단 신

마이크로파 조사 조건에서 $H_5PW_{10}V_2O_{40}$과 $H_5PMo_{10}V_2O_{40}$을 촉매로 사용하여 알코올로부터 아세트산 알킬을 합성하기(Part 2)

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Synthesis of Some Alkyl Acetates From Alcohols Catalyzed by $H_5PW_{10}V_2O_{40}$ and $H_5PMo_{10}V_2O_{40}$ Under Microwave Irradiation(Part 2)

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INTRODUCTION

Esters are important chemical compounds which can be synthesized *via* esterification of carboxylic acids with alcohols. The 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 etc), 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 protably used in homogeneous, biphasic, or heterogeneous systems.[5-7]
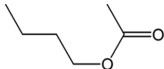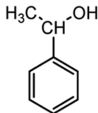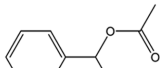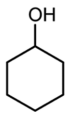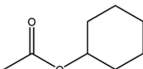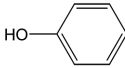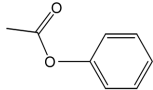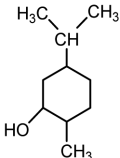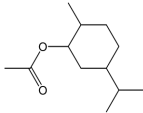
Herein, in continuation of our ongoing research program on using heteropolyoxometalates in organic synthesis,[8-16] we wish to describe the protection of alcohols under the environmentally benign microwave approach by the mediation of $H_5PMo_{10}V_2O_{40}$ and $H_5PW_{10}V_2O_{40}$ as vanadium-containing 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[26]

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 cond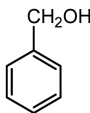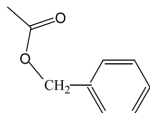itions. Reactions were performed in short times with medium to high conversions, except for (±) menthol and phenol, and with excellent selectivities (~100%). $H_5PW_{10}V_2O_{40}$ and $H_5PMo_{10}V_2O_{40}$ were effective catalysts in the acetylation of 1-phenyl ethanol and 1-butanol and led to >78% of conversion after <4 min. It seems that Lewis and Brönsted acidity of the cat-

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]
$H_5PW_{10}V_2O_{40}$			80	4	100	3529
$H_5PMo_{10}V_2O_{40}$			78	4	100	3441
$H_5PW_{10}V_2O_{40}$			90	2	100	7941
$H_5PMo_{10}V_2O_{40}$			85	3	100	5000
$H_5PW_{10}V_2O_{40}$			45	8	100	992
$H_5PMo_{10}V_2O_{40}$			40	10	100	706
$H_5PW_{10}V_2O_{40}$			<4	5	100	<1411
$H_5PMo_{10}V_2O_{40}$			5	10	100	882
$H_5PW_{10}V_2O_{40}$			80	3	>98	4705
$H_5PMo_{10}V_2O_{40}$			78	4	>97	3441
$H_5PW_{10}V_2O_{40}$			20	10	100	352
$H_5PMo_{10}V_2O_{40}$			20	12	100	294

[a]Conditions: 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 ^{1}H-NMR spectroscopy and/or comparison of their bp or mp with authentic samples. [b]Turnover frequency (TOF) was calculated by the expression [Product]/[catalyst]×time (h^{-1}).
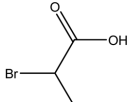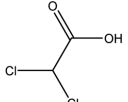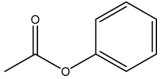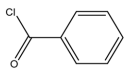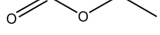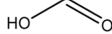
alysts, inner coordination sphere of the metal ions, and structural features of the catalysts at the molecular levels contribute to the catalytic activity of the catalysts in the protection process.

Protection of 1-butanol with different acetylating agents catalyzed by $H_5PW_{10}V_2O_{40}$[26]

Table 2 describes protection of 1-butanol with 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 findings,[17] benzoyl chloride is obviously more effective than acetic acid

Table 2. Protection of 1-butanol to the corresponding acetate with different acetylating agents catalyzed by $H_5PW_{10}V_2O_{40}$ under microwave[a]

Entry	Protecting agent	Conv.% (min)	Selec.%	TOF
1		80(4)	100	352
2		90(6)	100	2647
3		95(2)	100	8382
4		95(10)	100	1676
5[b]		90(1)	100	15882
6[b]		50(2)	100	4411
7[b]		65(2)	100	5735

[a]The reactions were carried out as described below *Table* 1. [b]The ratio of protecting agent: alcohol was 1:1.

and obtained fast (<1min) 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), 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 $H_5PW_{10}V_2O_{40}$[26]

The 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

Table 3. Effect of microwave power on the acetylation of 1-butanol with acetic acid catalyzed by $H_5PW_{10}V_2O_{40}$[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

[a]The reactions were carried out as described below *Table* 1.

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[26]

To study the recycle ability and stability of the catalyst, $H_5PW_{10}V_2O_{40}$ was regenerated at 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 bands belonging to the *Keggin* structure at 1088 ν(P-O); 998 ν(W-Ot); 890 ν(W-Ob-M, M=W and V); and 778 ν(W-Oc-M).[18] Ot and Ob,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 the 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. The progress of 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 was added. The reaction mixture was washed with 5% $NaHCO_3$ solution, then with H_2O, and dried with $MgSO_4$. 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, $H_5[PMo_{10}V_2O_{40}]$

$H_5[PMo_{10}V_2O_{40}]$ was prepared according to the procedure of Tsigdinos *et al.*[24] Sodium metavanadate (12.2 g, 100 mmol) was dissolved in 50 mL of boiling water and then mixed with Na_2HPO_4 (3.55 g, 25 mmol) in 50 mL of water. After cooling the solution to room temperature, *conc* sulfuric acid (17 M, 5 mL, 85 mmol) was added, and the solution developed a red color. Then, $Na_2MoO_4.2H_2O$ (60.5 g, 250 mmol) was dissolved in 100 mL of water and was added to the resulting red solution with vigorous stirring, followed by slow addition of *conc* sulfuric acid (17 M, 42 mL, 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 (yield, 78%).

Preparation of 10-tungsto-2-vanadophosphoric acid, $H_5[PW_{10}V_2O_{40}]$[25]

Sodium metavanadate ($NaVO_3$, 12.2 g, 100 mmol) was dissolved in 50 mL of boiling water and mixed with disodium hydrogen phosphate (Na_2HPO_4, 3.55 g, 25 mmol), dissolved in 50 mL of water. After cooling the resulting solution to room temperature, *conc* sulfuric acid (17 M, 5 mL, 85 mmol) was added to give a red solution. Sodium tungstate dihydrate ($Na_2WO_4.2H_2O$, 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 *conc* sulfuric acid (17 M, 42 mL, 714 mmol). Extraction of the solution with diethyl ether (500 mL), followed by evaporation in air, afforded $H_5[PW_{10}V_2O_{40}]$ 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 $H_5PM_{10}V_2$ (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 $H_5PMo_{10}V_2O_{40}$ and $H_5PW_{10}V_2O_{40}$ acted not only as Brönsted acid but also as Lewis acid in the acetylation reaction.

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