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An efficient and simple synthesis of 4-hydroxy coumarin derivatives using PMA-silica catalyst

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ABSTRACT

A convenient facile regioselective, quantitative synthesis of ortho derivatives of 4-hydroxy coumarins (3a-3i) by using Phosphomolybdic acid (PMA) Silica supported BF_3 : Etharate as a catalyst, at room temperature with excellent yield. This synthesis offers the advantage of mild reaction condition, very short reaction time, regioselective product at room temperature with good yield.

Keywords: 4-hydroxy coumarin, PMA Silica supported $BF_3:OEt_2$ catalyst, Solvent free synthesis, regioselective, ortho substitution.

INTRODUCTION

In the organic synthesis, heterogeneous catalyst plays an important role and consider as a method of choice for application in large number of diverse chemical reactions. Reactions involving the heterogeneous catalyst having advantage like easy workup of the reaction by simple filtration techniques increase simplicity, with high yield of product, reusability of catalyst.

A large number of solid supported reagents or catalysts like silica supported sulfuric acid [1], polyphospharic acid supported on silica, P-TSA catalyzed KSF solid supported, clay supported HPA catalyst [2], Zirconium supported phosphotungastic acid as catalyst [3], etc. have been developed over a period of time and have been used in many chemical transformations.

In the synthetic procedure of coumarins and 4-hydroxy coumarins and their derivatives have been modified by using several pathways [4-6] like microwave irradiation, ionic catalyst, heteropolyacids, solid supported catalyst, Lewis acid catalyst, silicon catalyst, EPZ-10 catalyst, mineral acid catalyst, transition metal catalyst. This work is attempt of synthesis and use of a new heterogeneous catalyst during the regioselective substitution reaction of Coumarin. Preparation of PMA-Silica supported BF₃:OEt₂ catalyst is simple and it can be store for long time over CaCl₂. During the course of reaction we got encouraging result, which underline possibility of wide usability spectrum of this heterogeneous catalyst.

Herein, we report as PMA-Silica supported catalysed synthesis of 4-hydroxy coumarins derivative under solvent free condition with excellent yield. (Scheme 1)

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Reaction Scheme 1. Synthesis of 4-hydroxy coumarins derivatives catalyzed by PMA-Silica supported Boron trifluoride: Etharate catalyst

MATERIALS AND METHODS

General

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. H¹ NMR spectra were recorded on a DRX-300Bruker FT-NMR spectrophotometer in CDCl₃. 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 catalyst

An equimolar amount of PMA and silica was taken in a 50 ml of RBF then $BF_3:OEt_2$ in excess amount were added, and stirred for 15 minutes at room temperature, PMA silica supported $BF_3:OEt_2$ catalyst was obtained as a free flowing powder after evaporation of $BF_3:OEt_2$ at room temperature then this powder dried at 120°C for 2 hr. and stored in dessicator over CaCl₂.

Table 1. Optimization of reaction condition for synthesis of 3-bromo-4-hydroxy coumarin^a

Entry	Catalyst	Relative mole %	Yield ^b in %
1	PMA-Silica-BF ₃ :OEt ₂	00%	NR
2	PMA-Silica-BF ₃ :OEt ₂	05%	42%
3	PMA-Silica-BF ₃ :OEt ₂	10%	66%
4	PMA-Silica-BF ₃ :OEt ₂	15%	79%
5	PMA-Silica-BF ₃ :OEt ₂	20%	88%
6	PMA-Silica-BF3:OEt2	25%	89%
7	PMA-Silica-BF3:OEt2	30%	85%

Reaction Condition^a4-hydroxy coumarin (1 mmol), NBS (1.5 mmol) catalyst 20 mol %, at r.t. grinding for 30 minutes. ^bIsolated yield

General Procedure for the synthesis of 3-substituted-4-hydroxy coumarins.

4-hydroxy coumarin (1 eq.) and 2 (a-i) (1.5 eq.) were taken with 20 mol % of PMA-Silica supported catalyst and grind for few minutes (Table 2) in mortar and pestle at r.t., after completion of reaction (monitored by TLC) ethyl acetate (10 ml \times 2) was added to reaction mixture and filtered to remove solid catalyst. Organic layer was wash with water and evaporated in reduced pressure to obtained solid products (**3a-3i**). Recrystallized from suitable solvents.

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Entry	Reagent (2a-i)	Product	Yield ^b (%)	Time (min.)	M.P.°C
1	NBS	3a	88	15	189-192
2	NCS	3b	72	40	115-117
3	Iodic acid	3c	84	15	150-153
4	NaNO ₃	3d	80	18	171-173
5	FeSO ₄ / Cat.H ₂ SO ₄	3e	81	30	91-95
6	HMTA	3f	40	70	160-162
7	AcOH	3g	76	30	135-139
8	HCHO/DMA	3h	71	20	144-147
9	Allyl bromide	3i	51	70	159-161

RESULTS AND DISCUSSION

In our previous study we have reported, [7-11] present few synthesis methods of Coumarins by Green protocol. In continuation to previous work we have developed simple, efficient and regioselective method for the 4-hydroxy coumarins derivatives. Present method gives significant yield of product at room temperature. This method gives product without any column chromatographic separation, simple recrystallization affords analytically pure compound.

Initially to optimized reaction condition, we have performed set of reactions keeping 4-hydroxy coumarins and NBS as model reaction by varying mole % of PMA-Silica-BF₃:OEt₂ catalyst. (Table 1) On increasing amount of catalyst from 20 mol %, no significant enhancement of yield was observed. Careful analyzed of yield of products provide best match of mole % of catalyst for this reaction. Keeping 20 mol % of catalyst as standard quantity, further reactions performed and acceptable results were obtained. (Table 2)

While performing series of reactions (Table 2; Entry 1-9) it was observed that Iodination and bromination of 4hydroxy coumarins were done smoothly with excellent yield and reaction required less time. Present method proven to be efficient protocol for obtaining 3-substituted 4-hydroxy coumarins.

Characterization of products:

(3a) (Yield 88 %, M.P. 189-192 °C) ¹H NMR (CDCl₃) δ : >13 (s; 1H, -OH), 7.42-7.86 (m, 4H, Ar-H) ES/MS, m/z: M⁺ 242, 240.

(**3b**) (Yield 72 %, M.P. 115-117 °C) ¹H NMR (CDCl₃) δ : >13 (s; 1H, -OH), 7.44-7.92 (m, 4H, Ar-H) ES/MS, m/z : M⁺ 198, 196.

(3c) (Yield 84 %, M.P. 150-153 °C) ¹H NMR (CDCl₃) δ : >13 (s; 1H, -OH), 7.35-7.55 (m, 4H, Ar-H) ES/MS, m/z : M⁺ 289, 288.

(3d) (Yield 80 %, M.P. 171-173°C) ¹H NMR (CDCl₃) δ : >13 (s; 1H, -OH), 7.66-8.23 (m, 4H, Ar-H) ES/MS, m/z : M⁺ 208, 207.

(3e) (Yield 81 %, M.P. 91-95 °C) ¹H NMR (CDCl₃) δ : >13 (s; 2H, -OH; -SO₃H), 7.71-8.65 (m,4H, Ar-H) ES/MS, m/z : M⁺ 243, 242.

(**3f**) (Yield 40 %, M.P. 160-162 °C) ¹H NMR (CDCl₃) δ : >13 (s; 1H, -OH), 10.12(s; 1H, -CHO), 7.33-7.64 (m,4H, Ar-H) ES/MS, m/z : M⁺ 242, 240.

(**3g**) (Yield 76 %, M.P. 135-139 °C) ¹H NMR (CDCl₃) δ : >13 (s; 1H, -OH), 2.40 (s; 3H,-CH₃), 7.36-7.63 (m,4H, Ar-H) ES/MS, m/z : M⁺ 205, 204.

(**3h**) (Yield 71 %, M.P. 144-147 °C) ¹H NMR (CDCl₃) δ : >13 (s; 1H, -OH), 3.02 (s; 6H, -N-CH₃), 4.19 (s; 2H, -CH₂), 7.41-7.76 (m,4H, Ar-H) ES/MS, m/z : M⁺ 220, 219.

(3i) (Yield 51 %, M.P. 159-161 °C) ¹H NMR (CDCl₃) δ : >13 (s; 1H, -OH), 2.58(d; 2H,-CH₂), 5.68 (m; 1H,- CH), 4.87 (dd; 1H,-CH), 4.83 (dd; 1H,-CH), 7.42-7.86 (m,4H, Ar-H) ES/MS, m/z : M⁺ 203, 202.

CONCLUSION

In conclusion, we reported PMA: Silica supported $BF_3:OEt_2$ as a heterogeneous catalyst for the synthesis of 3-substituted 4-hydroxy coumarins. Simple preparation method of catalyst and easy handling is the key feature of present methodology.

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