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A New Method for Preparation of Alcohols from Olefins with Molecular Oxygen and Phenylsilane by the Use of Bis(acetylacetonato)cobalt(II)

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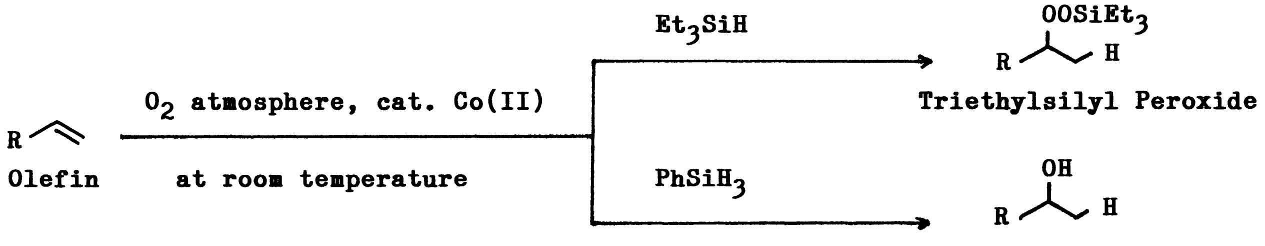
In the presence of a catalytic amount of bis(acetylacetonato)-cobalt(II), various olefins react smoothly with molecular oxygen and phenylsilane at room temperature to afford the corresponding alcohols in good yields under neutral conditions.

Much attention has been denoted to selective oxygenation of olefins with molecular oxygen by using cobalt complexes consisting of Schiff base ligands$^{1)}$ or porphyrin ligands.$^{2)}$ Recently, we found that bis(1,3-diketonato)cobalt(II) complexes effectively promote the Oxidation-Reduction Hydration of olefins into alcohols at 75°C by using secondary alcohols$^{3)}$ or triethylsilane$^{4)}$ (EtSiH$_3$) as reducing reagent under O$_2$ atmosphere. Further, we reported a novel peroxygenation reaction of olefins with O$_2$ and EtSiH$_3$ to produce the corresponding triethylsilyl peroxide at room temperature by the use of Co(II) complexes as catalysts.$^{5)}$ The above reaction provides an efficient method for the introduction of dioxygen functionality to the carbon-carbon double bond under mild conditions.

Now, various silanes were further screened in order to produce alcohols directly from olefins and we found that hydration of olefins successfully proceeds at room temperature when phenylsilane (PhSiH$_3$) is used in place of Et$_3$SiH in the above mentioned reaction. In this communication, we wish to describe a convenient method for hydration of olefins carried out at room temperature with O$_2$ and PhSiH$_3$ catalyzed by bis(acetylacetonato)cobalt(II) complex (Scheme 1).



Scheme 1.

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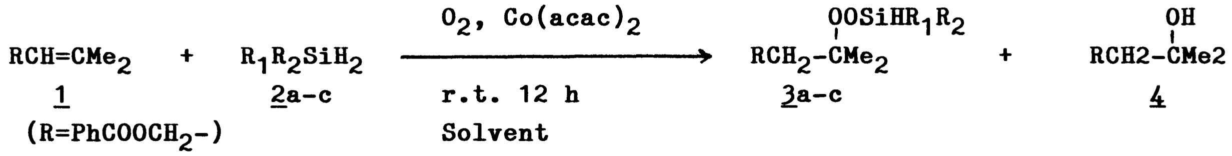
Table 1. Reaction of 1 with O_2 and Several Silanes[a]

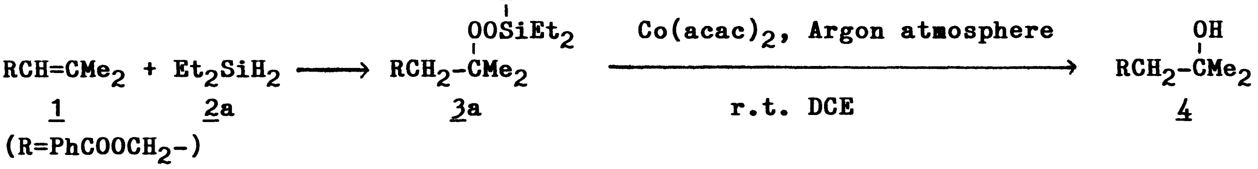


$$\underset{\substack{1\\(R=PhCOOCH_2-)}}{RCH=CMe_2} + \underset{2a-c}{R_1R_2SiH_2} \xrightarrow[\substack{r.t.\ 12\ h\\ Solvent}]{O_2,\ Co(acac)_2} \underset{3a-c}{RCH_2-\overset{OOSiHR_1R_2}{C}Me_2} + \underset{4}{RCH2-\overset{OH}{C}Me2}$$

Entry	$R_1R_2SiH_2$ 2a-c	Solvent	Conv. of 1 /%[b]	Yield /%[b]	
				3a-c	4
1	Et_2SiH_2 (2a)	$ClCH_2CH_2Cl$	quant.	90	5
2	Ph_2SiH_2 (2b)	$ClCH_2CH_2Cl$	85	60	20
3	$PhSiH_3$ (2c)	$ClCH_2CH_2Cl$	quant.	31[c]	60
4	$PhSiH_3$ (2c)	EtOAc	96	23[c]	70
5	$PhSiH_3$ (2c)	DME	quant.	6[c]	90
6	$PhSiH_3$ (2c)	THF	quant.	3[c]	93

a) All reactions were carried out by treating 1 mmol of 1 with 2 mmol of silane in the presence of 0.05 mmol of $Co(acac)_2$ under an oxygen atmosphere in 5 ml of solvent. b) Determined by HPLC. c) Isolated yield as hydroperoxide.

In the first place, the effect of substituents on silanes was examined taking 3-methyl-2-butenylbenzoate (1) as a model substrate. The reaction was performed by treating 1 (1 mmol) with silane 2 (2 mol) under O_2 in the presence of $Co(acac)_2$ (0.05 mmol). The results are summarized in Table 1. When the reaction of 1 was carried out in 1,2-dichloroethane (DCE) by using diethylsilane (2a), a small amount of desired alcohol 4 was obtained (Entry 1) along with diethylsilyl peroxide 3a[6], a major product, by column chromatography on silica gel. This diethylsilyl peroxide 3a was converted to the alcohol 4 at room temperature on treating with $Co(acac)_2$ under an argon atmosphere (Scheme 2). This result suggested that intramolecular or intermolecular reduction of the diethylsilyl peroxide 3a took place by promotion of Co(II) catalyst to afford the desired alcohol 4. The direct hydration of 1 also proceeded by using diphenylsilane 2b in DCE to give the desired alcohol 4 in 20% yield (Entry 2). Further, it was found that the alcohol 4 was obtained in 60% yield along with the corresponding phenylsilyl peroxide 3c when $PhSiH_3$ was used under the same reaction conditions (Entry 3).



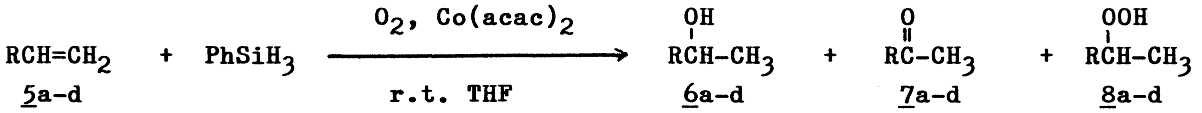
$$\underset{\substack{1\\(R=PhCOOCH_2-)}}{RCH=CMe_2} + \underset{2a}{Et_2SiH_2} \longrightarrow \underset{3a}{RCH_2-\overset{\overset{H}{|}}{\overset{OOSiEt_2}{C}}Me_2} \xrightarrow[r.t.\ DCE]{Co(acac)_2,\ Argon\ atmosphere} \underset{4}{RCH_2-\overset{OH}{C}Me_2}$$

Scheme 2.

In addition, a remarkable solvent effect was observed on the improvement of the yield of alcohol 4 in the present reaction (Entry 5 or 6). For example, when reaction was carried out in tetrahydrofuran (THF), the yield of alcohol 4 increased to 93%, and the yield of hydroperoxide decreased to only 3% (Entry 6). In the reactions of entries 4 and 5, it was assumed that phenylsilyl peroxide 3c could be produced in the first stage of this reaction. An attempt to isolate 3c from the above reaction mixture failed, instead the corresponding hydroperoxide was isolated by column chromatography.

Next, hydrations of several terminal olefins 5a-d were tried by using phenylsilane (Table 2). In all cases, reactions proceeded smoothly at room temperature and the corresponding secondary alcohols 6a-d were obtained in good yields (64-84% yields) along with methylketones 7a-d (7-24% yields). In the first stage of these reactions, the corresponding hydroperoxides 8a-d were detected by TLC analysis (silica gel) of the reaction mixture. While, in the reaction of 5-hexenylbenzoate (5a) or styrene (5b), each hydroperoxide disappeared completely in the final stage of the reaction (Entry 1 or 2). In case of 4-phenyl-1-butene (5c) or 1-decene (5d), hydroperoxide 8c or 8d still remained after 20-40 h (Entry 3 or 4). These hydroperoxides were easily reduced to alcohols on treatment with aqueous sodium thiosulfate. Thus, after completion of the reaction of 1-decene, the resulting reaction mixture was treated with aqueous sodium thiosulfate for half an hour and the yield of alcohol 6d apparently increased (Entry 5).

Table 2. Reaction of 5a-d with O_2 and Phenylsilane in THF[a]

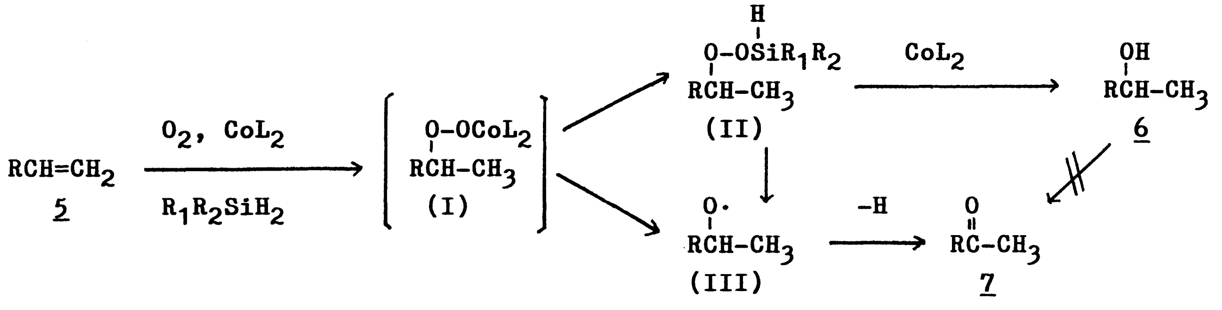


$$\underset{\mathbf{5a\text{-}d}}{RCH{=}CH_2} + PhSiH_3 \xrightarrow[\text{r.t. THF}]{O_2,\ Co(acac)_2} \underset{\mathbf{6a\text{-}d}}{\overset{OH}{RCH\text{-}CH_3}} + \underset{\mathbf{7a\text{-}d}}{\overset{O}{\overset{\|}{RC\text{-}CH_3}}} + \underset{\mathbf{8a\text{-}d}}{\overset{OOH}{RCH\text{-}CH_3}}$$

Entry	Olefin 5a-d	Reaction time /h	Conv. of 5 /%[b]	Yield /%[b]		
				6a-d	7a-d	8a-d
1	$PhCOO(CH_2)_4CH{=}CH_2$ (5a)	18	quant.	84	14	0
2	$PhCH{=}CH_2$ (5b)	20	quant.	70	24	0
3	$PhCH_2CH_2CH{=}CH_2$ (5c)	20	quant.	72	11	6
4	$CH_3(CH_2)_7CH{=}CH_2$ (5d)	40	quant.	64	7	12
5	$CH_3(CH_2)_7CH{=}CH_2$ (5d)	20[c]	quant.	82[d]	10[d]	0

a) All reactions were carried out using 1 mmol of an olefin, 2 mmol of phenylsilane and 0.05 mmol of $Co(acac)_2$ in 5 ml of THF under O_2 atmosphere. b) Isolated yield. c) After 20 h, the reaction mixture was treated with 10 ml of aqeous sodium thiosulfate for half an hour at room temperature. d) Determined by GC.

The pathway of this hydration reaction is considered as follows; the mechanism for the formation of silylperoxide (II) from olefin 5 is not yet made clear, however, it is assumed that an initially formed cobalt peroxide adduct (I) turns to the silylperoxide (II) by the metal exchange reaction between (I) and the silane. The silylperoxide (II) is in turn converted to the corresponding alcohol 6 by the promotion of Co(acac)$_2$ as evidenced in case of the reaction of diethylsilyl peroxide 3a with Co(acac)$_2$ catalyst (Scheme 3). On the other hand, time sequence of the reactions showed that ketones 7a-d were produced concomitantly with alcohols 6a-d and no significant conversion of alcohols into ketones was observed under these reaction conditions. So, it is postulated that the cobalt peroxide adduct (I) or silylperoxide (II) decomposes into an alkoxyl radical (III) by the O-O bond fission and successive release of the hydrogen atom from (III) would lead to the formation of ketone 7.



Scheme 3.

A typical procedure is described for the reaction of 5-hexenylbenzoate (5a); a mixture of 5a (204 mg, 1 mmol), phenylsilane (216 mg, 2 mmol) and bis(acetylacetonato)cobalt(II) (13 mg, 0.05 mmol) in THF (5 ml) was stirred at room temperature under O_2 for 18 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-benzoyloxy-5-hexanol (188 mg, 84% yield) and 1-benzoyloxy-5-hexanone (31 mg, 14% yield).

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6) 3a: Colorless oil. ^{1}H NMR ($CDCl_3$) δ = 0.75 (q, J=8 Hz, 4H, $SiCH_2$-), 1.00 (t, J=8 Hz, 6H, $-SiCH_2\underline{CH_3}$), 1.30 (s, 6H, 2Me), 2.12 (t, J=7 Hz, 2H, $-\underline{CH_2}CH_2O$), 4.35-4.55 (m, 3H, $-CH_2O-$ and -SiH), 7.38-7.46 (m, 3H, Ph), 7.95-8.05 (m, 2H, Ph). IR (neat) 2140 (-SiH), 1700, 1600, 1280, 1120 cm^{-1}.

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