mixture crystals of the amine-tartrate began to form. The mixture was well-stirred for 28 h. The solid was filtered, washed with isopropyl alcohol (25 mL), and suction dried. The amine was isolated by addition of the salt to a mixture of CH_2Cl_2 (100 mL) and 2.5 N NaOH (200 mL). The layers were separated, and the aqueous layer was washed with CH_2Cl_2 (100 mL). The combined organic layers were washed with brine (50 mL) and dried (Na_2SO_4). The filtered solution was concentrated to dryness (2.45 g, 49% yield of theory): $[\alpha]^{25}D$ -44.64° (c 2, ethanol) [lit.[26] $[\alpha]^{25}D$ -45° (c 2, ethanol)]. The amine was found to be 98.4:1.6 *R/S* by assay as the benzamide on a chiral Pirkle L-phenylglycine covalent column: hexanes-CH_2Cl_2-isopropyl alcohol (80:15:5); 1.5 mL/min; 230 nm; *S* enantiomer, 7.99 min; *R* enantiomer, 8.9 min.

***N*-((*R*)-1,2-Diphenylethyl)acetamide (1b).** The (*R*)-(-)-1,2-diphenylethylamine (2.29 g, 11.6 mmol) was acylated with acetic anhydride as for the racemate **1b** (2.68 g, 96%). A sample was purified by recrystallization from ethyl acetate-cyclohexane: mp 163.5-164.5 °C (lit.[12] mp 166-167 °C); $[\alpha]^{25}D$ 14.7° (c 2.2, ethanol) [lit.[12] $[\alpha]^{18}D$ 35.7° (c 1.5, ethanol)].

(*R*)-3,4-Dihydro-1-methyl-3-phenylisoquinoline (5b). The chiral acetamide **1b** (0.505 g, 2.11 mmol) was cyclized and the resultant oxalyl adduct converted to the 3,4-dihydroisoquinoline **5b** (0.417 g, 89% yield). The material was purified by column chromatography (silica gel, ethyl acetate/hexanes): mp 91-93 °C; $[\alpha]^{24}D$ 126° (c 2.05, ethanol). The enantiomeric ratio of the material was obtained by conversion of the 3,4-dihydroisoquinoline to the enamide: The imine (56.1 mg, 0.25 mmol) was dissolved in CH_2Cl_2 (5 mL). Triethylamine (37 μL, 0.27 mmol) and benzoyl chloride (31 μL, 0.27 mmol) were added separately and sequentially at room temperature. The mixture was stirred at room temperature for 1 h. The volatiles were removed by evaporation, and the residue was taken up in toluene (5 mL). The salts were filtered, and the filtrate was concentrated under vacuum. The residue was assayed on a Pirkle L-phenylglycine covalent column: 80:20:1 hexanes-CH_2Cl_2-isopropyl alcohol; 1.5 mL/min; 230 nm; *S* enantiomer, 7.1 min; *R* enantiomer, 8.3 min. The material was a 98.5:1.5 *R/S* mixture, indicating no epimerization of the chiral center.

3-Carbomethoxy-3,4-dihydro-1-methylisoquinoline (5n) was isolated as a light orange oil in 77% yield by silica gel chromatography (hexanes-ethyl acetate (1:1)). The material was shown to be racemic by conversion of the imine to the *N*-benzoyleneamide as for (*R*)-**5b** and assay on a Pirkle L-phenylglycine covalent column (hexanes-CH_2Cl_2-ethanol (90:10:2)): mp 175-176 °C dec as hydrochloride (ethanol-ethyl ether); IR 3100-2850, 1730, 1625, 1435, 1285, 1255, 1205, 1170 cm^{-1}; ^1H NMR δ 7.51 (br d, *J* = 7.4, 1 H), 7.38 (m, 1 H), 7.31 (m, 1 H), 7.21 (br d, *J* = 7.4, 1 H), 4.19 (m, 1 H), 3.82 (s, 3 H), 2.96 (m, 2 H), 2.45 (d, *J* = 2.3, 3 H); ^{13}C NMR δ 173.3, 165.8, 135.4, 131.1, 129.1, 127.5, 127.3, 125.6, 59.8, 52.4, 28.3, 23.3. Anal. Calcd for $C_{12}H_{14}ClNO_2$: C, 60.12; H, 5.90; N, 5.84. Found: C, 59.88; H, 5.85; N, 5.82.

Supplementary Material Available: Experimental procedures and data for the synthesis of the ketones and amides 1 (9 pages). Ordering information is given on any current masthead page.

(26) (a) Smith, H. E.; Chad, W. T. *J. Am. Chem. Soc.* 1971, *93*, 2282. (b) Reference 11.

Five-, Four-, and Three-Membered Carbocyclic Rings from 2-Deoxyribose by Intramolecular Nucleophilic Displacement Reaction

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1,3-Dithianes such as **4**, **9**, **11**, **13**, and **19** derived from 2-deoxy-D-ribose (**1**) undergo intramolecular displacement reactions to give three-, four-, and five-membered carbocyclic rings (**5**, **10**, **12**, **15**, and **20**). Cyclopropanes are favored over the cyclobutanes when starting from the epoxides **9** or **11**. Treatment of the tosylate **19** gives only a small yield of the corresponding cyclobutane **20**, the major product being the ketone **21**.

Introduction

Carbohydrates are useful starting materials for the synthesis of enantiomerically pure noncarbohydrate compounds.[1a-e] The construction of carbocyclic derivatives from sugars is particularly interesting because many important classes of compounds such as prostaglandins,[2] terpenes,[3] pheromones,[4] antibiotics,[5] antiviral compounds,[6] nucleic acid derivatives,[7] and pseudo sugars[8] that are potential enzyme inhibitors[9] can be prepared in enantiomerically pure form.

In many cases, the carbocyclic framework is constructed by cycloaddition reactions and the carbohydrate serves merely as a chiral template. Methods for the conversion of a carbohydrate to a carbocycle involving predominantly the carbon atoms of the starting sugar are rare,[10] and only

(1) (a) Fraser-Reid, B.; Anderson, R. C. Carbohydrate Derivatives in the Asymmetric Synthesis of Natural Products. In *Fortsch. Chem. Org. Naturst.*; Springer-Verlag: Wien, 1980; pp 1-61. (b) Vasella, A. Chiral Building Blocks in Enantiomer Synthesis-ex Sugars. In *Modern Synthetic Methods 1980*; Scheffold, R., Ed.; Salle und Sauerländer: Frankfurt and Aarau: 1980; Vol. 2, pp 174-267. (c) Hanessian, S. *Total Synthesis of Natural Products: The 'Chiron' Approach*; Pergamon: Oxford, 1983. (d) Baer, H. H. New Approaches to the Synthesis of Nitrogenous and Deoxy sugars and Cyclitols. In *Trends in Synthetic Carbohydrate Chemistry*; Horton, D., Hawkins, L. D., McGarvey, G. J., Eds.; American Chemical Society: Washington, DC, 1989; Chapter 2, pp 22-44. (e) Mulzer, J.; Altenbach, H.-J.; Braun, M.; Krohn, K.; Reissig, H.-U. Chiral Building Blocks from Carbohydrates. In *Organic Synthesis Highlights*; VCH Verlagsgesellschaft: Weinheim, 1991; pp 251-260.

(2) Ferrier, R. J.; Prasit, P. *Pure Appl. Chem.* 1983, *55*, 565.

(3) Dickson, J. K., Jr.; Tsang, R.; Llera, J. M.; Freiser-Reid, B. *J. Org. Chem.* 1989, *54*, 5350.

(4) Kandil, A. A.; Slessor, K. N. *J. Org. Chem.* 1985, *50*, 5649.

(5) Parry, R. J.; Bornemann, V.; Subramanian, R. *J. Am. Chem. Soc.* 1989, *111*, 5819.

(6) Wolfe, M. S.; Anderson, B. L.; Borcherding, D. R.; Borchardt, R. T. *J. Org. Chem.* 1990, *55*, 4712.

(7) Ali, S. M.; Ramesh, K.; Borchardt, R. T. *Tetrahedron Lett.* 1990, *31*, 1509.

(8) Tadano, K.; Habakuba, K.; Kimura, H.; Ogawa, S. *J. Org. Chem.* 1989, *54*, 276.

(9) Anderson, F. O.; Classon, B.; Samuelsson, B. *J. Org. Chem.* 1990, *55*, 4699.

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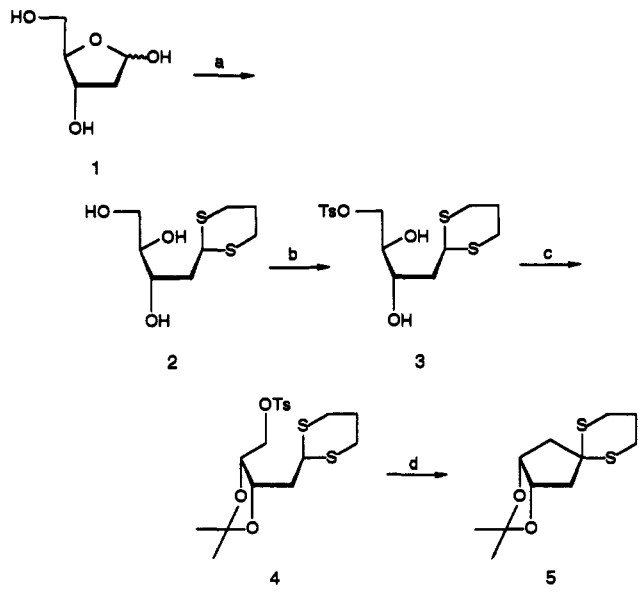
Scheme I[a]



[a] (a) $CHCl_3$, 6 N HCl, 1,3-propanedithiol; (b) TsCl, *n*-Bu_2SnO, Py; (c) DMP, TsOH; (d) THF, 1 equiv of *n*-BuLi, −30 °C.

a few examples are known where the nucleophilic center was generated from nitro sugars,[1d] dicarbonyl derivatives,[11] or vinyl ethers, as in the Ferrier reaction.[12]

In our work we anticipated the creation of a nucleophilic center within the sugar framework by polarity inversion (Umpolung) of the electrophilic aldehyde group to 1,3-dithianes. 2-Lithio-1,3-dithianes have rarely been used for intramolecular addition reactions, but the feasibility of that reaction has been demonstrated in model studies.[13] A prerequisite for the realization of this synthetic scheme is the absence of leaving groups at the neighboring position at C-2 to avoid 1,2-eliminations during anion formation. For that reason we selected the commercially available 2-deoxy-D-ribose (1) as the starting material for our initial studies to explore the possibility of constructing five-, four-, and three-membered carbocycles from sugars by the umpolung strategy.

Five-Membered Ring

2-Deoxy-D-ribose (1) was converted in 90% yield to the known[14] dithioacetal 2 as shown in Scheme I. The selective tosylation at the primary hydroxy group was achieved by the addition of dibutyltin oxide to yield 59% of 3. The monotosylate 3 was converted to the acetonide 4 to avoid epoxide formation and Payne rearrangements at the stage of the subsequent base treatment. A clean cyclization to give the achiral cyclopentane derivative 5 in 71% yield occurred upon treatment of 4 with *n*-butyllithium at −30 °C in THF.

Three-Membered Rings

Three-membered carbocyclic rings from sugars have mainly been constructed by external addition of diazomethane, sulfur ylides, or carbenes to unsaturated sugars (for a recent review see ref 15). There are only a few reports on the internal displacement reactions involving nitro sugars.[1d] In our plans we wanted to create an epoxide next to the nucleophilic dithiane center. Stork and Cohen[16] have shown that cyclobutanes were formed in an epoxynitrile cyclization in preference to cyclopentanes, and it was interesting to see whether three- or four-membered rings would result from the intramolecular dithiane cyclization.

Dithiane 2 was tritylated at the primary position to afford 6 in 81% yield as shown in Scheme II. The monotosylation of the two secondary hydroxy groups in 6 gave a 3:1 mixture of 7 and 8 (69%) that could be separated by layer chromatography on silica gel. Treatment of the α-hydroxy tosylates 7 and 8 gave the enantiomeric epoxides 9 and 11 in essentially quantitative yield. Over 70% of the cyclopropane dithioacetals 10 and 12 were isolated upon cyclization of the epoxides under the same conditions as employed for the conversion of 4 to 5. In agreement with the Baldwin rules (3-*exo-tet* favored versus 4-*endo-tet*) the formation of the three-membered rings was observed exclusively. The products 10 and 12 are enantiomers as are the parent epoxides 9 and 11. This is confirmed by their opposite optical rotation of $[\alpha]^{20}_D = 9.1°$ for 10 and $[\alpha]^{20}_D = -9.2°$ for 12. Thus, the separation of the isomeric monotosylates results in an enantiodivergent synthesis of highly functionalized chiral cyclopropane derivatives.

Two sequential inversions occur at C-3 during epoxide formation from 7 to 9 followed by another S_N2 displacement during cyclization to 10. Thus, a net retention at C-3 in the formation of 10 results. An inversion at that center would result from replacement of a C-3 monotosylate. This monotosylate was prepared by acid-catalyzed acetonide formation of the mixture of the monotosylates 7 and 8 (Scheme III). The trityl protecting group is cleaved under these conditions, and the five- and six-membered acetonides 13 and 14 were isolated in 53 and 24% yield, respectively. Treatment of 14 with *n*-BuLi under the same conditions as described before gave a clean cyclization to the cyclopropane acetonide 15. However, no cyclobutane formation could be induced by BuLi treatment of 13 in agreement with model studies confirming that no S_N2 displacement reaction was possible with 13 for steric reasons.

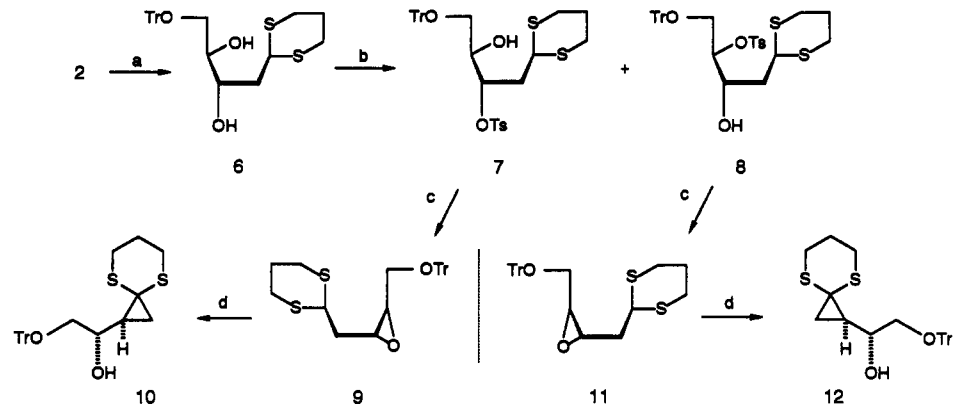
Four-Membered Ring

A more flexible system had to be chosen to investigate the formation of four-membered rings. For that purpose the anomeric mixture **16a/b** of the methyl glycosides derived from 2-deoxy-D-ribose (1) was converted to the methyl ethers **17a/b**.[17] At this stage small amounts of pyranoside methyl glycosides of 2-deoxy-D-ribose could be removed chromatographically (72% overall yield from 1). Thioacetalization of **17a/b** gave the 1,3-dithiane 18 in 81% yield, and tosylation of the free hydroxy group at C-4 afforded the desired monotosylate 19. Reaction of 19 at −50 °C gave two major reaction products. The less polar compound was identified as the desired cyclobutane derivative 20 (18%) and the polar product (35%) as the α-methoxy ketone 21 (Scheme IV).

A possible pathway for the formation of ketone 21 could involve deprotonation of the carbon atom bearing the tosylate, elimination of the methoxy group followed by hydrochloride addition, and saponification. We are currently

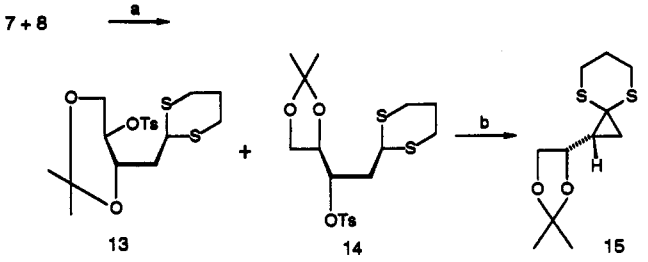
(10) Vite, G. D.; Alfonso, R.; Fraser-Reid, B. *J. Org. Chem.* **1989**, *54*, 2268.
(11) Achab, S.; Cosson, J.-P.; Das, B. C. *J. Chem. Soc., Chem. Commun.* **1984**, 1040.
(12) Barton, D. H. R.; Camara, J.; Dalko, P.; Gêro, S. T.; Quiclet-Sire, B.; Stütz, P. *J. Org. Chem.* **1989**, *54*, 3764.
(13) Seebach, D.; Jones, N. R.; Corey, E. J. *J. Org. Chem.* **1968**, *33*, 300.
(14) Sepulchre, A. M.; Vass, G.; Gero, S. D. *Tetrahedron Lett.* **1973**, 3619.
(15) Salaün, J. *Chem. Rev.* **1989**, *89*, 1247.
(16) Stork, G.; Cohen, J. F. *J. Am. Chem. Soc.* **1974**, *96*, 5270.
(17) Font, J.; Ortuno, R. M.; Ponsati, O.; Sanchez-Ferrando, F. *Nouv. J. Chim.* **1982**, *6*, 305.

Scheme II[a]



[a] (a) TrCl, Py; (b) TsCl, Py; (c) NaOMe, MeOH; (d) *n*-BuLi, THF, −30 °C.

Scheme III[a]



[a] (a) DMP, TsOH; (b) THF, 1 equiv of *n*-BuLi, −30 °C.

investigating methods of overcoming the poor yield in cyclobutane formation using different leaving groups (e.g., triflates).

In summary, the present work shows that five-, three-, and to a lesser extent four-membered carbocyclic rings can be prepared from 2-deoxy sugars by intramolecular nucleophilic displacement reactions. Small rings can be synthesized that have not yet been prepared via radical cyclization of sugars. The conversion of the aldehyde function into a dithane provides the sugar in a fixed open chain form that can be advantageous for further synthetic manipulations.

Experimental Section

For general and standard procedures see ref 18. The ^{1}H NMR were measured at 400 MHz and the ^{13}C NMR at 100 MHz.

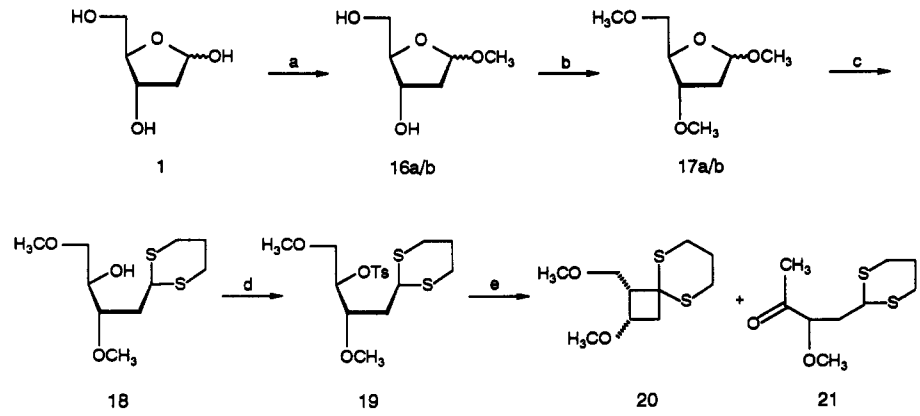
2-Deoxy-D-*erythro*-pentose Cyclic 1,3-Propanediyl Mercaptal (2). A solution of 2-deoxy-D-ribose (1, 3.0 g, 22.4 mmol) in $CHCl_3$ (10 mL) and 6 N HCl (16 mL) was cooled to 5 °C and treated with 1,3-propanedithiol (5 mL, 49.8 mmol, 2.2 equiv). The mixture is stirred for 4 h at 20 °C, and most of the product precipitates and is filtered off. The remaining product is isolated by neutralization of the solution with $PbCO_3$ and evaporation of the filtered solution under reduced pressure. The residue is extracted three times with hot chloroform (100 mL) and crystallized from $CHCl_3$ to afford 2 (4.5 g, 89.5%): mp 124–125 °C (lit.[14] mp 123–124 °C); $[\alpha]^{20}_D$ 31.7° (*c* 1.1, methanol); IR (KBr) 3404, 3275, 2943, 1416, 1279, 1093, 1030, 910, 774 cm^{-1}; ^{1}H NMR (CD_3OD) δ 1.70–1.89 (m, 2 H, 2-H), 2.05, 2.15 (m, 2 H, SCH_2CH_2), 2.78–3.00 (m, 4 H, SCH_2), 3.42 (ddd, $J_{3,4}$ = 6.6 Hz, $J_{4,5a}$ = 6.6 Hz, $J_{4,5b}$ = 3.8 Hz, 1 H, 4-H), 3.55 (dd, J_{gem} = 11.3 Hz, $J_{4,5a}$ = 6.5 Hz, 1 H, 5a-H), 3.71 (dd, J_{gem} = 11.3 Hz, $J_{4,5b}$ = 3.7 Hz, 1 H, 5b-H), 3.82 (ddd, $J_{2a,3}$ = 10.0 Hz, $J_{3,4}$ = 7.1 Hz, $J_{2b,3}$ = 2.4 Hz, 1 H, 3-H), 4.28 (dd, $J_{1,2b}$ = 11.0 Hz, $J_{1,2a}$ = 3.7 Hz, 1 H, 1-H); ^{13}C NMR (CD_3OD) δ 27.93 (t, SCH_2CH_2), 31.08 (t, SCH_2), 31.74 (t, SCH_2), 40.85 (t, C-2), 45.38 (d, C-1), 65.22 (t, C-5), 70.39 (d, C-4), 76.93 (d, C-3); MS (70 eV, FAB/pos, glycerine) *m/z* 225 (50) $(M + H)^+$, 185 (97), 117 (65), 93 (100).

2-Deoxy-5-*O*-[(4-methylphenyl)sulfonyl]-D-*erythro*-pentose Cyclic 1,3-Propanediyl Mercaptal (3). A solution of thioacetal 2 (1.50 g, 6.6 mmol) in 10 mL of anhydrous pyridine is treated with dibutyltin oxide (1.54 g). The mixture is stirred for 1 h at 20 °C and cooled to 0 °C, and the *p*-toluenesulfonyl chloride (1.41 g, 7.2 mmol) is added. The mixture is poured into ice–water (20 mL) after stirring for 24 h, extracted three times with 5 mL of CH_2Cl_2, washed with diluted HCl and aqueous saturated sodium hydrogen carbonate solution, and dried with Na_2SO_4. The solvent is removed under reduced pressure, and the residue is purified by column chromatography on silica gel (CH_2Cl_2/3% methanol) to afford 3 (1.47 g, 59%) as a colorless oil that solidified on storing at 0 °C; mp 110–111 °C; $[\alpha]^{20}_D$ −8.8° (*c* 0.5, CH_2Cl_2); IR (KBr) 3464, 3464 (OH), 3327 (OH), 2947, 2887, 1322, 1308, 1190, 1177, 1160, 1099, 1069, 1014, 938, 906, 875, 811, 708, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.80–1.91 (m, 2 H, SCH_2CH_2), 1.95 (ddd, $J_{2a,3}$ = 2.5 Hz, $J_{1,2a}$ = 9.4 Hz, J_{gem} = 14.4 Hz, 1 H, 2a-H), 2.05–2.14 (m, 1 H, 2b-H), 2.44 (s, 3 H, CH_3), 2.80–2.95 (m, 4 H, SCH_2), 3.38 (br s, 2 H, OH), 3.79 (dt, $J_{4,5a}$ = 3.7 Hz, J = 5.8 Hz, 1 H, 4-H), 3.95 (ddd, $J_{2a,3}$ = 2.7 Hz, $J_{3,4}$ = 5.6 Hz, $J_{2b,3}$ = 9.8 Hz, 1 H, 3-H), 4.08–4.16 (m, 2 H, 5-H), 4.22 (dd, $J_{1,2b}$ = 4.8 Hz, $J_{1,2a}$ = 9.6 Hz, 1 H, 1-H), 7.35 (d, J = 8.2 Hz, 2 H, Ar-H), 7.80 (d, J = 8.3 Hz, 2 H, Ar-H); ^{13}C NMR ($CDCl_3$) δ 21.80 (q, CH_3), 25.94 (t, SCH_2CH_2), 29.69 (t, SCH_2), 30.09 (t, SCH_2), 38.20 (t, C-2), 43.69 (d, C-1), 69.00 (d, C-3), 71.30 (t, C-5), 72.35 (d, C-4), 128.12 (d, Ar-C, 3 or 5), 130.17 (d, Ar-C, 2 or 6), 132.43 (s, Ar-C), 145.31 (s, Ar-C); MS (CI/neg; isobutane) *m/z* 378 (2) (M^+), 348 (10), 287 (100), 204 (22), 155 (27), 138 (12). Anal. Calcd for $C_{15}H_{22}O_5S_3$: C, 47.60; H, 5.86; S, 25.41. Found: C, 47.60; H, 5.98, S, 25.70.

2-Deoxy-3,4-*O*-(1-methyl-1,1-ethanediyl)-5-*O*-[(4-methylphenyl)sulfonyl]-D-*erythro*-pentose Cyclic 1,3-Propanediyl Mercaptal (4). A solution of the tosylate 3 (1.40 g, 3.7 mmol) in 2,2-dimethoxypropane (10 mL) is treated with *p*-toluenesulfuric acid (50 mg) and refluxed for 3 h. The cooled solution is neutralized with solid $NaHCO_3$, and the solvent is removed under reduced pressure. The residue is crystallized from diethyl ether to afford 4 (1.39 g, 90%); mp 108–109 °C, $[\alpha]^{20}_D$ 4.2° (*c* 1.1, $CHCl_3$); IR (KBr) 2987, 2898, 1367, 1186, 1177, 1081, 995, 835, 663, 554 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.31 (s, 3 H, $OCCH_3$), 1.34 (s, 3 H, $OCCH_3$), 1.79–1.95 and 2.06–2.16 (m, 4 H, 2-H and SCH_2CH_2), 2.45 (s, 3 H, $ArCH_3$), 2.75–2.95 (m, 4 H, SCH_2), 3.93 (dd, J_{gem} = 9.8 Hz, $J_{4,5a}$ = 6.0 Hz, 1 H, 5a-H), 3.98 (dd, J_{gem} = 9.7 Hz, $J_{4,5b}$ = 6.6 Hz, 1 H, 5b-H), 4.15 (t, J = 6.9 Hz, 1 H, 1-H), 4.26 (q, J = 5.9 Hz, 1 H, 4-H), 4.47 (q, J = 6.4 Hz, 1 H, 3-H), 7.37 (d, J = 8.0 Hz, 2 H, Ar-H), 7.80 (d, J = 8.2 Hz, 2 H, Ar-H); ^{13}C NMR ($CDCl_3$) δ 20.79 (q, $ArCH_3$), 24.53 (q, $OCCH_3$), 24.99 (t, SCH_2CH_2), 27.04 (q, $OCCH_3$), 28.67 (t, SCH_2), 29.25 (t, SCH_2), 34.01 (t, C-2), 42.61 (d, C-1), 66.66 (t, C-5), 72.11, 73.51 (d, C-3, C-4), 108.09 (s, $OCCH_3$), 127.12 (d, Ar-C), 128.97 (d, Ar-C), 131.54 (s, Ar-C), 144.27 (s, Ar-C-1); MS (70 eV) *m/z* 418 (12) (M^+), 403 (10) $(M^+ - CH_3)$, 246 (10), 155 (22), 132 (100), 119 (38), 97 (38), 91 (41). Anal. Calcd for $C_{18}H_{26}O_5S_2$: C, 51.64; H, 6.26; S, 22.98. Found: C, 51.23; H, 6.21; S, 22.95.

(18) Krohn, K.; Rieger, H.; Khanbabaee, K. *Chem. Ber.* **1989**, *122*, 2323.

Scheme IV[a]



[a] (a) MeOH, H_2SO_4; (b) MeI, NaH, THF; (c) $HS(CH_2)_3SH$, SiO_2/HCl, $ZnCl_2$, CH_2Cl_2; (d) TsCl, Py; (e) *n*-BuLi, −50 °C.

(3aα,6aα)-Tetrahydro-2,2-dimethylspiro[cyclopenta[1,3]-dioxole-5,2′-[1,3]dithiane] (5). A solution of the tosylacetonide 4 (800 mg, 1.9 mmol) in anhydrous THF (30 mL) is treated at −30 °C under nitrogen with 1.6 N *n*-butyllithium in *n*-hexane (1.2 mL, 1.9 mmol). The mixture is warmed to 20 °C and stirred for 4 h (TLC monitoring). The solution is poured into a saturated aqueous ammonium chloride solution (30 mL) and extracted with CH_2Cl_2. The organic phase is washed with water, dried with Na_2SO_4, and evaporated under reduced pressure. Layer chromatography on silical gel afforded 5 (330 mg, 71%), mp 98–99 °C. No optical rotation could be measured in CH_2Cl_2: IR (KBr) 2930, 2854, 1380, 1371, 1269, 1247, 1204, 1156, 1064, 911, 863 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (s, 3 H, CH_3), 1.40 (s, 3 H, CH_3), 1.84–1.94 (m, 2 H, SCH_2CH_2), 2.22 (dd, J_{gem} = 14.2 Hz, J = 3.1 Hz, 2 H, 4-H, 6-H), 2.43 (dd, J_{gem} = 15.4 Hz, J = 5.7 Hz, 2 H, 4-H, 6-H), 2.74–2.81 (m, 4 H, SCH_2), 4.66–4.74 (m, 2 H, 3a-H and 6a-H); ^{13}C NMR ($CDCl_3$) δ 24.57 (q, CH_3), 25.12 (t, C-5′), 26.74 (q, CH_3), 28.12 (t, C-4′, C-6′), 47.09 (t, C-4, C-6), 54.23 (s, C-5), 80.30 (d, C-3a, C-6a), 112.10 (s, $OCCH_3$); MS (70 eV) m/z 246 (100) (M^+), 231 (34) ($M^+ - CH_3$), 188 (25), 171 (75), 114 (42), 106 (32), 85 (32). Anal. Calcd for $C_{11}H_{18}O_2S_2$: C, 53.62; H, 7.36; S, 26.03. Found: C, 53.60; H, 7.34; S, 26.05.

2-Deoxy-5-*O*-(triphenylmethyl)-D-*erythro*-pentose Cyclic 1,3-Propanediyl Mercaptal (6). A solution of thioacetal 2 (1.00 g, 4.5 mmol) in anhydrous pyridine (10 mL) is treated with trityl chloride (1.37 g, 1.1 equiv). The mixture is stirred for 24 h at 20 °C (TLC monitoring). The solution is poured into ice–water (10 mL), extracted with CH_2Cl_2, washed successively with dilute HCl and aqueous sodium hydrogen carbonate solution and water, dried with Na_2SO_4, and evaporated under reduced pressure. The mixture is purified by column chromatography on silica gel (CH_2Cl_2) to afford oily 6 (1.70 g, 81%): $[\alpha]^{20}_D$ − 5.1° (*c* 0.9, CH_2Cl_2); IR (CCl_4) 3424 (OH), 3057, 3031, 3023, 2921, 2899, 1490, 1422, 1067, 1032, 908, 900 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.71–1.90 (m, 3 H, 2 × 2-H, SCH_2CH_2), 2.02–2.10 (m, 1 H, SCH_2CH_2), 2.63 (br s, 1 H, OH), 2.72 (br s, 1 H, OH), 2.74–2.89 (m, 4 H, SCH_2), 3.24 (dd, J_{gem} = 9.8 Hz, $J_{4,5a}$ = 6.1 Hz, 1 H, 5a-H), 3.35 (dd, J_{gem} = 9.8 Hz, $J_{4,5b}$ = 4.1 Hz, 1 H, 5b-H), 3.65 (ddd, $J_{4,5}$ = 4.9 Hz, $J_{3,4}$ = 10.0 Hz, 1 H, 4-H), 3.96–4.04 (m, 1 H, 3-H), 4.10 (dd, J = 4.9 and 9.4 Hz, 1 H, 1-H), 7.20–7.50 (m, 15 H, Ar-H); ^{13}C NMR ($CDCl_3$) δ 25.83 (t, SCH_2CH_2), 29.72 (t, SCH_2), 30.13 (t, SCH_2), 37.98 (t, C-2), 43.78 (d, C-1), 64.35 (t, C-5), 69.87 (d, C-4), 72.90 (d, C-3), 87.17 (s, CPh_3), 127.21, 128.52 (d, Ar-C), 143.51 (s, Ar-C); MS (70 eV) m/z 243 (52) (Ph_3C^+), 223 (25) ($M^+ - CPh_3$), 206 (10), 165 (29), 145 (36), 133 (28), 119 (100), 105 (22). Anal. Calcd for $C_{27}H_{30}O_3S_2$: C, 69.49; H, 6.48; S, 13.74. Found: C, 69.27; H, 6.48; S, 13.73.

2-Deoxy-3-*O*-[(4-methylphenyl)sulfonyl]-5-*O*-(triphenylmethyl)-D-*erythro*-pentose Cyclic 1,3-Propanediyl Mercaptal (7) and 2-Deoxy-4-*O*-[(4-methylphenyl)-sulfonyl]-5-*O*-trityl-D-*erythro*-pentose Cyclic 1,3-Propanediyl Mercaptal (8). A solution of trityl ether 6 (2.00 g, 4.3 mmol) in anhydrous pyridine (15 mL) is treated with *p*-toluenesulfonyl chloride (0.90 g, 1.1 equiv). After being stirred for 2 d at 20 °C, the solution was poured into ice–water (30 mL), extracted with CH_2Cl_2, and washed successively with diluted HCl, saturated aqueous sodium hydrogen carbonate, and water. The solution was dried with Na_2SO_4, the solvent was removed at reduced pressure, and the residue was purified by chromatography on silica gel to afford the isomeric mixture of the tosylates 7 and 8 as an oil (1.80 g, 67%). Separation of the isomers is achieved by layer chromatography on silica gel (diethyl ether/hexane (1:1)) to yield from the less polar fraction the tosylate 7 (1.35 g) and from the polar fraction the tosylate 8 (0.45 g).

Data for 7: $[\alpha]^{20}_D$ −11.1° (*c* 0.2, CH_2Cl_2); IR (CCl_4) 3063, 2937, 2902, 1492, 1449, 1373, 1276, 1215, 1189, 1178, 1122, 1097, 1075, 1034, 963, 947, 911 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.74–1.85 and 1.92–2.03 (m, 3 H, SCH_2CH_2, 2a-H), 2.04 (ddd, J_{gem} = 15.2 Hz, $J_{2b,3}$ = 9.3 Hz, $J_{1,2b}$ = 4.1 Hz, 1 H, 2b-H), 2.34 (d, J = 4.5 Hz, 1 H, OH), 2.44 (s, 3 H, CH_3), 2.60–2.80 (m, 4 H, SCH_2), 3.07 (dd, J_{gem} = 9.7 Hz, $J_{4,5a}$ = 6.3 Hz, 1 H, 5a-H), 3.23 (dd, J_{gem} = 9.7 Hz, $J_{4,5b}$ = 6.6 Hz, 1 H, 5b-H), 3.71 (dd, $J_{1,2a}$ = 10.6 Hz, $J_{1,2b}$ = 4.1 Hz, 1 H, 1-H), 4.04–4.11 (m, 1 H, 4-H), 5.00 (dt, $J_{2b,3}$ = 9.3 Hz, $J_{2a,3\text{ and }3,4}$ = 3.1 Hz, 1 H, 3-H), 7.23–7.41 (m, 17 H, Ar-H), 7.80 (d, J = 8.3 Hz, 2H, Ts-H); ^{13}C NMR ($CDCl_3$) δ 21.71 (q, CH_3), 25.65 (t, SCH_2CH_2), 28.84 (t, SCH_2), 29.49 (t, SCH_2), 34.93 (t, C-2), 42.07 (d, C-1), 63.75 (t, C-5), 71.71 (d, C-3), 80.96 (d, C-4), 87.19 (s, CPh_3), 127.24, 127.95, 128.12, 128.62, 129.83 (d, Ar-C), 133.66, 143.43, 144.96 (s, Ar-C); MS (70 eV) m/z 552 (0.05), 430 (0.8), 428 (1), 400 (0.8), 324 (12), 323 (9), 281 (6), 243 (100), 172 (36), 165 (79), 107 (20), 91 (48). Anal. Calcd for $C_{34}H_{36}O_5S_3$: C, 65.78; H, 5.85. Found: C, 65.64; H, 5.88.

Data for 8: $[\alpha]^{20}_D$ −14.4° (*c* 0.2, CH_2Cl_2); IR (KBr) 2927, 1449, 1216, 1177, 1122, 1033, 1011, 707, 682, 568 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.63 (ddd, $J_{1,2a}$ = 4.4 Hz, $J_{2a,3}$ = 10.2 Hz, J_{gem} = 14.5 Hz, 1 H 2a-H), 1.72 (ddd, $J_{2b,3}$ = 2.7 Hz, $J_{1,2b}$ = 10.1 Hz, J_{gem} = 14.1 Hz, 1 H, 2b-H), 1.79–1.95 and 2.02–2.11 (m, 2 H, SCH_2CH_2), 2.41 (s, 3 H, CH_3), 2.73–2.88 (m, 4 H, SCH_2CH_2), 3.32 (d, $J_{4,5}$ = 4.9 Hz, 2 H, 5-H), 4.12 (dd, $J_{1,2a}$ = 4.4 Hz, $J_{1,2b}$ = 10.1 Hz, 1 H, 1-H), 4.19 (ddd, $J_{2b,3}$ = 2.6 Hz, $J_{3,4}$ = 4.3 Hz, $J_{2a,3}$ = 10.3 Hz, 1 H, 3-H), 4.46–4.51 (m, 1 H, 4-H), 7.28–7.35 (m, 17 H, ArH), 7.78 (d, J = 8.3 Hz, 2 H, TsH); ^{13}C NMR ($CDCl_3$) δ 21.69 (q, CH_3), 25.87 (d, SCH_2CH_2), 29.43 and 29.93 (t, SCH_2), 37.73 (t, C-2), 43.23 (d, C-1), 62.48 (t, C-5), 68.10 (d, C-4), 83.35 (d, C-3), 87.37 (s, CPh_3), 127.25, 127.98, 128.56, 129.88 (d, Ar), 133.46, 143.17, 144.98 (s, Ar); MS (70 eV) m/z 582 (0.02), 340 (1), 260 (18), 243 (100), 183 (36), 165 (34), 105 (16). Anal. Calcd for $C_{34}H_{36}O_5S_3$: C, 65.78; H, 5.85. Found: C, 65.59; H, 5.78.

3,4-Anhydro-2-deoxy-5-*O*-(triphenylmethyl)-D-*threo*-pentose Cyclic 1,3-Propanediyl Mercaptal (9) and 3,4-Anhydro-2-deoxy-5-*O*-(triphenylmethyl)-L-*threo*-pentose Cyclic 1,3-Propanediol Mercaptal (11). A solution of the trityl tosylates 7 or 8 (120 mg, 0.19 mmol) in anhydrous methanol (5 mL) is treated with a 1 N solution of sodium methanolate (0.2 mL), stirred for 3 h (TLC monitoring) and then neutralized with solid NH_4Cl. The methanol is removed under reduced pressure, and the residue is dissolved in CH_2Cl_2, filtered, and evaporated to afford, respectively, 11 as an oil (82 mg, 97%) [$[\alpha]^{20}_D$ 7.7° (*c* 0.1, CH_2Cl_2)] and oily 9 (83 mg, 98%): $[\alpha]^{20}_D$ −7.1 ° (*c* 0.1, CH_2Cl_2); IR (CCl_4) 3063, 2937, 2903, 1277, 1221, 1183, 1091, 1069, 1034 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.76–2.09 (m, 4 H, 2-H and SCH_2CH_2),

2.74–2.91 (m, 4 H, SCH_2), 2.99 (ddd, $J_{4,5a}$ = 5.0 Hz, $J_{4,5b}$ and $J_{3,4}$ = 2.7 Hz, 1 H, 4-H), 3.05 (dt, $J_{2,3}$ = 5.8 Hz, $J_{3,4}$ = 2.0 Hz, 1 H, 3-H), 3.13 (dd, J_{gem} = 10.8 Hz, $J_{4,5a}$ = 5.4 Hz, 1 H, 5a-H), 3.30 (dd, J_{gem} = 10.8 Hz, $J_{4,5b}$ = 3.2 Hz, 1 H, 5b-H), 4.21 (dd, $J_{1,2}$ = 7.7 and 6.2 Hz, 1 H, 1-H), 7.18–7.30 and 7.43–7.47 (m, 15 H, Ar-H); ^{13}C NMR ($CDCl_3$) δ 25.55 (t, SCH_2CH_2), 30.14 (t, SCH_2), 30.33 (t, SCH_2), 37.95 (t, C-2), 44.50 (d, C-1), 53.42 (d, C-4), 57.59 (d, C-3), 64.13 (t, C-5), 86.67 (s, CPh_3), 126.99, 127.79, 128.61 (d, Ar-C), 143.76 (s, Ar-C); MS (70 eV) m/z 448 (12) (M^+), 387 (2), 243 (100), 205 (38), 165 (43), 145 (10), 132 (8), 119 (23), 105 (19). Anal. Calcd for $C_{27}H_{28}O_2S_2$: C, 72.29; H, 6.30. Found: C, 72.15; H, 6.38 for **9** and C, 72.18; H, 6.39 for **11**.

[*S*-(*R,*R**)]-1-(4,8-Dithiaspiro[2.5]oct-1-yl)-2-(triphenylmethoxy)ethanol (10) and [*R*-(*R**,*R**)]-1-(4,8-Dithiaspiro[2.5]oct-1-yl)-2-(triphenylmethoxy)ethanol (12).** A solution of the epoxides **9** and **11** (70 mg, 0.16 mmol) in anhydrous THF (10 mL) is treated under nitrogen at −50 °C with an 1.6 N solution of *n*-BuLi in *n*-hexane (0.1 mL, 0.16 mmol). The solution is stirred for 3 h at 20 °C (TLC monitoring) and then poured into a diluted aqueous ammonium chloride solution (10 mL). Excess THF is removed at reduced pressure, and the product is extracted with CH_2Cl_2 and washed with water. The organic phase is dried with Na_2SO_4 and evaporated to dryness, and the residue is separated by layer chromatography on silica gel to give, respectively, the oily spiro compound **10** (52 mg, 74%) [$[\alpha]^{20}_D$ 9.1° (*c* 0.1, CH_2Cl_2)] and oily **12** (50 mg, 71%): $[\alpha]^{20}_D$ −9.2° (*c* 0.1, CH_2Cl_2); IR (CCl_4) 3064, 2926, 1090, 1071, 1034, 909 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.09 (t, J_{gem} and $J_{1a,2}$ = 5.9 Hz, 1 H, 2a-H), 1.21 (dd, $J_{1,2b}$ = 9.0 Hz, J_{gem} = 5.4 Hz, 1 H, 1b-H), 1.52 (dt, $J_{1,2b}$ = and $J_{1,1'}$ = 8.5 Hz, $J_{1,2a}$ = 6.6 Hz, 1 H, 1-H), 1.64 (br s, 1 H, OH), 1.86–1.94 (m, 2 H, SCH_2CH_2), 2.40–2.81 (m, 4 H, SCH_2), 3.20 (dd, J_{gem} = 9.4 Hz, $J_{1'2'a}$ = 6.6 Hz, 1 H, 2'a-H), 3.33 (dd, J_{gem} = 9.4 Hz, $J_{1',2'b}$ = 3.3 Hz, 1 H, 2'b-H), 3.72 (dt, $J_{1',2'a}$ and $J_{1,1'}$ = 7.3 Hz, $J_{1',2'b}$ = 3.3 Hz, 1 H, 1'-H), 7.14–7.26 and 7.33–7.42 (m, 15 H, Ar-H), ^{13}C NMR ($CDCl_3$) δ 21.21 (t, C-2), 24.87 (t, C-6), 28.21 (s, C-3), 29.13, 29.40 (t, C-5 or C-7), 32.60 (d, C-1), 66.77 (t, C-2'), 70.24 (d, C-1'), 85.77 (s, CPh_3), 126.11, 126.91, 127.70 (d, Ar-C), 142.73 (s, Ar-C); MS (EI, 70 eV) m/z 419 (0.2), 387 (1.5), 243 (100), 205 (54) (M^+ − CPh_3), 165 (52), 145 (44), 105 (10). Anal. Calcd for $C_{27}H_{28}O_2S_2$: C, 72.29; H, 6.30. Found: C, 72.14; H, 6.34 for **10** and C, 72.20; H, 6.33 for **12**.

2-Deoxy-3,5-*O*-(1-methyl-1,1-ethanediyl)-4-*O*-[(4-methylphenyl)sulfonyl]-D-*erythro*-pentose Cyclic Propane-1,3-diyl Mercaptal (13) and 2-Deoxy-4,5-*O*-(1-methyl-1,1-ethanediyl)-3-*O*-[(4-methylphenyl)sulfonyl]-D-*erythro*-Pentose Cyclic Propane-1,3-diyl Mercaptal (14). A solution of the tosylates **7** and **8** (1.15 g, 1.86 mmol) in 2,2-dimethoxypropane (15 mL) is treated with *p*-toluenesulfonic acid (250 mg), and the mixture is stirred for 1 d at 20 °C. The solution is neutralized with solid sodium hydrogen carbonate and filtered, and the 2,2-dimethoxypropane is removed under reduced pressure. The residue is dissolved in CH_2Cl_2, washed with water, and dried with Na_2SO_4, and the solvent is removed under reduced pressure. Layer chromatographic separation on silica gel yields from the polar fraction of the 4,5-acetonide **14** (410 mg, 53%) [mp 119 °C; $[\alpha]^{20}_D$ −34.1° (*c* 0.7, chloroform)] and the 3,5-acetonide **13** (190 mg, 24%) [mp 80 °C; $[\alpha]^{20}_D$ −31.1° (*c* 0.5, CH_2Cl_2)].

Data for 13: IR (KBr) 2975, 2946, 2905, 1366, 1349, 1270, 1216, 1191, 1177, 1064, 957, 915, 845, 818, 768, 674, 556, 532 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.31 (s, 3 H, $OCCH_3$), 1.38 (s, 3 H, $OCCH_3$), 1.79–1.91 and 2.00–2.15 (m, 4 H, 2-H and SCH_2CH_2), 2.46 (s, 3 H, $ArCH_3$), 2.54–2.86 (m, 4 H, SCH_2), 3.75 (dd, $J_{1,2}$ = 8.0 and 6.3 Hz, 1 H, 1-H), 3.78 (dd, J_{gem} = 8.8 Hz, $J_{4,5a}$ = 5.4 Hz, 1 H, 5a-H), 4.01 (dd, J_{gem} = 8.9 Hz, $J_{4,5b}$ = 6.7 Hz, 1 H, 5b-H), 4.22 (q, J = 5.6 Hz, 1 H, 4-H), 4.86 (q, J = 5.5 Hz, 1 H, 3-H), 7.36 (d, Ar-H, J = 8.1 Hz, 2 H), 7.84 (d, J = 8.3 Hz, 2 H, Ar-H); ^{13}C NMR ($CDCl_3$) δ 20.68 (q, Ar-CH_3), 23.96 (q, CH_3), 24.67 (t, SCH_2CH_2), 25.21 (q, CH_3), 28.02 (t, SCH_2), 28.53 (t, SCH_2), 41.11 (d, C-1), 65.08 (t, C-5), 75.52 and 78.27 (2 d, C-4, C-3), 109.22 (s, O-*C*-CH_3), 126.98 (d, Ar-C), 128.83 (d, Ar-C), 132.98 (s, Ar-C), 143.94 (s, Ar-C-1)); MS (70 eV) m/z 418 (63) (M^+), 403 (90), 360 (22), 315 (25), 283 (10), 246 (36), 188 (36), 155 (32), 145 (78), 119 (77), 101 (100), 91 (84), 73 (28). Anal. Calcd for $C_{18}H_{26}O_5S_3$: C, 51.64; H, 6.26. Found: C, 52.16; H, 6.45.

Data for 14: IR (CCl_4) 2996, 2943, 2803, 1382, 1354, 1266, 1226, 1203, 1191, 1180, 1163, 1130, 1098, 1081 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (s, 3 H, $OCCH_3$), 1.42 (s, 3 H, $OCCH_3$), 1.51 (ddd, J_{gem} = 14.2 Hz, $J_{2a,3}$ = 10.2 Hz, $J_{1,2a}$ = 3.8 Hz, 1 H, 2a-H), 1.80–1.92 (m, 2 H, H-2b and SCH_2CH_2), 2.02–2.14 (m, 1 H, SCH_2), 2.46 (s, 3 H, $ArCH_3$), 2.68–2.82 (m, 4 H, SCH_2), 3.74 (dd, J_{gem} = 11.9 Hz, $J_{4,5a}$ = 7.8 Hz, 1 H, 5a-H), 3.88 (dd, J_{gem} = 12.0 Hz, $J_{4,5b}$ = 5.2 Hz, 1 H, 5b-H), 3.98–4.05 (m, 2 H, 1-H and 4-H), 4.15 (dt, $J_{4,5a}$ = 8.2 Hz, $J_{3,4}$ = 8.2 Hz, $J_{4,5b}$ = 5.3 Hz, 1 H, 4-H), 7.38 (d, J = 8.0 Hz, 2 H, Ar-H), 7.80 (d, J = 8.2 Hz, 2 H, Ar-H); ^{13}C NMR ($CDCl_3$) δ 19.86 (q, $OCCH_3$), 21.70 (q, $ArCH_3$), 25.96 (t, SCH_2CH_2), 27.44 (q, $OCCH_3$), 28.72 (t, SCH_2), 29.31 (t, SCH_2), 37.13 (t, C-2), 41.76 (d, C-1), 62.21 (t, C-5), 67.17 (d, C-4), 75.78 (d, C-3), 99.65 (s, $OCCH_3$), 128.01 (d, Ar-C), 130.11 (d, Ar-C), 133.11 (s, Ar-C), 145.50 (s, Ar-C-1); MS (70 eV) m/z 418 (22) (M^+), 403 (22) (M^+ − CH_3), 360 (14), 315 (5), 246 (16), 227 (10), 188 (100), 155 (49), 133 (47), 119 (61), 91 (70). Anal. Calcd for $C_{18}H_{26}O_5S_3$: C, 51.64; H, 6.26. Found: C, 52.23; H, 6.31.

[*S*-(*R,*S**)]-1-[2,2-Dimethyl[1,3]dioxolan-4-yl)-4,8-dithiaspiro[2.5]octane (15).** A solution of tosyl acetonide **14** (400 mg, 1 mmol) in anhydrous THF (15 mL) is treated at −50 °C under nitrogen with 1.6 N *n*-butyllithium solution in *n*-hexane (0.66 mL, 1 equiv). The mixture is poured into a saturated aqueous ammonium chloride solution (10 mL). The THF is removed at reduced pressure, and the aqueous phase is extracted with CH_2Cl_2, dried with Na_2SO_4, and separated by layer chromatography on silica gel to yield **15** (180 mg, 73%) as an oil: $[\alpha]^{20}_D$ 27.5° (*c* 0.2, CH_2Cl_2); IR (KBr) 2989, 2937, 2904, 1371, 1276, 1066 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.76 (t, J_{gem} and $J_{1,2a}$ = 6.2 Hz, 1 H, 2a-H), 1.18 (dd, J_{gem} = 6.0 Hz, $J_{1,2b}$ = 9.0 Hz, 1 H, 7b-H), 1.37 (s, 3 H, CH_3), 1.50 (s, 3 H, CH_3), 1.54 (dt, $J_{1,4'}$ and $J_{1,2b}$ = 9.2 Hz, $J_{1,2a}$ = 6.5 Hz, 1 H, 1-H), 1.94–2.06 and 2.15–2.23 (m, 2 H, SCH_2CH_2), 2.61–2.68 and 2.74–2.84 (m, 2 H, SCH_2), 3.07 (ddd, J = 2.4/11.4/13.7 Hz, 1 H, SCH_2), 3.36 (ddd, J = 2.4/11.8/14.0 Hz, 1 H, SCH_2), 3.80 (dd, J_{gem} = 7.8 Hz, $J_{4',5'a}$ = 6.4 Hz, 1 H, 5'a-H), 3.91 (dt, $J_{1,4'}$ = 9.3 Hz, $J_{4',5'a/b}$ = 6.2 Hz, 1 H, 4'-H), 4.04 (dd, J_{gem} = 7.7 Hz, $J_{4',5'b}$ = 5.9 Hz, 1 H, 5'b-H); ^{13}C NMR ($CDCl_3$) δ 19.67 (t, C-7), 25.88 (q, CH_3), 25.90 (t, SCH_2CH_2), 27.29 (q, CH_3), 29.80 (t, SCH_2), 29.96 (s, C-3), 30.83 (t, SCH_2), 34.95 (d, C-1), 68.52 (t, 5'-10), 77.66 (d, C-4'), 109.30 (s, OCO); MS (70 eV) m/z 246 (36) (M^+), 231 (36) (M^+ − CH_3), 218 (12), 188 (10), 171 (20), 145 (100), 132 (20), 101 (53). Anal. Calcd for $C_{11}H_{18}O_2S_2$: C, 53.62; H, 7.36. Found: C, 53.59; H, 7.38.

α- and β-Methyl 2-Deoxy-D-*erythro*-pentofuranoside (16a/b). A solution of 2-deoxy-D-ribose (**1**; 5.00 g, 0.037 mol) in anhydrous MeOH (80 mL) is treated at 5 °C with concd H_2SO_4 (0.5 mL) and stirred for 40 min. The solution is neutralized with basic exchange resin, and the solvent is removed under reduced pressure to afford 5.50 g of an oily mixture of the anomeric methyl glycosides **16a/b** that is used without purification.

α- and β-Methyl 2-Deoxy-3,5-*O*-dimethyl-D-*erythro*-pentofuranoside (17a/b). A suspension of 80% NaH (2.33 g, 2.1 equiv, washed with *n*-pentane) in anhydrous THF (100 mL) is treated dropwise under nitrogen with a solution of the crude anomeric mixture of **16a/b** (5.50 g) in THF (30 mL). After the solution is stirred for 1 h at 50 °C, methyl iodide (4.8 mL) is added at 20 °C and stirring is continued for 18 h. The mixture is neutralized with 3 N HCl, filtered, and evaporated at reduced pressure. The residue is dissolved in diethyl ether, washed with water, dried with Na_2SO_4, and separated by column chromatography on silica gel to afford oily **17a/b** (4.58 g, 72% over two steps): ^1H NMR ($CDCl_3$) δ 1.98–2.10 and 2.15–2.27 (m, 2 H, 2-H), 3.31–3.56 (m, 11 H, 2 × 5-H, 3 × OCH_3), 3.75–3.81 and 3.88–3.94 (m, 1 H), 4.10–4.20 (m, 1 H), 5.05–5.10 (m, 1 H, 1-H); ^{13}C NMR ($CDCl_3$ δ 38.43 and 39.95 (t, C-2), 54.96 and 55.21/57.17 and 57.48/59.19 and 59.36 (q, 3 × OCH_3), 73.20 and 74.77 (t, C-5), 81.47 and 82.02/81.96 and 82.39 (d, C-3 and C-4), 105.29 and 105.44 (d, C-1).

2-Deoxy-3,5-*O*-dimethyl-D-*erythro*-pentose Cyclic 1,3-Propanediyl Mercaptal (18). A suspension of silica gel (20 g) in CH_2Cl_2 (20 mL) is treated with vigorous stirring with 1 mL of 6 N HCl and then $ZnCl_2$ (2 g) and 1,3-propanedithiol (2 mL), a solution of α,β-methyl 3,5-*O*-dimethyl-2-deoxy-D-*erythro*-ribofuranoside (**17a/b**; 1.70 g, 9.7 mmol) in CH_2Cl_2 (5 mL) is added, and stirring is continued for 3 h at 20 °C. The suspension is filtered, and the silica gel is washed three times with 100 mL of diethyl ether. The filtrate is evaporated at reduced pressure, and the oily residue is dissolved in diethyl ether, washed with water,

dried with Na_2SO_4, evaporated, and purified by layer chromatography on silica gel (CH_2Cl_2/2% MeOH) to afford oily **18** (1.99 g, 81%) as a crystalline mass: mp 40 °C, $[\alpha]^{20}_D$ 8.9° (*c* 0.58, CH_2Cl_2); IR (KBr) 3398, 2936, 2902, 1421, 1247, 1193, 1101, 1085, 998, 878, 877 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.82–2.02 (m, 3 H, 2 × 2-H and SCH_2CH_2), 2.09–2.18 (m, 1 H, SCH_2CH_2), 2.75 (d, J = 3.6 Hz, 1 H, OH), 2.80–2.96 (m, 4 H, SCH_2), 3.40 (s, 3 H, OCH_3), 3.44 (s, 3 H, OCH_3), 3.44 (d, J = 5.9 Hz, 2 H, 5-H), 3.50–3.56 (m, 1 H, 3-H), 3.85–3.92 (m, 1 H, 4-H), 4.21 (dd, J = 5.1 and 9.3 Hz, 1 H, 1-H); ^{13}C NMR ($CDCl_3$) δ 26.22 (t, SCH_2CH_2), 30.09 u, 30.54 (t, SCH_2), 36.51 (t, C-2), 43.92 (d, C-1), 58.62 and 59.38 (q, OCH_3), 71.27 and 78.43 (d, C-3/C-4), 73.60 (t, C-5); MS (EI, 70 eV) m/z 252 (16) $(M)^+$, 220 (14) $(M - CH_4O)^+$, 175 (6), 145 (76), 119 (100), 113 (16), 87 (18). Anal. Calcd for $C_{10}H_{20}O_3S_2$: C, 47.59; H, 7.99; S, 25.41. Found: C, 47.60; H, 8.04; S, 25.40.

2-Deoxy-3,5-di-*O*-methyl-4-*O*-[(4-methylphenyl)-sulfonyl]-D-*erythro*-pentose Cyclic 1,3-Propanediyl Mercaptal (19). A solution of dithioacetal **18** (1.80, g 7.1 mmol) in anhydrous pyridine (20 mL) is treated with *p*-toluenesulfonyl chloride (1.49 g, 1.1 equiv) and stirred for 2 d at 20 °C. The mixture is poured into ice-cold 1 N HCl (20 mL) and extracted three times with CH_2Cl_2 (100 mL). The organic phase is washed with aqueous saturated sodium hydrogen carbonate solution, dried with Na_2SO_4, and evaporated at reduced pressure. The residue is separated by column chromatography on silica gel (CH_2Cl_2) to afford oily **19** (2.20 g, 76%): $[\alpha]^{20}_D$ −9.0° (*C* 1.35, CH_2Cl_2); IR (CH_2Cl_2) 3055, 2987, 2936, 1423, 1363, 1122, 1097, 1033, 1011, 910, 897, 816 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.80–1.92 (m, 3 H, 2 × 2-H and SCH_2CH_2), 2.06–2.14 (m, 1 H, SCH_2CH_2), 2.44 (s, 3 H, Ar-CH_3), 2.78–2.91 (m, 4 H, SCH_2), 3.25 (s, 3 H, OCH_3), 3.31 (s, 3 H, OCH_3), 3.48–3.59 (m, 2 H, 5-H), 3.68–3.73 (m, 1 H, 3-H), 4.09 (t, J = 7.4 Hz, 1 H, 1-H), 4.64–4.69 (m, 1 H, 4-H), 7.33 (d, J = 8.0 Hz, 2 H, Ar-H), 7.81 (d, J = 8.1 Hz, 2 H, Ar-H); ^{13}C NMR ($CDCl_3$) δ 21.65 (q, Ar-CH_3), 25.90 (t, SCH_2CH_2), 29.52 and 30.07 (t, SCH_2), 36.54 (t, C-2), 43.38 (d, C-1), 58.65 and 59.08 (q, OCH_3), 70.74 (t, C-5), 76.55 and 80.86 (d, C-3/C-4), 127.98 and 129.61 (d, C-Ar), 133.93 and 144.67 (s, C-Ar); MS (DCI, NH_3, pos) m/z 424 (100) $(M + NH_4)^+$, 407 (7) $(M + H)^+$, 373 (5), 270 (18), 203 (32), 178 (76), 162 (18). Anal. Calcd for $C_{17}H_{26}O_5S_3$: C, 50.22; H, 6.45; S, 23.66. Found: C, 50.23; H, 6.49; S, 23.55.

Cyclization of Tosylate 19. A solution of dithioacetal **19** (1.10 g, 2.7 mmol) in anhydrous THF (30 mL) is treated under nitrogen at −50 °C within 0.5 h with a solution of 1.6 N *n*-BuLi (1.7 mL) in *n*-hexane and stirred for 2 h at 20 °C. An aqueous ammonium chloride solution (3 mL) is added, and the THF is removed at reduced pressure. The residue is dissolved in diethyl ether, washed with water, dried with Na_2SO_4, evaporated, and separated by layer chromatography (ether:hexane (1:1)) to afford oily **20** (114 mg, 18%) from the less polar fraction $[\alpha]^{20}_D$ 43.7° (*c* 1.9, CH_2Cl_2)] and oily **21** (208 mg, 35%) from the polar fraction $[\alpha]^{20}_D$ −22.3° (*c* 1.5, CH_2Cl_2)].

(1*S*-*cis*)-2-Methoxy-1-(methoxymethyl)-5,9-dithiaspiro-[3.5]nonane (20): IR (film) 2930, 2896, 2827, 1221, 1131, 1103, 1044 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.87–2.09 (m, 2 H, SCH_2CH_2), 2.21 (dd, J_{gem} = 12.7 Hz, $J_{2,3}$ = 7.1 Hz, 1 H, 3a-H), 2.58–2.67 (m, 2 H, 3b-H, 1-H), 2.75–2.82 and 2.84–2.92 (m, 2 H, SCH_2), 3.05–3.12 (m, 2 H, SCH_2), 3.26 (s, 3 H, OCH_3), 3.39 (s, 3 H, OCH_3), 3.66 (dd, J_{gem} = 10.0 Hz, $J_{1a',1}$ = 5.4 Hz, 1 H, 1a'-H), 3.72 (dd, J_{gem} = 10.0 Hz, $J_{1'b,1}$ = 8.6 Hz, 1 H, 1b'-H), 4.16 (q, J = 7.2 Hz, 1 H, 2-H); ^{13}C NMR ($CDCl_3$) δ 25.17 (t, SCH_2CH_2), 28.52 and 28.60 (t, SCH_2), 43.61 (t, C-3), 46.60 (s, C-4), 53.27 (d, C-1), 56.82 (q, OCH_3), 58.61 (q, OCH_3), 69.90 (t, C-1'), 72.36 (d, C-2); MS (70 eV) m/z 234 (5) $(M)^+$, 202 (2), 189 92), 176 (4), 161 (4), 145 (10), 132 (100), 101 (10), 85 (6), 71 (10). HRMS 234.0748, calcd for $C_{10}H_{18}O_2S_2$ 234.074826. Anal. Calcd for $C_{10}H_{18}O_2S_2$: C, 51.25; H, 7.74. Found: C, 51.02; H, 7.73.

(*S*)-4-(1,3-Dithian-2-yl)-3-methoxy-2-butanone (21): IR (film) 2985, 2934, 2902, 1715, 1422, 1355, 1119, 909 cm^{-1}, ^1H NMR ($CDCl_3$) δ 1.85–1.96 (m, 1 H, SCH_2CH_2), 2.04–2.15 (m, 3 H, 1 × SCH_2CH_2 and 2 × 4-H), 2.20 (s, 3 H, CCH_3), 2.78–2.92 (m, 4 H, SCH_2), 3.41 (s, 3 H, OCH_3), 3.88 (dd, J = 5.2 and 7.8 Hz, 1 H, 3-H), 4.16 (dd, J = 5.2 and 8.3 Hz, 1 H, 2'-H); ^{13}C NMR ($CDCl_3$) δ 25.54 (q, C-1), 25.83 (t, SCH_2CH_2), 29.23 and 29.62 (t, SCH_2), 37.30 (t, C-4), 42.50 (d, C-2'), 58.55 (q, OCH_3), 83.71 (d, C-3), 210.41 (s, C-2); MS (70 eV) m/z 220 (2) $(M)^+$, 177 (1.5), 145 (1.5), 133 (92), 119 (100), 103 (8), 88 (24); HRMS 220.0591 ±2 ppm (M^+) calcd for $C_9H_{16}O_2S_2$ 220.05917. Anal. Calcd for $C_9H_{16}O_2S_2$: C, 49.06; H, 7.32. Found: C, 49.22; H, 7.44.

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Registry No. **1**, 533-67-5; **2**, 50907-65-8; **3**, 135598-34-4; **4**, 135598-35-5; **5**, 135598-36-6; **6**, 135598-37-7; **7**, 135598-38-8; **8**, 135598-39-9; **9**, 135598-40-2; **10**, 135619-08-8; **11**, 135598-41-3; **12**, 135598-42-4; **13**, 135598-43-5; **14**, 135598-44-6; **15**, 135598-45-7; **16a**, 51255-17-5; **16b**, 51255-18-6; **17a**, 83149-37-5; **17b**, 83149-38-6; **18**, 135598-46-8; **19**, 135598-47-9; **20**, 135598-48-0; **21**, 135598-49-1; 1,3-propanedithiol, 109-80-8.

Spontaneous Oxygenation of Cyclic Olefins: Effects of Strain[1]

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Reactivity of strained olefins **1–3**, **41**, and **44** toward spontaneous oxygenation has been evaluated. Angle-strained olefins **1**, **32**, and **35** react spontaneously with ground-state triplet oxygen, at room temperature, to yield quantitatively, not copolymers or hydroperoxides, but epoxides and diketones in approximately a 2:1 ratio. The autoxidation of **1** is carried out with various solvents, inhibitors, initiators, and in the presence of **2** and 1,2-dimethylcyclohexene to determine the mechanistic details. Compared with **1**, autoxidation of **2** and **3** follows a different route yielding mainly hydroperoxides along with other products. The mechanism of the spontaneous autoxidation is discussed in light of these results.

Introduction

The familiar examples of olefins becoming oxygenated under mild conditions follow a few well-defined models. One[2] is olefin autoxidation involving a chain reaction initiated by a free radical, generally from a thermally unstable peroxide or azo compound. Depending on the nature of the olefinic target, different chain steps at different points lead to allylic hydroperoxides, carbonyl-bearing cleavage products, epoxides, and other special products from oxygenated radicals. A second model[3] is the

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(2) Mayo, F. R.; *Acc. Chem. Res.* **1968**, *1*, 193.

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