Synthesis of Branched Triangulanes

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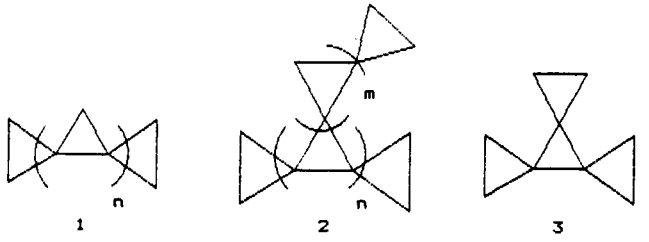
A method for the preparation of branched triangulanes (polyspirocyclopropanes) has been developed and used to synthesize tetraspiro[2.0.0.2.0.2.0.1]undecane and three isomeric pentaspirotridecanes.

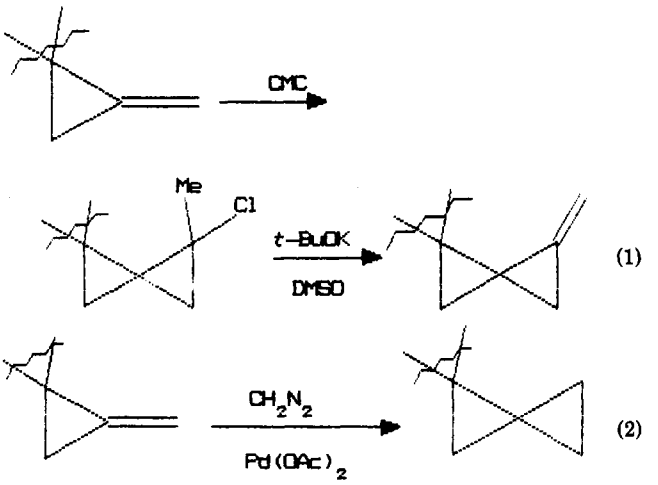
Recently we defined *triangulanes* as a unique class of polycyclic hydrocarbons constructed from spiroannulated cyclopropanes.[1] These compounds are expected to be highly strained and can exhibit unusual chemical behavior.[2] On the other hand, synthesis of compounds with a triangulane skeleton may present an intriguing problem.

Depending on their structure, the triangulanes can be subdivided into two classes: the linear triangulanes (LT), 1, and the branched triangulanes (BT), 2. Previously we



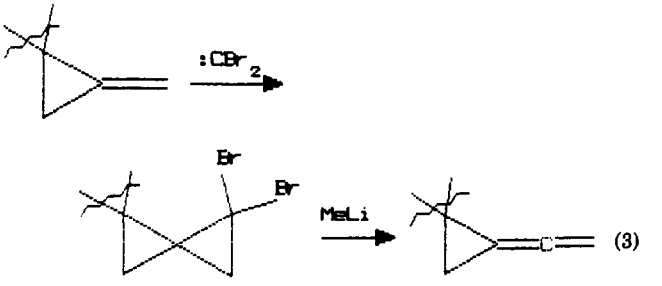
have studied the stereoisomerism in linear triangulanes[1] and developed a general[3] approach to their synthesis.[1,4] This method is based on two sequential structural transformations, namely, construction of cyclopropane moieties (extension of a synthetic chain) and cyclopropanation of a terminal methylenecyclopropane double bond (termination of a synthetic chain). A preparative version of the first transformation included cycloaddition of chloromethylcarbene (CMC)[5] to an appropriate methylenecyclopropane, followed by dehydrochlorination with potassium *tert*-butoxide in DMSO (eq 1).[1,4,5] The best results in the terminating cyclopropanation were obtained when the methylenecyclopropane double bond was treated with diazomethane under conditions of palladium(II) acetate catalysis (eq 2).[1,4]

This methodology could also be applied to the synthesis of branched triangulanes: for this purpose the corresponding polyspirocyclopropane with an internal double bond is required as the starting material. For example, the application of procedures 1 and 2 to bicyclopropylidene gave the simplest branched triangulane: trispiro[2.0.2.0.2.0]nonane (3).[3,4,6] However, the inaccessibility of higher polyspirocyclopropanes, possessing the bicyclopropylidene moiety, requires a new approach to the synthesis of branched triangulanes.



In this paper we describe a method of preparation of branched triangulanes, which includes (i) transformations 1 and 2 mentioned above as well as (ii) new procedures for chain branching and for independent chain extension in two directions.

The first of the new methods is based on transformation of a methylenecyclopropane moiety into a vinylidenecyclopropane. In practice, this was achieved by the cycloaddition of dibromocarbene to the methylenecyclopropane double bond and subsequent treatment of the resulting dibromocyclopropane derivative with methyllithium (eq 3). Two chains of spiroannulated cyclopropanes could be constructed from the allene prepared by this procedure, permitting chain branching to take place.



Independent construction of cyclopropane rings in two directions was achieved by use of two different vinylidene synthons for preparation of the methylenecyclopropane moiety. The first approach, utilizing CMC, was described above (eq 1) and was found useful in the preparation of linear triangulanes. The second approach includes the cycloaddition of (ethoxycarbonyl)carbene to one of the two double bonds of an allenic hydrocarbon, prepared during chain branching. Reduction of the ester group results in the formation of a cyclopropylcarbinol, which is trans-

(1) Zefirov, N. S.; Kozhushkov, S. I.; Kuznetzova, T. S.; Kokoreva, O. V.; Lukin, K. A.; Ugrak, B. I.; Tratch, S. S. *J. Am. Chem. Soc.* **1990**, *112*, 7702.

(2) For reviews, see: (a) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Wasserman, H. H., Eds.; Academic Press: New York, 1978; pp 1–406. (b) Strained organic compounds. *Chem. Rev.* **1989**, *89*, *No. 5*. pp 973–1270.

(3) For earlier syntheses of simple LTs, see: Fitjer, L.; Conia, J. M. *Angew. Chem.* **1973**, *85*, 349, 832.

(4) Zefirov, N. S.; Lukin, K. A.; Kozhushkov, S. I.; Kuznetzova, T. S.; Domarev, A. M.; Sosonkin, I. M. *Zh. Org. Khim.* **1989**, *25*, 312.

(5) Arora, S.; Binger, P. *Synthesis* **1974**, *No. 11*, 801.

(6) Erden, J. *Synth. Commun.* **1986**, *16*, 117.

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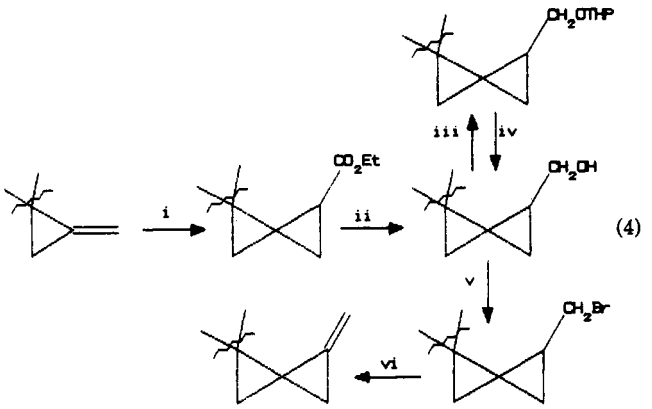
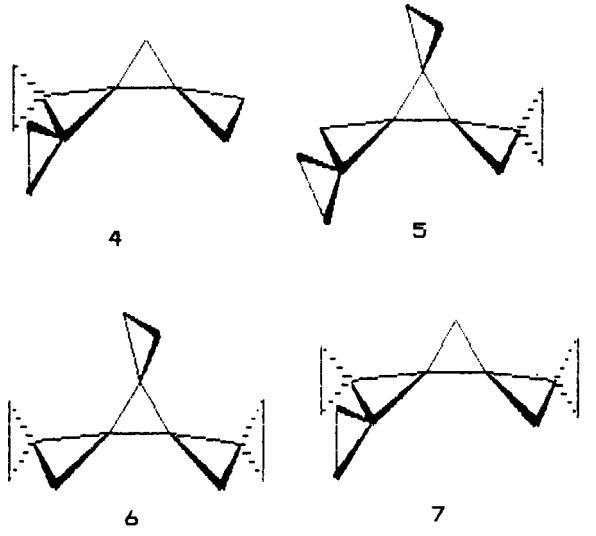
formed into a methylenecyclopropane via halogenation–dehydrohalogenation. While procedure 1 is used for construction of a chain of cyclopropanes, the hydroxyl group is protected as the tetrahydropyran-2-yl derivative (eq 4).[7]



(4)

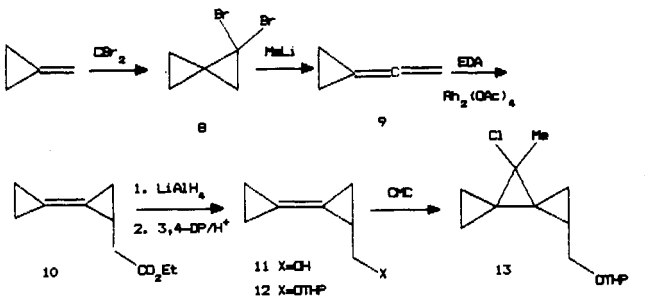
The application of such an approach to the synthesis of branched triangulanes was demonstrated by the preparation of hydrocarbons 4–7.



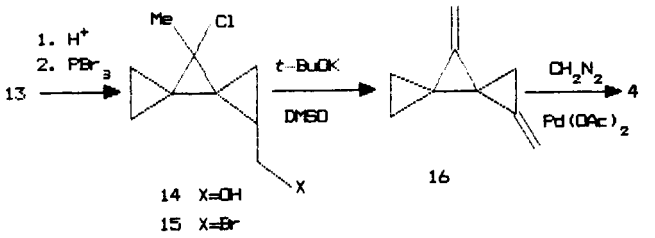
Cycloaddition of dibromocarbene (generated under phase-transfer conditions) to methylenecyclopropane and subsequent treatment of the resulting dibromospiropentane 8 with methyllithium gave vinylidenecyclopropane 9.[8] The study of reactions of this diene with CMC[9] and (ethoxycarbonyl)carbene showed that only in the latter case was the reaction selective. Bicyclopropylidene 10 (the adduct utilizing the terminal double bond of allene 9) was the only product when dirhodium tetraacetate was used as a catalyst for the decomposition of ethyl diazoacetate.[10] Reduction of ester 10 gave alcohol 11, which was in turn converted into the tetrahydropyran-2-yl derivative 12, which appeared to be a 55:45 mixture of diastereomers according to the ^{13}C NMR spectrum. Cycloaddition of CMC to olefin 12 resulted in a mixture of stereoisomeric derivatives of dispiro[2.0.2.1]heptane (13) (Scheme I).

Synthetic chains of spiroannulated cyclopropanes could be constructed from compound 13 in two directions, thus allowing the synthesis of a large number of BTs. For example, preparation of the hydrocarbon 4 requires construction of one cyclopropane moiety in each direction. In this case, both the generation of methylenecyclopropane

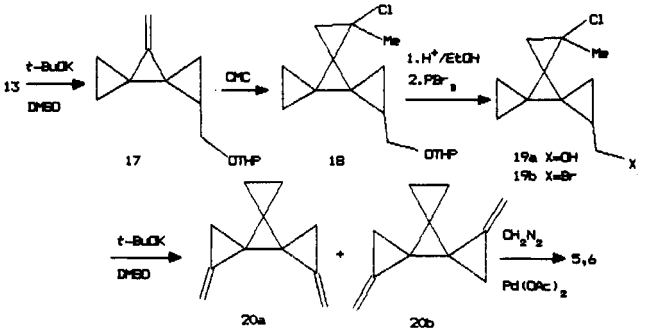
Scheme I



Scheme II



Scheme III

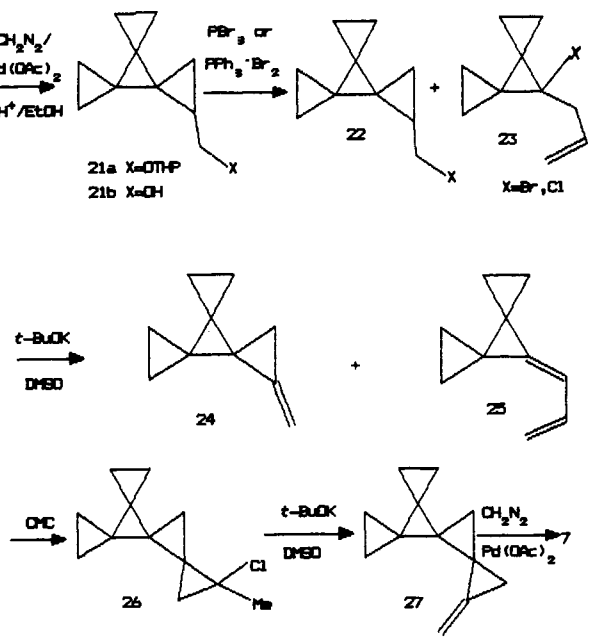


fragments and their cyclopropanation could be carried out simultaneously. As outlined in Scheme II, this was achieved by deprotection and bromination with PBr_3[11] of alcohol 14 and subsequent dehydrohalogenation of compound 15 with potassium *tert*-butoxide in DMSO. The palladium acetate promoted cyclopropanation of the resulting methylenecyclopropane 16 with diazomethane gave the tetraspiroundecane 4, which was characterized by ^1H and ^{13}C NMR spectra.

The synthesis of triangulanes 5 and 6 from dispiroheptane 13 required the construction of three cyclopropane rings in two directions. As outlined in Scheme III, dehydrohalogenation of compound 13 gave olefin 17, which was a mixture of two of the four possible stereoisomers in 57:43 ratio. This stereoselectivity can be accounted for by assuming CMC cycloaddition to olefin 12 from the less hindered side of the double bond. Further cycloaddition of CMC to methylenecyclopropane 17 afforded trispirononane 18. In this case equal steric accessibility of both faces of the double bond leads to the formation of precursors for both triangulanes 5 and 6. In fact, after deprotection, bromination, and dehydrohalogenation of compound 18, a mixture of dienes 20a,b was obtained. These dienes appeared to be unstable compounds and decomposed under conditions of isolation. Preparative GC allowed the isolation and characterization of only one isomer of dienes 20. Nevertheless, direct cyclopropanation

(7) Baldwin, J. E.; Parker, D. W. *J. Org. Chem.* **1987**, *52*, 1475.
(8) Lukin, K. A.; Zefirov, N. S. *Zh. Org. Khim.* **1987**, *23*, 2548.
(9) Lukin, K. A.; Masunova, A. Yu.; Kozhushkov, S. I.; Kuzneztova, T. S.; Ugrak, B. I.; Zefirov, N. S. *Zh. Org. Khim.* **1991**, *27*, 488.
(10) Doyle, M. P.; Leusen, D.; Tamblyn, H. *Synthesis* **1981**, *No. 10*, 787.
(11) Baldwin, J. E.; Ching-Chang, G. E. *Tetrahedron* **1982**, *38*, 825.

Scheme IV



of the pentane extract of products of dehydrohalogenation of compound **19** afforded a mixture of hydrocarbons **5** and **6** in a 60:40 ratio. ^{13}C NMR spectra provided the assignment of configuration for the triangulanes **5** and **6**, which was based on the differences in the symmetry of their structures. Atoms C-11 and C-12 are equivalent in the anti isomer **5** (C_2 symmetry) and nonequivalent in the syn isomer **6** (C_s symmetry).

Finally, the synthesis of triangulane **7**, starting from compound **13**, required construction of three cyclopropanes in two directions. As outlined in Scheme IV, this goal was achieved by a palladium-catalyzed cyclopropanation of olefin **17** with diazomethane and subsequent deprotection and bromination of alcohol **21b**. The bromination product was unstable and decomposed during attempted purification. Dehydrobromination of the crude product gave a mixture of olefins **24** and **25** in a 30:70 ratio. These data allow us to propose that direct bromination of alcohol **21** competes with rearrangement and results in bromides **22** and **23**. Even the milder halogenation conditions using triphenylphosphine dibromide[12] did not suppress the opening of the cyclopropane unit completely; however, the ratio of olefins **24** to **25**, obtained after dehydrohalogenation, was 87:13 in this case. Cycloaddition of CMC to olefin **24** and further dehydrohalogenation gave compounds **26** and **27**, respectively. Cyclopropanation of olefin **27** afforded the desired pentaspirotridecane **7**, the structure of which was supported by ^1H and ^{13}C NMR spectra.

In conclusion, we have developed a synthetic approach to branched triangulanes, which includes procedures for branching of a synthetic chain of spiroannulated cyclopropanes, extension of a synthetic chain, and its termination. The scope of the method was demonstrated by the synthesis of tetraspiroundecane **4** and the isomeric pentaspirotridecanes **5–7**.

Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$. GC analysis was carried out with a 3000 × 3 mm column packed with SE-30 on Inerton NAW phase. Preparative GC was performed on a 5000 × 5 mm column packed with SE-30 on Inerton NAW phase. Mass spectra were obtained at 12 eV.

1,1-Dibromospiropentane (**8**) and vinylidenecyclopropane (**9**) were prepared according to a literature procedure.[8]

Ethyl Bicyclopropylidene-1-acetate (10). To a solution of allene **9** (2.45 g, 37 mmol) and dirhodium tetraacetate (0.16 g, 0.37 mmol) in ether (20 mL) was added dropwise, in two equal portions, a solution of ethyl diazoacetate (4.4 g, 40 mmol) in ether (15 mL). The first portion was added at a rate of 10 mmol/h and the second portion at 5 mmol/h. The reaction mixture was then filtered through silica gel. Evaporation of the solvent and distillation gave ester **10** (2.93 g, 52%): bp 51–53 °C (3 mm); n^{20}_D 1.4889; ^1H NMR (250 MHz) δ 1.15–1.35 (m, 4 H), 1.25 (t, J = 7 Hz, 3 H), 1.71 (m, 1 H), 1.89 (m, 1 H), 2.32 (m, 1 H), 4.14 (q, J = 7 Hz, 1 H); ^{13}C NMR δ 3.42 (t, J = 164 Hz), 3.64 (t, J = 164 Hz), 11.79 (t, J = 166 Hz), 14.25 (q, J = 127 Hz), 18.36 (d, J = 169 Hz), 60.63 (t, J = 147 Hz), 111.06 (s), 112.51 (s), 172.73 (s). Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.73; H, 7.94.

Bicyclopropylidene-1-methanol (11). Ester **10** (9 g, 59 mmol) in ether (25 mL) was added dropwise to a suspension of $LiAlH_4$ (2.2 g, 59 mmol) in dry ether (70 mL), at a rate allowing gentle boiling of a solvent. The reaction mixture was then stirred for 3 h, cooled to 0 °C, and quenched with a saturated solution of Na_2SO_4. The residue was extracted with ether, and the combined organic layers were dried with $MgSO_4$. Removal of the solvent and distillation gave the alcohol **11** (4.8 g, 74%): bp 55–56 °C (2 mm); mp 30 °C; ^1H NMR (250 MHz) δ 1.08 (m, 1 H), 1.20 (m, 1 H), 1.44 (m, 1 H), 1.70 (br s, 1 H), 1.90 (m, 1 H), 3.55 (dd, J = 11, 7 Hz, 1 H), 3.62 (dd, J = 11, 6.5 Hz, 1 H); ^{13}C NMR δ 3.15 (t, J = 162 Hz, 2 C), 8.59 (t, J = 163.9 Hz), 18.39 (d, J = 160.5 Hz), 65.81 (t, J = 146 Hz), 111.68 (s), 112.46 (s).

1-[(Tetrahydropyran-2-yloxy)methyl]bicyclopropylidene (12) (55:45 Mixture of Diastereomers). To a solution of alcohol **11** (2.2 g, 20 mmol) and 4-toluenesulfonic acid (0.3 g, 0.2 mmol) in dry dioxane (40 mL)[13] was added 3,4-dihydropyran (5.7 mL, 60 mmol) dropwise during 2 min. The reaction mixture was stirred until all the alcohol was reacted (TLC monitoring) and quenched with a saturated solution of ammonia in methanol. The solvent was evaporated, and the residue was dissolved in $CHCl_3$ (100 mL), washed with 15% $NaHCO_3$, and dried with $MgSO_4$. Evaporation of the solvent and column chromatography on silica gel (eluenet ether–pentane, 1:10) gave acetal **12** (3.38 g, 87%): ^1H NMR (60 MHz) δ 0.9–1.3 (m, 6 H), 1.3–1.9 (m, 7 H), 3.0–3.9 (m, 4 H), 4.6 (m, 1 H); ^{13}C NMR δ 2.91, 3.05, 8.82, 9.32 (CH_2, cyclopropane), 15.76 (2 C), 19.58, 19.49 (CH, cyclopropane), 25.54 (2 C), 30.67, 30.77, 70.01, 70.21 (CH_2, heterocycle), 62.02, 62.15 (CH_2O), 98.03, 98.15 (OCHO), 111.45, 111.58, 112.42, 112.97 (=C=). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.30. Found: C, 74.28; H, 9.18.

General Procedure for Cycloaddition of Chloromethylcarbene to Olefins 12, 17, and 24. Preparation of Chloromethylcyclopropanes 13, 18, and 26. To a solution of an olefin (50 mmol) and 1,1-dichloroethane (75 mmol, 6.3 mL) in dry ether (30 mL) was added butyllithium (60 mmol, 45 mL of 1.5 N solution in pentane) dropwise over 3 h at −35 to −40 °C under Ar. The reaction mixture was allowed to warm to rt and quenched with cold water. The organic phase was separated, washed with water, and dried with $MgSO_4$. Solvent was evaporated, and distillation gave cyclopropanes **13**, **18**, **26**.

7-Chloro-7-methyl-1-[(tetrahydropyran-2-yloxy)methyl]-dispiro[2.0.2.1]heptane (13) was obtained in 85% yield: bp 103–104 °C (2 mm); n^{20}_D 1.4902; ^1H NMR (60 MHz) δ 0.7–1.3 (m, 6 H), 1.3–2.0 (m, 10 H), 3.1–3.9 (m, 4 H), 4.5 (m, 1 H). Anal. Calcd for $C_{14}H_{21}O_2Cl$: C, 65.48; H, 8.24. Found: C, 65.45; H, 8.58.

1-Chloro-1-methyl-5-[(tetrahydropyran-2-yloxy)methyl]-trispiro[2.0.2.0.2.0]nonane (18) was obtained in 82% yield: 110–115 °C (2 mm); n^{20}_D 1.4958; ^1H NMR (60 MHz) δ 0.5–1.2 (m, 8 H), 1.2–1.9 (m, 10 H), 3.1–3.9 (m, 4 H), 4.5 (m, 1 H). Anal. Calcd for $C_{16}H_{23}O_2Cl$: C, 67.09; H, 8.19. Found: C, 68.02; H, 8.05.

1-Chloro-1-methyltetraspiro[2.0.0.2.0.2.0.1]undecane (26) was obtained in 79% yield as a 1:1 mixture of diastereomers: bp 77 °C (1 mm); ^1H NMR (60 MHz) δ 0.6–0.9 (m, 18 H), 0.95–1.5 (m, 8 H), 1.60 (s, 3 H), 1.66 (s, 3 H). Anal. Calcd for $C_{12}H_{15}Cl$: C, 77.02; H, 7.77. Found: C, 73.83; H, 8.21.

General Procedure for Deprotection of Acetals 13, 18, and 21a to the Alcohols 14, 19a, and 21b. A solution of acetal (10 mmol) and hydrochloric acid (0.5 mL of 0.1 N solution) in ethanol (50 mL) was refluxed until all the acetal was reacted according

(12) Horner, L.; Oediger, H.; Hoffmann, H. *Justus Liebigs. Ann. Chem.* **1959**, *626*, 26.

to TLC (20–40 min). After evaporation of the solvent, alcohols **14**, **19a**, and **21b** were isolated by distillation or column chromatography (eluent ether–pentane, 4:6).

7-Chloro-7-methyldispiro[2.0.2.1]heptane-1-methanol (14) was obtained in 80% yield: bp 75–76 °C (3 mm); n^{20}_D 1.4938; ^{1}H NMR (60 MHz) δ 0.7–1.6 (m, 7 H), 1.65 (s, 3 H), 2.5 (s, 1 H), 3.2–3.5 (m, 2 H).

1-Chloro-1-methyltrispiro[2.0.2.0.2.0]nonane-5-methanol (19a) was obtained in 76% yield: 98–100 °C (2 mm); n^{20}_D 1.5090; ^{1}H NMR (60 MHz) δ 0.4–1.4 (m, 8 H), 1.4–1.6 (br s, 4 H), 2.5 (s, 1 H), 3.3–3.6 (m, 2 H).

Trispiro[2.0.2.0.2.0]nonane-1-methanol (21b) was obtained in 77% yield: bp 83–85 °C (3 mm); ^{1}H NMR (250 MHz) δ 0.63 (t, J = 4.5 Hz, 1 H), 0.7–0.9 (m, 8 H), 0.95 (dd, J = 7.5, 4.5 Hz, 1 H), 1.50 (dq, J = 4.5, 7.2 Hz, 1 H), 3.49 (d, J = 7 Hz, 2 H); ^{13}C NMR δ 4.69, 4.81, 4.87, 4.98, 9.65, 17.16, 18.31, 20.67, 22.37, 65.49.

General Procedure for Bromination of Alcohols 14, 19a, and 21b to Halides 15, 19b, 22, and 23. To a cooled (−78 °C) solution of alcohol (10 mmol) in dry ether (25 mL) was added PBr_3 (0.34 mL, 3.6 mmol) dropwise under an argon atmosphere. The reaction mixture was stirred at −78 °C for 0.5 h and allowed to stand overnight at 0 °C. Then it was quenched with saturated $NaHCO_3$ (10 mL); the organic phase was separated, washed with water, and dried with $MgSO_4$. Removal of the solvent gave halides **15**, **19b**, **22**, and **23**.

1-(Bromomethyl)-7-chloro-7-methyldispiro[2.0.2.1]heptane (15) was obtained in 60% yield and dehalogenated without further purification: ^{1}H NMR (60 MHz) δ 0.75–1.4 (m, 6 H), 1.6 (s, 3 H), 1.9–2.1 (m, 1 H), 3.0–3.5 (m, 2 H).

5-(Bromomethyl)-2-chlorotrispiro[2.0.2.0.2.0]nonane (19b) was obtained in 61% yield and purified by column chromatography: ^{1}H NMR (60 MHz) δ 0.6–1.4 (m, 8 H), 1.5–2.0 (m, 1 H), 1.6 (s, 3 H), 3.0–3.7 (m, 2 H). Anal. Calcd for $C_{11}H_{14}BrCl$: C, 50.50; H, 5.39. Found: C, 51.26; H, 6.01.

A mixture of 1-(bromomethyl)trispiro[2.0.2.0.2.0]nonane (22) and 7-allyl-7-bromodispiro[2.0.2.1]heptane (23), which was obtained in the bromination of alcohol **21b**, was dehydrobrominated without further purification.

General Procedure for Dehydrohalogenation of Halides 15, 19b, 22, 23, and 26 to Olefins 16, 17, 20, 24, 25, and 27. To a solution of sublimed potassium *tert*-butoxide (3.35 g, 30 mmol) in DMSO (15 mL) was added a halide (24 mmol) dropwise at 20 °C. The reaction mixture was stirred for 2–5 h and then quenched with cold water. Pentane (20 mL) was added, and the organic phase was separated, washed with water, and dried with $MgSO_4$. The pentane solution was concentrated, and olefins **16**, **17**, **20**, **24**, **25**, and **27** were isolated by distillation or preparative GC.

1,7-Dimethylenedispiro[2.0.2.1]heptane (16) was obtained in 45% yield: ^{1}H NMR (250 MHz) δ 1.1–1.2 (m, 4 H), 1.56 (ddd, J = 8, 2.5, 1.5 Hz, 1 H), 1.68 (ddd, J = 8, 2.5, 1.5 Hz, 1 H), 5.13 (s, 1 H), 5.15 (s, 1 H), 5.27 (t, J = 2.5 Hz, 1 H), 5.34 (t, J = 1.9 Hz, 1 H); ^{13}C NMR δ 9.31 (t), 9.72 (t), 12.70 (t), 17.99 (s), 18.95 (s), 95.11 (t), 100.00 (t), 136.17 (s), 141.63 (s); MS m/e 118 (M^+), 116 (base), 104, 92, 78, 65, 51.

1,5-Dimethylenetrispiro[2.0.2.0.2.0]nonanes (20) were isolated in 40% yield as a pentane solution. GC isolation of unstable dienes **20** afforded only one isomer: ^{1}H NMR (250 MHz) δ 0.82–0.95 (m, 4 H), 1.36 (br s, 4 H), 5.31 (t, J = 2.5 Hz, 2 H), 5.33 (t, J = 1.8 Hz, 2 H); MS m/e 144 (M^+), 143, 142, 129 (base), 116, 92, 78, 65.

1-Methylenetrispiro[2.0.2.0.2.0]nonane (24) and 7-allylidenedispiro[2.0.2.1]heptane (25) were obtained in dehydrohalogenation of bromides and chlorides **22** and **23** in 70% yield. Olefin **24**: bp 50–51 °C (15 mm); ^{1}H NMR (250 MHz) δ 0.7–1.0 (m, 8 H), 1.31 (s, 2 H), 5.24 (t, J = 2 Hz, 1 H), 5.30 (br s, 1 H); ^{13}C NMR δ 5.11 (2 C), 5.50 (2 C), 9.08 (1 C), 99.75 (1 C) (CH_2), 22.63 (3 C), 135.51 (1 C) (=C=). Anal. Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.44; H, 8.81. Diene **25** was isolated by prepatative GC: ^{1}H NMR δ 0.8–1.0 (m, 6 H), 1.1 (m, 2 H), 4.8–5.3 (m, 2 H), 6.0–6.4 (m, 2 H); ^{13}C NMR δ 9.20 (t), 9.44 (t), 15.86 (s), 16.15 (s), 113.10 (d), 114.11 (d).

1-Methylenetetraspiro[2.0.0.2.0.2.0.1]undecane (27) was obtained in 82% yield: ^{1}H NMR (250 MHz) δ 0.6–0.9 (m, 8 H), 1.35 (ddd, J = 7.6, 2.4, 1.7 Hz, 1 H), 1.38 (d, J = 4 Hz, 1 H), 1.43 (br d, J = 7.6 Hz, 1 H), 1.48 (d, J = 4.0 Hz, 1 H), 5.12 (t, J = 2.4 Hz, 1 H), 5.39 (t, J = 1.7 Hz, 1 H); ^{13}C NMR δ 3.70 (1 C), 4.31 (2 C), 4.80 (1 C), 8.83 (1 C), 15.05 (1 C), 99.71 (1 C) (CH_2), 17.1 (1 C), 18.12 (1 C), 18.77 (1 C), 25.85 (1 C), 135.30 (1 C) (=C=). Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.96; H, 8.86.

7-Methylene-1-[(tetrahydropyran-2-yloxy)methyl]dispiro[2.0.2.1]heptane (17) was obtained as 1:1 mixture of diastereomers in 78% yield: ^{1}H NMR (60 MHz) δ 0.7–1.4 (m, 6 H), 1.4–1.9 (m, 7 H), 3.0–3.9 (m, 4 H), 4.5 (m, 1 H), 4.95 (s, 2 H); ^{13}C NMR δ 9.03 (t), 9.20 (t), 14.05 (t, 2 C), 14.57 (s, 2 C), 18.48 (s, 2 C), 22.16 (d, 2 C), 140.81 (s, 2 C) (dispiroheptane moiety), 19.58 (t), 19.64 (t), 25.52 (t, 2 C), 30.67 (t), 30.80 (t), 68.52 (t), 69.14 (t), 98.55 (d), 98.67 (d) (heterocycle), 62.28 (t, 2 C, CH_2O), 94.14 (t, 2 C, CH_2=). Anal. Calcd for $C_{14}H_{20}O$: C, 76.32; H, 9.15. Found: C, 75.95; H, 9.22.

General Procedure for Cyclopropanation of Olefins 16, 17, 20, 24, and 27 to Cyclopropanes 4–7 and 21. A solution of diazomethane (prepared from 5 g of *N*-nitroso-*N*-methylurea) in ether (50 mL) was added dropwise at −5 to +3 °C to a solution of olefin (5 mmol) or diene (2.5 mmol) and $Pd(OAc)_2$ (50 mg, 0.22 mmol) in ether (15 mL). The solvent was evaporated, and the residue was distilled into a cold trap (−78 °C) or diluted with pentane (10 mL) and filtered through silica gel. Subsequent distillation or preparative GC gave cyclopropanes **4–7**, and **21**.

Tetraspiro[2.0.0.2.0.2.0.1]undecane (4) was obtained in 80% yield: ^{1}H NMR (250 MHz) δ 0.55–0.62 (m, 2 H), 0.68–0.84 (m, 10 H), 1.08 (s, 2 H); ^{13}C NMR δ 3.78 (t, 2 C), 3.85 (t, 2 C), 4.44 (t, 2 C), 11.56 (t, 1 C), 14.50 (s, 1 C), 18.31 (s, 2 C), 21.80 (s, 1 C). Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.02; H, 9.30.

Pentaspiro[2.0.0.2.0.0.2.1.0.1]tridecanes (5 and 6) were obtained as a 60:40 mixture of isomers in 75% yield: ^{1}H NMR (400 MHz) δ 0.6–0.9 (m, 12 H), 1.06 (d, J = 3.2 Hz, 2 H), 1.16 (d, J = 3.2 Hz, 2 H) (isomer **6**); 0.6–0.9 (m, 12 H), 0.95 (d, J = 3.5 Hz, 2 H), 1.14 (d, J = 3.5 Hz, 2 H) (isomer **5**); ^{13}C NMR δ 2.52 (t, 1 C), 3.83 (t, 1 C), 3.96 (t, 2 C), 6.63 (t, 2 C), 11.55 (t, 2 C), 14.21 (s, 2 C), 17.87 (s, 1 C), 23.17 (s, 2 C) (isomer **6**); 3.14 (t, 2 C), 3.76 (t, 2 C), 3.85 (t, 2 C), 10.30 (t, 2 C), 13.80 (s, 2 C), 17.87 (s, 1 C), 21.54 (s, 2 C) (isomer **-5**); MS m/e 172 (M^+), 156, 143, 129 (base), 117, 91, 79.

Pentaspiro[2.0.2.0.0.0.2.1.1.0]tridecane (7) was obtained in 91% yield: ^{1}H NMR (250 MHz) δ 0.6–0.9 (m, 12 H), 0.97 (d, J = 3.7 Hz, 1 H), 1.10 (m, 2 H), 1.22 (d, J = 3.7 Hz, 1 H); ^{13}C NMR δ 3.93 (t), 4.37 (t), 4.56 (t), 5.13 (t), 6.56 (t), 7.36 (t), 10.59 (t), 11.20 (t), 13.55 (s), 17.91 (s), 18.64 (s), 20.53 (s), 23.42 (s). Anal. Calcd for $C_{13}H_{16}$: C, 90.63; H, 9.36. Found: C, 90.90; H, 9.66.

1-[(Tetrahydropyran-2-yloxy)methyl]trispiro[2.0.2.0.2.0]nonane (21a) was obtained in 85% yield: ^{1}H NMR (60 MHz) δ 0.5–1.1 (m, 8 H), 1.1–1.9 (m, 9 H), 3.0–3.9 (m, 4 H), 4.5 (m, 1 H). Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.47. Found: C, 77.05; H, 9.83.

Supplementary Material Available: NMR spectra (^{13}C and ^{1}H) for the **5–6** mixture, **11**, **15**, **16**, **19a**, **21b**, and **25** (9 pages). Ordering information is given on any current masthead page.