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Lewis Acid Induced Alkoxyalkylation of Allylsilanes with Acetals (the Sakurai Reaction): Regio- and Stereo-chemical Aspects

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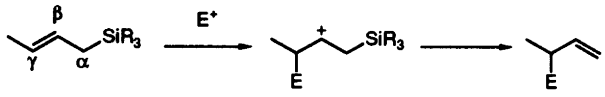
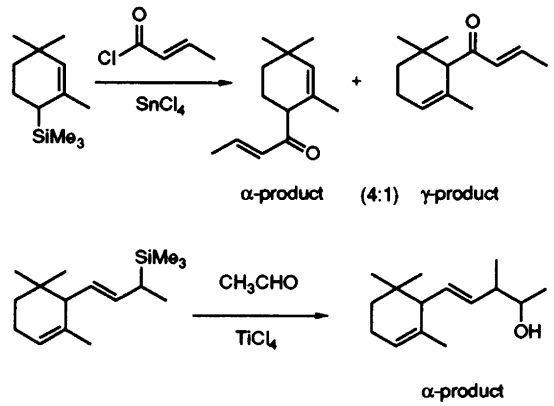
The electrophile generated from 1,1-diethoxyethane and TMSOTf reacts with allylic silanes **1a,b** to give the expected γ-substitution products. However, when the γ-position is sterically hindered as in **1c** substitution occurs at the α-position, presumably due to prior protodesilylation followed by electrophilic alkylation of the resulting olefin. This protodesilylation pathway may also explain similar results reported by other groups.

Allylic silanes have become an increasingly important class of compound in organic synthesis and it is well known that allylsilanes react with electrophiles in the presence of Lewis acids by selective attack at the γ-carbon to give an overall allylic rearrangement (Scheme 1).[1–4]



Scheme 1.

To our knowledge there are only two examples in the literature where the products are derived from an attack of the electrophile at the α-carbon of the allylsilane and so far no mechanistic explanation has been given for the formation of these α-products (Scheme 2).[5,6] We



Scheme 2.

now present a new example of α-substitution together with evidence consistent with a mechanism involving protodesilylation of the allylsilane prior to attack of the electrophile.

Table 1 shows the results of the Lewis acid catalyzed reactions of the allylsilanes **1a–c** and the olefin **2** with 1,1-diethoxyethane. The unhindered allylsilanes **1a** and **1b** react with 1,1-diethoxyethane in the presence of a catalytic amount of trimethylsilyl triflate (TMSOTf) to give only the expected γ-products **3a** and **3b**, respectively, (Scheme 4). Both compounds **3a** and **3b** were obtained as 1:1 diastereomeric mixtures.[7] The more substituted allylsilane **1c**, on the other hand, gave mainly the α-compounds **4/5** (ratio 2.3:1 determined by ^{1}H NMR spectroscopy). Since **4/5** could not be separated chromatographically the TBDMS protecting group was removed to give **8/9** which were separated on silica gel. The structures of **8** and **9** were then determined from their DEPT, HETCOR and PECOSY spectra. Owing to severely overlapping signals the coupling constants were measured from the PECOSY spectra. The use of other Lewis acids such as $SnCl_4$, BF_3–Et_2O, $AlCl_3$ and Et_2AlCl together with compound **1c** and 1,1-diethoxyethane

Table 1. Lewis acid catalyzed reaction between allylsilanes and 1,1-diethoxyethane.[a]

Olefin	Lewis acid	Product yield (%)	Ratio (**3**:**4**+**5**)
1a	TMSOTf[b]	84	>95:5[d]
1b	TMSOTf[b]	79	>95:5[d]
1c	TMSOTf[b]	90	15:75
1c	$TiCl_4$[c]	64	>95:5[d]
2	TMSOTf[c]	80	<5:95[d]

[a] All reactions were performed in CH_2Cl_2 (0.3 M) at −78 °C. [b] 0.1 equiv. [c] 1.0 equiv. [d] The minor component could not be detected.

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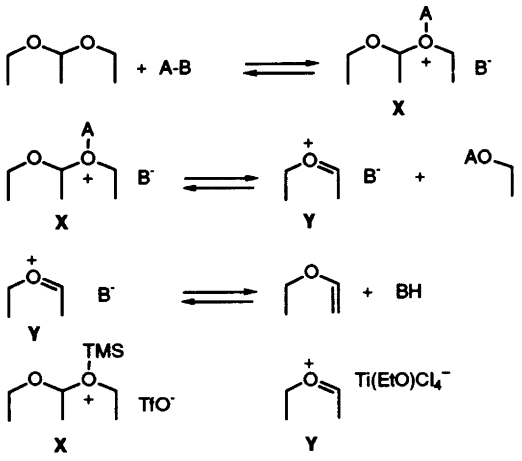
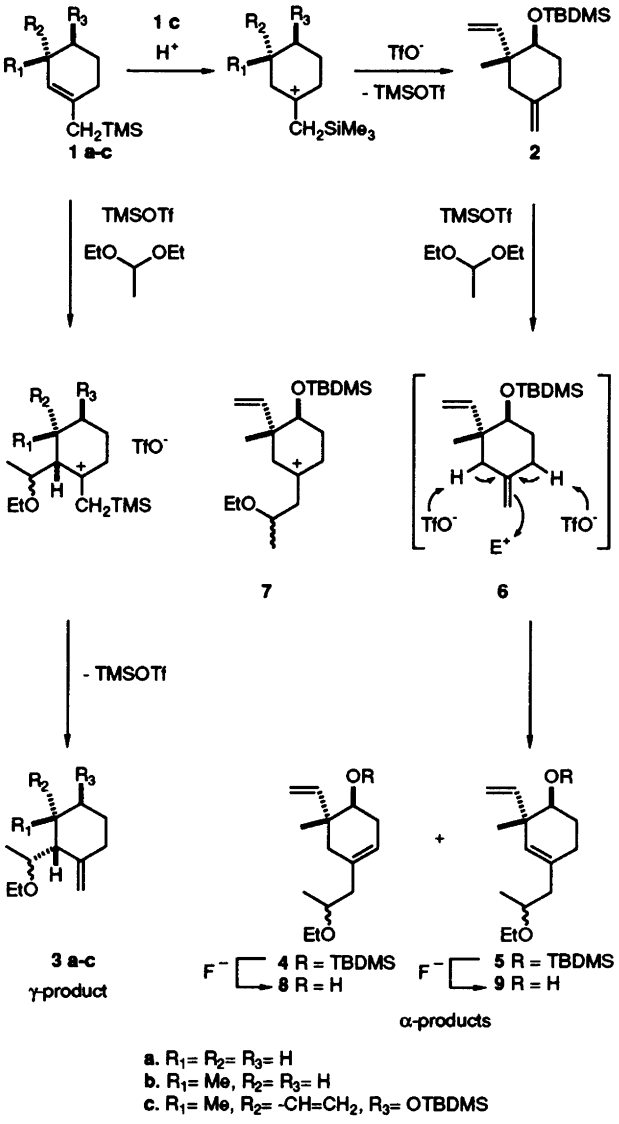
gave mixtures of **3c** and **4/5** along with unidentified by-products.

Two pathways could lead to α-products: (1) 1,3-trimethylsilyl migration followed by γ-attack of the electrophile or (2) protodesilylation followed by electrophilic attack at the less substituted olefinic position. Allylsilanes are known to be rather stable towards 1,3-allylic rearrangement undergoing this reaction only at higher temperatures (275 °C)[8] or in the presence of fluoride ions.[9] Clearly the 1,3-migration pathway is very unlikely under our reaction conditions (−78 °C, catalytic TMSOTf). In the second alternative only a catalytic amount of protons is required and may be unintentionally introduced together with the reagents or the glassware (e.g., the surface silanol groups may provide protons). Protons may also become available via the reaction of the acetal with the Lewis acid A–B as shown in Scheme 3, step 3. To test this idea the proposed intermediate **2** was subjected to the appropriate reaction conditions (1,1-diethoxyethane, TMSOTf, −78 °C). Indeed, in this reaction **2** produced the same mixture of the olefins **4/5** (80% yield) as did **1c**.



Scheme 3.

As judged from the literature the major electrophilic species formed from the acetal and TMSOTf is the complex **X** (Scheme 3).[10] The proton obviously competes successfully with the much larger electrophile **X** for attack at the hindered γ-position of allylsilane **1c** to give the carbocation intermediate, which subsequently loses the TMS group to give **2**. This compound then reacts with **X** to give the observed products in a reaction which is probably concerted with respect to the electrophilic attack and the loss of the respective protons (**6**, Scheme 4). If the reaction were stepwise, giving carbocation **7** as an intermediate, one would expect also the olefinic isomer(s) having an *exo* double bond to be formed, which is not the case. This protodesilylation–alkylation route may explain the results reported by Fleming *et al.*[5] and by Taddei *et al.*[6] (Scheme 2). The use of the stronger Lewis acid $TiCl_4$ together with the acetal generates the more reactive



Scheme 4.

electrophile **Y** (Scheme 3).[10, 11] This electrophile competes successfully with the proton and this time even the crowded silane **1c** gave **3c** exclusively. The relative configuration of **3c** was determined from the NOESY spectrum (cross peaks as indicated in Fig. 1).

Molecular-mechanics calculations [MM2(91)] indicate that the two obvious half-chair forms of **1c** have rather

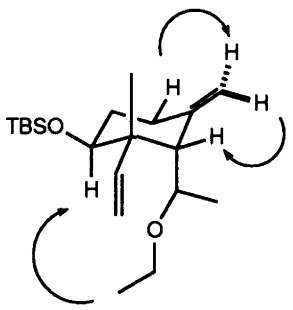
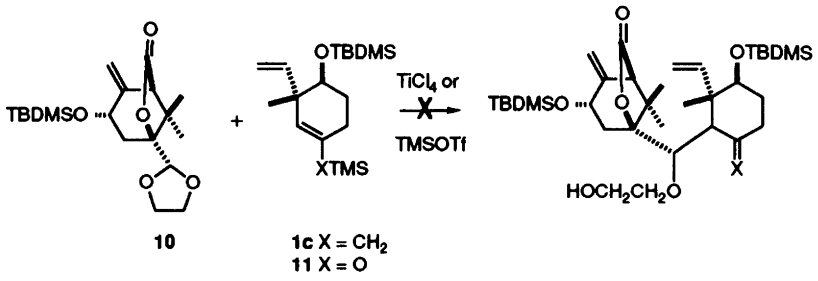


Fig. 1.



Scheme 5.

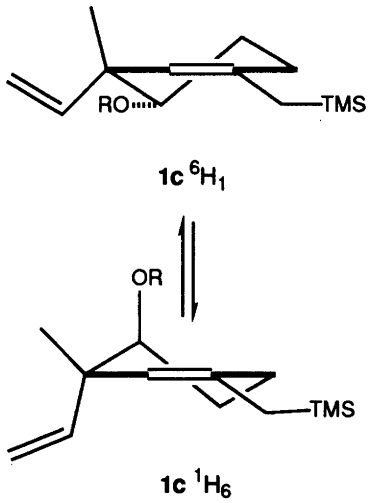


Fig. 2.

similar steric energies and thus may be almost equally populated at equilibrium (Fig. 2). However, conformer **1c** $^1H_6$ having an axial C–O bond seems very hindered from the β-face which gives the electrophile the option of attacking only conformer **1c** $^6H_1$ according to the Fürst–Plattner rule.

We reported earlier that the taxol A-ring derivative **10** was unreactive towards the silyl enol ether **11** under Lewis acid catalysis.[12] Not surprisingly the combination of allylsilane **1c** and **10** fail to give the desired taxane A–C system in the presence of $TiCl_4$ or TMSOTf (Scheme 5).

Experimental

All liquid chromatography separations were performed using Merck SiO_2 60 (0.040–0.063 mm) silica gel. TLC analyses were done on Merck SiO_2 60 F_{254} precoated aluminum sheets and the spots were visualized with UV light and by charring with 5% molybdophosphoric acid in ethanol. ^{1}H NMR spectra were recorded at 23 °C with a Varian XL-300 spectrometer at 299.94 MHz using $CDCl_3$ as the solvent and $CHCl_3$ as the internal standard (δ 7.26 ppm as compared with Me_4Si). Mass spectra were recorded on a Finnigan 4021 spectrometer and a Jeol JMS-SX 102 for the high resolution mass spectra (HRMS). Magnesium sulfate was used as the drying reagent for organic extracts. Dichloromethane was distilled from CaH_2. TMSOTf was distilled and stored under argon. 1,1-Diethoxyethane was distilled before use. The Lewis acids were transferred to the reaction flask with a dry syringe and with the needle inserted into a dry, argon filled glass tube sealed with a rubber septum at both ends. The molecular mechanics calculations were performed using the MacMIMIC-MM2(91) computer program commercially available from Instar Software, Ideon Research Park, S-223 70 Lund, Sweden. In the calculations the allylic trimethylsilyl group was approximated by a Bu′-group owing to lack of parameters.

3-Methyl-1-trimethylsilylmethylcyclohexene (**1b**). $Ni(acac)_2$ (0.53 g, 1.63 mmol) and $TMSCH_2MgCl$ (58 ml of a 1.4 M solution in diethyl ether, 81.5 mmol) were added to a solution of 3-methyl-1-trimethylsilyloxycyclohexene[13] (3.0 g, 16.3 mmol) in diethyl ether (40 ml).[14] The mixture was refluxed for 16 h, cooled and diluted with diethyl ether. The organic solution was washed successively with 2.0 M hydrochloric acid and saturated sodium hydrogencarbonate. The organic phase was dried and concentrated under reduced pressure. The crude product was distilled at 60–65 °C (4 mmHg) to give **1b** (2.73 g, 92%). ^{1}H NMR: δ 5.06 (1 H, s, 2-H), 2.04–2.21 (1 H, m, 3-H), 1.40–1.90 (6 H, m), 1.39 [2 H, s, $CH_2Si(CH_3)_3$], 0.93 (3 H, d, *J* 9.3 Hz, CH_3), 0.00 [9 H, s, $Si(CH_3)_3$]. HRMS (EI) Found: 182.1489. Calc. for $C_{11}H_{22}Si$: 182.1485.

t-*4*-(tert-*Butyldimethylsilyloxy*)-*3*-*methyl*-*1*-*trimethylsilylmethyl*-r-*3*-*vinylcyclohexene* (**1c**). Compound **1c** was prepared from $Ni(acac)_2$ (0.39 g, 1.2 mmol) and $TMSCH_2MgCl$ (42.8 ml of a 1.4 M solution in diethyl ether, 60.0 mmol) and *t*-4-(*tert*-butyldimethylsilyl)oxy-3-methyl-1-(trimethylsilyl)oxy-*r*-3-vinylcyclohexene[12] (4.1 g, 12.0 mmol) in diethyl ether (40 ml)[14] as described for compound **1b**. Flash chromatography (heptane–EtOAc 10:1) of the crude product gave **1c** (3.8 g, 94%). ^{1}H NMR: δ 5.76–5.85 (1 H, m, vinyl), 4.98 (1 H, dd, *J* 1.8, 6.5 Hz, vinyl), 4.93 (1 H, m, vinyl), 4.83 (1 H, s, 2-H), 3.58 (1 H, dd, *J* 3.7, 7.4 Hz, 4-H), 1.81–1.94 (1 H, m, 6-H), 1.96–2.08 (1 H, m, 6-H), 1.59–1.70 (2 H, m, 5-H), 1.44 [2 H, dd, *J* 13.5 Hz, $CH_2Si(CH_3)_3$], 1.02 (3 H, s, CH_3), 0.88 [9 H, s, $SiC(CH_3)_3$], 0.03, 0.04 [6 H, 2 s, $Si(CH_3)_2$], 0.02 [9 H, s, $Si(CH_3)_3$]. Anal. $C_{19}H_{38}OSi_2$: C, H. EIMS (70 eV): *m/z* 338 (*M*).

t-*2-(*tert-*Butyldimethylsilyloxy)-1-methyl-5-methylene-*r-*1-vinylcyclohexane* (**2**). A solution of methylenetriphenylphosphorane in THF was prepared as follows: BuLi (0.89 ml of a 2.1 M solution in hexane, 1.86 mmol) was added dropwise to a suspension of methyltriphenylphosphonium bromide (0.67 g, 1.86 mmol) in THF (1 ml). The reaction mixture was stirred for 60 min before use.

A solution of methylenetriphenylphosphorane (≈0.37 mmol) was added to a solution of 4-(tert-butyldimethylsilyloxy)-3-methyl-3-vinylcyclohexanone[12] (100 mg, 0.37 mmol) in THF (1 ml). The reaction mixture was stirred for 15 min. Water (6.7 µl, 0.37 mmol) was added and the mixture was stirred for another 15 min.[15] A further portion of methylenetriphenylphosphorane was then added. This cycle was repeated five times. Diethyl ether was added and the suspension was washed successively with 1.0 M hydrochloric acid, saturated sodium hydrogencarbonate and brine. The organic phase was dried and concentrated. Flash chromatography (heptane–EtOAc 10:1) of the crude product gave **2** (90 mg, 91%). ^{1}H NMR: δ 5.88 (1 H, m, vinyl), 4.95–5.02 (2 H, m, vinyl), 4.60, 4.71 (2 H, 2 m, exocyclic methylene), 3.51 (1 H, dd, *J* 3.4, 7.5 Hz, 2-H), 2.28–2.38 (1 H, m, 4-H), 2.10 (2 H, 2 d, *J* 13.5 Hz, 6-H), 1.97–2.07 (1 H, m, 4-H), 1.65–1.75 (1 H, m, 3-H), 1.49–1.60 (1 H, m, 3-H), 0.95 (3 H, s, CH_3), 0.89 [9 H, s, $C(CH_3)_3$], 0.04 [6 H, s, $Si(CH_3)_2$]. HRMS (EI) Found: 266.2062. Calc. for $C_{16}H_{30}OSi$: 266.2058.

1-(1-Ethoxyethyl)-2-methylenecyclohexane (**3a**). TMSOTf (33 µl, 0.18 mmol) was added to a solution of compound **1a** (0.30 g, 1.78 mmol) and 1,1-diethoxyethane (0.51 ml, 3.57 mmol) in dichloromethane (15 ml) at −75 °C under argon. The mixture was stirred at −75 °C for 180 min. Saturated sodium hydrogencarbonate (2 ml) was then added, followed by diethyl ether. The organic phase was dried and concentrated. Flash chromatography (dichloromethane) of the crude product gave **3a** (0.25 g, 84%) as a mixture of diastereomers (1:1). ^{1}H NMR for the more polar isomer: δ 4.57, 4.73 (2 H, 2 s, exocyclic methylene), 3.52–3.70 (2 H, m, OCH_2CH_3), 3.36–3.44 (1 H, m, C*H*OEt), 1.90–2.30 (3 H, m, 2-H, 6-H), 1.20–1.75 (6 H, m, 3-H, 4-H, 5-H), 1.17 (3 H, t, *J* 7.0 Hz, CH_3), 1.16 (3 H, d, *J* 6.1 Hz, CH_3). CIMS *m/z* 186 ($M + NH_4$). HRMS (CI, CH_4) Found: 167.1434. Calc. for $C_{11}H_{19}O$ ($M - 1$): 167.1431. ^{1}H NMR for the less polar isomer: δ 4.66, 4.62 (2 H, 2 m, exocyclic methylene), 3.51–3.73 (2 H, m, OCH_2CH_3), 3.29–3.44 (1 H, m, C*H*OEt), 1.90–2.18 (3 H, m, 2-H, 6-H), 1.20–1.77 (6 H, m, 3-H, 4-H, 5-H), 1.19 (3 H, t, *J* 10.3 Hz, CH_3), 1.07 (3 H, d, *J* 9.2 Hz, CH_3). CIMS *m/z* 186 ($M + NH_4$). HRMS (CI, CH_4) Found: 167.1437. Calc. for $C_{11}H_{19}O$ ($M - 1$): 167.1431.

2-(1-Ethoxyethyl)-1-methyl-3-methylenecyclohexane (**3b**). Compound **1b** (0.39 g, 2.11 mmol) was treated with 1,1-diethoxyethane (0.60 ml, 4.22 mmol) and TMSOTf (38 µl, 0.21 mmol) as described for **1a**. Flash chromatography (dichloromethane) of the crude product gave **3b** (0.30 g, 79%) as a mixture of diastereomers (1:1). ^{1}H NMR for the more polar isomer: δ 4.79, 4.63 (2 H, 2 m, exocyclic methylene), 3.45–3.70 (2 H, m, OCH_2CH_3), 3.26–3.42 (1 H, m, C*H*OEt), 1.45–2.25 (7 H, m), 1.18 (3 H, d, *J* 9.2 Hz, CH_3), 1.13 (3 H, t, *J* 10.3 Hz, CH_3), 0.95 (3 H, d, *J* 10.1 Hz, CH_3). ^{1}H NMR for the less polar isomer: δ 4.74, 4.63 (2 H, 2 m, exocyclic methylene), 3.53–3.74 (2 H, m, OCH_2CH_3), 3.30–3.45 (1 H, m, C*H*OEt), 2.28–2.45 (1 H, m, 2-H), 2.02–2.15 (1 H, 2 m, 4-H), 1.54–1.96 (6 H, m), 1.20 (3 H, t, *J* 10.3 Hz, CH_3), 1.02 (3 H, d, *J* 9.0 Hz, CH_3), 0.92 (3 H, d, *J* 10.6 Hz, CH_3). CIMS *m/z* 200 ($M + NH_3$). HRMS (CI, CH_4) Found: 181.1620. Calc. for $C_{12}H_{21}O$ ($M - 1$): 181.1587.

t-*6-(*tert-*Butyldimethylsilyloxy)-*c-*2-(1-ethoxyethyl)-1-methyl-3-methylene-*r-*1-vinylcyclohexane* (**3c**). $TiCl_4$ (0.9 ml of a 1.0 M solution in dichloromethane, 0.9 mmol) was added dropwise over 30 min to a solution of compound **1c** (0.10 g, 0.29 mmol) and 1,1-diethoxyethane (0.13 ml, 0.90 mmol) in dichloromethane (2 ml) at −75 °C under argon. The reaction mixture was stirred at −75 °C for 5 min. Saturated sodium hydrogencarbonate (0.5 ml) was added, followed by diethyl ether. The organic phase was dried and concentrated. Flash chromatography (heptane–EtOAc 100:1) gave **3c** (65 mg, 64%). ^{1}H NMR: δ 5.89 (1 H, m, vinyl), 4.92–5.02 (2 H, m, vinyl), 4.66, 4.83 (2 H, 2 m, exocyclic methylene), 4.18–4.28 (1 H, m, –O–C*H*<), 3.47–3.61 (2 H, m, –O–C*H*<), 3.27–3.38 (1 H, m, –O–C*H*<), 2.16–2.28 (1 H, m, 4-H), 2.10 (1 H, d, *J* 7.9 Hz, 2-H), 1.90–1.98 (1 H, m, 4-H), 1.71–1.83 (1 H, m, 5-H), 1.55–1.64 (1 H, m, 5-H), 1.18 (3 H, s, CH_3), 1.16 (3 H, t, *J* 6.9 Hz, CH_3), 1.01 (3 H, d, *J* 6.0 Hz, CH_3), 0.92 [9 H, s, $C(CH_3)_3$], 0.09, 0.06 [6 H, 2 s, $Si(CH_3)_2$]. HRMS (EI) Found: 338.2648. Calc. for $C_{20}H_{38}O_2Si$: 338.2641.

Reaction of **1c** *with 1,1-diethoxyethane and TMSOTf to give compounds* **3c** *and* **4/5** (**8/9**). Compound **1c** (2.0 g, 5.95 mmol) was treated with 1,1-diethoxyethane (1.69 ml, 11.9 mmol) and TMSOTf (105 µl, 0.580 mmol) as described for **1a**. Flash chromatography (heptane–EtOAc 20:1) of the crude product gave **3c** (0.30 g, 15%) together with a mixture of *t*-4-(*tert*-butyldimethylsilyloxy)-1-(2-ethoxypropyl)-5-methyl-*r*-5-vinylcyclohexene and *t*-4-(*tert*-butyldimethylsilyloxy)-1-(2-ethoxypropyl)-3-methyl-*r*-3-vinylcyclohexene (1.51 g, 75%, isomer ratio 2.3:1, respectively, as determined by ^{1}H NMR spectroscopy; the integrals for the signals of H-5 and H-3 were compared). All attempts to separate the isomers by TLC or column chromatography failed. The mixture of silyl ethers was instead hydrolyzed to give the corresponding alcohols (**8/9**) for characterization.

$Bu_4NF{-}3H_2O$ (1.9 g, 6.0 mmol) was added to a solution of compounds **4/5** (1.45 g, 4.28 mmol) in THF (5 ml). The reaction mixture was stirred overnight and diluted with diethyl ether. The solution was washed with saturated sodium chloride, dried and concentrated. Flash

chromatography (heptane–EtOAc 5:1) gave the expected alcohols **8**/**9** (401 mg, 42% and 174 mg, 18% for the fast and slow moving compounds, respectively) together with some overlapping fractions. ^{1}H NMR for the fast moving 4-(2-ethoxypropyl)-*c*-6-methyl-6-vinylcyclohex-3-en-*r*-1-ol (**8**): δ 5.73–5.84 (1 H, m, vinyl), 5.29–5.34 (1 H, m, 3-H), 5.14 (1 H, dd, *J* 1.3, 4.7 Hz, vinyl), 5.09 (1 H, dd, *J* 1.3, 2.5 Hz, vinyl), 3.35–3.57 (3 H, m, –O–CH<), 3.58 (1 H, dd, *J* 5.2, 7.8 Hz, 1-H), 2.30–2.41 (1 H, 2 m, $J_{6a,6b}$ 17 Hz, $J_{6,1}$ 7.8 Hz, $J_{6,5}$ 4 Hz, 2-H), 2.19–2.28 (1 H, 2 m, $J_{1'a,1'b}$ 14 Hz, $J_{1',5}$ 3 Hz, 1'-H), 2.00–2.11 (1 H, 2 m, $J_{3a,3b}$ 17 Hz, $J_{3,5}$ 3 Hz, 5-H), 1.92–2.02 (1 H, m, $J_{6a,6b}$ 17 Hz, $J_{6,1}$ 5.2 Hz, 2-H), 1.94–1.99 (1 H, 2 m, $J_{1'a,1'b}$ 14 Hz, 1'-H), 1.82–1.91 (1 H, 2 m, $J_{3a,3b}$ 17 Hz, $J_{3,5}$ 2 Hz, 5-H), 1.70 (1 H, m, OH), 1.16 (3 H, t, *J* 6.0 Hz, CH_3), 1.09 (3 H, d, *J* 6.2 Hz, CH_3), 1.00 (3 H, s, CH_3). HRMS (EI) Found: 224.1777. Calc. for $C_{14}H_{24}O_2$: 224.1770.

^{1}H NMR for the slow moving 4-(2-ethoxypropyl)-*c*-2-methyl-2-vinylcyclohex-3-en-*r*-1-ol (**9**): δ 5.79 (1 H, m, vinyl), 5.02–5.12 (3 H, m, vinyl, 3-H), 3.63 (1 H, dd, $J_{1,6}$ 3.1, 8.7 Hz, 1-H), 3.35–3.59 (3 H, m, –O–CH<), 2.21–2.30 (1 H, m, $J_{1'a,1'b}$ 14 Hz, $J_{1',3}$ 2.5 Hz, 1'-H), 1.97–2.05 (1 H, m, $J_{1'a,1'b}$ 14 Hz, $J_{1',3}$ 2.5 Hz, 1'-H), 2.04–2.11 (2 H, m, $J_{5,3}$ 3 Hz, $J_{5,6a}$ 6 Hz, $J_{5,6b}$ 7 Hz, 5-H), 1.65–1.89 (2 H, m, $J_{6a,6b}$ 13 Hz, $J_{6a,5}$ 6 Hz, $J_{6b,5}$ 7 Hz, $J_{6,1}$ 3.1, 8.7 Hz, 6-H), 1.17 (3 H, t, *J* 6.9 Hz, CH_3), 1.12 (3 H, d, *J* 6.0 Hz, CH_3), 1.08 (3 H, s, CH_3). HRMS (EI) Found: 224.1800. Calc. for $C_{14}H_{24}O_2$: 224.1770.

Mixture of **4**/**5** *from olefin* **2**. TMSOTf (11 µl, 0.06 mmol) was added to a solution of compound **2** (16 mg, 0.060 mmol) and 1,1-diethoxyethane (17 µl, 0.12 mmol) in dichloromethane (0.5 ml) at −75 °C under argon. The mixture was stirred at −75 °C for 15 min. Then saturated sodium hydrogencarbonate (0.2 ml) was added, followed by diethyl ether. The organic phase was dried and concentrated. Flash chromatography (heptane–EtOAc 10:1) gave the mixture **4**/**5** (16 mg, 80%, isomer ratio 2.3:1, respectively) with ^{1}H NMR data as mentioned.

Acknowledgments. We thank the Swedish Natural Science Research Council for financial support.

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