7 as a viscous oil (2.85 g, 6.90 mmol, 99.5% mass recovery). The product was thermally labile (80 °C) and acid sensitive and was reduced directly.

Hydroxylamine 9. The reaction of *p*-menth-3-ylhydrazine (8) (12.5 g, 73.2 mmol, 3 equiv), lead dioxide (35.0 g, 146 mmol, 6 equiv), and nitroso-*tert*-octane (3.5 g, 24.4 mmol) as described for the preparation of 7 afforded 9 (10.3 g, 24.4 mmol). The product was reduced directly.

***exo*- and *endo*-2-Bornyl-*tert*-octylamines (1 and 2).** Ammonia (50 mL) was condensed into a 250-mL flask at −78 °C and hydroxylamine 7 was added in 50 mL of THF. The solution was allowed to warm to −30 °C, and sodium pieces (1.0 g, 43.4 mmol, 8.6 equiv) were added in four portions over 6 h. The reaction was carefully quenched with 30% isopropanol–hexanes, and ammonia was removed under a nitrogen stream. The product was extracted into 1 N HCl, and the extracts were neutralized with saturated sodium bicarbonate. Extraction into ether, drying over sodium sulfate, and evaporation gave a 1:1 mixture of the amines 1 and 2 (1.06 g, 3.99 mmol, 79.4%). Chromatography on silica gel (hexane → 90% ethyl acetate–hexane) afforded the pure amines. *exo*-2-Bornyl-*tert*-octylamine (1): $[\alpha]^{22}_D$ −71.0° (*c* 2.5, chloroform); ^{1}H NMR ($CDCl_3$) δ 2.50 (m, 1 H), 2.0–1.0 (m, 7 H), 1.35 (s, 2 H), 1.04 (s, 6 H), 1.00 (s, 9 H), 0.94 (s, 3 H), 0.86 (s, 3 H), 0.78 (s, 3 H); MS, *m/e* 265 (M^+). *endo*-2-Bornyl-*tert*-octylamine (2): $[\alpha]^{22}_D$ +31.0° (*c* 3.7, chloroform); ^{1}H NMR 2.70 (m, 1 H), 2.4–1.0 (m, 7 H), 1.40 (s, 2 H), 1.08 (s, 6 H), 1.02 (s, 9 H), 0.87 (s, 3 H), 0.86 (s, 3 H), 0.78 (s, 3 H).

***p*-Menth-3-yl-*tert*-octylamines (3 and 4).** The reduction of hydroxylamine 9 (36.7 g, 87 mmol) as described for hydroxylamine 7 afforded 3 and 4 (16.5 g, 61.7 mmol, 71%) in a ratio of 20:1, respectively. 3: $[\alpha]^{22}_D$ −46.0° (*c* 2.5, chloroform); ^{1}H NMR ($CDCl_3$) δ 2.88 (m, 1 H), 2.0–1.0 (m, 9 H), 1.40 (s, 2 H), 1.11 (d, 6 H), 1.00 (s, 9 H), 0.90, 0.88, 0.82 (total 9 H); MS, *m/e* 267 (M^+). 4: $[\alpha]^{22}_D$ −35.0° (*c* 2.5, chloroform); ^{1}H NMR 3.03 (m, 1 H), 2.0–1.0 (m, 9 H), 1.39 (s, 2 H), 1.12 (d, 6 H), 1.02 (s, 9 H), 0.93, 0.85, 0.81 (total 9 H). MS, *m/e* 267 (M^+).

***N*-Isobornylcamphor Imine (14).** Isobornylamine (25.0 g, 163 mmol), (+)-camphor (6.6 g, 43.3 mmol), and 200 mL of toluene were placed in a 250-mL flask. Titanium tetrachloride (4.13 g, 21.7 mmol) was added, and the reddish-brown solution was heated to reflux for 14 h. The reaction mixture was cooled to room temperature and filtered to remove isobornylamine hydrochloride. Removal of solvent and chromatography on silica gel (5% ether–hexane) gave 14 (7.7 g, 26.27 mmol, 60.6%): $[\alpha]^{22}_D$ −41.0° (*c* 0.8, chloroform); ^{1}H NMR ($CDCl_3$) δ 3.1 (dd, 1 H), 2.55 (m, 2 H), 2.0–1.0 (m, 12 H), 1.14 (s, 3 H), 0.90 (s, 3 H), 0.88 (s, 3 H), 0.82 (s, 3 H), 0.74 (s, 3 H), 0.70 (s, 3 H); MS, *m/e* 287 (M^+).

Diisobornylamine (12). The imine 14 (7.7 g, 26.27 mmol), 30 mL of ethanol, and 500 mg of 5% platinum on carbon were placed in a Parr pressure bottle. The bottle was charged with hydrogen (45 psi), and the reaction mixture was shaken for 18 h. The catalyst was recovered by filtration and the filtrate concentrated. Chromatography on silica gel (5% ether–hexane, R_f 0.75) gave 12 as a white solid (6.7 g, 23.1 mmol, 87.9%). Recrystallization from methanol gave an analytical sample: mp 60 °C (lit. mp 60 °C[4]); $[\alpha]^{22}_D$ −140.0° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 2.46 (dd, 2 H), 1.5 and 1.05 (m, 15 H), 0.95 (s, 6 H), 0.79 (s, 6 H), 0.78 (s, 6 H); MS, *m/e* 289 (M^+).

A Practical and Efficient Synthesis of α,β-Unsaturated Acylsilanes

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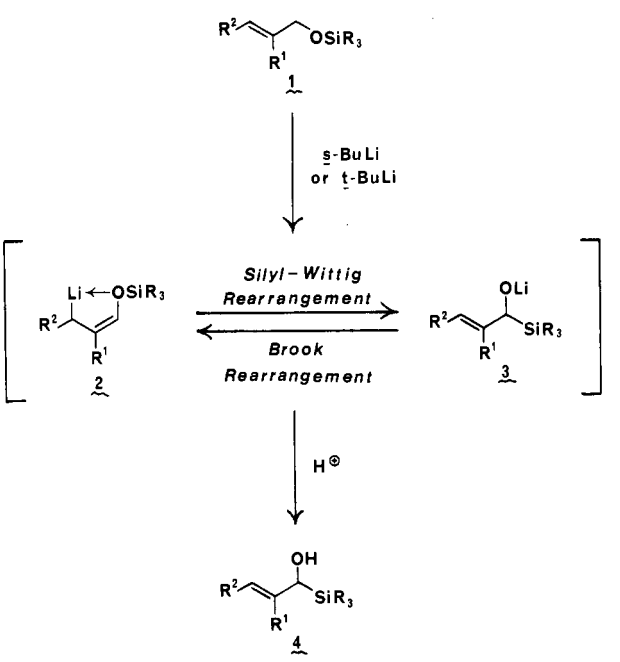
In recent years, α,β-unsaturated acylsilanes have emerged as valuable building blocks for the synthesis of complex organic compounds. Functioning as α,β-unsaturated carbonyl derivatives, they readily participate in a variety of carbon–carbon bond forming processes, including organocuprate conjugate additions,[2] $TiCl_4$-mediated conjugate allylations,[3] Diels–Alder reactions,[2] 1,3-dipolar cycloadditions,[4] and the [3 + 2] annulation reaction recently developed in our laboratory.[4,5] The synthetic utility of these reactions is enhanced by the fact that the product acylsilanes are subject to a variety of useful further transformations,[6] including, for example, Brook reactions,[2,7] oxidation to carboxylic acids,[8] and fluoride-promoted conversion to ketones and aldehydes.[8b,9]

Scheme I



Although several general synthetic approaches to α,β-unsaturated acylsilanes have previously been reported,[2-4,8b,10] these methods have proved less than satisfactory when applied to the synthesis of compounds lacking β-substituents such as the acryloyl and methacryloyl derivatives **7a** and **7b**. Not surprisingly, these simple but highly

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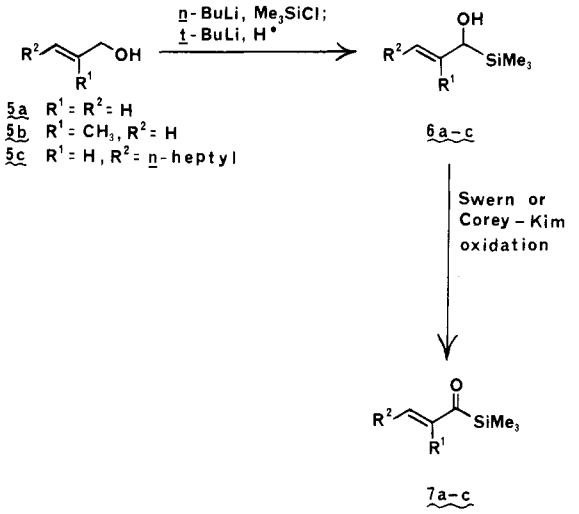
Scheme II



reactive acylsilanes are extremely sensitive to acid and base and readily undergo polymerization. We consequently have been unable to prepare these compounds by employing the classic Corey–Brook strategy,[11] as all our attempts to hydrolyze the dithianes corresponding to **7a** and **7b** have resulted in the partial destruction of the desired acylsilane products. To date, the best method for the preparation of the sensitive acryloyl derivative **7a** is that recently developed by Reich and co-workers.[2] Their route involves a total of four steps starting with propargyl alcohol and proceeds in 45% overall yield. The first synthesis of methacryloyltrimethylsilane was recently achieved in our laboratory[4] via the α-methylenation of propionyltrimethylsilane. This route delivers **7b** in an overall yield of 63–70%.

In this paper we now describe a general method for the synthesis of α,β-unsaturated acylsilanes from readily available allylic alcohols. The new route involves only two synthetic operations and constitutes a particularly convenient method for the preparation of the more unstable (and less accessible) acylsilane derivatives such as **7a** and **7b**. The design of this strategy was based on the expectation that (α-hydroxyallyl)silanes **4** would serve as useful intermediates which could be transformed to the desired acylsilanes under mild conditions employing Moffatt-type oxidizing agents.[12] As outlined in Scheme I, our plan for the synthesis of the requisite (α-hydroxyallyl)silanes[13] was based on the earlier observation in several laboratories that metalation of allyl silyl ethers generates a rapidly interconverting mixture of two organometallic species, **2** and **3**.[14,15] Although the alkylation of this mixture of organometallic derivatives generally proceeds at the C-3 position (via **2**), "hard" electrophiles such as Me_3SiCl react predominantly at the oxygen atom of the alkoxide intermediate **3**, and it was consequently expected that protonation would lead to the formation of the desired (α-hydroxyallyl)silanes **4**.

In practice, it proved possible to execute this strategy by using two simple synthetic operations (Scheme II). In the first step, an allylic alcohol is converted to the corresponding trimethylsilyl ether by sequential treatment with 1.05–1.1 equiv each of *n*-butyllithium and chlorotrimethylsilane in THF. Addition of 1.2 equiv of *tert*-butyllithium (3.0 equiv when R^2 = alkyl) then generates the desired mixture of organolithium species, which can be protonated by the addition of either saturated aqueous NH_4Cl solution or acetic acid. The (α-hydroxyallyl)silanes produced in this one-flask procedure exhibit limited thermal stability and are best isolated by carefully distilling off solvents and volatile impurities at bath temperatures below 70 °C. The alcohols **6a–c** obtained in this fashion were determined to be 94–95% pure by gas chromatographic analysis and were suitable for use in the next step without further purification.

In our experience, *tert*-butyllithium[14f] has proven to be superior to *sec*-butyllithium[14a–e] for effecting the metalation of allyl trimethylsilyl ethers. The rate of metalation has been found to vary from case to case. Thus, the lithiation of allyl trimethylsilyl ether itself proceeds to completion at −78 °C in 2 h, while the corresponding methallyl derivative requires 3.5 h at −33 °C. The metalation of silyl ether derivatives of γ-substituted allylic alcohols (e.g., **5c**) also takes place relatively slowly and is best carried out using 3.0 equiv of *tert*-butyllithium at −30 °C for 6 h.

A variety of methods were examined for the conversion of the (α-hydroxyallyl)silanes **6a–c** to the corresponding acylsilanes. It has previously been noted[12] that many conventional oxidizing agents have limited utility for the oxidation of α-trialkylsilyl alcohols, and we were in fact unable to achieve the clean conversion of **6a–c** to the desired acylsilanes using either manganese dioxide or a variety of chromium-based reagents. The desired transformations were eventually accomplished by employing the class of mild oxidation methods which proceed via the intermediacy of alkoxysulfonium species. Thus, Swern oxidation[16] of **6a** proceeded smoothly at −78 °C to furnish the acryloylsilane **7a** in 64% overall yield from allyl alcohol; the methacryloyl derivative **7b** was obtained in 79% overall yield (from methallyl alcohol) in a similar fashion. It should be noted that the use of freshly distilled oxalyl chloride and carefully dried Me_2SO proved crucial to the success of these reactions, since even traces of HCl were observed to promote significant decomposition of the (α-hydroxyallyl)silane starting materials. The oxidation of the γ-substituted allylic alcohol **6c** proceeded in somewhat higher yield when *N*-chlorosuccinimide–dimethyl sulfide[17] was used in place of the Swern reagent. The β-substituted acylsilane **7c** was thus obtained in 64% overall yield from 2-decenol employing the Corey–Kim procedure.

In summary, the α,β-unsaturated acylsilanes **7a–c** have been prepared in two steps in 64–79% overall yield starting with the allylic alcohols **5a–c**. This procedure can be conveniently carried out on a 10–25-g scale and constitutes

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(13) Reich and Eisenhart[10i] have recently reported the synthesis of an (α-hydroxyallyl)silane via the addition of (phenyldimethylsilyl)lithium to methacrolein. As a practical method for the synthesis of (α-hydroxyalyl)trimethylsilanes, we consider this alternative strategy to be less attractive than our approach because of the relative expense and inconvenience associated with the generation of trimethylsilyllithium on a large scale.[14b]

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(15) Analogous anionic migrations involving metalated *benzyl* trialkylsilyl ethers and (α-hydroxybenzyl)trialkylsilane salts have also been observed. For a detailed study, see: Wright, A.; West, R. *J. Am. Chem. Soc.* **1974**, *96*, 3214.

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a practical and efficient method for the synthesis of a variety of α,β-unsaturated acylsilanes.

Experimental Section

Instrumentation. Infrared spectra were obtained using a Perkin-Elmer 1320 grating spectrophotometer. ^{1}H NMR spectra were measured with a Bruker WM-250 (250 MHz) spectrometer, and ^{13}C NMR spectra were determined on a Bruker WM-270 (67.9 MHz) spectrometer. Chemical shifts are expressed in ppm (δ) downfield from tetramethylsilane. UV spectra were measured on a Varian Cary Model 118 UV–vis spectrophotometer. Low-resolution mass spectra (MS) and high-resolution mass spectra (HRMS) were determined on a Finnegan MAT 8200 instrument. Gas chromatography was performed employing a Hewlett-Packard 5710A instrument. Boiling points are uncorrected.

Materials. Commercial grade reagents and solvents were used without further purification except as indicated below. Allyl alcohol, methallyl alcohol, dimethyl sulfide, dimethyl sulfoxide, triethylamine, chlorotrimethylsilane, and dichloromethane were distilled from calcium hydride. Tetrahydrofuran was distilled from sodium benzophenone dianion. Oxalyl chloride was fractionally distilled under argon immediately before use. *n*-Butyllithium and *tert*-butyllithium were titrated by the method of Watson and Eastham.[18]

General Procedures. All reactions were performed in flame-dried glassware under a positive pressure of argon. Reaction mixtures were stirred magnetically unless otherwise indicated. Sensitive liquids and solutions were transferred via syringe or cannula and were introduced into reaction vessels through rubber septa. Reaction product solutions were concentrated with a Buchi rotary evaporator at 15–20 mmHg unless otherwise indicated. Column chromatography was performed using E. Merck silica gel 60 (230–400 mesh). Ethyl acetate and hexane were distilled prior to use as eluents.

(1-Hydroxy-2-propenyl)trimethylsilane (6a). A 1-L, three-necked, round-bottomed flask was equipped with two 150-mL pressure-equalizing dropping funnels and an argon inlet adapter. The flask was charged with allyl alcohol (10.00 g, 172.2 mmol) and 220 mL of tetrahydrofuran and then cooled at −78 °C while *n*-butyllithium solution (78.3 mL of a 2.31 M solution in hexane, 180.8 mmol, 1.05 equiv) was added dropwise over 40 min. After 1 h, a solution of chlorotrimethylsilane (19.64 g, 180.8 mmol, 1.05 equiv) in 20 mL of tetrahydrofuran was added dropwise over 20 min, and the resulting colorless solution was stirred at −78 °C for 1.25 h, and then treated dropwise over 40 min with 129.1 mL of a 1.60 M solution of *tert*-butyllithium in pentane (206.6 mmol, 1.20 equiv). After 2 h, the cold bath was removed, and 50 mL of saturated NH_4Cl solution was added to the yellow reaction mixture. The resulting solution was stirred for 5 min and then diluted with 50 mL of water and 300 mL of pentane. The organic phase was separated and washed with four 100-mL portions of water, and three 50-mL portions of saturated NaCl solution, dried over Na_2SO_4, filtered, and concentrated by carefully distilling off the solvents at atmospheric pressure through a 10-cm Vigreux column. The residual pale yellow liquid was transferred to a 50-mL round bottomed flask, and the remaining volatile impurities were removed by distillation at 15 mmHg through a 4-cm column packed with glass helices, leaving 19.75 g of **6a** as a pale yellow oil used in the next step without further purification. The purity of this material was determined to be 95% by gas chromatographic analysis (10% OV-101 on 100–120 mesh Chromosorb W, 6 ft × $^1/_8$ in., program: 50 °C for 2 min and then 50–250 °C at 32 °C/min): IR (film) 3420, 2955, 2895, 2820, 1625, 1410, 1245, 1138, 1095, 990, 900, 840 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.89 (ddd, J = 5.5, 11, 17 Hz, 1 H), 4.98 (ddd, J = 2, 2, 17 Hz, 1 H), 4.86 (ddd, J = 2, 2, 11 Hz, 1 H), 3.88 (m, 1 H), 2.86 (br s, 1 H), 0.05 (s, 9 H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 139.9, 109.4, 68.9, −4.4; HRMS, m/e calcd for $C_6H_{14}OSi$ (M^+) 130.0813, found 130.0810.

(1-Oxo-2-propenyl)trimethylsilane (7a).[2] A 1-L, three-necked, round-bottomed flask was equipped with a mechanical stirrer and two pressure-equalizing dropping funnels, one of which was fitted with an argon inlet adapter. The flask was charged with oxalyl chloride (21.78 g, 171.6 mmol, 1.15 equiv) and 250 mL of dichloromethane, and then cooled to −78 °C while a solution of dimethyl sulfoxide (29.10 g, 372.5 mmol, 2.5 equiv) in 50 mL of dichloromethane was added dropwise over 45 min. After 1 h, a solution of the alcohol **6a** (19.43 g, 149.2 mmol) in 100 mL of dichloromethane was added dropwise over 1 h, and the resulting colorless solution was stirred at −78 °C for 1 h and then treated dropwise over 30 min with triethylamine (78.13 g, 775.8 mmol, 5.2 equiv). After 1 h, the cold bath was removed, and the reaction mixture was poured into 150 mL of water and 300 mL of pentane. The organic phase was separated and washed successively with six 50-mL portions of 5% HCl solution, three 100-mL portions of H_2O, and two 100-mL portions of saturated NaCl solution, dried over Na_2SO_4, filtered, and concentrated by carefully distilling off the solvents at atmospheric pressure through a 10-cm Vigreux column. The residual yellow oil was transferred to a 100-mL round-bottomed flask containing ca. 40 mg of 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide and distilled through a 4-cm column packed with glass helices to afford 12.28 g (64% overall yield from allyl alcohol) of **7a** as a brilliant yellow oil: bp 64–68 °C (30 mmHg) [lit.[2] bp 40–60 °C (50 mmHg)]; IR (film) 2960, 2900, 1635, 1600, 1590, 1415, 1390, 1255, 1185, 985, 960, 845 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.38 (dd, J = 11, 18 Hz, 1 H), 6.13 (dd, J = 1, 18 Hz, 1 H), 5.94 (dd, J = 1, 11 Hz, 1 H), 0.23 (s, 9 H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 237.9, 141.3, 128.5, −2.2.

(1-Hydroxy-2-methyl-2-propenyl)trimethylsilane (6b). A 1-L, three-necked, round-bottomed flask was equipped with two 150-mL pressure-equalizing dropping funnels and an argon inlet adapter. The flask was charged with 2-methyl-2-propen-1-ol (10.00 g, 138.7 mmol) and 250 mL of tetrahydrofuran and then cooled at −78 °C while *n*-butyllithium solution (66.1 mL of a 2.31 M solution in hexane, 152.6 mmol, 1.1 equiv) was added dropwise over 20 min. After 1.25 h, a solution of chlorotrimethylsilane (16.58 g, 152.6 mmol, 1.1 equiv) in 10 mL of tetrahydrofuran was added dropwise over 30 min, and the resulting colorless solution was stirred at −78 °C for 1 h and then treated dropwise over 1.5 h with 100.8 mL of a 1.65 M solution of *tert*-butyllithium in pentane (166.4 mmol, 1.2 equiv). The reaction mixture was stirred at −78 °C for 15 min and at −33 °C for 3.5 h, and then the cold bath was removed and a solution of acetic acid (9.99 g, 166.4 mmol, 1.2 equiv) in 10 mL of tetrahydrofuran was added in one portion. After 15 min, the reaction mixture was diluted with 100 mL of saturated $NaHCO_3$ solution and 300 mL of pentane. The organic phase was separated and washed successively with five 100-mL portions of water and two 150-mL portions of saturated NaCl solution, dried over Na_2SO_4, filtered, and concentrated by carefully distilling off the solvents at atmospheric pressure through a 10-cm Vigreux column. The residual pale yellow liquid was transferred to a 50-mL round-bottomed flask, and the remaining volatile impurities were removed by distillation at 15 mmHg through a 4-cm column packed with glass helices, leaving 15.42 g of **6b** as a pale yellow oil, used in the next step without further purification. This material was determined to be 94% pure by gas chromatographic analysis (10% OV-101 on 100–120 mesh Chromosorb W, 6 ft × $^1/_8$ in., program: 50 °C for 2 min and then 50–250 °C at 32 °C/min): IR (film) 3450, 3080, 2960, 1635, 1250, 1142, 920, 840 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.93 (s, 1 H), 4.89 (s, 1 H), 4.00 (s, 1 H), 1.82 (s, 3 H), 1.79 (br s, 1 H), 0.20 (s, 9 H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 148.2, 106.2, 71.4, 20.5, −3.6; HRMS, m/e calcd for $C_7H_{16}OSi$ (M^+) 144.0970, found 144.0966.

(2-Methyl-1-oxo-2-propenyl)trimethylsilane (7b).[4] A 1-L, three-necked, round-bottomed flask was equipped with a mechanical stirrer and two pressure-equalizing dropping funnels, one of which was fitted with an argon inlet adapter. The flask was charged with oxalyl chloride (15.18 g, 119.6 mmol, 1.15 equiv) and 220 mL of dichloromethane and then cooled at −78 °C while a solution of dimethyl sulfoxide (20.31 g, 260.0 mmol, 2.5 equiv) in 50 mL of dichloromethane was added dropwise over 50 min. After 20 min, a solution of the alcohol **6b** (15.00 g, 104.0 mmol) in 100 mL of dichloromethane was added dropwise over 1 h, and the resulting colorless solution was stirred at −78 °C for 1 h and then treated dropwise over 20 min with triethylamine (54.72 g, 540.8 mmol, 5.2 equiv). After 1 h, the cold bath was removed, and the reaction mixture was poured into 100 mL of water and 300 mL of pentane. The organic phase was separated and washed

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successively with four 50-mL portions of 5% HCl solution, four 50-mL portions of H_2O, and two 50-mL portions of saturated NaCl solution, dried over Na_2SO_4, filtered, and concentrated by carefully distilling off the solvents at atmospheric pressure through a 10-cm Vigreux column. The residual yellow oil was transferred to a 50-mL round-bottomed flask containing ca. 40 mg of 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide and distilled through a 4-cm column packed with glass helices to furnish 11.52 g (79% overall yield from methallyl alcohol) of **7b**[4] as a brilliant yellow oil: bp 68–72 °C (35 mmHg); IR (film) 2960, 2922, 1630, 1604, 1450, 1429, 1373, 1300, 1255, 1042, 932, 844 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.06 (s, 1 H), 5.94 (s, 1 H), 1.72 (s, 3 H), 0.24 (s, 9 H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 237.3, 149.6, 128.5, 15.6, −1.2; UV max (isooctane) 425 nm (ϵ 77), 222 (5990); HRMS, *m/e* calcd for $C_6H_{11}OSi$ (M^+ − 15) 127.0576, found 127.0579.

(*E*)-(1-Hydroxy-2-decenyl)trimethylsilane (6c). A 100-mL, three-necked, round-bottomed flask was equipped with an argon inlet adapter and two rubber septa. The flask was charged with (*E*)-2-decenol[19] (2.34 g, 15.0 mmol) and 20 mL of tetrahydrofuran and then cooled at −78 °C while *n*-butyllithium solution (6.50 mL of a 2.48 M solution in hexane, 16.1 mmol, 1.07 equiv) was added dropwise by syringe over 3 min. The resulting pale yellow solution was stirred at 0 °C for 15 min and then cooled at −78 °C while chlorotrimethylsilane (1.80 g, 16.5 mmol, 1.1 equiv) was added in one portion by syringe. The colorless reaction mixture was next stirred at 0 °C for 15 min and then cooled to −78 °C and treated dropwise over 10 min with 26.0 mL of a 1.74 M solution of *tert*-butyllithium in pentane (45.2 mmol, 3.0 equiv). The resulting solution was stirred at −30 °C for 6 h, and then the cold bath was removed and 6 mL of saturated aqueous NH_4Cl solution was added in one portion. The reaction mixture was diluted with 100 mL of additional saturated NH_4Cl solution and then extracted with two 100-mL portions of ether. The combined organic phases were dried over Na_2SO_4, filtered, and concentrated to provide 3.93 g of **6c** as a yellow oil, used in the next step without further purification.

Column chromatography on silica gel (elution with ethyl acetate–hexane) furnished a pure sample of **6c**: IR (film) 3450, 2980, 2940, 2875, 1710, 1675, 1470, 1255, 1085, 980, 850 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 5.61 (ddd, J = 1, 7, 15 Hz, 1 H), 5.50 (ddt, J = 1, 7, 15 Hz, 1 H), 3.94 (dd, J = 1, 7 Hz, 1 H), 2.07 (apparent q, J = 7 Hz, 2 H), 1.47–1.66 (br s, 1 H, OH), 1.24–1.47 (m, 10 H), 0.91 (t, J = 7 Hz, 3 H), 0.07 (s, 9 H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 131.0, 127.9, 68.5, 32.4, 31.8, 31.7, 29.7, 29.1, 22.6, 14.0, 0.1; HRMS, *m/e* calcd for $C_{13}H_{28}OSi$ (M^+) 228.1910, found 228.1908.

(*E*)-(1-Oxo-2-decenyl)trimethylsilane (7c). A 100-mL, three-necked, round-bottomed flask was equipped with an argon inlet adapter and two rubber septa. The flask was charged with *N*-chlorosuccinimide (3.04 g, 22.8 mmol, 1.5 equiv) and 40 mL of dichloromethane and then cooled at 0 °C while 2.30 mL of dimethyl sulfide (1.95 g, 31.3 mmol, 2.1 equiv) was added dropwise over 10 min by syringe. After 45 min, the reaction mixture was cooled to −25 °C, and a solution of the unpurified alcohol **6c** (3.93 g) produced in the previous reaction in 20 mL of dichloromethane was added dropwise by syringe over 5 min. The resulting mixture was stirred at −25 °C for 2.5 h and at room temperature for 30 min and then cooled at −20 °C while 3.2 mL of triethylamine (2.32 g, 23.0 mmol, 1.5 equiv) was added dropwise by syringe over 5 min. The reaction mixture was diluted with 100 mL of water and then extracted with two 100-mL portions of dichloromethane. The combined organic phases were dried over Na_2SO_4, filtered, and concentrated to afford a yellow oil. Column chromatography on silica gel (elution with ethyl acetate–hexane) provided 2.174 g (64% overall yield from 2-decenol) of **7c** as a brilliant yellow oil: IR (film) 2960, 2930, 2855, 1645, 1635, 1590, 1460, 1250, 1190, 975, 845 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.73 (dt, J = 7, 17 Hz, 1 H), 6.17 (dt, J = 1, 17 Hz, 1 H), 2.21 (apparent dq, J = 1, 7 Hz, 2 H), 1.18–1.54 (m, 10 H), 0.85 (t, J = 7 Hz, 3 H), 0.22 (s, 9 H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 236.4, 148.9, 136.4, 32.7, 31.6, 29.0, 28.9, 28.1, 22.5, 13.9, −2.0; UV max (isooctane) 424 nm (ϵ 68), 225 (10,584); HRMS, *m/e* calcd for $C_{13}H_{26}OSi$ (M^+) 226.1754, found 226.1752.

(19) (*E*)-2-Decenol was prepared in 72–92% yield from 2-decyn-1-ol by reduction with 1.5 equiv of $LiAlH_4$ in the presence of 3.0 equiv of NaOMe in THF at reflux for 3.5 h.

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Sn(II)–Al-Promoted Allylation of Aldehydes with Allyl Chloride in an Aqueous Solvent System

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Intensive studies have been accumulated on the regio- and stereoselective allylation of carbonyl compounds with allyl metallic reagents.[1] Among them, allyl stannanes are of particular value for allylation of aldehydes and ketones,[1] enones,[2] pyridinium salt,[3] and allyl acetate.[4] However, there has been no study on the recycle use of the allyl metallic reagents for allylation. Recently, we have developed a novel electrochemical recycle system for organotin reagent promoted allylation in which 2–20 mol % of metallic tin in MeOH–H_2O–AcOH can be effectively recycled for allylation of aldehydes and ketones[5] with allyl bromide. However, allyl chloride is unreactive toward metallic tin in the electrolysis conditions to make a recycling system. Because of the low cost of allyl chloride as compared with allyl bromide, it is worthy to develop an allylation with allyl chloride by the aid of recycling tin reagents.

In contrast to facile oxidative addition of metallic tin to allyl bromide[6] and iodide,[7] allyl chloride was found to be less reactive so that no successful allylation by a combination of allyl chloride and metallic tin has appeared. Recently, Nokami and Okawara[8] showed that a combination of a stoichiometric amount of metallic tin and aluminum leads to a successful allylation of carbonyl compounds using various kinds of allylic bromides. This finding suggests a possibility of activation of allyl chloride with aluminum. Meanwhile, concerning regeneration of Sn(0) from Sn(II) and Sn(IV), aluminum would be a promising metal since aluminum is less electronegative than tin so as to reduce in principle a di- and tetravalent tin to a zerovalent one. On these bases we have studied an aluminum-promoted and tin-recycled allylation process with allyl chloride where aluminum affects both oxidative addition of metallic tin to allyl chloride and reductive regeneration of Sn(0) from Sn(II) and Sn(IV) for a recycle use.

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