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Novel catalytic acetylation and formylation of alcohols with potassium dodecatungstocobaltate trihydrate $(K_5CoW_{12}O_{40}\cdot 3H_2O)$

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Abstract—Acetylation and formylation reactions of alcohols with ethyl acetate, acetic acid and ethyl formate were catalyzed with potassium dodecatungstocobaltate trihydrate ($K_5CoW_{12}O_{40}\cdot 3H_2O$) in a mild, efficient and convenient method with high to excellent yields. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

The acetylation and formylation of the hydroxy group is one of the most widely used transformations in organic synthesis.[1,2] A direct esterification of carboxylic acids with alcohols is generally avoided because the equilibrium that is established between the reagents and the products requires the use of excess reagents or elimination of water from the reaction mixture to drive the process to completion. Many useful methods for esterification have been reported in the literature.[3–5] Some of the recently developed methods involve the use of organic reagents, such as imidate esters,[6–8] inorganic[9] and organometallic reagents.[10] However, most of these methods suffer from one or more of the following disadvantages: long reaction times,[6–8] vigorous reaction conditions,[10] the occurrence of side reactions,[10] and unavailability of the reagents, as well as poor yields of the desired product in many cases.

Recently, scandium(III) or lanthanum(III) triflates were used as catalyst for the acylation of alcohols with acetic acid,[11] also $La(OPr^i)_3$ and $CoCl_2$ have been reported[12,13] to promote the efficient acylation of alcohols with acetic anhydride. Acylation of alcohols can also be brought about by the action of Lewis acidic reagents in conjunction with carboxylic acids, but the Lewis acid is destroyed in the work-up procedure. From an industrial point of view, anhydrides are more expensive than the corresponding carboxylic acids. More recently zeolite HSZ-360[14] and LaY[15] have been reported to promote the acylation of alcohols. The acetylation and formylation of alcohols in acetic acid, ethyl acetate and ethyl formate by catalytic amount of $Ce(OTf)_4$ have also been reported.[16]

Formylation is a very important process in organic chemistry. Although various formylating reagents have been reported previously,[17–27] there are still serious limitations for the preparation of formats due to the drastic reaction conditions,[18] the use of uncommon reagents,[19–25] formation of undesirable or toxic by-products,[24–26] the application of expensive catalysts for preparation of formylating agents,[25] hygroscopicity[26] and thermal instability of the reagents.[27] Due to the instability of the anhydride and acid chloride of formic acid, formylation of alcohols by ethyl formate is an important synthetic reaction.

The use of heterogeneous catalysts in different areas of the organic synthesis has now reached significant levels, not only for the possibility to perform environmentally benign synthesis, but also for the good yields frequently, accompanied by excellent selectivities that can be achieved. Catalysis by heteropoly acids (HPAs) and related compounds is a field of increasing importance.[28–36] HPAs have several advantages as catalysts which make them economically and environmentally attractive. On the one hand, HPAs have a very strong Bronsted acidity approaching the superacid region; on the other, 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 chemical composition. Solid HPAs possess a discrete 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 to exhibit an extremely high proton mobility and a 'pseudoliquid phase',[31] while heteropolyanions can

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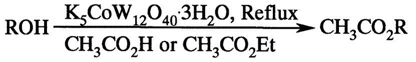

$$ROH \xrightarrow[CH_3CO_2H \text{ or } CH_3CO_2Et]{K_5CoW_{12}O_{40}\cdot 3H_2O, \text{ Reflux}} CH_3CO_2R$$

Scheme 1.

stabilize cationic organic intermediates.[34] On top of that, HPAs have a very high solubility in polar solvents and fairly high thermal stability in the solid state. These properties render HPAs potentially promising acid, redox, and bifunctional catalysts in homogeneous as well as in heterogeneous systems. HPAs are widely used as model systems for fundamental research, providing unique opportunities for mechanistic studies on the molecular level. At the same time, they have become increasingly important for applied catalysis. In the last two decades, the broad utility of HPA acid and oxidation catalysis has been demonstrated in a wide variety of synthetically useful selective transformations of organic substrates.[29–36] Several new industrial processes based on heteropolyanion catalysis, such as oxidation of methacrolein, hydration of olefins, polymerization of tetrahydrofuran, etc., have been developed and commercialized.[33] In continuation of our research on the application of polyoxometalate in organic synthesis,[37] we wish to report for the first time the applicability of a novel

Table 1. Acetylation of alcohols with acetic acid in the presence of 0.01 mol equiv. of $K_5CoW_{12}O_{40}\cdot 3H_2O$ at reflux

Entry	Alcohols	Esters	Time/min	Yields (%)[a]
1	$C_6H_5CH_2OH$	$C_6H_5CH_2OAc$	60	90
2	$4\text{-}CH_3OC_6H_4CH_2OH$	$4\text{-}CH_3OC_6H_4CH_2OAc$	45	98
3	$3\text{-}CH_3OC_6H_4CH_2OH$	$3\text{-}CH_3OC_6H_4CH_2OAc$	45	97
4	$2\text{-}CH_3OC_6H_4CH_2OH$	$2\text{-}CH_3OC_6H_4CH_2OAc$	50	97
5	$4\text{-}O_2NC_6H_4CH_2OH$	$4\text{-}O_2NC_6H_4CH_2OAc$	45	98
6	$3\text{-}O_2NC_6H_4CH_2OH$	$3\text{-}O_2NC_6H_4CH_2OAc$	45	96
7	$2\text{-}O_2NC_6H_4CH_2OH$	$2\text{-}O_2NC_6H_4CH_2OAc$	90	98
8	$4\text{-}ClC_6H_4CH_2OH$	$4\text{-}ClC_6H_4CH_2OAc$	45	92
9	$4\text{-}BrC_6H_4CH_2OH$	$4\text{-}BrC_6H_4CH_2OAc$	45	95
10	$C_6H_5CH_2CH_2CH_2OH$	$C_6H_5CH_2CH_2CH_2OAc$	60	98
11	$C_6H_5CH_2CH_2OH$	$C_6H_5CH_2CH_2OAc$	60	98
12	$C_6H_5CH(OH)CH_3$	$C_6H_5CH(OAc)CH_3$	45	87
13	$C_6H_5COCH(OH)C_6H_5$	$C_6H_5COCH(OAc)C_6H_5$	45	97
14	$C_6H_5CHCHCH_2OH$	$C_6H_5CHCHCH_2OAc$	60	92
15	$C_6H_{11}OH$ (Cyclohexanol)	$C_6H_{11}OAc$	150	80
16	(−)-Menthol	(−)-Menthyl acetate	240	70
17	Adamantanol	Adamantanyl acetate	60	82
18	$(C_6H_5)_3COH$	$(C_6H_5)_3COAc$	120	85
19	$CH_3(CH_2)_6CH_2OH$	$CH_3(CH_2)_6CH_2OAc$	45	96
20	$CH_3(CH_2)_5CH_2OH$	$CH_3(CH_2)_5CH_2OAc$	30	98
21	$CH_3(CH_2)_3CH(C_2H_5)CH_2OH$	$CH_3(CH_2)_3CH(C_2H_5)CH_2OAc$	45	99
22	$CH_3(CH_2)_3CH_2OH$	$CH_3(CH_2)_3CH_2OAc$	60	97
23	$CH_3(CH_2)_2CH_2OH$	$CH_3(CH_2)_2CH_2OAc$	30	98

All of the products were characterized by a comparison of their spectral and physical data with those of known samples.[44–46]

[a] Yields refer to isolated products.

Table 2. Acetylation of alcohols with ethyl acetate in the presence of 0.05 mol equiv. of $K_5CoW_{12}O_{40}\cdot 3H_2O$ at reflux

Entry	Alcohols	Esters	Time (h)	Yields (%)[a]
1	$C_6H_5CH_2OH$	$C_6H_5CH_2OAc$	3	94
2	$4\text{-}CH_3OC_6H_4CH_2OH$	$4\text{-}CH_3OC_6H_4CH_2OAc$	1.5	80
3	$3\text{-}CH_3OC_6H_4CH_2OH$	$3\text{-}CH_3OC_6H_4CH_2OAc$	3.5	89
4	$2\text{-}CH_3OC_6H_4CH_2OH$	$2\text{-}CH_3OC_6H_4CH_2OAc$	4	85
5	$4\text{-}O_2NC_6H_4CH_2OH$	$4\text{-}O_2NC_6H_4CH_2OAc$	5	90
6	$3\text{-}O_2NC_6H_4CH_2OH$	$3\text{-}O_2NC_6H_4CH_2OAc$	5	87
7	$2\text{-}O_2NC_6H_4CH_2OH$	$2\text{-}O_2NC_6H_4CH_2OAc$	5	50
8	$4\text{-}ClC_6H_4CH_2OH$	$4\text{-}ClC_6H_4CH_2OAc$	4	96
9	$4\text{-}BrC_6H_4CH_2OH$	$4\text{-}BrC_6H_4CH_2OAc$	4	94
10	$C_6H_5CH_2CH_2CH_2OH$	$C_6H_5CH_2CH_2CH_2OAc$	2	94
11	$C_6H_5CH_2CH_2OH$	$C_6H_5CH_2CH_2OAc$	2	95
12	$C_6H_5CH(OH)CH_3$	$C_6H_5CH(OAc)CH_3$	5	55
13	$C_6H_5COCH(OH)C_6H_5$	$C_6H_5COCH(OAc)C_6H_5$	2	98
14	$C_6H_5CHCHCH_2OH$	$C_6H_5CHCHCH_2OAc$	2	90
15	$C_6H_{11}OH$ (Cyclohexanol)	$C_6H_{11}OAc$	6	72
16	(−)-Menthol	(−)-Menthyl acetate	8	35
17	$(C_6H_5)_3COH$	$(C_6H_5)_3COAc$	5	80
18	$CH_3(CH_2)_6CH_2OH$	$CH_3(CH_2)_6CH_2OAc$	3	95
19	$CH_3(CH_2)_5CH_2OH$	$CH_3(CH_2)_5CH_2OAc$	2	93
20	$CH_3(CH_2)_3CH(C_2H_5)CH_2OH$	$CH_3(CH_2)_3CH(C_2H_5)CH_2OAc$	2	91
21	$CH_3(CH_2)_3CH_2OH$	$CH_3(CH_2)_3CH_2OAc$	2	90
22	$CH_3(CH_2)_2CH_2OH$	$CH_3(CH_2)_2CH_2OAc$	2	92

All of the products were characterized by a comparison of their spectral and physical data with those of known samples.[44–46]

[a] Yields refer to isolated products.

$$ROH \xrightarrow[HCO_2Et]{K_5CoW_{12}O_{40}\cdot 3H_2O,\ Reflux} HCO_2R$$

Scheme 2.

recyclable catalyst, potassium dodecatungstocobaltate trihydrate ($K_5CoW_{12}O_{40}\cdot 3H_2O$) for efficient esterification of acetic acid and the acetylation and formylation of alcohols. This catalyst is readily available and easily prepared from the sodium tungstodicobalt(II)ate, cobaltous acetate and the sodium tungstate in acetic acid and water at pH 6.5–7.5.[37,47–50]

2. Results and discussion

The acetylation of alcohols in the presence of catalytic amounts of $K_5CoW_{12}O_{40}\cdot 3H_2O$ was performed in acetic acid (Scheme 1) to produce the desired esters in high to excellent yields (Table 1).

Benzylic alcohols carrying both electron-withdrawing and electron-donating groups were acetylated without formation of any oxidative side products with 0.01 mol equiv. of catalyst. The acetylation of a bulky tertiary alcohol like adamantan-1-ol (Table 1, entry 17) was also performed in acetic acid under reflux and gave 82% of isolated yield after 1 h. We have observed that $K_5CoW_{12}O_{40}\cdot 3H_2O$ can bring about the acetylation of (−)-menthol with high yield and retention of the configuration in refluxing acetic acid (Table 1, entry 16).

We extended the scope of this process by performing the reaction in ethyl acetate (Scheme 1). It was observed that $K_5CoW_{12}O_{40}\cdot 3H_2O$ (0.05 mol equiv.) could catalyze the acetylation reaction of alcohols in refluxing ethyl acetate with high to excellent yields (Table 2). Under these conditions, triphenylmethanol reacted with ethylacetate in 80% yields (Table 2, entry 17). Benzylic and linear aliphatic alcohols were acetylated with ethyl acetate in high to excellent yields (Table 2). These reactions, in comparison with similar reactions, which have been performed in an autoclave at 150–200°C in the presence of hydrated zirconium oxide[38] occur more efficiently and under milder reaction conditions.

The formylation of alcohols in ethyl formate (Scheme 2) can be performed at reflux in the presence of 0.01 mol equiv. of $K_5CoW_{12}O_{40}\cdot 3H_2O$ with high to excellent yields (Table 3). The formylation of (−)-menthol with this catalyst was also investigated in ethyl formate (Table 3, entry 18).

In addition, we have 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. The yield of 1-heptylacetate produced from the reaction of 1-heptanol with acetic acid promoted by the recovered catalyst for four times remained 98% and after seven times was 85%.

Since publication of Chester's work in 1970, $CoW_{12}O_{40}{}^{5-}$ and related polyoxometalate anions have been used as a well-defined outer-sphere electron transfer agent in over 50 published studies.[39] Meanwhile, the potential utility of numerous polyoxometalate anions as electron-transfer agents in the selective catalytic oxidations of organic substrates of practical importance has been fully recognized.[40–43] The possibility of a concerted electron transfer mechanism was strongly supported by a large decrease of the reaction rate with addition small amount of acrylonitrile

Table 3. Formylation of alcohols with ethyl formate in the presence of 0.01 mol equiv. of $K_5CoW_{12}O_{40}\cdot 3H_2O$ at reflux

Entry	Alcohols	Esters	Time (min)	Yields (%)[a]
1	$C_6H_5CH_2OH$	$C_6H_5CH_2OCOH$	180[b]	89
2	$C_6H_5CH_2OH$	$C_6H_5CH_2OCOH$	60	90
3	$4\text{-}CH_3OC_6H_4CH_2OH$	$4\text{-}CH_3OC_6H_4CH_2OCOH$	20	98
4	$3\text{-}CH_3OC_6H_4CH_2OH$	$3\text{-}CH_3OC_6H_4CH_2OCOH$	75	97
5	$2\text{-}CH_3OC_6H_4CH_2OH$	$2\text{-}CH_3OC_6H_4CH_2OCOH$	90	87
6	$4\text{-}O_2NC_6H_4CH_2OH$	$4\text{-}O_2NC_6H_4CH_2OCOH$	20	92
7	$3\text{-}O_2NC_6H_4CH_2OH$	$3\text{-}O_2NC_6H_4CH_2OCOH$	45	94
8	$2\text{-}O_2NC_6H_4CH_2OH$	$2\text{-}O_2NC_6H_4CH_2OCOH$	75	94
9	$4\text{-}ClC_6H_4CH_2OH$	$4\text{-}ClC_6H_4CH_2OCOH$	45	97
10	$4\text{-}BrC_6H_4CH_2OH$	$4\text{-}BrC_6H_4CH_2OCOH$	45	98
11	$C_6H_5CH_2CH_2CH_2OH$	$C_6H_5CH_2CH_2CH_2OCOH$	15	92
12	$C_6H_5CH_2CH_2OH$	$C_6H_5CH_2CH_2OCOH$	40	97
13	$C_6H_5CH(OH)CH_3$	$C_6H_5CH(OCOH)CH_3$	180	90
14	$C_6H_5COCH(OH)C_6H_5$	$C_6H_5COCH(OCOH)C_6H_5$	30	99
15	$C_6H_5CHCHCH_2OH$	$C_6H_5CHCHCH_2OCOH$	30	94
16	α-Tetralol	α-Tetralyl formate	90	70
17	$C_6H_{11}OH$ (Cyclohexanol)	$C_6H_{11}OCOH$	45	80
18	(−)-Menthol	(−)-Menthyl formate	60	81
19	$(C_6H_5)_3COH$	$(C_6H_5)_3COCOH$	75	80
20	$CH_3(CH_2)_6CH_2OH$	$CH_3(CH_2)_6CH_2OCOH$	30	95
21	$CH_3(CH_2)_5CH_2OH$	$CH_3(CH_2)_5CH_2OCOH$	30	96
22	$CH_3(CH_2)_3CH(C_2H_5)CH_2OH$	$CH_3(CH_2)_3CH(C_2H_5)CH_2OCOH$	30	95
23	$CH_3(CH_2)_3CH_2OH$	$CH_3(CH_2)_3CH_2OCOH$	20	98
24	$CH_3(CH_2)_2CH_2OH$	$CH_3(CH_2)_2CH_2OCOH$	20	92

All of the products were characterized by a comparison of their spectral and physical data with those of known samples.[44–46]

[a] Yields refer to isolated products.

[b] Room temperature.

(as a radical scavenger) in the reaction of alcohols with ethyl formate in the presence of $K_5CoW_{12}O_{40}\cdot 3H_2O$.

3. Conclusion

We have shown that efficient acetylation and formylation of alcohols are promoted by a cheap, recyclable and easily prepared potassium dodecatungstocobaltate trihydrate ($K_5CoW_{12}O_{40}\cdot 3H_2O$). This method could be useful for efficient esterification of acetic acid, and for the acetylation and formylation of alcohols, which are often required in complex synthetic schemes. The possibility of performing the reaction in ethyl acetate or ethyl formate, the high stereospecificity of the reaction of (−)-menthol in both the acetylation and formylation reactions, and the simple procedure and work up makes this method a useful addition to the present methodologies.

4. Experimental

All of the products were characterized by a comparison of their spectral and physical data with those of known samples.[44–46] All yields refer to isolated products. NMR spectra were recorded on a Bruker AW 80 MHz. IR spectra were run on a Shimadzu IR-435 spectrophotometer. Mass spectra were recorded on an AMD 604 spectrometer, EI-mode at 70 eV, FT-mode at 0.005 V. The purity of the substances and the progress of the reactions were monitored by TLC on silica gel or by a Shimadzu Gas Chromatograph GC-16A instrument with a flame ionization detector.

4.1. Preparation of the catalyst[37,47–50]

The synthesis of potassium dodecatungstocobaltate trihydrate ($K_5CoW_{12}O_{40}\cdot 3H_2O$) starts with the preparation of sodium tungstodicobalt(II)ate from cobaltous acetate (2.5 g, 0.01 mol) and sodium tungstate (19.8 g, 0.06 mol) in acetic acid and water at pH 6.5–7.5. The sodium salt is then converted to the potassium salt by treatment with potassium chloride (13 g).

Finally the cobalt(II) complex is oxidized to the cobalt(III) complex by potassium persulfate (10 g) in 40 mL of 2 M H_2SO_4. The crystals of $K_5CoW_{12}O_{40}\cdot 20H_2O$ were dried at 200°C, after recrystallization with methanol, and potassium dodecatungstocobaltate trihydrate ($K_5CoW_{12}O_{40}\cdot 3H_2O$) was obtained.

4.2. Typical procedure for acetylation of alcohols with $K_5CoW_{12}O_{40}\cdot 3H_2O$ in acetic acid

$K_5CoW_{12}O_{40}\cdot 3H_2O$ (0.01 mmol, 32 mg) was added to a solution of 1-heptanol (1 mmol, 116 mg) in acetic acid (2 mL). The reaction mixture was stirred for 30 min at reflux and the progress of reaction was monitored by GC. Acetic acid was removed under reduced pressure and ether (20 mL) was added. The reaction mixture was washed with a 10% aqueous solution of $NaHCO_3$, then washed with water and dried (Na_2SO_4). Evaporation of the organic solution was followed by column chromatography on a short column of silica gel using petroleum ether as an eluent. 1-Heptyl acetate was obtained as a liquid in 98% yield.

4.3. Typical procedure for acetylation of alcohols with $K_5CoW_{12}O_{40}\cdot 3H_2O$ in ethyl acetate

To a solution of 1-butanol (1 mmol, 74 mg) in ethyl acetate (2 mL) was added $K_5CoW_{12}O_{40}\cdot 3H_2O$ (0.05 mmol, 160 mg). The reaction mixture was stirred for 2 h at reflux. The progress of reaction was monitored by GC. Ethyl acetate was removed under reduced pressure and ether (20 mL) was added. Evaporation of the organic solution was followed by column chromatography on a short column of silica gel using petroleum ether as an eluent. 1-Butyl acetate was obtained as a liquid in 92% yield.

4.4. Typical procedure for formylation of alcohols with $K_5CoW_{12}O_{40}\cdot 3H_2O$ in ethyl formate

1-Octanol (1 mmol, 130 mg) and $K_5CoW_{12}O_{40}\cdot 3H_2O$ (0.01 mmol, 32 mg) were mixed together in ethyl formate (2 mL). The reaction mixture was stirred for 30 min. at reflux. The progress of the reaction was monitored by GC. The solution was evaporated under reduced pressure and ether (30 mL) was added. The mixture was washed with water and dried with Na_2SO_4. Evaporation of organic solution was followed by column chromatography on a short column of silica gel using petroleum ether as an eluent. 1-Octyl formate was obtained as a colorless liquid in 95% yield.

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