Facile Generation of Alkenes and Dienes from Tosylates

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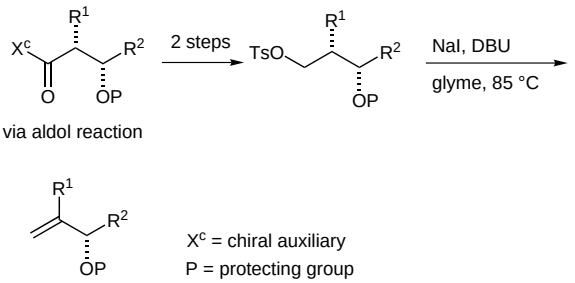
Abstract: Several aldol products resulting from Evans aldol reactions were converted to primary alcohols. After conversion to the corresponding tosylates, heating with NaI and DBU in dimethoxyethane (glyme) effected clean elimination to the terminal olefin. This simple one-pot procedure was applied to other tosylates and a tosylate derived from a homoallylic alcohol. The latter gave rise to a diene.

Key words: aldol reactions, alkenes, eliminations

Terminal alkenes are important functional groups in organic synthesis due to the great variety of addition reactions. In general, alkenes are prepared by elimination reactions, cross-coupling reactions, double bond formation (Julia, McMurry, Wittig), or repositioning reactions. A particular useful functionalization of alkenes is the hydroboration reaction that allows the introduction of a hydroxyl function or the use of the intermediate borane in subsequent Suzuki cross-coupling reactions. In the context of asymmetric synthesis the hydroboration reaction is also of interest in that the use of secondary allylic alcohol derivatives $R^1CH(OX)C(R^2)=CH_2$ proceeds with good stereocontrol.[1] However, the synthesis of such substrates in optically pure form is in general not easy. Possibilities include the Sharpless kinetic resolution,[2] enantioselective addition reactions to 2-substituted propenal derivatives,[3] or a synthesis from the chiral pool.[4] In this paper we demonstrate that protected chiral alkenols of type **18**–**22** and **24** and the alkene **23** can be obtained by elimination from the corresponding primary tosylates in a one-step procedure with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in the presence of sodium iodide. While the conversion of a tosylate to the corresponding alkene is a common strategy, the elimination is usually done in two steps.[5] Thus, the tosylates are generally converted first to the iodide and then subjected to elimination, occasionally in a one-pot reaction.[6] However, since iodides are somewhat unstable (sensitive to light and to solvolysis), the yield for the two-step procedure is usually not very high. Moreover, long reaction times are necessary. The present one-pot method works well for terminal alkenes, exocyclic enol ethers and 1,3-dienes, and results in very clean products (Scheme 1).

A range of tosylates was prepared from the corresponding alcohols by standard procedures.[7] The primary alcohol precursors of the tosylates **6**, **7**, and **8** in turn were ultimately obtained by Evans aldol reactions[8,9] followed by protection of the secondary hydroxyl function and reductive removal[10] of the chiral auxiliary. A typical sequence for the synthesis of the tosylate **6** is illustrated in Scheme 2. Thus, aldol reaction of the propionyloxazolidinone **1** with 3-[(*tert*-butyldimethylsilyl)oxy]propanal[11] (**2**) in the presence of sparteine (2.5 equiv) according to a procedure of Crimmins[12] gave the Evans *syn*-product **3** in good yield. A subsequent silylation [0.1 M in CH_2Cl_2, 2.5 equiv of 2,6-lutidine, 1.3 equiv of *tert*-butyldimethylsilyl triflate (TBDMSOTf), 23 °C, 12 h] of the secondary hydroxyl function led to compound **4**. This was followed by reductive removal of the chiral auxiliary using sodium borohydride in aqueous THF [0.11 M in THF, 0 °C, add 4 equiv of $NaBH_4$ (2.3 M in H_2O), then 23 °C, 2 h].[10] The final tosylation of the primary alcohol **5** furnished the tosylate **6** (0.36 M in pyridine, add 2.2 equiv of TosCl at 0 °C, 23 °C, 2 h) in 95%. The alcohol precursors of tosylates **7** and **8** are known compounds[13] and were also prepared by the aldol sequence.



Scheme 1 Conversion of primary tosylates, generated from aldol products to terminal alkenes (2-methylprop-2-enyl ether) (glyme = 1,2-dimethoxyethane)

The alcohol precursor of the tosylate[14] **9** is a known compound. The tosylates **10**[15] and **11**[16] were prepared according to the literature.

Finally, the homoallylic alcohol **16** was prepared with the question in mind whether the elimination can be extended to the formation of 1,3-dienes (Scheme 3). Accordingly, an Evans aldol reaction of aldehyde[17] **13** with the butenoyloxazolidinone[18] **12** was used to prepare the hydroxy compound **14**.[19] As described before, protection of the hydroxyl function as its *tert*-butyldimethylsilyl ether **15** followed by reductive removal of the oxazolidinone provided the primary alcohol **16**. The alcohol **16** was then converted to the tosylate **17**.

The elimination of the tosylate was initially tried with several bases, such as *t*-BuOK in THF or DBU in CH_2Cl_2.

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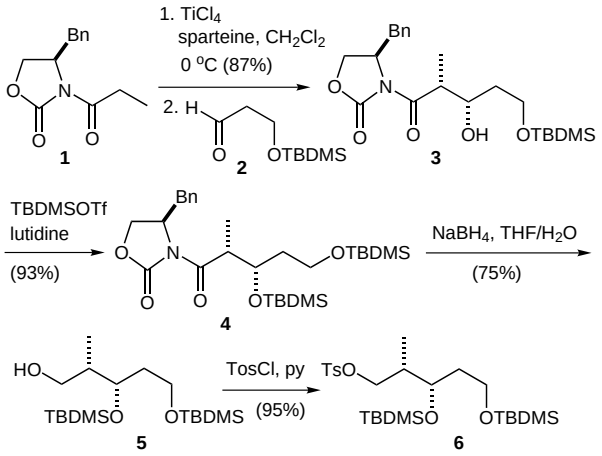
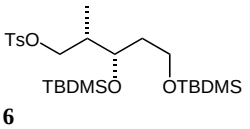
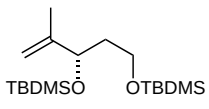
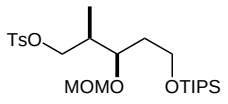
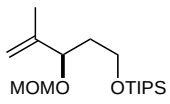
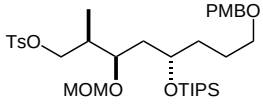
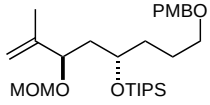
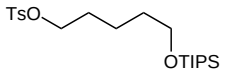
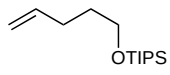
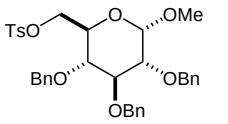
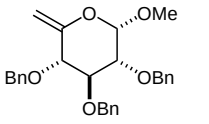
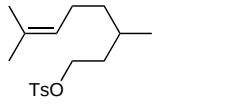
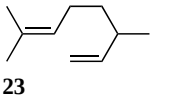
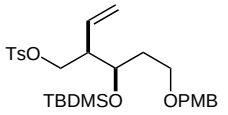
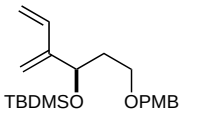


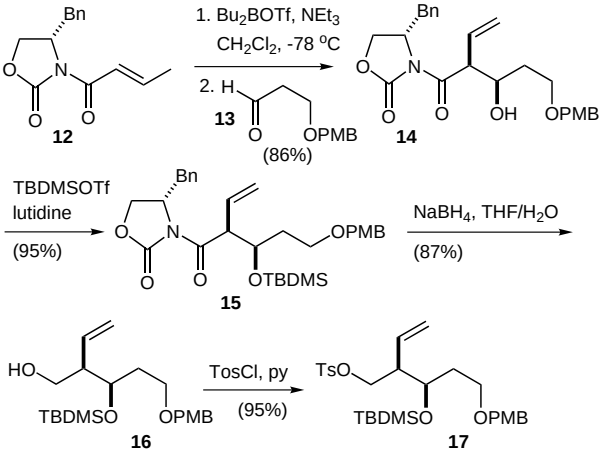
Scheme 2 Synthesis of the tosylate **6** by a *syn*-selective Evans aldol reaction

While elimination could be observed, the yields were low and the reactions were not very clean and high-yielding. However, performing the elimination in the presence of NaI in dimethoxyethane effected an efficient conversion to the desired alkenes (Table 1). Extractive workup gave the unsaturated products with high purity and yield. The alkenes **18**, **19**, and **20** have been used in diastereoselective hydroboration reactions.[13,20] Alkene **21** found use in hydroboration and transmetallation reactions.[21] The exocyclic enol ether[22] **22** has been employed in a Ferrier rearrangement reaction.[23] The somewhat lower yield of citronellene[24] (**23**) is attributed to the high volatility of the product during work-up. Compound **17** is an example where a homoallylic alcohol is transformed to a 1,3-diene. While compounds such as **24** are available by homoallenylboration,[25] the present route offers a practical alternative. Most likely, the reaction proceeds through an intermediate iodide. Indicative of this is the fact that usually within 45 minutes disappearance of the starting material is observed while a new intermediate – the putative iodide – arises.

Table 1 Elimination of Various Tosylates to the Corresponding Alkenes or Dienes, Respectiveley[a]

Entry	Tosylate	Product	Yield (%)
1	 **6**	 **18**	95
2	 **7**	 **19**	98
3	 **8**	 **20**	99
4	 **9**	 **21**	95
5	 **10**	 **22**	95
6	 **11**	 **23**	87
7	 **17**	 **24**	98

[a] TBDMS = *tert*-butyldimethylsilyl, MOM = methoxymethyl, TIPS = triisopropylsilyl, PMB = *p*-methoxybenzyl, Bn = benzyl.



Scheme 3 Synthesis of the tosylate **17** by an Evans aldol reaction of the crotonic acid derivative **12** with aldehyde **13** (PMB = *p*-methoxybenzyl)

In summary, we could demonstrate the facile conversion of Evans aldol products to chiral terminal alkenes containing a secondary alcohol function. These elimination conditions were also used to produce some other terminal alkenes and the diene **24**. Key to the sequence is the elimination reaction of the primary tosylate with the reagent combination NaI/DBU in the solvent dimethoxyethane.

^{1}H and ^{13}C NMR: Bruker Avance 400, spectra were recorded in $CDCl_3$; chemical shifts are calibrated to the residual proton and carbon resonance of the solvent: $CDCl_3$ (δ_H 7.25, δ_C 77.00). Melting points: Büchi Melting Point B-540, uncorrected. Polarimeter: Jasco Polarimeter P-1020. IR: Jasco FT/IR-430. EI-MS: Finnigan Triple-Stage-Quadrupol (TSQ-70). HRMS (FT-ICR): Bruker Daltonic APEX 2 with electron spray ionization (ESI). Flash chromatography: J. T. Baker silica gel 43–60 μm. TLC: Machery-Nagel Poly-

gram Sil G/UV$_{254}$. Solvents were distilled prior to use; petroleum ether with a boiling range of 40–60 °C was used.

The alcohol **6** was prepared as described in Scheme 2[10–12] and the alcohols **7** and **8** have been reported by us previously.[13] The general procedure followed for the preparation of tosylates listed in Table 1 is the same as the one given below for **9**.

5-[(Triisopropylsilyl)oxy]pentyl 4-Methylbenzenesulfonate (9); Typical Procedure

A solution of 5-[(triisopropylsilyl)oxy]pentan-1-ol[14] (0.42 g, 1.61 mmol) in pyridine (5 mL) was treated with *p*-toluenesulfonyl chloride (0.37 g, 1.94 mmol) at 0 °C. The resulting mixture was stirred for 2 h at r.t., followed by addition of H_2O (40 mL) and Et_2O (60 mL). After separation of the layers, the Et_2O layer was washed with 1 N HCl (20 mL), sat. aq $NaHCO_3$ solution (20 mL), and brine. The organic layer was dried ($MgSO_4$), filtered, and concentrated. Flash chromatography (petroleum ether–EtOAc, 9:1) of the residue provided the tosylate **9** as a colorless oil (0.55 g, 82%); R_f 0.50 (petroleum ether–EtOAc, 9:1).

IR (film): 2942, 2866, 1462, 1361, 1189, 1177 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.3 Hz, 2 H), 7.33 (d, *J* = 8.1 Hz, 2 H), 4.01 (t, *J* = 6.6 Hz, 2 H), 3.61 (t, *J* = 6.3 Hz, 2 H), 2.43 (s, 3 H), 1.73–1.58 (m, 2 H), 1.54–1.41 (m, 2 H), 1.40–1.29 (m, 2 H), 1.12–0.90 (m, 21 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.56, 133.24, 129.74, 127.82, 70.56, 62.90, 32.15, 28.62, 21.77, 21.55, 17.95, 17.65, 11.92.

MS (EI): *m*/*z* (%) = 285 (100), 257 (6), 243 (3), 155 (3), 115 (3), 91 (7).

HRMS (FT-ICR-ES): *m*/*z* calcd for $C_{21}H_{38}O_4SSiNa$ [M + Na]$^+$, 437.21523; found, 437.21526.

(4*S*)-4-Benzyl-3-((2*S*)-2-{(1*R*)-1-hydroxy-3-[(4-methoxybenzyl)oxy]propyl}but-3-enoyl)-1,3-oxazolidin-2-one (14)

To a stirred solution of imide **12** (1.0 g, 4.1 mmol) in CH_2Cl_2 (15 mL) was added dibutylboron trifluoromethansulfonate (4.5 mL, 1 M in CH_2Cl_2, 4.5 mmol) at –78 °C. After stirring for 5 min, the mixture was treated with Et_3N (0.8 mL, 5.7 mmol), then kept for 1 h at –78 °C, and 20 min at 0 °C, and recooled to –78 °C. At this point, a solution of the aldehyde **13** (1.18 g, 6.1 mmol) in CH_2Cl_2 (5 mL) was added dropwise. The reaction was kept for 1 h at –78 °C and 1 h at 0 °C, before it was quenched by addition of pH 7 buffer (5 mL) followed by MeOH (18 mL). After 5 min, 30% H_2O_2 (5 mL) was added and the mixture stirred for 1 h at 0 °C. Most of the solvent was removed in vacuo and the aqueous remainder extracted with EtOAc (3 × 30 mL). The organic phase was washed with 1 N HCl (20 mL), 5% aq $NaHCO_3$ (20 mL), brine (20 mL), dried (Na_2SO_4), filtered, and concentrated. The crude product was purified by flash chromatography (30% EtOAc in petroleum ether) to give **14** (1.54 g, 86%) as an oil; R_f 0.15 (petroleum ether–EtOAc, 7:3); $[\alpha]_D^{24}$ +23.3 (*c* = 1.57, CH_2Cl_2).

IR (film): 3503, 2930, 2862, 1780, 1694, 1612, 1513, 1386, 1360 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.11 (m, 7 H), 6.87 (d, *J* = 8.6 Hz), 6.15–5.97 (m, 1 H), 5.39 (dd, *J* = 12.9, 3.0 Hz, 2 H), 4.76–4.64 (m, 1 H), 4.56 (dd, *J* = 8.8, 4.3 Hz, 1 H), 4.44 (s, 2 H), 4.29–4.20 (m, 1 H), 4.19–4.09 (m 2 H), 3.80 (s, 3 H), 3.72–3.58 (m, 2 H), 3.42 (br s, 1 H), 3.26 (dd, *J* = 13.4, 2.8 Hz, 1 H), 2.76 (dd, *J* = 13.4, 9.6 Hz, 1 H), 1.94–1.82 (m, 1 H), 1.80–1.68 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.46, 159.18, 152.93, 135.04, 131.65, 130.12, 129.43, 129.33, 128.92, 127.35, 121.03, 113.03, 72.86, 70.54, 67.74, 65.95. 55.25, 52.53, 37.55, 33.85.

MS (EI): *m*/*z* (%) = 351 (3), 285 (1), 259 (10), 244 (8), 216 (10), 168 (10), 137 (19), 121 (100), 91 (29).

HRMS (FT-ICR-ES): *m*/*z* calcd for $C_{25}H_{29}NO_6Na$ [M + Na]$^+$, 462.18871; found, 462.18816.

(4*S*)-4-Benzyl-3-((2*S*)-2-{(1*R*)-1-{[*tert*-butyl(dimethyl)silyl]-oxy}-3-[(4-methoxybenzyl)oxy] propyl}but-3-enoyl)-1,3-oxazolidin-2-one (15)

To a solution of **14** (0.5 g, 1.15 mmol) and 2,6-lutidine (0.31 g, 2.87 mmol) in CH_2Cl_2 (10 mL) was added *tert*-butylsilyltrifluoromethane sulfonate (0.394 g, 0.34 mL, 1.49 mmol) and the solution was stirred overnight. The mixture was treated with H_2O (20 mL), stirred for 30 min, and then the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The organic phase was washed with 1 N HCl (20 mL), sat. aq $NaHCO_3$ (20 mL), brine (20 mL), dried (Na_2SO_4), filtered, and concentrated. Flash chromatography of the residue (10% EtOAc in petroleum ether) yielded 605 mg (95%) of the TBS-ether **15** as a gum; R_f 0.42 (petroleum ether–EtOAc, 4:1); $[\alpha]_D^{24}$ +42.3 (*c* = 0.52, CH_2Cl_2).

IR (film): 2954, 2930, 2856, 1782, 1696, 1612, 1513, 1383, 1353 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.24 (m, 5 H), 7.21 (d, *J* = 7.8 Hz, 2 H), 6.87 (d, *J* = 8.6 Hz, 2 H), 6.10–5.94 (m, 1 H), 5.34–5.22 (m, 2 H), 4.67–4.51 (m, 2 H), 4.43 (d, *J* = 11.6 Hz, 1 H), 4.39 (d, *J* = 11.6 Hz, 1 H), 4.25 (dd, *J* = 11.4, 5.1 Hz, 1 H), 4.07 (dd, *J* = 9.1, 2.0 Hz, 1 H), 3.89 (t, *J* = 8.3 Hz, 1 H), 3.80 (s, 3 H), 3.67–3.56 (m, 1 H), 3.55–3.43 (m, 1 H), 3.26 (dd, *J* = 13.4, 2.8, 1 H), 2.73 (dd, *J* = 13.4, 9.6, 1 H), 1.93 (m, 2 H), 0.89 (s, 9 H), 0.05 (s, 3 H), 0.04 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 127.37, 159.04, 152.77, 135.35, 134.05, 130.65, 129.43, 129.22, 128.85, 127.23, 119.43, 113.64, 72.51, 71.07, 65.78, 65.69, 55.38, 55.22, 53.15, 37.49, 35.24, 25.77, 17.96, –4.49, –4.63.

MS (EI): *m*/*z* (%) = 359 (3), 309 (4), 302 (13), 251 (2), 234 (3), 211 (2), 173 (6), 137 (3), 121 (100), 91 (5).

HRMS (FT-ICR-ES): *m*/*z* calcd for $C_{31}H_{43}NO_6SiNa$ [M + Na]$^+$, 576.27519; found, 576.27557.

(2*R*)-2-((1*R*)-1-{[*tert*-Butyl(dimethyl)silyl]oxy}-3-[(4-methoxybenzyl)oxy]propyl)but-3-en-1-ol (16)

To a stirred solution of **15** (144 mg, 0.27 mmol) in THF (10 mL) was added a solution of $NaBH_4$ (51 mg, 1.3 mmol) in H_2O (2 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 5 min and then for 3 h at r.t. The reaction was quenched by addition of sat. aq NH_4Cl solution (5 mL) and the mixture stirred for 1 h. The mixture was extracted with EtOAc (2 × 20 mL), the combined organic layers were washed with sat. aq $NaHCO_3$ solution (10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (20% EtOAc in petroleum ether) to give 89 mg (87%) of alcohol **16** as a colorless oil; R_f 0.3 (petroleum ether–EtOAc, 4:1); $[\alpha]_D^{23}$ +9.1 (*c* = 0.9, CH_2Cl_2).

IR (film): 3450, 2954, 2930, 2857, 1613, 1513, 1250 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 8.6 Hz, 2 H), 6.88 (d, *J* = 8.5 Hz, 2 H), 5.79–5.64 (m, 1 H), 5.22–5.03 (m, 2 H), 4.40 (d, *J* = 11.6 Hz, 1 H), 4.34 (d, *J* = 11.6 Hz, 1 H), 4.05–3.94 (m, 1 H), 3.80 (s, 3 H), 3.78–3.69 (m, 1 H), 3.66–3.54 (m, 1 H), 3.46 (t, *J* = 6.3 Hz, 2 H), 2.48–2.35 (m, 1 H), 2.22 (s, 1 H), 1.88–1.70 (m, 2 H), 0.89 (s, 9 H), 0.09 (s, 3 H), 0.06 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.12, 135.46, 130.44, 129.22, 118.44, 113.71, 72.52, 70.78, 66.45, 63.43, 55.22, 51.19, 33.98, 25.79, 17.95, –4.62.

MS (EI): *m*/*z* (%) = 309 (5), 251 (1), 173 (11), 137 (9), 121 (100), 91 (6), 77 (8).

HRMS (FT-ICR-MS): *m*/*z* calcd for $C_{21}H_{36}O_4SiNa$ [M + Na]$^+$, 403.22751; found, 403.22770.

(2*R*)-2-((1*R*)-1-{[*tert*-Butyl(dimethyl)silyl]oxy}-3-[(4-methoxybenzyl)oxy]propyl)but-3-enyl 4-Methylbenzenesulfonate (17)

To a stirred solution of alcohol **16** (84 mg 0.22 mmol) in pyridine (1 mL) was added *p*-toluenesulfonyl chloride (84 mg, 0.44 mmol) at 0 °C. After stirring for 2 h at r.t., H_2O (10 mL) and Et_2O (10 mL) were added and the organic layer separated. The etheral layer was washed with 1 N HCl (10 mL), sat. aq $NaHCO_3$ solution (10 mL), and brine (15 mL). The organic layer was dried (Na_2SO_4), filtered, and concentrated. Filtration of the residue over a short pad of silica gel (10% EtOAc in petroleum ether) and evaporation of the solvent gave the pure tosylate **17** as a colorless oil (113 mg, 95%); R_f 0.48 (petroleum ether–EtOAc, 4:1); $[\alpha]_D^{23}$ –1.2 (*c* = 1.19, CH_2Cl_2).

IR (film): 2953, 2929, 2892, 1612, 1513, 1463, 1364, 1177 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.3 Hz, 2 H), 7.31 (d, *J* = 7.8 Hz, 2 H), 7.23 (d, *J* = 8.6 Hz, 2 H), 6.87 (d, *J* = 8.6 Hz, 2 H), 5.67–5.51 (m, 1 H), 5.14 (d, *J* = 11.4 Hz, 1 H), 5.05 (d, *J* = 17.2 Hz, 1 H), 4.40 (d, *J* = 11.6 Hz, 1 H), 4.33 (d, *J* = 11.6 Hz, 1 H), 4.10 (dd, *J* = 9.4, 6.6 Hz, 1 H), 4.01–3.88 (m, 2 H), 3.80, (s, 3 H), 3.37 (t, *J* = 6.44 Hz, 2 H), 2.52–2.35 (m, 4 H), 1.80–1.53, (m, 2 H), 0.79 (s, 9 H), 0.01 (s, 3 H), –0.03 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.14, 144.64, 133.28, 133.01, 130.37, 129.74, 129.22, 127.96, 119.60, 113.75, 72.55, 70.37, 68.67, 66.18, 55.25, 48.43, 34.46, 25.73, 21.58, 17.92, –4.43, –4.87.

MS (EI): *m*/*z* (%) = 368 (6), 348 (4), 241 (3), 229 (100), 185 (5), 172 (11), 149 (18), 121 (14), 91 (34).

HRMS (FT-ICR-ES): *m*/*z* calcd for $C_{28}H_{42}O_6SSiNa$ $[M + Na]^+$, 557.23636; found, 557.23588.

Elimination of the Tosylates 6–11,17; General Procedure

A stirred solution of the tosylate (Table 1) (0.1 M) in glyme containing NaI (3 equiv) and DBU (2 equiv) was refluxed for 3 h. Thereafter it was cooled to r.t., diluted with Et_2O (20 mL per 1 mmol of tosylate) and H_2O (20 mL per 1 mmol of tosylate), and stirred for 10 min. The layers were separated and the aqueous phase was extracted with Et_2O (2 ×). The combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (usually petroleum ether–EtOAc, 9:1), yielding the elimination products in almost quantitative yield (Table 1). For the analytical and spectral properties of alkenes **18**–**20**, see Refs.[13,20]

4-Pentenyltriisopropylsilylether (21)

The tosylate **9** (160 mg, 0.38 mmol), dissolved in glyme (5 mL) was converted to the alkene **21** according to the general procedure using NaI (173 mg, 1.15 mmol) and DBU (117 mg, 0.77 mmol). Filtration of the crude product over a short pad of silica gel (5% EtOAc in petroleum ether) gave the pure alkene **21** (89 mg, 95%) as a colorless oil; R_f 0.68 (petroleum ether–EtOAc, 9:1).

IR (film): 2941, 2866, 1463, 1384, 1105 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 5.91–5.74 (m, 1 H), 5.01 (dd, *J* = 16.9, 1.8 Hz, 1 H), 4.94 (br dd, *J* = 10.4 Hz, 1 H), 3.69 (t, *J* = 6.6 Hz, 2 H), 2.13 (q, *J* = 7.1 Hz, 2 H), 1.63 (quint, *J* = 7.2 Hz, 2 H), 1.16–0.93 (m, 21 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.67, 114.42, 62,76, 32.22, 30.08, 18.02, 17.67, 12.03.

MS (EI): *m*/*z* (%) = 199 (70), 157 (100), 129 (94), 113 (14), 101 (50), 87 (13), 75 (58).

Methyl 2,3,4-Tri-*O*-benzyl-α-d-xylo-hex-5-enopyranoside (22)

The tosylate **10** (517 mg, 0.83 mmol), dissolved in glyme (8 mL) was converted to the alkene **22** according to the general procedure using NaI (376 mg, 2.5 mmol) and DBU (254 mg, 1.7 mmol). Filtration of the crude product over a short pad of silica gel (20% EtOAc in petroleum ether) gave the pure alkene **22** (356 mg, 95%) as a colorless solid; mp 55–56 °C; R_f 0.42 (petroleum ether–EtOAc, 4:1).

IR (film): 3004, 2928, 2867, 1663, 1496, 1454, 1162, 1093 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.27 (m, 15 H), 4.99–4.89 (m, 3 H), 4.88–4.77 (m, 3 H), 4.77–4.61(m, 3 H), 4.08–3.89 (m, 2 H), 3.64 (dd, *J* = 9.4, 3.3 Hz, 1 H), 3.45 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.58, 138.60, 138.00, 137.92, 128.38, 128.27, 127.99, 127.93, 127.66, 98.96, 96.74, 81.09, 79.44, 79.21, 75.64, 74.38, 73.49, 55.35.

MS (EI): *m*/*z* (%) = 413 (2), 391 (2), 355 (3), 313 (2), 289 81), 265 (5), 223 (4), 181 (19), 164 (15), 135 (6), 105 (6), 91 (100), 65 (3).

3,7-Dimethylocta-1,6-diene (23)

The tosylate **11** (310 mg, 1.0 mmol), dissolved in glyme (10 mL) was converted to the diene **23** according to the general procedure using NaI (449 mg, 3.0 mmol) and DBU (384 mg, 2.0 mmol). In this case, pentane was used instead of Et_2O for extraction. Filtration of the pentane solution over a short pad of silica gel gave the pure diene **23** (132 mg, 87%) as a colorless oil; R_f 0.90 (petroleum ether–EtOAc, 9:1)

IR (film): 2962, 2924, 1471, 1454 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 5.77–5.55 (m, 1 H), 5.14–5.01 (t, *J* = 7.3 Hz, 1 H), 4.89 (t, *J* = 11.1 Hz, 2 H), 2.09 (quint, *J* = 6.8 Hz, 1 H), 2.02–1.86 (m, 2 H), 1.65 (s, 3 H), 1.56 (s, 3 H), 1.42–1.16 (m, 2 H), 0.96 (d, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.66, 131.14, 124.59, 112.37, 37.28, 36.68, 25.66, 20.06, 17.58.

MS (EI): *m*/*z* (%) = 123 (42), 109 (21), 95 (100), 82 (85), 67 (94).

***tert*-Butyl[((1*R*)-1-{2-[(4-methoxybenzyl)oxy]ethyl}-2-methylenebut-3-enyl)oxy]dimethylsilane (24)**

The tosylate **17** (101 mg, 0.19 mmol), dissolved in glyme (5 mL) was converted to the diene **24** according to the general procedure using NaI (85 mg, 0.57 mmol) and DBU (57 mg, 0.38 mmol). Filtration of the crude product over a short pad of silica gel (5% EtOAc in petroleum ether) gave the pure diene **24** (67 mg, 98%) as a colorless oil; R_f 0.60 (petroleum ether–EtOAc, 9:1); $[\alpha]_D^{23}$ +44.7 (*c* = 0.66, CH_2Cl_2).

IR (film): 2954, 2929, 1613, 1513, 1463, 1248, 1094 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 8.6 Hz 2 H), 6.87 (d, *J* = 8.8 Hz, 2 H), 6.30 (dd, *J* = 17.9, 11.1 Hz, 1 H), 5.35 (d, *J* = 17.9 Hz, 1 H), 5.19 (s, 1 H), 5.06 (d, *J* = 12.4, 2 H), 4.56 (dd, *J* = 8.1, 3.3 Hz, 1 H), 4.43 (d, *J* = 11.4 Hz, 1 H), 4.39 (d, *J* = 11.4 Hz, 1 H), 3.80 (s, 3 H), 3.64–3.56 (m, 1 H), 3.51–3.39 (m, 1 H), 2.00–1.86 (m, 1 H), 1.83–1.66 (m, 1 H), 0.89 (s, 9 H), 0.03 (s, 3 H), –0.02 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.04, 149.40, 135.96, 130.76, 129.16, 114.17, 113.69, 72.55, 69.54, 66.80, 55.25, 38.01, 25.82, 18.17, –4.73, –5.27.

MS (EI): *m*/*z* (%) = 305 (2), 213 (4), 171 (2), 131 (5), 121 (100), 91 (4).

HRMS (FT-ICR-ES): *m*/*z* calcd for $C_{21}H_{34}O_3SiNa$ $[M + Na]^+$, 385.21694; found, 385.21680.

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