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NOTE

Synthesis of 3,5-Diaryl-4-benzoyl-1-pyridoyl Pyrazoles by Oxidation of Pyrazolines using DMSO-I_2 Solvent

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Some new 3,5-diaryl-4-benzoyl-1-pyridoyl pyrazoles have been synthesized by the oxidation of pyrazolines, by using I_2 in DMSO solvent. The structures of these compounds have been established by spectral analysis (IR, NMR and UV) and elemental analysis.

Key Words: Synthesis, Oxidation, Pyrazolines, 3,5-Diaryl-4-benzoyl-1-pyridoyl pyrazoles.

Literature survey reveals the importance of chalcones and flavanones as a valuable starting material for the synthesis of heterocycles like pyrazolines, pyrazoles, isoxazoles, *etc*. Formation of pyrazolines have been reported[1-3] by the action of hydrazine or phenyl hydrazines on chalcones and flavanones in solvents like DMSO, ethanol, *etc*.

Pyrazoles have been reported by oxidation of pyrazolines by chromic acid, potassium permangnate, silver nitrate, potassium ferricynide, lead oxide and manganese dioxide[4]. Nitro pyrazoles have been synthesized from nitro pyrazolines using DMSO-I_2 as a solvent[5]. Sharma *et al*.[6] obtained pyrazoles form pyrazolines using lead tetra acetate as an oxidizing agent in benzene medium. Pyrazoles and their derivatives were prepared by the action of DMSO-I_2-H_2SO_4 and DMSO-I_2 system[7] on pyrazolines and its derivatives. 1,3,5-Trisubstituted pyrazoles were prepared by the oxidation of pyrazolines using 1,3-dibromo-5,5-dimethyl hydantoin[8]. Pyrazole is a class of compounds which are widely used in drugs and dyes[9,10]. These compounds also shows physiological activities[11-17].

Thus, it was thought of interest to study the reactions of 3,5-diaryl-4-benzoyl-1-pyridoyl-Δ^2-pyrazolines with DMSO-I_2 system to yield pyrazoles.

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Melting points are uncorrected. IR spectra in KBr was recorded on FT-IR spectrophotometer Schimadzu-8101, at Department of Pharmaceutical Sciences, Nagpur University, Nagpur. PMR spectra was recorded on AMX-400 MHz high resolution FT NMR spectrometer at Regional Sophisticated Instruments Center, Indian Institute of Sciences, Bangalore. The purity of the compounds was checked on Silica Gel-G coated plates.

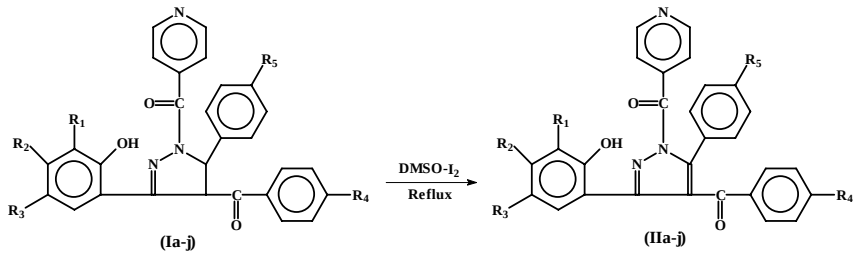
Synthesis of 3,5-diaryl-4-benzoyl-1-pyridoyl-Δ^2-pyrazolines (Ia-j): 3,5-Diaryl-4-benzoyl-1-pyridoyl-Δ^2-pyrazolines were prepared by known method[18].

Synthesis of 3,5-diaryl-4-benzoyl-1-pyridoyl pyrazoles (IIa-j): 3,5-Diaryl-4-benzoyl-1-pyridoyl-Δ^2-pyrazolines (**Ia-j**) were suspended in DMSO (20 mL) and a crystal of iodine was added to it. The reaction mixture was refluxed for 1 h, cooled and diluted with water to get corresponding pyrazoles. It was then washed with 20 % sodium thiosulphate to remove iodine and finally washed with water and crystallized from ethanol-acetic acid mixture to obtained white crystalline solid (yield 60-80 %) (Table-1).

TABLE-1
PHYSICAL CHARACTERIZATION DATA OF SYNTHESIZED COMPOUNDS

Compd.	R_1	R_2	R_3	R_4	R_5	m.f.	m.p. (°C)	% N Found (Calcd.)
IIa	-H	-H	$-CH_3$	-H	-H	$C_{29}H_{21}N_3O_3$	252	8.9 (9.1)
IIb	-H	-H	$-CH_3$	-H	$-OCH_3$	$C_{30}H_{23}N_3O_4$	232	8.4 (8.5)
IIc	-Br	-H	$-CH_3$	-H	-H	$C_{29}H_{20}N_3O_3Br$	215	7.5 (7.8)
IId	-Br	-H	$-CH_3$	-H	$-OCH_3$	$C_{30}H_{22}N_3O_4Br$	245	7.1 (7.3)
IIe	$-CH_3$	-H	-H	-H	-H	$C_{29}H_{21}N_3O_3$	270	8.9 (9.1)
IIf	$-CH_3$	-H	-H	-H	$-OCH_3$	$C_{30}H_{23}N_3O_4$	231	8.1 (8.5)
IIg	-H	$-CH_3$	-H	-H	-H	$C_{29}H_{21}N_3O_3$	240	9.8 (9.1)
IIh	-H	$-CH_3$	-H	-H	$-OCH_3$	$C_{30}H_{23}N_3O_4$	234	8.3 (8.5)
IIi	-H	-H	-H	-H	-H	$C_{28}H_{19}N_3O_3$	215	9.2 (9.4)
IIj	-H	-H	-H	-H	$-OCH_3$	$C_{29}H_{21}N_3O_4$	210	8.5 (8.8)

Spectral interpretation of IIa: IR (KBr, ν_{max}, cm^{-1}) 3350 (-OH), 1620 (-C=N of pyrazole str.), 1625 (C=O str.), 1500 (C=C str.), 1390 (-C-N) str.), 1033 (C-O str.). PMR (δ ppm): 1.9 (S, 3H, $-CH_3$), 7.22-7.6 (m, 17H, Ar-H), 12 (S, 1H, -OH). UV (λ_{max}): 256 nm.



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