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Hydration of Olefins with Molecular Oxygen and Triethylsilane Catalyzed by Bis(trifluoroacetylacetonato)cobalt(II)

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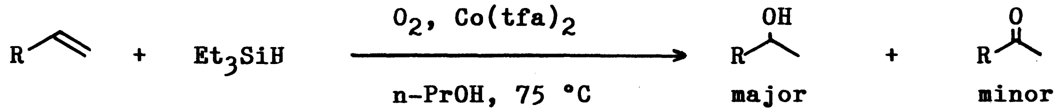
In the presence of a catalytic amount of bis(trifluoroacetylacetonato)cobalt(II), various olefins react smoothly with molecular oxygen (oxidant) and triethylsilane (reductant) to afford the corresponding alcohols regioselectively in good yields along with ketones.

Transition metal catalyzed oxygenation of olefins with molecular oxygen is one of important processes in organic synthesis. Recently, metalloporphyrin catalyzed oxygenations of olefins combined with several reductants have been widely studied in connection with enzymatic oxidations by cytochrome P-450. In these systems, tetrahydroborate[1,2] or molecular hydrogen over colloidal platinum[3-5] is employed as reductant to produce ketones, alcohols, and epoxides. On the other hand, Drago[6,7] and Nishinaga[8] reported cobalt Schiff base complexes catalyzed oxygenations of olefins by using primary alcohols as a reductant giving ketones along with alcohols.

We have already reported a convenient method for hydration of olefins promoted by bis(1,3-diketonato)cobalt(II) complexes in 2-propanol (reductant) under O_2 atmosphere.[9,10] In the course of our continuing study, we found that triethylsilane also acts as an effective reductant in the above reaction. For example, various olefins were smoothly hydrated with molecular oxygen and triethylsilane catalyzed by bis(trifluoroacetylacetonato)cobalt(II) $Co(tfa)_2$ in 1-propanol at 75 °C. Triethylsilane is frequently employed as useful reducing agent of organic compounds,[11,12] however, as far as we know, the above reaction is the first example of the use of silane in combination with molecular oxygen. In this communication, we wish to report the Oxydation-Reduction Hydration of olefins with O_2



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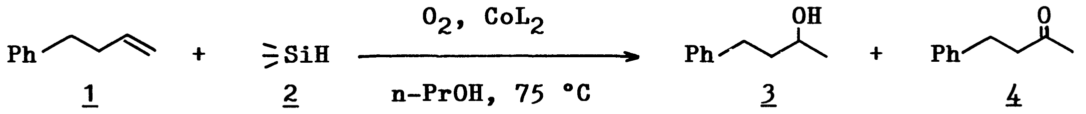
(oxidant) and triethylsilane (reductant).

In the first place, the effects of ligands of catalysts and those of substituents of silanes were screened taking the hydration of 4-phenyl-1-butene (1) as a model reaction (Table 1).

Table 1. Reactions of 4-Phenyl-1-butene (1)[a]



Entry	Silane (2)	Catalyst[b] (CoL_2)	Reaction time /h	Conv. of 1 /%[c]	Yield /%[c] 3	Yield /%[c] 4
1	Et_3SiH	$Co(tfa)_2$	8	100	67	8.0
2	Et_3SiH	$Co(acac)_2$	4	65	35	4.2
3	Et_3SiH	$Co(ppdo)_2$	8	60	32	3.8
4	$PhMe_2SiH$	$Co(tfa)_2$	8	15	8	4.0
5	$PhMe_2SiH$	$Co(acac)_2$	4	11	6	2.2
6	Ph_2SiH_2	$Co(tfa)_2$	20	6	0	2.0
7	Ph_3SiH	$Co(tfa)_2$	20	0	-	-
8	$i\text{-}Pr_3SiH$	$Co(tfa)_2$	20	0	-	-
9	$(MeO)_3SiH$	$Co(tfa)_2$	20	0	-	-

a) All reactions were carried out by treating 1 mmol of 4-phenyl-1-butene with 4 mmol of silane in the presence of 0.05 mmol of Co(II) complex under an oxygen atmosphere in 5 ml of n-PrOH at 75 °C.

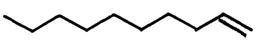
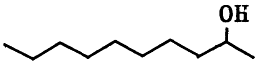
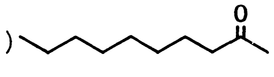
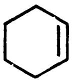
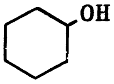
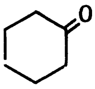
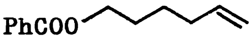
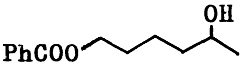
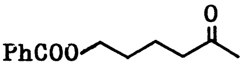
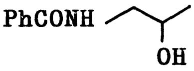
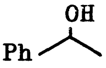
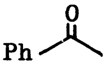
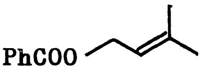
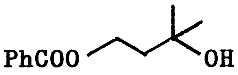
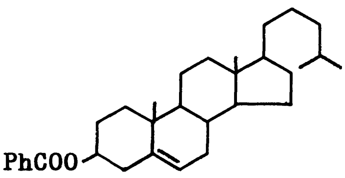
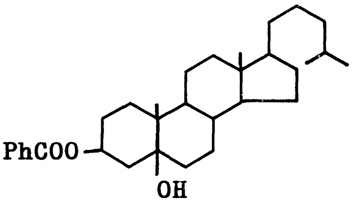
b) $Co(acac)_2$; bis(acetylacetonato)cobalt(II), $Co(ppdo)_2$; bis(1-phenyl-1,3-propanedionato)cobalt(II): All catalysts were dried over 70 °C in vacuo.

c) Determined by GC.

As shown in Table 1, $Co(tfa)_2$ effectively promoted the reaction of 1 with molecular oxygen and triethylsilane affording 4-phenyl-2-butanol (3) in 67% yield along with 4-phenyl-2-butanone (4) (Entry 1). The hydration of 1 was also catalyzed by $Co(acac)_2$ or $Co(ppdo)_2$, however, the yield of 3 was only 35% or 32%, respectively. In the above experiments, 4-phenyl-1-butanol, the regioisomer of 3, was not detected by gas chromatography analysis of the resulting reaction mixture. In addition, when dimethylphenylsilane or diphenylsilane was used as reductant, the yields of 3 became very low (Entries 4-6) and no reaction took place when triphenylsilane, triisopropylsilane, or trimethoxysilane was used instead of triethylsilane (Entries 7-9).

Several examples of the hydration reactions were demonstrated in Table 2. In every case, the reactions smoothly proceeded at 75 °C to afford the corresponding alcohols in good yields.

Table 2. The Co(tfa)$_2$ Catalyzed Reactions of Olefins with Molecular Oxygen and Triethylsilane in 1-Propanol at 75 °C.$^{a)}$

Entry	Olefin	Time /h	Products (Yield /%)$^{b)}$			
1		4		(73)$^{c)}$		(10)$^{c)}$
2		12		(60)$^{c)}$		(18)$^{c)}$
3		12		(82)$^{d)}$		(12)$^{d)}$
4		24		(72)$^{d)}$		(12)$^{d)}$
5		12		(53)$^{c)}$		(29)$^{c)}$
6		8		(87)$^{d)}$		
7		5		(85)$^{d)}$		

a) Molar ratio; Et$_3$SiH: olefin: Co(tfa)$_2$ = 4.0: 1.0: 0.05.

b) All the products gave satisfactory NMR and IR spectra.

c) Determined by GC.

d) Isolated yield.

A typical procedure is described for the reaction of 1-benzoylamino-2-propene; a mixture of 1-benzoylamino-2-propene (161 mg, 1 mmol), triethylsilane (464 mg, 4 mmol) and bis(trifluoroacetylacetonato)cobalt(II) (19 mg, 0.05 mmol) in 1-propanol (5 ml) was stirred at 75 °C under an oxygen atmosphere for 24 h. After completion of the reaction, the volatile materials were evaporated under reduced pressure and then the crude product was purified by preparative TLC (silica gel) to afford 1-benzoylamino-2-propanol (129 mg, 72%) and 1-benzoylamino-2-propanone (21 mg, 12%).

It is noted that, according to the present method, various olefins are readily converted to the corresponding alcohols in good yields under neutral conditions. Further extention of this type of reaction is now under investigation.

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