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.

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

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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

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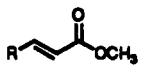
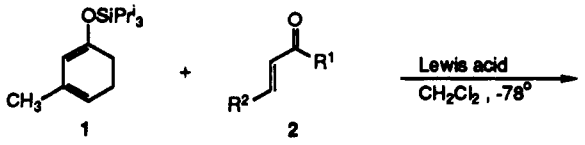
Table I. Endo/Exo Selectivity in Lewis Acid Catalyzed [4 + 2] Cycloaddition Reactions of 3-Methyl-1-(triisopropylsiloxy)-1,3-cyclohexadiene (1) with Various Dienophiles (See eq 1)

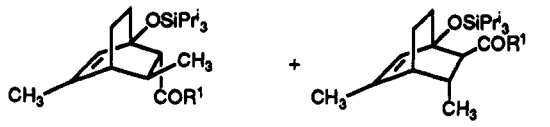
entry	R	equiv of Lewis Acid	endo:exo[a]	yield (%)[b]
				
1	OCH_3	0.25 $EtAlCl_2$	12.5:1	85
2	OCH_3	0.25 Et_2AlCl	8:1	85
3	OCH_3	0.25 $AlCl_3$	9:1	83
4	CH_3	1.5 $EtAlCl_2$	6:1	20
5	CH_3	1.5 Me_3Al	endo	33
6	oxazolidone	1.5 $EtAlCl_2$	2.3:1	31
7	oxazolidone	0.25 $EtAlCl_2$	2.6:1	75
8	CH_2OBn	1.5 Et_2AlCl	2.1:1	51
9	CH_2OBn	0.25 Et_2AlCl	1.7:1	62
10	H	1.0 Et_2AlCl	5.0:1	22
11	H	0.2 Et_2AlCl	1:1.9	41
12	H	1.5 Me_3Al	5.4:1	46
13	H	0.25 Me_3Al	1.75:1	42
14	H	1.5 $PhOAlMe_2$	1.5:1	51
				
15	CH_3	1.5 $EtAlCl_2$	1:1	76
16	CH_2Br	0.25 $EtAlCl_2$	5.6:1	71
17	CH_2OBn	1.5 Et_2AlCl	7:0	71
18		0.25 Et_2AlCl	-	0

[a] The ratios were obtained by ^1H NMR integrations of the vinyl hydrogens. [b] Isolated endo–exo mixtures using flash chromatography.

focus on the structural features of the dienophiles which influence the stereoselectivity of the cyclohexadiene/dienophile Diels–Alder reactions. The diene we have chosen for this study is 3-methyl-1-(triisopropylsiloxy)-1,3-cyclohexadiene (1).[4] Initial Diels–Alder reactions were carried out under thermal conditions in the absence of Lewis acid and resulted in low stereoselectivity. Thus, the Diels–Alder reactions in these studies were carried out under Lewis acid catalysis (eq 1). Extensive experimentation was performed with a variety of Lewis acids. Highest stereoselectivities were observed with aluminum Lewis acids. The stereoselectivity of these reactions are highly temperature sensitive. The reactions were carried out in a −78 °C bath, and the temperature of the reaction must be kept constant especially on the addition of substrate or reagent.



(1)

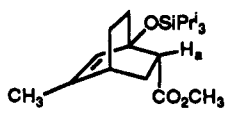


a, R^1=OCH_3, R^2=H
b, =CH_3, =H
c, =CH_2OBn, =H
d, =H, =H
e, =Oxazolidinone, R^2=H
f, R^1=OCH_3, R^2=CH_3
g, =OCH_3, =CH_2Br
h, =OCH_3, =CH_2OBn

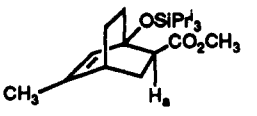
Table I summarizes the stereoselectivity of the corresponding reaction where the carbonyl activating group and the β-substituent were varied. Good stereoselectivities were obtained with methyl acrylate (entries 1–3), methyl vinyl ketone (entries 4 and 5), and acrolein (entries 10 and 12) with the proper choice of Lewis acids. However, only 2.3 and 2.6 to 1 endo selectivity was observed with acrylate carboximides (entries 6 and 7). Similar ratios were observed with (α-benzyloxy)methyl vinyl ketone (entries 8 and 9). The yields of these Diels–Alder reactions range from 85 to 20%, and the yields depend on the compatibility of the Lewis acid with the dienophile. For example, with acrolein 41–51% yields were obtained with mild Lewis acids such as trimethylaluminum and dimethylaluminum phenoxide (entries 12, 13, and 14) or catalytic amounts of stronger Lewis acids such as diethylaluminum chloride (entry 11). The weak Lewis acids, trimethylaluminum and dimethylaluminum phenoxide, successfully catalyzed the more reactive acrolein, but reaction with the less reactive dienophiles resulted in no reaction or gave complex reaction mixtures.

Good to excellent stereoselectivity was observed when R^2 of the methyl ester is a hydrogen, bromomethyl, or (benzyloxy)methyl group (entries 1–3, 16, and 17). However, when R^2 was a methyl group, the reaction was not stereoselective (entry 15).

Establishing that the reaction is a kinetic process, the endo adduct of methylacrylate was resubmitted to the reaction conditions. No exo isomer was observed. The ratio of endo to exo isomers was established on the basis of ^1H NMR spectral analysis.[5]



∂H_a = 2.75 ppm
J = 9.8, 5.9 Hz



∂H_a = 2.53 ppm
J = 11.4, 5.5, 1.9 Hz

With the exception of acrylate carboximide and (α-benzyloxy)methyl vinyl ketone, good stereoselectivites were observed with various carbonyl activators. The yields can also be in the excellent to acceptable range with properly

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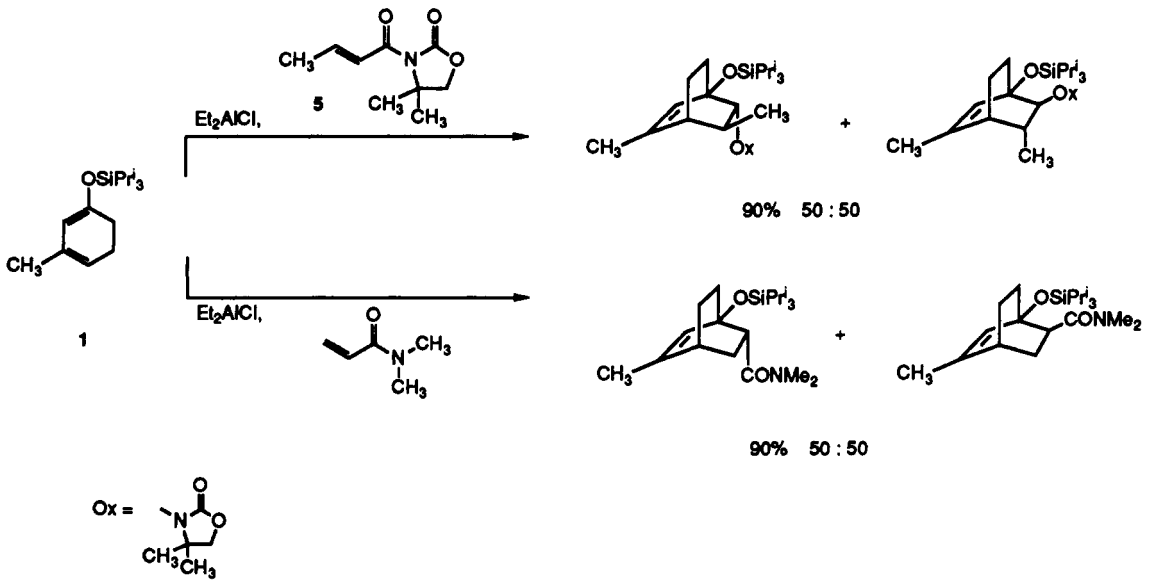
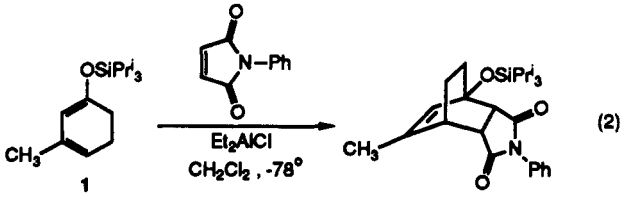
Scheme I



matched Lewis acids. The electron-withdrawing groups at the β-position, which increase the reactivity of the dienophile, also enhance the stereoselectivity. Following this trend *N*-phenylmaleimide gave complete endo selectivity (eq 2). This trend is in accord with the argument



(2)

that the electron-withdrawing group at the β-position can enhance the stabilizing secondary orbital interaction to give better endo selectivity.[6] The possibility that stereoselectivity was due to two different reacting conformations of the dienophile (s-cis or s-trans) was eliminated by investigating the Diels–Alder reactions of *N,N*-dimethylacrylamide and oxazolidinone **5**, which exist predominantly in the s-cis conformation (Scheme I).[7] Even with the single dienophile conformation, the reaction gave no selectivity. It has been shown that oxazolidinones undergo highly stereoselective Diels–Alder reactions with more reactive dienes,[8] but this is not the case with the less reactive cyclohexadiene **1**.

An interesting item to note is the stereoselectivity of dienophiles containing a second point of chelation (entries 6–9, Table I). The stereoselectivity of methyl vinyl ketone (entries 4 and 5) should be comparable to that of (α-benzyloxy)methyl vinyl ketone rather than the ratio observed.

In conclusion, we have shown that under proper conditions high stereoselectivities can be obtained in the Diels–Alder reactions of (triisopropylsiloxy)-1,3-cyclohexadiene with aldehydes, ketones, and ester dienophiles.

Experimental Section

General. CH_2Cl_2 was distilled from CaH_2 at atmospheric pressure. The Lewis acids were purchased from Aldrich Chemical Co. or Texas Alkyl. TLC and column chromatography were done with E. Merk silica gel. All reactions were run under argon or nitrogen atmosphere, and concentrations were performed under reduced pressure with a rotary evaporator. The purity of all title compounds was judged to be >97% by capillary GC and ^1H NMR determinations.

The general procedure for the Diels–Alder reactions is represented by the following case. All products were obtained as colorless liquids.

Methyl 5-Methyl-1-(triisopropylsiloxy)bicyclo[2.2.2]-oct-5-ene-2-carboxylate (*endo*-3a and *exo*-4a) Using 0.25 Equiv of Ethylaluminum Dichloride. To a stirred solution of ethylaluminum dichloride (0.30 mL of 25% in heptane, 0.46 mmol) in 11.5 mL of CH_2Cl_2 at −78 °C was added freshly distilled methyl acrylate (0.25 mL, 2.8 mmol). Twenty minutes later diene **1** (0.50 g, 1.88 mmol) was added dropwise in 0.5 mL of CH_2Cl_2. After 90 min, the reaction was quenched with 10 mL of saturated $NaHCO_3$ solution and warmed to room temperature. The layers were separated, and the aqueous phase was extracted (3 × 10 mL CH_2Cl_2). The combined organic phases were dried (Na_2SO_4) and concentrated. Flash chromatography (SiO_2, 1:1 hexanes–ether) gave 0.56 g (85%) products as a colorless oil. ^1H NMR integration shows an endo:exo ratio of 12.5:1. Analytical samples of *endo*-**3a** and *exo*-**4a** were prepared by flash chromatography.

endo-**3a**: R_f = 0.57 (SiO_2, 4:1 hexanes–ether); ^1H NMR (250 MHz, $CDCl_3$) δ 5.77 (1 H, s, H-6), 3.59 (3 H, s, CH_3O), 2.75 (1 H, dd, J = 9.8, 5.9 Hz, H-2), 2.29 (1 H, br s, H-4), 1.83 (3 H, d, J = 1.5 Hz, CH_3-5), 1.75–1.90 (1 H, m), 1.2–1.8 (5 H, m), 1.05 (18 H, br s, $(CH(CH_3)_2)_3$), 0.9–1.1 (3 H, m); ^{13}C NMR (63 MHz, $CDCl_3$) δ 175.7, 140.1, 129.0, 77.5, 51.3, 51.0, 36.2, 35.1, 33.0, 25.2, 20.1, 17.9, 13.6; IR (CCl_4) 2943, 2865, 1736, 1199, 875 cm^{-1}; MS (CI, isobutane) m/e 353 (MH^+, 100), 309 (78), 106 (49).

exo-**4a**: R_f = 0.67 (SiO_2, 4:1 hexanes–ether); ^1H NMR (250 MHz, $CDCl_3$) δ 5.86 (1 H, s, H-6), 3.62 (3 H, s, CH_3O), 2.53 (1 H, ddd, J = 11.4, 5.5, 1.9 Hz, H-2), 2.25 (1 H, m, H-4), 1.76 (3 H, d, J = 1.6 Hz, CH_3-5), 1.04 (18 H, br s, $(CH(CH_3)_2)_3$), 0.8–1.9 (m, 9 H); ^{13}C NMR (63 MHz, $CDCl_3$ δ 175.8, 141.4, 131.8, 77.1, 51.4, 50.3, 35.3, 30.8, 29.9, 25.9, 20.2, 18.4, 13.15; IR (CCl_4) 2959, 1730, 1346, 1188, 1158 cm^{-1}; MS (EI) m/e 352 (M^+, 18), 309 (100), 266 (40), 224 (22).

5-Methyl-2-(1-oxoethyl)-1-(triisopropylsiloxy)bicyclo-[2.2.2]oct-5-ene (*endo*-3b): ^1H NMR (360 MHz, $CDCl_3$) δ 5.74 (1 H, s), 2.88 (1 H, dd, J = 6 Hz, 10 Hz), 2.29 (1 H, s); ^{13}C NMR (90 MHz, $CDCl_3$) δ 211.07, 140.48, 128.56, 77.54, 58.05, 36.43, 34.86, 31.51, 24.98, 19.87, 18.35, 17.88, 13.41; IR (neat) 1709, 1720 cm^{-1}. Anal. Calcd: C, 71.37; H, 10.78. Found: C, 71.25; H, 10.72.

2-(2-(Benzyloxy)-1-oxoethyl)-5-methyl-1-(triisopropylsiloxy)bicyclo[2.2.2]oct-5-ene (*endo*-3c, *exo*-4c). *endo*-**3c**: ^1H NMR (360 MHz, $CDCl_3$) δ 7.34 (5 H, m), 5.69 (1 H, s), 4.56 (2 H, s), 4.35 (1 H, d, J = 18 Hz), 4.09 (1 H, d, J = 18 Hz), 2.87 (1 H, dd, J = 6 Hz, 9 Hz), 2.31 (1 H, s), 1.81 (3 H, s), 1.75–1.35 (6 H, m), 1.03 (21 H, s); ^{13}C NMR (90 MHz, $CDCl_3$) δ 208.79, 140.87,

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137.69, 128.26, 128.10, 127.87, 127.63, 77.63, 76.00, 75.96, 53.84, 36.14, 34.83, 31.41, 25.13, 19.06, 12.37; IR (neat) 1730 cm^{-1}. Anal. Calcd: C, 73.25; H, 9.56. Found: C, 73.14; H, 9.48.

exo-**4c**: ^1H NMR (360 MHz, $CDCl_3$) δ 7.35 (5 H, m), 5.84 (1 H, s), 4.58 (2 H, s), 4.44 (1 H, d, J = 18 Hz), 4.09 (1 H, d, J = 18 Hz), 2.69 (1 H, dd, J = 6 Hz, 9 Hz), 2.28 (1 H, s), 1.77 (3 H, s), 1.75–1.29 (6 H, m), 1.03 (2 H, s); ^{13}C NMR (90 MHz, $CDCl_3$) δ 209.70, 141.84, 137.66, 131.29, 128.56, 128.35, 127.97, 127.74, 77.69, 73.15, 52.33, 35.05, 31.57, 29.77, 25.36, 18.39, 13.40; IR (neat) 1730 cm^{-1}.

5-Methyl-1-(triisopropylsiloxy)bicyclo[2.2.2]oct-5-ene-2-carboxaldehyde (*endo*-3d, 4d). *endo*-**3d**: R_f = 0.71 (SiO_2, 2:1 hexanes–ether); ^1H NMR (300 MHz, $CDCl_3$) δ 9.65 (1 H, d, J = 2.9 Hz, CHO), 5.79 (1 H, s, H-6), 2.62 (1 H, m, H-2), 2.34 (1 H, br s, H-4), 1.79 (3 H, d, J = 1.4 Hz, CH_3), 1.18–1.45 (6 H, m), 104 (21 H, s, $Si(C_3H_7)_3$); IR (neat) 1724.0 cm^{-1}; MS (CI, positive ion) m/e (323 (MH^+, 100), 279 (M – C_3H_7, 8); MS (EI) m/e 322.2351 (322.2378 calcd for $C_{19}H_{34}O_2Si$). Anal. Calcd: C, 70.75; H, 10.62; Found: C, 70.56, H, 10.61.

exo-**4d**: R_f = 0.71 (SiO_2, 2:1 hexanes–ether); ^1H NMR (300 MHz, $CDCl_3$) δ 10.05 (1 H, d, J = 1.4 Hz, CHO), 5.92 (1 H, s, H-6), 2.53 (1 H, ddd, J = 9.0, 2.1, 4.3 Hz, H-2), 2.29 (1 H, br s, H-4), 2.01 (1 H, ddd, J = 13.1, 2.3, 2.4 Hz, H-3), 1.79 (3 H, d, J = 1.4 Hz, -CH_3), 1.74 (1 H, td, J = 11.6, 2.8 Hz), 1.58 (1 H, m), 1.5–1.3 (3 H, m), 1.08 (21 H, s, $Si(C_3H_7)_3$); IR (neat) 1721.4 cm^{-1}; MS (CI) m/e 323 (MH^+, 100), 279 (M – isopropyl, 20); MS (EI) m/e 322.2306 (322.2328 calcd for $C_{19}H_{34}O_2Si$), 279.1768 (M – C_3H_7).

***N*-[[5-Methyl-1-(triisopropylsiloxy)bicyclo[2.2.2]oct-5-en-2-yl]carbonyl]-2-oxazolidinone (3e and 4e).** *endo*-**3e**: R_f = 0.68 (SiO_2, ether); R_f = 0.35 (SiO_2, 1:2 hexanes–ether); ^1H NMR (250 MHz, $CDCl_3$) δ 5.79 (1 H, s, H-6), 4.3 (2 H, m, OCH_2), 3.94 (2 H, t, J = 8.03 Hz, NCH_2), 2.31 (1 H, br s, H-4), 191 (1 H, ddd, J = 3.0, 10.0, 12.4 Hz), 1.82 (3 H, d, J = 1.1 Hz, CH_3), 1.75 (1 H, m), 1.64 (1 H, m), 1.55–1.35 (2 H, m), 1.03 (21 H, s, Si $(C_3H_7)_3$), 1.95 (2 H, m); IR ($CHCl_3$) 1779.4, 17005 cm^{-1}; MS (CI, positive ion) m/e 408 (MH^+, 100), 364 (M – isopropyl, 5); MS (EI) m/e 407.2515 (407.24916 calcd for $C_{22}H_{37}NO_4Si$, 9.2), 364.1948 (M – C_3H_7, 100).

exo-**4e**: R_f = 0.85 (SiO_2, ether); R_f = 0.44 (SiO_2, 1:2 hexanes–ether); ^1H NMR (250 MHz, $CDCl_3$) δ 5.93 (1 H, s, H-6), 4.3 (2 H, m, OCH_2), 4.02 (2 H, m, NCH_2), 2.30 (2 H, br s, H-4, H-2), 1.78 (3 H, d, J = 1.6 Hz, CH_3), 1.66 (2 H, m), 1.5–1.2 (2 H, m), 1.04 (21 H, s, $Si(C_3H_7)_3$), 1.95 (2 H, m); IR (neat) 1760.4, 1693.3 cm^{-1}.

Methyl 3,5-Dimethyl-1-(triisopropylsiloxy)bicyclo-[2.2.2]oct-5-ene-2-carboxylates (3f, 4f). *endo*-**3f**: R_f = 0.60 (SiO_2, 4:1 hexanes–ether); ^1H NMR (300 MHz, $CDCl_3$) δ 5.74 (1 H, s, H-6), 3.60 (3 H, s, CH_3), 2.20 (1 H, d, J = 6.6 Hz, H-2), 1.94 (1 H, br s, H-4), 1.82 (3 H, d, 1.3 Hz, CH_3), 1.80 (1 H, m, H-3), 1.57 (1 H, dt, J = 3.9, 10.9 Hz), 1.45 (1 H, dt, J = 4.3, 11.17 Hz), 1.25 (2 H, m), 1.03 (24 H, s, CH_3, $Si(C_3H_7)_3$); IR (neat) 1740.7 cm^{-1}; MS (EI) m/e 366.2570 (366.2590 calcd for $C_{21}H_{38}O_3Si$), 323.2029 (322.2042 calcd for M – C_3H_7).

exo-**4f**: R_f = 0.67 (SiO_2, 4:1 hexanes–ether); ^1H NMR (300 MHz, $CDCl_3$) δ 5.86 (1 H, br s, H-6), 3.64 (3 H, s, OCH_3), 2.23 (1 H, dt, J = 3.1, 10.3 Hz, H-4), 2.05 (3 H, m, H-2, H-3), 1.79 (3 H, d, J = 1.4 Hz, CH_3), 1.73 (1 H, tdd, J = 10.4, 1.5, 3.8 Hz), 1.37 (1 H, tt, J = 12.0, 3.5 Hz), 1.22 (1 H, m), 1.08 (21 H, s, $SiC_3H_7)_3$), 0.85 (3 H, d, J = 6.34 Hz, CH_3); IR (neat) 1734.4 cm^{-1}; MS (EI) m/e 366.2614 (366.2590 calcd for $C_{21}H_{38}O_3Si$).

Methyl 3-(Bromoethyl)-5-methyl-1-(triisopropylsiloxy)-bicyclo[2.2.2]oct-5-ene-2-carboxylates (3g and 4g). *endo*-**3g**: R_f = 0.39 (SiO_2, 4:1 hexanes–ether); ^1H NMR (250 MHz, $CDCl_3$) δ 5.78 (1 H, s, H-6), 3.62 (3 H, s, OCH_3), 3.48 (1 H, dd, J = 7.4, 10.1 Hz, CHBr), 3.33 (1 H, dd, J = 8.6, 10.1 Hz, CHBr), 2.40 (2 H, br s, H-4), 2.31 (1 H, d, J = 6.6 Hz, H-2), 2.22 (1 H, m, H-3), 1.86 (3 H, d, J = 1.6 Hz, CH_3), 1.70 (1 H, m), 1.55 (2 H, d-quintet, J = 4.7, 11.7 Hz), 1.30 (1 H, m), 1.04 (21 H, br s, $Si(C_3H_7)_3$); IR (neat) 2946, 2858, 1737 cm^{-1}; MS (CI) m/e 447 (MH^+, 100), 445 (Br – isotope, 96.8); MS (EI) m/e 446 (M^+, 8.3, 403 (M – C_3H_7, 100), 401 (Br – isotope, 100).

exo-**4g**: R_f = 0.46 (SiO_2, 4:1 hexanes–ether); ^1H NMR (250 MHz, $CDCl_3$) δ 5.92 (1 H, s, H-6), 3.67 (3 H, s, OCH_3), 3.08 (2 H, d of AB quartet, J = 8.1 Hz, J_{AB} = 9.8 Hz, ν_{AB} = 11.6 Hz, CH_2Br), 2.49 (1 H, br s, H-4), 2.44 (1 H, m, H-3), 2.18 (1 H, dt, J = 3.7, 10.7 Hz), 2.13 (1 H, dd, J = 2.0, 5.6 Hz), 1.81 (3 H, d, J = 1.6 Hz, CH_3), 1.79 (1 H, m), 1.44 (1 H, tt, J = 3.5, 12.3 Hz, H-8), 1.26 (1 H, m), 1.05 (21 H, br s, $Si(C_3H_7)_3$); MS (CI, a positive ion) m/e 447 (MH^+, 100), 445 (Br – isotope, 97.4), 403 (M – C_3H_7, 16.2), 401 (Br – isotope, 15.1); MS (EI) m/e 446 (M^+, 8.2), 444 (Br – isotope, 8.2), 403 (M – C_3H_7, 100), 401 (Br – isotope, 98.7).

Methyl 3-[(Benzyloxy)methyl]-5-methyl-1-(triisopropylsiloxy)bicyclo[2.2.2]oct-5-ene-2-carboxylates (3h and 4h). *endo*-**3h**: R_f = 0.41 (SiO_2, 4:1 hexanes–ether); ^1H NMR (250 MHz, $CDCl_3$) δ 7.33 (5 H, m, Ph), 5.79 (1 H, s, H-6), 4.50 (2 H, AB q, ν_{AB} = 13.0 Hz, J_{AB} = 12.1 Hz), 3.59 (3 H, s, OCH_3), 3.50 (1 H, dd, J = 6.8, 9.4 Hz, CHO), 3.40 (1 H, t, J = 8.9 Hz, CHO) 2.33 (1 H, br s, H-4), 2.27 (1 H, d, J = 6.7 Hz, H-2), 2.14 (1 H, qt, J = 8.2, 1.6 Hz, H-3), 1.85 (3 H, d, J = 1.5 Hz, (1 H, td, J = 11.03, 4.32 Hz, H-7), 1.25 (1 H, m, H-8), 1.04 (21 H, br s, $Si(CH_3H_7)_3$); IR (neat) 2925, 2860, 1740 cm^{-1}; MS (CI, positive ion) m/e 473 (MH^+, 100), 429 (M^+ – C_3H_7, 20); MS (EI) m/e 472.2993 (472.3009 calcd for $C_{28}H_{44}O_4Si$).

exo-**4h**: R_f = 0.51 (SiO_2, 4:1 hexanes–ether); ^1H NMR (250 MHz, $CDCl_3$) δ 7.32 (5 H, m, H-6), 4.45 (2 H, AB q, ν_{AB} = 11.7 Hz, J_{AB} = 12.1 Hz, OCH_2Ph), 3.64 (3 H, s, CH_3), 3.10 (2 H, d, J = 7.5 Hz, CH_2O), 2.39 (1 H, br s, H-4), 2.33 (1 H, dq, J = 3.9, 10.9 Hz, H-3), 2.07 (1 H, d, J = 4.9 Hz, H-2), 1.79 (1 H, m, H-7), 1.76 (3 H, d, J = 1.6 Hz, =CH_2), 1.40 (1 H, m, H-7), 1.26 (2 H, m, H-8), 1.05 (21 H, br s, $Si(C_3H_7)_3$); IR (neat) 2950, 2870, 1730 cm^{-1}; MS (CI, isobutane) m/e 473 (MH^+, 100) 429 (M^+ – C_3H_7, 21); MS (EI) m/e 472.3019 (472.3009 calcd for $C_{28}H_{44}O_4Si$).

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Supplementary Material Available: ^1H NMR spectra for **3a–h**, **4a**, and **4d–h** (14 pages). Ordering information is given on any current masthead page.

Synthesis and Molecular Structure of Two New Crystalline 6,8-Dioxabicyclo[3.2.1]octanes

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The ever-growing number of natural products possessing the 6,8-dioxabicyclo[3.2.1]octane skeleton[1-4] spurs a con-

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