

# Irradiation of Tungsten Light: A Useful Energy Source for Synthesis of 4,5-Dihydro-pyrazole-1-carbaldehyde Derivatives

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**Abstract:** In the present communication, reported the easy, convenient route for the synthesis of *N*-formyl pyrazolines from  $\alpha,\beta$ -unsaturated ketone. The aqueous 2-methoxyethanol was used as reaction media for the synthesis of titled compounds. All synthesized compounds were confirmed on the basis of IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and CHN analysis.

**Keywords:** aqueous 2-methoxyethanol; hydrazine hydrate; irradiation of tungsten light; *N*-formyl-2-pyrazoline;  $\alpha,\beta$ -unsaturated ketone

## 1. INTRODUCTION

Amongst five-membered heterocycles, Nitrogen containing heterocyclic compounds represents a wide range of pharmacological applications and pronounced biological properties [1-8]. Pyrazolines are useful synthons in organic chemistry and also important in the development of theory in heterocyclic chemistry [9-10]. A classical synthesis of these compounds involves the condensation of  $\alpha,\beta$ -unsaturated carbonyl compounds with hydrazines [11].

The three components one step synthesis has great current interest towards development of novel synthetic organic compounds. One of the three component one step reaction involve, synthesis of *N*-formyl pyrazolines in which  $\alpha,\beta$ -unsaturated ketone reacts with hydrazine hydrate and formic acid [12-14]. In view of these observations and in continuation of earlier research work on synthesis of substituted 4,5-dihydro-pyrazole-1-carbaldehyde derivative [15-17], herein first time reported the synthesis of titled compound using irradiation of tungsten light as a useful energy in organic synthesis.

## 2. MATERIAL AND METHODS

### Chemical

All chemicals, solvents and reagents used in the present study were of analytical grade purchased from Sigma, SD Fine, or Spectrochem.

### Instrumentation

Melting points were determined in an open capillary tube and are uncorrected. The reactions were carried out in aqueous 2-methoxyethanol solvent (10 mL:10 mL, v/v) using 200 watt tungsten bulb light. Purification of the compounds was indicated using TLC (mixture of ethyl acetate and hexane, 0.20 mL:0.20 mL, vv). IR spectra were recorded in KBr pellets on a Perkin-Elmer FT-IR Shimadzu spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained in DMSO-*d*<sub>6</sub> on Avance 300 MHz spectrometer using TMS as an internal standard. The mass spectra were recorded on EI-Shimadzu-GC-MS spectrometer. Elemental analyses were performed on a Carlo Erba 106 Perkin-Elmer model 240 analyzer.

**General Procedure for synthesis of 4,5-dihydro-pyrazole-1-carbaldehyde derivative:** In 50 mL beaker, a mixture of  $\alpha,\beta$ -unsaturated ketones **1** (0.01 mol), hydrazines hydrate **2** (0.01mmol) and formic acid **3** (0.01 mmol) was dissolved in aqueous 2-methoxyethanol (20 mL) by warming. To this hot

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reaction solution acetic acid (0.001 mmol) was added and irradiated under tungsten light (200 Watt) for 40-54 min, and progress of reaction was monitored on TLC. After completion of reaction, the resultant mixture was poured with stirring into water (20 mL). The precipitate formed was filtered through simple büchner funnel under vacuum pressure and crystallized from ethanol to yield 2-pyrazolines (Scheme 1).

**5-(4-Fluoro-phenyl)-3-[2-(4-fluoro-phenyl)-vinyl]-4,5-dihydro-pyrazole-1-carbaldehyde. (4a):** IR (KBr): 1628 (C=O), 1578 (C=N)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz, DMSO-*d*6)  $\delta$  3.25 (dd,  $J = 5.0, 17.8$  Hz, 1H,  $\text{H}_A$ ),  $\delta$  3.65 (dd,  $J = 12.0, 17.8$  Hz, 1H,  $\text{H}_B$ ),  $\delta$  5.49 (dd,  $J = 5.1, 12.1$  Hz, 1H,  $\text{H}_X$ ),  $\delta$  6.78 (d,  $J = 16.2$  Hz, 1H,  $\text{H}_\alpha$ ),  $\delta$  7.17 (d,  $J = 16.2$  Hz, 1H,  $\text{H}_\beta$ ),  $\delta$  7.31-7.68 (m, 8H, Ar-H),  $\delta$  8.90 (s, 1H, CHO).  $^{13}\text{C}$  NMR (DMSO-*d*6) 160.42 (C=O), 143.70 (C=N), 135.28 ( $\text{C}_\beta$ , C=C double bond), 137.88 (C, Ar-C), 135.57 (C, Ar-C) 134.74 (2CH, of two Ar-C), 130.53 (2CH, of two Ar-C), 128.50 (2CH, of two Ar-C), 120.42 (2CH, of two Ar-C) 118.32 ( $\text{C}_\alpha$ , C=C double bond), 50.47 (-CH), 38.42 (-CH<sub>2</sub>). MS  $m/z$ : 312 (M<sup>+</sup>). Anal. Calcd for  $\text{C}_{18}\text{H}_{14}\text{F}_2\text{N}_2\text{O}$ : C, 69.23; H, 4.48. Found: C, 69.35; H, 5.53.

**5-(3-Iodo-4,5-dimethoxy-phenyl)-3-[2-(3-iodo-4,5-dimethoxy-phenyl)-vinyl]-4,5-dihydro-pyrazole-1-carbaldehyde. (4d):** IR (KBr): 1632 (C=O), 1585 (C=N)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz, DMSO-*d*6)  $\delta$  3.76 (s, 12H, four  $\text{OCH}_3$ ),  $\delta$  3.27 (dd,  $J = 5.0, 17.8$  Hz, 1H,  $\text{H}_A$ ),  $\delta$  3.62 (dd,  $J = 12.0, 17.8$  Hz, 1H,  $\text{H}_B$ ),  $\delta$  5.50 (dd,  $J = 5.1, 12.1$  Hz, 1H,  $\text{H}_X$ ),  $\delta$  6.78 (d,  $J = 16.2$  Hz,

1H,  $\text{H}_\alpha$ ),  $\delta$  7.17 (d,  $J = 16.2$  Hz, 1H,  $\text{H}_\beta$ ),  $\delta$  7.29-7.74 (m, 4H, Ar-H),  $\delta$  8.90 (s, 1H, CHO).  $^{13}\text{C}$  NMR (DMSO-*d*6) 167.12 (4C of two *para* Ar-ome) 160.47 (C=O), 143.77 (C=N), 135.30 ( $\text{C}_\beta$ , C=C double bond), 137.67 (C, Ar-C), 135.61 (C, Ar-C) 134.75 (2CH, of two Ar-C), 130.50 (2CH, of two Ar-C), 128.55 (2CH, of two Ar-C), 120.48 (2CH, of two Ar-C) 118.32 ( $\text{C}_\alpha$ , C=C double bond), 50.43 (-CH), 38.48 (-CH<sub>2</sub>). MS  $m/z$ : 648 (M<sup>+</sup>). Anal. Calcd for  $\text{C}_{22}\text{H}_{22}\text{O}_5\text{I}_2\text{N}_2$ : C, 40.74; H, 3.39. Found: C, 40.81; H, 3.43.

### 3. RESULTS AND DISCUSSION

Recently we reported the synthesis of 2-pyrazolines from 2'-hydroxychalcones in presence of catalytic amount of acetic acid under irradiation of tungsten light [18]. In view these observations we tried to implement the same reaction condition for cyclisation of  $\alpha,\beta$ -unsaturated ketone to afford N-formyl pyrazolines. Initially we attempted the condensation of 1,5-Bis-(4-fluoro-phenyl)-penta-1,4-dien-3-one with hydrazine hydrate and formic acid using acetic acid in aqueous 2-methoxyethanol in combination with irradiation of tungsten light. The reaction went to completion within 40 min and corresponding product **4a** obtained in 88% yield (Table 1).

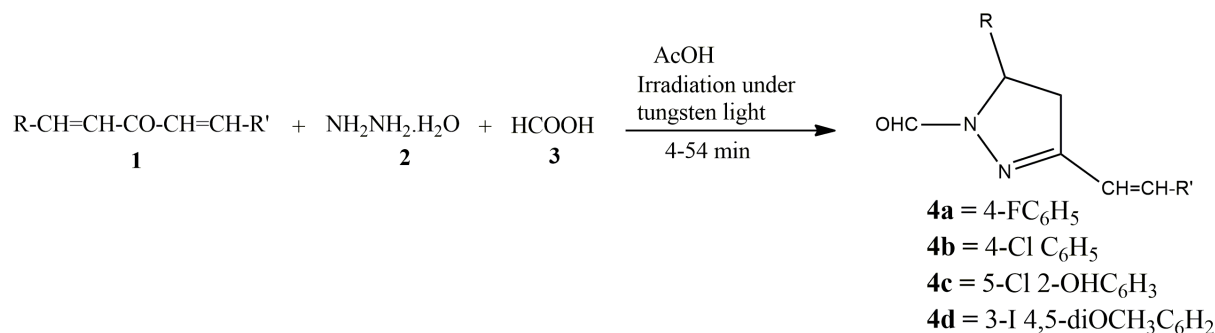
In order to optimize the reaction conditions, we made comparison between by carried out the above reaction through conventional pathway, and we found that the method using irradiation of tungsten light is efficient in terms of clean reaction conditions, not expensive, yields and environmentally eco-friendly.

**Table 1.** Synthesis of 4,5-dihydro-pyrazole-1-carbaldehyde derivatives.

Product	Method A			Method B		
	Reaction Time (min)	Yield (%) <sup>†</sup>	M. p. (°C)	Reaction time (h)	Reported Yield (%)	Reported M. p. (°C)
<b>4a</b>	40	88	140	03	79	138-140 [16]
<b>4b</b>	48	86	120	03	80	118-120 [16]
<b>4c</b>	54	83	137	03	76	135-137 [16]
<b>4d</b>	45	90	148	03	83	147-149 [16]

Method A: Irradiation under tungsten light, Aqueous 2-methoxyethanol, AcOH.

Method B: Aqueous 2-methoxyethanol, Reflux for 3 h.



**Scheme 1.** Synthesis of 4,5-dihydro-pyrazole-1-carbaldehyde derivatives.

#### 4. CONCLUSION

In summary, present communication reported the synthesis of 4,5-dihydro-pyrazole-1-carbaldehyde derivatives starting from  $\alpha,\beta$ -unsaturated ketone in aqueous 2-methoxyethanol under irradiation of tungsten light. The advantage of methods in comparison with classical synthesis, which includes clean reaction procedure, easy isolation of products, short reaction time and no need of special apparatus device.

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