A One-Pot Preparation of Allylsilanes and (*Z*)-Alk-2-enylsilanes

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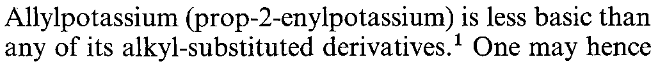
Metalation of alk-1-enes, using the mixture of butyllithium and potassium *tert*-butoxide in tetrahydropyran, followed by stereohomogenization and ultimate treatment with chlorotrimethylsilane afforded a series of alk-2-enyltrimethylsilanes in good yield and with (*Z*/*E*) ratios ranging from 95:5 to 98:2. The deprotonation of propene can be rapidly and readily accomplished with a stoichiometric amount of the superbase suspended in pentane on a 1 mol scale.

Allylpotassium (prop-2-enylpotassium) is less basic than any of its alkyl-substituted derivatives.[1] One may hence expect it to form with particular ease. In reality, propene is only slowly attacked by the butyllithium/potassium *tert*-butoxide mixed-metal reagent, requiring 5 h of vigorous stirring while being kept under reflux by means of a dry ice condenser.[2] Even when a 3-fold excess of the olefin is employed, the yield remains moderate (e.g., 63 % of pent-4-en-1-ol after trapping with oxirane).

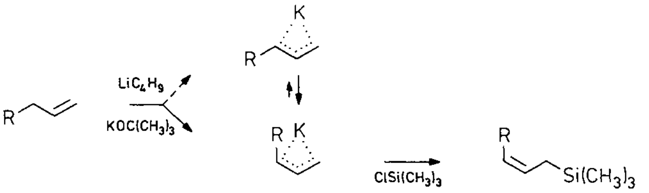
The sluggishness of the reaction may have merely practical reasons. Most of the exceptionally volatile olefin (bp −48 to −47 °C) can be assumed to accumulate in the head space of a non-pressurized vessel, thus avoiding the contact with the reagent. Actually, the transmetalation is virtually complete after 1 h if it is accomplished in a round-bottom flask closed with a Scotch-tape secured rubber stopper while the temperature is raised from −25 °C to +25 °C. Treatment of the thus generated allylpotassium (contaminated by allyllithium and lithium *tert*-butoxide) with triethylsilyl, *tert*-butyldimethylsilyl and *tert*-butyldiphenylsilyl chloride affords the corresponding silanes **1a–c** in 69, 77 and 83 % yield.



a: $R = R' = C_2H_5$ (69%)
b: $R = C(CH_3)_3$, $R' = CH_3$ (77%)
c: $R = C(CH_3)_3$, $R' = C_6H_5$ (83%)

These products had previously to be prepared by condensation of the silyl chloride with allylmagnesium chloride or bromide[3,4] or by addition of a lithium bissilylcuprate onto allene.[5] These methods[6] are, of course, far more expensive than the one described above and, moreover, less suited for scale-up.

Allylsilanes being versatile building blocks for organic synthesis, we wanted to demonstrate the universality of our superbase[7] approach. To this end we have metalated hex-1-ene, hept-1-ene, oct-1-ene, non-1-ene, dec-1-ene, undec-1-ene and dodec-1-ene and submitted the organometallic intermediates to torsional equilibration[8] before interception with trimethylsilyl chloride to obtain the corresponding (*Z*)-alk-2-enyltrimethylsilanes **2–8** in 52–75 % yield, (*Z*/*E*) ratios ranging from 95:5 to 98:2. Previously we had analogously converted the branched alkenes, isobutene, 2-methylbut-2-ene ("trimethylethylene") and 2-ethyl-but-2-ene into (2-methylallyl)-, (*Z*)-(2-methylbut-2-enyl)- and (*Z*)-(2-ethylbut-2-enyl)trimethylsilane in 50, 45 and 51 % yield, respectively.[9]



2: $R = H_7C_3$ (60%)
3: $R = H_9C_4$ (52%)
4: $R = H_{11}C_5$ (70%)
5: $R = H_{13}C_6$ (70%)
6: $R = H_{15}C_7$ (72%)
7: $R = H_{17}C_8$ (75%)
8: $R = H_{19}C_9$ (67%)

The literature does not provide information regarding the deprotonation of short-chain, medium-chain or long-chain alkenes using *N,N,N',N'*-tetramethylethylenediamine (TMEDA) activated alkyllithiums. Cyclic monoterpenes such as limonene, α-pinene and 2-carene do undergo metalation when treated with butyllithium in the presence of TMEDA.[10] Generally, however, long reaction times (e.g., 48 h at 25 °C or 8 h at reflux temperatures) and two molar equivalents of the substrate are required. Nevertheless, the average yield is poor (16–58 %). Allyllithium can be generated using a five-fold excess of propene and TMEDA-activated butyllithium (15 h between −75 °C and +25 °C; approx. 80 % yield of derivatives)[11] while partial dilithiation occurs when an excess of butyllithium in the presence of TMEDA is employed.[12] Allylsodium is formed when an over-stoichiometric (two-fold) amount of propene is exposed to the action of pentylsodium in hexane (1 h at −50 °C, 25 h at 25 °C; 28 % of but-3-enoic acid after carboxylation).[13]

Starting materials were purchased from Fluka (CH-9470 Buchs), Aldrich (D-89552 Steinheim) and Merck (D-64271 Darmstadt), unless literature sources or details of the preparation are given. Solutions of butyllithium in hexane (1.5 M and "11.5 M", i.e. containing the organometallic reagent to the extent of 90 %) were supplied by CheMetall (D-60271 Frankfurt), potassium *tert*-butoxide by Callery (Pittsburgh, PA 15230). All commercial reagents were used without further purification. Air and moisture sensitive compounds were stored in Schlenk tubes or Schlenk burettes. They were protected by and handled under an atmosphere of 99.995 % pure N_2 (glassware: Glasgerätebau Pfeifer, D-98711 Frauenwald).

Pentane was obtained anhydrous by treating it for 2 h with finely powdered CaH_2 under stirring and reflux before distillation, other paraffinic or aromatic hydrocarbons (e.g., hexane, benzene and toluene) by careful azeotropic distillation. Et_2O, tetrahydropyran and THF were dried by distillation from Na wire after the characteristic blue color of in situ generated sodium diphenyl ketyl[14] had been found to persist. Ethereal extracts were dried with Na_2SO_4. Before distillation of compounds prone to radical polymerization or sensitive to acids a spatula tip of hydroquinone or, respectively, K_2CO_3 was added.

The temperature of dry ice/MeOH baths is consistently indicated at $-75\,°C$ and "room temperature" (22-26 °C) as 25 °C. Melting ranges (mp) are reproducible after resolidification, unless stated otherwise ('dec.'), and are corrected by using a calibration curve which was established with authentic standards. If no melting points are given, it means that all attempts to crystallize the liquid product have failed even at temperatures as low as $-75\,°C$. If reduced pressure is not specified, boiling ranges were determined under ordinary atmospheric conditions (729 ± 25 mmHg). Silica gel (Merck Kieselgel 60) of 70–230 mesh (0.06–0.20 mm) particle size was used for column chromatography. The solid support was suspended in hexane and, when all air bubbles had escaped, was sluiced into the column. When the level of the liquid was still some 3–5 cm above the silica layer, the dry powder, obtained by adsorption of the crude product mixture on 15–20 g silica gel and subsequent evaporation of the solvent, was poured on top of the column.

Whenever reaction products were not isolated, their yields were determined by gas chromatography comparing their peak areas with that of an internal standard and correcting the ratios by calibration factors. Product ratios were determined and the purity of distilled compounds was checked on at least two columns loaded with stationary phases of different polarity. Chromosorb G-AW of 80–100 and 60–80 mesh particle size was used as the support for packed analytical or preparative columns (2 or 3 m long, 2 mm inner diameter and 3 or 6 m long, 1 cm inner diameter, respectively). Packed columns were made of glass, while quartz was the material for coated, Grob type capillary columns ($\geq$ 10 m long). In the case of programmed temperature increase a rate of 10 °C/min was maintained. The stationary phases employed are encoded as DB-1 (silicone type) and DB-Wax (polyethylene glycol type).

Nuclear magnetic resonance spectra of ^1H nuclei in $CDCl_3$ solution were recorded at 400 MHz. Chemical shifts δ refer to the signal of tetramethylsilane. Coupling constants (J) are measured in Hz. Coupling patterns are abbreviated as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), hex (hextet), hept (heptet), oct (octet), non (nonet), td (triplet of doublets) and m (multiplet). Mass spectra were obtained at 70 eV ionization potential maintaining a source temperature of 200 °C. Whenever no molecular peak was observed under standard conditions, chemical ionization ('c.i.') in an ammonia atmosphere at 100 °C source temperature was applied. Elementary analyses were executed by the laboratory of I. Beetz, D-96301 Kronach. The expected numbers are calculated on the bases of atomic weights according to the 1986 IUPAC recommendations.

Allyltriethylsilane [Triethylprop-2-enylsilane, 1a]:

Without inert gas protection, a 250 mL round-bottom flask was cooled to $-75\,°C$ and filled with a concentrated (approx. 11 M) solution of BuLi (0.25 mol) in hexane (23 mL), pentane (80 mL) and $KOC(CH_3)_3$ (28 g). Propene (20 mL, 11 g, 0.25 mol) was added being transferred from a Schlenk tube kept at $-75\,°C$ by means of a precooled pipet. The flask was closed with a rubber stopper in the middle of which a hole was drilled to fix a thermometer. The mixture was vigorously stirred for 15 min at $-25\,°C$ (salt-ice/MeOH bath), 15 min at 0 °C (ice bath) and 30 min at 25 °C. At $-25\,°C$, trimethylsilyl chloride (35 mL, 25 kg, 0.25 mol) was added dropwise. Without any further workup, the product was isolated by distillation; bp 166–168 °C (lit.[3] bp 170–172 °C); n_D^{20} 1.4437; 27 g (69 %).

^1H NMR: $\delta = 5.80$ (1 H, ddt, $J = 17.0, 10.1, 8.2$), 4.86 (1 H, ddt, $J = 17.0, 2.2, 1.4$), 4.80 (1 H, ddt, $J = 10.0, 2.0, 1.1$), 1.55 (2 H, dt, $J = 8.3, 1.3$), 0.94 (9 H, t, $J = 7.8$), 0.53 (6 H, q, $J = 7.9$).

Allyl-tert-butyldimethylsilane [(tert-Butyl)dimethyl(prop-2-enyl)silane, **1b**]:

As described for silane **1a** though on a 1.0 mol scale. To attenuate the strongly exothermal reaction, *tert*-butyldimethylsilyl chloride (0.17 L, 0.15 kg, 1.0 mol) was added at $-25\,°C$ in the course of 30 min. Direct distillation gave 95 g (61 %) of the product; another 25 g (16 %) were obtained after treatment of the residue with H_2O (0.2 L) and extraction with pentane (3 × 0.1 L); bp 150–152 °C (lit.[4] bp 65–66 °C/47 mmHg); n_D^{20} 1.4363.

^1H NMR: $\delta = 5.81$ (1 H, ddt, $J = 16.7, 10.0, 8.1$), 4.86 (1 H, dm, $J = 16.6$), 4.83 (1 H, dm, $J = 9.6$), 1.54 (2 H, d, $J = 7.9$), 0.90 (9 H, s), -0.04 (6 H, s).

Allyl-tert-butyldiphenylsilane [(tert-butyl)diphenyl(prop-2-enyl)silane, **1c**]:

As described for silane **1a**, though on a 50 mmol scale; bp 115–118 °C/0.5 mmHg; n_D^{20} 1.5673; 11.6 g (83 %).

^1H NMR (compatible with lit.[5]): $\delta = 7.6$ (4 H, m), 7.4 (6 H, m), 5.77 (1 H, ddt, $J = 16.9, 10.0, 7.8$), 4.90 (1 H, ddt, $J = 16.9, 2.2, 1.4$), 4.79 (1 H, ddt, $J = 10.0, 2.1, 1.3$), 2.19 (2 H, dt, $J = 7.9, 1.3$), 1.07 (9 H, s).

(*Z*)-Hex-2-enyltrimethylsilane (2):

At $-25\,°C$, precooled tetrahydropyran (20 mL), hex-1-ene (5.0 mL, 3.4 g, 40 mmol) and $KOC(CH_3)_3$ (4.5 g, 40 mmol) were consecutively added to BuLi (20 mmol) from which the commercial solvent (hexane) had beforehand been stripped off. After 3 h of vigorous stirring at 0 °C, the mixture was kept 72 h at $-25\,°C$ (deep freezer). After the addition of chlorotrimethylsilane (4.9 mL, 4.2 g, 40 mmol) at $-75\,°C$, the mixture was allowed to reach 25 °C under stirring before being poured into H_2O (25 mL). The aqueous phase was extracted with Et_2O (2 × 20 mL). The combined organic layers were washed with brine (2 × 10 mL), dried and evaporated. Upon distillation of the residue, product **2** was collected as a colorless liquid; (Z/E) ratio 95:5 according to gas chromatography (30 m, DB-1, 80 °C; 30 m, DB-Wax, 50 °C); bp 55–60 °C/25 mmHg (lit.[15] bp 60–61 °C/20 mmHg); n_D^{20} 1.4272 (lit.[15] 1.4241); 1.9 g (60 %).

^1H NMR: $\delta = 5.40$ (1 H, dtt, $J = 10.8, 8.6, 1.6$), 5.27 (1 H, dtt, $J = 10.8, 7.0, 1.6$), 1.97 (2 H, q, $J = 7.2$), 1.49 (2 H, d, $J = 8.5$), 1.37 (2 H, hex, $J = 7.5$), 0.92 (3 H, t, $J = 7.0$), 0.10 (9 H, s).

(Z)-Hept-2-enyltrimethylsilane (**3**):

As described for silane **2**, but using hept-1-ene (5.6 mL, 3.9 g, 40 mmol); (Z/E) ratio 95:5 according to gas chromatography (30 m, DB-1, 80 °C; 30 m, DB-Wax, 50 °C); bp 68–71 °C/25 mm Hg (lit.[16] bp 100–102 °C/58 mm Hg); n_D^{20} 1.4309; 1.8 g (52 %).

^1H NMR: $\delta = 5.38$ (1 H, ddt, $J = 10.8, 8.6, 1.6$), 5.27 (1 H, dtt, $J = 10.8, 7.0, 1.6$), 2.0 (2 H, m), 1.47 (2 H, d, $J = 8.5$), 1.3 (4 H, m), 0.91 (3 H, t, $J = 7.0$), 0.12 (9 H, s).

(Z)-Trimethyloct-2-enylsilane (**4**):

As described for silane **2**, but using oct-1-ene (6.3 mL, 4.5 g, 40 mmol); (Z/E) ratio 95:5 according to gas chromatography (30 m; DB-1, 100 °C; 30 m, DB-Wax, 60 °C); bp 28–30 °C/0.3 mm Hg (lit.[17] bp 100 °C/2 mm Hg); n_D^{20} 1.4412; 2.6 g (70 %).

^1H NMR: $\delta = 5.38$ (1 H, ddt, $J = 10.8, 8.6, 1.6$), 5.27 (1 H, dtt, $J = 10.8, 7.0, 1.6$), 1.98 (2 H, q, $J = 7.3$), 1.47 (2 H, d, $J = 8.5$), 1.3 (6 H, m), 0.89 (3 H, t, $J = 7.0$), 0.10 (9 H, s).

(Z)-Trimethylnon-2-enylsilane (**5**):

As described for silane **2**, but using non-1-ene (6.9 mL, 5.0 g, 40 mmol); (Z/E) ratio 98:2 according to gas chromatography (30 m; DB-1, 120 °C; 30 m, DB-Wax, 70 °C); bp 49–51 °C/0.5 mm Hg (lit.[18] bp of a (Z/E) mixture 120–130 °C/20 mm Hg); n_D^{20} 1.4423; 2.8 g (70 %).

^1H NMR: $\delta = 5.38$ (1 H, dtt, $J = 10.8, 8.6, 1.6$), 5.27 (1 H, dtt, $J = 10.8, 7.0, 1.6$), 1.98 (2 H, q, $J = 7.3$), 1.47 (2 H, d, $J = 8.5$), 1.3 (8 H, m), 0.90 (3 H, t, $J = 7.0$), 0.12 (9 H, s).

(Z)-Dec-2-enyltrimethylsilane (**6**):

As described for silane **2**, but using dec-1-ene (7.6 mL, 5.6 g, 40 mmol); (Z/E) ratio 95:5 according to gas chromatography (30 m;

DB-1, 130 °C; 30 m, DB-Wax, 80 °C); bp 60–62 °C/0.2 mm Hg; n_D^{20} 1.4438; 3.1 g (72 %).

^{1}H NMR: $\delta = 5.38$ (1 H, dtt, $J = 10.8$, 8.6, 1.6), 5.27 (1 H, dtt, $J = 10.8$, 7.0, 1.6), 1.98 (2 H, q, $J = 7.3$), 1.47 (2 H, d, $J = 8.5$), 1.3 (10 H, m), 0.90 (3 H, t, $J = 7.0$), 0.12 (9 H, s).

Analysis: calc. for $C_{13}H_{28}Si$ (212.45) C 73.50, H 13.28; found C 73.96, H 13.11 %.

(Z)-Trimethylundec-2-enylsilane (**7**):

As described for silane **2**, but using undec-1-ene (8.2 mL, 6.2 g, 40 mmol); (*Z*/*E*) ratio 98 : 2 according to gas chromatography (30 m; DB-1, 150 °C; 30 m, DB-Wax, 120 °C); bp 83–88 °C/1 mm Hg; n_D^{20} 1.4461; 3.4 g (75 %).

^{1}H NMR: $\delta = 5.4$ (2 H, m), 1.98 (2 H, q, 6.6), 1.47 (2 H, dm, $J = 8.1$), 1.3 (12 H, m), 0.89 (3 H, t, $J = 7.0$), 0.12 (9 H, s). Upon double irradiation at 1.46 the multiplet assigned to the olefinic hydrogen atoms was simplified to analyzable signals: 5.38 (1 H, d, $J = 10.8$), 5.27 g (1 H, dt, $J = 10.8$, 6.4).

Analysis: calc. for $C_{14}H_{30}Si$ (226.48) C 74.25, H 13.25; found C 74.42, H 13.31 %.

(Z)-Dodec-2-enyltrimethylsilane (**8**): As described for silane **2**, but using dodec-1-ene (8.9 mL, 6.7 g, 40 mmol); (*Z*/*E*) ratio 97 : 3 according to gas chromatography (30 m; DB-1, 170 °C; 30 m, DB-Wax, 140 °C); bp 100–105 °C/1 mm Hg; n_D^{20} 1.4452; 3.2 g (67 %).

^{1}H NMR: $\delta = 5.37$ (1 H, dtt, $J = 10.9$, 8.6, 1.3), 5.26 (1 H, dtt, $J = 10.9$, 7.0, 1.3), 1.97 (2 H, q, $J = 7.0$), 1.46 (2 H, d, $J = 8.6$), 1.3 (14 H, m), 0.89 (3 H, t, $J = 7.0$), 0.01 (9 H, s).

Analysis: calc. for $C_{15}H_{32}Si$ (240.50) C 74.91, H 13.41; found C 75.66, H 12.81 %.

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