stirring suspension of lithium aluminum hydride (LAH) in anhydrous ether–THF (2:1) solvent mixture (150 mL). The reaction mixture was heated at reflux for 24 h and then cooled to 0 °C. Ether (100 mL) was added and the excess LAH was quenched by the cautious successive addition of water (4 mL), 15% NaOH solution (4 mL), and water (12 mL). The aluminum salts were filtered and the organic layer was concentrated in vacuo to give an oil. The oil was dissolved in ether (150 mL) and extracted with 10% HCl solution. The aqueous acidic layer was basified to pH 9 and extracted with ether. The dried (Na_2SO_4) ethereal layer was concentrated to dryness in vacuo to give an oil (4.9 g, 76%) that was homogeneous on TLC (MeOH–EtOAc): ^1H NMR ($CDCl_3$) δ 7.25 (m, 5 H), 6.80 (m, 3 H), 4.65 (t, J = 6 Hz, 1 H), 3.65 (s, 3 H), 3.70 (s, 3 H), 3.2 (d, J = 6 Hz, 2 H), 1.60 (br, 2 H; exchangeable with D_2O).

***N*-[2-(Phenylthio)-2-(2,5-dimethoxyphenyl)ethyl]formamide (5).** A solution of 1-(2,5-dimethoxyphenyl)-1-(phenylthio)-2-aminoethane (0.218 g, 0.75 mmol) in THF (10 mL) was added dropwise to a solution of acetic formic anhydride (prepared by a literature procedure) at −15 °C. The reaction mixture was allowed to warm to room temperature and the volatiles were removed in vacuo. The residue was dissolved in ether and washed successively with water (50 mL), saturated $NaHCO_3$ solution and dried over anhydrous K_2CO_3. The ether was removed in vacuo to yield an oil that was triturated with an ethyl acetate–hexane mixture to give a crystalline colorless solid (0.21 g, 91%): mp 84–86 °C; IR 3244, 1648, 1500 cm^{-1}; ^1H NMR δ 8.0 (s, 1 H), 7.25 (m, 5 H), 7.03 (br, 1 H; exchangeable with D_2O), 6.80 (m, 3 H), 4.85 (t, J = 7.5 Hz, 1 H), 3.80 (br, 2 H) 3.75 (s, 3 H), and 3.70 (s, 3 H). Anal. Calcd for $C_{17}H_{19}NO_3S$: C, 64.33; H, 6.03; N, 4.41; S, 10.10. Found: C, 64.43; H, 6.08; N, 4.40; S, 10.00.

***N*-[2-(Phenylsulfinyl)-2-(2,5-dimethoxyphenyl)ethyl]formamide.** A solution of sodium metaperiodate (0.14 g, 0.66 mmol) in a minimal amount of water was added dropwise to a solution of **5** (0.21 g, 0.66 mmol) in 10 mL of methanol cooled to 0 °C. The reaction was then stirred at room temperature for 24 h. The solids were filtered and the precipitate washed several times with ethyl acetate (100 mL). The combined filtrate and washings were concentrated in vacuo to give an oil (0.23 g, 100%). The sulfoxide was used in the next step without further purification.

(*E*)-*N*-[2-(2,5-Dimethoxyphenyl)ethenyl]formamide (6). Sodium carbonate (1.59 g, 15.07 mmol) was added to a solution of *N*-[2-(phenylsulfinyl)-2-(2,5-dimethoxyphenyl)ethyl]formamide (5.025 g, 15.07 mmol) in toluene (100 mL). The reaction mixture was heated at reflux for 6 h and then cooled and filtered. The filtrate was concentrated in vacuo and the residue was subjected to column chromatography over silica gel. Elution with chloroform yielded a solid that was recrystallized from ethyl acetate to give colorless crystals (2.9 g, 94%): mp 87–88 °C; IR 3279, 1669, 1521 cm^{-1}; NMR δ 9.20 (br, 1 H; exchangeable with D_2O), 8.15 (s, 1 H), 7.60 (dd, J = 12 Hz, J = 15 Hz, 1 H), 6.95 (d, J = 3 Hz, 1 H), 6.75 (dd, J = 9 Hz, J = 3 Hz, 2 H), 6.47 (d, J = 15 Hz, 1 H), 3.75 (s, 3 H), 3.70 (s, 3 H). Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; N, 6.76. Found: C, 63.82; H, 6.33; N, 6.69.

(*E*)-*N*-[2-(2,5-Dihydroxyphenyl)ethenyl]formamide (1) (Erbstatin). A stirred, cold (−78 °C) solution of **6** (100 mg, 0.483 mmol) in anhydrous methylene chloride (5 mL) under nitrogen was treated, over a period of 7 min, with a 1.0 M solution of boron tribromide in methylene chloride [1.45 mL (1.45 mmol, 3 equiv)]. The resulting white mixture was stirred at −78 °C for 1 h under nitrogen and then allowed to warm to ambient temperature over a 1-h period. The reaction was stirred for 1.5 h at ambient temperature and the nitrogen atmosphere removed. The reaction mixture was cooled to −10 °C (2-propanol–ice bath) and quenched by the dropwise addition of water (5 mL) over a 10-min period. The cooling bath was removed and the mixture was stirred for 10 min (while warming to ambient temperature) and diluted with ethyl acetate (120 mL). This mixture was stirred for 20 min. The organic layer was washed with water (10 mL), dried (Na_2SO_4), and filtered, and the filtrate was reduced in vacuo (without heating) to dryness, venting with nitrogen. The residue was dissolved in 10% methanol in chloroform (20 mL) and reduced in vacuo (without heating), venting with nitrogen. The oil was dissolved in 10% methanol in chloroform (4 mL) and this solution was diluted with chloroform to faint turbidity (3 mL); the mixture was cooled (4 °C) for 6 h to give 80.2 mg (79% yield) of a white crystalline solid: mp (after drying at −78 °C in vacuo, 2 h) 149–151 °C; TLC (10% methanol in methylene chloride, 250 μm thick, Analtech GF silica gel plates) R_f 0.18 (R_f dimethylerbstatin is 0.62); UV (methanol) 278 (λ_{max}), 286 (shoulder), 331 nm; IR (after drying at 78 °C in vacuo, 2 h) 3352 (br), 1639, 1505, 1393, 1259, 1195, 949, and 780 cm^{-1}; ^1H NMR (360 MHz) δ 9.30–9.02 (br s, 1 H, N*H*; exchanges with D_2O), 8.19 (s, 1 H, CHO), 7.99–7.55 (s br, 2 H, OH; exchanges with D_2O), 7.65 [dd, J = 11 Hz, J = 15 Hz, 1 H, H-8, collapses to d (J = 15 Hz) with D_2O], 6.83 (d, J = 3 Hz, H-6), 6.71 (d, J = 9 Hz, H-3), 6.53 (dd, J = 9 Hz, J = 3 Hz, H-4), 6.47 (d, J = 15 Hz, H-7); ^{13}C NMR δ 159.3, 151.3, 148.2, 124.7, 122.5, 117.2, 115.1, 113.3, and 110.4.

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A Novel Synthesis of 3-Alkyl-Substituted Isoprenylsilanes

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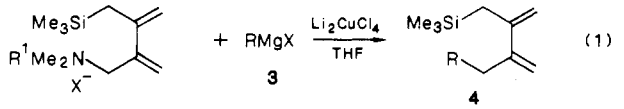
We have previously reported that 2-[(trimethylsilyl)methyl]-1,3-butadiene (isoprenylsilane) and related compounds are important reagents not only for the nucleophilic isoprenylation as allylsilanes but also for the building blocks of terpene synthesis as regioselective Diels–Alder dienes.[1] Moreover, we have recently found that 2-[(dimethylamino)methyl]-3-[(trimethylsilyl)methyl]-1,3-butadiene (**1**) is a synthon of the 2,2′-biallyl diradical.[2] In an extension of the studies on the application of **1** to organic synthesis, we now report a novel method for preparing 3-alkyl-substituted isoprenylsilanes **4** by the cross-coupling reaction between the ammonium salt **2** of **1** and the Grignard reagent **3** in the presence of dilithium tetrachlorocuprate as a catalyst (eq 1). The results are summarized in Table I.



2a: R^1 = Me, X = I
b: R^1 = *n*-Bu, X = I
c: R^1 = $PhCH_2$, X = Cl

For the purpose of coupling reactions between **2** and *n*-butylmagnesium bromide (**3a**), a copper salt,[3] in par-

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Table I. 3-Alkyl-Substituted Isoprenylsilanes 4[a]

entry	NH_4^+ salt	RMgX	molar ratio of 3 to 2	product	yield, %
1	2a	BuMgBr (3a)	1.2	4a	11
2	2a	3a	4.1	4a	88
3	2a	3a[b]	4.1	4a	36
4	2a	3a[c]	4.1	4a	29
5	2a	3a[d]	4.1	4a	49
6	2b	3a	1.2	4a	38
7	2b	3a	2.5	4a	52
8	2c	3a	2.5	4a	92
9	2a	$PhCH_2MgCl$ (3b)	8.4	4b	91
10	2b	3b	3.5	4b	72
11	2c	3b	3.5	4b	92
12	2a	PhMgBr (3c)	8.4	4c	84
13	2b	3c	3.5	4c	65
14	2c	3c	3.5	4c	85
15	2a	Me_3SiCH_2MgCl (3d)	8.4	4d	87
16	2b	3d	3.5	4d	79
17	2c	3d	3.5	4d	89

[a] All reactions were carried out in tetrahydrofuran at −40 to −20 °C for 3 h and then −20 °C to room temperature for 3.5 h in the presence of dilithium tetrachlorocuprate, unless otherwise stated. [b] Cuprous chloride was used as a catalyst. [c] Cuprous bromide was used. [d] Cuprous iodide was used.

ticular, such as dilithium tetrachlorocuprate was effective[4] and the expected 3-pentyl-2-[(trimethylsilyl)methyl]-1,3-butadiene (**4a**) was obtained in excellent yield. However, use of cuprous chloride, cuprous bromide, and cuprous iodide as catalysts did not give satisfactory results. The yield of **4** depends on the ratio of **2** to **3**. Thus, a large excess of the Grignard reagent is required to attain improvement of the yield.

It is noteworthy that the butylammonium salt **2b** and the benzylammonium salt **2c** give more satisfactory results than **2a**, presumably due to the higher solubility of the ammonium salt in the reaction medium.

Thus, alkyl and aryl Grignard reagents react with **2** to afford the desired 3-substituted isoprenylsilanes **4**, which can be viewed as useful nucleophilic reagents for the introduction of a 1,3-diene skeleton and as highly reactive 1,3-dienes. The present reaction might be applicable to other functionalized Grignard reagents and open a way to a variety of functionalized isoprenylsilanes, useful in organic synthesis, that are otherwise inaccessible.

Experimental Section

3-Alkyl-Substituted Isoprenylsilanes 4. General Procedure. The ammonium salt **2** was prepared from **1** (116 mg, 0.59 mmol) and a small excess of the corresponding alkyl halide in dry THF (5 mL) at room temperature under argon. Without isolation of **2**, the Grignard reagent **3**, which was prepared from the halide (2.1–2.7 mmol) and an excess of magnesium in THF in a separate flask, was added to the solution of **2** in the presence of dilithium tetrachlorocuprate[5] (0.10 mmol, 2 mL of 0.05 M THF solution) at −40 °C. The resulting mixture was stirred magnetically for 3 h at −40 to −20 °C and for 3.5 h at −20 °C to room temperature. After hydrolysis with water (10 mL), extractive workup with ether (20 mL × 3), and drying over sodium sulfate, the solvent was evaporated and the residue was subjected to preparative TLC (silica gel) using hexane as an eluent to give pure **4**.

Because of the similarity of structures for **4**, spectral data are reported in the following tabulation.

3-Methylene-2-[(trimethylsilyl)methyl]-1-octene (**4a**): ^1H NMR (CCl_4) δ 0.07 (s, 9 H), 0.98 (t, J = 6.8 Hz, 3 H), 1.14–1.76 (m, 4 H), 1.84 (br s, 2 H), 2.17–2.42 (m, 2 H), 4.79 (br s, 1 H), 4.98 (br s, 1 H), 5.00–5.10 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −1.17 (q), 14.10 (q), 22.59 (t), 24.28 (t), 28.72 (t), 31.92 (t), 34.14 (t), 109.80 (t), 112.08 (t), 145.18 (s), 148.70 (s); IR (CCl_4) 2920 (s), 2860 (s), 1590 (w), 1460 (m), 1250 (m), 1165 (w), 910 (s), 880 (s), 855 (s) cm^{-1}; EIMS (70 eV), m/e (relative intensity) 210 (3, M^+), 118 (8), 93 (5), 82 (5), 75 (11), 74 (9), 73 (100), 59 (6), 44 (6), 44 (5); HRMS calcd for $C_{13}H_{26}Si$ 210.1804, found 210.1806.

3-Methylene-5-phenyl-2-[(trimethylsilyl)methyl]-1-pentene (**4b**): ^1H NMR (CCl_4) δ 0.00 (s, 9 H), 1.78 (br s, 2 H), 2.37–2.88 (m, 4 H), 4.76 (br s, 1 H), 4.90 (br s, 1 H), 5.02 (br s, 2 H), 7.11 (br s, 5 H); ^{13}NMR ($CDCl_3$) δ −1.17 (q), 24.15 (t), 35.51 (t), 36.10 (t), 109.99 (t), 112.67 (t), 125.66 (t), 128.21 (d), 142.17 (s), 144.79 (s), 147.72 (s); IR (CCl_4) 3020 (w), 2920 (s), 2840 (m), 1585 (w), 1450 (m), 1245 (m), 890 (m), 875 (s), 850 (s) cm^{-1}; EIMS (70 eV) m/e (relative intensity) 244 (5, M^+), 170 (4), 121 (4), 91 (19), 75 (5), 74 (9), 73 (100), 59 (5), 45 (6), 44 (5); HRMS calcd for $C_{16}H_{24}Si$ 244.1645, found 244.1622.

3-Methylene-4-phenyl-2-[(trimethylsilyl)methyl]-1-butene (**4c**): ^1H NMR (CCl_4) δ −0.01 (s, 9 H), 1.76 (br s, 2 H), 3.50 (br s, 2 H), 4.70 (br s, 1 H), 4.83 (br s, 1 H), 4.99 (br s, 1 H), 5.15 (br s, 1 H), 7.13 (br s, 5 H); ^{13}C NMR ($CDCl_3$) δ −1.17 (q), 24.22 (t), 40.54 (t), 111.03 (t), 114.95 (t), 125.79 (d), 128.07 (d), 128.73 (d), 140.15 (s), 144.46 (s), 146.94 (s); IR (CCl_4) 3020 (m), 2950 (s), 2850 (m), 1590 (m), 1450 (m), 1250 (s), 905 (s), 880 (s), 850 (s), 700 (s) cm^{-1}; EIMS (70 eV), m/e (relative intensity) 230 (28, M^+), 187 (8), 182 (13), 156 (14), 143 (14), 135 (14), 91 (66), 74 (9), 73 (100), 59 (17); HRMS calcd for $C_{15}H_{22}Si$ 230.1490, found 230.1470.

3-Methylene-2-[(trimethylsilyl)methyl]-5-(trimethylsilyl)-1-pentene (**4d**): ^1H NMR (CCl_4) δ 0.11 (s, 9 H), 0.12 (s, 9 H), 0.71–0.95 (m, 2 H), 1.22–1.49 (m, 2 H), 1.88 (br s, 2 H), 4.82 (br s, 1 H), 5.03–5.14 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ −1.11 (q), −1.76 (q), 16.25 (t), 24.41 (t), 28.26 (t), 109.67 (t), 111.10 (t), 145.11 (s), 151.18 (s); IR (CCl_4) 3080 (m), 2910 (s), 2850 (m), 1410 (m), 1250 (s), 1160 (w), 910 (s), 855 (s), 835 (s), 690 (m) cm^{-1}; EIMS (70 eV), m/e (relative intensity) 240 (8, M^+), 137 (11), 135 (6), 124 (6), 121 (9), 74 (9), 73 (100), 59 (5), 45 (7), 44 (11); HRMS calcd for $C_{13}H_{28}Si_2$ 240.1729, found 240.1731.

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Convenient Preparation of 1,3-Bis(2,3,4,5-tetramethylcyclopentadienyl)-propane: Use of 2,3,4,5-Tetramethylcyclopent-2-enone Enolate as a Synthetic Equivalent for the Tetramethylcyclopentadienyl Anion

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The preparation and reactivity of organometallic complexes containing bridged tetramethylcyclopentadienyl ligands is of considerable current interest.[1-5] Unfortu-

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