

An Efficient and Highly Stereoselective Synthesis of Trimethylsilylvinylcyclopropane Derivatives *via* an Organotelluronium Salt: First Example of Catalytic Wittig-type Cyclopropanation

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A one-pot reaction of 3-trimethylsilylprop-2-enyl(diisobutyl)telluronium bromide **1** with α,β -unsaturated ketones gives, by way of Michael addition in the presence of caesium carbonate under solid-liquid phase-transfer conditions, trimethylsilylvinylcyclopropanes both in high to excellent yields and with high stereoselectivity. A similar high-yielding cyclopropanation occurs in THF/trace of water with diisobutyl telluride as catalyst in a one-pot reaction of (*E*)-3-bromo-1-trimethylsilylprop-1-ene with α,β -unsaturated ketones in the presence of caesium carbonate.

Much attention has been paid to the synthetic application of several heteroatom ylides other than phosphorus. As early as 1962, Bestman and his co-workers reported that the reaction of methylenetriphenylphosphorus with a crotonic ester gave cyclopropanes.¹ Later, Corey *et al.*,² Johnson³ and Trost⁴ described the synthesis of cyclopropanes by use of sulfonium ylides, respectively. In 1980, Huang *et al.* found that the reaction of arsonium ylide with α,β -unsaturated esters also afforded cyclopropanes.⁵

With the development of phosphonium, arsonium and sulfonium ylides in organic synthesis, there has recently been much interest in the synthetic application of organotelluronium ylides.⁶ In our previous communication, we reported a facile and stereoselective synthesis of trimethylsilylvinylcyclopropanes by way of Michael addition of a silylated telluronium allylide to α,β -unsaturated esters.⁷ However, all these methods suffered from severe reaction conditions. We now report a useful and practical synthesis of trimethylsilylvinylcyclopropanes.

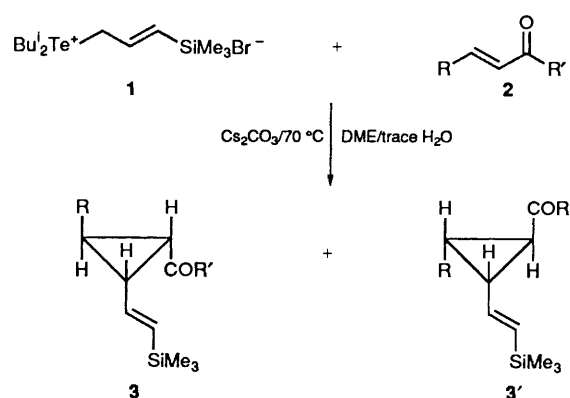
Results and Discussion

3-Trimethylsilylprop-2-enyl(diisobutyl)telluronium bromide **1** was prepared from the reaction of diisobutyl telluride with (*E*)-3-bromo-1-trimethylsilylprop-1-ene as described in the literature.^{6a} A one-pot reaction of the telluronium salt **1** with α,β -unsaturated ketones **2** in the presence of adequate base gives the desired trimethylsilylvinylcyclopropanes **3** (Scheme 1).

In order to optimize the reaction, we carried it out under a variety of reaction conditions (Table 1). As shown in Table 1, since the basicity of triethylamine is too weak to generate the silylated telluronium allylide, no product was detected (entry 1). Although potassium carbonate, KOH, $K_2CO_3 \cdot Al_2O_3$ and $KF \cdot Al_2O_3$ could promote the cyclopropanation, caesium carbonate was the most effective base. In short, the system of Cs_2CO_3 /DME (trace water) is the most convenient for this reaction, a variety of α,β -unsaturated ketones being transformed by it into trimethylsilylvinylcyclopropanes both in high yields and with high stereoselectivity (Scheme 1); experimental results are summarized in Table 2.

It is noteworthy that in the above reaction no α,β -unsaturated epoxides were detected and, further, when an α,β -unsaturated aldehyde was used as a substrate, the reaction was complex.

It is significant that this cyclopropanation is highly stereoselective. The configuration of the main product is shown as follows: both benzoyl group and trimethylsilylvinyl group are



Scheme 1

on the same side of the cyclopropane ring and are orientated *trans* to a phenyl or a substituted phenyl group. The configurations of the cyclopropanes **3a-e** were established on the basis of ¹H NMR, NOE and chemical shift reagent results. We now use **3d** to illustrate how the configurations were determined.

The ¹H NMR results for compound **3d** showed chemical shifts at δ 3.4, 3.09 and 2.5, which were assigned to three cyclopropane protons. Shen *et al.* have analysed the ¹H NMR spectra of trisubstituted cyclopropanes, showing that the ring proton chemical shifts are strongly influenced by the nature of the substituents on the ring, substituents of higher electronegativity causing a downfield chemical shift.⁸ Since the electronegativity of both phenyl and benzoyl groups are higher than that of the trimethylsilylvinyl group, we assign the upfield chemical shift, *i.e.* 2.5 ppm, to H_c. This assignment is consistent with the coupling patterns. From the ¹H-¹H NOESY spectra, strong NOE effects between H_e and H_c, H_a and H_b are observed. Furthermore, by using a shift reagent, the chemical shift of H_a and H_b was shown to move further downfield than that of H_c. Accordingly, on the basis of this evidence together with that of the coupling constants, we concluded that the benzoyl group and the trimethylsilylvinyl group are on the same side of the cyclopropane ring and orientated *trans* to the *p*-methylphenyl group (see Scheme 2).

The reaction mechanism shown in Scheme 3 would account for the high stereoselectivity.

In the presence of caesium carbonate, the trimethylsilylated diisobutyltelluronium allylide **4** was generated from the

Table 1 Cyclopropanation of chalcone with the telluronium salt **1** under a variety of conditions

Entry	Base	Solvent	Temp. (°C)	Reaction time (h)	Yield (%) ^a
1	Et ₃ N	THF/trace H ₂ O	70	12	0
2	K ₂ CO ₃	THF/trace H ₂ O	70	12	42
3	Cs ₂ CO ₃	THF/trace H ₂ O	70	12	84
4	K ₂ CO ₃ ·Al ₂ O ₃	THF/trace H ₂ O	70	12	62
5	KF·Al ₂ O ₃	THF/trace H ₂ O	70	12	51
6	KOH	THF/trace H ₂ O	70	12	75
7	Cs ₂ CO ₃	MeCN	80	9	60
8	Cs ₂ CO ₃	DME/trace H ₂ O	70	9	93
9	Cs ₂ CO ₃	DMSO	80	9	76
10	Cs ₂ CO ₃	THF	70	12	75
11	Cs ₂ CO ₃	DME	70	12	80

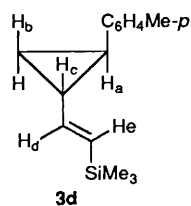
^a Isolated yield based on chalcone.**Table 2** Highly stereoselective synthesis of trimethylvinylcyclopropane derivatives in the system Cs₂CO₃/DME (trace of water)

3

	R ¹	R ²	R ³	R ⁴
a	H	Bz	Ph	H
a'	Bz	H	H	Ph
b	H	Bz	<i>p</i> -ClC ₆ H ₄	H
b'	Bz	H	H	<i>p</i> -ClC ₆ H ₄
c	H	Bz	<i>p</i> -O ₂ NC ₆ H ₄	H
c'	Bz	H	H	<i>p</i> -O ₂ NC ₆ H ₄
d	H	Bz	<i>p</i> -MeC ₆ H ₄	H
d'	Bz	H	H	<i>p</i> -MeC ₆ H ₄
e	H	PhCH=CHCO	Ph	H
e'	H	Ph	PhCH=CHCO	H

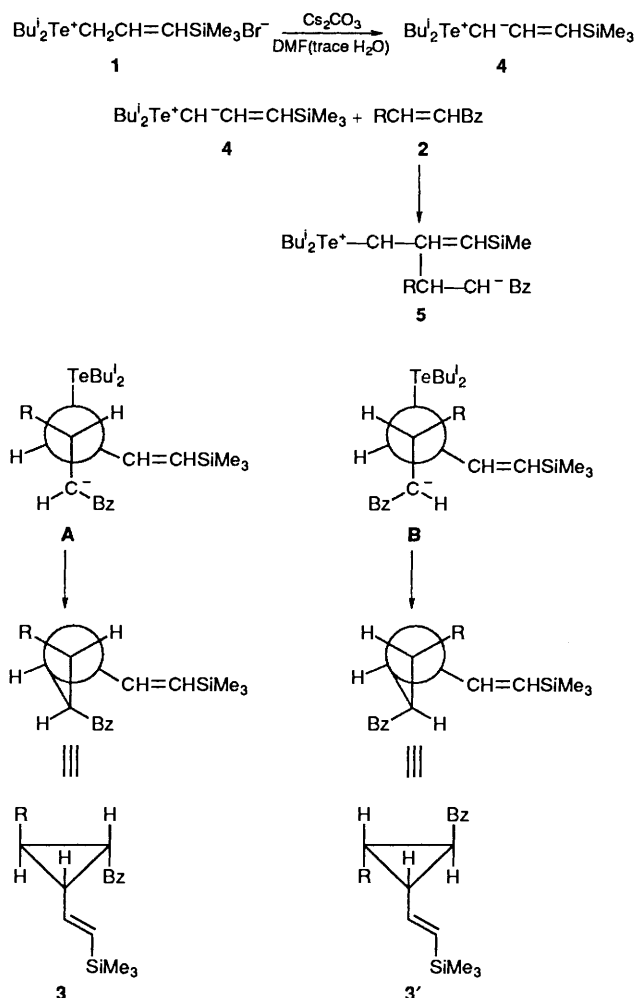
Entry	Substrate	Product ^a	Yield (%) ^b
1	PhCH ^ε CHCOPh	3a (92:8) 3a'	93
2	<i>p</i> -ClC ₆ H ₄ CH ^ε CHCOPh	3b (97:3) 3b'	77
3	<i>p</i> -O ₂ NC ₆ H ₄ CH ^ε CHCOPh	3c (95:5) 3c'	94
4	<i>p</i> -MeC ₆ H ₄ CH ^ε CHCOPh	3d (>99:1) 3d'	95 ^c
5	PhCH ^ε CHCOCH ^ε CHPh	3e (>99:1) 3e'	66 ^c

^a The configuration of the product was determined by ¹H NMR spectroscopy (300 MHz, ¹H NMR, ¹H-¹H NOESY and with a chemical shift reagent). The ratio of compounds **3/3'** was also determined by ¹H NMR (300 MHz) except for **3b** and **3b'** which was determined by capillary GC. ^b Isolated yield based on α,β-unsaturated ketones. ^c In entries 4 and 5, together with the product, some starting material was recovered.

**Scheme 2**

telluronium salt **1**. The telluronium allylide **4** attacked nucleophilically the carbon-carbon double bond, by way of a Michael addition, forming an intermediate **5**, which has two conformations, **A** and **B**. It was expected that conformation **B** would be destabilized as a result steric interaction of R and the trimethylsilylvinyl group, the preferred conformation **A** then undergoing cyclization to give the product.

The ready reaction of diisobutyl telluride with trimethylsilyl-

**Scheme 3**

allyl bromide to form a telluronium salt and the conversion of this with an α,β-unsaturated ketone by way of a Michael addition in the presence of caesium carbonate under phase-transfer conditions into cyclopropanes, led us to consider the possibility of a catalytic ylide cyclopropanation. A one-pot reaction of chalcone, caesium carbonate, trimethylsilylallyl bromide and diisobutyl telluride (1 equiv.), gave the cyclopropanation product in 65% yield (Scheme 4); the same yield of product was obtained when the amount of diisobutyl telluride was reduced. This demonstrates that the reaction is catalysed by diisobutyl telluride: Table 3 lists the results of various conditions.

Table 3 Reaction results from trimethylsilylvinyl bromide with chalcone under a variety of conditions^a

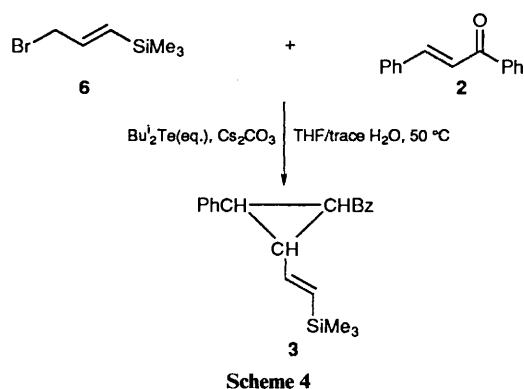
Entry	Amount of catalyst (equiv.)	Base	Solvent	Yield (%) ^b
1	0.2	Cs ₂ CO ₃	DME/trace H ₂ O	54
2	0.2	Cs ₂ CO ₃	CH ₃ CN	60
3	0.2	Cs ₂ CO ₃	DMSO	40 ^c
4	0.2	Cs ₂ CO ₃	THF/trace H ₂ O	63
5	0.2	Cs ₂ CO ₃	DME + hexane/trace H ₂ O	59
6	0.2	KF·Al ₂ O ₃	THF/trace H ₂ O	43
7	0.2	K ₂ CO ₃ ·Al ₂ O ₃	THF/trace H ₂ O	56
8	0.2	K ₂ CO ₃	THF/trace H ₂ O	52
9	0.2	KOH	THF/trace H ₂ O	50
10	0.2	Et ₃ N	THF/trace H ₂ O	0
11	1.0	Cs ₂ CO ₃	THF/trace H ₂ O	65
12	0.5	Cs ₂ CO ₃	THF/trace H ₂ O	65
13	0.1	Cs ₂ CO ₃	THF/trace H ₂ O	30

^a The reaction was performed as follows. A mixture of catalyst and base in certain solvent system was stirred at 50 °C for 24 h. ^b Isolated yield based on chalcone except where specially noted. ^c Determined by ¹H NMR.

Table 4 Highly stereoselective synthesis of trimethylsilylvinylcyclopropane derivatives **3** catalysed by diisobutyl telluride

Entry	Substrate	Product	Yield (%) ^a
1	PhCH ₂ CHCOPh	3a (>98:2) 3a'	70
2	<i>p</i> -ClC ₆ H ₄ CH ₂ CHCOPh	3b (>99:1) 3b'	64
3	<i>p</i> -O ₂ NC ₆ H ₄ CH ₂ CHCOPh	3c (>99:1) 3c'	83
4	<i>p</i> -MeC ₆ H ₄ CH ₂ CHCOPh	3d (>98:2) 3d'	70
5	PhCH ₂ CHCOCH ₂ CHPh	3e (>99:1) 3e'	58

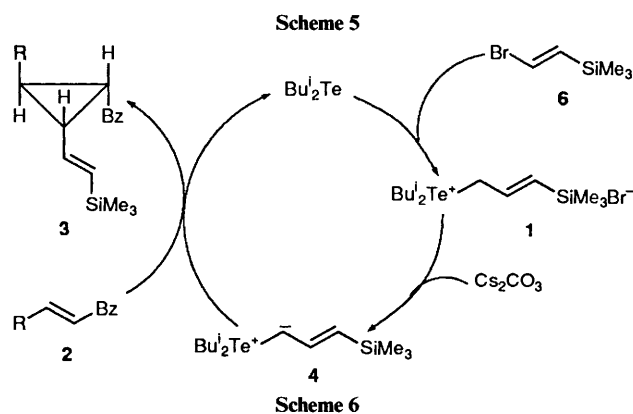
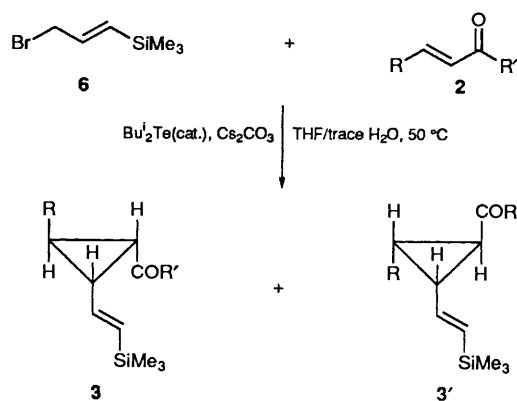
^a Isolated yields based on α,β -unsaturated ketones.



As can be seen, in the absence of catalyst, there is no reaction. Further, triethylamine is too weakly basic to promote the reaction and, whilst KF·Al₂O₃, K₂CO₃·Al₂O₃ and KOH could effect the reaction, cyclopropanation is most convenient with caesium carbonate. As for the solvent, we see that THF–trace H₂O is most effective whilst 0.2 equiv. of diisobutyl telluride are sufficient as catalyst. Thus, after α,β -unsaturated ketones, caesium carbonate, trimethylsilylallyl bromide and a catalytic amount of diisobutyl telluride in THF–trace H₂O had been stirred for 48 h at 50 °C, work-up afforded the desired product (Scheme 5). The results are shown in Table 4.

The reaction path is proposed as shown in Scheme 6. Diisobutyl telluride reacts with the silylated allyl bromide **6** to form 3-trimethylsilylallyl(diisobutyl)telluronium bromide **1** which, in the presence of caesium carbonate, generates the silylated telluronium allylide **4**. The *in situ* generated telluronium allylide **4** rapidly reacts with α,β -unsaturated ketones to afford the desired cyclopropanes and the diisobutyl telluride is regenerated.

Recent interest in unsaturated organosilicon compounds has arisen because of their synthetic potential.⁹ Thus, vinyl-¹⁰ and



dienyl-silanes¹¹ have been used in numerous carbon–carbon bond-forming reactions. There is also interest both in the biological activity shown by natural products with a cyclopropane moiety,¹² and, because of this, the vinylcyclopropanes–cyclopentanes rearrangement.¹³ Thus, the trimethylsilylvinylcyclopropanes reported herein are expected to be useful because of their novel structures and varied functionality which enables them to undergo further elaboration.¹⁴

Conclusions.—In the presence of caesium carbonate under solid–liquid phase-transfer conditions, 3-trimethylsilylallyl(diisobutyl)telluronium bromide reacted directly with α,β -unsaturated ketones to afford trimethylsilylvinylcyclopropane derivatives; this cyclopropanation is catalysed by diisobutyl telluride. The simplicity of our reported procedure together with the mildness of the reaction conditions, the high stereoselectivity shown, and especially the use of only catalytic amounts of diisobutyl telluride demonstrate its practical utility.

Experimental

All reactions were carried out under N₂ and solvents used were redistilled before use. The ¹H-¹H NOESY spectra were measured at 300 MHz. MS data were obtained with electron ionization.

Diisobutyl telluride,¹⁵ (*E*)-3-bromo-1-trimethylsilylprop-1-ene¹⁶ and 3-trimethylsilylprop-2-enyl(diisobutyl)telluronium bromide,^{6a} were prepared according to the reported method.

Highly Stereoselective Synthesis of Trimethylsilylvinylcyclopropane Derivatives 3: General Procedure.—With telluronium salt: **Method A.** A mixture of trimethylsilylprop-2-enyl(diisobutyl)telluronium bromide **1** (0.33 g, 0.75 mmol), caesium carbonate (0.25 g, 0.75 mmol), chalcone (0.5 mmol), and DME (5 cm³) and water (5 mm³) was heated at 70 °C for specific periods of time. When the reaction was complete (monitored by TLC), the resulting mixture was eluted with ethyl acetate through a short column of silica gel. Removal of the solvent and flash chromatography on silica gel gave the desired pure product, of purity >98% (GC).

With a catalytic amount of diisobutyl telluride: Method B. Chalcone (0.5 mmol), caesium carbonate (1.0 mmol), (*E*)-3-bromo-1-trimethylsilylprop-1-ene **6** (0.75 mmol), diisobutyl telluride (0.1 mmol), and THF (5 cm³) and water (5 mm³) were mixed in a reaction tube and stirred at 50 °C for a specific period of time. After 28 h, additional trimethylsilylallyl bromide **6** (0.25 mmol) was added and stirring continued for 20 h. When the reaction was complete (monitored by TLC), work-up as for method A and flash chromatography of the residue on silica gel afforded the product, of purity >98% (GC).

1-Benzoyl trans-2-phenyl-cis-3-trimethylsilylvinylcyclopropane 3a: Method A, 150 mg, 93%; Method B, 112 mg, 70%; m.p. 96–98 °C; δ_H(C₆H₆/TMS, 300 MHz) 0.09 (s, 9 H), 2.45 (d of t, *J*₁ 6.3, *J*₂ 8.9, 1 H), 2.96 (dd, *J*₁ 5.7, *J*₂ 8.9, 1 H), 3.46 (t, *J* 5.9, 1 H), 5.95 (d, *J* 18.6, 1 H), 6.45 (dd, *J*₁ 8.9, *J*₂ 18.6, 1 H), 6.96 (m, 8 H) and 7.83 (d, *J* 7.2, 2 H); *m/z* (EIMS) (rel. intensity) 320 (M⁺, 6), 105 (C₇H₅O⁺, 100), 77 (C₆H₅⁺, 24), 73 (SiMe₃⁺, 60), 45 (10) and 43 (7); ν_{max}(film)/cm⁻¹ 1650s, 1600s, 1590m, 1420m, 1240s, 1220s, 1080m, 1010s, 840s and 820s (Found: C, 79.0; H, 7.5. Calc. for C₂₁H₂₄O₂Si: C, 78.70; H, 7.54%).

1-Benzoyl trans-2-(p-chlorophenyl)-cis-3-trimethylsilylvinylcyclopropane 3b: Method A, 133 mg, 77%; Method B, 105 mg, 64%; m.p. 132–133 °C; δ_H(C₆H₆/TMS, 300 MHz) 0.04 (s, 9 H), 2.35 (d of t, *J*₁ 6.3, *J*₂ 8.9, 1 H), 2.86 (dd, *J*₁ 5.78, *J*₂ 9.3, 1 H), 3.16 (t, *J* 5.9, 1 H), 5.95 (d, *J* 18.6, 1 H), 6.38 (dd, *J*₁ 8.9, *J*₂ 18.6, 1 H), 6.58 (d, *J* 8.7, 2 H), 7.08 (m, 5 H) and 7.85 (m, 2 H); *m/z* (EIMS) (rel. intensity) 354 (M⁺, 26), 105 (C₇H₅O⁺, 100), 77 (C₆H₅⁺, 15), 73 (SiMe₃⁺, 43), 45 (6) and 43 (18); ν_{max}(film)/cm⁻¹ 1670s, 1610m, 1590m, 1490m, 1450m, 1355m, 1245s, 1225s, 860s, 840s, 820s, 745s and 700s (Found: C, 71.2; H, 6.4. Calc. for C₂₁H₂₃ClO₂Si: C, 71.06; H, 6.53%).

1-Benzoyl trans-2-(p-nitrophenyl)-3-trimethylsilylvinylcyclopropane 3c: Method A, 172 mg, 94%; Method B, 150 mg, 83%; m.p. 134–136 °C; δ_H(C₆H₆/TMS, 300 MHz) 0.04 (s, 9 H), 2.25 (d of t, *J*₁ 6.1, *J*₂ 8.8, 1 H), 2.88 (dd, *J*₁ 5.8, *J*₂ 8.9, 1 H), 3.14 (d, *J* 5.8, 1 H), 5.96 (d, *J* 18.5, 1 H), 6.3 (dd, *J*₁ 8.8, *J*₂ 18.5, 1 H), 6.48 (d, *J* 8.8, 2 H), 7.05 (m, 3 H), 7.70 (d, *J* 8.7, 2 H) and 7.78 (d, *J* 8.7, 2 H); *m/z* (EIMS) (rel. intensity) 365 (M⁺, 47), 105 (C₇H₅O⁺, 100), 77 (C₆H₅⁺, 13), 73 (SiMe₃⁺, 13), 45 (5) and 43 (18); ν_{max}(film)/cm⁻¹ 1660s, 1600s, 1505s, 1450s, 1340s, 1240s, 1220s, 1100m, 1020m, 920m, 840s, 825s and 740s (Found: C, 68.8; H, 6.3; N, 3.7. Calc. for C₂₁H₂₃NO₃Si: C, 69.01; H, 6.34; N, 3.83%).

1-Benzoyl trans-2-(4-p-tolyl)-cis-3-trimethylsilylvinylcyclopropane 3d: Method A, 160 mg, 95%; Method B, 117 mg, 70%; m.p. 129–130 °C; δ_H(C₆H₆/TMS, 300 MHz) 0.07 (s, 9 H), 2.08 (s, 3 H), 2.50 (d of t, *J*₁ 6.4, *J*₂ 8.9, 1 H), 3.08 (dd, *J*₁ 5.4, *J*₂ 8.9, 1 H), 3.40 (t, *J* 5.9, 1 H), 6.00 (d, *J* 18.5, 1 H), 6.54 (dd, *J*₁ 8.5, *J*₂

18.5, 1 H), 7.06 (m, 7 H) and 7.91 (d, *J* 8, 2 H); δ_H(C₆H₆/TMS-shift reagent, 300 MHz) 0.10 (s, 9 H), 2.12 (s, 3 H), 2.62 (m, 1 H), 3.22 (m, 1 H), 3.74 (m, 1 H), 6.10 (d, *J* 18.5, 1 H), 7.10 (m, 8 H) and 8.00 (m, 2 H); *m/z* (EIMS) (rel. intensity) 334 (M⁺, 7), 105 (C₇H₅O⁺, 100), 92 (C₇H₈⁺, 3), 77 (C₆H₅⁺, 14), 73 (SiMe₃⁺, 40), 45 (6) and 43 (10); ν_{max}(film)/cm⁻¹ 1660s, 1600m, 1420m, 1400m, 1355m, 1240s, 1220s, 940m, 920m, 880m, 860s, 850s, 835s and 740s (Found: C, 78.85; H, 7.8. Calc. for C₂₂H₂₆O₂Si: C, 78.99; H, 7.83%).

trans-2-Phenyl-1-phenylvinylcarbonyl-cis-trimethylsilylvinylcyclopropane 3e: Method A, 115 mg, 68%; Method B, 100 mg, 58%; m.p. 108–109 °C; δ_H(C₆H₆/TMS, 300 MHz) 0.01 (s, 9 H), 2.38 (d of t, *J*₁ 6.4, *J*₂ 6.8, 1 H), 2.55 (dd, *J*₁ 5.5, *J*₂ 8.8, 1 H), 3.23 (t, *J* 5.9, 1 H), 5.86 (d, *J* 18.5, 1 H), 6.50 (m, 2 H), 6.98 (m, 10 H) and 7.45 (d, *J* 16, 1 H); *m/z* (EIMS) (rel. intensity) 346 (M⁺, 13), 131 (C₉H₇O⁺, 100), 103 (C₈H₇⁺, 19), 73 (SiMe₃⁺, 48), 45 (5) and 43 (3); ν_{max}(film)/cm⁻¹ 1660s, 1600s, 1240m, 1195m, 1170s, 995m, 980m, 840s and 715s (Found: C, 79.6; H, 7.5. Calc. for C₂₃H₂₆O₂Si: C, 79.72; H, 7.56%).

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