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TETRAHEDRON

Preparation of 9,9-Dimethoxytetracyclo[8.5.0.0^{2,8}.0^{7,11}]pentadeca-3,5,12,14,-tetraene and Conversion to Hexacyclo[8.5.1.1^{4,7}.0^{5,14}.0^{6,12}.0^{11,15}.0^{16,17}]heptadeca-2,8-diene-13-one using a Domino Diels-Alder Reaction.[†,1]

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Abstract: The easily prepared bishomosecoheptaprismane ring system of **1** was converted to the tetracyclo[8.5.0.0^{2,8}.0^{7,11}]pentadeca-3,5,12,14-tetraene ring system of **10** using a photochemical decarbonylation/fragmentation reaction as the key step. The closely held face-to-face butadiene units in **10** undergo [4+4]cycloaddition under photochemical conditions and participate in domino Diels-Alder reactions with maleic anhydride and dicyanoacetylene. The maleic anhydride domino Diels-Alder adduct **18** was converted to the previously unreported hexacyclo[8.5.1.1^{4,7}.0^{5,14}.0^{6,16}.0^{11,15}.0^{16,17}]heptadecane ring system embodied in **19**. A single crystal X-ray analysis of **20**, one member of this new ring system, is reported and the results are compared with ab initio molecular orbital calculations.

We have been interested in the synthesis of higher order prismanes[2] and have recently reported the preparation of bishomohexaprismanedione (**3**).[3] Our synthesis started with conversion of the conveniently available bishomosecoheptaprismanedione (**1**)[4] to diene **2** followed by its further manipulation to **3**. As we reported, diene **2** does not undergo [2+2] photochemical ring closure to produce the bishomoheptaprismane ring system of **4** under either sensitized or direct irradiation conditions. We attributed this failure to the 80 kcal/mol increase in strain energy which accompanies the transformation of **2** to **4**. This value is above the 55 kcal/mol threshold suggested by Osawa[5] as the maximum increase in strain energy tolerated in a [2+2] photoreaction. Because of this limitation of the [2+2]photoreaction in the synthesis of multi-strained ring compounds, other methods need to be developed to synthesize higher order prismanes.

[†] Dedicated to our colleague and friend Professor Madeleine M. Joullié in celebration of forty years of distinguished teaching and research at the University of Pennsylvania.

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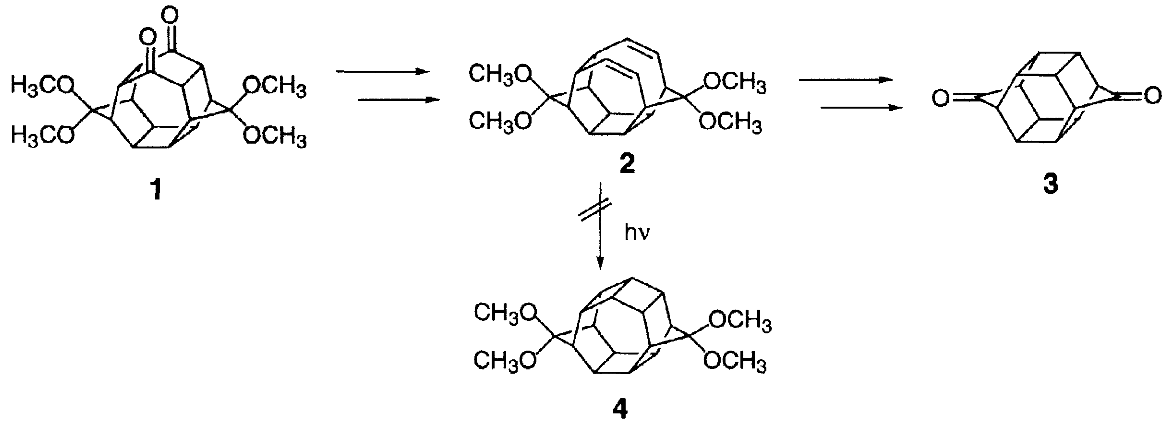
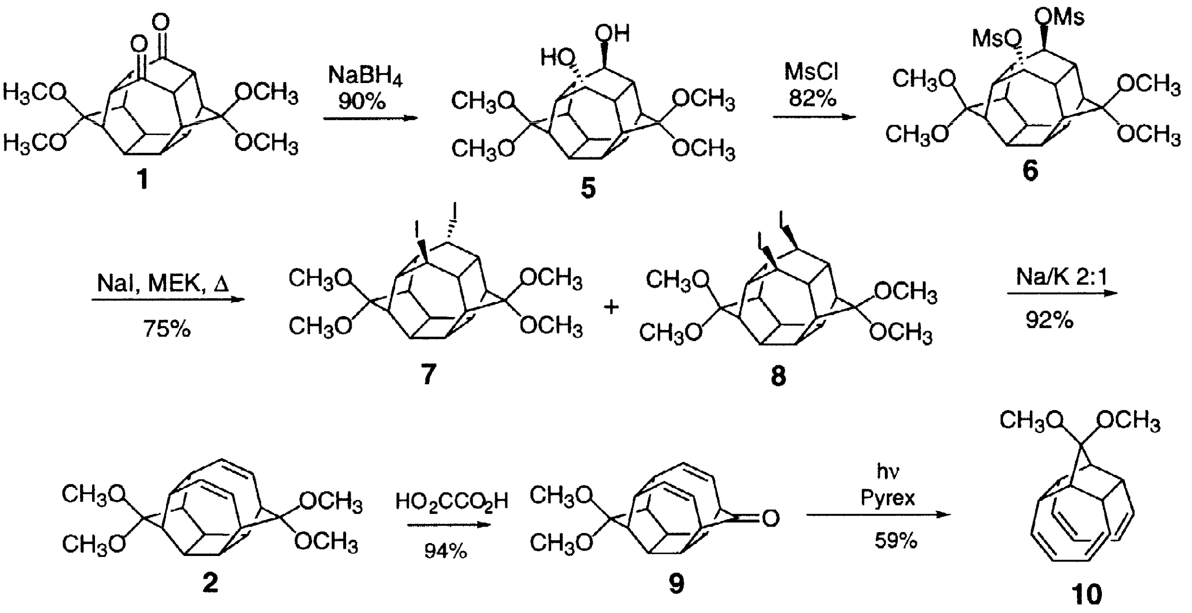


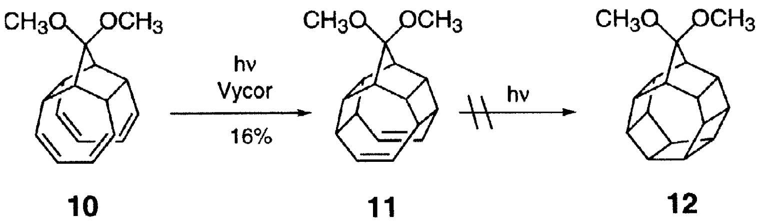
In this paper we report the full experimental details for the preparation of diene **2** and its further conversion to the interesting tetraene **10**. The photochemistry of tetraene **10** and its conversion to the previously unreported hexacyclo[$8.5.1.1^{4,7}.0^{5,14}.0^{6,12}.0^{11,15}.0^{16,17}$]heptadecane ring system using domino Diels-Alder reactions are described. The structure of one member of this ring system was determined by x-ray crystallagraphy and the results are compared with ab initio molecular orbital calculations.

Results and Discussion

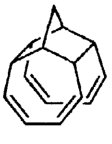
Fragmentation of **1** to diene **2** was accomplished via a multi-step sequence similar to that reported for the compound lacking methoxy groups.[6] Diketone **1** was converted to diol **5** in high yield using sodium borohydride. Treatment of **5** with methanesulfonyl chloride/pyridine gave dimesylate **6** in 82% yield which, when treated with sodium iodide in 2-butanone, produced a diastereomeric mixture of diiodides **7** and **8** in 75% yield. If desired, the two diastereomers could be separated by careful flash chromotagraphy on silica gel but the mixture was routinely carried through to the next reaction. Reductive Grob fragmentation of the diastereomeric mixture of diiodides **7** and **8** with 2:1 sodium-potassium alloy in THF at room temperature produced diene **2** in 92% yield. Mild selective hydrolysis of **2** using aqueous oxalic acid gave a high yield of ketone **9**. When irradiated using a medium pressure mercury arc through Pyrex, **9** smoothly underwent decarbonylation/fragmention to produce tetraene **10** in 59% yield. The photoextrusion of carbon monoxide in related systems is a well precedented process.[7] Tetraene **10** is a low melting solid which has its longest wavelength band at 238 nm (ε=11,700). If kept cold and under inert atmosphere, **10** is indefinitely stable.



Further direct irradiation (λ > 220 nm) of tetraene **10** produced the [4+4]photoadduct **11** in low yield. Diene **11** was resistant to further photochemical ring closure and yielded no traces of the homoheptaprismane derivative **12** even upon extended photolysis. The identity of **11** was determined by analysis of the ^{1}H and ^{13}C NMR spectra which revealed the symmetrical nature of the compound. A related example of [4+4]photocyclization reaction[8] has been reported.[9]



As an aid in understanding the observed photochemistry, geometry optimized ab initio calculations were carried out using the Gaussian 94 package at the HF/6-31G* level.[10] In order to save computational expense the dedimethoxy derivatives **13**, **14**, **15** and **16** were used. The relative energies of the isomers are given below. The [4+4]photoadduct **14** is related to **15** by a simple Cope rearrangement and is calculated to be 3.0 kcal/mol more stable than the [2+2]photoadduct **15**. At this time it is not obvious whether **14** is formed directly from **13** or if the [2+2]photoadduct **15** is the initial photoproduct which then undergoes a facile Cope rearrangment to yield **14**. The large increase in energy calculated for the transformation of **14** to **16** is responsible for the lack of success of this transformation.



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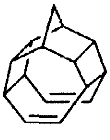

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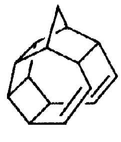

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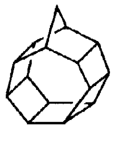
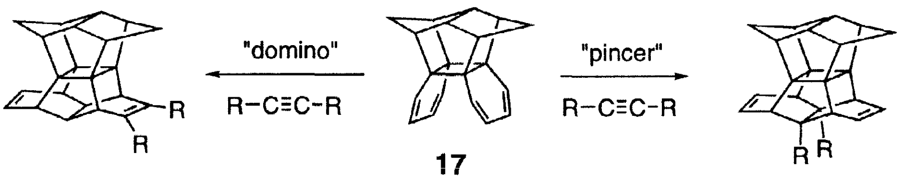


16

	13	14	15	16
Relative Energy (HF/6-31G*, Kcal/mol)	−21.0	0.0	3.0	63.0

We were intrigued by the possibility of performing tandem Diels-Alder reactions[11] with tetraene **10**. This system is reminiscent of **17**, an intermediate in Prinzbach's pagodane synthesis,[12] which undergoes tandem Diels-Alder reactions in both the domino and pincer modes.[13] Compound **10** consists of two cycloheptadiene units rather than two cyclohexadiene units as found in **17**. However, molecular models and ab initio calculations (see below) suggest that the two butadiene fragments of **10** should have a geometric relationship similar to that in **17**.



17

Before discussing the experimental results, it is informative to compare the structures of the two ring systems, **10** and **17**. Geometry optimized ab initio calculations at the HF/6-31G* level were carried out on **17** and the unsubstituted ring system **13** which serves as a model for **10**. The distances between the two diene units are similar for both **13** and **17** but are slightly shorter in **13**. The termini of the two diene units in **13** are calculated to be 2.95 Å apart while the ends of the two dienes are 3.07 Å apart in **17**. Thus the through space interaction between the two diene units should be approximately the same between the two compounds. Likewise, the steric interaction of dienophiles should be similar between the two systems. On the other hand because of properties of the cyclobutane ring, the amount of through bond interaction should be much greater in **17** than in **10**.

The amount of orbital interaction between the two alkene units can be judged by an analysis of their photoelectron (PE) spectra. Since ab initio calculations reproduce the PE spectra of organic compounds reasonably well, we have examined the orbital energies derived from geometry optimized HF/6-31G* calculations for **17** and **13**. The results are listed in Table 1 and are compared with the experimental results[14] in the case of **17**. The agreement between experiment and calculation is good. In agreement with the conclusions of Gleiter and coworkers[14], these results indicate that the through-bond orbital interactions are much more important than the though-space effect for **17** since the distance between the two dienes is smaller in **13** than **17** but the orbital splitting is much greater in **17** than **13**.

Table 1. Comparison between the measured vertical ionization energies and calculated orbital energies of **17** and **13** based on HF/6-31G* ab initio calculations. Values in eV.

Compound	Experimental Ionization Energies[a]	Calculated Orbital Energy
17	7.6	7.66
	8.1	8.08
	9.1	10.53
	9.65	10.70
13	-	8.05
	-	8.18
	-	10.60

[a] Experimental data taken from reference 14.

By analogy to Prinzbach's pagodane synthesis[12] using **17**, we have investigated the reaction of **10** with maleic anhydride and have found that the reaction proceeds in excellent yield to give **18**, the domino Diels-Alder adduct. Analysis of the crude reaction mixture by ^{1}H NMR produced no evidence for any other isomer in the reaction. The stereochemistry of the product was confirmed by single crystal x-ray analysis, although the R factor was poor. Diene **19** was produced in modest yield via oxidative decarboxylation. Hydrolysis gave ketone **20** which was subjected to single crystal x-ray analysis.[15] For comparison, the structure of **20** was calculated using ab initio molecular orbital theory at the HF/6-31G* level and a comparison of some selected bond lengths are shown in Table 2. The agreement is quite satisfactory.

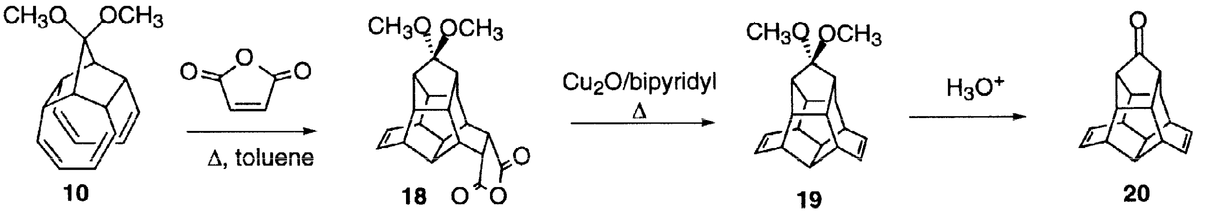
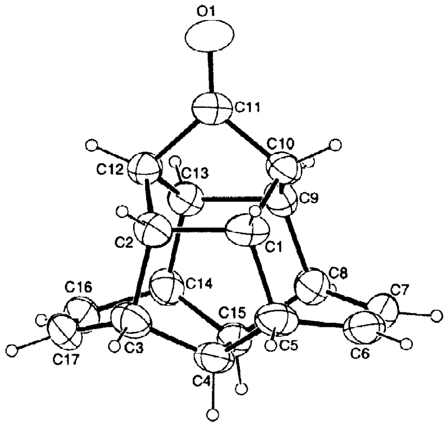
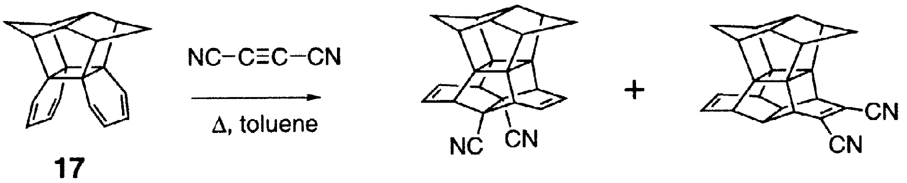


Table 2. Experimental and Calculated Bond Lengths in **20**.

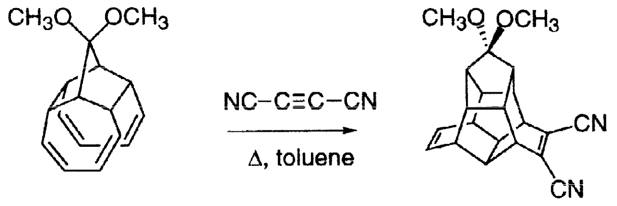
Bond	**X-ray(Å)**	**HF/6-31G***
C1- C2	1.568	1.571
C1-C5	1.548	1.545
C4-C5	1.544	1.545
C5-C6	1.482	1.507
C6-C7	1.305	1.319
C4-C15	1.536	1.551
C10-C11	1.528	1.523
C11-O1	1.208	1.186



Prinzbach and coworkers investigated various dienophiles[13] in the Diels-Alder reaction of **17** and discovered that most dienophiles gave the domino Diels-Alder adducts. The exception was dicyanoacetylene which, when heated with **17**, produced the pincer adduct **21** as the major product (74%) and the domino adduct **22** as the minor product (26%). We investigated the Diels-Alder reaction of tetraene **10** with dicyanoacetylene to determine whether any pincer adduct could be identified. In the event, reaction between tetraene **10** and dicyanoacetylene produced only the domino Diels-Alder adduct **23** in good yield. Analysis of the crude reaction product by ^{1}H NMR failed to reveal any other isomeric adducts. Given that the distance between the two diene units is almost identical in **10** and **17**, it is not clear why **10** did not produce any of the pincer adduct.



17 **21** **22**



10 **23**

Experimental Section

The general experimental methods were described in a previous paper.[16]

(11α,14β)-5,5,16,16-Tetramethoxyheptacyclo[7.6.1.$0^{2,8}$.$0^{3,7}$.$0^{4,13}$.$0^{6,12}$.$0^{10,15}$]hexadecane-11,14-diol (5)

To a solution of 6.83g (18.95 mmol) dione **1** in 120 mL of MeOH cooled in an ice-bath was added portionwise 575 mg (15.2 mmol) of $NaBH_4$. The reaction was stirred for an additional 30 minutes at 0°C, the methanol was concentrated in vacuo. The residue was treated with 250 mL of H_2O and was extracted three times with 250 mL of t-BuOH:CH_2Cl_2 (1:4). The combined organic layers were washed with water, dried ($MgSO_4$) and concentrated in vacuo to yield 6.89g of diol **5** (90%): m.p. 213-216 °C; R_F 0.25 (5:95-MeOH:$CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.42 (s, 4H, C$\underline{H}$C(OCH_3)$_2$), 2.89 (m, 4H, C$\underline{H}$-CHOH), 2.96 (s, 4H, cyclobutane's), 3.18 (s, 3H, OC$\underline{H}_3$), 3.23 (s, 3H, OC$\underline{H}_3$), 4.37 (m, 2H, C$\underline{H}$OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 38.2, 41.9, 43.6, 50.5, 50.8, 68.3, 116.2; IR (KBr) 3460, 2970, 2920, 2840, 1280, 1265, 1220, 1190, 1115, 1090, 1045 cm^{-1}; MS (CI) *m/z* calc'd for $C_{19}H_{25}O_5$ (-OCH_3): 333.1702, found 333.1706; 333 (100), 331 (10), 301 (10), 121 (10).

(11α,14β)-5,5,16,16-Tetramethoxyheptacyclo[7.6.1.$0^{2,8}$.$0^{3,7}$.$0^{4,13}$.$0^{6,12}$.$0^{10,15}$]hexadeca-11,14-dimesylate (6)

To a solution of 6.23g (17.1 mmol) of diol **5** in 120 mL of dry pyridine cooled to 0°C was added dropwise 6.9 mL (10.2g, 89.0 mmol) of methanesulphonyl chloride. The reaction mixture was stirred for 4h at rt, and was poured into water (400 mL). The aqueous layer was extracted with ethyl acetate (3 X 400 mL). The combined organic layers were washed with 10% HCl (5 X 300 mL), 10% $NaHCO_3$ (300 mL), water, were dried ($MgSO_4$) and concentrated in vacuo to yield 7.9 g of crude material. The residue was chromatographed on 30 g of silica with $CHCl_3$ as eluant. This furnished pure dimesylate **6** in 82% yield (7.28 g): m.p. 184-189 °C; R_F 0.2 (2:98-MeOH:$CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.46 (s, 4H), 2.99 (s, 4H), 3.02 (s, 6H, -SO_2C$\underline{H}_3$), 3.09 (m, 4H), 3.17 (s, 6H, -OC$\underline{H}_3$), 3.20 (s, 6H, -OC$\underline{H}_3$), 5.30 (m, 2H, $\underline{H}$C-OMs); ^{13}C NMR (125 MHz, $CDCl_3$) δ 37.99, 38.57, 40.74, 44.26, 59.60, 50.86, 78.97, 115.54; IR (KBr) 3031 m, 2980 vs, 2850 m, 1458 m, 1350 vs, 1282 s, 1268 s, 1248 m, 1223 w, 1175 vs, 1135 s, 1119 s, 1092 vs, 1060 m, 1040 s, 1010 m, 975 m, 940 vs, 899 vs, 867 vs, 800 m, 777 s, 745 w, 692 w, 608 m, 539 m, 497 s, 435 w cm^{-1}; MS (CI) *m/z* calc'd for $C_{22}H_{32}O_{10}S_2$(+ NH_4): 538.1781, found 538.1797; 538 (20), 489 (100), 474 (20), 439 (15), 395 (30); Analysis calc'd for $C_{22}H_{32}O_{10}S_2$: C, 50.75; H, 6.20; found: C, 50.68; H, 6.12.

Preparation of Diiodides 7 and 8

A mixture of 7.0 g of dimesylate **6** (13.5 mmol), excess sodium iodide (30 g, 200 mmol) and 130 mL of 2-butanone was stirred at reflux for three days under nitrogen. After cooling to rt, the reaction mixture was poured into water (200 mL). The aqueous layer was extracted with diethyl ether (3 X 400 mL) and the combined organic extracts were washed with water, were dried ($MgSO_4$) and were concentrated in vacuo. The residue was chromotographed on silica gel (25 g) with $CHCl_3$ as elutant to yield 5.93 g of diiodide (75%). This mixture was a 2:1 ratio of diastereomers (**7**:**8**) by ^1H NMR and was used in the next reaction. If desired, the isomers could be separated by careful flash chromatography (5% ethyl acetate/hexane).

(11α,14β)-11,14-Diiodo-5,5,16,16-Tetramethoxyheptacyclo[7.6.1.0^{2,8}.0^{3,7}.0^{4,13}.0^{6,12}.0^{10,15}]hexadecane **(7)** m.p. 121-123 °C; R_F 0.55 ($CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 2.81 (s, 4H), 3.00 (s, 8H), 3.17 (s, 6H, $-OC\underline{H}_3$), 3.20 (s, 6H, $-OC\underline{H}_3$), 5.07 (m, 2H, $\underline{H}$C-I); ^{13}C NMR (125 MHz, $CDCl_3$) δ 34.16, 37.68, 46.09, 50.43, 50.91, 51.37, 113.47; IR (KBr) 3004 w, 2960 s, 2840 m, 1460 br m, 1440 w, 1389 w, 1350 w, 1310 w, 1280 s, 1265 s, 1237 s, 1177 m, 1149 m, 1124 s, 1104 s, 1089 vs, 1049 s, 1038 m, 997 m, 960 m, 935 w, 892 m, 793 w, 753 w, 723 s, 692 w, 668 w, 657 w, 618 w, 501 w, 470 w, 418 w, 377 w, 290 m cm^{-1}; MS (CI) *m/z* calc'd for $C_{20} H_{26} 0_4 I_2(- OCH_3)$: 552.9736, found 552.9752; 553 (100), 538 (40), 457 (40), 427 (15), 299 (15); Analysis calc'd for $C_{20} H_{26} 0_4 I_2$: C, 41.12; H, 4.49; found: C, 41.15; H, 4.43.

(11β,14β)-11,14-Diiodo-5,5,16,16-Tetramethoxyheptacyclo[7.6.1.0^{2,8}.0^{3,7}.0^{4,13}.0^{6,12}.0^{10,15}]hexadecane **(8)** m.p. 180-182 °C; R_F 0.5 ($CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 2.52 (s, 2H), 2.62 (s, 2H), 2.92 (m, 4H, cyclobutane), 3.13 (s, 6H, $-OC\underline{H}_3$), 3.15-3.12 (m, 2H), 3.19 (s, 6H, $-OC\underline{H}_3$), 3.38-3.41 (m, 2H), 4.88 (s, 1H, $\underline{H}$C-I exo), 5.99 (dd, J_{app}=7.6 Hz, 1H, $\underline{H}$C-I endo); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.76, 34.73, 37.36, 37.52, 41.57, 49.25, 50.42, 50.53, 50.87, 50.90, 113.27; IR (KBr) 2955 s, 2844 m, 1785 w, 1775 w, 1740 w, 1475 w sh, 1470 m sh, 1460 m br, 1405 w br, 1389 w, 1364 w, 1350 m, 1308 m, 1268 s, 1228 w, 1215 m, 1180 s, 1152 m, 1123 s, 1090 s, 1035 s, 1000 m, 958 m, 938 w, 899 m, 875 w, 785 m, 762 w, 730 w, 699 w, 659 m, 648 m, 588 w, 504 w, 477 w, 432 w, 375 w, 315 w cm^{-1}; MS (CI) *m/z* calc'd for $C_{20} H_{26} 0_4 I_2(-OCH_3)$: 552.9736, found 552.9731; 553 (100), 538 (50), 457 (10), 427 (75), 412 (20), 381 (10), 299 (30); Analysis calc'd for $C_{20} H_{26} 0_4 I_2$: C, 41.12; H, 4.49; found: C, 41.22; H, 4.45.

5,5,16,16-Tetramethoxyheptacyclo[7.6.1.0^{2,8}.0^{3,7}.0^{4,13}.0^{6,12}]hexadeca-10,14-diene (2)

A solution of 8.20 g of diiodide mixture **7** and **8** (14.0 mmol) in 60 mL of dry THF was added to a mixture of 4.5 g Na/K(2:1) alloy (prepared by refluxing 3 g Na and 1.5 g K in toluene, cooling to room temperature, and removing the toluene via syringe) in 60 mL of dry THF. The resulting mixture was stirred at rt overnight under nitrogen. The mixture was filtered thru Celite and the filter cake was washed several times with anhydrous ether. The filtrate was concentrated, and the residue was redissolved in 400 mL of ether and washed with water, brine and dried ($MgSO_4$) and then concentrated to yield 4.28 g of diene **2** (92%). The diene was used as is in the next step. Flash chromatography on silica gel eluted with $CHCl_3$ furnished an analytically pure sample: m.p. 160-162.5 °C; R_F 0.3 ($CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 2.32 (s, 2H), 2.94 (m, 4H, cyclobutane), 3.00 (m, 2H), 3.14 (s, 3H), 3.18 (s, 3H), 3.26 (m, 5H), 3.31 (s, 3H), 5.41 (m, 2H, $=C\underline{H}$), 5.70 (dd, 2H, $=C\underline{H}$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 37.16, 37.39, 39.77, 44.47, 46.09, 48.19, 50.42, 50.78, 50.87, 115.03, 119.77, 129.66, 131.80; IR (KBr) 3010 m, 2960 vs, 2920 s, 2830 s, 1686 m, 1465 m, 1448 s, 1368 m, 1328 w, 1297 s, 1274 vs, 1262 vs, 1202 s, 1162 s, 1110 vs, 1070 vs, 1039 vs, 972 s, 918 m, 853 w, 834 s, 808 m, 772 s, 758 m, 742 w, 712 m, 690 m, 650 br w, 608 w, 495 w, 405 w, 352 m, 310 m cm^{-1}; MS (CI) *m/z* calc'd for $C_{20}H_{26}O_4$(- OCH_3): 299.1647, found 299.1659; 330 (10), 299 (100), 284 (20), 253 (15), 165 (10); Analysis calc'd for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93; found: C, 72.67; H, 7.77.

5,5,-Dimethoxyheptacyclo[7.6.1.0^{2,8}.0^{3,7}.0^{4,13}.0^{6,12}]hexadeca-10,14-dien-16-one (9)

To a solution of diene **2** (617 mg, 1.87 mmol) in 2 mL of CH_2Cl_2 was added 20 mL of 20% aqueous oxalic acid. The resulting mixture was stirred at room temperature for 3 days. Additional CH_2Cl_2 (50 mL) was added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 50 mL) and the combined organic layers were washed with water (100 mL), sat. $NaHCO_3$ (100 mL), brine (100 mL) and dried over $MgSO_4$. Flash chromatography on silica gel eluted with CH_2Cl_2 yielded 500 mg (94%) of pure ketodiene **9**: m.p. 150-153 °C; R_F 0.25 ($CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 2.38 (s, 2H, $(CH_3O)_2$-$C\underline{H}$), 3.12 (m, 4H, cyclobutane), 3.18 (s, 3H, $C\underline{H}_3O$), 3.28 (m, 5H), 3.42 (m, 2H), 5.38 (m, 2H, $=C\underline{H}$), 5.80 (dd, 2H, $=C\underline{H}$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 34.33, 38.84, 38.90, 44.68, 50.43, 50.88, 52.89, 114.02, 130.95, 131.57, 217.98; IR (KBr) 3012 m, 2960 s, 2930 sh, 2838 m, 1765 m, 1735 vs, 1668 m, 1449 w, 1408 w, 1365 w, 1352 w, 1302 w, 1279 s, 1262 m, 1215 m, 1195 w, 1180 m, 1140 s, 1128 vs, 1088 s, 1068 vs, 1026 s, 995 m, 950 w, 921 m, 882 w, 853 w, 815 w, 765 s, 740 m, 717 m, 685 m, 649 w, 615 w, 578 w, 490 w, 460 w, 410 w, 355 w cm^{-1}; MS (CI) *m/z* calc'd for $C_{18}H_{20}O_3$(+ NH_4): 302.1756, found 302.1759; 302 (55), 253 (100), 238 (40), 165 (15), 118 (10); Analysis calc'd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09; found: C, 75.81; H, 6.88.

9,9-Dimethoxytetracyclo[8.5.0.0^{2,8}.0^{7,11}]pentadeca-3,5,12,14,-tetraene (10)

A solution of 486 mg ketodiene **9** (1.71 mmol) in 50 mL of acetone was irradiated with a medium pressure mercury lamp for 3.5 hours thru Pyrex. The resulting solution was concentrated. The residue was chromatographed on silica gel with $CHCl_3$ elution to yield 257 mg of tetraene **10** (59%): m.p. 78-80 °C; R_F 0.6 ($CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 1.74 (s, 2H, $\underline{H}CC(OCH_3)_2$), 3.28 (s, 6H, -$OC\underline{H}_3$), 3.60 (m, 4H), 5.50-5.53 (m, 4H, $=C\underline{H}$), 5.78 (m, 4H, $=C\underline{H}$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 38.20, 43.47, 50.32, 112.57, 124.57, 132.39; IR (KBr) 3021 m, 2958 m, 2841 w, 1775 w, 1738 s, 1720 m, 1622 m, 1588 w, 1534 s, 1508 w, 1470 m, 1449 s, 1402 m, 1352 s, 1290 s, 1269 s, 1225 m, 1195 m, 1180 w, 1138 s, 1121 s, 1095 m, 1082 s, 1030 s, 1004 w, 980 m, 955 m, 930 w, 880 m, 855 w, 825 m, 785 m, 725 s, 653 m, 606 w, 525 w, 490 br w cm^{-1}; UV-Vis (Hexane) λ_{max} 238 nm (ϵ = 11,700); MS (CI) *m/z* calc'd for $C_{17}H_{20}O_2^+$: 256.1463, found .1468; 256 (40), 225 (100), 210 (15), 190 (10), 165 (20); Analysis calc'd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86; found: C, 79.80; H, 8.14.

9,9-Dimethoxytetracyclo[8.5.0.0^{2,8}.0^{3,15}.0^{6,12}.0^{7,11}]pentadeca-4,13-diene (11)

A deoxygenated solution of 92 mg (0.36 mmol) of tetraene **10** in 10 mL of dry ether was irradiated with a medium pressure mercury lamp thru a Vycor filter for 50 minutes. The solution was concentrated, and the residue was chromatographed on silica gel with gradent elution from hexane to 0.5% EtOAc / 99.5% hexane to yield 15 mg of pure diene **11** (16%): m.p. 94-96 °C; R_F 0.3 ($CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 2.41 (m, 2H, - $C\underline{H}C(OCH_3)$), 2.99 (m, 4H), 3.18 (s, 6H, -$OC\underline{H}_3$), 3.25 (m, 4H), 5.83 (d, 4H, =$C\underline{H}$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 35.72, 39.08, 43.24, 50.84, 117.90, 132.17; IR (KBr) 3010 m, 2957 s, 2818 w, 1260 m, 1195 w, 1149 m, 1115 m, 1089 s, 1065 m, 1015 m, 804 m, 785 m, 740 w, 720 w, 670 w, 655 w, 610 w, 465 w cm^{-1}; MS (CI) *m/z* calc'd for $C_{17}H_{20}O_2(-OCH_3)$: 225.1279, found 225.1284; 257 (10), 225 (100), 211 (40), 156 (10).

13,13-Dimethoxyhexacyclo[8.5.1.1^{4,7}.0^{5,14}.0^{6,12}.0^{11,15}.0^{16,17}]heptadec-8-ene-2-*anti*,3-*anti*-dicarboxylic acid Anhydride (18)

A solution of 189 mg (0.74 mmol) of tetraene **10** and 218 mg (2.22 mmol) of freshly sublimed maleic anhydride in 12 mL of dry toluene was stirred at reflux for 2 days. After concentration *in vacuo*, excess maleic anhydride was removed by sublimation under high vacuum to yield 262 mg (100 %) of pure adduct **18**: m.p. 192-194 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 1.76 (m, 1H, $O{=}CC\underline{H}$), 1.87 (m, 1H), 1.94 (m, 2H), 2.61 (m, 4H), 2.66 (m, 2H), 2.75 (m, 2H), 3.18 (s, 6H, - $OC\underline{H}_3$), 3.35 (s, 2H), 5.98 (m, 2H, =$C\underline{H}$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 37.70, 40.20, 40.90, 41.07, 41.46, 41.95, 42.13, 46.85, 50.35, 116.30, 130.04, 174.10; IR (thin film) 3045 w, 2950 s, 2840 m, 1860 br m, 1775 s, 1455 br w, 1285 m, 1228 m, 1195 w, 1105 s, 1049 s, 1000 m, 946 m, 925 s, 851 w, 810 w, 733 s cm^{-1}; MS (CI) *m/z* calc'd for $C_{21}H_{22}O_5H^+$: 355.1545, found 355.1541; 355 (60), 323 (100), 241 (10), 130 (15).

13,13-Dimethoxyhexacyclo[8.5.1.1^{4,7}.0^{5,14}.0^{6,12}.0^{11,15}.0^{16,17}]heptadeca-2,8-diene (19)

A mixture of anhydride **18** (100 mg, 0.28 mmol), 2,2'-bipyridyl (47 mg, 0.30 mmol), copper(I) oxide (87 mg, 0.61 mmol), water (20 μL), and quinoline (0.5 mL) was stirred vigorously and heated to reflux over 4 h. Heating at this temperature was continued for 12 h during which excess water was allowed to distill away. After a further 60 h at reflux, the dark mixture was cooled, diluted with ether-hexane (1:1), and filtered through a pad of Celite. The yellow filtrate was washed with 10% hydrochloric acid, saturated sodium bicarbonate solution, and then dried ($MgSO_4$). The solvent was evaporated and the residue was chromatographed over a short column of silica gel using $CHCl_3$ to give pure **19** (24 mg, 30%): m.p. 82-84 °C; R_F 0.4 ($CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 1.75 (m, 2H), 2.07 (m, 2H), 2.52 (m, 4H), 2.61 (s, 4H), 3.17 (s, 6H, $-OC\underline{H}_3$), 6.03 (m, 4H, $=C\underline{H}$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 42.13, 42.97, 43.33, 45.23, 50.17, 116.10, 130.59; IR (KBr) 3040 m, 2950 s, 2910 s, 2890 s, 2830 m, 1638 w, 1468 w, 1442 w, 1390 w, 1338 m, 1325 w, 1308 m, 1280 s, 1221 w, 1195 w, 1170 m, 1155 w, 1115 s, 1105 s, 1092 s, 1057 s, 1048 s, 1003 s, 910 m, 833 m, 815 w, 749 m, 738 m, 693 s, 664 m, 550 w, 470 w, 402 w cm^{-1}; MS (CI) *m/z* calc'd for $C_{19}H_{22}O_2^+$: 282.1620, found 282.1624; 282 (13), 251 (100), 236 (10).

Hexacyclo[8.5.1.1^{4,7}.0^{5,14}.0^{6,12}.0^{11,15}.0^{16,17}]heptadeca-2,8-diene-13-one (20)

A solution of **19** (20 mg, 0.07 mmol) in methylene chloride (5 mL) was vigorously stirred with 30% sulfuric acid (5 mL) for 5 days. The aqueous layer was separated and was extracted with methylene chloride (3 X 20 mL). The combined organic layers were washed successively with water and saturated sodium bicarbonate solution and then dried ($MgSO_4$). The solvent was evaporated and the residue was chromatographed over a short column of silica gel using $CHCl_3$ to give pure **20** (15 mg, 90%): m.p. 135-139 °C; R_F 0.4 ($CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 1.78 (m, 2H), 2.23 (m, 2H), 2.50 (m, 4H), 2.77 (s, 4H), 6.07 (m, 4H, $=C\underline{H}$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 38.84, 44.15, 44.85, 45.79, 130.30, 211.87; IR (KBr) 3030w, 2980w, 2920m, 2900m, 1780m, 1745s, 1140w, 830w, 740w, 690m cm^{-1}; MS (CI) *m/z* calc'd for $C_{17}H_{16}O\ H^+$: 237.1279, found 237.1275; 237 (45), 130 (15).

2,3-Dicyano-13,13-dimethoxyhexacyclo[8.5.1.1^{4,7}.0^{5,14}.0^{6,12}.0^{11,15}.0^{16,17}]heptadeca-2,8-diene (23)

A solution of 22 mg (0.74 mmol) of tetraene **10** and 200 mg (2.22 mmol) of dicyanoacetylene in 2 mL of dry toluene was stirred at reflux for 2 days. After concentration *in vacuo* the residue was purified by chromatography on silica gel with $CHCl_3$ to yield pure adduct **23**: m.p. 218-220 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 1.81(m, 2H), 2.30 (m, 2H), 2.64(m, 2H), 2.73 (m, 4H), 2.99 (m, 2H), 3.17 (s, 6H), 6.06 (m, 2H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 41.48, 41.75, 42.29, 42.75, 43.07, 44.79, 45.71, 50.36, 115.56, 115.64, 128.98, 129.97 ppm. MS (ammonia CI) *m/z* calc'd for $C_{21}H_{20}N_2O_2 + NH_4$: 350.1869, found 350.1882.

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REFERENCES AND NOTES

[1] Parts of this work are taken from the Ph. D. Dissertation of T. D. G. , University of Pennsylvania, 1996.

[2] For three recent [n]-prismane reviews see a.) Forman, M. A.; Dailey, W. P. *Org. Prep. Proc. Int.* **1994**, *26*, 291. b.) Mehta, G.; Padma,S., *Carbocyclic Cage Compounds*, Osawa, E.; Yonemitsu, O., Eds., VCH Publishers Inc., 1992. c.) Mehta, G.,*Strain and Its Implications in Organic Chemistry*, de Meijere; A.; Blechert, S., Eds., NATO ASI Series, Kluwer Academic Publishers: Dordrecht **1989**, *273*, 269.

[3] Golobish, T. G.; Dailey, W. P. *Tetrahedron Lett.* **1996**, *37*, 3239.

[4] Forman, M. A.; Dailey, W. P. *J. Org. Chem.* **1993**, *58*, 1501.

[5] Osawa, E. *J. Org. Chem.* **1977**, *42*, 2621.

[6] Mehta, G.; Padma, S.; Jemmis, E. D.; Leela, G.; Osawa, E.; Barbiric, D. A. *Tetrahedron Lett.* **1988**, *29*, 1613.

[7] For a review, see Givens, R. S. in **Organic Photochemistry**, Padwa, W., Ed., Marcel Dekker, Inc, New York, Vol 5, 1981, pp 228-331.

[8] For a recent review on [4+4]cycloadditions, see: Sieburth, S. Mcn.; Cunard, N. T. *Tetrahedron*, **1996**, 6251.

[9] Srinivasan, R.; Sunderbabu, G. *J. Org. Chem.* **1987**, *52*, 5037.

[10] Gaussian 94, Revision C.3: M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1995.

[11] Winkler, J. D. *Chem. Rev.* **1996**, *96*, 167.

[12] Fessner, W-D.; Sedelmeier, G.; Spurr, P. R.; Rihs, G.; Prinzbach, H. *J. Am. Chem. Soc.* **1987**, *109*, 4626.

[13] Fessner, W-D., Grund, C., Prinzbach, H. *Tetrahedron Lett.* **1989**, 3133.

[14] Gleiter, R., Zimmerman, H., Fessner, W-D., Prinzbach, H. *Chem. Ber.* **1985**, *118*, 3856.

[15] The results of the single crystal x-ray analysis have been deposited with the Cambridge Crystallographic data Centre.

[16] Golobish, T. D.; Dailey, W. P. *J. Org. Chem.* **1995**, *60*, 7865.