



A CaO Catalyzed Synthesis of Coumarin in Microwave

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Abstract

A Simple and efficient method for the synthesis of various coumarins from substituted phenols and ethylacetoacetate has been developed by using CaO as a catalyst in water under the microwave. The present methodology includes inexpensive catalyst, easy workup and basic reaction condition. The UV absorption of all the synthesised coumarine derivatives was recorded at λ_{max} at 380 nm. The compound was characterised by ¹H NMR, Mass spectroscopy.

Keywords: Coumarin, CaO, Phenols, UV absorption, Ethylacetoacetate.

Introduction

Coumarins are important organic compounds having several applications in perfume, cosmetic and pharmaceutical industrial production¹.

Perkin, Pechmann, Reformatsky, Wittig Knoevenagel reactions² are the most common synthetic methods to produce coumarins. Recently, room temperature ionic liquids have attracted interest in the field of green chemistry³⁻⁹.

CaO has also been applied as a solid base catalyst because of its high catalytic activity at mild reaction conditions, long lifetimes of catalyst and low catalyst cost. Microwave (MW) irradiation are used for a variety of applications including organic synthesis, wherein chemical reactions are accelerated by of selective absorption of MW radiation by molecules^{10,11}.

Here we present the reactions are catalyzed by using a base CaO, water as a solvent under microwave condition. Recently, it has been found that the use of microwave irradiation has considerable advantages over thermal reactions in organic reactions.

Materials and Methods

The organic materials were purchased from SdFine and Merck and were used without any additional purification. Merck, pre coated Silica gel 60 F₂₅₄ (Aluminum sheet) plates were used for analytical TLC. IR spectra were recorded on FTIR spectrophotometer, ¹H-NMR spectra of all the synthesized compounds were recorded in (CDCl₃/DMSO-d₆) on Bruker Advance-2 400MHz NMR Spectrophotometer using TMS as an internal standard. The melting point was determined in open capillary tubes using Pfit model.

Synthesis of 7-hydroxy-4-methyl-2H-chromen-2-one: A mixture of ethylacetoacetate (1mmol) substituted phenols (1mmol) and CaO (1mmol) was taken in a round bottom flask using water as a solvent. The reaction mixture was irradiated in microwave at 120^oC for a period of mentioned in the table II. Completion of the reaction was monitored by TLC.

The reaction mixture was poured in a beaker containing cold water. The solid obtained was purified by column chromatography (hexane/acetone 9:1) to furnish respective derivatives. The result was obtained in good yield.

Spectral data: Mass: m/z- 177.05, 121.06, 103.05, 77.03; IR (KBr) cm⁻¹: 1242 (C-O), 1604 (C=C), 1743 (O-C=O), 3082 (C=CH), 3204 (phenolic O-H). ¹H NMR (DMSO- d₆) 2.4 (s, 3H, -CH₃), 6.1 (s, 1H, -C=CH), 6.71 (d, 1H, J=2.4Hz, -C=CH), 6.79(dd, 1H, J=9, J=2.4Hz, -C=CH), 7.95 (d, 1H, J=9 Hz, -C=CH), 10.5 (s, 1H, Ar-OH) (Yield- 85%) (m.p.186-187).

Results and Discussion

A base catalysed synthesis of 4-methyl-7-hydroxycoumarin in 25 minutes, which was known to give blue fluorescence in UV light. 2-hydroxy-1-naphthaldehyde shows the maximum absorbance at 4.246 at 380nm (Table-1). The UV absorption for synthesized derivatives is depicted in Table-1

In order to establish the best reaction condition, (4) as a model reaction was performed using resorcinol, ethylacetoacetate, CaO with various solvent such as water, PEG-400, PEG-4000, Methanol, Ethanol, DMF and DMSO in microwave at 120^oC. The result summarised in Table-2.

Conclusion

Present methodology gives an base catalysed Pechmann condensation for the synthesis of coumarin derivatives.

Table-1
The derivatives prepared by using above methodology

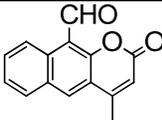
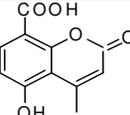
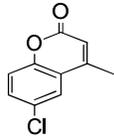
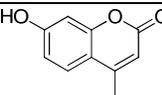
Entry	structure	Time required(min)	Absorbance
1		140	4.246
2		110	0.6724
3		90	0.4535
4		25	4.0610

Table-2
Reaction using different solvents

Entry	Solvent	Time(min)	Yield(%)
(4)	Water	25	85
	PEG-400	70	83
	PEG-4000	100	79
	Methanol	245	83
	Ethanol	125	80
	DMF	50	81
	DMSO	125	78

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