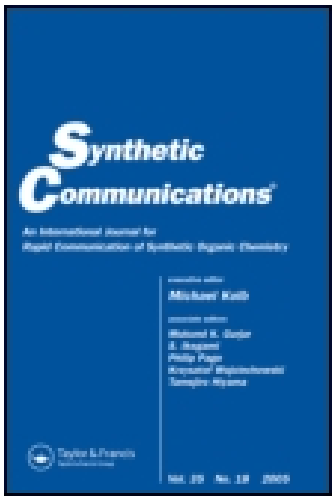

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COBALT POLYOXOMETALATE, AS A NEW REUSABLE CATALYST FOR THE DIRECT, FAST, AND EFFICIENT ACETYLATION OF ALCOHOLS AND PHENOLS UNDER SOLVENTLESS CONDITIONS

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COBALT POLYOXOMETALATE, $CoW_{12}O_{40}^{5-}$ AS A NEW REUSABLE CATALYST FOR THE DIRECT, FAST, AND EFFICIENT ACETYLATION OF ALCOHOLS AND PHENOLS UNDER SOLVENTLESS CONDITIONS

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ABSTRACT

Alcohols and phenols were efficiently acetylated with acetic anhydride without solvent in the presence of 0.01 molar equiv. of cobalt polyoxometalate ($CoW_{12}O_{40}^{5-}$).

The base catalyzed acylation of alcohols, phenols, amines and thiols by acetic anhydride or acyl chloride is an established procedure in organic synthesis.[1] Some procedures have also been developed wherein Lewis acid catalysts $COCl_2$,[2] $Sc(OTf)_3$,[3] TMSOTf,[4] Bu_3P,[5] $TaCl_5$,[6] montmorillonite

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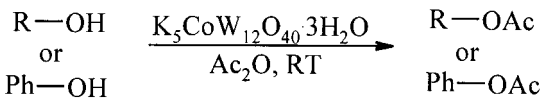
K-10 and KSF,[7] 4-(dimethylamino) pyridine (DMAP), 4-pyrrolidinopyridine (PPY),[8] $Cu(OTf)_2$,[9] etc.[10] have been used for acyl transfer reactions in alcohols. Moreover, silica gel-supported sodium hydrogen sulfate has been used for the selective monoacetylation of unsymmetrical diols.[11]

Polyoxometalates have been proven to be good catalysts in various oxidations. They are applied in bulk or supported forms, and both homogeneous and heterogeneous catalysis are possible. Due to their acidic and redox properties, heteropoly compounds (heteropoly acids and salts) are useful and versatile catalysts in a number of transformations.[12] In this research we present a cobalt polyoxometalate ($K_5CoW_{12}O_{40}\cdot 3H_2O$)[13] as an efficient, selective and reusable catalyst for direct acetylation of alcohols and phenols under solvent-free and room temperature conditions (scheme).



Scheme.

The reaction of alcohol or phenol (1 mmol) with acetic anhydride (2 ml) and cobalt polyoxometalate ($K_5CoW_{12}O_{40}\cdot 3H_2O$) (0.01 mmol) was performed at room temperature for a few minutes. High to excellent yields were observed in all cases (Tables 1, 2). This method tolerates other functionalities such as nitro, halides, ketones and methoxy groups. In addition, we found that cobalt polyoxometalate, $K_5CoW_{12}O_{40}\cdot 3H_2O$, can be reused several times without loss of activity, simply by filtering the catalyst, washing with acetone, drying and immediately reusing. Acetylation yield of benzyl alcohol promoted by the recovered catalyst for four times remained 99% and after seven times was about 95%. Cobalt polyoxometalate ($CoW_{12}O_{40}^{5-}$) shows good catalytic activity, which is independent of the different polarities of the reactions.

Typical procedure: Alcohols or phenols (1 mmol) and acetic anhydride (2 ml) were placed in a two-necked flask with stirring. After a few minute cobalt polyoxometalate ($K_5CoW_{12}O_{40}\cdot 3H_2O$) (0.01 mmol, 32 mg) was added and the mixture stirred for the appropriate time (see Tables 1, 2) at room temperature.

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

Entry	Alcohols	Esters	Time (min)	Yield[b] (%)
1	$C_6H_5CH_2OH$	$C_6H_5CH_2OAc$	1	99
2	*p*-$CH_3OC_6H_4CH_2OH$	*p*-$CH_3OC_6H_4CH_2OAc$	10	92
3	*m*-$CH_3OC_6H_4CH_2OH$	*m*-$CH_3OC_6H_4CH_2OAc$	1	99
4	*o*-$CH_3OC_6H_4CH_2OH$	*o*-$CH_3OC_6H_4CH_2OAc$	3	96
5	*p*-$O_2NC_6H_4CH_2OH$	*p*-$O_2NC_6H_4CH_2OAc$	1	99
6	*m*-$O_2NC_6H_4CH_2OH$	*m*-$O_2NC_6H_4CH_2OAc$	1	99
7	*o*-$O_2NC_6H_4CH_2OH$	*o*-$O_2NC_6H_4CH_2OAc$	1	99
8	*p*-$ClC_6H_4CH_2OH$	*p*-$ClC_6H_4CH_2OAc$	1	99
9	*p*-$BrC_6H_4CH_2OH$	*p*-$BrC_6H_4CH_2OAc$	1	99
10	$C_6H_5CH_2CH_2CH_2OH$	$C_6H_5CH_2CH_2CH_2OAc$	3	100
11	$C_6H_5CH_2CH_2OH$	$C_6H_5CH_2CH_2OAc$	3	98
12	$C_6H_5CH(OH)CH_3$	$C_6H_5CH(OAc)CH_3$	30	94
13	$C_6H_5COCH(OH)C_6H_5$	$C_6H_5COCH(OAc)C_6H_5$	5	94[c]
14	$C_6H_5CHCHCH_2OH$	$C_6H_5CHCHCH_2OAc$	2	96
15	α-Tetralol	α-Tetralylacetate	10	100
16	$C_6H_{11}OH$ (cyclohexanol)	$C_6H_{11}OAc$	5	97
17	(−)-Menthol	(−)-Menthylacetate	7	98
18	Adamantanol	Adamantanylacetate	40	90
19	$(C_6H_5)_3COH$	$(C_6H_5)_3COAc$	45	91
20	$CH_3(CH_2)_6CH_2OH$	$CH_3(CH_2)_6CH_2OAc$	4	96
21	$CH_3(CH_2)_5CH_2OH$	$CH_3(CH_2)_5CH_2OAc$	5	95
22	$CH_3(CH_2)_3CH(C_2H_5)CH_2OH$	$CH_3(CH_2)_3CH(C_2H_5)CH_2OAc$	8	100
23	$CH_3(CH_2)_3CH_2OH$	$CH_3(CH_2)_3CH_2OAc$	5	97
24	$CH_3(CH_2)_2CH_2OH$	$CH_3(CH_2)_2CH_2OAc$	10	93

[a]All of the products were characterized by comparison of their physical and spectral data with those of authentic samples.
[b]GC yields.
[c]Isolated yield.

After completion of reaction (monitored by GC or TLC) ether was added and the catalyst filtered off with a layer of silica gel. The reaction mixture was washed with a 10% aqueous solution of $NaHCO_3$, and after separation, organic solution dried with Na_2SO_4. After evaporation of the solvent, products could be purified by flash chromatography.

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

Entry	Phenols	Esters	Time (min)	Yield[b] (%)
1	C_6H_5OH	C_6H_5OAc	1	98
2	4-$O_2NC_6H_4OH$	4-$O_2NC_6H_4OAc$	2	99
3	2-$O_2NC_6H_4OH$	2-$O_2NC_6H_4OAc$	20	40
4	4-ClC_6H_4OH	4-ClC_6H_4OAc	1	100
5	4-$CH_3OC_6H_4OH$	4-$CH_3OC_6H_4OAc$	1	98
6	4-$CH_3COC_6H_4OH$	4-$CH_3COC_6H_4OAc$	30	60
7	2,5-$CH_3C_6H_3OH$	2,5-$CH_3C_6H_3OAc$	3	95
8	2,4,5-ClC_6H_2OH	2,4,5-ClC_6H_2OAc	15	96
9	Hydroquinone	Hydroquinoneacetate	2	97[c]
10	Resorsinol	Resorsinolacetate	3	98[c]
11	Catechol	Catecholacetate	5	98[c]
12	Pyrogalol	Pyrogalolacetate	5	94[c]
13	α-Naphthol	α-Naphthylacetate	10	100
14	β-Naphthol	β-Naphthylacetate	1	99

[a]All of the products were characterized by comparison of their physical and spectral data with those of authentic samples.
[b]GC yields.
[c]Isolated yields.

In conclusion we have shown that an efficient catalyst of alcohols and phenols with acetic anhydride is prompted by cobalt polyoxometalate ($K_5CoW_{12}O_{40}\cdot 3H_2O$). All acetates are obtained in high to excellent yields under simple experimental conditions. The catalyst can be reused several times without any loss of activity.

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