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Efficient One-Step Conversion of Tetrahydropyranyl Ethers into Acetates and Formates in the Presence of Potassium Dodecatungstocobaltate $K_5CoW_{12}O_{40}\cdot 3H_2O$*

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Abstract—Tetrahydropyranyl ethers derived from primary alcohols were directly and efficiently converted into the corresponding acetates and formates by the action of ethyl acetate, acetic acid, acetic anhydride, and ethyl formate in the presence of a catalytic amount of potassium dodecatungstocobaltate $K_5CoW_{12}O_{40}\cdot 3H_2O$. Tetrahydropyranyl ethers derived from secondary alcohols and phenols can also be transformed into the corresponding acetates with the use of acetic anhydride, but $K_5CoW_{12}O_{40}\cdot 3H_2O$ was ineffective for esterification with ethyl acetate, acetic acid, and ethyl formate.

Protection and subsequent deprotection of functional groups are important processes in multistep organic syntheses [1]. Tetrahydropyranyl ethers are widely used in organic chemistry to protect hydroxy groups, for these compounds are stable under various reaction conditions [2]; however, they are unsuitable in acidic medium. Acetate and formate moieties are also important hydroxy-protecting groups which are resistant to acidic reagents [2]; acetates and formates are usually prepared by esterification of the corresponding acids [3–5], transesterification [6], alkylation of carboxylate ions [7], acylation of alcohols and phenols [8–12], or cleavage of ethers [13]. Thus direct conversion of tetrahydropyranyl ethers into the corresponding acetates and formates is an important process in organic synthesis. Only a few reports on this topic are available from the literature [14, 15]. Therefore, introduction of new methods and reagents for such transformation of functional groups is still in demand.

We recently proposed to use $K_5CoW_{12}O_{40}\cdot 3H_2O$ as an efficient catalyst for removal of the tetrahydropyranyl protecting group from tetrahydropyranyl ethers [16] and for acetylation and formylation of alcohols with ethyl acetate, ethyl formate, acetic acid, and acetic anhydride [17, 18]. In continuation of our studies in this line, we now report a convenient method for direct esterification of tetrahydropyranyl ethers with the above acylating agents in the presence of $K_5CoW_{12}O_{40}\cdot 3H_2O$ (Scheme 1).

Scheme 1.

$$R^1OTHP \quad + \quad R^2C(O)OR^3 \xrightarrow{K_5CoW_{12}O_{40}\cdot 3\,H_2O} R^2C(O)OR^1$$

For R^1, see Tables 1, 2; $R^2 = CH_3$, H; R^3 = H, Et, CH_3CO.

Treatment of various tetrahydropyranyl ethers with acetic anhydride in the presence of $K_5CoW_{12}O_{40}\cdot 3H_2O$ (2 mol %) at room temperature afforded the corresponding acetates in good to excellent yields (Table 1). In order to extend the scope of application of this procedure we also examined esterification of tetrahydropyranyl ethers with less active acylating agents such as ethyl acetate, acetic acid, and ethyl formate. We found that tetrahydropyranyl ethers derived from primary alcohols were converted to the corresponding acetates and formates in good to excellent yields under reflux conditions (Tables 1, 2; run nos. 1–12). Under the same conditions, tetrahydropyranyl ethers derived from secondary alcohols and phenols turned out to be more resistant: they either remained intact or were transformed into the corresponding acetates and formates in relatively poor yields (Tables 1, 2; run nos. 13–15). We also found that the catalyst can be reused several times without loss in activity. It was regenerated simply by filtering, washing with acetone, and drying. The yield of benzyl acetate in the reaction of benzyl tetrahydropyranyl ether with ethyl acetate, promoted by five-fold recovered $K_5CoW_{12}O_{40}\cdot 3H_2O$, remained equal to 95%.

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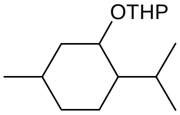
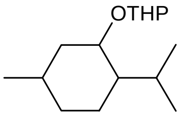
Table 1. Conversion of tetrahydropyranyl ethers into the corresponding acetates in the presence of $K_5CoW_{12}O_{40}\cdot 3H_2O$

Run no.	Initial ether	Yield of acetate,[a] %		
		ethyl acetate[b] (time, h)	acetic acid[b] (time, h)	acetic anhydride[c] (time, min)
1	3-$MeOC_6H_4CH_2OTHP$	94 (10)	96 (2.5)	90 (20)
2	4-$ClC_6H_4CH_2OTHP$	98 (6)	97 (2.25)	98 (3)
3	$PhCH{=}CHCH_2OTHP$	75 (0.5)	98 (0.4)	94 (8)
4	$PhCH_2CH_2OTHP$	98 (6)	95 (3.5)	91 (15)
5	$PhCH_2CH_2CH_2OTHP$	98 (5)	96 (2)	94 (3)
6	$PhCH_2OTHP$	98 (6)	95 (2)	94 (20)
7	$CH_3(CH_2)_6OTHP$	95 (6)	96 (2)	70 (13)
8	$CH_3(CH_2)_8OTHP$	90 (7)	92 (2.5)	84 (45)
9	$CH_3(CH_2)_3CH(Et)CH_2OTHP$	88 (8)	95 (2)	3 (25)
10		32 (8)	32 (2)	95 (7)
11	2,3-$(MeO)_2C_6H_4CH_2OTHP$	61 (1)	90 (1)	95 (30)
12	4-$O_2NC_6H_4CH_2OTHP$	53 (2)	45 (1)	50 (10)
13	4-$BrC_6H_4CH(CH_3)OTHP$	20 (2)	20 (1)	93 (17)
14	$Ph_2CHOTHP$	90 (3.5)	96 (0.25)	97 (10)
15	2-$C_{10}H_7OTHP$		30 (4)	80 (120)

[a] According to the GLC data.
[b] The reactions were carried out under reflux.
[c] The reactions were carried out at room temperature.

Table 2. Conversion of tetrahydropyranyl ethers into the corresponding formates in the presence of $K_5CoW_{12}O_{40}\cdot 3H_2O$ (under reflux conditions)

Run no.	Initial ether	Time, min	Yield,[a] %
1	3-$MeOC_6H_4CH_2OTHP$	40	83
2	4-$ClC_6H_4CH_2OTHP$	60	97
3	$PhCH{=}CHCH_2OTHP$	20	94
4	$PhCH_2CH_2OTHP$	45	91
5	$PhCH_2CH_2CH_2OTHP$	20	91
6	$PhCH_2OTHP$	5	90
7	$CH_3(CH_2)_6OTHP$	30	94
8	$CH_3(CH_2)_8OTHP$	30	93
9	$CH_3(CH_2)_3CH(Et)CH_2OTHP$	20	94
10		20	40
11	2,3-$(MeO)_2C_6H_4CH_2OTHP$	60	91
12	4-$O_2NC_6H_4CH_2OTHP$	30	50
13	4-$BrC_6H_4CH(CH_3)OTHP$	9 h	50
14	$Ph_2CHOTHP$	45	90
15	2-$C_{10}H_7OTHP$	10 h	0

[a] According to the GLC data.

Thus we have proposed a convenient procedure for acetylation and formylation of alcohols through the corresponding tetrahydropyranyl ethers. The procedure is advantageous due to easy isolation of the products and relatively low toxicity and reusability of the catalyst.

EXPERIMENTAL

Potassium dodecatungstocobaltate $K_5CoW_{12}O_{40}\cdot 3H_2O$ was prepared by the procedure described in [17].

Typical procedure for the conversion of tetrahydropyranyl ethers into the corresponding acetates

and formates. To a solution of 1 mmol of tetrahydropyranyl ether and 4 ml of acylating agent we added $K_5CoW_{12}O_{40}\cdot 3H_2O$ in an amount of 0.05 mmol for ethyl acetate, 0.01 mmol for acetic acid or ethyl formate, or 0.02 mmol for acetic anhydride. The mixture was stirred at room temperature or at the boiling point for a time indicated in Table 1 or 2. The progress of the reaction was monitored by GLC or TLC. The catalyst was filtered off, the filtrate was evaporated, 20 ml of diethyl ether was added to the residue, and the solution was washed with 5% aqueous $NaHCO_3$ and water, dried over Na_2SO_4, and evaporated. The products were isolated by chromatography on silica gel and were characterized by the IR and ^1H NMR spectra.

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