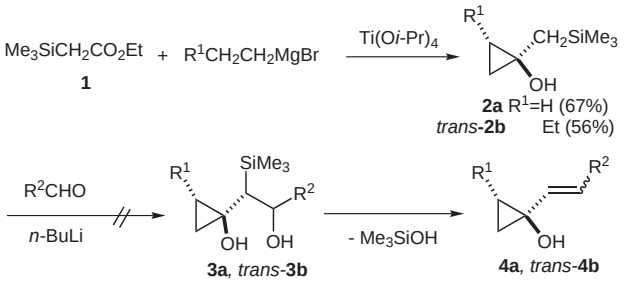
# Formation of 1-Ethenylcyclopropanols Involving Kulinkovich Cyclopropanation and Peterson Olefination of α-Trimethylsilylesters

Damien Hazelard, Jean Ollivier, Renée Paugam, Jacques Salaün*

Laboratoire des Carbocycles, UMR 8615, Institut de Chimie Moléculaire et des Matériaux d'Orsay, Université de Paris-Sud, 91405 Orsay, France
Fax +33(1)69156278; E-mail: jasalaun@icmo.u-psud.fr
*Received 26 April 2003*

**Abstract:** Mercuric iodide catalyzed condensation of bis-silylketene acetals with benzaldehyde provided a 1:1 *erythro* and *threo* mixture of α-trimethylsilylesters. Only the *threo* adducts underwent titanium(IV)-mediated cyclopropanation and acid induced Peterson olefination to provide (*Z*)-1-ethenylcyclopropanols of considerable synthetic potential.

**Key words:** condensation, elimination, ring closure, titanium, neighbouring group effect




**Scheme 1**

Functionalized cyclopropanes and particularly 1-vinylcyclopropanol derivatives provide building blocks of considerable synthetic potential. They not only undergo selective acid, base or thermally-induced $C_3 \rightarrow C_{4-8}$ ring expansions,[1] and fluoride ion-induced $C_3 \rightarrow C_{10,15,20}$ ring enlargements[2] but, their corresponding sulfonic esters (e.g., mesylates, tosylates) form significant π- or σ-1,1-ethylene allylmetal complexes, which then undergo regio- and diastereoselective nucleophilic[3] or electrophilic substitutions.[4] Syntheses of various frameworks and natural products have demonstrated the outstanding usefulness of these rearrangements and substitutions.[1–5] Consequently, ready accesses to these synthons are of crucial importance. Previously available from 1,3-dichloroacetone,[6] α-enone silylenol ethers,[7] cyclopropanone hemiacetals,[8] or 1-hydroxycyclopropanecarboxylic acids,[9] these compounds have been recently prepared from the titanium-mediated cyclopropanation[10] of ethyl 3,3-diethoxypropionate followed by modified Knoevenagel condensation with malonic acid under microwave irradiation,[11] or of β-haloesters followed by base-induced dehydrohalogenation,[12] which provided diastereoselectively pure *trans*-1-alkenyl-2-alkylcyclopropanols. On the other hand, titanium-mediated cyclopropanation of homoallyl alk-2-enoates furnished diastereomerically pure *cis*-1-(1-alkenyl)-2-(2-hydroxyethyl)cyclopropanols.[13]

We report herein our investigations to form these attractive synthons, alternatively from the commercially available ethyl α-(trimethylsilyl)acetate **1**. Thus, reaction of acetate **1** with EtMgBr and *n*-BuMgBr (2.2 equiv) in the presence of Ti(*i*-PrO)$_4$ (0.1 equiv) following reported procedures,[10d–12] gave the 1-(trimethylsilylmethyl)cyclopropanol **2a** ($R^1$ = H) and *trans*-**2b** ($R^1$ = Et) in 67% and 56% yields, respectively. Then, condensation with an aldehyde were expected to furnish the adducts **3a** and *trans*-**3b**, and after Peterson olefination[14] the required 1-ethenylcyclopropanols **4a** and *trans*-**4b** (Scheme 1).

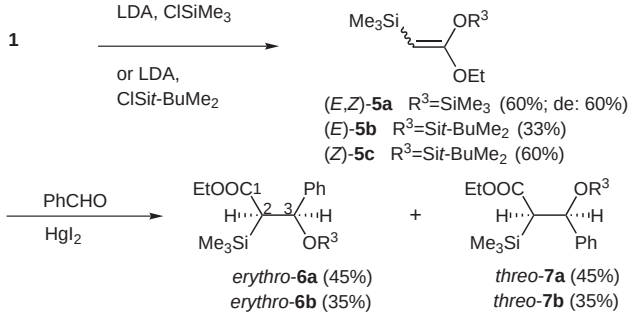
However, upon treatment with *n*-butyllithium (1 equiv) and benzaldehyde (1 equiv), **2a**,**b** underwent elimination of hydroxysilane to give non-isolated volatile products, likely methylenecyclopropane derivatives,[15] rather than the expected adducts **3a**,**b**.[16] Moreover, attempts to perform previous O-protection of the cyclopropanols **2a**,**b** (e.g., DHP, PPTs) before condensation, led also to elimination products.

In order to overcome the problem of the instability of the 1-[(trimethylsilyl)methyl]cyclopropanols **2a**,**b** revealed by this investigation,[17] we have first carried out tentatively the condensation of α-(trimethylsilyl)acetate **1** with benzaldehyde. A 8:2 diastereomeric mixture of (*E*)- and (*Z*)-bis(trimethylsilyl)ketene acetals **5a** ($R^3$ = $SiMe_3$) was obtained in 60% yield, upon treatment of **1** with 1 equivalent of lithium diisopropylamide (LDA, from 1.6 M *n*-BuLi in hexane and diisopropylamine) in the presence of TMSCl in THF at –78 °C. Then, $HgI_2$ (4.4%) induced condensation of the mixture of (*E*,*Z*)-**5a** with benzaldehyde in toluene provided in 90% yield, an unseparable 1:1 *erythro* and *threo* mixture of ethyl 3-phenyl-2-tri(methylsilyl)-3-(trimethylsilyloxy)propionate **6a** and **7a**.[18]

Otherwise, reaction of **1** with LDA and TBDMSCl led exclusively to the (*E*)-*t*-butyldimethylsilylketene acetal **5b** ($R^3$ = Si*t*-Bu$Me_2$) in 33% yield; while, in the presence of hexamethylphosphoramide (HMPT) as co-solvent, following a reported procedure,[19] the ketene acetal (*Z*)-**5c** was formed exclusively, in 60% yield. $HgI_2$ catalyzed condensation of (*E*)-**5b** with benzaldehyde gave also in

Synlett 2003, No. 8, Print: 24 06 2003.
Art Id.1437-2096,E;2003,0,08,1155,1159,ftx,en;G09403ST.pdf.
© Georg Thieme Verlag Stuttgart · New York

Downloaded by: Rutgers University. Copyrighted material.




**Scheme 2**

70% yield a 1:1 mixture of diastereomeric adducts *erythro*-**6b** and *threo*-**7b**, which were now readily separable by HPLC. Therefore, as reported for (*E*,*Z*)-**5a**,[18] the geometry of the double bond of (*E*)-**5b** has also been lost during the condensation reaction; on the other hand, attempted condensation of (*Z*)-**5c** under the same conditions led neither to *erythro*-**6b** nor to *threo*-**7b** (Scheme 2).

Titanium(IV)-mediated cyclopropanation[10] of the 1:1 diastereomeric mixture of *erythro*-**6a** and *threo*-**7a** by EtMgBr (2.2 equiv) in the presence of Ti(*i*-PrO)$_4$ (0.2 equiv) was expected to provide a mixture of cyclopropanols **8a** and **9a** ($R^1$ = H, $R^3$ = $SiMe_3$), which only differed in the configuration of their 1-substituents. However, the reaction performed in THF at room temperature for 4 h, gave in 52% yield (based on the reactant) the single cyclopropanol **9a**[20a] displaying in the $^1$H NMR spectrum of its 1-substituent [2-phenyl-1-(trimethylsilyl)-2-(trimethylsilyloxy)ethyl] two doublets at δ 0.71 ppm and 5.33 ppm [$J(H_{1'}H_{2'})$ = 4.95 Hz]; **9a** was always accompanied by various amounts of the corresponding diol **9a′** ($R^1$, $R^3$ = H)[20b] arising from partial O-deprotection (oxygentrimethylsilyl bond cleavage). The recovered unreacted bis-silylated adduct disclosed the persistent $^1$H NMR signals of *erythro*-**6a**, in particular a methylene signal at 4.08–4.26 ppm and a coupling constant $J(H_2H_3)$ = 10.7 Hz.[18]

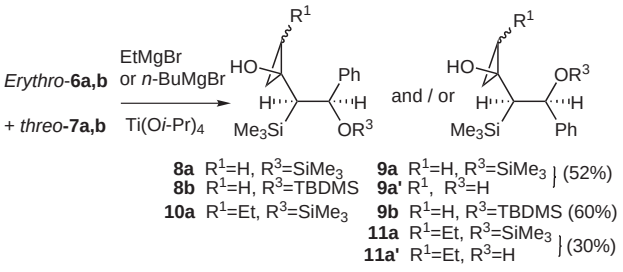
Likewise, titanium(IV)-mediated cyclopropanation of the pure silylated adduct *threo*-**7b** ($R^3$ = TBDMS), occurred to provide in 60% yield the single cyclopropanol **9b** [displaying in its $^1$H NMR spectrum two doublets at δ 0.67 ppm and 5.38 ppm for which $J(H_{1'}H_{2'})$ = 3.40 Hz]; while its isolated pure diastereomer *erythro*-**6b** appeared also unreactive towards this cyclopropanation reaction, irrespective of the experimental conditions [number of equivalents of Grignard reagents and of Ti(*i*-PrO)$_4$, temperature and time of reaction] (Scheme 3).

Otherwise, reaction of a 1:2 mixture of *erythro*-**6a** and *threo*-**7a** with *n*-BuMgBr (2.2 equiv) and Ti(*i*-PrO)$_4$ (0.2 equiv) in THF at room temperature, gave in 30% yield (based on the reactant) a 1:1 mixture of *cis*- and *trans*-2-ethyl-1-[2-phenyl-1-(trimethylsilyl)-2-(trimethylsilyloxy)ethyl] cyclopropanols **11a** ($R^1$ = Et, $R^3$ = $SiMe_3$), separable by liquid chromatography (eluent pentane/diethyl ether, 9:1), besides a 2:1 mixture of unreacted bissilylated esters **6a** and **7a**. The formation of the corresponding diols **11a′** ($R^1$ = Et, $R^3$ = H) was also observed. The configurations of these cyclopropanols were determined from their $^1$H and $^{13}$C NMR spectra, in particular *trans*-**11a** displayed one tertiary cyclopropanic proton at δ 0.17 ppm (t, *J* = 5.37 Hz, 1 H).[13]

Finally, O-desilylation and Peterson olefination were achieved upon treatment of these cyclopropanols under acidic conditions,[21] e.g., with concentrated $H_2SO_4$ in THF at –78 °C or with chlorotrimethylsilane in MeOH at room temperature, to provide the 1-(*Z*)-styrylcyclopropanol **12** ($R^1$ = H)[22] in 50% and 76% yield, respectively, from **9a**, while the *cis*- or *trans*-2-ethyl-1-[(*Z*)-styryl] cyclopropanol **13** ($R^1$ = Et) were obtained in 75% yield upon treatment of the corresponding *cis*- or *trans*-**11**a with TMSCl in MeOH. Indeed, comparison of the olefinic coupling constants of **12** and **13** (*J* = 13 Hz), with the reported coupling constants for the (*E*)-1-styrylcyclopropanol (*J* = 16 Hz),[23] and for the (*E*)- and (*Z*)-1-(2-*p*-tolylethenyl)cyclopropanols (*J* = 16 Hz and 12 Hz, respectively),[24] as well as their respective olefinic chemical shifts, [doublets at δ 5.70 ppm and 6.50 ppm for (*Z*)-**12** and at 5.92 and 6.62 ppm for (*E*)-**12**],[23] led to assign a (*Z*)-configuration for their styryl double bond.

As the acid-induced Peterson olefination was known to entail *anti* elimination of hexamethyldisiloxane,[25] the exclusive formation of the cyclopropanols (*Z*)-**12** and *cis*- and *trans*-(*Z*)-**13** led to assign a *threo* configuration for the 1-substituents as shown for **9a** and **11a** (Scheme 3). From these results it must be concluded that the configurations of adducts **6a** and **7a** had been previously assigned erroneously.[18] Moreover, X-ray crystallographic analyses of the solid diol **9a′** (recrystallized from hexane) have confirmed a *threo* configuration for its 1-substituent.[26] On the other hand, upon treatment with one equivalent of tetrabutylammonium fluoride (*n*-$Bu_4NF$) in THF at room temperature, **9b** underwent only O-desilylation to give exclusively the 1-[2-hydroxy-2-phenyl-1-(trimethylsilyl)ethyl]cyclopropanol **9a′**[20b] while, its reaction with $BF_3$·$Et_2O$ was ineffective (Scheme 4).

Titanium-mediated cyclopropanation of the β-hydroxyester derivatives **14** (X = THP, TBDMS; R = Me, Ph, 2-naphthyl) by EtMgBr and *n*-BuMgBr has been recently reported to provide in 54–65% yields, the cyclopropanols **15a** ($R^1$ = H) and diastereoselectively the cyclopropanols *trans*-**15b** ($R^1$ = Et; de:100%) (Scheme 5).[13b] Therefore, the presence of the α-trimethylsilyl substituent appeared

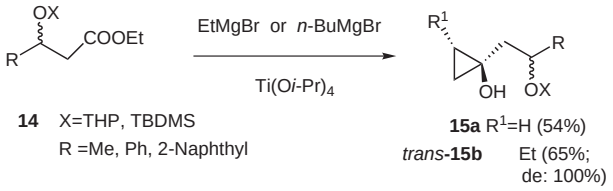



**Scheme 3**



Downloaded by: Rutgers University. Copyrighted material.

responsible for the surprising difference of reactivity observed between the diastereomeric silylated adducts *erythro*-**6a**,**b** and *threo*-**7a**,**b** and for the lack of stereoselectivity in these cyclopropanation reactions.




**14** X=THP, TBDMS
R =Me, Ph, 2-Naphthyl

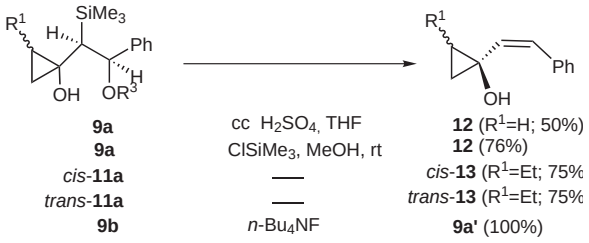
**15a** $R^1$=H (54%)
*trans*-**15b** Et (65%; de: 100%)

**Scheme 5**

This difference of reactivity towards the titanium-mediated cyclopropanation reaction which occurred between the stereoisomers *erythro*-**6a** and *threo*-**7a** was amazing. Apparently, it does not simply result from different steric hindrances around the carboxylate moiety of these α-silylesters. In order to elucidate this unexpected stereoselectivity, we have assumed that the reactivity of the silylated esters **6a** and **7a** is controlled by the formation of the intermediate titanafurans **A** and **B**. Therefore, we have undertaken computational studies of the transition structures resulting from the approaches of these esters by the titanacyclopropane **16**.[10] Taking into account the three chiral centers of **A** and **B**, calculations were carried out on the four possible approaches leading to the diastereomers *SRR*-**17** and *SSS*-**18** arising from *erythro*-**6a**, *SRS*-**19** and *SSR*-**20** arising from *threo*-**7a** (Schemes 6 and Figure 1). After determination of the chiral chain conformations of the esters by molecular dynamics simulations (MM2 force field type), all the structures were minimized by semi-empirical ZINDO method.[27] To confirm our model, Hessian calculations were carried out for each case and resulted in a transition structure, i.e., in a first-order saddle point with the Hessian having one negative eigenvalue.

The differences in energies between these four structures, $\Delta E$ = 3.1, 7.2, 0, and 9.0 kcal $mol^{-1}$, respectively, appeared consequently in full agreement with the difference of reactivity observed between the adducts *erythro*-**6a** and *threo*-**7a**, in this titanium(IV) induced cyclopropanation.

In conclusion, the titanium(IV)-mediated cyclopropanation by Grignard reagents of α-trimethylsilylesters arising from mercuric iodide catalyzed condensation of bissi-




**9a** — **12** ($R^1$=H; 50%)
**9a** — **12** (76%)
*cis*-**11a** — *cis*-**13** ($R^1$=Et; 75%
*trans*-**11a** — *trans*-**13** ($R^1$=Et; 75%
**9b** — **9a'** (100%)

**Scheme 4**

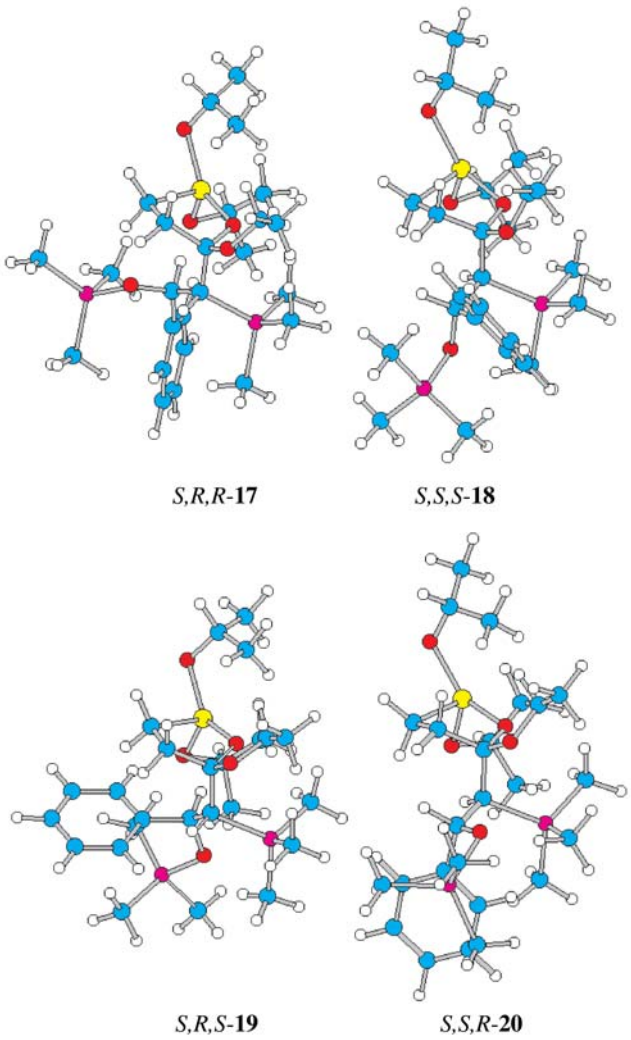
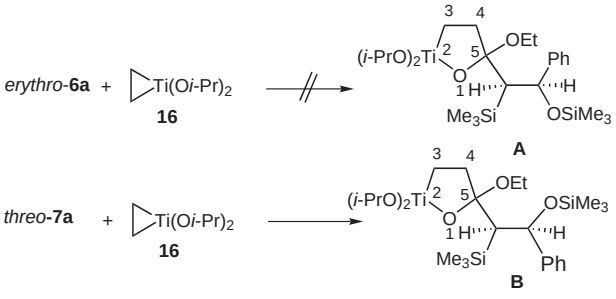



**Figure 1**

lylketene acetals **5a**,**b** with benzaldehyde, followed by acid induced Peterson olefination can provide 1-[1-(*Z*)-alkenyl]cyclopropanols **12** and *cis*- or *trans*-**13**; however, this three-membered ring formation appeared highly dependant on the configurations of the intermediate α-trimethylsilylester adducts **6a**,**b** and **7a**,**b**.




**Scheme 6**



Downloaded by: Rutgers University. Copyrighted material.

## References


(1) (a) Salaün, J. In *The Chemistry of the Cyclopropyl Group, Rearrangements Involving the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, **1987**, 809–878. (b) Salaün, J. *Top. Curr. Chem.* **1988**, *144*, 1; and references cited therein. (c) *Carbocyclic Three- and Four-membered Ring systems In, Houben-Weyl Methods of Organic Chemistry*, Vol. E 17a–f; de Meijere, A., Ed.; Thieme: Stuttgart, **1997**, and references cited therein.

(2) (a) Schnaubelt, J.; Ullmann, A.; Reissig, H.-U. *Synlett* **1995**, 1223. (b) Ulmann, A.; Reissig, H.-U.; Rademacher, O. *Eur. J. Org. Chem.* **1998**, 2541. (c) Palia, P. K.; Reissig, H.-U. *Synlett* **2001**, 33.

(3) (a) Stolle, A.; Ollivier, J.; Piras, P. P.; Salaün, J.; de Meijere, A. *J. Am. Chem. Soc.* **1992**, *114*, 4051. (b) Ollivier, J.; Dorizon, P.; Piras, P. P.; de Meijere, A.; Salaün, J. *Inorg. Chim. Acta* **1994**, *222*, 37. (c) Salaün, J. *Russian J. Org. Chem.* **1997**, *33*, 742.

(4) (a) Ollivier, J.; Girard, N.; Salaün, J. *Synlett* **1999**, 1539. (b) Paschetta, V.; Cordero, F. M.; Paugam, R.; Ollivier, J.; Salaün, J. *Synlett* **2001**, 1233.

(5) (a) Chevtchouk, T.; Ollivier, J.; Salaün, J. *Tetrahedron: Asymmetry* **1997**, *8*, 1005. (b) Chevtchouk, T.; Ollivier, J.; Salaün, J. *Tetrahedron : Asymmetry* **1997**, *8*, 1011. (c) Stolle, A.; Becker, H.; Salaün, J.; de Meijere, A. *Tetrahedron Lett.* **1994**, *35*, 3517. (d) Stolle, A.; Becker, H.; Salaün, J.; de Meijere, A. *Tetrahedron Lett.* **1994**, *35*, 3521. (e) Atlan, V.; Racouchot, S.; Rubin, M.; Bremer, C.; Ollivier, J.; de Meijere, A.; Salaün, J. *Tetrahedron: Asymmetry* **1998**, *9*, 1131. (f) Estieu, K.; Paugam, R.; Ollivier, J.; Salaün, J.; Cordero, F. M.; Goti, A.; Brandi, A. *J. Org. Chem.* **1997**, *62*, 8276. (g) Ferrara, M.; Cordero, F. M.; Goti, A.; Brandi, A.; Estieu, K.; Paugam, R.; Ollivier, J.; Salaün, J. *Eur. J. Org. Chem.* **1999**, 2725. (h) Pisaneschi, F.; Cordero, F. M.; Goti, A.; Paugam, R.; Ollivier, J.; Brandi, A.; Salaün, J. *Tetrahedron: Asymmetry* **2000**, *11*, 897. (i) Cordero, F. M.; Pisaneschi, F.; Goti, A.; Ollivier, J.; Salaün, J.; Brandi, A. *J. Am. Chem. Soc.* **2000**, *122*, 8075. (j) Delogu, G.; Salaün, J.; de Candia, C.; Fabbri, D.; Piras, P. P.; Ollivier, J. *Synthesis* **2002**, 2271.

(6) Salaün, J.; Conia, J. M. *Tetrahedron Lett.* **1972**, 2849.

(7) Denis, J. M.; Girard, C.; Conia, J. M. *Synthesis* **1972**, 549.

(8) Salaün, J. *Chem. Rev.* **1983**, *83*, 619.

(9) Salaün, J. *Chem. Rev.* **1989**, *89*, 1247.

(10) (a) Kulinkovich, O. G.; Sviridov, S. V.; Vasilevskii, D. A.; Pritcyckaja, J. S. *Zh. Org. Khim.* **1989**, *25*, 2245. (b) Kulinkovich, O. G.; Sviridov, S. V.; Vasilevskii, D. A. *Synthesis* **1991**, 234. (c) Kulinkovich, O. G.; Sviridov, S. V.; Vasilevskii, D. A.; Savchenko, A. I.; Pritytskaya, T. S. *Zh. Org. Khim.* **1991**, *27*, 294. (d) Kulinkovich, O. G.; de Meijere, A. *Chem. Rev.* **2000**, *100*, 2789; and references cited therein. (e) Kulinkovich, O. G. *Pure Appl. Chem.* **2000**, *72*, 1715; and references cited therein.

(11) Kozyrkov, Y.; Pukin, A.; Kulinkovich, O. G.; Ollivier, J.; Salaün, J. *Tetrahedron Lett.* **2000**, *41*, 6399.

(12) Sylvestre, I.; Ollivier, J.; Salaün, J. *Tetrahedron Lett.* **2001**, *42*, 4991.

(13) (a) Racouchot, S.; Ollivier, J.; Salaün, J. *Synlett* **2000**, 1729. (b) Racouchot, S.; Sylvestre, I.; Ollivier, J.; Kozyrkov, Y.-Y.; Pukin, A.; Kulinkovich, O. G.; Salaün, J. *Eur. J. Org. Chem.* **2002**, 2160.

(14) Chan, T. H. *Acc. Chem. Res.* **1977**, *10*, 442.

(15) Brandi, A.; Goti, A. *Chem. Rev.* **1998**, *98*, 589.

(16) Fleming, I.; Dunoges, J.; Smithers, R. *Org. React.* **1989**, *37*, 57.

(17) The cyclopropanol **2a** ($R^1$ = H) was previously isolated as 3,5-dinitrobenzoate from the alkylation-cyclization of ethyl 3-bromopropionate by $Me_3SiCH_2MgBr/SmI_2$, see: Fukuzawa, S.; Furuya, H.; Tsuchimoto, T. *Tetrahedron* **1996**, *52*, 1953.

(18) (a) Dicker, I. B. *J. Org. Chem.* **1993**, *51*, 2324. (b) In this article (ref.[18a]) the *J*(*threo*) > *J*(*erythro*) relationship for the $H_2H_3$ coupling constants, was erroneously based on the consideration of stronger intramolecular hydrogen bonds in the *threo* comparatively to the *erythro* adducts, see: House, H. O.; Crumrine, D. S.; Teranishi, A. Y.; Olmstead, H. D. *J. Am. Chem. Soc.* **1973**, *95*, 3310. (c) However, there are no intramolecular hydrogen bond in the O-silylated diastereoisomers **6a**,**b** and **7a**,**b**. The coupling constants of *erythro*-**6a** [*J*($H_2H_3$) = 10.7 Hz] and of *threo*-**7a** [*J*($H_2H_3$) = 10.4 Hz] were carefully measured by peak pickings.

(19) Colvin, E. W. In *Silicon Reagents in Organic Synthesis*; Academic Press: London/New York, **1988**, 101.

(20) To a solution of 4 g (11 mmol) of the 1:1 mixture of ethyl 3-phenyl-2-(trimethylsilyl)-3-(trimethylsilyloxy)propionate *erythro*-**6a** and *threo*-**7a** in 15 mL of THF containing 0.62 g (2.2 mmol; 0.2 equiv) of Ti(*i*-PrO)$_4$ was added dropwise a 2.54 M solution of ethylmagnesium bromide (11 mL, 27 mmmol; 2.5 equiv) in diethyl ether within 4 h. The reacting mixture was cooled to 0 °C (iced-water bath), then diluted with diethyl ether and hydrolyzed with 10 mL of aq $NH_4Cl$. After filtration through celite, the separated organic layer was washed with brine, dried on $Na_2SO_4$ and concentrated in vacuo. Flash chromatography of the residue (eluant: pentane/diethyl ether 9:1) gave two products:
(a) 1-[2-Phenyl-1-(trimethylsilyl)-2-(trimethylsilyloxy)ethyl]cyclopropanol **9a**: 1.94 g (52% yield); $^1$H NMR (250 MHz, $CDCl_3$) δ –0.08 (s, 9 H), 0.71 (d, *J* = 4.95 Hz, 1 H), 0.25–0.88 (m, 4 H), 3.24 (s, 1 H), 5.33 (d, *J* = 4.95 Hz, 1 H), 7.19–7.33 (m, 5 H); $^{13}$C NMR (66 MHz, $CDCl_3$): δ 0.21, 0.28, 13.27, 15.62, 46.13, 58.92, 78.75, 126, 126.9, 127.9, 144.4; IR 3463, 3379, 2974, 2949 cm$^{-1}$; MS *m/z* (EI) 322 (2) [$M^+$], 231 (42), 179 (31), 147 (17), 75 (36), 73 (100), 45 (16); MS *m/z* (CI with $NH_3$) 340 (0.1), 252 (17), 251 (61), 250 (100), 233 (40), 232 (44), 231 (74) 217 (18), 179 (21), 160 (21), 155 (15), 144 (26), 1433 (100).
(b) 1-(2-Hydroxy-2-phenyl-1-trimethylsilylethyl)cyclopropanol **9a′**: (various amounts 5–10%); white solid: mp 107 °C; $^1$H NMR (250 MHz, $CDCl_3$) δ –0.07 (s, 9 H), 0.76 (s, 1 H), 0.07–0.97 (m, 4 H), 2.58 (s, 1 H), 3.29 (s, 1 H), 5.44 (s, 1 H), 7.24–7.35 (m, 5 H); $^{13}$C NMR (66 MHz, $CDCl_3$) δ 0.32, 13.41, 16.02, 44.86, 59.97, 77.97, 125.17, 126.91, 128.09, 144.41; IR: 3468, 2955, 2898 cm$^{-1}$; MS *m/z* (EI) 231 (33), 159 (33), 145 (16), 131 (33), 115 (12), 103 (16), 79 (27), 77 (44), 75 (93), 73 (100), 79 (27), 45 (26); MS *m/z* (CI with $NH_3$) 251 (19), 250 (81) [$M^+$], 231 (10), 161 (16), 160 (13), 144 (13), 143 (100) 131 (8); Exact mass $M^+$ 250.1377 (calcd for $C_{14}H_{22}SiO_2$ 250.1389).

(21) Base-induced Peterson olefination of cyclopropanols **9a** and **11a** led to ring-opened derivatives (see ref. 1).

(22) To a stirred solution of 340 mg (1 mmol) of cyclopropanol **9a** in 5 mL of methanol at r.t. was added two drops of chlorotrimethylsilane. The reaction was complete within 2 h, as monitored by TLC. Then the solvent was removed in vacuo; flash chromatography of the residue (eluant: pentane/diethyl ether 9:1) gave 128 mg (76% yield) of 1-(*Z*)-styryl cyclopropanol **12.** $^1$H NMR (250 MHz, $CDCl_3$) δ 0.71–1.32 (m, 4 H), 2.16 (s, 1 H), 5.26 (d, *J* = 13 Hz, 1 H), 6.53 (d, *J* = 13 Hz, 1 H), 7.32–7.55 (m, 5 H); MS *m/z* (EI) 160 (41) [$M^+$], 159 (74), 145 (54), 131 (68), 127 (36), 115 (43), 103 (63), 91 (33), 77 (100), 51 (52); MS *m/z* (CI with $NH_3$) 178 (100), 161 (22), 160 (17), 159 (14), 143 (18), 131 (13).


Downloaded by: Rutgers University. Copyrighted material.

(23) Salaün, J.; Ollivier, J. *Nouv. J. Chem.* **1981**, *5*, 587.
(24) Ollivier, J. *PhD Thesis*; Université de Paris-Sud: Orsay France, **1986**.
(25) Colvin, E. W. In *Silicon Reagents in Organic Synthesis*; Academic Press: New York, **1988**, 65–69.
(26) X-ray crystallographic data of the diol **9a′**, will be published in *Zeitschrift fuer Kristallographie*.
(27) Molecular mechanics calculations (using a $MM^+$ force field) and semi-empirical ZINDO calculations have been performed with the Hyperchem software (version 5.1). The Ti-O and Ti-C bond lengths and the Ti-bond angles were in accord with reported RX data for titanium complexes. See: Gais, H. J.; Volhardt, J.; Linder, H. J.; Paulus, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1541.

Downloaded by: Rutgers University. Copyrighted material.