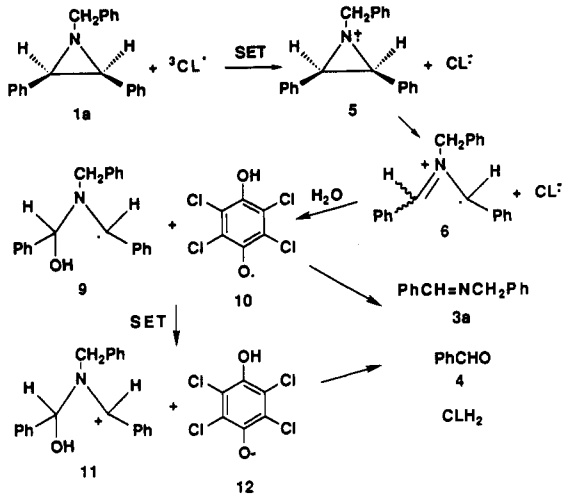
Scheme II



tonation–addition, which can compete with return to the aziridine ground state.

In contrast to the DCA-sensitized photoreactions, the photoreaction of **1a** and CL produced **3a**, **4**, and CLH_2. The overall reaction mechanism proposed for the CL processes is shown in Scheme II. The lack of formation of **2a** suggests that, in this case, the reaction **6** with H_2O to form **9** is faster than BET to form **7**. Slow BET in triplet ion radical pairs such as **6** and the CL anion radical is consistent with the above observation. Thus, the small effect of $LiClO_4$ on the product yields in the CL case can be radionalized by the rapid fragmentation of **6**, which is assisted by the combination of the CL anion radical and H_2O in the triplet-ion radical pair. In the ion radical pair, protonation of the basic CL anion radical by H_2O would occur.[10] This protonation assists the nucleophilic addition of H_2O to **6**. Then, fragmentation of the formed free radical **9**, assisted by hydrogen abstraction by **10**, gives **3a**, **4**, and CLH_2. Alternatively, SET from **9** to **10** followed by fragmentation of **11** involving ptoton transfer to **12** can also produce the observed compounds.

Summary

We have found that the photoinduced electron-transfer reaction of 1-substituted 2,3-diphenylaziridines **1** with DCA affords secondary amines and benzaldehyde, and the reaction of **1** with CL gives imines and benzaldehyde. The release of aziridine ring strain drives rapid bond cleavage of the cation radicals and may overcome the relatively lower electron-donating ability of azirizines compared to amines.[11] The results obtained in this study and related studies[2,3,12] indicate that aziridines should be reactive substances in other chemical or biological electron-transfer reactions.

Experimental Section

General Procedures.[13] 9,10-Dicyanoanthracene and chloranil were sublimed before use. Methylene chloride was distilled from calcium hydride after being treated with sulfuric acid, aqueous sodium hydroxide, and calcium chloride. Acetonitrile was distilled first from phosphorus pentoxide and then from calcium hydride. Aziridines **1a** and **1b** were prepared in three steps from *trans*-stilbene oxide.[14] **1a**: mp 56–56.5 °C (lit.[15] mp 52.5–53.5 °C); ^1H NMR ($CDCl_3$) δ 3.03 (s, 2 H), 3.85 (s, 2 H), 7.00–7.40 (m, 15 H). **1b**: mp 97–98 °C (lit.[16] 92–93 °C); ^1H NMR ($CDCl_3$) δ 1.15 (s, 9 H), 3.14 (2 H, s), 7.02–7.18 (m, 10 H).

Photolyses were performed in Pyrex tubes in a water bath with a 500-W Xe–Hg lamp with glass cut-off filters (Toshiba L-39 for DCA, Toshiba UV-37 for CL). The photoproducts were identified by direct comparison of their ^1H NMR spectra with those of authentic samples.

DCA-Sensitized Photoreactions of 1. Aziridine **1** (0.10–0.11 mmol) was dissolved in 3 mL of a methylene chloride or an acetonitrile solution of DCA ($4.0–4.4 \times 10^{-4}$ M). The appropriate additive (H_2O, 0.1 mL; MeOH, 0.1 mL; $LiClO_4$, 0.53 mmol) was added if necessary, and then the solution was purged with nitrogen or oxygen for 15 min. Then, the solution was irradiated ($\lambda > 360$ nm). Concentration of the photolysate at ambient temperature afforded a residue, which was subsequently analyzed by ^1H NMR with triphenylmethane as an internal standard.

Deuterium-Labeling Experiments in DCA-Sensitized Photoreactions of 1a in Methylene Chloride. D_2O (99.8% D, 0.1 mL) or MeOD (99.5% D, 0.1 mL) was added to a methylene chloride (3 mL) solution of **1a** (0.17–0.18 mmol) and DCA (0.0013 mmol). This solution was purged with nitrogen and irradiated for 40 min. the photolysate was extracted with 1 N HCl. The aqueous layer was basified with 2 N NaOH and subsequently extracted with methylene chloride. The extract was dried over anhydrous Na_2SO_4 and concentrated. Then, the ratio of the ^1H NMR peak integration of the aromatic protons to the benzylic protons of dibenzylamine was obtained. Ratios for D_2O and MeOD reactions were 3.4 and 3.3, respectively. In control experiments, H_2O or MeOH was added to the solution before irradiation, and D_2O or MeOD was added to the photolysate before workup. Ratios for these experiments were about 2.6.

Photoreactions of 1a with CL. **1a** (0.10–0.11 mmol), CL (0.054 mmol), and the additive were dissolved in 3 mL of methylene chloride or acetonitrile. This solution was purged with nitrogen for 15 min and then irradiated ($\lambda > 340$ nm) for 15 min. The product yields were obtained by ^1H NMR after concentration of the photolysate.

To isolate tetrachlorohydroquinone, a methylene chloride (11 mL) solution of **1a** (0.48 mmol) and CL (0.48 mmol) was purged with nitrogen and then irradiated for 60 min. Concentration of the phoyolysate was followed by the addition of chloroform. The solid obtained by filtration was identified as tetrachlorohydroquinone by comparing the IR spectrum of the product with that of an authentic sample.[17] The filtrate was concentrated and analyzed by ^1H NMR. The conversion of **1a** was 81%, and the yields of tetrachlorohydroquinone, **3a**, and **4** were 66%, 71%, and 60%, respectively.

(10) It is reported that quinone anion radicals are more basic than the DCA anion radical. Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1986**, *108*, 7356.

(11) We have briefly explored DCA-sensitized photoreactions of tribenzylamine in acetonitrile. However, more than 90% of the tribenzylamine was recovered (60-min irradiation) even though the electron-donating ability of tribenzylamine (E_p^{ox} = 1.17 V)[5] is much higher than that of **1a**.

(12) (a) Gassman, P. G.; Nishiguchi, I.; Yamamoto, H. *J. Am. Chem. Soc.* **1975**, *97*, 1600. (b) Kossai, R.; Simonet, J. *Tetrahedron Lett.* **1980**, *21*, 3575.

(13) See general procedures in ref 9d.

(14) Huisgen, R.; Matsumoto, K. Ross, C. H. *Heterocycles* **1981**, *15*, 1131.

(15) Loeppky, R. N.; Smith, D. H. *J. Org. Chem.* **1976**, *41*, 1578.

(16) Bartnik, R.; Mloston, G. *Synthesis* **1983**, 924.

(17) Ramirez, F.; Dershowitz, S. *J. Am. Chem. Soc.* **1956**, *78*, 5614.

A Cyclic Sulfate Route to Methylenecyclopropanes

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Hypoglycine A, an unusual amino acid, (+)-α-amino-2-methylenecyclopropanepropionic acid (**1**), found in the unripe ackee fruit (*Blighia sapida*), has been implicated in the Jamaican vomiting sickness.[1] The actual causative

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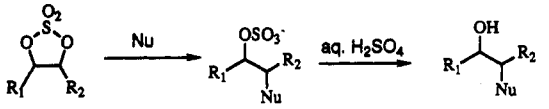
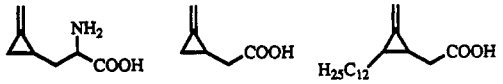
Scheme I



Nu = H^-, N_3^-, F^-, $RCOO^-$, NO_3^-, SCN^-

agent of the sickness has been identified to be methylenecyclopropaneacetic acid, **2**, resulting from metabolic degradation of hypoglycine A, involving enzymatic transdeamination to methylenecyclopropanepyruvic acid followed by oxidative decarboxylation to (*R*)-2-methylenecyclopropaneacetic acid, **2**.[2] The toxicity of **2** has been shown to stem from the inactivation of the flavin-dependent general acyl-CoA dehydrogenase resulting from the irreversible, covalent binding to flavin adenosine dinucleotide. Biological studies at Sandoz using substituted methylenecyclopropaneacetic acids have shown that the dodecyl-substituted **3** is of particular interest.[3] We report here an efficient synthesis of the enantiomers of **3** using 1,2-cyclic sulfates.



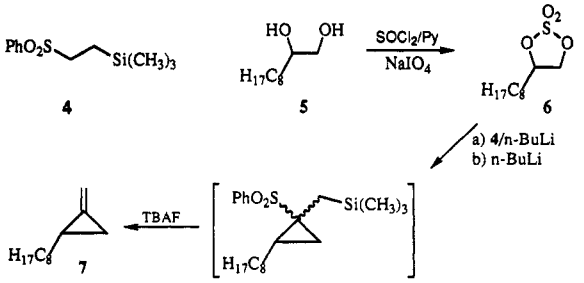
1 **2** **3**

Sharpless et al. have recently demonstrated a nucleophilic ring opening reaction of vicinal diol-derived cyclic sulfates with several nucleophiles[4] (Scheme I) including diethyl malonate. The synthesis of substituted aziridines was also reported recently via 1,2-cyclic sulfates.[5] In connection with the synthesis of enantiomers of **3**, it occurred to us that a double displacement of the sulfate moiety in 1,2-cyclic sulfates using β-(trimethylsilyl)ethyl phenyl sulfone,[6] **4**, followed by the elimination of the silyl and sulfone groups should lead to an efficient synthesis of methylenecyclopropanes. Since the reaction is stereospecific, enantiopure cyclic sulfates would give enantiopure methylenecyclopropanes. The usefulness of **4** in the synthesis of methylenecyclopropanes from epoxides has been demonstrated earlier.[6,7]

At the outset we tested the above strategy using the commerically available decane-1,2-diol **5** (Scheme II). The desired cyclic sulfate **6** was readily obtained in 90% yield from the reaction of **5** with thionyl chloride followed by oxidation with $NaIO_4$ using the procedure of Sharpless.[4] Sulfate **6** underwent facile double nucleophilic displacement on treatment with the lithium salt of β-(trimethylsilyl)ethyl phenyl sulfone followed by the addition of another equivalent of *n*-BuLi; the crude mixture on treatment with tetra-*n*-butylammonium fluoride gave the desired methylenecyclopropane **7** in an overall yield of 74%.

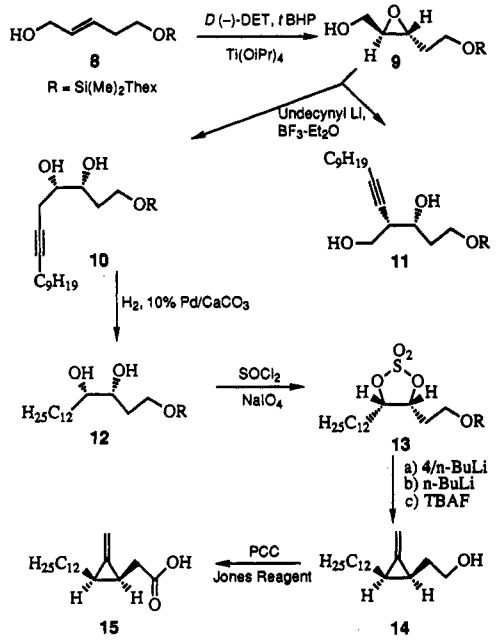
Next, we turned our attention to the synthesis of enantiomers of **3**. The optically pure *erythro*-1,2-diol **10**, which is the key intermediate in the present approach, was made in two steps from olefin **8** (Scheme III). Thus Sharpless epoxidation[8] of the trans-olefinic alcohol **8**[9] using

Scheme II



4 **5** **6** **7**

Scheme III



8 **9** **10** **11** **12** **13** **14** **15**

diethyl D-(−)-tartrate afforded the (2*R*,3*R*)-epoxy alcohol **9** in 78% chemical yield and 96% optical purity.[10] Subjecting **9** to an excess of undecynyllithium in the presence of boron trifluoride etherate[12] in THF at −78 °C led to two regioisomeric products, **10** and **11**, in ~4:1 ratio, from which the desired product **10** (resulting from the attack of the nucleophile at C(1) of the epoxide derived from Payne rearrangement of **9**) was isolated in 75% yield by flash chromatography. Hydrogenation of **10** was carried out in the presence of Pd–$CaCO_3$ to give the diol **12** in 85% yield. Conversion of **12** to the cyclic sulfate **13** was carried out using the literature procedure[4] in 91% yield. Reaction of **13** with the anion derived from **4** at −78 °C to rt, followed by the addition of another equivalent of *n*-BuLi(−78 °C to rt) and refluxing the reaction mixture with tetra-*n*-butylammonium fluoride, gave (methylenecyclopropanyl)ethanol **14**, in 36% yield. Oxidation of **14** to the carboxylic acid **15** was carried out in a two-step process, first with pyridinium chlorochromate over molecular sieves

(1) Lai, M.-T.; Liu, L.-D.; Liu, H.-W. *J. Am. Chem. Soc.* **1991**, *113*, 7388–7397 and references therein.

(2) (a) Von Holt, C. *Biochim. Biophys. Acta* **1966**, *125*, 1–21. (b) For a optically active synthesis of **2**, see: Lai, M.-T.; Oh, E.; Shih, Y.; Liu, H.-W. *J. Org. Chem.* **1992**, *57*, 2471–2676.

(3) Unpublished results, Sandoz Research Institute, East Hanover, NJ 07936.

(4) Gao, Y.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 7538–7539.

(5) Lohray, B. B.; Gao, Y.; Sharpless, K. B. *Tetrahedron Lett.* **1989**, *30*, 2623–2626.

(6) Hsiao, C.-N.; Shechter, H. *J. Org. Chem.* **1988**, *53*, 2688–2699.

(7) (a) Hsiao, C.-N.; Hannick, S. M. *Tetrahedron Lett.* **1990**, *31*, 6609–6612. (b) Kabat, M. M.; Wicha, J. *Tetrahedron Lett.* **1991**, *32*, 531–532.

(8) Johnson, R. A.; Sharpless, K. B. Addition reactions with formation of carbon–oxygen bonds: (ii) Asymmetric methods of epoxidation. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Ley, S. V., Eds.; Pergamon Press: New York, 1991; Vol. 7, p 389.

(9) Olefin **8** was prepared from 3-butyn-1-ol via silylation (dimethylthexylchlorosilane, NEt_3, DMAP, CH_2Cl_2), hydroxymethylation (*n*-BuLi, paraformaldehyde, THF, 0 °C, cf. *Preparative Acetylenic Chemistry*, 2nd ed.; Brandsma, L., Ed.; Elsevier: New York, 1988; p 81) followed by reduction (Red-Al (Aldrich), toluene, ether, 0 °C; cf. Jones, T. K.; Denmark, S. E. *Org. Synth.* **1985**, *64*, 182–188).

(10) Optical purities of the epoxy alcohol **9** and its enantiomer were determined by ^{31}P NMR spectroscopic technique described in ref 11.

(11) Alexakis, A.; Mutti, S.; Normant, J. F.; Manganey, P. *Tetrahedron Asym.* **1990**, *1*, 437–440.

(12) Yamaguchi, M.; Hirao, I. *J. Chem. Soc., Chem. Commun.* **1984**, 202–203.

and Celite followed by Jones reagent, in an overall 65% yield.

Similar sequence of reactions using L-(+)-tartrate in the Sharpless epoxidation, gave the other enantiomer of **15**. The somewhat higher ee (99%, see the Experimental Section) of the Sharpless epoxidation may be due to higher optical purity of the natural tartrate.

Experimental Section

^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, in $CDCl_3$. IR spectra were recorded as film enclosed between sodium chloride plates. Undecyne was obtained from Farchan Laboratories, and the other chemicals were purchased from Aldrich Chemical Co. and were used without purification. Flash chromatography[13] was performed on Merck silica gel 60 (230–400 mesh). Enantiomeric excesses (ee) of the epoxy alcohols were determined by Alexakis's method[11] using a diazaphospholidine derived from (*R,R*)-*N,N'*-dimethylcyclohexane-1,2-diamine. The purity of all new compounds is documented by the proton and carbon NMR spectra which are available as supplementary material.

3-*n*-Octyl-2,5-dioxathiolane 1,1-Dioxide (6). To a well-stirred solution of 7.0 g (40 mmol) of 1,2-decanediol and 8.0 g (101 mmol) of pyridine in 40 mL of CCl_4, cooled in an ice bath, was added a solution of 6.5 g (55 mmol) of $SOCl_2$ in 5 mL of CCl_4 over 2 min, and the reaction mixture was stirred at 0 °C for an additional 30 min. The reaction mixture was diluted with 200 mL of hexane and washed with 3 × 50 mL of water. The organic solution was passed through a 20-g pad of SiO_2, and the pad was eluted with 25 mL of 10% ether in hexane. The combined organic solution was evaporated, and the residual oil was dissolved in 40 mL of acetonitrile; at 0 °C was added 13 g (60.7 mmol) of $NaIO_4$ followed by 8 mg of $RuCl_3$ hydrate and 50 mL of water with vigorous stirring. The cooling bath was removed, and stirring was continued at rt for 3.5 h. The reaction mixture was diluted with 200 mL of hexane and worked up as above for the cyclic sulfite to give 8.47 g (36 mmol, 90% yield, colorless oil) of **6**: ^1H NMR ($CDCl_3$) δ 0.87 (t, 3 H, J = 7), 1.20–1.54 (m, 12 H), 1.72 (m, 1 H), 1.92 (m, 1 H) 4.34 (dd, 1 H, J = 8.5, 6), 4.70 (dd, 1 H, J = 8.5, 6), 4.97 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.97, 22.53, 24.48, 28.94, 28.99, 29.14, 31.69, 32.15, 72.94, 83.17; IR 1468, 1387, 1212 cm^{-1}; MS (NH_3 DCI) m/z 254 ($M + NH_4^+$).

1-Methylene-2-*n*-octylcyclopropane (7). To a solution of 1.44 g (6 mmol) of **4** in 7.5 mL of THF cooled to −70 °C was added 3.8 mL of 1.6 M (6.1 mmol) *n*-BuLi, and the resulting golden yellow solution was stirred at −70 °C for 1.5 h. A solution of 1.18 g (5 mmol) of **6** in 2 mL of THF was added; stirring was continued, allowing the reaction mixture to warm to rt, for 18 h. The reaction mixture was cooled to −70 °C, and an additional 3.8 mL of 1.6 M *n*-BuLi was added; the reaction mixture was allowed to warm to rt over the next 18 h. Tetra-*n*-butylammonium fluoride trihydrate (2.5 g) was added, the reaction mixture was refluxed for 1.5 h, and the solvent was evaporated in vacuo. The residue was dissolved in 50 mL of hexane, washed with 2 × 20 mL of water, 10 mL of 2 N HCl, and 20 mL of water, and concentrated in vacuo, and the residue was chromatographed on a 50-g column of SiO_2 using hexane to give 0.612 g (3.69 mmol, 74% yield) of **7** as a colorless oil: ^1H NMR ($CDCl_3$) δ 0.71 (m, 1 H), 0.88 (t, J = 3 H), 1.14–1.51 (m, 16 H), 5.32 (m, 1 H), 5.38 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 9.32, 14.02, 15.81, 22.66, 29.33, 29.37, 29.43, 29.59, 31.92, 33.13, 102.17, 137.20; IR 883 cm^{-1}; MS (NH_3 DCI) m/z 184 ($M + NH_4^+$).

2(*R*),3(*R*)-Epoxy-5-((dimethylthexylsilyl)oxy)pentan-1-ol (9). To a stirred suspension of 6 g of 4A molecular sieves in 50 mL of CH_2Cl_2, cooled to −23 °C, were added successively 9.0 mL (10.8 g, 52.4 mmol) of diethyl D-(−)-tartrate and 13 mL (12.41 g, 43.7 mmol) of titanium tetraisopropoxide. The reaction mixture was stirred for 10 min, and a 5.5 M solution (14.5 mL, 80 mmol) of *tert*-butyl hydroperoxide in isooctane and a solution of 9.76 g (40 mmol) of **8** in 25 mL of CH_2Cl_2 were successively added, while maintaining the inner temperature below −23 °C. The reaction mixture was kept stirring for 18 h at −23 °C, the temperature was allowed to rise to −10 °C, and after stirring for another 1 h, 50 mL of water was added. The mixture was stirred at rt for 1 h, then 10 mL of aqueous NaOH containing 5 g of NaOH was added, and stirring was continued for 2 h. The reaction mixture was extracted twice with CH_2Cl_2, and the combined organic layers were dried ($MgSO_4$) and the solvent stripped off to give a turbid oil. Flash chromatography on 150 g of SiO_2 using 0–30% ethyl acetate in hexane afforded 8.10 g (78% yield, colorless oil) of the epoxy alcohol **9**: ee 96%; ^1H NMR ($CDCl_3$) δ 0.13 (s, 6 H), 0.85 (s, 6 H), 0.91 (d, 6 H, J = 7.0), 1.61 (sep, 1 H, J = 7), 1.79 (m, 2 H), 1.93 (bm, 1 H), 2.97 (dt, 1 H, J = 2.5, 4.8), 3.08 (dt, 1 H, J = 2.5, 5.7), 3.61 (ddd, 1 H, J = 4.4, 7.2, 12.5), 3.73 (dd, 2 H, J = 5.6, 6.0), 3.92 (ddd, 1 H, J = 2.5, 5.6, 12.5), ^{13}C NMR ($CDCl_3$) δ −3.51, 18.50, 20.31, 25.10, 34.18, 34.95, 53.81, 58.61, 59.53, 61.77; $[\alpha]_D$ +28.63° ($CHCl_3$, c 2.81); by replacing the (−)- with (+)-tartrate, the other enantiomer was obtained: ee 99%, $[\alpha]_D$ −28.49° ($CHCl_3$, c 3.00).

Reaction of 9 with Undecynyllithium. 1-Undecyne, 9.12 g (60 mmol) in 60 mL of THF, was cooled to −20 °C and deprotonated with 24 mL of 2.5 M (60 mmol) *n*-BuLi. The stirred solution was allowed to warm up to rt and stirred for 15 min. The reaction mixture was cooled to −100 °C in a liquid N_2/EtOH slush bath, and 4.1 g of epoxy alcohol **9** in 10 mL of THF was added. After stirring at −100 °C for 5 min, 7.5 mL of $BF_3{\cdot}Et_2O$ was added over 2 min, followed by 25 mL of THF while maintaining the inner temperature at −100 °C. The reaction mixture was allowed to warm to −78 °C, and the liquid N_2 bath was replaced by a dry ice/acetone slush bath. The reaction mixture was stirred for an additional 1 h at this temperature. Saturated aqueous $NaHCO_3$ (25 mL) was added, and the mixture was allowed to warm to rt. The organic layer was separated, and the aqueous solution was extracted once with 60 mL of diethyl ether. The combined organic layers were concentrated in vacuo. The turbid residue was dissolved in 200 mL of a 3:1 mixture of diethyl ether and hexane when separation of the aqueous layer occurred. The organic layer was concentrated, and the residue was flash chromatographed on a 150-g column of SiO_2 to give 4.88 g (75% yield) of **10** as a colorless oil [^1H NMR ($CDCl_3$) δ 0.13 (s, 6 H), 0.85 (s, 6 H), 0.88 (d, 6 H, J = 7), 0.89 (t, 3 H, J = 7), 1.20–1.50 (m, 14 H), 1.61 (sep, 1 H, J = 7), 1.66 (m, 2 H), 2.15 (m, 2 H), 2.48 (m, 3 H), 3.50 (d, 1 H), 3.65 (m, 1 H), 3.80–3.95 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ −3.63, 13.99, 18.42, 18.72, 20.15, 20.23, 22.60, 23.00, 25.03, 28.86, 28.94, 29.10, 29.22, 29.44, 31.82, 33.42, 34.09, 61.89, 72.44, 73.50, 75.81, 83.12; IR 3600–3100, 2225, 1085 cm^{-1}; MS (NH_3 DCI) m/z 430 ($M + NH_4^+$); $[\alpha]_D$ −9.61°; $[\alpha]_{365}$ −26.28° ($CHCl_3$, c 1.05) [enantiomer]: $[\alpha]_D$ +9.32°; $[\alpha]_{365}$ + 26.14° ($CHCl_3$, c 1.48)]] and 1.14 g (17.5% yield, colorless oil) of **11** as a colorless oil: ^1H NMR ($CDCl_3$) δ 0.13 (s, 6 H), 0.85 (s, 6 H), 0.88 (d, 6 H, J = 7), 0.89 (t, 3 H, J = 7), 1.20–1.95 (m, 20 H), 2.15 (m, 2 H), 2.61 (m, 1 H), 3.6–4.15 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ −3.61, −3.59, 14.08, 18.45, 18.48, 18.69, 20.21, 20.28, 22.67, 25.07, 28.83, 28.91, 29.09, 29.27, 29.50, 31.89, 34.13, 36.41, 40.81, 62.70, 65.22, 75.75, 77.36, 84.79; IR 3600–3100, 2225, 1085 cm^{-1}; MS (NH_3 DCI) m/z 413 ($M + H^+$), 430 ($M + NH_4^+$).

(3*R*,4*S*)-1-((Dimethylthexylsilyl)oxy)hexadecane-3,4-diol (12). A solution of 2.89 g (7.0 mmol) of **10** in 15 mL of methanol was hydrogenated in the presence of 0.200 g of 10% Pd–$CaCO_3$ at 0 °C for 3 h. The catalyst was removed by filtration through a pad of Celite. Evaporation of the solvent, followed by flash chromatography on a 150-g column of SiO_2 using 10–30% ethyl acetate in hexane gave 2.48 g (85% yield) of **12** as an oil: ^1H NMR ($CDCl_3$) δ 0.13 (s, 6 H), 0.85 (s, 6 H), 0.88 (d, 6 H, J = 7), 0.89 (t, 3 H, J = 7), 1.20–1.85 (m, 25 H), 2.30 (bs, 1 H), 3.60 (bm, 2 H), 3.70–3.95 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ −3.54, −3.51, 14.12, 18.49, 18.53, 20.25, 20.33, 22.72, 25.12, 26.07, 29.40, 29.66, 29.69, 29.71, 29.79, 31.97, 32.27, 32.36, 34.17, 62.13, 74.26, 74.74; IR 3600–3100, 1085 cm^{-1}; MS (NH_3 DCI) m/z 417 ($M + H^+$), 434 ($M + NH_4^+$); $[\alpha]_D$ −12.03°; $[\alpha]_{365}$ −35.09° ($CHCl_3$, c 1.03); enantiomer: $[\alpha]_D$ +11.69°; $[\alpha]_{365}$ +35.73° ($CHCl_3$, c 1.26).

(3*R*,4*S*)-(2-((Dimethylthexylsilyl)oxy)ethyl)-4-*n*-dodecyl-2,5-dioxathiolane 1,1-Dioxide (13). To a solution of 0.630 g (1.51 mmol) of **12** and 0.615 g (7.8 mmol) of pyridine in 5 mL of CCl_4 stirred in an ice bath was added a solution of 0.348 g (2.9 mmol) of $SOCl_2$ in 1 mL of CCl_4, and stirring was continued at 0 °C for 30 min. The reaction mixture was diluted with 50 mL of hexane and washed with water (2 × 5 mL), and the organic solution was passed through a 2-g pad of SiO_2. Evaporation of

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the solvent gave 0.721 g of cyclic sulfite as a colorless oil, which showed two spots by TLC, for the cis and trans isomers, with respect to the oxygen on the sulfur and the carbon substituents. The oil was dissolved in 5 mL of acetonitrile and cooled to 0 °C, and 1.5 g of $NaIO_4$ was added, followed by 2.5 mL of water and 5 mg of $RuCl_3$; the cooling bath was removed, and stirring was continued at rt for 3.5 h. The reaction mixture was worked up as above to give 0.656 g (91% overall yield) of **13** as a colorless oil: ^1H NMR ($CDCl_3$) δ 0.10 (s, 3 H), 0.11 (s, 3 H), 0.84 (s, 6 H), 0.88 (t, 3 H, J = 7), 0.88 (d, 6 H, J = 7), 1.10–1.40 (m, 20 H), 1.52–1.66 (m, 3 H), 1.87 (m, 2 H), 3.76 (m, 2 H), 4.95 (ddd, 1 H, J = 3.5, 5.3, 5.3), 5.12 (ddd, 1 H, J = 3.5, 5.3, 5.3); ^{13}C NMR ($CDCl_3$) δ -3.63, -3.60, 14.09, 18.46, 20.27, 22.67, 25.19, 28.67, 29.09, 29.29, 29.32, 29.43, 29.55, 29.61, 31.23, 31.90, 34.14, 57.84, 83.35, 86.27; IR 1466, 1384, 1210, 1100, 831 cm^{-1}; MS (NH_3 DCI) m/z 479 (M + H^+), 496 (M + NH_4^+); $[\alpha]_D$ +18.7°; $[\alpha]_{365}$ +57.93° ($CHCl_3$, c 0.84); enantiomer: $[\alpha]_D$ -19.52°; $[\alpha]_{365}$ -58.18° ($CHCl_3$, c 0.82).

2-[2′(*R*)-Dodecyl-3′-methylenecyclopropan-1′(*S*)-yl]-ethanol (14). To a well-stirred solution of 0.777 g (3.21 mmol) of the sulfone **4** in 5 mL of THF cooled in a dry ice/acetone slush bath was added 2 mL of 1.6 M (3.2 mmol) of *n*-BuLi, and the resulting golden yellow solution was stirred at -78 °C for 2 h. A solution of 0.62 g (1.30 mmol) of **13** in 2 mL of THF was added over 1 min. Stirring was continued over the next 3.75 h, allowing the reaction mixture to warm up to rt. The reaction mixture was cooled to -78 °C, and an additional 2 mL of 1.6 M (3.2 mmol) *n*-BuLi was added; stirring was continued over the next 18 h, allowing the reaction mixture to warm to rt. Tetra-*n*-butylammonium fluoride trihydrate (1.5 g) was added, and the mixture was refluxed for 1.5 h. The reaction mixture was cooled, diluted with 50 mL of hexane, washed with 2 × 5 mL of water and 5 mL of 2 M HCl, and concentrated in vacuo. The residual oil was flash chromatographed on a 30-g column of SiO_2 using up to 25% of ethyl acetate in hexane to give 0.124 g (36% yield) of **14**: MS (NH_3 DCI) m/z 284 (M + NH_4^+); ^1H NMR ($CDCl_3$) δ 0.87 (t, 3 H, J = 7), 1.17–1.62 (m, 26 H), 1.78 (m, 1 H), 3.73 (m, 2 H), 5.31 (m, 1 H), 5.33 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.13, 16.28, 19.56, 22.71, 27.58, 29.37, 29.51, 29.63, 29.67, 29.95, 30.58, 31.94, 63.27, 101.63, 141.85; IR 3600–3150, 883 cm^{-1}; $[\alpha]_D$ -5.90°; $[\alpha]_{365}$ -25.1° ($CHCl_3$, c 0.9); enantiomer $[\alpha]_D$ +6.0°; $[\alpha]_{365}$ +24.9° ($CHCl_3$, c 1.05).

2-[2′(*R*)-Dodecyl-3′-methylenecyclopropan-1′(*S*)-yl]acetic Acid (15). To a well-stirred mixture of 70 mg of pyridinium chlorochromate, 70 mg of Celite, and 40 mg of activated, powdered 4A molecular sieves in 2.5 mL of CH_2Cl_2 was added a solution of 26 mg (0.1 mmol) of **14** in 0.5 mL of CH_2Cl_2, and the reaction mixture was stirred for 18 h; it was diluted with 10 mL of ether and filtered through a 1-g pad of SiO_2; the solvent was evaporated, and the residue was dissolved in 1 mL of acetone and oxidized with 0.5 mL of 6 M Jones reagent at rt for 6 h; excess of the reagent was reduced with the addition of 2-propanol, and the reaction mixture was diluted with 20 mL of a 1:1 hexane and ether mixture, washed several times with water, and concentrated. The residue, upon chromatography on a 5-g column of SiO_2 using 20–100% ethyl acetate in hexane gave 17 mg (65% yield, colorless oil) of **15**: MS (NH_3 DCI) m/z 298 (M + NH_4^+); ^1H NMR ($CDCl_3$) δ 0.89 (t, 3 H, J = 7), 1.20–1.50 (m, 22 H), 1.61 (m, 1 H), 1.82 (m, 1 H), 2.40 (dd, 1 H, J = 8.4, 16.8), 2.46 (dd, 1 H, J = 7.4, 16.8), 5.37 (m, 1 H), 5.42 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.10, 14.69, 19.60, 22.69, 27.64, 29.36, 29.42, 29.60, 29.67, 31.93, 32.37, 102.72, 139.88, 179.44; IR 3500–2550, 1713, 889 cm^{-1}; $[\alpha]_D$ -10.28°; $[\alpha]_{365}$ -44.86° ($CHCl_3$, c 0.7); enantiomer: $[\alpha]_D$ +10.36°; $[\alpha]_{365}$ +45.12° ($CHCl_3$, c 0.8).

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Supplementary Material Available: ^1H and ^{13}C NMR spectra of compounds **6–15** (20 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.

Selective Hydrosilylation of Alkenes Catalyzed by an Organoyttrium Complex

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Metal-catalyzed hydrosilylation procedures provide perhaps the most efficient and economical route to organosilanes, and a variety of catalysts have been developed for this reaction.[3] Curiously, relatively little effort has been made to develop general, synthetically useful procedures for hydrosilylation of polyolefins and functionalized alkenes.[3] In this context we have found that $(\eta^5\text{-}C_5Me_5)_2YCH(SiMe_3)_2$ serves as an efficient and selective precatalyst for the hydrosilylation of monosubstituted and 1,1-disubstituted olefins.

While this work was in progress, a related study utilizing an organoneodymium catalyst was reported.[3d] In that effort, unfunctionalized olefins (decene and styrene) were hydrosilylated in modest (GC) yields. Nearly all of the reactions described required 2 days at 80 °C for complete reaction. Left open was the question of whether any type of functionality could be tolerated in this process. This is a critical point owing to the extreme Lewis acidity of organolanthanides and group 3 organometallics which renders them incompatible with many functional groups.[4] For example, even ethers have been found to inhibit the catalytic activity of these organometallics because such Lewis bases complex irreversibly with the metal or are readily cleaved by the complexes, either of which destroy the activity of the catalyst.

From the outset our focus was on the development of a convenient, synthetically useful procedure which would take place at ambient temperatures. As illustrated in Table I, the organoyttrium-catalyzed hydrosilylation procedure fulfills all of these requirements. The process works extremely well for a variety of unhindered alkenes, and reactions can be performed in benzene or toluene utilizing 3 mol % catalyst at ambient temperatures. Furthermore, 1,1-disubstituted alkenes (entries 4, 7, and 9) are much less reactive than monosubstituted olefins, leading to considerable selectivity in hydrosilylation of dienes possessing both types of olefins (entry 7). With the exception of the highly reactive norbornylene (entry 2), more highly hindered alkenes (e.g., cyclohexene and *cis*-1,3-dimethyl-2-methylenecyclohexane) are virtually inert at ambient temperature.[5] Consequently, excellent chemoselectivity can be achieved in hydrosilylation of dienes containing a terminal olefin and any internal olefin (entries 5–9).

The extreme sensitivity of this particular catalyst to steric effects led us to examine the selective hydrosilylation of α,ω-dienes in which the two olefins were differentiated only by allylic substitution of one of the alkenes (entry 12).

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(5) At 60 °C over 42 h, *trans*-3-hexene reacts to provide a mixture of products in which the terminal organosilane predominates.

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