

which connects the molecules related by a twofold screw axis parallel to the *b* axis. The N-H group of Gly<sup>3</sup> points also to the C=O group of Gly<sup>4</sup>, but the distance of N...O, 3.37 Å, is too long for hydrogen bonding. One more hydrogen donor available, N-H of Val<sup>1</sup>, does not participate in any hydrogen bonds; its closest intermolecular approach is N(1)...O(2S), 3.56 Å.

There are two rather short intermolecular C-H...O interactions, (Pro<sup>2</sup>)C<sup>β</sup>-H...O=C(Gly<sup>3</sup>) and (Gly<sup>4</sup>)C<sup>α</sup>-H...O=C(Boc). Their geometries shown in Table IV are favorable for weak hydrogen bonds. These might be considered as hydrogen bonds.

All the other intermolecular contacts correspond to van der Waals interactions.

**Solvent Molecule.** The solvent ethyl acetate molecule seems to have an appropriate dimension to the crystal packing, and plays a role of space filling in the crystal. This is well shown by the fact that only an ethyl acetate solution gives a crystal, while neither an ethanol nor an acetone solution could give a crystal.

As shown in Figure 4 the ethyl acetate molecule, however, is very loosely packed in the crystal, and is not involved in any hydrogen bonds. Thus the fugacity of the solvent molecule from the crystal may not be negligible. This may explain first the unusually large temperature factors due to the nonstoichiometric occupancy of the solvent molecule, and second the significant decrease of the diffraction intensities during the X-ray experiment. The loose packing may explain also an evidence of the partially disordered structure of the solvent molecule with the head and tail interchanged at the same site.

## Conclusion

The X-ray analysis has established the crystal structure of Boc-Val-Pro-Gly-Gly-OBzl, showing that the basic conformation of this peptide is a type II β turn with Pro<sup>2</sup>-Gly<sup>3</sup> at the corner. This feature is the same as that suggested for Boc-Val-Pro-Gly-Gly-OMe<sup>7</sup> and the high polymer of the tetrapeptide<sup>24</sup> from NMR and conformational energy calculations. Thus for this tetrapeptide unit of elastin, the β turn structure has been shown to be a favorable conformation in crystal as well as in solution. On the other hand we previously reported that the pentapeptide, Boc-Val-Pro-Gly-Val-Gly-OH, is not in a β turn conformation but in an extended form, making an antiparallel β sheet structure.<sup>10</sup> It is worth noting that the molecular conformation is thoroughly changed by an insertion of a Val residue. Thus for the pentapeptide unit, a β turn structure does not seem to be a preferred conformation at least in the crystalline state. At the present stage of the structural studies of the repeating peptides in elastin, both of the β sheet and β turn conformations are said to play important parts in the structure and the function of elastin.

**Supplementary Material Available:** Listing of the observed and calculated structure factors and anisotropic thermal parameters of nonhydrogen atoms (16 pages). Ordering information is given on any current masthead page.

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## A Study of the Synthesis and Properties of [2<sub>5</sub>](1,2,3,4,5)Cyclophane<sup>1</sup>

Paulo F. T. Schirch and V. Boekelheide\*

Contribution from the Department of Chemistry, University of Oregon, Eugene, Oregon 97403.  
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**Abstract:** As part of an overall program investigating the behavior of π-electron systems forced into close proximity, a synthesis of [2<sub>5</sub>](1,2,3,4,5)cyclophane (**11**) has been accomplished in six steps, as shown in Scheme I, with an overall yield of 31%. The key to the successful synthesis was the formation of four bridges in a single step, via *o*-xylylene-type intermediates, during gas-phase pyrolysis of 1,2-bis[(1,2,4,5)dicyclobutaphenyl]ethane (**10**). X-ray crystallographic analysis of [2<sub>5</sub>](1,2,3,4,5)cyclophane (**11**) shows the mean interdeck distance between benzene rings to be 270 pm. From photoelectron spectral studies the first ionization energy of **11** is found to be 7.67 eV. [2<sub>5</sub>](1,2,3,4,5)Cyclophane is thermally stable, showing no evidence of bridge cleavage even on heating at 350 °C. Electrophilic substitution, bromination and Rieche formylation occur readily with **11** and in high yield. Chloromethylation of **11** is anomalous, though, giving 4-formyl-13-methyl[2<sub>5</sub>](1,2,3,4,5)cyclophane (**16**). Conversion of **16** to the corresponding tosylhydrazone **18**, followed by treatment with base and irradiation, gives superphane (**19**) in 80% yield, providing a useful alternate synthesis for this important member of the [2<sub>*n*</sub>]cyclophane series. Both dicyanoacetylene and perfluoro-2-butyne undergo normal Diels-Alder additions with [2<sub>5</sub>](1,2,3,4,5)cyclophane to give the corresponding barrellene adducts **20** and **21**. Treatment of [2<sub>5</sub>](1,2,3,4,5)cyclophane (**11**) with bis(η<sup>6</sup>-*p*-cymene)dichlorodi-μ-chloro-diruthenium(II), or bis(η<sup>6</sup>-hexamethylbenzene)dichlorodi-μ-chloro-diruthenium(II), readily gives the corresponding ruthenium complexes **22** and **23**, whereas irradiation of a solution of **11** and (η<sup>6</sup>-*p*-xylene)(η<sup>5</sup>-cyclopentadienyl)iron(II) hexafluorophosphate gives the corresponding iron complex (**24**).

The discovery that the gas-phase dimerization of benzocyclobutenes can be employed to synthesize multibridged cyclophanes<sup>2</sup> led to a rapid elaboration of all of the remaining, previously unknown, symmetrical [2<sub>*n*</sub>]cyclophanes.<sup>3</sup> The properties of these molecules are of particular interest because of the insight they provide regarding the effect of forcing two benzene π-electron

clouds together face to face at very short distances. In the previous paper of this series, we described the synthesis and properties of [2<sub>6</sub>](1,2,3,4,5,6)cyclophane (**19**, superphane), the ultimate in multibridging of a [2<sub>*n*</sub>]cyclophane.<sup>4</sup> In the present paper we describe a synthesis and some of the properties of [2<sub>5</sub>](1,2,3,4,5)cyclophane (**11**), the penultimate member of the series.

As an extension of our approach to utilize the dimerization of benzocyclobutene units to provide multibridged cyclophanes, the

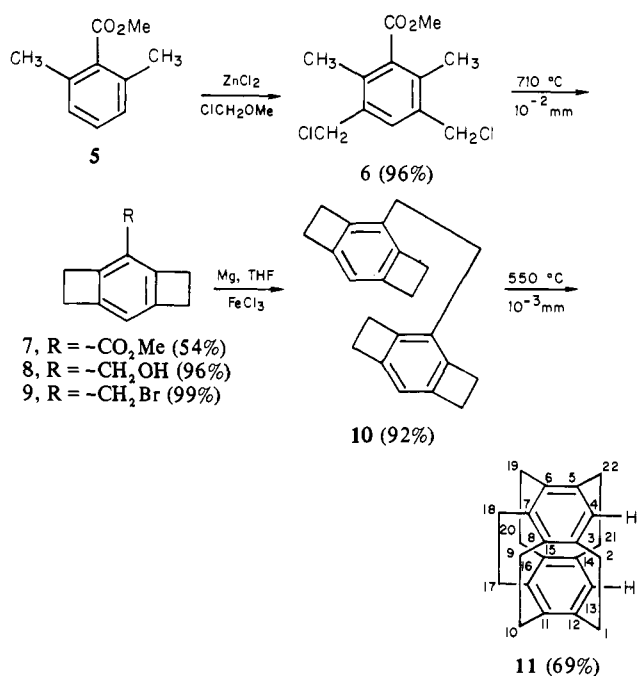
(1) For a preliminary account for this work, see: Schirch, P. F. T.; Boekelheide, V. *J. Am. Chem. Soc.* 1979, 101, 3125.

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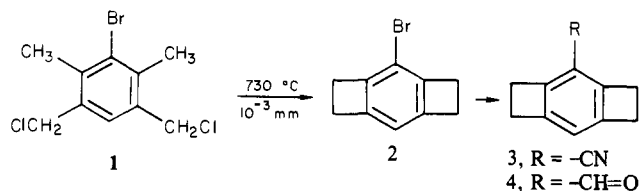
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## Scheme I



obvious precursor of [2<sub>5</sub>](1,2,3,4,5)cyclophane (11) is 1,2-bis-[1,2:4,5]dicyclobutaphenyl]ethane (10). Since dimerization of 3-bromomethylbenzo[1,2:4,5]dicyclobutene (9) via a Grignard coupling reaction would be expected to give 10 in good yield, our attention turned to the preparation of 9.

In exploring the general procedure of Gray et al.,<sup>5</sup> we found that gas-phase pyrolysis of bis(chloromethyl)mesitylene gave 3-methylbenzo[1,2:4,5]dicyclobutene in very poor yield. However, a similar gas-phase pyrolysis of 2,6-dimethyl-3,5-bis(chloromethyl)bromobenzene (1) readily gave 3-bromobenzo[1,2:4,5]dicyclobutene (2) in 53% yield. The further conversion of 2 to the corresponding cyanide 3, via the von Braun reaction, was successful; also 3 on reduction with diisobutylaluminum hydride readily gave the desired aldehyde 4. Unfortunately, the yield in the von Braun reaction was only 35%, and so we turned to an alternate route that might be easier to accomplish on a larger scale.



As shown in Scheme I, chloromethylation of methyl 2,6-dimethylbenzoate<sup>6</sup> (5) gave the corresponding bis(chloromethyl) derivative 6 in 96% yield. Gas-phase pyrolysis of 6 proceeded in 54% yield to the desired 3-carbomethoxybenzo[1,2:4,5]dicyclobutene (7). Lithium aluminum hydride reduction of 7 then gave the alcohol 8 in 96% yield, and this in turn was converted to the bromomethyl derivative 9 with phosphorus tribromide in 99% yield. Treatment of 9 with 0.5 equiv of magnesium in tetrahydrofuran followed by addition of a few milligrams of anhydrous ferric chloride led, as expected, to the desired dimer 10 in 92% yield. Gas-phase pyrolysis of 10 at 550 °C then gave [2<sub>5</sub>](1,2,3,4,5)cyclophane (11) in 69% yield, a remarkable reaction in which four bridges are introduced in a single step. This six-step synthesis of [2<sub>5</sub>](1,2,3,4,5)cyclophane (11) proceeds with an overall yield of 31% and is quite feasible for preparing multigram quantities,

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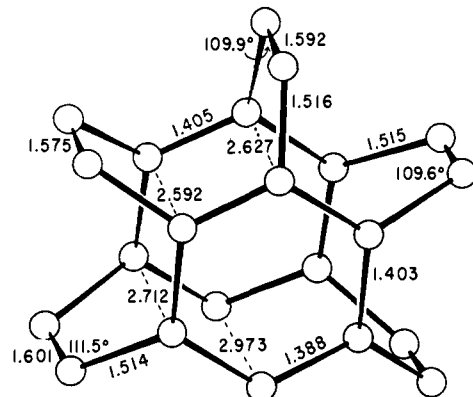


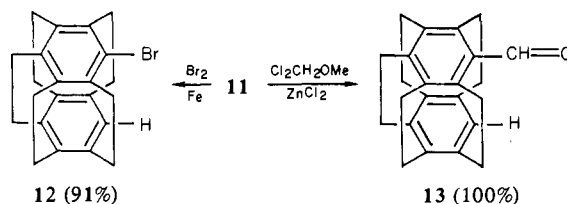
Figure 1. Geometry of [2<sub>5</sub>](1,2,3,4,5)cyclophane (11), giving bond lengths and interdeck distances (Å), determined from an X-ray crystallographic analysis.<sup>8</sup>

thus providing adequate quantities for studies of its properties.

[2<sub>5</sub>](1,2,3,4,5)Cyclophane (11) shows absorption maxima at 294 (ε, 352) and 313 nm (200). Its <sup>1</sup>H NMR spectrum has a singlet at δ 6.05 for the aromatic protons and a multiplet at δ 2.56-3.33 for the bridging methylene protons. In the mass spectrum of 11, the parent molecular ion (*m/e* 286) is the most intense signal with fragmentation peaks at 258 (loss of a bridging -CH<sub>2</sub>CH<sub>2</sub>-) and 243 (loss of -CH<sub>2</sub>CH<sub>2</sub>- and -CH<sub>3</sub>). The Raman spectrum of 11 has a symmetrical breathing vibration (Wilson Mode 1) at 578, ring stretch vibrations (Wilson Mode 8) at 1553 and 1570, and in-plane, ring stretch vibrations (Wilson Modes 6a and 6b) at 485 and 435 cm<sup>-1</sup>.

The molecular geometry of [2<sub>5</sub>](1,2,3,4,5)cyclophane, as determined by an X-ray crystallographic analysis,<sup>8</sup> is presented in Figure 1. As might be expected, the distance between decks of the benzene ring carbons bearing hydrogen (carbons 4 and 13) are farther apart (2.973 Å) than the bridged ring carbons (2.592-2.712 Å). Unexpectedly, though, the distance between decks at C<sub>7</sub>-C<sub>16</sub> is farther apart (2.627 Å) than at the adjacent positions of C<sub>8</sub>-C<sub>11</sub> and C<sub>6</sub>-C<sub>15</sub> (2.592 Å), giving a small, but definite boat shape to the benzene ring. In accord with the short distance between decks, the photoelectron spectrum of [2<sub>5</sub>](1,2,3,4,5)cyclophane has its first ionization potential at 7.67 eV, emphasizing the strong interaction of the two benzene π-electron systems.

[2<sub>5</sub>](1,2,3,4,5)Cyclophane (11) forms a 1:1 charge-transfer complex with tetracyanoethylene having its long wavelength absorption maximum at 570 nm, the shift of its charge transfer band to longer wavelengths being second only to superphane among the [2<sub>n</sub>]cyclophanes.<sup>4</sup> [2<sub>5</sub>](1,2,3,4,5)Cyclophane (11) readily undergoes electrophilic substitution, as shown by its bromination to give the corresponding monobromo derivative 12 and its formylation under Rieche conditions<sup>10</sup> to give 13.



When [2<sub>5</sub>](1,2,3,4,5)cyclophane was subjected to chloromethylation, using chloromethyl methyl ether and zinc chloride, the product was 4-methyl-13-formyl[2<sub>5</sub>](1,2,3,4,5)cyclophane (16).

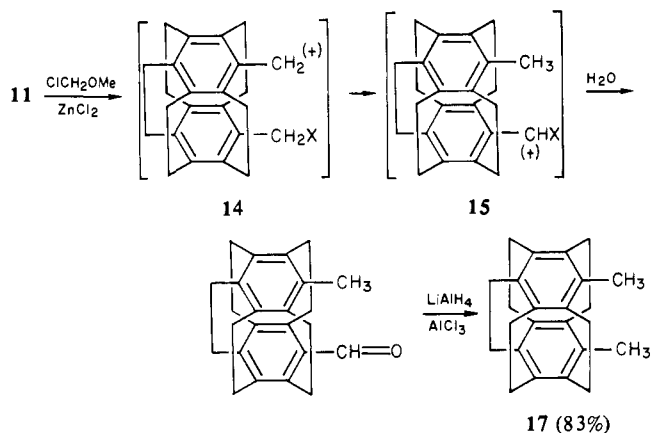
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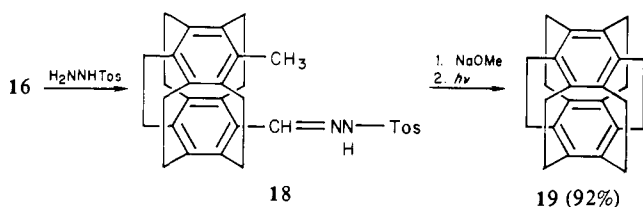
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Scheme 11



Our speculation is that an intermediate carbenium ion (**14**) undergoes transannular hydride abstraction to give a new carbenium ion (**15**) which, on hydrolysis, yields **16**. Although the formation of the methyl aldehyde **16** during attempted chloromethylation of **11** was unexpected, similar transannular carbenium ion-hydride abstractions to form gem methyl aldehydes have been recorded previously by Cram et al.<sup>11</sup> and by Gray and Boekelheide<sup>12</sup> in the [2.2]paracyclophane series. As confirmation of the structure assigned, **16** was reduced with a mixture of lithium aluminum hydride and aluminum chloride to give the known 4,13-dimethyl[2<sub>3</sub>](1,2,3,4,5)cyclophane (**17**).<sup>4</sup>

In view of the high yield (98%) observed for the formation of **16** and our past experience with the formation of bridges by carbene insertion reactions,<sup>12</sup> we investigated the possible elaboration of **16** to form superphane. Conversion of **16** to the corresponding tosylhydrazone **18**, followed by treatment with base and irradiation, gave superphane (**19**) in 82% yield. This route to superphane has advantages, both in the number of steps and in overall yield, to the original method published previously.<sup>4</sup>



Although cyclophanes have been employed as diene components in the Diels-Alder reaction, their reactivity varies widely. Whereas [2<sub>4</sub>](1,2,4,5)cyclophane is exceptionally reactive, [2.2]paracyclophane and [2<sub>3</sub>](1,2,4)cyclophane react with only certain dienophiles, and [2<sub>4</sub>](1,2,3,4)- and [2<sub>4</sub>](1,2,3,5)cyclophane, as well as superphane, are unreactive.<sup>4,12,13</sup> It was not anticipated, therefore, that [2<sub>3</sub>](1,2,3,4,5)cyclophane would undergo the Diels-Alder reaction. However, in fact, addition occurs with both dicyanoacetylene and with perfluoro-2-butyne to give the barrellene adducts **20** and **21**. There was no evidence for the formation of a 2:1 bis(barrellene) adduct in either case. Attempts to effect the Diels-Alder reaction with dimethyl acetylenedicarboxylate or with phenyl vinyl sulfoxide were unsuccessful.

In view of the methods developed recently for preparing transition metal complexes of [2.2]paracyclophane,<sup>14,15</sup> similar experiments were investigated with [2<sub>3</sub>](1,2,3,4,5)cyclophane.

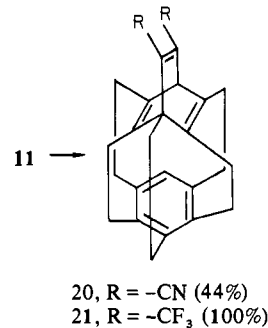
(11) Cram, D. J.; Hornby, R. B.; Truesdale, E.; Reich, H. J.; Delton, M. H.; Cram, J. M. *Tetrahedron* **1974**, *30*, 1757-68.

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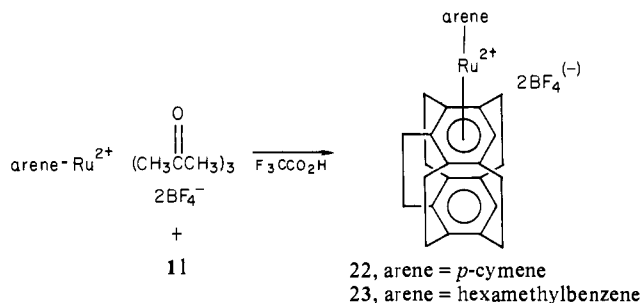
(13) Murad, A. F.; Kleinschroth, J.; Hopf, H. *Angew. Chem.* **1980**, *92*, 388-9; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 389-90.

(14) Laganis, E. D.; Finke, R. G.; Boekelheide, V. *Tetrahedron Lett.* **1980**, *21*, 4405-8.

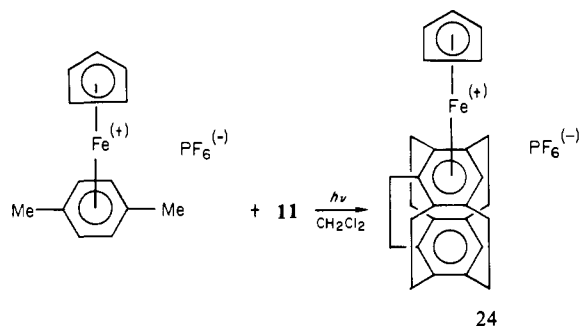
(15) Laganis, E. D.; Finke, R. G.; Boekelheide, V. *Proc. Natl. Acad. Sci. U.S.A.*, in press.



Treatment of a solution of bis(*p*-cymene)dichlorodi- $\mu$ -chlorodiruthenium(II) with silver perchlorate followed by addition of trifluoroacetic acid and [2<sub>3</sub>](1,2,3,4,5)cyclophane readily gave the ruthenium transition metal complex **22** in 77% yield. Similarly, the corresponding ruthenium transition metal complex **23**, where *p*-cymene is replaced by hexamethylbenzene, formed in 94% yield.

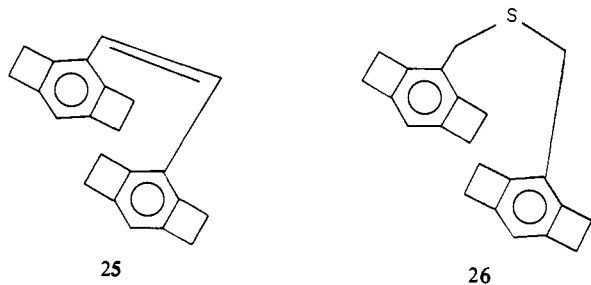


Irradiation of a solution of ( $\eta^6$ -*p*-xylene)( $\eta^5$ -cyclopentadienyl)iron(II) hexafluorophosphate and [2<sub>3</sub>](1,2,3,4,5)-cyclophane in dichloromethane led to the iron transition-metal complex **24** in 68% yield.



Before concluding, certain unsuccessful experiments attempted with [2<sub>3</sub>](1,2,3,4,5)cyclophane should be noted. For example, despite its high strain energy [2<sub>3</sub>](1,2,3,4,5)cyclophane is quite stable thermally and is recovered unchanged after prolonged periods of heating at 350 °C in *p*-diisopropylbenzene. Attempts to effect a Birch reduction of [2<sub>3</sub>](1,2,3,4,5)cyclophane, using lithium in liquid ammonia, led only to recovery of the unchanged starting material. When [2<sub>3</sub>](1,2,3,4,5)cyclophane was subjected to the conditions (concentrated H<sub>2</sub>SO<sub>4</sub> and zinc) of the mysterious bridge sulfur-insertion reaction encountered with superphane,<sup>4</sup> extensive polymerization occurred but no useful product could be isolated. Although [2<sub>3</sub>](1,2,3,4,5)cyclophane is not soluble in the common solvents used for catalytic hydrogenation and so could not be studied under favorable conditions, no uptake of hydrogen was observed on attempted catalytic hydrogenation of [2<sub>3</sub>](1,2,3,4,5)cyclophane over a palladium-on-charcoal catalyst in dichloromethane solution.

The remarkable formation of four bridges in a single step during pyrolysis of **10** led us to examine similar pyrolyses with other precursors that might yield an actual, or potential, olefinic bridge. For this purpose, the olefin **25** and the sulfide **26** were prepared. Surprisingly, though, neither of these compounds gave any useful product on attempted high-vacuum pyrolyses.



### Experimental Section<sup>16</sup>

**3-Methylbenzo[1,2,4,5]dicyclobutene.** A 3.73-g sample of bis(chloromethyl)mesitylene<sup>17</sup> was sublimed at  $10^{-2}$  mm Hg pressure into the hot zone (720 °C) of a quartz pyrolysis tube while collecting the exit gases on a cold finger held at  $-20$  °C. When the pyrolysis was complete, the material on the cold finger was removed by washing with chloroform and the combined chloroform washings were concentrated. Chromatography of the residual solid over silica gel, using hexane for elution, gave a white solid that was purified further by gas chromatography over a Carbowax column. This led to 210 mg (4.9%) of white crystals; mp 53–54 °C; <sup>1</sup>H NMR  $\delta$  6.64 (1 H, s, ArH), 3.05 (8 H, s, CH<sub>2</sub>), 2.05 (3 H, s, CH<sub>3</sub>); mass spectrum, *m/e* 144, 129, 115, 91, 63; molecular weight calcd for C<sub>11</sub>H<sub>12</sub> 144.093, found (high-resolution mass spectrum) 144.091.

**2,6-Dimethyl-3,5-bis(chloromethyl)bromobenzene (1).** A mixture of 7.0 g of 2-bromo-*m*-xylene,<sup>18</sup> 8 g of anhydrous zinc chloride, and 150 mL of chloromethyl methyl ether was stirred at room temperature for 30 h and then poured into 200 mL of ice water. The white solid, which separated, was collected by filtration and dried to give 10.67 g (100%) of white crystals; mp 113–115 °C; <sup>1</sup>H NMR,  $\delta$  7.22 (1 H, s, ArH), 4.60 (4 H, s, CH<sub>2</sub>Cl), 2.51 (6 H, s, CH<sub>3</sub>); mass spectrum, *m/e* 284, 282, 280, 249, 247, 245, 211, 209. Anal. (C<sub>10</sub>H<sub>11</sub>BrCl<sub>2</sub>) C, H.

**3-Bromobenzo[1,2,4,5]dicyclobutene (2).** A sample of 803 mg of 2,6-dimethyl-3,5-bis(chloromethyl)bromobenzene (1) was sublimed at  $5 \times 10^{-3}$  mm Hg pressure into the hot zone (730 °C) of a quartz pyrolysis tube while collecting the pyrolysate on a condenser held at  $-30$  °C. When the pyrolysis was complete, the condensate was removed by washing with chloroform and the combined chloroform washings were concentrated. The residual solid was chromatographed over a basic alumina column, using a 1:1 mixture of ether and benzene for elution. Sublimation of the resulting solid gave 317 mg (53%) of white crystals; mp 74–76 °C; <sup>1</sup>H NMR  $\delta$  6.73 (1 H, s, ArH), 3.09 (8 H, s, CH<sub>2</sub>); mass spectrum, *m/e* 210, 208, 129, 128, 127; molecular weight calcd for C<sub>10</sub>H<sub>9</sub><sup>79</sup>Br 207.988, found (high-resolution mass spectrum) 207.988.

**3-Cyanobenzo[1,2,4,5]dicyclobutene (3).** A mixture of 1.62 g of 3-bromobenzo[1,2,4,5]dicyclobutene (2) and 5.0 g of cuprous cyanide in 100 mL of *N*-methyl-2-pyrrolidone was heated at 115 °C with stirring under a nitrogen atmosphere for 4 days. The mixture was then poured into ammonium hydroxide and ice. When the resulting mixture had been allowed to stand overnight in a refrigerator, the solid which had separated was collected by filtration and dried. It was then placed in a Soxhlet apparatus and extracted with dichloromethane. Concentration of the dichloromethane extract gave a solid which was chromatographed over silica gel, using a 1:1 mixture of hexane and benzene for elution. The solid from the main fraction of eluate was recrystallized from ether to give 414 mg (35%) of white crystals; mp 102–103 °C; <sup>1</sup>H NMR  $\delta$  6.94 (1 H, s, ArH), 3.20 (8 H, m, CH<sub>2</sub>); mass spectrum, *m/e* 155, 154, 140, 127, 115; molecular weight calcd for C<sub>11</sub>H<sub>9</sub>N 155.073, found (high-resolution mass spectrum) 155.073.

**3-Formylbenzo[1,2,4,5]dicyclobutene (4).** To a solution of 155 mg of 3-cyanobenzo[1,2,4,5]dicyclobutene (3) in 100 mL of benzene was added with stirring 1.5 mL of a 20% solution of diisobutylaluminum hydride in hexane. After the resulting mixture had been stirred at room temperature for 1 h, it was decomposed by successive additions, with stirring, of 5 mL of methanol, 5 mL of a 1:1 mixture of methanol and water, and

100 mL of water. The mixture was then acidified with 10% aqueous hydrochloric acid and extracted with ether. After the ether extract had been dried, it was concentrated and the resulting white solid was recrystallized from benzene to give 131 mg of white crystals; mp 86–88 °C; <sup>1</sup>H NMR  $\delta$  10.08 (1 H, s, CH=O), 6.95 (1 H, s, ArH), 3.27 (8 H, m, CH<sub>2</sub>); IR (KBr pellet)  $\nu_{\max}$  1680 cm<sup>-1</sup> (–CH=O); mass spectrum, *m/e* 158, 130, 129, 128, 127, 105, 87; molecular weight calcd for C<sub>11</sub>H<sub>10</sub>O 158.073, found (high-resolution mass spectrum) 158.074.

**Methyl 2,6-Dimethyl-3,5-bis(chloromethyl)benzoate (6).** A mixture of 60.9 g of methyl 2,6-dimethylbenzoate<sup>6</sup> and 33 g of anhydrous zinc chloride in 100 mL of chloromethyl methyl ether was stirred at room temperature for 24 h before pouring it into 1 L of ice water. The resulting white precipitate was collected by filtration and then washed successively with ice water, an aqueous 10% solution of sodium bicarbonate, and water. Drying of the product under vacuum then gave 152.81 g (96%) of white crystals; mp 106.0–106.5 °C; <sup>1</sup>H NMR  $\delta$  7.32 (1 H, s, ArH), 4.57 (4 H, s, CH<sub>2</sub>Cl), 3.94 (3 H, s, OCH<sub>3</sub>), 2.32 (6 H, s, CH<sub>3</sub>); IR (CHCl<sub>3</sub>)  $\nu_{\max}$  1735 cm<sup>-1</sup> (C(=O)OCH<sub>3</sub>); mass spectrum, *m/e* 262, 260, 225, 192, 129, 128. Anal. (C<sub>12</sub>H<sub>14</sub>O<sub>2</sub>Cl<sub>2</sub>) C, H.

**3-Carbomethoxybenzo[1,2,4,5]dicyclobutene (7).** A sample of 22.5 g of methyl 2,6-dimethyl-3,5-bis(chloromethyl)benzoate was placed in the preheater zone of a pyrolysis apparatus and slowly sublimed at  $10^{-3}$  mm Hg pressure into the hot zone (710 °C) while collecting the pyrolysate on a condenser held at  $-20$  °C. The product was washed from the condenser with chloroform and the chloroform washings were concentrated. The resulting yellow solid was chromatographed over silica gel, using a 1:1 mixture of benzene and hexane for elution. The product from the main fraction of eluate was sublimed to give 8.18 g (54%) of white crystals. Recrystallization of this from methanol gave white crystals; mp 98.5–99.5 °C; <sup>1</sup>H NMR  $\delta$  6.90 (1 H, s, ArH), 3.87 (3 H, s, OCH<sub>3</sub>), 3.38–3.04 (8 H, m, CH<sub>2</sub>); IR (CHCl<sub>3</sub>)  $\nu_{\max}$  1712 cm<sup>-1</sup> (C(=O)OCH<sub>3</sub>); mass spectrum, *m/e* 188, 173, 145, 129, 128, 117, 115. Anal. (C<sub>12</sub>H<sub>12</sub>O<sub>2</sub>) C, H.

**3-Hydroxymethylbenzo[1,2,4,5]dicyclobutene (8).** To a slurry of 530 mg of lithium aluminum hydride in 100 mL of ether there was added dropwise with stirring a solution of 1.68 g of 3-carbomethoxybenzo[1,2,4,5]dicyclobutene (7) in 100 mL of ether. After the addition was complete, the mixture was stirred at room temperature for 4 h and then decomposed by dropwise addition of a saturated aqueous solution of sodium sulfate. The ether layer was separated, washed with water, dried, and concentrated. Recrystallization of the residual solid from ether gave 1.37 g (96%) of white crystals; mp 109–110 °C; <sup>1</sup>H NMR  $\delta$  6.72 (1 H, s, ArH), 4.63 (2 H, s, OCH<sub>2</sub>), 3.13 (8 H, s, CH<sub>2</sub>), 2.28 (1 H, d, *J* = 5 Hz, OH); mass spectrum, *m/e* 160, 131, 117, 115, 91. Anal. (C<sub>11</sub>H<sub>10</sub>O) C, H.

**3-Bromomethylbenzo[1,2,4,5]dicyclobutene (9).** To a solution of 1.12 g of 3-hydroxymethylbenzo[1,2,4,5]dicyclobutene (8) in 100 mL of benzene there was added 2 mL of phosphorus tribromide and the mixture was boiled under reflux for 4 h. After the solution had been cooled, ice water was slowly added. The benzene layer was separated and the aqueous layer was extracted with hexane. The combined benzene and hexane extracts were washed with aqueous brine, dried, and concentrated. The residual solid was sublimed to give 1.58 g (99%) of white crystals; mp 60–62 °C; <sup>1</sup>H NMR  $\delta$  6.70 (1 H, s, ArH), 4.33 (2 H, s, CH<sub>2</sub>Br), 3.11 (8 H, s, CH<sub>2</sub>); mass spectrum, *m/e* 224, 222, 145, 143, 128, 115, 91. Anal. (C<sub>11</sub>H<sub>11</sub>Br) C, H.

A sample of 9 was also prepared by irradiating a solution of 3-methylbenzo[1,2,4,5]dicyclobutene and *N*-bromosuccinimide in carbon tetrachloride. The product obtained on workup was identical in all respects with that described above. However, the yield in this case was only 10%.

**1,2-Bis([1,2,4,5]dicyclobutaphenyl)ethane (10).** A solution of 1.38 g of 3-bromomethylbenzo[1,2,4,5]dicyclobutene (9) in 50 mL of dry tetrahydrofuran was added to 75 mg of magnesium and stirred for 2 days. Then, a few milligrams of anhydrous ferric chloride was added and the mixture was stirred for 2 h more. Acidification of the cold reaction mixture with a 2% aqueous hydrochloric acid solution was followed by extraction of the organic layer with dichloromethane. The dichloromethane extract was washed with water, dried, and concentrated. Recrystallization of the residual solid from dichloromethane gave 808 mg (92%) of white crystals; mp 198.5–199.5 °C; <sup>1</sup>H NMR  $\delta$  6.63 (2 H, s, ArH), 3.04 (16 H, s, CH<sub>2</sub>), 2.77 (4 H, s, CH<sub>2</sub>); mass spectrum, *m/e* 286, 271, 258, 257, 243, 241, 147, 145, 143, 141; molecular weight calcd for C<sub>22</sub>H<sub>22</sub> 286.172, found (high-resolution mass spectrum) 286.172.

**[2,3]([1,2,3,4,5]Cyclophane (11).** A sample of 2.32 g of 1,2-bis([1,2,4,5]dicyclobutaphenyl)ethane (10) was placed in the preheater of a pyrolysis apparatus and slowly sublimed at  $10^{-3}$  mm Hg pressure into the hot zone (550 °C) of the quartz tube while collecting the pyrolysate on a condenser held at  $-20$  °C. When the sublimation was complete, the product was washed off the condenser with chloroform and the chloro-

(16) Elemental and mass spectral analyses were determined by Dr. Richard Wielesek of the University of Oregon microanalytical laboratories. All of the mass spectra were taken on a CEC-21B-110 instrument set at 70 eV. Melting points were taken with use of sealed, evacuated, melting-point tubes and are uncorrected. Infrared spectra were measured with use of a Beckman IR-7 instrument and visible and ultraviolet spectra with a Cary 15 spectrometer. NMR spectra were measured with a Varian XL-100 instrument, using deuteriochloroform as solvent and with residual chloroform ( $\delta$  7.27) as an internal standard (unless otherwise specified).

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form washings were concentrated. The residual pale yellow solid was chromatographed over silica gel, using a 1:1 mixture of benzene and hexane. Concentration of the main fraction of eluate gave 1.60 g (69%) of white crystals; mp 334–335 °C dec; <sup>1</sup>H NMR δ 6.05 (2 H, s, ArH), 3.32–2.56 (20 H, multiplet consisting of a singlet and an apparent AA'BB' doublet, CH<sub>2</sub>); <sup>13</sup>C NMR, proton decoupled, δ 145.0, 143.4, 143.1, 137.1, 35.5, 30.7, 29.3; UV (THF) λ<sub>max</sub> 294 nm (ε 352), 313 (200); IR (CHCl<sub>3</sub>) ν<sub>max</sub> 2900, 2865, 2840, 1510, 1485, 1225, and 1190 cm<sup>-1</sup>; mass spectrum, *m/e* 286, 258, 243, 128. Anal. (C<sub>22</sub>H<sub>22</sub>) C, H.

**Charge-Transfer Complex of Tetracyanoethylene and [2<sub>5</sub>](1,2,3,4,5)-Cyclophane.** Addition of pentane to the hot, purple solution of 10 mg of [2<sub>5</sub>](1,2,3,4,5)cyclophane and 15 mg of tetracyanoethylene<sup>18</sup> in 15 mL of chloroform followed by cooling caused the separation of 13.9 mg of black crystals; mp, turns colorless, at 200 °C; UV (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub> 570 nm. Anal. (C<sub>28</sub>H<sub>22</sub>N<sub>4</sub>) C, H, N.

**4-Bromo[2<sub>5</sub>](1,2,3,4,5)cyclophane (12).** To a hot solution of 37 mg of [2<sub>5</sub>](1,2,3,4,5)cyclophane (11) in 25 mL of carbon tetrachloride under a nitrogen atmosphere there was added a few milligrams of iron filings and 0.6 mL of bromine. After the mixture had been stirred at room temperature for 20 h, it was treated with 50 mL of a 20% aqueous solution of sodium bisulfite. The organic layer was extracted with 100 mL of dichloromethane, washed successively with aqueous sodium bicarbonate and water, dried, and concentrated. The residual yellow solid was chromatographed over silica gel, using a 1:1 mixture of dichloromethane and hexane as eluent. Concentration of the main fraction of eluate gave a solid which, on sublimation, yielded 43 mg (91%) of white, powdery crystals; mp >220 °C dec; <sup>1</sup>H NMR δ 6.62 (1 H, s, ArH), 3.71–2.69 (20 H, m, CH<sub>2</sub>); mass spectrum, *m/e* 366, 364, 338, 337, 323, 321, 199, 181; molecular weight calcd for C<sub>22</sub>H<sub>21</sub><sup>79</sup>Br 364.083, found (high-resolution mass spectrum) 364.081.

**4-Formyl[2<sub>5</sub>](1,2,3,4,5)cyclophane (13).** To a solution of 22 mg of [2<sub>5</sub>](1,2,3,4,5)cyclophane (11) in 5 mL of dichloromethane under a nitrogen atmosphere there was added 0.125 mL of stannic chloride and 0.064 mL of dichloromethyl methyl ether. After the reaction had been stirred at 0 °C for 24 h, it was brought to room temperature and stirred an additional 4 days. The resulting reddish-brown solution was poured into ice water and extracted with dichloromethane. The dichloromethane extract was washed with water, dried, and concentrated to give 24 mg (100%) of white crystals; mp >240 °C dec; <sup>1</sup>H NMR δ 10.15 (1 H, s, CHO), 6.00 (1 H, s, ArH), 3.82–2.60 (16 H, m, CH<sub>2</sub>), 3.03 (4 H, s, CH<sub>2</sub>); mass spectrum, *m/e* 314, 279, 271, 167, 149; molecular weight calcd for C<sub>23</sub>H<sub>22</sub>O 314.167, found (high-resolution mass spectrum) 314.167.

**4-Formyl-13-methyl[2<sub>5</sub>](1,2,3,4,5)cyclophane (16).** A mixture of 100 mg of [2<sub>5</sub>](1,2,3,4,5)cyclophane (11) and 300 mg of anhydrous zinc chloride in 10 mL of chloromethyl methyl ether was stirred at room temperature for 24 h. The reddish-brown solution was then poured into ice water, causing the separation of a flaky powder. This was extracted with dichloromethane and the dichloromethane extract was washed with water, dried, and concentrated. Recrystallization of the residual solid from a mixture of dichloromethane and methanol gave 113 mg (98%) of white crystals; mp >335 °C dec; <sup>1</sup>H NMR δ 9.98 (1 H, s, CHO), 3.94–2.90 (20 H, m, CH<sub>2</sub>), 1.89 (3 H, s, CH<sub>3</sub>); mass spectrum, *m/e* 328, 285, 190, 159; molecular weight calcd for C<sub>24</sub>H<sub>24</sub>O 328.183, found (high-resolution mass spectrum) 328.182.

**4,13-Dimethyl[2<sub>5</sub>](1,2,3,4,5)cyclophane (17).** A solution of 5 mg of 4-formyl-13-methyl[2<sub>5</sub>](1,2,3,4,5)cyclophane (16) in 10 mL of dry tetrahydrofuran was added dropwise to a boiling suspension of 2 mg of lithium aluminum hydride and 6.5 mg of aluminum chloride in 10 mL of tetrahydrofuran. After the mixture had been boiled under reflux for 12 h, it was quenched with water and extracted with dichloromethane. The dichloromethane extract was washed with water, dried, and concentrated. Recrystallization of the resulting solid from dichloromethane gave 4 mg (83%) of white crystals; mp 315 °C dec, identical in all respects with an authentic specimen.<sup>4</sup>

**Superphane (19).** To a solution of 113 mg of 4-formyl-13-methyl[2<sub>5</sub>](1,2,3,4,5)cyclophane (16) in 10 mL of tetrahydrofuran was added 73 mg of *p*-toluenesulfonylhydrazide, a few milligrams of *p*-toluenesulfonic acid, and a few drops of an aqueous 35% solution of hydrochloric acid. After the solution had been boiled under reflux for 4 h, thin-layer chromatography indicated the presence of starting material. Therefore, an additional 73 mg of *p*-toluenesulfonylhydrazide was added and the solution was boiled under reflux overnight. The solution was then placed in a quartz ring surrounding a 400 W, medium-pressure Hanovia lamp and degassed by a gentle stream of nitrogen. After addition of 1.0 g of solid sodium methoxide, the solution was irradiated for 10 h. The resulting mixture was concentrated, the residue was taken up in dichloromethane, and the dichloromethane extract was washed with water. Concentration of the dichloromethane extract gave a solid which was chromatographed over silica gel, using a 1:1 mixture of benzene and

hexane for elution. Concentration of the main fraction of eluate gave 89 mg (82%) of white crystals; mp 325–327 °C; identical in all respects with an authentic specimen of superphane (19).<sup>4</sup>

**Diels-Alder Adduct of [2<sub>5</sub>](1,2,3,4,5)Cyclophane (11) and Dicyanoacetylene (20).** A solution of 50 mg of [2<sub>5</sub>](1,2,3,4,5)cyclophane (11) and one drop of dicyanoacetylene in 50 mL of chloroform was heated at 60 °C for 3 days. After that, another drop of dicyanoacetylene was added and the solution was boiled under reflux overnight. The solution was then concentrated to give a yellow solid which was subjected to preparative thin-layer chromatography, using chloroform for elution. The main fraction gave 28 mg (44%) of yellow crystals; mp 238.5–239.5 °C dec; <sup>1</sup>H NMR δ 6.51 (1 H, s, ArH), 3.96 (1 H, s, CH), 3.38–1.98 (20 H, m, CH<sub>2</sub>); IR (KBr) ν<sub>max</sub> 2195 cm<sup>-1</sup> (–CN); mass spectrum, *m/e* 362, 287, 286, 259, 258, 257, 143; molecular weight calcd for C<sub>26</sub>H<sub>22</sub>N<sub>2</sub> 362.185, found (high-resolution mass spectrum) 362.178.

**Diels-Alder Adduct of [2<sub>5</sub>](1,2,3,4,5)Cyclophane (11) and Perfluoro-2-butyne (21).** To a mixture of 105 mg of [2<sub>5</sub>](1,2,3,4,5)cyclophane (11) in 10 mL of 1,2-dichloroethane placed in a thick-walled glass tube was added a large excess of 2-perfluoro-2-butyne and the tube was sealed under vacuum. After the tube had been heated at 100 °C for 1 week, the tube was opened and the white crystals, which had separated, were collected by filtration. Recrystallization from a 1:1 mixture of 1,2-dichloroethane and methanol gave 164 mg (100%) of white prisms; mp 286–288 °C; <sup>1</sup>H NMR δ 6.47 (1 H, s, ArH), 3.86 (1 H, s, CH), 3.29–1.88 (20 H, m, CH<sub>2</sub>); mass spectrum, *m/e* 449, 448, 420, 380, 379. Anal. (C<sub>26</sub>H<sub>22</sub>F<sub>6</sub>) C, H.

**(η<sup>6</sup>-*p*-Cymene)(η<sup>6</sup>-[2<sub>5</sub>](1,2,3,4,5)cyclophane)ruthenium(II) Bis(fluoroborate) (22).** After a solution of 54 mg of bis(*p*-cymene)dichloro-μ-chloro-diruthenium(II) and 69 mg of silver fluoroborate in 10 mL of acetone had been stirred at room temperature for 30 min, the precipitate of silver chloride was removed and 50 mg of [2<sub>5</sub>](1,2,3,4,5)cyclophane (11) was added together with 10 mL of trifluoroacetic acid. The mixture was boiled under reflux for 1 h and cooled and the insoluble precipitate removed. Addition of ether then caused the precipitation of a white powder. This was collected by filtration and recrystallized from ethanol to give 94 mg (77%) of pale yellow crystals; mp 270 °C dec; <sup>1</sup>H NMR (CD<sub>3</sub>CN) δ 6.69 (1 H, s, ArH), 6.52 (4 H, s, ArH), 5.69 (1 H, s, ArH), 3.77–2.57 (21 H, m, CH<sub>2</sub> and CH), 2.22 (3 H, s, CH<sub>3</sub>), 1.12 (6 H, d, *J* = 8 Hz, CH<sub>3</sub>). Anal. (C<sub>32</sub>H<sub>36</sub>RuB<sub>2</sub>F<sub>8</sub>) C, H.

**(η<sup>6</sup>-Hexamethylbenzene)(η-[2<sub>5</sub>](1,2,3,4,5)cyclophane)ruthenium(II) Bis(fluoroborate) (23).** The experimental procedure for preparing 23 was the same as that described for the preparation of 22 except that bis(hexamethylbenzene)dichloro-μ-chloro-diruthenium was substituted for bis(*p*-cymene)dichloro-μ-chloro-diruthenium(II). From 56 mg of [2<sub>5</sub>](1,2,3,4,5)cyclophane (11), there was isolated 132 mg (94%) of 23, after crystallization from ethanol, as yellow crystals; mp >270 °C dec; <sup>1</sup>H NMR (CD<sub>3</sub>CN) δ 6.59 (1 H, s, ArH), 5.40 (1 H, s, ArH), 3.61–2.49 (20 H, m, CH<sub>2</sub>), 2.23 (18 H, s, CH<sub>3</sub>). Anal. (C<sub>34</sub>H<sub>40</sub>RuB<sub>2</sub>F<sub>8</sub>·H<sub>2</sub>O) C, H.

**(η<sup>6</sup>-[2<sub>5</sub>](1,2,3,4,5)Cyclophane)(η<sup>5</sup>-cyclopentadienyl)iron(II) Hexafluorophosphate (24).** A nitrogen-deaerated solution of 89 mg of (η<sup>6</sup>-*p*-xylene)(η<sup>5</sup>-cyclopentadienyl)iron(II) hexafluorophosphate<sup>19</sup> and 68 mg of [2<sub>5</sub>](1,2,3,4,5)cyclophane (11) in 30 mL of dry dichloromethane was irradiated with visible light (General Electric reflector flood lamp, 150 W) for 4.5 h. The reaction mixture was filtered through glass wool before concentration. The resulting solid was washed with hot heptane to remove any free [2<sub>5</sub>](1,2,3,4,5)cyclophane and then recrystallized from ethanol to give 91 mg (68%) of reddish-orange crystals; mp >200 °C dec; <sup>1</sup>H NMR (Me<sub>2</sub>SO-*d*<sub>6</sub>) δ 6.22 (1 H, s, ArH), 5.18 (1 H, s, ArH), 4.74 (5 H, s, Cp-H), 3.34–2.60 (20H, m, CH<sub>2</sub>). Anal. (C<sub>27</sub>H<sub>27</sub>FePF<sub>6</sub>) C, H.

**1,2-Bis([1,2,4,5]dicyclobutaphenyl)ethene (25).** A solution of 221 mg of 3-bromomethylbenzo[1,2,4,5]dicyclobutene (9) and 269 mg of triphenylphosphine in 50 mL of dry tetrahydrofuran was boiled under reflux for 36 h. To the cooled reaction mixture was then added with stirring 2 mL of a 1.6 M solution of *n*-butyllithium in hexane. After the deep red solution had been stirred for 1 h, a solution of 158 mg of 3-formylbenzo[1,2,4,5]dicyclobutene (4) in 30 mL of dry tetrahydrofuran was added with stirring. After the solution turned yellow, 10 mL of ethanol was added and the mixture was concentrated. The resulting yellow solid was chromatographed over silica gel, using a 1:1 mixture of dichloromethane and hexane for elution. Concentration of the main fraction of eluate gave a solid which, after crystallization, yielded 105 mg (37%) of white crystals; mp, wide range (mixture of *cis* and *trans* isomers); <sup>1</sup>H NMR δ 6.84 (2 H, s, ArH), 6.65 and 6.48 (2 H, 2s, vinyl-H), 3.04–2.50 (16 H, m, CH<sub>2</sub>); mass spectrum, *m/e* 284, 283, 269, 239, 226; molecular weight calcd for C<sub>22</sub>H<sub>20</sub> 284.156, found (high-resolution mass spectrum) 284.156.

**Bis([1,2,4,5]dicyclobutabenzyl) Sulfide (26).** To a solution of 254 mg of 3-bromomethylbenzo[1,2,4,5]dicyclobutene (9) in 50 mL of degassed

benzene under a nitrogen atmosphere there was added dropwise with stirring a solution of 274 mg of sodium sulfide nonahydrate in 50 mL of a 1:1 mixture of ethanol and benzene. When the addition was complete, the solution was stirred overnight at room temperature. The mixture was then poured into 100 mL of a 10% aqueous solution of sodium bicarbonate and extracted with 200 mL of ether. The organic layer was washed with water, dried, and concentrated to give 170 mg (92%) of white crystals. Recrystallization of a sample from ethanol gave white

crystals; mp 131.5–133.0 °C;  $^1\text{H NMR}$   $\delta$  6.63 (2 H, s, ArH), 3.50 (4 H, s,  $\text{CH}_2\text{S}$ ), 3.30 (16 H, s,  $\text{CH}_2$ ); mass spectrum,  $m/e$  319, 318, 303, 289, 176, 175, 174, 173, 144, 143, 142, 141. Anal. ( $\text{C}_{22}\text{H}_{22}\text{S}$ ) C, H.

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## Formation of [9]- and [10]Paracyclophane Derivatives in Cycloaddition Reactions<sup>1</sup>

Fumio Kataoka, Shinya Nishida,\* Takashi Tsuji, and Masashi Murakami

Contribution from the Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Hokkaido 060, Japan. Received June 15, 1981

**Abstract:** Reactions of tetracyclopropylethylene (**1a**) and *cis*-1,2-dicyclopropylstilbene (**1b**) and its *trans* isomer (**1c**) with TCNQ gave 5,6-disubstituted [10]paracyclophane-4,6-dienes (**2**) in 50–70% yields. In a similar manner, 1-alkyl- or 1-phenyl-substituted 1-cyclopropyl-1,3-butadiene (**3a–g**) reacted with TCNQ to produce 5-substituted [9]paracyclophane-3,5-diene derivatives (**4**) in 15–89% yields. Reductive decyanation of **2** yielded hydrocarbons **5** and **6**, whereas the same reaction of **4** resulted in the cleavage of the cyclophane ring. All the products possessed a *cis,trans* configuration at the diene portion irrespective of the stereochemistry of the starting olefin **1** and **3**. The cycloaddition will, therefore, be most neatly rationalized by an assumption that it is a stepwise process involving a zwitterion possessing a *transoid* allylic cation portion. An intramolecular attack of the dicyano-bearing carbanion at the methylene carbon of the cyclopropyl group, which is activated by the allylic cation moiety, will produce **2** and **4** with the generation of the *cis* double bond. In contrast to **3a–g**, parent 1-cyclopropyl-1,3-butadiene (**3h**) failed to give a paracyclophanediene, but produced Diels–Alder adducts **9** and **10** in 34 and 28% yields, respectively. **10** is a cycloadduct of **3h** with methylenemalononitrile, which may be generated in situ by the fragmentation of **12**, a presumed [2 + 2] cycloadduct of **3h** with TCNQ. Supporting evidence was provided by the usage of **3h-d**<sub>2</sub> as the substrate.

Since a vinylcyclopropane moiety can be considered as a homo-1,3-diene unit, considerable efforts have been devoted to incorporate such a unit in the cycloaddition reactions.<sup>2–4</sup> We also studied sometime ago the reactions of several cyclopropyl-substituted ethylenes with a variety of reagents.<sup>5</sup> Although the reaction involving such a unit in the transformation has been

realized in some cases, somewhat unusual reactions, in which merely the cyclopropane  $\sigma$  bond is involved, have also been uncovered by us. For example, the reaction of tetracyclopropylethylene (**1a**)<sup>6</sup> and related olefins with ethenetetracarbonitrile (TCNE) does not produce a homo-Diels–Alder adduct, but gives a vinylcyclopentane.<sup>5a,b,k</sup> The reaction of dispiro[2.2.2]deca-4,9-diene has revealed another case.<sup>5h</sup> The dispiro compound reacts with a number of 1,3-dienes at 160 °C in a stepwise diradical fashion to afford an [8]paracyclophane derivative, but it reacts smoothly with 3,6-bis(dicyanomethylene)-1,4-cyclohexadiene (TCNQ) at a much lower temperature (60 °C), and a [3.3]paracyclophane is produced.<sup>5h</sup> Since the homolysis of the  $\sigma$  bond in the dispiro compound occurs very slowly at 60 °C, the cycloaddition should proceed in a process different from the diradical pathway in the [3.3]paracyclophane formation. Since smooth reactions are realized particularly in a donor–acceptor pairing of the two reactants, a plausible candidate of the reactive species, in which the prior rupture of the cyclopropane  $\sigma$  bond should occur, will be a cation radical<sup>7</sup> produced in an electron transfer from a cyclopropylethylene to a strongly electron-demanding TCNE or TCNQ. The fact that heavily substituted cyclopropylethylenes as well as the dispiro compound possess a

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