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Synthesis and Spectral Characterizations of Δ^2-Pyrazolines from Arylidene Furfurylidene Acetone

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Abstract

A variety of some new substituted Δ2-pyrazolines (11-15) have been synthesized by reactions from arylidene furfurylidene acetone (5-10) with hydrazine hydrate in presence of methanol as a solvent. Arylidene Furfurylidene Acetone (6-10) is prepared by the reaction substituted benzylideneacetone and furfuraldehyde in absolute ethanol is carried out in basic media. All newly synthesized compounds were established by spectral analysis.

*Keyword***:** benzylideneacetone, arylidene furfurylidene acetone, Δ2-pyrazolines, chalcones

Introduction

Pyrazolines are nitrogen-containing 5-membered heterocyclic compounds that have been produced using a variety of ways. Many pyrazoline derivatives have been discovered to exhibit significant biological actions, which has sparked interest in this topic. They have antimicrobial [1], anti-inflammatory [2], analgesic, anticancer [3], antidepressant [4], antioxidant [5] and anti-mycobacterial [6] activities.

Chalcones are a common step in the synthesis of a broad variety of heterocyclic compounds. Chalcones have a highly reactive, α,β-unsaturated carbonyl compounds that is responsible for a broad range of bioactivities. The essential intermediate chalcones are made using the Claisen-Schmidt condensation reaction in an alcohol medium, which involves aromatic aldehydes and ketones. Chalcones are a unique class of chemicals that have been shown to have anti-tubercular [7], anti-inflammatory [8], antiviral [9] and antimicrobial [10] properties. For this reason, our goal in the current research was to prepare these compounds (pyrazolines) because of their biological and pharmaceutical importance.

Experimental:

The melting points were determined by Electrothermal apparatus IA 9300 Digital – Series 1998 (uncorrected). 1H- NMR spectra (DMSO-d6, δ ppm) was recorded using Bruker advance 400 MHz (Germany). FT-IR spectra was recorded using FT-IR spectrometer (KBr, ν cm-1).

Synthesis of substituted benzalacetone (1-5) [11]:

place (63.5gm, 80 ml) of acetone (42gm, 40 ml) of benzaldehyde in presence (10 ml) of 10 % aq.NaOH added slowly (during about 30 minutes) at temperature 30° .Stir the mixture at room temperature for a 2 hrs. Render the upper organic layer , extract the lower aqueous layer, wash with (20 ml) of water, and dry by anhydrous $MgSO_4$, filtered and evaporated finally to yield product. Table1

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Table 1: Physical Properties of substituted benzalacetone (1-5).

Cpd	X	Color	m.p	Yield %
1	4-Cl	Yellow	123-124	53
2	2-Br	Yellow	230-232	71
3	2-NO2	Pale Yellow	110-113	67
4	2,4-DiCl	Yellow	138-141	60
5	2-Benzoyl	White	78-80	61

Synthesis of arylidene furfurylidene acetone (6-10) [12]:

To a cold stirred mixture of substituted benzylideneacetone (0.03 mol) and furfurdehyde (0.03 mol) in (50 ml) absolute ethanol (1 gm) of potassium hydroxide was added in a small portion to the mixture in a period of (15 min). The stirring was continued for additional (1 hr) at room temperature. The precipitate was then filtered out, washed with cold ethanol, and re-crystallized from ethanol to get a solid. Table 2

Synthesis of pyrazoline compounds (11-15) [13].

A mixture of (6-10) (0.01 mole) and $NH_2NH_2.H_2O$ (0.02 mole) in 50 ml MeOH was refluxed for 2h , The excess MeOH was distilled off, and the solution was stored overnight. a crystalline product was filtered and re-crystallized from ethanol. Table 3

Table 2: Physical Properties of arylidene furfurylidene acetone (6-10).

Cpd	X	Color	m.p	Yield %
6	4-Cl	Yellow	258-261	71
7	2-Br	Dark Yellow	100-103	53
8	2-NO_2	Dark Yellow	280-281	45
9	2,4-DiCl	Yellow	120-123	75
10	2-Benzoyl	Pale Yellow	238-241	60

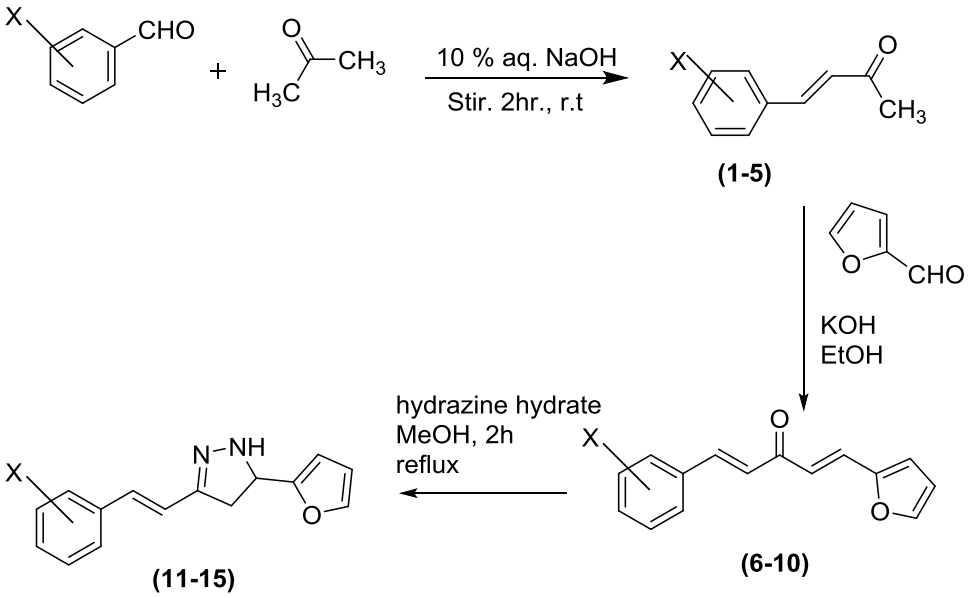
Table 3: Physical Properties of pyrazoline compounds (11-15).

Comp. No.	X	Color	m.p	Yield %
11	4-Cl	Brown	200-202	66
12	2-Br	Yellow	107-110	47
13	2-NO_2	Light Brown	200-203	26
14	2,4-DiCl	Yellow	140-143	58
15	2-Benzoyl	Light Brown	100-103	35

Result and Discussion

In this research some Δ2-pyrazolines compounds (11-15) have been synthesized via the key intermediates arylidene furfurylidene acetone (6-10) with hydrazine hydrate. Substituted benzalacetone (1-5) was synthesized in good yield through condensation substituted benzaldehyde with acetone in presence of NaOH. Arylidene furfurylidene acetone (6-10) was synthesized by the base-catalyzed Claisen–Schmidt condensation of Benzalacetone (1-5) and furfuraldehyde in ethanol and in presence of KOH. Table 4-7, Scheme1.

The structures of compounds (11-15) have been identified based on their FT-IR and 1H-NMR. The FT-I R spectra were characterized by the presence at the range (3402-3471 cm -1) due to (NH), the range (1585-1680 cm -1) refer to (C=N), the range (1554-1658 cm -1) due to (C=C), the disappearance of the carbonyl group frequency in the products is evidence of the reaction taking place. The assignment of the vibration ν(cm-1) of the IR absorption bands spectra was illustrated in Table (6). Whereas in 1H-NMR spectroscopy compounds (11-16) gave various absorption peaks as shown in (Table 7), the appearance of the pyrazoline proton peak at (δ ppm): (m,2H,2.4-2.61), (t,1H,3.28-5.23) and (s,1H, 8.52-8.88) respectively give a good indication that reaction was taking place and supporting the pyrazoline ring formation.



Scheme 1

Table 4: FT-IR data of Substituted Benzalacetone (1-5).

Comp.	FT-IR, ν (cm^{-1})			
	X	C = O	C = C	Others
1	4-Cl	1683	1591	(C-Cl) 761
2	2-Br	1693	1602	(C-Br) 711
3	2-NO2	1651	1600	(NO_2) Asym. 1531, Sym. 1346
4	2,4-DiCl	1654	1618	(C-Cl) 773
5	2-Benzoyl	1656, 1685	1631	----------

Table 5: FT-IR data of Arylidene Furfurylidene Acetone (6-10).

Comp.	FT-IR, ν (cm^{-1})			
	X	C = O	C = C	Others
6	4-Cl	1668	1612	(C-Cl) 705
7	2-Br	1693	1593	(C-Br) 719
8	2-NO2	1654	1599	(NO_2) Asym. 1516, Sym. 1344
9	2,4-DiCl	1654	1618	(C-Cl) 775
10	2-Benzoyl	1650, 1680	1591	----------

Table 6: FT-IR data of Δ2-pyrazolines compounds (11-15).

Comp.	FT-IR, ν (cm^{-1})				
	X	N-H	C = N	C = C	Others
11	4-Cl	3431	1597	1566	(C-Cl) 750
12	2-Br	3471	1680	1658	(C-Br) 682
13	2-NO2	3468	1593	1554	(NO_2) Asym. 1525, Sym. 1350
14	2,4-DiCl	3468	1585	1562	(C-Cl) 651
15	2-Benzoyl	3402	1587	1573	(C=O) 1647

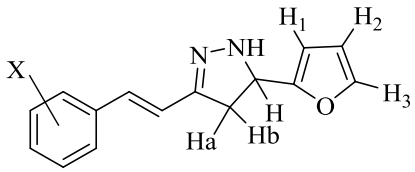


Table 7: The ^{1}H-NMR spectral data of Δ2-pyrazolines compounds (11-15).

Comp.	^{1}H-NMR, (ppm), DMSO-d6
11	2.41, 2.61(m, $2H_{a,b}$, -**CH_aH$_b$**-C=N), 5.04-5.23 (t, H, CH_2-**CH**-NH), 6.32-6.53 (m, $2H_{1,2,}$ Furan ring), 7.5 (d, 1H, CH=**CH**), 7.6 (d, 1H, **CH**=CH), 7.94 (d, $1H_{3,}$ Furan ring), 8.04-8.15 (d,d, 4H, Ar-**H**), 8.54 (s, 1H, -N**H**-)
13	2.41, 2.61(m, $2H_{a,b}$, -**CH_aH$_b$**-C=N), 3.9-4.1 (t, H, CH_2-**CH**-NH), 6.53-6.55 (m, $2H_{1,2,}$ Furan ring), 7.02 (d, 1H, CH=**CH**), 7.29 (d, 1H, **CH**=CH), 7.60 (d, $1H_{3,}$ Furan ring), 7.74-8.15 (m, 4H, Ar-**H**), 8.54 (s, 1H, -N**H**-)
14	2.41, 2.61(m, $2H_{a,b}$, -**CH_aH$_b$**-C=N), 3.28-3.47 (t, H, CH_2-**CH**-NH), 6.30-6.54 (m, $2H_{1,2,}$ Furan ring), 7.28-7.85 (m, 6H, **CH**=**CH**, 1H-Furan ring, Ar-**H**), 8.52 (s, 1H, -N**H**-)
15	2.41, 2.61(m, $2H_{a,b}$, -**CH_aH$_b$**-C=N), 5.02-5.06 (t, H, CH_2-**CH**-NH), 6.51-6.66 (m, $2H_{1,2,}$ Furan ring), 7.10 (d, 1H, **CH**=CH), 7.55 (d, $1H_{3,}$ Furan ring), 8.00-8.53 (m, 5H, CH=**CH**, Ar-**H**), 8.88 (s, 1H, -N**H**-)

Conclusion

A number of pyrazolines compounds were prepared and the reaction mechanism was determined through theoretical calculations, which showed that the preferred additive is the Michael addition in the preparation of these compounds, which is expected to have biological importance for these compounds, so this type of compounds was given attention in this research.

Conflicts of interest

There are no conflicts to declare.

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