

Synthesis and Characterization of 3,5-Diaryl-4-Benzoyl-1-Pyridoyl Pyrazoles

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

INTRODUCTION

The literature survey reveals the importance of chalcones and flavanones as a valuable starting materials for the synthesis of heterocycles like pyrazolines, pyrazoles isoxazolines etc. Formation of pyrazoles has been reported¹⁻³ by the action of hydrazines or phenyl hydrazines on flavones and chalcones in different solvents like methanol, DMSO, acetic acid, etc. Pyrazole is a class of compounds which are widely useful in drugs and dyes^{4,5}. These compounds also show physiological activities.⁶⁻¹² Trifluoromethyl-1-aryl derivatives of pyrazoles are used as analgesic, antipyretic and antiinflammatory agents.¹³ 1-phenyl derivatives are effective antidiabetics.¹⁴ Acyl amino and chloro pyrazoles have been found to be effective herbicides.^{15,16} Phenyl pyrazoles act as insecticides¹⁷ and alkyl pyrazoles are also used as hypolipidemic agents.¹⁸

The literature survey clearly indicates that 3,5-diaryl-4-benzoyl-1-pyridoyl pyrazoles are not yet synthesised. It was, therefore, thought of interest to synthesise 3,5-diaryl-4-benzoyl-1-pyridoyl pyrazoles (4) from 3-aryl flavones (3). Thus present work deals with the synthesis of some new 3,5-diaryl-4-benzoyl-1-pyridoyl pyrazoles (4) from 3-aryl flavones (3) (Scheme-I) and isoniazid in pyridine medium. Structures of these compounds have been established by elemental analysis and spectral analysis.

EXPERIMENTAL

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 239 OUV spectrophotometer.

(1) *Preparation of 1,3-diaryl-1,3-propanedione (1a-1j)*—2-Benzoyloxy acetophenone (0.05 M) 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 about 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-aryl 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. The structures of these compounds are confirmed by spectral analysis.¹⁹

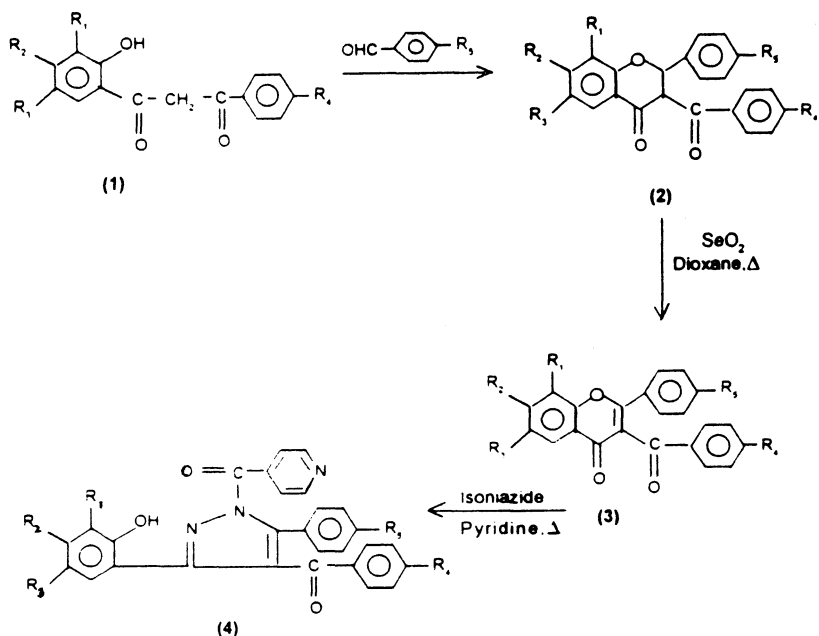
(3) *Preparation of 3-aryl flavones (3a–3j)*—3-Aroyl flavanones (2a–j) (0.01 M) and SeO₂ (0.001 M) were refluxed in dioxane for about 18 h. The reaction mixture was poured in cold water through a funnel fitted with glass wool. The solid separated was filtered, washed with sodium thiosulphate (5%) and water. It was recrystallized from ethanol-acetic acid mixture. Yield 80 to 95%.

Spectral interpretation of 3a:

IR (ν_{\max}) 1650 cm⁻¹ ν (C=O); 1615 cm⁻¹ ν (C=O); 1590–1585 cm⁻¹ ν (C=C); 1245 cm⁻¹ ν (C—O—C).

¹H NMR: δ 2.30 (s, 3H, Ar—CH₃); 3.80 (s, 3H, Ar—O—CH₃); 6.7–8.3 (m, 11H, Ar—H).

UV (λ_{\max}) 322 nm.



(Scheme-1)

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

TABLE-1
PHYSICAL CHARACTERISATION DATA OF SYNTHESISED COMPOUNDS
3-Aroyl Flavones (3a-3j)

Compound	R ₁	R ₂	R ₃	R ₄	R ₅	Yield (%)	m.p. (°C)	Molecular formula
3a	H	H	CH ₃	H	H	85	132	C ₂₃ H ₁₆ O ₃
3b	H	H	CH ₃	H	OCH ₃	85	156	C ₂₄ H ₁₈ O ₄
3c	Br	H	CH ₃	H	H	90	180	C ₂₃ H ₁₅ O ₃ Br
3d	Br	H	CH ₃	H	OCH ₃	92	195	C ₂₄ H ₁₇ O ₄ Br
3e	CH ₃	H	H	H	H	92	152	C ₂₃ H ₁₆ O ₃
3f	CH ₃	H	H	H	OCH ₃	77	176	C ₂₄ H ₁₈ O ₃
3g	H	CH ₃	H	H	H	70	148	C ₂₃ H ₁₆ O ₃
3h	H	CH ₃	H	H	OCH ₃	72	162	C ₂₄ H ₁₈ O ₄
3i	H	H	H	H	H	75	145	C ₂₂ H ₁₄ O ₃
3j	H	H	H	H	OCH ₃	80	185	C ₂₃ H ₁₆ O ₄

(4) Preparation of 3,5-diaryl-4-benzoyl-1-pyridoyl pyrazoles (4a-4j):

3-Aroyl flavones (3a-j) (0.01 M) were refluxed with isoniazide (0.2 M) for 8-10 h in pyridine solvent. The reaction mixture was decomposed by acidified water, filtered and washed with sufficient water. It was recrystallised from ethanol-acetic acid mixture to obtain a white crystalline solid. Yield 60-80%.

Spectral interpretation of 4a:

IR (ν_{\max}) 1625 cm⁻¹ ν (C=O); 3350 cm⁻¹ ν (OH); 1620 cm⁻¹ ν (C=N); 1500 cm⁻¹ ν (C=C); 1390 cm⁻¹ ν (C-N); 1035 cm⁻¹ ν (C-O) (phenol).

NMR: δ 1.9 (s, 3H, -CH₃); 7.2-7.6 (m, 17H, Ar-H); 12 (s, 1H, -OH).

UV (λ_{\max}) 256 nm.

Physical data of series (4a-4j) were recorded in Table-2.

TABLE-2
PHYSICAL CHARACTERISATION DATA OF SYNTHESISED COMPOUNDS
3,5-Diaryl-4-Benzoyl-1-Pyridoyl Pyrazoles :(4a-4j)

Compound	R ₁	R ₂	R ₃	R ₄	R ₅	Yield (%)	m.p. (°C)	Molecular formula	N % found (calc)
4a	H	H	CH ₃	H	H	70	252	C ₂₉ H ₂₁ O ₃ N ₃	8.9 (9.1)
4b	H	H	CH ₃	H	OCH ₃	71	232	C ₃₀ H ₂₃ O ₄ N ₃	8.4 (8.5)
4c	Br	H	CH ₃	H	H	65	215	C ₂₉ H ₂₀ O ₃ N ₃ Br	7.5 (7.8)
4d	Br	H	CH ₃	H	OCH ₃	77	245	C ₃₀ H ₂₂ O ₄ N ₃ Br	7.1 (7.3)
4e	CH ₃	H	H	H	H	67	270	C ₂₉ H ₂₁ O ₃ N ₃	8.9 (9.1)
4f	CH ₃	H	H	H	OCH ₃	72	231	C ₃₀ H ₂₃ O ₄ N ₃	8.1 (8.5)
4g	H	CH ₃	H	H	H	69	240	C ₂₉ H ₂₁ O ₃ N ₃	9.8 (9.1)
4h	H	CH ₃	H	H	OCH ₃	70	234	C ₃₀ H ₂₃ O ₄ N ₃	8.3 (8.5)
4i	H	H	H	H	H	70	215	C ₂₈ H ₁₉ O ₃ N ₃	9.2 (9.4)
4j	H	H	H	H	OCH ₃	75	210	C ₂₉ H ₂₁ O ₄ N ₃	8.5 (8.8)

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