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1,3-ASYMMETRIC INDUCTION IN RETRO-[1,4]-BROOK REARRANGEMENTS OF LITHIATED ALLYL METHYL ETHERS AND LITHIATED ALLYL MOM ETHERS

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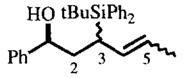
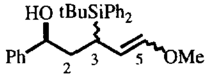
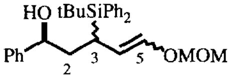
Abstract: The tBuPh$_2$Si-containing allyl methyl ether *cis*-**2** and its *trans* isomer were lithiated with sBuLi at -78°C in THF. Thereupon, diastereoselective retro-[1,4]-Brook rearrangements occurred which furnished the allylsilane *anti,trans*-**5** with 86-87% diastereocontrol. The analogous allyl MOM ethers *cis*- and *trans*-**3** underwent similar retro-[1,4]-Brook rearrangements upon treatment with sBuLi. They yielded the allylsilane *anti,trans*-**6** with 80-82% diastereoselectivity. © 1997 Elsevier Science Ltd.

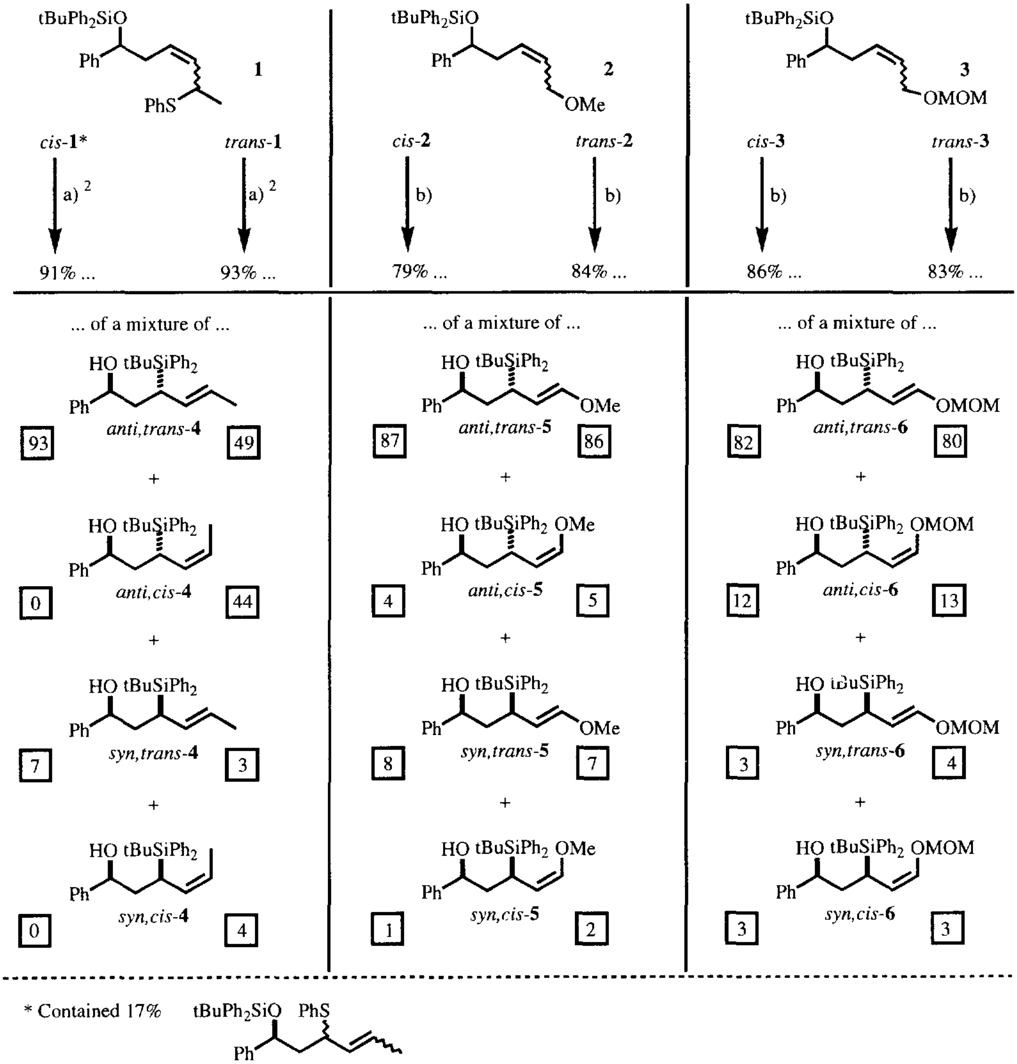
Studying retro-[1,4]-Brook rearrangements [1] of γ-siloxylated organolithium compounds as a stereoselective access to α-chiral allylsilanes with variable substitution patterns, we recently reported the reductive lithiation of the allyl phenyl sulfides *cis*- and *trans*-**1** and the stereochemistry of the ensueing rearrangements to the α-chiral γ-methylated allylsilanes **4** (Scheme 1) [2]. We now found that the γ-siloxylated allyl methyl ethers *cis*- and *trans*-**2** [3] and the analogous methoxymethyl („MOM") ethers *cis*- and *trans*-**3** [3] are lithiated with sBuLi at -78°C in THF; thereafter, smooth retro-[1,4]-Brook rearrangements occur leading to the α-chiral γ-methoxylated allylsilanes **5** and the analogous γ-MOMO-substituted allylsilanes **6**, respectively (Scheme 1).

Table 1. Structure-proving ^{1}H-NMR shifts in $CDCl_3$ of all diastereomers of the retro-Brook products **4** [2] (300 MHz), **5** (500 MHz), and **6** (500 MHz)

	4 					**5** 					**6** 				
Isomer:	2-H^A	2-H^B	3-H	5-H	tBu	2-H^A	2-H^B	3-H	5-H	tBu	2-H^A	2-H^B	3-H	5-H	tBu
anti,trans-	1.90	2.08	2.23	5.35	1.04	1.69	1.98	1.91	6.18	0.98	ca. 1.73	ca. 1.96	ca. 1.96	6.08	0.99
syn,trans-	ca. 1.62	2.21	3.12	5.48	1.18	1.41	1.99	2.71	6.34	1.09	1.40	ca. 1.95	ca. 2.7	6.24	1.10
anti,cis-	ca. 1.90	2.27	2.49	ca. 5.34	1.05	1.58	1.99	2.69	5.94	1.00	1.61	2.02	2.75	6.24	1.02
syn,cis-	1.51	2.28	3.47	ca. 5.54	1.19	1.44	1.93	3.23	6.06	1.09	1.44	1.96	3.29	6.33	1.10

After separating all diastereomers of the allylsilanes **5** and **6** by flash chromatography [4] the C=C bond configurations were deduced from the olefinic coupling constants $^3J_{trans}$ = 12.4-12.6 Hz vs. $^3J_{cis}$ = 6.0-6.4 Hz. The *syn* or *anti* orientations of the C^1–OH vs. C^3–$SiPh_2tBu$ bonds were inferred from consistently obeyed ^{1}H-NMR shift analogies with the reference compounds *anti,trans*-, *syn,trans*-, *anti,cis*-, and *syn,cis*-**4** (Table 1): The values of ($\delta_{2\text{-}H^B}$ - $\delta_{2\text{-}H^A}$), $\delta_{3\text{-}H}$, $\delta_{5\text{-}H}$, and δ_{tBu} were larger in all *syn* vs. *anti* isomers of a given C=C geometry.

The lithioether intermediates of Scheme 1 (central and right column) rearrange with moderate diastereoselectivities of 79-86% to the allylsilanes *anti,trans*-**5** and -**6**; this is independent from whether the starting material **2** or **3** is a *cis* or *trans* olefin. The total *anti* selectivities (91-94%) closely resemble the 93% *anti*-selectivities of the retro-[1,4]-Brook rearrangements starting from the sulfides *cis*-**1**/*iso*-**1** and *trans*-**1** (Scheme 1, left



Scheme 1. a) Lithium naphthalenide (2.5 equiv.), THF, -78°C, 30 min.– b) sBuLi (3.0 equiv.), THF, -78°C, 2 h.

column). Surprisingly, our lithioether rearrangements furnished the enol ethers **5** and the enol acetals **6** with 84-95% *trans* preference: Lithiated allyl methyl (or ethyl or phenyl) ether reacts at the γ-position with electrophiles so that the resulting C-CH=CH-OR moiety is *exclusively cis*-configurated [5]. We are unaware, though, of analogous results with lithiated γ-*substituted* allyl ethers which would model our rearrangement intermediates better. In our hands lithio-*trans*-1-methoxy-5-phenyl-2-propene reacted with D_2O (→85%) or Me_3SiCl (→66%) α and not γ to the MeO group which leaves open whether the MeO group was previously *cis* or *trans* oriented.

REFERENCES AND NOTES:

1. For background information cf. ref. 1-9 of Gibson, C.; Buck, T.; Noltemeyer, M.; Brückner, R. *Tetrahedron Lett.* **1997**, *38* (immediately preceding article in this issue).
2. Behrens, K.; Kneisel, B. O.; Noltemeyer, M.; Brückner, R. *Liebigs Ann.* **1995**, 385-400.
3. All new compounds gave satisfactory ^{1}H-NMR and IR spectra and a correct combustion analysis.
4. Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925.
5. D. A. Evans, G. C. Andrews, B. Buckwalter, *J. Am. Chem. Soc.* **1974**, *96*, 5560-5561.– W. C. Still, T. L. MacDonald, *J. Am. Chem. Soc.* **1974**, *96*, 5561-5563.

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