172. Capricious Stereoselectivities of Alkenylpotassium Formation under Kinetic and Thermodynamic Control Oxygen-Triggered Configurational Equilibration of an Allyl Type Organometallic Compound[1])

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Summary

(Z)-1-Alkylated propenes undergo metallation at an allylic site more rapidly than do their *(E)*-isomers, no matter in which configuration the resulting organometallic is thermodynamically more stable. A striking illustration is given by *(Z)*-4,4-dimethyl-2-pentenyl potassium which is formed 15 times faster than its *(E)*-isomer, although the latter is clearly favored under equilibrium conditions. The configurational reorganization of alkenylpotassium compounds in tetrahydrofuran solution is very slow. At least in one case, however, traces of oxygen efficiently catalyse the *Z/E* equilibration.

Organopotassium and organocaesium compounds [2] of the allyl type show a striking preference for the *endo-* (or *Z*-)configuration, though simple steric considerations would argue in favor of the *exo-(E-)*isomer. Thus, in the case of 2-butenylpotassium and 2-hexenylpotassium *Z/E* ratios of 120:1 and 40:1, respectively, were determined after the configurational equilibrium had been established in an hexane suspension [3][2]). These values were found to be reproducible within reasonably small limits of error [2]. However, equilibration in tetrahydrofuran solution when repeated several times, gave rise to significant aberrations. As we recognize now, this treacherous behavior is due to the interplay of two important factors:

- *Z/E* ratios produced by kinetically controlled metallation differ significantly from the equilibrium position;
- Configurational interchange occurs only slowly, particularly in tetrahydrofuran solution, but may be catalysed by oxygen or other impurities present in trace amounts.

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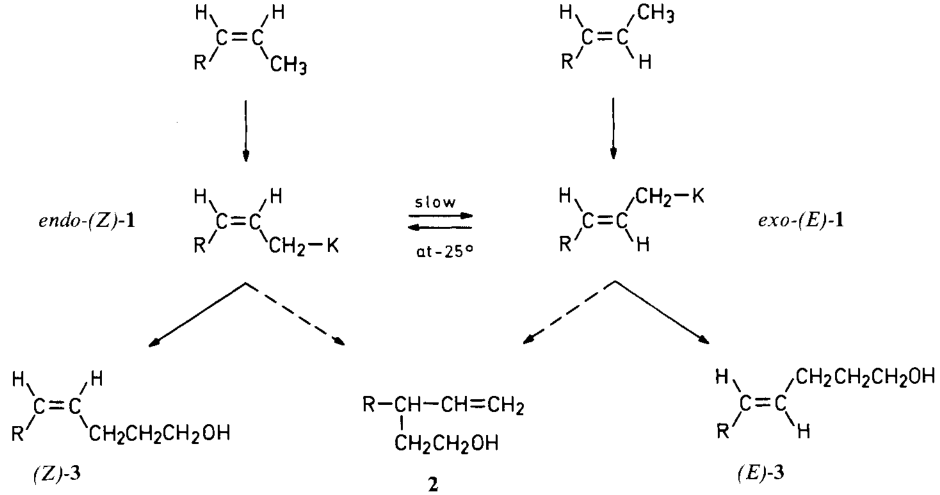
[1]) Part VI of the series 'Selective Syntheses with Organometallics'; for the preceding paper see [1].

[2]) If trimethylsilylmethyl potassium is used as the metallating agent and, therefore, no lithium *t*-butoxide is present in the hexane suspension, butenyl potassium and hexenyl potassium exhibit significantly less extreme positions: *Z/E* = 16 in both cases (see p. 1710).

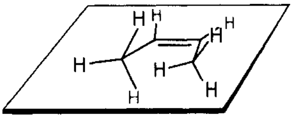
A 1:1 mixture of *cis* and *trans* 2-hexene treated with a limited quantity of trimethylsilylmethyl potassium [1] [4] in tetrahydrofuran at −55° produces an organometallic intermediate **1a** which reacts with oxirane to afford besides some 3-propyl-4-penten-1-ol (**2a**), *(Z)*- and *(E)*-4-octen-1-ol (*Z*-**3a** and *E*-**3a**) in a ratio of 4.6:1. Since under the given reaction conditions the organopotassium compounds **1a** are configurationally stable, this ratio reflects a same reactivity advance of the *Z*-isomer over the *E*-isomer ($\Delta\Delta G^{\neq} = 2.8$ kJ/mol $= 0.7$ kcal/mol).

Scheme 1



a: $R = H_7C_3$; b: $R = (H_3C)_3C$

The superiority of the *(Z)*-isomer in kinetic competition seems to establish another case of a 'sterically accelerated' metallation reaction [5]: As illustrated with the eclipsed-staggered conformation of *(Z)*-2-butene (**4**), the two methyl groups placed on the same side of the double bond approach each other close enough to suffer from substantial steric repulsion. In the corresponding butenyl anion (**5**) the interacting hydrogen atoms are further apart, mainly because the HCC angles in the methylene unity (around 120°) have been widened with respect to the same angles in the original methyl group (close to 110°). The detailed structure of the transition state of metallation is unknown. It can, however, be safely assumed to lie somewhere between the extreme geometries of the olefinic precursor and the corresponding carbanion **5**. Thus, in the *(Z)*-series, the hydrogen/metal exchange benefits from a decrease of intramolecular repulsions, while no such relief is operative in the strain-free *(E)*-series.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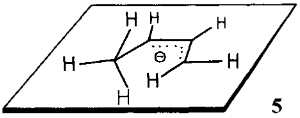
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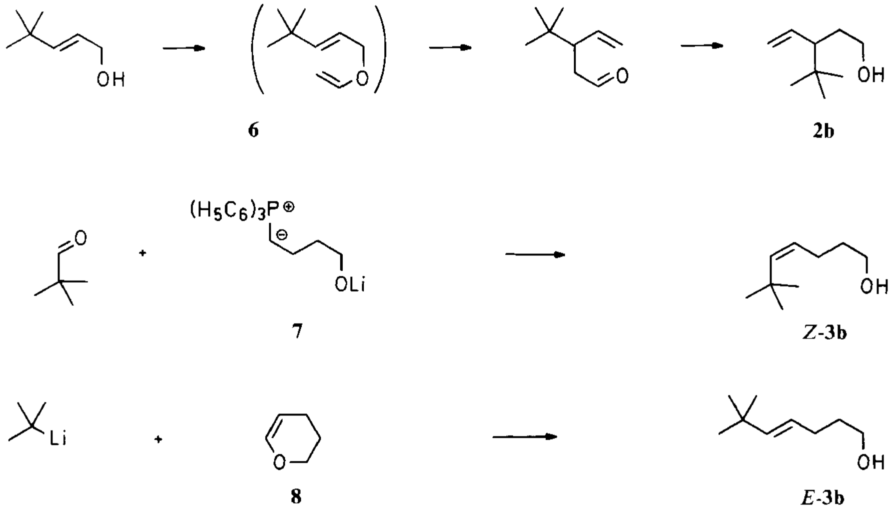
A more sterically crowded molecule would provide an even bigger driving force which assists to the departure of the hydrogen atom upon replacement by a metal. Thus, *(Z)*-4,4-dimethyl-2-pentene undergoes metallation to afford the corresponding organopotassium compound *(Z)*-**1b** at −45° in tetrahydrofuran 15 times more rapidly than its *(E)*-isomer to give *(E)*-**1b** ($\Delta\Delta G^{\neq} = 4.9$ kJ/mol (= 1.2 kcal/mol)). Starting out with a mixture rich in the *cis* isomer (as a 'salt-free' *Wittig* reaction [6] would furnish) it is almost exclusively the *(Z)*-component which will undergo metallation upon attack of trimethylsilylmethylpotassium. In other words, there is no need to dispose of pure *(Z)*-4,4-dimethyl-2-pentene in order to obtain derivatives with the *cis*-configuration (such as *(Z)*-**3b**) without notable contamination by the *trans*-isomer. On the other hand, products with *trans* double bonds (such as *(E)*-**3b**) can be obtained either by allowing for an equilibration step (see below) or by starting out with pure *(E)*-4,4-dimethyl-2-pentene. Varying amounts of a branched regioisomer (3-*t*-butyl-4-penten-1-ol (**2b**), when oxirane is chosen as the electrophile) notoriously accompany the straight-chain product **3**, no matter what configuration it has.

Compounds **2b**, *(Z)*-**3b** and *(E)*-**3b** were isolated and compared with authentic materials. These had been prepared by independent, though more lengthy routes (see *Scheme 2*), *i.e.*, 3-*t*-butyl-4-penten-1-ol (**2b**)³) by *Claisen/Cope*-rearrangement (*cf.* [8] [9]) of allyl vinyl ether **6**⁴) and subsequent sodium borohydride reduction of the resulting aldehyde; *(Z)*-6,6-dimethyl-4-hepten-1-ol (*Z*-**3b**) by *cis*-selective *Wittig* reaction [6] between pivalaldehyde and triphenylphosphonio-(4-lithiumoxy-

Scheme 2



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³) Furthermore, **2b** was identified as the sole volatile product after treatment of 1,2-dihydro-5*H*-pyran [7] with *t*-butylmagnesium chloride 6 h at 230°, but only in a 3.5% yield.

⁴) The *(E)*-4,4-dimethyl-2-penten-1-ol required for the preparation of **6** was obtained according to the *SCOOPY* procedure ([6] [10] [11]) or by applying the metallation/dialkoxyboration/oxidation sequence [12] to 4,4-dimethyl-2-pentene.

butylid) (**7**); *(E)*-6,6-dimethyl-4-hepten-1-ol (*E*-**3b**) by ring-opening addition ([13] [14]5)) of *t*-butyllithium onto 3,4-dihydro-2*H*-pyran (**8**).

Under equilibrium conditions the *(E)*-isomer of **1b** is clearly favored: $Z/E = 8:92$ and 13:87 in hexane and tetrahydrofuran, respectively [2]. Thus the ratios measured are not significantly different from data obtained for 4,4-dimethyl-2-pentenyllithium (3:97 and 4:96 in diethyl ether and tetrahydrofuran, respectively [2]). Unlike their lithium counterparts, however, alkenylpotassium compounds undergo configurational interconversion only very slowly [3]. In fact, equilibrium cannot be attained even after several days, if the isomerization is carried out in tetrahydrofuran solution (at −30°) with rigorous exclusion of air. It is possible, however, to catalyse the conversion of *(Z)*-**1b** into *(E)*-**1b** by traces of air (see *figure*).

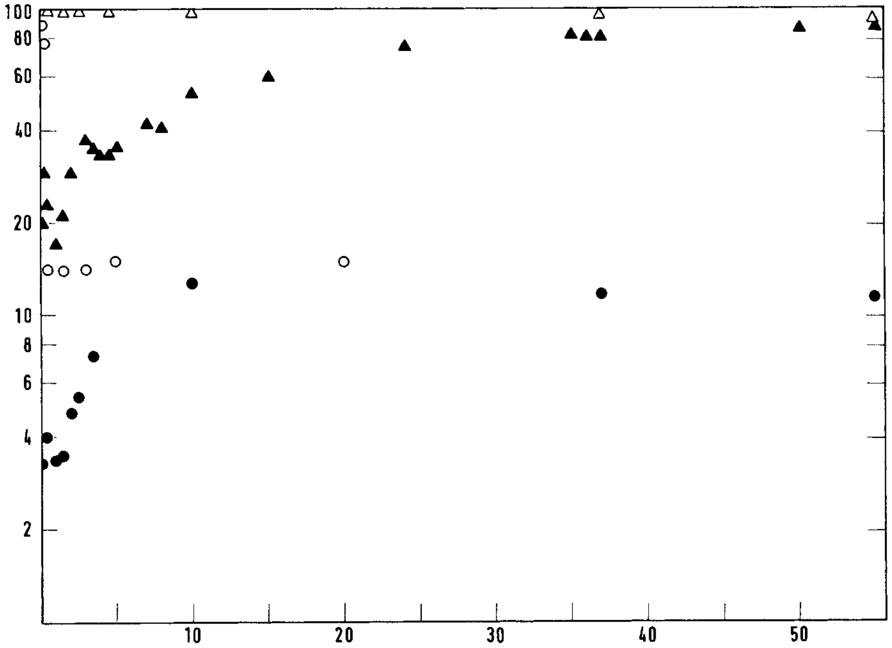

Figure. Endo/exo- (Z/E-)-*isomerization of allylpotassium derivatives* **1a** *and* **1b** *as a function of time* (on the ordinate: percentage of Z-isomer in the isomeric mixture; on the abscissa: reaction time in h).

△ *endo*-**1a** (trapped as Z-**3a**) ○ *endo*-**1b** (trapped as Z-**3b**)
▲ *exo*-**1a** (trapped as *E*-**3a**) ● *exo*-**1b** (trapped as *E*-**3b**)

Oxygen-triggering of torsional isomerizations was first observed in connection with studies of metallated enamines [16]. Oxygen is known to generate free radicals from organometallic compounds [17]. In general, an allyl type radical would not

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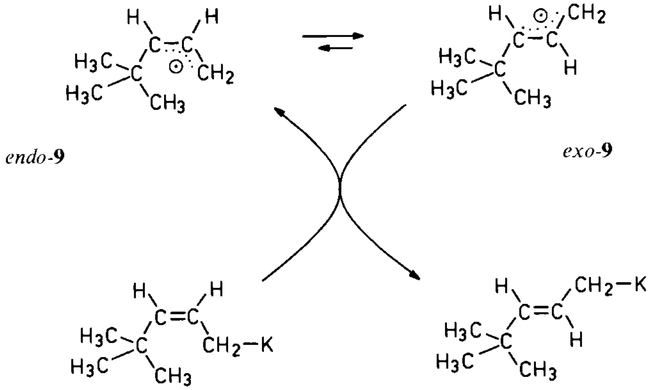
5) After refluxing a mixture of 2,3-dihydrofuran and butyllithium (2 equiv.) in hexane for 3 h, stereoisomerically pure 3-octen-1-ol (31%) was isolated. The coupling constant between the olefinic hydrogen atoms (measured in the presence of the praseodymium complex DC-1515 as a shift reagent) permitted unambiguous assignment of the *(E)*-configuration [15].

undergo rapid configurational interconversions since it must overcome a substantially high torsional barrier (> 17 kcal/mol [18]). The *endo*-4,4-dimethylpentenyl radical (*endo*-**9**), however, can lose a significant amount of steric strain upon torsional motion and therefore is separated from its *exo*-isomer (*exo*-**9**) by an exceptionally low barrier (10.3±0.9 kcal/mol [19]). After isomerization the *exo*-radical (*exo*-**9**) has only to abstract a potassium atom from the *(Z)*-isomer of the organometallic compound (*Z*-**1b**) in order to regenerate the *endo*-radical (*endo*-**9**) and thus to start and to maintain a chain process (see *Scheme 3*). Eventually the chain will be terminated by radical combination with oxygen or an hydroperoxide intermediate.

Scheme 3



The slowness in *Z*/*E*-isomerization of alkenylpotassium compounds casts doubt on any claimed *Z*/*E*-equilibration unless the same configurational mixture could be reached starting out from each of the two stereoisomeric precursors. Furthermore, the preference of *(Z)*-4,4-dimethyl-2-pentenyl potassium under kinetic control not only offers a preparatively useful option, but also has fundamental implications. Since its *(E)*-isomer is known to be thermodynamically more stable [2], the opposite trend in kinetic reactivity strongly argues against the view [20] that the predominance of *cis*-2-alkenes in the early stages of base-catalysed 1-alkene isomerisations must reflect an energetic advantage of *cis*(*endo*)-shaped alkenyl carbanions over their *trans*(*exo*)-analogues.

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Experimental part

General Remarks: see [3] [21].

1. Materials for comparison. - a) *4-Propyl-5-hexen-1-ol* (**2a**), (Z)-*2-octen-1-ol* (*Z*-**3a**) and (E)-*2-octen-1-ol* (*E*-**3a**) were obtained by metallation of *(Z)*- and *(E)*-2-octene followed by treatment with oxirane [3].

b) *3-*t*-Butyl-4-penten-1-ol* (**2b**). A hexane solution (1.60M) of butyllithium (62.5 ml, 100 mmol) was evaporated under reduced pressure (0.2 Torr) and the residue taken up at −78° in tetrahydrofuran (50 ml). *(Z)*-4,4-Dimethyl-2-pentene (10 ml, 0.07 mol) and potassium *t*-butoxide (0.07 mol) were added. After 42 h at −30°, the mixture was cooled down to −78° and treated first with fluorodimethoxyborane (10.2 g, 110 mmol) and then, 1 h later, with 30% hydrogen peroxide (12 ml, 0.12 mol) and aqueous sodium hydroxide (40 ml, 3N) [9]. The reaction mixture was allowed to reach 25°, was saturated with sodium chloride and stirred over night. Virtually pure 4,4-dimethyl-2-penten-1-ol was isolated by repeated extraction with diethyl ether (4×20 ml), washing, drying and evaporation of the solvent and distillation; $Z/E = 6:94$; yield 4.4 g (55%); b.p. 158-161°. - IR. (film): 3380 br. (O–H); 2970*s* and 2880*m* (C–H); 1370*m* (CH_3); 985*s* (–CH=CH–, *trans*). - ^{1}H-NMR.: 5.6 (*m*, 2 olefin. H); 4.39 (*s*, hydroxyl); 4.01 (*d*, $J = 4.5$, methylene adjacent to O); 1.02 (*s*, *t*-butyl). - MS. *(m/e)*: 114 (1.6%, M^+); 83 (100%).

$C_7H_{14}O$ (114.2) Calc. C 73.63 H 12.37% Found C 73.78 H 12.45%

4,4-Dimethyl-2-penten-1-ol (4.0 g, 35 mmol), mercuric acetate (0.4 g) and ethyl vinyl ether (100 ml) were heated 12 h under reflux. The mixture was cooled down and treated with potassium carbonate (1 g). After evaporation of the excess ethyl vinyl ether the residue was taken up in pentane (100 ml) and the solution filtered through a column filled with silica gel (10 g). Distillation afforded 3.2 g (65%) 4,4-dimethyl-2-penten-1-yl vinyl ether; b.p. 159-162°. - IR. (film): 2950*s* and 2865*m* (C–H); 1195*s* (C–O); 970*s* (–CH=CH–, *trans*); 810*m* (–O–CH=CH_2?). - ^{1}H-NMR.: 6.42 (*d*×*d*, $J = 14$ and 7 Hz, olefin. H next to O); 5.6 (*m*, 2 olefin. H, *trans* double bond); 4.0 (*m*, terminal methylene and methylene adjacent to O); 1.03 (*s*, *t*-butyl). - MS. *(m/e)*: 140 (0.8%, M^+); 55 (100%).

$C_9H_{16}O$ (140.2) Calc. C 77.09 H 11.50% Found C 77.22 H 11.61%

Small amounts of hydroquinone (0.05 g) and propionic acid (0.02 g) [9] were added to 4,4-dimethyl-2-penten-1-yl vinyl ether (1.8 g, 13 mmol). After 5 h heating at 190° under nitrogen all starting material had disappeared. Distillation yielded 1.5 g (83%) 3-*t*-butyl-4-pentenal; b.p. 51-53°/9 Torr. - IR. (film): 2965*s*, 2875*m* and 2720*w* (C–H); 1735*s* (C=O); 1370*m* (CH_3); 920*s* (–CH=CH_2). - ^{1}H-NMR.: 6.0-4.8 (*m*, vinyl); 2.4 (*m*, methine and methylene); 0.90 (*s*, *t*-butyl). - MS. *(m/e)*: 140 (0.8%, M^+); 57 (100%).

$C_9H_{16}O$ (140.2) Calc. C 77.09 H 11.50% Found C 76.79 H 11.32%

This aldehyde (0.90 g, 6.4 mmol) was dissolved in diethyl ether (15 ml) which contained sodium borohydride (0.76 g, 2.0 mmol). After 12 h heating under reflux, the mixture was treated with 3N HCl (10 ml), the organic phase was separated and the aqueous one extracted with diethylether (10 ml). The combined organic layers were washed, dried and evaporated. From the residue 0.43 g (47%) 3-*t*-butyl-4-penten-1-ol (**7**) were isolated by distillation; b.p. 61-62°/9 Torr. - IR. (film): 3320 br. (O–H); 2950*s* and 2860*m* (C–H); 1625*w* (C=C); 1360*m* (CH_3); 990*m* and 910*s* (–CH=CH_2). - ^{1}H-NMR.: 5.8-4.6 (*m*, vinyl); 4.30 (*s*, br., hydroxyl); 3.5 (*m*, methylene adjacent to O, diastereotopic hydrogen atoms); 2.0-1.1 (*m*, methine and other methylene); 0.88 (*s*, *t*-butyl). - MS. *(m/e)*: 142 (8.5%, M^+); 57 (100%).

The same product (**2b**) was obtained in only 3.5% yield, when 5,6-dihydro-2*H*-pyran (0.67 g, 8.0 mmol) [7] was added to an etheral solution of *t*-butylmagnesium chloride (8.0 mmol) and, after evaporation of the solvent, heated 6 h to 230°.

c) *(Z)-6,6-Dimethyl-4-hepten-1-ol* (*Z*-**3b**). 4-Hydroxybutyltriphenylphosphonium chloride (25.9 g, 70 mmol, prepared by heating triphenylphosphine and 4-chlorbutanol 72 h at 80°) was suspended in tetrahydrofuran (140 ml) and, under vigorous stirring, treated dropwise with butyllithium (140 mmol; 1.6M in hexane) at −78°. The yellow slurry was allowed to reach 25°. After 30 min cooled down again to −78°, it was treated with pivalaldehyde (6.0 g, 70 mmol) dissolved in tetrahydrofuran (10 ml). After 1 h stirring at 25° the mixture was worked up by hydrolysis (50 ml water), extraction with diethyl ether (3×50 ml), drying (magnesium sulfate) and evaporation of the solvent (*Widmer* column). The residue was treated with pentane (0.5 l) and the precipitated triphenylphosphine oxide filtered off. The liquid phase was concentrated again (*Widmer* column) and distilled; b.p. 84-88°/17 Torr; 2.6 g (26%) **3b**, *Z/E*-ratio 99.8:0.2 (according to GC., 20 m HB-5100*, 90° [16 min]→150°). - IR.: 3330*s* (O–H); 1655*w* (C=C); 1060*s* (C–O); 720*w* (–CH=CH–, *cis*, out-of-plane). - ^{1}H-NMR.: 5.2 (*m*, 2 olefin. H); 3.56 (*t*, $J = 6.5$, oxygen-bearing methylene); 3.45 (*s*, hydroxyl); 2.2 (*m*, *qa*-like, $J \sim 6.5$, allylic methylene);

1.6 (*m*, *qi*-like, $J \sim 6.5$, other methylene 1.10 (*s*, *t*-butyl). - MS. *(m/e)*: 142 (20%, M^+); 109 (75%); 83 (93%); 67 (57%); 55 (100%).

$C_9H_{18}O$ (142.2) Calc. C 76.00 H 12.76% Found C 76.20 H 12.62%

d) (E-)-*6,6-Dimethyl-4-hepten-1-ol* (*E*-**3b**). 3,4-Dihydro-2*H*-pyran were added dropwise to 1.46M *t*-butyllithium (100 mmol) in hexane (68.5 ml) over a period of 30 min. After 3 h heating under reflux, the mixture was hydrolysed at −20° and the aqueous phase extracted with ether (2× 10 ml). The combined organic layers were dried and evaporated. Bulb-to-bulb ('Kugelrohr') distillation of the residue afforded 1.56 g (22%) *(E)*-**3b**; b.p. 85-90°/12 Torr. Trace amounts of impurities were eliminated by prep. GC. (3 m, 20% Ap-L*, 135°). - IR. (film): 3340*s* br. (O−H); 2970*s* and 2880*m* (C−H); 1370*m* (CH_3); 980*s* (−CH=CH−, *trans*). - ^{1}H-NMR.: 5.4 (*m*, 1 olefin. H); 4.22 (*s*, hydroxyl); 3.58 (*t*, $J = 6.5$, methylene adjacent to O); 2.1 (*m*, allylic methylene); 1.6 (*m*, other methylene); 0.99 (*s*, *t*-butyl). - MS. *(m/e)*: 142 (43%, M^+); 109 (100%).

$C_9H_{18}O$ (142.2) Calc. C 76.00 H 12.76% Found C 75.96 H 12.80%

2. Metallation of alkenes and subsequent reaction with oxirane. - a) *With* (E)-*2-hexene.* Bis(trimethylsilylmethyl)mercury (0.467 g, 1.25 mmol), potassium/sodium alloy (0.3 ml) and pentane (7 ml) were stirred for 1 h at 25°. The solvent was evaporated under reduced pressure and replaced by precooled tetrahydrofuran (7 ml). *E*-2-hexene (0.74 ml, 5.1 mmol) was added to the organometallic solution at −25°. The mixture was kept 50 h at this temperature before being treated with oxirane (0.3 ml, 6.1 mmol); then it was allowed to warm up and was hydrolysed. The composition of the reaction mixture was analysed by GC. (20 m Ucon HB-5100*, 95°): 11% *3-propyl-4-hexen-1-ol* (**2a**) and 8.3% *4-octen-1-ol* (**3a**, $Z/E = 87:13$).

b) *With* (Z)- *and* (E)-*4,4-dimethyl-2-pentene.* A *Schlenk*-tube, filled with 4,4-dimethyl-2-pentene (4.4 g, 45 mmol), butyllithium (45 mmol, 2.5M solution in pentane)[6]) and potassium-*t*-butanolate (5.0 g, 45 mmol), was sealed under argon and shaken for 48 h on an horizontally moving machine. At 0° oxirane (3 ml, 0.06 mol) in pentane (10 ml) was added dropwise. After 30 min stirring at 25°, the mixture was poored into water (25 ml), extracted with pentane (3×25 ml), dried and evaporated (*Widmer* column). Distillation yielded a mixture of *3-*t*-butyl-4-penten-1-ol* (**2b**; 1.5 g, 21%) and (E)-*6,6-dimethyl-4-hepten-1-ol* (*E*-**3b**; 2.9 g, 48%); b.p. 81-84°/17 Torr; inseparable by prep. GC.

c) *With* (Z)-*4,4-dimethyl-2-pentene.* To a solution of trimethylsilylmethyl potassium (approximately 2.5 mmol) *Z*-4,4-dimethyl-2-pentene (0.37 ml, 2.5 mmol) was added at −78°. The mixture was kept 2 h at −48°, treated with oxirane (0.15 ml, about 3 mmol), hydrolysed with water (10 ml) and analysed by GC.: 8% *3-*t*-butyl-4-penten-1-ol* (**2b**) and 71% (Z)-*6,6-dimethyl-4-hepten-1-ol* (*Z*-**3b**).

d) *With* (E)-*4,4-dimethyl-2-pentene.* A hexane solution (1.6M) of butyllithium (20 mmol) was evaporated under reduced pressure. The residue was taken up in tetrahydrofuran (12.5 ml) at −78° and potassium *t*-butoxide (2.2 g, 20 mmol) and *E*-4,4-dimethyl-2-pentene (2.0 g, 20 mmol) were added. After 5 h at −55°, the reaction mixture was treated with oxirane (1.1 ml, about 23 mmol) and then allowed to warm up to 25°. It was poured into water (50 ml), the organic layer was separated and the aqueous phase was extracted with diethyl ether (15 ml). The organic layer was dried and evaporated. A distillation yielded 0.55 g of a fraction with b.p. 91-93°/113 Torr. composed of *3-*t*-butyl-4-penten-1-ol* (1.4%) and *6,6-dimethyl-4-hepten-1-ol* (18%; **3b**, $Z/E < 0.3:99.7$). About 2 g of polymeric material remained as a residue.

3. Kinetics of the configurational equilibrations. - a) *With 2-Hexene.* Pure *(Z)*- and *(E)*-isomers (about 30 mmol in each case) were added to a solution of trimethylsilylmethyl potassium (15 mmol) in tetrahydrofuran (30 ml), kept in a cold bath at −25° and containing a known amount of dodecane (about 0.04 g) as an 'internal standard' for analytical purposes. Right at the beginning and then at given times (first after 2 h, later after 10 h intervals) 0.5 ml air were injected into the reaction vessel by means of a syringe through a rubber septum. Periodically samples (1 ml) were withdrawn and added to precooled oxirane (about 1 mmol). After hydrolysis and extraction with hexane (1 ml), the organic phase was submitted to GC. analysis. The results are summarized in the table.

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[6]) The commercial hexane solvent was stripped off under reduced pressure and replaced by pentane.

Table. *Products derived from 2-hexene and 4,4-dimethyl-2-pentene as a function of the length of metallation time:* total yield of products; *ratio of branched* vs. *straight-chain substitution (α/γ-ratio)* (in parentheses) and ratio of *Z*/*E*-isomers resulting from 'γ-attack' (= straight-chain substitution, attack at the allylic methylene terminus)

Metallation time [h]	2-Hexene					
	Z-Isomer			*E*-Isomer		
0.1	57%	(39:61)	99.7:0.3	13%	(56:44)	20:80
0.2	98%	(49:51)	99.7:0.3	17%	(38:62)	29:71
0.4	99%	(50:50)	99.0:0.4	19%	(39:61)	23:77
1.0	90%	(46:54)	99.3:0.7	20%	(43:57)	17:83
1.5	99%	(48:52)	98.8:1.2	19%	(45:55)	21:79
2.0	98%	(49:51)	98.8:1.2	19%	(44:56)	29:71
2.5	72%	(48:52)	98.8:1.2	-	-	-
3.0	-	-	-	8%	(50:50)	37:63
3.5	80%	(46:54)	98.6:1.4	14%	(47:53)	35:65
4.0	-	-	-	20%	(45:55)	33:67
5.0	90%	(50:50)	95.9:4.1	25%	(44:56)	35:65
6.5	-	-	-	-	-	-
8.0	-	-	-	12%	(55:45)	41:59
10	-	-	-	21%	(48:52)	53:47
15	-	-	-	29%	(45:55)	60:40
24	-	-	-	12%	(54:46)	76:24
35	-	-	-	19%	(50:50)	83:17
36	-	-	-	31%	(48:52)	82:18
37	99%	(52:48)	95.6:4.4	29%	(48:52)	82:18
50	-	-	-	31%	(48:52)	87:13
55	100%	(53:47)	94.0:6.0	-	-	-
60	-	-	-	30%	(48:52)	88:12
90	84%	(50:50)	96.3:3.7	-	-	-
	4,4-Dimethyl-2-pentene					
	Z-Isomer[a]			*E*-Isomer		
0.1	17%	(9:91)	83:17	6.5%	(10:90)	0.9:99.1
0.2	33%	(12:88)	77:23	17%	(10:90)	3.3:96.7
0.4	-	-	-	32%	(13:87)	4.0:96.0
1.0	-	-	-	66%	(23:77)	3.4:96.6
1.5	75%	(30:70)	14:86	83%	(29:71)	3.5:96.5
2.0	-	-	-	92%	(33:67)	4.8:95.2
2.5	-	-	-	82%	(34:66)	5.2:94.8
3.0	89%	(33:67)	14:86	-	-	-
3.5	-	-	-	89%	(35:65)	7.3:92.7
4.0	-	-	-	-	-	-
5.0	84%	(33:67)	15:85	-	-	-
6.5	-	-	-	-	-	-
8.0	-	-	-	-	-	-
10	-	-	-	90%	(34:66)	12.6:87.4
15	-	-	-	-	-	-
24	93%[b]	(32:68)	14:86	-	-	-
35	-	-	-	-	-	-
36	-	-	-	-	-	-
37	-	-	-	80%	(34:66)	11.9:88.1
50	-	-	-	-	-	-
55	-	-	-	82%	(34:66)	11.8:88.2
60	-	-	-	-	-	-
90	-	-	-	88%	(32:68)	11.2:88.8

[a] At −48° instead of −25° as in the three other cases.

[b] After 20 h rather than 24 h.

b) *With 4,4-Dimethyl-1-pentene.* The same procedure was applied as with 2-hexene, except that the metallation and isomerization of the *(Z)*-isomer was carried out at − 48°.

Control experiments were performed to check the influence of the air injections. The rates of isomerization of the two hexenylpotassium isomers and of the *E*-4,4-dimethyl-pentenyl potassium turned out to be hardly effected by air or other impurities, whereas the *(Z)*-4,4-dimethyl-pentenyl potassium was found to undergo configurational changes only extremely slowly if at all, in a rigorously oxygen-free atmosphere.

4. Competitive metallation of stereoisomeric alkenes. - a) To a solution of trimethylsilylmethylpotassium (1.22 mmol; prepared as described on p. 1710) in tetrahydrofuran (7 ml) was added a 1:1 mixture of *(Z)*- and *(E)*-2-hexene (0.37 ml, 2.5 mmol) at − 78°. After 30 min at − 55°, the mixture was treated with oxirane (0.15 ml, 3 mmol) and hydrolysed with brine. According to GC. analysis (40 m C-20-M*, 125°) the organic layer contained 1.4% **2a** and 6.9% **3a**; *Z*/*E*-ratio = 82:18.

b) An analogous reaction with a 1:1 mixture of *(Z)*- and *(E)*-4,4-dimethyl-2-pentene afforded 0.8% **2b** and 10.4% **3b**; *Z*/*E*-ratio = 94:6 (25 m SE-30/S*, 80°).

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