Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2015, 7(5):899-902

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Perchloric acid modified cellulose: Solid acid catalyst for Pechmann condensation using grinding technic under solvent free condition

Omprakash S. Chavan*[1], S. A. Jadhav[2], M. G. Shioorkar[2], S. B. Chavan[3], M. A. Baseer[3] and Y. M. Pawar[3]

[1]*Department of Chemistry, Badrinarayan Barwale College, Jalna, (M.S.), India*
[2]*Department of Chemistry, Vivekanand College, Aurangabad (M.S.), India*
[3]*Department of Chemistry, Yashwant College, Nanded, (M.S.), India*

ABSTRACT

A simple, one pot green highly efficient condition for Pechmann condensation for synthesis of Coumarins involving grinding technic of phenols and ethyl aceto acetate under solvent free condition at room temperature catalyzed by biodegradable a versatile novel heterogeneous solid acid catalyst has been described . The remarkable features of this environmentally benign protocol are short reaction time, use of inexpensive heterogeneous catalyst and high yield of product via simple experimental procedure.

Keywords: Coumarins, Pechmann reaction, Perchloric acid: cellulose catalyst, solvent free condition, green synthesis.

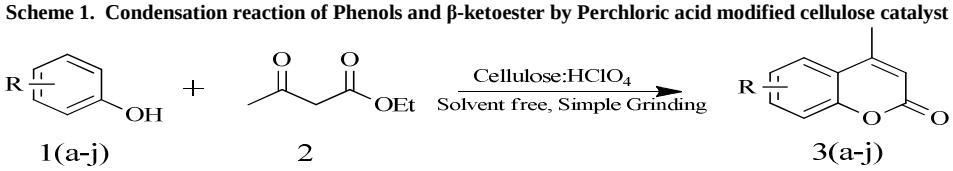
INTRODUCTION

Coumarins [1] are the very important class of naturally occurring oxygen containing heterocyclic compounds exhibit useful and diverse biological properties such as antibacterial [2], anti-cancer [3], anti-inflammatory [4], anti-pyretic, anti-biotic [5], anti-fungal [6], and also reported for exhibiting photochemical properties [7].

Due to biological importance of Coumarins, continuous efforts have been made to achieve simple, and efficient procedure, many routes are available for synthesis of Coumarins such as Pechmann [8], Perkins [9], Knoevengeal [10], Reformatsky [11] and Wittig Reaction [12]. Most of these, Pechmann is one of the most important reaction due to simple staring materials and catalyzed by acid catalyst like chlorosulphonic acid,[13] sulphuric acid, melamine formaldehyde resin supported H^+ ion catalyzed,[14] ionic liquid,[15] oxalic acid catalyzed,[16] silica triflate catalyzed, heterogeneous catalyzed, zirconia supported catalyst $CuFe_2O_4$nano-particle [17] and molecular iodine catalyst,[18] etc. Some of the above mentioned condition, use of harsh reaction condition, hazardous chemicals, expensive and large amount of reactant and catalyst, longer reaction times, use of solvents and conventionally supplement of energy, use of elevated temperature and formation of hazardous byproduct with exothermic workup.

In continuation of our research work[19] [20] to develop simple procedure for synthesis of coumarins via Pechmann condensation using grinding technic at room temperature with the help of versatile, biodegradable, Perchloric acid modified cellulose, solid acid catalyst under solvent free condition. (Scheme 1)

Scheme 1. Condensation reaction of Phenols and β-ketoester by Perchloric acid modified cellulose catalyst



1(a-j) 2 3(a-j)

Scheme 1.

Table 1. Investigation of Effect of Catalyst on reaction of Resorcinol and Ethyl acetoacetate[a]

Entry	Catalyst	Relative mole %	Yield[b] in %
1	Cellulose:$HClO_4$	00%	00%
2	Cellulose:$HClO_4$	10%	40%
3	Cellulose:$HClO_4$	20%	70%
4	Cellulose:$HClO_4$	30%	96%
5	Cellulose:$HClO_4$	40%	97%
6	Cellulose:$HClO_4$	50%	97%

[a]Reaction Condition: Resorcinol (1 mmol), EAA (1mmol), catalyst (Table 1) grind for 20 min. under solvent free condition. [b]Isolated yield

EPERIMENTAL SECTION

All the compounds used in synthesis were of analytical grade, the melting points of the compounds were determined in open head capillary and are uncorrected. The IR spectra of the compounds were recorded in the region of 4000-400 cm^{-1} by using KBr pallet on FT-IR Perkin spectrophotometer. H^1 NMR spectra were recorded on a DRX-300 Bruker FT-NMR spectrophotometer in $CDCl_3$. Satisfactory elemental analysis was obtained on a Perkin Elmer CHN analyzer. The values of chemical shift are expressed in δ ppm as a unit. All the compounds were checked for purity by thin layer chromatography (TLC).

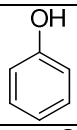
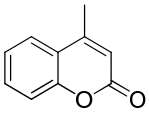
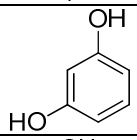
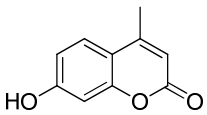
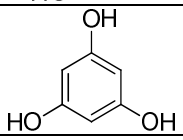
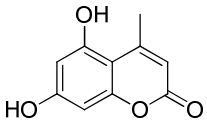
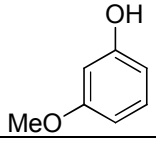
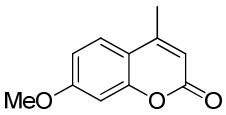
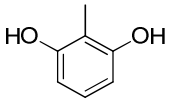
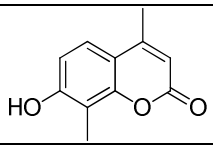
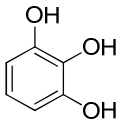
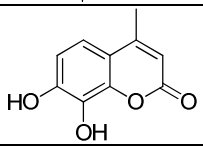
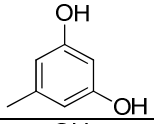
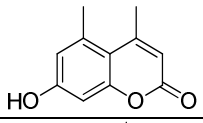
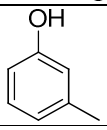
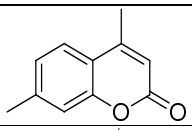
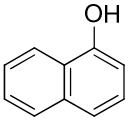
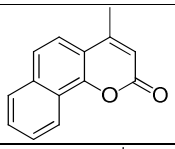
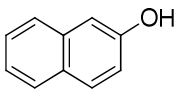
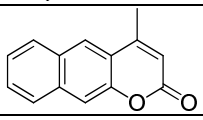
Procedure for Preparation of Perchloric acid modified cellulose Catalyst: Cellulose $HClO_4$ was prepared by the drop wise addition of Perchloric acid (1.0 g, 10mmol) to a magnetically stirred mixture of cellulose (5.0 g) in n hexane (20 ml) at 0 ^{0}C for 2 hr., after complete addition, the mixture was stirred for another 2 hr. The mixture was filtered, washed with acetone (30 ml) and dried at room temperature to affords cellulose- $HClO_4$ as white powder.

Spectral data of catalyst: IR (KBr, ν/*cm*$^{-1}$): 3441(br OH str), 1159 9 (asym C-O str), 10559 (C-C str), 904 (C-H str) of glucose.

General procedure for the synthesis of Coumarin derivatives under solvent free condition at room temperature: Substituted Phenols (1 mmol) and β- ketoester (EAA) (1 mmol), were taken with 30 mol % of Perchloric acid modified cellulose catalyst grind for few minutes (10-20 min) in mortar and pestle at room temperature, after completion of reaction (monitored by TLC) ethyl acetate (10 ml × 2) was added to reaction mixture and filtered to remove solid catalyst. Organic layer was wash with water (50 ml × 2) and evaporated in reduced pressure to obtained solid products **(3a-3j)** finally recrystallized from suitable solvent.

Spectral data of 3b: yellowish prism (yield 96 %, mp 183-184 °C). **^{1}H NMR** ($CDCl_3$) 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). **IR (KBr, ν/*cm*$^{-1}$):** 2985, 1740, 1625. ES/MS, *m/z*: 175 (M-H).

Table 2. **Synthesis of Coumarins via Pechmann condensation of phenols with ethyl acetoacetate catalyzed by Cellulose Perchloric acid modified Catalyst**

Comp.	Phenols	Coumarins	Yield	Melting point	Lit. M.P.
3a			61%	81-82°C	81°C[23]
3b			96%	183-184°C	185°C[21]
3c			82%	280-281°C	283°C[21]
3d			90%	154-155°C	156°C[22]
3e			86%	134-135°C	138°C[23]
3f			80%	240-241°C	244°C[21]
3g			79%	254-255°C	252°C[22]
3h			91%	129-130°C	132°C[21]
3i			69%	153-154°C	152°C[21]
3j			55%	172-173°C	182°C[23]

RESULTS AND DISCUSSION

Herein, we report that, synthesis of Coumarins by von Pechmann condensation in presence of cellulose Perchloric acid as a biodegradable heterogeneous solid acid catalyst under solvent free condition by using simple grinding technic at room temperature. This methodology with this catalyst is very simple and catalyst can be removed easily by simple filtration, hence there will not any unnecessary acidic waste to produce environmental pollution.

To optimized reaction condition, mixture of equimolar quantities of resorcinol and ethyl acetoacetate was treated with cellulose perchloric acid catalyst and grind for 20 min. to give the corresponding Coumarins (3b) in 96% yield, (m.p. 183-184°C; Table 2, Entry 2).

In this methodology used substrate having electron donating group which help to produce maximum yields under above reaction condition in short period of time. All the products were identified by comparison of analytical data of these reported for authentic sample.

CONCLUSION

In conclusion, we have developed a simple & efficient synthesis of coumarins via Pechmann reaction using cellulose perchloric acid as a modified catalyst under solvent free condition. Moreover, low cast of catalyst, solvent free condition, low toxicity of catalyst, fast reaction time, simple experimental condition, recyclability of catalyst & high yield of product, are the advantages.

We believe that our procedure will find important application in the synthesis of Coumarins.

Acknowledgment
Authors are thankful to the Principal, Yashwant Mahavidhyalaya, Nanded for constant encouragement and providing necessary facilities for this work and one of the author (Chavan O.S.) is thankful to UGC, New Delhi, for providing financial Assessment.

REFERENCES

[1] R. O'Kennedy, R. D. Thornas, Coumarins: Biology, Application and Mode of Action, Wiley and Sons, Chichester, **1997**.
[2] O Kayser, H Kolodziej, *Planta Med.* **1997**, 63, 508-510.
[3] CJ Wang, YJ Hsieh, CY Chu, YL Lin, TH Tseng, *Cancer Lett.* **2002**, 183, 163-168.
[4] AC Luchini, OP Rodrigues, SH Cestary, LN Seito, A Witaicenis, CH Pelizzon, LCD Stasi, *Bio.Pharma. Bull.* **2008**, 31, 1343-1350.
[5] DA Erans, CE Sacks, WA Kleschick, TR Taber, *J. Am. Chem. Soc.* **1979**, 101, 6789.
[6] M Yamato, *J. Pharma. Soc. Japan*,**1992**, 112, 81.
[7] G Kokotos, C Tzougraki, *J.Chem. Soc. Perkin Trans.* **1991**, 2, 495.
[8] H Pachmann, C Duisberg, *Chem.Bar.* **1883**, 16, 2119.
[9] JR Jonson, *Org. React.***1942** ,1, 210.
[10] F Bigi, L Chesini, R Maggi, G Sartori, *J. Org. Chem.* **1999**, 64, 1033.
[11] RL Shirner, *Org. React.* **1942**, 1, 1.
[12] I Yavari, R HekmatShoar, A Zonuzi, *Tet. Lett.* **1998**, 39, 2391.
[13] SA Kotharkar, SS Bahekar, DB Shinde, *Mendeleev Comm.*, **2006**, 16 (4), 241.
[14] R Rezaei, L Dorosty, M Rajabzadeh, R Khalifeh, *Chinese Chem. Lett.*, **2011**, 22, 1313.
[15] S Das, A Majee, A Hajra, *Green Chem. Lett. & Review*, **2011**, 4 (4), 349.
[16] ND Kokare, JN Sanghshetti, DB Shinde, *Chinese Chem. Lett.*, **2007**, 18, 1309.
[17] SM Baghbanian, M Farhang, *Syn. Comm.*, **2014**, 44, 697.
[18] JD Grote, S Tyndall, KF Wong, MVA Parris, *Tetrahedron Lett.*, **2014**, 55, 6715.
[19] OS Chavan, SB Chavan, MA Baseer, *Der Pharma Chemica*, **2015**, 7(1), 197-200.
[20] OS Chavan, MA Baseer, *Der Chemica Sinica*, **2014**, 5(5), 67-70.
[21] S Farhad, M Katayoun, HT Nahzomi, MA Zolfigol, *Chinese Chem. Lett.* **2007**,18, 909-911.
[22] K Niknam, SA Sajadi, R Hosseini, M Baghernejad, *Iranian J. of Catalysis.* **2014**, 4(3), 163-173.
[23] V Vahabi, F Hatamjafari, *Molecules*, **2014**, 19, 13093-13103.