



## SYNTHESIS AND SPECTRAL CHARACTERIZATION OF SOME NEW PYRAZOLINE DERIVATIVES

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### ABSTRACT

The title compounds were synthesized by condensation azachalcones with ethylacetoacetate to get intermediate 3-(pyridyl)-5-aryl-6-ethylcarboxylate-2-cyclohexenone which were subsequently treated with hydrazine hydrate to afford the title compounds 4-(pyridyl)-6-aryl-7one-5,6-dihydro-1Hindazol or pyrazoline derivatives.<sup>[1-10]</sup> The structures of the final products were supported by spectral data (UV, IR, <sup>1</sup>HNMR) in addition to their physical properties.

**KEYWORDS:** Azachalcones, Cyclohexenones, condensation, Indazol, Pyrazoline.

### INTRODUCTION

In recent year as significant portion of research in heterocyclic chemistry has been devoted to pyrazolines containing different aryl group as substituents.<sup>[1]</sup> Pyrazolines are compounds with noteworthy application pyrazolines are well known and important nitrogen-containing five member heterocyclic compounds.<sup>[2]</sup> Numerous pyrazoline derivatives have been found to possess considerable biological activities. Which stimulated the research activity in this field.<sup>[3]</sup> It has been demonstrated to have an important therapeutic potential mainly as anti-inflammatory<sup>[4]</sup>, antidepressant<sup>[5]</sup>, molluscicidal<sup>[6]</sup>, antibacterial<sup>[7]</sup>, antifungal<sup>[8]</sup> and antitumor<sup>[9]</sup> agents been cited in literature. pyrazoline derivatives such as antipyrine, aminopyrine and dipyrone are known as antipyretic and analgesic substances and their pharmacological action.<sup>[10]</sup>

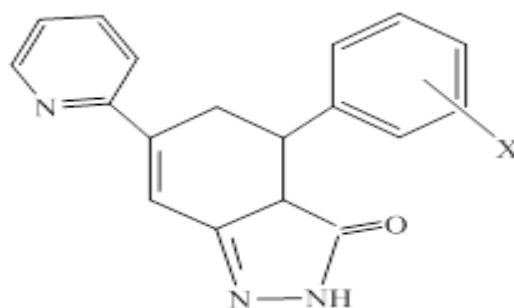
### Instrumentation

Melting points were measured on an electro thermal (Stuart melting point spm 30). IR spectra were recorded on a Bruker optics (FT –IR) spectrophotometer co. using KBr – disk. <sup>1</sup>H-NMR

spectra were recorded on B. Bruker Avance III400- MHz spectrometer (Gazi Osman basa University / Turkey) using TMS as an internal standard and DMSO – d<sub>6</sub> as a solvent. UV spectra were recorded by Shimadzu UV – visible recording UV -160 spectrophotometer. Theoretical study of the heat of formation (H.F) and steric energy (S.E) was achieved by using AM1(Austin–Model1) to explain the effect of different groups (electron donating or drawing) on the reaction.

General method for the synthesis of pyrazoline (indazole).<sup>[11]</sup>

A solution of cyclohexenone<sup>[12]</sup> (0.01 mol) in ethanol absolute (25 ml) was treated with hydrazine hydrate 80% and anhydrous sodium acetate (0.01 mol) in 100 ml round-bottomed flask and refluxed for (8 h). The mixture was cooled and then poured over crushed ice the crude products were recrystallized using ethanol as solvent a ford the product. See Table.<sup>[1]</sup>



X=(1-10)

## RESULTS AND DISCUSSION

The physical properties of the final products (1-10) (melting points, colours) supply an evidence to their formation. The spectral data of (1-10) series support strongly the formation of such compounds. The spectral data of compound number (1) has been discussed as a representative model.

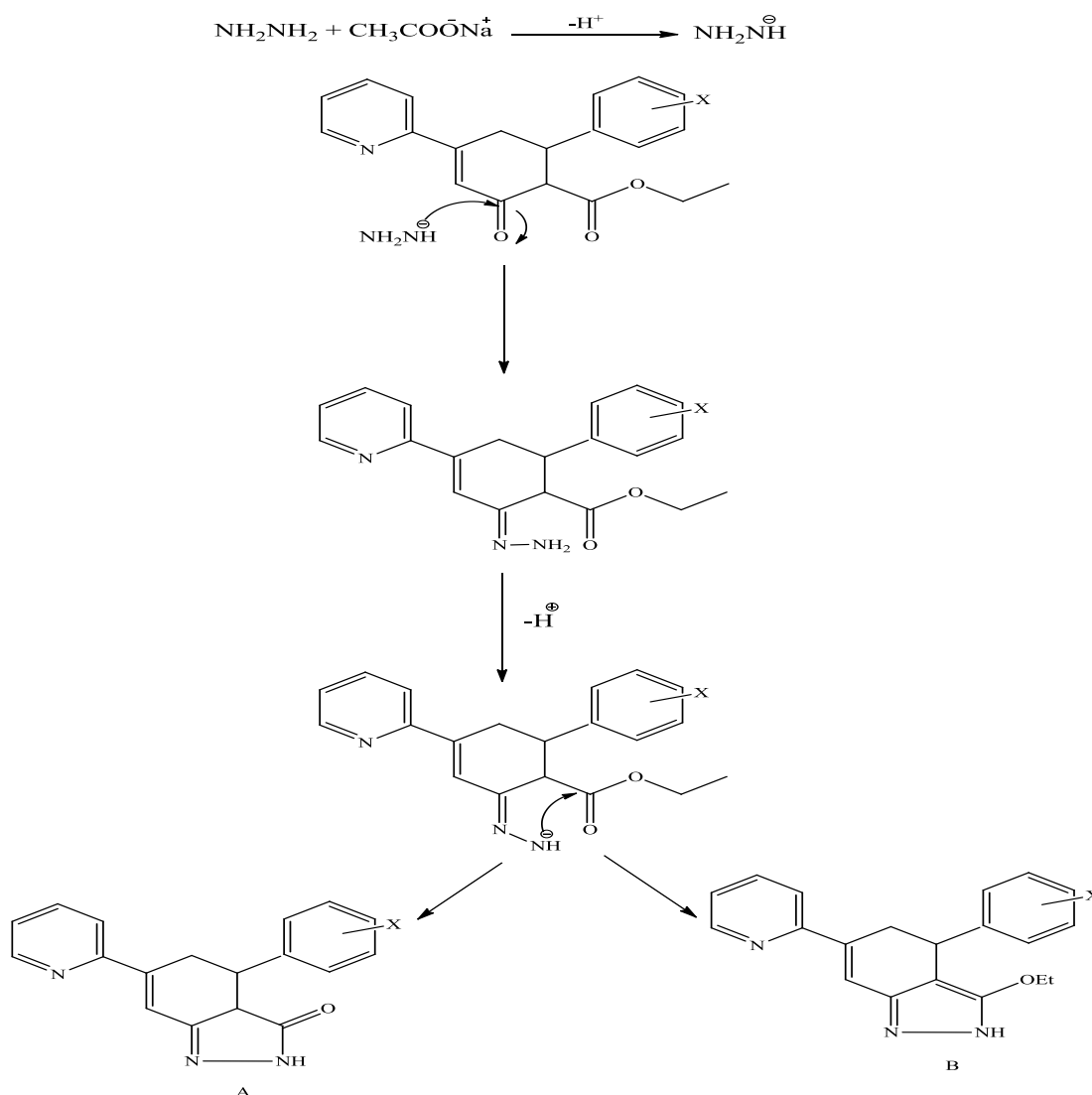
The <sup>1</sup>HNMR spectrum of (1) showed a doublet signal for tow protons (H4) resonate at δ(2) ppm. The benzylic proton (H5) seemed to resonate at δ(3.9) ppm as a quartet signal, but (H6) watched to resonate at δ(3) ppm as a doublet signal. The olefinic proton (H2) looks like a singlet at δ(5.5) ppm, while the aromatic protons (4H from the phenyl & 3H from the pyridyl) reflect a multiplet signal at δ(7-8) ppm. The aromatic proton labeled (H9) on the pyridyl ring resonates at δ(8.5) ppm as a singlet signal and deshielded due to the adjacent nitrogen. The methoxy three protons found clearly as a singlet signal and resonate at δ(3.7) ppm. Finaly the

pyrazoline Proton (H8) found clearly as singlet signal and resonate at (2.6) ppm]. See Table (2).

The IR spectrum<sup>[13]</sup> of (1) showed many distinguished absorption bands at  $\nu(1736) \text{ cm}^{-1}$  related to the pyrazoline carbonyl and  $\nu(1685) \text{ cm}^{-1}$  due to the C=N. The olefinic C=C showed a stretching vibration at  $\nu(1509) \text{ cm}^{-1}$  whereas the aromatic C... N and C...C displayed on absorption bands at  $\nu(1538) \text{ cm}^{-1}$  and  $\nu(1432) \text{ cm}^{-1}$  respectively. Finally showed band at (3100) due to the N-H. See Table (3).

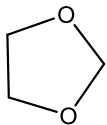
The UV spectrum<sup>[14]</sup> of (1) exhibited a red shift to a longer wavelength at maximum absorption  $\lambda_{\text{max}} = (232) \text{ nm}$  due to the increasing degree of conjugation. See Table (3).

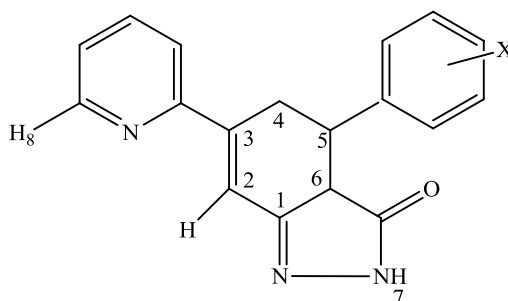
The suggested mechanisms for the reaction of cyclohexenone with hydrazine hydrate may pass through one of two routes.<sup>[15]</sup>



Finally. It is concluded that the most predominant product is (A) which is in full agreement with the spectral data.

**Table (1): Physical properties of pyrazolines.**

No	X	color	Yield%	m.p (°C)
1	p-OCH <sub>3</sub>	243-241	80	White
2	m-OCH <sub>3</sub>	215-213	94	White
3	p-CH <sub>3</sub>	232-235	85	White
4	p-NO <sub>2</sub>	190-192	77	White
5	2,4-DiCl	207-209	75	White
6	p-Cl	205-206	81	White
7	H	199-200	60	White
8		262-264	77	White
9	3-4DiCl	210-212	77	White
10	N.N-DiMe	237-235	70	White



**Table (2): The <sup>1</sup>H-NMR spectra data for some of prepared Pyrazoline.**<sup>[1,5,9,10]</sup>

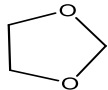


NO	X	<sup>1</sup> H-NMR(DMSO); δppm							
		H4	H6	H5	H2	H7.	Ar-H	Pyridyl-H8	Others
1	p-OCH <sub>3</sub>	2 1H,d	2.6 1H,d	3.9 1H,q	5.5 1H,s	6.6 1H,s	7.8-6.8 7H,m	8.5 1H,s	3.7 3H.S OCH <sub>3</sub>
9	NN-DiMe	2 1H,d	2.6 1H,d	3.9	6.6 1H,s	6.8 1H,s	7.3-8.2 7H,m	8.4 1H,s	2.8 CH <sub>3</sub> -N-CH <sub>3</sub> 3H.s
5	p-NO <sub>2</sub>	2 1H,d	2.7 1H,d	3.8 1H,q	5.6 1H,s	6.6 1H,s	7-8 7H,m	8.5 1H,s	---
10		2.5 1H,d	2.8 1H,d	3.5 1H,q	5.6 1H,s	6.5 1H,s	7.3-8.2 6H,m	8.6 1H,s	6 O-CH <sub>2</sub> -O 2H.S

Table (3): The IR and UV spectral data for Pyrazoline.

No.	IR $\nu$ $\text{cm}^{-1}$ (KBr)						Others	UV (CHCl <sub>3</sub> ) $\lambda_{\text{max}}$ (nm)
	X	C=O	N-H	C=N	C=C			
1	p-OCH <sub>3</sub>	1736	3100	1686	1509	1538 1432	Asy1146 (C-O-C) Sy 1093(C-O-C)	232
2	m-OCH <sub>3</sub>	1650	3178	1608	1485	1541 1431	Asy1159 (C-O-C) Sy 1034(C-O-C)	256
3	3,4-DiOCH <sub>3</sub>	1600	3150	1591	1483	1546 1434	Asy1146 (C-O-C) Sy 1028(C-O-C)	232
4	p-CH <sub>3</sub>	1700	2998	1655	1486	1587 1405	----	254
5	p-NO <sub>2</sub>	1647	3100	1709	1516	1583 1500	Asy1402(N---O) Sy 1346(N...O)	220
6	2,4-DiCl	1700	3011	1689	1486	1587 1405	789-742 (C-Cl)	232
7	P-Cl	1666	3150	1662	1577	1594 1433	783(C-Cl)	248
8	H	1685	3000	1597	1491	1585 1463	---	254
9		1660	3178	1600	1489	1543 1434	Asy1147(C-O-C) Sy 1039(C-O-C)	236
10	N,N-DiMe	1650	3135	1612	1520	1591 1471	1346(C-N)	254

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