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Protection of some alcohols with carboxylic acids under microwave irradiation catalyzed by $H_5PM_{10}V_2O_{40}$, M= W, Mo

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ABSTRACT

A fast and efficient method is introduced for the protection of various alcohols with carboxylic acids under microwave irradiation in the presence of *Keggin*-type $H_5PM_{10}V_2O_{40}$, M= W, Mo. Water is the only by-product of this green protocol and the catalytic system was inefficient in the absence of heteropoly acid catalyst. © 2011 Trade Science Inc. - INDIA

KEYWORDS

Protection;
Heteropolyoxometalate;
Microwave;
Catalytic;
Alcohol;
Green.

INTRODUCTION

Esters are important chemical compounds which can be synthesized via esterification of carboxylic acids with alcohols. Conversion of alcohol to ester as an important industrial functional group transformation is generally catalyzed by usual mineral acids. Considering the importance of environmental health problems in chemical technology, the eco-friendly green approaches have been expanded with the aim to diminish generation of unwanted hazardous and dangerous byproducts. Accordingly, the practical feasibility of microwave assisted solvent-free protocols in various organic transformations by the mediation of inorganic catalysts provided a number of advantages of environmental interest, including easy isolation and recovery from the reaction medium^[1,2].

Keggin-type heteropolyoxovanadates with the general formula of $H_{3+x}PM_{12-x}V_xO_{40}$ (M= W, Mo and x = 0, 1, 2 and 3) are known to exhibit interesting physical and chemical properties with relevance to catalysis, biochemical processes, and materials science^[3-5]. These types of heteropolyoxometalates are strong Brønsted

acid and most of them are stronger in acidity than the usual inorganic acids (HCl, H_2SO_4 , HNO_3 , HBr), even stronger than $HClO_4$ and CF_3SO_3H . This is of fundamental importance for their applications in acid catalysis. The difference in the acid strength between heteropoly acids and typical inorganic acids can be due to the fact that heteropoly anions are large anions bearing high negative charge density than inorganic acids. Therefore, the strength of bonding between the proton and heteropoly anions should be lower, which implies that the dissociation constants should be lower compared to the usual acids. Polyoxometalates show acidity as well as oxidative ability and can be profitably used in homogeneous, biphasic, or heterogeneous systems^[5-7].

Herein, in continuation of our ongoing research program on using heteropolypolyoxometalates in organic synthesis^[8-16], we wish to describe the protection of alcohols under the environmentally benign microwave approach by the mediation of $H_5PMo_{10}V_2O_{40}$ and $H_5PW_{10}V_2O_{40}$ as vanadium-containing mixed-addenda heteropolyoxometalates with *Keggin* primary structure.

RESULTS AND DISCUSSION

Protection of some alcohols catalyzed by $H_5PW_{10}V_2O_{40}$ and $H_5PMo_{10}V_2O_{40}$ under microwave irradiation

TABLE 1 shows protection of some alcohols catalyzed by $H_5PW_{10}V_2O_{40}$ and $H_5PMo_{10}V_2O_{40}$ under microwave irradiation in solvent free conditions. Reactions were performed in short times with medium to high conversions, except for (\pm) menthol and phenol, and with excellent selectivities ($\sim 100\%$). $H_5PW_{10}V_2O_{40}$ and $H_5PMo_{10}V_2O_{40}$ were effective catalysts in the acetylation of 1-phenyl ethanol and 1-butanol and led to $>78\%$ of conversion after <4 min. It seems that Lewis and Bronsted acidity of the catalysts, inner coordination sphere of the metal ions, and structural features of the catalysts at the molecular levels contribute to the catalytic activity of the catalysts in the protection process.

Protection of 1-butanol with different acetylating agents catalyzed by $H_5PW_{10}V_2O_{40}$

TABLE 2 describes protection of 1-butanol with

TABLE 1 : Protection of some alcohols catalyzed by $H_5PW_{10}V_2O_{40}$ and $H_5PMo_{10}V_2O_{40}$ under microwave irradiation^a

Catalyst	Substrate	product	Conv. %	Time (min)	Selec. %	TOF ^b
$H_5PW_{10}V_2O_{40}$	1-Butanol	1-Butyl acetate	80	4	100	3529
$H_5PMo_{10}V_2O_{40}$			78	4	100	3441
$H_5PW_{10}V_2O_{40}$	1-Ph-ethanol	1-Ph-ethyl acetate	90	2	100	7941
$H_5PMo_{10}V_2O_{40}$			85	3	100	5000
$H_5PW_{10}V_2O_{40}$	Cyclohexanol	Cyclohexyl acetate	45	8	100	992
$H_5PMo_{10}V_2O_{40}$			40	10	100	706
$H_5PW_{10}V_2O_{40}$	Phenol	Phenyl acetate	<4	5	100	<1411
$H_5PMo_{10}V_2O_{40}$			5	10	100	882
$H_5PW_{10}V_2O_{40}$	Benzyl alcohol	Benzyl acetate	80	3	>98	4705
$H_5PMo_{10}V_2O_{40}$			78	4	>97	3441
$H_5PW_{10}V_2O_{40}$	Menthol	Menthyl acetate	20	10	100	352
$H_5PMo_{10}V_2O_{40}$			20	12	100	294

^aConditions: Catalyst (0.034 mmol), was dissolved in a solution of acetic acid (50 mmol) and alcohol (10 mmol) and subjected to microwave irradiation with full power. Microwave irradiations were carried out with pulses of 15s followed by a 5s cooling periods. All acetylated products were known compounds and were identified by means of IR and 1H -NMR spectroscopy and/or comparison of their b.p. or m.p. with authentic samples; ^bTurnover frequency (TOF) was calculated by the expression [Product]/[catalyst] \times time (h^{-1})

different acetylating agents catalyzed by $H_5PW_{10}V_2O_{40}$ under microwave. Clearly, more electron deficient carboxylic groups caused higher tendency of 1-butanol toward acetylation. Dichloroacetic acid, as the most electron deficient carboxylic acid, led to the highest activity and produced 95% of conversion after only 2 min.; whereas, acetic acid gave 80% of product after 4 min. 2-bromopropionic acid was less effective than acetic acid and obtained 90% of product after 6 min. Phenyl acetate showed low reactivity compared to acetic acid and gave 95% of product after 10 min. In accord with our previous findings¹⁷, benzoyl chloride is obviously more effective than acetic acid and obtained fast (<1 min) and effective protection of 1-butanol ($>90\%$). Ethyl formate and formic acid were also less effective than acetic acid. Although, these two acetylating agents were effective at short time (<2 min), however, the protection reactions were stopped at 50-65% and no more conversions were achieved at longer reaction times.

Influence of microwave power on the acetylation of 1-butanol with acetic acid catalyzed by $H_5PW_{10}V_2O_{40}$

Influence of microwave power on the progress of 1-butanol acetylation with acetic acid in the presence of a catalytic amount of $H_5PW_{10}V_2O_{40}$ has also been studied (TABLE 3). The reactions were carried out under 17-100% microwave power. Rationally, protection was increased along with enhancing power. For example, conversion% was increased from 30 to 65% by enhancing power from 17% to 50% during 8 min. However, utilizing full power (100%) led to the highest conversion (80%) in short time (4 min). At this power, temperature of the reaction vessel was measured to be 72-75°C in repeated experiments. Moreover, performing control experiments in an equipped research microwave oven (Micro-SYNTH labstation), confirmed acceptable reproducibility of the obtained data.

Studying reproducibility of the catalyst

To study the recycle ability and stability of the catalyst, $H_5PW_{10}V_2O_{40}$ was regenerated the end of the protection reaction. The catalyst was washed with dichloromethane, dried at room temperature and finally was heated to 130 °C for 3 h. FT-IR spectrum of the regenerated catalyst showed the four characteristic

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bands belonging to the Keggin structure at 1088 ν (P–O); 998 ν (W–O_t); 890 ν (W–O_b–M, M=W and V); and 778 ν (W–O_c–M)^[18]. O_t and O_{b,c} refer to terminal and bridging oxygen atoms, respectively, in the Keggin anionic framework. These results clearly demonstrated that the *Keggin* structure is retained after completion of the acetylation reaction. Therefore, the recycled catalyst could be reused for several times without considerable loss of activity. Effects of different reaction parameters on the acetylation of alcohols with acetic acid catalyzed by other heteropoly acids were also investigated^[19].

MATERIALS AND METHODS

Typical experimental procedure for acetylation of alcohols with acetic acid catalyzed by heteropolyoxometalates under microwave irradiation

In an open vessel test tube (10 ml) equipped with a magnetic stirrer, the catalyst (0.034 mmol) was dissolved in acetic acid (50 mmol). Then, the corresponding alcohol (10 mmol) was added. The mixture was properly stirred with the help of a magnetic stirrer (15 s) and then irradiated under safe conditions in a microwave oven (Panasonic NN-GT546W operating at 2450 MHz providing a maximum output of 1000 W) for the required reaction time. Microwave irradiations were carried out with pulses of 15 s followed by a 5 s cooling periods. Progress of the reactions was followed by GLC. After completion of the reaction, the contents of the test tube were cooled to room temperature. Thereafter, acetic acid was removed under reduced pressure and 20 ml of ether were added. The reaction mixture was washed with 5% NaHCO₃ solution, then with H₂O, and dried with MgSO₄. Evaporation of the solvent followed by silica-gel chromatography provided the pure acetate. The catalysts were prepared and characterized according to literature procedures^[20-25].

Preparation of 10-molybdo-2-vanadophosphoric acid, H₅[PMo₁₀V₂O₄₀]

H₅[PMo₁₀V₂O₄₀] was prepared according to the procedure of Tsigdinos et al.^[24]. Sodium metavanadate (12.2 g, 100 mmol) was dissolved by boiling in 50 ml of water and then mixed with (3.55 g 25 mmol) of Na₂HPO₄ in 50 ml of water. After the

TABLE 2 : Protection of 1-butanol to the corresponding acetate with different acetylating agents catalyzed by H₅PW₁₀V₂O₄₀ under microwave^a

Entry	Protecting agent	Conv.% (min)	Selec.%	TOF
1	Acetic acid	80(4)	100	352
2	2-Br-Propanoic acid	90(6)	100	2647
3	Dichloro acetic acid	95(2)	100	8382
4	Phenyl acetate	95(10)	100	1676
5 ^b	Benzoyl chloride	90(1)	100	15882
6 ^b	Ethyl formate	50(2)	100	4411
7 ^b	Formic acid	65(2)	100	5735

^aThe reactions were carried out as described below TABLE 1;

^bProtecting agent: alcohol ratio was 1 : 1

TABLE 3 : Effect of microwave power on the acetylation of 1-butanol with acetic acid catalyzed by H₅PW₁₀V₂O₄₀^a

Entry	Power (%)	Conv.% (min)	Selec. (%)
1	17	35(7)	100
2	34	60(9)	100
3	50	60(7)	100
4	67	80(6)	100
5	84	90(6)	>98
6	100	80(4)	>98

The reactions were carried out as described below TABLE 1

solution was cooled, (5 ml, 17 M, 85 mmol) of concentrated sulfuric acid was added, and the solution developed a red color. Then, (60.5 g, 250 mmol) of Na₂MoO₄·2H₂O was dissolved in 100 ml of water and was added to the red solution with vigorous stirring, followed by slow addition of concentrated sulfuric acid (42 ml, 17 M, 714 mmol). The hot solution was allowed to cool to room temperature. The 10-molybdo-2-vanadophosphoric acid was then extracted with 500 ml of diethyl ether. Air was passed through the heteropoly etherate (bottom layer) to free it from ether. The solid remaining behind was dissolved in water and then allowed to crystallize. The large red crystals that formed were filtered, washed with water, and air-dried.

Preparation of 10-tungsto-2-vanadophosphoric acid, H₅[PW₁₀V₂O₄₀]^[25]

Sodium metavanadate (NaVO₃, 12.2 g, 100 mmol) was dissolved in 50 ml of boiling water and mixed with di-sodium hydrogen phosphate (Na₂HPO₄, 3.55 g, 25 mmol), dissolved in 50 ml of water. After cooling the resulting solution to room temperature, concentrated sulfuric acid (5 ml, 17 M, 85 mmol) was added to give

a red solution. Sodium tungstate di-hydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, 82.5 g, 250 mmol) was dissolved in 100 ml of water and was added to the red solution with vigorous stirring, followed by slow addition of concentrated sulfuric acid (42 ml, 17 M, 714 mmol). Extraction of the solution with diethyl ether (500 ml), followed by evaporation in air, afforded $\text{H}_5[\text{PW}_{10}\text{V}_2\text{O}_{40}]$ as a crystalline, orange-red solid (yield, 74%).

CONCLUSION

In conclusion, an efficient and fast method for acetylation of alcohols using microwave irradiation is introduced. Catalytic amounts of cheap and simple *Keggin*-type $\text{H}_5\text{PM}_{10}\text{V}_2$, M= W, Mo led to protection of alcohols with acetic acid in high yields, with reduced reaction times under solvent free conditions. It seems that $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ and $\text{H}_5\text{PW}_{10}\text{V}_2\text{O}_{40}$ acted not only as Brønsted acid but also as Lewis acid in the acetylation reaction.

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