

## Catalytic Hydrogenation of [2.2]Paracyclophane. Unsaturated Intermediates<sup>1</sup>

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The catalytic hydrogenation of [2.2]paracyclophane (**1**) was repeated to determine whether the claim that **1** yields an octahydro[2.2]paracyclophane (**2**) which contains a 1,4-cyclohexadienic structural unit can be substantiated. Decahydro[2.2]paracyclophane and three isomeric dienes (I–III), as well as perhydroparacyclophane, are isolated. The NMR spectra (<sup>1</sup>H and <sup>13</sup>C) of the dienes are inconsistent with the earlier proposal, and the failure of the dienes to be aromatized by treatment with DDQ indicates that the trisubstituted double bonds reside in different six-membered rings. Computations of conformational energies aid the assignment of structures to the dienes.

The hydrogenation of [2.2]paracyclophane (**1**) over reduced platinum oxide has been reported to yield a diene in which both double bonds are in the same ring, **2**.<sup>5</sup> The assigned structure was based upon the interpretation of the ultraviolet and infrared spectra and the inspection of space filling models which appeared to indicate that a structure in which the double bonds are in different rings was much more strained than the one which the authors preferred. Although no claim for the isolation of either a 1,4- or 1,3-cyclohexadiene from the catalytic hydrogenation of any aromatic hydrocarbon has been confirmed, the possibility that the unique structure of [2.2]paracyclophane might yield a 1,4-diene was plausible enough to warrant verification, even though the kinetics of hydrogenation of dialkylbenzenes indicate that the formation of a diene is the rate-controlling surface reaction.<sup>6</sup> The detection and/or isolation of cyclohexenes from the hydrogenation of aromatic hydrocarbons is well documented, although the amounts found are generally small unless the arene is appropriately substituted with bulky substituents as, for example, in 1,2- or 1,4-di-*tert*-butylbenzene.<sup>7–11</sup> More recently, conditions have been described which lead to the formation of cyclohexene as

the main initial product of hydrogenating benzene on platinum and ruthenium.<sup>12,13</sup>

We have repeated the hydrogenation of [2.2]paracyclophane under the conditions given by Cram and Allinger and have obtained three dienes, one of which has properties similar to the one they described but it does not have the structure which was proposed.<sup>5</sup> The dienes contain two symmetrically (or pseudosymmetrically) arranged double bonds which are present in different six-membered rings. On the basis of their chemical and spectral properties and with the aid of computations using various procedures, the structures of two of the isolated dienes can be assigned with some confidence and that of the third to one of two additional possibilities. The four possible formal structures (**5–8**), two of which are chiral (**5** and **7**), are represented in Scheme 1.

### Results

Upon repeating the hydrogenation of **1** dissolved in a mixture of acetic acid and ethyl acetate with reduced platinum oxide as catalyst, we isolated and characterized three dienes and one monoene (**3**). These unsaturated compounds are transformed by catalytic hydrogenation to perhydro[2.2]paracyclophane (**4**).

The dienes were designated I, II, and III according to the order of their elution from a GLC column of Carbowax 600/750 on Chromosorb W. For example, the chromatogram of a reaction mixture which contained unreduced **1** showed an additional five peaks, first the monoene followed by dienes I, II, and III, the perhydro product appearing as a shoulder on the peak for diene I. The mixture, dissolved in cyclohexane, was separated at first by chromatography on a 20% silver nitrate on alumina column. Elution with petroleum ether removed the saturated product **4**, but solvent which contained increasing amounts of benzene affected the elution of the unsaturated components, the elution order being the monoene **3**, followed by dienes II, I, and III. Later, more

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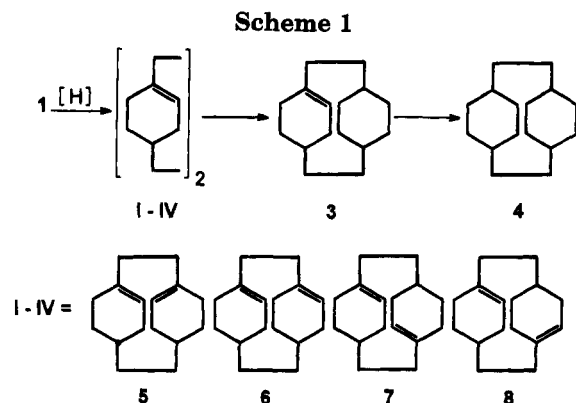
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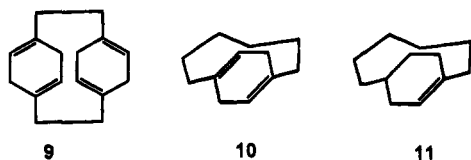
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efficient separations but with the same elution order were obtained with a column of 5% silver nitrate on silica gel (70–230 mesh) using hexane as the mobile phase. The change in the elution order of dienes I and II from that observed in the GLC on Chromosorb W indicates that  $\text{Ag}^+$  binds more tightly to diene I than to diene II and, since diene III follows I, III is even more tightly bound than is I. Accordingly, since  $\text{Ag}^+$ -olefin binding constants can be correlated with the strain in the ligand,<sup>14</sup> strain energy seems to increase in the order  $\text{II} < \text{I} < \text{III}$ .

The unsaturated intermediates have trisubstituted double bonds, as indicated by their IR spectra, e.g. adsorption in the range of 850–790  $\text{cm}^{-1}$ , none at 730–665  $\text{cm}^{-1}$ .<sup>15</sup> This was later confirmed by  $^{13}\text{C}$  NMR (see below). The dienes exhibit only end absorption in their UV spectra and accordingly the double bonds are not conjugated.

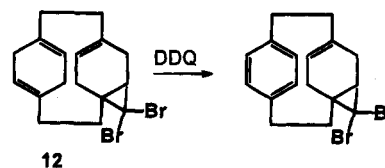
The  $^1\text{H}$  NMR spectra (250 MHz, ca. 22 °C) of the isolated compounds are reported in Table 1, including the data of model compounds 9, 10, and 11. The spectrum of diene I differs strikingly from those of dienes II and III by its much more complex pattern of the aliphatic resonance lines (ca. 1.1. to 2.5 ppm). Thus the number of magnetically nonequivalent proton sites in I is higher than in II and III. Furthermore, couplings of the olefinic protons (5.44 ppm) of I are partly resolved, whereas for II and III (5.29 and 5.18 ppm) as well as for the monoene 3 (5.76 ppm) broader unresolved singlets are observed.



The  $^{13}\text{C}$  NMR spectra (at ca. 25 °C, Table 2) of the dienes I, II, and III exhibit 8 lines each, whereas for the monoene 14 lines are resolved. The number of lines indicate that 25 °C is above the fast conformational exchange limit. Therefore the  $^{13}\text{C}$  as well as  $^1\text{H}$  chemical shifts are averaged values, since all possible minimum energy conformations (Figure 1 only gives the lowest minimum conformers for isomers 5–8) contribute more or less—corresponding to their populations—to these values. The olefinic carbon atoms of all four compounds (135.43 to 138.20 and 119.58 to 127.90 ppm) under off-

resonance decoupling<sup>16</sup> are observed as singlets and doublets, respectively, confirming that all the double bonds are trisubstituted. Thus, each of the isomers I–III has two quaternary bridgehead carbons and the monoene one (Scheme 1).

**Reaction of Dienes with DDQ.** DDQ (4,5-dichloro-3,6-dioxo-1,4-cyclohexene-1,2-dicarbonitrile) readily aromatizes tetrahydro[2.2]paracyclophane (9).<sup>17</sup> Similarly, it aromatizes the 1,4-cyclohexadienyl group in 12.<sup>18</sup> Treatment of the dienes I–III with DDQ leaves dienes I or II unaltered but causes the isomerization of diene III to diene I. Aromatization does not occur.



**Calculation of Low Energy Conformations.** Molecular mechanics calculations were performed on the four isomeric dienes 5–8. Due to the presence of the 12-membered ring, a large number of allowed conformations exist for each isomer—an example of the multiple minimum problem.<sup>19</sup> The search for the global minimum for each isomer was performed using an internal coordinate Monte Carlo method,<sup>20</sup> as implemented in the MACRO-MODEL program.<sup>21</sup> The calculations were performed using the MM3\* force field, which is the Macromodel implementation of Allinger's MM3 force field.<sup>22</sup> The lowest energy conformation found in each isomer is shown in Figure 1.

For 6, ten low energy conformations are found, including the global minimum. All are asymmetric in the sense that the two cyclohexene rings do not have identical geometries. These ten conformations come in five pairs, where each pair has the same structure except for the interchange of the cyclohexene rings. It is reasonable to conclude that any low energy conformation of 6 must be asymmetric.

For dienes 5, 7, and 8, the lowest energy conformations are symmetric. Isomer 5 has eight additional low energy conformations, six are asymmetric (four in two pairs; the pairs of the fifth and sixth conformations were simply not found among the limited number of trial conformations), and two are symmetric. Isomer 7 has additionally two asymmetric (paired) and one symmetric conformation. Isomer 8 has additionally three asymmetric (two of them paired) and one symmetric conformation. The conclusion is that symmetric conformations are certainly allowed for these isomers and that a symmetric global minimum is at least possible, even likely, for each isomer.

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Table 1. <sup>1</sup>H NMR Data of 3–7, 9, 10, and 11 (in CDCl<sub>3</sub>)

3 <sup>a</sup>	4 <sup>a</sup>	5 (≡ III) <sup>a</sup>	6 (≡ I) <sup>a</sup>	7 (≡ II) <sup>a</sup>	9 <sup>b</sup>	10 <sup>b</sup>	11 <sup>b</sup>
1.17–2.45 (m, 25H)	1.36–2.05 (m, 28H)	1.56–2.25 (m, 22H)	1.14–2.49 (m, 22H)	1.23–2.39 (m, 22H)	2.3 (m, 16H)	0.20–0.52 (m, 2H)	0.90–2.60 (m, 19H)
5.76 (br s, 1H)		5.18 (br s, 2H)	5.44 (m, 2H)	5.29 (br s, 2H)	5.3 (m, 4H)	0.68–2.80 (m, 14H)	5.66 (br d, 1H)

<sup>a</sup> 250 MHz. <sup>b</sup> 100 MHz (9,<sup>17</sup> 10,<sup>28</sup> 11<sup>29</sup>).

Table 2. <sup>13</sup>C NMR Data of 3, 7, 9, 10, and 11 (in CDCl<sub>3</sub>)

3 <sup>a</sup>	CH <sub>2</sub>	20.16, 24.06, 24.60, 27.78, 28.59 (2C), 30.37 (2C), 30.59, 31.07, 33.98
	CH	26.59, 26.76, 29.13
	olefinic C	127.90 (CH), 138.20 (>C=)
4 <sup>a</sup>	CH <sub>2</sub>	24.30 (8C), 30.87 (4C)
	CH	27.42 (4C)
5 <sup>b</sup> (≡ III)	CH <sub>2</sub>	23.98, 27.06, 27.45, 29.15, 34.36
	CH	27.30
	olefinic C	124.12 (CH), 135.43 (>C=)
6 <sup>c</sup> (≡ I)	CH <sub>2</sub>	23.40, 25.52, 28.68, 29.74, 35.39
	CH	28.22
	olefinic C	125.67 (CH), 137.62 (>C=)
7 <sup>a</sup> (≡ II)	CH <sub>2</sub>	26.51, 26.90, 29.83, 31.13, 33.27
	CH	28.72
	olefinic C	119.58 (CH), 138.03 (>C=)
9 <sup>d</sup>	CH <sub>2</sub>	38.0, 44.0
	olefinic C	125.6 (CH), 137.4 (>C=)
10 <sup>e</sup>	CH <sub>2</sub>	26.6, 29.9, 33.0, 38.1
	olefinic C	126.6 (CH), 145.3 (>C=)
11 <sup>e</sup>	CH <sub>2</sub>	24.89 (2C), 27.49, 27.61 (2C), 29.16, 29.89, 35.90, 38.38
	CH	30.33
	olefinic C	124.06 (CH), 138.23 (>C=)

<sup>a</sup> 22.63 MHz. <sup>b</sup> 62.86 MHz. <sup>c</sup> 22.49 MHz. <sup>d</sup> 25.14 MHz.<sup>17</sup> <sup>e</sup> 15.01 MHz (10,<sup>28</sup> 11<sup>29</sup>).

The calculations permit some speculations for assigning dienes I–III to the possible structures 5–8, as discussed below. However, the computed relative energies should not be considered reliable. Firstly, the calculations were performed in the absence of solvent. Secondly, each global minimum was reoptimized using additional methods, namely MM2\* (the MacroModel implementation of Allinger's MM2<sup>23</sup> force field), and the semiempirical quantum mechanical methods, MNDO,<sup>24</sup> AM1,<sup>25</sup> and PM3<sup>26</sup> implemented in MOPAC.<sup>27</sup> Even the order of relative stabilities are different for the different methods. For MM3\*, the order (most stable to least) is 8 > 5 > 7 > 6; for MM2\*, 8 > 7 > 5 > 6; for MNDO, 8 = 7 > 6 > 5; for AM1, 5 > 6 > 7 = 8; for PM3, 8 > 7 > 6 > 5. The energy differences between the lowest and highest energy isomers are quite small; they range from 1.5 (AM1) to 4.4 kcal/mol (MM3\*). Thus, it would not be prudent to base any conclusions on these relative energies.

### Discussion

That the monoene must have structure 3 is demonstrated by its <sup>13</sup>C NMR spectrum (trisubstituted double bond).

The chemical together with spectral properties suggest structures 5–8 as alternatives for dienes I–III. The

failure of aromatization of I–III by DDQ, in contrast to 9 and 12, excludes that the possibility that any of the dienes possesses a 1,3- or 1,4-cyclohexadiene moiety. Instead, the double bonds reside in different six-membered rings and, as proved by the <sup>13</sup>C spectra, are trisubstituted (>C= singlet and –CH= doublet).

The chemical evidence for double bonds in different rings is further supported by comparison with model compounds 10<sup>28</sup> and 11.<sup>29</sup> Bicyclo[6.2.2]dodeca-8,11-diene (10), because of its 1,4-cyclohexadiene moiety, is a rigid molecule as the 1,4-cyclohexadiene derivative 2 would be.<sup>30</sup> 2 and 10 have two C–H bonds pointing toward the cyclohexadiene ring, the hydrogens being in the shielding region of at least one double bond. Therefore 10 exhibits a high-field multiplet (0.20–0.52 ppm) for two protons. In contrast to 10, the monoenes 3 and bicyclo[6.2.2]dodeca-8-ene (11) as well as dienes 5–8 are more flexible molecules.<sup>30</sup> They have no hydrogens shielded by a double bond. That some hydrogens in 11 and some additional ones in 10, averaged over all minimum conformations, are closer to the double bonds (shielded or deshielded) than any in 3 and I–III can be seen from the chemical shift range of the aliphatic protons (0.68–2.80) (10) and 0.90–2.60 ppm (11) compared to 1.14–2.49 ppm for the olefins and 1.36–2.05 ppm for 4). Furthermore the <sup>13</sup>C spectrum of diene 10 differs from those of monoenes 3 and 11 and the dienes I–III in that it has the resonance line for the quaternary carbon atoms at 145.4 ppm (3, 11, and I–III at 135.4 to 138.2 ppm), indicating the strain in the 1,4-cyclohexadiene ring.

If we assume that isomerization of the dienes occurs most likely via a single 1,3-H shift, only the isomer pairs 5/6 and 7/8 are expected to isomerize with DDQ (all other double bond migrations require two or three consecutive 1,3-H shifts). Thus the DDQ-induced isomerization of III to I indicates that these two dienes are related to each other by the migration of a double bond which remains attached to the original ethano bridge; migration to the other ethano bridge would require isomerization via at least one additional less stable isomer which is likely to be a slower process.<sup>31</sup>

Since <sup>1</sup>H and <sup>13</sup>C NMR spectra at ambient temperature obviously were observed above fast exchange limits, diene I with the highest number of magnetically different proton sites is likely to be isomer 6 because all of its low energy conformations are asymmetric. If so, it follows that diene III is isomer 5 since it is isomerized by DDQ to diene I.

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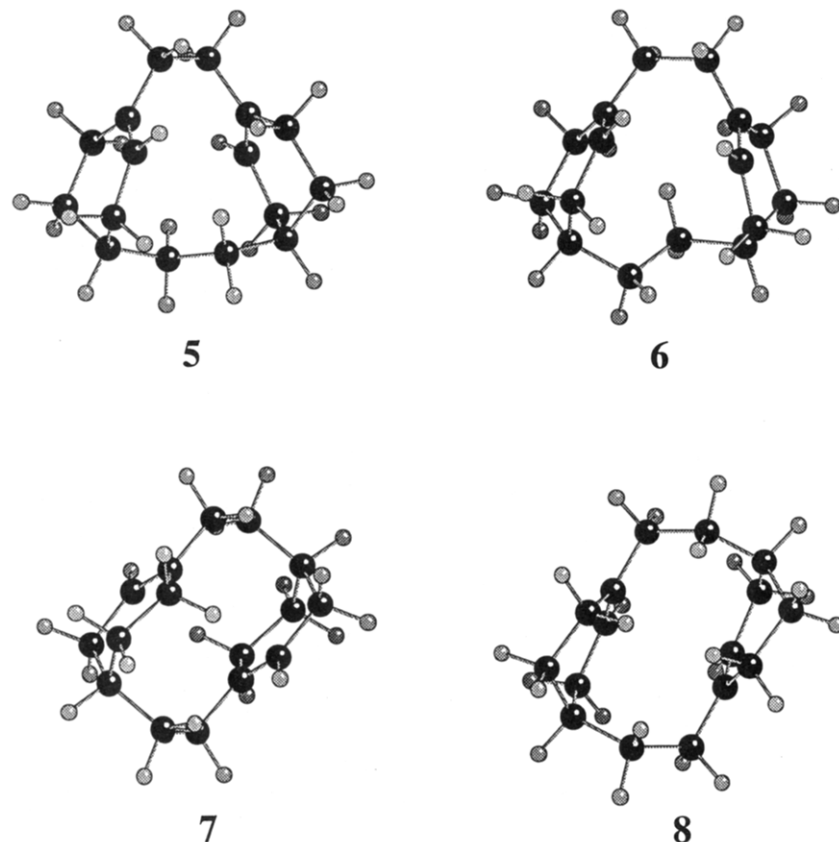


Figure 1. Lowest energy conformations of dienes 5–8.

Inspection of molecular models of isomer pair 7/8 indicates that in 8 one olefinic proton, directly above the double bond of the other cyclohexene ring, should be shifted to high field (as in 10). In 7 the two double bonds are parallel and above each other. Since a high-field proton for II is not observed, it follows that it is isomer 7. The high-field shift of the  $-\text{CH}=\text{C}$  carbons of 7 (119.58 compared to 124.12–127.90 for 3, 5, and 6) could account for the position of the double bonds above each other.

Summarizing,  $^{13}\text{C}$  NMR spectroscopy proves structure 3 for the monoene and oxidation results with DDQ as well as NMR spectroscopy indicate that none of the dienes is a 1,3- or 1,4-cyclohexadiene derivative. The tentative assignment (without direct spectroscopic proof) for the dienes is I  $\equiv$  6, II  $\equiv$  7, and III  $\equiv$  5. Molecular mechanics and semiempirical quantum mechanical calculation indicate only small energy differences between the isomeric dienes and all their minimum energy conformations. Nevertheless, a qualitative inspection of bond and torsion angles and bond lengths in the isomeric minimum energy conformations 5 to 8 suggests the order of stability 5  $\sim$  6 < 7  $\sim$  8, which is in agreement with results from MM2\*, MNDO, and PM3. This order of stability also is in agreement with relative binding constants to  $\text{Ag}^+$  implicated by the results from chromatography.

### Experimental Section

**General.**  $^1\text{H}$  NMR spectra were recorded at 60 or 250 MHz and  $^{13}\text{C}$  NMR at 22.49, 22.63, or 62.86 MHz at ambient temperature (ca. 22 and 25  $^\circ\text{C}$ , respectively). GLC separations were accomplished with an instrument equipped with a hydrogen flame detector. Hydrogenations were done using a Parr low pressure hydrogenation apparatus. Melting points

were corrected using known compounds. Microanalyses were performed by Micro Tech-Laboratories, Skokie, IL.

**Analytical Chromatography.** A column 10 ft by  $1/8$  in. was packed with 2 $1/2\%$  Carbowax 600 and 2 $1/2\%$  Carbowax 750 on Chromosorb W (60/80). At 115  $^\circ\text{C}$  and a flow rate of 25 mL  $\text{min}^{-1}$  of He, this column separated the reaction mixture into five components (one of which was a shoulder on the second peak and identified as the perhydro[2.2]paracyclophane (4)) and starting material. Retention times for all components but starting material were 4 h.

**[2.2]Paracyclophane (1).** The starting material was obtained from Friton Labs. It was a white crystalline material with a melting point of 280–284  $^\circ\text{C}$ .  $^1\text{H}$  NMR (60 MHz,  $\text{CCL}_4$ )  $\delta$  2.99 (s, 8H), 6.26 (s, 8H). UV (cyclohexane) ( $\lambda_{\text{max}}$ , nm (log  $\epsilon$ )) 226 (4.15).

**Decahydro- and Octahydro[2.2]paracyclophanes (Dienes I–III).** Paracyclophane (0.80 g,  $3.8 \times 10^{-3}$  mol) dissolved in a mixture of glacial acetic acid (50 mL) and ethyl acetate (100 mL) was hydrogenated over platinum oxide (300 mg,  $1.3 \times 10^{-3}$  mol) for 6 to 12 h at an initial pressure of 10 psig (1.7 atm). Cyclohexane (100 mL) was added to the reaction mixture and the catalyst filtered. The reaction mixture was neutralized with aqueous sodium hydroxide. The organic layer was separated and dried over sodium sulfate. The solvent was stripped and the resulting solid was dissolved in cyclohexane and placed on a 20%  $\text{AgNO}_3/\text{Al}_2\text{O}_3$  (basic) column, 22 cm by 1.2 cm (o.d.). The column was eluted with 250 mL of petroleum ether and then 200 mL each of mixtures of petroleum ether and benzene, respectively, 97%–3%, 75%–25%, 50%–50%, 25%–75%, and 300 mL of benzene. Twenty-five milliliter fractions were collected. The solvent was evaporated and the fractions were analyzed by GLC; those containing pure compounds were sublimed (80  $^\circ\text{C}$ , 2 mmHg) and analyzed further as described below. A GLC analysis of the crude product obtained after 6 h showed ca. 2% unchanged paracyclophane and, of the hydrogenation products, 12% 3, 62% diene I, 10% diene II, and 17% diene III.

**Decahydro[2.2]paracyclophane (tricyclo[8.2.2.2 $^{4,7}$ ]-hexadec-4-ene, 3)** is the first unsaturated compound which

follows the elution of the perhydro product **4** from the AgNO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> column. To obtain a quantity larger than that found in the above procedure, the quantities of reactants were halved and the hydrogenation proceeded for 15 h initially at 30 psig (~2.5 atm) of hydrogen. The material, which has a retention time corresponding to the first peak of the mixture's GLC, was collected and sublimed (80 °C and 2 mmHg) to yield monoene **3**, 105 mg (25%), mp 100–102 °C. IR (CS<sub>2</sub>) 3035 (w), 795 (m), 890 (m) cm<sup>-1</sup>. UV (cyclohexane) end absorption only; (λ, nm (log ε)) 210 (3.45), 220 (3.19), 230 (2.56). This compound appears to absorb oxygen readily as indicated by the elemental analysis which yields the correct C:H ratio but the percent of C and H diminish with time. The <sup>1</sup>H NMR (60 MHz) spectrum of a sample, obtained shortly after it was isolated, indicates that the signal of the vinyl proton, δ 5.76, has the relative intensity expected for the monoene. Anal. Calcd for C<sub>16</sub>H<sub>26</sub>: C, 88.00; H, 12.00; C/H, 7.33. Found: (5 days after preparation) C, 83.46; H, 11.28; C/H, 7.40; (3 days later) C, 79.43; H, 10.62; C/H, 7.48.

**Octahydro[2.2]paracyclophane (diene II, tricyclo[8.2.2.2<sup>4,7</sup>]hexadeca-4,10-diene, 7).** This compound elutes from the AgNO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> column after the monoene **3**, and its GLC chromatogram has a retention time corresponding to that of the third peak of the mixture; mp 90–96 °C. IR (CS<sub>2</sub>) 1665 (very weak), 802 (m), 870 (m) cm<sup>-1</sup>. UV (hexane) end absorption only; (λ, nm (log ε)) 210 (3.92), 215 (3.72), 220 (3.44), 230 (2.70). Anal. Calcd for C<sub>16</sub>H<sub>24</sub>: C, 88.82; H, 11.18. Found: C, 88.59; H, 11.46.

**Octahydro[2.2]paracyclophane (diene I, meso-tricyclo[8.2.2.2<sup>4,7</sup>]hexadeca-4,12-diene, 6).** This white substance elutes from the AgNO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> column after diene II and shows a single peak with a retention time the same as that of the second peak of the mixture's GLC chromatogram. This was the major component; mp 93–96 °C. IR (CS<sub>2</sub>) 1670 (m), 808 (m), 895 (m) cm<sup>-1</sup>. UV (*n*-hexane) end absorption only; (λ, nm (log ε)) 210 (3.81), 215 (3.60), 220 (3.27), 230 (2.48). Anal. Calcd for C<sub>16</sub>H<sub>24</sub>: C, 88.82; H, 11.18. Found: C, 88.83; H, 11.38.

**Octahydro[2.2]paracyclophane (diene III, dl-tricyclo[8.2.2.2<sup>4,7</sup>]hexadeca-4,12-diene, 5).** This compound follows diene I from the AgNO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> column and has a retention time corresponding to the fourth peak in a GLC chromatograph of a mixture of the hydrogenation products. A sample which was 80% diene III and 20% diene I exhibited only end absorption in the UV. A pure sample, isolated later by chromatography on a 5% AgNO<sub>3</sub>/SiO<sub>2</sub> column and eluted with hexane, gave the spectroscopic data in Tables 1 and 2.

**Perhydro[2.2]paracyclophane (tricyclo[8.2.2.2<sup>4,7</sup>]hexadecane, 4).** To obtain a larger quantity of **4**, paracyclophane (0.200 g, 9.6 × 10<sup>-4</sup> mol) dissolved in glacial acetic acid (200 mL) was hydrogenated over platinum oxide (1.0 g, 4.4 × 10<sup>-3</sup> mol) for 60 h under 75 psig (~6 atm) of hydrogen. The separation of the hydrogenation products from the catalyst and solvent proceeded as above but the crude, white solid was dissolved in petroleum ether and placed on a basic alumina column. It was eluted with petroleum ether and the first 40 mL were collected. The solvent was evaporated and the

product sublimed (100 °C, 6 mm) to yield 53 mg (25%) of a white solid, mp 111–112 °C. IR (KBr) 3040 (m), 2920 (s), 1445 (m) cm<sup>-1</sup>. UV (cyclohexane) blank. Anal. Calcd for C<sub>16</sub>H<sub>28</sub>: C, 87.20; H, 12.80. Found: C, 87.02; H, 13.08.

**Experiments with DDQ: Dehydrogenation of Tetrahydroparacyclophane (9).** A mixture of DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) (220 mg, 0.97 mmol) and **9** (100 mg, 0.47 mmol) in 30 mL of benzene was stirred at room temperature for 1 h. The mixture was then passed through 20 g of neutral alumina using benzene (100 mL) as the eluent. The benzene solutions were combined and evaporated under reduced pressure to give 93 mg (93%) of a white solid. The compound was identified as [2.2]paracyclophane by comparison of its IR and <sup>1</sup>H NMR spectra with those of an authentic sample.

**Attempted Dehydrogenation of Dienes I, II, and III.** These experiments were carried out in NMR tubes and monitored by their <sup>1</sup>H NMR spectroscopy. DDQ (10 mg) and diene (10 mg) were mixed with 0.5 mL of C<sub>6</sub>D<sub>6</sub> containing TMS. In these experiments, diene III was converted to diene I within 10 min; a mixture of diene III and diene II was converted to a mixture of diene I and diene II within 5 min. The mixture of diene II and diene I and pure diene I remained unchanged after 24 h. None of these experiments gave rise to an aromatic product.

**Calculations.** The molecular mechanics calculations were performed using the MACROMODEL program, version 3.5a,<sup>21</sup> on a Silicon Graphics Indigo R4000 workstation. In the conformational search, a total of 100 trial conformations were generated for each of dienes **5**–**8**, and their energies were minimized. Duplicate conformations and those with energies 50 kJ/mol above the current global minimum were rejected. The calculations employed a cutoff scheme for nonbonded interactions where electrostatic interactions were truncated at 20 Å and van der Waals interactions at 8 Å.

The semiempirical calculations (MNDO, AM1, PM3) were performed using the MOPAC program,<sup>27</sup> also on the Silicon Graphics workstation.

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