Potassium dodecatangestocobaltate trihydrate (K$_5$CoW$_{12}$O$_{40}$·3H$_2$O): a mild and efficient catalyst for deprotection of dioxolanes and trimethylsilyl ethers

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Abstract—Mild and easy deprotection of benzylic dioxolanes to carbonyl compounds (in refluxing dry acetone) and trimethylsilyl ethers to alcohols in acetonitrile at ambient temperature has been carried out in excellent yields under K$_5$CoW$_{12}$O$_{40}$·3H$_2$O (0.01 molar equiv.) catalysis. © 2001 Elsevier Science Ltd. All rights reserved.

There are many published procedures for the cleavage of acetals and ketals into carbonyl compounds,[1] but the development of new improved methods continues to attract attention.[2] Generally, this deprotection is carried out by acid-catalyzed aqueous hydrolysis.[3] However, very often this method is incompatible with the presence of some other functional group in the molecule, e.g. a protected hydroxyl group. Several nonacidic methods for cleavage of acetals, such as wet silica gel[4] or lithium tetrafluoroborate in wet acetonitrile[5] have been employed. A few nonaqueous methods utilizing phosphorous triiodide and diphosphorous tetraiodide,[6] boron trifluoride–iodide ion,[7] titanium (IV) chloride,[8] iodotrimethylsilane,[9] chlorotrimethylsilane–samarium trichloride,[10] chlorotrimethylsilane–sodium iodide[11] and cerium(III) chloride[12] have been reported for deprotection of acetals to carbonyl compounds. Many of these procedures suffer from lack of selectivity, unsatisfactory yields, cost or toxicity of the reagents, or necessity of anhydrous conditions. These limitations prompted us to investigate further a new catalyst, which is able to carry out the cleavage of acetals and ketals with excellent yields.

The conversion of alcohols into trimethylsilyl ethers is a widely used method of protection in organic synthesis.[1] Selective removal of the trimethylsilyl (TMS) group has been achieved by using aqueous HF–MeCN,[13] KF–Crown ether,[14] BF$_3$·Et$_2$O–CHCl$_3$,[15] N-bromo succinimide,[16] CF$_3$SO$_3$SiMe$_3$–CH$_2$Cl$_2$,[17] NH$_4$F–MeOH,[18] SiF$_4$–MeCN,[19] aqueous acid,[20] tetrabutylammonium fluoride (TBAF),[21] K$_2$CO$_3$,[22] Lewis acids[23] and neutral alumina.[24] However, while fluoride ions are very basic, especially under anhydrous conditions, and therefore cannot be used for base-sensitive molecules,[25,26] other procedures are not acceptable for acid-sensitive systems and, consequently, the development of alternative methods of deprotection under neutral conditions would be desirable.

Heteropoly compounds provide a good basis for the design of mixed oxide catalysts and they have high capability for practical uses. This is because the relationships among the following four levels of information can be established on a molecular basis: (i) catalytic performance; (ii) chemical and physical properties; (iii) molecular and bulk composition and structure; and (iv) the method of synthesis of catalysts in which these relationships are most useful for the design of practical catalysts. The catalytic function of heteropoly compounds has attracted much attention and they are used in solution as well as in the solid state. The
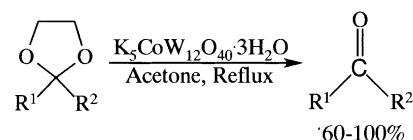
Scheme 1.

reason why heteropoly catalysts are attractive is their variety and high potential as catalysts.[27–29] Polyoxometalates have proved to be good catalysts for 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.[30,31] In continuation of our investigation on application of polyoxometalates in organic synthesis,[32] we wish to describe here that the deprotection of benzylic dioxolanes, which remains the most usual protecting group for the ketone functionality, can be effectively realized under mild conditions by a cheap and easily prepared cobalt heteropoly compound ($K_5CoW_{12}O_{40}\cdot3H_2O$) in acetone (Scheme 1).

The *para*-chlorobenzaldehyde 1,3-dioxolane (Table 1, entry 2) is transformed to the corresponding carbonyl compound after 10 minutes by treatment with 0.01 molar equivalents of $K_5CoW_{12}O_{40}\cdot3H_2O$ (95% yield). The deprotection of *para*-chlorobenzaldehyde 1,3-dioxolane were studied in different solvents and acetone turned out to be the best solvent for the deprotection of 1,3-dioxolanes. As shown in Table 1, in the presence of dodecatangestocobaltate ($K_5CoW_{12}O_{40}\cdot3H_2O$), a number of benzylic dioxolanes were heated in refluxing acetone for 0.1–6 h to provide the corresponding carbonyl compounds in excellent yields. The structures of the carbonyl compounds were confirmed by comparison of their boiling points or melting points, R_f values on TLC and spectroscopic data with authentic samples.

This procedure appears to be quite efficient for acetals and ketals. In conclusion, we provide an efficient and practical procedure for cleavage of dioxolanes to acetals and ketals.

Also, we have found that cleavage of trimethylsilyl ethers occurs efficiently in excellent yields at ambient temperature using $K_5CoW_{12}O_{40}\cdot3H_2O$ as the catalyst. This reaction takes place when 0.01 molar equivalents of $K_5CoW_{12}O_{40}\cdot3H_2O$ is mixed with the trimethylsilyl ether in acetonitrile at ambient temperature (Scheme 2).

As shown in Table 2, when trimethylsilyl ethers were allowed to react at room temperature with $K_5CoW_{12}O_{40}\cdot3H_2O$ in MeCN, cleavage of the ethers occurred and the corresponding alcohols were obtained readily in 3–45 min with excellent yields (96–100%). Phenolic trimethylsilyl ethers are resistant toward deprotection with this catalyst and only 5% of product was obtained from the reaction mixture (Table 2, entry 18).

In addition, we found that cobalt polyoxometalate, $K_5CoW_{12}O_{40}\cdot3H_2O$, can be reused several times without loss of activity, simply by filtering the catalyst, washing with acetone, drying and immediately reusing.

Preparation of the catalyst: The synthesis of potassium dodecatangestocobaltate trihydrate ($K_5CoW_{12}O_{40}\cdot3H_2O$) starts with the preparation of sodium tangesto-

Table 1. Deprotection of 1,3-dioxolanes using $K_5CoW_{12}O_{40}\cdot3H_2O^a$

Entry	1,3-Dioxolane	Time (min)	Yields (%)[b]
1		60 (r. t.)	97
2		10	95
3		60	97
4		60	99
5		75	80[c]
6		10	97
7		10	92
8		300	85
9		360	66
10		10	97
11		10	97[c]
12		10	100
13		30	87[c]
14		360	60[c]

[a] All carbonyl products were identified by comparison of their physical and spectroscopic data with authentic samples.

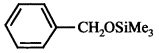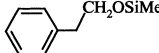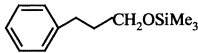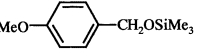[b] GC Yields.

[c] Isolated yields.

$$R\!-\!OSi(CH_3)_3 \xrightarrow[CH_3CN,\ R.\ T.]{K_5CoW_{12}O_{40}\cdot3H_2O} R\!-\!OH$$

96-100%
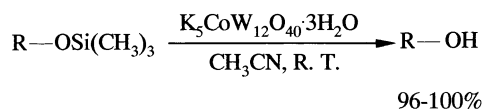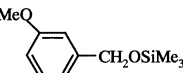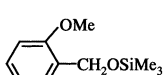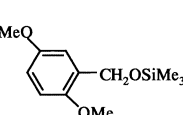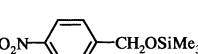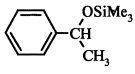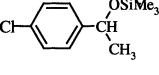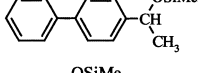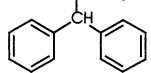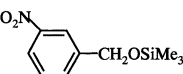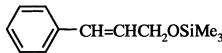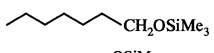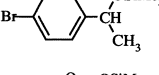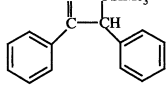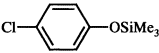
Scheme 2.

Table 2. Deprotection of silylethers catalyzed by $K_5CoW_{12}O_{40} \cdot 3H_2O^a$

Entry	Silyl Ether	Time (min)	Yields (%)[b]
1	Ph–CH$_2$OSiMe$_3$	25	100
2	Ph–CH$_2$CH$_2$OSiMe$_3$ (benzyl)	10	100
3	Ph–CH$_2$CH$_2$–CH$_2$OSiMe$_3$	5	100
4	MeO–C$_6$H$_4$–CH$_2$OSiMe$_3$	25	100
5	*m*-MeO–C$_6$H$_4$–CH$_2$OSiMe$_3$	20	100
6	*o*-OMe–C$_6$H$_4$–CH$_2$OSiMe$_3$	15	100
7	(MeO)(OMe)–C$_6$H$_3$–CH$_2$OSiMe$_3$	25	100
8	O$_2$N–C$_6$H$_4$–CH$_2$OSiMe$_3$	15	100
9	Ph–CH(OSiMe$_3$)CH$_3$	3	100
10	Cl–C$_6$H$_4$–CH(OSiMe$_3$)CH$_3$	10	100
11	biphenyl–CH(OSiMe$_3$)CH$_3$	40	96[c]
12	Ph$_2$CH–OSiMe$_3$	45	96[c]
13	*m*-O$_2$N–C$_6$H$_4$–CH$_2$OSiMe$_3$	15	100
14	Ph–CH=CHCH$_2$OSiMe$_3$	20	100
15	CH$_3$(CH$_2$)$_4$–CH$_2$OSiMe$_3$	10	100
16	Br–C$_6$H$_4$–CH(OSiMe$_3$)CH$_3$	10	100
17	Ph–C(O)–CH(OSiMe$_3$)–Ph	30	100
18	Cl–C$_6$H$_4$–OSiMe$_3$	75	5

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

[b] GC Yields.

[c] Isolated yields.

dicobalt(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 into 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$_2$SO$_4$. The crystals of K$_5$CoW$_{12}$O$_{40} \cdot$20H$_2$O were dried at 200°C after recrystallization with methanol, potassium dodecatangestocobaltate trihydrate (K$_5$CoW$_{12}$O$_{40} \cdot$3H$_2$O) was obtained. K$_5$Co$^{(III)}$W$_{12}$O$_{40} \cdot$3H$_2$O as catalyst was completely identified using chemical analysis, IR spectra, magnetic susceptibility and other spectral data and compared with reported physical and spectral data.[33–36]

General procedure for deprotection of 1,3-dioxolanes with K$_5$CoW$_{12}$O$_{40} \cdot$3H$_2$O: Dodecatangestocobaltate (K$_5$CoW$_{12}$O$_{40} \cdot$3H$_2$O) (32 mg, 0.01 mmol) was added to a stirred solution of *para*-chlorobenzaldehyde 1,3-dioxolane (174.5 mg, 1 mmol) in acetone (5 mL) and the resulting mixture was refluxed for 10 min. (entry 2, Table 1). After cooling, the catalyst was removed by filtration through a layer of silica gel and washed with diethyl ether (20 mL). The solvent was evaporated under reduced pressure and the residue was further purified by column chromatography on silica gel (eluent: ether–petroleum ether, 1:1) to give *para*-chlorobenzaldehyde (yield 95%).

General procedure for deprotection of tetramethylsilyl ethers with K$_5$CoW$_{12}$O$_{40} \cdot$3H$_2$O: To a mixture of C$_6$H$_5$CH$_2$OSiMe$_3$ (1 mmol, 183 mg) and acetonitrile (5 mL) was added K$_5$CoW$_{12}$O$_{40} \cdot$3H$_2$O (32 mg, 0.01 mmol). The mixture was stirred for 3 min. at room temperature (followed by TLC or GC), filtered through a short column of silica gel, washed with small amount of CHCl$_3$ and purified by column chromatography to afford the benzyl alcohol in excellent yields (100%).

Acknowledgements

References

1. Greene, T. W.; Wuts, P. G. M. *Protection Groups in Organic Synthesis*, 2nd ed.; John Wiley & Sons: New York, 1991 and references cited therein.
2. For example, see: (a) Johnstone, C.; Kerr, W. J.; Scott, J. S. *Chem. Commun.* **1996**, 341; (b) Kantam, M. L.; Swapna, V.; Santhi, P. L. *Synth. Commun.* **1995**, *25*, 2529; (c) Caballero, G. M.; Gros, E. G. *Synth. Commun.* **1995**, *25*, 395; (d) Eash, K. J.; Pulia, M. S.; Wieland, L. C.; Mohan, R. S. *J. Org. Chem.* **2000**, *65*, 8399; (e) Chiang, C.-C.; Chen, Y.-H.; Hsieh, Y.-T.; Luh, T.-Y. *J. Org. Chem.* **2000**, *65*, 4694–4697 and references cited therein.
3. Kocienski, P. J. *Protecting Groups*; Thieme: New York, 1994.

4. Huet, F.; Lechevalier, A.; Pellet, M.; Conia, J. M. *Synthesis* **1978**, 63.
5. Lipshutz, B. H.; Harvey, D. F. *Synth. Commun.* **1982**, *12*, 267.
6. Denis, J. N.; Krief, A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1006.
7. Mandal, A. K.; Shrotri, P. Y.; Ghogare, A. D. *Synthesis* **1985**, 221.
8. Balme, G.; Gore, J. *J. Org. Chem.* **1983**, *48*, 3336.
9. Jung, M. E.; Andrew, W. A.; Ornstein, P. L. *Tetrahedron Lett.* **1977**, 4175.
10. Ukaji, Y.; Konmoto, N.; Fujisawa, T. *Chem. Lett.* **1989**, 1623.
11. Olah, G. A.; Hussain, A.; Singh, B. P.; Malhotra, A. K. *J. Org. Chem.* **1983**, *48*, 3667.
12. Marcantoni, E.; Nobili, F. *J. Org. Chem.* **1997**, *62*, 4183–4184.
13. Collington, E. W.; Finch, H.; Smith, I. J. *Tetrahedron Lett.* **1985**, *26*, 681.
14. Liotta, C. L.; Harris, H. P. *J. Am. Chem. Soc.* **1974**, *96*, 2250.
15. Kelly, D. R.; Roberts, S. M.; Newton, R. F. *Synth. Commun.* **1979**, *9*, 295.
16. Battone, R. J.; Dixon, N. J.; Taylor, R. J. K. *Synthesis* **1980**, 234.
17. Bou, V.; Vilarrasa, J. *Tetrahedron Lett.* **1990**, *31*, 567.
18. Zhang, W.; Robins, M. J. *Tetrahedron Lett.* **1992**, *33*, 1177.
19. Corey, E. J.; Yi, K. Y. *Tetrahedron Lett.* **1992**, *33*, 2289.
20. Newton, R. F.; Reynolds, D. P.; Finch, M. A. W.; Kelly, D. R.; Roberts, S. M. *Tetrahedron Lett.* **1979**, 3981.
21. Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190.
22. Nilson, N. S.; Keay, B. A. *Tetrahedron Lett.* **1997**, *38*, 187.
23. Cort, A. D. *Synth. Commun.* **1990**, *20*, 157.
24. Fabian, J.; Capdevila, A.; Camps, F.; Guerrero, A. *J. Chem. Soc., Chem. Commun.* **1992**, 1451.
25. Clark, J. H. *Chem. Rev.* **1980**, *80*, 429.
26. Feixas, J.; Camps, F.; Guerrero, A. *Bioorg. Med. Chem. Lett.* **1992**, *2*, 467.
27. Mizuno, N.; Misono, M. *Chem. Rev.* **1998**, *98*, 199.
28. Okuhara, T.; Mizuno, N.; Misono, M. *Adv. Catal.* **1996**, *41*, 113.
29. Misono, M. In *Future Opportunities in Catalytic and Engineering Technology*; Misono, M.; Moro-oka, Y.; Kimura, S., Eds.; Elsevier: Amsterdam, 1990; p. 13.
30. Misono, M. *Stud. Surf. Sci. Catal.* **1993**, *75*, 69.
31. Izumi, C.; Urabe, Y.; Onaka, M. *Zeolite, Clay and Heteropoly Acid in Organic Reactions*; Kodansha: Tokyo/ VCH: New York, 1993; Chapter 3.
32. Habibi, M. H.; Tangestaninejad, S.; Mohammadpoor-Baltork, I.; Mirkhani, V.; Yadollahi, B. *Tetrahedron Lett.* **2001**, *42*, 2851.
33. Baker, L. C. W.; McCutcheon, T. P. *J. Am. Chem. Soc.* **1956**, *78*, 4503.
34. Baker, L. C. W.; Simmons, V. E. *J. Am. Chem. Soc.* **1959**, *81*, 4744.
35. Walmsley, F. *J. Chem. Ed.* **1992**, *69*, 936.
36. Simmons, V. E. Ph.D. Dissertation, Boston University, 1963.