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METAL DEPENDENT 1,3-ASYMMETRIC INDUCTION IN THE RETRO-[1,4]-BROOK REARRANGEMENT OF A SILYLATED TIGLYL ALKALIMETAL COMPOUND

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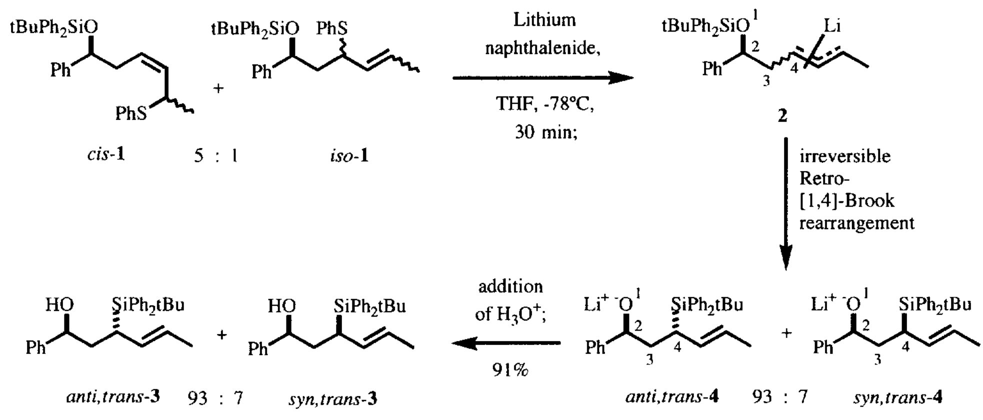
Abstract: At -78°C in THF, the tiglyl phenyl sulfide **5** and lithium naphthalenide gave a tiglyl lithium species which underwent an irreversible retro-[1,4]-Brook rearrangement giving rise to a 22:78 mixture of the *anti,trans* and the *syn,trans* diastereomer of the tiglyl silane **6**. The same sulfide **5** and potassium naphthalenide provided the same products *anti,trans*- and *syn,trans*-**6** as a 96:4 mixture. This time they arose from the reversible retro-[1,4]-Brook rearrangement of a tiglyl potassium intermediate.

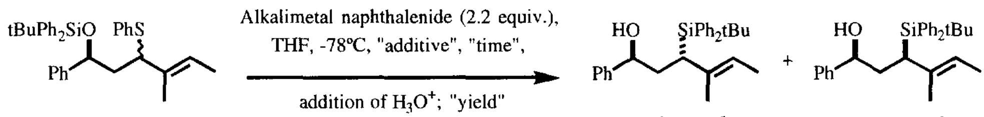
The retro-[1,*n*]-Brook rearrangement is an O→C shift of a SiR_3 group over *n* centers [1]. Retro-[1,*n*]-Brook rearrangements are encountered in (*n*-1)-siloxy-substituted alkalimetal compounds, so that retro-[1,4]-Brook rearrangements in particular occur in 3-siloxy-substituted alkalimetal compounds. However, certain 3-siloxy-substituted anionic species like carboxylic amide enolates [2], C≡N-substituted „carbanions“ [3], $PhSO_2$-substituted „carbanions“ [4], $Ph_2P(=O)$-substituted „carbanions“ [5], dithianes [6], $(R_3Si)_2$-substituted „carbanions“ [5], a benzyl „anion“ [7], and perhaps also a Me_3Si-substituted allyl „anion“ [8] are more stable than their retro-[1,4]-Brook rearrangement products. In fact, each of the mentioned 3-siloxy-substituted anionic species forms from its retro-[1,4]-Brook rearangement product through a C→O SiR_3 migration known as the [1,4]-Brook rearrangement [1]. This means that the driving force difference between retro-[1,4]-Brook rearrangements and [1,4]-Brook rear-



Scheme 1 [10]

rangements is small. One would therefore also expect that certain retro-[1,4]-Brook rearrangements are reversible. One such rearrangement was found by Corey and Chen (at 23°C) [7]. Another of these rearrangements is presented here; it was was reversible even at -78°C and exhibited, remarkably, 96% diastereoselectivity.

The motiviation for the present investigation was our observation that the retro-[1,4]-Brook rearrangements of 3-(*tert*-butyldiphenylsiloxylated) allyl [9] and crotyl lithium compounds [10] exhibit diastereoselectivities of up to 97:3 and 93:7, respectively. For instance (Scheme 1), the reductive lithiation [11] of a mixture of the phenyl sulfides *cis*-**1** and *iso*-**1** gave a crotyl lithium species **2** which rearranged at -78°C within 30 min to a 93:7 mixture of the diastereomeric alcoholates *anti,trans*-**4** and *syn,trans*-**4**. Protonation led to a 93:7 mixture of the corresponding alcohols *anti,trans*-**3** and *syn,trans*-**3**. When we deprotonated the $SiPh_2Me$ analogs of the $SiPh_2tBu$-containing alcohols **3** with nBuLi and left the resulting alcoholates at -78°C twice as long as their prior formation through a retro-[1,4]-Brook rearrangement had lasted no *anti,trans*/*syn,trans* interconversion occurred [10]. This proved that at -78°C the last-mentioned retro-[1,4]-Brook rearrangement was irreversible and indicated that the analogous rearrangement **2**→**4** in the $SiPh_2tBu$ series was probably irreversible, too.

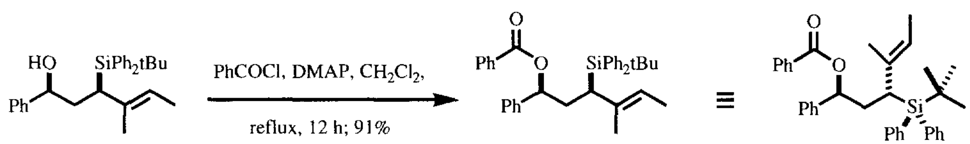


syn,anti-**5** *anti,trans*-**6** *syn,trans*-**6**

Alkalimetal	Additive	Time	Yield	*anti,trans*-**6** : *syn,trans*-**6**
lithium		60 min	89%	22 : 78
"		2 min	96%	23 : 77
"	TMEDA	60 min	91%	22 : 78
sodium		40 min	64%	37 : 63
potassium		50 min	98%	96 : 4
"	18-crown-6	80 min	-	(complex mixture)

Scheme 2

Trying to expand the scope of such retro-[1,4]-Brook rearrangements as a general synthesis of stereodefined allylsilanes with variable substitution patterns in the allyl moiety [12] we synthesized the higher homolog *syn,anti*-**5** (Scheme 2) of the phenyl sulfide *iso*-**1** [13]. Its reductive lithiation [11] furnished a tiglyl lithium intermediate which at -78°C in THF rearranged within 2 min to 96% of a 23:77 mixture of the lithium salts of the alcohols *anti,trans*- and *syn,trans*-**6** [13]. These alcohols were separable by flash chromatography on silica gel [14]. The stereostructure of the major rearrangement product *syn,trans*-**6** was determined by X-ray crystallography of the derived (Scheme 3) benzoate *syn,trans*-**7** (Fig. 1) [13,15]. The C=C bond configuration of the minor rearrangement product *anti,trans*-**6** – according to a H,H-NOESY spectrum – was also *trans*. This observation imp-



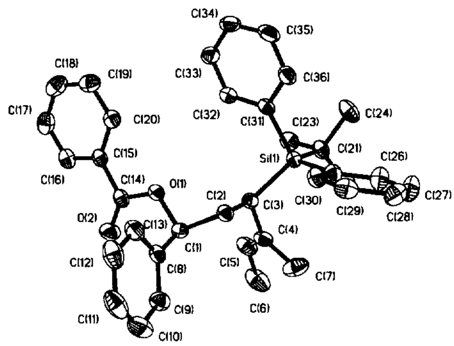
syn,trans-**6** *syn,trans*-**7** **8**

Scheme 3

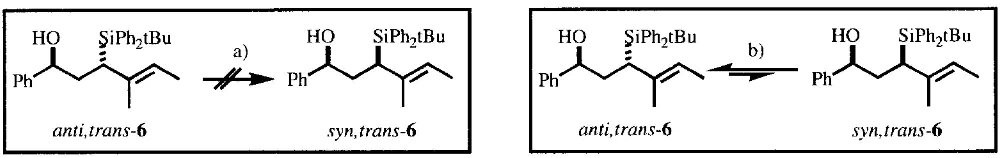
lies that the C–OH and C–$SiPh_2tBu$ bonds of this compound are *anti*-oriented, i. e. differently than in the stereoisomeric but equally *trans*-configurated rearrangement product *syn,trans*-**6**.

All retro-[1,4]-Brook rearrangements of the tiglyl lithium derivative of sulfide **5** led to the same 23(22):77(78) mixture of the alcohols *anti,trans*-**6** and *syn,trans*-**6** irrespective of whether we worked up after 2 min or 1 h and also irrespective of whether we had added 4 equiv. of TMEDA or not (Scheme 2). Treating the sulfide **5** with sodium naphthalenide led to the same rearrangement products **6** with decreased yield (64%) and diminished *anti,trans*:*syn,trans* selectivity (37:63). The reaction between sulfide **5** and potassium naphthalenide initiated a very high-yielding (98%) retro-[1,4]-Brook rearrangement to a quite differently composed 96:4 mixture of alcohols *anti,trans*-**6** and *syn,trans*-**6**. In the presence of 18-crown-6 the tiglyl potassium derivative of sulfide **5** reacted far less selectively.

Figure 1. X-ray crystal structure of benzoate *syn,trans*-**7** (conformer **8**)

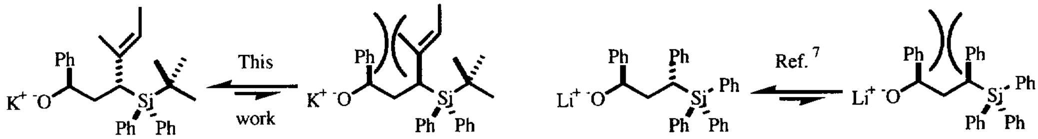


Why is there such a metal dependence of the stereochemical outcome of the retro-[1,4]-Brook rearrangement of the lithium vs. the potassium derivative of sulfide **5**? We re-subjected the minor diastereomer of the lithium naphthalenide induced rearrangement – compound *anti,trans*-**6** – to the rearrangement conditions (Scheme 4). It did not isomerize to the major diastereomer – compound *syn,trans*-**6** – which this rearrangement had produced. This proves that those retro-[1,4]-Brook rearrangements of Scheme 2 which proceed via tiglyl *lithium* compounds are *irreversible*. Consequently, their stereochemical outcome is kinetically controlled. When we re-exposed the minor diastereomer of the potassium naphthalenide induced rearrangement – compound *syn,trans*-**6** – to the rearrangement conditions most of it gave the former major diastereomer (*anti,trans*-**6**). In fact, the *syn,trans*:*anti,trans* ratio became 95:5 which is almost identical with the 96:4 ratio in which these compounds had been formed upon treating sulfide **5** with potassium naphthalenide. This proves that the retro-[1,4]-Brook rearrangement of the tiglyl *potassium* derivative of sulfide **5** is *reversible*. Therefore, its stereochemistry is determined by thermodynamic control.



Scheme 4. a) Lithium naphthalenide (2.3 equiv.), THF, -78°C, 50 min; 98% *anti,trans*-**6** recovered.– b) Potassium naphthalenide (2.5 equiv.), THF, -78°C, 2 h; 76% *anti,trans*-**6** isolated and 4% *syn,trans*-**6** recovered.

Our results can be summarized as follows: ① The stereochemistry of the retro-[1,4]-Brook rearrangement of the tiglyl lithium derivative of sulfide **5** (Scheme 2) and of the crotyl lithium compound **2** (Scheme 1) is kinetically controlled. The stereochemical outcomes differ from one another because sulfide **5** reacts with *syn* preference while intermediate **2** rearranges *anti* selectively. No interpretation of this discrepancy can be given. ② Other than the lithium derivative of sulfide **5** the potassium derivative undergoes a reversible retro-[1,4]-Brook rearrangement. An explanation is still sought. ③ The stereochemical outcome of the retro-[1,4]-Brook rearrangement of the tiglyl potassium intermediate of Scheme 2 – it produces a 96:4 equilibrium mixture of the potassium alcoholates pre-*syn,trans*-**6** and pre-*anti,trans*-**6** (Scheme 5) – is comparable to that of Corey´s earlier mentioned reversible retro-[1,4]-Brook rearrangement which delivered a 200:1 equilibrium mixture of the lithium alcoholates pre-*syn*-**9** and pre-*anti*-**9** (Scheme 5) [7]. It is suggested that the M^+ $^-$O–C–C–C–Si–tBu backbone of these alcoholates adopts the shown all-*anti* conformation. This conformation should be favored for steric reasons if these alcoholates form aggregates with their M^+ $^-$O moieties [16]. The predominating alcoholates pre-*syn,trans*-**6** and pre-*syn*-**9** then represent those diastereomers which – other then the epimeric minor alcoholates pre-*anti,trans*-**6** and pre-*anti*-**9** – do not suffer from *syn*-pentane strain [17].



pre-*syn,trans*-**6** pre-*anti,trans*-**6** pre-*syn*-**9** pre-*anti*-**9**

Scheme 5

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