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A Convenient Method for the Direct Preparation of Ketones from Vinylsilanes with Molecular Oxygen Catalyzed by Cobalt(II) Complex

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Various vinylsilanes are directly converted to the corresponding ketones in high yields on treatment with molecular oxygen in the presence of a catalytic amount of cobalt(II) complex under neutral condition.

Vinylsilanes are frequently employed as useful synthetic intermediates and various methods for the preparation of vinylsilanes have been reported.[1] Of their reactions, the conversion of vinylsilanes into carbonyl compounds by a stepwise method consisted of epoxidation of vinylsilanes with m-chloroperbenzoic acid and successive treatment of epoxysilanes with acids has been reported by Stork and co-workers.[2] The second step in the above method frequently requires relatively harsh conditions, therefore, the conversion of vinylsilanes having acid sensitive functional groups, such as acetal, ester or epoxide groups, still remains as a synthetic problem.

Recently, we reported that various olefinic compounds are hydrated with molecular oxygen in secondary alcohol by use of a catalytic amount of bis(1,3-diketonato)cobalt(II) complex to afford the corresponding alcohols under neutral condition (Oxidation-Reduction Hydration).[3,4]

During our continuing study, we found that various vinylsilanes smoothly react with molecular oxygen in secondary alcohol in the presence of a catalytic

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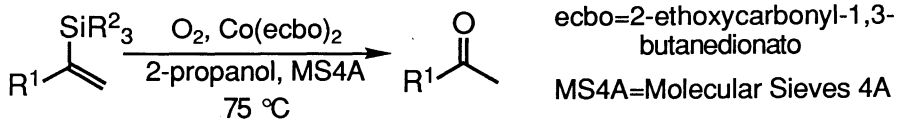
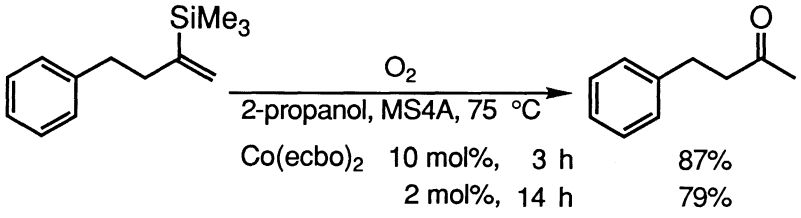
amount of a bis(1,3-diketonato)cobalt(II) complex to afford the corresponding ketones in high yields (Scheme 1). In the present communication, we would like to describe a new and convenient method for direct preparation of ketones from vinylsilanes under neutral condition.



Scheme 1.

First, we tried the reaction of 4-phenyl-2-trimethylsilyl-1-butene with molecular oxygen in 2-propanol in the presence of 10 mol% of bis(2-ethoxycarbonyl-1,3-butanedionato)cobalt(II) ($Co(ecbo)_2$)[4] and Molecular Sieves 4A[5] at 75 °C. The reaction proceeded smoothly to afford the corresponding ketone, 4-phenyl-2-butanone, in 87% yield (Scheme 2). Similarly, when 2 mol% of $Co(ecbo)_2$ was employed in the above reaction, 4-phenyl-2-butanone was obtained in 79% yield (Scheme 2).

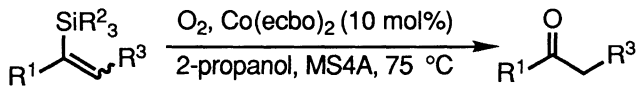


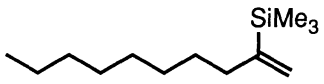
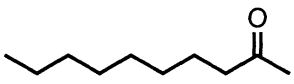
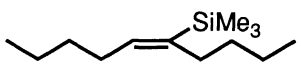
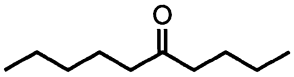
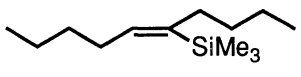
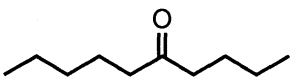
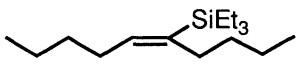
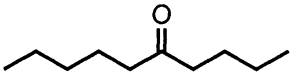
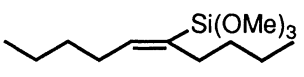
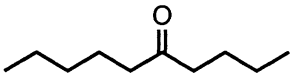
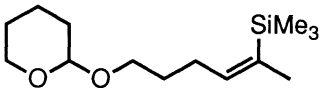
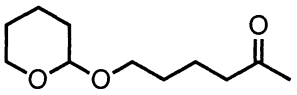
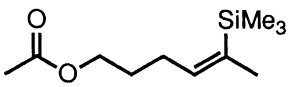
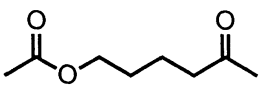
Scheme 2.

Then, we examined the conversion of various vinylsilanes into the corresponding ketones according to the above procedure. As shown in Table 1, the reactions of aliphatic vinylsilanes proceeded smoothly to give the corresponding ketones in high yields (Entry 1 and 2). The reactions of both (E)- and (Z)-vinylsilanes gave the same results (Entry 2 and 3). Also in the cases of sterically hindered triethyl- and trimethoxy-vinylsilanes, the reactions took place readily to afford the corresponding ketones (Entry 4 and 5). It is noteworthy to mention that vinylsilanes having functional groups, such as tetrahydropyranyl ether and ester groups, are also converted into the corresponding ketones in 90% and 82% yields, respectively, without destroying the functional groups (Entry 6 and 7). According to the conventional method consisted of epoxidation and successive treatment with acid, it was shown that derivation to ketone from vinylsilane having tetrahydropyranyl ether was not carried out successfully.[6]

On the other hand, the conversion of 4-phenyl-1-trimethylsilyl-1-butene into the corresponding aldehyde by the present procedure was unsuccessful.[7]

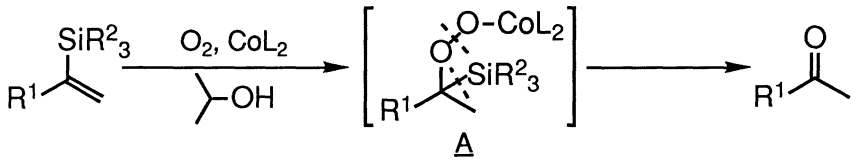
Table 1. The Reaction of Various Vinylsilanes with Molecular Oxygen[a)]



Entry	Vinylsilane	Ketone[b)]	Time / h	Yield / %
1			4	89[c)]
2			4	83[c)]
3			4	87[c)]
4			5	91[c)]
5			5	91[c)]
6			4	90[d)]
7			4	82[d)]

a) Reaction conditions; vinylsilane 1.0 mmol, $Co(ecbo)_2$ 0.1 mmol, 2-propanol 5 ml, Molecular Sieves 4A 0.5 g, 75 °C, under O_2 atmosphere. b) Satisfactory NMR and IR were obtained. c) Determined by GC analysis. d) Isolated yield.

The mechanism is not yet made clear in detail, however, it is assumed as follows; similar to Oxidation-Reduction Hydration,[3,4)] the peroxygenated intermediate A is initially generated by the reaction of vinylsilane with molecular oxygen and 2-propanol. The intermediate A is in turn converted to the corresponding ketone by way of a cleavage of O-O bond and elimination of silyl group (Scheme 3).



Scheme 3.

A typical experimental procedure is described for the reaction of 6-(2-tetrahydropyranoxy)-2-trimethylsilyl-2-hexene: To a solution of 6-(2-tetrahydropyranoxy)-2-trimethylsilyl-2-hexene (256 mg, 1.0 mmol) in 2-propanol (5 ml) was added bis(2-ethoxycarbonyl-1,3-butanedionato)cobalt(II) (37 mg, 0.1 mmol) and Molecular Sieves 4A (activated powder, 500 mg). After stirring for 4 h at 75 °C under oxygen atmosphere, Molecular Sieves 4A was filtered and the filtrate was concentrated under reduced pressure. Then the resulted crude product was purified by silica gel column chromatography (hexane-ethyl acetate) to afford 1-(2-tetrahydropyranoxy)-5-hexanone (180 mg, 90% yield).

Thus, it is noted that the reaction of vinylsilanes with molecular oxygen catalyzed by bis(2-ethoxycarbonyl-1,3-butanedionato)cobalt(II) ($Co(ecbo)_2$) provides a useful and convenient method for the preparation of ketones in high yields directly from vinylsilanes under neutral condition.

References

1) E. W. Colvin, "Silicon in Organic Synthesis," Butterworths, London (1981), Chaps. 7 and 8.
2) G. Stork and E. Colvin, J. Am. Chem. Soc., 93, 2080 (1971); G. Stork and M. E. Jung, ibid., 96, 3682 (1974).
3) 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.
4) K. Kato, T. Yamada, T. Takai, S. Inoki, and S. Isayama, Bull. Chem. Soc. Jpn., submitted.
5) In the previous paper,[4] we reported that water formed during the Oxidation-Reduction Hydration deactivates the cobalt(II) catalyst. In the present reaction, the formation of water was also confirmed by GC analysis (TCD), therefore, Molecular Sieves 4A, a dehydration reagent, was added in order to avoid the deactivation of cobalt(II) catalyst.
6) To a solution of 6-(2-tetrahydropyranoxy)-2-trimethylsilyl-2-hexene (256 mg, 1.0 mmol) in CH_2Cl_2 (5 ml) was added m-chloroperbenzoic acid (181 mg, 1.05 mmol) at 0 °C. After stirring for 1 h at 0 °C and 6 h at r. t., the corresponding epoxysilane was obtained after quenching by a usual manner. The corresponding ketone was not obtained at all on treatment of the epoxysilane with formic acid (5 ml) at r. t. for 30 min, though the epoxysilane was completely consumed.
7) A mixture of various products was obtained.

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