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THE WITTIG REARRANGEMENT AS A PRACTICAL METHOD FOR ALDEHYDE SYNTHESIS

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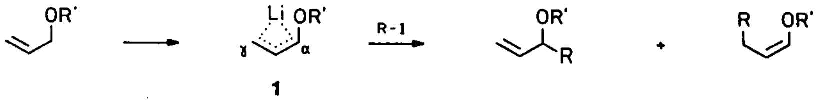
Summary : If the rearrangement of metalated allyl ethers **2** (or **4**) is accomplished in the presence of potassium *tert*-butoxide, primary alkyl groups preferentially migrate to the unsubstituted allylic terminus (γ-position). Enolates **7** and 1-vinylalcoholates **6** (by alkyl migration to the α-position, adjacent to the oxygen atom) are produced in an approximate ratio of 9 : 1. Because of the *endo*-configuration of their organometallic precursors, the enolates exclusively emerge in the (*Z*)-configuration as shown by trapping with chlorotrimethylsilane and isolation of the resulting *O*-silyl (*Z*)-enethers. Hydrolysis of the latter affords the corresponding aldehydes with good yields. - The rearrangement is mechanistically still obscure. A concerted process as the main reaction mode is unlikely. The intermediacy of zwitterionic metallomers **18** and solvent caged radical pairs **17** is tentatively suggested.

In 1974, we [1] and others [2, 3] have studied the alkylation of metalated allyl ethers **1** [OR' = OC_2H_5, OC_6H_5, $OSi(C_2H_5)_3$ *etc.*]. With methyl iodide or primary alkyl iodide, substitution was found to occur preferentially at the unsubstituted γ-position while 1 : 2 or 1 : 1 mixtures of α-alkylated allyl ethers and enethers were obtained with secondary alkyl halides (see table 1, following page).



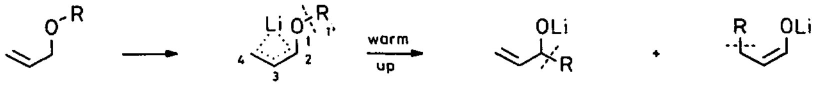
More recently, Hoppe *et al.* [4] have disclosed methods which offer almost perfect regiocontrol in either sense and which rely on allyl carbamates [OR' = $OCON(^iC_3H_7)_2$] as key substrates and, in addition, on metal variation [*e.g.*, $Ti(O^iC_3H_7)_3$ instead of Li]. Thus, chain-lengthened enethers, branched or unbranched, carrying or not functional groups, have become readily accessible. As "masked" aldehydes they are very useful for synthetic purposes.

Table 1. Alkylation of metalated allyl phenyl ether [OR' = OC_6H_5] [a], allyl *tert*-butyl ether [OR' = $OC(CH_3)_3$] [b] and allyl triethylsilyl ether [OR' = $OSi(C_2H_5)_3$] [c] : ratios of attack at the α- and γ-position as a function of the alkylating agent.

alkylating agent	OR' = OC_6H_5 [1]	OR' = $OC(CH_3)_3$ [2]	OR' = $OSi(C_2H_5)_3$ [3]
H_3C-I	25 : 75 [d]	-	5 : 95
RCH_2-I (RCH_2Br) [e]	15 : 85 (-)	10 : 90 (20 : 80)	15 : 85 (25 : 75)
$(H_3C)_2CH$-I	-	35 : 65	40 : 60

a) Reaction conditions : both, metalation (with butyllithium in the presence of potassium *tert*-butoxide) and alkylation in hexane at -30°C.
b) Reaction conditions : both, metalation (with *sec*-butyllithium) and alkylation in tetrahydrofuran at -65°C.
c) Reaction conditions : metalation (with *sec*-butyllithium) in tetrahydrofuran at -75°C and alkylation, at the same temperature, after addition of 5 vol% hexamethylphosphoric triamide.
d) Metalation with butyllithium in tetrahydrofuran and treatment with methyl iodide, both at -75°C, produces an α : γ ratio of 20 : 80.
e) Primary alkyl halide : R = ethyl, propyl, butyl or hexyl.

Despite these achievements we wanted to explore another approach to aldehyde synthesis from allyl ethers. The alkyl group would be transferred *intra- rather than intermolecularly* if a suitable metalated allyl ether **2** were allowed to undergo a Wittig rearrangement [5], giving α-vinylalcoholates (by 1,2-migration) and enolates (by 1,4-migration), rather than being intercepted with an electrophile. In this way, it should be possible to attach even tertiary alkyl, cyclopropyl, aryl, 1-alkenyl or 1-alkynyl groups to the allyl moiety. In contrast, the previously described alkylations of metalated allyl ethers or carbamates are restricted to the narrow scope of S_N2-type reactions. It would be of considerable practical importance if these limitations could be overcome.



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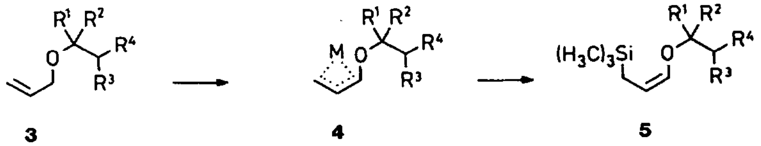
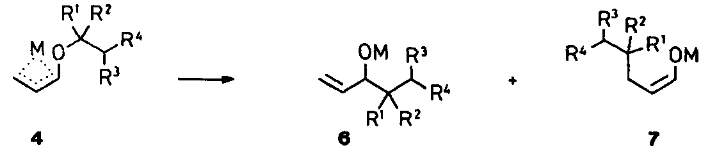
The Wittig rearrangement of bis(allyl) and allyl 2-alkynyl ethers has been abundantly studied and many examples of application to organic synthesis have been reported [6]. In general, the electronically [7] and geometrically attractive 3,2-mode [8, 9] of rearrangement prevails over the 1,2-mode [8], while the 1,4-mode [10] and the 3,4-mode [9] become competitive only in exceptional cases. Data on the rearrangement of metalated allyl aryl or allyl alkyl ethers are much more scarce. Felkin *et al.* [11] were the first to explore this kind of isomerizations. They identified both 1-alken-3-ols and aldehydes in the product mixtures obtained after hydrolysis. The yields, however, were poor and did not exceed 30% for either component.

In order to repeat and extend this work we selected a representative series of model substrates 3 (R^1, R^2, R^3, R^4 = H or alkyl). First of all we established experimental conditions which allow virtually quantitative metalation of these allyl ethers without simultaneous rearrangement. The organometallic intermediates 4 [M = Li] were generated with *sec*-butyllithium in neat tetrahydrofuran at -75°C and were regioselectively trapped with chlorotrimethylsilane to afford alkyl 3-trimethylsilyl-1-propenyl ethers 5 with high yields. The (*Z*)-configuration of the latter confirms the expected [12] *endo*-shape of the (alkoxy)allyllithium precursors. Quenching of the reaction with water gives alkyl 1-propenyl ethers.

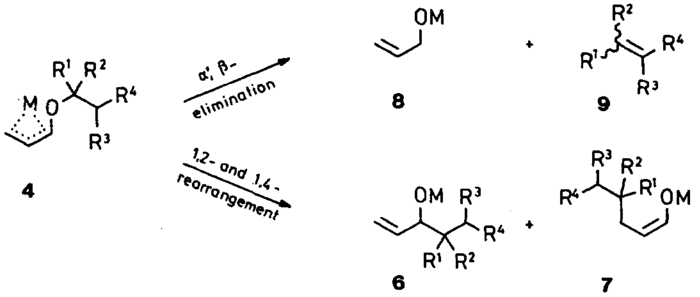


When the solutions containing intermediate 4 were stored 2 h at -25°C before being acidified, no allyl or propenyl ethers were present any more. On the other hand, only small quantities of aldehydes and alcohols were detected and many attempts to improve the mass balance failed. Finally we decided to avoid any aqueous work-up and to convert the two types of isomerization products, lithium 1-alken-3-olates 6 [M = Li] and lithium enolates 7 [M = Li] to the corresponding *O*-trimethylsilyl derivatives prior to isolation. This time both, high global yields (mostly in the range of 70 - 90%) and high proportions of the *O*-silyl enethers 7 [M = $Si(CH_3)_3$] [13] were obtained at least from all migrations in which simple primary alkyl groups were involved. The (*Z*)-configuration of these enolate derivatives demonstrates that no *cis/trans*-isomerization had taken place during or after the 1,4-rearrangement.



The *O*-silyl enethers 7 [M = $Si(CH_3)_3$] were readily and selectively cleaved under alkaline conditions to set free the corresponding aldehydes. The latter were found to be fairly stable even under such conditions which had been previously recognized to be fatal in the case of direct hydrolysis. We explain this apparent paradox by the well known strong aggregation of lithium enolates [14]. Whatever precautions may be taken, direct hydrolysis will give birth to a molecule of aldehyde being momentarily entangled in an enolate cluster fragment. Extensive destruction by aldol condensation processes and Cannizzaro-type dismutations appears to be inevitable under such circumstances.

The rearrangement products **6** and **7** (M = Li, isolated as the corresponding allyl alcohols and aldehydes, respectively) were always accompanied by lithium allyl alcoholate **8** (isolated as its *O*-trimethylsilyl ether) and an olefin **9**. They must have originated from an α',β-elimination [15] which had consumed approximately 25% of the intermediate **4**.



In a first attempt to suppress this side reaction the temperature dependence of the reaction was studied using allyl nonyl ether (**3c**; $R^1=R^2=R^3=H$, $R^4=C_7H_{15}$) as the model substrate (see table 2). Lowering the temperature to -50°C had little effect on the competition between rearrangement and elimination but did improve the ratio of 1,4- *vs*. 1,2-migration. On the other hand, the reactions required impractically long periods of time to go to completion. If, however, a stoichiometric amount of potassium *tert*-butoxide was added to the lithiated intermediate **4c**, the latter underwent smooth isomerization with quite satisfactory typo- and regioselectivities even at room temperature (see table 2).

Table 2. Transformation of 1-(nonyloxy)allylmetal intermediates **4c** under various reaction conditions : total yields of volatile products as well as ratios of rearrangement vs. scission and 1,2- vs. 1,4-rearrangement.

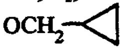
metal M	reac. time and temp.	total yield	rearr. vs. scission ([**6** + **7**] : **9**)	1,2- vs. 1,4-rearr. (**6** : **7**)
Li	2 h -25°C	89%	76 : 24	22 : 78
Li	24 h -50°C	81%	77 : 23	10 : 90
Li	4 h -50°C	40%	69 : 31	12 : 88
Li	24 h -75°C	< 5% a)	-	-
Li + K	240 h -50°C	70% b)	91 : 9	5 : 95
Li + K	2 h +25°C	82%	89 : 11	11 : 89

a) Much nonyl 3-trimethylsilyl-1-propenyl ether (**5c**, 81%) was obtained by interception of unconsumed **4c**.

b) Besides 12% of unchanged starting material, 14% of 3-trimethylsilyl-1-propenyl ether were obtained.

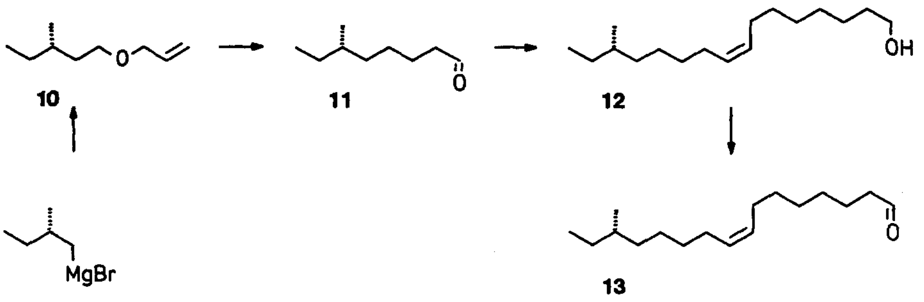
Addition of potassium *tert*-butoxide increased the amount of the 1,4- at the expense of the 1,2-migration product also in the case of all other allyl ether rearrangements (see table 3). Enolates **7** [M = $Si(CH_3)_3$], however, were obtained with sufficient (~ 90%) regioisomeric purity only if a resonance inactive primary alkyl group (such as butyl, 3-methylbutyl or nonyl) was allowed to migrate. The migration of secondary or tertiary alkyl groups (1-ethylpropyl, *tert*-butyl) or even the cyclopropylmethyl moiety led to 2 : 3 or 1 : 1 mixtures of 1-alken-3-olates **6** and enolates **7** (table 3).

Table 3. Isomerization of 1-(alkoxy)allyllithium intermediates **2** or **4** after 2 h at 25°C in the absence (M = Li) or presence (M = Li + K) of potassium *tert*-butoxide : total yields and, in parentheses, ratios ("α/γ ratios") of 1,2- and 1,4-rearrangement products [a].

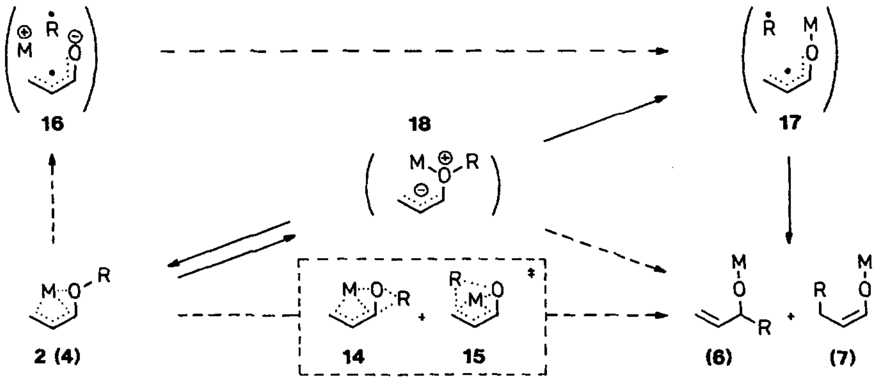
2 (4)	OR	M = Li	M = Li + K
a	OC_4H_9	-	66% (13 : 87)
b	$OCH_2CH_2CH(CH_3)_2$	73% (23 : 77)	73% (10 : 90)
c	OC_9H_{19}	-	70% (10 : 90)
d		85% (75 : 25) [b]	65% (40 : 60) [b]
e	$OCH(C_2H_5)_2$	77% (50 : 50)	71% (37 : 63)
f	$OC(CH_3)_3$	77% (70 : 30)	70% (54 : 46)

a) Yields and product ratios were determined by gas chromatography using an internal standard and, for comparison, authentic samples which had been isolated from independent runs (in general, carried out on a 50 mmol scale).
b) By coinjection of 3- and (*Z*)-1-trimethylsilyloxy-1,6-heptadiene it was shown that the reaction mixture did not contain any (< 1%) ring opened products which could have arisen from the very fast isomerization [25] of cyclopropylmethyl to 3-butenyl ("homoallyl") radicals.

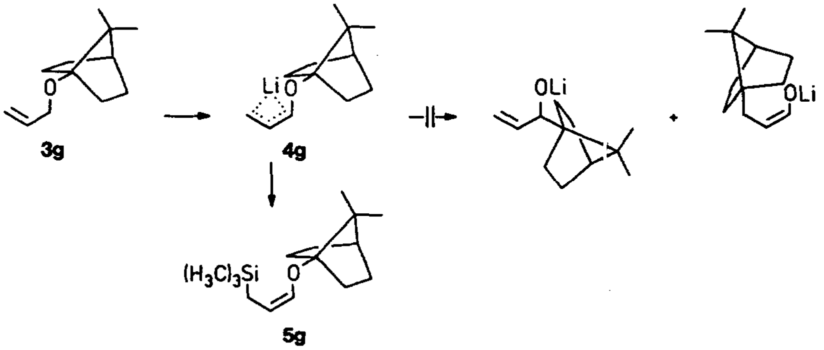
To demonstrate its practical utility, the potassium *tert*-butoxide controlled Wittig rearrangement was employed as the key step in a new pheromone synthesis which we feel is superior to previous ones [16, 17]. Commercial (*S*)-2-methyl-1-butanol was converted to the bromide and the corresponding Grignard reagent before being submitted to a C_1 + C_3 chain elongation by condensation with allyl chloromethyl ether and metalation of the new allyl ether **10** with *sec*-butyllithium followed by addition of potassium *tert*-butoxide. After warming up, keeping at 25°C and trapping with chlorotrimethylsilane a mixture of two *O*-silyl ethers was isolated. When treated with diluted aqueous sodium hydroxide the minor component, the derivative of a 1-alken-3-ol, remained unaffected while the principal product, an enolate derivative, was hydrolyzed to afford pure (*S*)-6-methyloctanal **11** with 64% yield (after distillation). A *cis*-selective Wittig reaction [18] with triphenylphosphonio-8-sodiooxyoctanide [19] finished the sequence. The *cis*-alkenol **12** (*cis/trans* ratio 97 : 3) obtained from aldehyde **11** can be oxidized [17] to give the *cis*-alkenal **13**, the sex attractant of the coleoptera species *trogoderma inclusum* and *trogoderma variabile* [20].



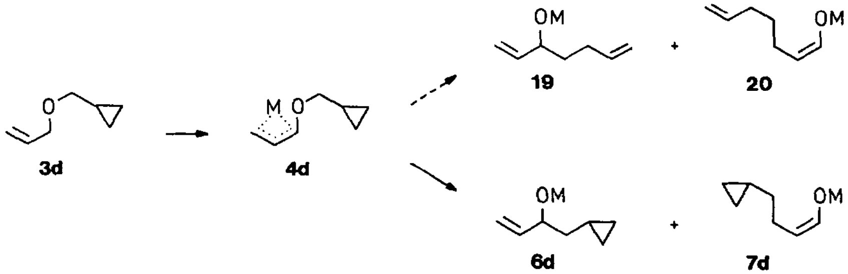
We would like to draw attention to a particular detail which has mechanistic implications. As a comparison of the required reaction times reveals (table 2), the addition of potassium *tert*-butoxide to the lithiated intermediates **2** (or **4**) by no means accelerates the subsequent Wittig rearrangement but rather retards it. These findings are in striking contrast with what is known about 3-metaloxy-1,5-hexadienes, the potassium derivatives of which undergo the Cope rearrangement several orders of magnitude faster than the lithium analogs [21]. In the latter case the reactivity order can be considered as normal : it well reflects the extent of resonance stabilization which the resulting enolates experience as a consequence of the tighter or looser binding between the metal and the oxygen atom. If now the 1-(alkoxy)allylmetal intermediates **2** (or **4**) show the opposite behavior, their structural reorganization must be triggered by the *electrophilic potential of the metal rather than the electron excess at the hetero-atom*. These characteristics are hardly compatible with a "dyotropic" [22] process (transition states **14** and **15**) nor with the intermediacy of a metal cation/radical/radical ion triplet **16**. All the evidence taken together [23] speaks for the solvent caged 1-(alkoxy)-allyl radical/alkyl radical pair **17** as a major transient species. We now speculate that it may be preceded by the zwitterionic metallomer **18**, an *O*-lithio(oxonia)-propenide, which either may collapse to the radical pair **17** or, in borderline cases, directly isomerize to provide the rearrangement products of type **6** and **7**.



The concerted process (**18** → **6** + **7**) would imply the *nucleophilic displacement* of the migrating group from the alkoxy moiety and its transfer to the α- or γ-allylic carbon atom *with retention of configuration*. Apparently for this reason it is disfavored and cannot take place with simple alkyl groups. In this way we explain why we were unable to bring about the Wittig rearrangement of lithiated allyl 1-(7,7-dimethyl)bicyclo[2.2.1]heptyl ether (allyl 1-apocamphyl ether, **4g**). This parallels previous findings according to which metalated benzyl norbornyl ether is stable under conditions which promote the Wittig rearrangement of metalated 1-adamantyl benzyl ether [24]. Due to its imposed pyramidal geometry, the 1-bicyclo[2.2.1]heptyl radical has a higher free energy than any primary alkyl or even methyl, not to speak of an ordinary acyclic tertiary radical (always when compared with the corresponding valence saturated hydrocarbons) [25].



On the other hand, the life time of the radical pair **17** must be extremely short, below 10^{-8} s. This was monitored by one of the best studied "radical clock" reactions, the isomerization of the cyclopropylmethyl to the 3-butenyl ("homoallyl") radical [26]. If the rearrangement of the lithiated allyl cyclopropyl methyl ether **4d** [M = Li] did collapse to generate radical fragments, the latter must have recombined much faster than ring opening occurred. Cyclopropane derivatives **6d** and **7d** [isolated as the *O*-silyl ethers, M = $Si(CH_3)_3$] were found to be the main products. Only trace amounts (< 1%) of acyclic compounds **19** and **20** were detected in the product mixture, if at all.



Similar results had been reported for the rearrangement of lithiated benzyl cyclopropylmethyl ether [27]. Moreover, the very ephemeral nature of radical pairs **17** is corroborated by the failure to detect any CIDNP (chemically induced dynamic nuclear polarization) signals in nmr investigations [28].

Finally it should be pointed out that the mechanistic profile of Wittig rearrangements heavily depends on the nature of the migrating group. Metalated allyl 1-alkenyl or aryl ethers [29 - 31] appear to follow the behavior of metalated benzyl 1-propenyl ether [30] and benzyl phenyl ether [32]. Transient bridged species of the 2-(1-lithioalkyl)oxirane type are presumably involved [33].

EXPERIMENTAL PART

1. General remarks

Starting materials have been purchased from Fluka AG, Buchs, Aldrich-Chemie, Steinheim, or Merck-Schuchardt, Darmstadt, unless literature sources or details for the preparation are given. *Butyllithium* and *potassium tert-butoxide* were supplied by CheMetall, Frankfurt, and Hüls-Troisdorf. All commercial reagents were used without further purification.

Air and moisture sensitive compounds were stored in Schlenk tubes or Schlenk burettes. They were protected by and handled under an atmosphere of 99.995% pure nitrogen.

Tetrahydrofuran was obtained anhydrous by distillation from sodium wire after the characteristic blue color of in situ generated sodium diphenylketyl [34] was found to persist. In case of poor quality it was, in addition, pretreated with cuprous chloride [35] and potassium hydroxide pellets.

Ethereal extracts were dried with sodium sulfate. Before distillation of compounds prone to radical polymerization or sensitive to acids a spatula tip of *hydroquinone* or, respectively, *potassium carbonate* was added.

The temperature of dry ice-methanol baths is consistently indicated as -75°C, "room temperature" (22 - 26°C) as 25°C. If no reduced pressure is specified, *boiling ranges* were determined under ordinary atmospheric conditions (720 ± 25 mmHg).

Whenever reaction products were not isolated, their yields were determined by *gas chromatography* comparing their peak areas with that of an internal standard and correcting the ratios by calibration factors. The purity of distilled compounds was checked on at least two columns loaded with stationary phases of different polarity. Chromosorb G-AW of 80 - 100 and, respectively, 60 - 80 mesh particle size were used as the support for packed analytical or preparative columns (2 or 3 m long, 2 mm inner diameter and 3 or 6 m long, 1 cm inner diameter, respectively). All packed columns were made of glass, while quartz was chosen as the material for coated, SCOT-type capillary columns ($\geq$ 10 m long). The type of the stationary phase used is abbreviated as SE-30 (silicone rubber) and Ap-L (Apiezon L hydrocarbon). In the case of programmed temperature increase a rate of 10°C/min was chosen.

Infrared spectra were recorded of films if the sample was liquid at room temperature, while solid substances were embedded in potassium bromide pellets. The intensities of absorption bands are abbreviated : s (strong), m (moderate), w (weak) and b (broad).

Nuclear magnetic resonance spectra of hydrogen nuclei were recorded in the 360 MHz field. Chemical shifts refer to the signal of tetramethylsilane (δ = 0 ppm). The shift numbers of silylated compounds were determined relative to the residual solvent peak (CD_5H : δ = 7.16 ppm, $CHCl_3$: δ = 7.27 ppm). Coupling constants (*J*) are measured in Hz. Coupling patterns are described by abbreviations : *s* (singulet), *d* (doublet), *t* (triplet), *q* (quadruplet), *pent* (pentuplet), *hex* (hexuplet), *td* (triplet of a doublet) and *m* (multiplet).

Mass spectra were obtained at a 70 eV ionisation potential. *Elementary analyses* were performed by the laboratory of I. Beetz, D-8640 Kronach.

2. Metalation and Rearrangement of Alkyl Allyl Ethers

a) Allyl Butyl Ether (3a)

Consecutive treatment of allyl butyl ether (2.9 g, 25 mmol) with *sec*-butyllithium (28 mmol, from which the original isopentane solvent had been stripped off) in tetrahydrofuran (25 mL), 1 h at -75°C, and with chlorotrimethylsilane (3.8 mL, 3.3 g, 30 mmol), 1 h at +25°C (after addition at -75°C), gave **butyl (*Z*)-3-trimethylsilyl-1-propenyl ether** [**5a**, M = $\mathrm{Si(CH_3)_3}$]; 3.4 g (73%), bp 81 - 82°C/15 mmHg, n_D^{20} 1.4358. - IR : 3045 (w, ν[=C-H]), 1665 (s, ν[C=C]), 1250 (s, ν[C-O-C]). - ^{1}H-NMR (C_6D_6): 5.84 (1 H, *dt*, *J* 6.3, 1.3), 4.40 (1 H, *dt*, *J* 8.5, 6.0), 3.43 (2 H, *t*, *J* 6.4), 1.64 (2 H, *dd*, *J* 8.5, 1.3), 1.4 (2 H, *m*), 1.3 (2 H, *m*), 0.79 (3 H, *t*, *J* 7.4), 0.80 (9 H, *s*). - MS : 186 (2%, M^+), 129 (15%), 73 (100%). - Calc. for $C_{10}H_{22}OSi$ (186.37) C 64.45, H 11.90; found C 64.40, H 11.77%.

A solution of *sec*-butyllithium (53 mmol; from which the original isopentane solvent had been stripped off) and allyl butyl ether (5.7 g, 50 mmol) in tetrahydrofuran (100 mL) was kept 1 h at -75° and 2 h at +25°C. After addition of chlorotrimethylsilane (10.9 g, 100 mmol) and *N,N,N',N'*-tetramethylethylenediamine (15.0 mL, 11.6 g, 100 mmol) the solvent was evaporated. Distillation afforded a 1 : 3 mixture of **6a** [M = $\mathrm{Si(CH_3)_3}$] and **7a** [M = $\mathrm{Si(CH_3)_3}$]; 6.6 g (71%), bp 58 - 63°C/20 mmHg. The components were identified by gas chromatographic comparison with authentic materials (3 m, 5% Ap-L, 75 → 200°C; 3 m, 5% SE-30, 75 → 200°C; tetradecane as an "internal standard"). The minor product **3-trimethylsilyloxy-1-heptene** [**6a**, M = $\mathrm{Si(CH_3)_3}$] was identified by gas chromatographic comparison with an authentic sample which was prepared by treating 1-hepten-3-ol (4.0 mL, 3.4 g, 29 mmol) with chlorotrimethylsilane (5.0 mL, 4.3 g, 40 mmol) in the presence of triethylamine (11 mL, 8.1 g, 80 mmol); 77%, bp 52 - 53°C/10 mmHg, n_D^{20} 1.4154. - IR : 3020 (w, ν[=C-H]), 1650 (w, ν[C=C]), 1260 (s, ν[C-O-C]). - ^{1}H-NMR (C_6D_6) : 5.79 (1 H, *ddd*, *J* 17.0, 10.2, 6.0), 5.15 (1 H, *ddd*, *J* 17.0, 2.0, 1.5), 4.96 (1 H, *ddd*, *J* 10.2, 2.0, 1.5), 4.0 (1 H, *m*), 1.6 (2 H, *m*), 1.4 (2 H, *m*), 1.3 (2 H, *m*), 0.87 (3 H, *t*, *J* 7.0), 0.13 (9 H, *s*). - MS : 171 (3%, M^+ - 15), 129 (45%), 73 (100%). - Calc. for $C_{10}H_{22}OSi$ (186.37) C 64.45, H 11.90; found C 64.55, H 11.80%.

The main product **(*Z*)-1-trimethylsilyloxy-1-heptene** [7a, M = $\mathrm{Si(CH_3)_3}$] [36] was isolated from a reaction carried out in the presence of potassium *tert*-butoxide (see chapter 4) by distillation; 68%, bp 69 - 70°C/10 mmHg, n_D^{20} 1.4216. - IR : 3060 (w, ν[=C-H]), 1655 (s, ν[C=C]), 1265 (s, ν[C-O-C]). - ^{1}H-NMR (C_6D_6) : 6.18 (1 H, *dt*, *J* 5.9, 1.4), 4.58 (1 H, *td*, *J* 7.0, 5.9), 2.29 (2 H, *tdd*, *J* 7.4, 7.2, 1.4), 1.4 (2 H, *m*), 1.3 (2 H, *m*), 0.87 (3 H, *t*, *J* 7.0), 0.08 (9 H, *s*). - MS : 186 (3%, M^+), 171 (5%), 129 (26%), 73 (100%). - Calc. for $C_{10}H_{22}OSi$ (186.37) C 64.45, H 11.90; found C 64.26, H 12.07%.

b) Allyl 3-Methylbutyl Ether (3b)

As described for allyl butyl ether (Section a), allyl 3-methylbutyl ether was consecutively treated with *sec*-butyllithium in tetrahydrofuran (1 h at -75°C) and with chlorotrimethylsilane (1 h at +25°C) to give **3-methylbutyl (*Z*)-3-trimethylsilyl-1-propenyl ether** [**5b**, M = $\mathrm{Si(CH_3)_3}$]; 75%, bp 83 - 85°C/10 mmHg, n_D^{20} 1.4362. - IR : 3020 (w, ν[=C-H]), 1655 (m, ν[C=C]), 1250 (s, ν[=C-O]). - ^{1}H-NMR (C_6D_6) : 5.85 (1 H, *dt*, *J* 6.0, 1.3), 4.40 (1 H, *td*, *J* 8.5, 6.2), 3.48 (2 H, *t*, *J* 6.7), 1.65 (2 H, *dd*, *J* 8.5, 1.3), 1.5 (1 H, *m*), 1.37 (2 H, *q*, *J* 6.7), 0.80 (6 H, *d*, *J* 6.8), 0.08 (9 H, *s*). - MS : 200 (1%; M^+), 129 (14%), 73 (100%). - Calc. for $C_{11}H_{24}OSi$ (200.40) C 65.93, H 12.07; found C 65.86, H 11.90%.

As described for allyl butyl ether (Section a), allyl 3-methylbutyl ether was consecutively treated with *sec*-butyllithium in tetrahydrofuran (1 h at -75°C and 2 h at +25°C) and chlorotrimethylsilane. The 1 : 3 mixture (68%, bp 75 - 82°C/10 mmHg) of **6b** [M = $\mathrm{Si(CH_3)_3}$] and **7b** [M = $\mathrm{Si(CH_3)_3}$] was separated by preparative gas chromatography (3 m, 10% Ap-L, 160°C). - **6-Methyl-3-trimethylsilyloxy-1-heptene** [**6b**, M = $\mathrm{Si(CH_3)_3}$] : n_D^{20} 1.4176. - IR : 3085 (w, ν[=C-H]), 1645 (w, ν[C=C]), 1250 (s, ν[C-O]). - ^{1}H-NMR (C_6D_6) : 5.79 (1 H, *ddd*, *J* 17.2, 10.2, 6.2), 5.15 (1 H, *ddd*, *J* 17.0, 2.0, 1.3), 4.97 (1 H, *ddd*, *J* 10.2, 2.0, 1.3), 4.03 (1 H, *ddt*, *J* 6.8, 5.8, 1.3), 1.5 (3 H, *m*), 1.3 (2 H, *m*), 0.89 (3 H, *d*, *J* 7.0), 0.88 (3 H, *d*, *J* 7.0), 0.17 (9 H, *s*). - MS : 200 (1%, M^+), 185 (9%), 129 (100%), 73 (76%). - Calc. for $C_{11}H_{24}OSi$ (200.40) C 65.93, H 12.07; found C 65.86, H 12.08%. - **(*Z*)-6-Methyl-1-trimethylsilyloxy-1-heptene** [**7b**, M = $\mathrm{Si(CH_3)_3}$] : n_D^{20} 1.4230. - IR : 3030 (w, ν[=C-H]), 1655 (m, ν[C=C]), 1255 (s, ν[=C-O]). - ^{1}H-NMR (C_6D_6) : 6.18 (1 H, *dt*, *J* 5.9, 1.5), 4.58 (1 H, *td*, *J* 7.2, 5.9), 2.28 (2 H, *tdd*, *J* 7.4, 7.2, 1.5), 1.5 (1 H, *m*), 1.4 (2 H, *m*), 1.2 (2 H, *m*), 0.86 (6 H, *d*, *J* 6.7), 0.07 (9 H, *s*). - MS : 200 (6%, M^+), 185 (12%), 129 (44%), 73 (100%). - Calc. for $C_{11}H_{24}OSi$ (200.40) C 65.93, H 12.07; found C 66.01, H 11.88%.

The starting material, **allyl 3-methylbutyl ether (3b)** [37], was prepared by stirring a mixture of 3-methylbutanol (44 g, 0.50 mol), allyl bromide (80 g, 0.66 mol), tetrabutylammonium bisulfate (20 g, 60 mmol) and sodium hydroxide (150 g, 3.6 mol) in water (0.15 L) 12 h at +25°C; 40 g (62%), bp 130 - 133°C, n_D^{20} 1.4100.

c) Allyl Nonyl Ether (3c)

As described for allyl butyl ether (Section a), allyl nonyl ether was consecutively treated with *sec*-butyllithium in tetrahydrofuran (1 h at -75°C) and with chlorotrimethylsilane to afford **nonyl (*Z*)-3-trimethylsilyl-1-propenyl ether [5c, M = $\mathrm{Si(CH_3)_3}$]**; 91%, bp 84 - 86°C/1 mmHg, n_D^{20} 1.4452. - IR : 3040 (w, ν[=C-H]), 1655 (m, ν[C=C]), 1250 (s, ν[=C-O]). - ^{1}H-NMR (C_6D_6) : 5.87 (1 H, *dt*, *J* 6.0, 1.2), 4.41 (1 H, *td*, *J* 8.5, 6.0), 3.47 (2 H, *t*, *J* 6.5), 1.66 (2 H, *dd*, *J* 8.6, 1.2), 1.5 (2 H, *m*), 1.3 (12 H, *m*), 0.90 (3 H, *t*, *J* 7.0), 0.09 (9 H, *s*). - MS : 256 (1%, M^+), 129 (100%), 73 (86%). - Calc. for $C_{15}H_{32}OSi$ (256.51) C 70.24, H 12.58; found C 70.05, H 12.46%.

As described for allyl butyl ether (Section a), allyl nonyl ether was consecutively treated with *sec*-butyllithium in tetrahydrofuran (1 h at -75°C and 2 h at -25°C) and chlorotrimethylsilane. The rearrangement products **6c** [M = $\mathrm{Si(CH_3)_3}$] and **7c** [M = $\mathrm{Si(CH_3)_3}$] as well as the by-products were identified by gas chromatographic comparison with authentic materials (3 m, 5% Ap-L, 100 → 200°C; 3 m, 5% SE-30, 100 → 200°C). - **3-Trimethylsilyloxy-1-dodecene** [**6c**, M = $\mathrm{Si(CH_3)_3}$] was identified by comparison with an authentic sample obtained by treatment of 1-dodecen-3-ol [38, 39] (prepared by addition of vinylmagnesium bromide [40] to decanal) with chlorotrimethylsilane in the presence of triethylamine as described for **6a** (in Section a); 78%; bp 67 - 68°C/1 mmHg; n_D^{20} 1.4320. - IR : 3080 (w, ν[=C-H]), 1645 (m, ν[C=C]), 1250 (s, ν[C-O]), 995 (w, δ[CH=CH_2]). - ^{1}H-NMR (C_6D_6) : 5.81 (1 H, *ddd*, *J* 16.8, 10.2, 6.0), 5.17 (1 H, *ddd*, *J* 16.8, 2.0, 1.5), 4.98 (1 H, *ddd*, *J* 10.2, 2.0, 1.5), 4.04 (1 H, *q*, broad, *J* 5.7), 1.6 (1 H, *m*), 1.5 (2 H, *m*), 1.3 (1 H, *m*), 1.27 (12 H, *s*), 0.90 (3 H, *t*, *J* 6.9), 0.15 (9 H, *s*). - MS : 256 (2%, M^+), 241 (9%), 129 (100%), 73 (86%). - Calc. for $C_{15}H_{32}OSi$ (256.51) C 70.24, H 12.58; found C 70.27, H 12.43%.

(*Z*)-1-Trimethylsilyloxy-1-dodecene [**7c**, M = $\mathrm{Si(CH_3)_3}$] was separately prepared by heating a mixture of dodecanal ("lauraldehyde", 11 mL, 9.2 g, 50 mmol), chlorotrimethylsilane (7.6 mL, 6.5 g, 60 mmol), triethylamine (14 mL, 10 g, 0.10 mol) and dimethylformamide (20 mL) 24 h to reflux temperature. Dilution with hexane (100 mL), washing with 5% aqueous hydrochloric acid (2 x 20 mL) and a saturated aqueous solution of sodium bicarbonate (3 x 20 mL) and distillation gave a 3 : 1 mixture of (*Z*)- and (*E*)-**7c**. The (*Z*)-isomer was isolated by preparative gas chromatography (3 m, 10% C-20M, 180°C); bp 96 - 98°/1 mmHg, n_D^{20} 1.4359. - IR : 3040 (w, ν[=C-H]), 1655 (m, ν[C=C]), 1255 (s, ν[=C-O]). - ^{1}H-NMR (C_6D_6) : 6.18 (1 H, *dt*, *J* 5.8, 1.5), 4.59 (1 H, *dt*, *J* 7.5, 5.8), 2.32 (2 H, *tt*, *J* 7.4, 1.5), 1.4 (2 H, *m*), 1.3 (14 H, *s*, broad), 0.90 (3 H, *t*, *J* 7.0), 0.08 (9 H, *s*). - MS : 256 (4%, M^+), 219 (5%), 129 (41%), 73 (100%). - Calc. for $C_{15}H_{32}OSi$ (256.51) C 70.24, H 12.58; found C 70.02, H 12.36%.

As described in the preceding Section for dodecanal, propanal was treated with chlorotriethylsilane in the presence of triethylamine to afford a 3 : 2 mixture of **(*Z*)- and (*E*)-1-triethylsilyloxy-1-propene**; 70%, bp 110 - 116°C/80 mmHg. - IR : 3040 (w, ν[=C-H]), 1660 (s, ν[C=C]), 1260 (s, ν[=C-O]). - ^{1}H-NMR (C_6D_6) : 6.29 (0.4 H, *dq*, *J* 11.8, 1.7), 6.23 (0.6 H, *dq*, *J* 5.8, 1.8), 5.12 (0.4 H, *dq*, *J* 12.5, 6.8), 4.52 (0.6 H, *dq*, *J* 7.5, 5.8), 1.71 (0.6 x 3 H, *dd*, *J* 6.8, 1.7), 1.47 (0.4 x 3 H, *dd*, *J* 6.8, 1.5), 0.98 (0.4 x 9 H, *t*, *J* 8.0), 0.96 (0.6 x 9 H, *t*, *J* 8.0), 0.61 (0.4 x 6 H, *q*, *J* 8.0), 0.58 (0.6 x 6 H, *q*, *J* 8.0). - MS : 172 (16%, M^+), 143 (93%), 116 (100%) 87 (63%). - Calc. for $C_9H_{20}OSi$ (172.34) C 62.72, H 11.70; found C 62.73, H 11.51%.

3-Triethylsilyloxy-1-propene [**8**, M = $\mathrm{Si(CH_3)_3}$] [41] : As described for **6a** (Section a), this *O*-silyl allyl ether was prepared by treating allyl alcohol with chlorotriethylsilane in the presence of triethylamine; 78%, bp 62 - 64°C/15 mmHg, n_D^{20} 1.4284. - IR : 3090 (w, ν[=C-H]), 1645 (w, ν[C=C]), 1180 (w, ν[C-O-C]), 1010 (w, δ[CH=CH_2]). - ^{1}H-NMR (C_6D_6) : 5.85 (1 H, *ddt*, *J* 17.2, 10.5, 4.5), 5.32 (1 H, *dq*, *J* 17.5, 2.0), 5.03 (1 H, *dq*, *J* 10.5, 2.0), 4.05 (2 H, *dt*, *J* 4.5, 2.0), 0.99 (9 H, *t*, *J* 7.5), 0.59 (6 H, *q*, *J* 7.5). - MS : 172 (26%, M^+), 143 (92%), 115 (99%), 87 (100%). - Calc. for $C_9H_{20}OSi$ (172.34) C 62.72, H 11.70; found C 62.80, H 11.67%.

As described for allyl 3-methylbutyl ether (Section b), the starting material, **allyl nonyl ether (3c)** [43] was prepared from 1-nonanol and allyl bromide under phase transfer conditions; 83%, bp 54 - 56°C/0.5 mmHg, n_D^{20} 1.4310. - IR : 3090 (w, ν[=C-H]), 1650 (m, ν[C=C]), 1180 (m, ν[C-O-C]), 1000 (w, δ[CH=CH_2]). - ^{1}H-NMR

($CDCl_3$) : 5.90 (1 H, *ddt, J* 17.2, 10.2, 5.6), 5.26 (1 H, *dq, J* 17.2, 1.8), 5.16 (1 H, *dq, J* 10.2, 1.8), 3.95 (2 H, *dt, J* 5.6, 1.8), 3.41 (2 H, *t, J* 6.8), 1.6 (2 H, *m*), 1.28 (12 H, *s*, broad), 0.88 (3 H, *s*). - MS : 184 (1%, M^+), 87 (100%), 71 (79%). - Calc. for $C_{12}H_{24}O$ (184.32) C 78.20, H 13.12; found C 78.32, H 13.05%.

d) Allyl Cyclopropylmethyl Ether (3d)

As described for allyl butyl ether (Section a), consecutive treatment of allyl cyclopropylmethyl ether with *sec*-butyllithium in tetrahydrofuran (15 min at -50°C) and chlorotrimethylsilane (30 min at +25°C) gave **cyclopropylmethyl (*Z*)-3-trimethylsilyl-1-propenyl ether [5d, M = $Si(CH_3)_3$]**; 75%, bp 72 - 73°C/10 mmHg, n_D^{20} 1.4507. - IR : 3040 (w, ν[=C-H]), 1665 (m, ν[C=C]), 1250 (s, ν[=C-O]). - ^{1}H-NMR (C_6D_6) : 5.88 (1 H, *dt, J* 6.2, 1.2), 4.42 (1 H, *td, J* 8.2, 6.2), 3.27 (2 H, *d, J* 6.8), 1.67 (2 H, *dd, J* 8.2, 1.2), 0.9 (1 H, *m*), 0.3 (2 H, *m*), 0.09 (9 H, *s*), 0.0 (2 H, *m*). - MS : 184 (14%, M^+), 130 (48%), 74 (70%), 57 (100%). - Calc. for $C_{10}H_{20}OSi$ (184.36) C 65.15, H 10.94; found C 64.99, H 10.92%.

As described for allyl butyl ether (Section a), allyl cyclopropylmethyl ether was consecutively treated with *sec*-butyllithium in tetrahydrofuran (1 h at -50°C, 15 h at -25°C and 2 h at +25°) and chlorotrimethylsilane. The 3 : 1 mixture (82%) of **6d** [M = $Si(CH_3)_3$] and **7d** [M = $Si(CH_3)_3$] was separated by preparative gas chromatography (3 m, 10% Ap-L, 140°C). - **4-Cyclopropyl-3-trimethylsilyloxy-1-butene [6d**, M = $Si(CH_3)_3$] : bp 50 - 51°C/10 mmHg, n_D^{20} 1.4278. - IR : 3010 (w, ν[=C-H]), 1645 (m, ν[C=C]), 1250 (s, ν[C-O]), 990 (w, δ[CH=CH_2]). - ^{1}H-NMR ($CDCl_3$) : 5.87 (1 H, *ddd, J* 17.0, 10.5, 6.0), 5.16 (1 H, *ddd, J* 17.0, 2.0, 1.5), 5.04 (1 H, *ddd, J* 10.5, 2.0, 1.5), 4.2 (1 H, *m*), 1.5 (2 H, *m*), 0.8 (1 H, *m*), 0.4 (2 H, *m*), 0.11 (9 H, *s*), 0.1 (2 H, *m*). - MS : 169 (6%, M^+ - 15), 130 (63%), 75 (86%). - Calc. for $C_{10}H_{20}OSi$ (184.4) C 65.15, H 10.94; found C 65.09, H 11.36%. - **(*Z*)-4-Cyclopropyl-1-trimethylsilyloxy-1-butene [7d**, M = $Si(CH_3)_3$]; bp 64 - 65°C/10 mmHg, n_D^{20} 1.4339. - IR : 3020 (w, ν[=C-H]), 1660 (m, ν[C=C]), 1250 (s, ν[=C-O]). - ^{1}H-NMR ($CDCl_3$) : 6.13 (1 H, *dt, J* 6.0, 1.5), 4.55 (1 H, *td, J* 7.1, 6.0), 2.17 (2 H, *ddd, J* 7.7, 7.5, 1.5), 1.24 (2 H, *dt, J* 7.7, 7.0), 0.7 (1 H, *m*), 0.4 (2 H, *m*), 0.18 (9 H, *s*), 0.0 (2 H, *m*). - MS : 184 (4%, M^+), 169 (10%), 129 (44%), 74 (100%). - Calc. for $C_{10}H_{20}OSi$ (184.36) C 65.15, H 10.94; found C 65.07, H 11.15%.

Trace amounts of the ring opened products **19** and **20** were identified by gas chromatographic comparison (2 m 5% SE-30, 50 → 200°C; 2 m 5% ApL, 65 → 200°C) with authentic samples prepared by treatment of 1,6-heptadien-3-ol [43], and respectively, 6-heptenal [44] with chlorotrimethylsilane in the presence of triethylamine. - **3-Trimethylsilyloxy-1,6-heptadiene** [**19**, M = $Si(CH_3)_3$] : bp 59 - 60°C/15 mmHg, n_D^{20} 1.4248. - IR : 3080 (w, ν[=C-H]), 1645 (m, ν[C=C]), 1250 (s, ν[C-O]), 990 (m, δ[CH=CH_2]). - ^{1}H-NMR (C_6D_6) : 5.8 (2 H, *m*), 5.11 (1 H, *dt, J* 17.2, 1.6), 5.01 (1 H, *dq, J* 17.2, 1.8), 5.0 (2 H, *m*), 4.06 (1 H, *qt, J* 6.3, 1.2), 2.1 (2 H, *m*), 1.6 (1 H, *m*), 1.5 (1 H, *m*), 0.08 (9 H, *s*). - MS : 183 (0.2%, M^+ - 1), 169 (4%), 129 (100%), 73 (60%). - Calc. for $C_{10}H_{20}OSi$ (184.36) C 65.15, H 10.94; found C 64.99, H 10.93%. - **(*Z*)-1-Trimethylsilyloxy-1,6-heptadiene** [*Z*-**20**, M = $SI(CH_3)_3$] : bp 66 - 68°C/10 mmHg, n_D^{20} 1.4312. - IR : 3035 (w, ν[=C-H]), 1655 (m, ν[C=C]), 1255 (s, ν[=C-O]), 995 (w, δ[CH=CH_2]). - ^{1}H-NMR (C_6D_6) : 6.16 (1 H, *dt, J* 6.0, 1.5), 5.80 (1 H, *ddt, J* 17.2, 10.2, 6.5), 5.02 (1 H, *ddt*, 17.2, 2.0, 1.5), 4.96 (1 H, *ddt, J* 10.2, 2.0, 1.2), 4.52 (1 H, *td, J* 7.2, 6.0), 2.25 (2 H, *dtd, J* 7.5, 7.2, 1.5), 2.06 (2 H, *dddt, J* 7.5, 6.5, 2.0, 1.2), 1.46 (2 H, *pent, J* 7.5), 0.06 (9 H, *s*). - MS : 169 (1%, M^+ - 15), 142 (5%), 129 (19%), 73 (100%). - Calc. for $C_{10}H_{20}OSi$ (184.36) C 65.15, H 10.94; found C 64.98, H 10.80%. - **(*E*)-1-Trimethylsilyloxy-1,6-heptadiene (*E*-20)** : bp 66 - 68°C/10 mmHg, n_D^{20} 1.4332. - IR : 3040 (w, ν[=C-H]), 1665 (m, ν[C=C]), 1255 (s, ν[=C-O]), 995 (w, δ[CH=CH_2]). - ^{1}H-NMR (C_6D_6) : 6.27 (1 H, *dt, J* 12.0, 1.2), 5.74 (1 H, *ddt, J* 17.0, 10.2, 6.8), 5.13 (1 H, *dt, J* 12.0, 7.5), 5.01 (1 H, *ddt, J* 17.2, 2.0, 1.2), 4.97 (1 H, *ddt, J* 10.2, 2.0, 1.2), 1.98 (2 H, *dddt, J* 7.5, 6.8, 2.0, 1.2), 1.85 (2 H, *qd, J* 7.3, 1.2), 1.35 (2 H, *pent, J* 7.5), 0.10 (9 H, *s*). - MS : 169 (1%, M^+ - 15), 142 (6%), 129 (28%), 73 (100%). - Calc. for $C_{10}H_{20}OSi$ (184.4) C 65.15, H 10.94; found C 65.14, H 10.81%.

The starting material, **allyl cyclopropylmethyl ether** [45] was prepared from cyclopropylmethanol and allyl bromide again under phase transfer conditions (see Section b); 91%, bp 81 - 82°C/165 mmHg, n_D^{20} 1.4300. - IR : 3020 (w, ν[=C-H]), 1650 (m, ν[C=C]), 1260 (m, ν[C-O-C]). - ^{1}H-NMR (C_6D_6) : 5.93 (1 H, *ddt, J* 17.2, 10.3, 5.58), 5.28 (1 H, *dq, J* 17.0, 1.7), 5.16 (1 H, *dq, J* 10.3, 1.5), 4.00 (2 H, *dt, J* 5.8, 1.3), 3.28 (2 H, *d, J* 7.0), 1.07 (1 H, *ttt*, 8.0, 7.0, 4.8), 0.53 (2 H, *ddd, J* 8.0, 6.2, 4.8), 0.21 (2 H, *dt, J* 6.2, 4.8). - MS : 112 (0.1%, M^+), 84 (10%), 55 (100%).

e) Allyl 1-Ethylpropyl Ether (3e)

As described for allyl butyl ether (Section a), allyl 1-ethylpropyl ether (3e) was consecutively treated with *sec*-butyllithium in tetrahydrofuran (1 h at -75°C) and chlorotrimethylsilane to give **1-ethylpropyl (*Z*)-3-trimethylsilyl-1-propenyl ether [5e, M = $Si(CH_3)_3$]**; 82%, bp 77 - 78°C/10 mmHg, n_D^{20} 1.4366. - IR : 3040 (w ν[=C-H]), 1655 (m, ν[C=C]), 1245 (s, ν[=C-O]). - ^{1}H-NMR (C_6D_6) : 5.87 (1 H, *dt*, *J* 6.2, 1.2), 4.35 (1 H, *td*, 8.4, 6.2), 3.2 (1 H, *m*), 1.63 (2 H, *dd*, *J* 8.4, 1.2), 1.4 (4 H, *m*), 0.84 (6 H, *t*, *J* 7.4), 0.08 (9 H, *s*). - MS : 200 (5% M^+), 129 (6%), 73 (100%). - Calc. for $C_{11}H_{24}OSi$ (200.40) C 65.93, H 12.07; found C 65.97, H 12.05%.

As described for allyl butyl ether (Section a), allyl 1-ethylpropyl ether (3e) was consecutively treated with *sec*-butyllithium in tetrahydrofuran (1 h at -75°C and 2 h at 25°C) and chlorotrimethylsilane (2 h at +25°C). A 1 : 1 mixture (77%) of **6e** [M = $Si(CH_3)_3$] and **7e** [M = $Si(CH_3)_3$] was obtained and separated by preparative gas chromatography (3 m, 10% Ap-L, 155°C). - **4-Ethyl-3-trimethylsilyloxy-1-hexene [6e, M = $Si(CH_3)_3$]** : n_D^{20} 1.4229. - IR : 3080 (w, ν[=C-H]), 1645 (m, ν[C=C]), 1255 (s, ν[C-O]), 995 (w, δ[CH=CH_2]). - ^{1}H-NMR (C_6D_6) : 5.78 (1 H, *ddd*, *J* 17.1, 10.3, 6.3), 5.16 (1 H, *dt*, *J* 17.1, 1.7), 5.02 (1 H, *ddd*, *J* 10.4, 2.0, 1.3), 4.1 (1 H, *m*), 1.4 (4 H, *m*), 1.3 (1 H, *m*), 0.90 (3 H, *t*, *J* 7.5), 0.89 (3 H, *t*, *J* 7.5), 0.13 (9 H, *s*). - MS : 185 (2%, M^+ - 15), 129 (66%), 73 (100%). - Calc. for $C_{11}H_{24}OSi$ (200.40) C 65.93, H 12.07; found C 65.99, H 12.03%. - **(*Z*)-4-Ethyl-1-trimethylsilyloxy-1-hexene [7e, M = $Si(CH_3)_3$]** : n_D^{20} 1.4280. - IR : 3040 (*w*, ν[=C-H]), 1655 (*m*, ν[C=C]), 1255 (*s*, ν[=C-O]). - ^{1}H-NMR (C_6D_6) : 6.22 (1 H, *dt*, *J* 5.8, 1.5), 4.54 (1 H, *td*, *J* 7.5, 5.8), 2.29 (2 H, *ddd*, *J* 7.5, 5.8, 1.5), 1.4 (4 H, *m*), 1.3 (1 H, *m*), 0.92 (6 H, *t*, *J* 7.5), 0.08 (9 H, *s*). - MS : 200 (1%, M^+), 185 (2%), 129 (36%), 73 (100%). - Calc. for $C_{11}H_{24}OSi$ (200.40) C 65.93, H 12.07; found C 66.02, H 11.85%.

The starting material, **allyl 1-ethylpropyl ether (3e)**, was prepared from 3-pentanol and allyl bromide under phase transfer conditions (see Section b); 26%, bp 129 - 130°C, n_D^{20} 1.4109. - IR : 3080 (w, ν[=C-H]), 1640 (m, ν[C=C]), 1180 (m, ν[C-O-C]), 995 (w, δ[CH=CH_2]). - ^{1}H-NMR ($CDCl_3$) : 5.93 (1 H, *ddt*, *J* 17.3, 10.3, 5.7), 5.28 (1 H, *dq*, *J* 17.0, 1.7), 5.15 (1 H, *ddt*, *J* 10.1, 1.6, 1.5), 3.99 (2 H, *dt*, *J* 5.7, 1.3), 3.19 (1 H, *pent*, *J* 5.8), 1.53 (4 H, *qd*, *J* 7.4, 5.8), 0.92 (6 H, *t*, *J* 7.4). - MS : 99 (1%, M^+ - 29), 57 (100%). - Calc. for $C_8H_{16}O$ (128.22) C 74.94, H 12.58; found C 74.92, H 12.66%.

f) Allyl *tert*-Butyl Ether (3f)

As described for allyl butyl ether (Section a), allyl *tert*-butyl ether (3f) was treated with *sec*-butyllithium in tetrahydrofuran just 1 h at -75°C and subsequently with chlorotrimethylsilane to give ***tert*-butyl (*Z*)-3-trimethylsilyl-1-propenyl ether [5f, M = $Si(CH_3)_3$]**; 43%, bp 60 - 61°C/12 mmHg, n_D^{20} 1.4306. - IR : 3030 (w, ν[=C-H]), 1645 (m, ν[C=C]), 1240 (s, ν[=C-O]). - ^{1}H-NMR (C_6D_6) : 6.11 (1 H, *dt*, *J* 6.2, 1.2), 4.48 (1 H, *td*, *J* 8.5, 6.2), 1.66 (2 H, *dd*, *J* 8.5, 1.2), 1.09 (9 H, *s*), 0.09 (9 H, *s*). - MS : 186 (2%, M^+), 130 (10%), 115 (25%), 73 (100%). - Calc. for $C_{10}H_{22}OSi$ (186.37) C 64.45, H 11.90; found C 64.55, H 11.83%.

As described for allyl butyl ether (Section a), allyl *tert*-butyl ether (3f) was consecutively treated with *sec*-butyllithium in tetrahydrofuran (1 h at -75°C and 3 h at +25°C) and chlorotrimethylsilane (2 h at +25°C). The resulting 2 : 1 mixture (69%, bp 40 - 64°C/17 mmHg) of **6f** [M = $Si(CH_3)_3$] and **7f** [M = $Si(CH_3)_3$] was separated by preparative gas chromatography (3 m, 10% Ap-L, 125°C). - **4,4-Dimethyl-3-trimethylsilyloxy-1-pentene [6f, M = $Si(CH_3)_3$]** : n_D^{20} 1.4136. - IR : 3065 (w, ν[=C-H]), 1635 (m, ν[C=C]), 1245 (s, ν[C-O]). - ^{1}H-NMR (C_6D_6) : 5.80 (1 H, *ddd*, *J* 17.0, 10.2, 6.2), 5.08 (1 H, *ddd*, *J* 17.0, 2.0, 1.0), 5.00 (1 H, *ddd*, *J* 10.2, 2.0, 1.0), 3.63 (1 H, *ddd*, *J* 6.2, 2.0, 1.0), 0.92 (9 H, *s*), 0.12 (9 H, *s*). - MS : 171 (2%, M^+ - 15), 129 (45%), 73 (100%). - Calc. for $C_{10}H_{22}OSi$ (186.37) C 64.45, H 11.90; found C 64.54, H 12.03%. - **(*Z*)-4,4-Dimethyl-1-trimethylsilyloxy-1-pentene [7f, M = $Si(CH_3)_3$]** : n_D^{20} 1.4182. - IR : 3025 (w, ν[=C-H]), 1645 (m, ν[C=C]), 1250 (s, ν[=C-O]). - ^{1}H-NMR (C_6D_6) : 6.24 (1 H, *dt*, *J* 6.0, 1.2), 4.61 (1 H, *td*, *J* 7.8, 6.0), 2.22 (2 H, *dd*, *J* 7.8, 1.2), 0.98 (9 H, *s*), 0.06 (9 H, *s*). - MS : 186 (6%, M^+), 171 (6%), 129 (49%), 73 (100%). - Calc. for $C_{10}H_{22}OSi$ (186.37) C 64.45, H 11.90; found C 64.94, H 12.00%.

The starting material **allyl *tert*-butyl ether (3f)** [46] was prepared by adding allyl bromide (20 mL, 29 g, 0.24 mol) in the course of 15 min to a solution of potassium *tert*-butoxide (23 g, 0.20 mol) and 1,4,7,10,13,16-hexaoxacyclooctadecane ("18-crown-6", 2.7 g, 10 mmol) in tetrahydrofuran (0.10 L) [47]. After keeping the mixture 15 h at +25°C, it was diluted with water (0.25 L) and extracted with pentane (3 x 50 mL). Distillation by means of a Fischer "Spaltrohr" column allowed to collect an analytically pure product; 7.0 g (31%; bp 96 - 97°C; n_D^{20} 1.4011).

g) **Allyl 1-(7,7-Dimethylbicyclo[2.2.1]heptyl) Ether (3g)**

As described for allyl butyl ether (Section a), allyl 1-(7,7-dimethylbicyclo[2.2.1]heptyl ether (**3g**) was consecutively treated with *sec*-butyllithium in tetrahydrofuran (1 h -75°C) and with chlorotrimethylsilane to afford **1-(7,7-dimethylbicyclo[2.2.1]heptyl (*Z*)-3-trimethylsilyl-1-propenyl ether** [**5g**, M = Si(CH$_3$)$_3$]; 64%; bp 180 - 190°C/ 1 mmHg; n_D^{20} 1.4760. - IR : 3040 (w, ν[=C-H]), 1655 (m, ν[C=C]), 1250 (s, ν[=C-O]). - ^{1}H-NMR (C$_6$D$_6$) : 6.14 (1 H, *dt*, *J* 6.4, 1.5), 4.45 (1 H, *td*, *J* 8.5, 6.0), 1.7 (4 H, *m*), 1.67 (2 H, *dd*, *J* 8.5, 1.2), 1.5 (2 H, *m*), 1.4 (1 H, *m*), 1.1 (2 H, *m*), 0.89 (6 H, *s*), 0.11 (9 H, *s*). - MS : 252 (40%, M^+), 237 (6%), 129 (100%). - Calc. for $C_{15}H_{28}OSi$ (252.47) C 71.36, H 11.18; found C 71.24, H 11.05%.

Under a variety of reaction conditions no rearrangement products were found. Only small amounts of 7,7-dimethylbicyclo[2.2.1]heptan-1-ol (or, after trapping with chlorotrimethylsilane, of the corresponding *O*-trimethylsilyl ether) and (*Z*)-**5g** as well as traces of (*E*)-**5g** were identified.

The starting material, **allyl 1-(7,7-dimethylbicyclo[2.2.1]heptyl) ether** (**3g**), was prepared by refluxing a solution of 7,7-dimethylbicyclo[2.2.1]heptan-1-ol [48] (4.6 g, 33 mmol) in tetrahydrofuran (30 mL) 2 h in the presence of potassium hydride (1.5 g, 37 mmol) before adding allyl bromide (12.0 g, 99 mmol). After 15 h at 25°C the mixture was absorbed on silica gel (15 g) and the dry powder was poured on top of a column filled with fresh silica gel (35 g). Elution with hexane (0.2 L) and distillation gave a colorless oil; 4.5 g (76%), bp 35 - 37°C/ 1 mmHg, n_D^{20} 1.4692. - IR : 3090 (w, ν[=C-H]), 1650 (m, ν[C=C]), 1180 (w, ν[C-O-C]). - ^{1}H-NMR (C$_6$D$_6$) : 5.89 (1 H, *ddt*, *J* 16.8, 10.5, 5.1), 5.31 (1 H, *dq*, *J* 17.2, 1.9), 5.04 (1 H, *dq*, *J* 10.5, 1.9), 3.84 (2 H, *dt*, *J* 4.9, 1.9), 1.8 (2 H, *m*), 1.6 (2 H, *m*), 1.5 (2 H, *m*), 1.4 (1 H, *m*), 1.2 (2 H, *m*), 1.04 (6 H, *s*). - MS : 180 (4%, M^+), 165 (10%), 55 (100%). - Calc. for $C_{12}H_{20}O$ (180.29) C 79.94, H 11.18; found C 80.04, H 11.07%.

3. Temperature Threshold for the Rearrangement

At -75°C, allyl nonyl ether, allyl 1-ethylpropyl ether or allyl *tert*-butyl ether (5.0 mmol in each case) was added to a solution of *sec*-butyllithium (5.3 mmol, from which the original isopentane solvent had been removed) in tetrahydrofuran (10 mL). After 1 h at -75°C the desired temperature was adjusted and kept constant during the specified period (see table 4). Then chlorotrimethylsilane (1.3 mL, 1.1 g, 10 mmol) and *N,N,N',N'*-tetramethylethylenediamine (3 mL) were added. After 2 h at 25°C the mixture was diluted with hexane (20 mL) and washed with 2% aqueous sulfuric acid (2 x 5 mL), with a saturated solution of sodium bicarbonate (2 x 5 mL) and water (5 mL). The product composition was analyzed by gas chromatography (3 m, 5% Ap-L or C-20M, 80 → 180°C).

Table 4. Transformation of metalated alkyl allyl ethers as a function of reaction time and temperature.

$H_2C=CH-CH_2OR$	react.time and temp.	recov'd start.mat.	silylated start.mat.	olefin by α',β-cleavage	1.2-rearr. product	1.4-rearr. product
OR = OC_9H_{19}	24h - 75°C	6%	81%	1%	1%	1%
	4h - 50°C	5%	54%	9%	~ 3%	28%
	24h - 50°C	4%	6%	25%	7%	49%
	2h - 25°C	4%	< 2%	21%	15%	53%
OR = $OCH(C_2H_5)_2$	24h - 75°C	1%	80%	a)	< 1%	< 1%
	4h - 50°C	1%	55%	a)	6%	6%
	24h - 50°C	1%	28%	a)	25%	29%
	2h - 25°C	1%	2%	a)	35%	38%
OR = $OC(CH_3)_3$	24h - 75°C	7%	76%	a)	6%	1%
	4h - 50°C	5%	22%	a)	47%	13%
	24h - 50°C	8%	4%	a)	60%	17%
	2h - 25°C	8%	2%	a)	59%	20%

a) Not determined.

4. The Potassium *tert*-Butoxide Effect on the Rearrangement

As described in the preceding chapter, the alkyl allyl ether (5.0 mmol) was reacted with *sec*-butyllithium (5.3 mmol) in tetrahydrofuran (10 mL) 1 h at -75°C before potassium *tert*-butoxide (5.8 mmol) was added. After 2 h at +25°C, the mixture was treated with chlorotrimethylsilane (1.3 mL, 1.1 g, 10 mmol) and *N,N,N',N'*-tetramethylethylenediamine (3 mL), diluted with hexane (20 mL), washed and analyzed by gas chromatography (using 3 m long 5% Ap-L and 5% SE-30 columns as well as an internal standard).

5. Pheromone Synthesis

Allyl (*S*)-4-Methylhexyl Ether (10)

After addition of magnesium turnings (1.5 g, 61 mmol), a solution of (*S*)-3-methylpentyl bromide [49] (7.6 g, 50 mmol), prepared by treating the corresponding alcohol with *N*-bromosuccinimide and triphenylphosphine [50] in tetrahydrofuran (25 mL), was heated 1 h to reflux, then filtered through glass wool and added dropwise, in the course of 15 min, to allyl chloromethyl ether [51] (5.6 g, 53 mmol). After 2 h heating to reflux, the mixture was poured into water (50 mL) and extracted with hexane (2 x 25 mL). Distillation afforded **10** as a colorless liquid; 5.5 g (77%), bp 82 - 85°C/50 mmHg, n_D^{20} 1.4188, $[\alpha]_D^{20}$ +8.5° (ethanol, *c* 5.1). - IR : 3080 (w, ν[=C-H]), 1640 (w, ν[C=C]), 1180 (m, ν[C-O-C]), 990 (w, δ[CH=CH$_2$]). - ^{1}H-NMR (CDCl$_3$) : 5.93 (1 H, *ddt*, *J* 16.8, 10.5, 5.6), 5.28 (1 H, *ddt*, *J* 16.8, 1.7, 1.5), 5.18 (1 H, *ddt*, *J* 10.5, 1.7, 1.5), 3.98 (2 H, *dt*, *J* 5.6, 1.5), 3.5 (2 H, *m*), 1.6 (1 H, *m*), 1.5 (1 H, *m*), 1.4 (2 H, *m*), 1.2 (1 H, *m*), 0.87 (3 H, *d*, *J* 6.2), 0.86 (3 H, *t*, *J* 7.5). - MS : 142 (12%, M^+), 113 (26%), 85 (13%), 71 (100%). - Calc. for $C_9H_{18}O$ (142.24) C 76.00, H 12.76; found C 76.05, H 12.86%.

(*S*)-6-Methyloctanal (11)

Allyl (*S*)-4-methylhexyl ether (5.4 g, 38 mmol) was added to a solution of *sec*-butyllithium (40 mmol) in tetrahydrofuran (50 mL) at - 75°C. After 1 h potassium *tert*-butoxide (5.0 g, 45 mmol) is added. The mixture was kept 0.5 h at - 75°C, 72 h at - 30°C and 1.5 h at + 25°C before being treated with chlorotrimethylsilane (10.1 mL, 8.7 g, 80 mmol) and *N,N,N',N'*-tetramethylethylenediamine (15 mL). After 2 h at 25°C, a 1 M aqueous solution of sodium hydroxide (50 mL) was added to the mixture. After 1.5 h of vigorous stirring, the organic layer was separated and the aqueous one extracted with hexane (3 x 50 mL). The combined organic phases were washed with 2% aqueous sulfuric acid (2 x 50 mL), a saturated aqueous solution of sodium bicarbonate (2 x 50 mL) and brine (50 mL). Upon evaporation remained a residue which was absorbed on silica gel and eluted with a 1 : 20 mixture of diethyl ether and hexane (0.5 L). Distillation under reduced pressure gave **11** [52] as a colorless liquid; 3.65 g (64%), bp 71 - 72°C/10 mmHg, n_D^{20} 1.4246, α_D^{20} +9.3° (chloroform, *c* 1.4). - IR : 1715 (s, ν[C=O]). - ^{1}H-NMR (CDCl$_3$) : 9.79 (1 H, *t*, *J* 1.8), 2.44 (2 H, *td*, *J* 7.5, 1.8), 1.6 (2 H, *m*), 1.3 (5 H, *m*), 1.1 (2 H, *m*), 0.9 (6 H, *m*). - MS : 142 (1%, M^+), 124 (3%), 113 (6%), 95 (48%), 57(100%). - Calc. for $C_9H_{18}O$ (142.24) C 76.00, H 12.76; found C 75.93, H 12.71%.

(*S,Z*)-14-Methyl-8-hexadecen-1-ol (12)

At -90°C (*S*)-6-methyloctanal (2.8 g, 20 mmol) in tetrahydrofuran (10 mL) was added dropwise to an "instant ylid" [19] preparation of triphenylphosphonio-8-sodiooxyoctanide (30 mmol) in tetrahydrofuran (100 mL). After 1 h at + 25°C, hexane (200 mL) was added, the precipitate removed by filtration, the filtrate washed with water (2 x 50 mL), concentrated and distilled. A colorless liquid was collected; 3.9 g (76%), bp 123 - 124°C/0.1 mmHg (lit. [17] : 132 - 133°C/0.2 mmHg), n_D^{20} 1.4583 (lit. [17] : n_D^{20} 1.4580), α_D^{20} +5.3° (chloroform, *c* 4.6; lit. [17] : α_D^{20} +5.3°). - IR : 3610 (m, ν[O-H]), 3450 (s, ν[O-H]), 3005 (w, ν[=C-H]), 1645 (m, ν[C=C]). - ^{1}H-NMR (CDCl$_3$) : 5.4 (2 H, *m*), 3.65 (2 H, *t*, *J* 6.8), 2.0 (4 H, *m*), 1.68 (1 H, *s*), 1.6 (2 H, *m*), 1.34 (15 H, *s*, broad), 1.1 (2 H, *m*), 0.9 (6 H, *m*). - MS : 254 (6%, M^+), 236 (1%), 225 (1%), 41 (100%).

A (*Z/E*)-ratio of approximately 97 : 3 was determined by multifold integration of the singulet-like signals of *cis*- and *trans*-olefinic hydrogen nuclei (δ 5.34 and 5.38 ppm, respectively), while the allylic positions (δ 2.0 ppm) were irradiated.

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