non-hydrogen atoms were refined by full-matrix least squares with anisotropic temperature factors; H atoms were found from difference Fourier maps and not refined. The final difference maps showed maximum positive peaks of 0.53 e $Å^{-3}$ and $(\Delta/\sigma) < 0.80$ for compound 2, and 0.20 e $Å^{-3}$ and $(\Delta/\sigma) < 0.03$ for compound 11. For the calculations, a VAX 6410 computer and the "X-Ray 76 System"[30] program were used. Scattering factors were taken from the literature.[31]

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Supplementary Material Available: Crystal data and data collection characteristics (Table IV), tables of atomic coordinates, thermal parameters, bond lengths, bond angles, and torsion angles for compounds 2 and 11 (13 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Stereospecific Synthesis of a Novel Allenic Cyclohexanoid Epoxide from the Fungus *Eutypa lata*

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The stereospecific synthesis of the novel allenic cyclohexanoid epoxide **13** is reported. Key steps include Diels–Alder reaction between a 1,4-dioxygenatedbuta-1,3-diene **1** and a ketene equivalent **2** and the coupling of a mixed isopropenyl cuprate with propagylic sulfinate **10**.

Recently we reported the isolation of a novel allenic epoxycyclohexane **13**[1] from the fungus *Eutypa lata*, the pathogen responsible for the vineyard dieback observed in recent years in Switzerland and France.[2] The structure of **13** was elucidated by classic spectroscopic techniques and confirmed by an X-ray study. Due to the novel structure of **13** and the small quantity isolated, we thought it interesting to carry out its total synthesis, eventually with a view to assign its absolute configuration by carrying out the synthesis enantioselectively.

Compound **13** shows a large structural similarity to the recently isolated asperpentyn[3] and contains the same epoxy-1,4-diol system found in eupenoxide.[4] Our retrosynthetic analysis suggested a ketone of type **7** as a key intermediate, which we thought would be obtainable by a Diels–Alder reaction between a 1,4-dioxygenated butadiene and a ketene equivalent.[5] Most Diels–Alder reactions between dienes and ketene equivalents have been used to form bicyclic systems where the questions of double-bond migration and epimerization of the functionality α to the newly formed ketone have not posed problems. In our case, we needed to choose from among the wide range of available ketene equivalents one which would be transformed under conditions mild enough not to cause these problems. For the diene we chose the bis(silyloxy) diene **1** that Duke and Rickards used in their synthesis of eupenoxide.[4]

Results and Discussion

Heating the diene **1** with 1-acetoxy-1-cyanoethylene (**2**) in a sealed tube a 110 °C for 4 days gave the required cycloadducts **3a** and **3b** (ratio by NMR ca. 8:1). Recrystallization gave **3a** in 50–65% yield. In most cases both unreacted diene and dieneophile could be recovered and reused. The double bond of the cycloadduct proved unreactive to peracid under standard conditions (CH_2Cl_2, rt), probably due to the presence of two allylic oxygen functions, but heating **3a** under reflux in dichloroethane with *m*-CPBA in the presence of a radical inhibitor[6] gave a single epoxide **4** in quantitative yield. We were relying on the directing influence of the two bulky TBDMS groups to give the epoxidation on the rear face of the molecule. That the epoxidation had in fact taken place in the desired manner was proven by the following NMR experiments. A NOE difference experiment based on the irradiation of the signal centered at δ 1.75 led to a 7% enhancement of the signal at δ 4.12 (2-H) and an 8% enhancement of the triplet at δ 4.27 (5-H) leading its assignment as H-4endo. A second experiment irradiating the signal at δ 2.62 led to a 2% enhancement of the triplet at δ 4.27 (5-H) leading to its assignment as H-4exo. Irradiation of the signal at δ 3.21 (6-H) revealed a W-type coupling (J = 0.7 Hz) with the signal at δ 2.62 (H-4exo). This information taken with the very small coupling constants $J_{1,2}$ (0.5 Hz) and $J_{5,6}$ (1.3 Hz) show that epoxidation had occurred on the required face of the molecule. Further NMR experiments were

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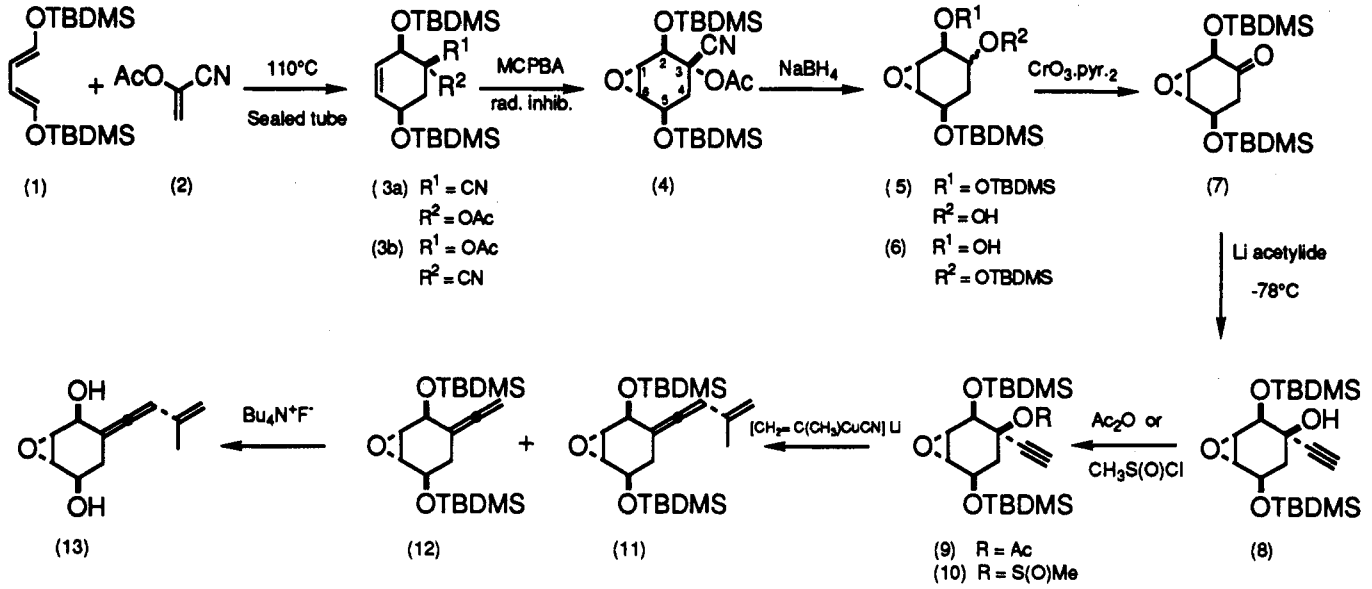
Scheme I



undertaken to determine the stereochemistry at C-3. In the proton-coupled ^{13}C NMR spectrum of **4** the cyanide signal appeared as a doublet of doublet at δ 115.46 (J = 2.1, 5.3, and 8.0 Hz). Selective decoupling of the signal at δ 4.12 (H-2) removed the 5.3-Hz coupling, while decoupling the signal at δ 1.75 (H-4exo) removed the 2.1-Hz coupling. Thus, the cyanide group must be trans to H-4endo (J = 8 Hz) and gauche to H-4exo (J = 2.1 Hz)[7] and is therefore on the same face of the molecule as the two silyloxy functions. The result is that expected from secondary orbital considerations in the Diels–Alder reaction.

The unmasking of the ketone function proved somewhat more problematic. Under the conditions developed by Vögel et al.[8] (K_2CO_3, MeOH, formalin) we obtained a complex mixture of products in which the epoxide had been cleaved and the oxygen function α to the newly formed ketone group had lost its stereochemical integrity. We got around this problem by treating the cyano acetate **3a** with sodium borohydride in ethanol,[9] effectively trapping the thus-formed ketone as an alcohol before epimerization could take place. Under these conditions we observed substantial migration of the TBDMS group from C-2 to the newly formed alcohol function. The lability of the TBDMS group in diol systems under basic conditions has been noted on numerous occasions[10] and has even been put to good use.[11] The migration proved not too problematic as the nonrearranged material **5** could be isolated easily by column chromatography, and further **5** was obtained by reequilibration of **6** under the original reaction conditions. At this stage we tried to change the TBDMS protecting groups for others reportedly less prone to this sort of migration (TBDPS[12] and TIPS[13]); although in both cases the respective bis(silyloxy) dienes were prepared in reasonable yield, the Diels–Alder reaction with **2** proved unsuccessful. Oxidation of the mixture of alcohols **5** with chromium trioxide–pyridine complex gave the ketone **7** in good yield.

For the addition of the required allenic moiety the coupling of a isopropenyl cuprate with a propargylic acetate appeared to us to be the most promising route. The coupling of alkyl cuprates with propargylic esters has been accepted, after some controversy, as occurring in an anti-S_N2' manner.[14] We therefore required the propargylic alcohol **8** in which the acetylenic group is on the same face of the molecule as the epoxide function. Here again we were relying on the two bulky TBDMS groups to direct acetylide attack to the required face of the ketone **7**. Treatment of ketone **7** with lithium acetylide[15] in THF at −78 °C gave a 65% yield of the required propargylic alcohol **8**. The stereochemistry of the product was confirmed by the following NMR experiments. In the ^1H NMR spectrum of **8** the hydroxyl proton appeared as a sharp singlet at δ 4.17. A NOE difference experiment based on irradiation of this signal led to, as well as a 2% enhancement of the signal at δ 3.86 (2-H), a 1% enhancement of both the epoxide proton signals [δ 3.4 (1-H) and δ 3.19 (6-H)] showing that the hydroxyl group was on the opposite face of the molecule to the epoxide oxygen. Acetylation of the tertiary alcohol in **8** proved extremely difficult, and under forcing conditions (Ac_2O, Et_3N, DMAP)[16] we obtained a disappointing 60% yield of the acetate **9** and again observed some migration of the TBDMS group.

Treatment of propargylic acetate **9** with diisopropenylcopper lithium led to almost exclusive recovery of alcohol **8**, and only trace amounts of allene **11** could be detected by GC-MS. We therefore tried to modify the nature of the attacking metal centre to favor attack at the acetylenic carbon by using mixed cyano and hexynyl[17] cuprates but again obtained very disappointing results, observing, at best, a 2.5% yield of allene and again recovered alcohol **8**. Propargylic acetates have been used successfully for this type of reaction[18] and were also completely satisfactory in our model studies. We therefore

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decided to change the acetate for methanesulfinate ester as we expected this to be a more efficient leaving group.[19] Already in the esterification step the advantages of this group were clear, in that treatment of the alcohol 8 with triethylamine and methanesulfinyl chloride[20] in dichloromethane at −50 °C gave a greater than 90% yield of the methanesulfinate 10 in under 10 min.

Treatment of the sulfinate ester 10 with lithium isopropenyl cyanocuprate in ether at −78 °C gave a 35% yield of the allene 11, 17% of the terminal allene 12, and a 46% recovery of alcohol 8. The origin of terminal (nonalkylated) allenes in this type of coupling reaction is thought to arise from hydrolysis of the proposed trivalent copper intermediate,[21] and longer reaction times are recommended to increase the yield of alkylated product; however, in our hands increased reaction times did not significantly change the product ratios. Removal of the two TBDMS protecting groups gave the hydroxy allene 13 which was identical to the natural material (^{1}H NMR, GC-MS, HPLC-UV, IR, and TLC).

Conclusion

The stereospecific synthesis of allene 13 in eight steps (7.4% overall yield) has been achieved. Investigations are now underway to make the synthesis enantiospecific by using a chiral ketene equivalent.

Experimental Section

Melting points were recorded in open capillaries and are uncorrected. ^{1}H and ^{13}C NMR spectra (δ) were recorded in $CDCl_3$ at 250 and 62.9 MHz, respectively, and the ^{1}H NOE experiments carried out at 360 MHz. All commercially available reagents were bought from Fluka AG and used without further purification.

(1*S,2*R**,5*S**)-1-Acetoxy-2,5-bis[(*tert*-butyldimethylsilyl)oxy]cyclohex-3-ene-1-carbonitrile (3).** (*E*,*E*)-1,4-bis-[(*tert*-butyldimethylsilyl)oxy]buta-1,3-diene[1] (1) (3.0 g, 9.5 mmol) and 1-acetoxy-1-cyanoethylene (2) (5 mL, Fluka) were placed in a glass tube, and the contents were degassed, and the tube was sealed. After being heated for 4 d at 110 °C the tube was opened. Unreacted dienophile was removed by distillation (65 °C (10 mmHg)). The brown residual oil was chromatographed on a silica column. Elution with hexane led to the recovery of unreacted diene. Further elution with toluene gave a mixture of the cycloadducts. Recrystallization from MeOH gave the title compound (3) (2.6 g, 65%) as colorless needles, mp 66–9 °C: IR (KBr) 1760 cm^{-1} (acetate); ^{1}H NMR 0.09 (6 H, s, SiMe), 0.13, 0.20 (2 × 3 H, s, SiMe), 0.90, 0.92 (2 × 9 H, s, *t*-Bu), 2.09 (3 H, s, C(O)Me), 2.46 (2 H, m), 4.22 (1 H, t, J = 6 Hz), 4.35 (1 H, d, J = 3.5 Hz), 5.58 (1 H, ddd, J = 1.5, 4, and 9 Hz), 5.79 (1 H, dd, J = 2 and 9 Hz); *m*/*e* 368 (5), 299 (3), 211 (25), 117 (25), 75 (45), and 73 (100). Anal. Calcd for $C_{21}H_{39}O_4Si_2N$: C, 59.26; H, 9.24; N, 3.29. Found: C, 59.26; H, 9.28; N, 3.29.

(1*S,2*S**,5*R**,6*R**)-3-Acetoxy-2,5-bis[(*tert*-butyldimethylsilyl)oxy]-7-oxabicyclo[4.1.0]heptane-3-carbonitrile (4).** A solution of cycloadduct (3) (5.0 g, 11.8 mmol), *m*-CPBA (4.0 g), and 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulphide (150 mg) in dichloroethane (100 mL, Aldrich) was heated under reflux. After 2 h further *m*-CBPA (1.5 g) was added, and reflux was continued for 1 h. The contents of the flask were then cooled, diluted with CH_2Cl_2, and washed in turn with solutions of Na_2SO_3, $NaHCO_3$, and brine. After the solution was dried over Na_2SO_4, the solvents were removed in vacuo to give a yellow crystalline solid which was adsorbed onto silica column. Elution with toluene gave, after crystallization from MeOH, the title compound 4 (4.5 g, 87%) as needles, mp 124–5 °C: IR (KBr) 1760 cm^{-1} (acetate); ^{1}H NMR 0.15, 0.18 (2 × 3 H, s, SiMe), 0.20 (6 H, s, SiMe), 0.97 (18 H, s, *t*-Bu), 1.78 (1 H, dd, J = 14 and 4 Hz), 2.09 (3 H, s, OAc), 2.62 (1 H, dd, J = 14 and 4 Hz), 3.21 (2 H, s), 4.12 (1 H, s), 4.27 (1 H, t, J = 7 Hz); ^{13}C NMR 168.44 (C=O acetate), 115.46 (CN), 73.61, 70.16, 64.46, 56.30, 55.39, 33.18, 25.62, 21.09, 18.07, 18.02, −4.71, −4.90, −6.81; *m*/*e* 426 (1), 384 (7), 117 (40), 73 (100). Anal. Calcd for $C_{21}H_{39}O_5Si_2N$: C, 57.11; H, 8.91; N, 3.17. Found: C, 56.84; H, 9.00; N, 3.31.

Reduction of 4 with Sodium Borohydride. To a solution of epoxide 4 (800 mg, 1.8 mmol) in EtOH (30 mL) was added $NaBH_4$ (700 mg) and the mixture was stirred at rt until GC indicated that all the starting material had been consumed (4 h). The reaction mixture was then quenched by the addition of a solution of NH_4Cl, diluted with H_2O, and extracted with Et_2O (×3). The organic extracts were dried over $MgSO_4$ and the solvents removed in vacuo to yield a colorless oil. Chromatography on a silica column eluting with toluene gave a mixture of **(1*S**,2*S**,3*S**,5*R**,6*R**)-** and **(1*S**,2*S**,3*R**,5*R**,6*R**)-2,5-bis[(*tert*-butyldimethylsilyl)oxy]-7-oxabicyclo[4.1.0]heptan-3-ols (5)** (410 mg, 1.09 mmol) as a colorless oil: IR (liq film) 3500, 1250, 830 cm^{-1}; ^{1}H NMR 0.13 (6 H, s, SiMe), 0.165, 0.17 (2 × 3 H, s, SiMe), 0.92, 0.95 (2 × 9 H, s, *t*-Bu), 1.72 (2 H, m), 3.13 (1 H, t, J = 3 Hz), 3.18 (1 H, d, J = 3 Hz), 3.67 (1 H, br m), 4.01 (1 H, d, J = 3 Hz), 4.12 (1 H, t, J = 4 Hz); *m*/*e* 317 (20), 225 (15), 157 (32), 117 (30), 75 (70), 73 (100); exact mass (EI) calcd for $C_{14}H_{29}O_4Si_2$ (M^+ − *t*-Bu) 317.1604, found (M^+ − *t*-Bu) 317.1601; IR (liquid film) 3500, 1255, 835 cm^{-1}; ^{1}H NMR 0.11 (6 H, s, SiMe), 0.16, 0.18 (2 × 3 H, s, SiMe), 0.92, 0.94 (2 × 9 H, s, *t*-Bu), 1.62 (2 H, m), 3.07 (2 H, br s), 3.69 (1 H, s), 3.71 (1 H, m), 4.32 (1 H, br s); *m*/*e* 317 (5), 185 (25), 147 (30), 75 (70), 73 (100); exact mass (EI) calcd for $C_{14}H_{29}O_4Si_2$ (M^+ − *t*-Bu) 317.1604, found (M^+ − *t*-Bu) 317.1605. Adding 1% Et_2O to the eluent gave a mixture of **(1*R**,2*S**,3*S**,5*R**,6*R**)-** and **(1*R**,2*S**,3*R**,5*R**,6*R**)-3,5-bis[(*tert*-butyldimethylsilyl)oxy]-7-oxabicyclo[4.1.0]heptan-2-ols (6)** first as a white crystalline solid (140 mg, 0.3 mmol), mp 73–74.5 °C [IR (liquid film) 3520, 1250, 835 cm^{-1}; ^{1}H NMR 0.08 (6 H, s, SiMe), 0.10, 0.11 (2 × 3 H, s, SiMe), 0.89, 0.91 (2 × 9 H, s, t-Bu), 1.6 (1 H, br m), 2.63 (1 H, s), 3.1 (1 H, d, J = 3 Hz), 3.40 (1 H, br s), 3.67 (1 H, dt, J = 12 and 4.5 Hz), 3.96 (1 H, dd, J = 10 and 7 Hz), 4.12 (1 H, br s); *m*/*e* 317 (12), 299 (12), 185 (25), 117 (60), 75 (90), 73 (100). Anal. Calcd for $C_{18}H_{38}O_4Si_2$: C, 57.72; H, 10.23. Found: C, 57.60; H, 10.28], and then as a colorless oil (90 mg, 0.24 mmol) [IR (liquid film) 3460, 1252, 835 cm^{-1}; ^{1}H NMR 0.84 (3 H, s, SiMe), 0.10 (6 H, s, SiMe), 0.12 (3 H, s, SiMe), 0.89, 0.92 (2 × 9 H, s, *t*-Bu), 1.54 (2 H, m), 3.01 (1 H, br s), 3.17 (1 H, d, J = 3 Hz), 3.63 (1 H, d, J = 8 Hz), 3.81 (1 H, m), 4.32 (1 H, br s); *m*/*e* 317 (4), 235 (10), 185 (25), 75 (70), 73 (100); exact mass (EI) calcd for $C_{14}H_{29}O_4Si_2$ (M^+ − *t*-Bu) 317.1604, found (M^+ − *t*-Bu) 317.1636].

(1*S,2*R**,5*R**,6*R**)-2,5-Bis[(*tert*-butyldimethylsilyl)oxy]-7-oxabicyclo[4.1.0]heptan-3-one (7).** To a solution of the mixture of alcohols 5 (410 mg, 1.09 mmol) in CH_2Cl_2 (20 mL) was added $CrO_3{\cdot}C_5H_5N$ complex (1.5 g) portionwise over 5 h. The reaction mixture was decanted from the insoluble residue, which was washed thoroughly with CH_2Cl_2. The washings were combined and washed with water (×3) and dried over $MgSO_4$ and the solvent removed in vacuo to give a brown oil which was adsorbed onto a silica column. Elution with toluene–hexane (70:30) gave the title compound 7 (310 mg, 0.83 mmol) as a white crystalline solid, mp 29–33 °C: IR (KBr) 1730 cm^{-1}; ^{1}H NMR 0.09 (6 H, s, SiMe), 0.12, 0.15 (2 × 3 H, s, SiMe), 0.88, 0.92 (2 × 9 H, s, *t*-Bu), 2.33 (1 H, dd, J = 14 and 4 Hz), 2.58 (1 H, dd, J = 14 and 4 Hz), 3.25 (1 H, t, J = 3 Hz), 3.33 (1 H, dt, J = 1 and 3 Hz), 4.25 (1 H, s), 4.64 (1 H, m); *m*/*e* 357 (2), 315 (47), 297 (19), 259 (9), 183 (11), and 73 (100). Anal. Calcd for $C_{18}H_{36}O_4Si_2$: C, 58.03; H, 9.75. Found: C, 58.17; H, 9.83.

(1*S,2*R**,3*R**,5*R**,6*R**)-2,5-Bis[(*tert*-butyldimethylsilyl)oxy]-3-ethynyl-7-oxabicyclo[4.1.0]heptan-3-ol (8).** Acetylene (20 mL) was introduced to a flask containing THF (30 mL) stirred at −78 °C by means of a gas-tight syringe. To this solution was added *n*-BuLi (0.3 mL of a 1.6 M solution) and the mixture stirred for 30 min. A solution of ketone 7 (100 mg, 0.26 mmol) in THF (5 mL) was added by means of a canula. The solution was stirred at −78 °C for 30 min and then allowed to warm to rt over 1 h. A solution of NH_4Cl was added, and the products were extracted into Et_2O (×3). The organic extracts were washed with brine and dried over $MgSO_4$. Removal of the solvents gave a colorless oil which was chromatographed on a silica column

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eluting with toluene–hexane (1:1) to give the title compound 8 (56 mg, 0.14 mmol), mp 64–66 °C: IR (KBr) 3400 cm^{-1}; ^1H NMR 0.155, 0.16 (2 × 3 H, s, SiMe), 0.21 (6 H, s, SiMe), 0.93, 0.97 (2 × 9 H, s, *t*-Bu), 1.805 (1 H, dd, J = 14 and 4 Hz), 2.08 (1 H, dd, J = 14 and 4 Hz), 2.40 (1 H, s), 3.14 (1 H, d, J = 3.5 Hz), 3.19 (1 H, d, J = 3.5 Hz), 3.86 (1 H, s), 4.17 (1 H, s, OH), 4.30 (1 H, br s); m/z 341 (10). Anal. Calcd for $C_{20}H_{38}O_4Si_2$: C, 60.27; H, 9.62. Found: C, 59.96; H, 9.56.

(1*S,2*R**,3*R**,5*R**,6*R**)-3-Acetoxy-2,5-bis[(*tert*-butyldimethylsilyl)oxy]-3-ethynyl-7-oxabicyclo[4.1.0]heptane (9).** To a mixture of Et_3N (3 mL), Ac_2O (1.5 mL), and DMAP (10 mg) was added the alcohol 8 (110 mg, 0.28 mmol). After being stirred at rt overnight the reaction mixture was diluted with Et_2O and washed in turn with solutions of dilute HCl, $NaHCO_3$, and brine. The organic extracts were dried over $MgSO_4$ and the solvent removed in vacuo to give a yellow oil. Chromatography gave the title compound **9**, mp 67–73 °C: IR (KBr) 1760 cm^{-1}; ^1H NMR 0.12, 0.14 (2 × 3 H, s, SiMe), 0.93, 0.94 (2 × 9 H, s, *t*-Bu), 2.00 (1 H, dd, J = 6 and 13 Hz), 2.01 (3 H, s, OAc), 2.42 (1 H, dd, J = 5.5 and 13 Hz), 2.50 (1 H, s), 3.15 (2 H, s), 4.15 (1 H, t, J = 6 Hz); m/e 383 (7), 341 (20), 323 (16), 147 (30), 117 (50), 73 (100); exact mass (EI) calcd for $C_{18}H_{31}O_5Si_2$ (M – *t*-Bu) 383.1710, found (M – *t*-Bu) 383.1741.

(1*S,2*R**,3*R**,5*R**,6*R**)-2,5-Bis[(*tert*-butyldimethylsilyl)oxy]-3-ethynyl-3-(methanesulfinoyl)-7-oxabicyclo[4.1.0]heptane (10).** To a stirred solution of the propargylic alcohol 8 (100 mg, 0.25 mmol) and Et_3N (0.5 mL) in dry CH_2Cl_2 (10 mL) at –50 °C was added methanesulfinyl chloride (0.4 mL). After 15 min the reaction mixture was diluted with further CH_2Cl_2 and washed in turn with solutions of 5% HCl, Na_2SO_4, and brine. The solvents were removed in vacuo after drying over $MgSO_4$ to give a diastereoisomeric mixture methanesulfinates **10** as a brown oil (110 mg, 0.24 mmol), which could be separated on a silica column eluting with CH_2Cl_2. First eluted: IR (CCl_4) 3310, 1258, 1147 cm^{-1}; ^1H NMR 0.11, 0.13 (2 × 3 H, s, SiMe), 0.19 (6 H, s, SiMe), 0.94, 0.96 (2 × 9 H, s, *t*-Bu), 1.93 (1 H, dd, J = 4 and 15 Hz), 2.25 (1 H, dd, J = 4 and 15 Hz), 2.64 (2 H, s, S(O)Me), 2.80 (1 H, s), 3.04 (1 H, d, J = 3.5 Hz), 3.17 (1 H, d, J = 3.5 Hz), 3.91 (1 H, s), 4.21 (1 H, br t, J = 4 Hz); m/e 403 (8), 381 (5), 323 (20), 137 (60), 73 (100). Second eluted: mp 125–6 °C; IR (CCl_4) 3310, 1259, 1151 cm^{-1}; ^1H NMR 0.13, 0.20 (2 × 6 H, SiMe), 0.92, 0.96 (2 × 9 H, s, *t*-Bu), 1.90 (1 H, dd, J = 5.5 and 13 Hz), 2.15 (1 H, dd, J = 5.5 and 13 Hz), 2.65 (3 H, s, S(O)Me), 2.79 (1 H, s), 3.15 (1 H, d, J = 3.5 Hz), 3.19 (1 H, d, J = 3.5 Hz), 4.02 (1 H, s), 4.20 (1 H, t, J = 5.5 Hz); m/e 403 (8), 381 (5), 323 (20), 137 (60), 73 (100). Anal. Calcd for $C_{21}H_{40}O_5SSi_2$: C, 54.76; H, 8.76. Found: C, 54.58; H, 8.85.

Reaction of Sulfinate Esters 10 with Organocuprate. To a stirred suspension of copper(I) cyanide (100 mg, 1.1 mmol) in Et_2O (10 mL) at –50 °C was added isopropenyllithium (2.2 mL of a 0.5 M ethereal solution). The mixture was allowed to stir at this temperature for 30 min and then added to a solution of sulfinate esters **10** (80 mg, 0.17 mmol) in Et_2O stirred at –50 °C. The reaction mixture was stirred at this temperature for 30 min then allowed to stir to rt over 2 h. Saturated NH_4Cl solution was added, the two phases were separated, and the aqueous phase was extracted with Et_2O (×2). The organic extracts were unified and dried over $MgSO_4$, and the solvents were removed in vacuo to give a yellow oil, separation on a preparative plate (toluene–hexane) gave, in order of migration, **(1*S**,2*S**,5*R**,6*R**)-2,5-bis[(*tert*-butyldimethylsilyl)oxy]-3-(3-methylbuta-1,3-dienylidene)-7-oxabicyclo[4.1.0]heptane (11)** (25 mg, 35%) as a colorless oil [IR (CCl_4) 1960 cm^{-1}; ^1H NMR 0.07 (3 H, s, SiMe), 0.10 (6 H, s, SiMe), 0.12 (3 H, s, SiMe), 0.91, 0.92 (2 × 9 H, s, *t*-Bu), 1.74 (3 H, br s), 2.25 (2 H, br m), 3.14 (2 H, br s), 3.97 (1 H, dd, J = 4.5 and 5 Hz), 4.50 (1 H, s), 4.84, 4.92 (2 × 1 H, br s, C=CH_2), 5.90 (1 H, s, C=C=CH); m/e 365 (8), 233 (25), 147 (80), 73 (100); exact mass calcd for $C_{19}H_{33}O_3Si_2$ (M^+ – *t*-Bu) 365.1968, found (M^+ – *t*-Bu) 365.1966], **(1*S**,2*S**,5*R**,6*R**)-2,5-bis[(*tert*-butyldimethylsilyl)oxy]-3-ethenylidene-7-oxabicyclo[4.1.0]heptane (12)** (11 mg, 17%) as a colorless oil [IR (CCl_4) 1965, 1257 cm^{-1}; ^1H NMR 0.08 (3 H, s, SiMe), 0.11 (6 H, s, SiMe), 0.12 (3 H, s, SiMe), 0.91, 0.92 (2 × 9 H, s, *t*-Bu), 2.24 (2 H, m), 3.13 (2 H, m), 3.99 (1 H, t, J = 8 Hz), 4.50 (1 H, s), 4.72 (2 H, br s, C=C=H_2); m/e 325 (20), 193 (23), 171 (25), 147 (100), 73 (75); exact mass (EI) calcd for $C_{16}H_{29}O_3Si_2$ (M^+ – *t*-Bu) 325.1655, found (M^+ – *t*-Bu) 325.1631], and the propargylic alcohol 8 (31 mg, 46%).

(1*R,2*S**,5*R**,6*S**)-2,5-Dihydroxy-3-(3-methylbuta-1,3-dienylidene)-7-oxabicyclo[4.1.0]heptane (13).** To a solution of allene 11 (12 mg, 0.03 mmol) in THF (5 mL) was added TBAF (50 mg, 0.16 mmol) and the mixture stirred for 1 h. The reaction mixture was diluted with Et_2O (15 mL) and washed with brine (2 × 10 mL); after the mixture was dried over $MgSO_4$ the solvents were removed in vacuo to give a colorless oil which was placed on a preparative plate. Development with chloroform–methanol (9:1) gave the title compound **13**[1] as a white amorphous solid (5 mg, 90%): IR (KBr) 3400, 1960 cm^{-1}; ^1H NMR 1.75 (3 H, s), 2.28 (1 H, dd, J = 4 and 15 Hz), 2.51 (1 H, dt J = 5 and 15 Hz), 3.32 (2 H, m), 4.32 (1 H, br s), 4.55 (1 H, s), 4.91 (1 H, s), 4.99 (1 H, s), 6.17 (1 H, s); m/e 194 (15), 175 (4), 161 (7), 147 (20), 133 (20), 121 (30), and 91 (100).

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