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Ring-Opening of *N*-*tert*-Butanesulfinylethynylaziridines with Lithium Tris(dimethylphenylsilyl)zincate: Stereoselective Access to 4-Amino-1-allenylsilanes

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Abstract: The ring-opening of *N*-*tert*-butanesulfinylethynylaziridines with lithium tris(dimethylphenylsilyl)zincate is reported. The reaction is demonstrated to be both stereoselective and stereospecific and to proceed through an *anti*-S_N2' process. Further deprotection of the nitrogen atom under mild conditions allows access to 4-amino-1-(dimethylphenylsilyl)allenes with high yields and levels of stereoselectivity.

Keywords: allenes; asymmetric synthesis; aziridines; diastereoselectivity; zincates

Since 4-aminoallenes **I** (Figure 1) constitute valuable building blocks for organic synthesis,[1] their synthesis has attracted much attention in the past decade.[2–8] Surprisingly, despite an obvious synthetic potential as propargylic anion equivalents in S_E2' substitution reactions,[9] only a few reports deal with the synthesis of 4-amino-1-allenylsilanes **II** (Figure 1).[3a,8a,b,10]

The S_N2' ring-opening of ethynylaziridines provides a straightforward access to 4-aminoallenes.[11] In particular, alkylcopper reagents have been reported to readily react with *N*-Mts, *N*-Mtr and *N*-Ts[12] ethynylaziridines to give the corresponding 4-aminoallenes with high levels of stereoselectivity and excellent yields through an *anti*-S_N2' process (Scheme 1).[10,13] Nevertheless, this easy-to-implement method has never been used in synthesis probably because of the harsh reaction conditions required for the removal of the arylsulfonyl group. On the other hand, the Ns group, easily cleavable under mild conditions,[14] has been reported not to be compatible with these reactions.[13b]

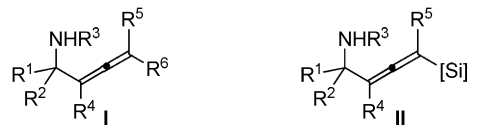
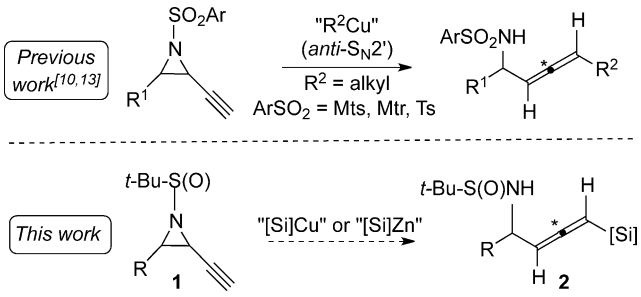


Figure 1. Structure of 4-aminoallenes **I** and 4-amino-1-allenylsilanes **II**.

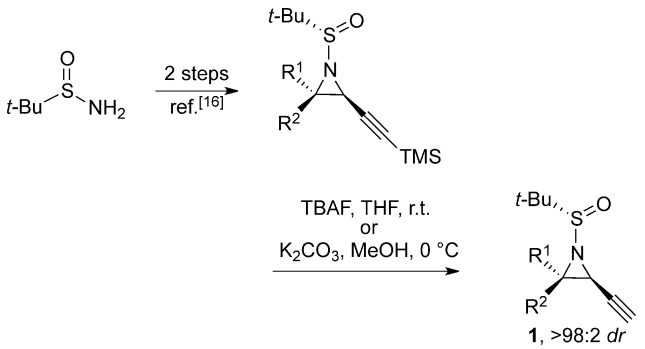
In this context, we reasoned that developing a straightforward and stereoselective synthesis of 4-amino-1-allenylsilanes **2** would be synthetically useful. The *tert*-butanesulfinyl group is indeed known to be easily removed under mild acidic conditions compatible with most functional groups,[15] allowing possible post-functionalizations. We thus aimed to obtain compounds **2** by the reaction of *N*-*tert*-butanesulfinylethynylaziridines **1** with silylcopper or silylzinc reagents (Scheme 1).

The study was initiated with the stereoselective synthesis of racemic *N*-*tert*-butanesulfinylethynylaziridines **1** obtained as pure *trans* and *cis* isomers in 3 steps following a methodology developed in our group (Scheme 2).[16]

We first investigated the reaction of aziridine **1a** with cyano cuprate **M1**.[17] At −80 °C in THF, we were



Scheme 1. Planned access to 4-amino-1-allenylsilanes **2**.



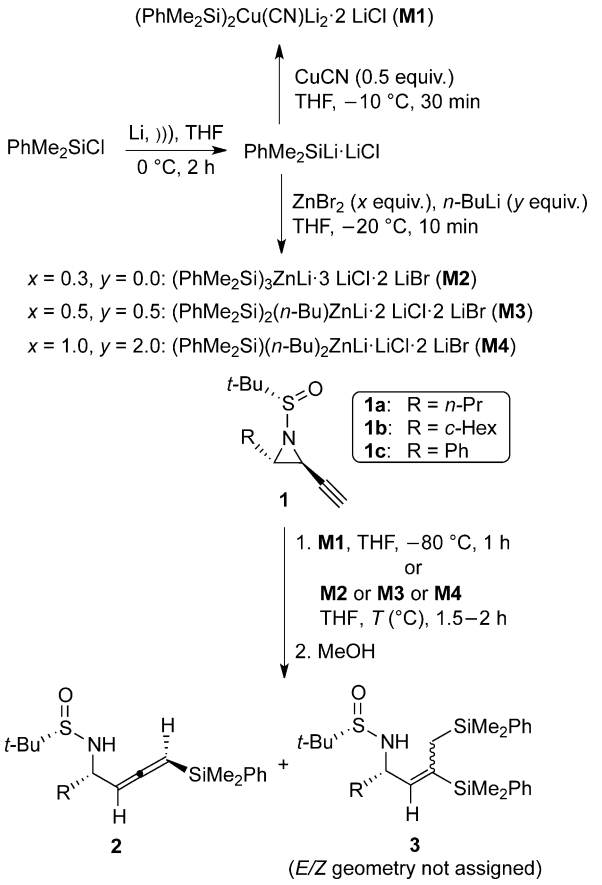
Scheme 2. Synthesis of racemic aziridines **1**.

pleased to observe the formation of the desired adduct **2a** as a single isomer as seen by ^{1}H NMR analysis.

Although encouraging, this result was however not fully satisfactory because of the unexpected formation of vinylsilane **3a**. The side-product **3a** was assumed to be formed through the nucleophilic attack of the copper species onto *in situ* generated **2a**. Despite many efforts, the formation of **3a** could not be avoided. Our best result was obtained by adding a slight sub-stoichiometric amount of **M1** (0.9 equiv.) to a THF solution of **1a** at −80 °C. Under such conditions, a full conversion was observed within 1 h and a **2a**:**3a** ratio of 80:20 was attained (Table 1, entry 1). The same trend was observed with 2° alkyl and aromatic aziridines **1b** and **1c** for which the corresponding side-products **3b** and **3c** were detected in the crude reaction mixture by ^{1}H NMR analysis in **2b**:**3b** = 72:28 and **2c**:**3c** = 84:16 ratios (Table 1, entries 2 and 3).

Being unable to avoid the formation of disilylated side-product **3**,[18] we thus planned to employ zincate **M2**[19] instead of cuprate **M1**. To our great delight, when carried out at −80 °C in THF, the reaction with aziridine **1a** was complete within 2 h and afforded **2a** in 66% isolated yield as a single isomer (Table 1, entry 4). The yield could be improved to 80% by adding **1a** to **M2** in THF at −60 °C and then running the reaction at −30 °C for 1.5 h (Table 1, entry 5), whereas using a stoichiometric amount of zincate species **M2** resulted in an incomplete conversion and a significantly lower 47% isolated yield (Table 1, entry 6). It is worthy of note that, in all these cases, no formation of the side-product **3a** was observed as seen by ^{1}H NMR analysis. As in this reaction two $PhMe_2Si$ groups were lost, we next envisaged to use mixed lithio zincates **M3** and **M4**. Unfortunately, at −30 °C degradation was observed leading to modest yields, albeit a high *dr* of 96:4 was attained with **M4** (Table 1, entry 8). In addition, in our hands, these results were not reproducible both in terms of stereoselectivity and yield. This was assumed to result from the difficulty in controlling the stoichiometry of these

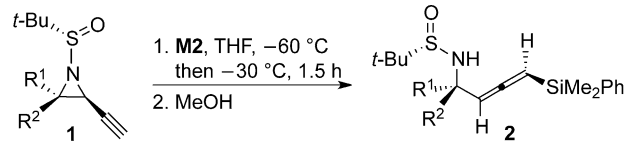
Table 1. Screening of the reaction conditions.

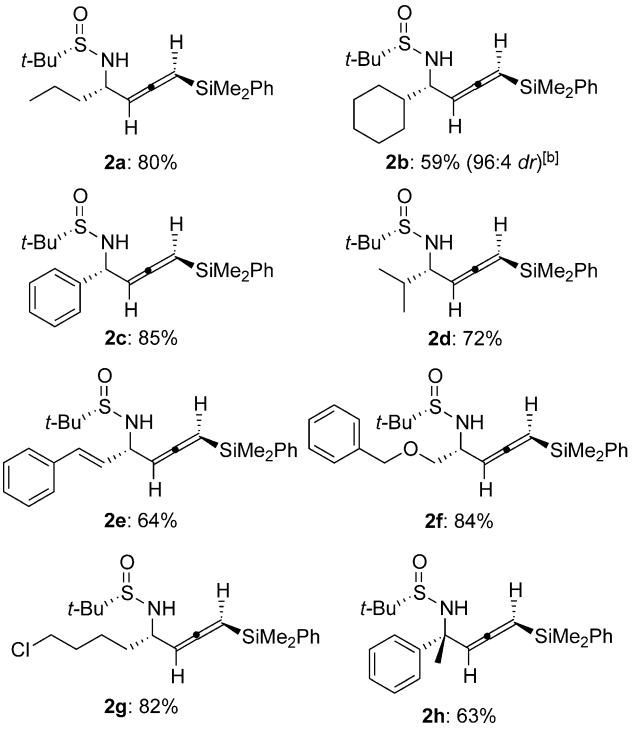


Entry	**1**	**M**	equiv.	*T* [°C]	**2**:**3**[a]	*dr*[b]	**2**, yield [%][c]
1	**1a**	**M1**	0.9	−80	80:20	>98:2	**2a**, 63[d]
2	**1b**	**M1**	0.9	−80	72:28	>98:2	**2b**, 66[e]
3	**1c**	**M1**	0.9	−80	84:16	>98:2	**2c**, 63[d]
4	**1a**	**M2**	2.2	−80	>98:2	>98:2	**2a**, 66
5	**1a**	**M2**	2.2	−30[f]	>98:2	>98:2	**2a**, 80
6	**1a**	**M2**	1.1	−30[f]	>98:2	>98:2	**2a**, 47[g]
7	**1a**	**M3**	2.2	−30[f]	>98:2	(75:25)[h]	**2a**, (57)[i]
8	**1a**	**M4**	2.2	−30[f]	>98:2	(96:4)[h]	**2a**, (78)[i]

[a] Ratio determined by ^{1}H NMR analysis of the crude reaction mixture.
[b] The *dr* of major product **2** was determined by ^{1}H NMR analysis of the crude reaction mixture.
[c] Unless otherwise stated, isolated yield of diastereomerically pure major product **2**.
[d] Minor product **3** could not be isolated.
[e] Isolated yield of 24% for minor product **3b**.
[f] Aziridine **1a** was added to the organometallic species **M** in THF at −60 °C and the resulting solution warmed to −30 °C.
[g] Conversion of 80% by ^{1}H NMR analysis.
[h] The stereoselectivity was not reproducible.
[i] Unidentified side-products were observed by ^{1}H NMR analysis. The yield of crude **2a** was not reproducible.

Table 2. Synthesis of 4-amino-1-allenylsilanes **2**.[a]

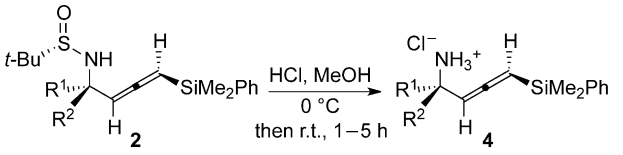


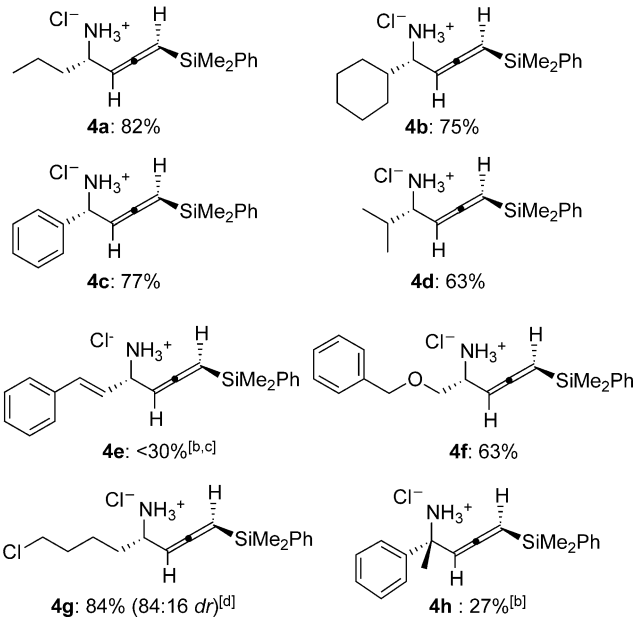


[a] Isolated yields of **2** after chromatography over silica gel. Unless otherwise stated, all 4-amino-1-allenylsilanes **2** were isolated in a diastereomerically pure form (>98:2 *dr*).

[b] The *dr* was determined by ^{1}H NMR analysis of the crude reaction mixture. The two diastereoisomers could not be separated by flash chromatography over silica gel.

Table 3. Synthesis of 4-amino-1-allenylsilane salts **4**.[a]





[a] Isolated yields. Unless otherwise stated, all salts **4** were isolated as diastereomerically pure products (>98:2 *dr*).

[b] Many side-products were observed.

[c] Salt **4e** could not be satisfactorily purified.

[d] The reaction was carried out 5 h at 0 °C. The *dr* was determined by ^{1}H NMR analysis of the crude reaction mixture. The two diastereomers could not be separated by chromatography over silica gel.

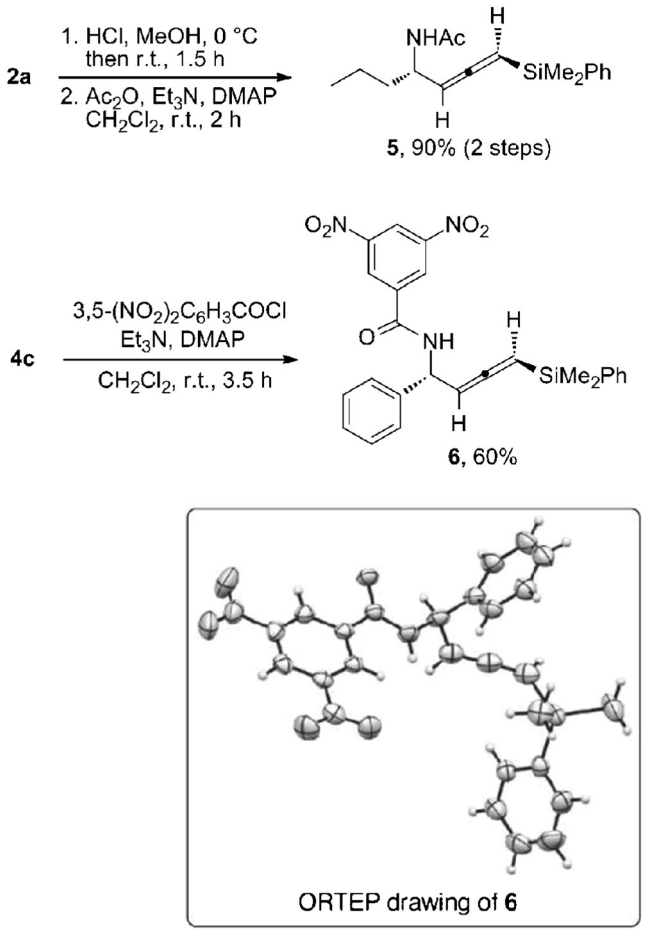
mixed zincates, presumably because the accurate titration of the $PhMe_2SiLi$ solution is impossible.[20]

The reactivity of **M2** was next investigated with other aziridines (Table 2). When subjected to the above optimized conditions, all disubstituted aziridines tested, bearing 2° alkyl, alkenyl, phenyl or even functionalized substituents, afforded the corresponding 4-amino-1-allenylsilanes **2a–g** in good yields (59–85%) and high *dr* (≥96:4). Interestingly, the reaction could also be efficiently applied to the synthesis of **2h** possessing a tetrasubstituted stereogenic carbon atom.

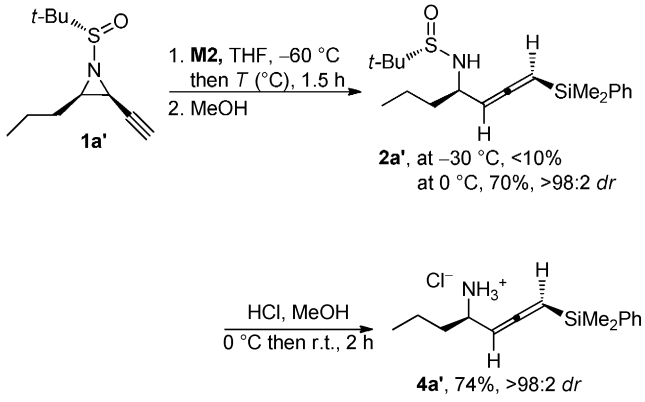
At this stage we thus had a general method for the stereoselective synthesis of 4-amino-1-allenylsilanes **2**. In order to demonstrate the synthetic potential of this method, we then considered the removal of the *N-tert*-butanesulfinyl chiral auxiliary. As well documented,[15] this group, whose reactivity is comparable with that of the Boc group, could be easily removed by treatment with dry HCl in MeOH. In most cases, hydrochloride salts **4** were obtained in good yields and high *dr* (Table 3). In the cases of compounds **2e** and **2h** degradation was however observed to some extent.

Furthermore, we have demonstrated that the *N*-acetylation of salt **4a** under basic conditions provided *N*-acetyl derivative **5** in 90% isolated yield over 2 steps (Scheme 3). The relative configuration of compounds **2** was unambiguously assigned by the single crystal X-ray analysis of the 3,5-dinitrobenzoyl derivative **6**[21] obtained in 60% yield through the reaction of salt **4c** with 3,5-$(NO_2)_2C_6H_3COCl$ under the same conditions.

We next explored the reactivity of **M2** with *cis* aziridine **1a′**. The latter was proven to be less reactive than its *trans* isomer **1a**. Only partial conversion of ~30% was indeed reached within 1.5 h at −30 °C in THF leading to less than 10% isolated yield of **2a′**. However, increasing the reaction temperature to 0 °C afforded **2a′** in 70% yield as a single isomer within 1.5 h (Scheme 4). Further removal of the *N-tert*-buta-

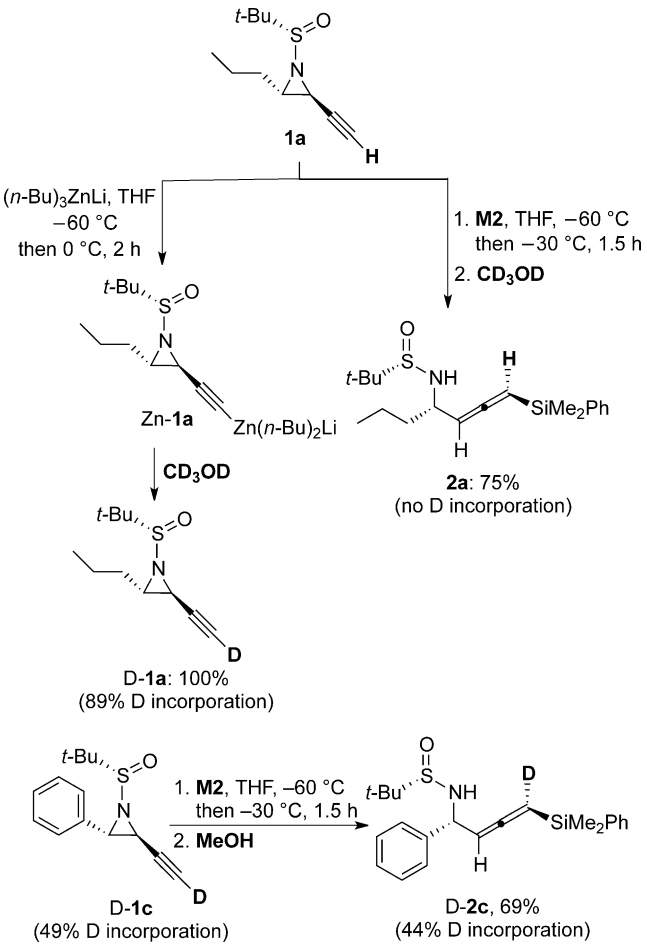


Scheme 3. Determination of the relative configuration of compounds **2**.



Scheme 4. Synthesis of **2a′** and **4a′**.

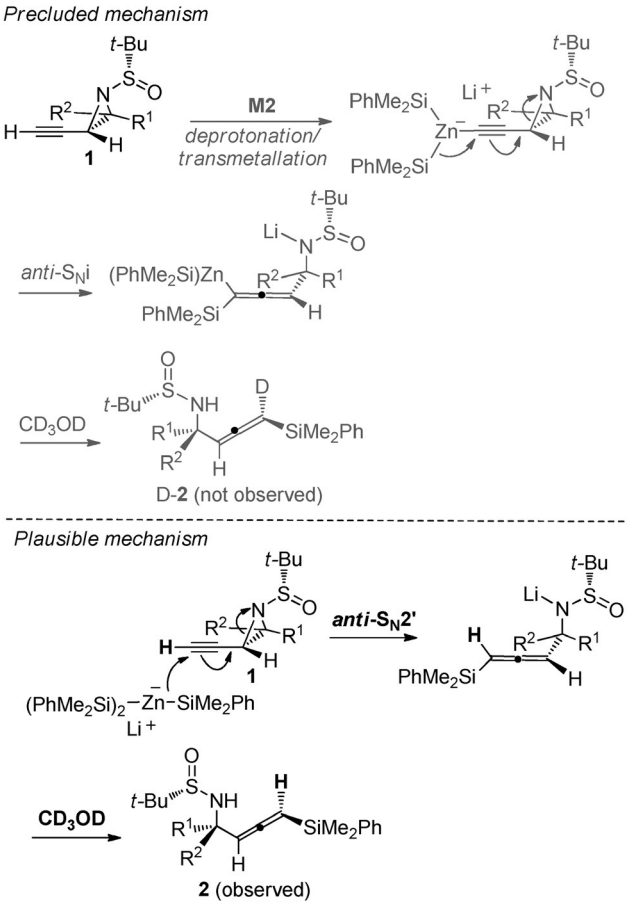
nesulfinyl moiety produced hydrochloride salt **4a′** in 74% yield. The ^{1}H NMR spectrum of **4a′** was found to be different from that of **4a**. This allowed us to deduce the relative configuration of **4a′** since **4a** and **4a′** only differ in the configuration of the stereogenic carbon atom α to the allenyl moiety.



Scheme 5. Mechanistic investigation.

To gain further insight into the mechanism, aziridine **1a** was reacted with $(n\text{-Bu})_3$ZnLi *in situ* generated by mixing *n*-BuLi (3 equiv.) with $ZnBr_2$ (1 equiv.) at −20 °C for 10 min.

Whereas no reaction occurred at −30 °C in THF, deuterated aziridine D-**1a** was quantitatively obtained when the reaction was performed for 2 h at 0 °C and then quenched with CD_3OD (Scheme 5). This result indicates that $(n\text{-Bu})_3$ZnLi is able to afford acetylenic zincate Zn-**1a** (through deprotonation and subsequent transmetallation), but that the transfer of an *n*-Bu group *via* an S_Ni mechanism does not take place in contrast with the reactivity observed by Oku et al. with propargylic electrophiles.[19,22] On the other hand, two supplementary experiments were performed with **M2**. Under our optimized conditions, upon quenching with CD_3OD, 4-amino-1-allenylsilane **2a** was obtained in 75% yield from **1a**, with no incorporation of deuterium atom. Additionally, from deuterium-labelled aziridine D-**1c** no significant loss of deuterium incorporation was noted upon quenching with MeOH. These results suggest that a mechanism reminiscent of that occuring for ethynylepoxides[23] that would entail deprotonation and subsequent *anti*-S_Ni transfer of



Scheme 6. Mechanistic rationale.

$PhMe_2Si$ is unlikely. Such a process would afford the deuterated 4-amino-1-allenylsilane D-**2** (Scheme 6, *top*). Conversely, a direct *anti*-S_N2' pathway fully accounts for the results (Scheme 6, *bottom*).

All these results point out that the stereoselectivity of the ring-opening only depends on the configuration of the progargylic stereogenic carbon atom on the aziridine. In particular, they indicate that the chiral *tert*-butanesulfinyl group on the nitrogen atom has no impact on the stereochemical outcome these reactions.

In conclusion, we have disclosed a rapid and highly stereoselective access to 4-amino-1-allenylsilanes by the reaction of lithium tris(dimethylphenylsilyl) zincate, $(PhMe_2Si)_3ZnLi{\cdot}3\,LiCl{\cdot}2\,LiBr$ **M2**, with *N*-*tert*-butanesulfinylethynylaziridines. The reaction was shown to be stereospecific and to proceed through an *anti*-S_N2' pathway. The use of these compounds in S_E2' substitution reactions is currently being investigated in our group.

Experimental Section

Representative Procedure for the Ring-Opening of Aziridines 1 with M2

Under argon, Li (557 mg, 80.0 mmol) was washed with anhydrous THF (×3). TMSCl (5.12 mL, 40.0 mmol) and THF (20 mL) were added. After 15 min of sonication, Li was washed with anhydrous THF (×4) and then taken up in anhydrous THF (40 mL). After an additional 5 min of sonication under argon, $PhMe_2SiCl$ (3.30 mL, 20.0 mmol) was added and the resulting mixture was sonicated for 2 h at 0 °C to give a dark-red THF solution of $PhMe_2SiLi$ (~0.4 M). The solution could be stored at −18 °C for 3 weeks.

Under argon, to the above solution of $PhMe_2SiLi$ (~0.4 M in THF, 28.50 mL, ~11.40 mmol) was added dropwise a solution of $ZnBr_2$ (1.00 M in THF, 3.80 mL, 3.80 mmol) at −20 °C, giving, after 10 min, a dark-green solution of **M2**. This solution was cooled to −60 °C and aziridine **1a** (369.3 mg, 1.73 mmol) in THF (17 mL) was added. After warming to −30 °C, the reaction mixture was stirred for 1.5 h and quenched with MeOH. The layers were separated and the aqueous one extracted with Et_2O (×3). The combined organic layers were washed with H_2O then brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under vacuum. The crude product was purified by flash chromatography over silica gel (EtOAc/cyclohexane 20:80) to afford analytically pure **2a** as a yellow oil; yield: 484.1 mg (80%).

Acknowledgements

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