Available online at www.sciencedirect.com

ScienceDirect

Catalysis Communications 8 (2007) 1886–1890

CATALYSIS COMMUNICATIONS

www.elsevier.com/locate/catcom

Highly efficient synthesis of coumarin derivatives in the presence of $H_{14}[NaP_5W_{30}O_{110}]$ as a green and reusable catalyst

Majid M. Heravi [a,*], Marzieh Khorasani [a], Fatemeh Derikvand [a], Hossein A. Oskooie [a], Fatemeh F. Bamoharram [b]

[a] *Department of Chemistry, School of Sciences, Azzahra University, Vanak, Tehran, Iran*
[b] *Department of Chemistry, Islamic Azad University – Mashhad Branch, Mashhad, Iran*

Received 15 November 2006; received in revised form 21 February 2007; accepted 28 February 2007

Abstract

A variety of heteropolyanions including: Keggin, Dawson, Preyssler, mixed addenda and sandwich types, catalyzed the formation of 4-methylnaphtho-(1,2-*b*)-pyran-2-one (coumarin) from the condensation of α-naphthol and ethylacetoacetate in a solvent free system and under heating conditions. Our data vividly indicate that sodium30–tungsto pentaphosphate, $[NaP_5W_{30}O_{110}]^{14-}$, which so-called Preyssler's anion, with high hydrolytic (pH 0–12) and thermal stability is the catalyst of choice. This catalyst catalyzed the synthesis of other coumarin derivatives in high yields and good selectivity.

Keywords: Coumarin; Heteropolyacid; Preyssler catalyst; Pechmann

---

1. Introduction

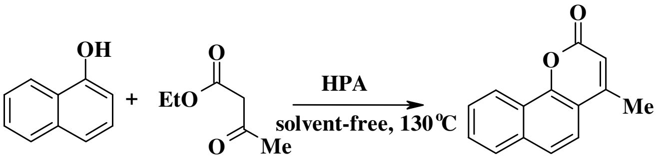
Coumarin and its derivatives form an elite class of compounds; they represent the ring systems of several important groups of natural products. They have been used as anticoagulants [1,2], additives in food and cosmetics [3], and in the preparation of insecticides, optical brighteners [4] and dispersed fluorescent and laser dyes [5]. Coumarins have been synthesized by several routes including Pechmann [6], Perkin [7], Knoevenagel [8], Reformatsky [9], Wittig reaction [10] and Flash Vacuum Pyrolysis [11]. The von Pechmann is one of the most significant and simple methods which consists the condensation of phenols with β-ketoesters to produce 4-substituted coumarins [12]. Several acid catalysts have been used in this reaction including H_2SO_4 [6], $HClO_4$ [13], P_2O_5 [14], CF_3COOH [15] and many more [16–18]. However, some of these catalysts have to be used in excess, for example, sulfuric acid in ten to twelve equivalents, trifluoroacetic acid in three to four equivalents and phosphorous pentoxid is required in a five-fold excess. Moreover, in some cases, long reaction times have been reported and undesired side products such as chromones were also isolated. Consequently, there is scope for further development of milder reaction conditions, using green and reusable catalysts.

In recent years considerable emphasis has been placed on improvement in the environmental impact of industrial chemical processes. The broad utility of heteropolyacids (HPAs) as acid and oxidative catalysts in solution as well as in the solid state for various industrial processes has been demonstrated for a wide variety of synthetically useful transformations of organic substrates. HPAs are strong Bronsted acids composed of heteropolyanions and protons as the counter cations. They are stronger than many conventional solid acids such as mixed oxides, zeolites and so forth. Recently, the synthesis of coumarins by a Wells-Dawson type heteropolyacid has been reported by Romanelli et al. [16]. To the best of our knowledge, there are no examples of other type of heteropolyacids as catalyst in Pechmann reaction. In view of the importance of solid acids as reusable catalysts in organic synthesis and in

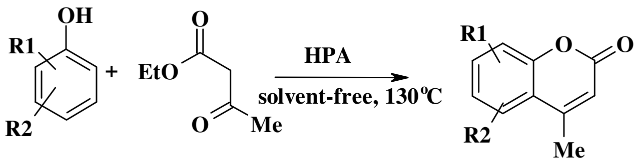
---

[*] Corresponding author. Fax: +98 2188047861.
E-mail address: mmh1331@yahoo.com (M.M. Heravi).

1566-7367/$ - see front matter
doi:10.1016/j.catcom.2007.02.030



Scheme 1.



Scheme 2.

continuation of our work on catalytic properties of heteropolyacids, [19–30] herein we wish to report the study of catalytic activity of a long range of heteropolyacids including Preyssler, Wells-Dawson, Keggin and sandwich types (Scheme 1) in the synthesis of 6-hydroxyl-4-methyl-coumarin and synthesis of other coumarin derivatives in the presence of $H_{14}[NaP_5W_{30}O_{110}]$, Preyssler type heteropolyacid, as the catalyst of choice (Scheme 2).

2. Experimental

All compounds were known and their physical and spectroscopic data were compared with those of authentic samples and found to be identical. Yields were obtained using GC analysis. In addition the isolated yields are also reported in some cases. All of the heteropolyacids were prepared in accordance with our earlier works and the literature [19–30,36].

2.1. *Synthesis of 4-methylcoumarins: General procedure*

A mixture of a phenol derivative or naphthol (1 mmol) and ethylacetoacetate (1 mmol) was made with a catalytic amount of heteropolyacid (1 mol %) and stirred at 130 °C. The progress of reaction was monitored by TLC and GC. After completion of the reaction, the mixture was extracted with hot toluene (3 × 5 ml). The solvent was evaporated and crude product was re-crystallized from a mixture of water and ethanol yielding each of pure 4-methyl coumarins. The catalyst could be washed with hot toluene and diethyl ether and reused.

3. Results and discussion

3.1. *Choice of reaction media*

To choose the most appropriate medium in this heterocyclization reaction, synthesis of 4-methylnaphtho-(1,2-*b*)-pyran-2-one from the condensation of α-naphthol and ethylacetoacetate in the presence of a catalytic amount of $H_{14}[NaP_5W_{30}O_{110}]$ was selected as a model reaction. The model reaction was examined under solvent-free conditions and using toluene, chloroform, acetic acid and DMF (Table 1). Reaction under solvent-less conditions, an approach that is gaining popularity as it eliminates the use of volatile organic solvents in synthesis, afforded the highest yield (89%). The reaction in chloroform was a failure, as the yield was less than 25%. Although the boiling point of DMF is more than 130 (153), the reaction time is longer than that in the solvent free conditions. So the reaction temperature can not be the reason of this differences (Table 1, entry 4). The PK_a of HPAs depends on the solvent; this may be one of the reasons for the distinctions.

3.2. *Effect of the catalyst on the synthesis of 4-methylnaphtho-(1,2-b)-pyran-2-one*

The results of the synthesis of 6-hydroxy-4-methyl-coumarin using a variety of heteropolyacids as catalyst in a solvent free system at 130 °C are shown in Table 2. Comparison of $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_4SiMo_{12}O_{40}$, $HNa_2[PMo_{12}O_{40}]$ (Keggin series), $K_7PW_{11}CuO_{40}$, $K_7PW_{11}CoO_{40}$ (mixed addenda Keggins), $H_{14}NaP_5W_{30}O_{110}$ (Preyssler's anion), $H_6P_2W_{18}O_{62}$ (Dawson catalyst), $K_{10}P_2W_{18}Zn_4(H_2O)_2O_{62} \cdot 20H_2O$ and $K_{10}P_2W_{18}Co_{40}(H_2O)_2O_{62} \cdot 20H_2O$ (sandwich types) showed that the higher activity and selectivity could be achieved using $H_{14}NaP_5W_{30}O_{110}$. This catalyst is more efficient than

Table 1
Effect of the solvent on the synthesis of 4-methylnaphtho-(1,2-*b*)-pyran-2-one using a catalytic amount of $H_{14}[Na\ P_5W_{30}O_{110}]$

Entry	Solvent	Temperature (°C)	Time (min)	Yield (%)[a]
1	$C_6H_5CH_3$	110	420	69
2	$CHCl_3$	60	420	15
3	CH_3COOH	153	250	87
4	$(Me)_2NCHO$	102	420	35
5	Solvent Free	130	30	89

[a] Yields were obtained using GC analysis.

Table 2
Effect of the catalyst on the synthesis of 4-methylnaphtho-(1,2-*b*)-pyran-2-one

Entry	Catalyst	Time (min)		Yield (%)[a]	
1	$H_3PW_{12}O_{40}$	60	30	95	60
2	$H_4SiW_{12}O_{40}$	100	30	95	50
3	$H_4SiMo_{12}O_{40}$	80	30	90	55
4	$K_7PW_{11}CuO_{40}$	120	30	35	10
5	$K_7PW_{11}CoO_{40}$	90	30	78	14
6	$HNa_2PW_{12}O_{40}$	220	30	90	10
7	$H_6P_2W_{18}O_{62}$	40	30	87	75
8	$H_{14}NaP_5W_{30}O_{110}$	30		98	
9	$K_{10}P_2W_{18}Co_4(H_2O)_2O_{62} \cdot 20H_2O$	135	30	60	17
10	$K_{10}P_2W_{18}Zn_4(H_2O)_2O_{62} \cdot 20H_2O$	100	30	55	15

[a] Yields were obtained using GC analysis.