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MICROWAVE ASSISTED SYNTHESIS OF 1-(3 -CHLOROPHENYL)-3, 5- DIARYL – PYRAZOLES

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ABSTRACT

Esterification of substituted acetophenone with aromatic acids followed by B.V. transformation gives β - diketone, which on microwave irradiation with m-chlorophenyl hydrazine hydrochloride give 1-(3-chlorophenyl)-3,5-diaryl–pyrazoles **(2a-f)**. The structures of these compounds were established by elemental, chemical and spectral analysis (IR, NMR). The properties of these compounds are found to be similar to the compounds obtained by usual method.

Key words : Microwave synthesis, Pyrazoles

INTRODUCTION

Refluxing is the most common method used in the synthesis of organic compounds. Since last decade the reaction rate has been accelerated by using the microwave dielectric heating[1,2]. This method has been popularized due to environmental benign reagents[3] and solvent free conditions[4-8] using microwave irradiation.

Pyrazoles play a vital role in the pharmaceuticals, possessing antimicrobacterial[9], and physiological activity[10]. Hence, it was thought to synthesize substituted pyrazoles by heating with microwave radiation.

Hydroxy chalcones and β-diketones are best starting compounds of the pyrazole derivatives in different solvents like pyridine, DMF, ethanol, acetic acid etc. and these are synthesized by the usual method. Present work deals with the microwave synthesis of 3,5-diaryl- pyrazoles and their characterization by elemental analysis, IR, ^{1}H NMR analysis and comparison of their properties with the compounds synthesized by conventional method.

EXPERIMENTAL

The melting points of the synthesized compounds were taken in silicon oil bath with open capillary tubes and are uncorrected. The purity of the compounds was checked by thin layer chromatography on silica gel-G. IR spectra were recorded on a Nicolet-Impact 400 FT-IR spectrometer. ^{1}H NMR spectra were recorded on a Brucker AC300 FNMR spectrometer (300MHz), using TMS as an internal standard. Microanalysis of nitrogen was obtained on colman 29-N analyzer.

Preparation of 1,3-diaryl-propane-1,3-dione (1a)

2'-Hydroxy-5'-methyl-acetophenone esterifies with benzoic acid to give the product which gives 1, 3-diaryl-propane-1, 3-dione **(1a)** by B.V. transformation. The product was washed and recrystallized with ethanol. The structures of this compound was confirmed by chemical and spectral analysis (m.p.146^{0}C, yield 70 %).

Spectral interpretation of (1a)

IR (ν_{max}) (cm^{-1}) : 1646 v(C=O), 1549 v(-CH=CH-), 1186 v(-C-O stretching),

NMR δ ppm : 2.32 (s, 3H, CH_3), 6.71-7.89 (m, 8H, Ar-H), 2.53 (s, 2H, $-CH_2-$), 13.61 (s, 1 H, -OH).

Similarly, 1, 3-diaryl-propane-1, 3-dione **(1b-f)** were prepared and their physical data are given in Table 1.

Preparation of 1-(3-chlorophenyl)-3,5-diaryl –pyrazoles (2a).

1,3-Diaryl-propane-1,3-dione **(1a)** was mixed with 3-chlorophenyl hydrazine hydrochloride (1 : 1) and the mixture irradiated with microwave radiation, in house hold 2450 Hz microwave oven at 600 watts for 3 minutes to give 1-(3-chlorophenyl) -3, 5-diaryl –pyrazoles **(2a)**. The product was washed and recrystallized with ethanol. The structure of this compound was confirmed by chemical and spectral analysis (m. p. 214ºC, yield 86 %).

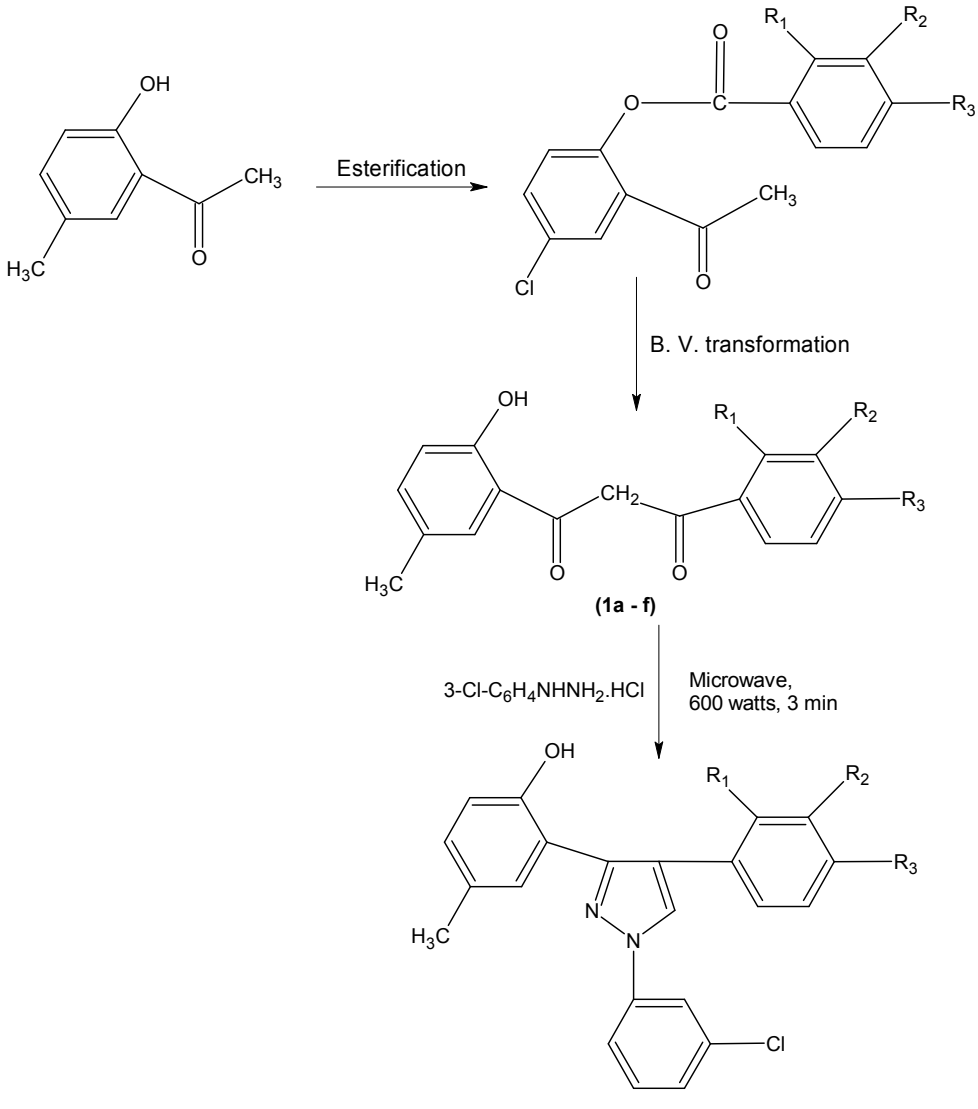
Spectral interpretation of (2a)

IR (ν_{max}) (cm^{-1}): 3148 v (-OH phenolic), 2853 v (-CH), 1623 v (>C=N), 1479 v (-C=C-), 1282 v (-C-O).

NMR δ ppm: 2.37 (s, 3H, $-CH_3$), 3.72 (s, 1H, -CH), 6.79-7.51 (m, 12H, Ar-H),

10.5 (s, 1H, Ar-OH).

Similarly, 1-(3-chlorophenyl)–3,5- diaryl–pyrazoles **(2b-f)** were prepared and their physical data are given in Table 1.



R_1 = -H, -OCH_3, -Cl, -Br ; R_2 = H, OCH_3, -Cl, -Br; R_3 = -H, -OCH_3, -Cl, -Br

Scheme 1

Table 1. Physical data of synthesized compounds

Compound	R_1	R_2	R_3	M. P. (ºC)	Yield old (M/W) %	%N Found (Calculated)
(1a)	H	H	H	146	70	
(1b)	Br	H	H	153	73	
(1c)	Cl	H	H	168	69	
(1d)	H	H	Cl	180	77	
(1e)	OCH_3	H	H	167	64	
(1f)	H	H	OCH_3	170	74	
(2a)	H	H	H	214	73 (86)	7.77 (7.70)
(2b)	Br	H	H	182	75 (88)	6.37 (6.22)
(2c)	Cl	H	H	179	79 (87)	7.09 (6.98)
(2d)	H	H	Cl	185	69 (89)	7.09 (6.89)
(2e)	OCH_3	H	H	206	72 (91)	7.17 (7.11)
(2f)	H	H	OCH_3	218	70 (90)	7.17 (7.15)

RESULTS AND DISCUSSION

Pyrazoles obtained from β-diketones and 3-chlorophenyl hydrazine hydrochloride by microwave irradiation were found to have same characteristics as that of compounds prepared by usual method. The rate of the organic reaction is accelerated and product obtained within 3 minutes, which required 6 hours in the routine method. % Yield of the product obtained was also found more than the usual method. Hence, this method is quite beneficial to the usual method as it avoids pollution.

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