Facile and Highly Stereoselective Synthesis of *cis*-Trimethylsilylethynyl Epoxides *via* a Silylated Telluronium Ylide

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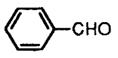
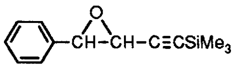
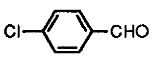
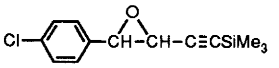
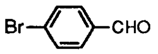
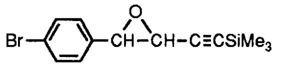
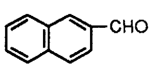
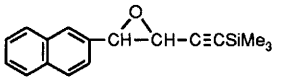
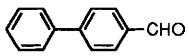
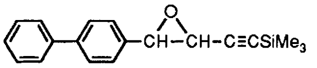
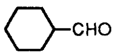
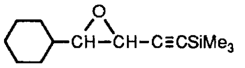
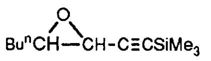
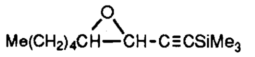
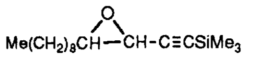
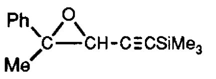
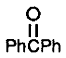
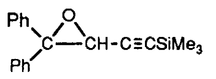
Diisobutyltelluronium trimethylsilylpropynyl ylide, generated from 3-trimethylsilylprop-2-ynyldiisobutyltelluronium bromide with lithium 2,2,6,6-tetramethylpiperidide (LiTMP), reacts with carbonyl compounds to afford predominately *cis*-trimethylsilylethynyl epoxides in good to excellent yields.

The birth of the Wittig reaction in 1953 marked the entry of ylides into the arsenal of important synthetic tools.[1] Since then, there has been remarkable interest in the synthetic application of other heteroatom ylides.[2] Along with the development of sulfonium, sulfoxonium and selenonium ylides,[3] the application of several stabilized and moderately stabilized telluronium ylides in organic synthesis has been described.[4] In our previous communication, we reported that diphenyltelluronium methylide, the first non-stabilized telluronium ylide, reacted with aldehydes or ketones to form

Table 1 Highly stereoselective synthesis of *cis*-trimethylsilylethynyl epoxides **3**[a]

Entry	R^1R^2CO	Product **3**	*cis* : *trans*[b]	Total yield (%)[c]
1		 **3a**	82 : 18	76
2		 **3b**	98 : 2	80
3		 **3c**	98 : 2	80
4		 **3d**	81 : 19	95
5		 **3e**	88 : 12	95
6		 **3f**	99 : 1	86
7	Bu^nCHO	 **3g**	98 : 2	83
8	$Me(CH_2)_4CHO$	 **3h**	98 : 2	82
9	$Me(CH_2)_8CHO$	 **3i**	97 : 3	94
10	 $PhC(=O)Me$	 **3j**	86 : 14[d]	96
11	 $PhC(=O)Ph$	 **3k**	—	80

[a] All the products gave satisfactory elemental analysis and/or HRMS, ^1H NMR, mass and IR spectra.§ [b] Determined by 200 MHz ^1H NMR and/or NOE. [c] Isolated yields based on carbonyl compounds. [d] The configuration of *cis* and *trans* isomer was determined by NOE technique.

substituted oxiranes.[5] To our knowledge, no report dealing with silylated telluronium ylide and its reactivity towards carbonyl compounds has appeared in the literature. We now report that a silylated semi-stabilized telluronium ylide, diisobutyltelluronium trimethylsilylpropynyl ylide, reacted with carbonyl compounds to afford predominately *cis*-trimethylsilylethynyl epoxides in good to excellent yields.

Diisobutyl telluride reacted with 3-bromo-1-trimethylsilylprop-1-yne without solvent at room temperature to give 3-trimethylsilylprop-2-ynyldiisobutyltelluronium bromide **1** in 87% yield (eqn. 1), which gave satisfactory elemental analysis, ^1H NMR, FAB-mass and IR spectra.†

$$Bu^i{}_2Te + BrCH_2C{\equiv}C\text{–}SiMe_3 \xrightarrow[\text{no solvent}]{\text{room temp.}} Bu^i{}_2Te^+CH_2C{\equiv}C\text{–}SiMe_3\ Br^- \quad (1)$$

1

Attempts to generate the silylated telluronium ylide from salt **1** with potassium *tert*-butoxide were unsuccessful. However, lithium 2,2,6,6-tetramethylpiperidide (LiTMP) was effective for generating the ylide **2**, which reacted with carbonyl compounds to afford trimethylsilylethynyl epoxides **3** in excellent yields with high *cis* stereoselectivity (eqn. 2).‡ The results are shown in Table 1.§

As shown in Table 1, one can see that this new method for the direct epoxidation of carbonyl compounds is of wide

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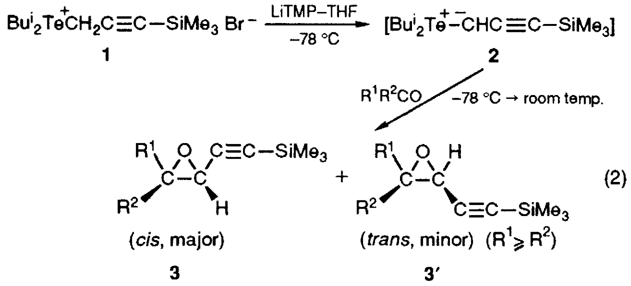
† *Data* for 3-trimethylsilylprop-2-ynyldiisobutyltelluronium bromide **1**: white solid, m.p. 102–104 °C; ^1H NMR (90 MHz, $CDCl_3$) δ 3.58 (s, 2 H), 3.00 (d, *J* 7 Hz, 4 H), 2.30 (m, 2 H), 2.04 (d, *J* 7.2 Hz, 6 H), 2.02 (d, *J* 7.2 Hz, 6 H) and 0.10 (s, 9 H); FAB-MS *m/z* (rel. intensity) 355 (C^+, ^{130}Te, 100), 353 (C^+, ^{128}Te, 93), 351 (C^+, ^{126}Te, 58), 298 ($Bu^iTe^+CH_2C{\equiv}C\text{–}SiMe_3$, 1), 296 ($Bu^iTe^+CH_2C{\equiv}C\text{–}SiMe_3$, 1), 294 ($Bu^iTe^+CH_2C{\equiv}C\text{–}SiMe_3$, 1), 244 ($Bu^i{}_2Te^+$, 4), 242 ($Bu^i{}_2Te^+$, 4), 240 ($Bu^i{}_2Te^+$, 3), 187 ($Bu^iTe^+$, 3), 185 ($Bu^iTe^+$, 3), 183 ($Bu^iTe^+$, 2), 789 ($[M + C]^+$, 0.8), 787 ($[M + C]^+$, 1.0) and 785 ($[M + C]^+$, 0.6); IR(KCl) ν/cm^{-1} 2950s, 2150s, 1380s and 1360s. Compound **1** gave satisfactory elemental analysis.

‡ *General procedure*: a solution of LiTMP (1.2 mmol) in tetrahydrofuran (2 ml) was added dropwise to a solution of 3-trimethylsilylprop-2-ynyldiisobutyltelluronium bromide **1** in 8 ml THF at −78 °C under N_2. The mixture was stirred for 30 min, and then carbonyl compound (1.0 mmol) in 2 ml THF was added. The reaction mixture was then allowed to warm to room temp. After the reaction was complete (monitored by TLC), usual work up and flash chromatography gave the pure product.

§ *Typical spectral data* for 1-(*p*-chlorophenyl)-2-trimethylsilylethynyl epoxide **3b**: ^1H NMR (200 MHz, CD_3COCD_3) δ 7.20 (s, 4 H), 3.90 (d, *J* 4 Hz, 1 H), 3.50 (d, *J* 4 Hz, 1 H) and 0.03 (s, 9 H); ^{13}C NMR (90 MHz, CD_3COCD_3–Me_4Si) δ 135.0, 130.1, 129.0, 101.4, 92.8, 59.2, 49.1, 0.5; EI-MS *m/z* (rel. intensity) 325 (M^+ + $SiMe_3$, ^{37}Cl, 52), 323 (M^+ + $SiMe_3$, ^{35}Cl, 100), 252 (M^+, ^{37}Cl, 29), 250 (M^+, ^{35}Cl, 66), 235(47), 215(33), 141(23) and 73(60); IR (neat) ν/cm^{-1} 2960m, 2150m, 1250s, 840s and 760s; HRMS *m/z* calc., for $C_{13}H_{15}\,^{35}ClOSi$: 250.0581, found 250.0580; calc. for $C_{13}H_{15}\,^{37}ClOSi$: 252.0551, found 252.0525.



1 2 3 3′

a; R^1 = Ph, R^2 = H
b; R^1 = p-ClPh, R^2 = H
c; R^1 = p-BrPh, R^2 = H
d; R^1 = 2-naphthyl, R^2 = H
e; R^1 = 4-biphenyl, R^2 = H
f; R^1 = cyclohexyl, R^2 = H
g; R^1 = Bu^n, R^2 = H
h; R^1 = n-C_5H_{11}, R^2 = H
i; R^1 = n-C_9H_{19}, R^2 = H
j; R^1 = Ph, R^2 = Me
k; R^1 = Ph, R^2 = Ph

scope and high *cis* stereoselectivity. The reaction works well with both enolizable and non-enolizable carbonyl compounds, including aromatic aldehydes, aliphatic aldehydes and ketones. The predominating *cis* forms of the products are in agreement with that of diisobutyltelluronium allylide reported by Osuka and Suzuki.[4b]

Recently, unsaturated organosilicon compounds have been extensively studied because of their potential in selective organic synthesis.[6] Thus vinyl[7] and dienyl silanes[8] have received much attention and their synthetic utility has been used in numerous carbon–carbon bond forming reactions. Alkynyl trimethylsilanes are also an important class of compounds and many useful transformations have been reported.[9]

The *cis*-trimethylsilylethynyl epoxides reported herein are expected to be useful in organic synthesis owing to their novel structure and the presence of several different functional groups. The epoxides can be reduced to *cis* terminal enynes,[10] which have attracted much attention owing to their biological properties.[11] Furthermore, the epoxides can also be ring-opened regiospecifically by a nucleophilic reagent to yield potentially useful β-substituted alcohols.[12]

In summary, a novel method for the direct synthesis of *cis*-trimethylsilylethynyl epoxides from carbonyl compounds has been established by the use of a silylated semi-stabilized telluronium ylide. It is expected that the above described reaction will find considerable application in the synthesis of acyclic molecules having adjacent chiral centres. Furthermore, we believe that the synthetic chemistry of the telluronium ylides will prove to be at least as rich as that associated with phosphonium ylides. Further work in this area is now in progress in our laboratory.

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