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The [2,3]-Wittig Rearrangements of Lithioalkyl Allyl Ethers Exhibit Different *cis,trans*-Selectivities Than [2,3] Shifts in their Lithiomethyl Analogues

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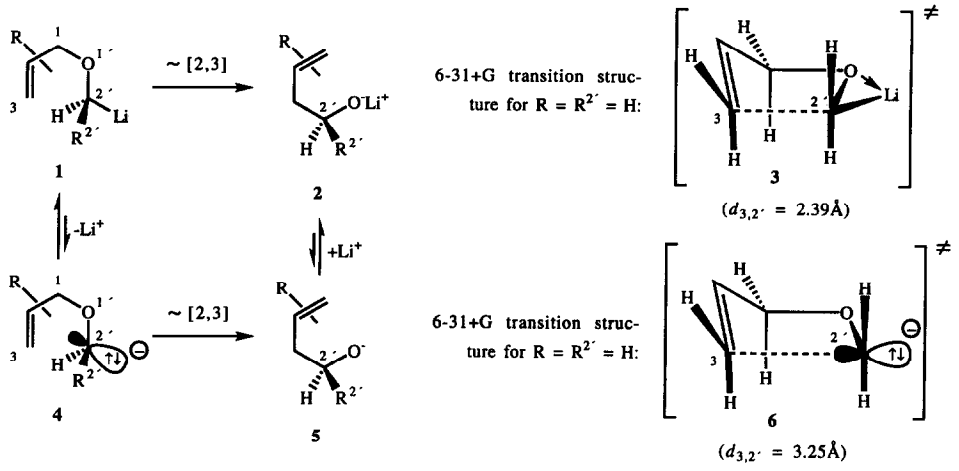
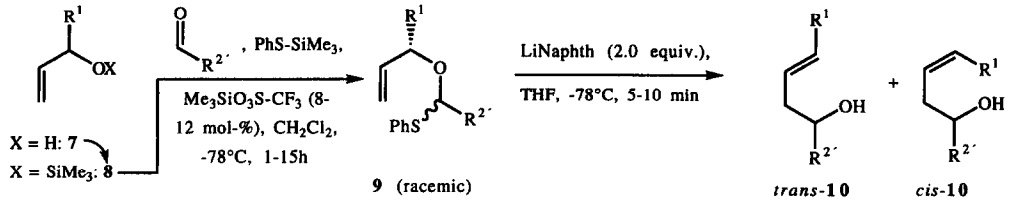
Abstract: The reductive lithiation of O,S-acetals **9a-d** initiated [2,3]-Wittig rearrangements whose *cis,trans*-selectivity depended on whether lithiomethyl (→ *cis*) or lithioalkyl allyl ethers reacted (→ *trans*). It is suggested that these rearrangements proceed via mixtures of the configurationally stable lithioether intermediates *syn*-**13** and *anti*-**13** and transition states $\mathbf{17}_{endo,exo}$ and $\mathbf{17}_{endo,endo}$, respectively.

[2,3]-Wittig rearrangements of lithiated allyl ethers which provide after aqueous workup homoallyl alcohols continue to arise synthetic [1], mechanistic [2], and theoretical interest [3]. Yet, until today one does not know whether the lithiated ethers **1** themselves rearrange to lithium alkoxides **2** or whether they react via the metal-free ether anions **4** to form metal-free alkoxide anions **5** [4] (Scheme 1). In any event, the [2,3] shift itself is believed to be concerted [1]. The [2,3]-Wittig rearrangement of lithiated ethers **1** with non-conjugated carbanionic centers ($R^{2'}$ = H, alkyl) was recently analyzed through ab-initio calculations by Houk *et al.* [3]. For the conversion of lithiomethyl allyl ether (**1**; R = $R^{2'}$ = H) into the lithium alkoxide **2** (R = $R^{2'}$ = H) they found a concerted mechanism and transition structure **3** [3a]. **3** consists of an envelope-shaped C=C-C-O-C moiety. In its main plane lies the lithium atom which bridges C-2' and the adjacent oxygen atom during its migration from the former to the latter. Alternatively, the same reaction was considered to proceed from ether anion **4** to the lithium free alkoxide **5** (R = $R^{2'}$ = H) [3b]. Again, one found a concerted mechanism and an envelope-like transition structure (**6**). It represents an earlier transition state than the lithium analogue **3** since the newly developing C-2'/C-3 bond is almost 1 Å longer. Both transition structures **3** and **6** reproduce correctly the experimental finding that in the course of the rearrangement an inversion of configuration takes place at the carbanion(ic) center [2].



Scheme 1.

Trying to learn more about the factors which determine the stereoselectivity of the [2,3]-Wittig rearrangement, we prepared the O,S-acetals **9b-d** (Scheme 2) from the trimethylsilylated allylic alcohol **8**, PhS-$SiMe_3$ [5], and acetaldehyde, propionaldehyde, and isobutyraldehyde, respectively [6]. They were isolated as inseparable mixtures of diastereomers after flash chromatography on silica [7]. O,S-acetal **9a** was prepared by a published route [8].

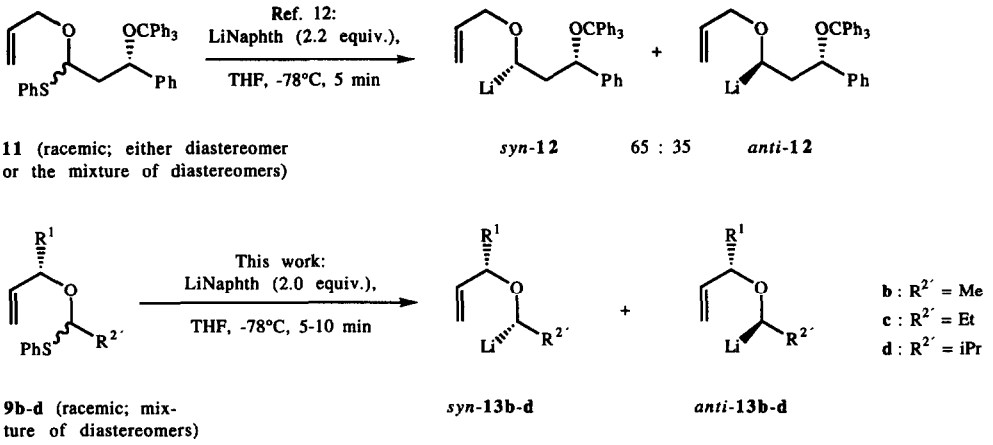


R^1 = CH_2-CH_2-*p*-C_6H_4OMe

Yield **9**	**9**	(diastereomer ratio)	$R^{2'}$	Yield **10**	**10** (*trans*:*cis*)	
(-)	**a**	(-)	H[8]	91%	**a**	(25:75)
52%	**b**	(92: 8)	Me	62%	**b**	(>95:<5)
88%	**c**	(55:45)	Et	66%	**c**	(>95:<5)
49%	**d**	(84:16)	iPr	72%	**d**	(>95:<5)

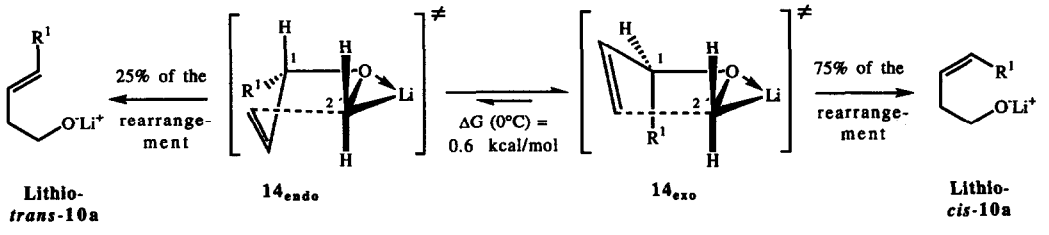
Scheme 2.

Reductive lithiation [9] of these O,S-acetals with lithium naphthalenide ("LiNaphth") led to the Wittig-rearrangement products **10b-d** as expected [8,10] (Scheme 2). However, according to the magnitude of their olefinic coupling constant $J_{H,H}$ = 15.3 Hz compounds **10b-d** were pure *trans* isomers. This contrasts with the observation that under similar conditions the lower homologue O,S-acetal **9a** gives a 75:25 *cis*:*trans* mixture of rearrangement product **10a** [8], i.e., shows the weak *cis*-preference known from the Wittig-Still modification of this reaction [11]. How to explain this discrepancy?



Scheme 3.

It was described earlier that the reduction of O,S-acetals **11** (Scheme 3) occurs with *little* 1,3-asymmetric induction, i.e., delivers a 65:35 ratio of diastereomeric lithio ethers *syn*-**12** and *anti*-**12** [12] which - importantly! - cannot have interconverted before undergoing [2,3]-Wittig rearrangements [13]. One expects an even lower 1,3-asymmetric induction in the reductive lithiation of O,S-acetals **9b-9d**. Therefore, the subsequent Wittig rearrangements will start from *mixtures* of the configurationally stable lithio ethers *syn*- and *anti*-**13b-d**. Due to the absence of a second stereocenter, the formaldehyde-based O,S-acetal **9a** ($R^{2'}$ = H) must react via a single lithioether.

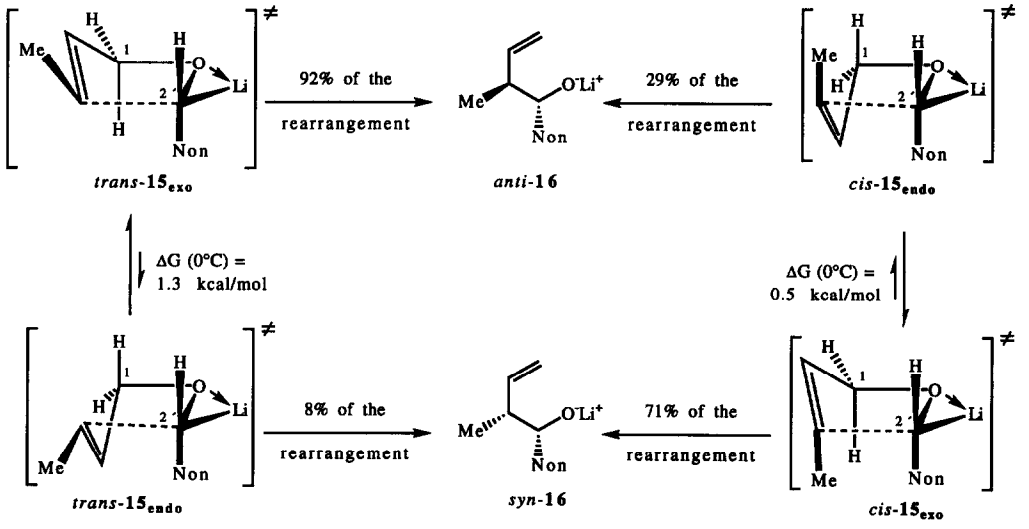


Scheme 4: Preferred orientation of a 1-substituent in the transition state of the [2,3]-Wittig rearrangement

Each of the substituents R^1 and $R^{2'}$ at the stereocenters of the aforementioned lithioether intermediates **13** has a preferred orientation in the transition state of the Wittig rearrangement. The orientational preference of *R^1 alone* is documented in the *cis*-favoring rearrangement of lithioether **13** ($R^{2'}$ = H) giving the alkoxide lithio-**10a** [8] via transition state $\mathbf{14}_{exo}$ rather than via $\mathbf{14}_{endo}$ (Scheme 4): R^1 is *exo*-oriented with respect to the envelope with a free enthalpy benefit of $\delta\Delta G$ = -0.6 kcal/mol.

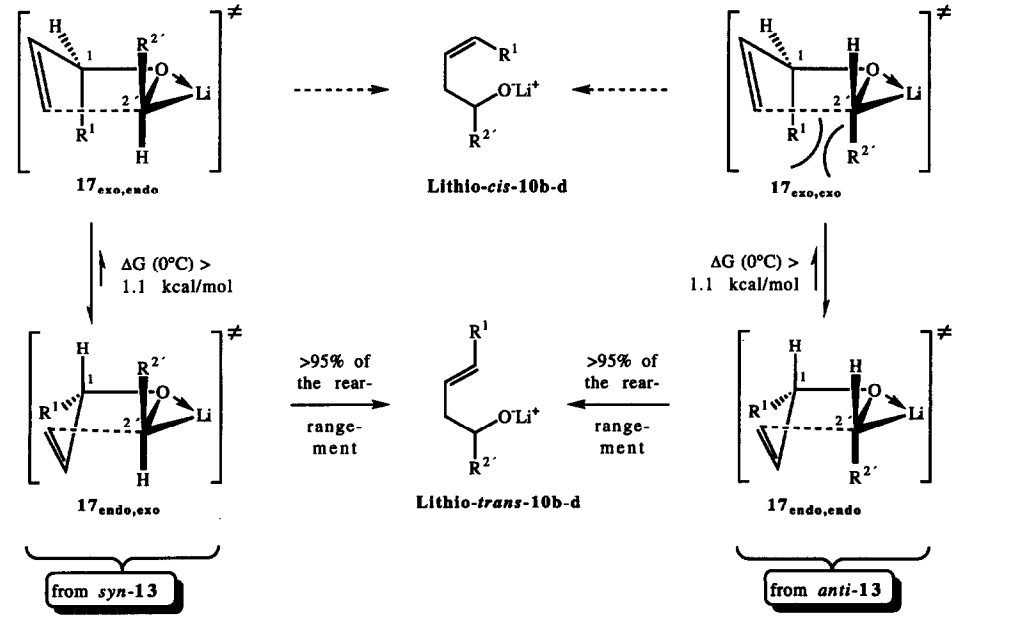
The orientational preference of a *substituent $R^{2'}$ alone* follows from the non-induced diastereoselectivity of Broka's [2,3]-Wittig rearrangements of lithiated *cis*- and *trans*-crotyl ethers [10] (Scheme 5). The favored transition states are *cis*- and *trans*-$\mathbf{15}_{exo}$ (giving alkoxides *syn*- and *anti*-**16**, respectively) rather than *cis*- and *trans*-$\mathbf{15}_{endo}$. I.e., R^2, too, has a free enthalpy advantage in an *exo* orientation with

respect to the envelope. It amounts to $\delta\Delta G$ = -1.3 kcal/mol in the *trans*- and -0.5 kcal/mol in the *cis*-series. Thus, in the absence of steric hindrance a substituent $R^{2'}$ strives *more* than R^1 towards the *exo*-orientation.



Scheme 5: Preferred orientation of a 2'-substituent in the transition state of the [2,3]-Wittig rearrangement

As a consequence, it is comprehensible why our lithioethers *syn*-**13b-d** rearrange via transition state $\mathbf{17}_{endo,exo}$ ($R^{2'}$ *exo*, R^1 *endo*) rather than via $\mathbf{17}_{exo,endo}$ (R^1 *exo*, $R^{2'}$ *endo*) and lead to *trans*-configurated alkoxides **10** (Scheme 6). The diastereomeric lithioethers *anti*-**13b-d**, however, cannot rearrange via transi-



Scheme 6: Combined effect of 1- and 2'-substituents in the transition state of the [2,3]-Wittig rearrangement

tion state $\mathbf{17}_{exo,exo}$ (although R^1 *and* $R^{2'}$ would be *exo*!): The *syn*-pentane strain [14] disfavors it at the expense of transition state $\mathbf{17}_{endo,endo}$ via which one then obtains *trans*-alkoxides **10**, too.

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EXPERIMENTAL

All reactions were performed in oven-dried (100°C) glassware ander dry nitrogen. During reductions with LiNaphth, stirring bars with glass coating were used. THF was freshly destilled from K/Na. The molarity of THF solutions of LiNphth was determined by dropwise addition to 4-*tert*-butylcyclohexanol in THF until the green color persisted. Products were purified by flash chromatography on Merck silica gel 60 (particle size 0.040-0.063 mm, 230-400 mesh ASTM) or Baker silica gel 60 (particle size 0.030-0.063 mm, 230-400 mesh ASTM); the eluent for acid labile O,S-acetals contained triethylamine (1 volume %); Na_2CO_3 (1 cm) was filled below and above silica gel; eluents given in brackets. Yields refer to analytically pure samples (combustion analyses: Table 1). Isomer ratios of diastereomeric mixtures were derived from ^1H NMR integrals.- ^1H NMR (tetramethylsilane or $CHCl_3$ internal standard in $CDCl_3$): Bruker AC-200, AC-250, AC-300, WM-400; integrals in accord with assignments; coupling constants in Hz; AB spectra: H_A refers to high- and H_B to low-field resonance.

5-(4-Methoxyphenyl)-1-penten-3-ol (7) [8]: A Grignard reagent was prepared from magnesium shavings (12.03 g, 0.4949 mol, 1.5 equiv.) and 2-(4-methoxyphenyl)ethyl chloride (50 ml, 56 g, 0.33 mol) in THF (400 ml) by heating for 2 h under reflux and stirring for 15 h at room temp.. At 0°C freshly distilled acrolein (22.1 ml, 18.5 g, 0.331 mol, 1.0 equiv.) was added. Stirring was continued for 4 h at room temp.. The reaction mixture was quenched by the addition of satd. aq. NH_4Cl solution and extracted with ether (5 x 100 ml). The organic phases were dried over $MgSO_4$. Removal of the solvent and distillation under reduced pressure (bp. 130-135°C/5 torr) yielded 7 (43.850 g, 69 %).- ^1H NMR (300 MHz): δ = 1.51 (d, $J_{OH,3}$ = 3.7, OH), 1.75-1.89 (m, 4-H_2), 2.65 (m_c, 5-H_2), 3.79 (s, OCH_3), 4.12 (br. m_c, 3-H), 5.13 (dm_c, J_{cis} = 10.4, 1-H^E), 5.24 (ddd, J_{trans} = 17.1 , $J_{1,3} = J_{gem}$ = 1.3, 1-H^Z), 5.90 (ddd, J_{trans} = 17.2, J_{cis} = 10.4, $J_{2,3}$ = 6.2, 2-H), AA'BB' signal centered at δ = 6.83 and δ = 7.12 (C_6H_4).

5-(4-Methoxyphenyl)-3-(trimethylsilyloxy)-1-pentene (8): 5-(4-Methoxyphenyl)-1-penten-3-ol (7; 30.0 g, 0.156 mol) in CH_2Cl_2 (150 ml) was added to imidazole (21.2 g, 0.312 mol, 2.0 equiv.). After stirring at 0°C for 30 min trimethylsilyl chloride (39.6 ml, 33.8 g, 0.312 mol, 2.0 equiv.) was added. After 15 h petroleum ether (100 ml) was added. A white precipitate formed and was removed by filtration. After evaporation of the solvent the residue was distilled under reduced pressure (bp. 110-115°C/10 torr) to give **8** (39.31 g, 95 %).- ^1H NMR (300 MHz): δ = 0.12 [s, $Si(CH_3)_3$], 1.67-1.87 (m, 4-H_2), 2.59 (m_c, 5-H_2), 3.79 (s, OCH_3), 4.10 (br. ddd, all *J* values ca. 6, 3-H), 5.06 (ddd, J_{cis} = 10.3, $J_{gem} = J_{1,3}$ = 1.4, 1-H^E), 5.16 (ddd, J_{trans} = 17.2, $J_{gem} = J_{1,3}$ = 1.5,

1-H^Z), 5.84 (ddd, J_{trans} = 17.2, J_{cis} = 10.3, $J_{2,3}$ = 6.1, 2-H), AA'BB' signal centered at δ = 6.81 and δ = 7.10 (C_6H_4).

Preparation of O,S-acetals: Method A: At -78°C TMSOTf (8-12 mol-%), the aldehyde (1.3 equiv.), and silylether **8** (1.0 equiv.) were added successively in 10 min intervals to trimethyl(phenylthio)silane (1.0-1.3 equiv.) in CH_2Cl_2. After stirring for 1-3 h the reaction was quenched with pyridine (0.5 ml) and extracted with satd. aq. Na_2CO_3 solution (5 ml) and petroleum ether (3 x 50 ml). The organic layer was dried (Na_2SO_4) and evaporated. Tetrabutylammonium fluoride (2.2 equiv.) in THF was added at room temp.. The O,S-acetals were purified by flash chromatography and isolated as mixtures of diastereomers (composition: Scheme 2). - Method B: At -78°C TMSOTf (8 mol-%) was added to trimethyl(phenylthio)silane (1.0 equiv.) in CH_2Cl_2 (2 ml) followed by addition of a mixture of isobutyraldehyde (1.0 equiv.) and silylether **8** (1.0 equiv.) in CH_2Cl_2. The mixture was stirred for 15 h at the same temp.; workup see method A.

5-(4-Methoxyphenyl)-3-[1-(phenylthio)ethoxy]-1-pentene (9b; method A): ^{1}H NMR (300 MHz): Major diastereomer: δ = 1.50 (d, $J_{2',1'}$ = 6.2, 2'-H_3), 1.69-1.99 (m, 4-H_2), 2.52-2.72 (m, 5-H_2), 3.79 (s, OCH_3), 4.27 (ddd, $J_{3,2} = J_{3,4}$ = 7.0, 3-H), 4.92 (q, $J_{1',2'}$ = 6.3, 1'-H), 5.07 (dm_c, J_{trans} = 17.3, 1-H^Z), 5.21 (dm_c, J_{cis} = 10.3, 1-H^E), 5.63 (ddd, J_{trans} = 17.2, J_{cis} = 10.3, $J_{2,3}$ = 8.1, 2-H), AA'BB' signal centered at δ = 6.83 and δ = 7.12 (C_6H_4), 7.27 and 7.45 (2m_c, 3 and 2 H, SC_6H_5).- Major diastereomer (unless superimposed by the other diastereomer): δ = 1.49 (d, $J_{2',1'}$ = 6.3, 2'-H_3), ca. 4.10-4.20 (m, 3-H), 4.99 (q, $J_{1',2'}$ = 6.3, 1'-H), 5.16 (dm_c, J_{cis} ≈ 11, 1-H^E), probably 5.62-5.77 (m, 2-H), part of AA'BB' signal centered at δ = 7.06 (C_6H_4).

5-(4-Methoxyphenyl)-3-[1-(phenylthio)propoxy]-1-pentene (9c; method A): ^{1}H NMR (250 MHz) of pure major diastereomer): δ = 0.97 (t, $J_{3',2'}$ = 7.4, 3'-H_3), 1.70-2.03 (m, 4-H_2, 2'-H_2), 2.52-2.71 (m, 5-H_2), 3.79 (s, OCH_3), 4.29 (br. ddd, all *J* values ca. 7, 3-H), 4.68 (t, $J_{1',2'}$ = 6.4, 1'-H), 5.02 (m_c, J_{trans} = 17.3, 1-H^Z), 5.20 (dd, J_{cis} = 10.2, $J_{gem} = J_{1,3}$ = 1.7, 1-H^E), 5.61 (ddd, J_{trans} = 17.2, J_{cis} = 10.3, $J_{2,3}$ = 8.4, 2-H), AA'BB' signal centered at δ = 6.83 and δ = 7.12 (C_6H_4), 7.21-7.32 and 7.39-7.50 (2m, 3 and 2 H, SC_6H_5).- ^{1}H NMR (300 MHz): Minor diastereomer: δ = 1.00 (t, $J_{3',2'}$ = 7.4, 3'-H_3), 1.69-2.10 (m, 4-H_2, 2'-H_2), 2.47-2.72 (m, 5-H_2), 3.78 (s, OCH_3), 4.21 (br. ddd, all *J* values ca. 7, 3-H), 4.71 (t, $J_{1',2'}$ = 6.4, 1'-H), 5.16 (dm_c, J_{cis} = 10.3, 1-H^E), 5.22 (dm_c, J_{trans} = 17.8, 1-H^Z), 5.79 (ddd, J_{trans} = 17.3, J_{cis} = 10.3, $J_{2,3}$ = 7.0, 2-H), AA'BB' signal centered at δ = 6.82 and δ = 7.06 (C_6H_4), 7.15-7.29 and 7.40-7.49 (2m, C_6H_5).

5-(4-Methoxyphenyl)-3-[2-methyl-1-(phenylthio)propoxy]-1-pentene (9d; method B): ^{1}H NMR (250 MHz): Major diastereomer: δ = 1.03 (d, $J_{2'\text{-}Me,2'}$ = 6.7, 3'-H_3), 1.05 (d, $J_{3',2'}$ = 6.6, 2'-CH_3), 1.66-2.12 (m, 2'-H, 4-H_2), ca. 2.56-2.70 (m, 5-H_2), 3.79 (s, OCH_3), 4.21 (ddd, all *J* values 7.2, 3-H), 4.59 (d, $J_{1',2'}$ = 5.8, 1'-H), 4.77 (dm_c, J_{trans} = 17.4, 1-H^Z), 5.10 (dd, J_{cis} = 10.3, J_{gem} = 1.7, 1-H^E), 5.55 (ddd, J_{trans} = 17.2, J_{cis} = 10.2, $J_{2,3}$ = 8.5, 2-H), AA'BB' signal centered at δ = 6.83 and δ = 7.12 (C_6H_4), 7.19-7.30 and 7.37-7.44 (2m à 3 and. 2 H, SC_6H_5).- ^{1}H NMR (300 MHz): Minor diastereomer: δ = 1.06 (d, $J_{3',2'}$ = 6.7, 3'-H_3), 1.08 (d, $J_{3',2'}$ = 6.6, 2'-CH_3), 1.67-2.10 (m, 2'-H, 4-H_2), 2.46 - ca. 2.59 (m, 5-H_2,), 3.79 (s, OCH_3), 4.18 (m_c, 3-H), 4.58 (d, $J_{1',2'}$ = 5.7, 1'-H), 5.10 (dm_c, J_{cis} = 10.3, 1-H^E, superimposed by major diastereomer), 5.18 (ddd, J_{trans} = 17.2, 1-H^Z), 5.73 (ddd, J_{trans} = 17.3, J_{cis} = 10.4, $J_{2,3}$ = 6.8, 2-H), AA'BB' signal centered at δ = 6.81 and δ = 7.05 (C_6H_4), 7.20-7.49 and 7.40-7.49 (2m, SC_6H_5).

Reductive cleavage of O,S-acetals: A solution of LiNaphth in THF was added to a stirred (glass-covered bar) solution of an O,S-acetal **9** in THF (1 ml) at -78°C. Stirring was continued for 5-10 min. The mixture was quenched with satd. aq. NH_4Cl solution (5 ml) and extracted with tBuOMe or ether. The organic layer was dried ($MgSO_4$), evaporated, and purified by flash chromatography.

*trans-7-(4-Methoxyphenyl)-4-hepten-2-ol (**10b**)*: ^1H NMR (250 MHz): δ = 1.14 (d, $J_{1,2}$ = 6.2, 1-H_3), 1.49 (br. d, $J_{OH,2}$ = 3.6, 2-OH), 1.96-2.25 (m, 3-H_2), 2.32 (br. dt, $J_{6,5} = J_{6,7}$ = 7.3, 6-H_2), 2.63 (t, $J_{7,6}$ = 7.3, 7-H_2), 3.64-3.81 (m, 2-H), superimposes 3.79 (s, OCH_3), AB signal (δ_A = 5.39, δ_B = 5.54, J_{AB} = 15.3, in addition split by $J_{A,3\text{-}H^1}$ = 7.7, $J_{A,3\text{-}H^2}$ = 6.4, $J_{B,6}$ = 6.5, A: 4-H, B: 5-H), AA'BB' signal centered at δ = 6.83 and δ = 7.08 (C_6H_4).

*trans-8-(4-Methoxyphenyl)-5-octen-3-ol (**10c**)*: ^1H NMR (250 MHz): δ = 0.93 (t, $J_{1,2}$ = 7.4, 1-H_3), 1.37-1.51 (m, signal intensity decreased upon addition of D_2O, 2-H_2, OH), A part of AB signal centered at 2.03 (J_{AB} ≈ 14, in addition split by $J_{A,5} = J_{A,6}$ ≈ 8, 4-H^A), 2.16-ca. 2.29 (m, 4-H^B), partly superimposed by 2.32 (br. dt, $J_{7,6} = J_{7,8}$ = 7.5, 7-H_2), 2.64 (t, $J_{8,7}$ = 7.5, 8-H_2), 3.40-3.52 (m, 3-H), 3.78 (s, OCH_3), AB signal (δ_A = 5.40, δ_B = 5.53, J_{AB} = 15.3, in addition split by $J_{A,4\text{-}H^A}$ = 7.6, $J_{B,7}$ = 6.5, $J_{A,4\text{-}H^B}$ = 6.4, A: 5-H, B: 6-H), AA'BB signal centered at δ = 6.83 and δ = 7.08 (C_6H_4).

*trans-8-(4-Methoxyphenyl)-2-methyl-5-octen-3-ol (**10d**)*: ^1H NMR (250 MHz): δ = 0.90 (d, $J_{2\text{-}Me,2}$ = 6.8, 2-CH_3), 0.92 (d, $J_{1,2}$ = 6.7, 1-H_3), 1.45 (d, $J_{OH,3}$ = 3.7, OH), 1.61 (m_c, 2-H), A part of AB signal centered at 2.02 (J_{AB} = 13.9, in addition split by $J_{A,5} = J_{A,6}$ ≈ 8, 4-H^A), 2.15-ca. 2.29 (m, 4-H^B), partly superimposed by δ = 2.32 (br. dt, $J_{7,6} = J_{7,8}$ = 7.5, 7-H_2), 2.64 (t, $J_{8,7}$ = 7.5, 8-H_2), 3.20-3.33 (m, 3-H), 3.79 (s, OCH_3), AB signal (δ_A = 5.41, δ_B = 5.54, J_{AB} = 15.3, in addition split by $J_{A,4\text{-}H^A}$ ≈ 7.7, $J_{A,4\text{-}H^B}$ ≈ 6.3, $J_{B,7}$ = 6.5, A: 5-H, B: 6-H), AA'BB' signal centered at δ = 6.83 and δ = 7.08 (C_4H_6); small unidentified signals at δ = 0.86 (d), 5.03-5.29 (m), and 5.64-5.70 (m).

Table 1. Combustion analyses

Compound	Molecular formula	Molecular mass	%C Calcd. (Found)	%H Calcd. (Found)
7	$C_{12}H_{16}O_2$	192.3	74.97 (74.66)	8.39 (8.58)
8	$C_{15}H_{24}O_2Si$	264.4	68.13 (68.36)	9.15 (8.90)
9b	$C_{20}H_{25}O_2S$	329.5	72.90 (72.89)	7.64 (7.59)
9c	$C_{21}H_{26}O_2S$	344.5	73.64 (73.56)	7.65 (7.84)
9d	$C_{22}H_{28}O_2S$	356.5	74.12 (73.95)	7.92 (7.86)
10b	$C_{14}H_{20}O_2$	220.3	76.32 (76.60)	9.15 (8.94)
10c	$C_{15}H_{22}O_2$	234.3	76.88 (76.89)	9.46 (9.80)
10d	$C_{16}H_{24}O_2$	248.3	77.37 (77.49)	9.74 (9.52)

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