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1,3-ASYMMETRIC INDUCTION IN RETRO-[1,4]-BROOK REARRANGEMENTS OF PROPARGYLLITHIUM COMPOUNDS TO PROPARGYLSILANES

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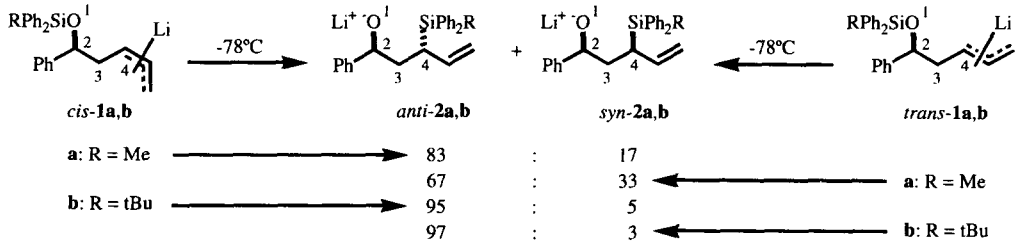
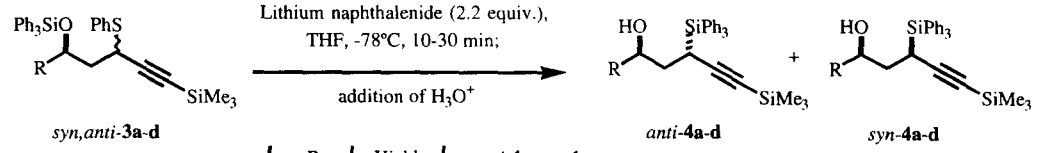
Abstract: The γ-siloxylated propargyl phenyl sulfides **3a-d**, **5**, and **6** were lithiated with lithium naphthalenide at -78°C in THF. They gave propargyllithium intermediates which rearranged within 10-30 min to the propargylsilanes **4a-d**, **7**, and **8**, respectively. In these compounds the relative orientations of γ-C–O vs. newly formed C–Si bonds were determined by a crystal structure analysis of the dinitrobenzoate *syn*-**10**, inferred from NMR shift homologies or found by a Karplus analysis of pertinent J_{vic} values. The *anti*:*syn* selectivities of these retro-[1,4]-Brook rearrangements are probably kinetically controlled. They range from 81:19 *anti*:*syn* starting from sulfide **3a** to 87:13 *syn*:*anti* starting from sulfide **3d**.

Retro-[1,4]-Brook rearrangements are silyl group shifts across the O^1–C^2–C^3–C^4 moiety of 4-lithio-2-siloxy substituted carbon-chains [1]. Retro-[1,4]-Brook rearrangements of siloxylated allyllithium compounds **1** can exhibit a high level of stereocontrol due to 1,3-asymmetric induction (Scheme 1) [2]. They react to allylsilanes **2** in which the inducing C^2–O^1 bond and the newly formed C^4-Si bond are preferentially oriented *anti*. The $tBuPh_2Si$-group migration in the allyllithium *trans*-**1b** exhibited the highest *anti*-selectivity of 97:3 and [1,4]-shifts of the $tBuPh_2Si$ group had a higher *anti*-preference than those of the $MePh_2Si$ group. The *anti*-selectivity of these retro-[1,4]-Brook rearrangements is probably in the same way kinetically controlled as the *anti*-selectivity of the retro-[1,4]-Brook rearrangements of analogous crotyllithium [3] and tiglyllithium compounds [4].



Scheme 1

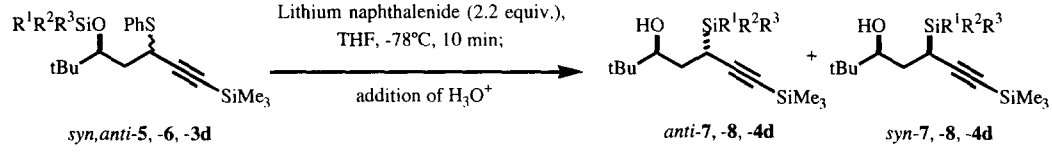
Schemes 2 and 3 show the first retro-[1,4]-Brook rearrangements of siloxylated propargyllithium compounds and which steric course they take under the influence of a 1,3-asymmetric induction. The starting propargyl phenyl sulfides **3a-d**, **5**, and **6** (53:47 - 63:37 mixtures of configurationally unassigned epimers) [5] were primed for these rearrangements at -78°C in THF through reductive lithiations with lithium naphthalenide [6] (the first ones, to the best of our knowledge, applied to *propargyl* phenyl sulfides). After 10-30 min we isolated the propargylsilanes **4a-d**, **7**, and **8** by flash chromatography [7] in 56-79% yield as an unseparable mixture of *anti* and *syn* isomers (**4a**) or as separated *anti* and *syn* isomers (**4b-d**, **7**, **8**).



syn,anti-**3a-d** *anti*-**4a-d** *syn*-**4a-d**

	R	Yield	*anti*-**4** : *syn*-**4**
a	Me	79%	81 : 19
b	nBu	72%	64 : 36
c	iPr	60%	57 : 43
d	tBu	56%	13 : 87

Scheme 2

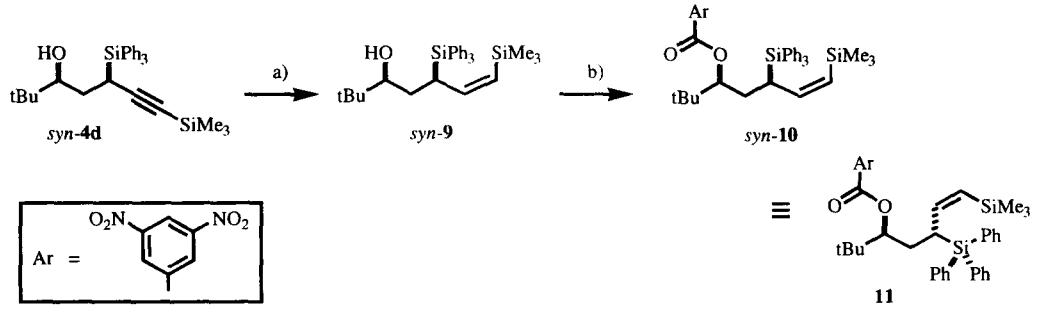


syn,anti-**5**, **-6**, **-3d** *anti*-**7**, **-8**, **-4d** *syn*-**7**, **-8**, **-4d**

	R^1	R^2	R^3	Yield	*anti* : *syn*
5, 7	Me	Me	Ph	77%	26 : 74
6, 8	Me	Ph	Ph	79%	19 : 81
3d, 4d	Ph	Ph	Ph	56%	13 : 87

Scheme 3

The stereostructures of these rearrangement products were determined in three ways. Firstly, the major epimer obtained from the retro-Brook rearrangement of the sulfide **3d** was semi-hydrogenated over Raney nickel to the *cis*-configurated ($J_{olefinic}$ = 14.0 Hz) alkenyl silane *syn*-**9** (Scheme 4). This compound was esterified to the 3,5-dinitrobenzoate *syn*-**10** from which a crystal structure analysis was made [8] (Fig. 1). It proved that the lithium derivative of sulfide **3d** had rearranged mainly to the propargylsilane *syn*-**4d**.



syn-**4d** *syn*-**9** *syn*-**10**

11

Scheme 4. a) H_2 (1.2 bar), Raney-Ni (30 weight-%), MeOH, ultrasound, 6 h; 94%.– b) 3,5-Dinitrobenzoyl chloride (6 equiv.), 4-(dimethylamino)pyridine, pyridine, reflux, 90 min; 80% (m.p. 179°C; recrystallized from MeOH/toluene).

Secondly, we collected the chemical shifts (as far as unequivocally assigned) of all protons and ^{13}C nuclei located between or by the stereocenters of the rearrangement products (Table 1). Since the X-ray structure of Fig. 1 allowed to identify the rearrangement products *anti*- and *syn*-**4d** we could compare the chemical shifts of the mentioned nuclei in diastereomer *anti*-**4d** vs. diastereomer *syn*-**4d**. In *anti*-**4d** one observes highfield shifts for $\delta_{1\text{-}H}$ and $\delta_{3\text{-}H}$ and lowfield shifts for $\delta_{2\text{-}H(A)}$, $\delta_{2\text{-}H(B)}$, $\delta_{C\text{-}1}$, $\delta_{C\text{-}2}$, $\delta_{C\text{-}3}$, and $\delta_{C\text{-}4}$. The assumption that the same shift orderings distinguish the *anti,syn* pairs of the other rearrangement products **4a-c**, **7**, and **8**, too, is the basis for their *anti,syn* assignments. That these assignments adhere to all eight shift orderings – as far as identifiable in the respective compounds – *without a single exception* is considered strong circumstancial evidence for their

correctness. These assignments signified also that all *anti* diastereomers of the rearrangement products **4b-d**, **7**, and **8** had eluted faster than their *syn* counterparts from the flash chromatography column (only exception: *anti*- and *syn*-**4a** co-eluted).

Our third access to stereostructures concerned the propargylsilanes **4d**, **7**, and **8** as well as the allylsilanes *syn*-**9** and *syn*-**10** derived from the first of these compounds. They all contain a $SiPhR^1R^2$ as well as a tBu group. Their bulkiness must ensure [9] that the respective molecule occurs exclusively as conformer with zigzag-shaped C_{tert}–C–C–C–Si backbone – as shown in the headline of Table 2 and for the dinitrobenzoate *syn*-**10** in the solid state structure **11** of Fig. 1, too. As a consequence, the proton 2-H(A) of each *anti*-diastereomer of Table 2 has dihedral angles of ≈180° to its vicinal protons. Therefore, it entertains two large couplings with them. Proton 2-H(B) of the same *anti*-configurated compounds, however, has dihedral angles of only ≈60° to the vicinal protons. Accordingly, both corresponding couplings are small. On the other hand, in all *syn*-configurated compounds of Table 2 each proton attached to C-2 is related to one vicinal proton by a dihedral angle of ≈180° and to another by a dihedral angle of ≈60°; each of them displays, therefore, one large and one small vicinal coupling.

Figure 1. X-ray crystal structure of 3,5-dinitrobenzoate *syn*-**10** (conformer **11**)

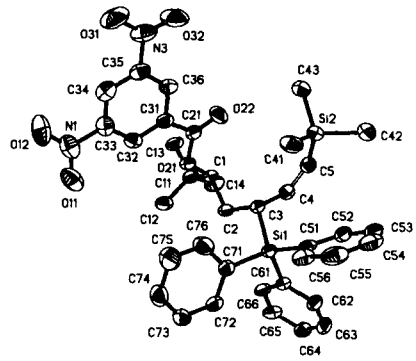
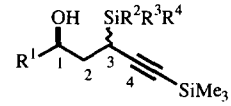


Table 1. Stereochemically relevant ^1H- and ^{13}C-NMR shifts ($CDCl_3$, 300 and 126 MHz, respectively) of the newly produced propargylsilanes. The numbering refers to the formula depicted at the right.



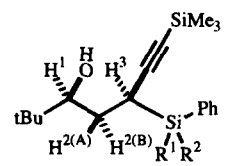
anti,syn-**4a-d**, **-7**, **-8**

Compound	R^1	R^2	R^3	R^4	$\delta_{1\text{-H}}$	$\delta_{2\text{-H(A)}}$	$\delta_{2\text{-H(B)}}$	$\delta_{3\text{-H}}$	$\delta_{C\text{-}1}$	$\delta_{C\text{-}2}$	$\delta_{C\text{-}3}$	$\delta_{C\text{-}4}$
anti-**4a**	Me	Ph	Ph	Ph	ca. 4.10	1.65	1.81	2.67	70.42	38.31	17.65	108.68
syn-**4a**	"	"	"	"	ca. 4.13	[a]	[a]	2.97	66.47	38.15	15.27	108.40
anti-**4b**	nBu	Ph	Ph	Ph	3.84	1.71	1.78	2.68	74.63	[b]	[b]	109.21
syn-**4b**	"	"	"	"	3.91	1.59	1.72	2.98	70.54	[b]	[b]	108.74
anti-**4c**	iPr	Ph	Ph	Ph	3.60	ca. 1.68	1.78	2.65	79.61	34.15	[b]	109.38
syn-**4c**	"	"	"	"	3.67	ca. 1.61	1.70	2.97	75.15	[c]	[b]	108.87
anti-**4d**	tBu	Ph	Ph	Ph	3.37	1.56	1.92	2.63	83.80	32.28	18.92	109.60
syn-**4d**	"	"	"	"	3.62	1.53	1.69	2.99	77.57	31.46	15.69	108.87
anti-**7**	tBu	Me	Me	Ph	3.29	1.36	1.67	1.95	82.98	31.51	20.22	109.76
syn-**7**	"	"	"	"	3.53	1.30	1.50	2.23	77.68	30.80	17.61	109.11
anti-**8**	tBu	Me	Ph	Ph	3.34	1.43	1.76	2.33	83.22	31.89	19.25	109.55
syn-**8**	"	"	"	"	3.57	1.38	1.57	2.63	77.61	31.13	16.44	108.89

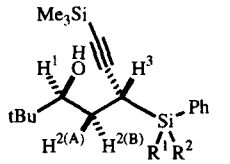
[a] Value not determinable in the solely available spectrum of the *anti,syn*-**4a** *mixture*.– [b] δ value of this carbon atom not unequivocally distinguishable from neighbouring resonances of R^1.– [c] δ = 33.61 or 33.87 (the other resonance belongs to R^1).

The 1,3-asymmetric induction established in the retro-[1,4]-Brook rearrangements of the lithium derivatives of the propargyl sulfides **3a-d**, **5**, and **6** is not uniform. According to Scheme 2 increasing the size of the substituent R at the inducing stereocenter from methyl over n-butyl and isopropyl to *tert*-butyl makes the migration of a $SiPh_3$ group change gradually from an 81:19 *anti*-preference to a totally opposite 87:13 *syn*-preference. According to Scheme 3, the *syn* preference of $SiPh_nMe_{3-n}$ group migrations in the *tert*-butylated substrates increases slightly from 74:26 to 87:13 for n = 1, 2, and 3.

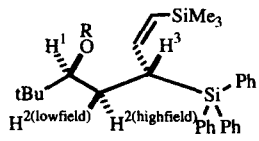
Table 2. Vicinal coupling constants (in Hz) of 2-H_2 in the tBu-containing propargylsilanes and derived allylsilanes



	anti-7	*anti*-8	*anti*-4d
R^1	Me	Me	Ph
R^2	Me	Ph	Ph



	syn-7	*syn*-8	*syn*-4d
R^1	Me	Me	Ph
R^2	Me	Ph	Ph



	syn-9	*syn*-10
R	H	3,5-dinitro-benzoyl

	anti-7	*anti*-8	*anti*-4d	*syn*-7	*syn*-8	*syn*-4d	*syn*-9 [a]	*syn*-10 [a]
$J_{2\text{-H(A)},1}$	9.4	9.4	9.1	10.2	10.1	10.2	10.4	9.4
$J_{2\text{-H(A)},3}$	11.1	11.1	11.4	3.4	3.4	3.4	1.6	1.0
$J_{2\text{-H(B)},1}$	1.3	1.2	1.2	1.9	1.7	1.9	≤1.0	1.0
$J_{2\text{-H(B)},3}$	4.0	3.7	3.3	11.9	12.1	12.1	12.5	11.7

[a] Couplings of $H^{2(lowfield)}$ listed under $J_{2\text{-H(A)}}$ and couplings of $H^{2(highfield)}$ under $J_{2\text{-H(B)}}$.

Too little is presently known about the detailed mechanism of retro-[Brook] rearrangements [1] and the structure, stereostructure, and stereodynamics of propargyllithium (vs. allenyllithium) compounds [10] to endeavor to explane these results. We gained just one more piece of information by re-subjecting the minor product – propargylsilane *anti*-**8** – and separately the major product – propargylsilane *syn*-**8** – of the retro-[1,4]-Brook rearrangement of the propargyllithium derivative of sulfide **6** to their formation conditions whereupon they were recovered unchanged in 96% and 89% yield, respectively. These experiments demonstrate that the stereochemical outcome of the retro-[1,4]-Brook rearrangement leading to compound **8** is kinetically controlled. By analogy, the same should be true for the other rearrangements of this study.

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8. Crystal data: $C_{37}H_{42}N_2O_6Si_2$, M = 666.91, monoclinic, space group $P2_1/c$, a = 1782.6(4), b = 1018.1(2), c = 2121.1(7) pm, α = 90°, β = 107.80(2)°, γ = 90°, V = 3.665(2) nm^3, Z = 4, D_c = 1.209 Mg/m^3, F(000) = 1416, crystal dimensions 0.60 × 0.60 × 0.60 mm.– Tables of atom positions, thermal parameters, and a complete listing of bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre.
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