The First Hydroxysilylation of Alkenes with Triethylsilane under Dioxygen Catalyzed by *N*-Hydroxyphthalimide

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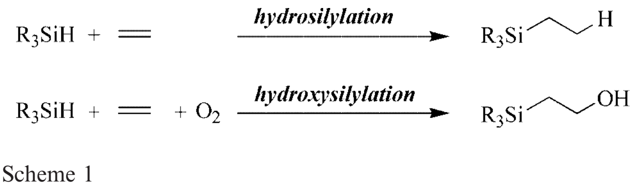
Catalytic hydroxysilylation of alkenes with trialkylsilane under dioxygen through a radical process was successfully achieved by the use of *N*-hydroxyphthalimide (NHPI) as a catalyst under mild conditions.

Introduction

The hydrosilylation of alkenes and alkynes with hydrosilanes is a frequently used and important method for the formation of complex organosilanes, such as vinylsilanes. These reactions can be brought about through catalysis by Pt and Rh compounds[1] as well as by radical processes, both photo- and radical-initiated.[2] The latter process is limited, however, to silanes such as $HSiCl_3$ or $MeSiCl_2H$,[2] and the introduction of trialkylsilanes to alkenes is not successful. Giese et al. have reported that tris(trimethylsilyl)silane (TTMSS) adds to carbon−carbon multiple bonds by a free-radical chain process to form the corresponding hydrosilanes.[3] Thus, a variety of substituted alkenes can be hydrosilylated successfully by TTMSS in the presence of a radical initiator, such as AIBN.[4] The simultaneous introduction, however, of both silyl and hydroxyl functions to carbon−carbon multiple bonds, which is referred to as hydroxysilylation, remained an unsolved reaction.[5]



Scheme 1

Recently, we have developed a novel catalytic method for the introduction of both alkyl and hydroxyl groups to alkenes by using *N*-hydroxyphthalimide (NHPI), which serves as a catalyst for producing alkyl radicals from alkanes.[6] Thus, our effort has been focused on the first catalytic hydroxysilylation of alkenes by the concomitant introduction of silyl and hydroxyl functions by the use of NHPI as a key catalyst under dioxygen.[7] In this paper, we report the first hydroxysilylations of substituted alkenes bearing electron-withdrawing groups by reacting them with triethylsilane and molecular oxygen under the influence of NHPI.

Results and Discussion

The hydroxysilylation of methyl acrylate (**1a**) with Et_3SiH under dioxygen, which is catalyzed by NHPI combined with a Co species, was chosen as a model reaction and was carried out under various reaction conditions (Table 1).

Table 1. Hydroxysilylation of methyl acrylate (**1a**) with Et_3SiH to **2a** by NHPI under various conditions.

Run[a]	NHPI (mol %)	$Co(OAc)_2$ (mol %)	$Co(acac)_3$ (mol %)	Conv.[b] (%)	Yield[b] (%)
1	10	0.1		63	57 (90)
2	10			<3	<3
3		0.1		<4	<4
4[c]	10	0.1		84	48 (57)
5	10	0.1	0.1	83	73 (88)
6[d]	5	0.1	0.1	79	74 (94)

[a] **1a** (3 mmol) was reacted with Et_3SiH (15 mmol) in EtOAc (2 mL) at 60 °C for 2 h under dioxygen (1 atm). [b] Based on the amount of **1a** used. Numbers in parentheses show the selectivity based on the amount of **1a** consumed. [c] 3 h. [d] 5 h.

As expected, the reaction of **1a** with Et_3SiH (5 equiv.) under 1 atm of dioxygen in the presence of NHPI (10 mol %) and $Co(OAc)_2$ (0.1 mol %) in ethyl acetate at 60 °C for 2 h produced methyl 2-hydroxy-3-triethylsilylpropionate (**2a**) in 57% yield (Run 1). We note that the hydroxysilylation of an alkene with a trialkyl silane, such as Et_3SiH,

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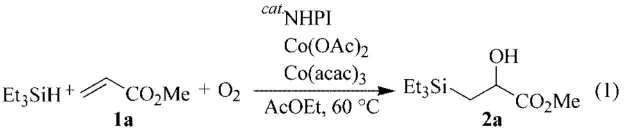
was first successfully achieved through a catalytic process by using NHPI as the catalyst. The same reaction in the absence of either NHPI or $Co(OAc)_2$ afforded **2a** in poor yield (Runs 2 and 3). When the reaction was prolonged to 3 h, the yield of **2a** decreased to 48%. This result shows that the adduct **2a** is not stable and decomposes to undesired side products. In fact, an independent reaction of **2a** under these conditions resulted in a complex mixture of cleaved products of **2a**. When the reaction was carried out in the presence of NHPI combined with Co^{II} (0.1 mol %) and Co^{III} (0.1 mol %), we obtained the adduct **2a** in 73% yield (Run 5). Previously, we observed a similar synergistic effect of both the Co^{II} and the Co^{III} in the NHPI-catalyzed coupling reaction of alcohols with **1a** leading to α-hydroxy-γ-butyrolactones.[8] By using both Co^{II} and Co^{III} as co-catalysts, the amount of NHPI required was reduced to 5 mol % (Run 6). In these reactions, oxygenated products derived from Et_3SiH, such as Et_3SiOH, were formed in 15−20 % yields based on the amount of Et_3SiH.



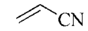
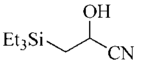
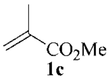
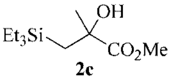
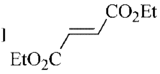
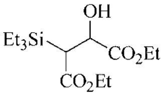
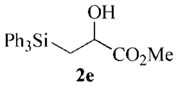
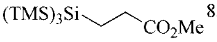
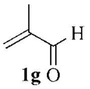
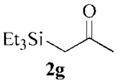
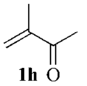
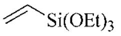
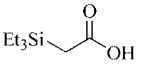
(1)

On the basis of these results, various olefinic compounds were reacted under selected conditions with Et_3SiH in the presence of both NHPI and the Co species (Table 2).

The reaction of acrylonitrile (**1b**) with Et_3SiH under dioxygen (1 atm) at 60 °C afforded 3-triethylsilyl-2-hydroxypropionitrile (**2b**) in 60% yield (Run 1). The reaction of methyl methacrylate (**1c**) with Et_3SiH occurred with some difficulty, probably because of the steric hindrance resulting from the methyl substituent on the olefinic unit of **1c**, to give hydroxysilylated product (**2c**) in 55% yield (Run 2). The hydroxysilylation of diethyl fumarate (**1d**) with Et_3SiH took place even at room temperature to form the corresponding adduct, **2d** (Run 3). The reaction of **1a** with Ph_3SiH afforded the hydroxysilylated product **2e**, while mainly hydrosilylation occurred in the reaction with $(TMS)_3Si-H$ to give **2f**, probably because of the lower bond-dissociation energy of $(TMS)_3Si-H$ (i.e., BDE [Et_3Si-H] = 96 kcal/mol and BDE [$(TMS)_3Si-H$] = 74 kcal/mol) (Runs 4 and 5).[9] It is interesting to note that under similar conditions methacrolein (**1g**) and 3-methyl-3-buten-2-one (**1h**) led to the same product, triethylsilylacetone (**2g**), in 52 and 42% yields, respectively, and is discussed later (Runs 6 and 7). Similarly, the cleavage product was obtained in the reaction of triethoxyvinylsilane (**1i**) (Run 8). The reaction of a simple alkene, such as 1-octene, with Et_3SiH was examined under these conditions, but no hydrosilylation product was obtained, probably because of polar effect of the Et_3Si· radical, which has nucleophilic character and prefers an electron-deficient alkene to an electron-rich one, such as 1-octene.

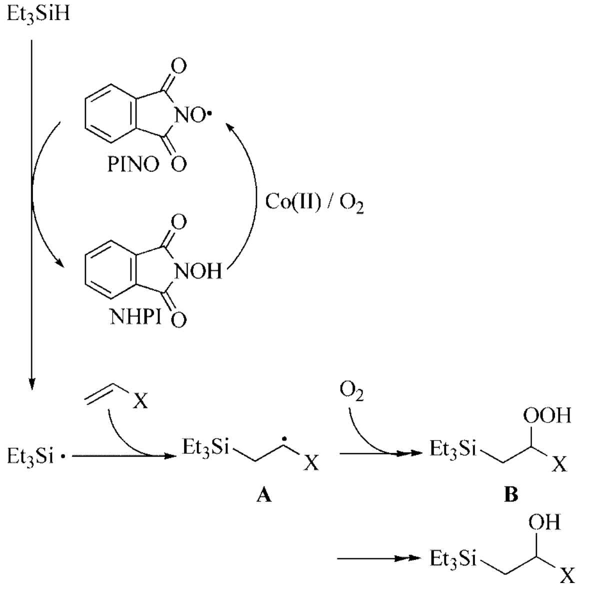
Scheme 2 illustrates a plausible reaction pathway for the present hydroxysilylation of alkenes with Et_3SiH under dioxygen catalyzed by NHPI combined with Co species.

Table 2. Hydroxysilylation of several alkenes (**1b**−**f**) with Et_3SiH catalyzed by NHPI.

Run	Substrate	Temp. / °C	Time / h	Conv. / %	Product	Select. / % [b]
1[c]	 **1b**	60	10	67	 **2b**	90
2[d]	 **1c**	50	10	57	 **2c**	97
3[e]	 **1d**	r.t.	12	99	 **2d**	66
4[f]	**1a**	r.t.	6	61	 **2e**	82
5[g]	**1a**	75	14	99	 **2f**	85
6[h]	 **1g**	70	4	-	 **2g**	52[i]
7[j]	 **1h**	70	4	78	**2g**	52
8[k]	 **1i**	70	2	68	 **2i**	77

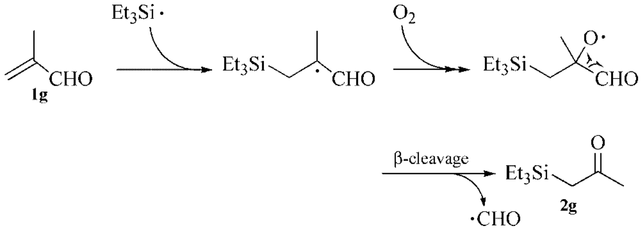
[a] Alkene (2 mmol) was reacted with Et_3SiH (15 mmol) in the presence of NHPI (10 mol %) and $Co(OAc)_2$ (0.5 mol %) in EtOAc (2 mL) under O_2 (1 atm). [b] Based on amount of alkene consumed. [c] **1b** (3 mmol), NHPI (5 mol %), $Co(OAc)_2$ (0.1 mol %), $Co(acac)_3$ (0.1 mol %). [d] Et_3SiH (20 mmol), NHPI (20 mol %) under N_2/O_2 (0.5:0.5 atm). [e] **1d** (3 mmol), CH_3CN (3 mL). [f] Ph_3SiH (6 mmol). [g] **1a** (1 mmol), $(TMS)_3SiH$ (5 mmol) under air. [h] Et_3SiH (20 mmol). [i] Based on amount of alkene used. [j] **1h** (3 mmol), $Co(OAc)_2$ (0.1 mol %), $Co(acac)_3$ (0.3 mol %). [k] **1i** (3 mmol), $Co(OAc)_2$ (0.1 mol %), $Co(acac)_3$ (0.1 mol %).

The reaction is initiated by the formation of phthalimide *N*-oxyl (PINO) from NHPI by the action of the cobalt−oxygen complex,[6,8,10] and then PINO abstracts a hydrogen atom from Et_3SiH to form the triethylsilyl radical Et_3Si·, which then adds to the alkene to form an adduct radical **A**. It is known that the hydrogen atom abstraction from trialkyl hydrosilane by an alkyl radical, such as **A**, occurs with difficulty. Hence, the abstraction of a hydrogen atom from Et_3SiH by the carbon-centered adduct radical **A** is probably a sluggish process.[3] Under the present reaction conditions, in which molecular oxygen is present, the resulting silylated alkyl radical **A** is readily trapped by dioxygen to form a hydroperoxide **B** that undergoes redox decomposition mediated by the cobalt species to convert it into an alcohol.



Scheme 2. A possible reaction pathway for the hydroxysilylation

The formation of triethyl silylacetone **2g** from alkenes **1g** and **1h** can be explained by the β-cleavage of the resulting hydroperoxide, as is shown in Scheme 3.[10]



Scheme 3. A possible reaction pathway for the reaction of **1g** with Et_3SiH

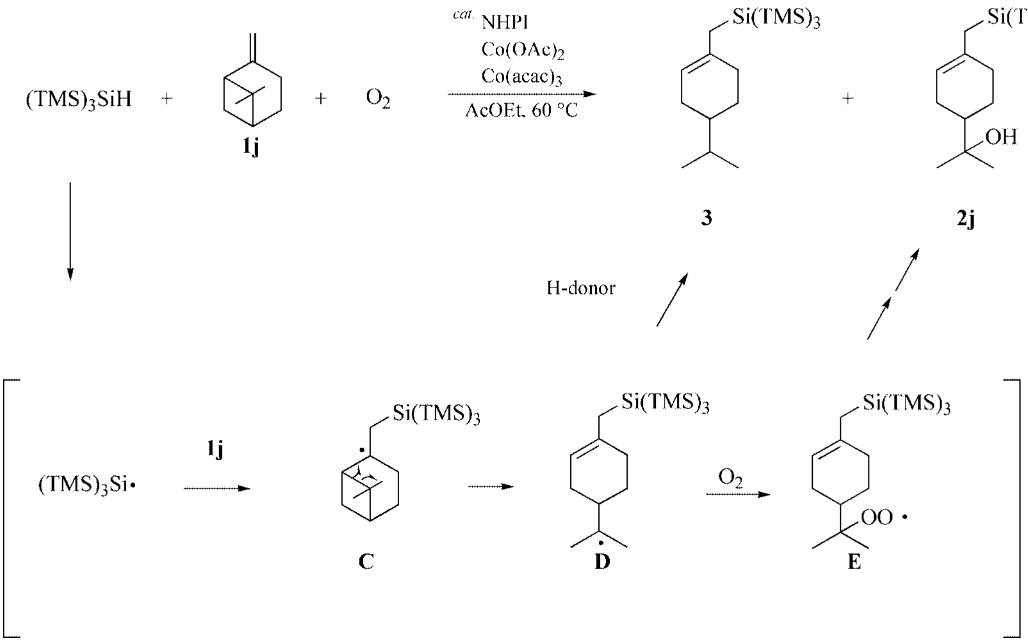
To obtain further information regarding the reaction pathway, the reaction of β-pinene (**1j**) was chosen to prove the radical nature of the reaction. It is known that the radical addition of **1j** proceeds through ring opening of its cyclobutane moiety. Unfortunately, the reaction of **1j** with Et_3SiH was difficult to achieve with selectivity. When the reaction of **1j** with $(TMS)_3SiH$ was carried out by the present reaction system, however, 2-(4-trimethylsilanylmethylcyclohex-3-enyl)propan-2-ol (**2j**) (2%) was obtained as a minor product, together with the hydrosilylated product **3** (31%), suggesting that the adduct formed between $(TMS)_3Si$ and **1j** underwent ring opening of the cyclobutane ring to give **D**, which subsequently underwent addition of O_2 to afford the corresponding adduct [Equation (2)].

In conclusion, we have achieved the first catalytic hydroxysilylation of electron-deficient alkenes with Et_3SiH and dioxygen by the use of NHPI as the key catalyst under mild conditions.

Experimental Section

General Procedures: All starting materials were commercially available and used without further purification. GLC analysis was performed with a flame-ionization detector using a 0.2 mm × 25 m capillary column (OV-1). ^1H and ^{13}C NMR spectra were measured at 400 MHz and 100 MHz, respectively, in $CDCl_3$ with Me_4Si as the internal standard. Infrared (IR) spectra were measured using NaCl plates.

Representative Procedure for the Hydroxysilylation of 1a with Et_3SiH: Compound **1a** (3 mmol) and Et_3SiH (15 mmol) were added to a solution of NHPI (0.3 mmol) and the transition metal salts in EtOAc (2 mL). The flask was equipped with a balloon filled with O_2 (1 atm). The mixture was stirred at 60 °C for 2 h. The product **2a** (ca. 1.8 mmol, 390 mg) was isolated by column chroma-



(2)

tography (230−400 mesh silica gel, *n*-hexane/ethyl acetate = 4:1). After the reaction was complete, GC and GC-MS analyses were performed. The conversions and yields of products were estimated from the peak areas, based on the internal-standard technique, observed using GC. Products **2f** and **3** have been reported previously.[3,4]

Methyl 2-Hydroxy-3-triethylsilylpropionate (2a): ^{1}H NMR: δ = 4.29−4.23 (m, 1 H), 3.77 (s, 3 H), 2.46 (br., 1 H), 1.26−1.11 (m, 2 H), 0.93 (t, J = 7.9 Hz, 9 H), 0.61 (q, J = 7.9 Hz, 6 H) ppm. ^{13}C NMR: δ = 177.0, 68.4, 52.3, 18.4, 7.2, 3.6 ppm. $C_{10}H_{22}O_3Si$ (218.4): calcd. C 55.00, H 10.15, O 21.98; Si 12.86; found C 54.95, H 10.06.

2-Hydroxy-3-triethylsilylpropionitrile (2b): ^{1}H NMR: δ = 4.53 (t, J = 7.8 Hz, 1 H), 3.72 (br., 1 H), 1.27 (d, J = 2.4 Hz, 2 H), 0.97 (t, J = 7.8 Hz, 9 H), 0.63 (q, J = 7.8 Hz, 6 H) ppm. ^{13}C NMR: δ = 121.3, 58.6, 20.0, 7.2, 3.4 ppm.

Methyl 2-Hydroxy-2-methyl-3-triethylsilylpropionate (2c): ^{1}H NMR: δ = 3.77 (s, 3 H), 3.09 (br., 1 H), 1.45 (s, 3 H), 1.23 (d, J = 14.8 Hz, 1 H), 1.16 (d, J = 14.8 Hz, 1 H), 0.93 (t, J = 7.9 Hz, 9 H), 0.55 (q, J = 7.9 Hz, 6 H) ppm. ^{13}C NMR: δ = 178.7, 74.0, 52.5, 29.6, 24.5, 7.26, 4.06 ppm.

Diethyl 2-Hydroxy-3-triethylsilylsuccinate (2d): ^{1}H NMR: δ = 4.23−4.11 (m, 5 H), 3.82 (br., 1 H), 2.74 (d, J = 2.8 Hz, 1 H), 1.26 (q, J = 7.2 Hz, 6 H), 0.99 (t, J = 7.6 Hz, 9 H), 0.74 (q, J = 7.6 Hz, 6 H) ppm. ^{13}C NMR: δ = 174.8, 174.0, 69.4, 61.3, 60.1, 38.2, 14.2, 7.1, 3.4 ppm.

Methyl 2-Hydroxy-3-triphenylsilylpropionate (2e): ^{1}H NMR: δ = 7.68−7.43 (m, 6 H), 7.43−7.23 (m, 9 H), 4.42−4.25 (m, 1 H), 3.43 (s, 3 H), 2.95 (br., 1 H), 1.24−1.86 (m, 2 H) ppm. ^{13}C NMR: δ = 175.8, 135.5, 134.1, 129.3, 127.6, 67.9, 51.9, 20.4 ppm. $C_{22}H_{22}O_3Si$ (362.5): calcd. C 72.89, H 6.12, O 13.24, Si 7.75; found C 72.76, H 6.20.

Triethylsilylacetone (2g): ^{1}H NMR: δ = 2.24 (s, 2 H), 2.12 (s, 3 H), 0.98 (t, J = 7.8 Hz, 9 H), 0.63 (q, J = 7.8 Hz, 6 H) ppm. ^{13}C NMR: δ = 207.9, 34.3, 31.8, 7.0, 3.5 ppm.

Methyl Triethylsilylacetate: ^{1}H NMR: δ = 3.62 (s, 2 H), 1.89 (s, 2 H), 0.96 (t, J = 7.9 Hz, 9 H), 0.62 (q, J = 7.9 Hz, 6 H) ppm. ^{13}C NMR: δ = 173.6, 51.1, 21.7, 7.0, 3.5 ppm.

2-(4-Trimethylsilanylmethylcyclohex-3-enyl)propan-2-ol (2j): ^{1}H NMR: δ = 5.30 (m, 1 H), 2.08−1.24 (m, 10 H), 1.18 (s, 6 H), 0.13 (s, 27 H) ppm. ^{13}C NMR: δ = 137.2, 118.5, 72.7, 44.8, 31.4, 27.5, 27.0, 26.3, 24.1, 17.5, 1.35 ppm.

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[1] [1a] J. Y. Corey, J. Braddock-Wilking, *Chem. Rev.* **1999**, *99*, 175−292. [1b] K. A. Horn, *Chem. Rev.* **1995**, *95*, 1317−1350. [1c] P. Braunstein, M. Knorr, *J. Organomet. Chem.* **1995**, *500*, 21−38. [1d] B. Marciniec, J. Gulinski, *J. Organomet. Chem.* **1993**, *446*, 15−23.

[2] [2a] L. H. Sommer, E. W. Pietrusza, F. C. Whitmore, *J. Am. Chem. Soc.* **1947**, *69*, 188−188. [2b] C. A. Barkhard, R. H. Krieble, *J. Am. Chem. Soc.* **1947**, *69*, 2687−2689. [2c] A. J. Barry, L. DePree, J. W. Gilkey, D. E. Hook, *J. Am. Chem. Soc.* **1947**, *69*, 2916−2916. [2d] F. W. Pietrusza, L. H. Sommer, F. C. Whitmore, *J. Am. Chem. Soc.* **1948**, *70*, 484−486. [2e] C. Eaborn, M. R. Harrison, D. R. M. Walton, *J. Organomet. Chem.* **1971**, *31*, 43−46. [2f] J. W. Wilt, in *Reactive Intermediates*, Vol. 3 (Ed.: R. A. Abramovitch), Pergamon Press, New York, **1983**, pp. 143−151. [2g]K. Miura, K. Oshima, K. Uchimoto, *Bull. Chem. Soc., Jpn.* **1993**, *66*, 2348−2355.

[3] B. Kopping, C. Chatgilialoglu, M. Zehnder, B. Giese, *J. Org. Chem.* **1992**, *57* 3994−4000.

[4] [4a] M. Ballestri, C. Chatgilialoglu, K. B. Clark, D. Griller, B. Giese, B. Kopping, *J. Org. Chem.* **1991**, *56*, 678−683. [4b] C. Chatgilialoglu, *Acc. Chem. Res.* **1992**, *25*, 188−194. [4c] C. Chatgilialoglu, *Chem. Rev.* **1995**, *95*, 1229−1251.

[5] The oxysulfuration has been reported previously: A. L. J. Beckwith, R. D. Wagner, *J. Org. Chem.* **1981**, *46*, 3638−3645.

[6] T. Hara, T. Iwahama, S. Sakaguchi, Y. Ishii, *J. Org. Chem.* **2001**, *66*, 6425−6431.

[7] Quite recently, the aerobic oxidation of silanes to silanols catalyzed by NHPI and Co salts was reported. See: F. Minisci, F. Recupero, C. Punta, C. Guidarini, F. Fontana, G. F. Pedullic, *Synlett* **2002**, 1173−1175.

[8] T. Iwahama, S. Sakaguchi, Y. Ishii, *Chem. Commun.* **2000**, 613−614.

[9] J. J. Lucas, P. M. Laarhoven, D. M. W. Danial, *Acc. Chem. Res.* **1999**, *32*, 342−349.

[10] K. Hirano, T. Iwahama, S. Sakaguchi, Y. Ishii, *Chem. Commun.* **2000**, 2687−2688.

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