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Novel Method for the Preparation of Triethylsilyl Peroxides from Olefins by the Reaction with Molecular Oxygen and Triethylsilane Catalyzed by Bis(1,3-diketonato)cobalt(II)

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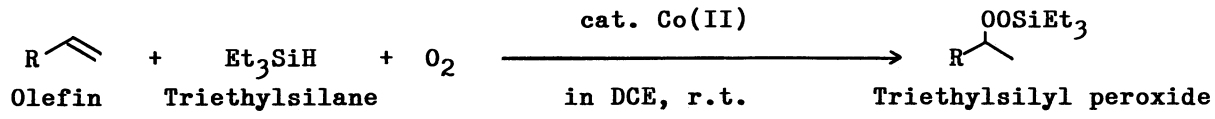
In the presence of a catalytic amount of bis(1,3-diketonato)-cobalt(II), various olefins react with molecular oxygen and triethylsilane at room temperature to give the corresponding triethylsilyl peroxides in high yields under neutral conditions. The reaction provides a new method for the preparation of various peroxides directly from olefins.

Selective olefin oxygenation by dioxygen activation is one of the most interesting topics in organic synthesis, and much attention has been focused on selective oxygenations of olefins with dioxygen-metal complexes yielding monooxygenated compounds, such as epoxides,[1-3] ketones,[4-6] and alcohols.[7-9]

In our previous communication,[10] we reported a new hydration reaction of olefins with molecular oxygen and triethylsilane catalyzed by bis(trifluoroacetylacetonato)cobalt(II) ($Co(tfa)_2$) in 1-propanol at 75 °C. In the course of our continuing study, we found that when the same reaction is carried out in aprotic solvents, such as 1,2-dichloroethane (DCE), at room temperature, various olefins are readily converted to the corresponding triethylsilyl peroxides in high yields (Scheme 1). In the present paper, we wish to report a novel and facile method for peroxygenation of olefins with molecular oxygen and triethylsilane catalyzed by bis(1,3-diketonato)cobalt(II).



Scheme 1.

In the first place, the effect of solvents was screened by taking the peroxygenation of 4-phenyl-1-butene (**1**) with triethylsilane as a model reaction.

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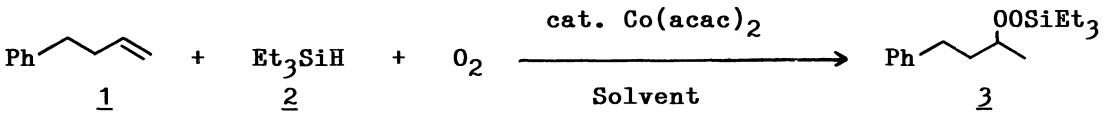
The reaction was carried out by treating 1 (1 mmol) with triethylsilane (2) (2 mmol) under an oxygen atmosphere at room temperature in the presence of a catalytic amount of $Co(acac)_2$ (0.05 mmol). When reaction was carried out in DCE (5 ml), olefin 1 was consumed within 5 h to give a sole product as detected by TLC. After evaporation of the solvent and excess of triethylsilane, the residue was purified by preparative TLC (silica gel) to give 2-triethylsilylperoxy-4-phenylbutane[11] (3) in 94% yield. The above reaction also proceeded in benzen or ethyl acetate, however, the yield of 3 was lower compared with that in DCE. While, no reaction took place in 1-propanol at room temperature.

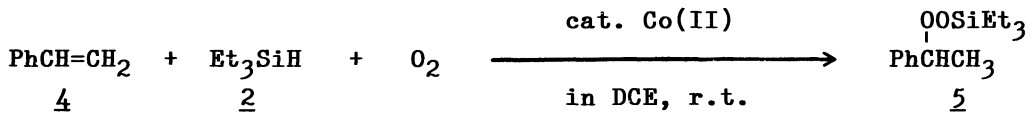
Table 1. Peroxygenation of 4-Phenyl-1-butene



Entry	Solvent	Reaction time /h	Conv. of 1 /%[a]	Yield of 3 /%[b]
1	DCE	5	100	94
2	Benzene	12	100	92
3	AcOEt	24	82	75
4	1-Propanol	24	0	0

a) Determined by GC. b) Isolated yield.

Similarly, the oxidation of styrene (4) in DCE was tried by using $Co(acac)_2$ as a catalyst and it was found that the reaction proceeded very slow and 4 still remained after 24 h. Thus, the desired product, 1-phenyl-1-triethylsilylperoxyethane (5), was obtained in 30% yield along with acetophenone. Then, we examined the effects of ligands of Co(II) complexes in the above reaction and it was found that various bis(1,3-diketonato)cobalt(II) complexes were effectively employed as catalysts. The results of several examples are summarized in Table 2. When $Co(tfa)_2$ was used as a catalyst, the peroxygenated product 5 was obtained in 73% yield with 82% conversion of styrene (Entry 2). In addition, $Co(dedp)_2$[13] and $Co(modp)_2$[14] showed excellent activities as catalysts. For example, styrene was completely consumed within 3 h and 5 was obtained in 96% yield in the presence of a catalytic amount of $Co(modp)_2$ (Entry 4). The $Co(modp)_2$ also promoted the same reaction under an air atmosphere affording 5 in high yield (Entry 5).



Scheme 2.

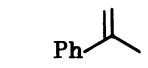
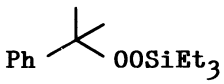
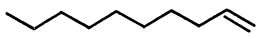
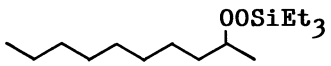
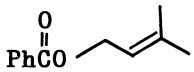
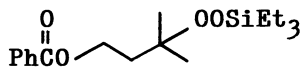
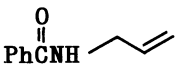
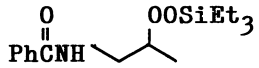
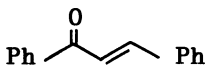
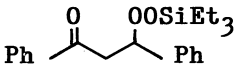
Table 2. Peroxygenation of Styrene Using Several Co(II) Complexes[a)]

Entry	Co(II)[b)]	Reaction time /h	Conv. of 4 /%[c)]	Yield of 5 /%[d)]
1	$Co(acac)_2$	24	52	30
2	$Co(tfa)_2$	12	82	73
3	$Co(dedp)_2$	3	100	94
4	$Co(modp)_2$	3	100	96
5	$Co(modp)_2$	6[e)]	100	92

a) All reactions were carried out at room temperature by treating 4 (1 mmol) with 2 (2 mmol) and Co(II) (0.05 mmol) under O_2 atmosphere in DCE (5 ml). b) Dried over 70 °C in vacuo. c) Determined by GC. d) Determined by HPLC. e) Reaction was carried out under an air atmosphere.

In order to study the scope of this procedure, the present reaction was applied to various olefins by using $Co(modp)_2$ as a catalyst (Table 3). In every case, the peroxygenation smoothly proceeded at 25 °C and the corresponding triethylsilyl peroxides obtained in good to high yields.

Table 3. Peroxygenation of Various Olefins with O_2 and Et_3SiH at 25 °C[a)]

Entry	Olefin	Time /h	Product[b)]	Yield /%[c)]
1		5		95
2		12		80
3		30		99
4		24		80
5		12		75

a) All reactions were carried out by treating 1 mmol of olefin with 2 mmol of triethylsilane and 0.05 mmol of $Co(modp)_2$ under an oxygen atmosphere in 5 ml of DCE. b) Satisfactory NMR and IR spectra were obtained. c) Isolated yield.

A typical procedure is described for the reaction of 1-decene; a mixture of 1-decene (1 mmol), triethylsilane (2 mmol) and $Co(modp)_2$ (0.05 mmol) in DCE (5 ml)

was stirred at 25 °C under O_2 atmosphere for 12 h. After completion of the reaction, the volatile materials were evaporated under reduced pressure, and then the residue was purified by preparative TLC (silica gel) to give 2-triethylsilylperoxydecane (230 mg, 80%).

It is noted that, according to the present method, various olefins are converted to the corresponding triethylsilyl peroxides in high yields under mild conditions. Further extension of this type of reaction is now under investigation.

References

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11) **3**: ^{1}H-NMR ($CDCl_3$) δ = 0.68 (q, J=8 Hz, 6H, $-SiCH_2-$), 0.99 (t, J=8 Hz, 9H, $-SiCH_2\underline{CH_3}$), 1.24 (d, J=7 Hz, 3H, Me), 1.72-2.10 (m, 2H, $PhCH_2\underline{CH_2}-$), 2.65-2.76 (m, 2H, $PhCH_2-$), 4.00-4.10 (m, 1H, -CHOOSi-), 7.17-7.30 (m, 5H, Ph).
12) **5**: ^{1}H-NMR ($CDCl_3$) δ = 0.66 (q, J=8 Hz, 6H, $-SiCH_2-$), 0.96 (t, J=8 Hz, 9H, $-SiCH_2\underline{CH_3}$), 1.46 (d, J=5 Hz, 3H, Me), 4.98 (q, J=5 Hz, 1H, -CHOOSi-), 7.20-7.45 (m, 5H, Ph).
13) $Co(dedp)_2$: Bis(1-**di**ethylaminocarbamoyl-4,4-**d**imethyl-1,3-**p**entanedionato)-cobalt(II) was prepared as follows; to an aqueous solution (100 ml) of NaOH (800 mg, 20 mmol) and 1-diethylaminocarbamoyl-4,4-dimethyl-1,3-pentanedione (4.54 g, 20 mmol) was slowly added an aqueous solution (20 ml) of cobalt(II) chloride (1.3 g, 10 mmol). After being stirred at 60 °C for 2 h, the light brown powder was separated by filtration, washed with water, and dried in vacuo (1.6 g, 31%). Mp 233.6-236.4 °C (decomp.); IR (KBr) 2966, 1638, and 1607 cm^{-1}.
14) $Co(modp)_2$: Bis(1-**mo**rpholinocarbamoyl-4,4-**d**imethyl-1,3-**p**entanedionato)-cobalt(II) was prepared similarly as $Co(dedp)_2$ (light brown powder, 70% yield). Mp 278.0-279.4 °C (decomp.); IR (KBr) 2964, 1597, and 1517 cm^{-1}.

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