Cascade Rearrangement of 5-Cyclopentylidenecyclooctanones

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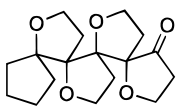
Acid-catalyzed rearrangement of 5-cyclopentylidenecyclooctanone derivatives **9a**−**c** was examined to obtain polyspiropolyquinanes **11a**−**c**, considered to have a unique helical structure, through cascade rearrangement pathways consisting of continuous transannular cyclization followed by successive 1,2-alkyl shifts. The substrates were prepared easily by use of the Wittig or McMurry reaction. Reaction of the 5-cyclopentylidenecyclooctanone (**9a**) with acid gave the expected dispirotriquinane ketone **11a** in high yield. The precise mechanism was elucidated by a deuterium-labeling experiment. In the case of the ketone **9b**, having another spiroannulated cyclopentane ring attached on **9a**, the trispirotetraquiane **11b** was not obtained but the bis-propellane-type tetrahydrofuran **25** was produced exclusively. The 5-(5′-cyclopentylidenecyclooctylidene)cyclooctanone (**9c**) afforded the polycyclic compounds **27**−**31**, depending on the acid used, instead of the desired tetraspiropentaquinane **11c**. The structures of the products were determined by NMR spectral data including 2D ^{13}C INADEQUATE spectra and X-ray crystallographic analyses. The unexpected rearrangement pathways are also discussed.

Introduction

Polyspiranes constitute an interesting structural type with novel helicity because of the primary bonding structure, differing from the shapes of helicenes and DNA which owe their helical topology to their secondary and tertiary structures.[1,2] From this viewpoint, two polyspiro compounds **1** and **2** have been synthesized by stepwise spiroannulation of a tetrahydrofuran ring[1b] or zipper-type cycloisomerization of polyolefins using a palladium catalyst.[3] The X-ray crystallographic analysis of **1** reveals that the cyclopentyl[4]helixane **1** is indeed a helix-shaped molecule.[1b]



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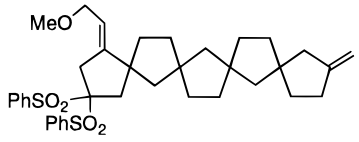
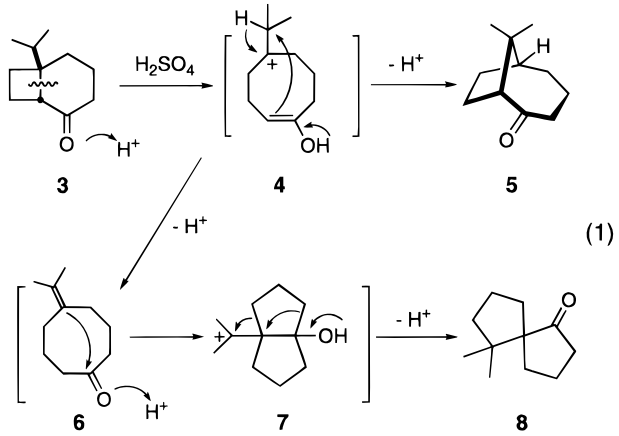


2

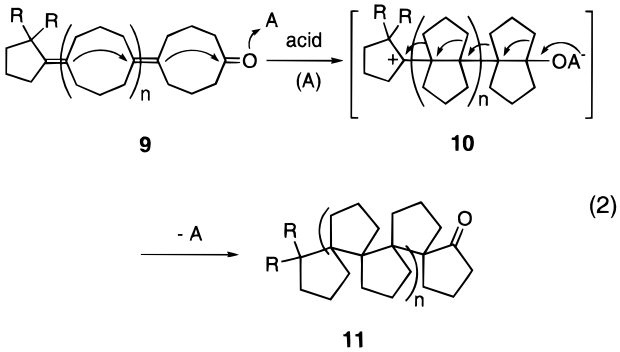
Recently, we reported a novel method for the synthesis of bicyclo[4.2.1]nonanes by acid-catalyzed rearrangement of 6-substituted bicyclo[4.2.0]octanones.[4] In the case of the isopropyl derivative **3**, a small amount of the spiroannulated diquinane ketone **8** was obtained as a byproduct along with the expected bicyclononanone **5**.[5] We considered a plausible reaction path to **8** as follows (eq 1).



3 **4** **5** **6** **7** **8** (1)

Deprotonation of the eight-membered ring cation **4**, generated through fission of the central cyclobutane bond, affords the intermediate **6**. Protonation followed by transannular cyclization forms the bicyclo[3.3.0] cation **7**, and a subsequent alkyl shift gives rise to the ketone **8**.

On the basis of this mechanism, we envisaged that a new type of polyspiroquinanes **11** could be synthesized by cascade rearrangement of 5-cyclopentylidenecyclooctanone derivatives **9** under the action of acid (eq 2).



9 **10** **11** (2)

Namely, continuous transannular cyclizations would generate the polybicyclo[3.3.0]octane intermediate **10**, and successive alkyl shifts would afford the novel polyspi-

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1996.

(1) (a) Meurer, K. P.; Vögtle, F. *Top. Curr. Chem.* **1985**, *127*, 1. (b) Gange, D.; Magnus, P.; Bass, L.; Arnold, E. V.; Clardy, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 2134 and references cited therein.

(2) The terms primary, secondary, and tertiary structure are used for classification of macromolecular structures and are briefly described as follows: primary, the structural formula of the monomer units, including bond length and bond angles, and leading to the resultant special geometry of the macromolecules; secondary, the manner in which monomer units are folded to generate simple structures, and nearly every secondary structure is helical; tertiary, the relative arrangement of the secondary structure(s), resulting from small periodic variations or the chain folding in secondary structure. For more extensive discussion, see: Hopfinger, A. J. *Conformational Properties of Macromolecules*; Academic Press: New York, 1973.

(3) Trost, B. M.; Shi, Y. *J. Am. Chem. Soc.* **1991**, *113*, 701; **1993**, *115*, 9421.

(4) Kakiuchi, K.; Fukunaga, K.; Matsuo, F.; Ohnishi, Y.; Tobe, Y. *J. Org. Chem.* **1991**, *56*, 6742.

(5) See the supplementary material in ref 4.

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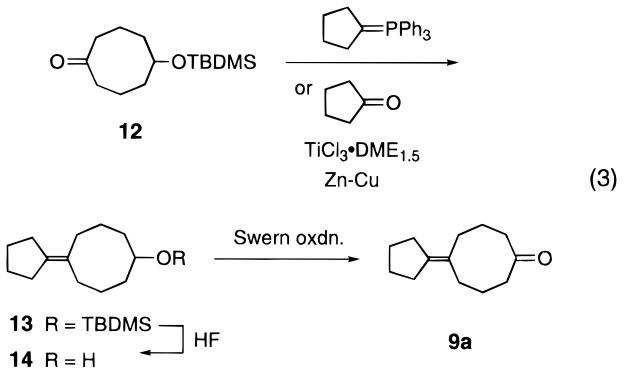
rocycles **11** regarded as the carbocyclic version of the polyoxapolyspiroquinane **1**. As our first approach to polyspiranes, we have investigated acid-catalyzed rearrangement of the ketones **9a** (n = 0, R = H), **9b** (n = 0; R, R = $-(CH_2)_4-$), and **9c** (n = 1, R = H). We wish to report herein the cascade rearrangements of ketone **9a** to the dispirotriquinane **11a** and those of ketones **9b** and **9c** to the interesting polycyclic structures **25** and **27**−**31** instead of the expected polyspiroquinanes **11b** and **11c**, respectively.

Results and Discussion

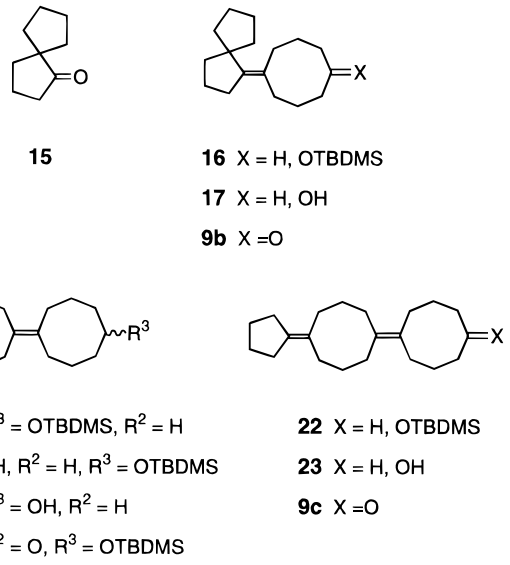
Synthesis of 5-Cyclopentylidenecyclooctanone Derivatives 9a−c. For construction of the cyclopentylidenecyclooctane (5−8) system, we used the Wittig reaction of siloxycyclooctanone **12**[6] and cyclopentylidenetriphenylphosphorane (eq 3). Thus, reaction of **12** in tol-



uene at ca. 80 °C with the ylide, which was generated from the corresponding phosphonium bromide[7] by treatment with $NaNH_2$ in toluene at ca. 70 °C,[8] gave the coupling product **13**. Deprotection of the TBDMS group in **13** with 23% HF gave the alcohol **14** in 32−58% overall yield. Since the Wittig reaction was irreproducible and the yields were not high due to the formation of byproducts, we used the hetero-McMurry coupling as an alternative method. Reaction[9] of **12** and excess cyclopentanone with $TiCl_3$•$DME_{1.5}$ complex and Zn−Cu couple in DME at reflux gave **13** in 95% yield which was subjected to deprotection as above to give **14** in 89% yield. Swern oxidation of **14** produced the 5-cyclopentylidenecyclooctanone (**9a**) in 79% yield.

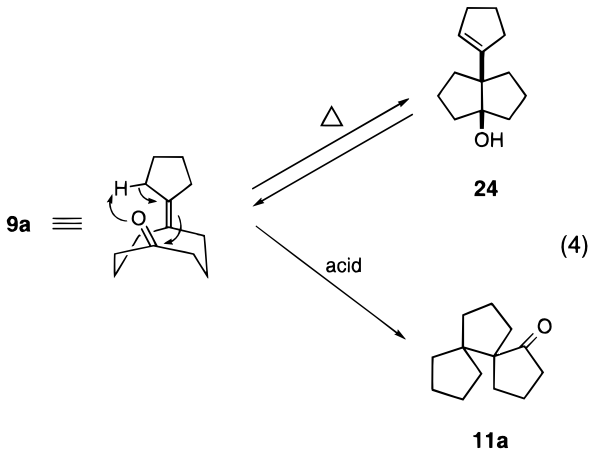
Similarly, 5-(cyclopentanespirocyclopentylidene)cyclooctanone (**9b**) was synthesized easily in 31% overall yield by McMurry coupling of **12** and spiro[4.4]nonan-1-one (**15**)[10] followed by deprotection of the olefin **16** and Swern oxidation of the resulting alcohol **17** (Chart 1). Furthermore, the higher homologue **9c** was synthesized by use of homo- and hetero-McMurry reactions. Homocoupling of **12** using $TiCl_3$·$DME_{1.5}$ complex and Zn−Cu couple followed by deprotection of the olefins **18** (a ca. 1:1 mixture of syn and anti isomers) as described above gave a mixture of the monoprotected alcohols **19** in 33% overall yield along with a mixture of the diols **20** in 27% overall yield. Selective protection[11] of **20** with TBDMSCl using

Chart 1



1 equiv of BuLi produced additional **19** in 46% yield. PDC oxidation of **19** followed by heterocoupling of the resulting ketone **21** with excess cyclopentanone afforded the olefin **22** in 73% overall yield. Deprotection and subsequent Swern oxidation of the alcohol **23** furnished 5-(5'-cyclopentylidenecyclooctylidene)cyclooctanone (**9c**) in 50% overall yield.

Cascade Rearrangement of Ketones 9a−c. Ketone **9a** showed interesting behavior upon GC analysis where two peaks appeared, suggesting a thermal conversion. To clarify this behavior, a solution of **9a** in xylene was heated at reflux to give the tertiary alcohol **24** in 60% yield as a white crystalline compound together with the starting ketone **9a** in 24% yield after column chromatography. The structure of **24** was assigned as shown in eq 4 from spectroscopic data. Namely, the ^{13}C NMR



spectrum showed 10 signals of which three methylene signals (δ 41.59, 38.66, and 23.16) showed double intensity, indicating the symmetrical structure of **24**. The data also indicated the presence of the trisubstituted olefin moiety and the quaternary sp^3 carbon (δ 90.50) having a hydroxyl group at the bridgehead position of a bicyclo[3.3.0]octane.[12] Similar heating of **24** in xylene furnished

(6) Yamago, S.; Nakamura, E. *Tetrahedron* **1989**, *45*, 3081.
(7) Ramirez, F.; Levy, S. *J. Am. Chem. Soc.* **1957**, *79*, 67.
(8) Schlosser, M.; Schaub, B. *Chimia* **1984**, *36*, 396.
(9) McMurry, J. E.; Lectka, T.; Rico, J. G. *J. Org. Chem.* **1987**, *54*, 3748.
(10) Hill, R. K.; Conley, R. T. *J. Am. Chem. Soc.* **1960**, *82*, 645.
(11) Roush, W. R.; Gillis, H. R.; Essenfeld, A. P. *J. Org. Chem.* **1984**, *49*, 4674

(12) For example, the chemical shifts of the bridgehead quaternary carbon having a hydroxyl group are 87.06 and 89.97 ppm for diquinane and angularly fused triquinane-type compounds; see: Kakiuchi, K.; Tsugaru, T.; Takeda, M.; Wakaki, I.; Tobe, Y.; Odaira, Y. *J. Org. Chem.* **1985**, *50*, 488.

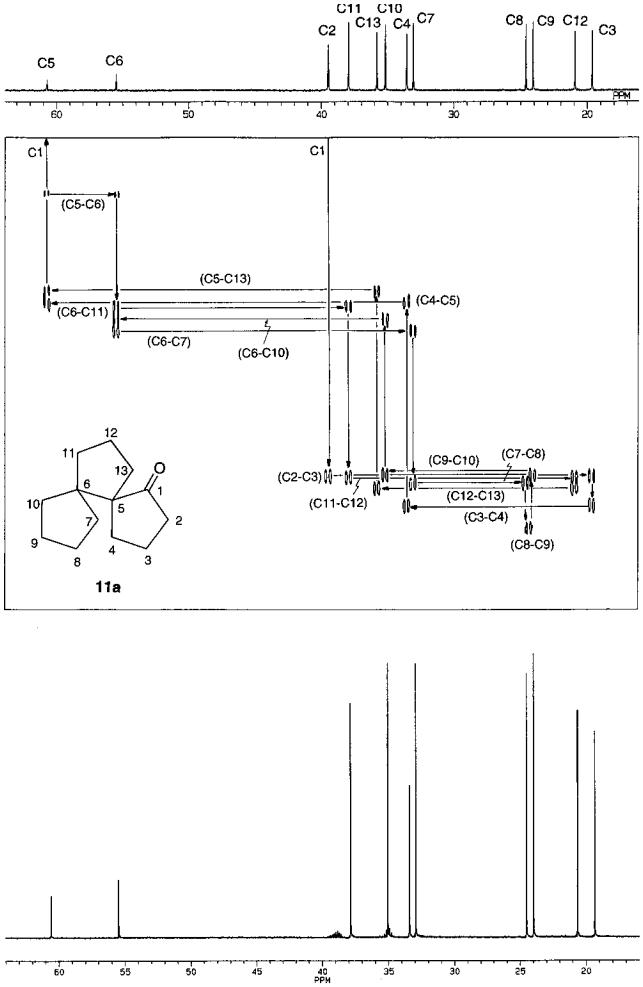
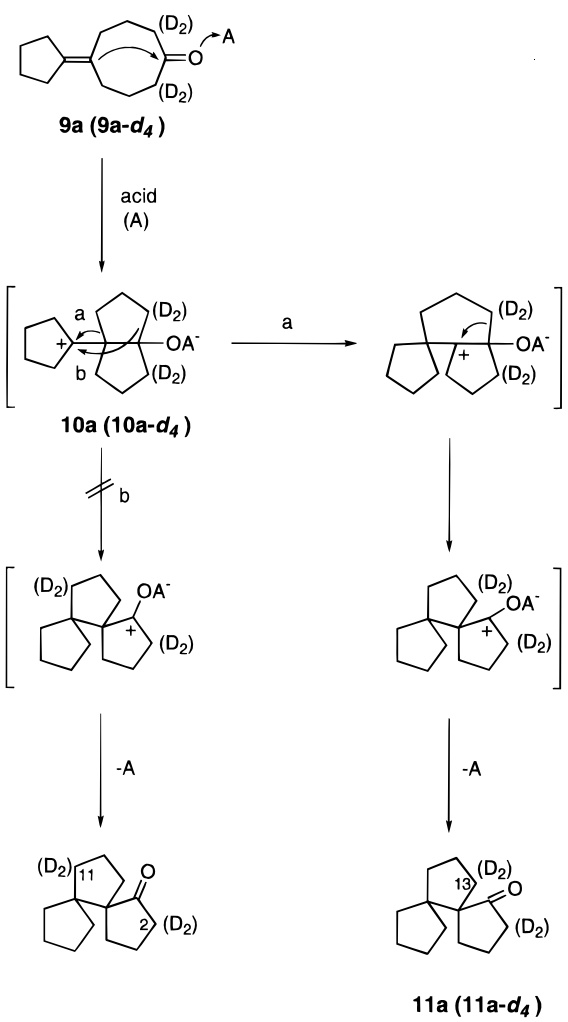


Figure 1. 100 MHz 2D ^{13}C INADEQUATE spectrum of **11a** (above) and 150 MHz ^{13}C NMR spectrum of **11a-*d*$_4$** in the region from 16 to 64 ppm.

a mixture of **24** and **9a** in almost the same ratio as above. The ratio of **9a** to **24** in DMSO-d_6 at 140 °C was determined to be 1.78 by an NMR experiment. It is noted that the difference in heats of formation (ΔH_f°) between **9c** (−49.38 kcal/mol) and **24** (−50.55 kcal/mol) calculated by MM2[13] reflects the equilibrium constant. Alcohol **24** can arise by an intramolecular ene reaction which proceeds through hydrogen abstraction by the carbonyl group and concerted transannular cyclization of the eight-membered ring.

Reaction of ketone **9a** with H_2SO_4 (0.5 equiv) in benzene at rt was complete within 10 min to give the ketone **11a** in 81% yield.[14] Similarly, with Lewis acids (0.5 equiv) such as $AlCl_3$, $TiCl_4$, and $FeCl_3$ in CH_2Cl_2, the ketone **11a** was obtained in 82%, 74%, and 83% yields, respectively. The structure of **11a** was determined unambiguously as a dispirotriquinane ketone by the 2D ^{13}C INADEQUATE spectrum shown in Figure 1. In the later stage of the cascade rearrangement, a 1,3-alkyl shift (path b) from intermediate **10a** is possible in addition to successive 1,2-alkyl shifts (path a) (Scheme 1). A 1,3-alkyl shift has also been postulated in the rearrangement

Scheme 1



of an angular triquinane to a [3.3.3]propellane system.[15] To elucidate the precise reaction path, we carried out a labeling experiment. For this purpose, we prepared the tetradeuterio ketone **9a-*d*$_4$** by treatment[16] of **9a** with Na in D_2O. Reaction of **9a-*d*$_4$** with H_2SO_4 and $AlCl_3$ gave ketone **11a-*d*$_4$** in 76% and 80% yields, respectively. The deuterium in **11a-*d*$_4$** was determined easily by the ^{13}C NMR spectrum (Figure 1) to be at C2 and C13, indicating that successive 1,2-alkyl shifts (path a, Scheme 1) proceed exclusively in this rearrangement. The 1,3-alkyl shift (path b, Scheme 1) from intermediate **10a-*d*$_4$** would lead to a ketone which should have deuterium at C2 and C11.

Next, to synthesize the higher homologue, trispirotetraquinane **11b**, we carried out the acid-catalyzed cascade rearrangement of ketone **9b**. Reaction of **9b** with H_2SO_4 or $AlCl_3$ as described above did not give the expected ketone **11b**, but afforded the crystalline compound **25** in 83% or 84% yield, respectively. The IR spectrum showed no carbonyl absorption, and the HRMS showed no change of molecular weight. The ^{13}C NMR spectrum indicated four quaternary sp^3 carbon signals including two low field signals (δ 103.08 and 97.39) and 13 methylene signals. The ^1H NMR spectrum showed no signals at lower field than δ 2.5. Since the structure of **25** was not defined

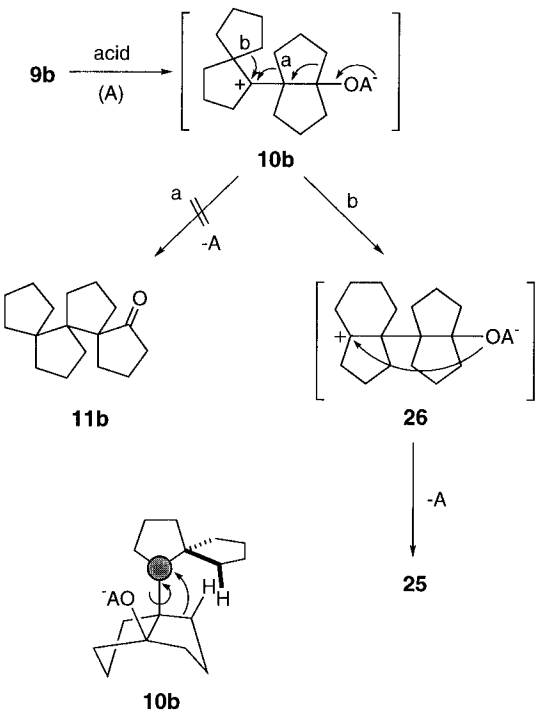
(13) Allinger, N. L. *QCPE No. MM2 (85)*. Also, calculations were performed with the MM2 program using an Iris Indigo R4000 computer. The output was recorded by using MOL-GRAPH program Ver. 2.8 by Daikin Industries, Ltd.

(14) A similar reaction of the alcohol **24** with H_2SO_4 did not give the ketone **11a**, and the starting material was recovered.

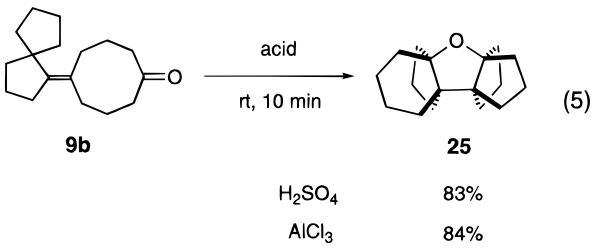
(15) Cargill, R. L.; Dalton, J. R.; O'Connor, S.; Michels, D. G. *Tetrahedron Lett.* **1978**, 4465.

(16) Lambert, J. B.; Clikeman, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 4203. Kakiuchi, K.; Ue, M.; Tsukahara, H.; Simizu, T.; Miyao, T.; Tobe, Y.; Odaira, Y.; Yasuda, M.; Shima, K. *J. Am. Chem. Soc.* **1989**, *111*, 3707.

Scheme 2

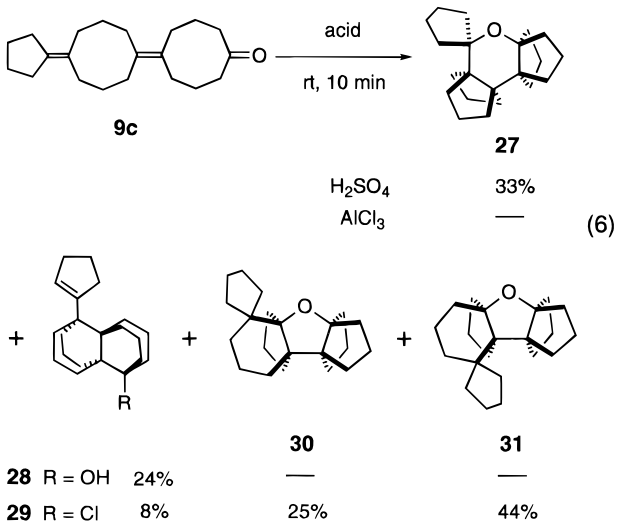


from these data, we carried out an X-ray crystallographic analysis which showed it to be the bis-propellane-type tetrahydrofuran derivative.[17]



The interesting rearrangement behavior of **9b** can be reasonably explained as shown in Scheme 2. In the cation **10b** generated through transannular cyclization of **9b**, successive 1,2-alkyl shifts (path a, Scheme 2) as described above would have given the desired tetraquinane **11b**. For the first 1,2-alkyl shifts to proceed smoothly, the vacant p orbital in **10b** should rotate so as to overlap with the migrating bond. A molecular model of **10b**, however, suggests that steric hindrance, as illustrated, prevents such rotation. Therefore, another alkyl shift (path b, Scheme 2) occurs to form cation **26** and subsequent cyclization gives the bis-propellane **25**. It is noted that the furan derivative **25** ($\Delta H_f° = -66.15$ kcal/mol, calculated by MM2[13]) is more stable than ketone **11b** ($\Delta H_f° = -60.09$ kcal/mol).

Furthermore, acid-catalyzed cascade rearrangement of the 5−8−8-type ketone **9c** gave a different polycycle from the expected tetraspiropentaquinane **11c** (eq 6). Reaction of **9c** with H_2SO_4 gave the tetrahydropyran derivative **27** and the tertiary alcohol **28** in 33% and 24% yields. In contrast, treatment of **9c** with $AlCl_3$ afforded the chloride **29** and two tetrahydrofuran derivatives **30** and **31** in 8%, 25%, and 44% yields, respectively. The symmetrical



structure of **27** was assigned from the ^{13}C NMR spectrum which revealed five quaternary sp^3 carbon signals and eight methylene signals. X-ray crystallographic analysis of **29** revealed the structure shown in Figure 2. Interestingly, the structure features a longer length of 1.601 Å for the C6−C14 bond compared to the C-C single bond standard of 1.54 Å.[18] The structure of **28** was assigned based on the similarity of its NMR spectra to those of **29**.[19] The 2D ^{13}C INADEQUATE spectra of **30** and **31** clarified their structures as bis-propellane-type tetrahydrofuran derivatives having a cyclopentane ring spiroannulated to the cyclohexane ring of **25** at different positions.

A plausible reaction path leading to the pyran and furan type polyquinanes **27**, **30**, and **31** is shown in Scheme 3. Continuous transannular cyclization from ketone **9c** generates the cation **10c**. Cyclization (path a, Scheme 3) of the cation **10c** with loss of a proton (A = H^+) gives the tetrahydropyran derivative **27**. Alternatively, a 1,2-alkyl shift (path b, Scheme 3) in cation **10c** followed by cyclization (path c, Scheme 3) affords the tetrahydrofuran derivative **30**. Further 1,2-alkyl shift (path d, Scheme 3) in cation **32** produces the cation **33**. It is reasonable that a steric argument similar to that discussed for **10b** also prevents continuous 1,2-alkyl shifts (path e, Scheme 3) for the formation of tetraspiropentaquinane **11c**. Therefore, another alkyl shift (path f, Scheme 3) produces the cation **34** and subsequent cyclization gives the other tetrahydrofuran derivative **31**, like **9b**. In the case of H_2SO_4, the absence of further rearranged products **30** and **31** may be due to kinetic control; that is, participation of the hydroxyl group in **10c** (A = H^+) to the cationic center occurs easier to give **27** than that of the alcoholate moiety (A = $AlCl_3$).[20]

The formation of the minor products **28** and **29** is explained by another type of cyclization of **9c** as shown in Scheme 4. Namely, bond formation between the

(17) The NMR data of **25** showed similarity to those of **30** and **31** which have bis-propellane-type tetrahydrofuran structures; see the Experimental Section and the supporting information.

(18) Allen, F.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1 (supplement).

(19) We carried out the transformation of the tertiary alcohol **28** to the chloride **29** using PCl_5-$CaCO_3$ in $CDCl_3$, which is reported to be a useful method for synthesis of tertiary chloride from the corresponding tertiary alcohols under extremely mild conditions; see: Carman, R. H.; Shaw, I. M. *Aust. J. Chem.* **1976**, *29*, 133. While some products including a small amount of **29** were detected by GLC analysis, we did not characterize them.

(20) The heats of formation of **27**, **30**, and **31** are calculated by MM2[13] to be −59.68, −70.42, and −67.74 kcal/mol, respectively.

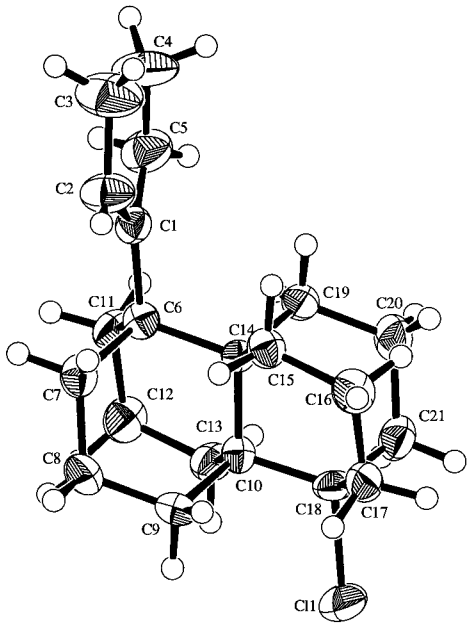
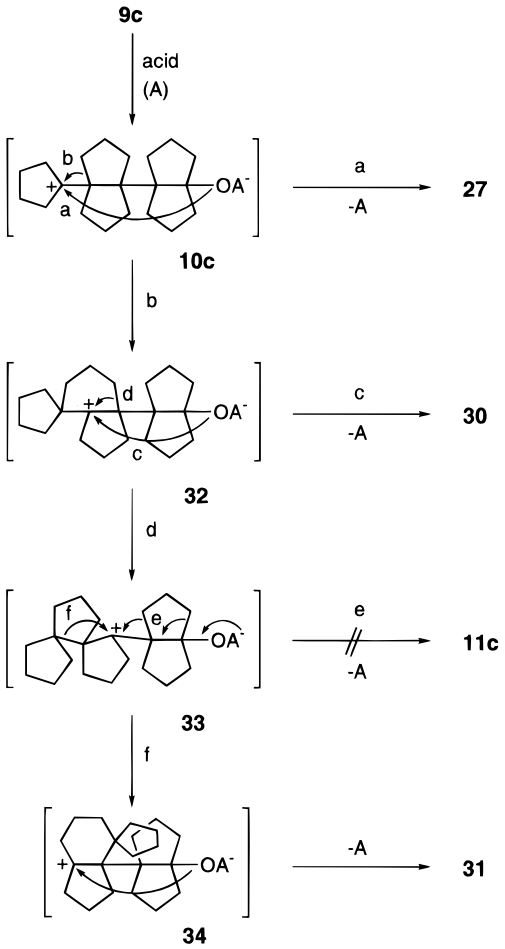


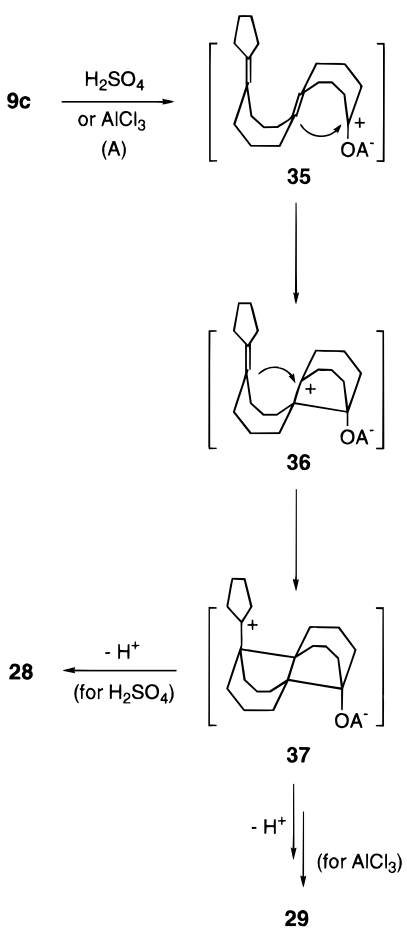
Figure 2. Molecular structure of chloride **29**.

Scheme 3



cationic center of the intermediate **35** and the exocyclic sp^2 carbon generates the cation **36**. Participation of the other double bond at the cationic center of **36** produces the cation **37**, and subsequent deprotonation affords the alcohol **28** in the case of H_2SO_4. Such a cyclization pathway has been demonstrated in the skeletal rearrangement of 5-cyclopropylidenecyclooctanone[6] and tetracyclo[8.2.2.$2^{2,5}$.$2^{6,9}$]-1,5,9-octadecatriene.[21] Although the formation of chloride **29** in the case of $AlCl_3$ can be depicted as displacement of the alcoholate moiety of **37** with chloride, the details are not clear at present.

Scheme 4



In conclusion, on the basis of our proposal, we have carried out the acid-catalyzed cascade rearrangement of 5-cyclopentylidenecyclooctanone derivatives **9a**−**c** to synthesize the unique polyspiropolyquinanes **11a**−**c**. The 5-cyclopentylidenecyclooctanone (**9a**) gave the expected dispirotriquinane **11a**. On the other hand, the 5-(cyclopentanespirocyclopentylidene)cyclooctanone (**9b**) did not afford the desired trispirotetraquinane **11b**, but produced the bis-propellane-type tetrahydrofuran **25** in high yield. Furthermore, the higher homologue, 5−8−8-type ketone **9c**, gave the polycyclic compounds **27**−**31** depending on the acid used, instead of the desired tetraspiropentaquinane **11c**. Although we could not synthesize the higher polyspiropolyquinane compounds such as **11b** and **11c**, the method used for the construction of 5−8- or 5−8−8-type compounds can be useful for oligo(cyclooctylidenes), whose analogues, oligo(cyclohexylidenes), have attracted attention in the area of nanochemistry.[22]

Experimental Section

All melting points were uncorrected. Instruments for the measurement of spectra and the technique of chromatography

(21) McMurry, J. E.; Haley, G. J.; Matz, J. R.; Clardy, J. C.; Van Duyne, G.; Gleiter, R.; Schäfer, W.; White, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 2932.

(22) Hoogesteger, F. J.; Havenith, R. W. A.; Zwikker, J. W.; Jenneskens, L. W.; Kooijman, H.; Veldman, N.; Spek, A. L. *J. Org. Chem.* **1995**, *60*, 4375 and references cited therein.

were the same as were used in the previous work.[4] Ketones **12**[6] and **15**[10] were prepared according to the literature.

1-(*tert*-Butyldimethylsiloxy)-5-cyclopentylidenecyclooctane (13). Wittig Method.[8] A mixture of $NaNH_2$ (320 mg, 8.0 mmol) and cyclopentyltriphenylphosphonium bromide[7] (3.29g, 8.0 mmol) in dry toluene (12 mL) was stirred at ca. 70 °C (oil bath temperature) for 5 h under argon. Then a solution of **12** (512 mg, 2 mmol) in dry toluene (7 mL) was added to the red suspension. The mixture was stirred at 80−90 °C for 24 h and then filtered. The filtrate was concentrated *in vacuo* to give the crude olefin **13** which was used for the next step without purification. The GLC analysis of the crude sample showed the existence of some unidentified impurities.

McMurry Method.[9] A mixture of $TiCl_3$·$DME_{1.5}$ (1.40 g, 4.80 mmol) and Zn−Cu (1.30 g, 8.40 mmol) in dry DME (20 mL) was stirred at reflux for 4 h under argon. A solution of cyclopentanone (66 mg, 1.56 mmol) and **12** (100 mg, 0.39 mmol) in dry DME (3 mL) was added to the black suspension. The mixture was stirred at reflux for 3 h and cooled. The mixture was diluted with pentane (10 mL) and filtrated through a pad of Florisil. The filtrate was concentrated *in vacuo* to give the crude material which was chromatographed on SiO_2 (elution with hexane) to give **13** (114 mg, 95%). We did not isolate other products derived by the respective homocoupling. **13**: colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.91 (m, 1H), 2.30−2.12 (m, 6H), 2.08−1.95 (m, 2H), 1.80−1.50 (m, 12H), 0.87 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 137.22 (s), 129.92 (s), 71.74 (d), 37.33 (t, 2C), 32.62 (t, 2C), 30.42 (t, 2C), 26.78 (t, 2C), 26.03 and 25.9 (br, q, 3C), 22.90 (t, 2C), 18.33 (s), −4.68 (q), −4.83 (q); IR (neat) 1240, 1050, 830, 770 cm^{-1}.

5-Cyclopentylidenecyclooctan-1-ol (14). A mixture of the above crude material, 46% HF (1.5 mL), and water (1.5 mL) in CH_3CN (25 mL) was stirred at rt for 1.5 h. Saturated $NaHCO_3$ solution was added to the cooled mixture. The mixture was extracted with ether, and the combined extracts were washed with brine and dried ($MgSO_4$). Evaporation of the solvent followed by column chromatography on SiO_2 (elution with ether/hexane, 2:8) gave **14** (225 mg, 58% from **12**). Reaction of **13** (110 mg, 0.36 mmol) obtained by McMurry coupling with 46% HF as described above gave **14** (62 mg, 89%): colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.85 (m, 1H), 2.22−2.06 (m, 8H), 1.80−1.71 (m, 4H), 1.68−1.55 (m, 8H), 1.49 (br s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.33 (s), 129.40 (s), 71.51 (d), 36.15 (t, 2C), 32.84 (t, 2C), 30.36 (t, 2C), 26.71 (t, 2C), 22.53 (t, 2C); IR (neat) 3320, 1040, 980 cm^{-1}; MS *m*/*e* (rel intensity) 194 (M$^+$, 80), 148 (100), 133 (55), 107 (53), 94 (76), 79 (76), 67 (57); HRMS calcd for $C_{13}H_{22}O$ 194.1671, found 194.1671.

5-Cyclopentylidenecyclooctan-1-one (9a). Swern Oxidation. To a solution of oxalyl chloride (80 μL, 0.80 mmol) in CH_2Cl_2 (3 mL) was added DMSO (120 μL, 1.70 mmol) dropwise at −60 °C under argon. The mixture was stirred at −60 °C for 5 min, and a solution of **14** (142 mg, 0.73 mmol) in CH_2Cl_2 (2 mL) was added. The mixture was stirred at −60 °C for 30 min, and Et_3N (0.52 mL 3.8 mmol) was added. The mixture was warmed to rt, and water was added. The mixture was extracted with CH_2Cl_2, and the combined extracts were dried ($MgSO_4$). Evaporation of the solvent followed by column chromatography on SiO_2 (elution with ether/hexane, 5:95) gave **9a** (111 mg, 79%): colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.36−2.29 (m, 4H), 2.23−2.11 (m, 8H), 2.04−1.96 (m, 4H), 1.65−1.53 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 215.40 (s), 143.51 (s), 126.19 (s), 41.87 (t, 2C), 33.05 (t, 2C), 30.58 (t, 2C), 26.32 (t, 2C), 24.22 (t, 2C); IR (neat) 1700, 1330, 860 cm^{-1}; MS *m*/*e* (rel intensity) 192 (M$^+$, 41), 174 (100), 145 (54), 131 (64), 93 (55); HRMS calcd for $C_{13}H_{20}O$ 192.1514, found 192.1492.

5-(Spiro[4.4]non-2-ylidene)cyclooctan-1-ol (17). McMurry coupling of **15** (300 mg, 2.2 mmol) and **12** (278 mg, 1.1 mmol) as described above gave the crude TBDMS ether **16**. Reaction of the ether **16** using 46% HF as described above gave **17** (130 mg, 45% overall) after column chromatography on SiO_2 (elution with ether/hexane, 5:95). A small amount of the diol **20** contaminated **17**. **17**: colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.91 (m, 1H), 2.32−2.10 (m, 6H), 2.06 (m, 1H), 1.92−1.45 (m, 20H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.85 (s), 129.96 (s), 71.31 (d), 52.81 (s), 45.75 (t), 39.80 (t), 39.54 (t), 36.82 (t), 34.35 (t), 33.00 (t), 32.73 (t), 32.61 (t), 25.93 (t), 25.93 (t), 24.03 (t), 23.11 (t), 21.91 (t); IR (neat) 3350, 1030 cm^{-1}; MS *m*/*e* (rel intensity) 248 (M$^+$, 64), 148 (41), 122 (100), 108 (79); HRMS calcd for $C_{17}H_{28}O$ 248.2140, found 248.2143.

5-(Spiro[4.4]non-2-ylidene)cyclooctan-1-one (9b). Swern oxidation of **17** (130 mg, 0.52 mmol) as described above gave **9b** (87 mg, 68%) after column chromatography on SiO_2 (elution with ether/hexane, 1:99): colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.44−2.41 (m, 2H), 2.34−2.31 (m, 2H), 2.27 (t, J = 6.1 Hz, 2H), 2.24 (t, J = 6.7 Hz, 2H), 2.17−2.14 (m, 2H), 2.13−2.08 (m, 2H), 1.91−1.81 (m, 3H), 1.76−1.45 (m, 11H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 215.43 (s), 149.09 (s), 126.84 (s), 52.89 (s), 45.47 (t), 44.89 (t), 39.64 (t, 2C), 39.19 (t), 33.20 (t), 32.72 (t), 32.28 (t), 26.29 (t), 25.88 (t, 2C), 23.85 (t), 21.76 (t); IR (neat) 1700, 1450 cm^{-1}; MS *m*/*e* (rel intensity) 246 (M$^+$, 100), 122 (53), 108 (52); HRMS calcd for $C_{17}H_{26}O$ 246.1984, found 246.1983.

5,5′-Bis(*tert*-butyldimethylsiloxy)-1,1′-bicyclooctylidene (18). McMurry coupling of **12** (1.07 g, 4.20 mmol) as described above gave a mixture (ca. 1:1) of syn and anti isomers of **18** (0.69 g, 65%) after column chromatography on SiO_2 (elution with hexane), which were not separated and therefore characterized as a mixture: white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.89−3.84 (m, 2H), 3.82−3.77 (m, 2H), 2.47−2.41 (m, 4H), 2.16 (t, J = 6.4 Hz, 8H), 1.93−1.87 (m, 4H), 1.81−1.72 (m, 8H), 1.69−1.44 (m, 24H), 0.87 (s, 18H), 0.85 (s, 18H), 0.01 (s, 12H), 0.00 (s, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 133.79 (s, 2C), 133.71 (s, 2C), 72.30 (d, 2C), 71.39 (d, 2C), 37.34 (t, 4C), 36.05 (t, 4C), 31.72 (t, 4C), 31.37 (t, 4C), 25.98 (q, 6C), 25.95 (q, 6C), 23.59 (t, 4C), 22.81 (t, 4C), 18.30 (s, 2C), 18.23 (s, 2C), −4.72 (q, 4C), −4.75 (q, 4C); IR (KBr) 1250, 1050, 1000, 910, 830, 770 cm^{-1}; MS *m*/*e* (rel intensity) 480 (M$^+$, trace), 423 (66), 215 (53), 135 (94), 109 (100), 75 (92); HRMS calcd for $C_{28}H_{56}O_2Si_2$ 480.3818, found 480.3832.

5′-(*tert*-Butyldimethylsiloxy)-5-hydroxy-1,1′-bicyclooctylidene (19) and 5,5′-Dihydroxy-1,1′-bicyclooctylidene (20). Reaction of **18** (496 mg, 1.03 mmol) with 46% HF as described above gave the recovered **18** (123 mg, 75% conversion), a mixture of syn and anti alcohol **19** (194 mg, 51%), and a mixture of syn and anti diol **20** (108 mg, 42%) after flash chromatography on SiO_2 (elution with ether/hexane, 3:7 for **19**, ether/methanol, 9:1 for **20**). **19**: colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.85−3.79 (m, 4H), 2.43−2.35 (m, 4H), 2.30−2.22 (m, 4H), 2.09−2.03 (m, 4H), 1.99−1.91 (m, 4H), 1.82−1.32 (m, 34H), 0.86 (s, 9H), 0.85 (s, 9H), 0.01 (s, 6H), −0.01 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 134.86 (s), 134.33 (s), 133.27 (s), 133.23 (s), 71.89 (d), 71.58 (d), 71.55 (d), 71.21 (d), 37.03 (t, 2C), 36.56 (t, 2C), 36.47 (t, 2C), 35.16 (t, 2C), 31.63 (t, 2C), 31.47 (t, 2C), 31.44 (t, 2C), 31.43 (t, 2C), 25.95 (q, 3C), 25.93 (q, 3C), 23.44 (t, 2C), 23.36 (t, 2C), 23.11 (t, 2C), 22.58 (t, 2C), 18.26 (s), 18.22 (s), −4.76 (q, 4C); IR (neat) 3320, 1260, 1060, 840, 780 cm^{-1}; MS *m*/*e* (rel intensity) 366 (M$^+$, trace), 291 (52), 135 (98), 121 (99), 109 (60), 75 (100); HRMS calcd for $C_{22}H_{42}O_2Si$ 366.2954, found 366.2959. **20**: white solid; mp 153−155 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.83−3.79 (m, 4H), 2.22−2.11 (m, 16H), 1.89−1.72 (m, 20H), 1.67−1.53 (m, 16H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 134.02 (s, 2C), 134.97 (s, 2C), 71.46 (d, 2C), 71.34 (d, 2C), 36.08 (t, 4C), 35.77 (t, 4C), 31.55 (t, 4C), 31.42 (t, 4C), 23.18 (t, 4C), 23.00 (t, 4C); IR (KBr) 3300, 1030, 970, 870 cm^{-1}; MS *m*/*e* (rel intensity) 252 (M$^+$, trace), 109 (58), 108 (100); HRMS calcd for $C_{16}H_{28}O_2$ 252.2089, found 252.2065.

To a solution of **20** (2.26 g, 8.97 mmol) in dry THF (30 mL) was added BuLi (1.5 M in hexane, 7.0 mL, 10.5 mmol) dropwise at −78 °C under argon. The mixture was warmed to rt for 1 h, and TBDMSCl (1.44 g, 9.50 mmol) and imidazole (200 mg) were added. The mixture was stirred at rt for 2 h, and saturated $NaHCO_3$ was added. The mixture was extracted with ether, and the combined extracts were dried ($MgSO_4$). Evaporation of the solvent followed by column chromatography on SiO_2 gave **18** (1.07 g, 25%), **19** (1.52 g, 46%), and the recovered **20** (0.58 g, 74% conversion).

5-(*tert*-Butyldimethylsiloxy)-5′-oxo-1,1′-bicyclooctylidene (21). To a stirred mixture of PDC (5.15 g, 13.5 mmol) and activated alumina (6.20 g) in CH_2Cl_2 (40 mL) was added

a solution of **19** (1.52 g, 4.15 mmol) in CH_2Cl_2 (10 mL) at rt. The mixture was stirred at rt for 6 h and diluted with ether (100 mL). The mixture was stirred for another 30 min and filtered through a pad of Florisil. The filtrate was concentrated *in vacuo*, and the residue was chromatographed on SiO_2 (elution with ether/hexane, 5:95) to give **21** (1.42 g, 94%): waxy white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.78 (m, 1H), 2.47−2.39 (m, 4H), 2.27−2.17 (m, 4H), 2.07−1.86 (m, 8H), 1.77−1.70 (m, 2H), 1.64−1.56 (m, 4H), 1.53−1.46 (m, 2H), 0.85 (s, 9H), −0.02 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 215.18 (s), 139.55 (s), 130.04 (s), 71.52 (d), 41.76 (t, 2C), 37.18 (t, 2C), 31.62 (t, 2C), 31.17 (t, 2C), 25.95 (q, 3C), 24.71 (t, 2C), 23.34 (t, 2C), 18.26 (s), −4.78 (q, 2C); IR (KBr) 1690, 1240, 1065, 830, 770 cm^{-1}; MS *m*/*e* (rel intensity) 364 (M$^+$, trace), 307 (70), 107 (100), 75 (61); HRMS calcd for $C_{22}H_{40}O_2Si$ 364.2797, found 364.2812.

5′-(*tert*-Butyldimethylsiloxy)-5-cyclopentylidene-1,1′-bicyclooctylidene (22). McMurry coupling of **21** (1.09 g, 3 mmol) and cyclopentanone (1.01 g, 12.0 mmol) as described above gave **22** (0.97 g, 78%) after column chromatography on SiO_2 (elution with hexane): colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.81 (m, 1H), 2.50−1.41 (m, 32H), 0.81 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 136.57 (s), 133.48 (s), 133.20 (s), 129.42 (s), 71.66 (d), 36.98 (t, 2C), 32.77 (t, 2C), 31.80 (t, 2C), 31.44 (t, 2C), 30.38 (t, 2C), 26.85 (t, 2C), 25.97 (q), 26.11 (q), 25.88 (q), 24.95 (t, 2C), 23.45 (t, 2C), 18.29 (s), −4.73 (q, 2C).

5-Cyclopentylidene-5′-hydroxy-1,1′-bicyclooctylidene (23). Reaction of **22** (0.97g, 2.33 mmol) with 46% HF as described above gave **23** (512 mg, 72%) after column chromatography on SiO_2 (elution with ether/hexane, 1:9): colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.78 (m, 1H), 2.27−2.03 (m, 16H), 1.78−1.50 (m, 17H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 136.67 (s), 134.57 (s), 132.70 (s), 129.46 (s), 71.34 (d), 35.85 (t, 2C), 32.83 (t, 2C), 31.77 (t, 2C), 31.50 (t, 2C), 30.37 (t, 2C), 26.81 (t, 2C), 25.11 (t, 2C), 23.15 (t, 2C); IR (neat) 3350, 1040 cm^{-1}; MS *m*/*e* (rel intensity) 304 (M$^+$, 69), 175 (75), 147 (96), 134 (82), 121 (79), 108 (86), 93 (100), 79 (89), 67 (94); HRMS calcd for $C_{21}H_{34}O$ 302.2609, found 302.2613.

5-Cyclopentylidene-5′-oxo-1,1′-bicyclooctylidene (9c). Swern oxidation of **23** (105 mg, 0.33 mmol) as described above gave **9c** (71 mg, 70%) after column chromatography on SiO_2 (elution with ether/hexane, 1:99): white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.30−2.27 (m, 4H), 2.20−2.11 (m, 8H), 2.10−2.05 (m, 8H), 1.97−1.92 (m, 4H), 1.75−1.70 (m, 4H), 1.58−1.54 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 215.36 (s), 139.42 (s), 136.83 (s), 129.32 (s), 129.16 (s), 41.71 (t, 2C), 32.70 (t, 2C), 31.59 (t, 2C), 31.41 (t, 2C), 30.41 (t, 2C), 26.85 (t, 2C), 24.83 (t, 2C), 24.50 (t, 2C); IR (film) 1690 cm^{-1}; MS *m*/*e* (rel intensity) 300 (M$^+$, 100), 176 (64); HRMS calcd for $C_{21}H_{32}O$ 300.2453, found 300.2430.

***cis*-5-(Cyclo-1-pentenyl)bicyclo[3.3.0]octan-1-ol (24).** A solution of **9a** (50 mg, 0.26 mmol) in xylene (10 mL) was heated at ca. 140 °C for 4 h under argon. The solution was cooled and concentrated *in vacuo*, and the residue was chromatographed on SiO_2 (elution with ether/hexane, 5:95) to afford **24** (30 mg, 60%) and the recovered **9a** (12 mg). **24**: white solid; mp 53−55 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.61 (t, J = 1.8 Hz, 1H), 2.41−2.34 (m, 4H), 2.10−2.03 (m, 2H), 1.89−1.66 (m, 9H), 1.59−1.49 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.38 (s), 125.67 (d), 90.50 (s), 57.02 (s), 41.59 (t, 2C), 38.66 (t, 2C), 34.34 (t), 32.39 (t), 23.70 (t), 23.16 (t, 2C); IR (KBr) 3350, 3020, 1620, 1280, 1100, 1030, 990 cm^{-1}; MS *m*/*e* (rel intensity) 192 (M$^+$, 36), 174 (100), 145 (54), 131 (64), 93 (53); HRMS calcd for $C_{13}H_{20}O$ 192.1514, found 192.1528.

Preparation of 9a-*d*$_4$. A sample of Na (150 mg, 6.52 mmol) was added to a solution of D_2O (5 mL) and 1,4-dioxane (3 mL) at rt under argon. The mixture was stirred at rt for 30 min, and a solution of **12** (150 mg, 0.78 mmol) in 1,4-dioxane (3 mL) was added. The mixture was stirred at 50 °C for 24 h, concentrated *in vacuo*, and extracted with ether. The combined extracts were dried ($MgSO_4$). Evaporation of the solvent followed by column chromatography on SiO_2 (elution with ether/hexane, 5:95) gave the deuterio ketone (145 mg, 95%) as a colorless oil. The mass spectrum showed the deuterium content as follows: 1.2% d_2, 6.6% d_3, 92.2% d_4.

General Procedure of Acid-Catalyzed Rearrangement. To a solution of ketone (50 mg) in CH_2Cl_2 (benzene for H_2SO_4, 5 mL) was added acid (0.5 equiv) at rt. The mixture was stirred at rt. The reaction was monitored with GLC or TLC. Saturated $NaHCO_3$ solution was added, and the mixture was extracted with ether. The combined extracts were dried ($MgSO_4$). Evaporation of the solvent was followed by flash chromatography on SiO_2 (elution with ether/hexane, 1:99).

Dispiro[4.0.4.3]tridecan-1-one (11a): colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.32 (m, 1H), 2.10 (m, 1H), 2.02−1.88 (m, 4H), 1.80−1.29 (m, 14H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 222.61(s), 60.73 (s), 55.51 (s), 39.47 (t), 37.96 (t), 35.83 (t), 35.15 (t), 33.54 (t), 33.03 (t), 24.56 (t), 24.03 (t), 20.88 (t), 19.54 (t); IR (neat) 1730, 1160 cm^{-1}; MS *m*/*e* (rel intensity) 192 (M$^+$, 28), 110 (75), 108 (43), 97 (100), 96 (50); HRMS calcd for $C_{13}H_{20}O$ 192.1514, found 192.1535.

[2,2,13,13-^{2}H$_4$]-Dispiro[4.0.4.3]tridecan-1-one (11a-*d*$_4$): ^{13}C NMR (150 MHz, $CDCl_3$) δ 222.84, 60.54, 55.47, 39.21 (triplet), 38.93 (quintet), 37.86, 35.05, 35.04 (quintet), 33.39, 32.94, 24.50, 23.97, 20.63, 19.32; deuterium content, 0.1% d_2, 12.8% d_3, 87.1% d_4.

Tetrahydrofuran derivative 25: white solid; mp 92−94 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.27 (m, 1H), 2.09−1.86 (m, 6H), 1.84−1.50 (m, 14H), 1.47 (m, 1H), 1.42−1.39 (m, 1H), 1.36−1.25 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 103.08 (s), 97.39 (s), 68.82 (s), 54.74 (s), 43.73 (t), 42.88 (t), 40.62 (t), 39.02 (t), 38.22 (t), 37.90 (t), 34.52 (t), 32.18 (t), 27.15 (t), 26.23 (t), 23.58 (t), 22.54 (t), 21.29 (t); IR (KBr) 1070, 1040, 1000 cm^{-1}; MS *m*/*e* (rel intensity) 246 (M$^+$, 16), 204 (100); HRMS calcd for $C_{17}H_{26}O$ 246.1984, found 246.1978.

Tetrahydropyran derivative 27: colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.28−2.22 (m, 2H), 2.11 (dt, J = 13.3, 9.4 Hz, 2H), 1.94−1.76 (m, 10H), 1.67−1.37 (m, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 90.64 (s), 87.44 (s), 56.70 (s), 56.08 (s), 53.14 (s), 44.11 (t, 2C), 41.17 (t, 2C), 39.06 (t, 2C), 37.89 (t, 2C), 36.74 (t, 2C), 24.04 (t, 2C), 23.82 (t, 2C), 21.51 (t, 2C); IR (neat) 1320, 1110, 1040 cm^{-1}; MS *m*/*e* (rel intensity) 300 (M$^+$, 57), 271 (100), 108 (32); HRMS calcd for $C_{21}H_{32}O$ 300.2453, found 300.2455.

Tertiary alcohol 28: waxy white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.37 (t, J = 2.0 Hz, 1H), 2.43−1.98 (m, 12H), 1.80−1.30 (m, 19H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.09 (s), 126.26 (d), 74.43 (s), 41.78 (s), 41.75 (s), 40.11 (s), 35.89 (t), 35.56 (t, 2C), 33.07 (t, 2C), 32.47 (t), 27.57 (t, 2C), 25.78 (t, 2C), 23.82 (t), 21.59 (t, 2C), 21.00 (t, 2C); IR (KBr) 3450, 1190, 970 cm^{-1}; MS *m*/*e* (rel intensity) 300 (M$^+$, 100), 282 (20), 272 (60); HRMS calcd for $C_{21}H_{32}O$ 300.2453, found 300.2443.

Chloride 29: white solid; mp 158−160 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.38 (t, J = 1.9 Hz, 1H), 2.67−2.59 (m, 2H), 2.44−2.25 (m, 10H), 2.22−2.06 (m, 4H), 2.00 (dd, J = 13.5, 7.6 Hz, 2H), 1.82−1.70 (m, 8H), 1.37−1.26 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.50 (s), 126.78 (d), 83.31 (s), 43.25 (s), 42.38 (s), 41.75 (s), 38.79 (t, 2C), 35.94 (t), 33.00 (t, 2C), 32.49 (t), 27.34 (t, 2C), 27.12 (t, 2C), 23.77 (t), 22.93 (t, 2C), 21.56 (t, 2C); IR (KBr) 810, 720 cm^{-1}; MS *m*/*e* (rel intensity) 320 (M$^+$ + 2, 37), 318 (M$^+$, 100), 147 (77), 121 (48), 108 (90); HRMS calcd for $C_{21}H_{31}Cl$ 318.2114, found 318.2115.

Tetrahydrofuran derivative 30: white solid; mp 63−65 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.22 (m, 1H), 2.16 (dt, J = 13.9, 9.2 Hz, 1H), 2.11−1.97 (m, 3H), 1.87 (dd, J = 12.0, 6.1 Hz, 1H), 1.82 (dt, J = 12.3, 6.6 Hz, 1H), 1.77−1.22 (m, 24H), 1.16 (dt, J = 13.1, 6.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 103.67 (s), 102.26 (s), 67.65 (s), 56.14 (s), 50.99 (s), 41.43 (t), 40.31 (t), 39.98 (t), 38.72 (t), 37.19 (t), 36.39 (t), 35.99 (t), 31.49 (t), 28.12 (t), 27.10 (t), 26.83 (t), 26.49 (t), 25.16 (t), 24.60 (t), 23.69 (t), 16.72 (t); IR (film) 1180, 1140, 1120, 1090, 1060, 1030 cm^{-1}; MS *m*/*e* (rel intensity) 300 (M$^+$, 34), 257 (95), 190 (100), 107 (34); HRMS calcd for $C_{21}H_{32}O$ 300.2453, found 300.2430.

Tetrahydrofuran derivative 31: colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.80 (dt, J = 12.6, 6.2 Hz, 1H), 2.29 (dt, J = 14.2, 9.6 Hz, 1H), 2.13−1.25 (m, 30H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 102.00 (s), 99.13 (s), 71.59 (s), 60.47 (s), 48.76 (s), 45.75 (t), 44.13 (t), 41.94 (t), 40.55 (t), 37.86 (t), 36.87 (t), 35.36 (t), 34.61 (t), 34.15 (t), 32.13 (t), 28.71 (t), 27.43 (t), 25.53 (t), 23.72 (t), 21.43 (t), 19.84 (t); IR (neat) 1070, 1040, 1010, 880

cm^{-1}; MS *m/e* (rel intensity) 300 (M^+, 23), 258 (100), 218 (46), 175 (90); HRMS calcd for $C_{21}H_{32}O$ 300.2453, found 300.2448.

X-ray Analysis. Data were collected at 23 °C on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation (λ = 071 069 Å). All the calculations were performed using the teXsan[23] crystallographic software package of Molecular Structure Corporation. **For 25**:[24] recrystallized from hexane. Crystal data: $C_{17}H_{26}O$, tetragonal $P42_1/m$ (#113), a = 10.3237(9) Å, c = 6.648(1) Å, V = 708.50(9) $Å^3$, Z = 2. The structure was solved by direct methods. The molecule itself lies on the crystallographic *mm* symmetry resulting in the disordered structure with the occupancies of 0.75 for cyclopentane rings and of 0.25 for cyclohexane rings, respectively. The structure was refined by the full-matrix least-square method. All non-hydrogen atoms were refined with isotropically to give R (Rw) = 0.24 (0.27) for 123 independent reflections of 526 unique reflections with $I > 3\sigma(I)$. **For 29**:[24] recrystallized from hexane. Crystal data: $C_{21}H_{31}Cl$, monoclinic $P2_1/n$ (#14), a = 12.371(2) Å, b = 11.642(2) Å, c = 12.708(2) Å, β = 112.490(9)°, V = 1691.1 (4) $Å^3$, Z = 4. The structure was solved by direct methods and expanded using Fourier technique and refined by the full-matrix least-square method. All non-hydrogen atoms were refined by anisotropically to give R (Rw) = 0.057 (0.050) for 1777 independent reflections of 4092 unique reflections with $I > 3\sigma(I)$.

(23) teXsan: Crystal Structure Analysis Package, Molecular Structure Corp. (1985 and 1992).

(24) The author has deposited atomic coordinates for **25** and **29** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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Supporting Information Available: ^1H and ^{13}C NMR spectra of **9a**−**c**, **11a**, **13**, **14**, **17**−**25**, and **27**−**31**, 2D ^{13}C-INADEQUATE spectra of **30** and **31**, and an ORTEP drawing of **25** (43 pages). This material is contained in 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.

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