CHEMISTRY LETTERS, pp. 519-522, 1989.

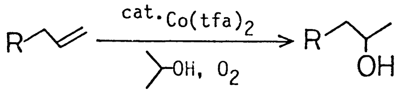
Novel Method for Oxidation of Secondary Alcohols into Ketones with Molecular Oxygen by Using Cobalt(II) Complex Catalyst

Tohru YAMADA and Teruaki MUKAIYAMA[†]
Basic Research Laboratories for Organic Synthesis,
Mitsui Petrochemical Industries, Ltd.,
Nagaura, Sodegaura-machi, Kimitsu-gun, Chiba 299-02

The oxidation of secondary alcohols into the corresponding ketones using a catalytic amount of cobalt(II) complex under an oxygen atmosphere is described. The effect of additives shows that Molecular Sieves is effective to improve the yield of ketones.

The oxidation of secondary alcohols into the corresponding ketones is one of the important reactions in organic synthetic methods, and many reagents have been developed for this purpose; for example, the Jones' reagent,1) the Collins' reagent,2) manganese oxide,3) silver carbonate,4) etc. These oxidation reagents contain poisonous metal (chromium, manganese, etc.), so they are usually employed to obtain ketones from secondary alcohols in a small scale, but not quite suitable for the mass production. On the other hand, molecular oxygen is one of the most available oxidants because of the abundance, cleanness and easiness to handle. Recently, several examples of the oxidation of secondary alcohols into the corresponding ketones using a catalytic amount of platinum,5) rhodium,6) or ruthenium7) compounds together with molecular oxygen are reported.

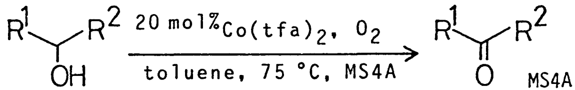
In the previous communications,8) we reported the "Oxidation-Reduction Hydration" of olefinic compounds using a catalytic amount of bis(1,3-diketonato) cobalt(II) complexes in secondary alcohol as solvent under an oxygen atmosphere (Scheme 1). In this reaction, olefinic compounds are hydrated into the corresponding alcohols, and it is confirmed that, at the same time, the secondary alcohol used as solvent is converted to the corresponding ketone.



tfa=trifluoroacetylacetonato

Scheme 1.

In this communication, we wish to report a new and convenient method for the oxidation of secondary alcohols into the corresponding ketones with molecular oxygen by using a catalytic amount of cobalt(II) complex (Scheme 2).

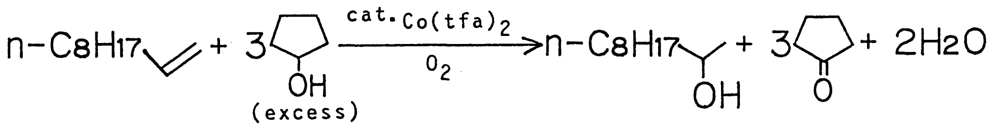


MS4A = Molecular Sieves 4A

Scheme 2.

[†] Address: Department of Applied Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162.

According to GC analysis, the molar ratio of the products in "Oxidation-Reduction Hydration", cyclopentanone (oxidized product of cyclopentanol used as solvent) : 2-decanol (hydrated product of 1-decene), was determined to be 3 : 1 (Scheme 3).



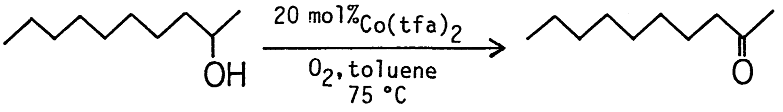
Scheme 3.

Based on the above result, we started to study the oxidation of secondary alcohol into ketone according to the following procedure; 2-decanol was treated in toluene at 75°C under an oxygen atmosphere in the presence of 20 mol% of bis(trifluoroacetylacetonato)cobalt(II),[9,10] and the corresponding ketone, 2-decanone, was obtained in 42% yield with 88% conversion (Table 1, Entry 1). Although 2-decanol was consumed under the above reaction conditions, the yield of 2-decanone was not increased as expected.[11]

During this reaction, molecular oxygen accepts hydrogen atoms from the secondary alcohol to form two molars of water, while secondary alcohol is converted into the corresponding ketone. Since water inhibited the catalytic activity of cobalt(II) catalyst or destroys cobalt(II) catalyst,[12] the reaction stopped at this stage, therefore, it was expected that the yield of ketone would increase by removal of water formed during the oxidation process.

Next, removal of the produced water was tried and as shown in Table 1, addition of powdered anhydrous sodium sulfate in the reaction mixture improved the yield of ketone up to 79% (Entry 2). Also azeotropic removal of water is effective to increase the yield (Entry 3), especially, addition of Molecular Sieves 4A (activated powder) in the reaction mixture is the most effective dehydrating method. The conversion and the yield were improved up to quantitatively and 97%, respectively (Entry 4).

Table 1. Removal of Water in Oxidation Using Cobalt(II) and Molecular Oxygen

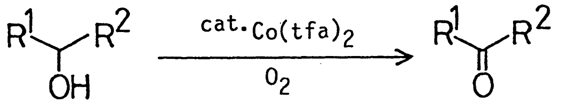


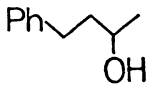
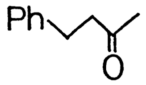
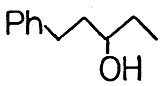
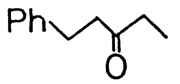
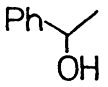
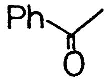
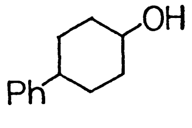
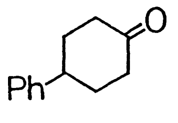
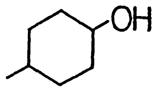
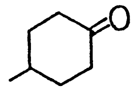
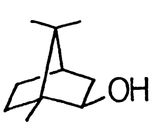
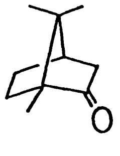
Entry	Dehydration method	Reaction time/h	Conversion/%	Yield/%[a]
1	None	12	88	42
2	Na_2SO_4[b]	10	83	79
3	azeotropic[c]	10	quant.	88
4	MS4A[d]	10	quant.	97

a) Determined by GC analysis.
b) 300 mg for 1.0 mmol of 2-decanol.
c) Azeotropic removal of water (toluene/water).
d) Molecular Sieves 4A : 300 mg for 1.0 mmol of 2-decanol.

The present procedure was applied to the oxidation of various secondary alcohols. As shown in Table 2, aliphatic secondary alcohols were oxidized into the corresponding ketones in high yield (Entries 1-4) and also in the case of alcohol having benzylic hydrogen (Entry 5). The cyclohexanol derivatives were converted to the corresponding cyclohexanone derivatives in good to high yields (Entries 6, 7). Similarly, hindered secondary alcohol, borneol, was smoothly oxidized into the ketone, camphor, in good yield (Entry 8).

Table 2. Oxidation of Various sec-Alcohols into Ketones a)



Entry	sec-Alcohol	Ketone b)	Reaction time/h	Yield/% c)
1			10	97
2			8	89 d)
3			3	98
4			6	82
5			5	quant.
6			6	73 e)
7			3	quant. e)
8			3	78

a) Reaction conditions; sec-alcohol 1.0 mmol, Co(tfa)$_2$ 0.2 mmol, solvent(toluene) 10 ml, Molecular Sieves 4A 300 mg, 75 °C, 1 atm O$_2$.
b) Satisfactory NMR and IR spectra were obtained.
c) Determined by GC analysis.
d) 5 mol% of Co(tfa)$_2$ was used.
e) Mixture of stereoisomers.

A typical experimental procedure is described for the oxidation of 2-decanol: To a toluene solution (10 ml) of 2-decanol (158 mg, 1.0 mmol) was added bis(trifluoroacetylacetonato)cobalt(II) (72 mg, 0.2 mmol),[10] and Molecular Sieves 4A (activated powder, 300 mg). The color of the solution changed from red into dark green soon. After being stirred for 10 h at 75°C under an oxygen atmosphere, the solvent was removed under reduced pressure and the crude product was purified by silica gel TLC (AcOEt-hexane) to afford 2-decanone (151 mg, 97% yield).

The mechanism of the present reaction is assumed as follows. Bis(1,3-diketonato)cobalt(II) (CoL_2) absorbs molecular oxygen to form an initial reactive intermediate, $L_2CoOO\cdot$,[13] which in turn accepts hydrogen atom from coexisted secondary alcohol, that is, secondary alcohol is oxidized into the corresponding ketone. On the other hand, without any dehydrating reagent, cobalt catalyst is destroyed by water formed during the oxidation step. Molecular Sieves accepts water to protect from undesirable interaction between catalyst and water leading to the regeneration of the original species, CoL_2.

Thus, it is noted that bis(trifluoroacetylacetonato)cobalt(II) is an excellent catalyst for the oxidation of secondary alcohols into the corresponding ketones with molecular oxygen. The addition of Molecular Sieves 4A is very effective to improve the yield of ketones.

References

1) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, J. Chem. Soc., 1946, 39.
2) J. C. Collins, W. W. Hess, and F. J. Frank, Tetrahedron Lett., 1968, 3363.
3) I. Y. Harrison, Proc. Chem. Soc., 1964, 110.
4) M. Fetizon and M. Golfier, C. R. Acad. Sci., Ser. C, 267, 900 (1968).
5) T. F. Blackburn and J. Schwartz, J. Chem. Soc., Chem. Commun., 1977, 158.
6) J. Martin, C. Martin, M. Faraj, and J.-M. Bregeault, Nouv. J. Chim., 8, 141 (1984).
7) B. Tang, S. E. Diamond, N. Neary, and F. Mares, J. Chem. Soc., Chem. Commun., 1978, 562.
8) T. Mukaiyama, S. Isayama, S. Inoki, K. Kato, T. Yamada, and T. Takai, Chem. Lett., submitted.
9) S. Inoki, K. Kato, T. Takai, S. Isayama, T. Yamada, and T. Mukaiyama, Chem. Lett., submitted.
10) Dried over 100 °C under reduced pressure (0.1 mmHg) for 10 h.
11) The reaction mixture became complicated system, and any product except 2-decanone could not be identified.
12) Also in "Oxidation-Reduction Hydration", it was confirmed that addition of water inhibited the reaction, and that removal of water improved the number of turnover based on Co(II) catalyst. K. Kato, T. Takai, T. Yamada, and T. Mukaiyama, Chem. Lett., submitted.
13) E. P. Talsi, Y. S. Zimin, and V. M. Nekipelov, React. Kinet. Catal. Lett., 27, 361 (1985).

(Received December 21, 1988)