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Synthesis of 3,5 Diaryl-4-Aroyl-1-Benzoyl-Δ^2-Pyrazolines

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Some new 3,5-diaryl-4-aroyl-1-benzoyl-Δ^2-pyrazolines (**3a–p**) have been synthesized by the action of benzhydrazide on 3-aroyl flavanones (**2a–p**) in pyridine medium. Structure of these compounds has been established on the basis of spectral analysis and elemental analysis.

Key words: 3,5-Diaryl-4-aroyl-1-benzoyl-Δ^2-pyrazolines, Synthesis.

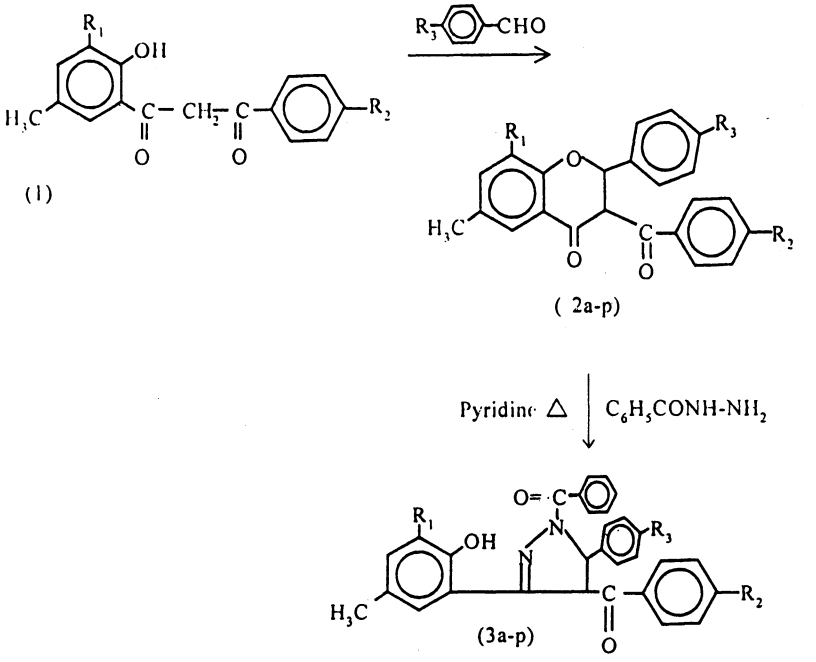
INTRODUCTION

The literature survey reveals that pyrazoline derivatives have been studied extensively because of their ready accessibility, diverse chemical reactivity, broad spectrum of biological activity[1–3] and variety of industrial applications[4,5]. Pyrazoline derivatives are known to have insecticidal[4], bactericidal[7] and fungicidal[8] properties. Some pyrazolines are found to show anti-inflammatory, antidiabetic, anasthetic and analgesic[9–12] properties.

Among the various methods for the synthesis of pyrazolines, the most convenient method for the synthesis of pyrazolines involves the action of hydrazine or phenylhydrazine on α,β-unsaturated carbonyl compounds. The synthesis of 3,5-diaryl-1-phenyl pyrazolines from flavanones and phenyl hydrazine hydrochloride in DMF solvent has been reported[13]. Chincholkar and Jamode[14] have reported some new 4-aroyl substituted pyrozolines by the condensation of hydrazine hydrate with 3-aroyl flavanones in pyridine. Synthesis of 3,5-diaryl-4-benzoyl-1-pyridoyl-Δ^2-pyrazolines has been reported[15]. After going through the literature it was clear that 3,5-diaryl-4-aroyl-1-benzoyl-Δ^2-pyrazolines have not yet been synthesized. It was therefore thought of interest to synthesize 3,5-diaryl-4 aroyl-1-benzoyl-Δ^2-pyrazolines in pyridine medium.

EXPERIMENTAL

All melting points were taken in silicon oil bath instrument in open capillary and are uncorrected. Purity of the compounds was checked by TLC on silica gel-G plates. IR spectra was recorded on Perkin-Elmer spectrophotometer and PMR spectra on Brucker AC-300 FNMR spectrophotometer at 30 MHz. UV spectra were recorded on Beckman DU-600. The nitrogen was estimated on Colman-N-analyzer-29.



Scheme-1

Preparation of 1-(2-hydroxy aryl)-3 aryl-1,3 propanediones (1): To a mixture of 2-aroyloxy acetophenones (0.01 mol) and pyridine (10 mL), pulvarized KOH (3.4 g) was added with constant stirring. The solution was warmed upto 60°C. It was kept overnight. Then the reaction mixture was acidified by adding ice-cold HCl (1 : 1); the brownish yellow product obtained was filtered, washed with sodium bicarbonate solution (2%) followed by water. The product obtained was crystallized from ethanol-acetic acid mixture.

Preparation of 3-aroyl flavanones (2a–p): 1-(2-hydroxy-aryl)-3-aryl-1,3-propanediones **(1)** (0.01 mol) and aromatic aldehyde (benzaldehyde/anisaldehyde/*p*-hydroxybenzaldehyde/*p*-dimethyl amino benzaldehyde) (0.02 mol) were refluxed for about 1/2 h in ethanol containing few drops of piperidine. The reaction mixture was cooled and poured in water along with addition of small amount of conc. HCl to neutralize piperidine. The product obtained was filtered and washed with water. It was crystallized from ethanol-acetic acid mixture. The physical characteristics are given in Table-1.

Spectral interpretation of (2i): IR (ν_{max}) (cm^{-1}): 3032 ν(Ar, C—H); 2931 ν(C—H); 1661 ν(C=O); 1602 ν(C=O, in ketone); 1455 ν(C=C); 1229 ν(C—O—C).

NMR: δ 2.23 (S, 3H, Ar—CH_3); 3.82 (S, 3H, O—CH_3); 5.02 (d, 1H); 5.92 (d, 1H); 6.83–7.79 (m, 12H Ar—H).

TABLE-1
PHYSICAL CHARACTERIzATION DATA OF SYNTHESIZED COMPOUNDS

Compd.	—R_1	—R_2	—R_3	Yield (%)	m.p. (°C)	m.f.
2a	H	H	H	75	122	$C_{23}H_{18}O_3$
2b	H	H	OCH_3	72	126	$C_{24}H_{20}O_4$
2c	H	H	OH	70	140	$C_{23}H_{18}O_4$
2d	H	H	$N(CH_3)_2$	67	145	$C_{25}H_{23}NO_3$
2e	Br	H	H	75	139	$C_{23}H_{17}O_3Br$
2f	Br	H	OCH_3	73	144	$C_{24}H_{19}O_4Br$
2g	Br	H	OH	68	135	$C_{23}H_{17}O_4Br$
2h	Br	H	$N(CH_3)_2$	65	142	$C_{25}H_{22}NO_3Br$
2i	H	OCH_3	H	70	132	$C_{24}H_{20}O_4$
2j	H	OCH_3	OCH_3	72	140	$C_{25}H_{22}O_5$
2k	H	OCH_3	OH	75	164	$C_{24}H_{20}O_5$
2l	H	OCH_3	$N(CH_3)_2$	68	148	$C_{26}H_{25}NO_4$
2m	Br	OCH_3	H	75	144	$C_{24}H_{19}O_4Br$
2n	Br	OCH_3	OCH_3	68	127	$C_{25}H_{21}O_5Br$
2o	Br	OCH_3	OH	70	170	$C_{24}H_{19}O_5Br$
2p	Br	OCH_3	$N(CH_3)_2$	65	149	$C_{26}H_{24}NO_4Br$

Preparation of 3,5 diaryl-4-aroyl-1-benzoyl-Δ^2-pyrazolines (3a–p): 3-Aroyl flavanones **(2a–p)** (0.01 mol) were refluxed with benzhydrazide (0.02 mol) in pyridine medium for 8 h. The reaction mixture was cooled and then diluted with water and acidified with conc. HCl. The product thus obtained was filtered and washed with sufficient water. It was crystallized from ethanol-acetic acid mixture. The physical characteristics of compounds **(3a–p)** are given in Table-2.

Spectral Interpretation of (3i): IR (ν_{max}) (cm^{-1}): 3181 ν(Ar—OH); 1642 ν(C=O); 1601 ν (C=N); 1446 ν(C=C); 1287 ν(C—N).

NMR: δ 2.46 (S, 3H, Ar—CH_3); 8.8 (S, 3H, Ar—OCH_3); 6.72 (d, 1H, —CH); 6.91 (d, 1H, —CH); 7.02–8.00 (m, 17H, Ar–H); 11.93 (S, 1H, —OH).

UVλ_{max}: 312 nm.

TABLE-2
PHYSICAL CHARACTERIZATION DATA OF SYNTHESIZED COMPOUNDS

Compd.	$-R_1$	$-R_2$	$-R_3$	Yield (%)	m.p. (°C)	m.f.	N% found (calc.)
3a	H	H	H	70	205	$C_{30}H_{24}N_2O_3$	5.81 (6.08)
3b	H	H	OCH_3	72	182	$C_{31}H_{26}N_2O_4$	5.63 (5.71)
3c	H	H	OH	72	230	$C_{30}H_{24}N_2O_4$	5.67 (5.88)
3d	H	H	$N(CH_3)_2$	68	200	$C_{32}H_{29}N_3O_3$	8.12 (8.34)
3e	Br	H	H	65	185	$C_{30}H_{23}N_2O_3Br$	5.08 (5.20)
3f	Br	H	OCH_3	67	192	$C_{31}H_{25}N_2O_4Br$	4.75 (4.92)
3g	Br	H	OH	66	202	$C_{30}H_{23}N_2O_{4Br}$	4.85 (5.05)
3h	Br	H	$N(CH_3)_2$	74	260	$C_{32}H_{28}N_3O_3Br$	7.03 (7.22)
3i	H	OCH_3	H	65	182	$C_{31}H_{26}N_2O_4$	2.20 (5.71)
3j	H	OCH_3	OCH_3	67	168	$C_{31}H_{28}N_2O_5$	5.25 (5.38)
3k	H	OCH_3	OH	68	210	$C_{31}H_{26}N_2O_5$	5.41 (5.53)
3l	H	OCH_3	$N(CH_3)_2$	68	216	$C_{33}H_{31}N_3O_4$	7.53 (7.87)
3m	Br	OCH_3	H	70	196	$C_{31}H_{25}N_2O_4Br$	4.63 (4.92)
3n	Br	OCH_3	OCH_3	73	178–180	$C_{32}H_{27}N_2O_5Br$	4.45 (4.68)
3o	Br	OCH_3	OH	65	290	$C_{31}H_{25}N_2O_5Br$	4.60 (4.79)
3p	Br	OCH_3	$N(CH_3)_2$	66	198–200	$C_{33}H_{30}N_3O_4Br$	6.51 (6.87)

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