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1,2-ELIMINATION OF ALCOHOL FROM HOMOALLYL ETHERS UNDER THE INFLUENCE OF MIXED METAL BASES

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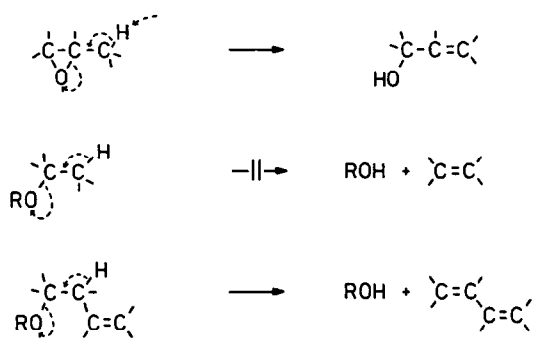
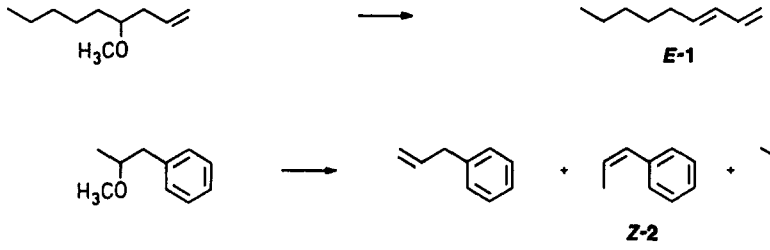
Summary : Lithium diisopropylamide in the presence of catalytic amounts of potassium *tert*-butoxide smoothly converts homoallyl or homobenzyl type ethers to dienes (*e.g.*, **1**, **3**, **5**, **26**) or styrenes (**2**). γ,δ-Unsaturated acetals give 1,3-dienyl ethers (*e.g.*, **4**) and 4-alkylidenetetrahydropyrans or dihydropyrans produce a variety of dienols (*e.g.*, **6 - 17, 20 - 22**). - If there is a choice, the new double bond is formed with high *trans*-selectivity while the configuration of existing double bonds is retained. - The elimination mode is *syn*-periplanar and concerted, though E1cb like.

Relief of ring strain provides a crucial driving force for the reaction of 2,3-dialkyl substituted oxiranes with potassium *tert*-butoxide activated lithium diisopropylamide ("LIDAKOR") to give allyl alcohols [1]. Ordinary ethers such as diethyl ether, tetrahydropyran and even tetrahydrofuran are inert towards this base mixture, at least below 25 °C. One can, however, immensely increase the propensity towards elimination by introducing insaturation in the γ,δ-position with respect to the ether function. In other words, acyclic or cyclic homoallyl (or homobenzyl) ethers readily undergo 1,2-elimination of alcohol to afford conjugated dienes (or styrenes) [2].

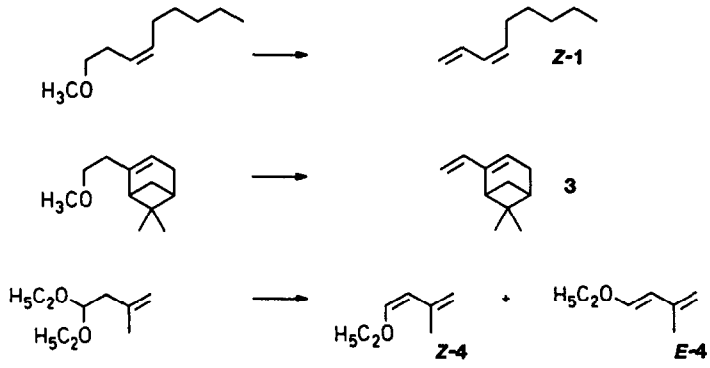


The present as the preceding and following article are dedicated to Dr. Gunther Ohloff, Geneva, former visiting professor at the University of Lausanne, on the occasion of his 65th birthday.

Thus, 4-methoxy-1-nonene leads to 1,3-nonadiene (*E*-**1**, 76%, *cis* : *trans* = 5 : 95) while 2-methoxy-1-phenylpropane produces 1-phenyl-1-propene (**2**, 86%, *cis* : *trans* = 30 : 70) and allylbenzene (10% presumably through base-catalyzed isomerization of **2**). In these as in other cases, best results were achieved with 0.1 molar equivalents of potassium *tert*-butoxide being added to the solution of lithium diisopropylamide in tetrahydrofuran at -50 °C.

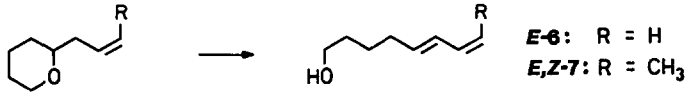


Alkyl substituents are tolerated not only at the α-, but also at the γ- and δ-position. The *cis*-configuration of (*Z*)-1-methoxy-3-nonene remains intact when this ether is converted to 1,3-nonadiene (*Z*-**1**, 80%, *cis* : *trans* > 95 : 5). The pinene derivative 2-(2-methoxyethyl)-6,6-dimethyl-2-bicyclo[3.1.1]heptene ("methyl nopyl ether") readily eliminates methoxide to give 6,6-dimethyl-2-vinyl-2-bicyclo[3.1.1]heptene (**3**, "nopadiene", 72%). Homoallylic acetals produce 1-alkoxy-1,3-dienes as exemplified by the formation of 1-ethoxy-3-methyl-1,3-butadiene (**4**, 91%, *cis* : *trans* = 1 : 1).



Alkyl branching at the β-position markedly slows down the reaction. Under standard conditions 3-methoxymethyl-1-octene gives with only a moderate yield 2-pentyl-1,3-butadiene (**5**, 58%).

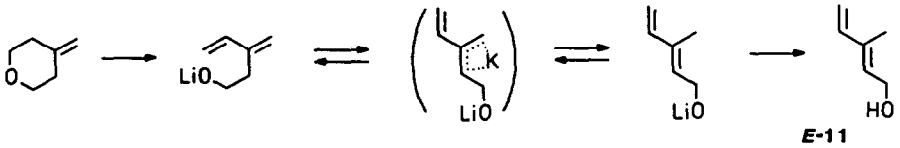
Incorporation of the ether function into a heterocycle does not alter the course of the elimination reaction. 2-Allyl- and (*Z*)-2-(2-butenyl)tetrahydropyran afford the corresponding elimination products, 5,7-octadien-1-ol (**6**, 72%) and (7*Z*)-5,7-nonadien-1-ol (**7**, 70%) with high *trans*-selectivity as far as the newly formed double bond is concerned.



In 4-methylenetetrahydropyrans the oxygen atom again occupies a homoallylic position. Therefore, such substrates are also prone to LIDAKOR promoted β-elimination as illustrated by the conversion of 2-methyl-4-methylenetetrahydropyran to 4-methylene-5-hexen-2-ol (**8**, 86%), of 2-ethyl-4-methylenetetrahydropyran to 5-methylene-6-hepten-3-ol (**9**, 87%) and of 2-(2-methylpropyl)-4-methylenetetrahydropyran to 2-methyl-6-methylene-7-octen-4-ol ("ipsenol", **10**, 83%). The latter compound has been identified as a major pheromone component of bark beetles [3].

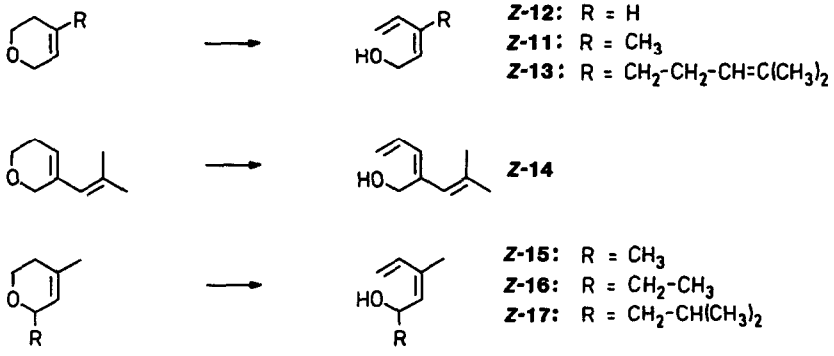
8: R = CH_3
9: R = CH_2-CH_3
10: R = CH_2-$CH(CH_3)_2$

The parent heterocycle 4-methylenetetrahydropyran should lead to 4-methylene-5-penten-1-ol. In this case, however, the original ring opening product can not be isolated as such. It rapidly undergoes base catalyzed isomerization to produce, after neutralization of the alcoholate, the thermodynamically more stable (*E*)-3-methyl-2,4-pentadien-1-ol (*E*-**11**, 48%).



E-**11**

Finally, 5,6-dihydro-2*H*-pyrans offer a simple and stereocontrolled entry to alkadienols, the *cis*-configuration of the double bond in the heterocyclic precursor being fully retained in the products. As shown by a few examples, a variety of pentadienyl type alcohols can be prepared by this method : (*Z*)-2,4-pentadien-1-ol (*Z*-**12**, 65%), (*Z*)-3-methyl-2,4-pentadien-1-ol (*Z*-**11**, 77%), (*Z*)-7-methyl-3-vinyl-2,6-octadien-1-ol (*Z*-**13**, 74%), (*Z*)-2-(2-methyl-1-propenyl)-2,4-pentadien-1-ol (*Z*-**14**, 55%), (*Z*)-4-methyl-3,5-hexadien-2-ol (*Z*-**15**, 81%), (*Z*)-5-methyl-4,6-heptadien-3-ol (*Z*-**16**, 87%) and (*Z*)-2,6-dimethyl-5,7-octadien-4-ol (*Z*-**17**, 58%).



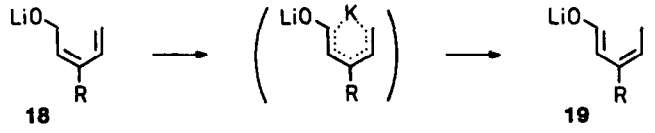
***Z*-12:** R = H
***Z*-11:** R = CH_3
***Z*-13:** R = CH_2-CH_2-CH=$C(CH_3)_2$

***Z*-14**

***Z*-15:** R = CH_3
***Z*-16:** R = CH_2-CH_3
***Z*-17:** R = CH_2-$CH(CH_3)_2$

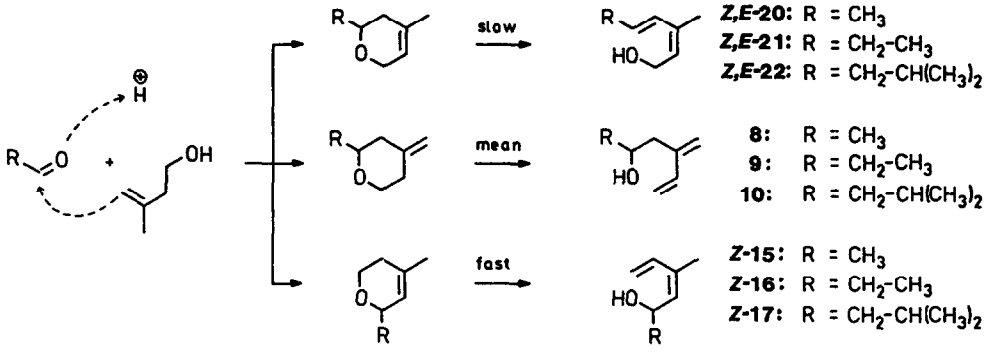
With $\beta,\gamma;\delta,\epsilon$-unsaturated alcohols the yields are obviously much lower than in the case of other ring opening products. (All percentage numbers refer, of course, to isolated and purified material.) This reflects, to some extent, losses during the work-up due to the particular sensitivity of pentadienyl type alcohols towards autoxida-

tion and acid catalyzed polymerization. Moreover, we suspect the 2,4-dien-1-olates **18** emerging from the ring opening elimination process to be particular prone to deprotonation [4] by strong bases. In this way, they may be isomerized to 1,3-dienolates **19** which then may be fatally consumed by autocondensation reactions. In order to minimize this threat it is preferable to use potassium *tert*-butoxide in catalytic (5 - 10 mol%) rather than stoichiometric amounts.



18 **19**

Unsaturated tetrahydropyrans are accessible by many expedient routes, among them the Kriewitz-Prins reaction and related modifications [5]. This latter method frequently provides a mixture of regioisomeric products. For example, treatment of 3-methyl-3-buten-1-ol with acetaldehyde, propanal or isovaleraldehyde and acid produces an approximate 20 : 50 : 30 mixture of 2-methyl-, 2-ethyl- or 2-isobutyl-4-methylenetetrahydropyran, 2-methyl-, 2-ethyl- or 2-isobutyl-4-methyl-3,6-dihydro-2*H*-pyran and 2-methyl-, 2-ethyl- or 2-isobutyl-4-methyl-5,6-dihydro-2*H*-pyran. Though, imperfect, a kinetic separation of these mixtures is possible. The substrates having the exocyclic double bond and leading to the alcohols **8**, **9** and **10** react roughly 3 times slower than the 5,6-dihydro-isomers (affording *Z*-**15**, *Z*-**16** and *Z*-**17**) and roughly 3 times faster than the 3,6-dihydro isomers (affording *Z,E*-**20**, *Z,E*-**21** and *Z,E*-**22**).



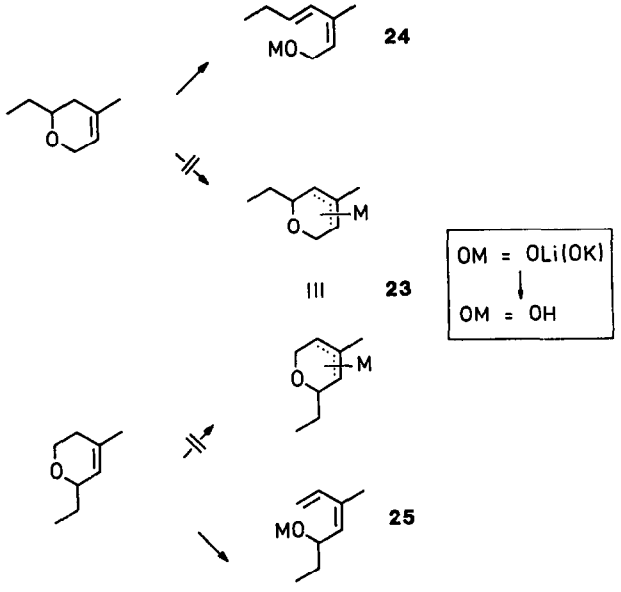
***Z,E*-20**: R = CH_3
***Z,E*-21**: R = CH_2-CH_3
***Z,E*-22**: R = CH_2-$CH(CH_3)_2$

8: R = CH_3
9: R = CH_2-CH_3
10: R = CH_2-$CH(CH_3)_2$

***Z*-15**: R = CH_3
***Z*-16**: R = CH_2-CH_3
***Z*-17**: R = CH_2-$CH(CH_3)_2$

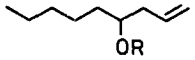
This demonstrates again the sensitivity of the LIDAKOR elimination reaction to steric bulk. 2-Alkyl-4-methylenetetrahydrofurans give rise to secondary alcohols (**8** - **10**) exclusively and none of the isomeric primary alcohols which would result from deprotonating attack at the other allylic position was ever detected. This strong positional discrimination must have its origin in a special elimination mechanism. The fact that homoallyl type ethers rapidly undergo LIDAKOR promoted elimination of alcohol while saturated analogs are perfectly stable could mean that we deal with a true E1cb mechanism. This hypothesis, however, can be rigorously ruled out. If a

carbanionic or organometallic intermediate **23** were involved in the ring-opening process, this transient species would be common to both precursors, 2- *and* 6-ethyl-5,6-dihydro-2*H*-pyran. Consequently, both should lead to the same mixture of reaction products **24** and **25** (OM = OH).

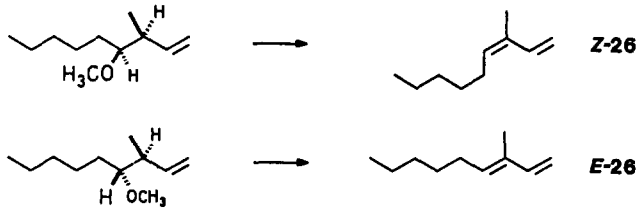


Kinetic measurements also argue against the E1cb mode. Upon a systematic variation of the alkoxy leaving group only pivaloate, when compared to methoxy, is found to accelerate moderately the rate of (*E*)-1,3-nonadiene formation while ethoxy, *tert*-butoxy, trimethylsilyloxy and methoxymethoxy cause a rate retardation in the range of 3 to 15 (see table).

Table. Relative rates k_{rel} of the LIDAKOR promoted 1,3-nonadiene formation from 1-nonen-4-ol derivatives.

	k_{rel}
OR = OCH_3	1.0
OR = OC_2H_5	0.3
OR = $OC(CH_3)_3$	0.2
OR = $OSi(CH_3)_3$	0.3
OR = OCH_2OCH_3	0.06
OR = $OCOC(CH_3)_3$	1.9

These data are well compatible with the assumption of a concerted mechanism having both, E1cb-like and push-pull character. Support for this view comes from a stereochemical study which reveals a *syn*-periplanar process to be operative. Both, *erythro*- and *threo*-4-methoxy-3-methyl-1-nonene [6a] react only sluggishly with the LIDAKOR mixture. Nevertheless, each of them produces a single individual stereoisomer, (*Z*)- and, respectively, (*E*)-3-methyl-1,3-nonadiene (*Z*- and *E*-**26**) with little if any mutual contamination. [6b]



EXPERIMENTAL PART

Generalities : see preceding article [1].

1. Acyclic and Carbocyclic Substrates

a) (*E*)-**1,3-Nonadiene** (*E*-**1**) [7] : From a solution of butyllithium (25 mmol) in hexane the solvent was stripped off under reduced pressure. Precooled (-75 °C) tetrahydrofuran (25 mL), diisopropylamine (3.5 mL, 2.5 g, 25 mmol), potassium *tert*-butoxide (0.28 g, 2.5 mmol) and 4-methoxy-1-nonene (3.9 g, 25 mmol) were consecutively added under stirring. After 2 h at -50 °C, the mixture was poured into water (250 mL) and extracted with pentane (3 x 50 mL). The combined organic layers were washed with brine (2 x 25 mL) and concentrated using a Widmer column of 30 cm length. Upon distillation, 2.4 g (76%) of *E*-**1** (*cis* : *trans* = 5 : 95) were collected; bp 150 - 154 °C, n_D^{20} 1.4541; ^{1}H-NMR : 6.32 (1 H, dt, *J* 17.0, 10.4), 6.06 (1 H, dddt, *J* 15.1, 10.4, 1.3, 1.0), 5.72 (1 H, dt, *J* 15.1, 7.3), 5.09 (1 H, dd, *J* 16.9, 1.4), 4.98 (1 H, dd, *J* 10.4, 1.6), 2.09 (2 H, q, *J* 7.2), 1.4 (6 H, m), 0.92 (3 H, t, *J* 7.0).

4-Methoxy-1-nonene was prepared by consecutive treatment of 1-nonen-4-ol [8] (8.5 g, 60 mmol), dissolved in dimethyl sulfoxide (60 mL), with sodium amide (2.7 g, 70 mmol) during 1 h and methyl iodide (10 g, 70 mmol) during 30 min at 25 °C. Addition of water (0.3 L), extraction with pentane (3 x 30 mL) and distillation afforded 7.0 g (75%) of analytically pure material; bp 57 - 59 °C/2 mmHg, n_D^{20} 1.4292; IR : 3095 (m, ν[=C-H]), 2930 (s, broad, ν[-C-H]), 2835 (w, ν[OC-H]), 1648 (m, ν[C=C]), 1100 (s, ν[C-O]), 910 (s, δ[=C-H]); ^{1}H-NMR (80 MHz) : 5.89 (1 H, ddt, *J* 17, 10, 7), 5.10 (1 H, d, *J* 17), 5.08 (1 H, d, *J* 11), 3.36 (3 H, s), 3.3 (1 H, m), 2.27 (2 H, t, *J* 7), 1.4 (8 H, m), 0.90 (3 H, t, *J* 6); MS : 115 (62%; M^+ - C_3H_5), 83 (100%); Analysis : calc. for $C_{10}H_{20}O$ (156.27) C 76.86, H 12.90; found C 77.12, H 12.70%.

b) (*Z*)-**1,3-Nonadiene** (*Z*-**1**) [9] : As described for 4-methoxy-1-nonene (Section 1a), *cis*-1-methoxy-3-nonene was converted to 2.5 g (80%) of *Z*-**1** (*cis* : *trans* = > 95 : 5); bp 90 - 94 °C/180 mmHg, n_D^{20} 1.4532; ^{1}H-NMR : 6.64 (1 H, dddd, *J* 17.0, 11.0, 10.1, 1.3), 6.00 (1 H, t, *J* 11.0), 5.46 (1 H, dt, *J* ~ 11, ~ 8), 5.17 (1 H, dd, *J* 17.0, 2.0), 5.08 (1 H, d, *J* 10.1), 2.20 (2 H, dq, *J* 7.8, 1.5), 1.39 (2 H, pent, *J* 7.0), 1.3 (4 H, m), 0.90 (3 H, t, *J* 7.0).

In order to prepare the starting material, a solution of 1-octene (11 g, 0.10 mol), butyllithium (0.10 mol) and potassium *tert*-butoxide [10] (11 g, 0.10 mol) in tetrahydrofuran (0.10 L) was kept 10 h at -50 °C before, at -75 °C, chloromethyl methyl ether [11] (7.6 mL, 8.1 g, 0.10 mol) was added. By distillation under reduced pressure 11 g (70%) of a 3 : 2 mixture of two isomers was isolated. Analysis : calc. for $C_{10}H_{20}O$ (156.27) C 76.86, H 12.90; found C 76.48, H 13.26%. The two components, 3-methoxymethyl-1-octene; (bp 68 - 72 °C/35 mmHg; n_D^{20} 1.4259) and *cis*-1-methoxy-3-nonene (bp 78 - 80 °C/35 mmHg; n_D^{20} 1.4320) were separated by distillation with a Fischer "Spaltrohr" column.

The two components were separated by fractionation using a Fischer Spaltrohr column : **3-Methoxymethyl-1-octene** (major component): bp 68 - 72 °C/35 mmHg, n_D^{20} 1.4259. - IR : 3095 (m, ν[=C-H]), 2925 (s, broad, ν[-C-H]), 2750 (w, ν[OC-H]), 1650 (m, ν[C=C]), 1130 (s, ν[C-O]), 915 (s, δ[=C-H]); ^{1}H-NMR : 5.64 (1 H, ddd, *J* 18.2, 9.9, 8.5), 5.1 (2 H, m), 3.35 (3 H, s), 3.31 (2 H, d, *J* 6.4), 2.30 (1 H, dpent, *J* ~ 7.5, ~ 5), 1.4 (8 H, m), 0.89 (3 H, t, *J* 7.0). - ***cis*-1-Methoxy-3-nonene** : bp 78 - 80 °C/35 mmHg, n_D^{20} 1.4320. - IR : 3025 (m, ν[=C-H]), 2900 (s, broad, ν[-C-H]), 1660 (w, ν[C=C]), 1120 (s, ν[C-O]), 720 (m, δ[=C-H]); ^{1}H-NMR : 5.49 (1 H, dtt, *J* 11.4, 7.0, 1.5), 5.38 (1 H, dtt, *J* 11.0, 7.0, 1.5), 3.40 (2 H, t, *J* 7.0), 3.37 (3 H, s), 2.34 (2 H, q, *J* 7.0), 2.06 (2 H, dt, *J* 7.6, 7.0), 1.3 (6 H, m), 0.90 (3 H, s).

c) **2-Pentyl-1,3-butadiene (5)** [12] : Under the conditions described above (Section 1a), 3-methoxymethyl-1-octene gave 58% of isolated product **5**; bp 74 - 76 °C/100 mmHg, n_D^{20} 1.4458; ^{1}H-NMR : 6.38 (1 H, dd, *J* 17.9, 10.9), 5.23 (1 H, d, *J* 17.9), 5.05 (1 H, dq, *J* 0.8, 10.9), 5.00 (2 H, d, *J* 4.1), 2.21 (2 H, ddd, *J* 1.1, 7.1, 8.0), 1.50 (2 H, tt, *J* 7.1, 8.2), 1.3 (4 H, m), 0.90 (3 H, t, *J* 7.1).

d) **(*Z*)-3-Methyl-1,3-nonadiene (*Z*-26)** : Under the conditions described above (Section 1a), but using lithium 2,2,6-tetramethylpiperidide instead of lithium diisopropylamide, *erythro*-4-methoxy-3-methyl-1-nonene (purified by preparative gas chromatography) gave approximately 5% of *Z*-**26** and 95% of the starting material was recovered. The product was identified by gas chromatographic comparison (3 m, 5% SE-30, 80 → 180 °C; 3 m, 10% Ap-L, 90 → 190 °C) with an authentic sample obtained by the reaction of (*E*)-3-methyl-2,4-pentadien-1-ol (*E*-**11**, see Section 3a) with two equivalents of butyllithium in hexane for 1 h at 0 °C [2]. It was purified by preparative gas chromatography (3 m, 10% SE-30, 50 → 150 °C at a rate of 5 °C/min); bp 63 - 65 °C/10 mmHg; IR : 3110 (m, ν[=C-H]), 3060 (w, ν[=C-H]), 2950 + 2880 (s, ν[-C-H]), 1652 + 1618 (m, ν[C=C]), 995 + 905 (s, δ[-CH=CH_2]); ^{1}H-NMR (80 MHz) : 6.80 (1 H, dd, *J* 18, 11), 5.43 (1 H, t, *J* 7), 5.20 (1 H, d, *J* 18), 5.08 (1 H, d, *J* 11), 2.2 (2 H, m), 1.81 (3 H, s), 1.3 (6 H, m), 0.88 (3 H, t, *J* 6); MS : 138 (12%, M^+), 109 (11%), 95 (16%), 81 (100%); Analysis : calc. for $C_{10}H_{18}$ (138.25) C 86.88, H 13.12; found C 86.99, H 12.99%.

In order to prepare the starting material, potassium *tert*-butoxide (11 g, 0.10 mol) and *cis*-2-butene *or* 1-butene (14 mL, 9.0 g, 0.16 mol) were rapidly added to a solution of butyllithium (0.10 mol) in neat tetrahydrofuran (50 mL) at -75 °C. After 10 min at -50 °C, the mixture was cooled to -75 °C and with fluorodimethoxyboron diethyl etherate (39 mL, 35 g, 0.30 mol). After 1 h and always at -75 °C, hexanal (14 mL, 11 g, 0.11 mol) and, after warming up to 25 °C, potassium hydroxide (20 g, 0.36 mol) and water (0.2 L). The mixture was vigorously stirred for three hours and then neutralized with 10% hydrochloric acid. The ethereal layer was separated and the aqueous phase was extracted with hexane (3 x 50 mL). The combined organic phases were washed with water (3 x 20 mL) and brine (50 mL), dried and evaporated. Distillation of the residue afforded 7.9 g (50%) *erythro*-**3-methyl-1-nonen-4-ol** [8, 13] having a diastereomeric ratio of 88 : 12 [14] (according to the gas chromatographic analysis : 3 m, 10% C-20M, 80 → 180 °C at a rate of 4 °C/min; subsequently purified by preparative gas chromatography); bp 54 - 58 °C/1 mmHg; n_D^{20} 1.4449; IR : 3390 (s, broad, ν[OH]), 3095 (m, ν[=C-H]), 2975 + 2945 (s, ν[-C-H]), 2885 + 2870 (m, ν[OC-H]), 1645 (m, ν[C=C]), 995 + 915 (m, δ[-CH=CH_2]); ^{1}H-NMR : 5.80 (1 H, ddd, *J* 17.9, 10.0, 7.3), 5.10 (1 H, dd, *J* 16.5, 1.0), 5.09 (1 H, d, broad, *J* 11.8), 3.50 (1 H, ddd, *J* 8.2, 5.1, 3.1), 2.28 (1 H, hex, *J* 6.9), 1.57 (1 H, s), 1.5 (2 H, m), 1.3 (6 H, m), 1.03 (3 H, d, *J* 7.0), 0.92 (3 H, t, *J* 6.9).

As described for 1-nonen-4-ol (Section 1a), the alcohol was converted to ***erythro*-4-methoxy-3-methyl-1-nonene** (68%); bp 58 - 61 °C/0.1 mmHg; n_D^{20} 1.4295; ^{1}H-NMR (80 MHz) : 5.85 (1 H, ddd, *J* 17, 10, 8), 5.03 (1 H, d, *J* 17), 5.00 (1 H, d, *J* 10), 3.36 (3 H, s), 3.0 (1 H, m), 2.4 (1 H, m), 1.3 (11 H, m), 0.95 (3 H, t, *J* 7); MS : 115 (60%, M^+ - C_4H_7), 99 (10%), 83 (100%); Analysis : calc. for $C_{11}H_{22}O$ (170.30) C 77.58, H 13.02; found C 77.52, H 12.95%.

e) **(*E*)-3-Methyl-1,3-nonadiene (*E*-26)** : Analogously, *threo*-4-methoxy-3-methyl-1-nonene gave virtually pure *E*-**25** (5%), identical with a sample prepared by treatment of (*Z*)-3-methyl-2,4-pentadien-1-ol (*Z*-**11**, see Section 4b) with two equivalents of butyllithium in hexane during 30 min at 25 °C and isolated with a 46% yield; IR : 3100 (m, ν[=C-H]), 3050 (w, ν[=C-H]), 2940 + 2875 (s, ν[-CH]), 1650 + 1610 (m, ν[C=C]), 990 + 890 (s, δ[-CH=CH_2]); ^{1}H-NMR (C_6D_6) : 6.46 (1 H, dd, *J* 17.9, 11.0), 5.47 (1 H, t, *J* 7.6), 5.16 (1 H, d, *J* 17.9), 4.98 (1 H, d, *J* 10.9), 2.04 (2 H, q, broad, *J* 7.9), 1.71 (3 H, s), 1.3 (6 H, m), 0.87 (3 H, t, *J* 7.0); MS : 138 (20%, M^+), 123 (5%), 109 (10%), 81 (70%), 67 (100%); Analysis : calc. for $C_{10}H_{18}$ (138.25) C 86.88, H 13.12; found C 87.13, H 12.83%.

threo-**3-Methyl-1-nonen-4-ol** [8, 13] was obtained following the same procedure as described for the *erythro* form but starting with *trans*-butene; 8.4 g (53%); bp 55 - 58 °C/1 mmHg, n_D^{20} 1.4450; *erythro/threo* ratio 3 : 97 [14]; IR : 3390 (s, broad, ν[O-H]), 3095 (m, ν[=C-H]), 1640 (m, ν[C=C])), 997 + 915 (m, ν[-CH=CH_2]); ^{1}H-NMR : 5.77 (1 H, ddd, *J* 16.6, 11.1, 8.0), 5.12 (1 H, d, *J* 11.0), 5.11 (1 H, d, *J* 17.0), 3.40 (1 H, ddd, *J* 9.0, 6.0, 3.1), 2.21 (1 H, hex, *J* 7.0), 1.69 (1 H, s, broad), 1.5 (2 H, m), 1.3 (6 H, m), 1.05 (3 H, d, *J* 7.0), 0.91 (3 H, t, *J* 6.9).

The alcohol was converted to *threo*-**4-methoxy-3-methyl-1-nonene** (73%) in the usual way; bp 57 - 60 °C/0.1 mmHg; n_D^{20} 1.4293; ^{1}H-NMR (80 MHz) : 5.92 (1 H, ddt, *J* 17, 10, 7), 5.1 (2 H, m), 3.32 (3 H, s), 3.07 (1 H, q, *J* 5), 2.5 (1 H, m), 1.3 (11 H, m), 0.98 (3 H, t, *J* 6); MS : 115 (47%, M^+ - C_4H_7), 99 (10%), 83 (100%); Analysis : calc. for $C_{11}H_{22}O$ (170.30) C 77.58, H 13.02; found C 77.96, H 12.90%.

f) **1-Ethoxy-3-methyl-1,3-butadiene (4)** [15] : Under the conditions described above (Section 1a), 4,4-diethoxy-3-methyl-1-butene [16] gave a 1 : 1 *cis/trans* mixture of 4 (91%) which was distilled at 25 °C under reduced pressure (0.001 mmHg); ^{1}H-NMR (80 MHz) signals assigned to the *cis*-isomer : 5.97 (1 H, d, *J* 7), 5.02 (1 H, s), 4.86 (1 H, d, *J* 7), 4.7 (?, 1 H, s), 3.87 (2 H, q, *J* 7), 1.98 (3 H, s), 1.29 (3 H, t, *J* 7); ^{1}H-NMR (80 MHz) signals assigned to the *trans*-isomer : 6.54 (1 H, d, *J* 13), 5.70 (1 H, d, *J* 13), 4.88 (1 H, s-like), 4.68 (1 H, s-like), 3.85 (2 H, q, *J* 7), 1.80 (3 H, s), 1.29 (3 H, t, *J* 7).

g) **6,6-Dimethyl-2-vinyl-2-bicyclo[3.1.1]heptene ("nopadiene", 3)** [17] : Under the conditions described above (Section 1a), 2-(2-methoxyethyl)-6,6-dimethyl-2-bicyclo[3.1.1]heptene ("methyl nopyl ether") gave 3 (72%); bp 66 - 71 °C/50 mmHg; n_D^{20} 1.5061; IR : 3100 + 3040 (m, ν[=C-H]), 2930 (s, ν[-C-H]), 2840 (m, ν[-C-H]), 1640 + 1595 (m, ν[C=C]), 990 + 890 (m + s, δ[-CH=CH_2]), 828 + 808 (m, δ[=C-H]); ^{1}H-NMR ($CDCl_3$, 80 MHz) : 6.41 (1 H, dd, *J* 18, 10), 5.60 (1 H, s), 5.16 (1 H, d, *J* 18), 4.91 (1 H, d, *J* 10), 2.4 (4 H, m), 1.66 (1 H, d, *J* 7), 1.34 (3 H, s), 1.13 (1 H, d, *J* 8), 0.81 (3 H, s); Analysis : calc. for $C_{11}H_{16}$ (148.25) C 89.12, H 10.88; found C 89.03, H 10.92%.

The starting material **2-(2-methoxyethyl)-6,6-dimethyl-2-bicyclo[3.1.1]heptene** was prepared (80%) from commercial (1*R*)-2-(6,6-dimethyl-2-bicyclo[3.1.1]hepten-2-yl)ethanol ("nopol", 0.13 kg, 0.80 mol). Its solution in hexane was poured to sodium hydroxide (82 g, 2.0 mol) and benzyltriethylammonium chloride (2.5 g, 11 mmol) dissolved in water (0.10 L). Dimethyl sulfate (0.12 kg, 0.95 mol) was added dropwise, over a period of 90 min, to the vigorously stirred two-phase mixture [18]. After additional 4 h, a 25% aqueous solution (25 mL) of ammonia was added and the stirring continued for another 30 min. Finally the organic layer was separated and the aqueous phase extracted with hexane (2 x 0.10 L). After evaporation of the solvent, the product was isolated by distillation under reduced pressure; 62 - 65 °C/1 mmHg, n_D^{20} 1.4720; IR : 3040 (m, ν[=C-H]), 3000 + 2930 + 2840 (m + s + m, ν[-C-H]), 2810 (w, ν[OC-H]), 1660 (w, ν[C=C]), 1120 (s, ν[C-O]); ^{1}H-NMR : 5.29 (1 H, s, fine structure), 3.40 (2 H, dt, *J* 7.1, 1.8), 3.34 (3 H, s), 2.38 (1 H, dt, *J* 8.2, 5.6), 2.3 (4 H, m), 2.1 (2 H, m), 1.28 (3 H, s), 1.16 (1 H, d, *J* 8.4), 0.84 (3 H, s); Analysis : calc. for $C_{12}H_{20}O$ (180.29) C 79.94, H 11.18; found C 79.82, H 11.21%.

h) **1-Phenyl-1-propene (2)** [19] : Treatment of 2-methoxy-1-phenylpropane [20] (20 mmol) with a solution of lithium diisopropylamide and potassium *tert*-butoxide (each 50 mmol) in tetrahydrofuran (50 mL) during 10 min at -50 °C sufficed to produce a mixture of three isomers in almost quantitative yield (96%) : allylbenzene, *Z*-**2** and *E*-**2** with a ratio of 10 : 25 : 65 (by gas chromatographic comparison).

2. 2-(2-Alkenyl)tetrahydropyrans as Substrates

a) (*E*)-**5,7-Octadien-1-ol** (*E*-**6**) : Under reduced pressure, the solvent was stripped off from a solution of butyllithium (50 mmol). Diisopropylamine (7.1 mL, 5.1 g, 50 mmol), potassium *tert*-butoxide (0.6 g, 5 mmol) and 2-allyltetrahydropyran [21] (6.3 g, 50 mmol) were added at -75 °C. After 2 h at -50 °C, the solvent was evaporated. Water (0.15 L) was added to the residue which was then extracted with hexane (3 x 50 mL). The combined organic layers were concentrated and *E*-**6** (*cis : trans* = 7 : 93) was isolated by distillation; 72%; bp 66 - 69 °C/1 mmHg; n_D^{20} 1.4882; IR : 3350 (s, broad, ν[O-H]), 3100 (m, ν[=C-H]), 3050 (w, ν[=C-H]), 2950 + 2870 (s + m, ν[-C-H]), 1650 + 1605 (w, ν[C=C]), 1060 (s, ν[C-O]), 1005 + 950 + 895 (s + m + s, δ=C-H]); ^{1}H-NMR : 6.66 (~0.1 H, ddt, *J* ~ 17, ~ 10, ~ 2), 6.32 (~ 0.9 H, dt, *J* 17.2, 10.2), 6.08 (1 H, dddt, *J* 15.2, 10.2, 1.3, 1.1), 5.70 (1 H, dt, *J* 15.1, 7.0), 5.10 (1 H, dd, *J* 17.2, ~ 2), 4.98 (1 H, dd, *J* 10.2, ~ 2), 3.66 (2 H, t, *J* 6.6), 2.15 (2 H, q, *J* 7.2), 1.70 (1 H, s), 1.5 (4 H, m); Analysis : calc. for $C_8H_{14}O$ (126.20) C 76.14, H 11.18; found C 75.77, H 11.35%.

b) **(5*E*,7*Z*)-5,7-Nonadien-1-ol** (*E,Z*-7): In the same way, *cis*-2-(2-butenyl)tetrahydropyran (3.5 g, 25 mmol) was converted to a 7 : 93 mixture of (5*Z*,7*Z*)- and (5*E*,7*Z*)-5,7-nonadien-1-ol; bp 72 - 74 °C/0.5 mmHg; n_D^{20} 1.4948; IR : 3350 (s, ν[O-H]), 3035 (s, ν[C=C]), 2950 + 2870 (s + m, ν[C-H]), 1660 + 1615 (w, ν[C=C]), 1065 (s, ν[C-O]), 984 + 950 + 710 (m, δ[=C-H]); ^{1}H-NMR : 6.35 (1 H, ddq, *J* 15.2, 11.0, 1.2), 5.98 (1 H, tq, *J* 11.0, 1.5), 5.63 (1 H, dt, *J* 15.1, 7.4), 5.39 (1 H, dq, *J* 10.9, 6.8), 3.66 (2 H, t, *J* 6.6), 2.16 (2 H, q, *J* 7.2), 1.74 (3 H, dd, *J* 7.2, 1.9), 0.6 (4 H, M), 1.36 (1 H, s); Analysis : calc. for $C_9H_{16}O$ (140.23) C 77.09, H 11.50; found : C 77.15, H 11.41%.

In order to prepare the starting material, potassium *tert*-butoxide (0.20 mol), *cis*-butene (0.30 mol) and, 10 min later, 2-chlorotetrahydropyran [21] (0.20 mol) were added to a solution of butyllithium (0.20 mol) in tetrahydrofuran at -50 °C. Evaporation of the solvent and distillation under reduced pressure afforded 21 g (75%) of a 3 : 1 mixture of 2-(1-methyl-2-propenyl)tetrahydropyran (*erythro/threo* ratio 1 : 1) and *cis*-2-(2-butenyl)tetrahydropyran; bp 50 - 80 °C/20 mmHg; Analysis : calc. for $C_9H_{16}O$ (140.23) C 77.09, H 11.50; found C 76.80, H 11.86%.

Fractional distillation using a Fischer Spaltrohr column allowed to remove the more volatile branched regioisomers (bp 66 - 72 °C/45 mmHg), and to obtain the ***cis*-2-(2-butenyl)tetrahydropyran** as a pure compound; bp 72 - 73 °C/25 mmHg; n_D^{20} 1.4542; IR : 3030 (m, ν[=C-H]), 2950 + 2860 (s + m, ν[-C-H]), 1660 (w, ν[C=C]), 1095 (s, ν[C-O]), 710 (m, δ[=C-H]); ^{1}H-NMR : 5.55 (1 H, dtq, *J* 11.0, 7.0, 1.5), 5.44 (1 H, dtq, *J* 11.0, 7.0, 1.5), 4.00 (1 H, ddt, *J* 11.7, 4.0, 2.0), 3.44 (1 H, dt, *J* 11.5, 2.8), 3.29 (1 H, ddt, *J* 11.1, 6.8, 2.1), 2.28 (1 H, dt, *J* 15.0, 7.0), 2.18 (1 H, dt, *J* 15.0, 7.0), 1.84 (1 H, d, *J* 10.0), 1.64 (3 H, ddt, *J* 6.9, 1.0, 0.8), 1.5 (4 H, m), 1.28 (1 H, ddt, *J* 12.7, 10.8, 4.0); MS : 140 (1%, M^+), 85 (100%).

3. 4-Methylenetetrahydropyrans as Substrates

a) **(*E*)-3-Methyl-2,4-pentadien-1-ol** (*E*-11) [22] : Under the conditions described above (Section 2a), 4-methylenetetrahydropyran (25 mmol) gave 48% of *E*-11; bp 46 - 47 °C/1 mmHg; n_D^{20} 1.4940; ^{1}H-NMR (C_6D_6): 6.38 (1 H, dd, *J* 18.0, 11.0), 5.67 (1 H, t, *J* 6.7), 5.11 (1 H, d, *J* 18.0), 4.97 (1 H, t, *J* 11.0), 4.14 (2 H, d, *J* 6.8), 3.27 (1 H, s, broad), 1.61 (3 H, s).

4-Methylenetetrahydropyran [23] was prepared by treating 4-tetrahydropyranone (10 g, 0.10 mol) with triphenylphosphonio-methanide (0.10 mol, as an "instant ylid" mixture [24]) in diethyl ether (0.15 L). After 30 min at 25 °C, 62% of the product were isolated by distillation; bp 104 - 107 °C; n_D^{20} 1.4498; ^{1}H-NMR (80 MHz) : 4.74 (2 H, s), 3.71 (4 H, t, *J* 6), 2.25 (4 H, t, *J* 6).

b) **4-Methylene-5-hexen-2-ol** (**8**) : Under the conditions described above (Section 2a), 2-methyl-4-methylenetetrahydropyran gave 86% of **8**; bp 67 - 70 °C/48 mmHg, n_D^{20} 1.4749; IR : 3400 (0, ν[O-H]), 3105 (m, ν[=C-H]), 3020 (w, ν[=C-H]), 2950 (s, ν[-C-H]), 1635 (w, ν[C=C]), 1600 (s, ν[C=C]), 1115 (s, ν[C-O]), 900 (s, δ[=C-H]); ^{1}H-NMR : 6.40 (1 H, ddd, *J* 17.9, 10.8, 0.7), 5.27 (1 H, d, *J* 17.8), 5.15 (1 H, d, *J* 10.7), 5.10 (2 H, s), 3.96 (1 H, ddq, j 12.7, 8.4, 4.2), 2.46 (1 H, dd, *J* 14.1, 1.0), 2.30 (1 H, dd, *J* 14.0, 0.9), 1.79 (1 H, s,), 1.24 (3 H, d, *J* 6.0). MS : 112 (18%, M^+), 97 (100%); Analysis : calc. for $C_7H_{12}O$ (112.65) C 74.95, H 10.78; found C 74.76, H 10.78%.

The starting material was prepared by adding in portions, in the course of 1 h, 3-methyl-3-buten-1-ol (86 g, 1.00 mol) and concentrated sulfuric acid (0.5 g, 5 mmol) to freshly distilled acetaldehyde (44 g, 1.00 mol), kept at 10 °C [25]. After 15 h at 25 °C, iodine (2 g, 8 mmol) was added and the temperature was progressively raised. In the boiling range 100 - 140 °C a crude product mixture (73 g, 65%) was collected. After a second distillation (bp 115 - 130 °C) it consisted of three isomers, 2-methyl-4-methylene-tetrahydropyran, 2,4-dimethyl-3,6-dihydro-2*H*-pyran and 2,4-dimethyl-3,6-dihydro-2*H*-pyran in the ratio of 20 : 50 : 30 and was otherwise pure. Analysis : calc. for $C_7H_{12}O$ (112.65) C 74.95, H 10.78; found C 74.78, H 11.02%.

Careful distillation using a Fischer Spaltrohr column allowed to separate the three components sufficiently well in order to obtain small quantities of pure samples. - **2-Methyl-4-methylenetetrahydropyran** [26] : bp 118 - 120 °C; n_D^{20} 1.4419; ^{1}H-NMR : 4.70 (2 H, s, fine structure), 4.05 (1 H, ddd, *J* 11.0, 5.8, 1.5), 3.4 (1 H, m), 3.38 (1 H, ddd, *J* 12.3, 10.9, 2.5), 2.29 (1 H, dt, fine structure, *J* 13.3, 6.5), 2.23 (1 H, dt, *J* 13.5, 2.0), 2.13 (1 H, d, fine structure, *J* 13.5), 1.98 (1 H, dq, *J* 12.2, 1.4), 1.28 (3 H, d, *J* 6.4); MS : 112 (100%, M^+), 97 (84%), 84 (50%). - **2,4-Dimethyl-3,6-dihydro-2*H*-pyran** [26] : bp 127 - 129 °C, n_D^{20} 1.4432; ^{1}H-NMR : 5.41 (1 H, s, fine structure), 4.2

(2 H, m), 3.62 (1 H, ddq, *J* 12.2, 6.1, 3.7), 1.9 (2 H, m), 1.70 (3 H, s, fine structure), 1.25 (3 H, d, *J* 6.2); MS : 112 (100%, M^+), 97 (93%), 83 (25%), 79 (20%). - **2,4-Dimethyl-5,6-dihydro-2*H*-pyran** [26] : bp 126 - 128 °C; ^{1}H-NMR : 5.32 (1 H, s, fine structure), 4.2 (1 H, m), 3.99 (1 H, ddd, *J* 11.2, 5.9, 2.3), 3.64 (1 H, ddd, *J* 11.3, 10.2, 4.0), 2.2 (1 H, m), 1.78 (1 H, d, fine structure, *J* ~ 17), 1.70 (3 H, s, fine structure), 1.20 (3 H, d, *J* 6.8); MS : 112 (50%, M^+), 97 (100%), 79 (18%).

c) **5-Methylene-6-hepten-3-ol (9)** : Under the conditions described above (Section 2a), 2-ethyl-4-methylenetetrahydropyran gave 87% of **9**; bp 62 - 65 °C/1 mmHg; n_D^{20} 1.4748; ^{1}H-NMR : 6.40 (1 H, dd, *J* 17.6, 10.8), 5.26 (1 H, d, *J* 17.6), 5.15 (1 H, dd, *J* 10.9, 0.9), 5.11 (2 H, s, broad), 3.69 (1 H, dddd, *J* 13.0, 8.9, 5.4, 3.8), 2.55 (1 H, ddd, *J* 13.8, 3.7, 1.0), 2.23 (1 H, dd, *J* 14.0, 9.1), 1.77 (1 H, s, broad), 1.55 (1 H, dq, *J* 7.5, 3.0), 1.53 (1 H, dq, *J* 7.5, 3.4), 1.0 (3 H, t, *J* 7.5); MS : 126 (19%, M^+), 111 (70%), 97 (100%); Analysis : calc. for $C_8H_{14}O$ (126.20) C 76.14, H 11.18; found C 76.23, H 11.17%.

The starting material was prepared and isolated according to the procedure described above (Section 3b) employing propanal instead of acetaldehyde. The crude product mixture was distilled a second time; Analysis : calc. for $C_8H_{14}O$ (126.20) C 76.14, H 11.18, found C 75.98, H 11.06%.

Three fractions were collected upon distillation using a Fischer Spaltrohrcolumn, only the first and the last of which contained pure isomers. - **2-Ethyl-4-methylenetetrahydropyran** : bp 62 - 64 °C/80 mmHg; n_D^{20} 1.4482; ^{1}H-NMR : 4.74 (2 H, d, fine structure, *J* 1.8), 4.08 (1 H, ddd, *J* 11.0, 5.8, 1.6), 3.38 (1 H, ddd, *J* 12.1, 11.0, 2.9), 3.16 (1 H, dddd, *J* 10.3, ~ 6.5, 5.4, 2.2), 2.30 (1 H, dt, *J* ~ 13, 5.5), 2.25 (1 H, dt, *J* 13.2, 1.9), 2.14 (1 H, d, fine structure, *J* ~ 13), 1.96 (1 H, t, fine structure, *J* ~ 12), 1.59 (1 H, ddq, *J* 13.5, 7.2, 6.9), 1.51 (1 H, ddq, *J* 13.5, 7.2, 5.5), 0.96 (3 H, t, *J* 7.4); MS : 126 (40%, M^+), 97 (100%), 81 (45%). - **2-Ethyl-4-methyl-3,6-dihydro-2*H*-pyran** [26] : bp 74 - 76 °C/80 mmHg; n_D^{20} 1.4479; ^{1}H-NMR : 5.39 (1 H, s, fine structure), 4.1 (2 H, m), 3.38 (1 H, dddd, *J* 9.5, 7.9, 5.9, 3.9), 1.8 (2 H, m), 1.70 (3 H, s, broad), 1.60 (1 H, ddq, *J* 13.5, 7.5, 7.0), 1.51 (1 H, ddq, *J* 13.5, 7.5, 5.9), 0.98 (3 H, t, *J* 7.5); MS : 126 (100%, M^+), 111 (35%), 97 (83%). - **2-Ethyl-4-methyl-5,6-dihydro-2*H*-pyran** [26] : bp 72 - 74 °C/80 mmHg.

d) **2-Methyl-6-methylen-7-octen-4-ol (10)** [3] : Under the conditions described above (Section 2b), 2-isobutyl-4-methylenetetrahydropyran was converted to **9** (83%); bp 82 - 86 °C/0.8 mmHg; n_D^{20} 1.4688; ^{1}H-NMR : 6.39 (1 H, dd, *J* 17.6, 10.8), 5.24 (1 H, d, *J* 17.8), 5.15 (1 H, d, *J* 2.0), 5.10 (1 H, d, *J* ~ 11), 5.08 (1 H, s-like), , 3.82 (1 H, symm. m), 2.48 (1 H, ddd, *J* 14.2, 3.8, 0.9), 2.22 (1 H, dd, *J* 14.0, 8.9), 1.8 (2 H, m), 1.47 (1 H, dd, *J* 13.8, 8.8, 5.5), 1.28 (1 H, ddd, *J* 13.8, 8.6, 4.3), 0.94 (3 H, d, *J* 6.7), 0.92 (3 H, d, 6.7).

The starting material was prepared and isolated according to the procedure described above (Section 3b) employing isovaleraldehyde instead of acetaldehyde. The crude product mixture (68%) was distilled a second time, Analysis : calc. for $C_{10}H_{18}O$ (154.25) C 77.87, H 11.76; found C 77.98, H 11.67%.

The three isomers, present in the ratio of 20 : 50 : 30 were separated by fractionation using a Fischer Spaltrohr column : **2-Isobutyl-4-methylenetetrahydropyran** [26] : bp 75 - 78 °C/40 mmHg; n_D^{20} 1.4492; ^{1}H-NMR : 4.73 (2 H, s, fine structure), 4.07 (1 H, ddd, *J* 11.0, 5.6, 1.8), 3.38 (1 H, ddd, *J* 12.1, 11.0, 2.8), 3.30 (1 H, dddd, *J* 10.9, 8.5, 4.5, 2.3), 2.31 (1 H, dt, fine structure, *J* 12.8, 6.0), 2.22 (1 H, dt, *J* 13.0, 1.9), 2.15 (1 H, ddt, *J* 13.5, 2.8, 1.5), 1.97 (1 H, t, fine structure, *J* 12.0), 1.80 (1 H, dhept, *J* 8.2, 6.6), 1.53 (1 H, ddd, *J* 14.0, 8.5, 5.7), 1.22 (1 H, ddd, *J* 14.0, 8.3, 4.2), 0.93 (3 H, d, *J* 6.7), 0.92 (3 H, d, *J* 6.7); MS : 154 (10%, M^+), 109 (5%), 97 (100%). - **2-Isobutyl-4-methyl-3,6-dihydro-2*H*-pyran** [26, 27] : bp 87 - 88 °C/40 mmHg; n_D^{20} 1.4502; ^{1}H-NMR : 5.41 (1 H, s, broad), 4.1 (2 H, m), 3.53 (1 H, dddd, *J* 10.1, 8.5, 4.9, 3.8), 1.8 (3 H, m), 1.69 (3 H, s), 1.53 (1 H, ddd, *J* 13.9, 8.3, 6.1), 1.25 (1 H, ddd, *J* 13.9, 8.2, 4.9), 0.92 (3 H, d, *J* 6.9), 0.91 (3 H, d, *J* 6.8); MS : 154 (30%, M^+), 139 (30%), 110 (40%), 97 (100%). - **2-Isobutyl-4-methyl-5,6-dihydro-2*H*-pyran** [26] (after purification by means of preparative gas chromatography : 3 m, 10% C-20 M, 60 → 180 °C at a rate of 5 °C/min) : bp 86 - 87 °C/40 mmHg; n_D^{20} 1.4484; ^{1}H-NMR : 5.33 (1 H, s, fine structure), 4.06 (1 H, m), 3.99 (1 H, ddd, *J* 11.3, 5.8, 2.8), 3.61 (1 H, ddd, *J* 11.2, 9.9, 4.0), 2.2 (1 H, m), 1.8 (2 H, m), 1.71 (3 H, d, *J* 1.1),, 1.47 (1 H, ddd, *J* 13.6, 8.9, 5.8), 1.21 (1 H, ddd, *J* 13.7, 8.5, 4.9), 0.93 (6 H, d, *J* 7.0); MS : 154 (4%, M^+), 139 (8%), 112 (10%), 97 (100%).

4. 3,6- and 5,6-Dihydro-2*H*-pyrans as Substrates

a) **(*Z*)-2,4-Pentadien-1-ol (*Z*-12)** [28] : Under the conditions described above (Section 2a), 65% of *Z*-**12** were obtained from 3,6-dihydro-2*H*-pyran [29]; bp 76 - 79 °C/12 mmHg; n_D^{20} 1.4975; ^{1}H-NMR : 6.63 (1 H, dddd, *J* 16.9,

11.1, 10.2, 1.0), 6.10 (1 H, t, fine structure, *J* 11.1), 5.64 (1 H, dt, *J* 10.5, 7.0), 5.28 (1 H, dd, *J* 17.0, 1.5), 5.19 (1 H, d, *J* 10.2), 4.32 (2 H, dd, *J* 7.0, 1.2),, 1.95 (1 H, s, broad).

b) **(*Z*)-3-Methyl-2,4-pentadien-1-ol (*Z*-11)** [30] : Under the conditions described above (Section 2a), 4-methyl-3,6-dihydro-2*H*-pyran [31] gave 77% of *Z*-11 (*Z*/*E* ≥ 97 : 3); bp 44 - 46 °C/1 mmHg; n_D^{20} 1.4965; IR : 3350 (s, broad, ν[O-H]), 3105 + 3030 (m, ν[=C-H]), 2960 (m, ν[-C-H]), 1650 (w, ν[C=C]), 1605 (s, ν[C=C]), 1040 (s, ν[C-O]), 910 (s, δ[=C-H]); ^{1}H-NMR (C_6D_6) : 6.65 (1 H, dd, *J* 18.0, 11.4), 5.49 (1 H, t, *J* 7.1), 5.14 (1 H, d, fine structure, *J* 18.0), 5.03 (1 H, d, fine structure, *J* 11.3), 4.12 (2 H, d, *J* 6.6), 1.92 (1 H, s, broad), 1.72 (3 H, s, broad); MS : 98 (24%, M^+), 83 (100%), 80 (34%); Analysis : calc. for $C_6H_{10}O$ (98.15) C 73.42, H 10.27, found C 72.93, H 10.24%.

c) **(*Z*)-7-Methyl-3-vinyl-2,6-octadien-1-ol (*Z*-13)** : Under the conditions described above (Section 2a), 4-(4-methyl-3-pentenyl)-3,6-dihydro-2*H*-pyran gave 74% of *Z*-13; bp 26 - 30 °C/10^{-6} mmHg; n_D^{20} 1.5032; IR : 3350 (s, broad, ν[O-H]), 3100 + 3050 (m + w, ν[=C-H]), 2960 + 2930 + 2875 (s, ν[-C-H]), 1640 (w, ν[C=C]), 1600 (s, ν[C=C]), 1050 (s, ν[C-O]), 985 + 950 + 905 (s + m + s, δ[=C-H]); ^{1}H-NMR (C_6D_6) : 6.53 (1 H, ddd, *J* 17.8, 11.0, 1.0), 5.51 (1 H, t, broad, *J* 6.7), 5.22 (1 H, dd, *J* 17.6, 1.0), 5.2 (1 H, m), 5.03 (1 H, dt, *J* 11.0,, 1.2), 4.08 (2 H, d, *J* 6.9), 2.2 (4 H, s, broad), 1.67 (3 H, d, *J* 0.8), 1.53 (3 H, d, *J* 0.8), 1.15 (1 H, s, broad); Analysis : calc. for $C_{11}H_{18}O$ (166.26) C 79.47, H 10.91, found C 78.90, H 10.91%.

4-(4-Methyl-3-pentenyl)-3,6-dihydro-2*H*-pyran [32] was prepared from myrcene and paraformaldehyde under acid catalysis [33] with a 56% yield; bp 108 - 111 °C/0.1 mmHg; n_D^{20} 1.4833; IR : 3050 (w, ν[=C-H]), 1670 + 1635 (w, ν[C=C]), 1130 (s, ν[C-O]); ^{1}H-NMR : 5.42 (1 H, s, fine structure), 5.11 (1 H, tq, *J* 6.9, 1.2), 4.13 (2 H, s, fine structure), 3.78 (2 H, t, *J* 5.5), 2.1 (6 H, m), 1.70 (3 H, d, *J* 1.2), 1.62 (3 H, s); MS : 166 (10%, M^+), 151 (40%), 123 (40%), 96 (65%), 83 (100%); Analysis : calc. for $C_{11}H_{18}O$ (166.26) C 79.47, H 10.91, found C 79.10, H 11.04%.

d) **(*Z*)- 2-(2-Methyl-1-propenyl)-2,4-pentadien-1-ol (*Z*-14)** : Diverging from the standard conditions (Section 2a), lithium diisopropylamide was replaced by lithium 2,2,6,6-tetramethylpiperidide and the reaction was carried out during 4 h at - 75 °C. 5-(2-Methyl-1-propenyl)-3,6-dihydro-2*H*-pyran gave 55% of 14; bp 79 - 82 °C/1 mmHg; n_D^{20} 1.4935; IR : 3350 (s, broad, ν[O-H]), 3100 + 3030 (m, ν[=C-H]), 2950 (m, ν[-C-H]), 1660 + 1590 (m, ν[C=C]), 1035 (s, ν[C-O]), 900 (s, δ[=C-H]); ^{1}H-NMR (C_6D_6) : 6.09 (1 H, dq, *J* 11.9, 1.4), 5.78 (1 H, d, broad, *J* 1.1), 5.65 (1 H, dt, *J* 11.9, 6.3), 5.00 (2 H, d, broad), 4.35 (2 H, dd, *J* 6.4, 1.9), 1.9 (1 H, m), 1.80 (3 H, d, *J* 1.4), 1.78 (3 H, d, *J* 1.4).

5-(2-Methyl-1-propenyl)-3,6-dihydro-2*H*-pyran was isolated with a 52% yield from the reaction between 3-(5,6-dihydro-2*H*-pyranyl)carbaldehyde (12 g, 0.10 mol) and an equimolar amount of triphenylphosphonio-1-methylethanide (as an "instant ylid" mixture [24]) in diethyl ether (0.15 L); bp 103 - 105 °C/45 mmHg, n_D^{20} 1.4952; ^{1}H-NMR : 5.64 (1 H, d, fine structure, *J* 1.8), 5.46 (1 H, d, *J* 1.4), 4.12 (2 H, dt, *J* 2.5, 2.0), 3.77 (2 H, t, *J* 5.5), 2.24 (2 H, d, broad, *J* 2.5), 1.78 (6 H, d, *J* 0.6); MS : 138 (30%, M^+), 123 (43%), 93 (100%), 77 (71%); Analysis : calc. for $C_9H_{14}O$ (138.21) C 78.21, H 10.21, found C 77.95, H 9.91%.

e) **(*Z*)-4-Methyl-3,5-hexadien-2-ol (*Z*-15)** : Under the conditions described above (Section 2a), 2,4-dimethyl-5,6-dihydro-2*H*pyran (see Section 3b) gave 87% of *Z*-15; bp 71 - 73 °C/1 mmHg; n_D^{20} 1.4857; ^{1}H-NMR (C_6D_6) : 6.68 (1 H, ddd, *J* 17.3, 10.9, 0.8), 5.33 (1 H, d, *J* 9.0), 5.15 (1 H, ddd, *J* 17.5, 1.8, 0.9), 5.03 (1 H, dt, *J* 11.0, 1.5), 4.62 (1 H, dq, *J* 8.7, 6.2), 1.70 (3 H, d, *J* 1.2), 1.64 (1 H, s), 1.16 (3 H, d, *J* 6.4); MS : 112 (6%, M^+), 97 (40%), 94 (30%), 79 (100%).

f) **(2*Z*,4*E*)-3-Methyl-2,4-hexen-1-ol (*Z*,*E*-20)** : A 2 : 1 mixture of 2,4-dimethyl-3,6- and 2,4-dimethyl-5,6-dihydro-2*H*-pyran (see Section 3b) were concomitantly treated with lithium diisopropylamide and catalytic amounts of potassium *tert*-butoxide as already described (Section 2a). After 5 h at -50 °C, a 5 : 3 mixture of **20** and *Z*-15 was obtained with a 72% yield; bp 72 - 77 °C/1 mmHg; Analysis : calc. for $C_7H_{12}O$ (112.65) C 74.95, H 10.78, found C 74.62, H 11.08%.

The major component **20** was separated by preparative gas chromatography (3 m, 10% SE-30, 80 → 180 °C at a rate of 5 °C/min), n_D^{20} 1.5018; ^{1}H-NMR (C_6D_6) : : 6.40 (1 H, ddq, *J* 15.5, 1.0, 0.9), 5.60 (1 H, dq, *J* 15.5, 6.9), 5.41 (1 H, t, *J* 6.9), 4.12 (2 H, d, *J* 7.0), 1.74 (3 H, d, *J* 1.2), 1.64 (3 H, dd, *J* 6.9, 1.4), 1.6 (1 H, s, broad); MS : 112 (21%, M^+), 97 (35%), 94 (30%), 79 (100%).

g) **(*Z*)-5-Methyl-4,6-heptadien-3-ol (*Z*-16)** and **(2*Z*,4*E*)-3-methyl-2,4-heptadien-1-ol (*Z*,*E*-21)** : A 1 : 1 mixture of 2-ethyl-4-methyl-3,6- and 2-ethyl-4-methyl-5,6-dihydro-2*H*-pyran (see Section 3c) were concomitantly submitted to the ring opening elimination reaction (see Sections 2a and 4f). After 5 h at -50 °C, a 2 : 1 mixture of *Z*-17 and *Z*,*E*-21 was obtained with a 68% yield; bp 72 - 78 °C/1 mmHg; Analysis : calc. for $C_8H_{14}0$ (126.20) C 76.14, H 11.18, found C 75.88, H 11.08%.

The regioisomeric dienols were separated by preparative gas chromatography (3 m, 5% SE-30, 120 → 180 °C at a rate of 10 °C/min). - *Z*-16 : n_D^{20} 1.4862; ^{1}H-NMR : 6.79 (1 H, dd, *J* 17.4, 11.0), 5.38 (1 H, d, broad, *J* 8.9), 5.30 (1 H, d, fine structure, *J* 17.4), 5.18 (1 H, dt, *J* 10.9, 1.5), 4.53 (1 H, dt, *J* 8.9, 6.5), 1.87 (3 H, d, *J* 1.3), 1.76 (1 H, s, broad), 1.65 (1 H, ddq, *J* 13.8, 7.2, 5.5), 1.51 (1 H, ddq, *J* 14.0, 7.2, 5.5), 0.93 (3 H, t, *J* 7.4); MS : 126 (3%, M^+), 111 (8%), 108 (20%), 97 (100%). - *Z*,*E*-21 : n_D^{20} 1.4996; ^{1}H-NMR : 6.43 (1 H, dq, *J* 15.1, 0.9), 5.83 (1 H, dt, *J* 15.3, 6.7), 5.49 (1 H, tq, *J* 6.8, 1.0), 4.30 (2 H, d, fine structure, *J* 7.2), 2.18 (2 H, ddq, *J* 8.0, 7.5, 1.2), 1.88 (3 H, d, *J* 1.0), 1.61 (1 H, s, broad), 1.05 (3 H, t, *J* 7.5); MS : 126 (22%, M^+), 111 (15%), 108 (25%), 97 (80%), 77 (100%).

h) **(*Z*)-2,6-Dimethyl-5,7-octadien-4-ol (*Z*-17)** : Under the conditions described above (Section 2a), 2-isobutyl-4-methyl-5,6-dihydropyran (Section 3d) gave 81% of *Z*-17 : bp 85 - 88 °C/1 mmHg; n_D^{20} 1.4777; IR : 3360 (s, broad, ν[O-H]), 3105 (m, ν[=C-H]), 3040 (w, ν[=C-H]), 2970+2940+2880 (s+s+m, ν[-C-H]), 1650 (w, ν[C=C]), 1603 (m, ν[C=C]), 1145 (m, ν[C-O]), 990+970+950+905+855+835 (s+m+m+s+w+m, δ[=C-H]); ^{1}H-NMR : 6.80 (1 H, dd, *J* 17.4, 11.0), 5.36 (1 H, d, broad, *J* 9.1), 5.29 (1 H, d, fine structur, *J* 17.4), 5.18 (1 H, dt, *J* 11.0, 1.5), 4.69 (1 H, ddd, *J* ~ 9, 7.3, 6.1), 1.86 (3 H, d, *J* 1.5), 1.69 (1 H, non, *J* 6.9), 1.64 (1 H, s, broad), 1.53 (1 H, ddd, *J* 13.5, 7.0, 6.1), 1.30 (1 H, ddd, *J* 13.5, 7.5, 7.0), 0.94 (3 H, d, *J* 6.6), 0.92 (3 H, d, *J* 6.6); ^{13}C-NMR : 134.4 (s), 133.6 (d, *J* 156), 133.3 (d, *J* 156), 115.5 (t, *J* 158), 65.7 (d, *J* 142), 46.9 (t, *J* 127), 24.6 (d, *J* 130), 23.1 (q, *J* 122), 22.6 (q, *J* 122) 19.8 (qt, *J* 128.9); MS : 154 (1%, M^+), 136 (17%), 121 (10%), 97 (89%), 79 (100%).

i) **(2*Z*,4*E*)-3,7-Dimethyl-2,4-octadien-1-ol (*Z*,*E*-22)** : A 2 : 1 mixture of 2-isobutyl-4-methyl-3,6- and 2-isobutyl-4-methyl-5,6-dihydro-2*H*-pyran (see Section 3d) were concomitantly submitted to the ring opening elimination reaction (see Sections 2a and 4f). After 5 h at -50 °C, a 5 : 3 mixture of 22 and *Z*-17 was obtained with a 69% yield; bp 81 - 89 °C/1 mmHg; Analysis : calc. for $C_{10}H_{18}O$ (154.25) C 77.87, H 11.76, found C 77.93, H 11.96%.

The major component was separated by preparative gas chromatography (3 m, 10% SE-30, 95 → 195 °C at a rate of 5 °C/min); n_D^{20} 1.4905; IR : 3350 (s, broad, ν[O-H]), 3050 + 3020 (w, ν[=C-H]), 2960 (m, ν[-C-H]), 1655 + 1630 (w, ν[C=C]), 1020 (0, ν[C-=]), 965 (s, δ[=-C-H]); ^{1}H-NMR : 6.41 (1 H, dd, *J* 15.5, 1.0), 5.78 (1 H, dt, *J* 15.5, 7.6), 5.49 (1 H, t, broad, *J* ~ 7.3), 4.30 (2 H, d, *J* 7.2), 2.05 (2 H, dt, *J* 7.0, 0.9), 1.88 (3 H, d, *J* 0.8), 1.68 (1 H, non, *J* 6.6), 1.50 (1 H, s, broad, 0.92 (6 H, d, *J* 6.8); ^{13}C-NMR : 135.8 (s), 131.9 (d, *J* 150), 127.4 (d, *J* 152), 126.2 (d, *J* 155), 58.5 (t, *J* 142), 42.6 (t, *J* 130), 28.7 (d, *J* 126), 22.4 (q, *J* 125), 20.6 (q, *J* 126); MS : 154 (7%, M^+), 136 (13%), 121 (11%), 93 (84%), 79 (100%).

5. Rate Comparisons

a) Competition between 4-ethoxy- and 4-methoxy-1-nonene : At -75 °C, the two ethers (2.5 mmol each) were dissolved in a solution of lithium diisopropylamide (2.5 mmol) and potassium *tert*-butoxide (0.25 mmol) in tetrahydrofuran (5 mL) containing also some octane (0.1 - 0.2 g) as an "internal standard". As soon as homogeneity was achieved, a sample was withdrawn, quenched with a methanolic solutio of acetic acid and analyzed by gas chromatography (3 m, 5% SE-30, 70 → 190 °C at a rate of 10 °C/min). The mixture was stored 30 min at -50 °C before a second sample was withdrawn and treated in the same way. The relative ether concentrations before and after the reaction were inserted into the equation for competitive kinetic measurements [34] and the ratio of rate constants was calculated. - In a separate run, pure 4-ethoxy-1-nonene gave 93% *E*-1.

4-Ethoxy-1-nonene was prepared from 1-nonen-4-ol (60 mmol) by consecutive treatment with sodium amide in dimethylsulfoxide and ethyl iodide (see also Section 1a); 6.7 g (66%); bp 40 - 44 °C/0.1 mmHg; n_D^{20} 1.4258; ^{1}H-NMR (80 MHz) : 5.92 (1 H, ddt, *J* 17, 10, 7), 5.08 (1 H, d, *J* 17), 5.06 (1 H, d, *J* 11), 3.5 (3 H, m), 2.25 (2 H, t, *J* 6), 1.4 (8 H, m), 1.19 (3 H, t, *J* 7), 0.90 (3 H, t, *J* 6); MS : 129 (44%, M^+ - C_3H_5), 99 (10%), 83 (100%); Analysis : calc. for $C_{11}H_{22}O$ (170.30) C 77.58, H 13.02, found C 78.06, H 12.97%.

b) Competition between 4-(1,1-dimethylethoxy- and 4-methoxy-1-nonene : The same procedure as described above (Section 5a) was applied. In a separate run, pure 4-(1,1-dimethylethoxy)-1-nonene gave 88% *E*-1.

4-(1,1-Dimethylethoxy)-1-nonene was obtained by heating a solution of 1-nonen-4-ol (50 mmol) in dichloromethane (0.10 L) with isobutene (0.15 kg, 2.7 mol) in the presence of concentrated (98%) sulfuric acid (5 mmol) [35]. After separation of the solution from a viscous, insoluble residue by centrifugation and evaporation of the volatile components, 4.5 g (46%) of a colorless liquid were collected in the boiling range 48 - 52 °C/0.1 mmHg; n_D^{20} 1.4326; ^{1}H-NMR (80 MHz) : 5.87 (1 H, ddt, *J* 17, 10, 7), 5.03 (1 H, d, *J* 16), 5.01 (1 H, d, *J* 11), 3.50 (1 H, pent, *J* 6), 2.21 (2 H, t, *J* 7), 1.3 (8 H, m), 1.19 (9 H, s), 0.88 (3 H, t, *J* 6); MS : 157 (100%, M^+ - C_3H_5), 127 (20%), 83 (98%); Analysis : calc. for $C_{13}H_{26}O$ (198.35) C 78.72, H 13.21, C 78.71, H 13.06%.

c) Competition between 4-trimethylsilyloxy- and 4-methoxy-1-nonene : The same procedure as described above (Section 5a) was applied. In a separate run, 4-trimethylsilyloxy-1-nonene gave 70% *E*-**1**. Treatment of 1-nonen-4-ol (50 mmol) during 6 h at 25 °C with chlorotrimethylsilane (2.2 g, 20 mmol) and bis(trimethylsilyl)amine (6.5 g, 40 mmol) in the presence of pyridine (40 mL) resulted in the formation of 7.2 g (67%) **4-trimethylsilyloxy-1-nonene**, isolated after filtration and evaporation of the pyridine by distillation; bp 44 - 46 °C/0.3 mmHg; n_D^{20} 1.4249; IR : 3095 (m, ν[=C-H]), 2965 (m, ν[-C-H]), 1647 (m, ν[C=C]), 1255 (s, δ[SiC-H]), 1090 (s, ν[C-O]=, 840 (s, ν[C-Si]); ^{1}H-NMR (80 MHz) : 5.82 (1 H, ddt, *J* 18, 9. 7), 5.0 (2 H, m), 3.65 (1 H, pent, *J* 6), 2.16 (2 H, t, *J* 6), 1.3 (8 H, m), 0.86 (3 H, t, *J* 6), 0.07 (9 H, s); MS : 199 (3%, M^+ - CH_3), 173 (34%), 143 (10%), 73 (100%); Analysis : calc. for $C_{12}H_{26}OSi$ (214.43) C 67.22, H 12.22, found C 67.41, H 12.30%.

d) Competition between 4-(methoxymethoxy)- and 4-methoxy-1-nonene : The same procedure as described above (Section 5a) was applied. In a separate run, 4-(methoxy-methoxy)-1-nonene gave 55% *E*-**1**.

In order to prepare the starting material, 1-nonene-4-ol (50 mmol) was treated during 72 h at 25 °C with dimethoxymethane (100 mL) in the presence of lithium bromide (30 mmol) and *p*-toluenesulfonic acid monohydrate (5 mmol) [36]. At the end, some of the alcohol remained unconsumed. The reaction mixture was absorbed on neutral aluminum oxide (Brockmann activity grade I, 100 mL) and the product, 5.9 g (63%) of **4-methoxymethoxy-1-nonene** eluted with pentane (400 mL); bp 46 - 49 °C/0.3 mmHg; n_D^{20} 1.4283; IR : 3095 (m, ν[=C-H]), 2950 (m, ν[-C-H]), 2795 (w, ν[OC-H]), 1645 (m, ν[C=C]), 1100 + 1045 (s, ν[C-O]), 918 (s, δ[=C-H]); ^{1}H-NMR (80 MHz) : 5.90 (1 H, ddt, *J* 18, 10, 7), 5.10 (1 H, d, *J* 17), 5.08 (1 H, d, *J* 11), 4.69 (2 H, s), 3.63 (1 H, pent, *J* 6), 3.40 (3 H, s), 2.30 (2 H, t, *J* 7), 1.4 (8 H, m), 0.90 (3 H, t, *J* 6); MS : 186 (5%, M^+), 145 (100%), 99 (84%), 83 (62%); Analysis : calc. for $C_{11}H_{22}O_2$ (186.30) C 70.92, H 11.90, found C 70.69, H 11.69%.

e) Competition between 1-pentyl-3-butenyl pivaloate (4-pivaloyloxy-1-nonene) and 4-methoxy-1-nonene : The same procedure as described above (Section 5a) was applied. In a separate run, 1-pentyl-3-butenyl pivaloate gave 84% *E*-**1**.

The starting material was prepared by keeping 1-nonen-4-ol (30 mmol) and pivaloyl chloride (50 mmol) in pyridine (30 mL) 10 h at 25 °C. After evaporation of the solvent, the residue was absorbed on silica gel (150 g) which was eluted with hexane (400 mL). Distillation afforded 3.1 g (46%) of **1-pentyl-3-butenyl pivaloate**; bp 53 - 57 °C/0.8 mmHg; n_D^{20} 1.4274; IR : 3095 (m, ν[=C-H]), 2970 (m, ν[-C-H]), 1740 (s, ν[C=O]), 1650 (s, ν[C=C]), 1170 (s, ν[C-O]), 915 (s, δ[=C-H]); ^{1}H-NMR (80 MHz) : 5.80 (1 H, ddt, *J* 18, 10, 7), 5.1 (2 H, m), 4.93 (1 H, pent, *J* 6), 2.30 (2 H, t, *J* 7), 1.3 (8 H, m), 1.17 (9 H, s), 0.88 (3 H, t, *J* 6); MS : 226 (4%, M^+), 185 (10%), 124 (11%), 85 (100%); Analysis : calc. for $C_{14}H_{26}O_2$ (226.4) C 74.29, H 11.58, found C 73.88, H 11.60%.

f) Competition between 2-ethyl-4-methylenetetrahydropyran, 2-ethyl-4-methyl-3,6-dihydro-2*H*-pyran and 2-ethyl-4-methyl-5,6-dihydro-2*H*-pyran : A 20 : 50 : 30 mixture (10 mmol) of the three isomers (see Section 3b) was added to a solution of lithium diisopropylamide (10 mmol) and potassium *tert*-butoxide (1 mmol) in tetrahydrofuran (20 mL) containing some 1-nonanol as an "internal standard" for gas chromatographic comparison of peak areas. Immediately after the addition of the isomeric substrates and 20 min later samples were withdrawn, quenched and analyzed. Relative rates of 3, 1 and, respectively, 9 were calculated [34].

g) Competition between 2-(1-methyl-2-propenyl)- and (*Z*)-2-(2-butenyl)tetrahydropyran : Under standard conditions only the latter compound reacted while the branched isomer was completely recovered. This means a difference in reaction rates by a factor of at least 20.

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