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ENVIROCAT EPZ-10: AN EFFICIENT CATALYST FOR SYNTHESIS OF COUMARINS BY PECHMANN REACTION UNDER SOLVENT FREE MICROWAVE IRRADIATION METHOD

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Abstract: EPZ-10 is a clay catalyst was found to be an efficient ecofriendly catalyst for the synthesis of coumarins by Von-Pechmann condensation which includes cyclocondensation of phenol with β-ketoester under solvent free conditions by using microwave irradiation with excellent yield and good purity. The advantage of present methods is use of EPZ-10 as an ecofriendly biodegradable clay catalyst under solvent free condition with better yield in shorter reaction time.

Keywords: EPZ-10 catalyst, Coumarins, Pechmann reaction, MWI, green synthesis.

Introduction

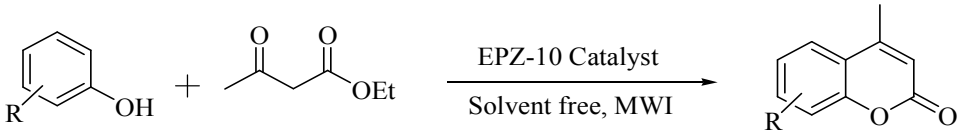
Coumarin occupied an important place in region of natural and synthetic organic chemistry[i], because of use as anticoagulants, antibacterial[ii], antiviral, anti-HIV[iii], anticancer[iv] and also used in additive in food, perfumes, and cosmetics in lesser dye and in optical brightener[v]. Coumarins have been synthesized by several synthetic routes including Pechmann[vi], Perkin[vii], Wittig[viii], Knoevenagel[ix], and Reformatsky[x] reactions. Among these Pechmann[vi] reaction is most common and versatile reaction this method involves condensation of phenols with β-ketoester in the presence of condensation agent. In original reaction used harsh reaction conditions with concentrated H_2SO_4 as catalyst as well as solvent. A wide varity of condensation agent have been developed for Pechmann reaction like chlorosulphonic acid[xi], sulphuric acid[vi], melamine formaldehyde resin supported H^+ ion catalyzed[xii], ionic liquid[xiii], oxalic acid catalyzed[xiv], silica triflate catalyzed, heterogeneous catalyzed, zirconia supported catalyst $CuFe_2O_4$ nano-particle[xv], and molecular iodine catalyst[xvi], etc. Most of these reactions suffer from several drawbacks including use of large amount of catalyst, longer reaction time, hazardous work up, formation of unwanted products and affect the yield.

Here we report that use of environmental catalyst EPZ-10 for synthesis of coumarins derivative by Pechmann condensation[xvii] under solvent free and microwave irradiation technique in shorter reaction time. (Scheme 1) EPZ-10 is a commercial available, green

catalyst having several applications in field of synthetic organic chemistry such as condensation reaction[xviii,xix] solid acid catalyst[xx] cycloaddition reaction[xxi], etc.

RESULT AND DISCUSSION

Here in, we report the applicability of this reagent EPZ-10 in acceleration of Von Pechmann condensation of phenols and ethyl acetoacetate under solvent free condition catalyzed by simple, efficient, ecofriendly, biodegradable catalyst. (Scheme 1) To establish the reaction condition, a mixture of equimolar quantities of resorcinol and ethyl acetoacetate was treated with EPZ-10 (20 mol %) and subjected to microwave at 300 watt for 60 sec to give the corresponding coumarins.[14] (Table 1, Entry 1) By encouraging above result, we carried out a series of substituted phenols with ethyl acetoacetate by using EPZ-10 as a catalyst under solvent free condition to synthesis corresponding coumarins derivatives in excellent yield. (Table 1)



Scheme: Synthesis of Coumarins derivative by Von-Pechmann condensation under solvent free condition.

EXPERIMENTAL

General:

All melting points (mp) were obtained on open head capillary and uncorrected. NMR spectra were recorded in solvent $CDCl_3$, ^1H at 400 MHz using TMS as the internal standard on a Bruker FT-400 spectrometer. Analytical thin-layer chromatography (TLC) was carried out on precoated plates (silica gel 60 F^{254}), and spots were visualized with ultraviolet (UV) light. All reactants and reagents were used as obtained from commercial sources without further purification.

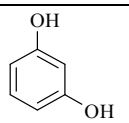
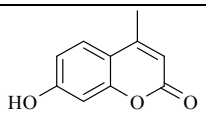
General procedure for synthesis of coumarins derivatives:

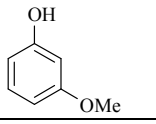
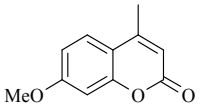
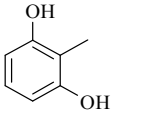
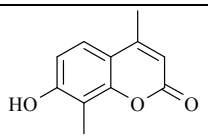
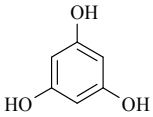
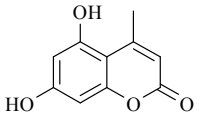
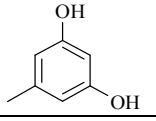
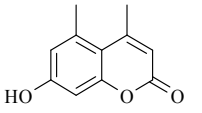
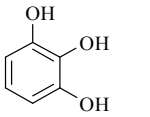
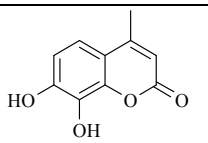
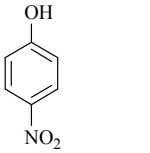
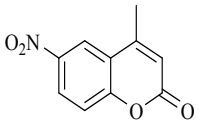
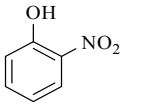
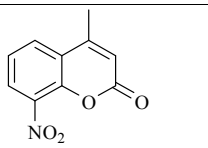
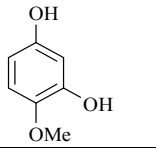
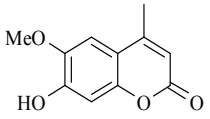
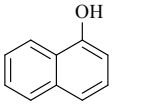
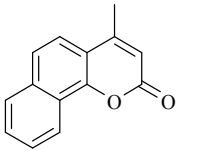
A mixture of substituted phenol (10mmol), ethylacetoacetate (10mmol) and EPZ-10 catalyst (20 mol %) were subjected to microwave irradiation at 300W for appropriate time (Table 1). After completion of reaction, as monitor by TLC, the reaction mixture was cooled to room temperature, water was added and stirred for another two minutes, precipitation was filtered off and recrystallized from methanol to afford pure product.

The spectral data and melting point in good agreement with those reported in literature[xiv]

Characteristic data of representative compound 1. Yellowish prism, yield 98 %, m.p. 184-186°C. IR (KBr pellet): 2985, 1740, 1625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.2 (s, 3H, Me), 6.1 (s, 1H), 6.83 (d, 1H, J 2.4 Hz), 6.97 (dd, 1H, J 8.7 and 2.4 Hz), 7.5 (d, 1H, J 8.7 Hz); MS (*m/z*): 175 (M^+ ion).

Table 1: Solvent free synthesis of 2-oxo-2H-chromen (coumarin) in presence of EPZ-10 as catalyst and MWI technique.

Entry	Substrate	Product[a]	Time in Sec.	M. P. in °C		Yield[b] (%)
				Obs.	Lit.	
1			60	184-86	185[xiv]	98

2			60	158-60	161[XIV]	95
3			60	138-39	138[XIV]	90
4			60	285-86	285[XIV]	90
5			60	257-58	258[XIV]	92
6			80	235-36	237[XIV]	89
7			110	147-49	150[XIV]	72
8			100	183-184	185[XIV]	79
9			90	164-165	165[XIV]	91
10			120	156-158	155[XIV]	87

[a]Products were characterized by their physical constant and spectral analysis.
[b]Isolated yield

CONCLUSION

In conclusion, the present green approach methodology offers several advantages such as, excellent yield, short reaction time, simple reaction procedure with solvent free condition, use of commercially available green biodegradable EPZ-10 as catalyst. We believe that, this method can be useful addition to present methodologies for synthesis of coumarins.

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