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Wittig Rearrangement of Lithiated Allyl Aryl Ethers: A Mechanistic Study

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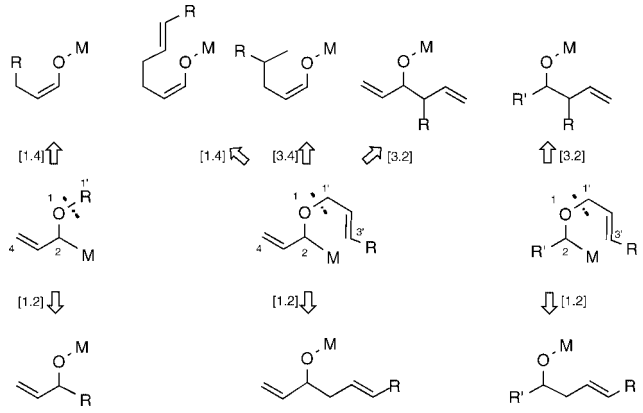
At –75 °C, α-lithiated allyl phenyl ether undergoes mainly the [1,2] Wittig rearrangement to afford, after acidic hydrolysis, 1-phenyl-2-propen-1-ol as the main product. A second metalation taking place at one of the *ortho* positions is the sole competing side reaction. Both, the significant decrease of the isomerization rate upon the introduction of a *tert*-butyl substituent in the *para* position of the aromatic ring and the complete absence of [1.4] rearrangement products suggest an intramolecular addition/elimination process bringing about the aryl migration. The first step, a nucleophilic attack of the α- to the *ipso*-carbon atom generates a spiro-connected oxiranylidene-cyclohexadienyllithium species. This short-lived intermediate collapses to the final product, a lithium alkoxide, by the nucleofugal departure of the oxygen atom which simultaneously binds the metal atom.

Introduction

What makes the Wittig rearrangement particularly fascinating is its complexity. The manifold of mechanistic possibilities is multiplied when allyl entities are involved as either the stationary or the migratory group.[1–6] In addition to the ubiquitous [1,2] migration pattern, three more rearrangement modes can thus become operational by connecting the [1,4], [3,2] or [3,4] sites (as shown in the center of Scheme 1).



Scheme 1. The four rearrangement modes available to metalated allylic ethers (M standing for metal).

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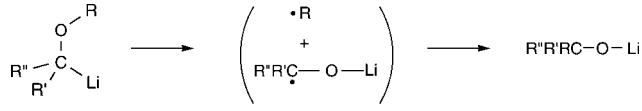
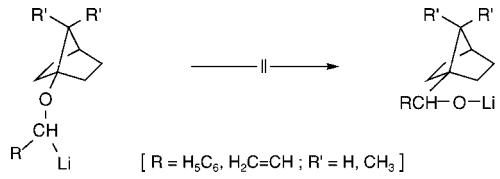
Whereas the [3.2] mode offers the opportunity to accomplish stereocontrolled carbon–carbon linking reactions and is therefore synthetically most attractive,[3–5] the [1.2] mode was in the focus of numerous mechanistic studies.[1,6] The principal features of the structural reorganization of α-(alkoxy)alkyllithiums are nowadays widely accepted (Scheme 2). During a two-stage process, the lithiated intermediate splits into an alkyl radical and an *O*-lithiated aldehyde (or, rarely, ketone) anion-radical, a so-called "ketyl", before these fragments recombine to afford a lithium alkoxide.[1]



Scheme 2. Homolytic cleavage of an α-(alkoxy)alkyllithium followed by instantaneous radical-pair recombination.

This two-step mechanism satisfies all crucial experimental observables. The migratory aptitude of the dislocated alkyl group mirrors the thermodynamical stability of the transient radical obeying the order methyl < *prim*-alkyl < *sec*-alkyl < *tert*-alkyl. As to be expected, 1-adamantyl behaves like *tert*-butyl,[7] whereas 1-(norbornyloxy)benzyllithium[7] and 1-(apocamphyloxy)allyllithium[8] prove reluctant to isomerize as the corresponding bridgehead radicals would have to be pyramidal, hence would be energetically unfavorable (Scheme 3).

The radical–ketyl pair must be extremely short-lived. Only if the recombination occurs at approximately the same rate as the radicals can tumble around one of their axes within the confinements of a solvent cage, it becomes intelligible why the configuration of a migrating *sec*-alkyl group[1]



Scheme 3. No migration of bridgehead-connected strained bicyclic rings.

is partially retained. The cyclopropylmethyl group, one of the most rapidly ticking "molecular clocks",[9] was found to undergo very little, if any, ring opening when traveling from the oxygen to the neighboring carbon atom.[8,10]

The rearrangement of α-aryloxy, as opposed to α-alkyloxy, substituted organolithium species has received much less attention. G. Wittig et al.[11–13] had recognized in their pioneering work a pronounced metal effect on the isomerization rate. Lithium species react faster than sodium analogs, and the latter faster than potassium derivatives.[11,12] Furthermore, they demonstrated the intramolecularity of the phenyl migration by a negative crossover experiment.[13] Although the authors finally found a concerted O → C shift of the phenyl ring more appealing, they took the alternative intramolecular nucleophilic addition/elimination mechanism explicitly into consideration.

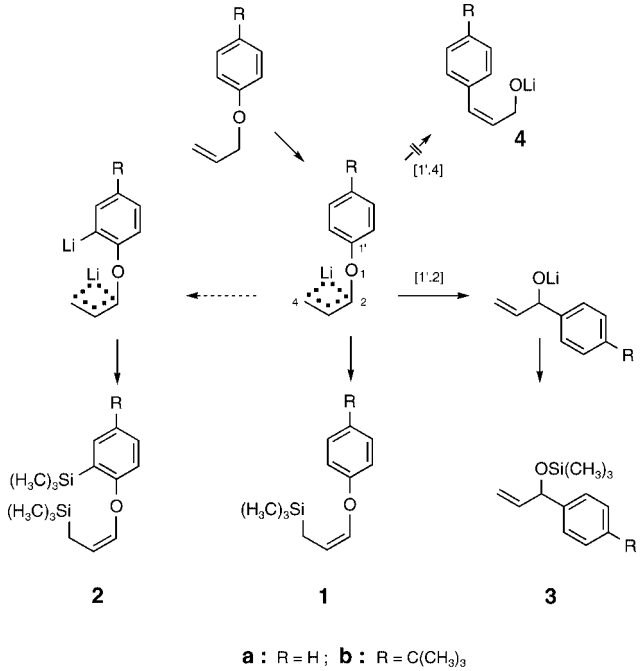
This intramolecular nucleophilic displacement, already tentatively favored by U. Schöllkopf,[1] was definitively resurrected when E. Grovenstein et al.[14] reinterpreted the retention of the (*Z*)- and (*E*)-1-propenyl configurations observed by V. Rautenstrauch, G. Büchi et al.[15] in the isomerization of α-metalated benzyl ethers. The Swiss authors for their part did not conceal their preference for another two-stage scenario consisting of the heterolytic cleavage and subsequent recombination of the fragments benzaldehydes and propenyllithium. Finally, J. J. Eisch et al.[16] rejected whatever mechanistic hypothesis so far proposed except the homolytic dissociation/recombination sequence.

Results

We intended to shed new light on this unsolved issue by applying two different probes. While monitoring to what extent a *para*-alkyl substituent accelerates or retards the rearrangement, we wanted also to check whether or not at least trace amounts of products attributable to the [1.4] mode[17] were detectable.

The *para* substituent was selected to satisfy two criteria: inertness toward strong bases and discrimination between radicals and carbanions by stabilizing one and destabilizing the other species. As we realized after long exploratory experimentation, *tert*-butyl is the sole substituent that meets both conditions. Unlike methyl and primary or secondary alkyl, it lacks benzylic C–H bonds and consequently resists any attempt of metalation. At the same time, it neither undergoes reductive degradation or elimination as halogen-bearing entities such as trifluoromethyl tend to do. Moreover, it destabilizes carbanions and organometallic derivatives thereof[18] while stabilizing, if weakly, aryl radicals.[19] All other common substituents favor both radical and carbanion formation although to a different degree. Thus, the comparison between the migratory aptitudes of a phenyl and a *p*-cymyl (4-*tert*-butylphenyl) group deemed us truly conclusive.

The metalation of both substrates, allyl phenyl ether and allyl *p*-cymyl ether, proceeded quickly with *sec*-butyllithium in tetrahydrofuran at –75 °C. After having trapped the lithiated species with chlorotrimethylsilane, (*Z*)-trimethyl(3-phenyloxy-2-propenyl)silane (**1a**, 77%) and (*Z*)-(3-*p*-cymyloxy-2-propenyl)trimethylsilane (**1b**, 83%), were isolated. When the reaction mixtures were brought to –25 °C, rearrangement set in. It turned out to be slow in the case of the lithiated phenyl ether and even almost ten times slower with the *p*-cymyl analog. Interception with chlorotrimethylsilane gave 1-phenyl-2-propenyl trimethylsilyl ether (**3a**, 25%) and 1-*p*-cymyl-2-propenyl trimethylsilyl ether (**3b**, 2.7%) as the main products. The bulk of the material was obtained without isomerization in form of the silanes **1a** (58%) and **1b** (70%) along with the bis(silanes) **2a** (6.5%) and **2b** (9.4%) as by-products resulting from a twofold metalation at both the α-allyl and an *ortho*-aryl position (Scheme 4). No other new compounds, in particular no (3-aryl-2-propenyloxy)trimethylsilanes derived from [1,4] migration products **4**, were identified.

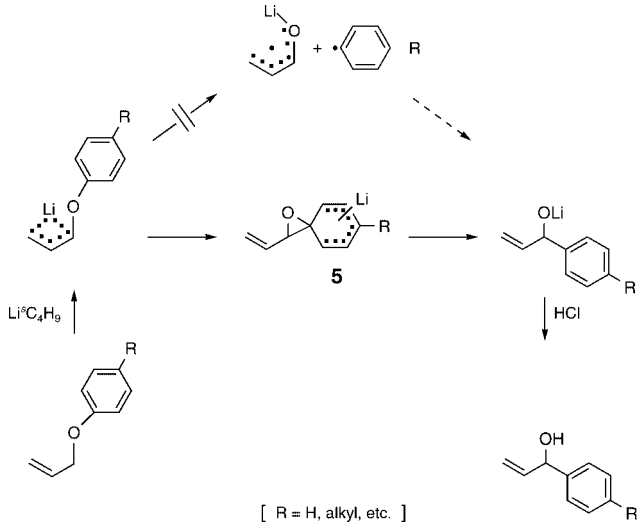


Scheme 4. Wittig rearrangement of α-lithiated phenyl and *p*-cymyl 2-propenyl ether.

Conclusions

The excellent mass balances of 96 and 91% with respect to *sec*-butyllithium and 95 and 94% with respect to the allyl aryl ethers (taking into account recovered starting material)

corroborate the claim that no 1,4-rearrangement products were formed. They should have inevitably emerged from the collapse of an aryl/ketyl radical pair. Thus, the homolysis/recombination mechanism can be ruled out. The substantial retardation of the isomerization rate caused by a *para*-alkyl substituent provides convincing evidence for a two-step mechanism initiated by intramolecular nucleophilic addition and terminated by nucleofugal elimination. It features 8-vinyl-7-oxyspiro[5.2]octa-3,5-dien-2-yllithium compounds **5** as the crucial intermediates in allyl aryl ether rearrangements (Scheme 5). This behavior is reminiscent of the well-established mechanism of the Smiles isomerization.[20–23]



Scheme 5. Rearrangement of α-metalated allyl aryl ethers according to the intramolecular nucleophilic addition/elimination (rather than the homolytic cleavage/recombination) mechanism.

Although the two competing intermediates, the hypothetical ketyl/aryl radical pair and the oxaspirooctadienyllithium **5** are not the rate-determining transition states, they should lie at almost the same energetic level. Relying on this plausible assumption we can compare the activation required for either process. The homolytic scission of the aryl–oxygen linkage costs some 95 kcal/mol, that of the allyl–lithium interaction about 50 kcal/mol. After deduction of the enthalpy of the newly formed O–Li bond of 120 kcal/mol[24] and the improved resonance due to the conversion of the allyl into the ketyl species by 5 kcal/mol remains a deficit of 20 kcal/mol. This barrier shrinks to approximately 15 kcal/mol if the intramolecular nucleophilic substitution mechanism is elicited. At the stage of intermediate **5** no bond scission nor lithium transfer has yet occurred. The spiro annulation builts up ring strain in the order of 25 kcal/mol. It is only partially compensated by the increase of the resonance energy in pentadienyllithium as opposed to allyllithium (30 vs. 20 kcal/mol). Even if the estimates made above are admittedly crude, they support the experimental findings which suggest an intramolecular nucleophilic substitution mechanisms to be operative and rule out a homolytic dissociation/recombination process.

The ultimate force driving the isomerization is the replacement of a weak[25,26] C–Li bond by a strong[24] O–Li bond. In order not to enter into high-energy regions, a sophisticated trajectory of metal delivery is mandatory. This will be the subject of forthcoming articles.[27,28]

Experimental Section

1. Generalities: For working routine and abbreviations, see related publications from this laboratory.[29–31] Unless specified otherwise, the ^{1}H NMR spectra were recorded at 360 MHz of samples dissolved in [D$_6$]benzene or, if marked by an asterisk, in [D$_6$]acetone.

2. Starting Materials and Compounds for Comparison

Allyl phenyl ether is commercial. Allyl *p*-cymyl ether and all reference compounds had to be prepared.

Trimethyl[(*Z*)-3-phenoxy-2-propenyl]silane (1a): At –75 °C, precooled tetrahydrofuran (25 mL) and allyl phenyl ether (2.7 g, 20 mmol) were added consecutively to *sec*-butyllithium (20 mmol) from which the customary hydrocarbon solvent had been stripped off beforehand. The mixture was kept 1 h at dry ice temperature before being treated with chlorotrimethylsilane (2.5 mL, 2.2 g, 20 mmol). Upon distillation a colorless liquid was collected; b.p. 114–115 °C/10 Torr; n_D^{20} = 1.5062; yield 3.17 g (77%). ^{1}H NMR: δ = 7.1 (m, 2 H), 6.9 (m, 2 H), 6.83 (tt, *J* = 7.5, 1.0 Hz, 1 H), 6.28 (dt, *J* = 6.0, 1.2 Hz, 1 H), 4.71 (td, *J* = 8.7, 6.0 Hz, 1 H), 1.65 (dd, *J* = 8.6, 1.2 Hz, 2 H), 0.04 (s, 9 H) ppm. MS: *m*/*z* (%) = 206 (4) [M$^+$], 191 (4), 73 (100). $C_{12}H_{18}OSi$ (206.36): calcd. C 69.84, H 8.79; found C 70.15, H 8.91.

Trimethyl[(*Z*)-2-(3-trimethylsilyl-1-propenyl)oxyphenyl]silane (2a): The same protocol as described in the preceding paragraph was applied, but 2 equiv. (40 mmol) of *sec*-butyllithium were allowed to react with the substrate for 20 h in a dry ice/methanol bath before the mixture was treated with chlorotrimethylsilane (4.9 mL, 4.3 g, 40 mmol); colorless oil; b.p. 84–85 °C/1 Torr; n_D^{20} = 1.5018; yield 3.12 g (75%). ^{1}H NMR*: δ = 7.4 (m, 2 H), 7.05 (td, *J* = 7.4, 1.0 Hz, 1 H), 6.99 (d, *J* = 8.2 Hz, 1 H), 6.43 (dt, *J* = 8.8, 6.0 Hz, 1 H), 4.92 (td, *J* = 8.8, 6.0 Hz, 1 H), 1.66 (dd, *J* 8.8, 1.2 Hz, 2 H), 0.32 (s, 9 H), 0.05 (s, 9 H) ppm. MS: *m*/*z* (%) = 206 (1) [M$^+$], 175 (25), 73 (100). $C_{15}H_{26}OSi$ (278.54): calcd. C 64.68, H 9.41; found C 64.79, H 9.41.

Trimethyl[(1-phenyl-2-propenyl)oxy]silane (3a): The mixture of 1-phenyl-2-propen-1-ol[32] (5.0 g, 37 mmol), chlorotrimethylsilane (6.2 mL, 5.4 g, 50 mmol) and triethylamine (14 mL, 10 g, 0.10 mol) was kept 12 h at +25 °C before being diluted with hexanes (20 mL) and washed with ice-cold 5% hydrochloric acid (2 × 10 mL) and a saturated aqueous solution (2 × 20 mL) of sodium hydrogen carbonate. Distillation gave a colorless oil; b.p. 52–56 °C/0.5 Torr; n_D^{20} = 1.4832; yield 6.11 g (80%). ^{1}H NMR: δ = 7.4 (m, 2 H), 7.2 (m, 2 H), 7.07 (tt, *J* = 7.0, 1.0 Hz, 1 H), 5.94 (ddd, *J* = 16.8, 10.2, 6.0 Hz, 1 H), 5.26 (ddd, *J* = 16.8, 2.0, 1.5 Hz, 1 H), 5.11 (broad d, *J* = 6.0 Hz, 1 H), 4.96 (ddd, *J* = 10.2, 2.0, 1.5 Hz, 1 H), 0.15 (s, 9 H) ppm. MS: *m*/*z* (%) = 206 (9) [M$^+$], 191 (8), 117 (38), 73 (100). $C_{12}H_{18}OSi$ (206.36): calcd. C 69.84, H 8.79; found C 70.03, H 8.75.

Trimethyl[(*Z*)-(1-phenyl-1-propenyl)oxy]silane: Precooled (–75 °C) tetrahydrofuran (10 mL) and 1-phenyl-2-propen-1-ol[32] (0.67 g, 5.0 mmol) were added consecutively to *sec*-butyllithium (5.5 mmol) from which before the commercial hydrocarbon solvent had been stripped off. After 170 h (1 week) at +25 °C, the mixture was poured into hexanes (20 mL) and washed with 2% sulfuric acid (2 × 5 mL), a saturated aqueous solution (2 × 5 mL) of sodium hy-

drogen carbonate and brine (5 mL). Upon evaporation of the volatiles and distillation of the residue, trimethyl[(1-phenyl-1-propenyl)-oxy]silane and its isomer **3a** were collected in a 9:1 ratio; b.p. 50–56 °C/0.5 Torr; yield 0.86 g (83%). The main component was purified by preparative gas chromatography (3 m, 10% Apiezon-L, 200 °C); n_D^{20} = 1.5040. ^{1}H NMR: δ = 7.5 (m, 2 H), 7.2 (m, 2 H), 7.06 (tt, J = 7.2, 1.2 Hz, 1 H), 5.28 (q, J = 6.8 Hz, 1 H) 1.73 (d, J = 6.8 Hz, 3 H), 0.09 (s, 9 H). MS: m/z (%) = 206 (12) [M$^+$], 205 (18), 105 (21), 75 (100). $C_{12}H_{18}OSi$ (206.36): calcd. C 69.84, H 8.79; found C 69.85, H 8.75.

Trimethyl[(*Z*)-(3-phenyl-1-propenyl)oxy]silane: A solution of 3-phenylpropanal[33] (13 g, 0.10 mol), chlorotrimethylsilane (15 mL, 13 g, 0.12 mol) and triethylamine (35 mL, 31 g, 0.25 mol) in dimethylformamide (50 mL) was heated to reflux for 24 h. After the addition of hexanes (0.10 L), the mixture was washed with ice-cold hydrochloric acid (2 ×0.10 L), a saturated aqueous solution (2×0.10 L) of sodium hydrogen carbonate and brine (0.10 L). Distillation afforded the product as a 2:1 mixture of (*Z*) and (*E*) isomers; b.p. 63–72 °C/1 Torr; yield 14.2 g (69%). The main component was purified by preparative gas chromatography (3 m, 10% Apiezon-L, 200 °C). ^{1}H NMR: δ = 7.2 (m, 4 H), 7.05 (tt, J = 7.0, 1.2 Hz, 1 H), 6.19 (dt, J = 5.8, 1.5 Hz, 1 H), 4.75 (td, J = 7.5, 5.8 Hz, 1 H), 3.59 (dd, J = 7.5, 1.2 Hz, 2 H), 0.05 (s, 9 H). MS: m/z (%) = 206 (11) [M$^+$], 191 (9), 117 (20), 73 (100). $C_{12}H_{18}OSi$ (206.36): calcd. C 69.84, H 8.79; found C 70.27, H 8.84.

Allyl *p*-Cymyl Ether (Allyl 4-*tert*-Butylphenyl Ether): Potassium carbonate (28 g, 0.20 mol) was added to a solution of 4-*tert*-butylphenol (30 g, 0.20 mol) and allyl bromide (24 g, 0.20 mol) in anhydrous acetone (25 mL). The mixture was heated to reflux for 9 h before being washed with water (0.10 L) and a 2.0 M aqueous solution (3×25 mL) of sodium hydroxide. The product was isolated by distillation under reduced pressure; b.p. 68–69 °C/0.5 Torr (lit.[34] 115–116 °C/3 Torr); 1.5069 (lit.[34] 1.5065); yield 20.6 g (54%). ^{1}H NMR: δ = 7.3 (m, 2 H), 6.9 (m, 2 H), 6.06 (ddt, J = 17.5, 10.5, 5.5 Hz, 1 H), 5.42 (dq, J = 17.5, 1.5 Hz, 1 H), 5.28 (dq, J = 10.5, 1.5 Hz, 1 H), 4.52 (dt, J = 5.5, 1.5 Hz, 2 H), 1.29 (s, 9 H) ppm. MS: m/z (%) = 190 (35) [M$^+$], 175 (100). $C_{13}H_{18}O$ (190.29): calcd. C 82.06, H 9.54; found C 82.34, H 9.47.

(*Z*)-(3-*p*-Cymyloxy-2-propenyl)trimethylsilane (1b): Prepared, analogously as the phenoxy compound **1a**, from allyl *p*-cymyl ether (3.8 g, 20 mmol); b.p. 101–102 °C/0.5 Torr; n_D^{20} = 1.5022; yield 4.34 g (83%). ^{1}H NMR: δ = 7.2 (m, 2 H), 7.0 (m, 2 H), 6.32 (dt, J = 6.0, 1.2 Hz, 1 H), 4.76 (dt, J = 8.7, 6.2 Hz, 1 H), 1.71 (dd, J = 8.6, 1.2 Hz, 2 H), 1.21 (s, 9 H), 0.06 (s, 9 H) ppm. MS: m/z (%) = 262 (8) [M$^+$], 247 (17), 205 (45), 73 (100). $C_{16}H_{26}OSi$ (262.47): calcd. C 73.22, H 9.99; found C 73.31, H 9.93.

{5-*tert*-Butyl-2[(*Z*)-(3-trimethylsilyl-1-propenyl)oxy]}trimethylsilane (2b): Prepared and isolated as described for the analog **2a**; b.p. 123–127 °C/1 Torr; n_D^{20} = 1.4996; yield 6.23 g (93%). ^{1}H NMR*: δ = 7.48 (d, J = 2.5 Hz, 1 H), 7.43 (dd, J = 8.5, 2.6 Hz, 1 H), 6.91 (d, J = 8.5 Hz, 1 H), 6.41 (dd, J = 6.0, 1.2 Hz, 1 H), 4.87 (td, J = 8.7, 6.2 Hz, 1 H), 1.66 (dd, J = 8.7, 1.2 Hz, 2 H), 1.31 (s, 9 H), 0.32 (s, 9 H), 0.05 (s, 9 H). $C_{19}H_{34}OSi_2$ (334.65): calcd. C 68.19, H 10.24; found C 68.18, H 10.28.

[(1-*p*-Cymyl-1-propenyl)oxy]trimethylsilane (3b): Prepared and isolated as described for the phenyl analog **3a**; b.p. 82–84 °C/0.5 Torr; n_D^{20} = 1.4841; yield 7.09 g (73%). ^{1}H NMR: δ = 7.4 (m, 2 H), 7.3 (m, 2 H), 6.02 (ddd, J = 17.0, 10.5, 6.0 Hz, 1 H), 5.33 (ddd, J = 10.5, 2.0, 1.5 Hz, 1 H), 5.18 (broad d, J = 6.0 Hz, 1 H), 5.02 (ddd, J = 10.5, 2.0, 1.5 Hz, 1 H), 1.21 (s, 9 H), 0.11 (s, 9 H). MS: m/z (%) = 262 (5) [M$^+$], 247 (19), 205 (100), 73(55). $C_{16}H_{26}OSi$ (262.47): calcd. C 73.22, H 9.99; found C 73.51, H 9.97.

3. Rearrangement of Allyl Phenyl Ether and Allyl *p*-Cymyl Ether

At –75 °C, precooled tetrahydrofuran (9.0 mL) and allyl phenyl ether (0.67 g, 5.0 mmol) were added consecutively to *sec*-butyllithium (5.0 mmol) from which the commercial hydrocarbon solvent had beforehand been stripped off. The mixture was kept for 2 h at –25 °C before being treated with chlorotrimethylsilane (1.3 mL, 1.1 g, 10 mmol) and *N,N,N′,N′*-tetramethylethylenediamine (1.5 mL, 1.2 g, 10 mmol). Gas chromatography (2 m, 5% silicon rubber SE-30, 80 °C [5 min] → 200 °C [10 °C/min]; 2 m, 5% hydrocarbon Apiezon-L, same temperature program; undecane as the calibrated internal standard) revealed the presence of the silane **1a** (58%), the bis(silane) **2a** (6.5%), the rearranged trimethylsilyl ether **3a** (19%) and its isomerization product trimethyl[(1-phenyl-1-propenyl)oxy]silane (5.8%). Not even trace amounts of trimethyl[(*Z*)-(3-phenyl-1-propenyl)oxy]silane were detected. Some unconsumed allyl phenyl ether (5.1%) was identified too.

The same protocol was applied to allyl *p*-cymyl ether (0.96 g, 5.0 mmol). Gas chromatographic analysis (same columns and temperature profiles as above; tetradecane as the calibrated internal standard) identified the silane **1b** (70%), the bis(silane) **2b** (9.4%) and the rearranged trimethylsilyl ether **3b** (2.7%). A moderate quantity (12%) of allyl *p*-cymyl ether was recovered.

Acknowledgments

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