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Synthesis of 3, 5 diaryl-4-benzoyl-1-pyridoyl pyrazoles by oxidation of pyrazolines using DMSO-I_2 solvent in microwave oven (Eco-friendly method)

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ABSTRACT

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. The reactions were carried out in microwave oven.

Key words: Synthesis, Oxidation, Microwave oven, I_2 in DMSO Solvent.

INTRODUCTION

Literature survey reveals the importance of chalocones and flavanones as a valuable starting material for the synthesis of heterocycles like pyrazolines, pyrazoles, isoxazoles., etc. Foramtion 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 from pyrazolines using lead tetra acetrate 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-dimenthyl hydantoin[8]. Pyrazole is a class of compounds which are widely used in drugs and dyes[9, 10]. These compounds also show physiological activities[11-17].

The above titled compounds were prepared by the oxidation of pyrazolines using I_2 in DMSO solvent [19] by traditional method, i.e. by using gas burners for heating and condensers. In this type of methods there is wastage of heat energy due to radiations, evaporation of reagents and wastage of water used in condensers.

Thus it was thought to prepare the titled compounds by following the principles of green chemistry to create an eco friendly technique which reduced evaporation of reagents, used of water for condensers, time of the reaction and ultimately reduced the cost of the reaction. This method is pollution free and hence eco-friendly.

The 12 principles[20] of green chemistry which were developed by Paul Anastas of the United States Environmental Protection Agency and John. C. Warner are

1. It is better to prevent waste than to treat or clean up waste after it is formed.
2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Wherever practicable, synthetic

methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and, innocuous when used.
6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. A raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable.
8. Reduce derivatives - Unnecessary derivatization (blocking group, protection/ deprotection, temporary modification) should be avoided whenever possible.
9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
11. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. Substances and the form of a substance used in a chemical process should be chosen to minimize potential for chemical accidents, including releases, explosions, and fires.

EXPERIMENTAL

Melting points are uncorrected. IR spectra in KBr were recorded on FT- IR spectrophotometer Schimadzu-8101, at Department of Pharmaceutical Sciences, Nagpur University, and Nagpur. PMR spectra were 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-Diary1-4-benzoyl-1-pyridoyl-Î^2-pyrazolines were prepared by known method [18].

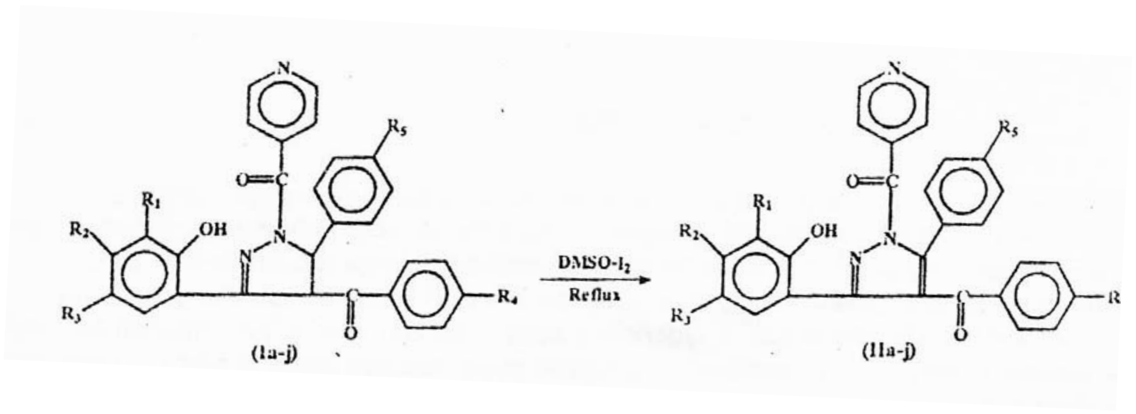
Synthesis of 3, 5 diaryl-4-benzoyl-1-pyridoyl pyrazoles (IIa-j)

Old Method

3, 5- Diaryl-4-benzoyl-1-pyridoyl -Δ^2-pyrazolines (Ia-j) were suspended in DMSO (20mL) and a crystal of iodine was added to it. The reaction mixture was refluxed for 1hour, 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 obtain white crystalline solid (yield 60-80%) (Table 1).

Microwave Method

When the above compounds (IIa-j) were prepared by using eco friendly technique (Microwave oven) the product was obtained in 5-6 minutes and the yield was in between 80-90%.



RESULTS AND DISCUSSION

Thus use of microwave oven for heating reduced time required, improved the yield and there was no need of condensers. Small amount of solvent was used, which ultimately reduced the cost of the reaction.

Spectral interpretation of IIa

IR (KBr, 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 (ppm)

1.9 (S, 3H, -CH_3) 7.22-7.6 (m, 17H, Ar-H), 12 (S, 1H,-OH).

UV (8max)

256 nm.

Table 1: Physical Characterization Data of Synthesized Compound

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)

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