residue flash chromatographed on silica gel eluting with 2.7:1 hexanes/ethyl acetate to afford 613 mg (77%) of **9a**, yellow needles from ethyl acetate/hexanes: mp 103–104.5 °C; 300-MHz ^{1}H NMR ($CDCl_3$) δ 1.27 (t, 3 H, J = 6.9 Hz), 2.65 (s, 3 H), 2.68 (dd, 1 H, J = 15.6 and 6.3 Hz), 2.87 (dd, 1 H, J = 15.6 and 7.2 Hz), 3.23 (dd, 1 H, J = 16.8 and 7.2 Hz), 3.69 (dd, 1 H, J = 16.8 and 9.6 Hz), 4.01 (s, 3 H), 4.19 (q, 2 H, J = 6.9 Hz), 5.24 (m, 1 H), 6.75 (d, 1 H, J = 7.5 Hz), 7.30–7.50 (m, 2 H), 11.35 (s, 1 H); IR (film) 3005, 1730, 1610, 1390, 1310, 1220, 1150, 1080 cm^{-1}; ^{13}C NMR 14.37, 32.50, 38.38, 41.09, 56.22, 60.64, 78.87, 105.40, 114.75, 115.08, 116.26, 118.56, 124.94, 128.62, 146.79, 154.03, 157.72, 170.40, 201.11 ppm; MS, m/e 344, 270, 257, 241; HRMS, m/e calcd 344.12599, found 344.1259.

***trans*-Ethyl [1-Hydroxy-9-methoxy-1-methyl-5,10-dioxo-3,4,5,10-tetrahydronaphtho[2,3-*c*]pyran-3-yl]acetate (10a).** To a solution of **9** (613 mg, 1.78 mmol) in 40 mL of acetonitrile at ambient temperature was added ceric ammonium nitrate (2.36 g, 4.30 mmol) in 8.5 mL of water. The reaction mixture was stirred 30 min at ambient temperature and poured into 50 mL of water containing 5 mL of a pH 7.5 phosphate buffer, and the layers were separated. The aqueous phase was extracted twice with 30-mL portions of methylene chloride, and the organic extracts were combined, washed with water, and dried over magnesium sulfate. The solvents were removed in vacuo and the residue was crystallized from methylene chloride/hexanes to afford 553 mg (91%) of **10a** as yellow needles: mp 153–154 °C; 300-MHz ^{1}H NMR ($CDCl_3$) δ 1.29 (t, 3 H, J = 7.2 Hz), 1.73 (s, 3 H), 2.28 (dd, 1 H, J = 18.7 and 11.1 Hz), 2.64 (dd, 1 H, J = 15.6 and 6.6 Hz), 2.76 (dd, 1 H, J = 15.6 and 6.6 Hz), 2.88 (dd, J = 18.7 and 2.7 Hz), 3.87 (br s, 1 H), 4.02 (s, 3 H), 4.19 (q, 2 H, J = 7.2 Hz), 4.48 (m, 1 H), 7.32 (dd, 1 H, J = 8.1 and 0.9 Hz), 7.64–7.80 (m, 2 H); IR ($CHCl_3$) 3600–3400, 3010, 1730, 1655, 1585, 1270 cm^{-1}; ^{13}C NMR 14.02, 27.64, 28.23, 40.09, 56.71, 60.69, 65.00, 94.30, 118.34, 119.06, 120.01, 133.97, 135.27, 140.35, 146.33, 159.84, 170.19, 182.02, 182.18 ppm; MS, m/e 342, 296, 268, 244, 229, 201; HRMS, m/e calcd 360.12091, found 360.12032.

***cis*-Ethyl [9-Methoxy-1-methyl-5,10-dioxo-3,4,5,10-tetrahydro-1*H*-naphtho[2,3-*c*]pyran-3-yl]acetate (11a).** To a solution of **10a** (102 mg, 0.30 mmol) in 15 mL of methylene chloride at −78 °C was added trifluoroacetic acid (0.14 mL, 1.8 mmol), and the resulting slurry was stirred at −78 °C for 15 min. To the slurry was added triethylsilane (0.29 mL, 1.8 mmol) at −78 °C. The reaction mixture was slowly warmed to ambient temperature over 3 h. The resulting yellow solution was concentrated in vacuo and the residue crystallized from diethyl ether/hexanes to afford 93 mg (95%) of **11a** as yellow needles: mp 118–119 °C [lit.[2c] mp 113–115 °C]; 300-MHz ^{1}H NMR ($CDCl_3$) δ 1.29 (t, 3 H, J = 7.2 Hz), 1.52 (d, 3 H, J = 6.6 Hz), 2.28 (ddd, 1 H, J = 18.1, 10.5, and 3.7 Hz), 2.60 (dd, 1 H, J = 15.6 and 7.5 Hz), 2.70 (dd, 1 H, J = 15.6 and 7.5 Hz), 2.83 (apparent dt, 1 H, J = 18.1, 2.5, and 2.5 Hz), 3.93 (m, 1 H), 4.00 (s, 3 H), 4.19 (q, 2 H, J = 7.2 Hz), 4.87 (m, 1 H), 7.28 (br d, 1 H, J = 8.4 Hz), 7.64 (t, 1 H, J = 7.8 Hz), 7.73 (dd, 1 H, J = 7.8 and 0.9 Hz); IR (film) 2980, 1730, 1660, 1585, 1270 cm^{-1}; MS, m/e 344, 298, 270, 257, 240; HRMS, m/e calcd 344.12599, found 344.1255.

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Supplementary Material Available: Experimental conditions and spectral data for compounds in the deoxyfrenolicin series (**7b**, **9b**, **10b**, and **11b**) (7 pages). Ordering information is given on any current masthead page.

Stereospecific Arylation of Alkenylsilanes with Arylpalladium Acetates

Kazutoshi Ikenaga*

Department of Industrial Chemistry, Kumamoto Institute of Technology, Ikeda, Kumamoto 860, Japan

Kiyoshi Kikukawa* and Tsutomu Matsuda

Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812, Japan

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Alkenyltrimethylsilanes ((*E*)- and (*Z*)-RCH=CHSiMe$_3$: R = H, Ph, *n*-C_6H_{13}, and CH_3OCH_2) stereospecifically reacted at 40 °C or room temperature with in situ generated phenylpalladium acetate to produce R(Ph)C=CHSiMe$_3$ and RCH=C(Ph)SiMe$_3$ with inversion of their geometry. The arylation of CH_2=CHSiMe$_3$ with arylpalladium acetates gave (*E*)-ArCH=CHSiMe$_3$ (Ar = XPh; X = H, 4-Me, 4-MeO, 4-Br, 4-I, 4-EtOCO, and 4-NO_2) in good yields.

Stereospecific transformations of alkenylsilanes by a variety of electrophiles have been developed and utilized in organic synthesis.[1] However, little is known concerning the reaction of alkenylsilanes with transition-metal organometallics or salts whose catalysis has an important role in C–C coupling of main group organometallics with carbon-based electrophiles.[2]

Reactions of (*E*)-PhCH=CHSiMe$_3$ or (*E*)-PhCH=CHSiF$_5^{2-}$ with palladium salts have been reported to give (*E*)-PhCH=CHPd intermediates through an addition–elimination[3] or transmetalation[4] mechanism. Palladium-catalyzed reactions of CH_2=CHSiMe$_3$ with aryl iodides yield aryl-desilylated products, ArCH=CH_2.[5] Recently

Scheme I

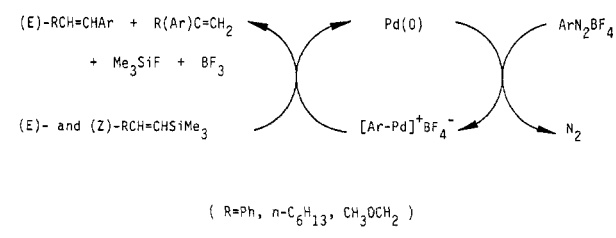

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Table I. Palladium-Catalyzed Stereospecific Phenylation of Alkenylsilanes 1

entry	1	source of PhPdOAc[a]	yields,[b] %	products composition,[c] %				regioselectivity
				2 (E/Z)	3 (E/Z)	4 (E/Z)	5	1-Ph/2-Ph
1	(E)-1a	A	69[d]	42 (5/95)	33	12 (83/17)	13	54/46
2	(E)-1a	B	66	53 (5/95)	35	12		53/47
3	(E)-1a	C	58[d]	56 (5/95)	34	10		56/44
4	(Z)-1a	A	67[d]	66 (95/5)	27	6 (99/1)	1	72/28
5	(Z)-1a	B	60	60 (95/5)	30	10		60/40
6	(Z)-1a	C	70[d]	56 (95/5)	19	25		56/44
7	(E)-1b	A	78[d]	6 (0/100)	62 (95/5)	0	32	6/94
8	(E)-1b	B	73	5 (0/100)	60 (98/2)	0	35	5/95
9	(E)-1b	C	46	3 (0/100)	75 (97/3)	0	22	3/97
10	(Z)-1b	A	56[d]	44 (86/14)	44 (36/64)	2	10	46/54
11	(Z)-1b	B	65	35 (94/6)	57 (30/70)	0	8	35/65
12	(Z)-1b	C	34	43 (86/14)	39 (44/56)	0	18	43/57
13	(E)-1c	A	55[d]	10 (20/80)	88 (7/93)	0	2	10/90
14	(Z)-1c	A	64[d]	45 (87/13)	52 (88/12)	2	1	47/53

[a] PhPdOAc was prepared in situ from the following sources: method A, $PhN(NO)COCH_3$, $Pd(dba)_2$, and an alkenylsilane in CH_3CN at 40 °C for 2 h; method B, Ph_3Sb, $Pd(OAc)_2$, and an alkenylsilane in CH_3CN at 25 °C for 2 h; and method C, Ph_3P, $Pd(OAc)_2$, and an alkenylsilane in CH_3CN at 40 °C for 2 h. [b] GLC yields based on $PhN(NO)COCH_3$ (method A) or on $Pd(OAc)_2$ (method B and C). [c] Determined by GLC. [d] Isolated yields.

we reported a facile aryl desilylation of (*E*)- and (*Z*)-RCH=CHSiMe$_3$ with arylpalladium tetrafluoroborates ([ArPd]$^+$BF$_4^-$) generated from ArN_2BF_4 and bis(dibenzylidenacetone)palladium(0) ($Pd(dba)_2$).[6-8] Both *E* and *Z* isomers give (*E*)-RCH=CHAr and R(Ar)C=CH$_2$ (Scheme I).

In contrast to these desilylating reactions, herein we report a stereospecific and nondesilylating arylation of (*E*)- and (*Z*)-RCH=CHSiMe$_3$ with arylpalladium acetates (ArPdOAc) generated from various sources.[9]

Results

Phenylation of (*E*)- and (*Z*)-RCH=CHSiMe$_3$ with PhPdOAc. The following three methods were employed to generate PhPdOAc because of their mild conditions and availability of starting materials (eq 1–3). With respect

method A[10]

$$PhN(NO)COCH_3 + Pd(0)(dba)_2 \rightarrow PhPdOAc + N_2 \quad (1)$$

method B[11]

$$Ph_3Sb + Pd^{II}(OAc)_2 \rightarrow PhPdOAc + Ph_2Sb(OAc) \quad (2)$$

method C[12]

$$Ph_3P + Pd^{II}(OAc)_2 \rightarrow PhPdOAc + Ph_2P(OAc) \quad (3)$$

to palladium, method A is catalytic, whereas methods B and C are stoichiometric. Irrespective of the method of generation, PhPdOAc easily reacted with (*E*)- and (*Z*)-RCH=CHSiMe$_3$ (R = Ph (**1a**), *n*-C$_6$H$_{13}$ (**1b**), and CH$_3$OCH$_2$ (**1c**)) at 25 °C or 40 °C for 2 h. The structure of **1** does not affect the rate, therefore the generation of PhPdOAc may determine the rate of phenylation. In contrast to the reactions with [PhPd]$^+$BF$_4^-$, either *E* or *Z* isomers stereospecifically produced phenylated alkenylsilanes **2** and **3** as major products (eq 4 and Table I).

$$\text{(E)- or (Z)-RCH=CHSiMe}_3 + PhPdOAc \rightarrow \underset{\textbf{1a–c}}{} \underset{\textbf{2a–c}}{RCH{=}C(Ph)SiMe_3} + \underset{\textbf{3a–c}}{R(Ph)C{=}CHSiMe_3} + \underset{\textbf{4a–c}}{RCH{=}CHPh} + \underset{\textbf{5a–c}}{R(Ph)C{=}CH_2} \quad (4)$$

a, R = Ph; **b**, R = *n*-C$_6$H$_{13}$; **c**, R = CH$_3$OCH$_2$

The exact isomer ratio of **2a** could not be determined because the retention time of (*Z*)-**2a** on GLC was very close to that of **3a**. After separation of the isomers by medium pressure column chromatography (silica gel–hexane), the ^{1}H NMR spectra of (*E*)-**2a** did not show the resonance of (*Z*)-**2a** and vice versa. The geometry of the starting silanes were inverted in the products, although the stereospecificity considerably varied with the structure of alkenylsilanes. In the case of (*E*)-**1b** and (*E*)-**1c**, 2-phenylated products **3** and **5** were selectively produced, whereas **1a**, (*Z*)-**1b**, and (*Z*)-**1c** yielded comparable amounts of 1- and 2-phenylated products.

Arylation of CH$_2$=CHSiMe$_3$ with ArPdOAc. The present results prompted us to examine the synthesis of substituted styrylsilanes by the arylation of CH$_2$=CHSiMe$_3$ (**6**) with ArPdOAc. Since a variety of substituted *N*-nitroso-*N*-arylacetamides (ArN(NO)COCH$_3$, **7a–g**) are easily available,[13] method A was employed to generate ArPdOAc. All substituents on **7** examined here could be successfully used in this arylation and (*E*)-ArCH=CHSiMe$_3$ (**8a–g**) were obtained as the main products (eq 5 and Table II). Pure **8a–g** were easily separated from the reaction mixture in good yields by medium pressure column chromatography (silica gel–hexane). Generally an electron-withdrawing group on **7** gave good results.

$$\underset{\textbf{6}}{CH_2{=}CHSiMe_3} + \underset{\textbf{7a–g}}{ArN(NO)COCH_3} \xrightarrow{Pd(dba)_2,\ 40\ ^\circ C\ in\ CH_3CN} \underset{\textbf{8a–g}}{\text{(E)-ArCH=CHSiMe}_3} + \underset{\textbf{9a–g}}{Me_3SiC(Ar){=}CH_2} + \underset{\textbf{10a–g}}{ArCH{=}CH_2} \quad (5)$$

a, Ar = Ph; **b**, Ar = 4-MePh; **c**, Ar = 4-MeOPh; **d**, Ar = 4-BrPh; **e**, Ar = 4-IPh; **f**, Ar = 4-EtOCOPh; **g**, Ar = 4-NO$_2$Ph

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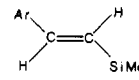
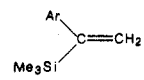
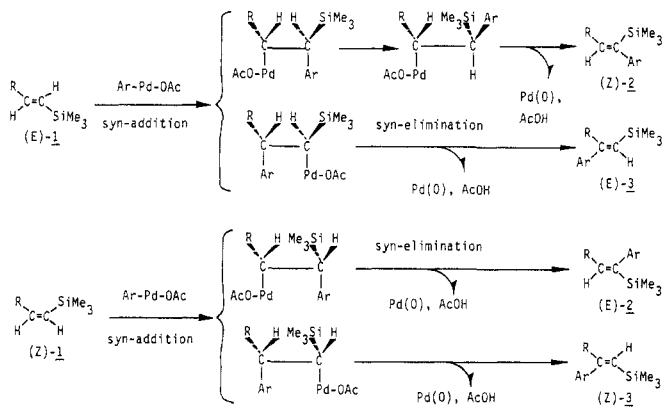
Table II. Palladium-Catalyzed Arylation of CH_2=$CHSiMe_3$ (6) with $ArN(NO)COCH_3$ (7a-g)

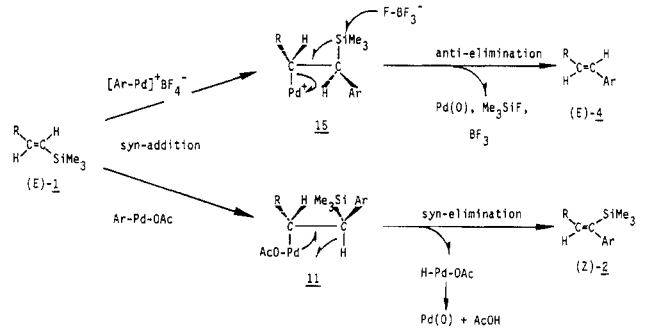
entry	Ar in 7	$Pd(dba)_2$, mol %	reactn time, h	yields,[a] %	products composition,[b] %		
							$ArCH$=CH_2
15[c]	Ph (**7a**)	2	1.0	79	(*E*)-**8a** (94)	**9a** (6)	*f*
16[c]	**7a**	10	2.0	80	(*E*)-**8a** (96)	**9a** (4)	*f*
17[d]	**7a**	20	0.3	82[e]	(*E*)-**8a** (92)	**9a** (5)	**10a** (3)
18[c]	4-MePh (**7b**)	10	1.5	50	(*E*)-**8b** (94)	**9b** (4)	**10b** (2)
19[d]	**7b**	10		54	(*E*)-**8b** (92)	**9b** (5)	**10b** (3)
20[c]	4-MeOPh (**7c**)	10	1.0	56	(*E*)-**8c** (92)	**9c** (5)	**10c** (3)
21[d]	4-BrPh (**7d**)	10	2.0	81	(*E*)-**8d** (94)	**9d** (5)	**10d** (1)
22[d]	4-IPh (**7e**)	10	1.5	75	(*E*)-**8e** (76)	**9e** (5)	**10e** (19)[g]
23[d]	4-NO_2Ph (**7f**)	10	1.5	75	(*E*)-**8f** (88)	**9f** (8)	**10f** (4)
24[c]	**7f**	20	2.0	56[e]	(*E*)-**8f** (83)	**9f** (9)	**10f** (8)
25[d]	4-EtOCOPh (**7g**)	10	1.0	83	(*E*)-**8g** (91)	**9g** (6)	**10g** (3)[g]

[a] Isolated yields based on **7**. [b] The mol % compositions of the products were determined by direct GC analysis of the crude mixture. [c] Employed **6** equivalent to **7**. [d] Used 3 mol of **6** to 1 mol of **7**. [e] GC yields based on **7**. [f] Not detected. [g] Involved unknown products.

Scheme II



Scheme III



Discussion

The stereochemistry of the present reactions can be easily explained in terms of syn addition of ArPdOAc and syn elimination of HPdOAc as in the Heck arylation (Scheme II).[14]

The marked difference between the reactions with $[ArPd]^+BF_4^-$ and ArPdOAc can be accounted for by the difference in the elimination pathway from the adducts formed by the syn addition of the ArPd species for each reaction (Scheme III). In the adduct **15**, the cationic nature of the palladium and the presence of BF_4^- may facilitate the elimination of the Me_3Si group.[6,7] On the contrary, the tighter coordination of OAc^- to palladium in the adduct **11** may promote the syn elimination of HPdOAc.

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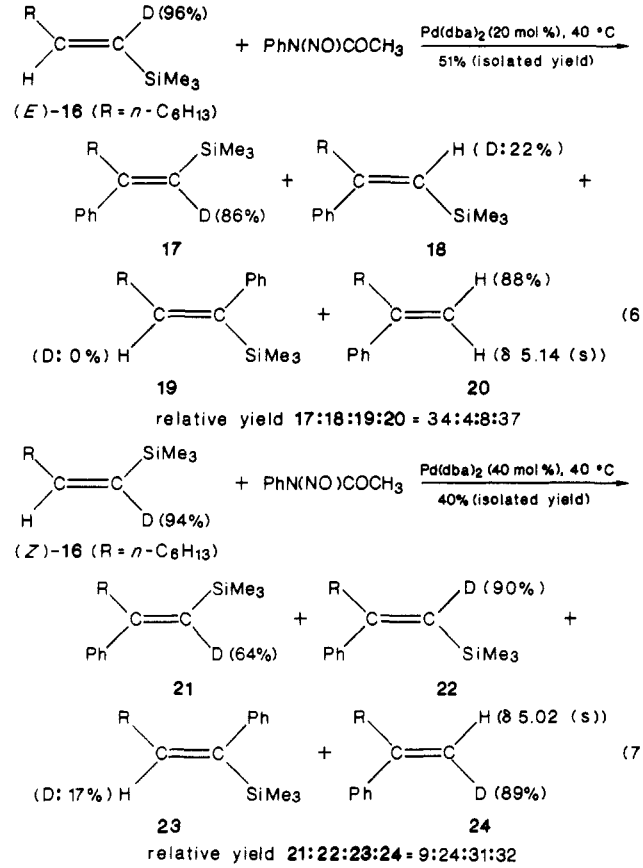
Deuteriated (*E*)- and (*Z*)-*n*-$C_6H_{13}CH$=$CDSiMe_3$ ((*E*)- and (*Z*)-**16**) were used to get more information about the stereochemistry of the present arylation (eq 6 and 7).



Since the minor products **18**, **19**, and **21** could not be isolated in pure form, the deuterium contents shown in parentheses in the equations were determined by ^1H NMR measurements of the product mixture. Thus the deuterium contents have considerable experimental errors. It can be concluded that (i) the deuterium in **16** was virtually retained in **17**, **20**, **22**, and **24** and was virtually lost in **18**, **19**, and **23** and (ii) some of the deuterium was lost in **21**. The reaction pathways described in Scheme II clearly explain the loss of deuterium in **19** and **23**.

The stereospecific formation of **20** from (*E*)-**16** and that of **24** from (*Z*)-**16** are noticeable. The following two processes can be considered for the formation of desilylated products: (i) protodesilylation from **17** (or **22**) and (ii) the direct elimination of $Me_3SiPd(OAc)$ moiety from the ad-

duct **25** and **26**. The desilylation of **17** (or **22**) was very slow under the present reaction conditions. The product ratios described in eq 6 and 7 were virtually constant during the reactions. Furthermore, protodesilylation generally proceed with retention of the geometry.[1] Therefore **20** and **24** must directly arise from the adduct **25** and **26**, respectively, as shown in Scheme IV.

The regiochemistry of the arylation depends on the substituents and the geometry of **1**. The electronic and steric factors of substituents on olefins affect the orientation of the addition of ArPdX. The aryl group of ArPdX usually binds to the carbon atom possessing the less bulky and more electron-donating group.[14] The order of electron-donating effect of 2-substituents on **1** (n-C_6H_{13} > CH_3OCH_2 > Ph) and the bulkiness (Ph > n-C_6H_{13} ≈ CH_3OCH_2) easily account for the order of regioselectivity for 2-phenylation in the substrates of the same geometry, i.e., **1b** ≳ **1c** > **1a**. At present, there is no clear-cut explanation for the remarkable difference in the regioselectivity between the E and Z substrates. The steric factor of the substituents on **1** seems to be a principal reason for the difference. Usually the steric effect works more effectively in E isomers than Z isomers in the coordination of olefins to palladium(II).[15] Since, the Me_3Si group is the most bulky substituent in **1**, its steric effect, giving 2-phenylated products, may be more effective in (*E*)-**1a–c** than (*Z*)-**1a–c**.

Since **7** with various substituents are easily available from aniline derivatives, the present arylation with **7** provides a convenient procedure for preparation of **8** a bearing polar functional group. The chemoselective formation of the halo-substituted **8** showed the high reactivity of N-nitrosoamide group to zero-valent palladium.

Experimental Section

IR and ^1H NMR spectra were measured by using JASCO Model IR-E spectrometer and Hitachi R24B NMR spectrometer using CH_2Cl_2 as the internal reference, respectively. GLC analyses were performed with a Shimazu GC-8A chromatography (FID) using a 2, 1, or 0.6 m × 4 mm column (5% SE-30 or 5% Thermon 1000). GLC yields were determined by using diamyl ether and dioctyl ether as internal standards.

Materials. Acetonitrile was distilled from phosphorus pentoxide (twice) and calcium hydride under nitrogen. Arylamines and triphenylantimony were obtained commercially. Liquid arylamines were distilled before use. $ArNHCOCH_3$ were prepared from $ArNH_2$ and Ac_2O and recrystallized from ethanol. $ArN(NO)COCH_3$ (**7a–g**) were prepared according to the modified method of Carcia et al.[13] N_2O_4 (10 times excess) generated from Cu-concentrated HNO_3 was introduced to a solution of $ArNHCOCH_3$ in Ac_2O with NaOAc at −40 to −20 °C. In the present method, CH_2Cl_2 was replaced by Ac_2O as a solvent because of the easy decomposition of **7** during the purification by column chromatography (silica gel–CH_2Cl_2). After ordinary workup from the resulting green solution, **7a–g** were obtained and stored under nitrogen at −20 °C. $Pd(dba)_2$[16] and $Pd(OAc)_2$[17] were prepared by the published methods. (*E*)-RCH=CHSiMe$_3$ (**1a–c**) and Z isomers were prepared through hydrosilation[18] of acetylenes and hydroalumination[19] of (trimethylsilyl)acetylenes, respectively. CH_2=CHSiMe$_3$ (**6**) was obtained by methylation of CH_2=CH-$SiCl_3$ with MeMgBr in dibutyl ether. (*E*)- and (*Z*)-n-C_6H_{13}CH=CDSiMe$_3$ (**16**) were prepared from hydrosilation of n-$C_6H_{13}C{\equiv}CD$ and deuterolysis of hydroalumination products of n-$C_6H_{13}C{\equiv}CSiMe_3$, respectively. The structure and purity of starting alkenylsilanes were confirmed by ^1H NMR and IR spectra and GC analysis. Isomeric purity estimated by GC of those alkenylsilanes was 99.9% or more except for (*Z*)-**1a** (96.0%) and (*E*)-**1c** (99.5%). Deuterium contents estimated by NMR of (*E*)-**16** and (*Z*)-**16** were 96% and 94%, respectively.

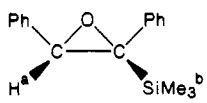
General Procedure of Arylation. Method A (eq 1). To a thermostated cell equipped with gas buret under nitrogen were added 0.5 mmol of N-nitroso-N-arylacetamide (**7**), 1 mmol of alkenyltrimethylsilane (**1**), 0.1 mmol of $Pd(dba)_2$, and 5 mL of dry acetonitrile. Smooth evolution of gas was started by warming the mixture to 40 °C. The mixture was stirred for 1 h. **Method B (eq 2).** The reaction was carried out by addition of 0.2 mmol of $Pd(OAc)_2$ to a solution of 0.2 mmol of Ph_3Sb, 0.5 mmol of **1**, and 5 mL of CH_3CN at 25 °C. The solution was stirred for 2 h. **Method C (eq 3).** The reaction was started by addition of 0.5 mmol of Ph_3P to a solution of 0.5 mmol of $Pd(OAc)_2$, 1 mmol of **1**, and 5 mL of CH_3CN at 40 °C. The mixture was stirred for 1 h. After reactions were completed, 50 mL of diethyl ether was added to the mixture. The diluted solution was filtered to remove precipitated palladium. The product ratios were determined by GC analysis of the filtrate after an appropriate internal standard was added. The mixture was washed with aqueous sodium bicarbonate and brine and then dried over anhydrous magnesium sulfate. The filtrate was condensed in vacuo. The residue was purified by column chromatography (silica gel–hexane) and/or distillation (Kugelrohr). The stereochemistries of (*E*)- and (*Z*)-**2a**, (*E*)-**2c**, and (*E*)- and (*Z*)-**3c** were assigned by NMR spectra of their epoxides which were prepared by the reaction with peroxybenzoic acid in $CHCl_3$.

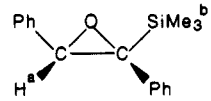
((*E*)-1,2-Diphenylvinyl)trimethylsilane ((*E*)-2a) ((*E*)-PhCH^a=C(Ph)SiMe$_3^b$): ^1H NMR ($CDCl_3$) δ H^a 6.7 (s, 1 H), H^b 0.14 (s, 9 H). Anal. Calcd for $C_{17}H_{20}Si$: C, 80.87; H, 8.00. Found: C, 80.90; H, 8.08.

((*Z*)-1,2-Diphenylvinyl)trimethylsilane ((*Z*)-2a) ((*Z*)-PhCH^a=C(Ph)SiMe$_3^b$): ^1H NMR ($CDCl_3$) δ H^a 7.24 (s, 1 H), H^b −0.06 (s, 9 H). Anal. Calcd for $C_{17}H_{20}Si$: C, 80.87; H, 8.00. Found: C, 81.02; H, 7.93.

(2,2-Diphenylvinyl)trimethylsilane (3a) (Ph$_2$C=CH^{a}SiMe$_3^b$): ^1H NMR ($CDCl_3$) δ H^a 6.21 (s, 1 H), H^b −0.13 (s, 9 H) [lit.[20] H^a 6.91, H^b −0.12]. Anal. Calcd for $C_{17}H_{20}Si$: C, 80.87; H, 8.00. Found: C, 80.93; H, 7.97.

Epoxide of (*E*)-2a: ^1H NMR ($CDCl_3$) δ H^a 4.13 (s, 1 H), H^b 0.22 (s, 9 H) [lit.[21] 4.24, H^b 0.32]. **Epoxide of (*Z*)-2a:** ^1H NMR ($CDCl_3$) δ H^a 3.95 (s, 1 H), H^b 0.05 (s, 9 H).





((*E*)-1-Phenyl-1-*n*-octenyl)trimethylsilane ((*E*)-2b) ((*E*)-*n*-C$_5$H$_{11}$CH$_2^a$CH^b=C(Ph)SiMe$_3^c$): ^1H NMR ($CDCl_3$) δ H^a 1.85–2.30 (br), H^b 5.96 (t, J_{ba} = 7.4 Hz, 1 H), H^c 0.11 (s, 9 H).

((*E*)-2-Phenyl-1-*n*-octenyl)trimethylsilane ((*E*)-3b) ((*E*)-*n*-C$_5$H$_{11}$CH$_2^a$C(Ph)=CH^{b}SiMe$_3^c$): ^1H NMR ($CDCl_3$) δ H^a 2.45–2.93 (br), H^b 5.77 (s, 1 H), H^c −0.15 (s, 9 H).

((*Z*)-2-Phenyl-1-*n*-octenyl)trimethylsilane ((*Z*)-3b) ((*Z*)-*n*-C$_5$H$_{11}$CH$_2^a$C(Ph)=CH^{b}SiMe$_3^c$): ^1H NMR ($CDCl_3$) δ H^a 2.30–2.76 (br), H^b 5.54 (t, J_{ba} = 1.33 Hz, 1 H), H^c 0.11 (s, 9 H).

((*E*)-3-Methoxy-1-phenylpropenyl)trimethylsilane ((*E*)-2c) ((*E*)-Me^{a}OCH$_2^b$CH^c=C(Ph)SiMe$_3^d$): ^1H NMR (CD-

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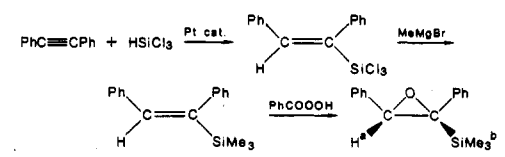
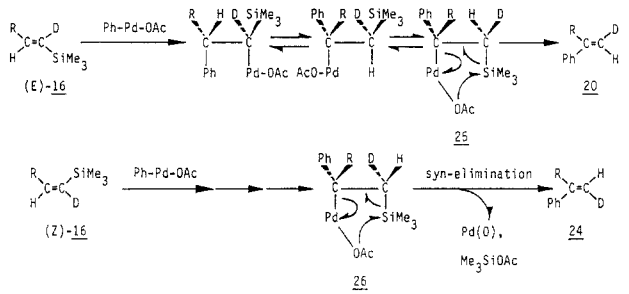
(21) The NMR spectra are those of authentic sample prepared from the following reactions. The NMR spectra of epoxide of (*E*)-**2a** were nearly in agreement with those of the authentic sample.



Scheme IV

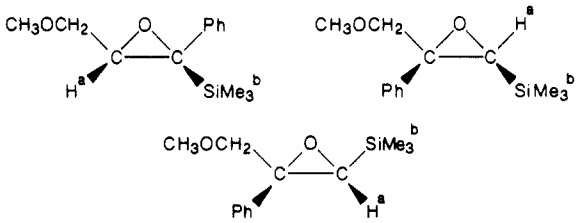


Cl_3) δ H^a 3.27 (s, 3 H), H^b 3.80 (d, J_{bc} = 5.87 Hz, 2 H), H^c 6.14 (t, J_{cb} = 5.87 Hz, 1 H), H^d 0.16 (s, 9 H).

((*E*)-3-Methoxy-2-phenylpropenyl)trimethylsilane ((*E*)-3c) ((*E*)-$Me^aOCH_2{}^bC(Ph)$=$CH^cSiMe_3{}^d$): ^1H NMR ($CDCl_3$) δ H^a 3.42 (s, 3 H), H^b 4.08 (d, J_{bc} = 1.47 Hz, 2 H), H^c 5.90 (t, J_{cb} = 1.47 Hz, 1 H), H^d −0.08 (s, 9 H).

((*Z*)-3-Methoxy-2-phenylpropenyl)trimethylsilane ((*Z*)-3c) ((*Z*)-$Me^aOCH_2{}^bC(Ph)$=$CH^cSiMe_3{}^d$): ^1H NMR ($CDCl_3$) δ H^a 3.42 (s, 3 H), H^b 4.43 (s, 2 H), H^c 6.12 (s, 1 H), H^d 0.36 (s, 9 H).

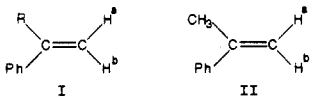
Epoxide of (*E*)-2c: ^1H NMR ($CDCl_3$) δ H^a 3.02 (s, 1 H), H^b −0.20 (s, 9 H). **Epoxide of (*E*)-3c**: ^1H NMR ($CDCl_3$) δ H^a 2.44 (s, 1 H), H^b 0.07 (s, 9 H). **Epoxide of (*Z*)-3c**: ^1H NMR ($CDCl_3$) δ H^a 2.15 (s, 1 H), H^b 0.33 (s, 9 H).



Arylation of Vinyltrimethylsilane. ((*E*)-2-Phenylvinyl)trimethylsilane (8a) and (1-Phenylvinyl)trimethylsilane (9a). The reaction was carried out through method A and employed 5 mmol (0.50 g) of vinyltrimethylsilane (**6**), 5 mmol (0.82 g) of **7a**, 0.5 mmol (0.29 g) of $Pd(dba)_2$, and 50 mL of CH_3CN. After completion of the gas evolution, the mixture was diluted with 100 mL of diethyl ether. The usual workup and purification by column chromatography (silica gel–hexane) gave **8a** and **9a** (0.71 g, 80%, **8a**:**9a** = 94:6). **(*E*)-PhCH=CHSiMe$_3$ (8a)**: Anal. Calcd for $C_{11}H_{16}Si$: C, 74.91; H, 9.16. Found: C, 74.76; H, 9.25. **(*E*)-4-MeC$_6$H$_4$CH=CHSiMe$_3$ (8b)**: Anal. Calcd for $C_{12}H_{18}Si$: C, 75.70; H, 9.55. Found: C, 75.91; H, 7.90. **(*E*)-4-$Me^aOC_6H_4CH^b$=$CH^cSiMe_3{}^d$ (8c)**: ^1H NMR ($CDCl_3$) δ H^a 3.87 (s, 3 H), H^b 6.90 (d, J_{bc} = 19.7 Hz, 1 H), H^c 6.24 (s, J_{cb} = 19.7 Hz, 1 H), H^d 0.40 (s, 9 H). Anal. Calcd for $C_{12}H_{18}OSi$: C, 69.83; H, 8.81. Found: C, 72.00; H, 9.16. **(*E*)-4-$CH_3{}^aCH_2{}^bOCOC_6H_4CH^c$=$CH^dSiMe_3{}^e$ (8g)**: ^1H NMR ($CDCl_3$) δ H^a 1.50 (t, J_{ab} = 6.0 Hz, 3 H), H^b 4.35 (q, J_{ba} = 6.0 Hz, 2 H), H^c 6.92 (d, J_{cd} = 1.87 Hz, 1 H), H^d 6.47 (d, J_{dc} = 18.7 Hz, 1 H), H^e 0.42 (s, 9 H). Anal. Calcd for $C_{14}H_{20}O_2Si$: C, 67.68; H, 8.13. Found: C, 68.20; H, 8.18. **4-EtOCOC$_6$H$_4$(Me$_3$Si)C=CH$_2{}^{a,b}$ (9g)**: ^1H NMR ($CDCl_3$) δ H^a 5.79 (d, J_{ab} = 2.9 Hz, 1 H), H^b 5.60 (d, J_{ba} = 2.9 Hz, 1 H).

Reactions of (*E*)- and (*Z*)-*n*-C$_6$H$_{13}$CH=CDSiMe$_3$ with PhN(NO)COCH$_3$. The same procedure with that described above was employed with 2.4 mmol (0.45 g) of (*E*)-**16**, 1.5 mmol (0.25 g) of **7a**, 0.6 mmol (0.35 g) of $Pd(dba)_2$, and 10 mL of CH_3CN, or with 2.4 mmol (0.45 g) of (*Z*)-**16**, 2.0 mmol (0.33 g) of **7a**, 0.4 mmol (0.23 g) of $Pd(dba)_2$, and 10 mL of CH_3CN. The ordinary workup and Kugelrohr distillation gave arylated alkenylsilanes and *n*-octenes in 51% (0.20 g) yield from (*E*)-**16** and in 40% (0.21 g) yield from (*Z*)-**16**. The stereochemistries of **17**–**20** and **21**–**24** were confirmed by NMR spectra of them and by their retention times on GC with those products from entries 7 and 10, respectively. Deuterium contents of products were estimated by NMR spectra of mixtures of them. **(*E*)-*n*-C$_6$H$_{13}$(Ph)C=CDH^a (20)**: ^1H NMR ($CDCl_3$) δ H^a 5.14(s).[22] **(*Z*)-*n*-C$_6$H$_{13}$(Ph)C=CH^{a}D (24)**: ^1H NMR ($CDCl_3$) δ H^a 5.02 (t, J = 1.3 Hz).[22]

(22) The NMR spectra were compared with those of I (R = *n*-C_6H_{13}) prepared from the palladium-catalyzed reaction of (*E*)-RCH=CHSiMe$_3$ with PhN_2BF_4: ^1H NMR ($CDCl_3$) δ H^a 5.09 (m), H^b 5.27 (m). Cf. the spectra were in fair agreement with those of α-methylstyrene (II): H^a 5.02, H^b 5.28; Jackman, L. M.; Wiley, R. H. *J. Chem. Soc.* **1960**, 2881.



I II

Synthesis and Base-Induced Methylation Reactions of *cis*-7a-Hydroxy-3a-(phenylsulfenyl)-3a,4,5,6,7,7a-hexahydro-4-indanone[1a,b]

Drury Caine,*[2] Candice J. McCloskey,[3] Jerry L. Atwood,[2] Simon G. Bott,[2] Hong-Ming Zhang,[2] and Donald VanDerveer[3a]

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332, and Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama 35487

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cis-7a-Hydroxy-3a-(phenylsulfenyl)-3a,4,5,6,7,7a-hexahydro-4-indanone (**2**) was prepared by reaction of 10-oxatricyclo[4.3.1.0]decan-2-one with sodium thiophenoxide in THF. Reaction of **2** with potassium hydride in THF/HMPA and an excess of a methylating agent gave *cis*-7a-methoxy-3a-(phenylsulfenyl)-3a,4,5,6,7,7a-hexahydro-4-indanone (**8**) and 1-methyl-7-(phenylsulfenyl)bicyclo[4.3.0]-6(7)-nonen-2-one (**9**), which apparently arose by a retroaldol reaction followed by recyclization, formation of a dienolate, and C-alkylation. The ratio of **8** and **9** was dependent upon the reaction conditions. When DME rather than THF was used as a solvent in some runs, **2** apparently underwent a 1,3-sigmatropic rearrangement of the phenylsulfenyl group because 3-(phenylsulfenyl)bicyclo[4.3.0]-1(6)-nonen-2-one (**14**) and its C-3 methylation product **15** were isolated.

We recently reported that upon base treatment monocyclic β-hydroxy α-phenylsulfenyl ketones undergo retroaldol reactions to generate acyclic keto (or aldehydo) enolates that can be trapped with electrophilic or nucleophilic reagents.[4] The possibility also existed that

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(2) The University of Alabama.

(3) (a) Georgia Institute of Technology. (b) Present address: Chemistry Department, Georgia State University, Atlanta, GA 30303.

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