

NOTE

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

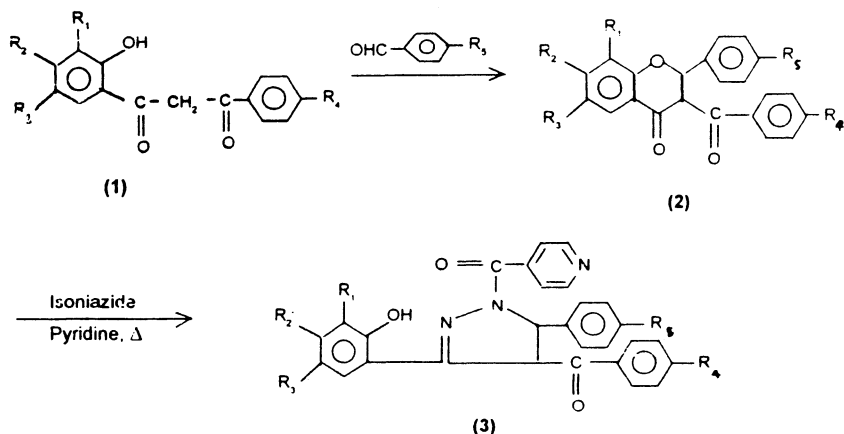
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Some new 3,5-diaryl-4-benzoyl-1-pyridoyl- Δ^2 -pyrazolines (3) have been synthesised by the action of isoniazid on 3-aryl flavanones (2) in pyridine medium. Structures of these compounds have been established by spectral analysis (NMR, IR and UV) and elemental analysis.

The literature survey reveals the importance of chalcones and flavanones as a valuable starting materials for the synthesis of heterocycles like pyrazolines, pyrazoles and isoxazolines etc. Formation of pyrazolines has been reported¹⁻³ by the action of hydrazines or phenyl hydrazines on chalcones and flavanones in different solvents like DMSO or ethanol, etc.

Pyrazolines were formally regarded only as an intermediate in the synthesis of pyrazoles, but these have recently come to notice for their use as effective bleaching agents, as luminescents, fluorescents⁴⁻⁸ and as oxidised forms in the development of cine films⁹ apart from drugs. Pyrazoline derivatives have been found to be effective insecticides,¹⁰ pharmaceuticals and fungicidal agents.¹¹ Thus from the survey of literature it is cleared that 3,5-diaryl-4-benzoyl-1-pyridoyl- Δ^2 -pyrazolines are not yet synthesised. It was, therefore, thought of interest to synthesise 3,5-diaryl-4-benzoyl-1-pyridoyl- Δ^2 -pyrazolines (3) from 3-aryl flavanones (2).

The present work deals with the synthesis of 3,5-diaryl-1-benzoyl-1-pyridoyl-



Δ^2 -pyrazoline (3) from 3-aroyle flavanones (2) and isoniazide in pyridine medium. Structures of these compounds have been established by elemental analysis and spectral analysis.

Melting points are uncorrected. IR spectra in KBr were recorded on PE-983/PE-781 IR spectrophotometer, NMR in DMSO on Varian EM 390-cw NMR spectrophotometer and UV on Varian Cary 2390 UV spectrophotometer.

(1) Preparation of 1,3-diaryl-1,3-propanedione (1a–1j)

2-Benzoyloxy acetophenone (0.05) was dissolved in dry pyridine (40 mL) (dried over KOH). The solution was warmed up to 60°C and pulverised KOH (0.1 M) was added slowly with constant stirring. After 4 h, 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%) and sufficient water. The product obtained was crystallised from ethanol-acetic acid mixture.

(2) Preparation of 3-aroyle flavanones (2a–2j)

1,3-Diaryl-1,3 propanediones (1) (0.01 M) and aromatic aldehyde (benzaldehyde and anisaldehyde) (0.01 M) were refluxed for about 1 h in ethanol (25 mL) containing a few drops of piperidine. The reaction mixture was cooled and the product separated was crystallised from ethanol-acetic acid mixture.

Spectral interpretation of 2d

IR (ν_{\max}) : 1625 cm^{-1} $\nu(\text{C}=\text{O})$; 1600 cm^{-1} $\nu(\text{C}=\text{O})$ (two $\text{C}=\text{O}$ groups); 552 cm^{-1} $\nu(\text{C}=\text{Br})$; 1235 $\nu(\text{C}-\text{O}-\text{C})$.

NMR : δ 2.32 (s, 3H, Ar—CH₃); 3.73 (s, 3H, O—CH₃); 5.04 (d, 1H); 5.91 (d, 1H); 6.3–7.8 (m, 10H, Ar—H).

UV (λ_{\max}) : 340 nm.

(3) Preparation of 3,5-diaryl-4-benzoyl-1-pyridoyl- Δ^2 -pyrazolines (3a–3j)

3-Aroyle flavanones (2a–j) (0.1 M) were refluxed with isoniazide (0.2 M) for 8–10 h. in pyridine solvent. The reaction was decomposed by acidified water, filtered and washed with sufficient water. It was crystallised from ethanol-acetic acid mixture to obtain a white crystalline solid. Yield 60–80%.

Spectral interpretation of 3d

IR (ν_{\max}) : 3400 cm^{-1} $\nu(\text{C}-\text{OH})$; 550 cm^{-1} $\nu(\text{C}-\text{Br})$; 1550 cm^{-1} $\nu(\text{C}=\text{N})$; 1200 cm^{-1} $\nu(\text{C}-\text{N})$; 1150 cm^{-1} $\nu(\text{C}-\text{O})$

NMR : δ 2.4 (s, 3H, —CH₃); 3.6 (d, 1H, —CH); 6.8 (d, 1H, —CH); 8 to 8.5 (m, 17H, Ar—H); 11.8 (s, 1H, —OH)

UV (λ_{\max}) : 280 nm

Physical data of series (3a–3j) were recorded in Table 1.

TABLE-1
 PHYSICAL CHARACTERISATION DATA OF SYNTHESISED COMPOUNDS
 3,5-Diaryl-4-benzoyl-1-pyridoyl- Δ^2 -pyrazoline (3a-3j)

Compound	R ₁	R ₂	R ₃	R ₄	R ₅	Yield (%)	m.p. (°C)	Molecular formula	N%, found (calcd.)
3a	H	H	CH ₃	H	H	67	250	C ₂₉ H ₂₃ O ₃ N ₃	8.5 (9.1)
3b	H	H	CH ₃	H	OCH ₃	70	215	C ₃₀ H ₂₅ O ₄ N ₃	7.8 (8.5)
3c	Br	H	CH ₃	H	H	65	237	C ₂₉ H ₂₂ O ₃ N ₃ Br	7.2 (7.7)
3d	Br	H	CH ₃	H	OCH ₃	72	227	C ₃₀ H ₂₄ O ₄ N ₃ Br	8.3 (7.3)
3e	CH ₃	H	H	H	H	66	256	C ₂₉ H ₂₃ O ₃ N ₃	9.7 (9.1)
3f	CH ₃	H	H	H	OCH ₃	65	225	C ₃₀ H ₂₅ O ₃ N ₃	8.1 (8.5)
3g	H	CH ₃	H	H	H	70	236	C ₂₉ H ₂₃ O ₃ N ₃	8.7 (9.1)
3h	H	CH ₃	H	H	OCH ₃	70	214	C ₃₀ H ₂₅ O ₄ N ₃	8.2 (8.5)
3i	H	H	H	H	H	79	215	C ₂₈ H ₂₁ O ₃ N ₃	8.9 (9.3)
3j	H	H	H	H	OCH ₃	75	210	C ₂₉ H ₂₃ O ₄ N ₃	7.5 (8.8)

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