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.

$$d[3]/d[4] = (k_1/k_2)/[ROH] \quad (2)$$

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.

(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.

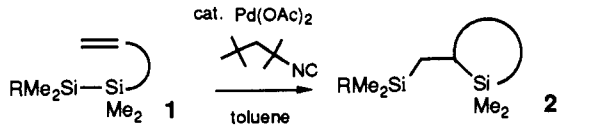
Intramolecular Bis-Silylation of Carbon–Carbon Double Bonds Leading to Stereoselective Synthesis of 1,2,4-Triols

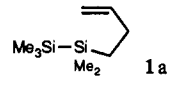
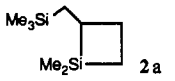
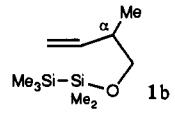
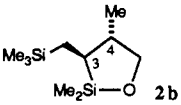
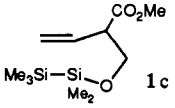
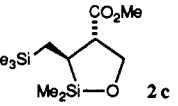
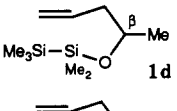
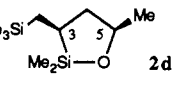
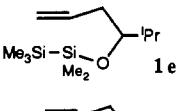
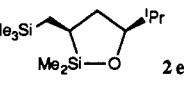
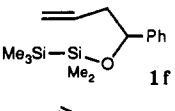
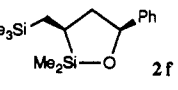
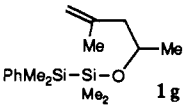
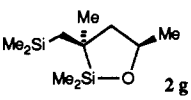
Masahiro Murakami, Pher G. Andersson,†
Michinori Suginome, and Yoshihiko Ito*

Department of Synthetic Chemistry, Faculty of Engineering
Kyoto University, Yoshida, Kyoto 606, Japan
Received January 2, 1991

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)

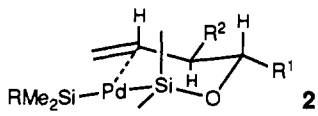
A solution of a terminal alkene **1** incorporating a disilyl group, palladium acetate (1–5 mol %), and 1,1,3,3-tetramethylbutyl isocyanide[6] in toluene[7] was stirred under the conditions specified in Table I. Subsequent Kugelrohr distillation furnished a cyclic bis-silylation product **2** in good 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

† On leave from the Department of Organic Chemistry, University of Uppsala, Sweden.
(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.

0002-7863/91/1513-3987$02.50/0

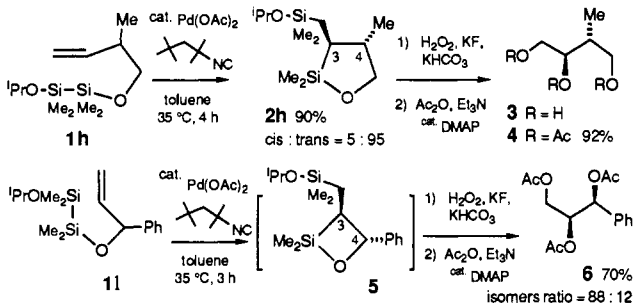
with an enhanced reactivity toward bis-silylation. The present bis-silylation did not require an electron-withdrawing group on the silicon atom (entry 1). Furthermore, a tertiary alkyl–silicon bond was readily formed by the bis-silylation of a geminally disubstituted olefin (entry 7). However, vicinally disubstituted olefins were found not to undergo bis-silylation.

It is noteworthy that bis-silylation of alkenes having an asymmetric center in the tether proceeded with high diastereoselection.[8] Alkenes having allylic substituents, i.e., α to the C=C bond, gave *trans*-**2** (entries 2 and 3), whereas substituents β to the C=C bond favored *cis*-**2** (entries 4–7). The stereoselectivity of the reaction is formulated as arising through a preference for a six-membered cyclic transition state **2t**, in which the substituents R^1 or R^2 are equatorial.



2t

The stereoselective intramolecular bis-silylation of olefinic disilanyl ethers, readily prepared from allylic and homoallylic alcohols, is synthetically useful. Thus, oxidation of the two carbon–silicon bonds of the bis-silylation products introduces two hydroxyl groups leading to the stereo- and regio-defined synthesis of triols as demonstrated in the **1h** to **4** and **1i** to **6** conversions. The use of isopropoxydisilyl ether derivatives of olefinic alcohols facilitates the ultimate oxidation of the silicon–carbon bond. The olefinic disilanyl ether **1h** underwent stereoselective bis-silylation to furnish **2h**, which was oxidized with retention of stereochemistry at carbon[9] to *threo*-3-methylbutane-1,2,4-triol (**3**), a versatile intermediate for the syntheses of δ-multistriatin[10] and ionophore antibiotic X-14547A.[11] Similarly, the olefinic disilanyl ether **1i** was converted to 1,2,3-triol triacetate **6** with moderate stereoselection (88:12) by intramolecular bis-silylation and subsequent oxidation. The stereochemistry of **6** suggests formation of the trans-disubstituted four-membered bis-silylation product **5** analogous to **2a**, although the four-membered silyl ether **5** was too unstable to be isolated and characterized.[12] Thus, intramolecular bis-silylation followed by oxidation offers a new entry to stereoselective dihydroxylation of olefins.



Acknowledgment. This work was supported in part by the Ministry of Education, Science and Culture, Japan (Grant-in-Aid for General Scientific Research 01430017). P.G.A. acknowledges fellowship support from the Royal Swedish Academy of Sciences and Japan Society for the Promotion of Science.

Supplementary Material Available: Experimental details for the synthesis and identification of **2a–h**, **4**, and **6** (6 pages). Ordering information is given on any current masthead page.

(8) Details of the assignment of stereochemistry are described in the supplementary material.

(9) Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* **1983**, *2*, 1694.

(10) Mori, K.; Iwasawa, H. *Tetrahedron* **1980**, *36*, 87.

(11) Nicolaou, K. C.; Papahatjis, D. P.; Claremon, D. A.; Magolda, R. L.; Dolle, R. E. *J. Org. Chem.* **1985**, *50*, 1440.

(12) The mixture was oxidized directly to triol after removal of catalyst by filtration through a short column of Florisil.

Models for Non-Heme Iron Oxygenases: A High-Valent Iron–Oxo Intermediate

Randolph A. Leising, Bridget A. Brennan, and Lawrence Que, Jr.*

Department of Chemistry, University of Minnesota Minneapolis, Minnesota 55455

Brian G. Fox and Eckard Münck*

Department of Chemistry, Carnegie Mellon University 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

Received November 27, 1990

The ferryl (Fe=O) species has been demonstrated to be an intermediate in heme peroxidase chemistry[1] and implicated in cytochrome P-450 catalyzed oxygenations.[2] By analogy to these heme enzymes, ferryl species are increasingly being proposed in the mechanisms of dioxygen activation by non-heme iron enzymes[3-6] and invoked in the chemistry of several non-heme alkane functionalization catalysts.[7] Although transient non-heme iron–oxo species have been reported, they have not been fully characterized,[8,9] and the actual viability of an iron(oxo) intermediate in the absence of a porphyrin ligand has yet to be firmly established. During the course of our alkane functionalization studies,[10] we have identified a reactive intermediate derived from the reaction of a (μ-oxo)diferric complex with hydrogen peroxide and report here the spectroscopic characterization of this novel high-valent non-heme iron species.

The reaction of $Fe(ClO_4)_3$ with TPA[11] in the absence of other coordinating anions affords $Fe_2TPA_2O(ClO_4)_4$ (**1**),[12] which has

(1) (a) Schulz, C. E.; Devaney, P. W.; Winkler, H.; Debrunner, P. G.; Doan, N.; Chiang, R.; Rutter, R.; Hager, L. P. *FEBS Lett.* **1979**, *103*, 102–105. (b) Roberts, J. E.; Hoffman, B. M.; Rutter, R.; Hager, L. P. *J. Biol. Chem.* **1981**, *256*, 2118–2121. (c) LaMar, G. N.; deRopp, J. S.; Smith, K. M.; Langry, K. C. *J. Biol. Chem.* **1981**, *256*, 237–243. (d) Hashimoto, S.; Teraoka, J.; Inubushi, T.; Yonetani, T.; Kitagawa, T. *J. Biol. Chem.* **1986**, *261*, 11110–11118. (e) Penner-Hahn, J. E.; Eble, K. S.; McMurry, T. J.; Renner, M.; Balch, A. L.; Groves, J. T.; Dawson, J. H.; Hodgson, K. O. *J. Am. Chem. Soc.* **1986**, *108*, 7819–7825.

(2) McMurry, T. J.; Groves, J. T. *Cytochrome P-450: Structure, Mechanism, and Biochemistry*; Ortiz de Montellano, P. R., Ed.; Plenum: New York, 1986; p 3 and references therein.

(3) Methane monooxygenase: (a) Fox, B. G.; Borneman, J. G.; Wackett, L. P.; Lipscomb, J. D. *Biochemistry* **1990**, *29*, 6419–6427. (b) Fox, B. G.; Froland, W. A.; Dege, J. E.; Lipscomb, J. D. *J. Biol. Chem.* **1989**, *264*, 10023–10033. (c) Green, J.; Dalton, H. *J. Biol. Chem.* **1989**, *264*, 17698–17703.

(4) Ribonucleotide reductase: (a) Sahlin, M.; Sjöberg, B.-M.; Backes, G.; Loehr, T.; Sanders-Loehr, J. *Biochem. Biophys. Res. Commun.* **1990**, *167*, 813–818. (b) Fontecave, M.; Gerez, C.; Atta, M.; Jeunet, A. *Biochem. Biophys. Res. Commun.* **1990**, *168*, 659–664.

(5) Phenylalanine hydroxylase: Dix, T. A.; Benkovic, S. J. *Acc. Chem. Res.* **1988**, *21*, 101–107.

(6) Isopenicillin N synthase: Baldwin, J. E.; Abraham, E. *Nat. Prod. Rep.* **1988**, *5*, 129–145.

(7) (a) Groves, J. T.; Van Der Puy, M. *J. Am. Chem. Soc.* **1976**, *98*, 5290–5297. (b) Sugimoto, H.; Sawyer, D. T. *J. Am. Chem. Soc.* **1976**, *98*, 4283–4285. (c) Vincent, J. B.; Huffman, J. C.; Christou, G.; Li, Q.; Nanny, M. A.; Hendrickson, D. N.; Fong, R. H.; Fish, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 6898–6900. (d) Barton, D. H. R.; Halley, F.; Ozbalik, N.; Young, E.; Balavoine, G.; Gref, A.; Boivin, J. *New J. Chem.* **1989**, *13*, 177–182. (e) Herron, N. *New J. Chem.* **1989**, *13*, 761–766.

(8) Proniewicz, L. M.; Bajdor, K.; Nakamoto, K. *J. Phys. Chem.* **1986**, *90*, 1760–1766.

(9) Stassinopoulos, A.; Caradonna, J. P. *J. Am. Chem. Soc.* **1990**, *112*, 7071–7073.

(10) Leising, R. A.; Norman, R. E.; Que, L., Jr. *Inorg. Chem.* **1990**, *29*, 2553–2555.

(11) Abbreviations used: TPA = tris(2-pyridylmethyl)amine; OAc = acetate; Por = porphyrin.

0002-7863/91/1513-3988$02.50/0