



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 (1-10). The structures of the final products were supported by spectral data (UV, IR, ¹HNMR) 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.^[1] Pyrazolines are compounds with noteworthy application pyrazolines are well known and important nitrogen-containing five member heterocyclic compounds.^[2] Numerous pyrazoline derivatives have been found to possess considerable biological activities which stimulated the research activity in this field.^[3] It has been demonstrated to have an important therapeutic potential mainly as anti-inflammatory,^[4] antidepressant,^[5] molluscicidal,^[6] antibacterial,^[7] antifungal,^[8] and antitumor^[9] agents been cited in literature. Pyrazoline derivatives such as antipyrine, aminopyrine and dipyrone are known as antipyretic and analgesic substances and their pharmacological action.^[10]

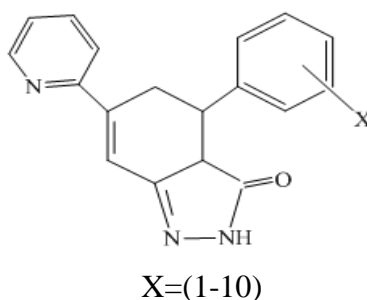
Instrumentation

Melting points were measured on an electro thermal (Stuart melting point spm30). IR spectra were recorded on a Bruker optics (FT –IR) spectrophotometer co. using KBr – disk. ¹H-NMR

spectra were recorded on B.Bruker Avance III400- MHz spectrometer (Gazi Osman basa University / Turkey) using TMS as an internal standard and DMSO – d₆ 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).^[11]

A solution of cyclohexenone^[12] (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 (1).



RESULTS AND DISCUSSION

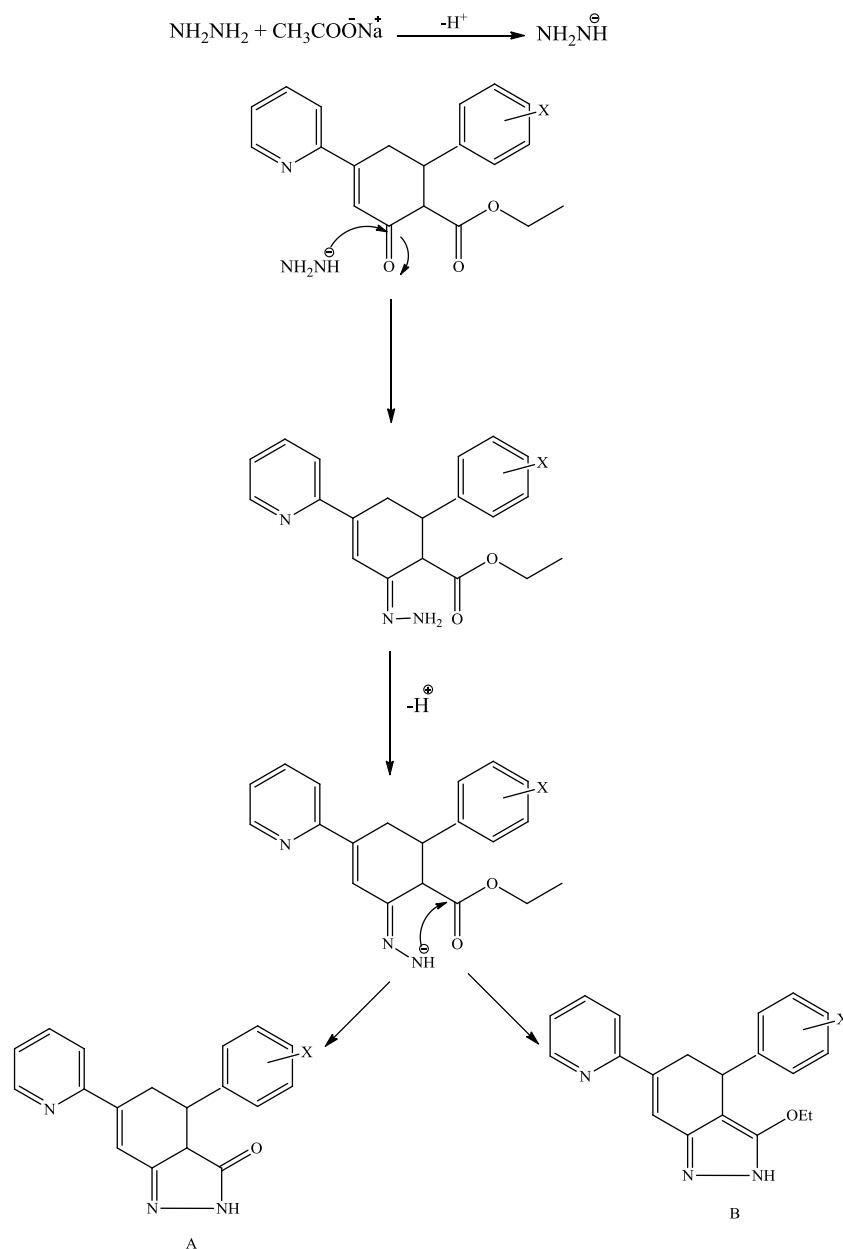
The physical properties of the final products (1-10) (melting points, colours) supply an evidence to their formation. The spectral data of (1-10) series support strongly the formation of such compounds. The spectral data of compound number (1) has been discussed as a representative model.

The ¹HNMR 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. Finally the pyrazoline Proton (H8) found clearly as singlet signal and resonate at (2.6) ppm]. See Table(2).

The IR spectrum^[13] 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).

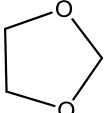
The UV spectrum^[14] of (1) exhibited a red shift to a longer wavelength at maximum absorption $\lambda_{\text{max}} = (232) \text{ nm}$ due to the increasing degree of conjugation. See Table (3).

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



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

Table 1: Physical properties of pyrazolines.

No	X	M.P (°C)	Yield%	Color
1	p-OCH ₃	243-241	80	White
2	m-OCH ₃	213-215	94	White
3	p-CH ₃	232-235	85	White
4	p-NO ₂	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 _e	237-235	70	White

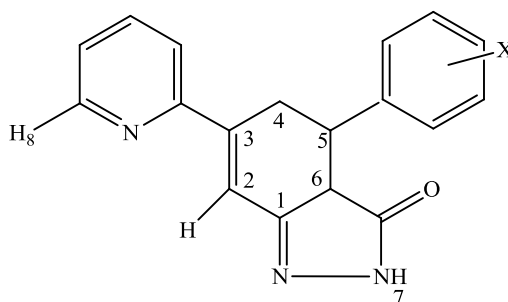


Table 2: The ¹H-NMR spectra data for some of prepared Pyrazoline(1,5,9,10).


NO	X	¹ H-NMR(DMSO);δppm							
		H4	H6	H5	H2	H7.	Ar-H	Pyridyl-H8	Others
1	p-OCH ₃	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 OCH3
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 CH3-N-CH3 3H.s
5	p-NO ₂	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-CH2-O 2H.S

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

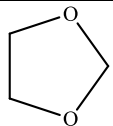
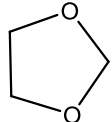
No.	IR ν cm^{-1} (KBr)					Ar } $\left. \begin{array}{l} \text{C}\dots\text{N} \\ \text{C}\dots\text{C} \end{array} \right\}$	Others	UV (CHCl ₃) λ_{max} (nm)
	X	C=O	N-H	C=N	C=C			
1	p-OCH ₃	1736	3100	1686	1509	1538 1432	Asy1146 (C-O-C) Sy 1093(C-O-C)	232
2	m-OCH ₃	1650	3178	1608	1485	1541 1431	Asy1159 (C-O-C) Sy 1034(C-O-C)	256
3	3,4-DiOCH ₃	1600	3150	1591	1483	1546 1434	Asy1146 (C-O-C) Sy 1028(C-O-C)	232
4	p-CH ₃	1700	2998	1655	1486	1587 1405	----	254
5	p-NO ₂	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

Table-4.

No	X	UV
4	p-CH ₃	322 270
5	p-NO ₂	282 256
11	H	364 260
12	OCH ₃	365 280
13	N,N-DiMe	336 280
14		385 270

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