20 eV) m/z 214 (M^+). Anal. Calcd for $C_{10}H_{22}OSi_2$: C, 56.01; H, 10.34. Found: C, 56.21; H, 10.57.

Synthesis of Homoallylic Alcohol 10. To a THF solution (1 mL) of **8** (67 mg, 0.25 mmol) was added a hexane solution of *n*-butyllithium (0.49 mmol) at -78 °C under nitrogen. The temperature of the mixture was allowed to rise to room temperature over 12 h, and then 1 N aqueous HCl (1 mL) was added. Extraction with ether and preparative TLC of the extract (*n*-hexane/ether = 9:1) afforded **10** (66 mg, 81%): IR (neat) 3324, 2964, 1252, 1040 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.20 (s, 6 H), 0.21 (s, 9 H), 0.24 (s, 9 H), 0.65–0.74 (m, 2 H), 0.89 (t, J = 6.6 Hz, 3 H), 1.26–1.43 (m, 4 H), 2.87 (t, J = 6.8 Hz, 2 H), 3.62 (t, J = 6.8 Hz, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 0.33, 3.50, 3.72, 13.64, 17.67, 26.21, 26.48, 46.78, 62.24, 167.99, 174.64; HREIMS (20 eV) calcd for $C_{16}H_{38}OSi_3$ 330.2231, found 330.2221.

Epoxidation of 9. To a dichloromethane solution (1 mL) of *m*-chloroperbenzoic acid (45 mg, 0.26 mmol) was added **9** (47 mg, 0.22 mmol) at 0 °C. The mixture was stirred for 45 min and was then extracted with ether. Evaporation of solvent from the extract afforded **11** (43 mg, 85%): IR (neat) 2968, 1254, 1064 cm^{-1}; ^1H NMR (200 MHz, C_6D_6) δ 0.05 (s, 9 H), 0.31 (s, 3 H), 0.42 (s, 3 H), 1.25 (s, 3 H), 1.57 (ddd, J = 14.1, 4.5, and 2.1 Hz, 1 H), 1.86–2.03 (m, 1 H), 3.88–4.05 (m, 2 H); ^{13}C NMR (50 MHz, C_6D_6) δ -2.02, -1.61, 0.36, 18.55, 36.83, 56.94, 63.42; EIMS (20 eV) m/z 230 (M^+). Anal. Calcd for $C_{10}H_{22}O_2Si_2$: C, 52.12; H, 9.62. Found: C, 51.84; H, 9.60.

Supplementary Material Available: ^1H and ^{13}C NMR spectra of compounds **6**, **7**, and **10** (6 pages). Ordering information is given on any current masthead page.

C-Centered Optically Active Organosilanes. A Rational Approach to an Efficient Silylated Chiral Auxiliary

Cristina Nativi,[‡] Nunziatino Ravidà,[†] Alfredo Ricci,[†,‡] Giancarlo Seconi,[§] and Maurizio Taddei*[,†]

Dipartimento di Chimica Organica "U.Schiff" dell'Università, Via G. Capponi 9, I-50121 Firenze, Italy, CNR, Centro Composti Eterociclici, Via G. Capponi 9 I-50121, Firenze, Italy, and CNR, Istituto Composti del Carbonio Contenenti Eteroatomi, Via della Chimica, Ozzano Emilia, Bologna, Italy

Received February 22, 1990

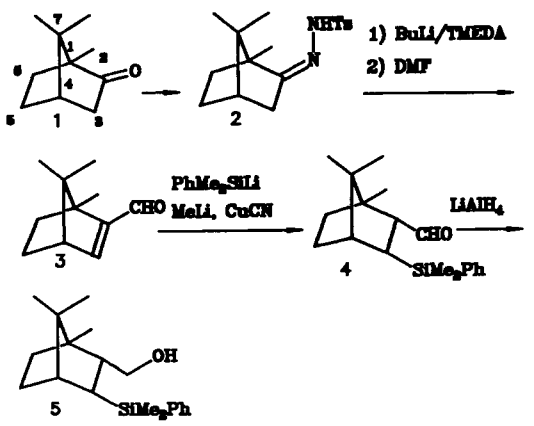
We recently reported the preparation[1] of some C-centered optically active organosilanes and their use[2] as chiral auxiliaries in the rections of allylsilanes with electrophiles. The modest enantiomeric excess (ee) values obtained in these reactions, comparable with results reported by other authors,[3] prompted us to consider a different approach to the preparation of such auxiliaries.

We looked at the possibility of performing an enantiocontrolled electrophilic attack at the double bond of an allylsilane by using a C-centered optically active auxiliary bonded to silicon, one which efficiently hinders one side of the double bond.

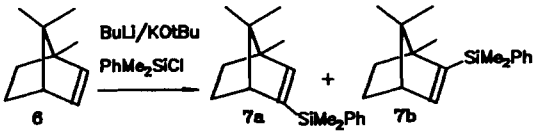
We report here the preparation of a chlorosilyl derivative with one of the ligands to silicon having a bornane-like structure, some applications which show the efficacy of this auxiliary in stereocontrolled reactions of allylsilanes, and some observations on the possible limitations of wider applications of this approach.

We first attempted to prepare a $PhMe_2Si$ derivative, as the precursor of a $ClMe_2Si$ group, by silyl cupration of the

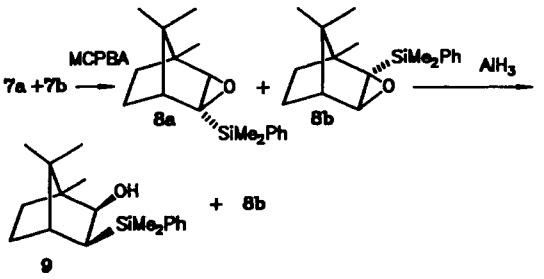
Scheme I



Scheme II



Scheme III



α,β-unsaturated bornyl aldehyde **3**, prepared by a modification of the Shapiro reaction[4] (Scheme I).

Aldehyde **3**, isolated in 56% yield,[5] underwent silyl cupration with $PhMe_2SiLi$ and CuCN at 0 °C, giving, after column chromatography, product **4** as the syn-endo isomer. The silyl cuprate attacks the double bond from the endo face, and the addition of the proton from the opposite direction[6] gives the product with the stereochemistry shown in Scheme I for **4**.

Aldehyde **4** was easily enolized by treatment with organometallic reagents such as BuLi, BuMgBr, $PhCH_2MgBr$, and MeLi. Reduction of **4** with $LiAlH_4$ gave alcohol **5** only in poor yield. These results suggested that **4** was not a suitable intermediate for preparation of the required auxiliary.

The introduction of the $PhMe_2Si$ group into the bornyl skeleton was then attempted by coupling $PhMe_2SiCl$ with

[†] Dipartimento di Chimica Organica "U. Schiff".
[‡] CNR, Centro Composti Eterociclici.
[§] CNR, Instituto Composti del Carbonio Contenenti Eteroatomi.

(1) Coppi, L.; Ricci, A.; Taddei, M. *Tetrahedron Lett.* **1987**, *28*, 965.
(2) Coppi, L.; Mordini, A.; Taddei, M. *Tetrahedron Lett.* **1987**, *28*, 969.
(3) (a) Chan, T. H.; Wang, D. *Tetrahedron Lett.* **1989**, *30*, 3041. (b) Jung, M. E.; Hogan, K. T. *Tetrahedron Lett.* **1988**, *29*, 6199. (c) Yi, G.; Wang, D.; Chan, T. H. *Youji Huaxue*, **1988**, *8*, 115; *Chem. Abstr.* **1989**, *110*, 75615c. (d) Walkup, R. D.; Obeyesekere, N. U. *J. Org. Chem.* **1988**, *53*, 923. (e) Tamao, K.; Kanatami, R.; Nada, M. K. *Tetrahedron Lett.* **1984**, *25*, 1913.
(4) (a) Shapiro, R. H. *Org. React.* **1975**, *23*, 405. (b) Shapiro, R. H.; Heath, M. J. *J. Am. Chem. Soc.* **1967**, *89*, 5734. Kaufman, G.; Cook, F.; Shechter, R.; Bayless, J.; Friedman, L. *J. Am. Chem. Soc.* **1967**, *89*, 5737.
(5) This product has been prepared by an analogous reaction starting from the camphor trisylhydrazone. Chamberlin, A. R.; Stemke, J. E.; Bond, F. T. *J. Org. Chem.* **1978**, *43*, 147.
(6) Bernahrd, W.; Fleming, I.; Waterson, D. *J. Chem. Soc., Chem. Commun.* **1984**, 28.

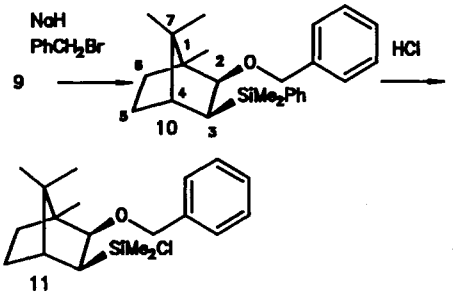
0022-3263/91/1956-1951$02.50/0

Table I. Products Obtained from Treatment of Allylsilanes 13a–c with MCPBA/TBAF

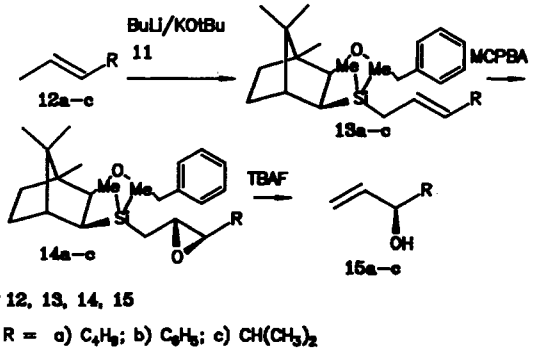
R =	product	de (%)[a]	reaction conditions	alcohol	yield[b] (%)	ee (%), absolute config
C_4H_9	13a	92	MCPBA (–10 °C, CH_2Cl_2, 2 h). TBAF (rt, THF, 12 h).	15a	62[c]	76, *R*
C_6H_5	13b	85	MCPBA (rt, CH_2Cl_2, 12 h). TBAF (rt, THF, 12 h).	15b	49[d]	32, *S*
$(CH_3)_2CH$	13c	97	MCPBA (–10 °C, CH_2Cl_2, 8 h). TBAF (rt, THF, 12 h)	15c	70[c]	87, *R*

[a] Determined by GLC analyses. [b] Yields of isolated products. [c] Isolated by bulb-to-bulb distillation. [d] Isolated by PTLC.

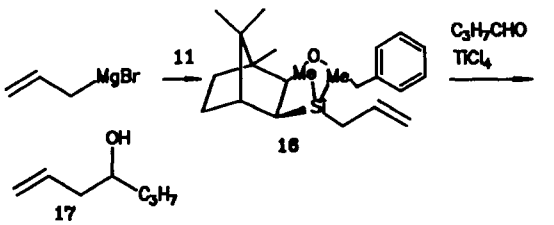
Scheme IV



Scheme V



Scheme VI



a bornyl anion, as shown in Scheme II.

2-Bornene **6** was obtained from tosylhydrazone **2** using the Shapiro reaction.[7] Metalation[8] of **6** with butyllithium and potassium *tert*-butoxide gave the potassium alkene which, after coupling with $PhMe_2SiCl$, gave products **7a** and **7b** as an 87:13 mixture (determined by GLC analysis). Attempts to separate **7a** and **7b** by chromatography on silica gel were unsuccessful. The stereochemistry of **7a** and **7b** was deduced from their ^1H NMR spectra, which showed, for **7a**, a singlet at δ 6.03 for H(2) and, for **7b**, a doublet at δ 6.35, relative to H(3) (see Scheme II).

The mixture of **7a** and **7b** was epoxidized with *m*-chloroperbenzoic acid (MCPBA) in $CHCl_3$ (Scheme III). The reaction was stereoselective, and only two regioisomers **8a** and **8b** were obtained as an 82:18 mixture.

Ring opening of the oxiranes **8** was attempted with several reducing agents. Product **9** was obtained in acceptable yield only with AlH_3 (prepared from $AlCl_3$ and $LiAlH_4$). Product **8b** was extremely unreactive toward AlH_3 so it was possible to isolate product **9** (derived from **8a**) as a single isomer after column chromatography on silica gel.

The stereochemistry of **9** was determined by ^1H NMR analysis. From the results of selective decoupling experiments, we assigned the resonances of H(2), H(3), and H(4) to δ 4.18, 1.21, and 1.91, respectively. After exchange of the hydroxyl proton with deuterium and irradiation at δ 1.91, the original multiplet was transformed to a clear doublet at δ 4.18 (J = 6 Hz). Further irradiation at δ 4.18 transformed the triplet-like signal at δ 1.21 to a sharp doublet (J = 0.5 Hz). These coupling constants are typical of a syn-exo arrangement of the substituents on the bornyl skeleton.[9] An analogous experiment with **10** showed a $J_{H(2)-H(3)}$ and a $J_{H(3)-H(4)}$ of 5 and 0.1 Hz, respectively. We also observed a relevant nuclear Overhouser effect (NOE) in product **9** between H(2) and H(6) and, with **10**, between the protons of the methyl groups bonded to silicon and those of the methyl group in position 7. The stereochemistry observed is consistent with the mechanism proposed by Whitham[10] for the ring opening of epoxysilanes by $LiAlH_4$. Recovered **8b** was shown to have an exo epoxide ring with a doublet at δ 3.32 (J = 0.7 Hz).

The OH group of **9** was protected with a benzyl group using NaH and benzyl bromide in the presence of *tetra-n*-butylammonium iodide (Scheme IV). Treatment of **10** with HCl have the chlorosilane **11**, which was isolated by distillation. Compound **11** was a thick oil which solidified below 0 °C, fumed in moist air, but could be stored under a nitrogen atmosphere for months.

From chlorosilane **11** we prepared allylsilanes **13a–c** by coupling with the potassium derivatives of olefins **12a–c**, obtained by deprotonation with butyllithium and potassium *tert*-butoxide.[11]

The products, isolated as crude materials, consisted of enriched mixtures of the *E* isomers (Table I). The stereochemistry around the double bond of **13a–c** was determined by selective decoupling. Irradiation of the protons of the CH_2 α to the silicon (at ca δ 1.6 for **13a**) produced a doublet at δ 5.65 (J = 16–18 Hz) attributed to the H(2′). This assignment was confirmed by the ir absorption δ_C-(C–H) of the C=C bond observed around 965 cm^{-1} for compounds **13a–c**.

Allylsilanes **13a–c** were treated with MCPBA followed by *tetra-n*-butylammonium fluoride (TBAF) to give allylic alcohols **15a–c**. The products were isolated from the reaction mixture by either preparative thin-layer chromatography (PTLC) or bulb-to-bulb distillation. The ee values were determined by gas chromatographic analysis of the corresponding esters of the Mosher acid. The results of the reactions shown in Scheme V are shown in Table I.

(7) Shapiro, R. H.; Duncan, J. H. *Org. Synth.* **1971**, *51*, 66.
(8) Schlosser, M.; Mordini, A. *Chimia* **1986**, *40*, 309.
(9) Gaudemar, A. In *Stereochemistry, Fundamentals and Methods*; Kagan, H. B., Ed.; Georg Thieme Verlag: Stuttgart, 1977; Vol. 1, p 108.
(10) Robbins, C. M.; Whitham, G. H. *J. Chem. Soc., Chem. Commun.* **1976**, 697.
(11) Mordini, A.; Palio, G.; Ricci, A.; Taddei, M. *Tetrahedron Lett.* **1988**, *29*, 4991 and references therein.

We were encouraged by the chemical yields and ee values obtained, except in the case of **15b**, where we started with a mixture of *E* and *Z* isomers and performed the oxidation at higher temperatures. Nevertheless, the results were consistent with a model showing hindrance of one side of the stereogenic center by the benzyl group. The results may also be related to the possibility that the methyl groups bonded to silicon can overlap the methyl of the camphor skeleton, introducing an additional element of strain in the molecule (no free rotation of the C–Si bond), as suggested by the relevant (38%) NOE effect between the protons of the two methyl groups.

The auxiliary described in this paper is thus efficient enough to control the epoxidation of the double bond of an allylsilane, but apparently cannot be employed in electrophilic reactions of allylsilanes, such as condensation with aldehydes. For example, we prepared allylsilane **16** (Scheme VI) and allowed it to react with butyraldehyde in the presence of $TiCl_4$. Product **17** was obtained in 61% yield and an ee of 18%.

The oxygen in the auxiliary does not appear to be in position for an efficient coordination with a Lewis acid to force the reaction toward a synclinal pathway, as in the case reported by Chan.[3a]

Our results demonstrate that it is possible to build an efficient C-centered optically active organosilane for synthesis of enantiomerically pure compounds, but the auxiliary must to be designed specifically for a reaction that proceeds by a well-known mechanism.[12] The use of such auxiliaries does not seem to be general. The condensation of allylsilanes and aldehydes, for example, does not seem to give chiral homoallylic alcohols with high enantiomeric excess as does the reaction of allylboranes or other allylic organometallic reagents and aldehydes.[13] Nevertheless, we believe other stereocontrolled reactions of organosilanes can be influenced by the approach described herein, and we are continuing to work in this direction.

Experimental Section

^1H and ^{13}C Nuclear magnetic resonance spectra ($CDCl_3$ solutions) were obtained at 300 and 75 MHz, respectively. Infrared spectra were obtained on liquid films. Gas chromatographic analyses were performed using a 30 m × 0.32 mm i.d. DB Wax capillary column (J & W scientific) and H_2 as carrier gas. GLC/MS analyses were performed with a Hewlett-Packard 5970/5790 GC–MS system equipped with a 15 m SE 30 capillary column.

Tetrahydrofuran (THF) and ether were purified by distillation from Na wire and subsequent distillation from $LiAlH_4$. Pentane, dichloromethane, and chloroform were washed with H_2SO_4 and water, dried ($CaCl_2$), and distilled from CaH_2 prior to use. Tetramethylethylenediamine (TMEDA) was distilled from CaH_2 prior to use. Column chromatography was performed under low pressure using Merck silica gel 60 (230–400 mesh ASTM). Preparative thin layer chromatography (PTLC) was performed with 2 mm thick Merk silica gel 60 plates. All reactions were carried out under a nitrogen atmosphere.

Compounds **2** and **6** were prepared as previously described.[4,7] (Phenyldimethylsilyl)lithium was prepared as described by Fleming.[14] The ee values of the products **15a–c** and **17** were determined after purification by GLC analysis of the corresponding esters prepared with the Mosher acid chloride (MPTA chloride).[15]

Compounds **15a–c** were prepared by reaction of vinylmagnesium bromide and the corresponding aldehyde (pentanal, benzaldehyde, and isobutyroaldehyde, respectively) in THF. Compound **17** was prepared by coupling of allyltrimethylsilane and butyraldehyde in the presence of $TiCl_4$.[16] Compounds **15a–c** and **17** were identified by GLC and GLC/MS comparison with authentic racemic samples.

NOE Experiments. Compounds **9** and **10** (15 mg) were dissolved in degassed $CDCl_3$ (0.7 mL) and the spectra recorded using the gated decoupling technique activated with the macro available on a Varian VXR 300 spectrometer. Irradiation of **9** at δ 1.62 produced a NOE at δ 4.18. Irradiation at δ 4.18 produced a NOE at δ 1.62 and also at δ 0.98 (low inensity 2–5%), suggesting this frequency was that of the methyl protons on C1. Irradiation of **10** at δ 0.33 produced a NOE at δ 0.96; irradiation at δ 3.9 produced a NOE at δ 1.55 and at δ 0.96, assigned to the methyl protons on C1.

1,7,7-Trimethylbicyclo[2.2.1]-2-heptene-2-carboxaldehyde (3). Tosylhydrazone **2** (10 g, 31.2 mmol) was dispersed in dry TMEDA (70 mL). The mixture was cooled to −45 °C, and butyllithium (78.1 mL of a 1.6 N solution in hexane, 125 mmol) was added slowly. The mixture was stirred for 1 h, warmed to room temperature, and again stirred for 1 h. The mixture was cooled to 0 °C and DMF (9.1 g, 125 mmol) was added slowly. The mixture was warmed to room temperature and stirred for 1 h. Water (100 mL) was added, followed by ether (100 mL). The organic layer was washed several times with saturated aqueous $CuCl_2$, followed by 2% aqueus HCl and brine. After drying (Na_2SO_4) and evaporation of solvent, the product was purified by column chromatography (hexane/ethyl acetate, 5:1) to give 2.9 g of **3** (56% yield): IR 3025, 2995, 2980, 2850, 2780, 1700, 1610 cm^{-1}; ^1H NMR (90 mHz) δ 0.75 (s, 3 H), 0.91 (s, 3 H), 1.31 (s, 3 H), 1.7–2.6 (m, 5 H), 5.7 (d, 1 H, J = 4 Hz), 9.61 (s, 1 H); MS m/e (%) 164 (M^+, 2), 136 (M^+ − CO, 14), 93 (100).

***endo*-3-(Phenyldimethylsilyl)-1,7,7-trimethylbicyclo[2.2.1]heptane-*endo*-2-carboxaldehyde (4).** Copper cyanide (1.0 g, 11.2 mmol) was dispersed in THF (5 mL) and cooled to 0 °C, and then a solution of (phenyldimethylsilyl)lithium (14 mL of a 0.08 M solution in THF, 11.2 mmol) was added slowly. After 10 min at 0 °C, methyllithium (7 mL of a 1.6 M solution in Et_2O 11.2 mmol) was added and the mixture was stirred for 20 min. After the was cooled mixture to −25 °C, a solution of **3** (1.5 g, 9.15 mmol) in dry THF (3 mL) was added. The mixture was warmed to room temperature and stirred overnight. The flask was cooled again to 0 °C and a 1:1 aqueous solution of NH_4Cl/NH_4OH (10 mL) was added. The mixture was extracted with ether (3 × 10 mL), and the ether extract was dried (Na_2SO_4). Removal of the solvent and purification of the residue by column chromatography (hexane/ethyl acetate, 10:1) gave 1.9 g of **4** (56% yield): IR 2980, 2950, 1720, 1250, 920, 860 cm^{-1}; ^1H NMR δ 0.38 (s, 6 H, $Si(CH_3)_2$), 0.68 (s, 3 H), 0.79 (s, 3 H), 1.08 (s, 3 H), 1.21–1.57 (m, 6 H), 2.56 (m, 1 H, CHCO), 7.33 and 7.55 (m, 5 H, ArH), 9.78 (d, 1 H, J = 1.5 Hz); MS m/e (%) 300 (M^+, 12), 135 (100). Product **4** was transformed into the corresponding phenylhydrazone, mp 136–137 °C for elemental analysis. Anal. Calcd for $C_{25}H_{34}N_2Si$: C, 76.82; H, 8.77. Found: C, 76.98; H, 8.67.

***endo*-3-(Phenyldimethylsilyl)-*endo*-2-(hydroxymethyl)-1,7,7-trimethylbicyclo[2.2.1]heptane (5).** To a dispersion of lithium aluminium hydride (0.061 g, 1.6 mmol) in THF (2 mL), cooled to −78 °C, was added aldehyde **4** (0.50 g, 1.6 mmol) by syringe. The mixture was warmed to room temperature and stirred overnight. The mixture was cooled to 0 °C, and saturated aqueous NH_4Cl (2 mL) was added. The mixture was extracted with ether (5 mL). The organic layer was washed with 1 M aqueous HCl, water, and brine. The extract was dried (Na_2SO_4), and the solvent was evaporated. Column chromatography of the residue (hexane/ethyl acetate, 6:1) gave 0.12 g of **5** (24% yield) and recovered starting material (ca. 25%): IR 3350, 2990, 2950, 1610, 1120 cm^{-1}; ^1H NMR δ 0.29 (s, 6 H, $Si(CH_3)_2$), 0.78 (s, 3 H),

(12) This statement is supported by a communication (Chan, T. H.; Pellon, P. *J. Am. Chem. Soc.* **1989**, *111*, 8737) published during the typing of this paper. The authors describe a highly enentioselective synthesis of carbinols using a suitable silylated auxiliary.

(13) Brown, H. C.; Jadhav, P. K.; Singram, B. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Springer Verlag: Berlin, 1984; Vol. 4, p 321 and references therein. Roush, W. R.; Ando, K.; Powers, D. B.; Halterman, R. L.; Palkowitz, A. D. *Tetrahedron Lett.* **1988**, *29*, 5579.

(14) Fleming, I.; Newton, T. W.; Roessler, F. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2527.

(15) Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512. Yamaguchi, S. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: London, 1983, Vol. 1, p 128.

(16) Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, *16*, 1295.

0.80 (s, 3 H), 0.95 (s, 3 H), 1.20–1.67 (m, 7 H), 2.38 (b, 1 H, OH), 3.38 (m, 2 H, CH_2O), 7.3 and 7.5 (m, 5 H, ArH); MS *m/e* (%) 302, (M^+, 10), 135 (100).

3-(Phenyldimethylsilyl)-1,7,7-trimethylbicyclo[2.2.1]-2-heptene (7a). A Schlenk tube was charged with butyllithium (29.5 mL of a 1.5 M solution in hexane, 44.1 mmol) and cooled to −78 °C. Potassium *tert*-butoxide (4.9 g, 44.1 mmol) was added in small portions. After 10 min bornene **6** (5 g, 36.7 mmol) in pentane (25 mL) was added slowly. The mixture was warmed to room temperature and stirred for 48 h. The mixture was again cooled to −78 °C, and phenyldimethylsilyl chloride (9.3 g, 55 mmol) in dry THF (30 mL) was added over 30 min. The mixture was warmed to room temperature, and saturated aqueous NH_4Cl was added, followed by pentane (100 mL). The organic layer was separated, washed with water and brine, and dried (Na_2SO_4). Removal of solvent and purification of the residue by column chromatography (hexane) gave 7.9 g of a mixture of **7a** and **7b** in a 7:1 ratio (overall yield 80%): ^1H NMR δ 0.323 (s, 6 H, $Si(CH_3)_2$), 0.751 (s, 6 H), 1.010 (s, 3 H), 1.5–1.8 (m, 4 H), 2.39 (m, 1 H), 6.03 (s, 1 H, =CH **7a**), 6.32 (d, 1 H, *J* = 3 Hz, =CH, **7b**), 7.26 and 7.35 (m, 5 H, ArH); ^{13}C NMR δ 3.4, 5.4, 13.3, 19.6, 19.8, 24.7, 31.7, 52.4, 52.9, 56.6, 126.8, 127.9, 128.7, 132.3, 139.8, 141.8, 143.7; MS *m/e* (%) 270 (M^+, 16), 135 (100). Anal. Calcd for $C_{18}H_{26}Si$: C, 79.92; H, 9.69. Found: C, 79.34; H, 9.54.

Epoxidation of the Mixture of 7a and 7b. The mixture of **7a** and **7b** (5 g, 18.5 mmol) was dissolved in chloroform (150 mL) and cooled to 0 °C. To this solution was added slowly $Na_2HPO_4 \cdot 12H_2O$ (9.9 g, 27.7 mmol), followed by MCPBA (5.6 g, 27.7 mmol). The resulting mixture was stirred at room temperature for 12 h. Methyl sulfide (0.5 mL) was added followed by ether (200 mL). The organic layer was washed with water and saturated aqueous Na_2CO_3 (3 × 100 mL) and dried (Na_2SO_4). Removal of solvent and purification of the residue by column chromatography (hexane/ethyl acetate, 10:0.1) gave 3.7 g of **8a** and **8b** (70% yield): ^1H NMR δ 0.30 (s, 3 H, $SiCH_3$), 0.37 (s, 3 H, $SiCH_3$), 0.73 (s, 3 H), 0.92 (s, 3 H), 0.93 (s, 3 H), 1.3–1.8 (m, 5 H), 3.11 (s, 1 H, CHO, **8a**), 3.20 (m, 1 H, CHO, **8b**), 7.4 and 7.6 (m, 5 H, ArH); MS *m/e* (%) 286 (M^+, 25), 135 (100).

***exo,exo*-3-(Phenyldimethylsilyl)-1,7,7-trimethylbicyclo-[2.2.1]heptan-2-ol (9).** Lithium aluminum hydride (0.29 g, 10.3 mmol) was dispersed in dry ether at 0 °C, and aluminum trichloride (0.33 g, 2.5 mmol) was added in small portions. The mixture was stirred at room temperature for 30 min and cooled again to 0 °C, and the mixture of epoxides **8a** and **8b** (2.9 g, 10.1 mmol) in ether (10 mL) was added slowly. After stirring 30 min at room temperature, the mixture was cooled to 0 °C and aqueous NH_4Cl was cautiously added. The organic layer was separated, washed with brine, and dried (Na_2SO_4). Removal of solvent and column chromatography (hexane/ethyl acetate, 15:1) gave 1.9 g of **9** (64% yield): $[\alpha]^{25}_D$ +10.5° (*c* 1.5, $CHCl_3$); IR 3400, 3040, 2900, 1580, 1480, 1250, 900 cm^{-1}; ^1H NMR δ 0.39 (s, 3 H, $SiCH_3$), 0.49 (s, 3 H, $SiCH_3$), 0.81 (s, 3 H, CH_3), 0.90 (s, 3 H, CH_3), 1.21 (s, 3 H, CH_3), 1.21 (dd, 1 H, *J*(H2–H3) = 6 Hz, *J*(H3–H4) = 0.5 Hz, H(3)), 1.44 (br d, 1 H, OH), 1.62 (m, 3 H), 1.85 (m, 1 H), 1.91 (m, 1 H, H(4)), 4.18 (d (after exchange with D_2O), 1 H, *J*(H2–H3) = 6 Hz, H(2)), 7.3 and 7.5 (m, 5 H, ArH); ^{13}C NMR δ 3.7, 3.9, 13.47, 19.6, 20.0, 26.0, 28.4, 39.1, 45.3, 48.7, 49.7, 77.5, 126.8, 127.9, 128.9, 132.5. Anal. Calcd for $C_{18}H_{18}OSi$: C, 74.93; H, 9.78. Found: C, 75.18; H, 9.80. Unreacted **8b** (0.02 g) was also recovered: ^1H NMR δ 0.29 (s, 3 H, $SiCH_3$), 0.44 (s, 3 H, $SiCH_3$), 0.90 (s, 3 H), 0.98 (s, 3 H), 1.15 (s, 3 H), 1.58 (m, 2 H), 1.66 (m, 1 H), 1.71 (m, 1 H), 1.82 (m, 1 H), 3.20 (d, 1 H, *J* = 0.7 Hz), 7.29 and 7.51 (m, 5 H, ArH); ^{13}C NMR δ 3.9, 4.8, 13.1, 18.0, 20.2, 28.7, 29.0, 37.9, 40.2, 56.7, 71.3, 126.9, 129.9, 131.0, 132.9; MS *m/e* (%) 286 (M^+, 5), 135 (100).

***exo*-3-(Phenyldimethylsilyl)-*exo*-2-(benzyloxy)-1,7,7-trimethylbicyclo[2.2.1]heptane (10).** Sodium hydride (0.3 g of 50% oil dispersion, 6.2 mmol) was washed several times with pentane and was than dispersed in dry THF (5 mL). After cooling the mixture to 0 °C, **9** (1.2 g, 4.16 mmol) was added. The mixture was stirred at room temperature for 2 h and then refluxed for 15 min. After the mixture was cooled to −78 °C, *tetra-n*-butylammonium iodide (1.5 g, 4.16 mmol) was added, followed by benzyl bromide (0.9 g, 5.4 mmol). The mixture was warmed to room temperature and refluxed for 24 h. After the mixture was cooled to 0 °C, water was added followed by ether (10 mL). The ether layer was separated, washed with saturated aqueous NH_4Cl and brine, and dried (Na_2SO_4). Removal of solvent and purification of the residue by column chromatography (hexane) gave 1.06 g of **10** (67% yield): $[\alpha]^{25}_D$ +5.5° (*c* 1.5, $CHCl_3$); ^1H NMR δ 0.33 (s, 3 H, $SiCH_3$), 0.36 (s, 3 H, $SiCH_3$), 0.80 (s, 3 H), 0.85 (m, 1 H), 0.96 (s, 3 H), 1.06 (s, 3 H), 1.26 (m, 1 H), 1.42 (m, 1 H), 1.55 (m, 1 H), 1.72 (m, 2 H), 3.95 (d, 1 H, *J* = 5 Hz, H(2)), 4.24 (AB system, 1 H, *J* = 11.7 Hz, CH_2Ph), 4.43 (AB system, 1 H, *J* = 11.7 Hz, CH_2Ph), 7.31 and 7.53 (m, 10 H, ArH); ^{13}C NMR δ −2.4, −2.3, 12.2, 19.9, 20.0, 25.1, 34.0, 36.9, 45.2, 48.2, 50.7, 72.6, 86.7, 126.8, 127.6, 127.9, 128.6, 129.0, 129.8, 133.8, 139.3; MS *m/e* (%) 363 (M^+ − 15, 2), 135 (100). Anal. Calcd for $C_{25}H_{34}OSi$: C, 79.30; H, 9.05. Found: C, 79.40; H, 9.10.

***exo*-3-(Chlorodimethylsilyl)-*exo*-2-(benzyloxy)-1,7,7-trimethylbicyclo[2.2.1]heptane (11).** Compound **10** (0.95 g, 25 mmol) was dissolved in chloroform (15 mL) and dry HCl was bubbled continuously through the solution for 6 h. The progress of the reaction was monitored by GC/MS analysis. When the starting material disappeared, solvent was evaporated using a vacuum nitrogen line, yielding a thick oil which fumed in air. The product (0.74 g, 88% yield) was 96% pure as indicated by GLC analysis and was used in the next step without further purification. A small sample was purified by bulb-to-bulb distillation (180 °C (10^{-2} mmHg) for spectroscopic characterization: ^1H NMR δ −0.120 (s, 3 H, $SiCH_3$), −0.100 (s, 3 H, $SiCH_3$), 0.809 (s, 3 H), 0.950 (s, 3 H), 0.990 (s, 3 H), 1.4–1.7 (m, 6 H), 3.37 (d, 1 H, *J* = 5 Hz, H(2)), 4.25 (m, 2 H, CH_2Ph), 7.2 and 7.4 (m, 5 H, ArH); ^{13}C NMR δ −7.6, −0.9, 14.2, 18.7, 20.3, 25.3, 29.7, 39.1, 47.9, 49.8, 50.6, 65.1, 77.5, 127.9, 129.3, 130.1, 133.8; MS *m/e* (%) 337 (M^+ + 1, 2), 336 (M^+, 8), 93 (58), 74 (100).

Preparation of Allylsilanes 13a–c. General Procedure. *exo*-3-[Dimethyl[(*E*)-2-hepten-1-yl]silyl]-*exo*-2-(benzyloxy)-1,7,7-trimethylbicyclo[2.2.1]heptane (13a). A Schlenk tube, cooled to −78 °C, was charged with butyllithium (0.47 mmol) in dry THF (1 mL), and potassium *tert*-butoxide (0.053 g, 0.47 mmol) was added. After 30 min at −78 °C, (*E*)-2-heptene **12a** (0.05 g, 0.51 mmol) was added, and after 1 h at − 78 °C, chlorosilane **11** (0.135 g, 0.4 mmol) in THF (1 mL) was added. The mixture was warmed to room temperature and stirred for 1 h. Aqueous NH_4Cl was added, followed by ether (10 mL). The ether layer was separated, washed with brine, and dried (Na_2SO_4). Removal of solvent and purification of the residue by column chromatography (pentane/diethyl ether, 15:1) gave 0.114 g of **13a** (72% yield). GLC analysis showed that the product was a 24:1 mixture of the *E* and *Z* isomers: IR 3020, 2980, 2890, 1620, 1420, 965 cm^{-1}; ^1H NMR δ 0.12 (s, 3 H, $SiCH_3$), 0.20 (s, 3 H, $SiCH_3$), 0.80 (s, 3 H), 0.95 (s, 3 H), 0.98 (m, 3 H), 1.01 (s, 3 H), 1.2–1.9 (m, 12 H), 2.31 (m, 2 H), 3.38 (d, 1 H, *J* = 5 Hz) 4.25 (m, 2 H), 5.27 (m, 1 H), 5.35 (m, 1 H), 7.3 and 7.4 (m, 5 H, ArH); ^{13}C NMR δ 1.8, 2.7, 13.4, 18.0, 18.8, 20.3, 22.8, 26.1, 28.4, 29.7, 31.7, 32.8, 38.9, 45.4, 48.4, 49.8, 66.1, 77.3, 124.9, 127.4, 127.8, 128.7, 132.3, 141.7; MS *m/e* (M^+, 2), 383 (15), 47 (100). Anal. Calcd For $C_{26}H_{42}OSi$: C, 78.32; H, 10.62. Found: C, 78.01; H, 10.4.

***exo*-3-[Dimethyl[(*E*)-3-phenyl-2-propen-1-yl]silyl]-*exo*-2-(benzyloxy)-1,7,7-trimethylbicyclo[2.2.1]heptane (13b).** The general procedure gave a gas chromatographically pure 9:1 mixture of the *E* and *Z* isomers: IR 3020, 3010, 2980, 2890, 1620, 1420, 965 cm^{-1}; ^1H NMR δ 0.16 (s, 3 H, $SiCH_3$), 0.20 (s, 3 H, $SiCH_3$), 0.81 (s, 3 H), 0.95 (s, 3 H), 0.99 (s, 3 H), 1.5–1.7 (m, 6 H), 2.31 (m, 2 H), 3.360 (d, 1 H, *J* = 5 Hz), 4.28 (m, 2 H), 6.36 (m, 1 H), 7.16 (m, 1 H), 7.3 and 7.5 (m, 10 H); ^{13}C NMR δ 1.0, 4.7, 13.7, 19.0, 20.5, 26.3, 28.7, 39.1, 45.5, 48.3, 49.8, 65.1, 77.5, 114.3, 126.8, 127.6, 127.9, 128.4, 129.0, 129.3, 137.6, 138.3, 141.8; MS *m/e* (%) 418 (M^+, 10), 77 (100). Anal. Calcd for $C_{28}H_{38}OSi$: C, 80.32; H, 9.15. Found: C, 79.96; H, 9.06.

***exo*-3-[Dimethyl[(*E*)-4-methyl-2-penten-1-yl]silyl]-*exo*-2-(benzyloxy)-1,7,7-trimethylbicyclo[2.2.1]heptane (13c):** IR 3010, 2980, 2890, 1630, 1420, 962 cm^{-1}; ^1H NMR δ 0.12 (s, 3 H), 0.20 (s, 3 H), 0.89 (s, 3 H), 0.92 (s, 3 H), 0.99 (s, 3 H), 1.05 (m, 6 H), 1.5–1.7 (m, 6 H), 2.11 (m, 2 H), 2.36 (m, 1 H), 3.751 (d, 1 H, *J* = 5 Hz), 4.36 (m, 2 H), 5.75 (m, 1 H), 5.85 (m, 1 H), 7.3 and 7.6 (m, 5 H); ^{13}C NMR δ 1.8, 3.9, 13.7, 14.3, 14.7, 18.9, 21.0, 25.9, 26.1, 28.5, 38.9, 39.8, 45.4, 48.1, 49.6, 64.9, 77.7, 125.6, 127.7, 127.8, 128.8, 135.6, 141.7; MS *m/e* (%) 384 (M^+, 2), 369 (15), 77 (100). Anal. Calcd for $C_{25}H_{40}OSi$: C, 78.06; H, 10.48. Found: C, 77.90; H, 10.36.

Reaction of Allylsilanes 13a–c with MCPBA and TBAF. General Procedure. 1-Hepten-3-ol (15a). MCPBA (0.12 g, 0.7 mmol), was dissolved in dry CH_2Cl_2 (10 mL). The solution was cooled to −10 °C after the addition of $Na_2PO_4 \cdot 12H_2O$ (0.26 g, 0.9 mmol). Allylsilane **13a** (0.28 g, 0.7 mmol), in dry CH_2Cl_2 (1 mL), was added slowly by syringe. After the mixture was stirred for 2 h at this temperature, methyl sulfide (0.1 mL) was added followed by aqueous Na_2CO_3. The organic layer was separated, washed with brine, and dried (Na_2SO_4). The solvent was evaporated, and the residue was dissolved in dry THF (2 mL), which was added to a solution of TBAF (0.21 g 0.8 mmol) in dry THF (2 mL). The mixture was stirred at room temperature for 12 h and then ether (5 mL) was added, followed by aqueous NH_4Cl. The ether layer was separated and dried (Na_2SO_4). After evaporation of the solvent bulb-to-bulb distillation (140 °C) of the residue gave 0.043 g of **15a** (62% yield): $[\alpha]^{25}_D$ −4.35° (*c* 0.5, $CDCl_3$) [lit.[17] $[\alpha]^{25}_D$ −6.01° (*c* 1, $CHCl_3$)]; ^1H NMR δ 0.86 (t, 3 H, *J* = 7 Hz), 1.2–1.8 (m, 6 H), 2.70 (b, 1 H, OH), 4.1 (m, 1 H, CHO), 5.20 (m, 2 H, CH_2=), 5.90 (m, 1 H, CH=). GLC of the MTPA esters (60 °C for 2 min followed by 60–140 °C programmed at 3 °C/min) gave peaks corresponding to the esters of (*S*)-**15a** (t_R 20.8 min, 12%) and (*R*)-**15a** (t_R 21.4 min, 88%), indicating 76% of optical purity.

1-Phenyl-1-propen-3-ol (15b). Following the above general procedure, after evaporation of solvent, PTLC (hexane/ethyl acetate, 8:1) gave 0.043 g of **15b** (49% yield): $[\alpha]^{25}_D$ −2.01° (*c* 2, $CDCl_3$) [lit.[18] $[\alpha]^{25}_D$ −7.8° (*c* 5, benzene) for a 95% ee sample]; ^1H NMR δ 2.90 (b, 1 H, OH), 5.30 (m, 2 H, CH_2=), 5.70 (m, 1 H, CHO), 6.10 (m, 1 H, CH=), 7.2–7.5 (m, 5 H, ArH). GLC of the MTPA esters (80 °C for 2 min followed by 90–180 °C programmed at 3 °C/min) gave peaks corresponding to the esters of (*S*)-**15b** (t_R 16.8 min, 66%) and (*R*)-**15b** (t_R 17.4 min, 34%), indicating 32% of optical purity.

4-Methyl-1-penten-3-ol (15c). Following the general procedure, after evaporation of solvent, bulb-to-bulb distillation (70 °C (30 mmHg)) gave 0.056 g of **15c** (70% yield): $[\alpha]^{25}_D$ +29.2° (*c* 1, $CDCl_3$); ^1H NMR δ 0.91 (d, 3 H, *J* = 7 Hz), 1.1 (t, 3 H, *J* = 7 Hz), 1.9 (m, 1 H), 2.6 (b, 1 H, OH), 3.8 (m, 1 H, CHO), 5.2 (m, 2 H, CH_2=), 6.0 (m, 1 H, CH=). GLC of the MTPA esters (60 °C for 2 min followed by 60–140 °C programmed at 3 °C/min) gave peaks corresponding to the ester of one enantiomer of **15c** (t_R 18.9 min, 6.5%) and of the other enantiomer of **15c** (t_R 19.4 min, 93.5%), indicating 87% of optical purity.

Determination of the Absolute Configuration of 15c. (*R*)-(+)-4-Methyl-1-pentyn-3-ol was prepared by the method of Noyori.[19] The product was obtained with 50% ee, as shown by the optical rotation $[\alpha]^{25}_D$ +13.0° (*c* 1, diethyl ether) [lit.[19] for the *S* enantiomer, $[\alpha]^{25}_D$ −15.4° (*c* 0.8, ether)] for a 54% ee sample. 4-Methyl-1-pentyn-3-ol (0.075 g, 0.76 mmol) was hydrogenated at atmospheric pressure in methanol (2 mL) in the presence of 5% Pd/$CaCO_3$ (80 mg, 0.02 mmol) at room temperature for 12 h. The solution was filtered through Celite. GLC analysis of the filtrate showed no starting material and complete conversion to the desired allylic alcohol. After evaporation of the solvent, bulb-to-bulb distillation (70 °C (30 mmHg)) of the residue gave 0.032 g of (*R*)-**15c** (50% ee, 43% yield) which showed the optical rotation value of the same sign as the product obtained from **13c**, $[\alpha]^{25}_D$ +17.3° (*c* 3.2, $CDCl_3$). GLC of the MTPA esters (60 °C for 2 min followed by 60–140 °C programmed at 3 °C/min) gave peaks corresponding to the esters of (*S*)-**15c** (t_R 19.1 min, 25%) and of (*R*)-**15c** (t_R 19.7 min, 75%). Comparison with the GLC analysis of the product obtained by reaction of **13c** with MCPBA and TBAF confirmed the assignment of the absolute configuration based on the observed optical rotation.

***exo*-3-[Dimethyl(1-propen-3-yl)silyl]-*exo*-2-(benzyloxy)-1,7,7-trimethylbicyclo[2.2.1]heptane (16).** To a solution of allylmagnesium bromide in ether (prepared from 0.12 g of allyl bromide and 0.072 g of magnesium turnings in 5 mL of ether), cooled to −78 °C, was added chlorosilane **11** (0.135 g, 0.4 mmol), in THF (5 mL). The mixture was warmed to room temperature and stirred for 1 h. Aqueous NH_4Cl was added, followed by ether (10 mL). The ether layer was separated, washed with brine, and dried (Na_2SO_4). Removal of solvent gave 0.100 g (73% yield) of product **16**, which was used in the next step without further purification: ^1H NMR δ 0.16 (s, 3 H, $SiCH_3$), 0.19 (s, 3 H, $SiCH_3$), 0.80 (s, 3 H), 0.98 (s, 3 H), 1.03 (s, 3 H), 1.30 (m, 1 H), 1.42 (m, 1 H), 1.55 (m, 1 H), 1.65 (m, 1 H), 1.88 (m, 2 H), 2.3 (m, 2 H), 3.89 (d, 1 H, *J* = 5 Hz), 4.26 (AB system, 1 H, *J* = 7 Hz), 4.43 (AB system, 1 H, *J* = 7 Hz), 5.45 (m, 2 H), 6.09 (m, 1 H), 7.31 and 7.50 (m, 5 H, ArH); ^{13}C NMR δ 1.9, 2.3, 13.5, 18.8, 20.4, 24.9, 26.2, 28.4, 38.8, 45.4, 48.2, 49.7, 65.0, 77.4, 113.1, 127.4, 127.8, 128.8, 135.6, 141.7; MS *m/e* (%) 342 (M^+, 5), 77 (100).

1-Hepten-4-ol (17). Butyraldehyde (0.03 g, 0.4 mmol) and $TiCl_4$ (0.076 g, 0.4 mmol) were mixed at 0 °C in CH_2Cl_2 (5 mL) and stirred for 10 min. The yellow solution was added via cannula to a cooled (−78 °C) solution of crude **16** (0.100 mg) in CH_2Cl_2 (2 mL). The mixture was stirred 1 h at 0 °C. After the mixture was cooled to −78 °C, saturated aqueous NH_4Cl (2 mL) was added, followed by ether (10 mL). The organic layer was dried (Na_2SO_4) and after evaporation of solvent, PTLC (hexane/ethyl acetate, 8:1) gave 20 mg of product **17** (60% yield): $[\alpha]^{25}_D$ +2.2° (*c* 2, $CDCl_3$) [lit.[20] $[\alpha]^{25}_D$ +10.37° (*c* 10, benzene) for a 72% ee sample]; ^1H NMR δ 0.68 (t, 3 H, *J* = 7 Hz), 1.2–1.9 (m, 4 H), 2.3 (m, 2 H), 2.7 (b, 1 H, OH), 3.7 (m, 1 H, CHO), 5.3 (m, 2 H, CH_2=), 6.05 (m, 1 H, CH=). GLC of the MTPA ester (65 °C for 2 min followed by 65–170 °C programmed at 2 °C/min) gave peaks corresponding to the esters of (*S*)-**17** (t_R 20.3 min, 59%) and (*R*)-**15b** (t_R 20.7 min, 41%), indicating 18% of optical purity.

Acknowledgment. This project was financially supported (in part) by Ministero per l'Università e la Ricerca Scientifica e Tecnologica, Rome (Fondi M.P.I. 60%).

(17) Aggarwal, S. K.; Bradshaw, J. S.; Eguchi, M.; Parry, S.; Rossiter, B. E.; Markides, K. E.; Lee, M. L. *Tetrahedron* **1987**, *43*, 451.
(18) Claremon, D. A.; Lumma, P. K.; Phillips, B. T. *J. Am. Chem. Soc.* **1986**, *108*, 8265.
(19) Noyori, R.; Tomino, I.; Yamada, M.; Nishizawa, M. *J. Am. Chem. Soc.* **1984**, *106*, 6717.
(20) Hoffmann, R. H.; Herold, T. *Chem. Ber.* **1981**, *114*, 375.

Lewis Acid Catalyzed Diels–Alder Reactions of 3-Methyl-1-(triisopropylsiloxy)-1,3-cyclohexadiene: Factors Influencing the Stereoselectivity

Paul N. Devine and Taeboem Oh*

Department of Chemistry, State University of New York, Binghamton, New York 13901

Received April 2, 1990

Diels–Alder reactions can generate 6-membered rings with remarkable regioselectivity and stereoselectivity which contribute to their great synthetic utility.[1] Elucidation of factors which control the regiochemistry and stereochemistry have challenged the organic chemist for many years.[2]

It is known that Diels–Alder reactions are generally endo selective. However, with a 1,3-cyclohexadiene, good stereoselectivity is not usually observed.[3,4] Our investigations

(1) (a) Desimoni, G.; Tacconi, G.; Bario, A.; Pollini, G. P. *Natural Product Syntheses Through Pericyclic Reactions*; ACS Monograph 180; American Chemical Society: Washington, DC, 1984; Chapter 5. (b) Paquette, L. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1984; Chapter 7. (c) Wurziger, H. *Kontakte (Darmstadt)* **1984**, 3. (d) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1984**, 876.
(2) For leading references, see: (a) Eisenstein, O.; Lefour, J. M.; Anh, N. T. *Tetrahedron* **1977**, *33*, 523. (b) Houk, K. N. *Acc. Chem. Res.* **1975**, *8*, 361. (c) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1976.
(3) (a) Monti, S. A.; Chen, S.-C.; Yang, Y.-L.; Yuan, S.-S.; Bourgeois, O. P. *J. Org. Chem.* **1978**, *43*, 4062. (b) Fleming, I. In *New Trends in Natural Products Chemistry*; A.-ur-Rahman, Le Quesne, P. W., Ed.; Elsevier Science: New York, 1986; p 83. (c) Ibuka, T.; Mori, Y.; Aoyama, T.; Inubushi, Y. *Chem. Pharm. Bull.* **1978**, *26*, 456. (d) Jung, M. E.; McCombs, C. A. *J. Am. Chem. Soc.* **1978**, *100*, 5207. (e) Still, W. C.; Tsai, M.-Y. *Ibid.* **1980**, *102*, 3654. (f) Spitzner, D. *Tetrahedron Lett.* **1978**, 3349. (g) Jung, M. E.; Pan, Y.-G. *Ibid.* **1980**, *21*, 3127. (h) Birch, A. J.; Macdonald, P.; Powell, V. H. *Ibid.* **1969**, 351. (i) Rubottom, G. M.; Krueger, D. S. *Ibid.* **1977**, 611.

0022-3263/91/1956-1955$02.50/0