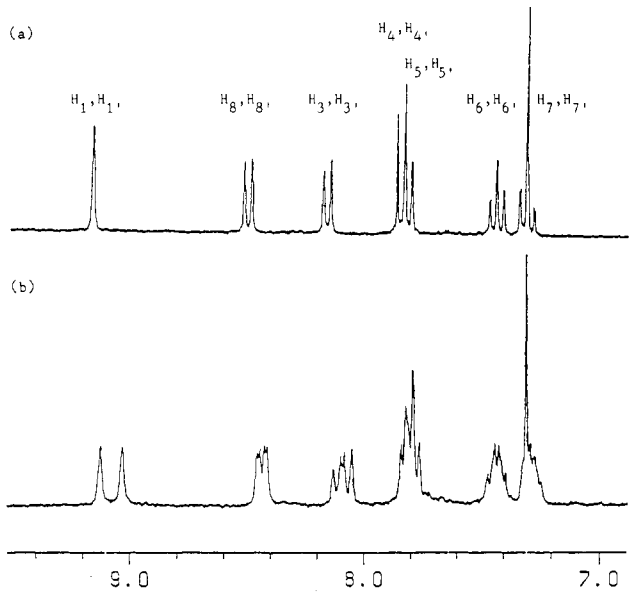
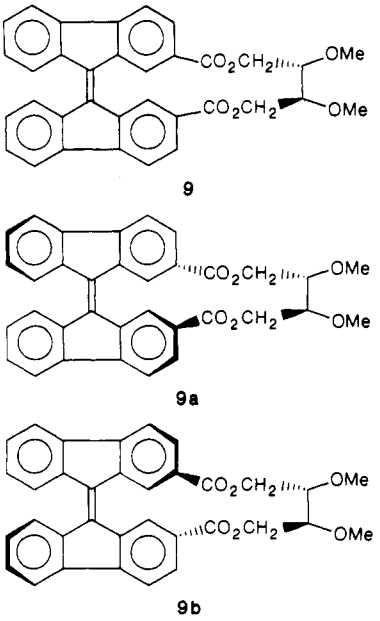


Figure 2. The partial ^1H NMR spectra of **9** at (a) 20 °C and (b) −60 °C. The singlet at δ 7.26 in both spectra is due to residual $CHCl_3$ absorption. Other signals: (a) (20 °C) 4.40–4.60 (br m, 4 H), 3.70–3.80 (br m, 2 H), 3.49 (s, 6 H); (b) (−60 °C) 5.05 (m, 1 H), 4.82 (m, 1 H), 4.15 (m, 1 H), 4.05 (m, 1 H), 3.79 (m, 1 H), 3.55 (m, including a singlet at 3.56, 4 H), 3.44 (s, 3 H).

In order to clarify this point, we synthesized a less rigid chiral bridged bifluorenylidene **9** ($[\alpha]^{22}_D$ +7.3° (*c* 0.19, $CHCl_3$), mp 265–285 °C)[6,8] from **3** in 30% yield by the usual manner.[10] It is important to note that **9** exhibited only one set of NMR absorptions at ambient temperature but two sets of signals at low temperature (Figure 2).[11] The coalescent temperature was −20 °C, which corresponds to a barrier[12] of 12 kcal/mol. These results clearly demonstrate that **9** consisted of a pair of diastereoisomers **9a** and **9b** which underwent rapid equilibrium. The wide range of the melting point of **9** further supports such fast interconversion.



9

9a

9b

The mechanism for the racemization of bifluorenylidenes is interesting. Direct interconversion via a planar bifluorenylidene transition state **10** (Scheme I) seems unlikely since the steric interaction between hydrogens at C_1 and $C_{1'}$ and between hydrogens at C_8 and $C_{8'}$ in **10** would be severe and the barrier should be much higher[3c] than that obtained in this investigation. Alternatively, pyramidalization[13] at C_9 and/or $C_{9'}$ might occur to give **11**, which might undergo rapid twist along the C_9–$C_{9'}$ bond to yield **12** followed by "depyramidalization" to afford the inversion product (Scheme II). The barrier for such an interconversion might be expected to be lower than that depicted in Scheme I.

In summary, we have demonstrated the first enantioselective synthesis of bifluorenylidenes and the activation barrier for the racemization of one such bifluorenylidene. Our results indicate that bifluorenylidene molecules could be chiral in rigid systems.

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(10) Treatment of **3** with **4c** (K_2CO_3, Bu_4NBr, DMF, 60 °C) yielded **5c** (90%, mp 202–204 °C, $[\alpha]^{22}_D$ +1.6° (*c* 0.38, $CHCl_3$)). Desulfurdimerization of **5c** with $W(CO)_6$ (4 equiv) afforded **9** (33%).

(11) It is noted that the chemical shifts were slightly different at different temperatures. The signals between δ 9.0 and 9.2 were employed for the coalescent study.

(12) Atta-ur-Rahman *Nuclear Magnetic Resonance: Basic Principles*; Springer Verlag: New York, 1986; p 133.

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(14) On leave from the Institute of Chemistry, Academia Sinica, Beijing.

General Methods for Alkaloid Synthesis via Intramolecular Diels–Alder Reactions. A Concise Formal Total Synthesis of (±)-Dendrobine

Summary: The tricyclic enone **2**, which previously served as a key intermediate in the total synthesis of (±)-dendrobine (**1**), has been prepared by a novel strategy that features the stereoselective, intramolecular Diels–Alder cycloaddition of the olefinic dienamide **13** to give **14**; several model studies related to this cyclization were performed.

Sir: The ornamental orchid "Jinchai Shihu" (*Dendrobium nobile* LINDL.) has been employed in traditional herbal

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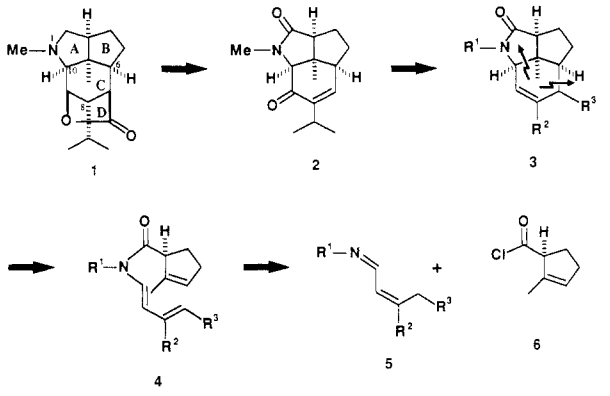
Scheme I



medicine in China as a tonic for the promotion of general health,[3] and dendrobine (1), which itself exhibits antipyretic and hypotensive activity,[4] is the major alkaloidal component isolated from this plant.[5] Inasmuch as 1 incorporates a total of seven stereogenic centers distributed among a mere 17 skeletal atoms arranged in four rings, it may be argued that dendrobine ranks as one of the most complex molecules of its size. Given its intricate architecture, it is thus not surprising that dendrobine has been selected as a target by a number of investigators,[6-12] and these efforts have culminated in four successful total syntheses of 1[6-9] together with the preparation of the C(8)-epimer of dendrobine.[10]

These significant advances not withstanding, we were nevertheless intrigued by the prospect of designing a concise, stereoselective entry to dendrobine (1) according to the strategy outlined in retrosynthetic format in Scheme I. There is a conceptual element of this approach that distinguishes it from prior art. Namely, the intramolecular Diels–Alder reaction of the olefinic dienamide 4 to give 3, which we reasoned should serve admirably as a precursor of 2, results in the *direct* formation of the ABC ring subunit of the dendrobine skeleton.[13,14] This strategy offered

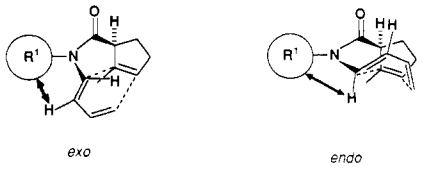
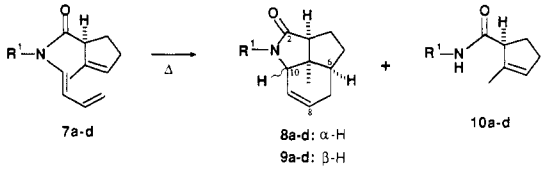


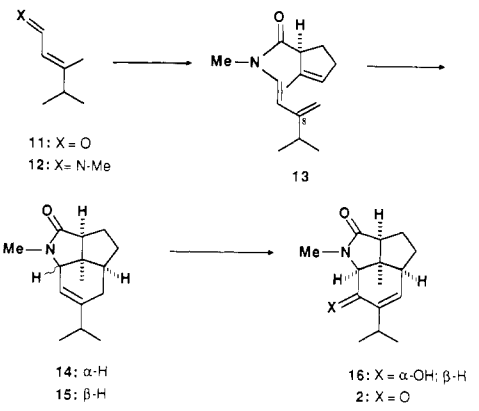
Figure 1.

Table I. Cycloadditions of Some Model Olefinic Dienamides



entry	R^1	temp, °C	α:β (% yield)	% 2° amide
a	Me	260	3.5:1 (14)	51
b	$PhCH_2$	240	5:1 (63)	<5
c	Ph(Me)CH	220	6:1 (68)	<5
d	Ph_2CH	170	9:1 (70)	<1

Scheme II



a means of circumventing some manipulations and refunctionalizations that were previously encountered in those plans that proceeded via initial construction of a *cis*-hydrindane BC ring synthon followed by sequential formation of the A and D rings. A high degree of convergency could be achieved by the maximal incorporation of substitution and functionality prior to the cycloaddition step. We now report some results of these studies that led to an efficient route to the tricyclic enone 2, which was a key intermediate in Inubushi's[6] total synthesis of 1.

Prior to undertaking the preparation of 2, we elected to assess the feasibility of the pivotal intramolecular Diels–

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(3) (a) *China's Pharmacopoeia*, Part I, The People's Health Sciences Publication Co.: Beijing, China, 1977; p 145. (b) *A Dictionary of Chinese Materia Medica*, Jiangsu Medical College; Shanghai Scientific Technology Press: Shanghai, China, 1977; p 586.

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(13) For other examples of the intramolecular [4 + 2] cycloadditions of dienamides, see: (a) Oppolzer, W.; Keller, K. *J. Am. Chem. Soc.* **1971**, *93*, 3836. (b) Oppolzer, W.; Fröstl, W. *Helv. Chim. Acta* **1975**, *58*, 590. (c) Oppolzer, W.; Fröstl, W.; Weber, H. P. *Ibid.* **1975**, *58*, 593. (d) Oppolzer, W.; Flaskamp, E. *Ibid.* **1977**, *60*, 204. (e) Stork, G.; Morgans, D. J., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 7110. (f) Keck, G. E.; Boden, E.; Sonnewald, U. *Tetrahedron Lett.* **1981**, *22*, 2615. (g) Magnus, P.; Gallagher, T.; Brown, P.; Pappalardo, P. *Acc. Chem. Res.* **1984**, *17*, 35 and references cited therein. (h) Magnus, P.; Cairns, P. M. *J. Am. Chem. Soc.* **1986**, *108*, 217.

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Alder reaction that was necessary to construct the ABC ring subunit. To this end, the model olefinic dienamides **7a–d** were prepared[15,16] in a straightforward fashion by the condensation of crotonaldehyde with selected primary amines (R^1NH_2; Et_2O; $MgSO_4$; 0 °C; 2 h) followed by N-acylation of the intermediate imines with the acid chloride **6**[17] ($C_6H_5NEt_2$; toluene; −78 °C → room temperature; 10 h). Thermolyses of **7a–d** were then conducted under a variety of experimental conditions, the best of which are summarized in Table I.[19] Examination of these results reveals that the size of the alkyl substituent on the nitrogen atom linking the dienophile and diene exerts a substantial effect.[20] As evidenced by the required reaction temperatures and times, increased steric bulk of the *N*-alkyl substituent R^1 in **7a–d** resulted in a qualitative decrease in the energy of activation for the intramolecular [4 + 2] cycloaddition. A modest increase in the stereoselectivity of the reaction favoring the production of the endo cycloadducts **8a–d**, which possess the α-orientation of the hydrogen at C(10) (dendrobine numbering), was also observed. At higher temperatures, fragmentation of the trienes **7a–d** ensued as a major side reaction to give the secondary amides **10a–d**.

For the cyclizations of **7a–d**, the observed ratios of cycloadducts **8a–d** and **9a–d** correspond to approximate energy differences between the endo transition state, which yielded the α-orientation of the C(10) hydrogen (e.g., **8a–d**), and the exo transition state, which afforded the β-orientation (e.g., **9a–d**), of approximately 1.3–1.9 kcal/mol. The preferential formation of the endo products **8a–d** may be rationalized upon inspection of molecular models. As the bulk of the *N*-alkyl group increases, the steric interactions of this residue with the diene moiety are more pronounced in the exo rather than in the endo transition state (Figure 1). Moreover, larger *N*-alkyl groups not only increase the ground-state population of the cisoid conformational isomer about the amide N–CO bond, which is required for cyclization, but the buttressing also compresses the dienophilic and dienoic moieties more closely together in the ground state, thereby rendering $\Delta S^{\ddagger}$ less negative;[20a] relief of steric strain emanating from this buttressing in both transition states contributes to the lowering of $\Delta H^{\ddagger}$ for each. Whether the enthalpic or the entropic term was the dominant factor in these processes must be resolved by further, more quantitative experiments.

Having established that an intramolecular Diels–Alder reaction could be exploited for construction of the ABC ring subunit of dendrobine, we set to the more demanding task of introducing additional substituents onto the precursor olefinic dienamide to enhance the convergency of the approach. One appealing tactic entailed the incorporation of an isopropyl group on the dienic partner at C(8). Thus, the requisite triene **13** was conveniently prepared by *N*-acylation of the imine derived from the known aldehyde **11**[21] [(a) CH_3NH_2; $MgSO_4$; Et_2O; 0 °C; 2 h. (b) $C_6H_5NEt_2$; **6**; −78 °C → room temperature; 10 h; 67% overall]; subsequent thermolysis of **13** (xylenes; 180 °C; 10 h) furnished a readily separable mixture (8:1, 55% combined yield) of the two cycloadducts **14** and **15**, respectively. It is notable that the isopropyl group at C(8) on **13**, which favors the s-cis conformation of the diene moiety in the ground state, facilitated the intramolecular [4 + 2] cycloaddition of **13** relative to **7a**. Indeed, its presence on the parent dienic array **7a** had a comparable effect upon both the diastereoselectivity and the rate of cyclization of the resulting olefinic dienamide **13** as was observed in the model study when the *N*-methyl substituent of **7a** was replaced with the bulky *N*-benzhydryl group (e.g., as in **7d**).

Further elaboration of the major cycloadduct **14** into the allylic alcohol **16** was then quickly achieved by highly stereoselective epoxidation (*m*-CPBA; CH_2Cl_2; 0 °C; 2 h; 95%) followed by rearrangement of the intermediate epoxide[22] [(a) TMSOTf;[23] 2,6-di-*tert*-butyl-4-methylpyridine; −78 °C → room temperature; 10 h. (b) 1 N HCl; room temperature; 2 h; 80% overall]. The structure of **16** was unequivocally established by single-crystal, X-ray analysis.[24] Finally oxidation of **16** (PDC;[25] CH_2Cl_2; room temperature; 6 h; 80%) afforded enone **2**, which had spectral characteristics identical with those previously described.[26] Since **2** was previously converted in seven steps into (±)-dendrobine (**1**),[6] the present preparation of **2**, which proceeds via a longest linear sequence requiring only nine

(15) For leading references of methods for the preparation of enamides and dienamides, see: (a) Oppolzer, W.; Fröstl, W. *Helv. Chim. Acta* **1975**, *58*, 587. (b) Overman, L. E.; Taylor, G. F.; Petty, C. B.; Jessup, P. J. *J. Org. Chem.* **1978**, *43*, 2164. (c) Oppolzer, W.; Bieber, L.; Francotte, E. *Tetrahedron Lett.* **1979**, 981. (d) Martin, S. F.; Tu, C.-Y.; Chou, T.-S. *J. Am. Chem. Soc.* **1980**, *102*, 5274. (e) Martin, S. F.; Desai, S. R.; Phillips, G. W.; Miller, A. C. *Ibid.* **1980**, *102*, 3294. (f) Martin, S. F.; Tu, C.-Y.; Kimura, M.; Simonsen, S. H. *J. Org. Chem.* **1982**, *47*, 3634. (g) See in ref 13 and 14.

(16) The structure assigned to each compound was in full accord with its spectral (^1H and ^{13}C NMR, IR, MS) characteristics. Analytical samples of all new compounds wre obtained by recrystallization or preparative HPLC and gave satisfactory data for elemental composition via combustion analysis (C, H, N) and/or high-resolution mass spectrometry. All yields are based on isolated, purified material judged >95% pure by ^1H NMR spectroscopy. Spectral data for selected intermediates are as follows. For **14**: (colorless oil); ^1H NMR (360 MHz) δ 5.46 (br s, 1 H), 3.40 (dd, 1 H, J = 2.5, 5.0 Hz), 2.77 (s, 3 H), 2.53 (br d, 1 H, J = 11.0 Hz), 2.21 (p, 1 H, J = 6.8 Hz), 2.10–1.67 (comp, 5 H), 1.47 (m, 1 H), 1.40–1.17 (comp, 4 H), 0.95 (d, 6 H, J = 6.8 Hz); ^{13}C NMR (90 MHz) δ 176.1, 145.6, 113.8, 64.0, 55.6, 45.7, 43.2, 35.4, 30.9, 29.1, 28.0, 27.7, 26.3, 20.9, 20.7. For **16**: (colorless crystals from ether, mp 127–128 °C); ^1H NMR (500 MHz) δ 5.49 (br d, 1 H, J = 1.7 Hz), 4.38 (br, 1 H), 3.58 (d, 1 H, J = 2.8 Hz), 2.76 (s, 3 H), 2.46 (dd, 1 H, J = 5.0, 8.0 Hz), 2.37–2.32 (comp, 2 H), 2.02–1.81 (comp, 3 H), 1.44–1.37 (comp, 5 H), 1.07 (d, 3 H, J = 6.7 Hz), 1.05 (d, 3 H, J = 6.7 Hz); ^{13}C NMR (125 MHz) δ 177.2, 141.9, 128.0, 68.6, 66.0, 55.5, 45.8, 43.2, 34.1, 33.5, 29.7, 28.4, 27.9, 21.8, 21.6. For **2**: (colorless oil); ^1H NMR (500 MHz) δ 6.55 (dd, 1 H, J = 1.0, 4.7 Hz), 3.54 (s, 1 H), 2.86 (tp, 1 H, J = 1.0, 6.9 Hz), 2.72 (s, 3 H), 2.55 (d, 1 H, J = 7.0 Hz), 2.46 (m, 1 H, J = 4.7, 8.0, 10 Hz), 2.26 (tdd, 1 H, J = 1.4, 6.0, 12.7 Hz), 2.06 (m, 1 H, J = 1.0, 7.0, 8.0, 10.0 Hz), 1.89 (m, 1 H, J = 6.0, 7.0, 12.5, 12.7 Hz), 1.38–1.27 (comp, 4 H), 1.03 (d, 3 H, J = 6.9 Hz), 0.96 (d, 3 H, J = 6.9 Hz); ^{13}C NMR (125 MHz) δ 194.7, 176.8, 143.9, 140.9, 70.4, 55.5, 47.1, 44.7, 33.9, 29.6, 28.7, 27.3, 26.9, 22.0, 21.1. The structures of the major cycloadducts **8c,d** were established by single-crystal X-ray analysis; the structures of the remaining cycloadducts were then made by comparisons of coupling patterns for the protons at C(4), C(5), and C(6).

(17) The acid chloride **6** was prepared from corresponding known methyl ester[18] [(a) KOH/aqueous MeOH; reflux; 4 h; 93%. (b) $(COCl)_2$; 0 °C; 2 h; 95%].

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(20) For other examples of the effect of substitution on a nitrogen in the chain linking the diene and dienophile, see: (a) Gschwend, H. W.; Lee, A. O. *J. Org. Chem.* **1973**, *38*, 2169. (b) Guy, A.; Lemaire, M.; Negre, M.; Guette, J. P. *Tetrahedron Lett.* **1985**, *26*, 3575. (c) Parker, K. A.; Adamchuk, M. R. *Ibid.* **1978**, 1689. For related examples of steric effects in all-carbon systems, see: (d) DeClecq, L. A.; Van Royen, L. A.; Mijngheer, R. *Ibid.* **1983**, *24*, 3145. (e) Boeckman, K., Jr.; Ko, S. S. *J. Am. Chem. Soc.* **1982**, *104*, 1033. (f) Sternbach, D. D.; Rossana, D. M.; Onan, K. D. *Tetrahedron Lett.* **1985**, *26*, 591. (g) Jung, M. E.; Gervay, J. *Ibid.* **1988**, *29*, 2429.

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(23) Noyori, R.; Murata, S.; Suzuki, M. *Tetrahedron* **1981**, *37*, 3899.

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(26) We thank Dr. Takashi Harayama of the Faculty of Pharmaceutical Sciences, Kyoto University, for providing IR and ^1H NMR spectra of authentic **2** that had been previously prepared in Professor Inubushi's laboratory.[6]

steps from commercially available starting materials, constitutes a formal total synthesis of the title alkaloid.

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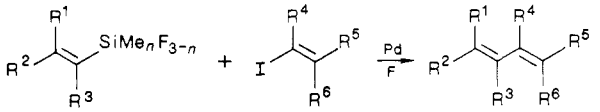
Alkenylfluorosilanes as Widely Applicable Substrates for the Palladium-Catalyzed Coupling of Alkenylsilane/F^- Reagents with Alkenyl Iodides

Summary: Introduction of fluorine(s) to the silyl groups of alkenylsilanes accelerated the rate of the coupling reaction with alkenyl iodides mediated by fluoride ion and palladium catalyst. The new version of the silicon-based coupling reaction has provided a general and highly stereospecific route to 1,3-dienes as well as alkenylarenes.

Sir: Organosilicon compounds are versatile synthetic reagents in that they are stable under normal conditions but activated to undergo nucleophilic reactions only in the presence of nucleophiles like fluoride ion.[1] The organic parts of organosilicons were recently found to be successfully transferred to a palladium complex in the presence of tris(diethylamino)sulfonium difluorotrimethylsilicate (TASF) to establish a catalytic cycle of the coupling reaction of the organosilanes with organic halides.[2] However, the scope of the reported reactions is severely limited mainly due to low reactivity of trimethylsilyl-substituted organosilanes compared with other organometallics.[3] For example, 1-(trimethylsilyl)-1-alkenes failed the coupling reaction under the standard conditions. We report that introduction of fluorine atom(s) into the silicon substituent extremely accelerates the cross-coupling reaction, and thus the silicon-based coupling reaction has now grown to be a powerful synthetic tool for carbon–carbon bond formation.



We first studied the substituent effect of the reaction of (*E*)-1-silyl-1-octenes with 1-iodonaphthalene in the presence of TASF[4] and $(\eta^3\text{-}C_3H_5PdCl)_2$[5] as a catalyst (50 °C). Results are given in the order of silyl group, reaction time, yield (%) of 1-[1(*E*)-octenyl]naphthalene: Me_3Si, 24 h, 0%; FMe_2Si, 10 h, 81%; F_2MeSi, 48 h, 74%; F_3Si, 24 h, 0%. Thus, (*E*)-1-(dimethylfluorosilyl)-1-octene (**1**) exhibited the highest reactivity, the reaction was complete within 10 h, and the coupled product was obtained in a yield of synthetic use. (E)-1-(Methyldifluorosilyl)-1-octene (**2**) was slightly less reactive and required a longer reaction time. To our surprise, trifluorosilyl in addition to the trimethylsilyl group was totally useless. The success of the reactions when **1** or **2** is used may be explained in terms of fluoride ion attacking the silicon atom of **1** or **2** to readily produce a pentacoordinate silicon species which is assumed to be the key intermediate of the coupling reaction.[6] Introduction of more fluorine might have strengthened the C–Si bond to prevent the transmetalation of alkenylsilanes with palladium complex or facilitated the formation of a hexacoordinated silicon species which presumably is unreactive toward the coupling reaction under the mild conditions.[7]

Using dimethylfluorosilyl-substituted alkenes as the substrate, we applied the reaction conditions to various iodoalkenes and iodoarenes. Results summarized in Table I clearly show the following salient features. Since the reaction proceeds with retention of the configuration of both the starting alkenylsilanes and the iodoalkenes, the method disclosed now is highly effective for the stereospecific syntheses of conjugated (*E*,*E*)-, (*E*,*Z*)-, and even (*Z*,*Z*)-dienes. In addition, a wide variety of carbonyl functionalities like ester and ketone tolerate the reaction conditions (entries 4, 5, 8, 9, and 13). It is worth noting that the conditions A [$(\eta^3\text{-}C_3H_5PdCl)_2$ catalyst and tetrahydrofuran (THF) solvent] employed for the coupling of (*E*)-1-(dimethylfluorosilyl)-1-decene, when applied to the reaction of (*Z*)-1-(dimethylfluorosilyl)-1-decene with (*E*)-1-iodo-1-octene, afforded a fair amount of (7*E*,9*E*)-7,9-octadecadiene, which is derived from $Z \rightarrow E$ isomerization of the desired (*E*,*Z*)-diene. The problem was soon cleared up by using $Pd(PPh_3)_4$ catalyst and dimethylformamide (DMF) solvent (conditions B), which reduced the extent of isomerization. Furthermore, when the reaction was monitored carefully, the isomerization was completely suppressed (entries 6–8).

TASF could be replaced by tetrabutylammonium fluoride (TBAF) (conditions C), especially in the reaction of 2-(dimethylfluorosilyl)-1-hexene (entries 9 and 10), wherein TASF caused methylation of iodoarenes to a fair extent.[8]

(1) (a) Furin, G. G.; Vyazankina, O. A.; Gostevsky, B. A.; Vyazankin, N. S. *Tetrahedron* **1988**, *44*, 2675. (b) Corriu, R. J. P.; Perz, R.; Reye, C. *Ibid.* **1983**, *39*, 999.

(2) (a) Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1988**, *53*, 918. (b) Hatanaka, Y.; Hiyama, T. *Tetrahedron Lett.* **1988**, *29*, 97.

(3) For other examples of palladium-catalyzed cross-coupling reactions using organometallic compounds of main group elements, see footnote 1a of ref 2a.

(4) Middleton, W. J. U.S. Patent 3940402, 1976; *Chem. Abstr.* **1976**, *85*, P6388j. Cf.: *Org. Synth.* **1985**, *64*, 221.

(5) Allylpalladium chloride dimer was purchased from Kanto Chemical Co., Inc., Japan.

(6) Many isolable pentacoordinate anionic silicon compounds possess more than two fluorine substituents on silicon, and double or more alkyl substitution reduces the stability of the pentacoordinate silicon species: Damrauer, R.; Danahey, S. E. *Organometallics* **1986**, *5*, 1490.

(7) Coordinative unsaturation of pentacoordinate anionic siliconates is essential for a smooth transmetalation reaction with palladium catalyst: Negishi, E. *Pure Appl. Chem.* **1981**, *53*, 2333. It was reported that coordinatively saturated hexacoordinate dianionic silicon species showed rather low reactivity in the palladium-catalyzed cross-coupling reaction with organic halides: Yoshida, J.; Tamao, K.; Yamamoto, H.; Kakui, T.; Uchida, T.; Kumada, M. *Organometallics* **1982**, *1*, 542. Indeed, a large excess of TASF (6 equiv) over the alkenylsilanes completely suppressed the reaction of (*E*)-1-(dimethylfluorosilyl)-1-octene with 1-iodonaphthalene catalyzed by $(\eta^3\text{-}C_3H_5PdCl)_2$.

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