A Facile Reaction of Unactivated Imines with Telluronium Allylide. Highly Stereoselective Synthesis of Vinylaziridines

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Supporting Information

General methods.

Infrared spectra were recorded on a Nicolet AVATAR-360 spectrometer. $^1$H NMR and $^1$C NMR spectra were recorded at Bruker AM-300 instruments. Low resolution mass spectra (m/z) were recorded on HP5989A. High-resolution mass spectra were recorded on Concept 1H or MALDI/DHB. Microanalyses were performed using a Elementar Vario EL. All reaction flasks were dried by flame. And all reactions were carried out under argon unless otherwise noted. THF and toluene were dried by distilled over sodium-benzophenone ketyl prior to use. N-aryl imines and $\alpha$-amidoalkyl-$p$-tolyl sulfones were prepared according to literature methods.$^1$

Typical procedure for the reaction of telluronium ylides and N-aryl imines.

To a solution of telluronium salt 1 (153 mg, 0.35mmol) in toluene or THF (5mL) was added LiHMDS (0.35mmol) and HMPA (1.05 mmol) at -78 °C. The resulting mixture was stirred for 20 minutes under Ar atmosphere, and then N-aryl imines ( 0.25 mmol ) in THF was added. After 4-5 hours, the reaction temperature was allowed to warm to rt. The mixture was filtrated through short silica gel and eluted by ethyl acetate. After the solvent was removed, the residue was purified by flash chromatography (silicon gel, eluted by petroleum ether/acetate, 15:1, Et$_3$N (~2% )) to afford the desired product.

Typical procedure for the reaction of telluronium ylides and $\alpha$–amidoalkyl–$p$-tolyl sulfones (N-Boc-imines).

To a solution of telluronium salt 1 (183 mg, 0.42mmol) was added NaHMDS (0.42mmol) at
-78 °C. After stirred for 20 minutes under Ar atmosphere, α-amidoalkyl-p-tolyl sulfones (0.2 mmol) 4 in THF (5mL) was added. After 2-3 hours, the reaction temperature was allowed to warm to rt. The mixture was filtrated through short silica gel column and eluted by ethyl acetate. After the solvent was removed under reduced pressure, the residue was purified by flash chromatography (silicon gel, eluted by petroleum ether/acetate, 25:1, Et3N (~2%)) to afford the desired product.

**N-phenyl-trans-2-( β-trimethylsilyl)vinyl-3-phenylaziridine (Table 2, Entry 1)**

Prepared according to general procedure. Yield: 61 mg (84%); trans/cis: 98/2; 

^{1}H NMR(300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.37-7.20 (m, 8H), 6.96-6.93 (m, 2H), 6.18 (d, \(J = 18.9\) Hz, 1H), 5.40 (dd, \(J = 18.3\) Hz, \(J = 9.3\) Hz 1H), 3.33 (d, \(J = 2.7\) Hz, 1H), 3.10 (dd, \(J = 9.0\) Hz, \(J = 2.7\) Hz, 1H), 0.01 (s, 9H). 

^{13}C NMR(75 MHz, CDCl\textsubscript{3}): 149.58, 142.10, 138.28, 136.24, 128.68, 128.42, 127.36, 126.34, 122.089, 120.68, 52.67, 48.40, -1.37. MS (m/z): 293 (25.27, \(M^{+}\)), 220 (100). IR (film) 1598, 1489 cm\(^{-1}\). HRMS Calcd for C\textsubscript{19}H\textsubscript{23}NSi: 293.159. Found: 293.159.

**N-phenyl-trans-2-( β-trimethylsilyl)vinyl-3-(p-methyl)phenylaziridine (Table 2, Entry 2)**

Prepared according to general procedure. Yield: 54 mg (70%); trans/cis: 99/1; 

^{1}H NMR (300 MHz, Aceton-\(\text{d}_6\)) \(\delta\) 7.28-7.14 (m, 6H), 6.96-6.91 (m, 3H), 6.23 (d, \(J = 18.9\) Hz, 1H), 5.46 (dd, \(J = 18.4\) Hz, \(J = 9.0\) Hz, 1H), 3.43 (d, \(J =2.7\) Hz, 1H), 3.09 (dd, \(J = 9.3\) Hz, \(J = 2.7\) Hz, 1H), 2.31 (s, 3H), 0.01 (s, 9H). 

^{13}C NMR (75 MHz, Aceton-\(\text{d}_6\)): 150.91, 143.29, 137.58, 136.43, 136.02, 129.83, 129.46, 127.12, 122.64, 121.44, 53.18, 48.58, 21.19, -1.22. MS (m/z): 307 (31.68, \(M^{+}\)), 234 (100). IR (film) 1598, 1489 cm\(^{-1}\). HRMS Calcd for C\textsubscript{20}H\textsubscript{25}NSi: 307.176. Found: 307.176.

**N-phenyl-trans-2-( β-trimethylsilyl)vinyl-3-(p-methoxy)phenylaziridine (Table 2, Entry 3)**
N-phenyl-trans-2-(β-trimethylsilyl)vinyl-3-(o-methoxy)phenylaziridine (Table 2, Entry 4)

Prepared according to general procedure. Yield: 56 mg (71%); trans/cis: 99/1; \(^1\)H NMR (300 MHz, Aceton-\(d_6\)) \(\delta\) 7.28-7.20 (m, 4H), 7.02-6.90 (m, 5H), 6.24 (d, \(J = 18.6\) Hz, 1H), 5.45 (dd, \(J = 18.6\) Hz, \(J = 9.0\) Hz, 1H), 3.89 (s, 3H), 3.70 (s, 3H), 3.08 (dd, \(J = 9.0\) Hz, \(J = 2.7\) Hz, 1H), 0.02 (s, 9H). \(^{13}\)C NMR (75 MHz, Aceton-\(d_6\)): 160.08, 152.22, 144.98, 137.19, 130.46, 130.19, 128.33, 128.06, 123.65, 122.38, 112.21, 56.93, 53.23, 44.99, -0.200. MS (\(m/z\)): 323 (19.28, M\(^+\)), 250 (100). IR (film) 1598, 1492 cm\(^{-1}\). HRMS (MALDI/DHB) Caled for C\(_{20}\)H\(_{26}\)NOSi\(^+\): 324.176. Found: 324.177.

N-phenyl-trans-2-(β-trimethylsilyl)vinyl-3-(p-chloro)phenylaziridine (Table 2, Entry 5)

Prepared according to general procedure. Yield: 68 mg (83%); trans/cis: 98/2; \(^1\)H NMR (300 MHz, Aceton-\(d_6\)) \(\delta\) 7.43-7.21 (m, 6H), 7.00-6.92 (m, 3H), 6.25 (d, \(J = 18.9\) Hz, 1H), 5.43 (dd, \(J = 18.6\) Hz, \(J = 9.0\) Hz, 1H), 3.51 (d, \(J = 2.4\) Hz, 1H), 3.11 (dd, \(J = 8.7\) Hz, \(J = 2.4\) Hz, 1H), 0.01 (s, 9H). \(^{13}\)C NMR (75 MHz, Aceton-\(d_6\)): 150.44, 143.20, 138.52, 136.63, 133.28, 129.45, 129.19, 128.77, 122.84, 121.40, 53.43, 47.80, -1.29. MS (\(m/z\)): 327 (29.42, M\(^+\)), 254 (100). IR (film) 1600, 1502 cm\(^{-1}\). HRMS Caled for C\(_{19}\)H\(_{22}\)NCIsi: 327.121. Found: 327.121.

N-phenyl-trans-2-(β-trimethylsilyl)vinyl-3-(p-trifluoromethyl)phenylaziridine (Table 2, Entry 6)
N-phenyl-trans-2-vinyl-3-phenylaziridine (Table 2, Entry 7)

Prepared according to general procedure. Yield: 21 mg (37%); trans/cis: 80/20;
Data for trans: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.39-7.21 (m, 7H), 7.00-6.95 (m, 3H), 5.51-5.45 (m, 1H), 5.29-5.21 (m, 2H), 3.27 (d, $J = 2.7$ Hz, 1H), 3.09 (dd, $J = 8.7$ Hz, $J = 2.7$ Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$): 149.54, 138.28, 134.59, 128.82, 128.45, 127.41, 126.25, 122.15, 120.68, 119.25, 50.99, 47.89. MS (m/z): 221 (100, M$^+$), 77 (88.26). IR (film) 1598, 1489 cm$^{-1}$. HRMS Calcd for C$_{16}$H$_{15}$N: 221.120. Found: 221.120.

Data for cis: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.46-7.24 (m, 7H), 7.07-6.98 (m, 3H), 5.54-5.43 (m, 2H), 5.20-5.16 (m, 1H), 3.49 (d, $J = 6.6$ Hz, 1H), 3.00 (t, $J = 6.6$ Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$): 154.30, 136.45, 134.01, 129.06, 128.13, 127.55, 127.17, 122.60, 119.91, 118.61, 48.72, 47.63. MS (m/z): 221 (86.16, M$^+$), 77 (100). IR (film) 1599, 1489 cm$^{-1}$. HRMS Calcd for C$_{16}$H$_{15}$N: 221.120. Found: 221.120.

N-Boc-cis-2-(3-trimethylsilyl)vinyl-3-(i-propyl)aziridine (Table 2, Entry 8)

Prepared according to general procedure. Yield: 41 mg (77%); cis/trans: 91/7;
$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 6.13 (d, $J = 18.6$ Hz, 1H), 5.83 (dd, $J = 18.6$ Hz, $J = 6.9$Hz, 1H), 3.01 (t, $J = 6.9$ Hz, 1H), 2.16 (dd, $J = 9.9$ Hz, $J = 6.9$Hz, 1H), 1.46 (s, 9H), 1.43-1.41 (m, 1H), 1.15 (d, $J = 6.6$ Hz, 3H), 0.88 (d, $J = 7.2$ Hz, 3H), 0.07 (s, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$):
162.47, 139.78, 135.65, 80.83, 50.76, 45.30, 27.86, 27.80, 20.77, 18.78, -1.41. MS (m/z): 57 (100), 73 (61.64), 182 (45.70). IR (film) 1723, 1617 cm⁻¹. Anal. Calcd. for C₁₅H₂₉NO₂Si: C, 63.55; H, 10.31; N, 4.94. Found: C, 63.68; H, 10.44; N, 4.75.

**N-Boc-cis-2-(β-trimethylsilyl)vinyl-3-(cyclohexyl)aziridine (Table 2, Entry 9)**

\[
\begin{align*}
\text{N-Boc} & \quad \text{Boc} \\
& \quad \text{TMS}
\end{align*}
\]

Prepared according to general procedure. Yield: 46 mg (71%); cis/trans: 97/3; \(^1\)H NMR (300 MHz, CDCl₃) δ 6.09 (d, J = 18.6 Hz, 1H), 5.81 (dd, J = 18.9 Hz, J = 6.9Hz, 1H), 2.97 (t, J = 6.6 Hz, 1H), 2.18 (dd, J = 9.0 Hz, J = 6.9Hz, 1H), 2.00-1.96 (m, 1H), 1.76-1.50 (m, 4H), 1.49 (s, 9H), 1.24-0.96 (m, 6H), 0.05 (s, 9H). \(^{13}\)C NMR (75 MHz, CDCl₃): 162.56, 139.82, 135.42, 80.82, 49.17, 44.85, 36.85, 31.20, 29.31, 27.90, 26.26, 25.55, 25.52, -1.36. MS (m/z): 77 (100), 222 (49.11), 73 (35.06). IR (film) 1722, 1617 cm⁻¹. Anal. Calcd. for C₁₅H₃₃NO₂Si: C, 66.82; H, 10.28; N, 4.33. Found: C, 67.07; H, 10.13; N, 4.30.

**N-Boc-cis-2-(β-trimethylsilyl)vinyl-3-(cyclohexyl)aziridine (Table 2, Entry 10)**

\[
\begin{align*}
\text{n-Bu} & \quad \text{N} \\
& \quad \text{Boc} \\
& \quad \text{TMS}
\end{align*}
\]

Prepared according to general procedure. Yield: 30 mg (50%); cis/trans: 86/14; \(^1\)H NMR (300 MHz, CDCl₃) δ 6.08 (d, J = 18.9 Hz, 1H), 5.80 (dd, J = 18.6 Hz, J = 6.6Hz, 1H), 2.99 (t, J = 6.9 Hz, 1H), 2.51-2.45 (m, 1H), 1.47-1.43 (m, 15H), 0.90 (t, J = 7.0 Hz, 3H), 0.06 (s, 9H). \(^{13}\)C NMR (75 MHz, CDCl₃): 162.53, 139.62, 135.67, 80.85, 44.95, 44.13, 29.09, 27.79, 27.38, 22.13, 13.93, -1.48. MS (m/z): 57 (100), 222 (52.36), 196 (4.28). IR (film) 1721, 1616 cm⁻¹. Anal. Calcd. for C₁₆H₃₁NO₂Si: C, 64.59; H, 10.50; N, 4.71. Found: C, 64.94; H, 10.36; N, 4.40.

**Reaction of silylated dimethyl sulfur allylide with N-phenyl aldimine.**¹

\[
\begin{align*}
\begin{array}{c}
\text{Me}_2\text{S} \quad \text{TMS}^+ \\
\text{Br} \quad \text{NPh} \\
\text{1'} \quad \text{2a} \quad \text{3}
\end{array}
\end{align*}
\]

To a solution of [3-(trimethylsilyl)allyl]dimethylsufonium 1' (89 mg, 0.35 mmol) in THF (5...
mL) was added LiHMDS (0.35 mmol) and HMPA (1.05 mmol) at -78 °C. The resulting mixture was stirred for 20 minutes under Ar atmosphere, and then N-aryl imines 2a (45 mg, 0.25 mmol) in THF was added. After stirring for 3-4 hours, the reaction temperature was allowed to warm to room temperature. The mixture was filtrated through short silica gel and eluted by ethyl ether. After the solvent was removed, the residue was purified by flash chromatography (silicon gel, eluted by petroleum ether/acetate, 15:1, Et3N (~2%)) to afford N-aryl imines 2a (35 mg, 0.19 mmol), benzaldehyde (4.8 mg, 0.045 mmol).

The stereochemical assignment of aziridines.

The configuration of the aziridines is determined by 1H NMR, 1H-1H NOESY and/or by a comparison with the 1H NMR of the known compounds. According to literatures,\(^ 2\) generally, the coupling constant of the H\(_a\) and H\(_b\) on aziridine ring for trans-isomer is between 2-4 Hz and for the cis-isomer, the corresponding coupling constant is 4-8 Hz. For N-phenyl-aziridines, some of the cis-isomers are known compounds.\(^ 2\) So, by comparing their 1H NMR, it’s easy to determine the configuration of our products. For the N-Boc aziridines, we first proposed that the major products are cis-isomer by comparing their 1H NMR with those of the similar aziridines.\(^ 3,4\) The assignment for N-Boc-imines 7 (Cis/trans = 91/9) is further confirmed by 1H-1H NOESY (attached).

**Figure 1** 1H-1H NOESY for compound 7

Preparation of 3-trimethylsilyl-2-propenyldiisobutyl telluronium bromide 1a.

\[
\text{Te} + \text{CH}_2\text{(OH)}\text{SO}_2\text{Na}_2 \text{H}_2\text{O} \xrightarrow{\text{NaOH}, \text{H}_2\text{O}, \text{reflux}} [\text{Na}_2\text{Te}] \xrightarrow{\text{iBuBr} / \text{EtOH}} \text{iBu}_2\text{Te} \rightarrow 5
\]

a) **Preparation of Telluride 5.**\(^ 5\) A mixture of tellurium (19.14 g, 150 mmol), Sodium
Formaldehyde Sulfoxylate 4 (61.65 g, 400 mmol) and NaOH (36 g, 900 mmol) in 200 mL of H₂O was refluxed for 30 min, then isobutylbromide (32.6 ml, 137 mmol) in ethanol was added dropwise. After the resulting mixture was refluxed for 4-5 hours, the organic layer was separated and the water layer was extracted with ethyl ether. The organic layers were combined, dried over CaCl₂, concentrated. The residue was distilled in vacuo to afford Telluride 5 (73-74°C/7mmHg). Yield: 16.7 g (44.8%). ¹H NMR (60 MHz, CDCl₃/TMS) δ 2.55 (d, J = 18.0 Hz, 4H), 2.1-1.6 (m, 2H), 1.8 (d, J = 10.0 Hz, 12H).

3-trimethylsilyl-2-propenylidisobutyl telluronium bromide 1a.⁶ (E)-3-bromo-1-trimethylsilyl-1-propene 6 (11.4 g, 59.1 mmol) and disobutyl telluride 5 (14.3 g, 59.1 mmol) were mixed and stirred at room temperature under N₂. The resulting solid was washed with ethyl ether to afford 3-trimethylsilyl-2-propenylidisobutyl telluronium bromide 1a. Yield: 21.2 g (82%). ¹H NMR (60 MHz, CDCl₃/TMS) δ 6.4-6.0 (m, 1H), 5.6-5.3 (m, 1H), 4.05 (d, J = 9.0 Hz, 2H), 3.1-2.3 (m, 6H), 1.15 (d, J = 9.0 Hz, 12H), 0.1 (s, 9H).

Possible mechanisms for the aziridination. In the case of aromatic imines, the trans-isomers are obtained as the major products. In this case, we proposed the mechanism is similar to that of the ylide aziridination reported by Hou.⁷ The ylide reacted with imine to afford intermediates A and B. A is favorable for it’s less steric hindrance and thus trans-aziridine is provided as the major one.
However, in the case of N-Boc-imines, we proposed that the C=O group of BOC played an important role to control the stereochemistry of this reaction. In this case, a possible mechanism could be envisioned to proceed via a chelating six-membered ring transition state, which is formed by coordination of telluronium ion with carbonyl oxygen and ylidylic carbanion simultaneously. Transition state TS-1 might be anticipated to be more stable than transition state TS-2. Thus, the formation of intermediate C in the initial condensation is favored over that of intermediate D. Following elimination leads to cis-isomers as the major product. A detailed mechanism awaits for further investigation.

Notes and references


8. There always has strong interaction between Te and O. For example, please see: Z.-Z. Huang, S. Ye, W. Xia, Y.-H. Yu and

7 (cis-isomer/trans = 91/9) \textsuperscript{1} H-\textsuperscript{1}H NOESY