



SYNTHESIS OF 3-(2-HYDROXY –3,4-BENZOPHENYL-5-METHOXY) 5-ARYL –1-SUBSTITUTED PYRAZOLINES

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ABSTRACT

1-(2-Hydroxy-3,4-benzophenyl-5-methoxy)-3-aryl-prop-2-ene-1-one and phenylhydrazine/semi-carbazide/thiosemicarbazide/isonicotinic acid hydrazide were added to DMF and refluxed for 2 hours. The cooled reaction mixture was diluted with water and the semisolid so obtained was triturated with ethanol to get a solid, which was recrystallised from ethanol–acetic acid mixture to get titled pyrazolines.

Key words: Synthesis, Pyrazolines.

INTRODUCTION

Pyrazolines and pyrazoles are well known and important nitrogen containing five-membered heterocyclic compounds and various methods have been worked out for their synthesis¹⁻⁴. Derivatives of pyrazolines have played a crucial role in the history of heterocyclic chemistry and these have been used extensively as important pharmacophores and synthons in the field of organic chemistry and drug designing.

Pyrazolines possess fungicidal⁵, bactericidal⁶ and insecticidal⁷ properties. Several pyrazolines are important as pharmaceuticals and they have been found to possess analgesic⁸, antipyretic⁹, and anti-inflammatory¹⁰ properties. Pyrazoline derivatives acquire anti-implantation activity¹¹ and cerebroprotective¹² also. Due to the vital biological role of pyrazolines derivatives^{13,14}, it was thought of interest to synthesize titled pyrazolines.

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It has been observed that substituted chalcones are best starting compounds for the preparation of the substituted pyrazolines. Present work deals with the synthesis of some new pyrazolines and their characterization by elemental analysis, IR and ^1H NMR analysis

EXPERIMENTAL

All the melting points were taken in silicon oil bath with open capillary tubes and are uncorrected. Thin layer chromatography on silica gel-G, was used to check the purity of the compounds. ^1H NMR spectra were recorded on a Bruker AC300 FNMR spectrometer (300 MHz), using TMS as an internal standard. IR spectra were recorded on a Nicolet-Impact 400 FT-IR spectrometer. Microanalysis of nitrogen was obtained on Colman 29-N analyzer.

Synthesis of 2-acetyl-4 methoxy-1-naphthol (2)

In hot glacial acetic acid (80 mL), fused ZnCl_2 (50 g) was added and refluxed till it was dissolved. Then powdered 4-methoxy-1-naphthol (30 g) was added and refluxed for about 8 hours. The reaction mixture was cooled and poured in acidulated water. The solid obtained was filtered, washed with water and recrystallized from rectified spirit to obtain compound (2). Physical data of the compounds are given in Table 1.

Synthesis of 1-(2-hydroxy-3,4-benzophenyl-5-methoxy)-3-aryl-prop-2-ene-1-one (3-6)

2-Acetyl-4 methoxy-1-naphthol (0.01mole) and aromatic aldehyde (0.02 mole) were added in ethanol solvent (20 mL). To this mixture, 10 % of KOH (10 mL) solution was added dropwise with constant stirring. The reaction mixture was kept overnight. Then this mixture was poured over crushed ice and HCl. The product was filtered and recrystallized from ethanol to obtain 1-(2-hydroxy-3,4-benzophenyl-5-methoxy)-3-aryl-prop-2-ene-1-one. Their physical data are given in Table 1.

Synthesis of 3-(2-hydroxy-3,4-benzophenyl-5-methoxy)-5-aryl-1-substituted pyrazolines (7-22)

1-(2-Hydroxy-3,4-benzophenyl-5-methoxy)-3-aryl-prop-2-ene-1-one (0.01 mole) and phenylhydrazine/semicarbazide/thiosemicarbazide/isonicotinic acid hydrazide (0.01 mole) were added to DMF (20 mL) and refluxed for 2 hours. The cooled reaction mixture was diluted with water and the semisolid so obtained was triturated with ethanol to get a solid, which was recrystallised from ethanol-acetic acid mixture to get titled pyrazolines in 42-72% yield and their physical data are given in Table 1.

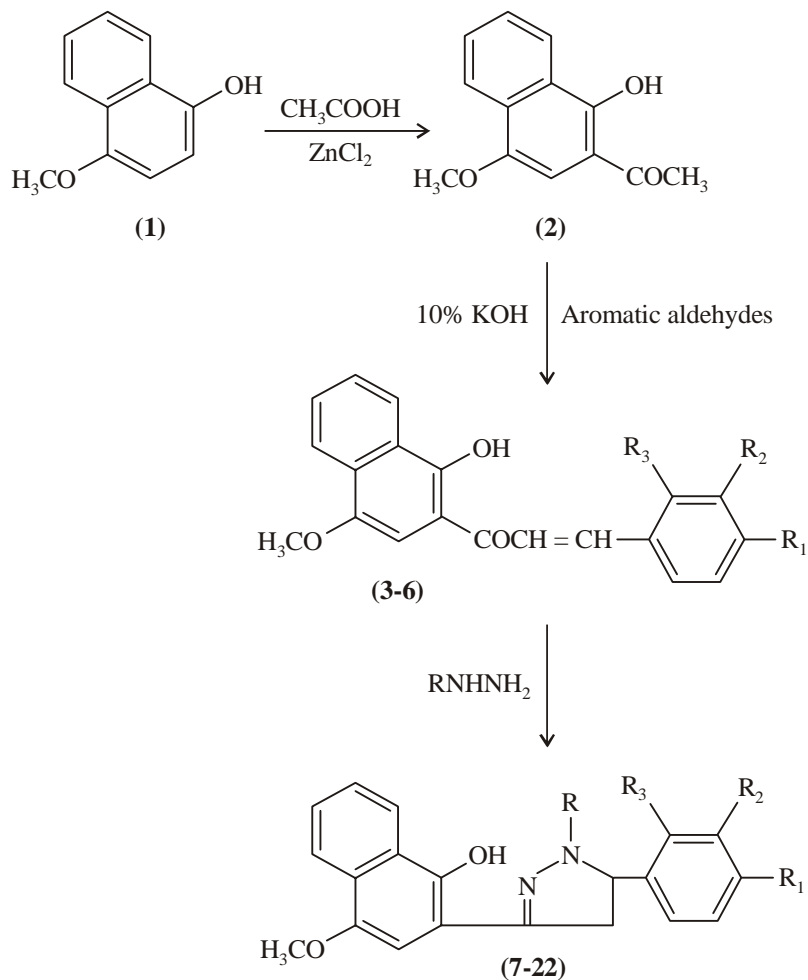
Spectral interpretation of (7)

IR (ν_{max}) (cm^{-1}): 3412 (OH str), 3215 (N-N pyrazoline), 1580 (C=N str), 1350 (C-O).

NMR (δ ppm): 3.099–3.174 (dd, 1H, H_A) J_{AB} = 17.74 Hz J_{AX} = 8.80 Hz, 3.638–3.738 (dd, 1H, H_B) J_{AB} = 17.74 Hz, J_{BX} = 11.68 Hz, 5.217–5.272, (dd, 1H, H_X) J_{AX} = 8.80 Hz, J_{BX} = 11.68 Hz, 7.35–7.75 (m, 11Ar-H), 10.98 (s, 1H, OH), 6.75 (s, 2H, NH₂).

Table 1: Physical data of synthesized compounds

Compd.	R	R ₁	R ₂	R ₃	Melting point (°C)	% Yield	% Nitrogen		R _f Value
							Found	Calculated	
2	--	--	--	--	99°C	75%	--	--	--
3	--	H	H	H	102°C	68%	--	--	--
4	--	H	H	OH	110°C	56%	--	--	--
5	--	OCH ₃	OCH ₃	H	160°C	54%	--	--	--
6	--	Cl	H	H	140°C	58%	--	--	--
7	C ₆ H ₅	H	H	H	206°C	46%	7.00	7.11	0.65
8	C ₆ H ₅	H	H	OH	196°C	41%	6.70	6.83	0.64
9	C ₆ H ₅	OCH ₃	OCH ₃	H	214°C	51%	6.11	6.17	0.56
10	C ₆ H ₅	Cl	H	H	227°C	48%	6.42	6.53	0.64
11	CONH ₂	H	H	H	208°C	40%	11.53	11.63	0.59
12	CONH ₂	H	H	OH	210°C	41%	11.06	11.14	0.56
13	CONH ₂	OCH ₃	OCH ₃	H	222°C	38%	9.84	9.98	0.57
14	CONH ₂	Cl	H	H	240°C	40%	10.58	10.62	0.65
15	CSNH ₂	H	H	H	199°C	39%	11.07	11.14	0.69
16	CSNH ₂	H	H	OH	219°C	36%	10.61	10.69	0.58
17	CSNH ₂	OCH ₃	OCH ₃	H	188°C	45%	9.58	9.61	0.56
18	CSNH ₂	Cl	H	H	274°C	49%	10.19	10.21	0.54
19	C ₅ H ₄ NCO	H	H	H	194°C	48%	9.88	9.95	0.53
20	C ₅ H ₄ NCO	H	H	OH	200°C	46%	9.48	9.59	0.58
21	C ₅ H ₄ NCO	OCH ₃	OCH ₃	H	216°C	48%	8.68	8.71	0.62
22	C ₅ H ₄ NCO	Cl	H	H	225°C	43%	9.10	9.20	0.63



R = C₆H₅, CONH₂, CSNH₂, C₃H₄NCO; R₁ = H, OCH₃, Cl; R₂ = OCH₃ and R₃ = H, OH

Scheme

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