Conformational Mobility and Preferences of Allyl-Type Organometallic Intermediates: Dodec-2-enylpotassium

Livia Franzini, Etienne Moret, and Manfred Schlosser*

Institut de Chimie organique de l'Université,
Bâtiment de Chimie (BCh), CH-1015 Lausanne-Dorigny, Switzerland

Received August 2, 1996

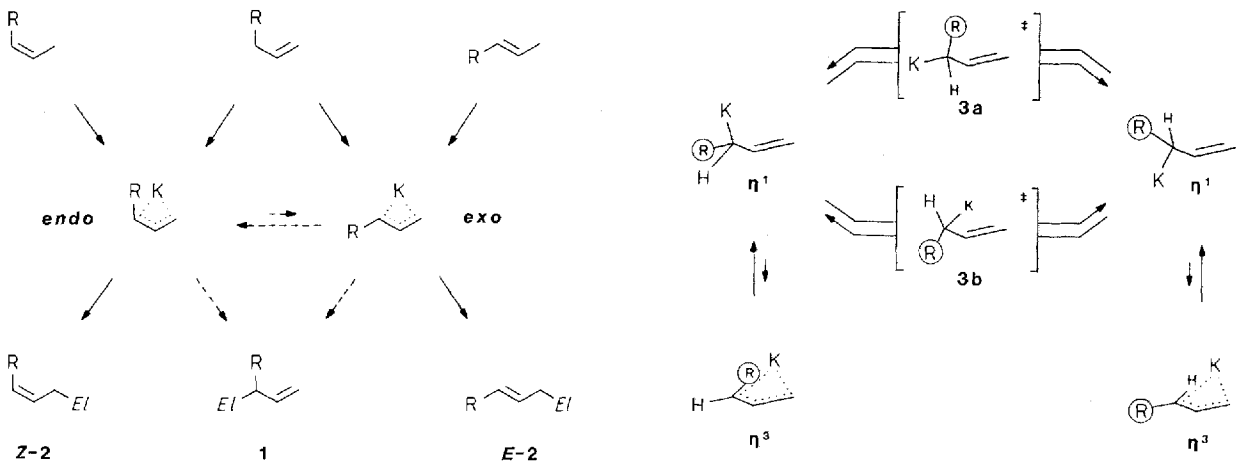
Keywords: Torsional (*Z*/*E*) isomerization / Selectivity, regio- and stereo- / Allylsilanes / Allylic oxidation

Alk-2-enylpotassium compounds having the *endo* conformation are synthetically very valuable precursors of (Z)-olefinic derivatives substituted at the outward allylic position. They may be generated by "stereoconservative" metalation of the readily available (Z)-alk-2-enes by using the superbasic mixture of butyllithium and potassium *tert*-butoxide or by metalation under similar conditions of stereorandom mixtures of alk-2-enes or alk-1-enes followed by torsional isomerization of the concomitantly formed *exo* conformers to the thermodynamically more stable *endo* species. The principal factors that dictate the rate and the extent of the *endo*/*exo* equilibration are the substrate geometry, the solvent, the temperature, the reagent stoichiometry, and catalysis.

Butyllithium activated by potassium *tert*-butoxide was the first mixed metal reagent conceived to promote the deprotonation of weakly acidic hydrocarbons[1]. As systematic investigations have revealed[2], it is far more selective and at the same time chemically more stable than other superbases such as butylpotassium. The butyllithium/potassium *tert*-butoxide adduct was in particular found to accomplish efficaciously the hydrogen/potassium exchange in linear[3] and cyclic[4] olefins, thus generating allyl-type organometallics. These versatile species may play a key role in organic synthesis[5] provided they are stereochemically uniform. Stereocontrol may be achieved in two ways[6,7]. One can use a stereoisomerically pure 2-alkene as the precursor and work under configuration-retaining conditions, thus converting a (*Z*)-olefin via an *endo* allylmetal into an electrophilically substituted (*Z*) derivative (*Z*-**2**) and an (*E*) olefin via an *exo* allylmetal into an (*E*) configurated product (*E*-**2**). Alternatively, one may start with any blend of *cis*/*trans*-2-alkenes or even with a 1-alkene, generate the organometallic intermediates as a mixture of *endo* and *exo* conformers and allow for their torsional equilibration. The latter favors the *endo* component and thus paves the way towards the (*Z*) product. Branched regioisomers (**1**) are generally formed in minor amounts, if at all.

(*Z*)-2-Alkenes can be conveniently obtained with 99% isomeric purity by the Wittig reaction of acetaldehyde with the corresponding triphenylphosphonioalkanide[8]. The equilibration approach to *endo*-alk-2-enylpotassium species is more tricky, but also more challenging. We would like to comment on some of the problems encountered and briefly explain how the inherent difficulties can be mastered.

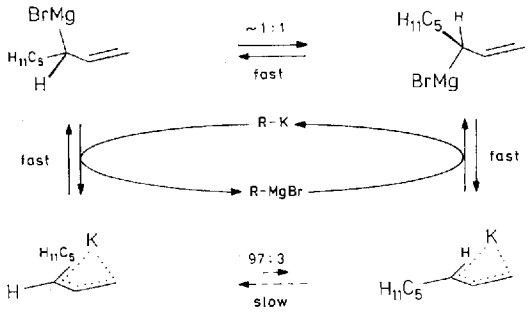
The torsional isomerization of allylic organoalkali metal compounds can only take place after its π-complex-like η^3-structure[9] has been abandoned in favor of a σ-bond-like η^1-interaction, which links the metal to the inner (C-3) terminus of the allyl entity[7]. The loss of coordination provided by the carbon backbone to the metal has to be compensated for by external donor ligands or aggregation. Now



  0009-2940/97/0101-0083 $ 15.00+.25/0

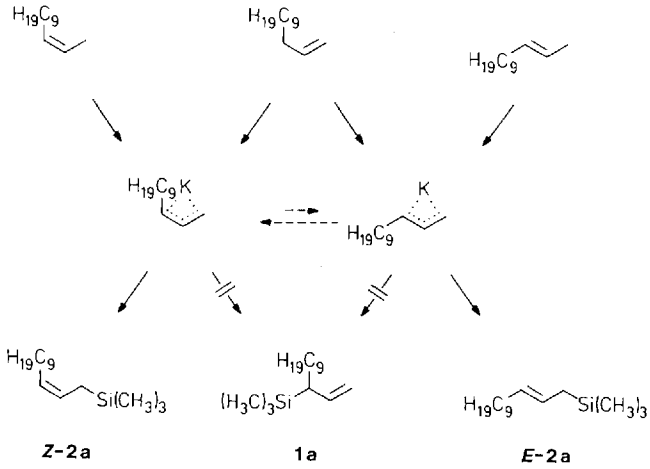
the stage is set for the crucial event, the rotation around the C(2)–C(3) axis. When the carbon-metal bond and the *p*-electrons of the double bond located between C(1) and C(2) occupy planes that are orthogonal to each other (transition states **3a** and **3b**), no more delocalization is possible. The sacrifice of the allylic resonance energy is certainly the most important factor that impedes torsional motion. Actually, the apparent[3,7,10] activation energies are approximately 20 kcal/mol with ethereal solutions and 22–25 kcal/mol with paraffinic suspensions. In other words, torsional equilibration requires many hours in tetrahydrofuran if, for reasons of stability, the temperature is kept in the range from −50 °C to −25 °C, or in hexane at +25 °C.

The resonance energy is high if the allyl moiety is combined with an electropositive metal such as potassium or cesium and much smaller with less electropositive ones. Allyllithium[11], allylmagnesium and allylzinc[13] species undergo rapid torsional equilibration already at −75 °C. This offers the opportunity to accelerate the torsional equilibration of alk-2-enylpotassium species (e.g., non-2-enylpotassium) by introducing catalytic amounts of organolithium or organomagnesium compounds. Lithium and magnesium halides have the same effect since they immediately react with the organopotassium intermediate under metal/metal exchange conditions.



These catalysts have to be employed in strictly limited quantities since the derivatives of less electropositive metals no longer exhibit a pronounced *endo* preference and, therefore, impair the (*Z*/*E*) ratios of final products. However, if appropriate precautions are taken, equilibration times can be substantially shortened. A typical example may illustrate this[14]. The metalation of oct-1-ene in tetrahydrofuran with butyllithium in the presence of potassium *tert*-butoxide or with trimethylsilylmethylpotassium[15] affords (*Z*)- and (*Z*)-oct-2-enylpotassium in a ratio of 81:19, as evidenced by the stereoisomeric composition of the products obtained after trapping with chlorotrimethylsilane. After addition of 3 mol-% of butylmagnesium bromide and storage of the solution for 25 h at −75 °C, an *endo*/*exo* ratio of 97:3 was attained whereas it would have taken 150 h at −50 °C to establish the equilibrium without added catalyst.

The catalytic process is not without drawbacks. First of all, the yields are unsatisfactory. Apparently, the metal/metal interconversion promotes alkenylpotassium-consuming side reactions. Thus, only 42% of oct-2-enylsilane was formed in the reaction described above, while 70% was isolated after the same time in the absence of a catalyst. Although the exact mode of decomposition is still unknown, one may suspect the solvent to be involved. Replacement of tetrahydrofuran by tetrahydropyran diminishes the vulnerability of the allylmetal intermediate without protecting it completely against catalyst-triggered destruction.



Z-**2a** **1a** *E*-**2a**

Another shortcoming is the immobilization of magnesium by functional groups. Under these circumstances, the optimum amount of catalyst has to be determined empirically. When undec-10-en-1-ol was metalated with two equivalents of trimethylsilylpotassium, it needed 0.75 equivalents of butylmagnesium chloride to bring about, in 40 h at −60 °C, the *endo*/*exo* equilibration to obtain, after trapping with methyl iodide, dodec-9-en-1-ol in a (*Z*/*E*) ratio of 96:4 besides small amounts of the regioisomeric 9-methylundec-10-en-1-ol[14b].

What increases the feeling of uneasiness is the occasional "overshooting" of the torsional equilibration process. The *endo*/*exo* ratios of most alk-2-enylpotassium compounds level out between 92:8 and 94:6 if kept long enough at tempertures around −75 °C, −50 °C or −25 °C. Now and then, however, ratios ranging from 94:6 to 99:1 are found. In the case of hex-2-enylpotassium[3,16] selective crystallization of the (*Z*) conformer, at least if present in high concentrations, seems to be at the origin of this phenomenon. Side reactions might be another source of artefacts if they discriminate against the (*E*) isomer by consuming it preferentially.

In order to explore how the internal mobility of allyl-type organometallics can be affected, we undertook a systematic study. Dodec-1-ene and the two stereoisomers of dodec-2-ene were selected as model compounds. So far, no long-chain alkenes have been investigated as substrates of metalation reactions. The dodec-2-enylpotassium intermediates were trapped with chlorotrimethylsilanes since this electrophile attacks only the terminal position. In other words, they do not form the "branched" regioisomer [trimethyl-(1-nonylprop-2-enyl)silane (**1a**)], but only the "linear" products [(*Z*)- and (*E*)-(dodec-2-enyl)trimethylsilane (*Z*-**2a** and *E*-**2a**)]. The time dependence of *endo*/*exo* equilibration was determined as a function of the olefin geometry (Table 1), the temperature (Table 2), the solvent (Table 3), the reagent stoichiometry

(Table 4), and the presence of an isomerization catalyst (Table 5).

Table 1. Metalation of (*Z*)- and (*E*)-dodec-2-ene with equivalent amounts of the LIC-KOR superbase in tetrahydrofuran (0.7 M) at −25 °C and subsequent trapping with chlorotrimethylsilane: stereoconvergence as a function of time

time	from (*Z*)-dodec-2-ene		from (*E*)-dodec-2-ene	
[h]	yield (**2**)	*Z*-**2**:*E*-**2**	yield (**2**)	*Z*-**2**:*E*-**2**
0.3	45%	97:3	25%	7:93
1	56%	97:3	–	–
3	69%	95:5	48%	18:82
24	74%	92:8	44%	41:59
72	75%	92:8	40%	59:41
150	70%	92:8	16%	92:8

Table 2. Metalation of dodec-1-ene with equivalent amounts of the LIC-KOR superbase in tetrahydrofuran at varying temperatures and subsequent trapping with chlorotrimethylsilane: yields and (*Z*/*E*) ratios of (dodec-2-enyl)trimethylsilanes **2** formed as a function of time

time	at −50 °C		at −25 °C		at 0 °C	
[h]	yield	*Z*-**2**:*E*-**2**	yield	*Z*-**2**:*E*-**2**	yield	*Z*-**2**:*E*-**2**
0.3	58%	79:21	41%	75:25	47%	84:16
1	57%	80:20	40%	75:25	44%	90:10
3	59%	80:20	38%	78:22	40%	91:9
24	51%	82:18	38%	91:9	40%	90:10
72	44%	85:15	36%	92:8	31%	90:10
150	38%	92:8	33%	93:7	17%	90:10

Table 3. Metalation of dodec-1-ene with equivalent amounts of the LIC-KOR superbase in tetrahydropyran at varying temperatures and subsequent trapping with chlorotrimethylsilane; yields and (*Z*/*E*) ratios of (dodec-2-enyl)trimethylsilanes **2** formed as a function of time

time	at −50 °C		at −25 °C		at 0 °C	
[h]	yield	*Z*-**2**:*E*-**2**	yield	*Z*-**2**:*E*-**2**	yield	*Z*-**2**:*E*-**2**
0.3	4%	71:29	41%	72:28	68%	82:18
1	5%	72:28	63%	77:23	70%	89:11
3	15%	77:23	72%	81:19	63%	90:10
24	39%	87:13	70%	88:12	78%	90:10
72	49%	91:9	68%	92:8	76%	90:10
150	61%	91:9	63%	93:7	69%	90:10

Table 4. Metalation of dodec-1-ene in tetrahydropyran at −25 °C using varying stoichiometric ratios of butyllithium and potassium *tert*-butoxide relative to the olefin (1.0 equiv.), followed by the treatment with chlorotrimethylsilane: yields (relative to dodec-1-ene) and (*Z*/*E*) ratios of the (dodec-2-enyl)trimethylsilanes **2** formed as a function of time

time	equivalents of LiC_4H_9 and $KOC(CH_3)_3$ used					
[h]	1.0:1.0		2.0:2.0		0.5:1.0	
0.3	41%	72:28	64%	75:25	34%	76:24
1	63%	77:23	77%	75:25	33%	75:25
3	72%	81:19	90%	80:20	32%	79:21
24	70%	88:12	90%	89:11	29%	96:4
72	68%	92:8	93%	92:8	22%	97:3
150	63%	93:7	92%	92:8	23%	97:3

What lessons can be learned from these data? There are some obvious conclusions and a few tentative suggestions:

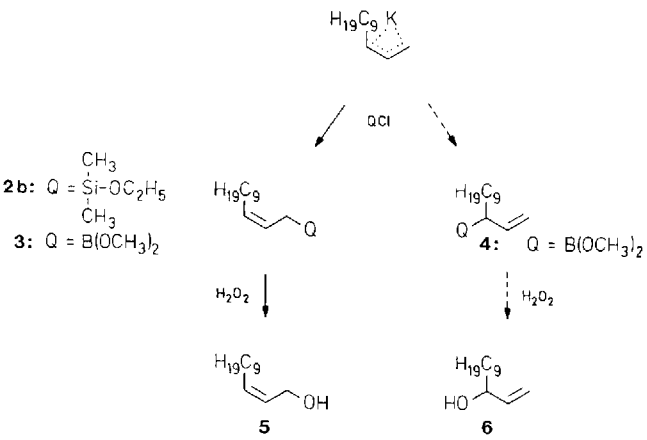
Table 5. Metalation of dodec-1-ene in tetrahydropyran at −25 °C in the presence or absence of an isomerization catalyst (0.02 mol-%) and subsequent trapping with chlorotrimethylsilane: yields and (*Z*/*E*) ratios of the (dodec-2-enyl)trimethylsilanes **2** formed as a function of time

time	catalyst					
[h]	none		$ClMgC_3H_7$		$Hg(CH_2Si(CH_3)_3)_2$	
0.3	41%	72:28	53%	78:22	55%	81:19
1	63%	77:23	61%	80:20	59%	88:12
3	72%	81:19	68%	90:10	56%	90:10
24	70%	88:12	68%	93:7	53%	91:9
72	68%	92:8	67%	92:8	51%	91:9
150	63%	93:7	60%	93:7	45%	92:8

- Tetrahydrofuran is not inert enough towards allylic organometallics[17] and, therefore, yields are unsatisfactory even at −50 °C. Tetrahydropyran is a better choice (Tables 2 and 3).
- (*Z*)-Alk-2-enes undergo rapid deprotonation and the (*Z*/*E*) ratios of the products formed by electrophilic trapping of the organometallic intermediates after a few hours still reflect the isomeric purity of the olefinic starting material ("stereoconservative reaction sequence", Table 1). On the other hand, (*E*)-2-alkenes react more sluggishly (Table 1) and it is advisable to work at high concentrations (1−2 M) to shorten the metalation stage to a minimum of time, thus preserving the original geometry.
- If terminal olefins (alk-1-enes) are the precursors, then optimum (*Z*/*E*) ratios are generally obtained at −25 °C (Table 3). However, it may be advantageous to carry out the metalation rapidly at 0 °C and torsional equilibration subsequently at a lower temperature (see Experimental).
- Use of the superbase in excess considerably improves the yields but does not affect the stereochemistry. In contrast, the (*Z*/*E*) ratios increase when twice the amount of potassium *tert*-butoxide is used relative to butyllithium (Table 4). One can only speculate about the origin of this change: the alcoholate either purges the allylpotassium intermediate of contaminating allyllithium inclusions[18] or promotes the selective consumption of the organometallic *exo* species by hydrogen/metal interconversion with dodec-1-ene or (*Z*)-dodec-2-ene, which are both present in significant amounts [after 150 h of metalation and equilibration, respectively 7% and 3% besides 3% of (*E*)-dodec-2-ene].
- Both butylmagnesium chloride and bis(trimethylsilylmethyl)mercury accelerate the *endo*/*exo* equilibration noticeably (Table 5). The mode of action of the organomercurial is yet unknown. It may participate in a metal/metalloid exchange, thus reversibly producing an alk-2-enylmercury[19] species with can undergo rapid torsional isomerization (like allylic Grignard reagents too[12]) or it may, while being reduced to the elementary state, set free conformationally mobile allyl radicals and thus initiate an equilibrating chain process[16].

Allylsilanes are versatile intermediates for organic synthesis. They react with a variety of electrophiles, either directly[20] or after lithiation of the silicon-adjacent position[22]. A final option consists in their oxidation to allyl alcohols pro-

vided the metalloid atom carries at least one hetero substituent[23]. To compare this possibility with the well-established borylation/oxidation sequence[24], we treated *endo*-dodec-2-enylpotassium in parallel reactions with fluorodimethoxyborane and chloroethoxydimethylsilane. The alkoxysilane **2b** thus formed was heated with alkaline hydrogen peroxide to afford regioisomerically pure dodec-2-en-1-ol (**5**) in a (*Z*/*E*) ratio of 96:4 in 52% overall yield. The same product **5** was obtained in a (*Z*/*E*) ratio of 93:7 and 69% overall yield, but concomitantly with 3.5% of the secondary alcohol **6** via the dimethyl boronates **3** and **4**.



This work was financially supported by the *Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung*, Bern (grants 20-92'838-90, 20-36'385-92 and 20-41'887-94).

Experimental Section

1. *Generalities, Starting Materials and Materials for Comparison*

For laboratory routine and formalities, see related articles[25,26]. – ^{1}H NMR: spectra were recorded in deuteriochloroform solutions at 250 MHz or, if marked by an asterisk, at 400 MHz.

(Z)-Dodec-2-ene[27]: A suspension of the "instant ylide"[28] mixture (0.10 mol) containing ethyltriphenylphosphonium bromide and sodium amide in tetrahydrofuran (0.10 l) was stirred vigorously for 30 min at 25°C. At −75°C and with continuous stirring, decanal (caprinaldehyde; 19 ml, 16 g, 0.10 mol) was added dropwise over 30 min. As soon as the mixture had reached 25°C, hexane (0.25 l) was added. After centrifugation, the supernatant liquid was decanted and the residue thoroughly extracted with hexane (0.15 l). The combined organic solution was filtered through silica gel (0.2 kg) and concentrated. Distillation of the residue afforded a colorless oil, b.p. 59−62°C/2 mmHg; n_D^{20} = 1.4396; 76%. – (*Z*/*E*) ratio 95:5 according to gas chromatography (30 m DB-1, 120→220°C; 30 m DB-Wax, 100→180°C). – ^{1}H NMR*: δ = 5.4 (2H, m), 2.04 (2H, q, *J* = 6.4 Hz), 1.62 (3H, dq, *J* = 5.9, 1.1 Hz), 1.3 (12H, m), 1.27 (12H, s), 0.90 (3H, t, *J* = 6.9 Hz). – $C_{12}H_{24}$ (168.32): calcd. C 85.63, H 14.37; found C 85.58, H 14.28.

(E)-Dodec-2-ene[27]: As previously described[29], (*E*)-but-2-enyl acetate[30] (11 g, 0.10 mol) and octylmagnesium bromide (prepared from 0.11 mol of 1-bromooctane and 0.14 mol of magnesium turnings) in tetrahydrofuran (0.10 l) were consecutively added to a solution of dilithium trichlorocuprate (2 mmol) in tetrahydrofuran (20 ml) kept at −75°C. The resulting solution was allowed to reach 25°C over 2 h. Immediately afterwards it was filtered through a pad of diatomite and concentrated. Distillation of the residue yielded a colorless liquid; b.p. 61−62°C/2 mmHg: n_D^{20} = 1.4341; 73%. – (*Z*/*E*) ratio 1:99 according to gas chromatography (conditions: see above). – ^{1}H NMR*: δ = 5.4 (2H, m), 1.98 (2H, q-like m, *J* ≈ 6.0 Hz), 1.66 (3H, dt, *J* = 4.9, 1.3 Hz), 1.3 (12H, m), 1.29 (12H, s), 0.90 (3H, t, *J* = 7.0 Hz). – $C_{12}H_{24}$ (168.32): calcd. C 85.63, H 14.37; found C 85.64, H 14.03.

Trimethyl(1-nonylprop-2-enyl)silane (**1**): At −25°C and with stirring, precooled (−75°C) tetrahydropyran (20 ml), dodec-1-ene (8.9 ml, 6.7 g, 40 mmol) and potassium *tert*-butoxide (4.5 g, 40 mmol) were consecutively added to butyllithium (20 mmol) from which the commercial solvent (hexane) had previously been evaporated. After 3 h at 0°C, a solution of dilithium trichlorocuprate (5 mmol) in tetrahydrofuran (7.0 ml) was added. The orange suspension turned black. It was stirred for another 3 h at 0°C, before being cooled to −25°C and treated with chlorotrimethylsilane (5.1 ml, 4.4 g, 40 mmol). Evaporation and distillation gave a mixture containing approximately equal amounts of **1** and **2**, the latter in a (*Z*/*E*) ratio of 4:1; 69%. – Isomer **1** was purified by preparative gas chromatography (3 m, 5% SE-30, 140°C). – ^{1}H NMR*: δ = 5.60 (1H, ddd, *J* = 18.3, 10.4, 9.4 Hz), 4.86 (1H, dd, *J* = 10.5, 2.1 Hz), 4.80 (1H, ddd, *J* = 18.1, 2.1, 1.0 Hz), 1.4 (3H, m), 1.25 (14H, s), 0.89 (3H, t, *J* = 6.7 Hz), −0.04 (9H, s). – $C_{15}H_{32}Si$ (240.51): calcd. C 74.91, H 13.41; found C 75.66, H 13.27.

(Z)-(Dodec-2-enyl)trimethylsilane[26] (*Z*-**2a**): At −25°C and with stirring, precooled (−75°C) tetrahydropyran (20 ml), dodec-1-ene (8.9 ml, 6.7 g, 40 mmol) and potassium *tert*-butoxide (4.5 g, 40 mmol) were consecutively added to butyllithium (20 mmol) from which the commercial solvent (hexane) had been evaporated. After 3 h at 0°C, the orange-colored suspension was placed for 72 h in a cooling bath at −25°C. At −75°C, chlorotrimethylsilane (5.1 ml, 4.4 g, 40 mmol) was added all at once whereupon immediate decoloration occurred. Evaporation and distillation gave a colorless oil; b.p. 100−105°C/2 mmHg; n_D^{20} = 1.4452; 67%. – (*Z*/*E*) ratio 97:3 according to gas chromatography (30 m DB-1, 170°C; 30 m DB-Wax, 140°C). – ^{1}H NMR*: δ = 5.37 (1H, dtt, *J* = 10.9, 8.6, 1.3 Hz), 5.26 (1H, dtt, *J* = 10.9, 7.0, 1.3 Hz), 1.97 (2H, q, *J* = 7.0 Hz), 1.46 (2H, dm, *J* = 8.6 Hz), 1.3 (14H, m), 0.89 (3H, t, *J* = 7.0 Hz), 0.01 (9H, s).

(E)-(Dodec-2-enyl)trimethylsilane[31] (*E*-**2a**): A stirred solution of (*Z*)-(dodec-2-enyl)trimethylsilane (3.5 g, 15 mmol) and diphenyl sulfide (4.7 g, 21 mmol) in hexane (25 ml) was irradiated for 2 h with a mercury lamp (HPK Philips, 125 W)[32]. The material was absorbed on silica gel (10 g) and the dry powder was placed on the top of a column filled with more silica gel (90 g). Elution with hexane and evaporation of the solvent gave an oil wich after gas chromatographic purification (3 m, 5% SE-30, 200°C) proved to consist of *Z*-**2a** and *E*-**2a** in a ratio of 17:83; 91%. – ^{1}H NMR*: δ = 5.36 (1H, dtt, *J* = 15.2, 7.8, 1.1 Hz), 5.24 (1H, dtt, *J* = 15.2, 6.9, 1.1 Hz), 2.0 (2H, m), 1.40 (2H, dd, *J* = 8.0, 0.9 Hz), 1.3 (14H, m), 0.89 (3H, t, *J* = 7.1 Hz), 0.0 (9H, s).

2. *Stereoequilibration Studies*

General Procedure: The precooled ethereal solvent (15 ml), dodec-1-ene (2.2 ml, 1.7 g, 10 mmol), undecane (as a gas chromatographic reference compound; approximately 1 mmol), and potassium *tert*-butoxide (1.1 g, 10 mmol) were consecutively added to solvent-free butyllithium (10 mmol) at −75°C. As soon as the alcoholate had dissolved, the mixture was placed in a cooling bath to maintain the desired temperature over a total of 150 h. Small quantities (approximately 0.1 ml) of the solution were withdrawn after given intervals and treated at −75°C with chlorotrimethylsilane (approx. 0.1 ml). After partitioning between hexane (1 ml) and water (1 ml), the products in the organic layer were identified by

comparison of their retention times with those of authentic samples on capillary columns (30 m DB-1; 30 m DB-Wax; both 100→220 °C [10 °C/min]) and their amounts were determined by comparing their peak areas with that of the "internal standard" after correction with predetermined calibration factors. In this way, the yields of dec-1-ene, (*Z*)- and (*E*)-dodec-2-ene, and (*Z*)- and (*E*)-(dodec-2-enyl)trimethylsilane (*Z*-**2** and *E*-**2**) were monitored as a function of time, the numbers being listed in Tables 1–5; only trace amounts (1–2%) of trimethyl(1-nonylprop-2-enyl)silane were detected.

3. *Conversion of Dodec-1-ene into Dodec-2-en-1-ol*

According to the Boronate Route: At −25 °C, precooled (−75 °C) tetrahydropyran (20 ml), dodec-1-ene (8.9 ml, 6.7 g, 40 mmol) and potassium *tert*-butoxide (4.5 g, 40 mmol) were consecutively added to butyllithium (20 mmol) from which the commercial solvent (hexane) had been removed. After 3 h at 0 °C, the mixture was kept for 72 h at −25 °C before being treated with fluorodimethoxyborane diethyl etherate (9.3 ml, 8.3 g, 50 mmol). The color of the suspension instantly changed from orange-red to white. At 0 °C, 30% aqueous hydrogen peroxide (6.0 ml, 2.0 g, 59 mmol) was added and the two-phase mixture was vigorously stirred for 1 h at 25 °C. The aqueous layer was saturated with sodium chloride and extracted with diethyl ether (3 × 25 ml). The combined organic layers were washed with brine (3 × 10 ml), dried and the solvent was evaporated. According to gas chromatography (30 m DB-1, 150 °C; 30 m DB-Wax, 150 °C), the residue contained 1-nonylprop-1-ene-ol[33] (**6**; 3.5%) and dodec-2-en-1-ol[34] (**5**; 69%). Since no separation of dodec-2-en-1-ols *Z*-**5** and *E*-**5** was achieved, a sample of the crude reaction product was treated with a slight excess (1.1 equiv.) of acetyl chloride and pyridine in dichloromethane (0.8 M solution) for 2 h at 25 °C. The resulting (*Z*)- and (*E*)-dodec-2-enyl acetates[35] could now be well identified by using authentic samples for comparison. The (*Z*/*E*) ratio was found to be 93:7 (30 m DB-1, 150 °C; 30 m DB-Wax, 150 °C). – $C_{14}H_{26}O_2$ (226.36): calcd. C 74.29, H 11.58; found C 74.29, H 11.53. – The bulk of the crude product was distilled to give *Z*-**5**, slightly contaminated by its regioisomer **6**; b.p. 75–77 °C/0.3 mmHg; n_D^{20} = 1.4541; 68%. – $C_{12}H_{24}O$ (184.32): calcd. C 78.20, H 13.12; found C 78.11, H 12.95.

According to the Alkoxysilane Route: In an analogous reaction starting with dodec-1-ene (40 mmol), fluorodimethoxyborane was replaced by chloro(ethoxy)dimethylsilane[36]. Upon oxidation with hydrogen peroxide, dodec-2-enyl(ethoxy)dimethylsilane (**2b**) was isolated as described in the preceding paragraph; b.p. 85–90 °C/0.2 mmHg; n_D^{20} = 1.4485; 54%. – The (*Z*/*E*) ratio was 96:4 according to gas chromatography (30 m DB-1, 180 °C; 30 m DB-Wax, 180 °C). – ^{1}H NMR*: δ = 5.39 (1H, dt, *J* = 10.4, 8.6 Hz), 5.30 (1H, dt, *J* = 10.4, 7.0 Hz), 3.69 (2H, q, *J* = 6.9 Hz), 2.00 (2H, q, *J* = 7.0 Hz), 1.59 (2H, d, *J* = 8.1 Hz), 1.3 (14H, m), 1.20 (3H, t, *J* = 7.0 Hz), 0.89 (3H, t, *J* = 7.0 Hz), 0.12 (6H, s). – $C_{16}H_{34}OSi$ (270.53): calcd. C 71.04, H 12.67; found C 71.13, H 12.70. – A solution of silane **2b** (5.4 g, 20 mmol) and potassium hydrogen carbonate (2.0 g, 20 mmol) in 30% aqueous hydrogen peroxide (27 ml, 30 g, 0.27 mol), methanol (40 ml) and tetrahydrofuran (40 ml) was heated at reflux for 1 h with stirring. The volatile components were evaporated and the residue was extracted with dichloromethane (3 × 10 ml). Distillation afforded dodec-2-en-1-ol (**5**) as a colorless liquid; (*Z*/*E*) ratio 96:4; b.p. 75–80 °C/0.3 mmHg; n_D^{20} = 1.4543; 95%.

[1] M. Schlosser, *J. Organomet. Chem.* **1967**, *8*, 9–16.
[2] M. Schlosser, S. Strunk, *Tetrahedron Lett.* **1984**, *25*, 741–744.
[3] M. Schlosser, J. Hartmann, V. David, *Helv. Chim. Acta* **1974**, *57*, 1567–1576; M. Schlosser, J. Hartmann, *J. Am. Chem. Soc.* **1976**, *98*, 4674–4676.
[4] J. Hartmann, M. Schlosser, *Synthesis* **1975**, 328–329; G. Rauchschwalbe, M. Schlosser, *Helv. Chim. Acta* **1975**, *58*, 1094–1099.
[5] M. Schlosser, *Pure Appl. Chem.* **1988**, *60*, 1627–1634; M. Schlosser, F. Faigl, L. Franzini, H. Geneste, G. Katsoulos, G.-F. Zhong, *Pure Appl. Chem.* **1994**, *66*, 1423–1446.
[6] H. Bosshardt, M. Schlosser, *Helv. Chim. Acta* **1980**, *63*, 2393–2403.
[7] M. Schlosser, O. Desponds, R. Lehmann, E. Moret, G. Rauchschwalbe, *Tetrahedron* **1993**, *49*, 10175–10203.
[8] M. Schlosser, G. Müller, K. F. Christmann, *Angew. Chem.* **1966**, *78*, 677–678; *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 667–668; M. Schlosser, B. Schaub, J. de Oliveira-Neto, S. Jeganathan, *Chimia* **1986**, *40*, 244–245.
[9] M. Schlosser, M. Stähle, *Angew. Chem.* **1980**, *92*, 497–499; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 487–488; M. Stähle, M. Schlosser, *J. Organomet. Chem.* **1981**, *220*, 277–283; see also: S. Brownstein, S. Bywater, D. J. Worsfold, *J. Organomet. Chem.* **1980**, *199*, 1–8; U. Schümann, E. Weiss, H. Dietrich, W. Mahdi, *J. Organomet. Chem.* **1987**, *322*, 299–307.
[10] T. B. Thompson, W. T. Ford, *J. Am. Chem. Soc.* **1979**, *101*, 5459–5964.
[11] P. West, J. I. Purmort, S. V. McKinley, *J. Am. Chem. Soc.* **1968**, *90*, 797–798.
[12] J. E. Nordlander, J. D. Roberts, *J. Am. Chem. Soc.* **1959**, *81*, 1769–1770; G. M. Whitesides, J. E. Nordlander, J. D. Roberts, *J. Am. Chem. Soc.* **1962**, *84*, 2010–2011.
[13] G. Wilke, B. Bogdanović, P. Hardt, P. Heimbach, W. Keim, M. Kröner, W. Oberkirch, K. Tanaka, E. Steinrücke, D. Walter, H. Zimmermann, *Angew. Chem.* **1966**, *78*, 157–172; *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 151–198.
[14] E. Moret, Doctoral Thesis, University of Lausanne, **1980**, (a) pp. 12–13 and 55, (b) pp. 32–33 and 79–83.
[15] J. Hartmann, M. Schlosser, *Helv. Chim. Acta* **1976**, *59*, 453–466.
[16] M. Stähle, J. Hartmann, M. Schlosser, *Helv. Chim. Acta* **1977**, *60*, 1730–1738.
[17] E. Moret, O. Desponds, M. Schlosser, *J. Organomet. Chem.* **1991**, *409*, 83–91.
[18] M. Schlosser, J. Hartmann, *Angew. Chem.* **1973**, *85*, 544–545; *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 508–509.
[19] H. E. Zieger, J. D. Roberts, *J. Org. Chem.* **1969**, *34*, 2826–2828.
[20] T. H. Chan, I. Fleming, *Synthesis* **1979**, 761–786, spec. 775; A. W. Colvin, *Silicon Reagents in Organic Synthesis*, Academic Press, London, **1988**; G. Majetich, in *Organic Synthesis: Theory and Application* (Ed.: T. Hudlicky), Jai Press, Greenwich, **1989**, pp. 173–240.
[21] A. Mordini, G. Palio, A. Ricci, M. Taddei, *Tetrahedron Lett.* **1988**, *29*, 4991–4994.
[22] E. Moret, L. Franzini, M. Schlosser, *Chem. Ber.*, in press.
[23] K. Tamao, N. Ishida, T. Tanaka, M. Kumada, *Organometallics* **1983**, *2*, 1694–1696.
[24] G. Rauchschwalbe, M. Schlosser, *Helv. Chim. Acta* **1975**, *58*, 1094–1099.
[25] O. Desponds, M. Schlosser, *J. Organomet. Chem.* **1996**, *507*, 257–261.
[26] O. Desponds, L. Franzini, M. Schlosser, manuscript submitted.
[27] L. Soják, J. Hrivňák, A. Simkovicová, J. Janak, *J. Chromatogr.* **1972**, *71*, 243–249; A. R. Katritzky, A. M. El-Mowafy, *J. Org. Chem.* **1982**, *47*, 3506–3511.
[28] M. Schlosser, B. Schaub, *Chimia* **1982**, *36*, 396–397.
[29] G. Fouquet, M. Schlosser, *Angew. Chem.* **1974**, *86*, 50–51; *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 82; M. Schlosser, H. Bossert, *Tetrahedron* **1991**, *47*, 6287–6292.
[30] W. G. Young, H. E. Green, A. F. Diaz, *J. Am. Chem. Soc.* **1971**, *93*, 4782–4787.
[31] H. Iio, M. Ishii, M. Tsukamoto, T. Tokoroyama, *Tetrahedron Lett.* **1988**, *29*, 5965–5968.
[32] Method: C. Moussebois, J. Dale, *J. Chem. Soc. [C]* **1966**, 260–264.
[33] J. H. Babler, B. J. Invergo, S. J. Sarussi, *J. Org. Chem.* **1980**, *45*, 4241–4243.
[34] D. L. J. Clive, G. Chittattu, N. J. Curtis, S. M. Menchen, *J. Chem. Soc., Chem. Commun.* **1978**, 770–771.
[35] A. Martinez, A. C. Villalobos, M. O. Ruiz, *Synthesis* **1988**, 58–60.
[36] L. M. Shorr, *J. Am. Chem. Soc.* **1954**, *76*, 1390–1391.

[96160]