Synthesis and Structural Properties of Two Biscyclopropenes

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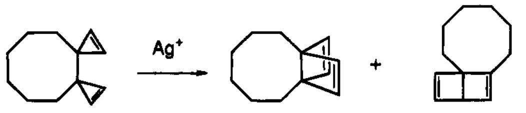
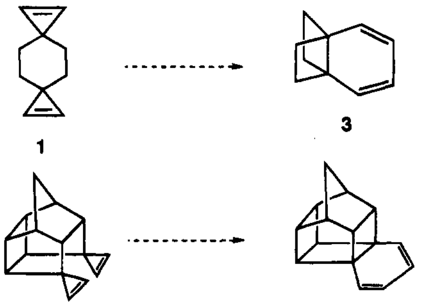
The synthesis of two biscyclopropenes, **1** and **2**, are described. Both compounds are moderately sensitive to oxygen and Lewis acids. The conformational properties of **1** were examined by dynamic ^{1}H NMR spectroscopy. The structure of **2** was determined by low-temperature X-ray crystallography. Ab initio calculations successfully reproduce the structure for **2** and the conformational properties of **1**.

On a per carbon basis, the cyclopropene functional group is one of the most highly strained all-carbon systems that can be manipulated and studied.[1] We have been interested in preparing systems that contain multiple cyclopropene groups for use as potential high-energy density materials. Several biscyclopropenes have been reported in which the cyclopropene groups are located on vicinal carbon atoms.[2] In certain cases, these highly energetic biscyclopropenes can be isomerized to the more stable dewar benzenes (eq 1).[3]



(1)

We were interested in investigating the longer range interactions between two cyclopropene groups having a 1,4 relationship such as found in **1** and **2**. In connection with our interest in new synthetic methods for the preparation of prismanes,[4] we envisioned that such an interaction in **1** and **2** together with an appropriate catalyst might lead to C−C bond-forming reaction across the cyclohexane ring and the formation of compounds such as **3** and **4** which contain a cyclohexadiene group fused onto a bicyclo[2.2.0]hexane unit. Simple Benson group additivity[5] predicts that reaction of **1** leading to **3** is exothermic by 60 kcal/mol. While we have not yet discovered conditions that will allow this process to take place, we have prepared two new biscyclopropenes, **1** and **2**, designed to investigate this interaction. In addition, we report a high-quality low-temperature X-ray structural determination for **2** and information about dynamic conformational effects for **1**. Ab initio calculations have been used to investigate **1** and **2** and the results are compared with experiment.



1 **3** **2** **4**

Results and Discussion

Synthesis of **1** and **2** followed standard procedures. The synthesis of **1** is shown in Scheme 1. Commercially available 1,4-bis(hydroxymethyl)cyclohexane (**5**) was converted to the bis(bromomethyl) compound with PBr_3.[6] Double dehydrobromination using potassium hydroxide in diethylene glycol[7] produced 1,4-bis(methylene)cyclohexane (**6**)[8] in 36% yield for two steps. Addition of dibromocarbene using phase-transfer conditions[9] produced the bis(dibromocyclopropane) **7**[10] as a mixture of two diastereomers in 56% yield. Tin hydride reduction[11] of the mixture afforded a diastereomeric mixture of dibromides **8** in 76% yield. Double dehydrobromination using *tert*-butoxide in dimethyl sulfoxide at room temperature produced the biscyclopropene **1** in 61% yield. The compound is a liquid at room temperature and is moderately sensitive to oxygen or Lewis acids.

The caged-ring compound **2** was prepared in a manner similar to that of **1** (Scheme 2). Shen and Kuebler reported that the readily available dione **9** could be converted in 50% yield to diene **10** using a double Wittig reaction.[12] Marchand and Kaya were unable to reproduce this preparation and instead reported a three-step procedure for the preparation of diene **10** in 52% overall yield.[13] We have found that dione **9** can be converted directly to **10** in 63% yield using the Lombardo reagent.[14] The Lombardo reagent is a Lewis acidic reagent and has

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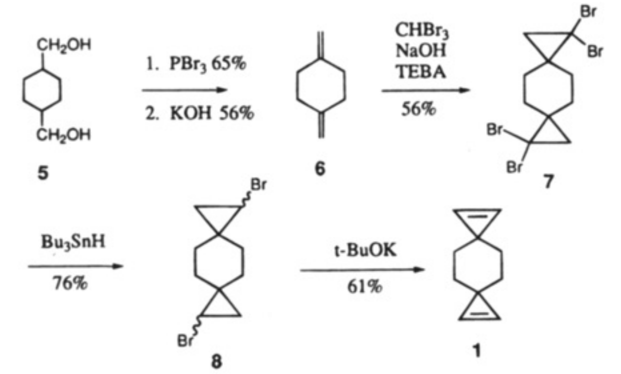
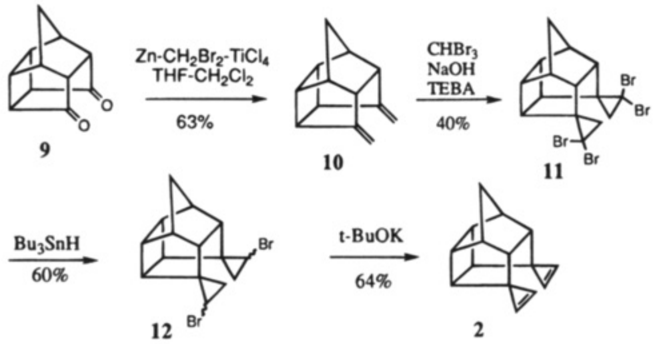
Scheme 1



Scheme 2



found use for methylenation of base-sensitive carbonyl compounds. Dione **9** undergoes transannular reactions under basic conditions.[13] Dibromocarbene addition to diene **10** produced the bis(dibromocarbene) adduct as one isomer **11**. Reduction of **11** produced bis(dibromocyclopropane) **12** as a mixture of diastereomers. Base-induced elimination of **12** produced the biscyclopropene **2** which after multiple vacuum sublimations was a crystalline solid. Biscyclopropene **2** was much more sensitive to oxygen than compound **1**.

Structural Properties and ab Initio Calculations for 1 and 2

Since **1** is a functionalized cyclohexane, it was expected to exhibit conformational properties similar to other subsituted cyclohexanes.[15] To investigate this, a conformational study of **1** was undertaken by dynamic ^{1}H NMR. At room temperature the ^{1}H NMR for **1** consists of two singlets. Upon cooling, each of these peaks broadens and splits into two peaks. At −90 °C, the vinylic resonances are not yet baseline resolved. The methylene protons are baseline resolved with a separation of 580 Hz but do not yet show any splittings. At 500 MHz, the coalescence temperature for the methylene protons is −70 °C which[16] leads to a value of 8.8 kcal/mol for the free energy of activation for the site exchange process in **1**. This can be compared with the value obtained for cyclohexane ($\Delta G^{\ddagger} = 10.3$ kcal/mol at −67 °C)[17] and that obtained for 1,1,4,4-tetramethylcyclohexane (11.4 kcal/mol at −62 °C).[18] The chair conformation (**13c**), the transition structure for conversion of the chair to the twist boat (**13ts**), and the twist boat conformation (**13tb**) of cyclohexane were located using geometry optimized HF/6-31G* calculations.[19] That the transition structure **13ts** interconnected the chair **13c** and twist boat **13tb** was confirmed by using the intrinsic reaction coordinate (IRC) algorithm. The optimized structures are shown in Figure 1. The total energies are given in Table 1. The difference in energy between the chair and the transition structure is calculated to be 12.2 kcal/mol.

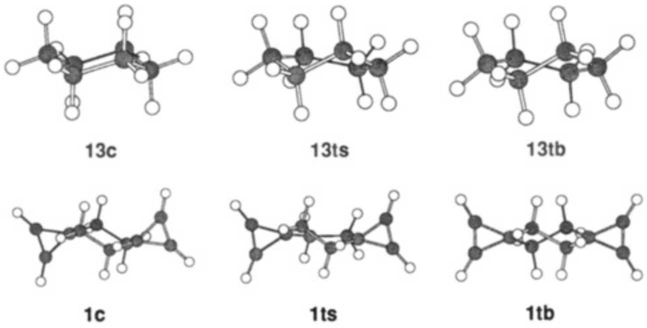


Figure 1. Structures for the chair, transition structure leading from chair to twist boat, and twist boat of cyclohexane (**13c**, **13ts**, **13tb**) and **1** (**1c**, **1ts**, **1tb**).

Table 1. Total and Relative Energies for Several Conformers of Cyclohexane and 1 Calculated at the HF/6-31G* Level

structure	-*E* (hartrees)	relative *E* (Kcal/mol)[a]
13c	234.20801	0.0
13ts	234.18845	12.3
13tb	234.19723	6.8
1c	385.47506	0.0
1c	385.45938	9.8
1tb	385.46722	4.9

[a] 1 Hartree = 627.5 kcal/mol.

In a similar manner, the chair conformation of **1** (**1c**), the transition structure for conversion of the chair to the twist boat (**1ts**), and the twist boat conformation (**1tb**) of biscyclopropene **1** were calculated. IRC calculations confirmed the interconnectivity of the structures. The optimized structures are shown in Figure 1. The total energies are given in Table 1. The difference in energy between the chair **1c** and the transition structure **1ts** is calculated to be 9.8 kcal/mol, or 2.4 kcal/mol less that that calculated for the parent cyclohexane. This is in reasonable agreement with our value derived from dynamic NMR measurements. The reason for the lower barrier is due to the fewer eclipsing interactions present in the transition state as compare with cyclohexane. The three-membered rings naturally reduce the eclipsing interactions by virtue of the smaller CCC bond angle compared with a HCH bond angle.

The structure of **2** was confirmed by single-crystal X-ray analysis. The collection of the data was carried out at −40 °C. An ORTEP of the structure is shown in Figure 2. For comparison, the structure of **2** was calculated at the geometry optimized HF/6-31G* level.

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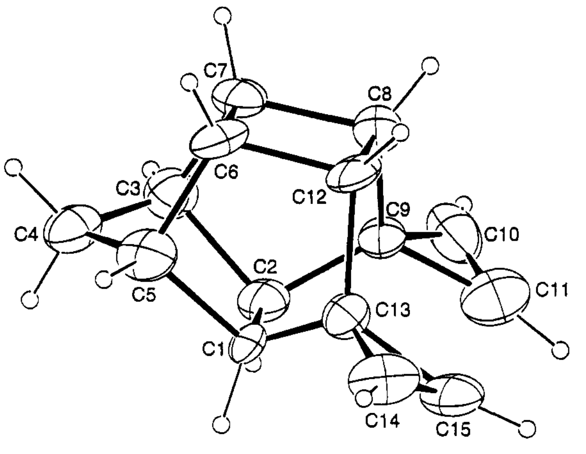

Figure 2. Structure of **2** determined by X-ray crystallography. Ellipsoids are drawn at the 30% level.

Table 2. Comparison of Experimental and Calculated Structure of 2

bond	distance (Å) observed (X-ray)	distance (Å) calculated (HF/6-31G*)
C(1)–C(2)	1.554(3)	1.553
C(1)–C(5)	1.543(3)	1.551
C(1)–C(10)	1.559(3)	1.556
C(2)–C(3)	1.539(3)	1.551
C(2)–C(9)	1.560(3)	1.556
C(3)–C(4)	1.525(3)	1.528
C(3)–C(7)	1.545(3)	1.549
C(4)–C(5)	1.520(3)	1.528
C(5)–C(6)	1.542(3)	1.549
C(6)–C(7)	1.582(3)	1.582
C(6)–C(11)	1.521(3)	1.527
C(7)–C(8)	1.515(3)	1.527
C(8)–C(9)	1.511(3)	1.522
C(8)–C(12)	1.503(3)	1.494
C(8)–C(13)	1.500(3)	1.488
C(9)–C(10)	1.567(3)	1.568
C(10)–C(11)	1.515(3)	1.522
C(11)–C(14)	1.505(3)	1.494
C(11)–C(15)	1.488(3)	1.488
C(12)–C(13)	1.280(4)	1.281
C(14)–C(15)	1.273(4)	1.281

A comparison of the experimental and HF/6-31G* calculated structure is listed in Table 2. The agreement is outstanding. Typically values for bond lengths calculated at the HF/6-31G* level are too short.[20]

There are relatively few structural studies of 3,3-dialkylcyclopropenes or simple cyclopropenes.[21] The structure of 3,3-dimethylcyclopropene was determined by microwave spectroscopy.[22] The C=C length was determined to be 1.294 and the C–C length 1.52 Å. The C=C length may be contrasted with the corresponding bond lengths in **2** which are 1.280 and 1.273 Å. Boese and co-workers have recently reported the low-temperature X-ray structure for 3-vinylcyclopropene.[23] Their reported C=C cyclopropene bond length (1.279 Å) is the same as that determined for the two cyclopropene double bonds in **2** while their C–C cyclopropene bond lengths (1.516 and 1.517 Å, respectively) are slightly longer than those determined in **2** (1.503, 1.500, 1.505, and 1.488 Å). Boese and co-workers also have reported the low-temperature X-ray structure for 3,3′-bicyclopropenyl.[24] The C=C were found to be 1.290 Å and the C–C were determined to be 1.510 and 1.513 Å. Overall, the structure determined for **2** matches that found for other simple cyclopropenes.

Summary

The preparation of two new biscyclopropenes, **1** and **2**, is described. The conformation of **1** was analyzed by dynamic ^{1}H NMR in solution. Chair–chair interconversion takes place with a free energy activation of 8.8 kcal/mol. Ab initio calculations predict a slightly higher barrier for this process (10.8 kcal/mol) but the difference between the values calculated for cyclohexane compared with **1** are well reproduced. The structure of **2** was determined using low-temperature X-ray crystallography. The structure is extremely well reproduced at the geometry optimized HF/6-31G* level.

Experimental Section

***cis*- and *trans*-1,4-Bis(bromomethyl)cyclohexane.** A mixture of *cis*- and *trans*-1,4-bis(hydroxymethyl)cyclohexane (200 g, 1.4 mol) was added dropwise (some heating is necessary to melt diol) over 1 h to a stirred solution of PBr_3 (370 g, 1.4 mol) in 300 mL of benzene at 15 °C. The solution was then refluxed for 75 min, cooled, and poured slowly onto 200 g of crushed ice. The aqueous layer was separated and washed with CH_2Cl_2 (3 × 400 mL). The combined organic layers were washed with saturated $NaHCO_3$ (3 × 500 mL) and then with distilled water (3 × 500 mL). The organic layer was dried over $MgSO_4$, filtered, and evaporated. Distillation of the residue at ~120 °C (0.1 mm) gave 244 g of dibromide (65%) as a mixture of *cis* and *trans* isomers: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.9–1.16 (m, 3H), 1.40–1.69 (m, 4H), 1.79–2.02 (m, 3H), 3.25 (d, J = 6.6 Hz, 3H), 3.34 (d, J = 6.6 Hz, 1H).

1,4-Dimethylenecyclohexane (6). A 2-L three-necked round bottom flask equipped with a dropping funnel fitted with a nitrogen inlet, mechanical stirrer, and Vigreaux column leading to a still head was charged with 370 g of powered KOH (6.59 mol) and 460 mL of diethylene glycol. The system was stirred vigorously and heated to 180 °C while a slow stream of nitrogen was passed through the flask. The collection flask was cooled to 0 °C and a mixture of *cis*- and *trans*-1,4-bis(bromomethyl)cyclohexane (244 g, 0.9 mol) was added dropwise over 1 h. A mixture of product and water was collected at a head temperature of 110 °C. Heating was continued for 1 h after addition of the dibromide was complete. The water layer was removed from the product using a separatory funnel, and the product was dried ($MgSO_4$). The crude product, 55.1 g (56%), was used in the next step without further purification. Spectral data matched those reported: ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.08 (s, 8H), 4.56 (s, 4H); the product was 98% pure by ^{1}H NMR.

***syn*- and *anti*-1,1,7,7-Tetrabromodispiro[2.2.2.2]decane (7).** To a vigorously stirred mixture of 62 mL of bromoform (180.7 g, 0.72 mol), 19.34 g (0.179 mol) of crude 1,4-dimethylenecyclohexane, 0.72 g of triethylbenzylammonium chloride (TEBA), and 1.5 mL of ethanol was added 180 mL of a 50% aqueous NaOH solution over 10 min while the temperature was maintained at 40–50 °C by intermittent cooling with a cold water bath. After the addition, the mixture was maintained at this temperature for 3 h. Up to an additional 40 mL of CH_2Cl_2 was added if the reaction mixture became too thick. The mixture was then poured into 500 mL of water, the organic layer was separated (at this step do not shake to avoid emulsions), and the aqueous layer was extracted with CH_2Cl_2 (3 × 300 mL). The combined organic layers were

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washed with water, 1 N HCl, and water and dried (MgSO$_4$). Recrystallization from 95% ethanol with decolorizing carbon yielded white crystals (44.9 g, 56%) of *syn*- and *anti*-1,1,7,7-tetrabromodispiro[2.2.2.2]decane: mp 179–181 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.45–1.55 (m, 8H), 1.65–1.76 (m, 4H), 1.78 (s, 2H), 1.8 (s, 2H), 1.95–2.05 (m, 8H); ^{13}C NMR (500 MHz, CDCl$_3$) δ 31.08, 33.08, 33.41, 33.48, 33.51, 37.79, 37.93; IR (KBr) 2980, 2918, 2860, 1450, 1430, 1290, 1280, 1050, 1040, 1035, 690 cm^{-1}; MS (EI) *m/e* 448 (M$^+$, 5), 450 (18), 452 (25), 454 (17), 456 (4). Anal. Calcd for C$_{10}$H$_{12}$Br$_4$: C, 26.85; H, 2.68. Found: C, 26.53; H, 2.61.

***syn*- and *anti*-1,7-Dibromodispiro[2.2.2.2]decane (8).** Under nitrogen, a solution of 42 mL (45.45 g, 0.157 mol) of freshly distilled tributyltin hydride in 50 mL of dry THF was added dropwise to a solution of 33.31 g (0.074 mol) of *syn*- and *anti*-1,1,7,7-tetrabromodispiro[2.2.2.2]decane in 300 mL of dry THF. Some heating (35 °C) may be used to initiate the reaction. The mixture was stirred for 3 h and then concentrated under reduced pressure. The residue was chromatographed twice on a column of Al$_2$O$_3$ (250 g) using hexane as the eluent. A third chromatography using silica gel with hexane removed any over-reduced monobrominated side products [R_f 0.8 (hexane) for monobromo]. An inseparable mixture of *syn*- and *anti*-1,7-dibromodispiro[2.2.2.2]decane was obtained in 76% yield (16.5 g) as an oil: R_f 0.7 (hexane); ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.66–0.71 (m, 2H), 0.95–1.05 (m, 2H), 1.20–1.28 (m, 1H), 1.32–1.42 (m, 2H), 1.45–1.56 (m, 1H), 1.57–1.72 (m, 3H), 1.75–1.85 (m, 1H), 2.80–2.88 (m, 2H); ^{13}C NMR (500 MHz, CDCl$_3$) δ 21.51, 21.53, 21.70, 21.73, 23.49, 23.64, 28.70, 31.25, 31.39, 33.82, 33.87; IR (neat) 2940, 2830, 1445, 1395, 1335, 1300, 1230, 1035, 965, 910 cm^{-1}; MS *m/e* calcd for C$_{10}$H$_{14}$Br$_2$ 291.9462 (M$^+$); found 291.9475.

Dispiro[2.2.2.2]deca-1,7-diene (1). Under nitrogen, a solution of 1.4 g (4.8 mmol) of *syn*- and *anti*-1,7-dibromodispiro[2.2.2.2]decane in 4 mL of dry DMSO (distilled from CaH$_2$) was slowly added dropwise to a stirred solution of 1.6 g (14.4 mmol, freshly sublimed) of potassium *tert*-butoxide in 16 mL of dry DMSO. Stirring was continued for 3 days at rt. The brownish-black mixture was poured into 60 mL of ice–water and extracted 5 times with 20 mL of *n*-pentane. The combined pentane layers were washed with water (2 × 10 mL) and brine (10 mL) and were dried with Na$_2$SO$_4$. At this point all glassware used was washed with a 5% EDTA solution, two 2 times with distilled water, and once with concentrated NH$_4$OH and then dried. The pentane solution was then concentrated in vacuo to yield a crude liquid. The liquid was transfered to a bulb under reduced pressure to yield 386 mg (61%) of dispiro[2.2.2.2]deca-1,7-diene as an oil: ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.46 (s, 8H), 7.56 (s, 4H); ^{13}C NMR (500 MHz, CDCl$_3$) δ 23.90, 38.94, 124.09; IR (neat) 2940, 2910, 2860, 1640, 1610, 1450, 1280, 1145, 1130, 1015, 950 cm^{-1}; MS *m/e* calcd for C$_{10}$H$_{13}$ 133.1017 (MH); found 133.1014; purity by GC was 98.4%.

8,11-Dimethylenepentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (10). Into a 3 L, round-bottomed flask fitted with a magnetic stirrer and a pressure equalizing dropping funnel connected to argon balloon were placed 86.25 g (1.32 mol) of activated zinc powder, 750 mL of dry THF, and 31 mL (0.44 mol) of dibromomethane. The mixture was stirred and cooled with a dry ice–acetone bath at −40 °C. To the stirred mixture was added dropwise 35 mL (0.32 mol) of titanium tetrachloride over 30 min. The cooling bath was removed and the mixture was stirred often at 5 °C for 3 days under argon atmosphere. The dark gray slurry was then cooled with an ice–water bath and 150 mL of dry dichloromethane was added. To the stirred mixture was added 17.42 g (0.10 mol) pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione in 150 mL of dry dichloromethane over a period of 30 mins. The cooling bath was removed, and the mixture was stirred at room temperature (20 °C) for 1.5 h. The mixture was then diluted with 900 mL of pentane and a slurry of 450 g of sodium bicarbonate in 240 mL of water was added cautiously over 1 h. The clear organic solution was poured off into a 4 L Erlenmeyer flasks and the residue was washed three times with 150 mL portions of pentane. The combined organic solutions were dried over a mixture of 300 g of sodium sulfate and 60 g of sodium bicarbonate and filtered through a sintered glass funnel, and the solid desiccant was thoroughly washed with pentane. The solvent was removed in vacuo, and the residue was filtered through a short plug of silica gel (pentane eluent) to yield 10.72 g of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-diene (63%). This material was used as is in the next reaction: ^{1}H NMR (250 MHz, CDCl$_3$) δ 1.35 (d, J = 10.5 Hz, 1H), 1.75 (d, J = 10.5 Hz, 1H), 2.4 (m, 2H), 2.72 (m, 4H), 2.95 (m, 2H), 4.52 (d, J = 2.0 Hz, 2H), 4.6 (d, J = 2.0 Hz, 2H); the product was 95% pure by ^{1}H NMR.

Dispiro[pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,1′-(2′,2′-dibromocyclopropane)-11,1″-(2″,2″-dibromocyclopropane)] (11). To a stirred mixture of 22 mL of bromoform (63.67 g, 0.25 mol), 10.8 g (0.063 mol) of crude 8,11-dimethylenepentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane, 0.25 g triethylbenzylammonium chloride (TEBA), and 0.5 mL of ethanol was added 65 mL of a 50% aqueous NaOH solution over 10 min at 40–50 °C (cooling with cold water). After the addition, the mixture was maintained at this temperature for 3 h. Up to an additional 20 mL of CH$_2$Cl$_2$ was added if the reaction mixture became too thick. The mixture was then poured into 200 mL of water, and the organic layer was separated (at this step do not shake to avoid emulsions) and extracted three times with 100 mL of methylene chloride. The combined organic layers were washed with water, 1 N HCl, and again with water, dried with anhydrous magnesium sulfate, and concentrated in vacuo to yield a very dark residue. This residue was then filtered through a plug of silica gel using hexane as the eluent and concentrated in vacuo. Recrystallization from 95% ethanol with decolorizing carbon yielded white crystals (12.85 g, 40%) of dispiro[pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,1′-(2′,2′-dibromocyclopropane)-11,1″-(2″,2″-dibromocyclopropane)]: mp 152–153 °C; R_f 0.4 (hexane); ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.45 (d, J = 10.7 Hz, 1H), 1.58 (d, J = 7.42 Hz, 2H), 1.71 (d, J = 7.42 Hz, 2H), 1.77 (d, J = 10.7 Hz, 1H), 2.37 (s, 2H), 2.68 (s, 2H), 2.80 (s, 2H), 2.83 (s, 2H); ^{13}C NMR (500 MHz, CDCl$_3$) δ 50.9, 46.1, 44.2, 42.0, 40, 35.7, 35.4, 30.9; IR (KBr) 2980, 2885, 1542, 1480, 1290, 1270, 1240, 1070, 1040, 1030, 895, 695 cm^{-1}; MS (EI) *m/e* 510 (M$^+$, 0.7), 512 (3), 514 (4.5), 516 (2.5), 518 (0.5). Anal. Calcd for C$_{15}$H$_{14}$Br$_4$: C, 35.06; H, 2.75. Found: C, 35.32; H, 2.89.

Dispiro[pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,1′-(2′-bromocyclopropane)-11,1″-(2″-bromocyclopropane)] (12). Under nitrogen, a solution of freshly distilled tributyltin hydride 2.88 mL (3.12 g, 11.0 mmol) in 5 mL of dry THF was added dropwise to a solution of 2.6 g (5.06 mmol) of dispiro[pentacyclo[5.4.0.02,6.03,10.05,9]undecane-8,1′-(2′,2′-dibromocyclopropane)-11,1″-(2″,2″-dibromocyclopropane)] in 30 mL of dry THF. The mixture was heated at 35 °C and stirred for 3 h and then concentrated. The residue was chromatographed twice on a column of basic Al$_2$O$_3$ (60 g) with hexane as the eluent and concentrated. The residue was chromatographed a third time on a column of silica gel (40 g) with hexane to remove any residual tin. A 1.09 g sample of dispiro[pentacyclo[5.4.0.0^{2,6}.0^{3,1}0.0^{5,9}]undecane-8,1′-(2′-bromocyclopropane)-11,1″-(2″-bromocyclopropane)] was obtained in 60% yield as a mixture of three diastereomers: R_f 0.4 (hexane Ce(SO$_4$)$_2$); ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.8–1.82 (complex multiplets, 8H), 2.0–2.39 (complex multiplets, 2H), 2.49–2.85 (complex multiplets, 6H); ^{13}C NMR (500 MHz, CDCl$_3$) δ 18.45, 18.73, 26.27, 26.46, 26.79, 26.91, 27.01, 30.85, 31.12, 31.21, 31.35, 31.39, 35.04, 35.29, 36.65, 41.96, 42.18, 42.36, 42.46, 42.59, 42.67, 42.75, 42.97, 44.24, 44.31, 44.36, 44.51, 44.60, 44.73, 45.94, 46.02, 46.10, 46.17, 46.24, 46.37, 46.53, 46.59, 48.72, 48.76, 49.04, 50.80, 50.86, 50.91, 51.17, 51.26; IR (neat) 2980, 2880, 1470, 1460, 1440, 1380, 1300, 1270, 1235, 1225, 1200, 1120, 1070, 1040, 980, 960, 915, 895, 825, 695 cm^{-1}; MS *m/e* calcd for C$_{15}$H$_{16}$Br$_2$ 353.9612 (M$^+$); found 353.9624.

Dispiro[pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,1′-(cyclopropene)-11,1″-(cyclopropene)] (2).[15] Under nitrogen,

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(25) The author has deposited atomic coordinates for this structure 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.

a solution of 450 mg of dispiro[pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]-undecane-8,1′-(2′-bromocyclopropane)-11:1″-(2″-bromocyclopropane)] (1.26 mmol) in 2 mL of dry DMSO (distilled from CaH_2) was slowly added dropwise to a stirred solution of 440 mg of potassium *tert*-butoxide (3.92 mmole, freshly sublimed) in 5 mL of dry DMSO. Stirring was continued for 3 days. The brownish-black mixture was poured into 20 mL of ice–water and extracted 5 times with 10 mL of *n*-pentane. The combined pentane layers were washed with water (2 × 10 mL) and brine (10 mL) and dried with Na_2SO_4. At this point all glassware used was washed with a 5% EDTA solution, two times with distilled water, and once with NH_4OH and then dried. The pentane solution was then concentrated in vacuo to yield 157 mg (64%) of crude cage biscyclopropene which was 80% pure by NMR. This sample was sublimed three times to give X-ray-quality crystals: softening point 48–50 °C; R_f 0.8 (hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24 (d, J = 10 Hz, 1H), 1.47 (s, 2H), 1.54 (d, J = 10 Hz, 1H), 1.80 (m, 2H), 2.48 (m, 2H), 2.64 (m, 2H), 7.48 (d, J = 1.2 Hz, 2H), 7.57 (d, J = 1.2 Hz, 2H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 30.63, 35.38, 41.80, 45.83, 47.21, 54.01, 123.44, 123.56; IR (neat) 2970, 2880, 1690, 1630, 1460, 1020 cm^{-1}; MS m/e calcd for $C_{15}H_{15}$ 195.1174 (MH^+); found 195.1171. Sublimation of the material (40 °C, 0.001 Torr) onto an ice-cooled cold finger, produced white crytals, suitable for X-ray analysis. The material is sensitive to oxygen and Lewis acids and forms a white polymeric material after a short time.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for compounds **1**, **2**, **8**, **12**, and HF/6-31G*-optimized cartesian coordinates for **1c**, **1ts**, **1tb**, **13c**, **13ts**, **13tb**, **2** (12 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 for ordering information.

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