Synthesis of a Substituted Bi[cyclohepta-3,5(3′,5′)-dienyl]: A Possible Building Block for Domino Diels−Alder Reactions

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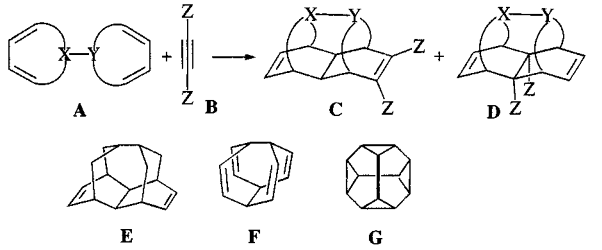
A versatile 13-step synthesis of 1,1′-dimethoxy-4,4′,5,5′-tetrakis(trimethylsilyloxy)bicyclohepta-3,3′,5,5′-dienyl (**11**) is described. **11** represents a potential building block for the construction of polycyclic cage compounds through domino Diels–Alder and pincer reactions.

Introduction

Ever since their popularization by Paquette,[1] domino Diels−Alder reactions have attracted interest as a very efficient means of constructing certain polycyclic compounds. Typically, two dienes connected to each other through a number of saturated atoms (**A**) are treated with an activated acetylene (**B**). Isomers are sometimes obtained, i.e. the standard asymmetrical domino Diels−Alder adduct (**C**) and a symmetrical isomer called a "pincer" adduct[1−3] (**D**). Cases have appeared in the literature where the cyclic dienes are connected through a single bond and are located (a) in two five-membered rings,[1,2] or (b) in a seven- and a five-membered ring.[1] There have also been examples where the dienes are fixed in a polycyclic cage, being incorporated in (c) two six-membered rings[3] or (d) two seven-membered units[4] (Scheme 1).

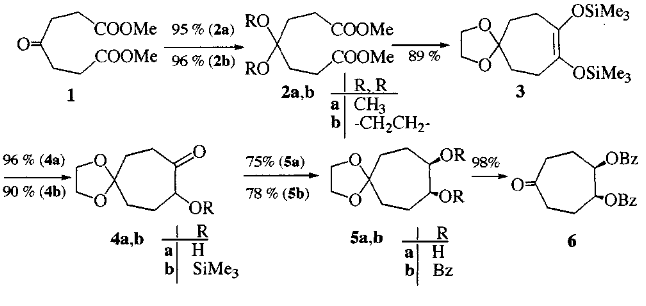


Scheme 1

We report herein on an efficient synthesis of a particular bi(cycloheptadienyl), but the reaction sequence can easily be adapted for the preparation of other congeners. The title compound and closely related analogues thereof represent building blocks for the construction of a number of cage compounds. For example, both the pincer and domino adducts with dialkyl butynoate would consist of a C_{16} skeleton (**E**). It should be possible to transform this into a substituted tricyclo[5.5.0.0^{4,10}]dodecatetraene (**F**) by a sequence involving cleavage of the double bonds, degradation of the formed side chains, and the subsequent introduction of new double bonds.[5] **F** has been predicted to be the photochemical precursor of "truncahedrane" (**G**) by Woodward and Hoffmann[6] (Scheme 1).

Results and Discussion

Our synthesis starts from dimethyl 4-oxoheptanedioate (**1**), which can be prepared from furfural by means of a Knoevenagel condensation with malonic acid[7] (84%) and subsequent ring opening/ester formation[8] (63%). Direct acid-catalyzed ketal formation from **1** using ethylene glycol, as proposed by Lukes,[9] gave only poor yields in our hands. Consequently, we chose to follow the "detour" **1** → **2a** → **2b**, which gave excellent yields in both steps, i.e. (a) ketalization with methyl orthoformate and (b) ketal exchange with $ZnCl_2$/ethylene glycol (Scheme 2). Acyloin cyclization of **2b** was accomplished by the Rühlmann method[10,11] in the presence of chlorotrimethylsilane to give **3**. An attempted direct acyloin reaction of **2a** led to an unpleasant mixture of several products.



Scheme 2

Catalytic hydrogenation of **3** was impracticable, but the compound could be hydrolyzed in dioxane/water to give **4a**. Its $LiAlH_4$ reduction resulted in the formation of approximately equal amounts of *cis* and *trans* diols. This was considered as being less desirable since it meant that more complex and potentially difficult to purify diastereomer mixtures were to be expected in the subsequent steps. Therefore, **4a** was converted into the trimethylsilyl derivative **4b** and

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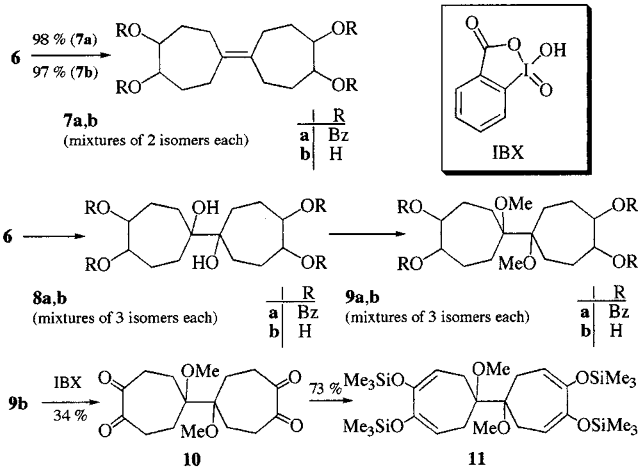
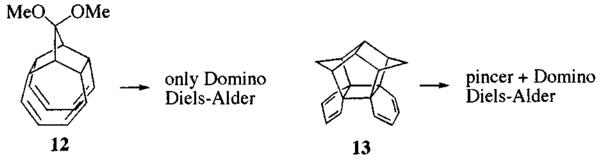
reduced with the somewhat modified hydride $LiAlH_3(OiPr)$ to exclusively afford the *cis*-diol **5a**. Benzylation (→ **5b**) and cleavage of the ketal (→ **6**) were followed by a McMurry coupling with $TiCl_3/LiAlH_4$/THF, which yielded **7a** (98%) as an inseparable mixture of the two possible stereoisomers (Scheme 3). Catalytic hydrogenation of **7a** with H_2 (4 bar) in the presence of Pd/C led to **7b**, in which the double bond had been retained.



Scheme 3

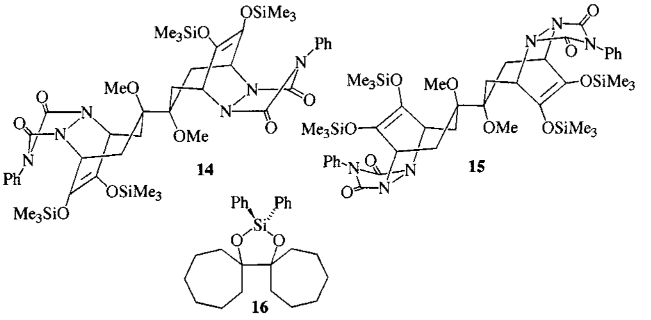
When the coupling of compound **6** was performed with $TiCl_4$/Mg(Hg) in a variant introduced by Corey,[12] the pinacol product **8a** was obtained as an inseparable mixture of three stereoisomers (98% yield). Hydrogenolysis of **8a** to give **8b** (76%) and the methylation **8a** → **9a** (96%) did not present any problems. However, the analogous transformation of **9a** into **9b** could only be achieved in 30% yield due to difficulties associated with the purification and crystallization of the stereoisomer mixture. The isomer mixture **9b** was subsequently oxidized to homogeneous **10** utilizing Santagostino's reagent *o*-iodoxybenzoic acid ("IBX", cf. Scheme 3) in DMSO.[13−15] The yield for this step was again relatively low (34%), apparently due to the sensitivity of the two α-diketone units in the molecule. The ultimate generation of the tetrakis(trimethylsilyloxyenol) ether **11** seemed critical as intramolecular condensations were to be avoided. Therefore, Simchen's method (trimethylsilyl triflate/triethylamine)[16] was applied, which has been shown to be useful with other α-diketones.[17] A yield of 73% was realized.

In principal, compound **11** is an electron-rich substrate suitable for potential pincer and domino Diels−Alder cycloadditions. It must be realized, however, that the necessary side selectivity for the pincer reactions is likely to be difficult to control in this simple but flexible case. The only known example of a domino Diels−Alder reaction of two cycloheptadiene units is that involving the cage compound **12**, which has a rigid arrangement of the dienes. In this case, no pincer reaction occurs with dicyanoacetylene.[4] In contrast, Prinzbach's cage compound **13** (with two cyclohexadiene units) undergoes both types of cycloadditions (domino/pincer = 1:3) with the same alkyne (Scheme 4).[3] This is quite remarkable because calculations indicate that the distance between the two diene units is almost identical.[4]



Scheme 4

In a first test of its reactivity, **11** was treated with two equivalents of *N*-phenyltriazolindione at −80 °C. An immediate decoloration indicated a very fast cycloaddition. A single product was obtained on workup, which was found to have a symmetrical structure giving rise to just one methoxy and one trimethylsilyloxy group signal in the NMR spectra. Of the two possible structures, **14** and **15** (Scheme 5), the former seemed to be the more likely. A preorientation effected by the methoxy substituent should result in an attack of the dienophile from the CH_3O-bearing side so as to give **14**.



Scheme 5

When **11** was treated with dicyanoacetylene at room temperature, a dark-blue color developed and a polymerization occurred. Lowering the temperature to −80 °C and slowly allowing the mixture to warm to room temperature resulted in a slower development of the coloration and the formation of a complex mixture. The ^1H NMR spectrum of the crude product gave no indication that the desired products might be present. **11** was found not to react with dimethyl butynoate at room temperature within 24 h, whereas intractable mixtures were formed at higher temperatures.

Clearly, further studies are necessary to find suitable conditions and substitution patterns for optimizing the desired reactions. An obvious problem is the conformational preference of compound **11**, which is undoubtedly not the ideal one for domino and pincer reactions. This might be controlled by introducing a bridge between the two hydroxy groups. As a model structure, compound **16** has been prepared.

Experimental Section

General: NMR spectra were recorded in $CDCl_3$ with TMS as internal standard with Bruker AC 250-P (^1H: 250 MHz, ^{13}C: 62.89 MHz) or DRX 500 (^1H: 500 MHz, ^{13}C: 125.78 MHz) instruments. − IR: Genesis FT instrument (Mattson). − MS: VG

AutoSpec from Fisons Instruments. − Melting points: Büchi apparatus after Dr. Tottoli. − Boiling points in kugelrohr distillations refer to air-bath temperatures.

Dimethyl 4,4-Dimethoxypimelate (2a): A solution of dimethyl 4-oxopimelate (**1**)[8] (101.1 g, 500 mmol) in dry methanol (500 mL) was treated with trimethyl orthoformate (109 mL, 1.0 mol) and toluenesulfonic acid (0.5 g) and the resulting mixture was heated for 15 h under reflux. The volatile components were then removed in vacuo and the residue was neutralized with saturated aq. $NaHCO_3$ solution (100 mL). Diethyl ether was added, the layers were separated, and the aqueous phase was extracted with further ether. The combined organic extracts were dried (Na_2SO_4), the solvent was removed in a rotary evaporator, and the product was purified by kugelrohr distillation. It was finally crystallized from a small volume of hexane. Yield: 117.7 g (95%); b.p. 100−105 °C/0.1 Torr; m.p. 30 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.91 (m, 4 H), 2.31 (m, 4 H), 3.16 (s, 6 H), 3.68 (s, 6 H). − 13C NMR ($CDCl_3$): δ = 27.7, 28.8, 48.0, 51.7, 101.9, 173.6. − IR (film): $\tilde{\nu}$ = 1739 cm^{-1}. − MS (EI, 70 eV); *m/z* (%): 217 (37), 161 (100), 157 (87), 125 (53), 101 (85), 97 (76), 59 (51). − $C_{11}H_{20}O_6$ (248.3): calcd. C 53.22, H 8.12; found C 53.17, H 7.88.

2,2-Bis(2-methoxycarbonylethyl)-1,3-dioxolane (2b): 2a (124.1 g, 500 mmol) was heated with ethylene glycol (31.3 g, 505 mmol), trimethyl orthoformate (2.65 g, 25 mmol), and zinc chloride (100 mg) at 100 °C in a distillation apparatus. Most of the methanol formed was distilled at atmospheric pressure. A vacuum was subsequently applied to remove the volatile components. The residue was distilled under high vacuum. Yield: 118.5 g (96%); b.p. 131−133 °C/0.04 Torr. − ^{1}H NMR ($CDCl_3$): δ = 1.97 (m, 4 H), 2.37 (m, 4 H), 3.67 (s, 6 H), 3.94 (s, 4 H). − ^{13}C NMR ($CDCl_3$): δ = 28.7, 32.2, 51.6, 65.2, 110.0, 173.8. − IR (film): $\tilde{\nu}$ = 2954, 2888, 1739, 1438, 1311, 1261, 1199, 1137, 1049, 890 cm^{-1}. − MS (CI); *m/z* (%): 247 (21), 215 (100), 159 (80), 99 (53). − $C_{11}H_{18}O_6$ (246.3): calcd. C 53.65, H 7.37; found C 53.51, H 7.35.

8,9-Bis(trimethylsilyloxy)-1,4-dioxaspiro[4.6]undec-8-ene (3): Freshly cut sodium (28.7 g, 1.25 mol) in toluene (300 mL) was heated to a gentle reflux, then dispersed under vigorous stirring. The mixture was cooled to room temp., whereupon chlorotrimethylsilane (174 mL, 1.38 mol) was added.[11] The resulting mixture was heated to a mild reflux once more and then a few mL of a solution of **2b** (61.6 g, 250 mmol) in toluene (200 mL) was added dropwise. The start of the reaction was indicated by a blue-violet coloration. The remainder of the solution of **2b** was added over a period of 6 h under vigorous reflux, and this was maintained for 15 h until most of the Na had been consumed. The mixture was cooled and then filtered through an inverted frit. The removed solids were washed twice with hexane, the combined filtrate and washings were concentrated in vacuo, and the residue was purified by kugelrohr distillation. Yield: 73.7 g (89%); b.p. 100−110 °C/0.1 Torr (ref.[18]: 110−120 °C/1 Torr). − ^{1}H NMR ($CDCl_3$): δ = 0.15 (s, 18 H), 1.78 (m, 4 H), 2.21 (m, 4 H), 3.91 (s, 4 H). − ^{13}C NMR ($CDCl_3$): δ = 0.5, 27.9, 35.2, 64.1, 110.9, 135.5. − IR (film): $\tilde{\nu}$ = 2954, 2881, 1681, 1442, 1373, 1349, 1253, 1207, 1106, 883, 844 cm^{-1}.

9-Hydroxy-1,4-dioxaspiro[4.6]undecan-8-one (4a): 3 (64.9 g, 196 mmol) was refluxed for 15 h in a mixture of 1,4-dioxane (200 mL) and water (40 mL) and then the solution was concentrated in vacuo. The residue was taken up in diethyl ether (200 mL), the by-products were filtered off, and the filtrate was concentrated once more. The residual pale-yellow oil was purified by kugelrohr distillation. Yield: 35.1 g (96%), b.p. 130−140 °C/0.1 Torr. − ^{1}H NMR ($CDCl_3$): δ = 1.84 (m, 4 H), 2.05 (m, 2 H), 2.64 (m, 2 H), 3.95 (m, 4 H), 4.29 (m, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 28.4, 32.5, 34.4, 35.3, 64.4, 64.7, 76.9, 109.3, 212.5. − IR (film): $\tilde{\nu}$ = 3455, 2950, 2885, 1704, 1450, 1369, 1276, 1187, 1083, 948, 856 cm^{-1}. − MS (CI); *m/z* (%): 186 (87), 168 (97), 157 (47), 128 (41), 100 (39), 98 (97), 86 (76), 85 (100).

9-Trimethylsilyloxy-1,4-dioxaspiro[4.6]undecan-8-one (4b): 4a (93.1 g, 500 mmol) was dissolved in dry diethyl ether (500 mL) and then triethylamine (79.7 mL, 575 mmol) and chlorotrimethylsilane (59.8 mL, 550 mmol) were simultaneously added dropwise with cooling at 0 °C. The mixture was stirred for 15 h at room temp. Pentane (500 mL) was then added, the resulting slurry was stirred for 10 min, and the triethylamine hydrochloride formed was filtered off. The filtrate was concentrated in vacuo, the residue was taken up in fresh pentane, this solution was filtered, and the filtrate was concentrated once more. The remaining yellowish oil was purified by kugelrohr distillation. Yield: 116.8 g (90%); b.p. 90−100 °C/0.1 Torr (ref.[19]: no b.p. given). − ^{1}H NMR ($CDCl_3$): δ = 0.13 (s, 9 H), 1.70−2.16 (m, 6 H), 2.38−2.64 (m, 2 H), 3.92 (m, 4 H), 4.26 (m, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 0.5, 28.9, 32.2, 33.5, 35.2, 64.4, 64.4, 78.0, 109.9, 211.1. − IR (film): $\tilde{\nu}$ = 2954, 2888, 1716, 1446, 1369, 1253, 1095, 995, 887, 844 cm^{-1}. − MS (CI); *m/z* (%): 225 (13), 186 (47), 168 (59), 157 (33), 128 (33), 100 (34), 98 (83), 85 (100).

***cis*-8,9-Dihydroxy-1,4-dioxaspiro[4.6]undecane (5a):** Lithium aluminium hydride (24.7 g, 650 mmol) was suspended in dry diethyl ether (1000 mL) and then acetone (48 mL, 650 mmol) in diethyl ether (100 mL) was added dropwise at such a rate that mild boiling occurred. Following the addition, the mixture was refluxed for 30 min, and then cooled to −30 °C. At this temperature, a solution of **4b** (122.6 g, 475 mmol) in diethyl ether (150 mL) was slowly added dropwise over a period of 4 h. After stirring the mixture for a further 1 h in the cold, it was allowed to warm to room temp. over a period of 3 h and then refluxed for 15 h. The excess hydride was then carefully decomposed with water under cooling with ice. More water was added, the two-phase mixture was heated for 1 h under reflux, and then the layers were separated. The aqueous suspension was extracted with five 300 mL portions of ethyl acetate with vigorous mixing. The combined organic phases were dried (Na_2SO_4) and concentrated in vacuo. The remaining slightly pinkish oil was crystallized from *tert*-butyl methyl ether. Yield: 67.4 g (75%); m.p. 89 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.63 (m, 4 H), 1.94 (m, 4 H), 3.21 (m, 2 H), 3.79 (m, 2 H), 3.89 (s, 4 H). − ^{13}C NMR ($CDCl_3$): δ = 26.1, 31.8, 64.1, 73.3, 112.2. − IR (KBr): $\tilde{\nu}$ = 3378, 2939, 2877, 1442, 1384, 1249, 1141, 1052, 1002, 941 cm^{-1}. − MS (EI, 70 eV); *m/z* (%): 189 (3), 171 (33), 129 (28), 99 (100), 86 (76), 83 (36), 73 (36). − $C_9H_{16}O_4$ (188.2): calcd. C 57.43, H 8.57; found C 57.21, H 8.40.

***cis*-8,9-Dibenzyloxy-1,4-dioxaspiro[4.6]undecane (5b):** Under argon, 23.0 g of 60% sodium hydride (13.8 g, 576 mmol NaH) was washed free of oil with hexane. Dry THF (50 mL) and a small amount of tetrabutylammonium iodide was then added. Under stirring, a solution of **5a** (36.1 g, 192 mmol) in THF (250 mL) was added over a period of 60 min. Once the evolution of hydrogen had ceased, a solution of benzyl bromide (57.0 mL, 480 mmol) in THF (50 mL) was added and the resulting mixture was stirred for 15 h at room temp. followed by 24 h under reflux. The excess NaH was destroyed with water under cooling in an ice bath, and further water was added until all the solids had dissolved. The phases were separated, and the aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with saturated brine, dried (Na_2SO_4), and concentrated. The residual solid was recrystallized from hexane. Yield: 55.2 g (150 mmol); m.p. 87 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.58−1.68 (m, 4 H), 1.93−2.16 (m, 4 H), 3.68 (d, J = 8.4 Hz, 2 H), 3.87 (s, 4 H), 4.59 (s, 4 H), 7.24−7.37 (m, 5 H). − ^{13}C NMR ($CDCl_3$): δ = 24.2, 32.3, 63.9, 64.2, 71.0, 79.7, 112.3, 127.3, 127.4, 128.2, 139.2. − IR (KBr): ṽ = 3031, 2942, 2858, 1454, 1373, 1218, 1103, 944, 748 cm^{-1}. − MS (CI); m/z (%): 369 (0.1), 277 (6), 181 (16), 171 (13), 91 (100). − $C_{23}H_{28}O_4$ (368.5): calcd. C 74.97, H 7.66; found C 74.73, H 7.62.

***cis*-4,5-Dibenzyloxycycloheptanone (6): 5b** (15.0 g, 40.7 mmol) was stirred in a mixture of THF (120 mL), H_2O (40 mL), methanol (20 mL), and conc. HCl (6 mL) for 24 h at room temp. The reaction mixture was then neutralized by the addition of solid $NaHCO_3$ and repeatedly extracted with diethyl ether. The combined organic phases were dried (Na_2SO_4) and concentrated. The pale-yellow residual liquid was purified by kugelrohr distillation. Yield: 12.9 g (98%); b.p. 195−200 °C/0.1 Torr. − ^{1}H NMR ($CDCl_3$): δ = 1.66−1.75 (m, 2 H), 2.14−2.33 (m, 4 H), 2.65−2.75 (m, 2 H), 3.66 (m, 2 H), 4.60 (s, 4 H), 7.25−7.33 (m, 10 H). − ^{13}C NMR ($CDCl_3$): δ = 24.2, 37.9, 71.2, 79.4, 127.4, 127.5, 128.3, 138.7, 213.4. − IR (film): ṽ = 3062, 3027, 2935, 2869, 1700, 1454, 1199, 1099, 1068, 740 cm^{-1}. − MS (CI); m/z (%): 323 (7), 269 (10), 231 (15), 181 (11), 180 (71), 178 (13), 125 (13), 90 (100). − $C_{21}H_{24}O_3$ (324.4): calcd. C 77.75, H 7.46; found C 77.55, H 7.54.

***cis*-4,5-Dibenzyloxy-1-(*cis*-4′,5′-dibenzyloxycycloheptylidene)-cycloheptane (Isomer Mixture 7a):** $TiCl_3$ (6.17 g, 40 mmol) was taken up in THF (100 mL) and the resulting solution was treated with small portions of $LiAlH_4$ (760 mg, 20 mmol in total) over a period of 15 min and then refluxed. After ca. 30 min, a solution of **6** (6.49 g, 20 mmol) in THF (50 mL) was added, and the mixture was vigorously stirred under reflux for 48 h. Under cooling, water (20 mL) was very carefully added, and most of the solvent was removed in a rotary evaporator. The residue was treated with saturated brine (50 mL) and repeatedly extracted with 100 mL portions of diethyl ether. The combined extracts were washed with brine, dried with a mixture of Na_2SO_4 and silica gel, filtered, and concentrated to give a colorless oil. Crude yield: 5.63 g (9.1 mmol, 91%). Part of the product was chromatographed on silica gel eluting with hexane/*tert*-butyl methyl ether (2:1) to give a sample for elemental analysis (R_f = 0.56). As **7a** was obtained as a mixture of two isomers, its NMR spectra showed mostly unresolved multiplets. − ^{1}H NMR ($CDCl_3$): δ = 1.18−1.77 (m, 8 H), 1.92−2.23 (m, 8 H), 3.63−3.72 (m, 4 H), 4.53−4.60 (m, 8 H), 7.20−7.34 (m, 20 H). − ^{13}C NMR ($CDCl_3$): δ = 22.1−32.8, 70.4−71.4, 79.0−81.1, 126.8−129.6, 138.2−140.5. − IR (film): ṽ = 3062, 3027, 2923, 2861, 1496, 1454, 1365, 1203, 1099, 1068 cm^{-1}. − $C_{42}H_{48}O_4$ (616.8): calcd. C 81.78, H 7.84; found C 81.68, H 7.98.

1-(*cis*-4′,5′-Dihydroxycycloheptylidene)-*cis*-4,5-dihydroxycycloheptane (Isomer Mixture 7b): 7a (3.08 g, 5.0 mmol) was hydrogenated in methanol (100 mL) and ethyl acetate (50 mL) in the presence of 10% palladium on charcoal (500 mg) at a pressure of ca. 4 bar for 15 h at room temp. The catalyst was then filtered off and washed with hot methanol. The solvents were removed from the combined filtrate and washings and the residue was crystallized from methanol. Yield: 1.12 g (87%); m.p. 235 °C. **7b** thus obtained was found to consist of a mixture of two isomers in an approximate ratio of 5:1. The given NMR-spectroscopic data refer to the major component. − ^{1}H NMR ([D_6]DMSO): δ = 1.34−1.43 (m, 4 H), 1.74−1.87 (m, 4 H), 2.12 (t, J = 6.1 Hz, 8 H), 3.55 (m, 4 H), 4.16 (d, J = 4.2 Hz, 4 H). − ^{13}C NMR ([D_6]DMSO): δ = 25.0, 29.9, 72.7, 131.7. − IR (KBr): ṽ = 3309, 2908, 1465, 1365, 1342, 1292, 1268, 1187 cm^{-1}. − MS (CI); m/z (%): 256 (28), 238 (17), 221 (48), 220 (15), 203 (100), 185 (71), 175 (64), 159 (25). − $C_{14}H_{24}O_4$ (256.3): calcd. C 65.60, H 9.44; found C 65.60, H 9.37.

***cis*-4,5,*cis*-4′,5′-Tetrabenzyloxy-1,1′-dihydroxybicycloheptyl (Isomer Mixture 8a):** Magnesium turnings (3.65 g, 150 mmol) and $HgCl_2$ (1.09 g, 4.0 mmol) were stirred in THF (100 mL) for 30 min at room temp. The supernatant solution became turbid and the Mg acquired a dark-grey color. The mixture was then cooled to −10 °C, whereupon freshly distilled $TiCl_4$ (8.3 mL, 75 mmol) was added dropwise over a period of 15 min. At this temperature, the resulting greenish-yellow suspension was combined with a solution of ketone **6** (16.2 g, 50 mmol) and stirring was continued at the same temperature for a further 30 min followed by 90 min at room temp. In the course of the reaction, the color changed through olive-green and brown to deep black. For workup, water (10 mL) was added at 0 °C, and the resulting suspension was poured into a cold (0 °C) mixture of saturated brine (100 mL) and diethyl ether (400 mL). After stirring for a few min, the ethereal phase was decanted off, and the aqueous layer was stirred with further portions of ether to complete the extraction. The combined ethereal extracts were washed with saturated brine, dried with Na_2SO_4 and silica gel, then concentrated in a rotary evaporator to leave a turbid, viscous oil. Crude yield: 16.0 g (98%). Part of the product was chromatographed on silica gel eluting with *tert*-butyl methyl ether to obtain a sample for spectra and analysis (R_f = 0.61). As **8a** was obtained as a mixture of three stereoisomers, the obtained NMR spectra featured unresolved multiplets. − ^{1}H NMR ($CDCl_3$): δ = 1.37−2.27 (m, 16 H), 3.53−3.74 (m, 4 H), 4.59 (m, 8 H), 7.24−7.35 (m, 20 H). − ^{13}C NMR ($CDCl_3$): δ = 23.3−32.0, 70.9−71.7, 77.3−77.6, 79.6−80.6, 127.2−128.5, 138.3−139.4. − IR (film): ṽ = 3432, 3062, 3027, 2931, 2865, 1454, 1365, 1091, 1064, 1029 cm^{-1}. − $C_{42}H_{50}O_6$ (650.9): calcd. C 77.51, H 7.74; found C 77.33, H 7.48.

1,1′,*cis*-4,5,*cis*-4′,5′-Hexahydroxybicycloheptyl (Isomer Mixture 8b): 8b was obtained from **8a** in a similar manner as described for the preparation of **7b** from **7a**. Yield: 2.20 g (76%); m.p. 145−150 °C. As **8b** was obtained as a mixture of three isomers, its NMR spectra consisted only of unresolved multiplets. − ^{1}H NMR ([D_6]DMSO): δ = 1.06−1.95 (m, 16 H), 3.53−3.61 (m, 4 H). − ^{13}C NMR ([D_6]DMSO): δ = 24.1−30.4, 72.4−72.7, 78.2−79.1. − IR (KBr): ṽ = 3370, 3282, 2919, 2858, 1434, 1396, 1342, 1037, 937 cm^{-1}.

***cis*-4,5,*cis*-4′,5′-Tetrabenzyloxy-1,1′-dimethoxybicycloheptyl (Isomer Mixture 9a):** Under argon, 2.84 g of 60% sodium hydride (1.70 g, 71 mmol NaH) was washed free of oil with hexane. Dry THF (10 mL) was then added, and a solution of **8a** (11.5 g, 17.7 mmol) in THF (50 mL) followed by methyl iodide (4.4 mL, 71 mmol) of were added dropwise under stirring at room temp. The resulting mixture was refluxed for 15 h. It was then cooled and saturated aqueous NH_4Cl solution (20 mL) was added. After separation of the phases, the organic layer was repeatedly extracted with diethyl ether. The combined organic phases were dried (Na_2SO_4), concentrated, and the residue was taken up in *tert*-butyl methyl ether. The resulting solution was stirred with a little silica gel and charcoal (to remove impurities), then filtered, and concentrated once more. The residual colorless oil was used as such without further purification. Crude yield: 11.5 g (17.0 mmol, 96%). − IR (film): ṽ = 3062, 3027, 2935, 2877, 1454, 1365, 1110, 1060, 1029, 910 cm^{-1}. − From this mixture of three isomers, one component crystallized. After washing with hexane/*tert*-butyl methyl ether, the product gave the following data: m.p. 121−125 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.64−1.76 (m, 8 H), 2.00−2.10 (m, 8 H), 3.22 (s, 6 H), 3.50 (d, J = 8.1 Hz, 4 H), 4.57 (m, 8 H), 7.25−7.37 (m, 20 H). − ^{13}C NMR ($CDCl_3$): δ = 24.7, 50.2, 70.6, 79.8, 84.9, 127.3, 127.5, 128.2, 139.3. − IR (KBr): ṽ = 3062, 3027, 2935, 2888, 2854, 1492, 1454, 1361, 1199, 968 cm^{-1}. − $C_{44}H_{54}O_6$ (678.9): calcd. C 77.84, H 8.02; found C 77.77, H 7.98.

***cis*-4,5,*cis*-4′,5′-Tetrahydroxy-1,1′-dimethoxybicycloheptyl (Isomer Mixture 9b):** The compound was obtained from **9a** in a similar manner as described for the preparation of **7b** from **7a**. Yield: ca. 30%. The crude product was taken up in hot toluene/ethanol (10:1) whereupon one of the three isomers (about one-quarter of the product) crystallized (m.p. 156−158 °C), the rest remaining as a viscous oil. The following data relate to the isomer mixture. − ^1H NMR ([D$_4$]MeOH): δ = 1.52−1.75 (m, 8 H), 1.84−2.25 (m, 8 H), 3.27−3.35 (m, 6 H), 3.69 (m, 4 H). − ^{13}C NMR ([D$_4$]MeOH): δ = 25.9−26.2, 28.0−28.2, 51.0−51.7, 74.7−75.1, 86.7−87.4. − IR (KBr): ṽ = 3444, 3301, 2912, 2873, 1457, 1403, 1353, 1230, 979 cm^{-1}.

1,1′-Dimethoxybicycloheptyl-4,4′,5,5′-tetraone (10): IBX[13−15] (4.20 g, 15 mmol) was suspended in dimethyl sulfoxide (15 mL) and stirred for 10 min until the reagent had completely dissolved. **9b** (955 mg, 3 mmol) was added, and the mixture was stirred at room temp. A yellow coloration appeared and soon thereafter the onset of the deposition of a solid became noticeable. After 15 h, the suspension obtained was poured into 100 mL of an ice-cold phosphate buffer [pH = 7; 58.7 mL of aq. Na_2HPO_4 (11.87 g/L of $Na_2HPO_4 \cdot 2\,H_2O$) and 41.3 mL of aq. KH_2PO_4 (9.07 g/L)]. The mixture was stirred for a few min, then treated with dichloromethane (400 mL) and stirred vigorously once more. The solid formed was filtered off and washed with buffer (50 mL) and CH_2Cl_2 (150 mL). The filtrate was transferred to a separatory funnel, shaken vigorously, then the layers were allowed to separate. The aqueous phase was repeatedly extracted with further CH_2Cl_2 and the combined organic layers were dried (Na_2SO_4). Concentration left a residue, which was taken up in $CHCl_3$ (5 mL). Small portions of this solution were treated dropwise with diethyl ether until a slight turbidity persisted. Crystallization of the yellow compound occurred at 0 °C. Yield: 330 mg (34%); m.p. 136−138 °C. − ^1H NMR ([D$_6$]DMSO): δ = 1.91−2.03 (m, 4 H), 2.19−2.29 (m, 4 H), 2.60−2.78 (m, 8 H), 3.19 (s, 6 H). − ^{13}C NMR ([D$_6$]DMSO): δ = 28.4, 35.5, 51.8, 83.5, 198.0. − IR (KBr): ṽ = 3409, 2966, 2838, 1708, 1434, 1334, 1288, 1234, 1087, 941, 914 cm^{-1}. − MS (CI); *m*/*z* (%): 311 (4), 293 (11), 279 (29), 261 (38), 247 (53), 219 (19), 156 (21), 155 (100). − $C_{16}H_{22}O_6$ (310.3): calcd. C 61.92, H 7.15; found C 61.22, H 6.98.

1,1′-Dimethoxy-4,4′,5,5′-tetra(trimethylsilyloxy)bi(cyclohepta-3,3′,5,5′-dienyl) (11): 10 (420 mg, 1.4 mmol) in CH_2Cl_2 (40 mL) was treated with triethylamine (1.5 mL, 10.8 mmol) under stirring. Trimethylsilyl trifluoromethanesulfonate (1.0 mL, 5.5 mmol) was then added dropwise over a period of 30 min at −20 °C. Thereafter, the reaction mixture was stirred for 2 h at room temp. The solvent was then removed, and the residue was taken up in hexane (50 mL) and stirred for a few min. The supernatant hexane was then decanted off, and the undissolved solid was extracted with hexane (2 × 30 mL). The combined organic phases were stirred with active charcoal, filtered, and concentrated at room temperature. The solid that separated was recrystallized from pentane. Yield: 590 mg (73%); m.p. 106−110 °C. − ^1H NMR ($CDCl_3$): δ = 0.18 (s, 36 H), 2.07 (dd, *J* = 7.3, 13.8 Hz, 4 H), 2.28 (dd, *J* = 7.3, 13.8 Hz, 4 H), 3.30 (s, 6 H), 5.27 (t, *J* = 7.3 Hz, 4 H). − ^{13}C NMR ($CDCl_3$): δ = 0.3, 29.6, 52.4, 102.6, 112.0, 147.8. − IR (KBr): ṽ = 3054, 2958, 2908, 2834, 1643, 1619, 1461, 1373, 1249, 1199, 1157, 1099, 941, 887, 840 cm^{-1}. − MS (CI); *m*/*z* (%): 600 (2), 598 (7), 567 (11), 495 (6), 463 (5), 300 (19), 299 (100), 285 (25). − $C_{28}H_{54}O_6Si_4$ (599.1): calcd. C 56.14, H 9.09; found C 55.90, H 8.70.

4,4′-Diphenyl-11,11′,12,12′-tetrakis(trimethylsilyloxy)bi[2,4,6-triazatricyclo[5.3.0.0^{2,6}]dodec-11-en-11-yl]-3,3′,5,5′-tetraone (14 or 15): A solution of **11** (1.04 g, 1.7 mmol) in dichloromethane (20 mL) was cooled to −80 °C, whereupon a solution of *N*-phenyltriazolindione (610 mg, 3.5 mmol) in CH_2Cl_2 (25 mL) was slowly added. The intense coloration faded immediately. The mixture was allowed to warm to room temp. and left for 15 h. The solvent was then removed, and the residue was refluxed for a short time with hexane (50 mL) under vigorous stirring. The solid was collected by filtration and recrystallized from *tert*-butyl methyl ether/hexane, 1:1. Yield: 800 mg (50%); m.p. 175 °C (dec.). − ^1H NMR ($CDCl_3$): δ = 0.13 (s, 36 H), 2.14−2.40 (m, 8 H), 3.08−3.16 (m, 4 H), 3.21 (s, 6 H), 7.35−7.48 (m, 10 H). − IR (KBr): ṽ = 2958, 2834, 1774, 1708, 1500, 1427, 1253, 1106 cm^{-1}.

1,1′-Dioxy(diphenylsilylidene)bicycloheptyl (16): 1.60 g of 60% NaH (0.96 g, 40 mmol) was washed free of oil with THF and then suspended in THF (50 mL). 1,1′-Bicycloheptanediol (2.26 g, 10 mmol) (m.p. 78 °C[19]) in THF (20 mL) followed by freshly distilled dichlorodiphenylsilane (3.04 g, 12 mmol) were then added. The reaction mixture was refluxed for 15 h. After filtration, the solvent was removed, and the residue was crystallized from hexane. Yield: 3.25 g (80%); m.p. 119 °C. − ^1H NMR ($CDCl_3$): δ = 1.42−1.92 (m, 24 H), 7.30−7.47 (m, 6 H), 7.63−7.67 (m, 4 H). − ^{13}C NMR ($CDCl_3$): δ = 22.7, 29.5, 36.5, 88.2, 127.6, 130.3, 134.0, 135.1. − IR (KBr): ṽ = 3070, 3046, 2923, 2858, 1592, 1461, 1430, 1118, 1068, 1029, 937 cm^{-1}. − MS (CI); *m*/*z* (%): 407 (100), 406 (53), 199 (37), 189 (23), 139 (54). − $C_{26}H_{34}O_2Si$ (406.6): C 76.80, H 8.43; found C 76.77, H 8.20.

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