Monatshefte für Chemie 133, 323–327 (2002)

Monatshefte für Chemie
Chemical Monthly

Printed in Austria

Catalytic Acetylation of Alcohols and Phenols with Potassium Dodecatungstocobaltate Trihydrate

Mohammad H. Habibi[*], **Shahram Tangestaninejad**,
Valiollah Mirkhani, and **Bahram Yadollahi**

Chemistry Department, Isfahan University, Isfahan 81745-117, Iran

Summary. Alcohols and phenols are converted to esters in a mild, clean, and efficient reaction with acetic anhydride in the presence of a catalytic amount of potassium dodecatungstocobaltate trihydrate ($K_5CoW_{12}O_{40} \cdot 3H_2O$).

Keywords. Esterification; Catalysis; Polyoxometallates; Acetic anhydride; Alcohols; Phenols.

Introduction

The acetylation of alcohols and phenols is a fundamental process in organic chemistry and provides a cheap and efficient means for protecting OH groups [1]. 4-Dimethylaminopyridine and 4-pyrrolidinopyridine are known to catalyze the acylation of alcohols [2]. A variety of catalysts such as $TaCl_5$ [3], *TMS*O*Tf* [4], Sc(O*Tf*)$_3$ [5], Bu_3P [6], $CoCl_2$ [7], and others [8] have been used for acyl transfer reactions in alcohols and phenols. Recently, montmorillonite K-10 and KSF [9], Zeolite HSZ-360 [10], and Cu(O*Tf*)$_2$ [11] have been reported as remarkable acetylation catalysts. Silica gel supported sodium hydrogen sulfate has been used for the selective monoacetylation of unsymmetrical diols [12]. Although some of these methods produce good results, the use of harmful chlorinated solvents is required.

In recent years there has been a tremendous upsurge of interest in chemical transformations performed under heterogeneous catalysis [13]. Moreover, using inexpensive and non-corrosive heterogeneous catalysts, chemical transformations proceed with better efficiency, higher purity of products, easier work-up, and evident economic and ecological advantages, especially for industrial processes.

Catalysis by heteropoly acids (HPAs) and related compounds is a field of increasing importance [14–22], several features making them economically and environmentally attractive. On the one hand, they are very strong acids, approaching the superacid region; on the other hand, they are efficient oxidants exhibiting fast reversible multielectron redox transformations under rather mild conditions. Their acid–base and redox properties can be varied over a wide range by changing the

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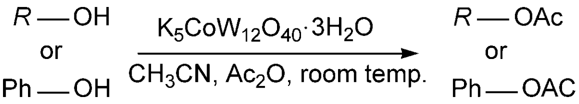
[*] Corresponding author. E-mail: habibi@sci.ui.ac.ir



Scheme 1

chemical composition. Solid HPAs possess an ionic structure comprising fairly mobile basic structural units – heteropolyanions and countercations (H^+, H_3O^+, $H_5O_2^+$, *etc.*) – unlike the network structure of *e.g.* zeolites and metal oxides. This unique structure manifests itself by an extremely high proton mobility and a 'pseudoliquid phase' [17] manifested by the ability of heteropolyanions to stabilize cationic organic intermediates [20]. Above all, HPAs are very soluble in polar solvents and fairly thermally stable in the solid state. These properties render them potentially promising acid, redox, and bifunctional catalysts in homogeneous as well as in heterogeneous systems. In the last two decades, the broad utility of HPAs has been demonstrated by a wide variety of synthetically useful selective transformations of organic substrates [15–22]. Several new industrial processes based on HPA catalysis, such as oxidation of methacrolein, hydration of olefins, polymerization of tetrahydrofuran, *etc.*, have been developed and commercialized [19].

In continuation of our research on the application of polyoxometalates [23] in organic synthesis we report for the first time the applicability of a novel recyclable catalyst for the efficient acetylation of alcohols and phenols according to Scheme 1.

Since the publication of *Chester*'s work [24] in 1970, $CoW_{12}O_{40}^{5-}$ and related polyoxometallate anions have been used as well-defined outer-sphere electron transfer agents in over 50 published studies [25]. Meanwhile, the potential utility of numerous polyoxometalate anions as electron transfer agents in the selective catalytic oxidation of organic substrates of practical importance has been fully recognized [26–29]. The possibility of a concerted electron transfer mechanism was strongly supported by a large decrease of the reaction rate upon addition of a small amount of acrylonitrile as a radical scavenger.

Results and Discussion

Treatment of benzyl alcohol with Ac_2O and $K_5CoW_{12}O_{40} \cdot 3H_2O$ in acetonitrile at ambient temperature provided the corresponding acetate in excellent yield (Table 1, entry 1). The acetylation reaction was extended to a variety of alcohols and phenols, and high to excellent yields were obtained in all cases (Tables 1, 2).

Tertiary alcohols (Table 1, entries 18, 19) were also acetylated in a satisfactory manner. Allylic (Table 1, entry 14) and benzylic (Table 1, entry 1–9) alcohols behaved uniformaly well. Phenols and naphthols also yielded the corresponding acetates in excellent yields (Table 2).

In addition, we have found that $K_5CoW_{12}O_{40} \cdot 3H_2O$ can be reused several times without loss of activity simply by filtering the catalyst, washing it with acetone, and drying. The yield of acetate starting from benzyl alcohol promoted by the catalyst recovered four times remained 98%; even after seven reuses, the yield was still about 85%.

In conclusion, we have shown that a mild and efficient catalytic esterification of alcohols and phenols with acetic anhydride is prompted by potassium dodecatungstocobaltate trihydrate ($K_5CoW_{12}O_{40} \cdot 3H_2O$). All acetates were

Table 1. Esterification of alcohols with Ac_2O in the presence of $K_5CoW_{12}O_{40} \cdot 3H_2O$ in CH_3CN[a]

Entry	Alcohol	t/min	Yield/%[b]
1	$C_6H_5CH_2OH$	5	98
2	4-$CH_3OC_6H_4CH_2OH$	240	87
3	3-$CH_3OC_6H_4CH_2OH$	40	94
4	2-$CH_3OC_6H_4CH_2OH$	60	90
5	4-$O_2NC_6H_4CH_2OH$	15	99
6	3-$O_2NC_6H_4CH_2OH$	15	98
7	2-$O_2NC_6H_4CH_2OH$	20	98
8	4-$ClC_6H_4CH_2OH$	15	98
9	4-$BrC_6H_4CH_2OH$	15	99
10	$C_6H_5CH_2CH_2CH_2OH$	20	95
11	$C_6H_5CH_2CH_2OH$	15	97
12	$C_6H_5CH(OH)CH_3$	240	100
13	$C_6H_5COCH(OH)C_6H_5$	10	60[c]
14	$C_6H_5CHCHCH_2OH$	20	91
15	α-Tetralol	150	55
16	$C_6H_{11}OH$	20	93
17	(−)-Menthol	75	94
18	Adamantanol	240	70
19	$(C_6H_5)_3COH$	240	90[c]
20	$CH_3(CH_2)_6CH_2OH$	20	99
21	$CH_3(CH_2)_5CH_2OH$	25	100
22	$CH_3(CH_2)_3CH(C_2H_5)CH_2OH$	60	95
23	$CH_3(CH_2)_3CH_2OH$	30	92
24	$CH_3(CH_2)_2CH_2OH$	100	95

[a] All products were characterized by comparison of their physical and spectroscopic data with those of authentic samples; [b] GC; [c] isolated yield

Table 2. Esterification of phenols with Ac_2O in the presence of $K_5CoW_{12}O_{40} \cdot 3H_2O$ in CH_3CN[a]

Entry	Phenol	t/min	Yield/%[b]
1	C_6H_5OH	15	97
2	4-$O_2NC_6H_4OH$	20	100
3	4-ClC_6H_4OH	15	100
4	4-$CH_3OC_6H_4OH$	15	98
5	2,5-$CH_3C_6H_3OH$	40	96
6	2,4,5-ClC_6H_2OH	180	55
7	Hydroquinone	15	98[c]
8	Resorcinol	45	96[c]
9	Catechol	25	97[c]
10	Pyrogallol	45	98[c]
11	1-Naphthol	120	92
12	2-Naphthol	20	96

[a] All products were characterized by comparison of their physical and spectroscopic data with those of authentic samples; [b] GC; [c] isolated yields

obtained in high to excellent yields under simple experimental conditions. The catalyst can be reused with only low loss of activity.

Experimental

$K_5CoW_{12}O_{40} \cdot 3H_2O$ was prepared according to Refs. [30–33].

General procedure for the conversion of alcohols to their corresponding acetates

In a typical procedure, 108 mg (1 mmol) benzyl alcohol and 153 mg (1.5 mmol) Ac_2O were added to a stirred solution of 32 mg $K_5CoW_{12}O_{40} \cdot 3H_2O$ (0.01 mmol) in 3 cm^3 CH_3CN. The mixture was stirred at room temperature for 5 min. After completion of the reaction (monitored by GC or TLC) the catalyst was filtered and the reaction mixture was washed with 10% $NaHCO_3$. Diethyl ether was added, and after separation of phases the organic solution was dried over Na_2SO_4. Evaporation of the organic solvent was followed by column chromatography on silica gel using petroleum ether as eluent. Benzyl acetate was obtained in 98% yield (Table 1, entry 1). The catalyst was reused seven times and then showed a small loss of activity (yield: 85%).

Acknowledgements

We are grateful to the Isfahan University Research Council for partial support of this work.

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Received August 27, 2001. Accepted (revised) October 29, 2001