Stereochemistry and Mechanism for the Addition of Alcohols to a Cyclic Silene[1]

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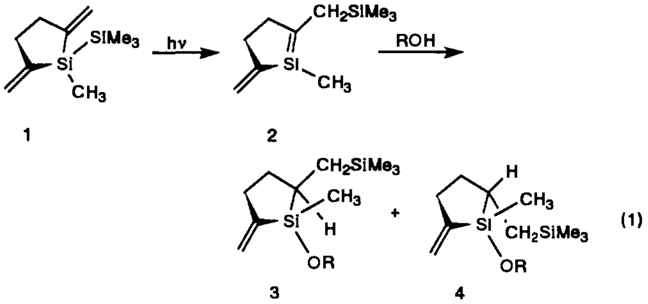
Silenes react efficiently with alcohols to give addition products,[2] but the stereochemistry and mechanism of the reaction are not yet fully elucidated. Nonstereospecific addition of methanol to isolable silenes has been observed by Brook et al.,[2a,3] while a silene reported by Jones et al. adds to methanol stereospecifically.[4] Wiberg has proposed a two-step mechanism involving the first formation of a silene–alcohol complex followed by proton migration to the carbon of the silene.[5] The mechanism may be compatible with the results by Brook et al., if rotation around the Si–C(silene) bond occurs faster than the proton migration.

We report herein that, in disagreement with the simple two-step or a concerted four-centered mechanism, alcohols add nonstereospecifically even to a cyclic silene where the bond rotation is prohibited. The stereochemical outcome for the addition of various alcohols to the silene depends remarkably on the concentration and on the acidity of the alcohols.[6] We propose a more elaborate mechanism for the reaction where the intramolecular proton transfer in the first generated silene–alcohol complex competes with the intermolecular proton transfer from another molecule of alcohol. The stereochemical complexity is fully explained by this mechanism.

Irradiation of a cyclic divinyldisilane **1** in various alcohols gave a mixture of cis (**3**) and trans adduct (**4**) of alcohols to a cyclic silene **2** (eq 1).[7,9] The reaction conditions and the product yields are shown in Table I.



(1)

a, R= CH_3; b, R= $CH_2CH_2CH_3$;
c, R= $CH(CH_3)_2$; d, R= $C(CH_3)_3$.

Table I. Product Distribution of the Photoreactions of **1** in Various Alcoholic Solvents[a]

alcohol	conversion of **1**, %	total yield of **3** and **4**, %	product ratio **3**/**4**
CH_3OH	59	71	27/73
$CH_3CH_2CH_2OH$	61	77	35/65
$(CH_3)_2CHOH$	65	76	46/54
$(CH_3)_3COH$	85	64	100/0

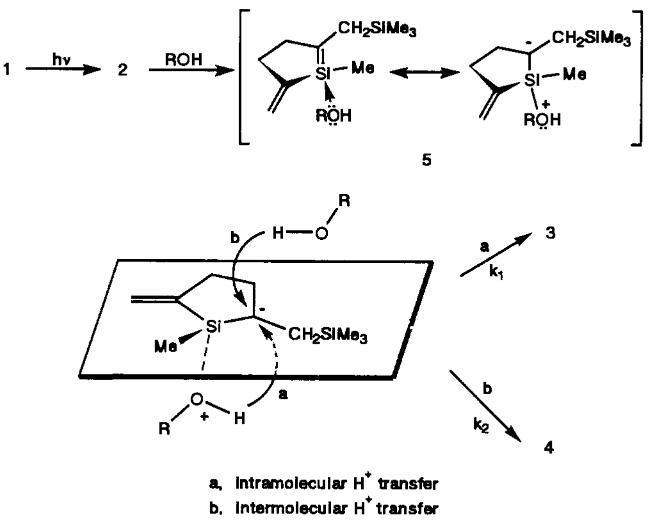
[a] A solution of **1** (ca. 0.01–0.05 M) in an alcohol in a quartz tube was irradiated for 4–45 min at ambient temperature by using a 125-W low-pressure Hg arc lamp. Yields were determined by GLC. [b] The yield is based on the consumed **1**.

Table II. Slope for Linear Plots of the Product Ratio **3**/**4** vs the Inverse of Alcohol Concentration for the Photolysis of **1** in Acetonitrile[a]

		pK_a	
ROH	slope[b]	ROH[c]	RO^+H_2[d]
CH_3OH	4.6 (0.28)	29.0	−2.2
$CH_3CH_2CH_2OH$	9.2 (−0.5)	(29.8)[e]	(−2.4)[f]
$(CH_3)_2CHOH$	32. (−2.2)	30.25	−3.2
$(CH_3)_3COH$	∞[g]	32.2	−3.8

[a] An acetonitrile solution of **1** (ca. 0.01 M) in the presence of an amount of a pertinent alcohol (1.46–20.1 M) was irradiated for 2–5 min by using a 125-W low-pressure Hg arc lamp, which conditions kept the conversion below 20%. Relative yields between **3** and **4** were determined by GLC. [b] As described in the text, the slope of a plot of [**3**]/[**4**] vs 1/[ROH] stands for k_1/k_2. The intercept, which is shown in parentheses, is meaningless under the present conditions. [c] pK_a's in DMSO from ref 11, unless otherwise noted. [d] pK_a's in H_2O from ref 12. [e] pK_a of CH_3CH_2OH in DMSO from ref 13. [f] pK_a of $CH_3CH_2O^+H_2$ in H_2O. [g] No trans isomer **4d** was detected even when *tert*-butyl alcohol was used as solvent.

Scheme I



The ratio **3**/**4** increased in the following order of the alcohols used: MeOH < *n*-PrOH <*i*-PrOH ≪ *t*-BuOH. *tert*-Butyl alcohol gave only a cis adduct. No interconversion between **3** and **4** was observed under irradiation. Further interesting findings are the dependence of the initial product ratio **3**/**4** on the concentration of alcohol. Thus, plots of **3**/**4** vs the inverse of alcohol concentration gave straight lines, when **1** was irradiated for 2–5 min in the presence of various amounts of alcohols in acetonitrile. The slope varied remarkably from 4.6 for MeOH to 32 for *i*-PrOH,

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(1) Chemistry of Organosilicon Compounds. 278.

(2) For recent reviews, see: (a) Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 1. (b) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.

(3) Brook, A. G.; Safa, K. D.; Lickiss, P. D.; Baines, K. M. *J. Am. Chem. Soc.* **1985**, *107*, 4339.

(4) Jones, P. R.; Bates, T. F. *J. Am. Chem. Soc.* **1987**, *109*, 913.

(5) (a) Wiberg, N.; Wagner, G.; Müller, G.; Riede, J. *J. Organomet. Chem.* **1984**, *271*, 381. (b) Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141.

(6) Recently, Fink et al. reported nonstereospecific addition of alcohols to a silacyclobutadiene in a glass matrix. The results have been explained, however, by the photoisomerization of an initially formed diastereomer. (a) Fink, M. J.; Puranik, D. B.; Johnson, M. P. *J. Am. Chem. Soc.* **1988**, *110*, 1315. (b) Puranik, D. B.; Fink, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 5951.

(7) Generation of silenes via 1,3-silyl migration under irradiation of the corresponding vinyldisilanes was evidenced by trapping experiments,[8] although no direct evidence for the existence of the silenes has been obtained until now. The possibility of direct photoreaction of **1** with alcohols as suggested by a referee can be precluded, since the conversion of **1** under irradiation was independent of alcohol concentration. Typically, the conversion after irradiation of **1** in acetonitrile for 210 s was 12.8 ± 3.5% in the methanol concentration range of 1.46–20.1 M. The 1,1-divinyldisilane **1** generates the conjugate 2-sila-1,3-butadiene **2**. We believe that the existence of a vinyl group on the silene does not change the proposed mechanism, but examination with a simple silene would be desirable. Photolysis of 1-(trimethylsilyl)-2-methylenesilacyclopentane was attempted for this purpose to generate a cyclic silaethene, but it did not react effectively under similar photochemical conditions.

(8) (a) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1976**, *98*, 7424. (b) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1978**, *149*, 37. (c) Conlin, R. T.; Bobbit, K. L. *Organometallics* **1987**, *6*, 1406.

(9) See the supplementary material for experimental details and spectral and analytical data of the new compounds.

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as shown in Table II. Virtually infinitely large slope was estimated for *t*-BuOH. The intercept falls always near 0, while it depends on the slope.

On the basis of these results, we propose a more elaborate mechanism for the addition of alcohol to a silaethene as shown in Scheme I. Thus, after the first formation of an alcohol–silene complex **5** as suggested by Wiberg,[5] the intramolecular proton migration in **5** (the first-order rate constant, k_1) competes with the intermolecular proton transfer from an extra alcohol to **5** (the second-order rate constant, k_2). These two processes give the cis and trans isomers, **3** and **4**, respectively.[10] The mechanism is fully compatible with the observed linear relationship between the product ratio **3**/**4** and 1/[ROH], since the initial product ratio should be represented by eq 2.

$$d[3]/d[4] = (k_1/k_2)/[ROH] \tag{2}$$

The slope, which means the relative rate constant (k_1/k_2), would thus reflect the relative ease between the intra- and intermolecular proton transfer. According to the Brønsted catalysis law, k_2 and k_1 are expected to increase with increasing acidity of ROH and the protonated alcohol, respectively. As shown in Table II, the pK_a values of alcohols decrease in the following order: MeOH > *n*-PrOH > *i*-PrOH > *t*-BuOH. The inverse order is known for the protonated alcohols, RO^+H_2: *t*-BuO^+H_2 > *i*-PrO^+H_2 > *n*-PrO^+H_2 > MeO^+H_2. The more acidic the alcohol is, the less acidic the corresponding protonated alcohol. Thus k_1/k_2 should increase in the following order: MeOH < *n*-PrOH < *i*-PrOH < *t*-BuOH. The observed dependence of the slope on the kind of alcohol is in good agreement with the above prediction.

Supplementary Material Available: Experimental and spectroscopic details, NOESY spectra of **3a** and a related compound, and plot of [**3a**]/[**4a**] vs $[MeOH]^{-1}$ (9 pages). Ordering information is given on any current masthead page.

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[10] If the intermolecular proton transfer occurs at the same side of the complexed alcohol with the rate constant of k_2', the intercept will correspond to k_2'/k_2. Apparently meaninglessly small values of the intercept suggest that the intermolecular syn addition can be neglected.

[11] Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.

[12] Arnett, E. M. *Prog. Phys. Org. Chem.* **1963**, *1*, 223.

[13] Olmsted, W. N.; Margolin, Z.; Bordwell, F. G. *J. Org. Chem.* **1980**, *45*, 3295.

Intramolecular Bis-Silylation of Carbon–Carbon Double Bonds Leading to Stereoselective Synthesis of 1,2,4-Triols

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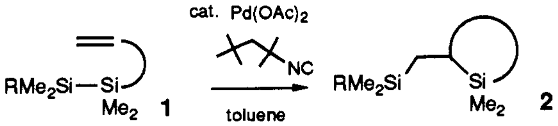
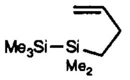
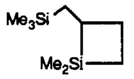
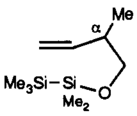
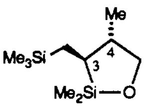
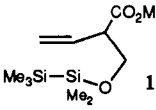
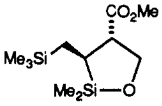
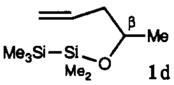
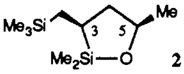
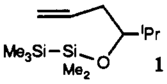
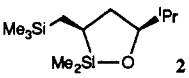
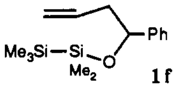
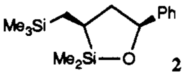
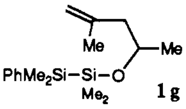
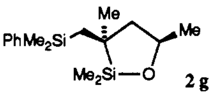
Reactions using organosilicon reagents have become a major tool in organic synthesis,[1] and a variety of pathways to such organosilicon reagents have been developed. Bis-silylation of functional groups such as carbon–carbon multiple bonds with Si–Si is potentially useful since two Si–C bonds are created at once. However, bis-silylation has attracted less attention than hydrosilylation[2] mainly because of the paucity of effective catalysts. Bis-silylation of ethene was achieved with a platinum catalyst, though satisfactory yields were limited to disilanes having electron-withdrawing groups.[3] We reported palladium-catalyzed bis-silylation of isocyanides[4] and very recently found that a new catalyst system, palladium acetate–*tert*-alkyl isocyanide, is extremely efficient for bis-silylation of alkynes with otherwise unreactive disilanes such as hexamethyldisilane.[5] Now we report *intra*molecular bis-silylation of C=C bonds catalyzed by palladium acetate–*tert*-alkyl isocyanide, which leads to stereoselective synthesis of 1,2,4-triols.

Table I. Intramolecular Bis-Silylation of Carbon–Carbon Double Bonds



entry	1	conditions	product (2)	yield, % (cis : trans)
1	 1a	reflux 1 h	 2a	83 (-)
2	 1b	25 °C 6 h	 2b	90 (7 : 93)
3	 1c	25 °C 8 h	 2c	85 (0 : 100)
4	 1d	25 °C 6 h	 2d	85 (96 : 4)
5	 1e	35 °C 10 h	 2e	97 (93 : 7)
6	 1f	75 °C 6 h	 2f	95 (97 : 3)
7	 1g	100 °C 1 h	 2g	96 (95 : 5)

A solution of a terminal alkene **1** incorporating a disilyl group, palladium acetate (1–5 mol %), and 1,1,3,3-tetramethylbutyl isocyanide[6] in toluene[7] was stirred under the conditions specified in Table I. Subsequent Kugelrohr distillation furnished a cyclic bis-silylation product **2** in good yield. Intramolecular stereo- and regioselective addition of the Si—Si linkage to a C=C bond readily took place with **1a–g**; **1a**, having two methylene groups between the C=C bond and the disilyl group, afforded a four-membered exo ring closure product **2a**. Exo ring closure also occurred with **1b–g** to give five-membered products **2b–g**. With disilanes tethered to a C=C bond by chains of more than four atoms, the intramolecular bis-silylation did not proceed. It is not surprising, therefore, that *inter*molecular bis-silylation of olefins with disilanes did not occur at all under similar conditions. Thus, C=C bonds appropriately juxtaposed with disilanes are endowed

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[1] Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988.

[2] Tamao, K.; Nakajima, T.; Sumiya, R.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1986**, *108*, 6090. Ojima, I. In *The chemistry of organic silicon compounds*; Patai, S., Rappoport, Z., Eds.; Wiley-Interscience: Chichester, 1989; Chapter 25.

[3] Hayashi, T.; Kobayashi, T.; Kawamoto, A. M.; Yamashita, H.; Tanaka, M. *Organometallics* **1990**, *9*, 280.

[4] Ito, Y.; Matsuura, T.; Murakami, M. *J. Am. Chem. Soc.* **1988**, *110*, 3692.

[5] Ito, Y.; Suginome, M.; Murakami, M. *J. Org. Chem.* **1991**, *56*, 1948.

[6] An excess of the isocyanide [1,1,3,3-tetramethylbutyl isocyanide/Pd-$(OAc)_2$ = 6–15] was added. Use of less than 6 equiv of isocyanide with respect to $Pd(OAc)_2$ seriously retarded the reaction. Detailed reaction conditions for each experiment are reported in the supplementary material.

[7] Use of THF as solvent gives similar chemical yields and diastereoselectivities.

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