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An Efficient Method for the Direct Peroxygenation of Various Olefinic Compounds with Molecular Oxygen and Triethylsilane Catalyzed by a Cobalt(II) Complex

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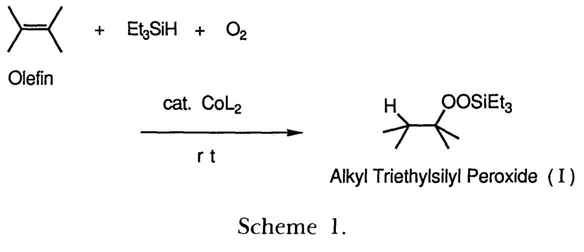
An efficient method for the direct peroxygenation of various olefinic compounds with molecular oxygen and triethylsilane (Et_3SiH) was developed by the use of a catalytic amount of a bis(1,3-diketonato)cobalt(II) complex. According to the above method, 1-phenyl-3-triethylsilydioxybutane (**2**) was directly produced from 4-phenyl-1-butene (**1**) by means of a reaction with O_2 and Et_3SiH at room temperature. Styrene (**3**) and ethyl acrylate (**5a**) were also smoothly peroxygenated to give 1-phenyl-1-triethylsilyldioxyethane (**4**) and ethyl 2-triethylsilyldioxypropionate (**6a**) by using a small amount of *t*-BuOOH as an initiator. The successive desilylation of **6a** and reduction of the resulting ethyl 2-hydroperoxypropionate (**8a**) afforded the corresponding alcohol, ethyl lactate (**10a**), in a high yield. The synthetic utility of the present peroxygenation reaction was demonstrated in the preparation of α-hydroxy esters **10a—e** from several α,β-unsaturated esters **5a—e** via the corresponding triethylsilyldioxy derivatives.

Much attention has been paid to selective oxygenations of olefinic compounds with molecular oxygen by using transition metal complexes containing various types of ligands.[1)] Recently, several oxygenation systems yielding mono-oxygenated compounds, such as ketones and alcohols, have been reported by using metalloporphyrins[2)] and cobalt Schiff-base complexes[3)] as catalysts. However, in these reactions, the substrates have been limited to several olefins, such as aromatic olefins and aliphatic olefins, little work is known concerning the oxygenation of a double bond having electron-withdrawing groups with molecular oxygen by the use of transition metal catalysts.

Previously, we have reported a series of Co(II)-catalyzed hydration reactions of olefins (Oxidation-Reduction Hydration) with molecular oxygen (oxidant) in secondary alcohol (reductant), thus forming the corresponding alcohols along with ketones.[4)] Various bis(1,3-diketonato)cobalt(II) complexes behaved as efficient catalysts in the above-mentioned reactions to give alcohols as the major products. On the other hand, it was found that triethylsilane (Et_3SiH) also behaves as an effective reductant (a hydrogen donor) in the hydration of olefin when bis(1,3-diketonato) cobalt(II) complex employs as a catalyst.[5)] On the other hand, an unexpected peroxygenated product, triethylsilyldioxy derivative, was obtained when the above reaction was carried out at room temperature (20 °C) (Scheme 1). For example, 4-phenyl-1-butene (**1**) reacted with O_2 and Et_3SiH at room temperature in the presence of a catalytic amount of bis(acetylacetonato)cobalt(II) complex to give the corresponding 1-phenyl-3-triethylsilyldioxybutane (**2**) in good a yield.

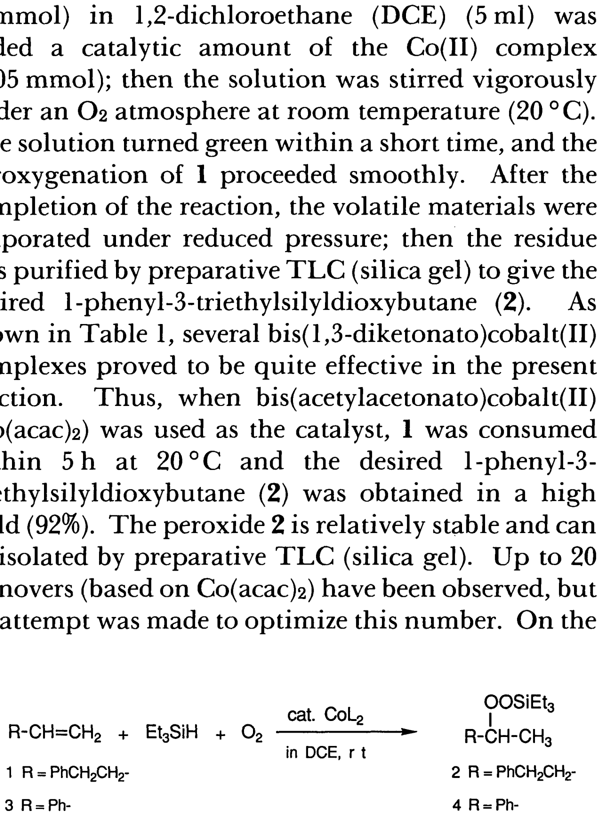


Scheme 1.

Thus, the above mentioned peroxygenation reaction provides a facile and efficient method for the direct introduction of dioxygen functionality into the carbon–carbon double bond of olefinic compounds under mild conditions. In addition, the triethylsilyldioxy derivative is considered to be a potentially useful synthetic intermediate; for example, the triethylsilyldioxy derivative was easily converted into the corresponding alcohol in a high yield by successive desilylation and reduction. During the course of our further study of the scope of the preparative utility of the present peroxygenation reaction, it was found that several α,β-unsaturated esters are also peroxygenated according to the present method to produce the corresponding triethylsilyldioxy derivatives. However, a rather long of induction period was observed in the peroxygenation of α,β-unsaturated esters or styrene, and the yields were relatively low. The induction period was, however, effectively shortened by the addition of a small amount of *t*-BuOOH as an initiator. According to this modified method, the peroxygenations of several α,β-unsaturated esters **5a—e** were successfully performed to yield the corresponding α-triethylsilyldioxy esters **6a—e** under mild conditions. Further, the successive desilylation of **6a—e** and reduction of the resulting hydroperoxides gave the corresponding α-hydroxy esters **10a—e** in good yields. Since it is known that the α-hydroxy esters are generally difficult to prepare by the direct hydration of α,β-unsaturated esters, the present procedure provides a convenient method for the preparation of α-hydroxy esters from α,β-unsaturated esters. In the present paper, we wish to describe in detail modified method for the peroxygenation of olefinic compounds and the hydration of several α,β-unsaturated esters **5a**—**e**.

Results and Discussion

Peroxygenation of 4-Phenyl-1-butene (1) and Styrene (3) with O_2 and Et_3SiH. The peroxygenation of 4-phenyl-1-butene (**1**) with Et_3SiH was examined first by using several cobalt(II) complexes as catalysts. The reactions were carried out according to the following procedure: To a mixture of **1** (1 mmol) and Et_3SiH (2 mmol) in 1,2-dichloroethane (DCE) (5 ml) was added a catalytic amount of the Co(II) complex (0.05 mmol); then the solution was stirred vigorously under an O_2 atmosphere at room temperature (20 °C). The solution turned green within a short time, and the peroxygenation of **1** proceeded smoothly. After the completion of the reaction, the volatile materials were evaporated under reduced pressure; then the residue was purified by preparative TLC (silica gel) to give the desired 1-phenyl-3-triethylsilyldioxybutane (**2**). As shown in Table 1, several bis(1,3-diketonato)cobalt(II) complexes proved to be quite effective in the present reaction. Thus, when bis(acetylacetonato)cobalt(II) ($Co(acac)_2$) was used as the catalyst, **1** was consumed within 5 h at 20 °C and the desired 1-phenyl-3-triethylsilyldioxybutane (**2**) was obtained in a high yield (92%). The peroxide **2** is relatively stable and can be isolated by preparative TLC (silica gel). Up to 20 turnovers (based on $Co(acac)_2$) have been observed, but no attempt was made to optimize this number. On the other hand, when Co(salen)[7] or Co(smdpt)[8] was used as the catalyst, although a small amount of olefin **1** was consumed, the desired peroxygenation reaction did not take place and the generation of **2** was not detected under the same reaction conditions.



$$R\text{-}CH{=}CH_2 + Et_3SiH + O_2 \xrightarrow[\text{in DCE, r t}]{\text{cat. }CoL_2} R\text{-}\overset{OOSiEt_3}{\overset{|}{C}}H\text{-}CH_3$$

1 R = $PhCH_2CH_2$-
3 R = Ph-
2 R = $PhCH_2CH_2$-
4 R = Ph-

Scheme 2.

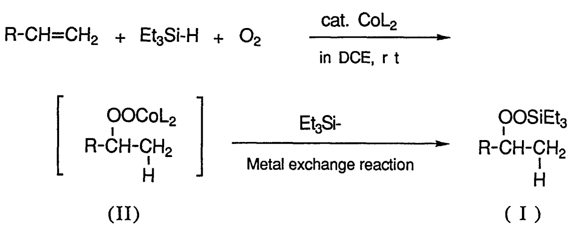
Styrene (**3**) was also peroxygenated under the same reaction conditions by using the $Co(acac)_2$ catalyst to give 1-phenyl-1-triethylsilyldioxyethane (**4**) in a 30% yield, along with acetophenone, after an induction period of a certain length. The time sequence of the reaction of **3** by the use of $Co(acac)_2$ showed that the generation of **4** can be detected after 5 h, though the starting material **3** still remained even after 24 h.

A similar induction period was observed in the same peroxygenation of **3** by using several bis(1,3-diketonato)cobalt(II) complexes as catalysts. For example, when $Co(tfa)_2$ was used as the catalyst, the peroxygenation reaction did not start for at least 6 h, and the yield of **4** was relatively low. On the other hand, when $Co(modh)_2$ or $Co(dpm)_2$ was used as the catalyst in the above reaction, the peroxygenation of **3** proceeded smoothly without any induction period to give **4** in a high yield. Therefore, it may be inferred that the length of the induction period apparently depends on the structures both of the olefins and the ligands of cobalt(II) complexes. The induction period can be effectively shortened by the addition of a small amount of *t*-BuOOH as an initiator to the reaction mixture. Thus, when a small amount of *t*-BuOOH (0.05 mmol) was added to a mixture of **3** (1 mmol), Et_3SiH (2 mmol), and a catalytic amount of $Co(acac)_2$ (0.05 mmol) at room temperature (20 °C), the reaction mixture immediately turned green and the peroxygenation reaction began smoothly without any induction period. Styrene was consumed within 5 h, and the desired product **4** was obtained in an 85% yield. The α-cumenyl hydroperoxide (CHP) also acts as an effective initiator in the above reaction. On the other hand, no effect was observed when $(t\text{-}BuO)_2$ was added

Table 1. Peroxygenation of Olefins **1** and **3**[a]

Entry	Olefin	CoL_2[b]	Additive[c]	Reaction time/h	Conv. of olefin/%	Yield of peroxide/%
1	**1**	$Co(acac)_2$	—	5	100	94
2	**1**	$Co(dpm)_2$	—	5	100	90
3	**1**	$Co(tfa)_2$	—	12	90	80
4	**1**	$Co(modh)_2$	—	3	100	92
5	**1**	Co(salen)	—	24	12	0
6	**1**	Co(smdpt)	—	24	10	0
7	**3**	$Co(acac)_2$	—	24	52	30
8	**3**	$Co(tfa)_2$	—	12	82	73
9	**3**	$Co(modh)_2$	—	3	100	96
10	**3**	$Co(acac)_2$	*t*-BuOOH	5	100	85
11	**3**	$Co(acac)_2$	CHP[f]	5	100	82
12	**3**	$Co(tfa)_2$	*t*-BuOOH	5	100	85

a) All reactions were carried out in 1,2-dichloroethane under an O_2 atmosphere at room temperature (20 °C). Molar ratio of olefin : Et_3SiH : CoL_2=1 : 2 : 0.05. b) Dried in vacuo at 80 °C before use. c) A catalytic amount of hydroperoxide was used. *t*-BuOOH; anhydrous 3 mol dm^{-3} solution in 2,2,4-trimethylpentane. d) Determined by GC. e) Isolated yields. f) CHP=α-cumenylhydroperoxide.



Scheme 3.

to the reaction mixture.

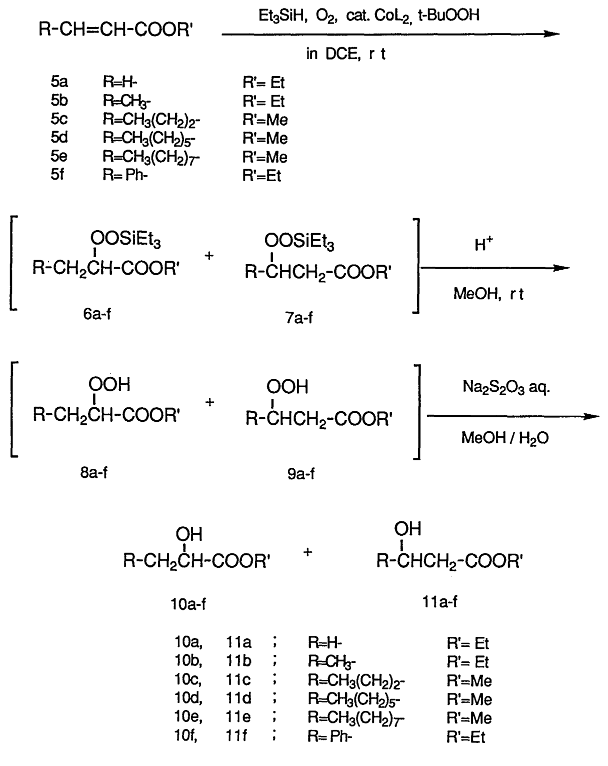
The mechanistic role of hydroperoxide has not yet been made clear, however, it is assumed that hydroperoxide participates directly in the generation of a cobalt peroxide adduct (**II**) by the oxidation of the Co(II) complex into a Co(III) complex. The key intermediate **II** is in turn, changed into the desired alkyl triethylsilyl peroxide (**I**) by means of the metal-exchange reaction between the cobalt peroxide adduct (**II**) and triethylsilane. In the absence of hydroperoxide, an initiator, the rate of the generation of **II** from CoL_2 is strongly influenced by the structures of both olefins and the ligands of cobalt(II) complexes, as is demonstrated in Table 1. Therefore, it is noted that the generation of the cobalt peroxide adduct (**II**) is an essential step in the present peroxygenation reaction.

Peroxygenation of α,β-Unsaturated Esters. From the synthetic point of view, it is strongly desirable to develop an efficient method for the oxygenation of an olefinic bond having electron-withdrawing substituents, such as esters and ketones, with molecular oxygen. Now, it was found that the present modified catalyst system ($Co(acac)_2$+*t*-BuOOH) effectively promotes the peroxygenation of α,β-unsaturated esters to give the corresponding α-triethylsilyldioxy esters under mild conditions. Thus, even ethyl acrylate (**5a**), which is difficult to introduce oxygen into its α position according to conventional methods, was easily peroxygenated at room temperature without any induction period to give the ethyl 2-triethylsilyldioxypropionate (**6a**) in a good yield (see Entries 3—5 in Table 2). Although the desired product **6a** was also obtained in the absence of *t*-BuOOH, the yield of **6a** was low and a long induction period (ca. 6 h) was observed (Entries 1 and 2 in Table 2). In general, the triethylsilyldioxy compounds are relatively stable and are easily isolated by means of preparative TLC (silica gel) or column chromatography (silica gel). Further, the triethylsilyldioxy compound **6a** can be purified by distillation under reduced pressure without decomposition. As far as we kwow, the α-triethylsilyldioxy ester **6a** is one of a new class of peroxides and can be expected to be a useful synthetic intermediate.[9]

Table 2. Preparation of **6a** from Ethyl Acrylate (**5a**)[a]

Entry	CoL_2	Additive[b]	Time/h	Yield/%[c]
1	$Co(acac)_2$	—	24	25
2	$Co(modh)_2$	—	24	18
3	$Co(acac)_2$	*t*-BuOOH	12	65
4	$Co(dpm)_2$	*t*-BuOOH	12	54
5	$Co(modh)_2$	*t*-BuOOH	12	50

a) All the reactions were carried out in 1,2-dichloroethane under an O_2 atmosphere at room temperature (25 °C). b) Anhydrous 3 mol dm^{-3} solution in 2,2,4-trimethylpentane. c) Isolated yield.



Scheme 4.

Preparation of α-Hydroxy Esters 10a—e via α-Triethylsilyldioxy Esters 6a—e. Next, the preparation of several α-hydroxy esters from α,β-unsaturated esters was examined in order to demonstrate the synthetic utility of the present peroxygenation reaction. The triethylsilyldioxy derivative **6a** was easily converted into the corresponding alcohol, ethyl lactate (**10a**), by successive desilylation and reduction. Thus, **6a** was smoothly desilylated in acidic MeOH to give ethyl 2-hydroperoxypropionate (**8a**), which was then isolated; its structure was confirmed by means of the ^{1}H NMR spectra. The hydroperoxide **8a** was subsequently reduced into ethyl lactate (**10a**) in a high yield on treatment with an aqueous solution of $Na_2S_2O_3$ at room temperature. Based on the above results, we examined a one-pot procedure for the preparation of α-hydroxy esters from α,β-unsaturated esters via the corresponding triethylsilyldioxy derivatives. As is shown in Table 3 (Entries 1—5), the peroxygenation of α,β-unsaturated esters **5a—e** proceeded smoothly within 5—21 h at room temperature

Table 3. One-Pot Procedure for Hydroxy Esters from α,β-Unsaturated Esters **5a—f**

Entry	Ester	Reaction time/h	Yield/%	
			8	**9**
1	**5a**	5	55	0
2	**5b**	21	58	6
3	**5c**	21	70	5
4	**5d**	21	83	3
5	**5e**	21	71	5
6	**5f**	5	0	82

a) Peroxygenations were carried out in 1,2-dichloroethane under an O_2 atmosphere at room temperature (25 °C). The crude products were treated by acidic MeOH and then stirred with additional $Na_2S_2O_3$ aq. for 60 min at room temperature. b) Reaction time of peroxygenations. c) Determined by GC.

when a small amount of *t*-BuOOH was used as an initiator. After the successive treatment of the crude peroxygenated products with an acidic MeOH and an aqueous $Na_2S_2O_3$ solution, the desired α-hydroxy esters **10a—e** were obtained in good yields, along with small amounts of the β-hydroxy esters **11a—e**. It may be noted that the above reaction provides a new and facile method for the preparation of α-hydroxy esters from α,β-unsaturated esters. On the other hand, when ethyl cinnamate (**5f**) was used as a substrate, the peroxygenation proceeded on its β-position to give the β-hydroxy ester, ethyl 3-hydroxy-3-phenylpropionate (**11f**), in an 82% yield. Thus, it may be noted that the regioselectivities of the above peroxygenation reactions are strongly influenced by the substituents attached to the double bond.

It is concluded that the combined use of a bis(1,3-diketonato)cobalt(II) complex and *t*-BuOOH effectively promotes the peroxygenation of a wide range of olefinic compounds with molecular oxygen and triethylsilane to give the corresponding triethylsilyldioxy derivatives in good yields. These triethylsilyldioxy derivatives are easily converted into the corresponding alcohols by successive desilylation and reduction. Thus, the present reaction provides a facile and efficient method for the preparation of peroxides directly from olefinic compounds under mild conditions. Further, the synthetic utility of the above reaction is demonstrated by the preparation of the α-hydroxy ester from the α,β-unsaturated ester via the corresponding triethylsilydioxy derivative.

Experimental

General. The melting points were measured on a Mettler FP62 apparatus and are uncorrected. The IR spectra were obtained by using a JASCO Model IR-700 infrared spectrometer on KBr pellets or liquid film on NaCl. The ^1H NMR spectra were recorded with a JEOL Model FX270 spectrometer, using $CDCl_3$ as the solvent and with tetramethylsilane as the internal standard. The FD-mass spectra were recorded with a JEOL Model JSM=DX300 mass spectrometer. Preparative TLC was performed on Merck PLC apparatus (Art. 5717 and Art. 13895). Column chromatography was conducted under silica gel (Daisogel IR-60). The GLC analyses were performed on a Shimadzu GC-14A chromatograph using a capillary column (CBP-20 M-25 0.25×25000 mm) while the peak areas were calculated on a Shimadzu chromatopack CR-5A. The triethylsilane was purchased from the Shin-Etsu Chemicals Co. and was used without further purification. The *t*-BuOOH was purchased from the Aldrich Co. as an anhydrous 3 mol dm^{-3} solution in 2,2,4-trimethylpentane. The α-cumenyl hydroperoxide was purchased from Nacalai Tesuque. The 1,2-dichloroethane was stored over 4A Molecular Sieves. The 4-phenyl-1-butene (**1**), styrene (**3**), ethyl acrylate (**5a**), ethyl crotonate (**5b**), and ethyl cinnamate (**5f**) were purchased from the TCI Co., Ltd., and were freshly distilled before use. The other α,β-unsaturated esters[10] (**5c—e**) were prepared from the corresponding α,β-unsaturated carboxylic acids, which has themselves been purchased from the TCI Co., Ltd.

Bis(1,3-diketonato)cobalt(II) Complexes. The bis(2,4-pentanedionato)cobalt(II), bis(acetylacetonato)cobalt(II), (Co(acac)$_2$), and bis(1,1,1-trifluoro-2,4-pentanedionato)cobalt(II) (Co(tfa)$_2$) were purchased from the TCI Co., Ltd., and were dried at 70 °C under a reduced pressure before use.

Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)cobalt(II) (bis(dipivaloylmethanato)cobalt(II), Co(dpm)$_2$), was prepared according to the previously reported method[11] and then purified by sublimation (120 °C, 0.5 mmHg; 1 mmHg≈133.322 Pa). Bis(1-morpholino-5,5-dimethyl-1,2,4-hexanetrionato)cobalt(II) (Co(modh)$_2$).

a) Preparation of Ligand: To a suspension solution of *t*-BuOK (11.2 g, 0.1 mol) in toluene (200 ml) was added a toluene solution (50 ml) of 3,3-dimethyl-2-butanone (12 g, 0.12 mol) and ethyl morpholineglyoxalate[12] (18.7 g, 0.1 mol) at 100 °C. The resulting suspension was stirred vigorously for 0.5 h, quenched with a 10% aqueous HCl solution (100 ml), and extracted with ether. The organic layer was washed with brine, and dried over Na_2SO_4. After the removal of the solvent, the residue was purified by column chromatography (Disogel, IR-60, hexane–EtOAc) to give 1-morpholino-5,5-dimethyl-1,2,4-hexanetrione (**12**) (8.7 g, 36%); ^1H 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.

b) Preparation of Co(II) Complex: To an aqueous solution (100 ml) of NaOH (800 mg, 20 mmol) and **10** (4.82 g, 20 mmol) was slowly added an aqueous solution (20 ml) of cobalt(II) chloride (1.3 g, 10 mmol). After the mixture had been stirred at 60 °C for 2 h, the precipitate was separated by filtration, washed with water, and dried in vacuo to give Co(modp)$_2$ as a light brown powder (yield 3.77 g, 70%); mp 278.0—279.4 °C (decomp); IR (KBr) 2964, 1597, 1517, 1112, and 1066 cm^{-1}; FD-MS *m/z* 539 (M^+). Found: *m/z* 539.18105. Calcd for $C_{24}H_{36}N_2O_8Co$: M, 539.18037.

General Procedure for Peroxygenation of Olefins. A solution of olefin (1 mmol), Et_3SiH (232 mg, 2 mmol), *t*-BuOOH (0.05 mmol, if needed), and a catalytic amount of the cobalt(II) complex (0.05 mmol) was stirred vigorously under an oxygen atmosphere at room temperature (20 °C).

After the completion of the reaction, the volatile materials were evaporated under reduced pressure; then the residue was purified by preparative TLC (silica gel) to give the desired triethylsilyldioxy derivatives.

1-Phenyl-3-triethylsilyldioxybutate (2): Colorless oil; Bp 120—122 °C (0.05 mmHg); ^{1}H NMR ($CDCl_3$) δ=0.68 (6H, q, J=8 Hz), 0.99 (9H, t, J=8 Hz), 1.24 (3H, d, J=7 Hz), 1.72—2.10 (2H, m), 2.65—2.76 (2H, m), 4.00—4.10 (1H, m), 7.17—7.30 (5H, m); Found: C, 68.38; H, 10.26; Si, 10.30%; Calcd for $C_{16}H_{28}O_2Si$: C, 68.51; H, 10.06; Si, 10.02%.

1-Phenyl-1-triethylsilyldioxyethane (4): Colorless oil; Bp 102—104 °C (0.05 mmHg); ^{1}H NMR ($CDCl_3$) δ=0.65 (6H, q, J=8 Hz), 0.95 (9H, t, J=8 Hz), 1.49 (3H, d, J=6 Hz), 4.98 (1H, q, J=6 Hz), 7.27—7.34 (5H, m); Found: C, 66.60; H. 9.33; Si, 11.32%; Calcd for $C_{14}H_{24}O_2Si$: C, 66.61; H, 9.58; Si, 11.13%.

Ethyl 2-Triethylsilyldioxypropionate (6a): Colorless oil; Bp 91—92 °C (0.05 mmHg); ^{1}H NMR ($CDCl_3$) δ=0.71 (3H, q, J=8 Hz), 0.99 (3H, t, J=8 Hz), 1.30 (3H, t, J=7 Hz), 1.34 (3H, q, J=7 Hz), 4.23 (2H, q, J=7 Hz), 4.48 (1H, q, J=7 Hz); Found: C, 53.19; H, 9.79; Si, 11.60%; Calcd for $C_{11}H_{24}O_2Si$: C, 53.19; H, 9.74; Si, 11.31%; IR (neat) 1758, 1754, and 1199 cm^{-1}.

Preparation of Ethyl Lactate (10a): To a methanol solution (10 ml) of **6a** (248 mg, 1 mmol) was added a drop of 10% hydrochloric acid at room temperature; the resulting mixture was stirred at the ambient temperature for 30 min. The reaction mixture was then poured into water (30 ml), and the product was extracted with ether (20 ml×3), washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by preparative TLC (silica gel) to give 123 mg of **8a** as a colorless oil (yield 90%). ^{1}H NMR ($CDCl_3$); δ=1.32 (3H, t, J=7 Hz), 1.41 (3H, d, J=7 Hz), 4.26 (2H, q, J=7 Hz), 4.62 (1H, q, J=7 Hz), 9.38 (1H, s, -OOH); IR (neat) 3406, 1737, 1218, and 1153 cm^{-1}. To a methanol solution (10 ml) of **8a** (123 mg, 0.92 mmol) was added an aqueous $Na_2S_2O_3$ solution (saturated, 10 ml); the resulting mixture was stirred under an argon atmosphere for 1 h. The product was extracted with ethyl acetate, and the organic layer was washed with brine, dried over Na_2SO_4, and evaporated. The residue was purified by preparative TLC (silica gel) to give 104 mg of **10a** as a colorless oil (yield 96% from **8a**). ^{1}H NMR ($CDCl_3$); δ=1.30 (3H, t, J=7 Hz), 1.33 (3H, d, J=7 Hz), 4.25 (2H, q, J=7 Hz), 4.25 (1H, m); IR (neat) 3450 and 1737 cm^{-1}.

Preparation of α-Hydroxy Esters. A Typical Method: Ethyl 2-Hydroxybutyrate (10b): To a solution of **5b** (114 mg, 1 mmol), triethylsilane (228 mg, 2 mmol), and $Co(acac)_2$ (13 mg, 0.05 mmol) in 1,2-dichloroethane was added t-BuOOH (12 mg of 3 mol dm^{-3} solution in 2,2,4-trimethylpentane, 0.05 mmol); the reaction mixture was then stirred vigorously under an oxygen atmosphere at room temperature for 5 h. Then the volatile materials were evaporated under reduced pressure, and the resulting residue was treated with MeOH (10 ml) containing a drop of concentrated hydrochloric acid at room temperature for 0.2 h. To the reaction mixture was then added an additional aqueous $Na_2S_2O_3$ solution; the mixture was stirred vigorously for 1 h and then quenched with brine, and extracted with ethyl acetate. The organic layer was combined and dried over Na_2SO_4. The solvent was evaporated, and the residue was purified by preparative TLC (silica gel) to give **10b** (58%) and **11b** (6%).

^{1}H NMR and IR Spectra of the Hydrated Products (in Table 3): The ^{1}H NMR spectra, the IR spectra, and the retention time in GC analysis are in good agreement with those of authentic samples.

Ethyl 2-Hydroxybutyrate (10b): ^{1}H NMR ($CDCl_3/D_2O$) δ=0.97 (3H, t, J=7 Hz), 1.30 (3H, t, J=7 Hz), 1.60—1.90 (2H, m), 4.14 (1H, dd, J=4 and 6 Hz), 4.25 (2H, q, J=7 Hz): IR (neat) 3456 and 1739 cm^{-1}.

Ethyl 3-Hydroxybutyrate (11b): ^{1}H NMR ($CDCl_3/D_2O$) δ=1.24 (3H, t, J=7 Hz), 1.28 (3H, t, J=7 Hz), 2.44 (2H, AB of ABX, 8 peaks), 4.17 (2H, q, J=7 Hz), 4.10—4.20 (1H, m): IR (neat) 3476 and 1738 cm^{-1}.

Methyl 2-Hydroxyhexanoate (10c): ^{1}H NMR ($CDCl_3/D_2O$) δ=0.91 (3H, t, J=7 Hz), 1.25—1.45 (4H, m), 1.55—1.90 (2H, m), 3.79 (3H, s), 4.19 (1H, dd, J=4 and 6 Hz): IR (neat) 3500 and 1740 cm^{-1}.

Methyl 3-Hydroxyhexanoate (11d): ^{1}H NMR ($CDCl_3/D_2O$) δ=0.90 (3H, t, J=7 Hz), 1.22—1.42 (4H, m), 2.46 (2H, AB of ABX, 8 peaks), 3.72 (3H, s), 3.97 (1H, br.s): IR (neat) 3468 and 1739 cm^{-1}.

Methyl 2-Hydroxynonanoate (10d):(13) ^{1}H NMR ($CDCl_3/D_2O$) δ=0.88 (3H, t, J=7 Hz), 1.23 (10H, br.s), 1.55—1.90 (2H, m), 3.79 (3H, s), 4.15 (1H, dd, J=4 and 7 Hz): IR (neat) 3456 and 1739 cm^{-1}.

Methyl 3-Hydroxynonanoate (11d): ^{1}H NMR ($CDCl_3/D_2O$) δ=0.88 (3H, t, J=7 Hz), 1.29 (10H, br.s), 2.48 (2H, AB of ABX, 8 peaks), 3.72 (3H, s), 3.99 (1H, br.s): IR (neat) 3474 and 1739 cm^{-1}.

Methyl 2-Hydroxyundecanoate (10e):(14) ^{1}H NMR ($CDCl_3/D_2O$) δ=0.88 (3H, t, J=7 Hz), 1.26 (14H, br.s), 1.50—1.75 (2H, m), 3.79 (3H, s), 4.18 (1H, dd, J=4 and 7 Hz): IR (neat) 3456 and 1738 cm^{-1}.

Methyl 3-Hydroxyundecanoate (11e) ^{1}H NMR ($CDCl_3/D_2O$) δ=0.88 (3H, t, J=7 Hz), 1.27 (14H, br.s), 2.50 (2H, AB of ABX, 8 peaks), 3.72 (3H, s), 4.03 (1H, br.s): IR (neat) 3456 and 1738 cm^{-1}.

Ethyl 3-Hydroxy-3-Phenylpropionate (11f) ^{1}H NMR ($CDCl_3/D_2O$) δ=1.24 (3H, t, J=7 Hz), 2.73 (2H, AB of ABX, 8 peaks), 4.18 (2H, q, J=7 Hz), 5.13 (1H, br.s), 7.20—7.50 (5H, m): IR (neat) 3452 and 1731 cm^{-1}.

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References

1) a) "Metal-catalyzed Oxidations," in "The Role of Oxygen in Chemistry and Biochemistry," ed by W. Ando and Y. Morooka, Elsevier, Amsterdam-Oxford-New York-Tokyo (1988), Part B, pp. 175—350, and references cited therein; b) I. Tabushi and N. Koga, *J. Am. Chem. Soc.*, **101**, 6456 (1979); I. Tabushi and A. Yamazaki, *ibid.*, **103**, 2884 (1983); I. Tabushi, M. Kodera, and M. Yokoyama, *ibid.*, **107**, 4466 (1985).

2) T. Okamoto and S. Oka, *J. Org. Chem.*, **49**, 1589 (1984); S. Inoue, Y. Ohkatsu, M. Ohno, and T. Ooi, *Nippon Kagaku Kaishi*, **1985**, 387.

3) A. Zombeck, D. E. Hamilton, and R. S. Drago, *J. Am. Chem. Soc,.* **104**, 6782 (1982); D. E. Hamilton, R. S. Drago, and A. Zombeck, *ibid.*, **109**, 374 (1987); B. B. Corden, R. S. Drago, and R. P. Periot, *ibid.*, **107**, 2903 (1985); A. Nishinaga, T. Yamada, H. Fujisawa, K. Ishizaki, H. Ihara, and T.

Matsuura, *J. Mol. Catal.*, **48**, 249 (1988); A. Nishinaga, H. Yamato, T. Abe, K. Maruyama, and T. Matsuura, *Tetrahedron Lett.*, **29**, 6309 (1988).

4) T. Mukaiyama, S. Isayama, S. Inoki, K. Kato, T. Yamada, and T. Takai, *Chem. Lett.*, **1989**, 449; S. Inoki, K. Kato, T. Takai, S. Isayama, T. Yamada, and T. Mukaiyama, *ibid.*, **1989**, 515.

5) S. Isayama and T. Mukaiyama, *Chem. Lett.*, **1989**, 569.

6) S. Isayama and T. Mukaiyama, *Chem. Lett.*, **1989**, 573.

7) Co(salen), bis(salicylideneethylenediamine)cobalt(II), was prepared by the previously reported procedure: A. Nishinaga, H. Tomita, K. Nishizawa, T. Matsuura, S. Ooi, and K. Hirotsu, *J. Chem. Soc., Dalton Trans.*, **1981**, 1504.

8) Co(smdpt), bis(salicylidene-γ-iminopropylmethylamine)cobalt(II), was prepared as previously described: B. B. Corden, R. S. Drago, and R. P. Periot, *J. Am. Chem. Soc.*, **107**, 2903 (1985).

9) The several methods for the preparation of organosilyl peroxides have been reported: D. Brandes and A. Blaschette, *J. Organomet. Chem.*, **78**, 1 (1974); R. L. Dannley and G. Jalics, *J. Org. Chem.*, **30**, 2417 (1965).

10) The α,β-unsaturated esters could be easily prepared from the corresponding acid chlorides of α,β-unsaturated carboxylic acids.

11) F. A. Cotton and R. H. Soderberg, *Inorg. Chem.*, **3**, 1 (1964).

12) V. L. Heinisch, C. Kuchler, and W. Kucheler, *Arzneim. Forsch.*, **18**, 1324 (1968).

13) H. Hagiwara, K. Kimura, and H. Uda, *J. Chem. Soc., Chem. Commun.*, **1986**, 860.

14) J. E. Thompson, *J. Org. Chem.*, **32**, 3947 (1967).