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Pentacyclo[8.2.1.1^{2,5}.1^{4,7}.1^{8,11}]hexadeca-1,7-diene and Its 4,5,10,11-Tetramethyl Derivative, Two Highly Hyperstable Slightly Pyramidalized Dienes

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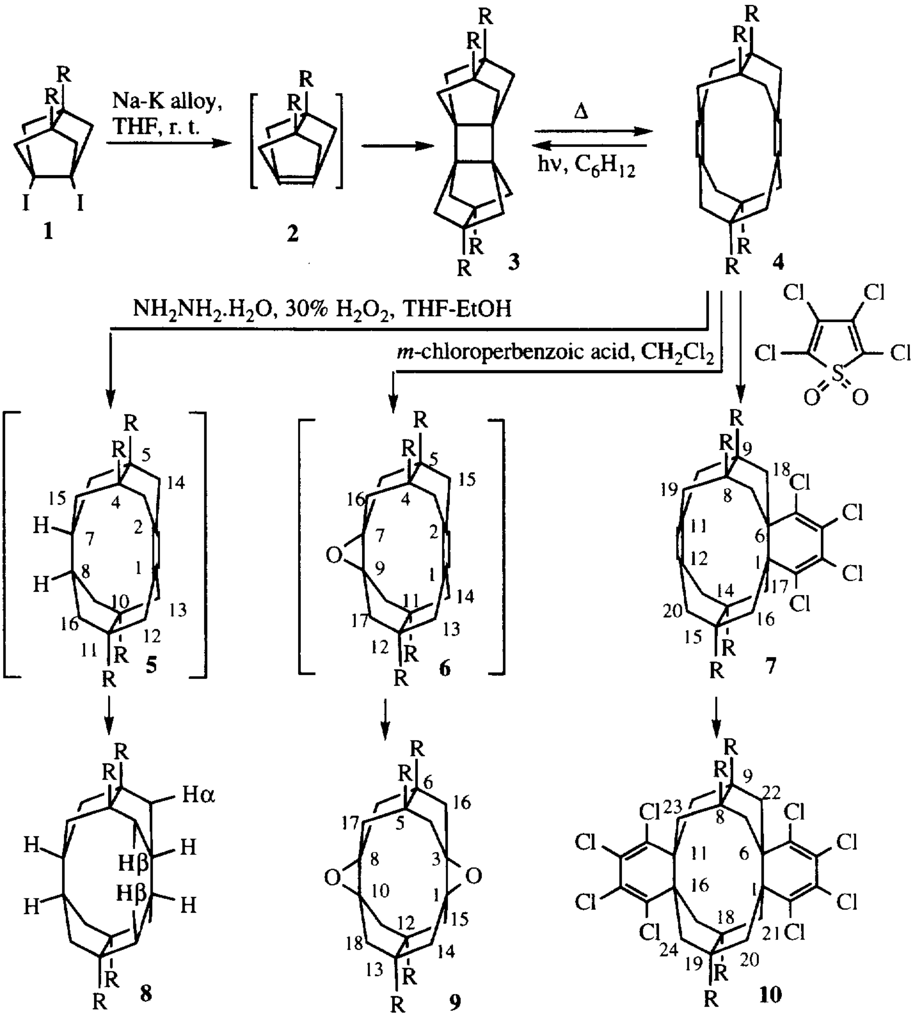
Abstract: Dienes **4a,b** and their monohydrogenation products **5a,b** have shown to be hyperstable alkenes which could be reduced with diimide or epoxidized with *m*-chloroperbenzoic acid. Moreover dienes **4a,b** show slightly pyramidalized carbon-carbon double bonds which must be responsible for its long-wave lengh UV absorption which allows their photochemical [2 + 2] conversion into cyclobutanes **3a,b** in the absence of any photosensitizer and, in the case of **4b**, its participation as a dienophile in an inverse-electron demand Diels-Alder reaction with tetrachlorotiophene-S,S-dioxide.

Recently, we described the synthesis of the highly pyramidalized alkene 3,7-dimethyltricyclo [3.3.0.0^{3,7}]oct-1(5)-ene, **2b**,[1] and its parent compound, **2a**,[2,3] from diiodides **1b** and **1a**, respectively (Throughout the text, compounds denoted as **a** have R = H, while those denoted as **b** have R = Me). These highly reactive alkenes undergo a spontaneous [2 + 2] cycloaddition to the corresponding cyclobutane dimers, **3b**,**a**, which under some reaction conditions (i.e.: dioxane under reflux) experience a [2 + 2] retrocycloaddition reaction to give the isomeric dienes, **4b**,**a**, respectively (Scheme 1). Cyclobutane compounds **3a**,**b**, could be obtained by [2 + 2] photocyclization of the corresponding dienes **4a**,**b**. In this paper we report some of the reactivity of dienes **4a** and **4b**, their hyperstability and pyramidalization.

In 1981 P. v. R. Schleyer et al.[4] introduced the concept of alkene hyperstability and later other autors[5] described several hyperstable alkenes. In general, the Strain Energy (E_{st}) of a cycloalkene is higher than that of the corresponding cycloalkane, i.e.: a cycloalkene usually has a positive Olefin Strain Energy (OSE). However, he found that several cycloalkenes showed negative OSE values. The strain energy increase in these cases is due to an increase in the vicinal and transannular hydrogen interactions. However, in spite of the OSE increase, the difference ΔH_f(alkene) - ΔH_f(alkane) show positive values, although they are lower than usual. These kinds of cycloalkenes were defined as hyperstable alkenes and are characterized by their reluctance to be hydrogenated even under drastic catalytic conditions, although they can be reduced with diimide or epoxidized with peroxycarboxylic acids or dimethyldioxirane.

The first indication about the hyperstability of the present compounds came when diene **4b** remained unchanged under quite drastic hydrogenation conditions (Pd-C or PtO_2 as catalyst, 50 °C, 20 atm H_2, several hours, different solvents). Molecular Mechanics Calculations (MM2 program)[6] allowed us to obtain the values for ΔH_f and E_{st} of dienes **4a,b**, their monohydrogenation products **5a,b**, and the fully saturated products **8a,b**, and the OSE values for dienes **4a,b** and alkenes **5a,b**, which are collected in Table 1.



1-6a and **8,9a**, R = H; **1-10b**, R = Me

Scheme 1. Synthesis and reactions of dienes **4a,b**.

As can be see from Table 1, compounds **4a,b** and **5a,b** are hyperstable alkenes. The OSE values for the transformations **4a** / **5a** and **5a** / **8a** are -12.0 and -7.2 kcal / mol, respectively. For the conversions **4b** / **5b** and **5b** / **8b**, the values are still higher, -14.6 and -10.9 kcal / mol, respectively. Only one case has recently been reported of a diene with OSE values[5c] higher than that of **4b**, although a bissecododecahedrene described by Prinzbach[5a,b] shows an OSE value very close to that of **4b**. On saturation of each double bond of **4a,b** the strain energy raises. Although there is a small decrease of the stretching and bending terms, the torsional and Van der Waal's ones increase, mainly because of the small dihedral angles formed by the new C-H bonds and by these bonds and the methylene C-Hα (1,2- and 1,3-interactions). Other important destabilizing terms arise from the approaching of the methylene Hβ protons from different C_8 subunits, and of the R-substituents (CH_3 or H) on the C4 / C5 and C10 / C11 atom pairs.

Table 1. ΔH_f and E_{st} of **4a,b**, **5a,b** and **8a,b** and OSE for **4a,b** / **5a,b** and **5a,b** / **8a,b** (kcal / mol), calculated by using the MM2 program.

	4a	**5a**	**8a**	**4b**	**5b**	**8b**
ΔH_f	32.3	20.5	4.0	-1.4	-10.4	-23.3
E_{st}	48.2	60.2	67.4	48.1	62.7	73.6
OSE	-12.0	-7.2	-	-14.6	-10.9	-

Table 2. Angle of pyramidalization, Φ (°) and distances between the olefinic or corresponding carbon atoms, d (Å), of compounds **4-6a** and **8,9a**.

	4a[a,b]	**5a**[a]	**6a**[b]	**8a**[a]	**9a**
d	2.889	3.303	3.012	3.744	3.165
Φ	10.6	10.6	10.4	-	-

[a] MM3: **4a** (d = 2.949, Φ = 11.7), **5a** (d = 3.376, Φ = 11.9) and **8a** (d = 3.800). [b] *ab initio* (HF/3-21G): **4a** (d = 2.970, Φ = 12.4), **6a** (d = 3.066 , Φ = 11.1).

Table 3. Angle of pyramidalization, Φ (°), and distance between the olefinic or corresponding carbon atoms, d (Å), of compounds **4-6b** and **8,9b**.

	4b[a,b,c]	**5b**[a]	**6b**	**8b**[a]	**9b**
d	2.845	3.243	2.967	3.676	3.092
Φ	9.8	8.6	8.7	-	-

[a] MM3: for **4b** (d = 2.891, Φ = 11.2), **5b** (d = 3.308, Φ = 11.8), and **8b** (d = 3.729). [b] *ab initio* (HF/3-21G): for **4b** (d = 2.923, Φ = 11.6). [c] X-ray: for **4b** (d = 2.989, Φ = 13.0).[1b]

Moreover, hydrogenation of the first double bond in **4a,b** raises the strain energy (-12.0 and -14.6 Kcal / mol for **4a** and **4b**, respectively) more than the hydrogenation of the second one (-7.2 and -10.9 Kcal / mol for **5a** and **5b**, respectively). This difference is due to the fact that alkanes **8a,b** can release part of the above cited interactions by twisting around the new single C-C bonds to a much greater extent than alkenes **5a,b**. Moreover, since the destabilization in passing from **4b** to **5b** and **8b**, due to the approaching of the eclipsed methyl substituents, is greater than that observed in passing from **4a** to **5a** and **8a**, where the approaching substituents are hydrogen atoms, alkenes **4b** and **5b** are more hyperstable than their parent compounds **4a** and **5a**.

Tetrasubstituted C=C double bonds can be saturated with diimide, a procedure used by Prinzbach et al.[5a,b] to reduce other hyperstable alkenes. When diene **4b** was reacted with a large excess of diimide, generated *in situ* by reaction of hydrazine hydrate with 30% hydrogen peroxide, a mixture of monohydrogenation product **5b** and alkane **8b** still containing starting **4b** (approximate ratio **4b** / **5b** / **8b** of 2:2:1 by ^{1}H-NMR) was obtained. Further reaction of this mixture with excess diimide gave a mixture of the same products in the approximate ratio of 1:5:4, which after four more treatments with excess diimide gave **8b** in 88% isolated yield. The approximate ratio of the products obtained after the successive diimide treatments show a quite similar reactivity for both C=C double bonds. A similar situation was found in the case of **4a**. However, in this case reduction took place more rapidly, in accord with the lower hyperstability of alkenes **4a** and **5a**.

Reaction of **4a** and **4b** with a large excess of *m*-chloroperbenzoic acid in CH_2Cl_2 gave the corresponding diepoxides **9a** and **9b**, quantitatively. Attempted monoepoxidation of **4b** by using one equivalent of an acetone solution of DMD[7] gave a mixture of **4b** / **6b** / **9b** in the approximate ratio of 79:13:8 (relative area by GC / MS). When the above mixture was reacted with a second equivalent of DMD solution, a new mixture of the same products in the approximate ratio of 38:44:18 was obtained. These figures show that the reactivity of **4b** and **6b** towards DMD is quite similar as it was also observed for the diimide reduction.

The UV spectra of dienes **4a,b** in hexane solution show maximum absorptions at λ 207 (ε = 3740) and 205 nm (ε = 9100), respectively, a fact that allows their conversion into the corresponding cyclobutane derivatives **3a,b** by direct irradiation with a 125 W medium-pressure mercury lamp in deoxygenated cyclohexane in the absence of any photosensitizer.[1b,2] The relatively high charge transfer absorptions of dienes **4a,b** might be due to the pyramidalization of the alkene subunits which lowers the LUMO and increases the HOMO energies,[8] and / or to a π-π interaction.[9] The X-Ray structure[1b] of diene **4b** shows the double bonds to be parallel and lightly pyramidalized. The experimental distance between the two double bonds [2.989(3) Å][2] is in reasonable agreement with MM2, MM3 and *ab initio* (HF/3-21G) calculations (see Table 3), but the experimental pyramidalization angle (13.0°) is somewhat higher than calculated. Tables 2 and 3 collect the pyramidalization angles of the olefinic carbon atoms of several of these compounds and the distance between the olefinic carbon atoms of **4a,b** or of the corresponding atoms in their derivatives **5a,b**, **6a,b**, **8a,b** and **9a,b**. As can be seen from these Tables, while on epoxidation of **4a,b** only a slight increase in the distance between the original olefinic carbon atoms is calculated, hydrogenation of these compounds has a profound influence on this distance, making the saturated compounds **8a,b** to addopt a more spheric shape.

Highly pyramidalized alkenes are known to react easily with electron-rich dienes.[1a,10] However, the slightly pyramidalized diene **4b** failed to react with cyclopentadiene and 11,12-dimethylene-9,10-dihydro-9,10-ethanoanthracene,[11] even under drastic conditions, although it did react with the electron-poor diene, tetrachlorothiophene-S,S-dioxide,[12] under drastic conditions (boiling toluene, great excess of diene and long reaction times), to give not only product **7b**, derived from the mono-Diels-Alder adduct by retro-chelotropic SO_2 elimination, but also product **10b**, probably derived from **7b** through a new Diels-Alder reaction followed by SO_2 elimination. As for the diimide reduction or DMD epoxidation, **7b** seems to be as reactive as **4b** towards this diene, a fact that must be due to its pyramidalization.

Moreover, reaction of **4b** with electrophilic reagents, such as bromine or iodine gave complex mixtures of products, from which no defined products could be isolated, in particular those derived from transannular reactions, as it has been observed in related cases.[10,13]

It is worth noting that a bissecododecahedradiene described by Prinzbach et al.[5a,b] is less hyperstable than its monoreduction product. Accordingly, this diene was selectively hydrogenated with diimide or reacted with tetrachlorotiophene-S,S-dioxide. In fact, complete saturation of this diene with diimide could not be carried out. While diepoxidation of this diene with *m*-chloroperbenzoic acid was easily effected, the second epoxidation was so much slow that it was possible to obtain the corresponding monoepoxide.[5a] In this case, a partial compensation of the hyperstability of the diene due to a destabilizing transannular π-π repulsion was suggested to explain the greater reactivity of the diene as compared with its derived monoenes.

For a series of dienes having close π-bonds (1,16-dodecahedradiene, a bisseco-, a seco- and a bishomo-derivative) a π-π interaction between the π-bonds has been clearly established by photoelectron spectroscopy.[14] This interaction has been shown to take place essentially through-space for distances between the olefinic carbon atoms lower than 3.00 Å. At longer distances the contribution of the through-bond interaction increased, the global magnitude being smaller. According to this study and taken into account the carbon-carbon distance between the olefinic carbon atoms, important mainly through-space π-π interactions are to be expected for dienes **4a,b**. A π-π repulsion in **4a,b**, not taken into account by the MM2 calculations, would render these dienes less stable and thus to make them as reactive as the less hyperstable alkenes **5a,b** or their related compounds **6a,b** and **7a,b**, which would explain the observed reactivity.

Experimental

Melting points (open capillary tubes) were determined on a Gallenkamp melting point apparatus, model MFB 595010M. IR and UV spectra were recorded on Perkin-Elmer spectrometers, FT / IR model 1600 and Lambda 2, respectively. 300 MHz ^{1}H and 75.4 MHz ^{13}C NMR spectra were taken on a Varian Gemini 300 spectrometer and 500 MHz ^{1}H NMR on a Varian VXR 500. Chemical shifts are given in ppm (δ scale) relative to internal TMS and coupling constants are given in Hertz (Hz). For the GC / MS analysis a gas chromatograph Hewlett-Packard model 5890 Series II connected to a mass spectrometer Hewlett-Packard HP-5989A and a 30-meter HP-5 (5% diphenyl- 95% dimethyl-polysiloxane) gas chromatographic column were used (conditions: 10 psi. 100 to 250 °C, 10 °C / min). The HRMS were performed on a AUTOSPEC-UG spectrometer. Molecular mechanics calculations were carried out on Hewlett-Packard computer Vectra N 486 working at 66 MHz, by using the MM2(91) and MM3(92) programs. For the *ab initio* calculations the GAUSSIAN 94, D.2 revision, program, run on an IBM SP/2 computer from the *Centre de Supercomputació de Catalunya* (CESCA), was used. Silica gel (SDS 60, 60-200 mm) was used without any pretreatment for column chromatography. For the TLC, silica gel 60 F254 (alugram R sil G / UV 254) was used. Mycroanalyses and HRMS were carried out, respectively, at the Mycroanalysis Service and at the Mass Spectrometry Service of the Centro de Investigación y Desarrollo, C.I.D., Barcelona, Spain.

4,5,10,11-Tetramethylpentacyclo[8.2.1.1^{2,5}.1^{4,7}.1^{8,11}]hexadecane (8b). To a solution of diene **4b** (27 mg, 0.1 mmol) in THF (8 mL) and ethanol (4 mL), stirred in an inert atmosphere at 0 °C, was added hydrazine hydrate solution (6 mL) and then slowly a 30% hydrogen peroxide solution (6 mL) and the mixture was stirred at 0 °C for 4 h and at room temperature for 14 h. The mixture was diluted with CH_2Cl_2 (60 ml) and washed with brine (2 x 25 ml). The organic phase was dried (Na_2SO_4) and concentrated in vacuo to give a mixture of **4b** / **5b** / **8b** in the approximate ratio of 2:2:1 (^{1}H NMR). The above procedure was repeated five more times giving rise to the following mixtures and ratios (^{1}H NMR): After the second treatment, mixture of the same products in the ratio of 1:5:4; after the third to fith treatments, mixtures of **5b** / **8b** in the ratios of 4.5:5.5, 3:7 and 1.7:8.3, respectively. Finally, after the sixth treatment, reduction was complete, and pure **8b** was obtained as colorless crystals after crystallization from chloroform (24 mg, 88% yield), mp 161-163 °C. IR (KBr), v: 2968 (s), 2922 (s), 2853 (s), 1462 (m), 1377 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.94 (s, 12 H, CH_3), 1.67 [dd, J = 15.0 Hz, J' = 10.7 Hz, 8 H, 3(6,9,12,13,14,15,16)-Hα], 2.20 [d, J = 15.0 Hz, 8 H, 3(6,9,12,13,14,15,16)-Hβ], 2.37 [m, 4 H, 1(2,7,8)-H]. ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 29.0 [CH_3, 4(5,10,11)-CH_3], 38.4 [CH, C1(2,7,8)], 45.6 [CH_2, C3(6,9,12,13,14,15,16)], 52.6 [C, C4(5,10,11)]. MS (EI): m/z (%) = 272 ($M^{\cdot+}$, 3), 257 [(M^+ -CH_3), 6], 243 (5), 231 (5), 230 (12), 229 (26), 136 (30), 135 (68), 134 (12), 121 (16), 119 (17), 109 (27), 108 (22), 107 (60), 105 (15), 95 (100), 94 (35), 93 (52), 91 (23), 81 (30), 79 (45), 77 (16), 69 (13), 67 (33), 55 (32), 53 (11). Anal. Calcd. for $C_{20}H_{32}$: C, 88.15%; H, 11.85%. Found: C, 88.12% H, 11.80%.

Pentacyclo[8.2.1.1^{2,5}.1^{4,7}.1^{8,11}]hexadecane (8a). **4a** (47 mg, 0.22 mmol) was reacted with diimide as previously described for **4b** using the same ratio of reagents. After the first treatment a mixture of **4a** / **5a** / **8a** in the approximate ratio of 12:3:2 (^{13}C NMR) was obtained. After two more treatments a mixture of **5a** and **8a** in which **8a** was the main component was obtained. After a fourth treatment, pure **8a** (47 mg, nearly quantitative yield) was obtained as colorless crystals, mp 173-174 °C (ethyl acetate). IR (KBr) v: 3008 (m), 2924 (s), 2861 (s), 1469 (s), 1450 (s), 1372 (m), 1262 (m), 1088 (s), 802 (m), 694 (m), 608 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.83 - 1.97 (m, 16 H, 8 CH_2), 2.47 [m, 4 H, 1(2,7,8)-H)], 2.60 [m, 4 H, 4(5,10,11)-H]. ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 36.5 [CH_2, C3(6,9,12,13,14,15,16)], 41.7 [CH, C4(5,10,11)], 45.9 [CH, C1(2,7,8)]. MS (EI): m/z (%) = 216 ($M^{\cdot+}$, 14), 187 (14), 175 (10), 174 (12), 173 (41), 135 (32), 134 (31), 108 (27), 107 (100), 106 (38), 105 (24), 93 (21), 92 (11), 91 (38), 85 (14), 83 (26), 81 (21), 80 (28), 79 (94), 77 (24), 67 (66), 66 (17), 65 (14), 53 (15). Anal. Calcd. for $C_{16}H_{24}$: C, 88.82%; H, 11.18%. Found: C, 88.52% H, 11.20%.

2,9-Dioxa-5,6,12,13-tetramethylheptacyclo[10.2.1.1^{3,6}.1^{5,8}.1^{10,13}.0^{1,3}.0^{8,10}]octadecane (9b). A solution of **4b** (15 mg, 0.06 mmol) in CH_2Cl_2 (5 mL) was stirred with *m*-chloroperbenzoic acid (30 mg, 0.17 mmol) at room temperature for 4 h. Then it was washed with aqueous 10% sodium thiosulfate solution (2 x 5 mL) and with aqueous 10% $NaHCO_3$ solution (2 x 5 mL), dried with anhydrous Na_2SO_4 and evaporated at reduced pressure to give **7b** (16 mg, quantitative yield) as colorless crystals, mp 188-192 °C (hexane). IR (KBr) ν: 2970 (s), 2924 (s), 2868 (s), 1457 (s), 1382 (m), 1311 (m), 1281 (m), 1261 (m), 1157 (s), 1134 (s), 1073 (m), 1003 (m), 972 (m), 950 (m), 898 (m), 794 (m), 698 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.16 (s, 12 H, 4 CH_3), 1.65 (d, J = 13.5 Hz, 8 H) and 1.96 (d, J = 13.5 Hz, 8 H) (8 CH_2). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 25.8 [CH_3, 5(6,12,13)-CH_3], 45.1 [C, C5(6,12,13)], 46.7 [CH_2, C4(7,11,14,15,16,17,18)], 71.4 [C, C1(3,8,10)]. MS (EI): m/z (%) = 301 (6), 300 ($M^{\cdot+}$, 27), 285 (M^+ - CH_3, 5), 258 (20), 257 (20), 243 (26), 242 (10), 199 (11), 191 (12), 190 (28), 185 (15), 177 (10), 175 (12), 162 (16), 151 (18), 150 [$(C_{10}H_{14}O)^{\cdot+}$, 63], 149 (53), 147 (11), 137 (10), 135 (29), 134 (24), 133 (20), 123 (19), 122 (10), 121 (18), 119 (32), 117 (13), 111 (39), 110 [$(C_7H_{10}O)^{\cdot+}$, 100], 109 (43), 108 (48), 107 (53), 106 (10), 105 (26), 95 (63), 94 (50), 93 (39), 92 (17), 91 (68), 83 (10), 82 (12), 81 (18), 79 (85), 78 (11), 77 (46), 69 (18), 68 (10), 67 (32), 65 (19), 55 (49), 53 (24). Anal. Calcd. for $C_{20}H_{28}O_2$: C, 79.95%; H, 9.40%. Found: C, 80.08%; H, 9.44%.

Reaction of 4b with dimethyldioxirane (DMD) in acetone. To a cold (- 25 °C) solution of **4b** (20.6 mg, 0.077 mmol) in CH_2Cl_2 (2 mL), was added dropwise a cold (- 25 °C) solution of DMD in acetone (0.144 M, 0.5 mL, 0.077 mmol).[7] The reaction mixture was allowed to warm to room temperature and stirred for 15 h at this temperature. The residue obtained after solvent removal analyzed by GC / MS showed to consist of a mixture of **4b / 6b / 9b** (**4b**: rt 11.0, **6b**: rt 11.8, **9b**: rt 12.4 min) in the approximate ratio of 79:13:8 (relative area by GC / MS). Treatment of this mixture with a second equivalent of DMD under similar reaction conditions gave a mixture of the same components in the approximate ratio of 38:44:18.

Significant NMR data of 8-oxa-4,5,8,12-tetramethylhexacyclo[9.2.1.1^{2,5}.1^{4,7}.1^{9,12}.0^{7,9}]heptadec-1-ene (**6b**) obtained from the spectra of the above mixture: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.18 (s, 12 H, CH_3), 1.63 (d, J = 13.5 Hz, 4 H) and 1.96 (d, J = 13.5 Hz, 4 H) [6(10,16,17)-H_2], 2.00 (d, J = 12.2 Hz, 4 H) and 2.35 (d, J = 12,2 Hz, 4 H) [3(13,14,15)-H_2]. ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 25.0 [CH_3, 4(5,11,12)-CH_3], 46.2 [C, C4(5,11,12)], 47.2 [CH_2, C6(10,16,17)], 47.9 [CH_2, C3(13,14,15)], 72.3 [C, C7(9)], 129.8 [C, C1(2)]. GC / MS (EI), rt = 11.7 min. m/z (%) = 285 (6), 284 ($M^{\cdot+}$, 25), 269 (M^+ -CH_3, 10), 227 (14), 211 (27), 210 (100), 199 (15), 195 (20), 187 (19), 186 (18), 185 (12), 175 (18), 173 (11), 171 (11), 159 (20), 157 (11), 145 (11), 135 (61), 134 (25), 133 (24), 131 (10), 123 (11), 121 (13), 119 (29), 117 (11), 110 (55), 109 (10), 107 (29), 105 (26), 95 (28), 94 (41), 93 (22), 91 (41), 81 (10), 79 (33), 77 (26), 69 (13), 67 (13), 65 (10), 55 (21), 53 (13).

2,9-Dioxaheptacyclo[10.2.1.1^{3,6}.1^{5,8}.1^{10,13}.0^{1,3}.0^{8,10}]octadecane (9a). 4a (15 mg, 0.07 mmol) was reacted with *m*-chloroperbenzoic acid as previously described for **4b**. In this way **9a** (16 mg, quantitative yield) was isolated as colorless crystals, mp 238-240 °C (hexane). IR (KBr) ν: 2953 (s), 2930 (s), 2860 (m), 1451 (s), 1318 (s), 1249 (s), 1172 (s), 1147 (s), 1109 (s), 1038 (s), 954 (s), 906 (s), 818 (s), 771 (m), 669 (s) cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.54 [d, J = 13.7 Hz, 8 H, 4(7,11,14,15,16,17,18)-Hβ], 2.21 (dd, J = 13.7 Hz, J' = 9.3 Hz, 8 H, 4(7,11,14,15,16,17,18)-Hα], 2.82 [m, 4 H, 5(6,12,13)-H]. ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 35.4 [CH, C5(6,12,13)], 37.8 [CH_2, C4(7,11,14,15,16,17,18)], 73.4 [C, C1(3,8,10)]. MS (CI, CH_4): m/z (%) = 273 (M^+ + 29, 19), 245 (M^+ +1, 72), 244 ($M^{\cdot+}$, 34), 243 (33), 228 (19), 227 (M^+ - OH, 100), 209 (10), 203 (29), 201 (13), 199 (14), 188 (12), 187 (79), 185 (19). Anal. Calcd. for $C_{16}H_{20}O_2$: C, 78.65%; H, 8.25%. Found: C, 78.77%; H, 8.38%.

2,3,4,5-Tetrachloro-8,9,14,15-tetramethylhexacyclo[12.2.1.1^{6,9}.1^{8,11}.1^{12,15}.0^{1,6}]icosa-2,4,11-triene (7b) and 2,3,4,5,12,13,14,15-octachloro-8,9,18,19-tetramethylheptacyclo[16.2.1.1^{6,9}.1^{8,11}.1^{16,19}.0^{1,6}.0^{11,16}]tetracosa-2,4,12,14-tetraene (10b). A solution of diene **4b**, (27 mg, 0.1 mmol) and 2,3,4,5-tetrachlorothiophene-S,S-dioxide (127 mg, 0.5 mmol) in anhydrous toluene (25 mL) was heated under reflux for 48 h in an argon atmosphere. The solvent was evaporated at reduced pressure to give a residue (130 mg) which was chromatographed (silica gel / hexane) to give in order of elution, pure **7b** (29 mg, 63% yield), mp > 250 °C ($CHCl_3$), and **10b** (15 mg) impurified with **7b**. The above mixture and 2,3,4,5-tetrachlorothiophene-S,S-dioxide (9 mg, 0.04 mmol) in anhydrous toluene (10 mL) was heated under reflux for 75 h in an inert atmosphere. The solvent was evaporated at reduced pressure to give pure **10b** (11 mg, 17% yield), mp > 250 °C ($CHCl_3$).

7b: IR ($CHCl_3$) ν: 2960 (s), 2857 (s), 1608 (s), 1473 (s), 1446 (s), 1382 (s), 1232 (s), 1212 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.20 (s, 12 H, 4 CH_3), 1.93 (d, J = 12.1 Hz, 4 H) and 2.44 (d, J = 12.1 Hz, 4 H) [10(13,19,20)-H_2], 2.26 (d, J = 16.5 Hz, 4 H) and 2.55 (d, J = 16.5 Hz, 4 H) [7(16,17,18)-H_2]. ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 25.3 [CH_3, 8(9,14,15)-CH_3], 47.1 [CH_2, C10(13,19,20)], 51.4 [C, C8(9,14,15)], 55.7 [CH_2, C7(16,17,18)], 59.6 [C, C1(6)], 129.5 [C, C11(12)], 140.8 [C, C2(5) or C3(4)], the other quaternary carbon was not observed. MS (EI): m/z (%) = 460 [$M^{\cdot+}$ ($^{35}Cl_2{}^{37}Cl_2$), 10], 458 [$M^{\cdot+}$ ($^{35}Cl_3{}^{37}Cl$), 20], 456 [$M^{\cdot+}$ ($^{35}Cl_4$), 16], 426 (6), 425 [M^+ - Cl, ($^{35}Cl{}^{37}Cl_2$), 25], 424 (21), 423 [M^+ - Cl, ($^{35}Cl_2{}^{37}Cl$), 74], 422 (28), 421 [M^+ - Cl ($^{35}Cl_3$), 75], 389 [$M^{\cdot+}$ - Cl - HCl ($^{37}Cl_2$), 14], 388 (21), 387 [M^+ - Cl -HCl ($^{35}Cl{}^{37}Cl$), 66], 386 (38), 385 [M^+ - Cl - HCl ($^{35}Cl_2$), 96], 384 (13), 367 (12), 365 (13), 353 (12), 351 (24), 350 (17), 349 (41), 345 (16), 343 (18), 331 (16), 327 (10), 317 (15), 315 (21), 314 (14), 313 (30), 311 (10), 309 (11), 307 (12), 305 (14), 303 (19), 301 (15), 299 (13), 297 (13), 295 (19), 294 (15), 293 (26), 292 (10), 291 (22), 288 (11), 287 (28), 285 (19), 283 (15), 282 (11), 281 (18), 280 (13), 279 (21), 278 (10), 277 (23), 275 (11), 274 (12), 273 (31), 272 (11), 271 (22), 269 (14), 268 (12), 267 (17), 266 (10), 265 (20), 264 (11), 263 (27), 262 (15), 261 (27), 260 (16), 259 (24), 258 (16), 257 (22), 256 (13), 255 (21), 254 (16), 253 (33), 252 (20), 251 (43), 250 (17), 249 (36), 248 (21), 247 (42), 246 (24), 245 (29), 239 (27), 237 (24), 227 (30), 225 (26), 217 (21), 215 (25), 213 (29), 211 (33), 203 (22), 199 (26), 187 (24), 186 (49), 185 (29), 175 (26), 173 (26), 171 (29), 165 (26), 159 (24), 157 (20), 147 (30), 145 (20), 143 (20), 141 (23), 135 (39), 134 (38), 133 (56), 131 (21), 129 (25), 128 (24), 121 (31), 119 (73), 117 (24), 115 (25), 109 (26), 107 (85), 105 (67), 95 (52), 94 (25), 93 (69), 91 (100), 81 (21), 79 (73), 77 (63), 69 (27), 67 (32), 65 (26), 55 (45), 53 (32). HRMS: Calcd.for $C_{24}H_{28}{}^{35}Cl_3{}^{37}Cl$: 458.091562. Found: 458.087820 (Δ = 3.7 mDa = 8.2 ppm).

10b: IR ($CHCl_3$) ν: 2959 (s), 2927 (s), 1604 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.30 (s, 12 H, CH_3), 2.38 (d, J = 17.0 Hz, 8 H) and 3.08 (d, J = 17.0 Hz, 8 H) [7(10,17,20,21,22,23,24)-H_2]. ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 26.9 [CH_3, 8(9,18,19)-CH_3], 52.5 [CH_2, C7(10,17,20,21,22,23,24)], 55.1 [C, C8(9,18,19)], 60.2 [C, C1(6,11,16)], 122.6 (C) y 140.2 (C), [C2(5,12,15) and C3(4,13,14)]. MS (EI): m/z (%) = 648 [$M^{\cdot+}$ ($^{35}Cl_6{}^{37}Cl_2$), 0.1], 646 [$M^{\cdot+}$ ($^{35}Cl_7{}^{37}Cl$), 0.1], 615 [M^+ - Cl, $^{35}Cl_4{}^{37}Cl_3$), 5], 613 [M^+ - Cl ($^{35}Cl_5{}^{37}Cl_2$), 11], 611 [M^+ - Cl ($^{35}Cl_6{}^{37}Cl$), 11], 609 [M^+ - Cl ($^{35}Cl_7$), 5], 579 [M^+ - 2 Cl ($^{35}Cl_3{}^{37}Cl_3$), 3], 577 [M^+ - 2 Cl ($^{35}Cl_4{}^{37}Cl_2$), 6], 575 [M^+ - 2 Cl ($^{35}Cl_5{}^{37}Cl$), 7], 573 [M^+ - 2 Cl ($^{35}Cl_6$), 3], 541 [M^+ - 2 Cl - HCl ($^{35}Cl_3{}^{37}Cl_2$), 4], 539 [M^+ - 2 Cl - HCl ($^{35}Cl_4{}^{37}Cl$), 5], 537 [M^+ - 2 Cl - HCl ($^{35}Cl_5$), 3], 289 (11), 287 (14), 285 (11), 265 (11), 263 (10), 261 (10), 255 (10), 253 (14), 251 (16), 249 (13), 247 (14), 245 (12), 241 (10), 239 (14), 237 (14), 236 (10), 235 (10), 227 (12), 233 (10), 225 (12), 219 (10), 217 (12), 215 (15), 213 (17), 211 (15), 203 (12), 201 (11), 199 (13), 197 (10), 193 (10), 189 (11), 185 (11), 181 (10), 179 (13), 178 (10), 177 (11), 167 (11), 166 (10), 165 (19), 163 (12), 153 (14), 152 (14), 151 (11), 149 (14), 143 (11), 141 (19), 139 (11), 137 (10), 129 (24), 128 (10), 127 (12), 125 (11), 123 (13), 121 (13), 119 (10), 115 (13), 111 (18), 110 (11), 109 (21), 107 (28), 105 (12), 99 (11), 98 (23), 97 (34), 96 (19), 95 (49), 94 (11), 93 (22), 91 (18), 85 (24), 84 (21), 83 (47), 82 (19), 81 (41), 79 (23), 77 (17), 73 (17), 71 (38), 70 (17), 69 (70), 68 (15), 67 (44), 60 (13), 57 (75), 56 (19), 55 (100), 54 (12), 53 (14). HRMS: Calcd. for $C_{28}H_{28}{}^{35}Cl_8$: 643.969923. Found: 643.967498 (Δ = 2.4 mDa = 3.8 ppm); Calcd. for $C_{28}H_{28}{}^{35}Cl_7{}^{37}Cl$: 645.966973. Found: 645.966733 (Δ = 0.2 mDa = 0.4 ppm). Calcd. for $C_{28}H_{28}{}^{35}Cl_6{}^{37}Cl_2$: 647.964023. Found: 647.966274 (Δ = - 2.3 mDa = - 3.5 ppm). Calcd. for $C_{24}H_{28}{}^{35}Cl_5{}^{37}Cl_3$: 649.961073. Found: 649.960859 (Δ = 0.2 mDa = 0.3 ppm).

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