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Michael Addition of Silylated Telluronium Allylide to α,β-Unsaturated Esters: Facile and Stereoselective Synthesis of Trimethylsilylvinylcyclopropane Derivatives

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Trimethylsilylated diisobutyltelluronium allylide, generated from 3-trimethylsilylprop-2-enyldiisobutyltelluronium bromide **1** with lithium 2,2,6,6-tetramethylpiperidide (LTMP), reacts with α,β-unsaturated esters to afford trimethylsilylvinylcyclopropane derivatives *via* Michael addition in excellent yields with high stereoselectivity.

Since the birth of the Wittig reaction, there has been remarkable interest in the synthetic application of other heteroatom ylides.[1] Along with the development of sulfonium, sulfoxonium and selenonium ylides,[2] the application of several stabilized and moderately stabilized telluronium ylides in organic synthesis has been described.[3] In our previous communications, we reported that diphenyltelluronium methylide, the first non-stabilized telluronium ylide, reacted with aldehydes or ketones to form substituted oxiranes.[4] We also reported that trimethylsilylated diisobutyltelluronium allylide, a silylated semistabilized telluronium ylide, reacted with carbonyl compounds to give trimethylsilylvinyloxiranes in excellent yields with high *cis* stereoselectivity *via* 1,2-addition.[5] However, to the best of our knowledge, the reactivity of telluronium ylides towards α,β-unsaturated systems has not appeared in the literature. We report herein that trimethylsilylated diisobutyltelluronium allylide, reacts with α,β-unsaturated esters to afford trimethylsilylvinylcyclopropane derivatives *via* Michael addition in excellent yields with high stereoselectivity.

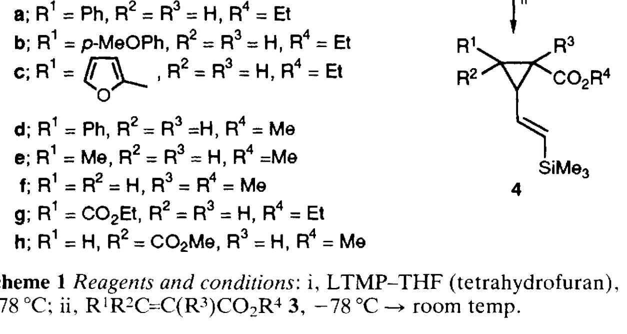
3-Trimethylsilylprop-2-enyldiisobutyltelluronium bromide **1** was prepared from the reaction of diisobutyl telluride with (*E*)-3-bromo-1-trimethylsilylprop-1-ene as described in ref. 5. The telluronium salt **1**, after being treated with lithium 2,2,6,6-tetramethylpiperidide (LTMP), is reacted with α,β-unsaturated esters to give trimethylsilylvinylcyclopropane derivatives **4** in excellent yields *via* silylated telluronium allylide **2** (Scheme 1).

Although potassium *tert*-butoxide (Bu^{t}OK) and lithium diisopropylamide (LDA) were effective for generating the silylated telluronium ylide **2**, LTMP was the most effective for the cyclopropanation reaction. The preparation of cyclopropane derivative **4** has been performed on a variety of structurally different α,β-unsaturated esters to determine the scope of the reaction. Some experimental results are summarized in Table 1 and illustrate the efficiency, the applicability, and the scope of the present method. The conversion of α,β-unsaturated esters into the trimethylsilylvinylcyclopropane derivatives usually proceeded completely when the mixture was allowed to warm to room temperature and further stirred for several hours.

It is significant that the reaction of silylated telluronium allylide **2** with β-aryl-substituted esters gave cyclopropane derivatives with high stereoselectivity. Only one isomer was formed (**4a–d**); the aryl and trimethylvinyl groups were on the same side of the cyclopropane ring and were oriented *trans* to alkoxycarbonyl group. However, the reactions of **2** with *trans*-methyl crotonate or methyl methacrylate afforded mixtures of two isomers (**4e** and **e**′, **4f** and **f**′). It is interesting to note that the reactions of **2** with either diethyl fumarate or dimethyl maleate afforded cyclopropane derivatives with the same configuration with the two alkoxycarbonyl groups oriented *trans* to each other.

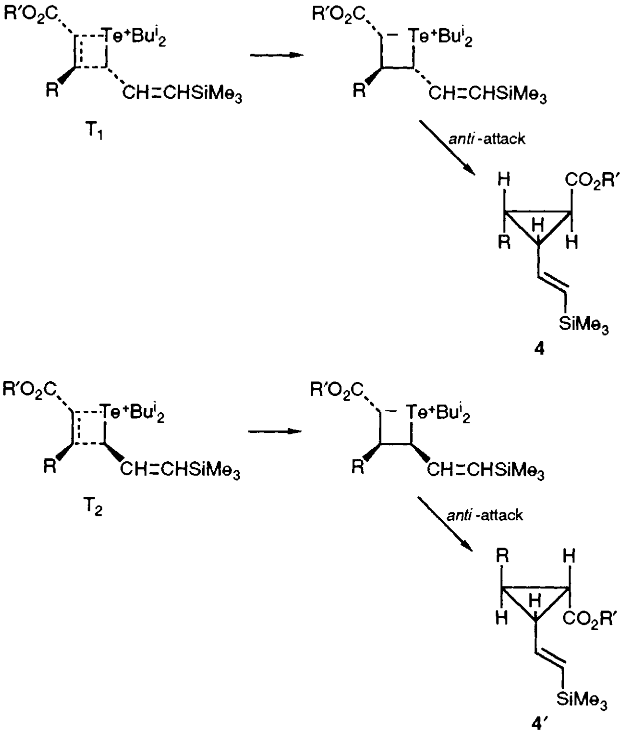
The mechanism illustrated in Scheme 2 would account for the stereoselectivity of the trimethylsilylvinylcyclopropane derivatives. Given the postulate that the reaction proceeds *via* four-membered transition states T_1 and T_2, similar to that of epoxidation of aldehydes with telluronium allylide,[3b] it might be anticipated that T_2 is destabilized relative to T_1 by steric interaction between the trimethylsilylvinyl and R groups.

Recently, unsaturated organosilicon compounds have been extensively studied because of their interesting 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. On the other hand, it is reported that some natural products with a cyclopropane moiety show biological activity.[9] The trimethylsilylvinylcyclopropane derivatives reported



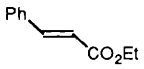
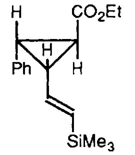
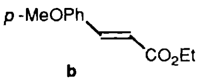
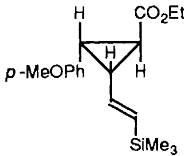
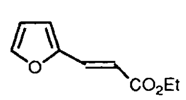
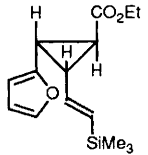
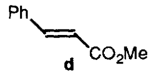
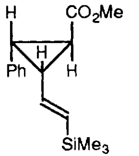
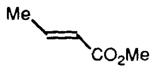
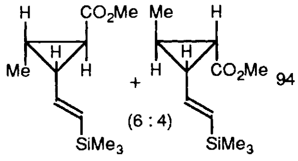
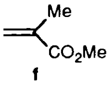
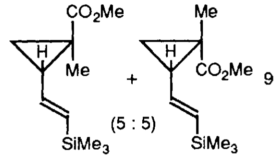
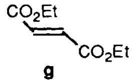
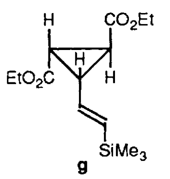
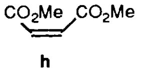
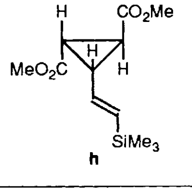
Scheme 1 *Reagents and conditions*: i, LTMP–THF (tetrahydrofuran), −78 °C; ii, $R^1R^2C{=}C(R^3)CO_2R^4$ **3**, −78 °C → room temp.

herein are expected to be useful in organic synthesis, since they have a novel structure and several functional groups. Furthermore, they are capable of undergoing many transformations.[10]



Scheme 2

Table 1 Stereoselective synthesis of trimethylsilylvinylcyclopropanes[a,b]

Entry	Base	Substrate 3	Product 4[c]	Yield %[d]
1	Bu^{t}OK	 a	 a	48
2	LDA	a	a	85
3	LTMP	a	a	97
4	LTMP	 b	 b	97
5	LTMP	 c	 c	93
6	LTMP	 d	 d	93
7	LTMP	 e	 e + e′ (6 : 4)	94
8	LTMP	 f	 f + f′ (5 : 5)	97
9	LTMP	 g	 g	74
10	LTMP	 h	 h	55

[a] *General procedure*: A solution of freshly prepared LTMP (1.2 mmol) in THF (2 ml) was added dropwise to a solution of 3-trimethylsilylprop-2-enyldiisobutyltelluronium bromide 1 (1.2 mmol) in THF (8 ml) at −78 °C under N$_2$. The mixture was stirred for 30 min, and then the α,β-unsaturated ester (1.0 mmol) in THF (2 ml) was added. The reaction mixture was then allowed to warm to room temp. After the reaction was completed (monitored by TLC), usual workup and flash chromatography gave the pure product. [b] All products gave satisfactory elemental analysis and/or high resolution mass spectrometry, ^{1}H NMR, mass and IR spectra.† [c] The configurations of the products were determined by 200, 300 and/or 600 MHz ^{1}H NMR. [d] Isolated yields based on α,β-unsaturated esters.

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† *Selected spectroscopic data* for trimethylsilylvinylcyclopropane derivatives **4a**, **e** and **h**. For **4a**: ^{1}H NMR (200 MHz, CDCl$_3$) δ 7.35 (m, 5H), 6.02 (d, J 18.5 Hz, 1H), 5.45 (dd, J_1 18.5, J_2 9 Hz, 1H), 4.32 (q, J 8 Hz, 2H), 3.05 (dd, J_1 9, J_2 5.5 Hz, 1H), 2.60 (d, of t, $J_1 = J_2$ 9, J_3 5.5 Hz, 1H), 2.35 (t, $J_1 = J_2$ 5.5 Hz, 1H), 1.38 (t, J 8 Hz, 3H), 0.02 (s, 9H); EIMS *m/z* (rel. intensity) 289 (M^+ + 1, 0.5), 288 (M^+, 1), 273 (M^+ − Me, 5), 243 (M^+ − OEt, 6), 215 (M^+ − SiMe$_3$, 7), 170 (21), 142 (23), 73 (SiMe$_3^+$, 100); IR ν/cm^{-1} (neat) 2990s, 2950s, 1730vs, 1618s, 1250s, 1030m, 860s, 840s.

For **4e**: ^{1}H NMR (200 MHz, CDCl$_3$) δ 5.86 (d, J 18 Hz, 1H), 5.66 (dd, J_1 18, J_2 8 Hz, 1H), 3.64 (s, 3H), 2.14 (ddd, J_1 9.5, J_2 8, J_3 4 Hz), 1.67 (m, 1H), 1.47 (t, $J_1 = J_2$ 4 Hz, 1H), 1.11 (d, J 3.5 Hz, 3H); EIMS *m/z* (rel. intensity) 212 (M^+, 1), 197 (M^+ − Me, 26), 181 (M^+ − OMe, 9), 165 (52), 139 (M^+ − SiMe$_3$, 14), 123 (18), 108 (26), 89 (67), 73 (SiMe$_3^+$, 100); IR ν/cm^{-1} (neat) 2950s, 2900m, 1730s, 1618m, 1440s, 1250s, 1170s, 860s and 840s.

For **4h**: ^{1}H NMR (200 MHz, CDCl$_3$) δ 6.00 (m, 2H), 3.72 (s, 6H), 2.48 (m, 3H), 0.04 (s, 9H); ^{1}H NMR (600 MHz, C$_6$D$_6$) δ 6.25 (dd, J_1 18.6, J_2 9.5 Hz, 1H), 5.88 (d, J 18.6 Hz, 1H), 3.24 (s, 3H), 3.21 (s, 3H), 2.65 (t, $J_1 = J_2$ 5.0 Hz, 1H), 2.62 (dd, J_1 9.5, J_2 5.0 Hz, 1H), 2.54 (d of t, $J_1 = J_2$ 9.5, J_3 5.0 Hz, 1H), 0.04 (s, 9H); EIMS *m/z* (rel. intensity) 257 (M^+ + 1, 0.4), 256 (M^+, 2), 241 (M^+ − Me, 14), 225 (M^+ − OMe, 4), 209 (16), 197 (M^+ − CO$_2$Me, 100), 183 (36), 165 (22), 141 (19), 143 (12), 121 (16), 89 (12), 73 (3); IR ν/cm^{-1} (film) 2980s, 2910s, 2850s, 1740s, 1618m, 1470s, 1380m, 1250m, 1160m, 860m and 840m.

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