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Cobalt(II)-catalyzed direct acetylation of alcohols with acetic acid

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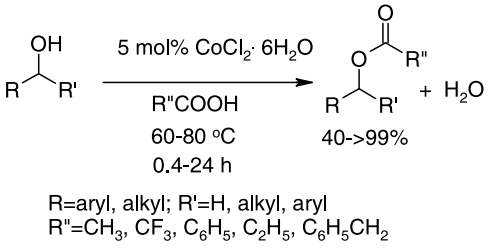
Abstract—Cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) efficiently catalyzes the acetylation of alcohols with AcOH in high yields. This protocol is also effective with other carboxylic acids, trifluoroacetic acid, propanoic acid, phenylacetic acid and benzoic acid, affording the corresponding acylated products in moderate to good yields. Removal of water is not necessary in these reactions. The catalyst can be filtered and recycled without loss of activity.

1. Introduction

Esterification of alcohols with carboxylic acids is among the fundamental and routinely used functional transformations in organic chemistry.[1] Traditionally, it is performed using mineral or sulfonic acids as catalysts in the presence of excess of either the alcohol or carboxylic acid to shift the equilibrium to the product side.[2] The use of strong mineral acids, however, leads to waste streams posing environmental problems for industrial processes. Alternatively, alcohols can be converted to the corresponding esters with carboxylic acids in the presence of a stoichiometric amount of DEAD[3] or DCC,[4] but these methods are uneconomical. Similarly, processes using anhydrides or acid chlorides are also significantly expensive routes compared to use of carboxylic acids.[5,6] Thus, from an industrial standpoint, there is a necessity to develop new methods for the esterification of alcohols with carboxylic acids. Graphite bisulfate has been used as a catalyst for the condensation of alcohols with carboxylic acids.[7] Later, microwave irradiation coupled with *p*-toluenesulfonic acid,[8] metal triflates,[9a–c] anhydrous $FeCl_3$,[9d] $HfCl_4 \cdot (THF)_2$[10a] and distannoxane[10b–c] have been studied for this purpose. Although most of these methods have been shown to be efficient, the catalysts involved are either expensive or water sensitive or both and are destroyed during the work-up procedure.[7–10]

Cobalt(II) chloride has recently been shown by Iqbal et al.[11] and ourselves[12] to catalyze condensation of β-ketoesters with aldehydes,[11a] cleavage of ethers,[11b] acylation of anisoles,[11c] conversion of allylic alcohols to amides,[11d] allylation of 1,3-dicarbonyl compounds,[11e] acylal synthesis,[11f] tosylation of alcohols[12a] and acetal synthesis.[12b] Since this catalyst is readily available, mild Lewis acid, inexpensive and less toxic, its further exploration to other functional group transformations will be quite useful. Herein we report the direct acetylation of alcohols with AcOH using cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) as a recyclable catalyst in high yields (Scheme 1). Other carboxylic acids, trifluoroacetic acid, phenylacetic acid, propanoic acid and benzoic acid, are also effective with this system affording the corresponding acylated products in moderate to good yields.



Scheme 1.

2. Results and discussion

Acetylation of benzyl alcohol **2a** was first studied with AcOH in acetonitrile. The reaction occurred to afford benzyl acetate **3a** in 45% yield when the reaction mixture was allowed to stir at 60 °C for 8 h over 5 mol% $CoCl_2 \cdot 6H_2O$ and 5 equiv of AcOH (Table 1, entry 1 and method A). Alternatively, the reaction could be driven to completion within 1 h in >99% yield of **3a** by performing the reaction in AcOH (method B). A control experiment of method A

Keywords: Acylation; Alcohol; Carboxylic acid; Cobalt(II) chloride; Catalyst.
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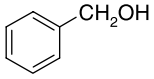
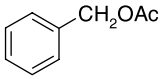
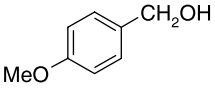
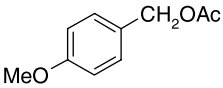
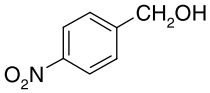
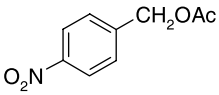
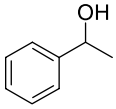
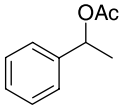
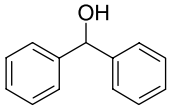
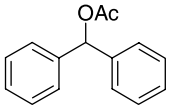
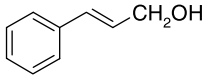
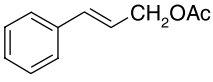
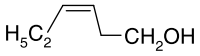
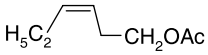
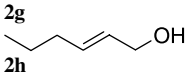
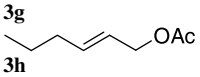
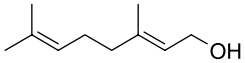
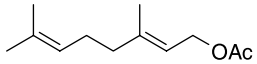
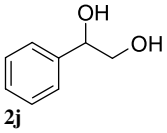
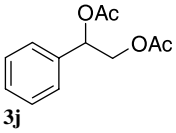
Table 1. Cobalt(II) catalyzed direct acetylation of benzylic and allylic alcohols with acetic acid

Entry	Substrate	Temp. (°C)	Time (h)	Product	Yield (%)[a,b]
1	 **2a**	60 60	8.0 1.0	 **3a**	45[c] 98
2	 **2b**	60	0.4	 **3b**	99
3	 **2c**	60	2.2	 **3c**	95
4	 **2d**	80	8.0	 **3d**	95
5	 **2e**	80	6.5	 **3e**	95
6	 **2f**	60	8.0	 **3f**	97
7	 **2g**	60	10.0	 **3g**	97
8	 **2h**	60	18.0	 **3h**	65
9	 **2i**	60	10.0	 **3i**	89
10	 **2j**	80	6.0	 **3j**	68

[a] Isolated yield.
[b] Substrate (3 mmol), $CoCl_2 \cdot 6H_2O$ (5 mol%) and AcOH (1.5–3.0 mL) were stirred for the appropriate time and temperature.
[c] Substrate (1 mmol), $CoCl_2 \cdot 6H_2O$ (5 mol%) and AcOH (5 mmol) were stirred in acetonitrile (1 mL) for the appropriate time and temperature.

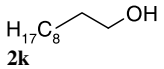
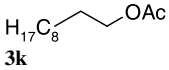
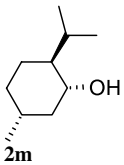
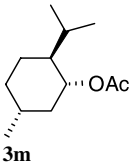
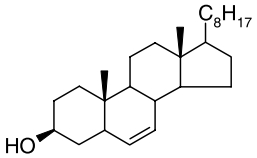
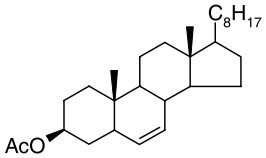
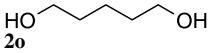
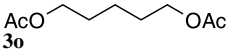
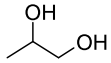
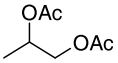
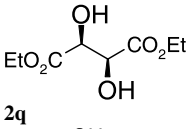
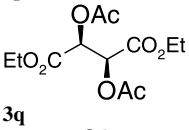
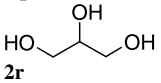
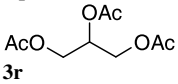
showed no reaction in the absence of cobalt salt, but, 12% of **3a** was obtained with method B.

To evaluate the scope of this reaction, acetylation of other alcohols was studied (Tables 1 and 2). Aromatic alcohols, 4-methoxy- and 4-nitrobenzyl alcohols, phenylethanol, diphenylmethanol and phenylglycol, were converted to the corresponding acetates in high yields (Table 1, entries 2–5 and 10). Allylic alcohols, cinnamyl alcohol, *cis*- and *trans*-hex-2-ene-1-ols and geraniol, were transformed to the respective acetates without affecting the carbon–carbon double bonds (Table 1, entries 6–9). Saturated alcohols, decanol, 2-butanol, (−)-menthol, cholesterol, pentane-1,5-diol, propane-1,2-diol, diethyl L-tartrate and 1,2,3-trihydroxypropane, took slightly longer reaction time compared to aromatic and allylic alcohols to afford the corresponding acetates (Table 2, entries 1–8). It is noteworthy that optically active alcohols did not undergo racemization. The reactivity of primary alcohols was greater compared to secondary alcohols. However, all hydroxy groups were acetylated in polyols. Acetylation of *tert*-alcohol, *tert*-butanol, and phenol was also studied but no reaction was observed (Table 2, entry 9).

Other carboxylic acids, trifluoroacetic acid, propanoic acid, benzoic acid and phenylacetic acid, were next studied for the acylation of benzyl and decyl alcohols (Table 3). Using method B, the reactions of trifluoroacetic acid and propanoic acid were studied to afford the corresponding acylated products **4a–b** and **4e–f** in high yields. In contrast, the reactions of benzoic acid and phenylacetic acid were investigated in acetonitrile to give the respective benzoates **4c–d** and **4g–h** in moderate yields (method A). These results suggest that this protocol can be applied for the acylation of alcohols with different carboxylic acids.

Regarding the mechanism, whether the reaction takes place

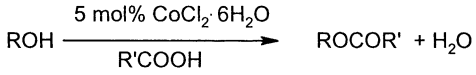
Table 2. Cobalt(II) catalyzed acetylation of saturated alcohols

Entry	Substrate	Temp. (°C)	Time (h)	Product	Yield (%)[a,b]
1	 **2k**	60	8	 **3k**	94
2	 **2l**	60	18	 **3l**	89
3	 **2m**	60	23	 **3m**	91
4	 **2n**	80	19	 **3n**	31[c]
5	 **2o**	60	14	 **3o**	95
6	 **2p**	80	15	 **3p**	92
7	 **2q**	80	24	 **3q**	56
8	 **2r**	80	23	 **3r**	68
9	 **2s**	80	20	No reaction	—

[a] Substrate (3 mmol), $CoCl_2 \cdot 6H_2O$ (5 mol%) and AcOH (1.5–3.0 mL) were stirred for the appropriate time and temperature.
[b] Isolated yield.
[c] Substrate (1 mmol), $CoCl_2 \cdot 6H_2O$ (5 mol%) and AcOH (5 mmol) were stirred in 1,2-dichloroethane (2 mL).

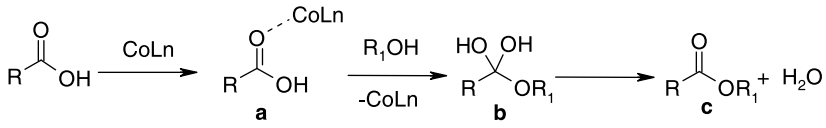
either by Lewis acid or Lewis acid assisted Brønsted acidity via intermediate **5**,[13] the acetylation of 4-methoxybenzyl alcohol was studied using a catalytic amount of HCl at 60 °C. The reaction took place efficiently affording a 2:1 mixture of 4-methoxybenzyl acetate and di(4-methoxybenzyl) ether in >99% yield at 0.3 h. In contrast, the corresponding $CoCl_2 \cdot 6H_2O$ catalyzed process afforded only 4-methoxybenzyl acetate with >99% selectivity. Furthermore, the FT-IR spectrum of the recovered cobalt salt was identical with that of $CoCl_2 \cdot 6H_2O$. Additionally, when the acetylation of 4-methoxybenzyl alcohol was studied with $Co(OAc)_2 \cdot 4H_2O$ as a catalyst, no significant effect was

Table 3. Cobalt(II) catalyzed acylation of alcohols with carboxylic acids



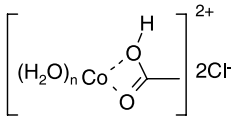
Entry	R	Temp. (°C)	Time (h)	R′	ROCOR′ (%)[a]
1	$C_6H_5CH_2$–**2a**	60	1.0	CF_3–(**4a**)	95[b]
2		60	1.2	C_2H_5–(**4b**)	93[b]
3		80	14.0	C_6H_5–(**4c**)	47[c]
4		80	15.0	$C_6H_5CH_2$– (**4d**)	44[c]
5	$H_{21}C_{10}$–**2k**	60	7.0	CF_3–(**4e**)	95[b]
6		60	8.5	C_2H_5–(**4f**)	93[b]
7		80	15.0	C_6H_5–(**4g**)	43[c]
8		80	18.0	$C_6H_5CH_2$–(**4h**)	40[c]

[a] Isolated yield.
[b] Substrate (1 mmol), $CoCl_2 \cdot 6H_2O$ (5 mol%) and carboxylic acid (1 mL) were stirred.
[c] Substrate (1 mmol), $CoCl_2 \cdot 6H_2O$ (5 mol%) and carboxylic acid (5 mmol) were stirred in acetonitrile (1 mL).



Scheme 2.

observed. These studies clearly suggest that the present methodology may take place by Lewis acid catalyzed process as shown in Scheme 2 and not by Lewis acid assisted Brønsted acidity.



5

To study the recyclability of the catalyst, the reaction mixture of benzyl alcohol **2a** and AcOH was treated with diethyl ether and water (Table 4). The organic layer was separated and successively washed with saturated $NaHCO_3$ solution, brine and water to provide benzyl acetate **3a** in >98% yield. The aqueous layer was concentrated under reduced pressure and the recovered cobalt(II) salt was further investigated for the acetylation of benzyl alcohol **2a** with AcOH under the same reaction conditions. As usual, the reaction occurred and the corresponding acetate **3a** was obtained in >97% yield. This process was repeated two times without loss of activity of the catalyst and the results are summarized in Table 4.

Table 4. Recycling of the catalyst

Run[a]	Benzylacetate [%]	Catalyst recovery [%]
1	>98	>99
2	>97	>98
3	>96	>97

[a] Benzyl alcohol (3 mmol), $CoCl_2 \cdot 6H_2O$ (5 mol%) and AcOH (1.5 mL) were stirred for 1 h at 60 °C.

3. Conclusions

The use of $CoCl_2 \cdot 6H_2O$ as a recyclable catalyst has been shown for the direct acetylation of alcohols using AcOH only as the acetyl source in high yields. These reaction conditions are also suitable for the esterification of alcohols with other carboxylic acids. Removal of water is not necessary in these reactions.

4. Experimental

4.1. General methods

$CoCl_2 \cdot 6H_2O$ was obtained from Loba India Ltd, Bombay. Alcohols and carboxylic acids were purchased either from Aldrich or Fluka and used without further purification. NMR spectra were recorded on DRX-300 (300 MHZ for ^1H and 75.5 MHZ for ^{13}C) spectrometer. Chemical shifts are given in δ units relative to the tetramethyl silane (TMS) signal as an internal reference. Coupling constants (J) are reported in hertz. IR spectra were recorded on Nicolet impact 410 spectrometer. Optical rotation was measured on Perkin Elmer Model 343 Polarimeter. Elemental analysis was conducted using Perkin Elmer 2400 series II CHNS analyzer. Column chromatography was preformed on silicagel (60–120 mesh) using ethyl acetate and hexane as eluent.

General procedure for the acylation of alcohols: method A. A solution of $CoCl_2 \cdot 6H_2O$ (5 mol%), alcohol (1 mmol) and carboxylic acid (5 mmol) in acetonitrile (1 mL) was stirred for the appropriate time and temperature (see Table 1 and 3). The reaction mixture was then cooled to room temperature and the aqueous acetonitrile was removed on a rotary evaporator under reduced pressure. The residue was treated with diethyl ether (10 mL) and water (1 mL). The organic layer was successively washed with saturated $NaHCO_3$ solution (3×5 mL), brine (2×5 mL) and water (2×5 mL). Drying (Na_2SO_4) and evaporation of the solvent under reduced pressure provided a residue which was passed through a short pad of silica gel (60–120 mesh) using ethyl acetate and hexane as eluent to provide the analytically pure acylated product. Concentration of the aqueous layer under reduced pressure provided the catalyst which can be recycled without loss of activity.

Method B. A solution of $CoCl_2 \cdot 6H_2O$ (5 mol%), alcohol (3 mmol) and AcOH (1.5–3.0 mL) was stirred for the appropriate time and temperature (see Table 1–4). The reaction mixture then treated with diethyl ether (25 mL) and water (2 mL). The organic layer was subjected to the work up and purification procedure as described in method A to provide the analytically pure acylated product. Concentration of the aqueous layer under reduced pressure afforded the catalyst (>99%) whose FT-IR spectrum was identical with that of $CoCl_2 \cdot 6H_2O$.

The following compounds are known and spectral data are consistent with those reported in the literature: benzyl acetate (**3a**),[19b] 4-methoxybenzyl acetate (**3b**),[6h] 4-nitrobenzyl acetate (**3c**),[6h] α-methylbenzyl acetate (**3d**),[6h] diphenylmethyl acetate (**3e**),[6h] cinnamyl acetate (**3f**),[19b] *trans*−2-hexenyl acetate (**3h**),[19a] geranyl acetate (**3i**),[19a] phenyl-1,2-ethyl diacetate (**3j**),[6j] decyl acetate (**3k**),[13] butyl-2-acetate (**3l**),[14] (−)-menthyl acetate (**3m**),[19a] cholesteryl acetate (**3n**),[19c] pentane-1,5-diacetate (**3o**),[6j] diethyl (L)-tartrate diacetate (**3q**),[15] 1,2,3-propyl triacetate (**3r**),[19a] benzyl trifluoroacetate (**4a**),[16] benzyl propanoate (**4b**),[17] benzyl benzoate (**4c**),[19b] decyl propanoate (**4f**),[18a] decyl benzoate (**4g**).[18b]

The following acetylated products are not reported in the literature.

4.1.1. *cis*-3-Hexenyl acetate (3g). Colorless liquid. Yield 97%. ^1H NMR ($CDCl_3$) δ 0.97 (t, 3H, J=7.5 Hz), 2.02 (s, 3H), 2.06–2.11 (m, 2H), 2.33–2.40 (m, 2H), 4.05 (t, 2H, J= 6.9 Hz), 5.27–5.35 (m, 1H), 5.46–5.54 (m, 1H); ^{13}C NMR

($CDCl_3$) δ 13.8, 20.2, 20.4, 26.4, 63.5, 123.4, 134.1, 170.5; IR (neat) 1741 cm^{-1}. Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.58; H, 9.94.

4.1.2. Propane-1,2-diacetate (3p). Colorless liquid. Yield 92%. ^1H NMR ($CDCl_3$) δ 1.25 (d, 3H, $J=6.6$ Hz), 2.06 (s, 3H), 2.08 (s, 3H), 4.05 (dd, 1H, $J=6.6$, 11.7 Hz), 4.17 (dd, 1H, $J=3.6$, 12.0 Hz), 5.08–5.18 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 16.4, 20.7, 21.1, 66.0, 68.2, 170.4, 170.7; IR (neat) 1742 cm^{-1}. Anal. Calcd for $C_7H_{12}O_4$: C, 52.49; H, 7.55. Found: C, 52.50; H, 7.53.

4.1.3. Benzyl phenylacetate (4d). Colorless liquid. Yield 44%. ^1H NMR ($CDCl_3$) δ 3.6 (s, 2H), 5.1 (s, 2H), 7.2–7.4 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 41.8, 67.0, 127.4, 128.5, 128.8, 129.6, 133.3, 134.2, 136.1, 171.5; IR (neat) 1750 cm^{-1}. Anal. Calcd for $C_{16}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.64; H, 6.25.

4.1.4. Decyl trifluoroacetate (4e). Colorless liquid. Yield 95%. ^1H NMR ($CDCl_3$) δ 0.9 (t, 3H, $J=7.0$ Hz), 1.28–1.37 (m, 14H), 1.73–1.76 (m, 2H), 4.3–4.4 (t, 2H, $J=7.0$ Hz); ^{13}C NMR ($CDCl_3$) δ 14.3, 23.0, 25.9, 28.4, 29.8, 29.9, 32.2, 68.5, 157.2, 157.7, 158.0, 158.2, 171.9; IR (neat) 1794 cm^{-1}. Anal. Calcd for $C_{12}H_{21}O_2F_3$: C, 56.68; H, 8.32. Found: C, 56.66; H, 8.33.

4.1.5. Decyl phenylacetate (4h). Colorless liquid. Yield 40%. ^1H NMR ($CDCl_3$) δ 0.9 (t, 3H, $J=6.8$ Hz), 1.3–1.5 (m, 14H), 1.5–1.7 (m, 2H), 3.6 (s, 2H), 3.9–4.2 (t, 2H, $J=6.8$ Hz), 7.1–7.4 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.6, 23.2, 29.3, 29.4, 29.7, 29.8, 30.0, 32.3, 65.3, 127.2, 128.7, 129.4, 134.4, 171.7; IR(neat) 1751 cm^{-1}. Anal. Calcd for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21. Found: C, 78.22; H, 10.18.

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