of the **9k** showed two singlets, the first at  $\delta$  6.89 ppm, corresponding to the resonance of the olefin CH proton and the second at  $\delta$  14.46 ppm corresponding to the hydrazone NH proton. The  $^{13}\text{C}$ -NMR has also showed the disappearance of the absorption signal of the carbon atom corresponding to the formyl carbonyl group and the appearance of a signal at  $\delta$  165.27 ppm for the carbon atom of the  $\text{HC}=\text{N}$  group. The IR of the **9l** showed an absorption band at  $3350\text{ cm}^{-1}$  of the NH group, as well as an absorption band at the rather low value of  $1684\text{ cm}^{-1}$  for the carbonyl group. This indicates that there is a hydrogen bond between the hydrazone NH hydrogen and the oxygen of the carbonyl group. Treatment of **6c** with secondary amines such as piperidine and morpholine afforded compounds **12a,b** in good yield (Scheme 3).

Arylhydrazones **6e,h** reacted with benzotriazolylacetone (**13**) in boiling ethanol in the presence of traces of pyridine as a catalyst to give **14a,b** by loss of a water molecule (Scheme 4). The structure of this product is proposed based on its elemental analysis and spectral data. The IR showed an absorption band at  $1674\text{ cm}^{-1}$  and another at  $1646\text{ cm}^{-1}$  for the carbonyl groups, as well as an absorption band at  $3308\text{ cm}^{-1}$  for the NH group. The  $^1\text{H}$ -NMR showed two singlets at  $\delta$  1.99 and 7.20 ppm, corresponding to the resonances of the  $\text{CH}_3$  protons and the olefin CH proton. Similar results were obtained when the reaction was performed under microwave irradiation.

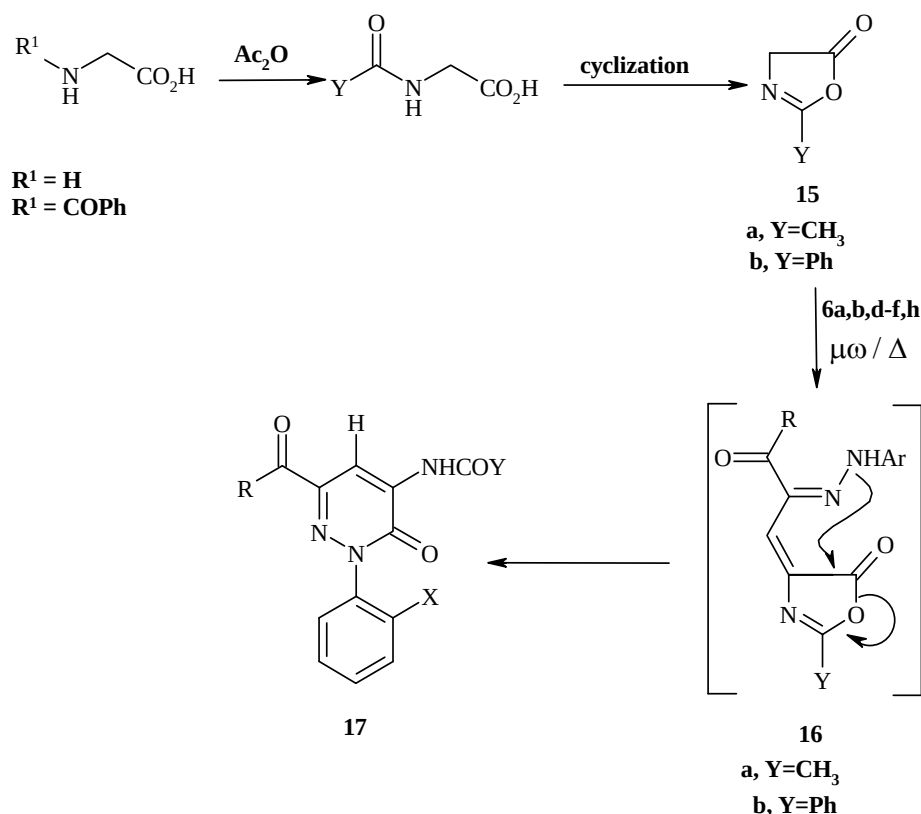
Scheme 4.



It was noted that the reaction of 3-arylhydrazone-4-butanals **6a,e** and 2-arylhydrazone-3-propanals **6b,d,f,h** with glycine or *N*-acetylglycine and with hippuric acid by boiling in acetic anhydride ( $\text{Ac}_2\text{O}$ ) gave similar compounds. The structural formulae **17a-g** are proposed for the resulting products based on their elemental analysis and spectral data. Thus the  $^1\text{H}$ -NMR of compound **17a** showed a singlet at  $\delta$  2.23 ppm corresponding to the protons of the  $\text{CH}_3$  attached to the amide group. Another singlet was

seen at  $\delta$  8.61 ppm, corresponding to the resonance of the pyridazine ring (HC-4) proton. A third singlet seen at  $\delta$  10.21 ppm was assigned to the amide group NH proton. The  $^{13}\text{C}$ -NMR showed a signal for the carbon atom of the methyl group attached to the amide group ( $\text{NHCOCH}_3$ ) at  $\delta$  24.83 ppm and an absorption at  $\delta$  171.98 ppm corresponding to the carbon atom of the amide group carbonyl ( $\text{NHCOCH}_3$ ). The same result was obtained when the reaction was performed by means of microwave irradiation in a microwave oven for 5-15 minutes, in yields of 35 %-50 % (Scheme 5).

Scheme 5.

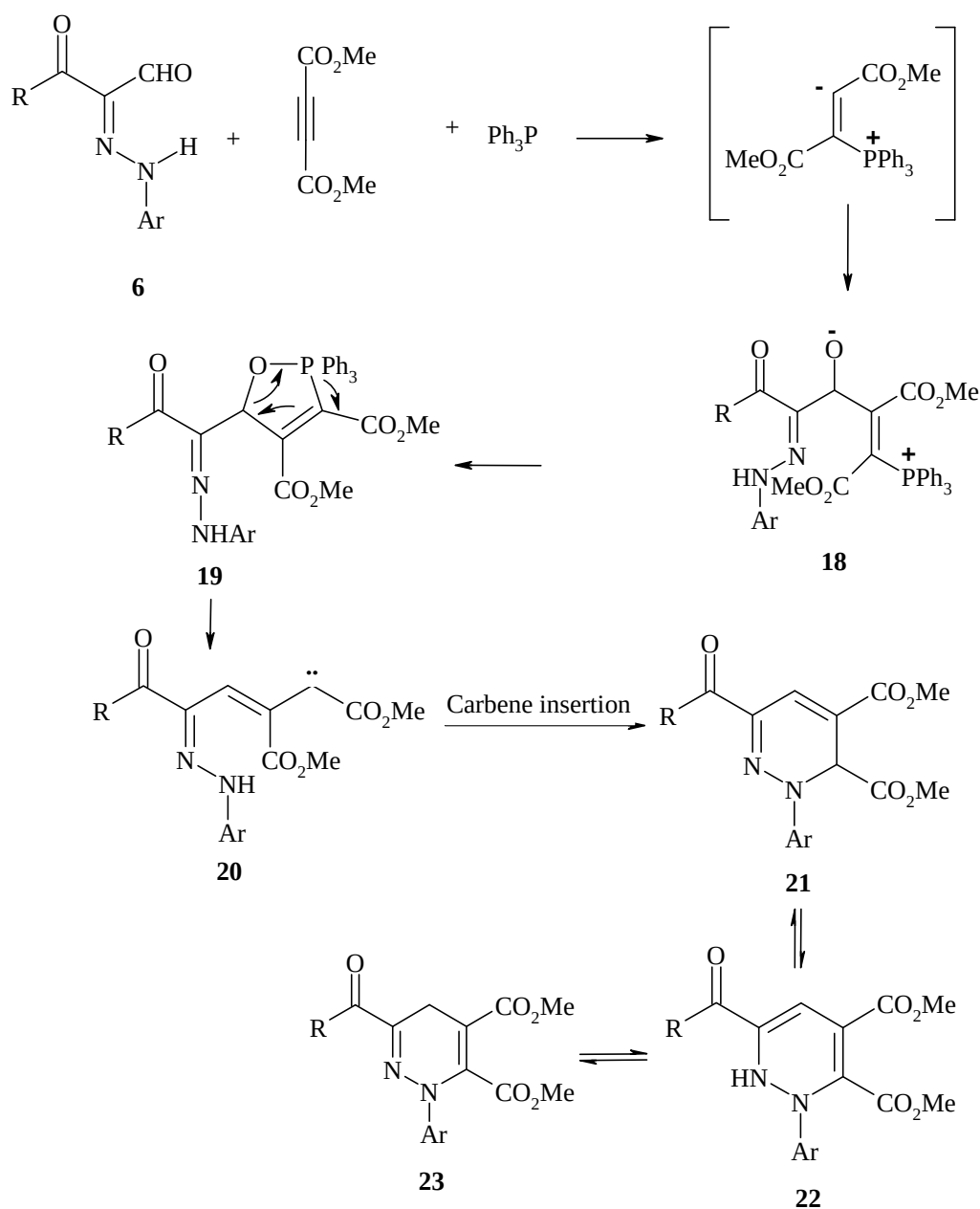


| 17 | R                                           | X                               | Y               |
|----|---------------------------------------------|---------------------------------|-----------------|
| a  | CH <sub>3</sub>                             | CO <sub>2</sub> CH <sub>3</sub> | CH <sub>3</sub> |
| b  | 2-furyl                                     | CO <sub>2</sub> CH <sub>3</sub> | CH <sub>3</sub> |
| c  | C <sub>6</sub> H <sub>4</sub> Cl- <i>p</i>  | CO <sub>2</sub> CH <sub>3</sub> | CH <sub>3</sub> |
| d  | CH <sub>3</sub>                             | CN                              | CH <sub>3</sub> |
| e  | 2-furyl                                     | CN                              | CH <sub>3</sub> |
| f  | C <sub>6</sub> H <sub>4</sub> -Cl- <i>p</i> | CN                              | CH <sub>3</sub> |
| g  | CH <sub>3</sub>                             | CO <sub>2</sub> CH <sub>3</sub> | Ph              |

It is proposed that when  $\text{Ac}_2\text{O}$  is present the glycine is acetylated to *N*-acetylglycine and then this compound cyclizes to form 2-methyloxazol-5-one (**15a**) and the latter in turn condensed with the arylhydrazone derivatives **6a,b,d-f,h** to form the intermediate **16** which cannot be isolated, but then rearranges to form pyridazinone derivatives **17a-f**. Similarly hippuric acid cyclized in the presence of  $\text{Ac}_2\text{O}$  to give 5-phenyloxazol-5-one (**15a**) and then this compound condensed with arylhydrazone derivative **6a** to gave pyridazinone derivative **17g** [28,29].

Recently Elnagdi *et al.* [10, 30, 31] have described a synthesis of pyridazine-5,6-dicarbonates **22a,b** *via* reaction of **6b,e** with dimethyl acetylenedicarboxylate in the presence of diphenylphosphine. The exact mechanism has never been discussed. In our hands, a similar reaction took place affording dimethyl-1,6-dihydropyridazines-5,6-dicarboxylate. We believe that the initial step in this reaction is the addition of triphenylphosphine to the dimethyl acetylenedicarboxylate to yield **18**, then this compound attacks the formyl carbonyl group yielding **19**, which cyclizes to **20** and the latter is then converted into the final product *via* intermediate **21** (Scheme 6).

Scheme 6



a: R= 2-furyl, Ar=  $\text{C}_6\text{H}_4-\text{CO}_2\text{CH}_3$ -o

b: R=  $\text{CH}_3$ , Ar=  $\text{C}_6\text{H}_4-\text{CN}$ -o

## Experimental

### General

All melting points were measured on a Gallenkamp Electrothermal melting point apparatus and are uncorrected. The IR absorption spectra (KBr disks) were measured on a Nicolet Magna 520FT IR Spectrophotometer.  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra were recorded in deuterated dimethylsulfoxide ( $\text{DMSO-d}_6$ ) or deuterated chloroform ( $\text{CDCl}_3$ ) at 200 MHz on a Varian Gemini NMR spectrometer or a Bruker DPX 400 MHz spectrometer using tetramethylsilane (TMS) as an internal reference and results are expressed as  $\delta$  values (ppm). Mass spectra were recorded on a Shimadzu GCMS-QP 1000 Ex mass spectrometer at 70 eV. Microwave irradiation was carried out using a commercial microwave oven (SGO 390W). Elemental analyses were carried out at the Microanalytical Center of Cairo University, Egypt.

### General Procedure for the preparation of enaminones **2a-g**

**Method I ( $\Delta$ ):** Dimethylformamide dimethylacetal (DMFDMA) (0.1 mol) was added to solution of methyl ketone (0.1 mol) in dry xylene (30 mL) or dry toluene (30 mL), and the reaction mixture was refluxed for 8 hours. Removal of the solvent under reduced pressure yielded the crude product, which was recrystallized from xylene.

**Method II ( $\Delta$  without solvent):** A mixture of dimethylformamide dimethylacetal (DMFDMA, 0.1 mol) and the corresponding methyl ketone (0.1 mol) was refluxed for 9 hours and was allowed to cool. The solid product formed was collected and recrystallized from xylene.

**Method III ( $\mu\omega$ ):** Dimethylformamide dimethylacetal (DMFDMA, 0.1 mol) and methyl ketone (0.1 mol) were placed in the microwave oven and irradiated at full power for 1-5 min., left to cool to room temperature and the solid formed was collected and recrystallized from xylene.

Yields and properties of the products are summarized in Table 1.

**Table 1.**

| NO.       | COMPOUND                                      | M.P./ $^{\circ}\text{C}$ | REF. |
|-----------|-----------------------------------------------|--------------------------|------|
| <b>2a</b> | 4-Dimethylamino-3-buten-2-one                 | -                        | 15   |
| <b>2b</b> | 3-Dimethylamino-1-(2-furyl)propenone          | 92                       | 15   |
| <b>2c</b> | 3-Dimethylamino-1-(2-pyrrolyl)propenone       | 94                       | 15   |
| <b>2d</b> | 3-Dimethylamino-1-(2-pyridyl)propenone        | 135                      | 15   |
| <b>2e</b> | 3-Dimethylamino-1-(2-hydroxyphenyl) propenone | 123                      | -    |
| <b>2f</b> | 3-Dimethylamino-1-(4-hydroxyphenyl) propenone | -                        | -    |
| <b>2g</b> | 3-Dimethylamino-1-(4-chlorophenyl) propenone  | 88                       | -    |



*Preparation of 2-arylhydrazono-3-oxo-3-substituted-propanals 6a-h* [15]

A cold solution of aryldiazonium salt (10 mmol) was prepared by adding a solution of sodium nitrite (1 g in 10 mL H<sub>2</sub>O) to a cold solution of aryl amine hydrochloride (10 mmol of aryl amine in 5 mL concentrated HCl) with stirring as described earlier [15]. The resulting solution of the aryldiazonium salt was then added to a cold solution of enaminone in EtOH (50 mL) containing sodium acetate (1g in 10 mL H<sub>2</sub>O). The mixture was stirred at room temperature for 1h and the solid product thus formed was collected by filtration and crystallized from the appropriate solvent.

*2-(2-methoxycarbonylphenylhydrazono)-3-oxo-butanal (6a)*. Orange crystals (from ethanol); yield 63%; m.p. 126 °C; IR  $\nu_{\max}$  cm<sup>-1</sup>: 3568 (br, NH), 2954 (CH aldehyde), 1695 (C=O ester), 1647 (C=O aldehyde), 1600 (C=O ketone); <sup>1</sup>H-NMR:  $\delta$  = 2.52, 2.65 (s, 3H, CH<sub>3</sub>), 4.02, 4.03 (s, 3H, OCH<sub>3</sub>), 7.20–8.15 (m, 4H, Ar-H), 9.59, 10.19 (s, 1H, CHO), 15.57, 15.89 (s, 1H, NH); MS: (M<sup>+</sup> +1) 249; Anal. Calcd. for C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub> (248.224): C, 58.07; H, 4.67; N, 11.28; Found: C, 58.37; H, 4.71; N, 11.58.

*3-(2-furyl)-2-(2-methoxycarbonylphenylhydrazono)-3-oxo-propanal (6b)*. Dark yellow crystals (from dioxane); yield 90%; m.p. 195 °C; IR  $\nu_{\max}$  cm<sup>-1</sup>: 3468 (br, NH), 2837 (CH aldehyde), 1705 (C=O ester), 1652 (C=O aldehyde) and 1615 (C=O ketone); <sup>1</sup>H-NMR:  $\delta$  = 4.05 (s, 3H, CH<sub>3</sub>), 6.60 (m, 1H, furyl H-4), 7.21–7.74 (m, 4H, Ar-H), 7.95–8.12 (m, 2H, furyl H-3, H-5), 10.23 (s, 1H, CHO) and 15.66 (s, 1H, NH) ppm; MS: (M<sup>+</sup>) 300; Anal. Calcd. for C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O<sub>5</sub> (300.256): C, 60.00; H, 4.00; N, 9.33; Found: C, 59.99; H, 4.01; N, 9.43.

*2-(2-methoxycarbonylphenylhydrazono)-3-oxo-3-(2-pyrrolyl)propanal (6c)*. Pale orange crystals (from dil. dioxane); yield 45%; m.p. 186 °C; IR  $\nu_{\max}$  cm<sup>-1</sup>: 3568 (br, NH), 2837 (CH aldehyde), 1720 (C=O ester), 1662 (C=O aldehyde) and 1645 (C=O ketone); MS: (M<sup>+</sup> +1) 298; Anal. Calcd. for C<sub>15</sub>H<sub>13</sub>N<sub>3</sub>O<sub>4</sub> (299.27): C, 60.20; H, 4.34; N, 14.05; Found: C, 60.31; H, 4.40; N, 14.12.

*3-(4-Chlorophenyl)-2-(2-methoxycarbonylphenylhydrazono)-3-oxo-propanal (6d)*. Yellow crystals (from ethanol); yield 80%; m.p. 189 °C; IR:  $\nu_{\max}$  cm<sup>-1</sup> (this compound shows a complex spectrum due to the to H-bond between O and NH): 3022 (CH aromatic), 1711 (C=O ester), 1650 (C=O aldehyde), 1638 (C=O ketone) and 1586 (C=N); <sup>1</sup>H-NMR:  $\delta$  = 4.05 (s, 3H, CH<sub>3</sub>), 7.20–8.09 (m, 8H, Ar-H), 10.25 (s, 1H, CHO) and 15.69 (s, 1H, disappeared after D<sub>2</sub>O exchange, NH); <sup>13</sup>C-NMR:  $\delta$  = 52.90 (COOCH<sub>3</sub>), 116.19, 116.40, 118.98, 128.36, 133.33, 138.75 (C<sub>6</sub>H<sub>4</sub>-CO<sub>2</sub>M-o), 124.98, 131.59, 131.89, 134.74, 135.50 (C<sub>6</sub>H<sub>4</sub>-Cl-p), 143.54 (C=N-N), 166.87 (COOCH<sub>3</sub>), 188.23 (C=O) and 190.49 (CHO); MS: (M<sup>+</sup>) 344; Anal. Calcd. for C<sub>17</sub>H<sub>13</sub>N<sub>2</sub>O<sub>4</sub>Cl (344.76): C, 59.23; H, 3.80; N, 8.13; Found: C, 59.33; H, 3.82; N, 8.15.

*2-(2-Cyanophenylhydrazono)-3-oxo-butanal (6e)*. Orange crystals (from ethanol); yield 80%; m.p. 130 °C; IR:  $\nu_{\max}$  cm<sup>-1</sup>: 3406 (br, NH), 2221 (CN), 1693 (C=O aldehyde) and 1670 (C=O ketone); <sup>1</sup>H-NMR:  $\delta$  = 2.52, 2.63 (s, 3H, CH<sub>3</sub>), 7.22–8.02 (m, 4H, Ar-H), 9.58, 10.26 (s, 1H, CHO) and 14.4, 15.4 (s, 1H, NH); MS: (M<sup>+</sup>) 215; Anal. Calcd. for C<sub>11</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub> (215.2): C, 61.39; H, 4.21; N, 19.53; Found: C, 61.48; H, 4.30; N, 19.58.

*3-(2-Furyl)-2-(2-cyanophenylhydrazono)-3-oxopropanal (6f)*. Orange yellowish crystals (from dioxane); yield 78%; m.p. 205 °C; IR  $\nu_{\max}$   $\text{cm}^{-1}$ : 3543 (br, NH), 2221 (CN), 1651 (C=O aldehyde) and 1648 (C=O ketone);  $^1\text{H-NMR}$ :  $\delta$  = 6.76 (m, 1H, furyl H-4), 7.34-7.52 (m, 4H, Ar-H), 7.56-8.10 (m, 2H, furyl H-3, H-5), 10.02 (s, 1H, CHO) and 14.49 (s, 1H, NH);  $^{13}\text{C-NMR}$ :  $\delta$  = 112.54, 115.30, 148.22, 149.63 (furoyl carbon), 116.09 ( $\text{CN}$ ), 122.08, 125.49, 133.66, 133.14, 143.70 ( $\text{C}_6\text{H}_4\text{-CN-o}$ ), 152 (C=N-N), 176.15 ( $\text{CHO}$ ) and 188.95 ( $\text{C=O}$ ); MS: ( $\text{M}^+$ ) 267; Anal. Calcd. for  $\text{C}_{14}\text{H}_9\text{N}_3\text{O}_3$  (267.23): C, 62.92; H, 3.37; N, 15.73; Found: C, 62.99; H, 3.40; N, 15.81.

*2-(2-Cyanophenylhydrazono)-3-oxo-3(2-pyrrolyl)propanal (6g)*. Pale brown crystals (from dioxane); yield 65%; m.p. 172 °C; IR  $\nu_{\max}$   $\text{cm}^{-1}$ : 3450 (br, NH), 2216 (CN), 1680 (C=O aldehyde) and 1648 (C=O ketone);  $^1\text{H-NMR}$ :  $\delta$  = 6.37 (m, 1H, pyrrolyl H-4), 7.15-7.31 (m, 4H, Ar-H), 7.64-7.91 (m, 2H, pyrrolyl H-3, H-5), 9.85 (br s, 1H, NH), 10.23 (s, 1H, CHO) and 14.98 (s, 1H, NH); MS: ( $\text{M}^+$ ) 266; Anal. Calcd. for  $\text{C}_{14}\text{H}_{10}\text{N}_4\text{O}_2$  (266.24): C, 63.16; H, 3.76; N, 21.05; Found: C, 63.23; H, 3.79; N, 21.07.

*3-(4-Chlorophenyl)-2-(2-cyanophenylhydrazono)-3-oxo-propanal (6h)*. Brown crystals (from 1:1 ethanol dioxane); yield 88%; m.p. 225 °C; IR  $\nu_{\max}$   $\text{cm}^{-1}$ : 3320 (NH), 3019 (CH aromatic), 2221 (CN), 1675 (C=O aldehyde) and 1640 (C=O ketone); MS: ( $\text{M}^+$ ) 311; Anal. Calcd. for  $\text{C}_{16}\text{H}_{10}\text{N}_3\text{O}_2\text{Cl}$  (311.73): C, 61.65; H, 3.23; N, 13.48; Found: C, 61.70; H, 3.15; N, 13.55.

#### General procedure for the preparation of bisazo compounds 7a,b

A cold solution of aryldiazonium salt (10 mmol, a slight excess) was prepared by adding a solution of sodium nitrite (1g in 10 mL  $\text{H}_2\text{O}$ ) with stirring to a cold solution of arylamine hydrochloride (10 mmol of arylamine in 5 mL concentrated HCl) as described earlier. The resulting solution of the aryldiazonium salt was then added to a cold solution of enaminone in EtOH (50 mL) containing sodium acetate (1g in 10 mL  $\text{H}_2\text{O}$ ). The mixture was stirred at room temperature for 1 h and the solid product thus formed was collected by filtration and crystallized from the appropriate solvent.

*3-[(2-cyanophenyl) diazo]-3-[(2-cyanophenyl)hydrazono]propan-2-one (7a)*. Brown crystals (from ethanol); yield 82%; m.p. 179 °C; IR  $\nu_{\max}$   $\text{cm}^{-1}$ : 3066 (CH aromatic), 2935 (CH aliphatic), 2222 (CN), 1666 (C=O);  $^1\text{H-NMR}$ :  $\delta$  = 2.63 (s, 3H,  $\text{CH}_3$ ), 7.20-7.81 (m, 8H, Ar-H), and 15.50 (s, 1H, NH);  $^{13}\text{C-NMR}$ :  $\delta$  = 52.26 ( $\text{CH}_3$ ), 117.05, 117.46 ( $2\text{C}\equiv\text{N}$ ), 100.67, 108.74, 117.96, 118.86, 125.05, 127.74, 133.39, 133.67, 134.10, 134.19, 134.35, 144.75 ( $2\text{C}_6\text{H}_4\text{-CN-o}$ ), 151.75 ( $\text{C=N-NH}$ ) and 197.41 ( $\text{C=O}$ ); MS: ( $\text{M}^+ - 1$ ) 315; Anal. Calcd. for  $\text{C}_{17}\text{H}_{12}\text{N}_6\text{O}$  (316.32): C, 64.55; H, 3.82; N, 26.57; Found: C, 64.60; H, 3.75; N, 26.49.

*1-(4-chlorophenyl)-2-[(2-cyanophenyl)diazo]-2-[(2-cyanophenyl)hydrazono]-ethan-1-one (7b)*. Dark brown crystals (from 1:1 ethanol/dioxane); yield 80%; m.p. 226 °C; IR  $\nu_{\max}$   $\text{cm}^{-1}$ : 3069 (CH aromatic), 2222 (CN), 1646 (C=O);  $^1\text{H-NMR}$ :  $\delta$  = 7.18-7.96 (m, 12H, Ar-H) and 15.75 (s, 1H, NH);  $^{13}\text{C-NMR}$ :  $\delta$  = 101.38, 107.99, 117.17, 119.84, 125.17, 127.56, 133.18, 133.54, 133.57, 134.17, 134.34, 145.48

(2C<sub>6</sub>H<sub>4</sub>-CN-*o*), 116.09, 116.36 (2C≡N), 151.74 (C=N-NH) and 190.07 (C=O); MS: (M<sup>+</sup>-1) 411; Anal. Calcd. for C<sub>22</sub>H<sub>13</sub>N<sub>6</sub>OCl (412.84): C, 64.01; H, 3.17; N, 20.36; Found: C, 64.15; H, 3.20; N, 20.39.

*Reaction of 2-Arylhydrazones with heterocyclic amines:*

*Method I (Δ):* A mixture of compounds **6a-h** (0.1 mol) and amine (0.1 mol) was refluxed in ethanol (30 mL) for 2 hours, then left to cool to room temperature and the solid was collected and crystallized from the appropriate solvent.

*Method II (μω):* A mixture of compounds **6a-h** (0.1 mol) and amine (0.1 mol) and a few drops of ethanol was placed in the microwave oven and irradiated at 390 w for 5 min., then left to cool to room temperature and the solid was collected and crystallized from the appropriate solvent.

*Methyl 2-{N'-[2-Oxo-1-(thiazol-2-yliminomethyl)-propylidene]hydrazino}benzoate (9a).* Brown crystals (from methanol); yield 80%; m.p. 145 °C; IR ν<sub>max</sub> cm<sup>-1</sup>: 3450 (br, NH), 3087 (CH aromatic), 2954 (CH aliphatic), 1706 (C=O ester), 1660 (C=O ketone) and 1571 (C=N); MS: (M<sup>+</sup>) 330; Anal. Calcd. for C<sub>15</sub>H<sub>14</sub>N<sub>4</sub>O<sub>3</sub>S (330.37): C, 54.54; H, 4.27; N, 16.96; Found: C, 54.56; H, 4.20; N, 16.90.

*Methyl 2-{N'-[2-Furan-2-yl-2-oxo-1-(thiazol-2-yliminomethyl)ethylidene]hydrazino}benzoate (9b).* Light brown crystals (from methanol); m.p. 162 °C; <sup>1</sup>H-NMR δ = 3.97 (s, 3H, CH<sub>3</sub>O), 6.79 (m, 1H, furyl H-4), 7.24 (d, 1H, furyl H-3), 7.3, 7.52 (d, 2H, thiazole H-4, H-5), 7.57-8.06 (m, 4H, Ar-H), 7.8 (s, 1H, CH olefinic), 8.13 (d, 1H, furyl H-5) and 15.37 (s, 1H, NH); MS: (M<sup>+</sup>) 382; Anal. Calcd. for C<sub>18</sub>H<sub>14</sub>N<sub>4</sub>O<sub>4</sub>S (382.40): C, 56.54; H, 3.69; N, 14.65; Found: C, 56.57; H, 3.70; N, 14.66.

*2-{N'-[2-Oxo-2-(1H-pyrrol-2-yl)-1-(thiazol-2-yliminomethyl)ethylidene]hydrazino}benzonitrile (9c).* Brown crystals (from ethanol); m.p. 201 °C; IR ν<sub>max</sub> cm<sup>-1</sup>: 3490 (br, NH), 3066 (CH aromatic), 2223 (CN), 1665 (C=O) and 1551 (C=N); MS: (M<sup>+</sup>) 348; Anal. Calcd. for C<sub>17</sub>H<sub>12</sub>N<sub>6</sub>OS (348.39): C, 58.61; H, 3.47; N, 24.12; Found: C, 58.67; H, 3.50; N, 24.15.

*Methyl 2-{N'-[2-(4-chlorophenyl)-2-oxo-1-(pyridin-2-yliminomethyl)ethylidene]hydrazino}benzoate (9d).* Orange crystals (from 2:1 ethanol/dioxane); m.p. 255 °C; IR ν<sub>max</sub> cm<sup>-1</sup>: 3320 (NH), 3007 (CH aromatic), 1645 (C=O ketone), and 1588 (C=N); <sup>1</sup>H-NMR: δ = 3.99 (s, 3H, OCH<sub>3</sub>), 7.25, 7.47 (m, 2H, pyridyl H-4, H-5), 7.62-8.03 (m, 8H, Ar-H), 8.63 (d, 1H, pyridyl H-3), 8.58 (d, 1H, pyridyl H-6), 9.66 (s, 1H, CH olefinic) and 15.73 (s, 1H, NH); MS: (M<sup>+</sup>) 420; Anal. Calcd. for C<sub>22</sub>H<sub>17</sub>N<sub>4</sub>O<sub>3</sub>Cl (420.86): C, 62.79; H, 4.07; N, 13.31; Found: C, 62.70; H, 4.20; N, 13.39.

*2-{N'-[2-Oxo-1-(pyridin-2-yliminomethyl)propylidene]hydrazino}benzonitrile (9e).* Dark orange crystals (from ethanol); m.p. 198 °C; IR ν<sub>max</sub> cm<sup>-1</sup>: 3317 (NH), 3065 (CH aromatic), 2920 (CH aliphatic), 2222 (CN), 1664 (C=O ketone) and 1553 (C=N); MS: (M<sup>+</sup>) 291; Anal. Calcd. for C<sub>16</sub>H<sub>13</sub>N<sub>5</sub>O (291.31): C, 65.97; H, 4.50; N, 24.04; Found: C, 65.87; H, 4.59; N, 24.35.

*2-{N'-[2-Oxo-1-(pyridin-2-yliminomethyl)-2-(1H-pyrrol-2-yl)-ethylidene]hydrazino}benzonitrile (9f).* Dark orange crystals (from ethanol); m.p. 232 °C; IR ν<sub>max</sub> cm<sup>-1</sup>: 3267 (2 NH), 3050 (CH aromatic),

2222 (CN), 1618 (C=O) and 1539 (C=N); MS: ( $M^+$ ) 342; Anal. Calcd. for  $C_{19}H_{14}N_6O$  (342.36): C, 66.66; H, 4.12; N, 24.55; Found: C, 66.56; H, 4.20; N, 24.59.

2-{*N'*-[2-Furan-2-yl-2-oxo-1-(pyridin-2-yliminomethyl)ethylidene]hydrazino}benzonitrile (**9g**). Brown crystals (from ethanol); m.p. 259 °C; IR  $\nu_{\max}$   $cm^{-1}$ : 3500 (br, NH), 3105 (CH aromatic), 2220 (CN), 1631 (C=O) and 1549 (C=N); MS: ( $M^+$ ) 343; Anal. Calcd. for  $C_{19}H_{13}N_5O_2$  (343.35): C, 66.47; H, 3.82; N, 20.40; Found: C, 66.50; H, 3.89; N, 20.35.

Methyl 2-(*N'*-{1-[(1*H*-Benzoimidazol-2-ylimino)-methyl]-2-furan-2-yl-2-oxo-ethylidene}hydrazino)benzoate (**9h**). Brown crystals (from 2:1 ethanol/dioxane); m.p. 240°C;  $^1H$ -NMR:  $\delta$  = 4.0 (s, 3H, OCH<sub>3</sub>), 6.83 (dd, 1H, furyl H-4), 7.22-7.25 (m, 4H, imidazole-H), 7.36 (m, 1H, furyl H-3), 7.63-7.99 (m, 4H, Ar-H), 8.08 (d, 1H, furyl H-5), 9.47 (s, 1H, CH olefinic), 12.11 (s, 1H, NH imidazole) and 15.85 (s, 1H, NH hydrazone) ppm; MS: ( $M^+$ ) 415; Anal. Calcd. for  $C_{22}H_{17}N_5O_4$  (415.41): C, 63.61; H, 4.12; N, 16.86; Found: C, 63.67; H, 4.22; N, 16.90.

Methyl 2-(*N'*-{1-[(1*H*-Benzoimidazol-2-ylimino)-methyl]-2-oxo-2-(1*H*-pyrrol-2-yl)-ethylidene}hydrazino)benzoate (**9i**). Dark yellow crystals (from 2:1 ethanol/dioxane); m.p. 281°C; IR  $\nu_{\max}$   $cm^{-1}$  (shows complex spectra due to H-bond between O and NH): 3480 (NH pyrrolyl), 3383 (NH imidazole), 3081 (CH aromatic), 1718 (C=O ester), 1656 (C=O ketone) and 1571 (C=N);  $^1H$ -NMR:  $\delta$  = 3.96 (s, 3H, OCH<sub>3</sub>), 6.54 (m, 1H, pyrrolyl H-4), 6.95-7.02 (m, 2H, pyrrolyl H-3, H-5), 7.21-7.32 (m, 4H, imidazole H), 7.54-7.97 (m, 4H, Ar-H), 9.22 (s, 1H, CH olefinic), 11.43 (s, 1H, NH pyrrolyl), 11.65 (s, 1H, NH imidazole) and 14.25 (s, 1H, NH hydrazone) ppm; MS: ( $M^+$ ) 414; Anal. Calcd. for  $C_{22}H_{18}N_6O_3$  (414.43): C, 63.76; H, 4.38; N, 20.28; Found: C, 63.79; H, 4.40; N, 20.30.

Methyl 2-(*N'*-{1-[(1*H*-Benzoimidazol-2-ylimino)-methyl]-2-(4-chlorophenyl)-2-oxo-2-ethylidene}hydrazino)benzoate (**9j**). Orange crystals (from 2:1 ethanol/dioxane); m.p. 257 °C; IR  $\nu_{\max}$   $cm^{-1}$ : (shows complex spectra due to H-bond between O and NH) 3354 (NH imidazole), 1690 (C=O ester), 1640 (C=O ketone) and 1586 (C=N); MS: ( $M^+$ -18) 441; Anal. Calcd. for  $C_{24}H_{18}N_5O_3Cl$  (459.90): C, 62.68; H, 3.95; N, 15.23; Found: C, 62.58; H, 3.90; N, 15.33.

Methyl 2-{*N'*-[1-(Benzothiazol-2-yliminomethyl)-2-oxo-2-(1*H*-pyrrol-2-yl)-ethylidene]-hydrazino}benzoate (**9k**). Brown crystals (from methanol); m.p. 189 °C; IR  $\nu_{\max}$   $cm^{-1}$ : 3492, 3224 (2NH), 3023 (CH aromatic), 1720 (C=O ester), 1664 (C=O ketone) and 1575 (C=N);  $^1H$ -NMR:  $\delta$  = 3.96 (s, 3H, OCH<sub>3</sub>), 6.41 (m, 1H, pyrrolyl H-4), 6.75 (d, 2H, pyrrolyl H-3), 6.89 (s, 1H, CH olefinic), 6.95 (d, 1H, pyrrolyl H-5), 7.22, 7.36 (d, 2H, benzothiazole H-4, H-7), 7.38-7.44 (m, 2H, benzothiazole H-5, H-6), 7.53 (s, 1H, NH pyrrolyl), 7.62-7.69 (m, 2H, Ar H-4, H-5), 7.89, 7.91 (d, 2H, Ar H-3, H-6), and 14.46 (s, 1H, NH hydrazone) ppm;  $^{13}C$ -NMR:  $\delta$  = 52.46 (OCH<sub>3</sub>), 110.33, 121.24, 126.57, 131.30 (pyrrolyl carbon), 113.21, 114.03, 116.90, 119.54, 134.21, 136.84 ( $C_6H_4$ -CO<sub>2</sub>Me-o), 121.58, 123.18, 124.77, 134.32, 137.45 ( $C_6H_4$ NS), 140.50 ( $C=N$ -N), 144.82 (N-C-S), 165.27 (HC=N), 167.31 (COOCH<sub>3</sub>) and 173.42 ( $C=O$ ) ppm; MS: ( $M^+$ ) 431; Anal. Calcd. for  $C_{22}H_{17}N_5O_3S$  (431.48): C, 61.24; H, 3.97; N, 16.23; Found: C, 61.34; H, 3.87; N, 16.40.

2-{*N'*-[1-(Benzothiazol-2-yliminomethyl)-2-oxo-propylidene]-hydrazino}-benzonitrile (**9l**). Brown crystals (from 2:1 ethanol/dioxane); m.p. 223 °C; IR  $\nu_{\max}$   $\text{cm}^{-1}$ : 3350 (NH), 3061 (CH aromatic), 2921 (CH aliphatic), 2216 ( $\text{C}\equiv\text{N}$ ), 1684 ( $\text{C}=\text{O}$ ) and 1560 ( $\text{C}=\text{N}$ );  $^1\text{H}$ -NMR:  $\delta$  = 2.60 (s, 3H,  $\text{CH}_3$ ), 7.24-7.99 (m, 8H, Ar-H), 9.50 (s, 1H, CH olefinic) and 15.29 (s, 1H, NH) ppm,  $^{13}\text{C}$ -NMR:  $\delta$  = 25.10 ( $\text{CH}_3\text{CO}$ ), 101.32, 115.80, 121.92, 134.23, 134.38, 145.82 ( $\text{C}_6\text{H}_4\text{-CN-o}$ ), 116.32 ( $\text{C}\equiv\text{N}$ ), 123.56, 125.45, 125.48, 126.81, 133.12 ( $\text{C}_6\text{H}_4\text{NS}$ ), 151.55 ( $\text{C}=\text{N-N}$ ), 153.50 ( $\text{N-C-S}$ ), 168.40 ( $\text{HC}=\text{N}$ ) and 196.56 ( $\text{C}=\text{O}$ ) ppm; MS: ( $\text{M}^+$ ) 347; Anal. Calcd. for  $\text{C}_{18}\text{H}_{13}\text{N}_5\text{OS}$  (347.40): C, 62.23; H, 3.77; N, 20.16; Found: C, 62.40; H, 3.97; N, 20.20.

2-{*N'*-[1-(Benzothiazol-2-yliminomethyl)-2-(4-chlorophenyl)-2-oxo-ethylidene]-hydrazino}-benzonitrile (**9m**). Brown crystals (from 2:1 ethanol/dioxane); m.p. 259 °C; IR  $\nu_{\max}$   $\text{cm}^{-1}$ : 3600 (br, NH), 3070 (CH aromatic), 2219 ( $\text{C}\equiv\text{N}$ ), 1650 ( $\text{C}=\text{O}$ ) and 1559 ( $\text{C}=\text{N}$ );  $^1\text{H}$ -NMR:  $\delta$  = 6.97-8.35 (m, 12H, Ar-H), 8.13 (s, 1H, CH olefinic) and 15.10 (s, 1H, NH) ppm; MS: ( $\text{M}^+$ ) 443; Anal. Calcd. for  $\text{C}_{23}\text{H}_{14}\text{N}_5\text{OClS}$  (443.92): C, 62.23; H, 3.18; N, 15.78; Found: C, 62.40; H, 3.28; N, 15.68.

Methyl 2-[2-piperidin-1-yl-1-(1H-pyrrol-2-carbonyl)-vinylazoethylidene] benzoate (**12a**). Brown crystals (from ethanol); m.p. 200 °C; IR  $\nu_{\max}$   $\text{cm}^{-1}$ : 3158 (NH pyrrolyl), 3009 (CH aromatic), 2932 (CH aliphatic), 1672 ( $\text{C}=\text{O}$  ester), 1573 ( $\text{C}=\text{O}$  ketone) and 1495 ( $\text{N}=\text{N}$ );  $^1\text{H}$ -NMR:  $\delta$  = 1.43-2.75 (m, 10H, piperidin H), 5.57 (s, 1H, NH pyrrolyl), 6.50 (m, 1H, pyrrolyl H-4), 6.82 (d, 1H, pyrrolyl H-3), 6.95-6.99 (m, 1H, Ar H-4), 7.21 (d, 1H, pyrrolyl H-5), 7.49-7.53 (m, 1H, Ar H-5), 7.86, 7.98 (d, 2H, Ar-H-3, H-6) and 8.12 (s, 1H, CH olefinic) ppm;  $^{13}\text{C}$ -NMR:  $\delta$  = 24.54, 26.18, 48.43 (piperidinyl carbons), 52.37 ( $\text{COOCH}_3$ ), 109.35, 112.88, 114.03 (pyrrolyl carbons), 116.13, 120.77, 123.43, 131.34, 134.32, 135.38 ( $\text{C}_6\text{H}_4\text{-CO}_2\text{M-o}$ ), 139.45 ( $\text{HC}=\text{C-N}$ ), 145.59 ( $\text{HC}=\text{C-N}$ ), 167.42 ( $\text{COOCH}_3$ ) and 174.40 ( $\text{C}=\text{O}$ ) ppm; MS: ( $\text{M}^+$ ) 366; Anal. Calcd. for  $\text{C}_{20}\text{H}_{22}\text{N}_4\text{O}_3$  (366.42): C, 65.56; H, 6.05; N, 15.29; Found: C, 65.69; H, 6.25; N, 15.15.

Methyl 2-[2-morpholin-4-yl-1-(1H-pyrrol-2-carbonyl)-vinylazo] benzoate (**12b**). Brown crystals (from ethanol); m.p. 190 °C; IR  $\nu_{\max}$   $\text{cm}^{-1}$ : 3115 (NH pyrrolyl), 3018 (CH aromatic), 2952 (CH aliphatic), 1697 ( $\text{C}=\text{O}$  ester), 1660 ( $\text{C}=\text{O}$  ketone) and 1495 ( $\text{N}=\text{N}$ );  $^1\text{H}$ -NMR:  $\delta$  = 2.47-2.79 (m, 4H, morpholinyl H), 3.58, 3.93 (d, 4H, morpholinyl H), 5.93 (s, 1H, NH pyrrolyl), 6.60 (m, 1H, pyrrolyl H-4), 6.87 (d, 1H, pyrrolyl H-3), 7.20 (d, 1H, pyrrolyl H-5), 7.55-7.97 (m, 4H, Ar-H) and 8.10 (s, 1H, CH olefinic) ppm; MS: ( $\text{M}^+$ ) 368; Anal. Calcd. for  $\text{C}_{19}\text{H}_{20}\text{N}_4\text{O}_4$  (368.40): C, 61.95; H, 5.47; N, 15.21; Found: C, 61.92; H, 5.50; N, 15.30.

*General procedure for the reaction of 2-arylhydrazono derivatives with active methylene compounds*

*With benzotriazolacetone*

**Method I** ( $\Delta$ ): A solution of compounds **6e,h** (0.1 mol) in ethanol (30 mL) was treated with benzotriazolylacetone (0.1 mol) in the presence of a few drops of piperidine and refluxed for 3 hours. The precipitated material was isolated by filtration and crystallized from the appropriate solvent

**Method II ( $\mu\omega$ ):** Compounds **6e,h** (0.1 mol) and benzotriazolylacetone (0.1 mol) in the presence of a few drops of piperidine was placed in the microwave oven and irradiated at 390 w for 2-15 min., then left to cool to room temperature and the solid was collected and crystallized from the appropriate solvent.

**5-Benzotriazolyl-3-(2-cyanophenylhydrazono)-4-hepten-2,6-dione (14a).** Brown crystals (from dioxane); m.p. 235 °C;  $^1\text{H-NMR}$ :  $\delta$  = 2.20, 2.30 (s, 3H, 2CH<sub>3</sub>), 6.64-7.98 (m, 9H, Ar-H + CH olefinic) and 14.12 (s, 1H, NH) ppm;  $^{13}\text{C-NMR}$ :  $\delta$  = 19.77, 19.80 (2C<sub>H</sub>), 112.11 (HC), 116.50 (CN), 110.11, 115.82, 119.20, 132.81, 133.65, 150.22 (C<sub>6</sub>H<sub>4</sub>CN-o), 128.59, 129.89, 130.23, 131.79 (benzotriazolyl carbons), 144.70 (N-C-CO), 155.39 (C=N-N) and 196.55, 199.75 (2C=O) ppm; MS: (M<sup>+</sup>) 372; Anal. Calcd. for C<sub>20</sub>H<sub>16</sub>N<sub>6</sub>O<sub>2</sub> (372.39): C, 64.51; H, 4.33; N, 22.57; Found: C, 64.65; H, 4.23; N, 22.59.

**4-Benzotriazolyl-1-(4-chlorophenyl)-2-(2-cyanophenylhydrazono)-3-hexaen-1,5-dione (14b).** Green crystals (from ethanol); m.p. 259 °C; IR  $\nu_{\text{max}}$  cm<sup>-1</sup>: 3400 (NH), 3068 (CH aromatic), 2320 (C $\equiv$ N), 1674 (C=O) and 1646 (C=O ketone);  $^1\text{H-NMR}$ :  $\delta$  = 1.99 (s, 3H, CH<sub>3</sub>), 7.20 (s, 1H, CH olefinic), 7.61-8.11 (m, 12H, Ar-H) and 13.89 (s, 1H, NH) ppm; MS: (M<sup>+</sup>) 468; Anal. Calcd. for C<sub>25</sub>H<sub>17</sub>N<sub>6</sub>O<sub>2</sub>Cl (468.91): C, 64.04; H, 3.65; N, 17.92; Found: C, 64.45; H, 3.59; N, 17.99.

*With glycine or N-acetylglycine or hippuric acid*

**Method I ( $\Delta$ ):** Each of compounds **6a,b,d,e,f,h** (0.1 mol) and glycine or N-acetylglycine or hippuric acid (0.1 mol) was refluxed in acetic anhydride (20 mL) for 1 hour, then left to cool at room temperature and poured into ice-cold water. The solid product so formed was collected by filtration and crystallized from the appropriate solvent.

**Method II ( $\mu\omega$ ):** Each of compounds **6a,b,d,e,f,h** (0.1 mol) and glycine or N-acetylglycine or hippuric acid (0.1 mol) and drops from acetic anhydride (20 mL) was placed in the microwave oven and irradiated at 390 W for 5-15 min., then left to cool to room temperature and the solid was collected and crystallized from the appropriate solvent.

**4-Acetylamino-6-acetyl-2-(2-methoxycarbonylphenyl)-2-hydropyridazin-3-one (17a).** Brown crystals (from ethanol); m.p. 238 °C;  $^1\text{H-NMR}$ :  $\delta$  = 2.23, 2.43 (s, 3H, 2CH<sub>3</sub>CO), 3.66 (s, 3H, OCH<sub>3</sub>), 7.66-8.01 (m, 4H, Ar-H), 8.61 (s, 1H, pyridazinyl H-5) and 10.21 (s, 1H, NH) ppm;  $^{13}\text{C-NMR}$ :  $\delta$  = 24.83 (NHCOCH<sub>3</sub>), 25.11 (CH<sub>3</sub>CO), 52.98 (COOCH<sub>3</sub>), 108.76, 136.98, 143.87 (pyridazine ring), 127.78, 128.99, 130.17, 130.90, 134.02, 140.89 (C<sub>6</sub>H<sub>4</sub>-CO<sub>2</sub>Me-o), 156.25 (C=O ring), 165.54 (COOCH<sub>3</sub>), 171.98 (NHCOCH<sub>3</sub>) and 195.66 (CH<sub>3</sub>CO) ppm; MS: (M<sup>+</sup>) 329; Anal. Calcd. for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>O<sub>5</sub> (329.32): C, 58.36; H, 4.59; N, 12.76; Found: C, 58.40; H, 4.55; N, 12.86.

**4-Acetylamino-6-(2-furylcarbonyl)-2-(2-methoxycarbonylphenyl)-2-hydropyridazin-3-one (17b).** Dark brown crystals (from ethanol); m.p. 214 °C;  $^1\text{H-NMR}$ :  $\delta$  = 2.25 (s, 3H, CH<sub>3</sub>CO), 3.66 (s, 3H, OCH<sub>3</sub>), 6.73 (m, 1H, furyl H-4), 7.51 (d, 1H, furyl H-3), 7.68-7.89 (m, 4H, Ar H), 8.02 (d, 1H, furyl H-5), 8.69

(s, 1H, pyridazinyl H-5) and 10.26 (s, 1H, NH) ppm; MS: ( $M^+$ ) 381; Anal. Calcd. for  $C_{19}H_{15}N_3O_6$  (381.35): C, 59.84; H, 3.96; N, 16.08; Found: C, 59.79; H, 3.99; N, 16.25.

**4-Acetylamino-6-(4-chlorophenylcarbonyl)-2-(2-methoxycarbonylphenyl)-2-hydropyridazin-3-one (17c).** Light yellow crystals (from ethanol); m.p. 246 °C; IR  $\nu_{\max}$   $\text{cm}^{-1}$ : 3285 (NH), 1713 (C=O ester and C=O ketone) and 1644 (C=O amide and C=O pyridazine ring);  $^1\text{H-NMR}$ :  $\delta$  = 2.21 (s, 3H,  $\text{CH}_3\text{CO}$ ), 3.85 (s, 3H,  $\text{OCH}_3$ ), 7.53–8.03 (m, 8H, Ar-H), 8.70 (s, 1H, pyridazinyl H-5) and 10.19 (s, 1H, NH) ppm; MS: ( $M^+$ ) 425; Anal. Calcd. for  $C_{21}H_{16}N_3O_5\text{Cl}$  (425.83): C, 59.23; H, 3.79; N, 9.87; Found: C, 59.35; H, 3.70; N, 9.96.

**4-Acetylamino-6-acethyl-2-(2-cyanophenyl)-2-hydropyridazin-3-one (17d).** Dark brown crystals (from ethanol); m.p. 244 °C; IR  $\nu_{\max}$   $\text{cm}^{-1}$ : 3323 (NH), 3107 (CH aromatic), 2900 (CH aliphatic), 2234 (C $\equiv$ N), 1702 (C=O ketone), 1656 (C=O amide) and 1608 (C=O pyridazine ring);  $^1\text{H-NMR}$ :  $\delta$  = 2.26, 2.49 (s, 3H,  $2\text{CH}_3\text{CO}$ ), 7.73–8.15 (m, 4H, Ar-H), 8.64 (s, 1H, pyridazinyl H-5) and 10.33 (s, 1H, disappeared after  $\text{D}_2\text{O}$  exchange, NH) ppm; MS: ( $M^+$ ) 296; Anal. Calcd. for  $C_{15}H_{12}N_4O_3$  (296.29): C, 60.81; H, 4.08; N, 18.91; Found: C, 60.91; H, 4.25; N, 18.75.

**4-Acetylamino-2-(2-cyanophenyl)-6-(2-furyl carbonyl)-2-hydropyridazin-3-one (17e).** Brown crystals (from ethanol); m.p. 242 °C; IR  $\nu_{\max}$   $\text{cm}^{-1}$ : 3295 (NH), 3037 (CH aromatic), 2236 (C $\equiv$ N), 1714 (C=O ketone), 1649 (C=O amide) and 1620 (C=O pyridazine ring);  $^1\text{H-NMR}$ :  $\delta$  = 2.28 (s, 3H,  $\text{CH}_3$ ), 6.76 (m, 1H, furyl H-4), 7.64, 8.13 (d, 2H, furyl H-3, H-5), 7.74–8.05 (m, 4H, Ar-H), 8.70 (s, 1H, pyridazinyl H-5) and 10.41 (s, 1H, NH) ppm; MS: ( $M^+$ ) 348; Anal. Calcd. for  $C_{18}H_{12}N_4O_4$  (348.32): C, 62.07; H, 3.47; N, 16.08; Found: C, 62.25; H, 3.40; N, 16.32.

**4-Acetylamino-6-(4-chlorophenylcarbonyl)-2-(2-cyanophenyl)-2-hydropyridazin-3-one (17f).** Brown crystals (from 1:1 ethanol/dioxane); m.p. 252 °C; IR  $\nu_{\max}$   $\text{cm}^{-1}$ : 3225 (NH), 3050 (CH aromatic), 2220 (CN), 1718 (C=O ketone), 1640 (C=O amide) and 1635 (C=O pyridazine ring); MS: ( $M^+$ ) 392; Anal. Calcd. for  $C_{20}H_{13}N_4O_3\text{Cl}$  (392.80): C, 61.16; H, 3.34; N, 14.26; Found: C, 61.25; H, 3.30; N, 14.29.

**6-Acetyl-4-Benzoylamino-2,3-dihydro-2-(2-methoxycarbonylphenyl)pyridazin-3-one (17g).** Brown crystals (from ethanol); m.p. 170 °C; IR  $\nu_{\max}$   $\text{cm}^{-1}$ : 3339 (NH), 3077 (CH aromatic), 1799 (C=O ester), 1750 (C=O ketone), 1690 (C=O amide) and 1640 (C=O pyridazine ring); MS: ( $M^+$ ) 391; Anal. Calcd. for  $C_{21}H_{17}N_3O_5$  (391.39): C, 64.45; H, 4.38; N, 10.74; Found: C, 64.55; H, 4.28; N, 10.80.

*General Procedure for the reaction of 2-arylhydrazono derivatives with dimethyl acetylenedicarboxylate (DMAD):*

**Method I ( $\Delta$ ):** To stirred solution of triphenylphosphine (0.1 mol) and each of compound **6b,e** (0.1 mol) in dichloroethane (10 mL) was added a few drops of DMAD solution (0.1 mol) in dichloroethane (10 mL) then left at room temperature overnight. The solvent was removed and the residue cooled to deposit a solid, which was crystallized from the appropriate solvent.

**Table 2.** Comparison between microwave and conventional heating reactions.

| Product | Time/min              |                          |             | Yield%                |                          |             |
|---------|-----------------------|--------------------------|-------------|-----------------------|--------------------------|-------------|
|         | $\Delta$ With Solvent | $\Delta$ Without Solvent | $\mu\omega$ | $\Delta$ With Solvent | $\Delta$ Without Solvent | $\mu\omega$ |
| 2a      | 2100                  | -                        | -           | -                     | -                        | -           |
| 2b      | 420                   | 480                      | 3           | 79                    | 85                       | 96          |
| 2c      | 420                   | 480                      | 5           | 89                    | 90                       | 97          |
| 2d      | 420                   | 480                      | 5           | 60                    | 77                       | 96          |
| 2e      | 420                   | 480                      | 1           | 75                    | 88                       | 99          |
| 2f      | 420                   | 480                      | 1           | 80                    | 87                       | 98          |
| 2g      | 420                   | 480                      | 5           | 61                    | 88                       | 97          |
| 9a      | 120                   | -                        | 5           | 65                    | -                        | 70          |
| 9b      | 120                   | -                        | 15          | 70                    | -                        | 75          |
| 9c      | 120                   | -                        | 5           | 54                    | -                        | 65          |
| 9d      | 120                   | -                        | 7           | 40                    | -                        | 95          |
| 9e      | 120                   | -                        | 15          | 60                    | -                        | 99          |
| 9f      | 120                   | -                        | 7           | 55                    | -                        | 73          |
| 9g      | 120                   | -                        | 15          | 73                    | -                        | 80          |
| 9h      | 120                   | -                        | 10          | 60                    | -                        | 99          |
| 9i      | 120                   | -                        | 10          | 56                    | -                        | 99          |
| 9j      | 120                   | -                        | 10          | 95                    | -                        | 98          |
| 9k      | 120                   | -                        | 10          | 46                    | -                        | 60          |
| 9l      | 120                   | -                        | 5           | 50                    | -                        | 70          |
| 9m      | 120                   | -                        | 15          | 65                    | -                        | 70          |
| 12a     | 180                   | -                        | 2           | 30                    | -                        | 70          |
| 12b     | 180                   | -                        | 2           | 50                    | -                        | 87          |
| 14a     | 180                   | -                        | 2           | 16                    | -                        | 25          |
| 14b     | 180                   | -                        | -           | 40                    | -                        | -           |
| 17a     | 60                    | -                        | -           | 20                    | -                        | -           |
| 17b     | 60                    | -                        | -           | 80                    | -                        | -           |
| 17c     | 60                    | -                        | 15          | 25                    | -                        | 35          |
| 17d     | 60                    | -                        | 5           | 25                    | -                        | 40          |
| 17e     | 60                    | -                        | -           | 61                    | -                        | -           |
| 17f     | 60                    | -                        | -           | 25                    | -                        | -           |
| 17g     | 60                    | -                        | 10          | 35                    | -                        | 50          |
| 22a     | 1440                  | -                        | -           | 27                    | -                        | -           |
| 22b     | 1440                  | -                        | 30          | 24                    | -                        | 60          |

*Method II* ( $\mu\omega$ ): Each of compounds **6b,e** (0.1 mol) and triphenylphosphine (0.1 mol) and a few drops of DMAD solution (0.1 mol), was placed in the microwave oven and irradiated at 390 W for 10-30 min., then left to cool to room temperature and the solid was collected and crystallized from the appropriate solvent.



*2,3-Dihydro-3,4-dimethoxycarbonyl-6-(2-furylcarbonyl)-2-(2-methoxycarbonylphenyl)pyridazine*

**(22a)**. Yellow crystals (from ethanol); m.p. 141 °C; IR:  $\nu_{\max}$   $\text{cm}^{-1}$ : 3305 (NH), 3077 (CH aromatic), 2962 (CH aliphatic), 1780, 1750 (3C=O ester) and 1681 (C=O ketone);  $^1\text{H-NMR}$ :  $\delta$  = 3.55, 3.70, 3.89 (s, 3H, 3CH<sub>3</sub>), 6.01 (s, 1H, pyridazine H-3), 6.48 (m, 1H, furyl H-4), 7.36-7.65 (m, 4H, Ar-H), 7.47, 7.77 (d, 2H, furyl H-3, H-5) and 7.83 (s, 1H, pyridazine H-5) ppm;  $^{13}\text{C-NMR}$ :  $\delta$  = 52.24, 52.68, 53.20 (3COOCH<sub>3</sub>), 57.88, 126.88, 141.01, 149.94 (pyridazine carbons), 112.29, 117.20, 121.94, 131.04, 132.34, 144.40 (C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>Me-o), 122.35, 123.91, 126.89, 147.20 (furyl carbons), 164.84, 167.03, 168.70 (3COOCH<sub>3</sub>) and 174.63 (C=O) ppm; MS: (M<sup>+</sup>) 426; Anal. Calcd. for C<sub>21</sub>H<sub>18</sub>N<sub>2</sub>O<sub>8</sub> (426.39): C, 59.16; H, 4.26; N, 6.57; Found: C, 59.10; H, 4.39; N, 6.69.

*2-(2-Cyanophenyl)-2,3-dihydro-3,4-dimethoxycarbonyl-6-acetylpyridazine (22b)*. Yellow crystals

(from ethanol); m.p. 175 °C; IR:  $\nu_{\max}$   $\text{cm}^{-1}$ : 3415 (NH), 3013 (CH aromatic), 2959 (CH aliphatic), 2221 (C≡N), 1746, 1717 (2C=O ester) and 1673 (C=O ketone);  $^1\text{H-NMR}$ :  $\delta$  = 2.20 (s, 3H, CH<sub>3</sub>), 3.67, 3.76 (s, 3H, 2OCH<sub>3</sub>), 6.20 (s, 1H, pyridazine H-3), 6.61-7.32 (m, 4H, Ar-H) and 7.80 (s, 1H, pyridazine H-5) ppm;  $^{13}\text{C-NMR}$ :  $\delta$  = 19.80 (CH<sub>3</sub>), 50.55, 50.81 (2CO-OCH<sub>3</sub>), 62.80, 126.85, 142.20, 150.45 (pyridazine carbons), 101.32, 113.00, 117.62, 132.81, 133.52, 147.82 (C<sub>6</sub>H<sub>4</sub>CN-o), 116.50 (CN), 165.05, 171.20 (2COOCH<sub>3</sub>) and 196.56 (C=O) ppm; MS: (M<sup>+</sup>+1) 342; Anal. Calcd. For C<sub>17</sub>H<sub>15</sub>N<sub>3</sub>O<sub>5</sub> (341.33): C, 59.82; H, 4.43; N, 12.31; Found: C, 59.98; H, 4.35; N, 12.48.

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