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Potassium dodecatangestocobaltate trihydrate ($K_5CoW_{12}O_{40}\cdot 3H_2O$): a mild and efficient catalyst for the tetrahydropyranylation of alcohols and their detetrahydropyranylation

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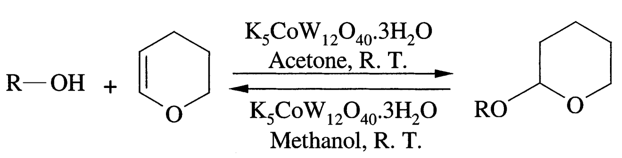
Abstract—A simple, mild and effective method for tetrahydropyranylation of a variety of alcohols and cleavage of their tetrahydropyranyl ethers at ambient temperature in the presence of $K_5CoW_{12}O_{40}\cdot 3H_2O$ as the catalyst with high turnovers is described. © 2001 Elsevier Science Ltd. All rights reserved.

The importance of selective introduction and removal of protecting groups in organic synthesis is well established. Tetrahydropyranylation is one of the most frequently used methods for the protection of hydroxyl groups in synthetic organic chemistry, in particular natural product chemistry, because of its easy installation, general stability to most nonacidic reagents, and easy removal under mild acidic conditions.[1,2]

A wide variety of catalysts have already been applied to the tetrahydropyranylation of alcohols and phenols, and their detetrahydropyranylation including the use of protic acids[3] (acetic acid, *p*-toluenesulfonic acid, boric acid), Lewis acids[4] (magnesium bromide in ether, dimethylaluminium chloride), Lewis acids (copper sulfate and iron(III) chloride) supported on silica gel,[5] electrogenerated acid,[6] pyridinium *p*-toluenesulfonate,[7] ion exchange resins[8] (amberlyst H-15, Dowex 50W-X8, Nafion-H), bentonitic earth,[9] organotin phosphate condensates,[10] triphenylphosphine dibromide (PPh_3Br_2)[11] and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ).[12] More recently, heteropolyacids,[13] lithium chloride,[14] expansive graphite,[15] reductive cleavage using sodium cyanoborohydride and $BF_3\cdot OEt_2$,[16] clay materials[17] (montmorilonite K-10 and H-Y zeolite), $ZnCl_2$,[18] CuCl[19] and NH_4Cl[20] have also been employed to this purpose. However, some of these procedures suffer due to the use of expensive and toxic reagents, high temperatures, strongly acidic conditions or formation of considerable amounts of side products. Consequently, there is a need to develop alternative methods for the protection of alcohols as well as deprotection of tetrahydropyranyl ethers.

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 is possible. Due to their acidic and redox properties, heteropoly compounds (heteropoly acids and salts) are useful and versatile catalysts in a number of transformations. Since they exhibit weak superacidic properties, they can be used in reactions requiring electrophilic catalysis.[21]

Having these factors in mind, we now wish to report that $K_5CoW_{12}O_{40}\cdot 3H_2O$[22] is an excellent and effective catalyst for tetrahydropyranylation and deprotection of tetrahydropyranyl ethers to their parent alcohols (Scheme 1).



Scheme 1.

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As shown in Table 1, the treatment of a series of alcohols with 3,4-dihydro-2*H*-pyran in the presence of only 0.01 mmol of the catalyst in acetone at room temperature, afforded the corresponding tetrahydropyranyl ether in high yields (60–100%) with high turnover per hour (about 1400 for benzyl alcohol). Under the same reaction conditions phenols reacted more slowly and the corresponding tetrahydropyranyl ethers were obtained in 5–55% yields (Table 1, entries 22–24).

In a typical procedure 3,4-dihydro-2*H*-pyran (2 mmol, 168 mg) dissolved in acetone (5 mL) was added to a stirred solution of benzyl alcohol (1 mmol, 108 mg) and $K_5CoW_{12}O_{40}\cdot 3H_2O$ (0.01 mmol, 32 mg) in acetone (5 mL) at ambient temperature for 5 min. The solution was first filtered through a short column of silica gel, washed with a small amount of CH_2Cl_2 and concentrated to give tetrahydropyranyl ether, the product was purified by column chromatography and the corre-

Table 1. Tetrahydropyranylation of alcohols catalyzed with $K_5CoW_{12}O_{40}\cdot 3H_2O$

Entry	Alcohols	THP–ethers[a]	Time (min)	Yield (%)[b]
1	$C_6H_5CH_2OH$	$C_6H_5CH_2OTHP$	5	97
2	$2\text{-}NO_2C_6H_4CH_2OH$	$2\text{-}NO_2C_6H_4CH_2OTHP$	15	75
3	$4\text{-}NO_2C_6H_4CH_2OH$	$4\text{-}NO_2C_6H_4CH_2OTHP$	10	80
4	$4\text{-}ClC_6H_4CH_2OH$	$4\text{-}ClC_6H_4CH_2OTHP$	5	97
5	$2\text{-}CH_3OC_6H_4CH_2OH$	$2\text{-}CH_3OC_6H_4CH_2OTHP$	5	97
6	$3\text{-}CH_3OC_6H_4CH_2OH$	$3\text{-}CH_3OC_6H_4CH_2OTHP$	5	97
7	$4\text{-}CH_3OC_6H_4CH_2OH$	$4\text{-}CH_3OC_6H_4CH_2OTHP$	5	95
8	$C_6H_5CH_2CH_2CH_2OH$	$C_6H_5CH_2CH_2CH_2OTHP$	5	98
9	$C_6H_5CH(OH)CH_3$	$C_6H_5CH(OTHP)CH_3$	10	95
10	$C_6H_5CH_2CH_2OH$	$C_6H_5CH_2CH_2OTHP$	5	98
11	$C_6H_5CHCHCH_2OH$	$C_6H_5CHCHCH_2OTHP$	10	85
12	$C_6H_5CH(OH)COC_6H_5$	$C_6H_5CH(OTHP)COC_6H_5$	10	80
13	$C_6H_{11}OH$ (Cyclohexanol)	$C_6H_{11}OTHP$	10	85
14	$CH_3(CH_2)_6CH_2OH$	$CH_3(CH_2)_6CH_2OTHP$	5	86
15	$CH_3(CH_2)_5CH_2OH$	$CH_3(CH_2)_5CH_2OTHP$	10	88.5
16	$CH_3(CH_2)_3CH_2OH$	$CH_3(CH_2)_3CH_2OTHP$	5	96
17	$CH_3(CH_2)_2CH_2OH$	$CH_3(CH_2)_2CH_2OTHP$	15	76
18	α-Tetralol	α-TetralolTHP	5	100
19	2-Ethyl-1-hexanol	2-Ethyl-1-hexanolTHP	5	68.5
20	(−)-Menthol	(−)-MentholTHP	15	82
21	Adamantanol	AdamantanolTHP	15	60
22	$2\text{-}NO_2C_6H_4OH$	$2\text{-}NO_2C_6H_4OTHP$	60	5
23	$4\text{-}NO_2C_6H_4OH$	$4\text{-}NO_2C_6H_4OTHP$	30	25
24	$CH_3COC_6H_4OH$	$CH_3COC_6H_4OTHP$	15	55

[a] All tetrahydropyranyl ethers were identified by comparison of their physical and spectral data with authentic samples.

[b] GC yields.

Table 2. Deprotection of THP–ethers of alcohols catalyzed by $K_5CoW_{12}O_{40}\cdot 3H_2O$

Entry	THP–ethers	Alcohol[a]	Time (min)	Yield (%)[b]
1	$4\text{-}CH_3OC_6H_4CH_2OTHP$	$4\text{-}CH_3OC_6H_4CH_2OH$	60	100
2	$3\text{-}CH_3OC_6H_4CH_2OTHP$	$3\text{-}CH_3OC_6H_4CH_2OH$	60	100
3	$4\text{-}ClC_6H_4CH(OTHP)CH_3$	$4\text{-}ClC_6H_4CH(OH)CH_3$	45	100
4	α-TetralolTHP	α-Tetralol	50	100
5	$C_6H_4CH(OTHP)CH_3$	$C_6H_4CH(OH)CH_3$	45	100
6	$C_6H_5CH(OTHP)C_6H_5$	$C_6H_5CH(OH)C_6H_5$	100	95[c]
7	Furfuryl alcoholTHP	Furfuryl alcohol	90	100
8	$2,5\text{-}CH_3OC_6H_4CH_2OTHP$	$2,5\text{-}CH_3OC_6H_4CH_2OH$	90	100
9	$C_6H_5CH_2CH_2OTHP$	$C_6H_5CH_2CH_2OH$	150	100
10	$C_6H_5CHCHCH_2OTHP$	$C_6H_5CH_2CH_2CH_2OH$	150	100
11	$4\text{-}C_6H_5C_6H_5CH(OTHP)CH_3$	$4\text{-}C_6H_5C_6H_5CH(OH)CH_3$	60	94[c]
12	$4\text{-}NO_2C_6H_4CH_2OTHP$	$4\text{-}NO_2C_6H_4CH_2OH$	40	100
13	$C_6H_5CH_2OTHP$	$C_6H_5CH_2OH$	80	100
14	$C_6H_{11}OTHP$	$C_6H_{11}OH$ (Cyclohexanol)	60	100
15	$C_6H_5CHCHCH_2OTHP$	$C_6H_5CHCHCH_2OH$	100	100
16	$CH_3(CH_2)_5CH_2OTHP$	$CH_3(CH_2)_5CH_2OH$	120	100

[a] All alcohols were identified by comparison of their physical and spectral data with authentic samples.

[b] GC yields.

[c] Isolated yields.

sponding benzyltetrahydropyranyl ether was obtained in 97% yield.

Deprotection of THP–ethers was also investigated. As shown in Table 2, these ethers are converted to their parent alcohols in excellent yields.

In a typical deprotection reaction, a solution of benzyltetrahydropyranyl ether (1 mmol, 192 mg) with $K_5CoW_{12}O_{40}\cdot 3H_2O$ (0.01 mmol, 32 mg) in methanol (5 mL) was stirred at ambient temperature for 80 min. Work-up as mentioned earlier for tetrahydropyranylation gave the pure benzyl alcohol in 100% yield.

In conclusion, our protocol provides a simple, fast and effective method for the protection and deprotection of tetrahydropyranyl ethers. In addition, recovery and industrial applicability of the catalyst, easy work-up, low reaction times and high yields are worthy advantages of this procedure.

Acknowledgements

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22. The synthesis of potassium dodecatangestocobaltate trihydrate ($K_5CoW_{12}O_{40}\cdot 3H_2O$) starts with the preparation of sodium tangestodicobalt(II)ate from cobaltous acetate (2.5 g, 0.01 mol) and sodium tangestate (19.8 g, 0.06 mol) in acetic acid and water at pH 6.5 to 7.5. The sodium salt is then converted to potassium salt by treatment with potassium chloride (13 g). Finally cobalt(II) complex is oxidized to 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 recrystalization with methanol, potassium dodecatangestocobaltate trihydrate ($K_5CoW_{12}O_{40}\cdot 3H_2O$) was obtained.