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Catalytic Oxidation-Reduction Hydration of Olefin with Molecular Oxygen in the Presence of Bis(1,3-diketonato)cobalt(II) Complexes

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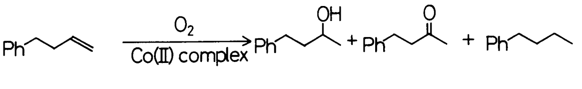
In the presence of a bis(1,3-diketonato)cobalt(II) complex, various olefins are converted to the corresponding hydrated products according to the Markownikov rule on treatment with molecular oxygen in secondary alcohol ("oxidation–reduction hydration"). Removal of water formed during the hydration reaction, especially by azeotropic method, is remarkably effective to improve yields of the hydrated products based on the cobalt(II) catalyst as bis(trifluoroacetylacetonato)cobalt(II) (Co(tfa)$_2$) or bis(2-ethoxycarbonyl-3-oxobutanalato)-cobalt(II) (Co(ecbo)$_2$).

Oxygenation of carbon–carbon double bond with molecular oxygen or air is one of the most important methods in organic synthesis and much effort has been made to develop the practical method of oxygenation by use of molecular oxygen. Especially, transition metal complexes coordinated by organic ligands are expected to be employed as promising catalysts in the above reaction, because catalytic activity would be controlled by changing the structure of the organic ligands. Several oxygenation reactions with molecular oxygen by the combined use of transition metal complexes and reducing agents have recently been studied by several groups; for example, (tetraphenylporphyrinate)manganese(III) complex/NaBH$_4$ (or colloidal Pt–H$_2$),[1] (tetraphenylporphyrinate)cobalt(II) complex/Et$_4$NBH$_4$[2] or NaBH$_4$[3] or [bis(salicylidene-γ-iminopropyl)methylamine]cobalt(II) complex/primary or secondary alcohol,[4–6] are shown to be effective as catalytic systems for oxygenations of olefins. However, there have been few reports concerning a selective oxygenation of olefins into the corresponding alcohols by use of molecular oxygen.

We have reported in the previous communication[7] that various olefins are smoothly oxygenated into the corresponding hydrated products (alcohols) along with minor products, ketones and the reduced products (alkanes), by use of bis(acetylacetonato)cobalt(II) (Co(acac)$_2$) as a catalyst. That is, when 4-phenyl-1-butene was treated with molecular oxygen in 2-propanol(solvent) at 75 °C in the presence of a catalytic amount of Co(acac)$_2$, the corresponding hydrated product, 4-phenyl-2-butanol (46% yield) was obtained along with 4-phenyl-2-butanone (8% yield) and 1-phenylbutane (17% yield)(Scheme 1).



Scheme 1.

Herein, we would like to discuss on improvement of yields of hydrated products based on the cobalt(II) catalysts and also on effect of structure of ligands in bis(1,3-diketonato)cobalt(II) complexes.

Results and Discussion

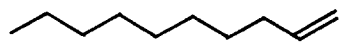
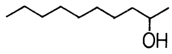
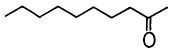
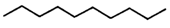
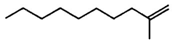
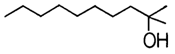
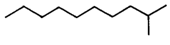
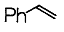
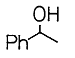
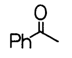
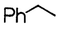
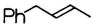
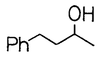
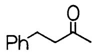
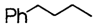
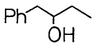
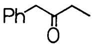
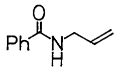
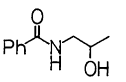
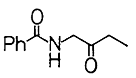
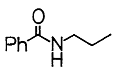
Effect of Solvents. First, effect of cobalt(II) complexes and that of alcohol solvents were studied taking the hydration of 4-phenyl-1-butene as a model reaction (Table 1). It was found that an olefinic compound, 4-phenyl-1-butene, was converted into corresponding alcohol, 4-phenyl-2-butanol, in good yields particularly in secondary alcohol, such as 2-propanol and cyclopentanol. On the contrary, when a primary alcohol, such as ethanol, or a tertiary alcohol, such as *t*-butyl alcohol, is used, no reaction takes place at all. Based on these results, it is suggested that secondary alcohol used as the reaction solvent acts as an effective reductant. That is, both the oxidation by molecular oxygen and the reduction by secondary alcohol simultaneously takes place onto the carbon–carbon

Table 1. Examination of Cobalt(II) Complexes and Solvents[a]

Entry	Co(II) complex	Solvent	Conversion/%	Yield/%[b]		
				Alcohol	Ketone	Alkane
1	Co(acac)$_2$	2-Propanol	100	46	8	17
2	Co(acac)$_2$	Cyclopentanol	100	45	9	16
3	Co(acac)$_2$	Ethanol	No reaction			
4	Co(acac)$_2$	*t*-Butyl alcohol	No reaction			
5	Co(salen)	2-Propanol	No reaction			

a) Reaction conditions; 4-phenyl-1-butene (2.0 mmol) and Co(II) complex (0.4 mmol) were heated in 10 ml of solvent at 75 °C for 1 h under O$_2$ atmosphere. b) Determined by GC analysis.

Table 2. Hydration of Various Olefins Catalyzed by $Co(acac)_2$$^{a)}$

Entry	Substrate	Products (yield/%)		
1		 $(45)^{b)}$ **1**	 $(7)^{b)}$	 $(22)^{b)}$
2		 $(57)^{b)}$ **2**	 $(43)^{b)}$	
3		 $(48)^{b)}$ **3**	 $(24)^{b)}$	 $(2)^{b)}$
4		 $(18)^{b)}$ **4a**	 $(7)^{b)}$	 $(19)^{b)}$
		 $(19)^{b)}$ **4b**	 $(7)^{b)}$	
5		 $(38)^{c)}$ **5**	 $(18)^{c)}$	 $(28)^{c)}$

a) Reaction conditions; 2.0 mmol of olefin and $Co(acac)_2$ (0.4 mmol) were heated in 10 ml of solvent at 75 °C for 1 h under O_2 atmosphere. b) Determined by GC analysis. c) Isolated yield.

double bond. Because of effective formation of hydrated products according to the above procedure, we proposed to classified this reaction as "oxidation–reduction hydration". It is noted that cobalt(II) complexes coordinated by 1,3-diketone type ligands are essential catalysts for the present "oxidation–reduction hydration". While, Co(II)(salen) complex[5] is not employed as effective catalyst at all.

Regioselectivity of Hydration. Various olefins are converted to the corresponding alcohols in good yields along with alkanes by "oxidation–reduction hydration" (see Table 2). The ketones are always formed as minor products except in the case of exo-olefin. It should be pointed out here that hydroxyl group is introduced onto the more substituted carbon atom according to the Markownikov rule. No regio-isomer was detected at all in hydration of any terminal or exo-olefin. On the other hand, a hydroxyl group is introduced without any regio-selection in the case of 1,2-disubstituted olefin.

Effect of Ligands on Catalytic Activities. Next, we examined catalytic activity of several cobalt(II) complexes having various 1,3-diketone type ligands. In order to clarify possible catalytic activity, the redox potentials of Co(II) complexes were measured at first (see Fig. 1).

As shown in Fig. 1, the catalytically active complexes are characterized by their redox potentials ($E_{1/2}$) between Co^{2+} and Co^{3+}. It was found that the complexes ranging in their redox potentials from 0 V to +0.5 V show the catalytic activities in the present reaction. Any complex having higher or lower redox potentials compared with the range mentioned above shows no catalytic activity at all (**14a**, **15a**, or **6a**).

The relationship between structure of the ligands and catalytic activity of cobalt(II) complexes can be explained as follows: in the cases of cobalt(II) complexes coordinated by ligands(L) with the electron-donating groups, such as 3-phenyl-2,4-pentanedione (**6b**), the redox potential indicates that the complex itself is easily oxidized by molecular oxygen. This oxidized complex shows no longer any catalytic activity in the present hydration. On the contrary, in the cases of cobalt(II) complexes coordinated by ligands(L) with strong electron-withdrawing groups such as hexafluoroacetylacetone (**15b**) or 4,4,4-trifluoro-1-phenyl-1,3-butanedione (**14b**), it is presumed that cobalt(II) complexes are hard to catch up molecular oxygen to exhibit no catalytic activity for the present reaction based on the measurement of the redox potential.

Next, effect of cobalt(II) complexes toward selectivity in the formation of alcohol were examined (see Table 3).[8] It was found there that formation of a minor product, alkane, was suppressed by the use of the cobalt(II) complexes coordinated by ligands having an electron-withdrawing group at 1-position of 1,3-diketone (**10b**, **11b**, **12b**, and **13b**) leading to

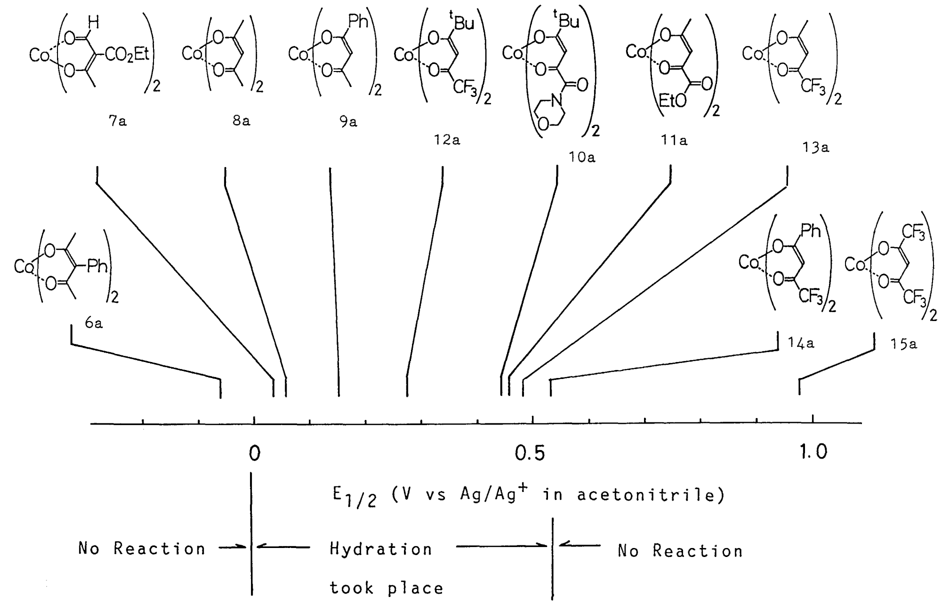
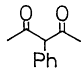
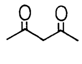
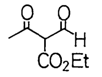
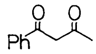
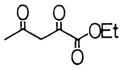
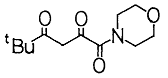
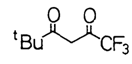
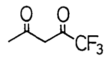
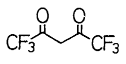


Fig. 1. Relationship of redox potentials and catalytic activities of Co(II) complexes.

Table 3. Selectivity for Alcohols in Oxidation-Reduction Hydration of 1-Decene Catalyzed by Co(II) Complexes[a]

Entry	Ligand (LH)		Time/h	Conversion/%	Yield/%[b]		
					Alcohol	Ketone	Alkane
1		**6b**		No reaction			
2		**8b** (Hacac)	2	100	45	7	22
3		**7b** (Hecbo)	1	100	72	14	2
4		**9b**	2	100	59	17	15
5		**11b**	19	87	65	10	2
6		**10b**[c]	8	94	74	7	5
7		**12b**	10	100	81	9	4
8		**13b** (Htfa)	15	100	81	13	2
9		**15b** (Hhfa)		No reaction			

a) Reaction conditions; 1-decene (2.0 mmol) and Co(II) complex (0.4 mmol) were heated in 10 ml of solvent at 75 °C under O_2 atmosphere. b) Determined by GC. c) 0.1 mmol of catalyst was used.

increased yield of the hydrated product (alcohol). The electron-withdrawing group at 2-position of 1,3-diketone (**7b**) is also effective to suppress the formation of alkane and to improve the selectivity in the formation of alcohol. However, no reaction took place when the cobalt(II) complex coordinated by ligand having two electron-withdrawing groups (**15b**) was employed.

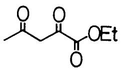
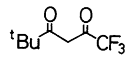
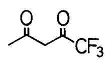
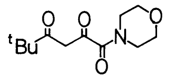
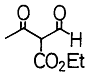
Improvement of Yield Based on the Catalyst. Further, we investigated to device a method to increase yield of alcohol based on the cobalt(II) catalyst. At first, effect of amount of cobalt(II) catalyst on yield of alcohol was examined by taking hydration of 1-decene as a model reaction (see Table 4). The reactions were carried out in the presence of 20 mol%, 5 mol%, and 2 mol% of Co(tfa)$_2$ (=bis(trifluoroacetylacetonato)-cobalt(II), **13a**) against 1-decene, respectively. When 5 mol% of **13a** was employed, the starting material, 1-decene, was almost completely consumed (94% conversion), and yield of hydrated product based on the catalyst increased up to 1390% compared with the yield (405%) by using 20 mol% of catalyst. On the contrary, in case of using 2 mol% of catalyst, the reaction stopped halfway and the conversion of 1-decene decreased to 39%, unexpectedly. Yield of hydrated product based on the catalyst (1370%) was found to be about the same to that when 5 mol% of catalyst was used (1390%). These results clearly indicated that the cobalt(II) catalyst was deactivated during the reaction.

Table 4. Yield of 2-Decanol Based on Co(tfa)$_2$[a]

Entry	Amount of Co(tfa)$_2$/mol%	Conversion/%	Yield/%[b]
1	20	100[c]	405
2	5	94[d]	1390
3	2	39[e]	1370

a) Reaction conditions; cobalt(II) complex and 1-decene (1.0 mmol) in 2-propanol (5 ml) were heated at 75 °C under O_2 atmosphere. b) Based on Co(tfa)$_2$ and determined by GC analysis. c) Reaction time; 15 h. d) Reaction time; 52 h. e) Reaction time; 52 h, and the reaction stopped.

Table 5. Yield of Alcohols Based on the Cobalt Catalysts

Entry	Ligand(LH)		Yield/%[a]
1		**11b**	300[b]
2		**12b**	750[c]
3		**13b**	1390[d]
4		**10b**	1490[d]
5		**7b**	3650[e]

a) Reaction conditions; 1-decene (2.0 mmol) and cobalt(II) complex in 2-propanol solution was heated at 75 °C under O_2 atmosphere until consumption of 1-decene stopped. Based on the cobalt(II) catalyst and determined by GC analysis. b) 20 mol% of cobalt(II) catalyst was used. c) 2 mol% of catalyst was used. d) 5 mol% of catalyst was used. e) 1 mol% of catalyst was used.

Next, the durability of several cobalt(II) catalysts was studied under the same reaction conditions (see Table 5). All the catalysts showed high selectivities toward the formation of an alcohol in the hydration of 1-decene. When the cobalt(II) complex **11a** or **12a** was employed as a catalyst, yield of 2-decanol based on the cobalt(II) catalyst decreased to 300% or 750%, respectively. On the contrary, it was found that cobalt(II) complex **7a** (bis(2-ethoxycarbonyl-3-oxobutanalato)-cobalt(II), Co(ecbo)$_2$) is hard to be deactivated under the present reaction conditions and the hydrated product was obtained in 3650% yield based on the catalyst.

As deactivation was observed even in the reaction catalyzed by Co(ecbo)$_2$, it is reasonable to assume that deactivation of cobalt(II) catalysts was caused by a co-product formed during the reaction. In the present reaction, it is suggested that secondary alcohol used as solvent (2-propanol or cyclopentanol) acts as a reductant, which subsequently turns into the corresponding ketone (acetone or cyclopentanone). Then, the amount of ketone was measured by taking the

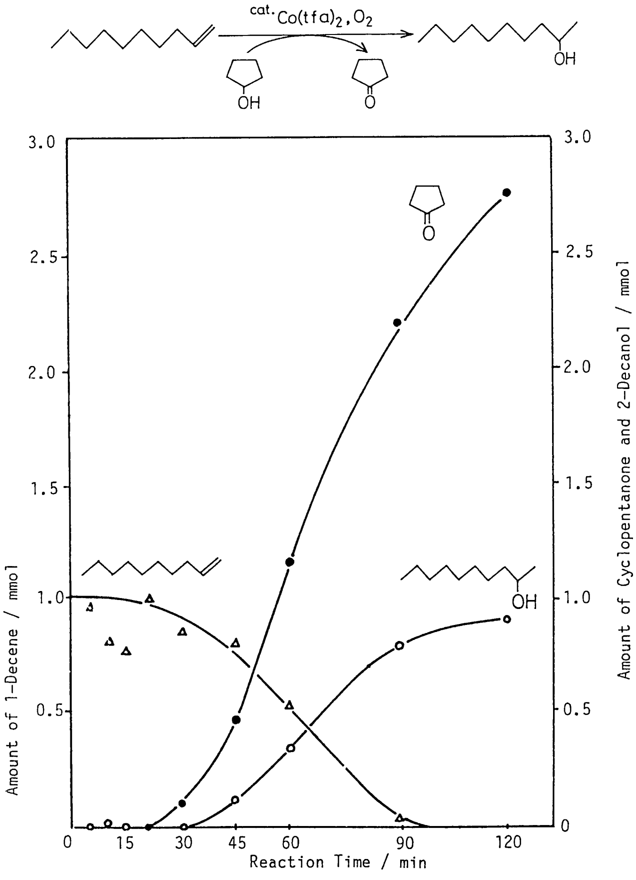


Fig. 2. Ratio of consumed reductant against hydrated product.

hydration of 1-decene in cyclopentanol as a model reaction (Fig. 2). And it was then found that the mole ratio of cyclopentanone (oxidized product of cyclopentanol) to 2-decanol (hydrated product of 1-decene) was nearly 3 : 1.

Also, it was considered that one oxygen atom of molecular oxygen is introduced into olefin to form the corresponding alcohol and another oxygen atom accepts two hydrogen atoms from secondary alcohol to form water. Then, the amount of water formed during the reaction was measured in the hydration of 1-decene in 2-propanol catalyzed by $Co(ecbo)_2$ (Fig. 3). It was observed then that the amount of water increased as the hydration proceeded and nearly two moles of water were formed along with one molar of 2-decanol.

These measurements indicate that the "oxidation-reduction hydration" of olefins with molecular oxygen catalyzed by bis(1,3-diketonato)cobalt(II) proceeds via the equation illustrated in Scheme 2.

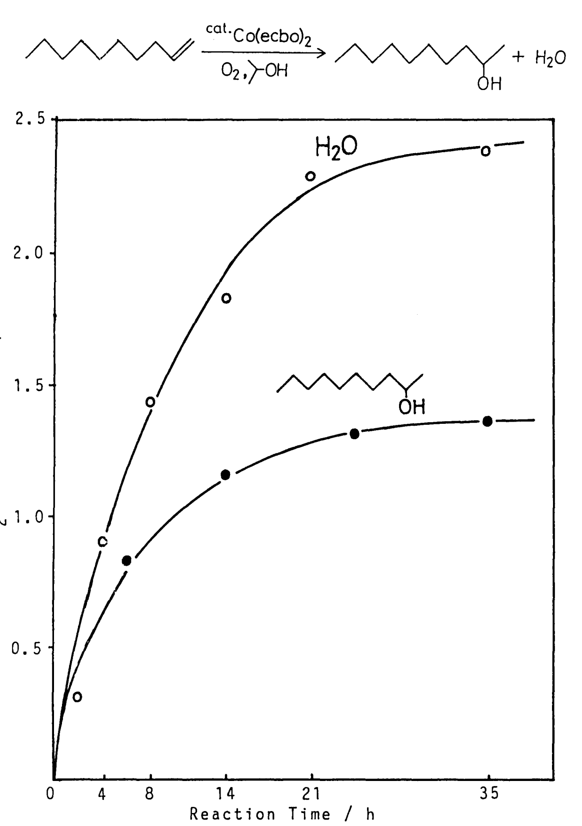
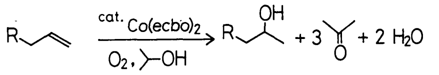


Fig. 3. Ratio of forming water against hydrated product.



Scheme 2.

During the hydration, amounts of ketone (oxidized product of secondary alcohol used as solvent) and water increases as the reaction proceeds. There is alternative possibility that ketone or water would deactivate cobalt(II) catalyst to result in insufficient yield of alcohol based on the cobalt(II) catalyst. Then, influence on yield was examined in the "oxidation-reduction hydration" of 1-decene by adding ketone or water into the reaction mixture (Table 6). By the addition of one molar of ketone (acetone) into the reaction mixture from the beginning, yield of 2-decanol was not affected at all. On the other hand, the addition of water extremely decreased yield of 2-decanol to 940% yield based on $Co(ecbo)_2$.

Therefore, it was expected that yield based on the cobalt(II) catalyst would be improved by the removal of water formed during the hydration.[9] Then, several methods for removal of water from reaction system were examined (Table 7). By addition of dehydration reagents, such as anhydrous Na_2SO_4 or Molecular Sieves 4A (activated powder, MS4A), into the reaction mixture, yields of 2-decanol based on the catalyst increased to 4120% or 8500%, respectively. Further, azeotropic procedure for removal of water was found to

Table 6. Addition of Acetone or H_2O in Oxidation-Reduction Hydration[a]

Entry	Additive[b]	Yield/%[c]
1	None	3190
2	Acetone	3040
3	H_2O	940

a) Reactions were carried out by treating 1-decene (4 mmol) and $Co(ecbo)_2$ (0.038 mmol) in 2-propanol (10 ml) under O_2 atmosphere at 75 °C for 21 h. b) To the reaction mixture was added 4 mmol of additive. c) Yield of 2-decanol based on $Co(ecbo)_2$ and determined by GC analysis.

Table 7. Effect of Removal of Water in Oxidation-Reduction Hydration[a]

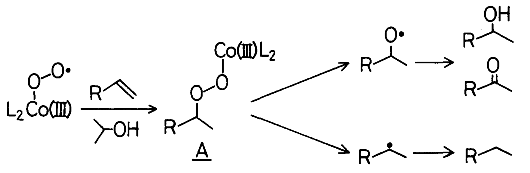
Entry	Dehydration method	Temperature/°C	Time/h	Yield/%[b]
1	None[c]	75	30	3650
2	Na_2SO_4[d]	75	30	4120
3	Molecular Sieves 4A[d]	75	30	8500
4	Azeotropic[e]	Reflux	42	9140

a) A solution of 1-decene (8 mmol) and $Co(ecbo)_2$ (0.038 mmol) in 2-propanol (20 ml) was heated under O_2 atmosphere. b) Yield of 2-decanol based on $Co(ecbo)_2$ and determined by GC analysis. c) 4 mmol of 1-decene was used. d) Dehydration reagent (2 g) was added. e) 2-Propanol (25 ml) and the apparatus shown in Fig. 4 were used.

be more effective and convenient and produce 2-decanol in 9140% yield based on Co(ecbo)$_2$ (Entry 4). It was also confirmed by GC analysis of reaction mixture that, according to azeotropic procedure, water is entirely removed during the reaction to increase yield of alcohol based on the catalyst. Therefore, it is noted that azeotropic procedure is remarkably effective to prevent from deactivation of cobalt(II) catalysts and to improve yields of alcohols based on the catalyst.

Thus, the procedure mentioned above was successfully applied to the "oxidation–reduction hydration" of various olefins. As shown in Table 8, both of acyclic and cyclic olefins are hydrated in high yields based on Co(ecbo)$_2$ (Entries 1—4). Especially, exo- and trisubstituted olefins were converted into the corresponding tertiary alcohol in more than 10000% yield based on Co(ecbo)$_2$ (Entries 2 and 4). Also, olefinic compounds having functional groups, such as ester, ether and amide groups, are hydrated into the corresponding alcohols in high yields without any decomposition of functional groups (Entries 5—7).

It was already reported that bis(1,3-diketonato)-cobalt(II) complex readily reacted with molecular oxygen to form the radical species, $L_2Co(III)OO\cdot$.[13]



Scheme 3.

As mentioned previously,[7] we assumed that the initial active oxidant is a radical species $L_2Co(III)OO\cdot$, which in turn reacts with both the carbon–carbon double bonds and secondary alcohols used as solvent to form the peroxygenated intermediate **A**. The intermediate **A** was subsequently decomposed into the corresponding alcohol, ketone or alkane.

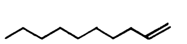
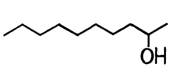
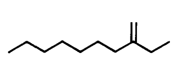
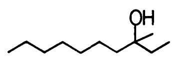
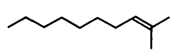
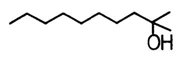
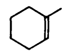
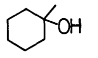
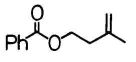
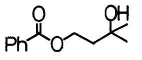
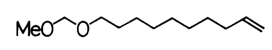
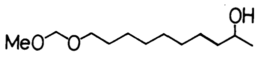
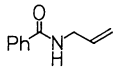
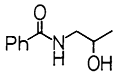
Conclusion

It is concluded that bis(1,3-diketonato)cobalt(II) complexes effectively catalyze the reaction of olefins with molecular oxygen (oxidant) in secondary alcohol (reductant) to form the corresponding alcohols in good yields along with alkanes ("oxidation–reduction hydration"). The formation of alkanes was suppressed by using Co(tfa)$_2$ or Co(ecbo)$_2$ as the catalyst, and the hydrated products (alcohols) are obtained selectively from the olefinic compounds. Further, it is referred that Co(ecbo)$_2$ is a quite effective catalyst and removal of water formed during the "oxidation–reduction hydration" remarkably improves yield of alcohols based on the catalyst. The azeotropic procedure was the most effective and convenient method to improve yields of hydrated products, alcohols. The present procedure thus provides a useful method for the preparation of alcohols directly from olefins under mild conditions.

Experimental

General: Melting points were measured on a Mettler FP62 apparatus and uncorrected.

Table 8. The Effective Oxidation–Reduction Hydration of Various Olefin by Using Co(ecbo)$_2$ and Azeotropic Method[a]

Entry	Olefinic compound	Alcohol		Time/h	Yield/%[b]
1			**1**	45	9080[c]
2			**16**	28	10110[c]
3			**2**	28	9780[c]
4			**17**	24	10370[c]
5			**18**	37	8700[d]
6			**19**	45	9340[c]
7			**5**	35	8340[d]

a) Mixture of 5.5 mmol of olefin, 0.043 mmol of Co(ecbo)$_2$, and 25 ml of 2-propanol was gently refluxed under O_2 atmosphere by using the apparatus shown in Fig. 4. b) Based on Co(ecbo)$_2$. c) Determined by GC analysis. d) Isolated yield based on Co(ecbo)$_2$.

(a) Spectrometers: IR spectra were obtained by using a JASCO Model IR-700 infrared spectrometer on KBr pellets or liquid film on NaCl. ^{1}H NMR spectra were recorded with a JEOL Model FX270 spectrometer using $CDCl_3$ as solvent and with tetramethylsilane as internal standard. FD-mass spectra were recorded with a JEOL Model JMS-DX300 mass spectrometer.

(b) Chromatography: Column chromatography was conducted under silica gel (Daisogel IR-60). Preparative TLC was carried out on silica gel (E. Merck, 5714). GC analyses were performed on a Shimadzu GC-15A or GC-14A chromatograph using a column packed with PEG20M (20%) supporting Chromosorb W (3 mm×2 m), and the peak areas were calculated on a Shimadzu chromatopack CR-5A.

(c) Solvents and Reagents: Methanol and 2-propanol were HPLC-grade and stored over molecular sieves. Ethanol, *t*-butyl alcohol, and cyclopentanol were purified by distillation and stored over molecular sieves. Molecular Sieves 4A (MS4A) was purchased from Aldrich Chemical Company, Inc. or Wako Pure Chemical Industries Ltd.

(d) Cyclic Voltammetry: All cyclic voltammograms were recorded with a BAS Model CV1B-120 in acetonitrile solution containing 0.1 M (M=mol dm^{-3}) tetrabutylammonium perchlorate (TBAP) and 0.001 M cobalt(II) complex. The working and auxiliary electrodes were platinum and the reference electrode was Ag/AgCl (Model RE-1B). Tetrabutylammonium perchlorate (TBAP) and acetonitrile (HPLC-grade) were purchased from TCI Co., Ltd. and Kanto Chemical Co., Ltd., respectively.

Preparations of 1,3-Diketones and Bis(1,3-diketonato)-cobalt(II) Complexes. Bis(acetylacetonato)cobalt(II) (**8a**, Co(acac)$_2$), bis(1,1,1-trifluoro-2,4-pentanedionato)cobalt(II) (**13a**, Co(tfa)$_2$), bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)-cobalt(II) (**15a**, Co(hfa)$_2$) were purchased from TCI Co., Ltd. Bis(3-phenyl-2,4-pentanedionato)cobalt(II) (**6a**),[14] bis(1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedionato)cobalt(II) (**12a**),[15] bis(1-phenyl-1,3-butanedionato)cobalt(II) (**9a**),[16] and bis-(1,1,1-trifluoro-4-phenyl-2,4-butanedionato)cobalt(II) (**14a**)[17] were prepared according to the reported method, respectively, and the ligands were purchased from DOJINDO laboratories (**6b** and **12b**) or TCI Co., Ltd. (**9b** and **14b**). Ethyl 2,4-dioxovalerate (**11b**) was prepared according to the reported method,[10] and 1-morpholino-5,5-dimethyl-1,2,4-hexanetrione (**10b**) was synthesized in a similar manner. **1-Morpholino-5,5-dimethyl-1,2,4-hexanetrione (10b).** Bp 160—170 °C (0.1 mmHg; 1 mmHg≈133.322 Pa, bath temp); ^{1}H NMR ($CDCl_3$) δ=1.21 (9H, s), 3.60—3.80 (8H, m), 6.03 (1H, s); IR (neat) 1721, 1695, and 1648 cm^{-1}; FD-MS *m/z* 241 (M$^+$); Found: *m/z* 241.13345. Calcd for $C_{12}H_{19}NO_4$: M, 241.13141. Found: C, 59.34; H, 8.09; N, 5.65%. Calcd for $C_{12}H_{19}NO_4$: C, 59.74; H, 7.94; N, 5.81%. The corresponding cobalt(II) complexes were prepared as follows; an alkaline (NaOH 0.1 mol) solution (50 ml) was added to aqueous methanol solution (100 ml) of 1,3-diketone (0.1 mol) at 0 °C and successively the aqueous solution (50 ml) of cobalt(II) chloride hexahydrate (0.05 mol) was added. After stirring for 0.5 h at room temperature under argon atmosphere, yellow (**11a**) or reddish brown (**10a**) precipitate was separated by filtration, washed with water, and dried in vacuo before use. **Bis(1-ethoxycarbonyl-1,3-butanedionato)cobalt(II) (11a).** Mp>300 °C; IR(KBr) 1792, 1675, 1607, and 1362 cm^{-1}. FD-MS *m/z* 373 (M$^+$); Found: *m/z* 373.03399. Calcd for $C_{14}H_{18}O_8Co$: M, 373.03337. **Bis(1-morpholino-5,5-dimethyl-1,2,4-hexanetrionato)cobalt(II) (10a).** Mp 278.0—279,4 °C; IR(KBr) 2964, 1597, 1517, 1112, and 1066 cm^{-1}. FD-MS *m/z* 539 (M$^+$); Found: *m/z* 539.18105. Calcd for $C_{24}H_{36}N_2O_8Co$: 539.18037. **Bis(2-ethoxycarbonyl-3-oxobutanalato)cobalt(II) (7a Co(ecbo)$_2$).** To a mixture of ethyl 2-(ethoxymethylene)-acetoacetate[12] (3.72 g, 0.02 mol) in water (29 ml) was added a solution of alkaline (NaOH 0.02 mol, 10 ml). After stirring for 0.5 h at room temperature, an aqueous solution (10 ml) of cobalt(II) chloride hexahydrate (2.38 g, 0.01 mol) was added, and the mixture was stirred for 0.5 h at room temperature under argon atmosphere. The pink powder was separated by filtration, washed with water (20 ml), and dried in vacuo at 90 °C for 5 h to afford Co(ecbo)$_2$ (3.43 g, 92% yield). Mp 224—226 °C, IR (KBr) 2980, 1705, and 1612 cm^{-1}, FD-MS found: *m/z* 373 (M$^+$). Found: *m/z* 373.03145. Calcd for $C_{14}H_{18}O_8Co$: M, 373.03337.

The "Oxidation-Reduction Hydration" of 4-Phenyl-1-butene Catalyzed by Co(acac)$_2$. Bis(acetylacetonato)cobalt(II) (0.4 mmol)[11] and 4-phenyl-1-butene (2.0 mmol) in 2-propanol (10 ml) were stirred at 75 °C under oxygen atmosphere for 1 h. 2-Propanol was then removed under reduced pressure. The residue was purified by TLC (silica gel) to give 4-phenyl-2-butanol (46%), 1-phenylbutane (17%), and 4-phenyl-2-butanone (8%).

The "Oxidation-Reduction Hydration" of 3-Methyl-3-butenyl Benzoate with Azeotropic Dehydration Method. Molecular Sieves 4A (1/8 pellet, Wako Pure Chemical Industries, Ltd., 4.0 g) was setted in the reaction apparatus (shown in Fig. 4) and a mixture of 3-methyl-3-butenyl benzoate (1.05 g, 5.5 mmol), Co(ecbo)$_2$ (16 mg, 0.043 mmol, 0.8 mol%), and 2-propanol (25 ml) was gently refluxed under oxygen atmosphere. After refluxing for 37 h, 2-propanol was evaporated in vacuo. The residue was purified by column chromatography on silica gel (1:1 hexane–ethyl acetate) to give 3-hydroxy-3-methylbutyl benzoate (779 mg, 8700% yield based on Co(ecbo)$_2$).

^{1}H NMR and IR Spectra of the Hydrated Products (in Table 2 or 8). 2-Decanol (1), 2-Methyl-2-decanol (2), 1-Phenylethanol (3), 4-Phenyl-2-butanol (4a), 4-Phenyl-3-butanol (4b), 3-Methyl-3-decanol (16), and 1-Methylcyclohexanol (17). ^{1}H NMR spectra, IR spectra, and retention time in GC analysis agreed with those of the authentic samples. **1-Benzoylamino-2-propanol (5);** ^{1}H NMR ($CDCl_3$) δ=1.24 (3H, d, *J*=6.0 Hz), 2.98 (1H, br), 3.30 (1H, ddd, *J*=14.0, 8.0, and 5.0 Hz), 3.65 (1H, ddd, *J*=14.0, 7.0, and 3.0 Hz), 4.03 (1H,

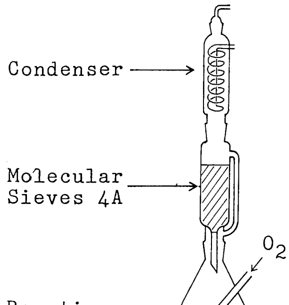


Fig. 4. Reaction apparatus.

m), 6.79 (1H, br), 7.42 (3H, m), 7.79 (2H, m); IR (KBr) 3248 and 1643 cm^{-1}. **3-Hydroxy-3-methylbutyl Benzoate (18);** ^{1}H NMR ($CDCl_3$) δ=1.33 (6H, s), 1.84 (1H, s), 1.99 (2H, t, *J*=7.0 Hz), 4.51 (2H, t, *J*=7.0 Hz), 7.43 (2H, m), 7.56 (1H, m), 8.30 (2H, m); IR (neat) 3248 and 1718 cm^{-1}. **10-Methoxymethoxy-2-decanol (19);** ^{1}H NMR ($CDCl_3$) δ=1.18, (3H, d, *J*=6.0 Hz), 1.31 (12H, m), 1.57 (2H, m), 3.36 (3H, s), 3.52 (2H, t, *J*=7.0 Hz), 3.78 (1H, m), 4.62 (2H, s); IR (neat) 3380 cm^{-1}.

Measurement of the Amount of the Consumed Reductant in "Oxidation-Reduction Hydration". A solution of 1-decene (280 mg, 2.0 mmol) and $Co(tfa)_2$$^{11)}$ (144 mg, 0.4 mmol, 20 mol%) in cyclopentanol (10 ml) were stirred at 75 °C under oxygen atmosphere. Amounts of the formed cyclopentanone and 2-decanol were measured by GC analysis (FID) with solvent (cyclopentanol) as internal standard.

Measurement of the Amount of Water Formed in "Oxidation-Reduction Hydration". A solution of 1-decene (560 mg, 4 mmol) and $Co(ecbo)_2$ (14 mg, 0.038 mmol, 0.95 mol%) in 2-propanol (20 ml) was heated at 75 °C under oxygen atmosphere. Amount of hydrated product (2-decanol) was determined by GC analysis with naphthalene as internal standard. And the amount of the formed water was measured by GC analysis (TCD) using a column packed with Porapak Type Q (3 mm×3 m) with 2-propanol (solvent) as internal standard.

Measurement of Cyclic Voltammetry. The acetonitrile solution containing 0.1 M TBAP and 0.001 M cobalt(II) complex was degassed by bubbling of argon for 15 min and the measurements were performed at the scan rate of 200 mV s^{-1}. The range of measurement was between −2.0 V and +2.0 V.

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