Synthesis and Absolute Stereochemistry of a Constitutionally New Spiroacetal from an Insect

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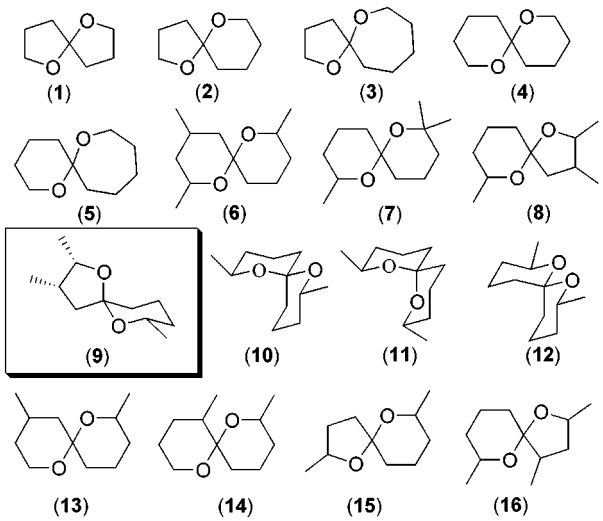
A group of about 30 constitutionally different spiroacetal structures have been characterized from insects[1] and represent five spiroacetal systems: 1,6-dioxaspiro-[4.4]nonane, 1,6-dioxaspiro[4.5]decane, 1,6-dioxaspiro-[4.6]decane, 1,7-dioxaspiro[5.5]undecane, and 1,7-dioxaspiro[5.6]decane, compounds **1**−**5** (Chart 1).

The characterized spiroacetals are very predominantly odd-numbered in carbon,[1,2] and only two, **6**[3] and **7**,[4] have branched carbon skeletons.

Recently we suggested[5] that an isomer of 2,3,7-trimethyl-1,6-dioxaspiro[4.5]decane (**8**) was a likely component of the dorsal abdominal gland secretion of the aposematic shield bug, *Cantao parentum* (White) (Hemiptera: Scutelleridae), on the basis of some mass spectral and chromatographic comparisons. We now wish to describe studies that confirm the occurrence of this unprecedented spiroacetal system (**8**) and the (2*S*,3*S*,-5*R*,7*S*) stereochemistry, as in (**9**). This completes the identification of the structurally and stereochemically most diverse suite of spiroacetals from an insect species.[1,2] This component (*B*)[6] (*M* = 184) was initially assumed to be the (*E*,*Z*)-diastereomer of 2,8-dimethyl-1,7-dioxaspiro[5.5]undecane (**10**), which often accompanies the (E,E)-diastereomer (**11**), component *A*,[6] in insects,[1,2] but retention time comparisons with the authentic (*E*,*Z*), (*E*,*E*), and (*Z*,*Z*) diastereomers **10**−**12**[7] disproved this. Arguments and data presented elsewhere[5] ruled out isomers of the 2,10- (**13**) or 2,11-dimethyldioxaspiro[5.5]-undecane (**14**) as possible structures, with the former being an 8-*des*-methyl relative of the thoroughly characterized system (**6**).[3] Other structures, of various ring sizes and methyl dispositions (with *M* = 184), were confidently eliminated.[8]

Chart 1



Detailed scrutiny of very low-level components with shorter retention times than (*B*) led to the identification of an isomer of 2,7-dimethyl-1,6-dioxaspiro[4.5]decane (*M* = 170) (**15**) by comparisons with an authentic sample.[9] Mass spectral comparisons of **15** with unknown component *B* indicated that *B* could be an isomer of either the 2,3,7- or 2,4,7-trimethyl-1,6-dioxaspiro[4.5]decane systems (**8**) and (**16**), respectively, both uncharacterized from natural sources.

The synthetic approach to these spiroacetals was based on addition of the anion of hydroxyl-protected 4-pentyn-2-ol (**17**) to appropriate[4,10] lactones **18**−**20**. Initially, a mixture of four isomers of the 2,4,7-trimethylspiro system **16** was synthesized in this way[11,12] (Scheme 1). Careful flash chromatography (silica, petroleum ether) provided the isomers (**16a**−**d**). These were of sufficient isomeric purity to permit ^{1}H and ^{13}C NMR analyses (including NOE experiments), which established the relative stereochemistry. Isomer **16d** coeluted with natural component *B* from two different GC columns, one of which had a β-cyclodextrin phase. Furthermore, the EIMS of both matched very well, except for a difference in the relative intensity of one ion (*m*/*z* 73).

This discrepancy encouraged the synthesis of spiro system **8**, initially as a stereoisomeric mixture, and one of the isomers matched *B* precisely, with respect to both coelution and mass spectra. Thus, *trans*-[13] and *cis*-lactones[14] **19** and **20**, along with an approximately 50:50

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(11) For the synthesis of the (racemic) tetrahydropyranyl ether of 4-pentyn-2-ol (**17**), see: (a) Bestmann, H. J.; Schobert, R. *Synthesis* **1989**, *6*, 419. (b) White, J. D.; Somers, T. C.; Reddy, G. N. *J. Org. Chem.* **1992**, *57*, 4991. (c) Alvarez, A.; Lera, A. R. *Tetrahedron*: *Asymmetry* **1998**, *9*, 3065.
(12) For the synthesis of the lactone 3,5-dimethyl-dihydrofuran-2-one (**18**), see: (a) Hullett, P.; Curigny, T.; Larchevêque, M.; Normant, H. *Can. J. Chem.* **1977**, *55*, 266. (b) Shum, T. J.; Marolewski, A. E.; Rezeuka, D. S.; Taylor, S. K. *J. Org. Chem.* **1989**, *54*, 2039.

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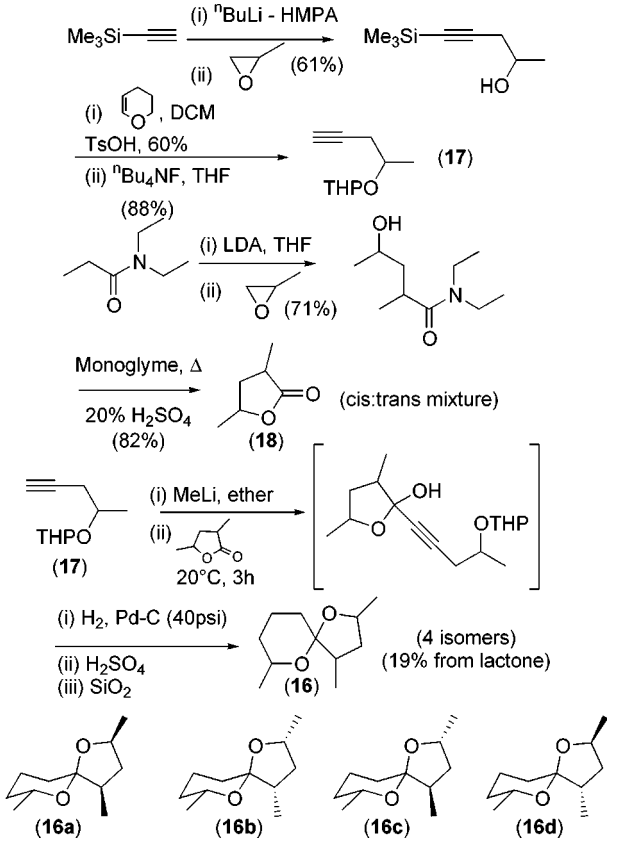
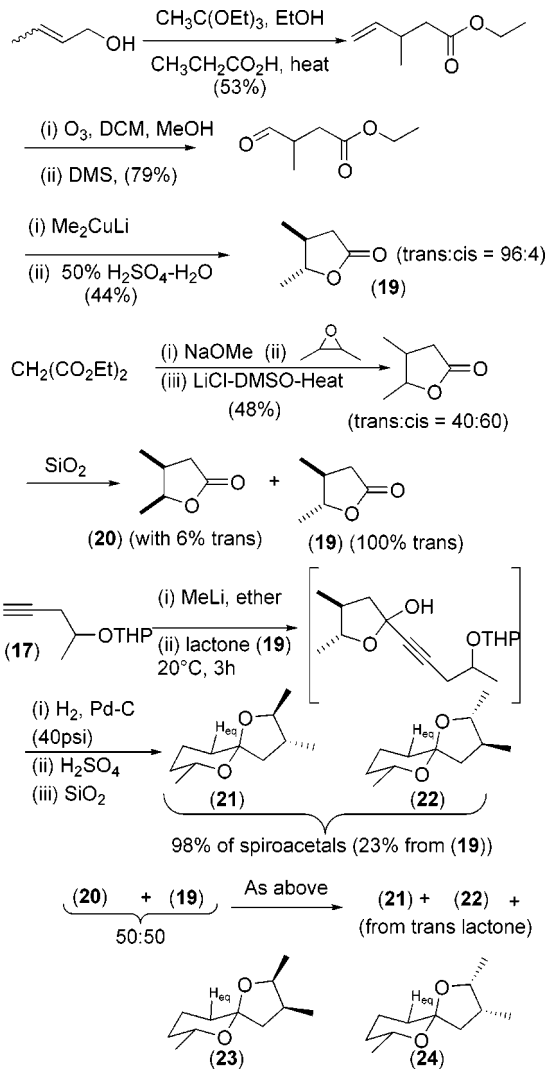
Scheme 1



mixture of each, were acquired as summarized in Scheme 2. Deprotonation of the protected 4-pentyn-2-ol (**17**) and addition to *trans*-lactone **19**, and also to the *cis*−*trans*-lactone mixture, afforded spiroacetals of system **8**. The pure *trans*-lactone **19** provided comparable amounts of spiroacetals **21** and **22** (together about 98%) and two minor isomers (∼2%), on the basis of GC−MS data. These minor isomers are probably epimers of **21** and **22** with the C_5-O_1 bond *equatorial*. The major isomers **21** and **22** were readily separated by flash chromatography and individually characterized. Lactone mixture **19** and **20** provided **21** and **22**, together with the additional spiroacetals **23** and **24**,[15] from the *cis*-lactone component **20**. The major isomers from each lactone were assigned as the anomerically stabilized ones. These outcomes are summarized in Scheme 2.

Co-injection studies, with a *β*-cyclodextrin column, showed that the natural isomer incorporated *cis-vic*-methyl groups and corresponded to a single enantiomer of one of the diastereomers **23** or **24**. Of these two, only **24** would be anticipated to exhibit NOE effects between $H10_{eq}$ and either of the C_2 and C_3 methyl groups, depending on the conformations. This conclusion could be supported by the observation of NOEs to the methyl groups from $H10_{eq}$ in each of the (separated) spiroacetals **21** and **22** that are derived from the *trans*-lactone.

Scheme 2



An enantioselective synthesis of stereoisomer **9** was developed that was based on (2*S*,3*S*)-2,3-epoxybutane (**26**), acquired from diethyl (2*R*,3*R*)-tartrate (**25**), as described by Mori and Tamada.[15] Epoxide **26** was converted to the (3*S*,4*S*)-lactone **27** with malonate ion as outlined in Scheme 2 for the racemates. Addition of the anion from THP-protected (2*S*)-4-pentyn-2-ol (**28**) to this lactone followed by reduction and cyclization afforded essentially a single isomer ($[\alpha]^{22}_D$ −16.5 (*c* 0.4, acetone)) assigned as **9** with the (2*S*,3*S*,5*R*,7*S*) configuration. The ee was >99% by enantioselective gas chromatography. A strong NOE was detected between the C-3 methyl group and H-10eq, consistent with **9** but inconsistent with the C-5 epimer, wherein the C_5-O_1 bond is *equatorial*. This and other observed NOEs are shown in Scheme 3. Comparisons of enantioselective gas chromatographic and mass spectral behavior and co-injection studies demonstrated that **9** was the natural component *B*.

This aposematic shield bug, *Cantao parentum* (White), has remarkable biosynthetic capability as evidenced by its production of the spiroacetals shown in Chart 2. These are listed in gas chromatographic elution order[6] and possess the indicated absolute stereochemistry.[3,5] This suite encompasses spiroacetals both odd- and even-numbered in carbon, of both linear and branched carbon skeletons and illustrating both the 1,7-dioxaspiro[5.5]-undecane and 1,6-dioxaspiro[4.5]decane systems.

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(15) Mori, K.; Tamada, S. *Tetrahedron* **1979**, *35*, 1279.

Scheme 3

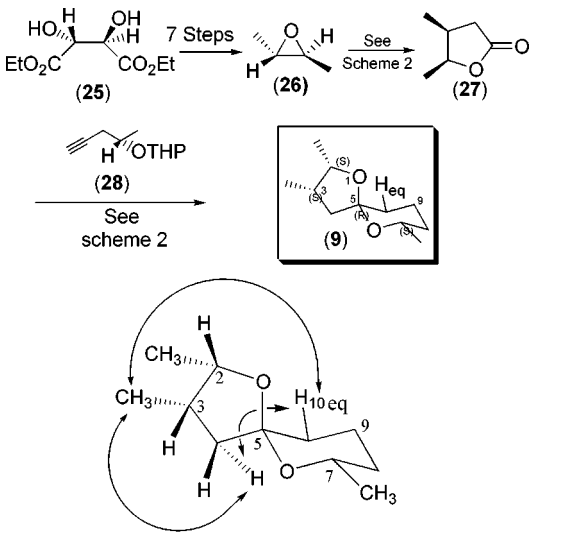
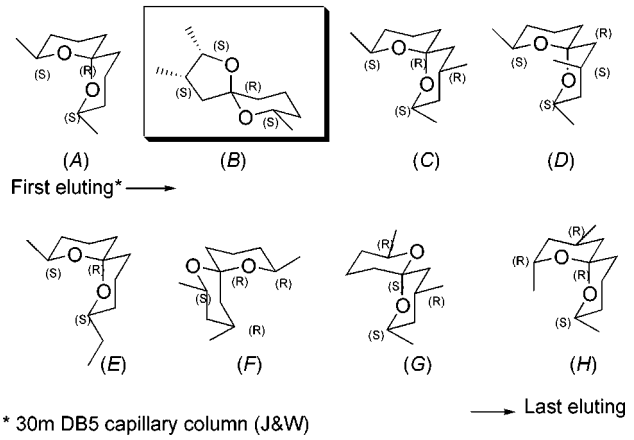


Chart 2



Experiments are being planned to establish the likely pathways to these diverse spiroacetal systems.[16]

Experimental Section

General Methods. ^{1}H NMR spectra were recorded at 400 MHz with either TMS ($\delta = 0$) or the signal for residual $CHCl_3$ in the $CDCl_3$ solvent (δ7.24), or the signal of benzene in the C_6D_6 solvent (δ7.15) as internal standards. ^{13}C NMR spectra were recorded at 100 MHz with either TMS ($\delta = 0$) or the central peak of the $CDCl_3$ triplet (δ 77.00 ppm, $CDCl_3$), or the multiplet of benzene (δ 128.00 ppm). *J* values are reported in Hz. Flash chromatography was performed with Kiesel S (0.032−0.063 mm). Enantioselective gas chromatography was conducted using a permethylated β-cyclodextrin column (SGE, 50 m, 0.25 μm).

2,4,7-Trimethyl-1,6-dioxaspiro[4.5]decanes (16a−d). Following the procedure of Williams and Smith,[10] MeLi (3.2 mmol) was added dropwise but rapidly with good stirring to a cooled solution (0 °C) of THP-protected 4-pentyn-2-ol (**17**) (3.2 mmol) in dry ether (10 mL) under an inert atmosphere. After 5 min, this solution was added to a solution of lactone **18**[12] (3.3 mmol) in dry ether (10 mL), and the resulting mixture was stirred at room temperature for 3 h. A 20% aqueous solution of NH_4Cl (5 mL) was added, and stirring was continued until all the precipitate had dissolved. The organic layer was separated, washed with 1 M aqueous $NaHCO_3$, dried ($MgSO_4$), and evaporated to give an oil. The crude oil was dissolved in MeOH (20 mL) and hydrogenated over 10% Pd/C (71 mg) at 40 psi for 2 h. Then, the mixture was filtered on Celite, and 2 drops of concentrated sulfuric acid were added. The mixture was stirred at room temperature overnight. Water (10 mL) was added and the mixture extracted with petroleum ether (3 × 20 mL). The organic layer was dried ($MgSO_4$) and concentrated. Spiroacetals **16a−d** so obtained were purified and separated on a silica column (1% ether in petroleum ether) in 19% yield.

Spiroacetal **16a**: ^{1}H NMR ($CDCl_3$) δ 0.94 (d, *J* 6.5, CH_3(4)), 1.04 (d, *J* 6.3, CH_3(7)), 1.09 (dddd, *J* 13.0, 13.0, 12.2. 4.0, H_{8ax}), 1.16 (d, *J* 6.4, CH_3(2)), 1.42 (dddd, *J* 13.1, 4.5, 1.8, 1.8, H_{10eq}), 1.51−1.58 (m, H_3), 1.52 (dm, *J* 13.0, H_{8eq}), 1.55 (dd, *J* 13.4, 12.4, H_{10ax}), 1.60 (dm, *J* 12.6, H_{9eq}), 1.80−1.84 (dm, *J* 12.6, H_{9ax}), 1.80−1.87 (m, H_4), 1.80−1.90 (m, H_3), 3.82 (dqd, *J* 12.6, 6.3, 2.2, H_7), 4.11 (dqd, *J* 14.4, 8.2, 6.4, H_2); ^{13}C NMR ($CDCl_3$) δ 12.7 (CH_3-(4)), 20.4 (C_9), 21.8(CH_3(7)), 23.7 (CH_3(2)), 31.0 (C_{10}), 32.9 (C_8), 39.0 (C_3), 41.9 (C_4), 65.5 (C_7), 71.5 (C_2), 105.6 (C_5); MS (*m*/*z*) 184 ($M^{\bullet+}$, 1.5), 169 (3.2), 140 (12.6), 125 (21.0), 115 (100), 112 (48.7), 97 (28.0), 73 (7.5), 69 (40.7), 55 (58.0), 43 (69.6), 41 (73.0); HRMS (ES, 70 eV) calcd for $C_{11}H_{21}O_2$ (M + 1) 185.153606, found 185.153282.

Spiroacetal **16b**: ^{1}H NMR ($CDCl_3$) δ 0.96 (d, *J* 6.8, CH_3(4)), 1.04 (d, *J* 6.2 (CH_3(7)), 1.09 (ddd, *J* 11.0, 4.0, 1.8, H_{8eq}), 1.22 (d, *J* 6.2, CH_3(2)), 1.42 (ddd, *J* 13.0.13.0, 4.5, H_{10ax}), 1.47 (ddd, *J* 11.6, 8.8, 8.8, H_3), 1.48−1.55 (m, H_{8ax}), 1.54 (ddd, *J* 13.8, 12.9, 4.8, H_{10eq}), 1.62 (dm, *J* 13.5, H_{9eq}), 1.79 (ddddd, *J* 13.5, 13.3, 13.3, 4.0, 4.0, H_{9ax}), 1.83 (dqd, *J* 8.8, 7.0, 6.8, H_4), 2.06 (ddd, *J* 11.7, 7.0, 7.0, H_3), 3.91 (dqd, J12.6, 6.3, 2.2, H_7), 4.11 (dqd, *J* 14.0, 8.8, 6.2, H_7); ^{13}C NMR ($CDCl_3$) δ 12.7 (CH_3(4)), 20.4 (C_9), 21.8 (CH_3(7)), 23.7 (CH_3(2)), 31.0 (C_{10}), 32.9 (C_8), 39.8 (C_3), 44.2 (C_4), 65.4 (C_7), 74.1 (C_2), 105.1 (C_5).

Spiroacetal **16c**. NMR resonances subtracted from a mixture of **16c** and **16d**, and some resonances were obscured: ^{1}H NMR ($CDCl_3$) δ 0.91 (d, *J* 7.2, CH_3(4)), 1.08 (d, *J* 6.4, CH_3(7)), 1.23 (d, *J* 6.2, CH_3(2)), 2.36 (ddd, *J* 12.2, 8.4, 7.2, H_3), 3.85 (dqd, *J* 12.6, 6.2, 2.1, H_7), 4.04 (dqd, *J* 13.4, 7.2, 6.2, H_2); ^{13}C NMR ($CDCl_3$) δ 17.5 (CH_3(4)), 20.2 (C_9), 21.7 (CH_3(7)), 22.1 (CH_3(2)), 29.7 (C_{10}), 32.9 (C_8), 40.9 (C_3), 43.1 (C_4), 66.2 (C_7), 71.8 (C_2), 107.7 (C_5).

Spiroacetal **16d**: ^{1}H NMR ($CDCl_3$) δ 0.88 (d, *J* 7.2, CH_3(4)), 1.07 (d, *J* 6.3, CH_3(7)), 1.08−1.14 (m, H_{8ax}), 1.14 (dddd, *J* 13.1, 13.1, 11.4, 4.2, H_{8eq}), 1.23 (d, *J* 6.2, CH_3(2)), 1.42 (ddd, *J* 13.0.13.0, 4.5, H_{10ax}), 1.54 (dd, *J* 12.9, 4.4, H_{10eq}), 1.61−1.69 (m, H_{9eq}), 1.63 (ddd, *J* 11.8, 6.9, 1.1, H_3), 1.76 (ddddd, *J* 13.7, 13.5, 13.3, 4.4, 4.1, H_{9ax}), 2.02 (ddd, *J* 11.8, 8.4, 7.2, H_3), 2.12 (dq, *J* 7.2, 7.2, H_4), 3.96 (dqd, *J* 12.7, 6.3, 2.2, H_7), 4.30 (dqd, *J* 14.7, 8.4, 6.2, H_2); ^{13}C NMR ($CDCl_3$) δ 15.7 (CH_3(4)), 20.3 (C_9), 21.9 (CH_3(7)), 23.6 (CH_3(2)), 29.6 (C_{10}), 32.8 (C_8), 39.6 (C_3), 43.7 (C_4), 65.8 (C_7), 74.6 (C_2), 107.9 (C_5).

(2*S*,3*S*)-2,3-Epoxybutane (26). Following a published procedure,[15] **26** was prepared in seven steps from diethyl (2*R*,3*R*)-tartrate (**25**) in 10% overall yield. NMR data were identical with whose listed by Mori:[15] $[\alpha]_D$ −54.7 (*c* 0.4, ether) (lit.[15] −61.7 (*c* 2.1, ether)).

(3*S*,4*S*)-Lactone 27. Following the Byström procedure,[14] **27** was prepared from epoxide **26** in 30% yield. NMR data were identical with those described by Byström.[14] $[\alpha]_D$ −53.4 (*c* 1.1, $CHCl_3$) (lit.[14c] + 54.1 (*c* 0.7, $CHCl_3$) for the (3*R*,4*R*)-isomer).

2,3,7-Trimethyl-1,6-dioxaspiro[4.5]decanes (9, 21−24). The procedure employed for the acquisition of **16a−d** was applied. Spiroacetals **9** and **21−24** were obtained in 19−23% yield from lactones **19**, **20**, or **27**.

Spiroacetal **21**: ^{1}H NMR (C_6D_6) δ 0.77 (d, 3H, *J* 6.5, CH_3(3)), 1.10−1.17 (m, H_{8ax}), 1.15 (d, *J* 6.3, CH_3(7)), 1.26 (dd, 1H, *J* 11.3, 11.3, H_4), 1.27 (d, 3H, *J* 6.1, CH_3(2)), 1.38−1.44 (dm, 1H, *J* 11.4, H_{8eq}), 1.52 (dm, 1H, *J* 12.2, H_{9ax}), 1.52−1.59 (m, 2H, H_{10ax} and H_{10eq}), 1.99−2.06 (m,1H, H_{9eq}), 2.10 (dd, 1H, *J* 11.6, 6.8, H_4), 2.13−2.22 (m, 1H, H_3), 3.6 (dq, 1H, *J* 8.0, 6.1, H_2), 4.13 (dqd, 1H, *J* 12.6, 6.3, 2.3, H_7); ^{13}C NMR (C_6D_6) δ 16.7 (CH_3(3)), 20.8 (C9), 21.4 (CH_3(2)), 22.3(CH_3(7)), 33.2 (C8), 34.1 (C10), 39.7 (C3), 48.2 (C4), 66.2 (C7), 83.1 (C2), 105.4 (C5); HRMS (ES, 70 eV) calcd for $C_{11}H_{21}O_2$ (M + 1) 185.153606, found 185.153434.

Spiroacetal **22**: ^{1}H NMR (C_6D_6) δ 0.88 (d,1H, *J* 6.7, CH_3(3)), 1.08−1.14 (m, 1H, H_{8ax}), 1.15 (d, 3H, *J* 6.2, CH_3(7)), 1.19 (d, 3H, *J* 6.0, CH_3(2)), 1.36−1.41 (dm, 1H, *J* 12.8, H_{8eq}), 1.45−1.53 (m, 1H, H_{9ax}), 1.49−1.57 (m, 1H, H_3), 1.54 (dd, 1H, *J* 12.9, 4.4, H_{10eq}), 1.62−1.67 (dm, 1H, *J* 12.9, H_{10ax}), 1.74 (dd, 1H, *J* 12.9, 7.7, H_4),

(16) See: (a) Hungerford, N. L.; Mazomenos, B.; Haniotakis, G.; Moore, C. J.; Fletcher, M. T.; Hübener, A.; DeVoss, J. J.; Kitching, W. *J. Chem. Soc., Chem. Commun.* **1998**, 863. (b) Stok, J. E.; Lang, C.-H.; Schwartz, B. D.; Fletcher, M. T.; Kitching, W.; DeVoss, J. J. *Org. Lett.* **2001**, *3*(3), 397−400.

1.92 (dd, 1H, *J* 12.9, 9.7, H_4), 2.01 (ddd, 1H, *J* 13.3, 4.2, 3.8, H_{9eq}), 3.76 (dq, 1H, *J* 8.5, 6.1, H_2), 4.09 (dqd, 1H, *J* 13.7, 6.2, 2.4, H_7); ^{13}C NMR (C_6D_6) δ 17.2 (CH_3(3)), 19.2 (CH_3(7)), 20.6 (C9), 22.5 (CH_3(2)), 31.8 (C8), 34.9 (C10), 40.9 (C3), 47.9 (C4), 66.7 (C7), 80.4 (C2), 105.4 (C5).

Spiroacetal **23**. NMR resonances for **23** were extracted from the spectra of a mixture of the four isomers, and some resonances were obscured: ^{1}H NMR (C_6D_6) δ 0.71 (d,1H, *J* 6.5, CH_3(3)), 1.17 (d, 3H, *J* 6.2, CH_3(2)), 1.18 (d, 3H, *J* 6.2, CH_3(7)), 3.69 (dq, 1H, *J* 8.8, 6.2, H_7), 4.08 (dq, 1H, *J* 6.5, 6.5, H_2); ^{13}C NMR (C_6D_6) δ 20.6 (C9), 33.0 (C8), 35.3 (C10), 40.2 (C3), 47.9 (C4), 67.0 (C7), 78.8 (C2), 104.8 (C5).

Spiroacetal **24**. NMR data were identical with those described for spiroacetal **9**.

Spiroacetal **9**: ^{1}H NMR (400 MHz, C_6D_6) δ 0.72 (d,1H, *J* 7.0, CH_3(3)), 1.05 (d, 3H, *J* 6.5, CH_3(2)), 1.11 (dddd, 1H, *J* 12.8, 12.3, 12.3, 4.0, H_{8ax}), 1.16 (d, 3H, J, 6.3, CH_3(7)), 1.30 (dd, 1H, *J* 12.4, 6.2, H_4), 1.40 (dm, 1H, *J* 12.8, H_{8eq}), 1.46−1.54 (dm, 1H, *J* 12.6, H_9), 1.59 (dd, 1H, *J* 11.8, 4.0, H_{10}), 1.59 (ddd, 1H, *J* 11.8, 4.0, 1.2, H_{10}), 1.67−2.07 (m, 1H, H_9), 2.21 (dd, 1H, *J* 12.4, 7.8, H_4), 2.28 (m, 1H, *J* 7.0, H_3), 4.09 (dqd, 1H, *J* 11.3, 6.2, 2.3, H_7), 4.27 (dq, 1H, *J* 6.5, 6.5, H_2); ^{13}C NMR (100 MHz, C_6D_6) δ 15.2 (CH_3-(3)), 16.2 (CH_3(2)), 20.8 (C9), 22.4 (CH_3(7)), 33.1 (C8), 34.8 (C3), 35.1 (C10), 47.5 (C4), 66.5 (C7), 76.1 (C2), 104.8 (C5); MS (*m*/*z*) 184 ($M^{\bullet+}$, 6.0), 169 (1.9), 140 (33.3), 125 (56.7), 115 (100), 112 (56.4), 97 (55.8), 73 (48.7), 69 (49.0), 55 (57.8), 43 (55.8), 41 (51.8); $[\alpha]_D$ −16.5 (*c* 0.4, acetone).

Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectra for spiroacetals **16a**−**d**, spiroacetal **9**, and spiroacetals **21** and **22**. This material is available free of charge via the Internet at http://pubs.acs.org.

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