Novel Reaction Course of Thiiranes to Vinyl Epoxides: 
Reaction of Benzyne with Thiiranes and Aldehydes

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Experimental Section
$^1$H NMR and $^{13}$C NMR chart
Experimental

**General**: All chemicals were obtained from commercial suppliers and were used without further purification. Analytical TLC was carried out on precoated plates (Merck silica gel 60, F254) and flash column chromatography was performed with silica gel (Merck, 70-230 mesh). NMR spectra ($^1$H at 400 MHz; $^{13}$C at 101 MHz) were recorded in CDCl$_3$, and chemical shifts are expressed in ppm relative to internal TMS for $^1$H- and $^{13}$C-NMR. $^{19}$F NMR (376 MHz) spectra were recorded on a Bruker AVANCE spectrometer and referenced against the external standard CFCl$_3$. EI and ESI-TOF mass spectra were recorded on a JEOL JMS-GCmateII and a JEOL JMS-T100CS spectrometer, respectively.

**Reaction of 2-trimethylsilylphenyl triflate with 2-phenylthiirane 2a in the presence of chloroform**

To a suspension of 2-trimethylsilylphenyl triflate 1a (90 g, 0.3 mmol) and CsF (137 mg, 0.9 mmol) in acetonitrile (2 mL) was added 2-phenylthiirane 2a (41 mg, 0.3 mmol) in chloroform (2 mL). After being stirred for 6 h, the reaction mixture was washed with water and extracted with dichloromethane. The combined extracts were dried over sodium sulfate, filtered, and evaporated to give pale brown oily crystals, which were chromatographed over silica gel by elution with hexane to afford ($E$)-but-1-enylphenyl sulfide 3a (54 mg, 0.26 mmol).

![Chemical structure of (E)-but-1-enylphenyl sulfide 3a](image)

(E)-but-1-enylphenyl sulfide 3a. Colorless oil (lit.$^1$ Colorless oil);$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 6.74$ (d, 1H, $J = 16$ Hz, CH), 6.89 (d, 1H, $J = 16$ Hz, CH), 7.27 - 7.21 (m, 2H), 7.37 - 7.27 (m, 6H), 7.44 - 7.40 (m, 2H).

$^1$H NMR (400 MHz, CDCl$_3$) 3a
Reaction of 2-trimethylsilylphenyl triflate (2 eq) with 2-phenylthiirane 2a in the presence of chloroform

To a suspension of 2-trimethylsilylphenyl triflate 1a (208 mg, 0.7 mmol) and CsF (320 mg, 2.1 mmol) in acetonitrile (2 mL) was added 2-phenylthiirane 2a (41 mg, 0.3 mmol) in chloroform (2 mL). After being stirred for 6 h, the reaction mixture was washed with water and extracted with dichloromethane. The combined extracts were dried over sodium sulfate, filtered, and evaporated to give a pale brown oil, which was chromatographed over silica gel by elution with hexane to afford diphenyl sulfide 4 (46 mg, 0.25 mmol).

![Image of diphenyl sulfide 4]

Diphenyl sulfide 4. Colorless oil (lit.² Colorless oil); ¹H NMR (400 MHz, CDCl₃) δ = 7.37 - 7.22 (m, 10H).

¹H NMR (400 MHz, CDCl₃) 4

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Reaction of 2-trimethylsilylphenyl triflate (2 eq) with 2-phenylthiirane 2a

To a suspension of 2-trimethylsilylphenyl triflate 1a (208 mg, 0.7 mmol), and CsF (320 mg, 2.1 mmol) in acetonitrile (2 mL) was added 2-phenylthiirane 2a (76 mg, 0.3 mmol) in acetonitrile (2 mL). After being stirred for 12 h, the reaction mixture was washed with water and extracted with dichloromethane. After being stirred for 12 h, the reaction mixture was washed with water and extracted with dichloromethane. The combined extracts were dried over sodium sulfate, filtered, and evaporated to give a pale yellow oil. Diethyl ether (10 mL) was added to the dichloromethane solution to afford diphenyl(styryl)sulfonium triflate 5a (79 mg 0.18 mmol).
diphenyl(styryl)sulfonium triflate 5a: Colorless oil (lit.\textsuperscript{3} white solid); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta = 7.49 - 7.39 \) (m, 3H), 7.71 - 7.62 (m, 6H), 7.82 - 7.77 (m, 2H), 7.89 (s, 2H, CH), 7.98 - 7.93 (m, 4H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta = 109.9, 127.2, 129.3, 129.6, 130.0, 121.5, 132.0, 132.7, 134.3, 153.4 \); \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}) \( \delta = -78.1 \); MS (ESI): Caled for C\textsubscript{20}H\textsubscript{17}S m/z = 289.10, Found; m/z = 289.15 [M]\textsuperscript{+}.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) 5a

\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) 5a
Reaction of triflate 1 with 2-phenylthiirane 2a followed by the addition of benzylamine in the presence of CsF.

To a suspension of triflate 1 (208 mg, 0.7 mmol) and CsF (320 mg, 2.1 mmol) in acetonitrile (2 mL) was added a solution of 2-phenylthiirane 2a (76 mg, 0.3 mmol) in acetonitrile (2 mL). After being stirred for 12 h, benzylamine (48 mg, 0.45 mmol) in acetonitrile (1 mL) was added to the reaction mixture at rt. After being stirred for 6 h, the reaction mixture was washed with water and extracted with dichloromethane (5 mL x 3). The combined extracts were dried over sodium sulfate, filtered, and evaporated to give pale brown oil, which was subjected to alumina chromatography by elution with hexane:dichloromethane (1:1) to afford diphenyl sulfide 4 and 1-benzyl-2-phenylaziridine 6 (177 mg, 0.26 mmol).

1-benzyl-2-phenylaziridine 6: pale yellow oil (lit. \(^4\) colorless oil); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 1.84\) (d, 1H, \(J = 7\) Hz, CHH), 1.99 (d, 1H, \(J = 3\) Hz, CHH), 2.50 (dd, 1H, \(J = 3, 7\) Hz, CH), 3.61 (d, 1H, \(J = 14\) Hz, CHH), 3.69 (d, 1H, \(J = 14\) Hz, CHH), 7.40 - 7.19 (m, 10H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 37.9, 41.5, 64.7, 126.3, 126.8, 126.9, 127.8, 128.3, 128.3, 139.1, 140.1\); MS (ESI): Calcd for C\(_{15}\)H\(_{15}\)N m/z = 209.12, Found; m/z = 209.09 [M+H]\(^+\).
Reaction of 2-trimethylsilylphenyl triflate (2 eq) with 2-ethylthiirane 2b and benzaldehyde
To a suspension of 2-trimethylsilylphenyl triflate 1a (208 g, 0.7 mmol), benzaldehyde (0.35 mg, 0.33 mmol) and CsF (320 mg, 2.1 mmol) in acetonitrile (2 mL) was added 2-ethylthiirane 2b (27 mg, 0.3 mmol) in acetonitrile (2 mL). After being stirred for 12 h, the reaction mixture was washed with water and extracted with dichloromethane. The combined extracts were dried over sodium sulfate, filtered, and evaporated to give a pale brown oil, which was chromatographed over silica gel by elution with dichloromethane: hexane (1:3) to afford isomer’s mixture of 2-phenyl-3-(prop-1-en-1-yl)oxirane 8aa (25 mg, 0.15 mmol).
2-phenyl-3-(prop-1-en-1-yl)oxirane 8aa: (1E, 3Z): (1Z, 3Z): (1E, 3E): (1E, 3Z) = 32:51:3:8; colorless oil (lit.⁵ colorless oil); MS (ESI): Calcd for C₁₁H₁₂O m/z = 160.09, Found: m/z = 161.03 [M+H]⁺.

(1E, 3Z) isomer:

¹H NMR (400 MHz, CDCl₃) δ = 1.79 - 1.75 (m, 3H), 3.95 (dd, 1H, J = 4, 9 Hz, CH), 4.25 (d, 1H, J = 4 Hz, CH), 4.99 (dd, 1H, J = 9, 10 Hz, CH), 5.76 (m, 1H), 7.40 - 7.27 (m, 5H); ¹³C NMR (101 MHz, CDCl₃) δ = 13.4, 54.8, 58.7, 125.4, 127.3, 128.0, 128.5, 131.4, 137.4.

(1Z, 3Z) isomer:

¹H NMR (400 MHz, CDCl₃) δ = 1.79 - 1.75 (m, 3H), 3.61 (d, 1H, J = 9 Hz, CH), 3.78 (d, 1H, J = 2 Hz, CH), 5.23 (dd, 1H, J = 9, 10 Hz, CH), 5.90 - 5.81 (m, 1H), 7.40 - 7.27 (m, 5H); ¹³C NMR (101 MHz, CDCl₃) δ = 13.4, 58.8, 59.8, 123.6, 126.5, 127.6, 128.1, 132.8, 135.5.
Other oxiranes were synthesized in a similar manner.

2-phenyl-3-vinylxirane 8ba: E/Z = 40/60; colorless oil (lit.\(^6\)); MS (ESI): Calcd for C\(_{10}\)H\(_{10}\)O m/z = 146.07, Found: m/z = 147.07 [M+H]\(^+\).

E isomer:
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 3.66 \text{ (dd, 1H, } J = 4, 8 \text{ Hz, } CH), 4.24 \text{ (d, 1H, } J = 4 \text{ Hz, } CH), 5.28 \text{ (dd, 1H, } J = 2, 11 \text{ Hz, } CH), 5.41 \text{ (ddd, 1H, } J = 11, 11, 7 \text{ Hz, } CH), 5.55 \text{ (dd, 1H, } J = 2, 17 \text{ Hz, } CH), 7.39 - 7.26 \text{ (m, 5H); } \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 58.8, 59.7, 121.8, 126.4, 127.4, 128.2, 132.0, 135.1.\)

Z isomer:
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 3.37 \text{ (dd, 2H, } J = 2, 8 \text{ Hz), 3.77 \text{ (d, 1H, } J = 2 \text{ Hz, })}, 5.34 \text{ (d, 1H, } J = 10 \text{ Hz), 5.53 \text{ (d, 1H, } J = 17 \text{ Hz), 5.74 \text{ (ddd, 1H, } J = 7, 10, 17 \text{ Hz), 7.39 - 7.26 \text{ (m, 5H); } \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 60.2, 62.9, 119.5, 125.5, 128.1, 128.5, 135.1, 137.0.\)\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) 8ba
2-(4-methylphenyl)-3-vinylloxirane 8bb: E/Z = 40/60; colorless oil (lit.\textsuperscript{7} colorless liquid); MS (ESI): Calcd for C\textsubscript{11}H\textsubscript{12}O m/z = 160.09, Found: m/z = 161.02 [M+H]\textsuperscript{+}.  
E isomer:
\( ^1\text{H} \text{NMR (400 MHz, CDCl}_3 \) \( \delta = 2.35 \) (s, 3H, CH\textsubscript{3}), 3.35 (dd, 1H, \( J = 2 \), 7 Hz, CH), 3.73 (d, 1H, \( J = 2 \) Hz, CH), 5.33 (d, 1H, \( J = 10 \) Hz, CH), 5.51 (d, 1H, \( J = 17 \) Hz, CH), 5.73 (ddd, 1H, \( J = 7 \), 10, 17 Hz, CH), 7.25 - 7.12 (m, 4H); \( ^{13}\text{C} \text{NMR (101 MHz, CDCl}_3 \) \( \delta = 21.1, 58.8, 59.8, 121.7, 126.4, 128.8, 132.0, 134.0, 137.4. \)

Z isomer:
\( ^1\text{H} \text{NMR (400 MHz, CDCl}_3 \) \( \delta = 2.35 \) (s, 3H, CH\textsubscript{3}), 3.64 (dd, 1H, \( J = 4 \), 8 Hz, CH), 4.21 (d, 1H, \( J = 5 \) Hz, CH), 5.27 (dd, 1H, \( J = 2 \), 10 Hz, CH), 5.41 (ddd, 1H, \( J = 8 \), 10, 17 Hz, CH), 5.54 (dd, 1H, \( J = 2 \), 17 Hz, CH), 7.25 - 7.12 (m, 4H); \( ^{13}\text{C} \text{NMR (101 MHz, CDCl}_3 \) \( \delta = 21.2, 60.2, 62.8, 119.3, 125.5, 129.2, 132.2, 135.2, 138.0. \)
$^1$H NMR (400 MHz, CDCl$_3$) 8bb

$^1$C NMR (101 MHz, CDCl$_3$) 8bb

2-(4-chlorophenyl)-3-vinyloxirane 8bc: E/Z = 35/65; colorless oil (lit.$^6$); MS (ESI): Calcd for C$_{10}$H$_9$ClO m/z = 180.03, Found: m/z = 181.10 [M+H]$^+$.  

E isomer:

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 3.66 (dd, 1H, $J$ = 4, 7 Hz, CH), 4.20 (d, 1H, $J$ = 4 Hz, CH), 5.40 - 5.25 (m, 2H, CH), 5.59 - 5.48 (m, 1H), 7.27 (d, 2H, $J$ = 8 Hz, CH), 7.38 - 7.29 (m, 2H); $^1$C NMR (101 MHz, CDCl$_3$) $\delta$ = 58.2, 59.7, 122.1, 127.8, 128.3, 133.5, 134.0, 135.6.

Z isomer:

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 3.31 (dd, 1H, $J$ = 2, 8 Hz, CH), 3.74 (d, 1H, $J$ = 2 Hz, CH), 5.40 - 5.25 (m, 1H), 5.59 - 5.48 (m, 1H), 5.72 (ddd, 1H, $J$ = 7, 10, 17 Hz,
CH, 7.21 (d, 2H, J = 8 Hz, CH), 7.38 - 7.29 (m, 2H); \( ^{13} \text{C} \) NMR (101 MHz, CDCl\(_3\)) \( \delta = 59.5, 62.9, 119.8, 126.8, 128.7, 131.6, 133.7, 134.7. \)

\( ^{1} \text{H} \) NMR (400 MHz, CDCl\(_3\)) \textbf{8bc}

\( ^{13} \text{C} \) NMR (101 MHz, CDCl\(_3\)) \textbf{8bc}

2-(4-bromophenyl)-3-vinylxirane \textbf{8bd}: E/Z = 40/60; colorless oil (lit.\(^8\)); MS (ESI): Calcd for C\(_{10}\)H\(_9\)BrO m/z = 223.98, Found: m/z = 224.87 [M+H]\(^+\).

E isomer:
\( ^{1} \text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta = 3.66 \) (dd, 1H, \( J = 4, 7 \) Hz, CH), \( 4.19 \) (d, 1H, \( J = 4 \) Hz, CH), \( 5.40 - 5.26 \) (m, 2H, CH), \( 5.58 - 5.48 \) (m, 1H), \( 7.21 \) (d, 2H, \( J = 8 \) Hz, ArH), \( 7.51 - 7.45 \) (m, 2H); \( ^{13} \text{C} \) NMR (101 MHz, CDCl\(_3\)) \( \delta = 58.3, 59.6, 121.7, 122.1, 128.2, 131.6, 134.2, 136.1. \)

Z isomer:
$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 3.31$ (dd, 1H, $J = 2$, 7 Hz, CH), 3.73 (d, 1H, $J = 2$ Hz, CH), 5.40 - 5.26 (m, 1H), 5.58 - 5.48 (m, 1H), 5.72 (ddd, 1H, $J = 7$, 10, 17 Hz, CH), 7.16 (d, 2H, $J = 8$ Hz, ArH), 7.51 - 7.45 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 59.6$, 62.9, 119.9, 122.2, 127.1, 131.5, 131.6, 134.7.

$^1$H NMR (400 MHz, CDCl$_3$) 8bd

[Chemical structure image]

$^{13}$C NMR (101 MHz, CDCl$_3$) 8bd

[Chemical structure image]

2-(4-nitrophenyl)-3-vinylxirane 8bf: E/Z = 35/65; pale yellow oil (lit. mp. 54-56°C); MS (ESI): Caled for C$_{10}$H$_9$NO$_3$ m/z = 191.06, Found: m/z = 191.10 [M+H]$^+$.

E isomer:

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 3.77$ (dd, 1H, $J = 4$, 7 Hz, CH), 4.31 (d, 1H, $J = 4$ Hz, CH), 5.34 - 5.27 (m, 2H), 5.61 - 5.53 (m, 1H), 7.52 (d, 2H, $J = 9$ Hz, ArH), 8.25 -
8.20 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 58.0, 59.9, 122.8, 123.4, 130.8, 134.1, 147.8.

Z isomer:

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 3.35 (dd, 1H, $J$ = 2, 7 Hz, CH), 3.87 (d, 1H, $J$ = 2 Hz, CH), 5.41 (d, 1H, $J$ = 10 Hz, CH), 5.61 - 5.53 (m, 1H), 5.74 (dd, 1H, $J$ = 7, 10, 17 Hz, CH), 7.46 (d, 2H, $J$ = 9 Hz, ArH), 8.25 - 8.20 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 59.1, 63.4, 120.6, 123.8, 126.2, 134.1, 144.5.

$^1$H NMR (400 MHz, CDCl$_3$) 8bf

$^{13}$C NMR (101 MHz, CDCl$_3$) 8bf

2-(4-fluorophenyl)-3-vinyloxirane 8bg: E/Z = 35/65; colorless oil (lit.); MS (ESI): Calcd for C$_{10}$H$_7$FO m/z = 164.06, Found: m/z = 164.12 [M+H]$^+$. E isomer:
$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 3.65$ (dd, 1H, $J = 4$, 8 Hz, CH), 4.21 (d, 1H, $J = 4$ Hz, CH), 5.41 - 5.25 (m, 2H), 5.59 - 5.49 (m, 1H), 7.04 (m, 2H), 7.30 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 58.3, 59.7, 115.1$ (d, $J_{C-F} = 22$ Hz), 122.0, 128.0 (d, $J_{C-F} = 8$ Hz), 130.7 (d, $J_{C-F} = 4$ Hz), 131.7, 162.3 (d, $J_{C-F} = 246$ Hz).

Z isomer:

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 3.32$ (dd, 1H, $J = 2$, 7 Hz, CH), 3.75 (d, 1H, $J = 2$ Hz, CH), 5.41 - 5.25 (m, 1H), 5.59 - 5.49 (m, 1H), 5.72 (ddd, 1H, $J = 7, 10, 17$ Hz, CH), 7.08 - 7.00 (m, 2H), 7.27 - 7.23 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 59.6, 62.8, 115.5$ (d, $J_{C-F} = 22$ Hz), 119.7, 127.1 (d, $J_{C-F} = 8$ Hz), 133.7 (d, $J_{C-F} = 4$ Hz), 134.8, 162.7 (d, $J_{C-F} = 246$ Hz).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$.

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$. 

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References: