Synthesis of Enaminones by Conventional and Microwave Irradiation Methods

R. K. JADHAV[1], B. K. KARALE[2*], P. V. RANDHAVANE[1], A.B. NIKUMBH [1] AND K. P. KAKDE[1]

[1]Department of Chemistry, S.S.G.M. College, Kopargaon, Dist. Ahmednagar- 423 601.
[2]Chhatrapati Shivaji College, Satara - 415 001.
Corresponding Author email: jadhavranjana2211@yahoo.co.in

ABSTRACT

Microwaves have become an important source of energy in many laboratory procedures as green approach. We followed the microwave assisted organic reactions using solvents. The chief goal of this work was to observe the reaction of secondary amine with 3-formylchromones using conventional and microwave assisted reactions.

Keywords: Conventional method, Microwave irradiation method, Green reaction

Introduction

3-Formylchromones have noticed as of influence of their biological activity and organic synthesis. 3-formylchromones are a group of naturally occurring compounds that are universal in nature predominantly in plants and helpful for use as precursor as green approach. They give versatile condensation reactions because of 3 electron deficient sites. A number of condensation reactions represent the ability of 3-formylchromones to give out as an excellent precursor for the synthesis. They are synthesized by the well-known procedure of Vilsmeyer Haak reaction[1, 2].

Since a couple of decades before, scores of major advances in practical aspects of organic chemistry have built-in novel synthetic strategies and methods as well as the commencement of an immense set of analytical techniques. In these environmentally vigilant days, the development in the technologies is focussed towards environmental sound and cleaner procedures.

With rising complexity of the problems and the accessibility of newer methods of creations of chemical reactions, researchers have reinstated to use wide diversity of techniques with ultrasound and microwave origin; their utility in chemistry has expanded thrust recently[3]. Microwaves have been employed to accelerate the chemical reaction in laboratories. On the electromagnetic spectrum the microwave radiation part is placed between infrared radiation and radio waves.

Microwaves directly couples with molecules of the whole reaction mixture with rapid rise in temperature. In microwave assisted reactions, using organic solvents, the reactants are usually dissolved in solvents, which are often coupled effectively with microwaves and thus acts as the energy transfer medium. Microwaves have become an important source of energy in many laboratory procedures[4-9]. We followed the microwave assisted organic reactions using solvents[10-11]. The chief target of this work was to observe the reaction of secondary amine with 3-formylchromones using conventional and microwave assisted reactions respectively. Synthesis under microwave irradiation keeps on extensively faster. The reaction time dropped down to 20-50 min under exposure to microwave at 500 to 700W and produced clean products in high yields.

Experimental Work

The melting points of all the synthesized compounds were studied in open capillary tubes and are uncorrected. Purity of all compounds was determined by TLC and column chromatography. TLC was performed on precoated silica-gel plates, which was observed under UV light. IR (KBr) spectra were recorded on a Perkin-Elmer (spectrum on a FT-IR) spectrophotometer. The ^{1}H NMR were recorded on a Bruker Avance II 400 MHz NMR spectrometer in $CDCl_3$ and DMSO as a solvent, chemical shift (δ) are expressed in ppm downfield from TMS and coupling constant (J) are expressed in hertz(Hz). Mass spectra were recorded on Waters, Q-TOF MICROMASS (LC-MS).

Materials and Method

Synthesis of the compounds was done by conventional method and Non conventional method. In the present investigation, we used saleable microwave with an IR sensor for scheming temperature up to 500^{0}C Model RG-311R manufactured by RAGA'S Microwave System having a maximum power output of 700 W capacities.

(*E*)-3-(N-cyclohexyl-N-methylamino)-1-(2-hydroxyphenyl) prop-2-en-1-one

Conventional Method: 3-Formylchromones (0.001 mole) and N-methylcyclohexanamine (0.002 mole) were dissolved in 15 mL of ethanol. The reaction contents were refluxed for 5 to 7 hr. The reaction was monitored by TLC. After completion of reaction, the reaction mixture was poured on crushed ice and acidified with conc. HCl. The resulting product was filtered and crystallized from ethanol to afford a pure compound. The various analogs of the synthesized compounds by above procedure are listed in **Table I**

Table : Data of the synthesized compounds

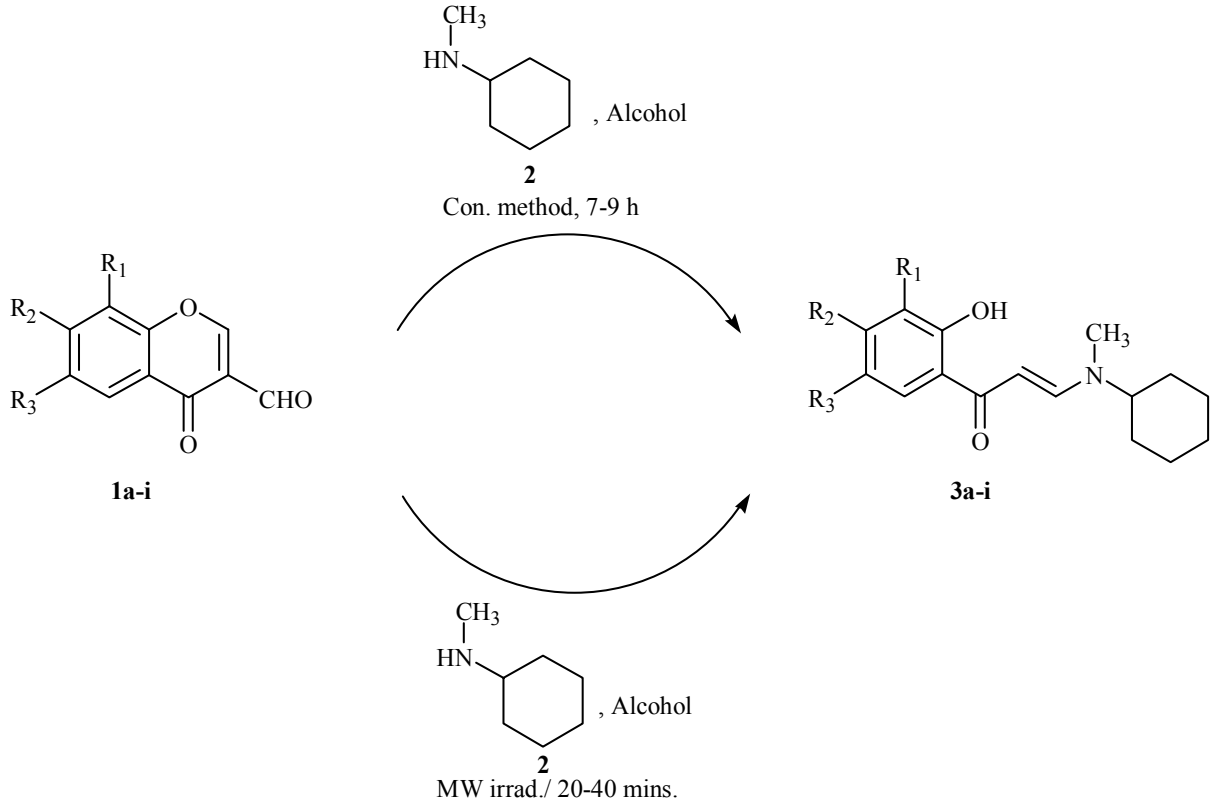
Sr. No.	R1	R2	R3	R4	Conventional method			Microwave method		
					MP (^{0}C)	Yield (%)	Time (Min)	MP (^{0}C)	Yield (%)	Time (Min)
3a	H	H	CH_3	H	65-75	62	480	70-75	78	45
3b	H	CH_3	H	H	Oil	60	540	Oil	74	50
3c	H	H	H	H	110-111	58	420	90-95	80	24
3d	H	H	Br	H	120	65	540	110-115	86	50
3e	Cl	H	Cl	H	60	66	540	55-60	82	45
3f	H	H	Cl	H	95-97	68	360	90	80	24
3g	H	CH_3	Cl	H	120	65	420	118	80	50
3h	H	H	C_2H_5	H	Oil	60	540	Oil	83	10
3i	H	H	H	CH_3	Oil	67	540	Oil	85	20

Microwave Irradiation Method: **Microwave method:** 3-Formylchromones (0.001 mole) and N-methylcyclohexanamine (0.002 mole) were dissolved in 15 mL of ethanol in flat bottomed flask. The reaction contents were subjected for microwave irradiation at 350-500W for time as shown in **Table** till completion of the reaction. The reaction was monitored by TLC. After completion of reaction, the reaction mixture was poured on crushed ice and acidified with conc. HCl. The resulting product was

filtered and crystallized from ethanol to afford a pure compound **5a-i**. Data of the synthesized compounds by above procedure are listed in **Table**.

3b: IR: (KBr) (cm^{-1}): 3400 (-OH stretching), 3061 (trans >C=C< stretching), 1632(C=O stretching), 1535 (-C=C- stretching), 1289 (C-N stretching); ^{1}H NMR: 1.1-1.8 δ, (10H, m), 2.28 δ, (3H, s), 2.92 δ, (3H, s), 3.19 δ, (1H, m), 5.79 δ, 1H, (d, J=12.04Hz), 6.83 δ, (1H, d, J = 8.36 Hz), 7.15 δ, (1H, dd, J = 8.36 &1.8 Hz), 7.4 δ, (1H, s), 8.0 δ, (1H, d, J = 12.04 Hz), 13.8 δ, (1H, s)**,** Mass: m/z 274 (M^+).

SCHEME:



Result and discussion

Synthesis of compounds **3a-e** was done by conventional and microwave irradiation method, as shown in **scheme**. The IR spectrum of compound **3a** showed the bands at 1632 and 1535 cm^{-1} for conjugated C=O and C=C bonds respectively. The ^{1}H NMR spectrum of this compound showed a singlet at δ 13.8 which shows the presence of O-H proton. The formation of the novel synthesized compounds also confirmed by mass spectrometry.

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