

1.27 (t, 3 H,  $J = 7$  Hz), 4.13 (q, 2 H,  $J = 7$  Hz), 6.7-7.5 (m, 6 H)], and (c) 2-amino-3-chloro-*N*-phenylmaleimide (**50**) [mp 138-141 °C; IR 3500, 3330 (NH<sub>2</sub>), 1725, 1670 (C=O) cm<sup>-1</sup>; NMR (acetone-*d*<sub>6</sub>) δ 7.10 (br s, 2 H), 7.47 (s, 5 H); MS (relative abundance),  $m/e$  224 (32, M<sup>+</sup> + 2), 222 (100, M<sup>+</sup>), 196 (9), 194 (29), 180 (5), 178 (11), 143 (39), 131 (9), 119 (21), 77 (31), 75 (57), 68 (30)].

Anal. Calcd for C<sub>10</sub>H<sub>7</sub>N<sub>2</sub>ClO<sub>2</sub>: C, 53.93; H, 3.14; N, 12.58, Cl, 15.95. Found: C, 53.49; H, 3.21, N, 12.31; Cl, 15.88.

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## A Study of the Synthesis and Properties of [2<sub>6</sub>](1,2,3,4,5,6)Cyclophane (Superphane)<sup>1</sup>

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**Abstract:** A synthesis of [2<sub>6</sub>](1,2,3,4,5,6)cyclophane (**9**) is described. This molecule, the ultimate in a multibridged [2<sub>*n*</sub>]cyclophane, has been given the trivial name "superphane" and was synthesized in ten steps, as outlined in Scheme I, starting from 2,4,5-trimethylbenzyl chloride (**14**). The key to the successful synthesis of superphane lay in employing gas-phase dimerization of *o*-xylylene intermediates to introduce more than one bridge at a time. This provides a convenient overall synthesis suitable for preparing superphane in multigram quantities. X-ray crystallographic analysis has shown superphane to be a highly symmetrical (*D*<sub>6h</sub>) molecule with the benzene decks being planar hexagons separated by 2.624 Å. The <sup>1</sup>H NMR spectrum of superphane shows a singlet at δ 2.98 and the <sup>13</sup>C NMR spectrum singlets at δ 144.2 and 32.2, reflecting this high degree of symmetry. Superphane forms hard, white crystals, mp 325-327 °C, which are rather insoluble and relatively inert, showing no evidence of thermal rupture of the bridges as occurs with many of the [2<sub>*n*</sub>]cyclophanes. However, superphane does exhibit the Birch reduction and undergoes electrophilic attack by alkyl cations and benzylic substitution with *N*-bromosuccinimide. Although superphane readily forms a charge-transfer complex with tetracyanoethylene (TCNE), it does not give the normal, Diels-Alder, barrelene-type adduct with either TCNE or dicyanoacetylene. In the presence of aluminum chloride, though, superphane reacts with dicyanoacetylene to form an unusual structure (**50**), involving formation of novel intramolecular bonds. With ethyl diazoacetate in the presence of cupric sulfate, superphane undergoes carbene addition to give **44**, which can be converted readily to the corresponding tropylium ion (**46**). In a remarkable reaction, the tropylium ion (**46**) in the presence of moisture regenerates superphane.

The cyclophane nomenclature and the cyclophane era were ushered in by the work of Cram and Steinberg in 1951.<sup>2</sup> The availability of [2.2]cyclophanes via 1,6-eliminations or by Wurtz coupling reactions<sup>3</sup> attracted much interest because the rigid geometry of these molecules made them ideal for studying questions of bonding, strain energy, and transannular π-electron interactions. The introduction of the dithiacyclophane-sulfur extrusion approach<sup>4,5</sup> greatly facilitated syntheses of cyclophanes and opened the possibility of preparing multibridged [2<sub>*n*</sub>]cyclophanes, as shown by the synthesis of [2<sub>3</sub>](1,3,5)cyclophane.<sup>6</sup> The possibility of constructing additional bridges with known cyclophanes by stepwise manipulation was exploited in syntheses of [2<sub>3</sub>](1,2,4)cyclophane<sup>7</sup> and [2<sub>4</sub>](1,2,4,5)cyclophane.<sup>8</sup> Further, Hopf introduced a very convenient method for synthesizing

multisubstituted [2.2]paracyclophanes.<sup>9</sup> Even so, the further elaboration of these substituted [2.2]paracyclophanes to give multibridged cyclophanes such as [2<sub>4</sub>](1,2,3,5)cyclophane<sup>10</sup> and [2<sub>4</sub>](1,2,3,4)cyclophane<sup>11</sup> remained a somewhat tedious chore.

In thinking about the further elaboration of multibridged cyclophanes and the possible synthesis of the ultimate member of the series, [2<sub>6</sub>](1,2,3,4,5,6)cyclophane (superphane<sup>12</sup>), we felt that a new approach was needed, especially if superphane were to be made available in sufficient quantity for adequate chemical studies. It had been shown by Cava and Deana that the pyrolysis of 1,3-dihydroisothianaphthene 2,2-dioxide (**1**) in diethyl phthalate solution at 300 °C gave [2.2]orthocyclophane (**3**) in 48% yield.<sup>13</sup> Presumably, this reaction proceeds via *o*-xylylene (**2**) as an intermediate. Similarly, Jensen, Coleman, and Berlin have shown that benzocyclobutene (**4**) dimerizes to [2.2]orthocyclophane (**3**), when being boiled under reflux.<sup>14</sup> However, Errede had found that pyrolysis of (2-methylbenzyl)trimethylammonium hydroxide (**5**) followed by condensation of the volatile products at low temperature gave mainly the spirotriene **6**, with only a modest quantity of **3** being formed.<sup>15</sup> Whereas the Diels-Alder dimerization of *o*-xylylene (**2**) to the spirotriene **6** is an allowed process in terms of the conservation of orbital symmetry, the

(1) (a) For a preliminary report of the synthesis of superphane, see: Sekine, Y.; Brown, M.; Boekelheide, V. *J. Am. Chem. Soc.* **1979**, *101*, 3126. (b) The chemistry of superphane was presented at the First Laaxer Conference on Chemistry, Sept 20-27, 1980, and we thank the participants at that conference for helpful suggestions, especially Professor Eschenmoser who first suggested structure **42** as a likely possibility for the oxidation product from **41**.

(2) Cram, D. J.; Steinberg, H. *J. Am. Chem. Soc.* **1951**, *73*, 5691-5706.

(3) For reviews, see: (a) Smith, B. H. "Bridged Aromatic Compounds"; Academic Press: New York, 1964. (b) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1971**, *4*, 204-214. (c) Misumi, S.; Otsubo, T. *Ibid.* **1978**, *11*, 251-256. (d) Vögtle, F.; Höhner, G. *Top. Curr. Chem.* **1978**, *74*, 1-31. (e) Boekelheide, V. *Acc. Chem. Res.* **1980**, *13*, 65-70.

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(5) (a) Mitchell, R. H.; Boekelheide, V. *J. Am. Chem. Soc.* **1970**, *92*, 3510. (b) *Ibid.* **1974**, *96*, 1547-1557.

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(8) (a) Gray, R.; Boekelheide, V. *Angew. Chem.* **1975**, *87*, 138. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 107. (b) Gray, R.; Boekelheide, V. *J. Am. Chem. Soc.* **1979**, *101*, 2128-2136.

(9) (a) Hopf, H. *Angew. Chem.* **1972**, *84*, 471-472. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 419-420. (b) Hopf, H.; Lenich, F. Th. *Chem. Ber.* **1974**, *107*, 1891-1902. (c) Böhm, I.; Herrmann, H. Menke, K.; Hopf, H. *Ibid.* **1978**, *111* 523-537.

(10) Gilb, W.; Menke, K.; Hopf, H. *Angew. Chem.* **1977**, *89*, 177. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 191.

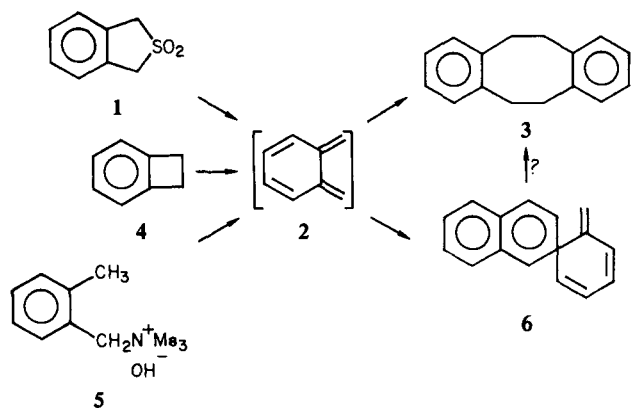
(11) Kleinschroth, J.; Hopf, H. *Angew. Chem.* **1979**, *91*, 336. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 329.

(12) We are indebted to Professor H. Hopf for suggesting the trivial name, superphane, for [2<sub>6</sub>](1,2,3,4,5,6)cyclophane.

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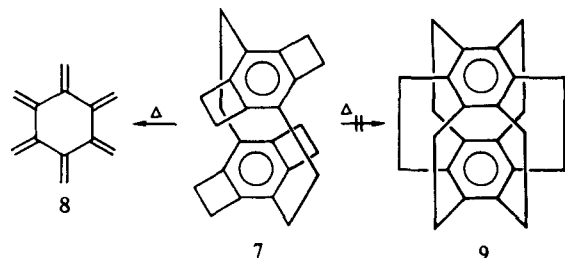
(14) Jensen, F. R.; Coleman, W. E.; Berlin, A. J. *Tetrahedron Lett.* **1962**, 15-18.

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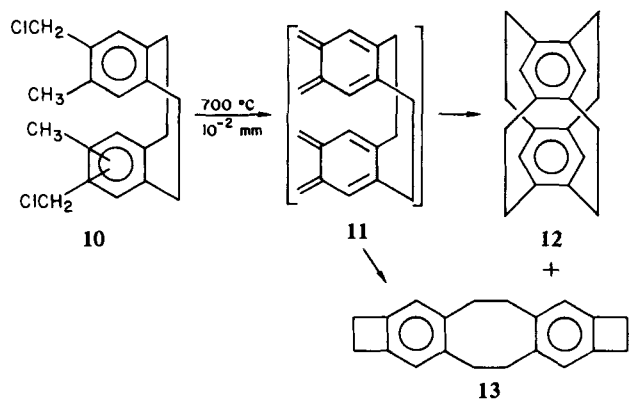


concerted conversion of **2** to **3** is forbidden.<sup>16</sup>

Thus, the dimerization of *o*-xylenes appeared to be an attractive method for introducing two bridges at a time in syntheses of multibridged [2<sub>n</sub>]cyclophanes. However, the question of whether **3** can be formed directly from **2** or is the result of a sigmatropic rearrangement of the spirodiene intermediate (**6**) could not be ignored. Examination of molecular models clearly showed that the conversion of two *o*-xylenes, attached to cyclophane decks, to a spirotriene intermediate such as **6** is impossible. This concern was also brought to the fore by the observation that the pyrolysis of cyclophane **7** gave hexaradialene **8** and not the sought for [2<sub>6</sub>](1,2,3,4,5,6)cyclophane **9**.<sup>17</sup>



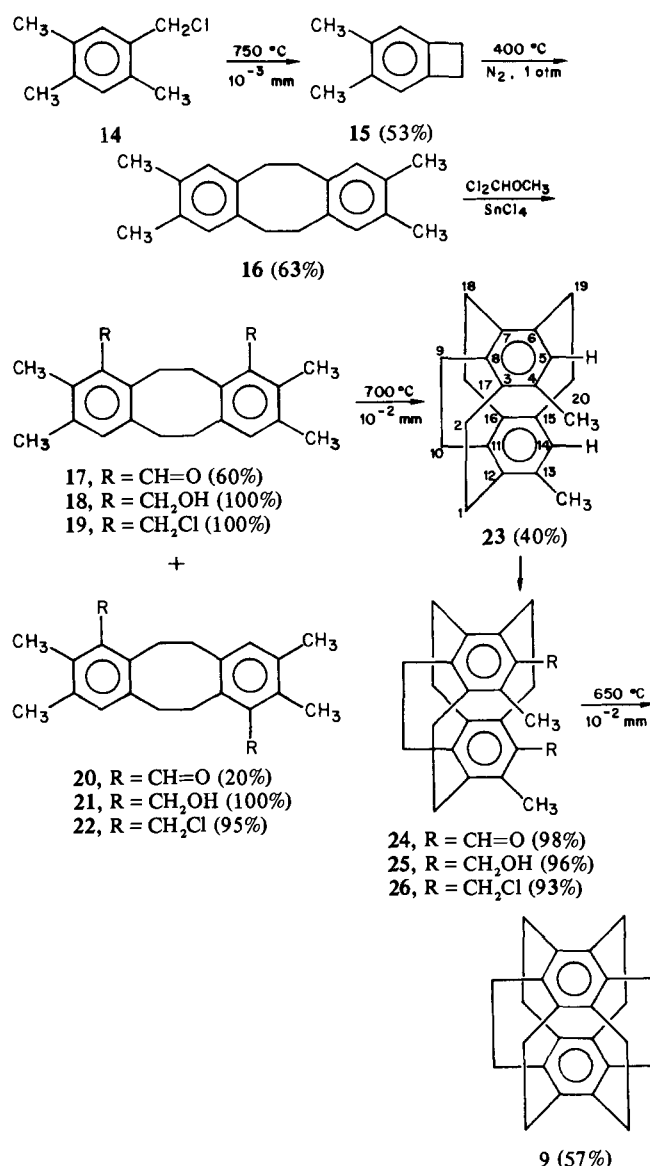
To test the question of *o*-xylene dimerization in cyclophanes, we pyrolyzed the [2.2]orthocyclophane derivative **10** in the gas



phase at 700 °C and found it to give a mixture of [2.2]-(1,2,4,5)cyclophane (**12**) and the benzocyclobutene derivative **13**, presumably via the intermediate bis(*o*-xylene) (**11**).<sup>18</sup> Thus, the principle of *o*-xylene dimerization as a method of simultaneously introducing two bridges into a cyclophane was established.

We then undertook the synthesis of superphane (**9**), as outlined in Scheme I. As can be seen, the proposed route depended heavily on gas-phase pyrolysis, a technique which in practice proved to be both convenient and efficient. Thus, the gas-phase pyrolysis of *o*-chloromethyltoluenes is a very convenient method for pre-

## Scheme I



paring benzocyclobutenes,<sup>19-21</sup> and the conversion of 2,4,5-trimethylbenzyl chloride (**14**) to 4,5-dimethylbenzocyclobutene (**15**) proceeds smoothly in 53% yield on runs of 60 g of material. The dimerization of the benzocyclobutene **15** to **16** was first carried out in boiling diethyl phthalate,<sup>1,13</sup> but the yields of **16** under these conditions are only fair and the procedure for isolating **16** is cumbersome and tedious. It seemed probable that this dimerization could be done more efficiently in the gas phase, if conditions were designed such that bimolecular collisions of the intermediate *o*-xylene would be favored. This proved to be the case. When finely ground **15** was slowly dusted into a stream of nitrogen (flow rate = 2 mL/s), which carried it into the hot zone (400 °C) of a vertical quartz tube, the dimer **16** was collected in a cold trap at the outlet and, after recrystallization, was isolated in 63% yield.

Formylation of **16**, via the Rieche reaction,<sup>22</sup> gave two products, **17** and **20**, as anticipated. The spectral data obtained for these products did not allow a decision as to which compound had which structure. To decide this each was separately carried out through the next stages and the corresponding individual chlorides, **19** and

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(20) Schiess, P.; Heitzmann, M.; Rutschmann, S.; Stäheli, R. *Tetrahedron Lett.* **1978**, 4569-4572.

(21) Gray, R. Harruff, L. G.; Krymowsky, J.; Peterson, J.; Boekelheide, V. *J. Am. Chem. Soc.* **1978**, *100*, 2892.

(22) Rieche, A. *Chem. Ber.* **1960**, *93*, 88.

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(17) Harruff, L. G.; Brown, M.; Boekelheide, V. *J. Am. Chem. Soc.* **1978**, *100*, 2893-2894.

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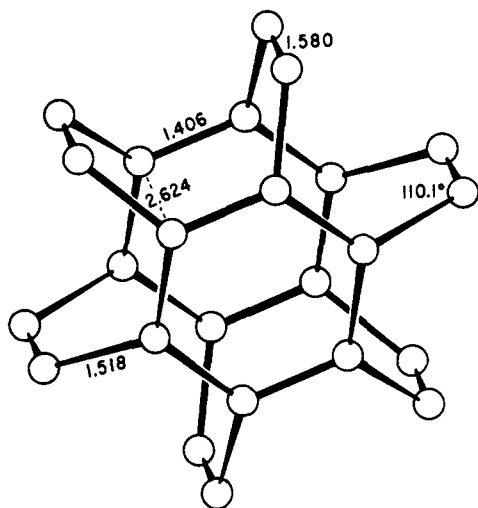


Figure 1. Geometry of [2<sub>6</sub>](1,2,3,4,5,6)cyclophane (9) from an X-ray crystallographic analysis.<sup>25</sup>

22, were subjected to gas-phase pyrolysis. Fortunately, the more abundant isomer 19 was converted smoothly to the desired 4,13-dimethyl[2<sub>4</sub>](1,2,3,4)cyclophane (23), whereas the other isomer, 22, gave only polymeric material on pyrolysis. At the time, the synthesis of 23 was the first example of a [2<sub>4</sub>](1,2,3,4)-cyclophane. However, simultaneously with our studies, Kleinschroth and Hopf reported the synthesis of the parent cyclophane.<sup>11</sup>

Formylation of 23, followed by reduction of 24 and treatment of the alcohol (25) with thionyl chloride, then gave the dichloride 26 in excellent yield. Pyrolysis of 26 at 650 °C 10<sup>-2</sup> mm of pressure proceeds smoothly to give superphane (9) in 57% yield. Thus, the synthesis of superphane has been accomplished in a ten-step synthesis with an overall yield of 4% and by procedures that allow the preparation of multigram quantities.

Superphane, on recrystallization, forms hard white crystals, melting at 325–327 °C without decomposition. Its ultraviolet spectrum shows absorption bands at 296 (ε 421), 306 (sh) (394), and 311 nm (sh, 324), a very similar pattern to the other multibridged cyclophanes.<sup>8b,23</sup> The high symmetry of the molecule is reflected in its NMR spectra: its <sup>1</sup>H NMR spectrum shows a singlet at δ 2.98 and its <sup>13</sup>C NMR spectrum (proton decoupled) has singlets at δ 144.2 and 32.2 (*J*<sup>13</sup>C-H = 126 Hz). The mass spectrum of superphane shows a very strong signal for the parent molecular ion at *m/e* 312, with signals at *m/e* 284 and 256, suggestive of the successive loss of ethylene bridges, and then an envelope of signals at *m/e* 156, 141, and 128, very similar to that observed in the mass spectrum of hexaradialene.<sup>24</sup>

The molecular geometry of superphane, as determined by an X-ray crystallographic analysis,<sup>25</sup> is given in Figure 1. The molecule is seen to have a highly symmetrical, *D*<sub>6h</sub>, eclipsed conformation with the benzene rings being regular hexagons separated by only 2.624 Å, the closest distance thus far attained between two aromatic rings in a stable molecule. Prior to its synthesis, Lindner calculated the geometry to be expected for superphane by using a π-SCF-force field method,<sup>26</sup> and his predictions are in very good agreement with the actual experimental values. Probably, the most surprising feature of superphane is the distortion of the bond angle of the sp<sup>2</sup>-sp<sup>3</sup> carbon-carbon bonds out of planarity with the benzene ring and toward the interior by 20.3°. Thus the π orbitals in superphane are not perpendicular to the ring plane but are deflected by ca. 10°, giving the contour representation of the π-electron cloud a bowl shape. Iwamura and Katoh have examined this point by an ab initio SCF

Table I. Position of the Longest Wavelength Band in the Ultraviolet Absorption Spectrum of [2<sub>*n*</sub>]Cyclophane-TCNE Complexes and Their Corresponding Methylated Benzene Analogues

[2 <sub><i>n</i></sub> ]cyclophane-TCNE complex	λ <sub>max</sub> , nm	methylated benzene analogues	λ <sub>max</sub> , nm
[2.2]paracyclophane	521	<i>p</i> -xylene <sup>a</sup>	460
[2 <sub>3</sub> ](1,2,3)cyclophane	493		
[2 <sub>3</sub> ](1,3,5)cyclophane	559	mesitylene <sup>a</sup>	461
[2 <sub>4</sub> ](1,2,4,5)cyclophane	addition <sup>b</sup>	durene <sup>a</sup>	480
4,13-dimethyl[2 <sub>4</sub> ](1,2,3,4)-cyclophane (23)	550	pentamethylbenzene <sup>a</sup>	520
[2 <sub>5</sub> ](1,2,3,4,5)cyclophane	570		
[2 <sub>6</sub> ](1,2,3,4,5,6)cyclophane	572	hexamethylbenzene <sup>a</sup>	545

<sup>a</sup> Reference 30. <sup>b</sup> The initial deep violet color of the complex disappeared within seconds, and the 1:1 Diels-Alder adduct was isolated in quantitative yield.

MO calculation and have concluded that the strain energy in the bowl-shaped benzene rings of superphane is 20.6 kcal/mol.<sup>27</sup> The loss in π-resonance energy is not considered to be serious but rather the strain in the σ framework is thought to be responsible for most of this destabilization.

Photoelectron spectroscopy is of particular value for understanding π-electron properties and a full study of the photoelectron spectra of all of the symmetrical [2<sub>*n*</sub>]cyclophanes has been reported.<sup>28</sup> It would be expected that, as the two benzene rings of the cyclophane are forced closer together, the "through-space" interaction should be greater, raising the energy of the HOMO and lowering that of the LUMO orbitals. In agreement with this concept the first ionization energy of superphane (7.55 eV) is the lowest of the [2<sub>*n*</sub>]cyclophanes. However, the anticipated additional effect of the bridges behaving as alkyl substituents to lower the first ionization energy is not realized due to the severe symmetry restriction imposed on "through-bond" interaction in the highly symmetrical superphane. Thus, although the superphane molecule clearly behaves as one overall π-electron system, it does not give up an electron as readily as might have been anticipated.

This behavior is also reflected in the ultraviolet absorption spectra of the charge-transfer complexes of the [2<sub>*n*</sub>]cyclophanes. These data are summarized in Table I, together with the values for the corresponding methylated benzenes. Cram and Bauer have previously discussed in some detail the properties and interpretation of the spectra of the tetracyanoethylene (TCNE) complexes of [2.2]paracyclophane derivatives.<sup>29</sup> If the effect of shortening the distance between benzene decks in [2<sub>*n*</sub>]cyclophanes and the alkyl effect due to increased bridges were independent and additive, the long wavelength absorption band of the TCNE-superphane complex would be predicted to occur at much longer wavelength than the 572 nm actually observed. The value for the TCNE-superphane complex is still the highest for any of the [2<sub>*n*</sub>]cyclophanes, even though the alkyl effect in the case of superphane is probably negligible.

Although superphane undoubtedly possesses the greatest total strain energy (estimated to be in the range of 60–79 kcal/mol)<sup>26</sup> of any of the [2<sub>*n*</sub>]cyclophanes, this strain is evenly distributed over a large number of bonds and so superphane would be expected to be thermally stable. [2.2]Paracyclophane (strain energy 31.3 kcal/mol<sup>31</sup>) and [2<sub>3</sub>](1,2,4)cyclophane undergo thermal rupture of an ethano bridge at 250 °C, and the resulting benzyl diradical can be trapped by reduction with a hydrogen donor molecule or by addition to dimethyl maleate.<sup>32–34</sup> In contrast, prolonged

(23) A laser Raman and infrared spectral study has been made of the [2<sub>*n*</sub>]cyclophanes, including superphane, and will be reported elsewhere.

(24) Harruff, L. G.; Brown, M.; Boekelheide, V. *J. Am. Chem. Soc.* **1978**, *100*, 2893–2894.

(25) Hanson, A. W.; Cameron, T. S. *J. Chem. Res., Synop.* **1980**, 336–337.

(26) Lindner, H. J. *Tetrahedron* **1976**, *32*, 753–757.

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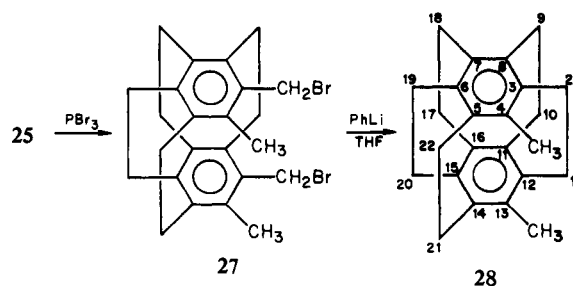
(29) Cram, D. J.; Bauer, R. H. *J. Am. Chem. Soc.* **1959**, *81*, 5971–5977.

(30) Merrifield, R. E.; Phillips, W. D. *J. Am. Chem. Soc.* **1958**, *80*, 2778–2782.

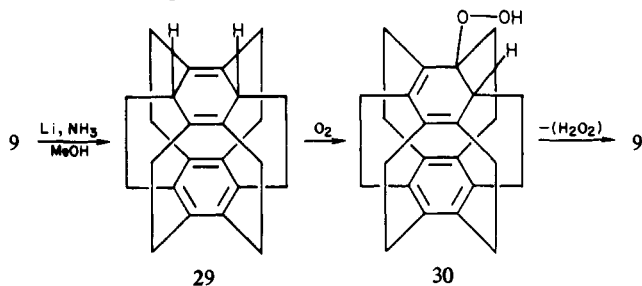
(31) Boyd, R. H. *Tetrahedron* **1966**, *22*, 119–122.

(32) Reich, H. J.; Cram, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 3517–3526.

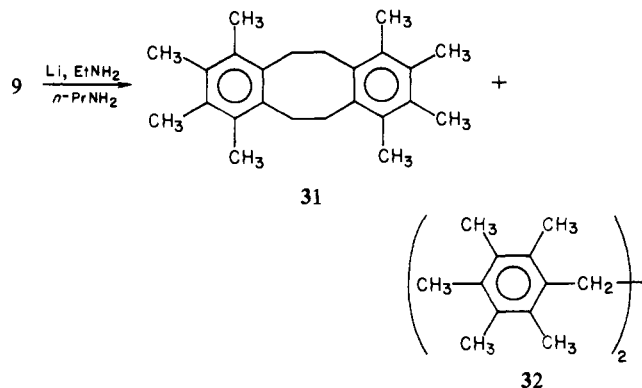
heating of superphane in the presence of trapping agents (diisopropylbenzene at 350 °C for 24 h or dimethyl maleate at 200 °C for 24 h) led only to the complete recovery of unchanged superphane. It seemed important to have a specimen of 4,13-dimethyl[2<sub>5</sub>](1,2,3,4,5)cyclophane (**28**) on hand to know its properties, in the event it was formed in the thermal rupture-reduction experiments and also for comparison with dihydrosuperphane (**29**), formed in the Birch reduction (*vide infra*). This was readily accomplished by converting diol **25** to the corresponding bromide **27** and treating this with phenyllithium.



The Birch reduction of [2.2]paracyclophane<sup>35</sup> and [2.4]-(1,2,4,5)cyclophane<sup>8b</sup> are very easy, high-yield reactions. However, subjecting superphane (**9**) to the usual conditions of the Birch

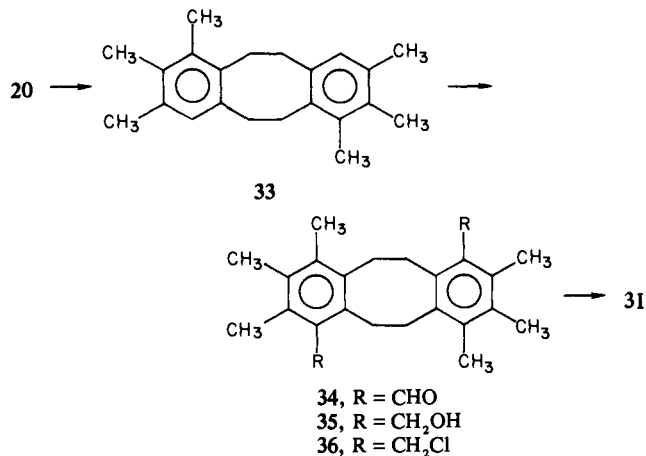


reduction gave dihydrosuperphane **29** only in poor yield. Furthermore, the dihydro derivative **29** reverts back to superphane with extreme ease in the presence of oxygen,<sup>36</sup> and this is probably the explanation for the poor yield encountered in its formation. Based on the behavior of other dihydrosuperphane derivatives (*vide infra*), we presume that **29** undergoes an "ene" reaction with oxygen to give **30** which, by loss of hydrogen peroxide, regenerates superphane (**9**). When the Birch reduction of superphane (**9**) is



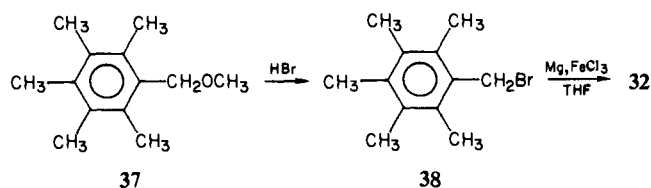
done under the more forcing conditions of lithium in a mixture of ethylamine and *n*-propylamine, rupture of the bridges occurs to give mainly **31** (57%) with a small amount of **32** (7%).

The structures of **31** and **32** were proved by independent syntheses. Reduction of **20** with a mixture of aluminum chloride and lithium aluminum hydride in tetrahydrofuran gave **33**.



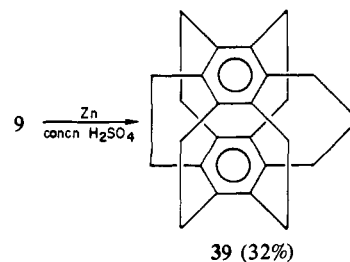
Formylation then led to the dialdehyde **34** which, on reduction with lithium aluminum hydride, yielded diol **35**, and this was converted to the dichloride **36** with thionyl chloride. A further reduction of **36** with lithium aluminum hydride then gave **31**, in all respects identical with the compound obtained from the Birch reduction of superphane.<sup>37</sup>

For the synthesis of **32**, pentamethylbenzyl methyl ether (**37**)<sup>38</sup>



was treated with 48% aqueous hydrobromic acid to give the bromide **38** which, via a Grignard coupling in the presence of ferric chloride, gave **32**, in all respects identical with the sample obtained from the Birch reduction of superphane.

Attempts to effect catalytic hydrogenation of superphane using Adams catalyst were unsuccessful. Quite possibly this is due to the extreme insolubility of superphane in polar solvents and the difficulty of effecting catalytic hydrogenation in solvents such as dichloromethane. Chemical reduction was tried by adding zinc dust to a solution of superphane in concentrated sulfuric acid. This did not lead to reduction but, instead, gave an unusual product in which sulfur has inserted into one of the bridged carbon-carbon bonds, as shown by structure **39**. One can only speculate on the



mechanism by which this reaction occurs. Thus far we have not found that any of the other [2<sub>n</sub>]cyclophanes behave in this manner, and so the reaction is apparently unique to superphane.

In the course of investigating the behavior of superphane toward electrophilic reagents, another route to dihydrosuperphane derivatives was discovered. Treatment of a chloroform solution of superphane with dimethoxycarbonium fluoroborate (Meerwein's reagent)<sup>39</sup> gave a deep red solution whose <sup>1</sup>H NMR spectrum is in accord with structure **40**. Addition of sodium borohydride in methanol to this solution led to a product whose composition and

(33) Cram, D. J.; Hornby, R. B.; Truesdale, E. A.; Reich, H. J.; Delton, M. H.; Cram, J. M. *Tetrahedron* **1974**, *30*, 1757-1768.

(34) Murad, A. E.-F. E.-S.; Hopf, H. *Chem. Ber.* **1980**, in press.

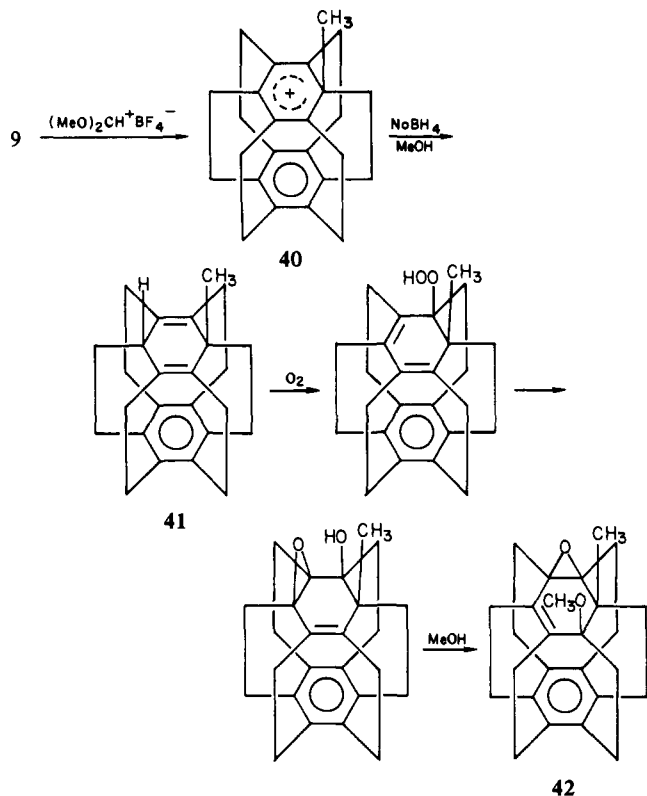
(35) Marshall, J. L.; Song, B.-H. *J. Org. Chem.* **1974**, *39*, 1342-1346.

(36) Hopf has observed that the Birch reduction products from [2.4]-(1,2,3,5)cyclophane similarly rearomatize thermally or by reaction with oxygen (private communication from Professor Hopf).

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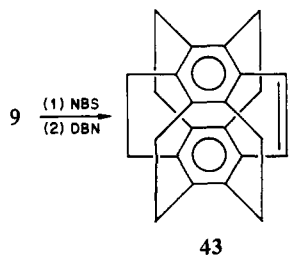
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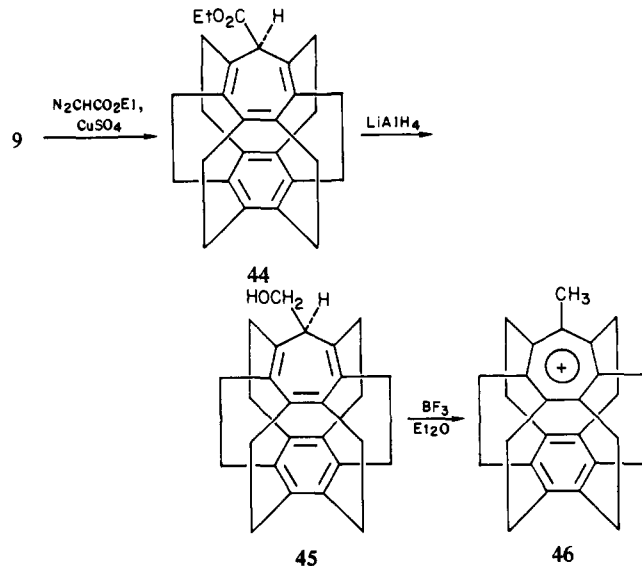
spectral properties are in agreement with those to be expected for the dihydro derivative **41**. Recrystallization of **41** from a mixture of dichloromethane and methanol in the presence of air, though, led to a new product whose composition and spectral properties are in accord with the assigned structure **42** (or an isomer). As a rationalization of this reaction, the dihydro derivative **41** could be expected to undergo easy reaction with oxygen, possibly via an "ene" reaction, to a hydroperoxide, as shown. This could then readily yield an epoxy carbinol which, on methanolysis, could give **42** (or a position isomer).

A superphane analogue of some theoretical interest would be that in which all six bridges contain carbon-carbon double bonds. In an attempt to see whether this could be accomplished directly, superphane was treated with an excess of *N*-bromosuccinimide in the presence of a radical initiator. The resulting mixture of bromides (mass spectral analysis indicated primarily the formation of a monobromide accompanied by traces of dibromides) was treated directly with 1,5-diazabicyclo[3.4.0]non-5-ene to give the monoolefin **43** in 20% yield. It is clear that a more efficient route



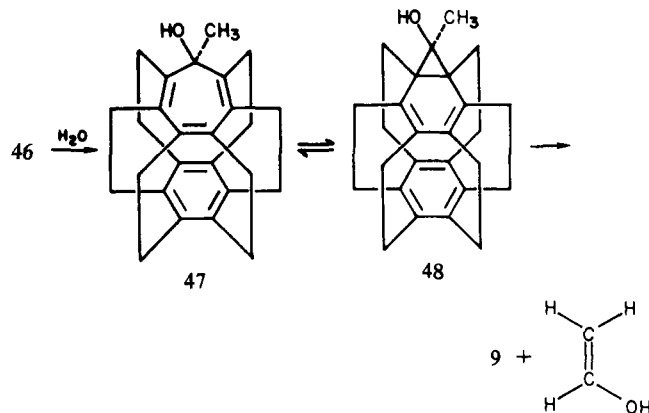
will be needed for the successful preparation of the corresponding hexaene.

Treatment of superphane with ethyl diazoacetate in the presence of anhydrous cupric sulfate led to a smooth carbene insertion and ring expansion to give **44** in 46% yield. The further conversion of the seven-membered ring to a tropylium ion was accomplished in a rather simple fashion. Reduction of the ester **44** with lithium aluminum hydride gave the alcohol **45**, and this, on treatment with boron trifluoride etherate, underwent a carbonium ion-hydride shift to give the tropylium ion **46** directly. The ultraviolet absorption spectrum of **46** showed a strong charge-transfer band at 375 ( $\epsilon$  2990) and 431 nm (1440) with a shoulder at 490 nm ( $\epsilon$



919). As would be expected, because of the shorter distance between decks and the decreased possibility for skewing of the decks in **46**, its charge-transfer band is at a longer wavelength than that for the analogous tropylium ion derived from [2.2]-paracyclophane ( $\lambda_{\text{max}}$  323 ( $\epsilon$  2,230), 353 (1590), 400 (sh) nm (524))<sup>40,41</sup> or that derived from [2<sub>4</sub>](1,2,4,5)cyclophane ( $\lambda_{\text{max}}$  351 ( $\epsilon$  2000), 400 (750), 460 (sh) nm (400)).<sup>8b</sup>

When recrystallization of **46** was attempted with aqueous



methanol or when **46** was allowed to stand exposed to air, a remarkable transformation occurred, regenerating superphane in 52% yield. A possible explanation is that **46** combines with moisture to form the carbinol **47**, which is in equilibrium with the noncaradiene valence tautomer **48**. By the usual arrow pushing, a bond reorganization of **48** can be visualized which would lead to ejection of the enol of acetaldehyde and the regeneration of superphane (**9**).

For many [2<sub>n</sub>]cyclophanes participation of a benzene deck as a diene in a Diels-Alder reaction relieves strain, and so such Diels-Alder reactions are a common phenomenon.<sup>7,8b,42,43</sup> In the case of superphane, 1,4-addition of a dienophile in the Diels-Alder reaction would be expected to increase strain rather than decrease it. It is not surprising, therefore, that our attempts to effect a Diels-Alder reaction with superphane, even using prolonged reaction times with such a powerful dienophile as dicyanoacetylene, have been fruitless. However, when a solution of superphane in dichloromethane was treated with an excess of dicyanoacetylene in the presence of aluminum chloride, a 1:2 adduct of superphane

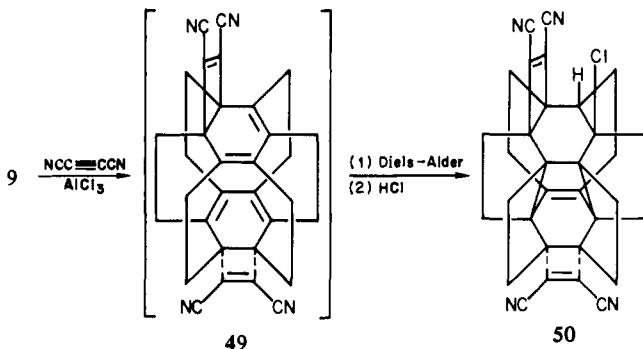
(40) Horita, H.; Otsubo, T.; Sakata, Y.; Misumi, S. *Tetrahedron Lett.* **1976**, 3899-3902.

(41) O'Connor, J. G.; Keehn, P. M. *J. Am. Chem. Soc.* **1976**, *98*, 8446-8450.

(42) Ciganek, E. *Tetrahedron Lett.* **1967**, 3321-3325.

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and dicyanoacetylene was formed in 40% yield. No obvious structure could be deduced from the spectral properties of this adduct. However, Dr. A. W. Hanson kindly performed an X-ray crystallographic analysis of this adduct and demonstrated that its correct structure is that given by formula **50**.<sup>44</sup> On the basis of structure **50**, a logical interpretation for the formation of the adduct can be made. Successive 1,2-additions of dicyanoacetylene to the separate decks of superphane could lead to intermediate **49** which, by an internal Diels–Alder reaction followed by addition



of hydrogen chloride to one of the isolated olefin bonds, would give the adduct having structure **50**.

In summary, superphane is, in some respects, rather inert, and several derivatives of superphane undergo amazing rearrangements to regenerate superphane, indicating that the molecule represents an energy well of surprising stability. The unusual structural features of the molecule are matched by its unusual chemistry.

#### Experimental Section<sup>45</sup>

**4,5-Dimethylbenzocyclobutene (15).** The preparation of 2,4,5-trimethylbenzyl chloride (**14**) was carried out on a molar scale by the reaction of 1,2,4-trimethylbenzene with paraformaldehyde in concentrated hydrochloric acid following a procedure described by von Braun and Nelles.<sup>46</sup> Distillation gave **14** in 71% yield as a colorless oil: bp 65 °C (10<sup>-1</sup> mm); <sup>1</sup>H NMR δ 2.21 (6 H, s, CH<sub>3</sub>), 2.38 (3 H, s, CH<sub>3</sub>), 4.56 (2 H, s, CH<sub>2</sub>Cl), 6.96 (1 H, s, ArH), 7.06 (1 H, s, ArH). Slow distillation of 59.62 g of **14** at 10<sup>-3</sup> mm of pressure into the hot zone (750 °C) of a 30 × 5 cm quartz tube, followed by collection of the exit gases at -40 °C, gave a pale yellow solid. This was sublimed at 60 °C (10<sup>-1</sup> mm) to give 24.70 g (53%) of pale yellow crystals: mp 66–68 °C; <sup>1</sup>H NMR δ 2.23 (6 H, s, CH<sub>3</sub>), 3.11 (4 H, s, CH<sub>2</sub>CH<sub>2</sub>), 6.83 (2 H, s, ArH); mass spectrum, *m/e* 132, 117; molecular weight calcd for C<sub>10</sub>H<sub>12</sub> 132.094, found (high-resolution mass spectrum) 132.094.

**5,6,14,15-Tetramethyl[2.2]orthocyclophane (16).** (A) **Solution Pyrolysis of 15.** A solution of 6.458 g of **15** in 31 mL of diethyl phthalate was boiled under reflux in an atmosphere of nitrogen for 1 h. After the reaction mixture had been added to 179 mL of an aqueous 15% solution of potassium hydroxide, it was stirred at room temperature for 12 h and then extracted with dichloromethane. The dichloromethane extract was washed with water, dried, and concentrated, followed by sublimation of the residue at 150 °C (10<sup>-2</sup> mm). The resulting sublimate was recrystallized from a mixture of dichloromethane and methanol to give 1.475 g (23%) of fine, white prisms: mp 238–241 °C; <sup>1</sup>H NMR δ 2.14 (12 H, s, CH<sub>3</sub>), 2.93 (8 H, s, CH<sub>2</sub>), 6.80 (4 H, s, ArH); mass spectrum, *m/e* 264, 249, 234; molecular weight calcd for C<sub>20</sub>H<sub>24</sub> 264.188, found (high-resolution mass spectrum) 264.188.

(B) **Gas-Phase Pyrolysis of 15.** A pyrolysis apparatus with a vertical 30 × 5 cm quartz tube in the hot zone (400 °C), having a 3-cm zone of quartz helices at the top, was employed, and 820 mg of finely ground **15** was slowly dusted into a nitrogen stream (2 mL/s) at atmospheric

pressure, carrying it into the hot zone, and the exit gases were passed through an ice-cooled trap. The solid product, which collected in the trap, was recrystallized from a mixture of dichloromethane and methanol to give 518 mg (63%) of white crystals (mp 238–241 °C) in all respects identical with the product obtained in A.

**Formylation of 16 via the Rieche Reaction.** To a solution of 26.15 g of **16** and 46.2 mL of stannic chloride in 2.5 L of dry dichloromethane held at 0 °C was added 35.8 mL of dichloromethyl methyl ether with stirring under a nitrogen atmosphere. After the mixture had been stirred at 0 °C for 4 h, it was allowed to warm to room temperature and then was stirred for an additional 2 days. The mixture was poured into ice water and extracted with dichloromethane, and the dichloromethane extract was washed with water, dried, and concentrated to give a pale yellow solid. This was purified by column chromatography over silica gel by using a 1:1 mixture of benzene and hexane as eluant.

**The first fraction of eluate** gave 19.10 g (60%) of **17** as white crystals. This was recrystallized from a mixture of dichloromethane and methanol to give fine, white needles: mp 195–196 °C; IR (KBr)  $\nu_{\max}$  1690 (C–H=O) cm<sup>-1</sup>; <sup>1</sup>H NMR δ 2.15 (6 H, s, CH<sub>3</sub>), 2.26 (6 H, s, CH<sub>3</sub>), 3.06 (4 H, s, CH<sub>2</sub>), 3.26 (4 H, s, CH<sub>2</sub>), 6.93 (2 H, s, ArH), 10.58 (2 H, s, CH=O); mass spectrum, *m/e* 320, 305, 291; molecular weight calcd for C<sub>22</sub>H<sub>24</sub>O<sub>2</sub> 320.178, found (high-resolution mass spectrum) 320.178.

**The second fraction of eluate** gave 7.10 g (20%) of crystalline **20**. This was recrystallized from a mixture of dichloromethane and methanol to give white cubes: mp 235–239 °C; IR (KBr)  $\nu_{\max}$  1681 (CH=O) cm<sup>-1</sup>; <sup>1</sup>H NMR δ 2.09 (6 H, s, CH<sub>3</sub>), 2.29 (6 H, s, CH<sub>3</sub>), 3.25 (8 H, br s, CH<sub>2</sub>), 6.86 (2 H, s, ArH), 10.60 (2 H, s, CH=O); mass spectrum, *m/e* 320, 305, 291; molecular weight calcd for C<sub>22</sub>H<sub>24</sub>O<sub>2</sub> 320.178, found (high-resolution mass spectrum) 320.178.

**Reduction of 20 with Sodium Borohydride To Give 21.** To a solution of 20.0 mg (0.06 mmol) of **20** in a mixture of 3 mL of methanol and 3 mL of benzene was added a solution of 3 mg (0.08 mmol) of sodium borohydride in 1 mL of methanol under nitrogen with stirring. After the mixture had been stirred at room temperature for 2 h, it was neutralized with acetic acid, 1 mL of water was added, and the mixture was extracted with dichloromethane. The dichloromethane extract was washed with water, dried, and concentrated to give a white powder. Recrystallization of this from chloroform gave 20.2 mg (100%) of **21** as white crystals: mp 204–205 °C; <sup>1</sup>H NMR δ 1.20 (2 H, s, OH), 2.10 (6 H, s, CH<sub>3</sub>), 2.20 (6 H, s, CH<sub>3</sub>), 2.93–3.30 (8 H, m, CH<sub>2</sub>), 4.72 (4 H, s, CH<sub>2</sub>OH), 6.65 (2 H, s, ArH); mass spectrum, *m/e* 324, 306; molecular weight calcd for C<sub>22</sub>H<sub>26</sub>O<sub>2</sub> 324.209, found (high-resolution mass spectrum) 324.208.

**Conversion of 21 to 22.** To a solution of 68 mg (0.21 mmol) of **21** in 4 mL of benzene at room temperature was added 0.06 mL (0.85 mmol) of thionyl chloride and a drop of pyridine under nitrogen with stirring. After the solution had been stirred for 2.75 h at room temperature, it was boiled under reflux for 1 h, concentrated, poured into ice water, and extracted with dichloromethane. The dichloromethane extract was washed successively with an aqueous sodium bicarbonate solution and water, dried, and concentrated. Recrystallization of the residual solid from tetrahydrofuran gave 72 mg (95%) of white, powdery crystals: mp 231–234 °C dec; <sup>1</sup>H NMR δ 2.10 (6 H, s, CH<sub>3</sub>), 2.20 (6 H, s, CH<sub>3</sub>), 3.02–3.24 (8 H, m, CH<sub>2</sub>), 4.69 (4 H, s, CH<sub>2</sub>Cl), 6.69 (2 H, s, ArH); mass spectrum, *m/e* 362, 360; molecular weight calcd for C<sub>22</sub>H<sub>26</sub>Cl<sub>2</sub> 360.141, found (high-resolution mass spectrum) 360.142.

Attempted pyrolysis of **22** at 700 °C and 10<sup>-2</sup> mm of pressure gave only tars and polymeric substances.

**Reduction of 17 with Sodium Borohydride To Give 18.** To a solution of 50 mg (0.16 mmol) of **17** in a mixture of 5 mL of methanol and 5 mL of benzene was added a solution of 12 mg (0.32 mmol) of sodium borohydride in 2 mL of methanol, and the mixture was stirred under nitrogen at room temperature for 2 h. After neutralization with acetic acid, the mixture was concentrated and 3 mL of water was added to the residue. It was then extracted with dichloromethane, washed with water, dried, and concentrated. The resulting white powder was recrystallized from a mixture of dichloromethane and methanol to give 15 mg (100%) of white, powdery crystals: mp 257–259 °C; <sup>1</sup>H NMR δ 2.12 (6 H, s, CH<sub>3</sub>), 2.19 (6 H, s, CH<sub>3</sub>), 2.43 (2 H, s, OH), 3.05 (4 H, s, CH<sub>2</sub>), 3.26 (4 H, s, CH<sub>2</sub>), 4.73 (4 H, s, CH<sub>2</sub>OH), 6.73 (2 H, s, ArH); mass spectrum, *m/e* 324, 306. Anal. (C<sub>22</sub>H<sub>26</sub>O<sub>2</sub>) C, H.

**Conversion of 18 to 19.** To a solution of 119 mg (0.37 mmol) of **18** in 4 mL of benzene was added at room temperature under nitrogen with stirring 0.1 mL of thionyl chloride and a drop of pyridine. After the solution had been stirred at room temperature for 2 h, it was boiled under reflux for 1 h, concentrated, and poured into ice water. The aqueous mixture was extracted with dichloromethane, and the dichloromethane extract was washed successively with an aqueous sodium bicarbonate solution and water, dried, and concentrated. Sublimation of the residual solid gave 133 mg (100%) of **19** as white, powdery crystals: mp 238–240 °C; <sup>1</sup>H NMR δ 2.17 (6 H, s, CH<sub>3</sub>), 2.23 (6 H, s, CH<sub>3</sub>O), 2.98 (4 H, s,

(44) The details of this X-ray crystallographic analysis will be published elsewhere. We express our deep appreciation to Dr. A. W. Hanson for carrying out this structural determination.

(45) 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 by using sealed, evacuated capillary melting point tubes. Infrared spectra were obtained by using 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 (δ 7.27) as an internal standard.

(46) (a) von Braun, J.; Nelles, J. *Ber. Disch. Chem. Ges. A* **1934**, *67*, 1094–1099. (b) Smith, L. I.; MacMullen, C. W. *J. Am. Chem. Soc.* **1936**, *58*, 629–632.

CH<sub>2</sub>), 3.15 (4 H, s, CH<sub>2</sub>), 4.73 (4 H, s, CH<sub>2</sub>Cl), 6.83 (2 H, s, ArH); mass spectrum, *m/e* 362, 360, 347, 345. Anal. (C<sub>22</sub>H<sub>26</sub>Cl<sub>2</sub>) C, H.

**4,13-Dimethyl[2<sub>4</sub>](1,2,3,4)cyclophane (23).** Slow sublimation at 10<sup>-2</sup> mm of pressure of 25 mg of **19** into the hot zone (700 °C) of a quartz tube followed by condensation of the exit gases on a cold finger at -40 °C gave a brown solid. This was purified by thin-layer chromatography over silica gel using a 1:1 mixture of benzene and hexane for elution. The product isolated from the main fraction of eluate was recrystallized from ether to give 8 mg (40%) of white plates: mp 219–220 °C; UV (CH<sub>2</sub>Cl<sub>2</sub>), λ<sub>max</sub> 287 nm (ε 384), 295 (sh) (354), 301 (sh) (319); <sup>1</sup>H NMR δ 2.06 (6 H, s, CH<sub>3</sub>), 2.40–3.25 (8 H, m, CH<sub>2</sub>), 2.88 (4 H, s, CH<sub>2</sub>), 3.01 (4 H, s, CH<sub>2</sub>), 6.17 (2 H, s, ArH); mass spectrum, *m/e* 288, 260, 245, 232, 144; molecular weight calcd for C<sub>22</sub>H<sub>24</sub> 288.183, found (high-resolution mass spectrum) 288.183.

**4,13-Dimethyl-5,14-diformyl[2<sub>4</sub>](1,2,3,4)cyclophane (24).** To a solution of 450 mg (1.56 mmol) of 4,13-dimethyl[2<sub>4</sub>](1,2,3,4)cyclophane (**23**) and 0.75 mL (6.43 mmol) of stannic chloride in 129 mL of dry dichloromethane held at 0 °C was added 0.57 mL (6.30 mmol) of dichloromethyl methyl ether under nitrogen with stirring. After the solution had been stirred at 0 °C for 5 h, it was warmed to room temperature and stirred an additional 8 h. Then the reaction mixture was poured into ice water and extracted with dichloromethane. The dichloromethane extract was washed with water, dried, and concentrated. Recrystallization of the residual solid from a mixture of ether and dichloromethane afforded 529 mg (98%) of fine, white needles: mp 305–309 °C dec; IR (KBr) ν<sub>max</sub> 1674 (CH=O) cm<sup>-1</sup>; <sup>1</sup>H NMR δ 2.25 (6 H, s, CH<sub>3</sub>), 2.80–3.55 (8 H, m, CH<sub>2</sub>), 3.03 (4 H, s, CH<sub>2</sub>), 3.11 (4 H, s, CH<sub>2</sub>), 10.25 (2 H, s, CH=O); mass spectrum, *m/e* 344, 316; molecular weight calcd for C<sub>24</sub>H<sub>26</sub>O<sub>2</sub> 344.178, found (high-resolution mass spectrum) 344.177.

**4,13-Dimethyl-5,14-bis(hydroxymethyl)[2<sub>4</sub>](1,2,3,4)cyclophane (25).** To a suspension of 186 mg of lithium aluminum hydride in 60 mL of ether was added dropwise with stirring a solution of 525 mg of **24** in 640 mL of ether. When the addition was complete, the reaction mixture was stirred at room temperature for an additional 20 h. Then, while the mixture was cooled in an ice bath, a saturated aqueous solution of sodium sulfate was added with stirring. The ether layer was separated, and the aqueous layer was extracted with dichloromethane. The combined organic extract was washed with water, dried, and concentrated. Recrystallization of the residual solid from a mixture of methanol and dichloromethane gave 508 mg (96%) of white prisms: mp 273–275 °C; <sup>1</sup>H NMR δ 2.17 (6 H, s, CH<sub>3</sub>), 2.97 (8 H, s, CH<sub>2</sub>), 3.08 (4 H, s, CH<sub>2</sub>), 3.18 (4 H, s, CH<sub>2</sub>), 3.69 (2 H, s, OH), 4.29 and 4.56 (4 H, two d, J<sub>A,B</sub> = 11.4 Hz, CH<sub>2</sub>OH); mass spectrum, *m/e* 348, 331, 303, 275; molecular weight calcd for C<sub>24</sub>H<sub>28</sub>O<sub>2</sub> 348.209, found (high-resolution mass spectrum) 348.209.

**4,13-Dimethyl-5,14-bis(chloromethyl)[2<sub>4</sub>](1,2,3,4)cyclophane (26).** A mixture of 4.2 mL of thionyl chloride and one drop of pyridine was added to 514 mg of **25**, and the resulting mixture was stirred at room temperature for 21 h and then boiled under reflux for 1 h. After removal of the excess thionyl chloride in vacuo, the residual solid was washed briefly with water and with methanol, dried, and sublimed at 180 °C at 10<sup>-2</sup> mm of pressure to give 530 mg (93%) of white crystals: mp 215–217 °C; <sup>1</sup>H NMR δ 2.08 (6 H, s, CH<sub>3</sub>), 2.92–3.24 (8 H, m, CH<sub>2</sub>), 2.96 (4 H, s, CH<sub>2</sub>), 2.99 (4 H, s, CH<sub>2</sub>), 4.43 and 4.56 (4 H, two d, J<sub>A,B</sub> = 11.4 Hz, CH<sub>2</sub>Cl); mass spectrum, *m/e* 386, 384; molecular weight calcd for C<sub>24</sub>H<sub>26</sub>Cl<sub>2</sub> 384.141, found (high-resolution mass spectrum) 384.140.

**[2<sub>6</sub>](1,2,3,4,5,6)Cyclophane (9, Superphane).** Slow sublimation of 530 mg of **26** at 10<sup>-2</sup> mm of pressure into the hot zone (650 °C) of a quartz tube in a pyrolysis apparatus with condensation of the exit gases at -40 °C gave a light tan solid on the cold finger. After removal of the solid by washing the cold finger with chloroform, the chloroform solution was concentrated and the residual solid sublimed at 200 °C (10<sup>-2</sup> mm). Recrystallization of the sublimate from dichloromethane gave 245 mg (57%) of white prisms: mp 325–327 °C; UV (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub> 296 nm (ε 421), 306 (sh) (394), 311 (sh) (324); IR (KBr) ν<sub>max</sub> 2980 and 2950 (C—H), 1510 (C=C), 1400, 1315, 1230 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 2.98 (s, CH<sub>2</sub>); <sup>13</sup>C NMR (proton decoupled) δ 144.2 and (J<sub>13C-1H</sub> = 126 Hz); mass spectrum, *m/e* 312, 284, 256, 156, 141, 128; molecular weight calcd for C<sub>24</sub>H<sub>24</sub> 312.188, found (high-resolution mass spectrum) 312.188.

**4,13-Dimethyl-5,14-bis(bromomethyl)[2<sub>4</sub>](1,2,3,4)cyclophane (27).** A solution of 14 mg of **25** and 0.05 mL of phosphorus tribromide in 2 mL of dry benzene was boiled under reflux in a nitrogen atmosphere for 4 h, cooled to 0 °C, and poured into ice water. The benzene layer was separated, and the aqueous layer was extracted with chloroform. The combined organic extracts were washed with water, dried, and concentrated. Sublimation of the residual solid gave 17 mg (89%) of white crystals: mp 207–209 °C; <sup>1</sup>H NMR δ 2.05 (6 H, s, CH<sub>3</sub>), singlets at 2.93, 2.97, 3.02, and 3.08 (4 H each, CH<sub>2</sub>), doublets at 4.35 and 4.52 (2 H each, J<sub>A,B</sub> = 11 Hz, CH<sub>2</sub>Br); mass spectrum *m/e* 476, 474, 472, 394, 393; molecular weight calcd for C<sub>24</sub>H<sub>26</sub>Br<sub>2</sub> 476.036 (474.038,

472.040), found (high-resolution mass spectrum) 476.036 (474.040, 472.038).

**4,13-Dimethyl[2<sub>4</sub>](1,2,3,4,5)cyclophane (28).** To a solution of 16 mg of **27** in 2.3 mL of dry tetrahydrofuran was added dropwise with stirring 1.67 mL of a solution of phenyllithium, prepared by diluting a 1.9 M solution of phenyllithium in hexane 25-fold with dry tetrahydrofuran. The resulting mixture was stirred at room temperature for 6 h, water was added, and the organic layer was extracted successively with ether and chloroform. The combined extracts were washed with water, dried, and concentrated. Purification of the residual solid by thin-layer chromatography over silica gel using a 1:5 mixture of benzene and hexane as eluant gave 3 mg of white crystals. These were recrystallized from dichloromethane to yield 2 mg (22%) of white prisms: mp 315 °C dec; UV (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub> 301 nm (ε 341), 313 (sh) 257) 318 (sh) (224); <sup>1</sup>H NMR δ 2.13 (6 H, s, CH<sub>3</sub>), 2.81 (8 H, s, CH<sub>2</sub>), 2.94 (4 H, s, CH<sub>2</sub>), 3.11 (8 H, s, CH<sub>2</sub>); mass spectrum, *m/e* 314, 299, 286, 271; molecular weight calcd for C<sub>24</sub>H<sub>26</sub> 314.203, found (high-resolution mass spectrum) 314.204.

**Birch Reduction of Superphane (9) To Give 29.** A solution of 10 mg of superphane (**9**) in 8 mL of tetrahydrofuran was added under nitrogen with stirring to a solution of 20 mg of lithium and one drop of methanol in 8 mL of liquid ammonia. After the mixture had been stirred for 4.5 h, the blue color of the solution was discharged by the addition of 1 mL of methanol. When the ammonia had been allowed to evaporate, the residue was extracted with chloroform, washed with water, dried, and concentrated. Preparative thin-layer chromatography over silica gel using a 1:1 mixture of benzene and hexane gave two fractions: (1) 2 mg of crystalline product and (2) recovery of 8 mg of superphane. The crystalline product was recrystallized from a mixture of dichloromethane and methanol to give 1 mg (10%) of white prisms: mp 279 °C dec; <sup>1</sup>H NMR δ 2.02–3.02 (m, CH<sub>2</sub> and CH); molecular weight calcd for C<sub>24</sub>H<sub>26</sub> 314.203, found (high-resolution mass spectrum, 314.204).

**Birch Reduction of Superphane (9) in Ethylamine and *n*-Propylamine To Give 31 and 32.** To a solution of 7 mg of superphane (**9**) in 6 mL of dry *n*-propylamine was added under nitrogen at room temperature 25 mg of lithium. The mixture was cooled to -68 °C, and 6 mL of dry ethylamine was added. The blue solution was allowed to warm to room temperature where it was stirred for 2 h. Another 25 mg of lithium was added, and the mixture was stirred an additional 8 h. After evaporation of the ethylamine, ether was added and the solution was cooled before adding an aqueous solution of 5% hydrochloric acid. The resulting mixture was extracted successively with ether and chloroform. The combined extracts were washed with water, dried, and concentrated. The residual solid was purified by preparative thin-layer chromatography over silica gel using a 1:5 mixture of benzene and hexane as eluant. The first fraction of eluate gave a white solid which, after being washed with ether, yielded 0.5 mg (7) of **32** as white plates: mp 176–178 °C; <sup>1</sup>H NMR δ 2.24 (18 H, s, CH<sub>3</sub>), 2.37 (12 H, s, CH<sub>2</sub>), 2.85 (4 H, s, CH<sub>2</sub>); molecular weight calcd for C<sub>24</sub>H<sub>34</sub> 322.266, found (high-resolution mass spectrum) 322.266.

The second fraction of eluate gave 5 mg of a white solid. This was recrystallized from a mixture of methanol and dichloromethane to give 4 mg (57%) of **31** as white prisms: mp 293–294 °C dec; UV (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub> 265 (sh) nm (ε 440), 272 (557), 276 (sh) (515), 279 (sh) (429); <sup>1</sup>H NMR δ 2.18 (12 H, s, CH<sub>3</sub>), 2.27 (12 H, s, CH<sub>2</sub>), 2.63–3.45 (9 H, m, CH<sub>2</sub>); mass spectrum, *m/e* 320, 305, 290, 160.

**Independent Synthesis of 31.** (A) **4,5,6,14,15,16-Hexamethyl[2.2]-orthocyclophane (33).** To a solution of 55 mg of **20** in 5 mL of tetrahydrofuran was added 39 mg of lithium aluminum hydride, and the mixture was stirred under nitrogen at room temperature for 30 min. Then, 136 mg of anhydrous aluminum chloride was added, and the mixture was boiled under reflux for 21 h. After the mixture had been cooled in an ice bath, a saturated aqueous solution of sodium sulfate was added and the organic layer was extracted with ether. An additional extraction of the aqueous layer was made with chloroform before the combined organic extracts were washed with water, dried, and concentrated. Sublimation of the residual solid gave 20 mg (40%) of **33** as white prisms: mp 205–206 °C; <sup>1</sup>H NMR δ 2.10 (6 H, s, CH<sub>3</sub>), 2.14 (6 H, s, CH<sub>3</sub>), 2.24 (6 H, s, CH<sub>3</sub>), 2.91–3.21 (8 H, m, CH<sub>2</sub>), 6.63 (2 H, s, ArH); mass spectrum, *m/e* 292, 277, 262, 249; molecular weight calcd for C<sub>22</sub>H<sub>28</sub> 292.219, found (high-resolution mass spectrum) 292.219.

(B) **4,5,6,14,15,16-Hexamethyl-7,13-diformyl[2.2]orthocyclophane (34).** To a solution of 22 mg of **33** and 0.04 mL of stannic chloride in 5 mL of dry dichloromethane was added 0.03 mL of dichloromethyl methyl ether with stirring at 0 °C. The mixture was stirred at 0 °C for 3 h and then an additional 67 h at room temperature, before being poured into water. After the organic layer had been extracted with dichloromethane, the dichloromethane extract was washed with water, dried, and concentrated. Recrystallization of the resulting pale yellow solid from a mixture of dichloromethane and tetrahydrofuran gave 24 mg (86%) of

**34** as fine, white needles: mp 261–262 °C; IR (KBr)  $\nu_{\max}$  1687  $\text{cm}^{-1}$  (CH=O);  $^1\text{H NMR}$   $\delta$  2.12 (6 H, s,  $\text{CH}_3$ ), 2.26 (6 H, s,  $\text{CH}_3$ ), 2.32 (6 H, s,  $\text{CH}_3$ ), 3.29 (8 H, br s,  $\text{CH}_2$ ), 10.59 (2 H, s, CH=O); mass spectrum,  $m/e$  348, 333, 319; molecular weight calcd for  $\text{C}_{24}\text{H}_{28}\text{O}_2$  348.209, found (high-resolution mass spectrum) 348.209.

(C) **4,5,6,14,15,16-Hexamethyl-7,13-bis(hydroxymethyl)[2.2]orthocyclophane (35)**. To a solution of 47 mg of **34** in 25 mL of ether was added 16 mg of lithium aluminum hydride, and the mixture was stirred at room temperature under nitrogen for 26 h. After the mixture had been decomposed by addition of an aqueous saturated sodium sulfate solution, it was extracted successively with ether and chloroform. The combined organic extracts were washed with water, dried, and concentrated. Recrystallization of the solid residue from chloroform gave 42 mg (86%) of **35** as white prisms: mp 295 °C dec;  $^1\text{H NMR}$   $\delta$  2.12 (12 H, s,  $\text{CH}_3$ ), 2.26 (6 H, s,  $\text{CH}_3$ ), 2.96–3.48 (8 H, m,  $\text{CH}_2$ ), 4.70 (4 H, br s,  $\text{CH}_2\text{OH}$ ); molecular weight calcd for  $\text{C}_{24}\text{H}_{32}\text{O}_2$  352.240, found (high-resolution mass spectrum) 352.238.

(D) **4,5,6,7,13,14,15,16-Octamethyl[2.2]cyclophane (31)**. A solution of 15 mg of **35**, 0.5 mL of thionyl chloride, and a drop of pyridine was stirred at 0 °C for 1 h and then at room temperature for 6 h. After the mixture had been poured into ice water, the organic layer was extracted with chloroform. The chloroform extract was washed successively with a sodium bicarbonate solution and water, dried, and concentrated to give 11 mg of **36** as white crystals (molecular weight calcd for  $\text{C}_{24}\text{H}_{30}\text{Cl}_2$  388.172, found (high-resolution mass spectrum) 388.171). A solution of these crystals plus 15 mg of lithium aluminum hydride in 7 mL of tetrahydrofuran was boiled under reflux in a nitrogen atmosphere for 12 h. After the mixture had been decomposed by addition of a saturated aqueous solution of sodium sulfate, it was extracted successively with ether and chloroform. The combined extracts were washed with water, dried, and concentrated. Purification of the residue by preparative thin-layer chromatography over silica gel using a 1:1 mixture of benzene and hexane for elution was followed by recrystallization of the product from a mixture of methanol and chloroform to give 6 mg (44%) of **31** as white prisms: mp 293–294 °C dec; in all respects identical with the sample of **31** obtained previously from the Birch reduction of superphane (**9**).<sup>37</sup>

**Independent Synthesis of 32. (A) Pentamethylbenzyl Bromide (38)**. When 0.5 mL of an aqueous 48% hydrobromic acid solution was added to a solution of 53 mg of pentamethyl methyl ether<sup>38</sup> in 0.8 mL of glacial acetic acid at room temperature, a crystalline precipitate separated almost instantaneously. This was collected and dissolved in dichloromethane, and the dichloromethane extract was washed with water, dried, and concentrated. The resulting crystalline solid was recrystallized from hexane to give 63 mg (94%) of **38** as white needles: mp 84–85 °C;  $^1\text{H NMR}$   $\delta$  2.21 (9 H, s,  $\text{CH}_3$ ), 2.32 (6 H, s,  $\text{CH}_3$ ), 4.64 (2 H, s,  $\text{CH}_2\text{Br}$ ); molecular weight calcd for  $\text{C}_{12}\text{H}_{11}\text{Br}$  242.049, 240.051, found (high-resolution mass spectrum) 242.049, 240.051.

(B) **1,2-Bis(pentamethylphenyl)ethane (32)**. A mixture of 112 mg of **38** and 7 mg of magnesium in 5 mL of tetrahydrofuran was boiled under reflux in a nitrogen atmosphere for 46 h. After addition of a few milligrams of anhydrous ferric chloride, the reaction mixture was boiled under reflux for an additional 24 h. The cold reaction mixture was acidified with an aqueous 2% hydrochloric acid solution and extracted with chloroform. The chloroform extract was washed with water, dried, and concentrated. Recrystallization of the residual solid from ether gave 54 mg (72%) of **32** as white plates: mp 176–178 °C; in all respects identical with the sample of **32** obtained from the Birch reduction of superphane (**9**).

**Reaction of Superphane (9) with Zinc and Sulfuric Acid To Give 39**. To a solution of 3 mg of superphane (**9**) in 1 mL of concentrated sulfuric acid was added 25 mg of zinc powder, and the mixture was stirred at room temperature for 1 h. It was then poured into ice water, and the organic product was extracted with chloroform. The chloroform extract was washed with water, dried, and concentrated. Purification of the residue by preparative thin-layer chromatography over silica gel using a 1:5 mixture of benzene and hexane for elution led to recovery of 1 mg of superphane and 2 mg of a new product. The new product was washed with ether and then recrystallized from tetrahydrofuran to give 1 mg (32%) of **39** as white prisms: mp >270 °C dec;  $^1\text{H NMR}$   $\delta$  2.59–3.71 (16 H, m,  $\text{CH}_2$ ), 2.99 (4 H, s,  $\text{CH}_2$ ), 4.06 (4 H, s,  $\text{CH}_2\text{S}$ ); mass spectrum,  $m/e$  344 ( $\text{M}^+$ ), 329 ( $\text{M}^+ - 15$ ), 316 ( $\text{M}^+ - \text{C}_2\text{H}_4$ ), 312 ( $\text{M}^+ - \text{S}$ ), 316; molecular weight calcd for  $\text{C}_{24}\text{H}_{24}\text{S}$  344.160, found (high-resolution mass spectrum) 344.162.

When the above experiment was repeated on a scale sixfold larger and in the presence of added sulfur, the yield of **39** and the recovery of superphane were the same as in the above experiment, showing that the presence of free sulfur does not promote formation of **39**.

**Conversion of Superphane (9) to 41 and 42**. When 10 mg of superphane (**9**) was treated with an excess of dimethoxycarbonium fluoro-

borate<sup>39</sup> in 3.5 mL of dry chloroform, the solution gradually became a deep red and it was stirred under nitrogen at room temperature for 4 days. A solution of 100 mg of sodium borohydride in 1 mL of methanol was then added, and the resulting mixture was stirred at room temperature for 6 h. After addition of water to the reaction mixture followed by neutralization with acetic acid, the organic constituents were extracted with chloroform. The chloroform extract was washed with water, dried, and concentrated. Purification of the residual solid by preparative thin-layer chromatography over silica gel using a 2:3 mixture of benzene and hexane led to a recovery of 2 mg (20%) of superphane and, from the main fraction of eluate, 3.5 mg (33%) of **41** as white crystals:  $^1\text{H NMR}$   $\delta$  0.62 (3 H, s,  $\text{CH}_3$ ), 2.12–3.22 (25 H, m,  $\text{CH}_2$  and CH); mass spectrum,  $m/e$  328, 313, 300; molecular weight calcd for  $\text{C}_{25}\text{H}_{28}$  328.219, found (high-resolution mass spectrum) 328.220.

Attempted recrystallization of **41** from a mixture of dichloromethane and methanol in the presence of air gave 3.5 mg of **42** as white prisms: mp >302 °C dec;  $^1\text{H NMR}$   $\delta$  0.97 (3 H, s,  $\text{CH}_3$ ), 1.93–3.51 (24 H, m,  $\text{CH}_2$ ), 3.03 (3 H, s,  $\text{OCH}_3$ ); molecular weight calcd for  $\text{C}_{26}\text{H}_{30}\text{O}_2$  374.225, found (high-resolution mass spectrum) 374.223.

**[2<sub>6</sub>](1,2,3,4,5,6)Cyclophane-1-ene (43)**. A solution of 10 mg of superphane (**9**), 37 mg of *N*-bromosuccinimide, and a small amount of benzoyl peroxide in 40 mL of carbon tetrachloride was boiled under reflux for 18 h. After removal of succinimide and concentration of the solution, the residual solid was purified by preparative thin-layer chromatography over silica gel using a 1:5 mixture of benzene and hexane for elution. The resulting 8 mg of solid appeared from mass spectra analysis to be mainly a monobromo derivative of superphane contaminated with a small amount of dibromide. Therefore, it was dissolved directly in 0.5 mL of 1,5-diazabicyclo[3.4.0]non-5-ene and heated at 80 °C for 11 h. Concentration of the solution followed by preparative thin-layer chromatography of the residual solid over silica gel using a 1:1 mixture of benzene and hexane led to a recovery of 3 mg (30%) of **9** and 2 mg of a white crystalline product. Sublimation of this product then gave 2 mg (20% from **9**) of **43** as white crystals: mp >310 °C dec;  $^1\text{H NMR}$   $\delta$  2.46–3.04 (20 H, m,  $\text{CH}_2$ ), 6.86 (2 H, s,  $\text{CH}=\text{CH}$ ); molecular weight calcd for  $\text{C}_{24}\text{H}_{22}$  310.172, found (high-resolution mass spectrum) 310.173.

**Reaction of Superphane (9) with Ethyl Diazoacetate To Give 44**. A solution of 16 mg (0.051 mmol) of superphane (**9**), 0.015 mL of ethyl diazoacetate and 4 mg of anhydrous cupric sulfate in 6 mL of dry chloroform was boiled under reflux in a nitrogen atmosphere for 3 h. The reaction mixture was taken up in chloroform, washed with water, dried, and concentrated. Purification of the residual, yellow solid by preparative thin-layer chromatography over silica gel using chloroform for elution led to the recovery of 6 mg (38%) of superphane and the isolation of 6 mg (30%) of product. Recrystallization of the product from a mixture of dichloromethane and methanol afforded 6 mg of **44** as white plates: mp 264–265 °C; IR (KBr),  $\nu_{\max}$  1719  $\text{cm}^{-1}$  (C(=O)OEt), 1500 (C=C);  $^1\text{H NMR}$   $\delta$  1.17 (3 H, t,  $\text{CH}_3$ ), 2.22–3.34 (25 H, m,  $\text{CH}_2$  and CH), 4.03 (2 H, q,  $\text{CH}_2\text{CH}_3$ ); mass spectrum,  $m/e$  398, 383, 369, 325; molecular weight calcd for  $\text{C}_{28}\text{H}_{30}\text{O}_2$  398.225, found (high-resolution mass spectrum) 398.224.

**Reduction of 44 To Give 45**. To a solution of 6 mg of **44** in 5 mL of tetrahydrofuran was added 5 mg of lithium aluminum hydride, and the mixture was stirred under nitrogen at room temperature for 4 h. After decomposition of the mixture by addition of a saturated, aqueous solution of sodium sulfate, it was extracted with chloroform. The chloroform extract was washed with a saturated, aqueous solution of sodium chloride, dried, and concentrated. This gave 6 mg of a somewhat air-sensitive white solid. Purification of this by preparative thin-layer chromatography over silica gel using a 1% methanol in chloroform mixture led to extensive loss of material due to decomposition but gave 1.5 mg (25%) of **45** as white prisms; mp 227–229 °C;  $^1\text{H NMR}$   $\delta$  1.68–3.36 (25 H, m,  $\text{CH}_2$  and CH), 3.89 (2 H, d,  $J = 9$  Hz,  $\text{CH}_2\text{OH}$ ); molecular weight calcd for  $\text{C}_{26}\text{H}_{28}\text{O}$  356.214, found (high-resolution mass spectrum) 356.212.

**Conversion of 45 to 46**. Addition of half a drop of boron trifluoride etherate to a solution of 0.79 mg of **45** in 0.3 mL of deuteriochloroform at room temperature led to a reddish brown color, after which the solution was allowed to stand for 35 min. Concentration of the solution gave **46** as a light, reddish brown solid. A solution of this in acetonitrile showed absorption maxima at 375 ( $\epsilon$  2990), 431 (1440), and 490 nm (sh) (919). Also, this product in deuteriochloroform gave  $^1\text{H NMR}$  signals at  $\delta$  2.72–3.61 (24 H, m,  $\text{CH}_2$ ) and 2.97 (3 H, s,  $\text{CH}_3$ ).

When **46** was allowed to stand exposed to the atmosphere or was treated with aqueous methanol, it was converted to superphane (0.36 mg, 52%), in all respects identical with an authentic sample.

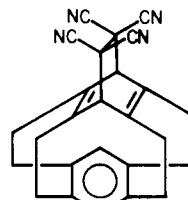
**Reaction of Superphane (9) with Dicyanoacetylene in the Presence of Aluminum Chloride To Give 50**. To a solution of 55 mg (0.176 mmol) of superphane (**9**) and an excess of dicyanoacetylene in 35 mL of dry dichloromethane was added 47 mg (0.352 mmol) of anhydrous aluminum



chloride under nitrogen with stirring at room temperature. The solution became a reddish brown and was stirred at room temperature for 3 days. A saturated, aqueous solution of sodium bicarbonate was added, and the organic layer was extracted with chloroform. The chloroform layer was washed with water, dried, and concentrated. The residual solid was purified by preparative thin-layer chromatography over silica gel using chloroform as eluant to give 37 mg of pale, yellow crystals. Recrystallization of these from chloroform then gave 35 mg (40%) of **50** as white prisms; mp 220 °C dec; UV (CHCl<sub>3</sub>) λ<sub>max</sub> 297 nm (ε 223); <sup>1</sup>H NMR δ 1.75-3.26 (m, CH<sub>2</sub> and CH); mass spectrum, *m/e* 502, 500, 464, 386, 312. Anal. (C<sub>32</sub>H<sub>25</sub>N<sub>4</sub>Cl) C, H, N.

Structure **50** for this substance has been established by an X-ray crystallographic analysis.<sup>43</sup>

**Diels-Alder Addition of Tetracyanoethylene to [2<sub>4</sub>](1,2,4,5)Cyclophane To Give 51.** Addition of tetracyanoethylene (19 mg) at room temperature to a solution of 10 mg of [2<sub>4</sub>](1,2,4,5)cyclophane<sup>8b</sup> in 20 mL of chloroform led to an immediate deep blue color. The color disappeared in a few seconds and white crystals separated from the solution. These



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were collected by filtration and dried to give 12 mg (100%) of **51** as white crystals: mp >215 °C dec; <sup>1</sup>H NMR δ 2.20-3.12 (16 H, m, CH<sub>2</sub>), 3.60 (2 H, s, CH), 6.76 (2 H, s, ArH); mass spectrum, *m/e* 260 (M<sup>+</sup> - TCNE), 245, 128. Anal. (C<sub>26</sub>H<sub>20</sub>N<sub>4</sub>) C, H, N.

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## Preparation and Chemistry of Penta- and Hexacoordinated Phosphorus Compounds Containing Trifluoroethoxy Groups

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**Abstract:** Tris(trifluoroethyl) phosphite, bis(trifluoroethyl) phenylphosphonite, trifluoroethyl diphenylphosphinite, and triphenylphosphine all react with 2 mol of trifluoroethyl benzenesulfonate to give pentacoordinated phosphorus compounds in which two trifluoroethoxy groups have been added to the original tricoordinated phosphorus compound. When tris(trifluoroethyl) phosphite was allowed to react with 1 mol of trifluoroethyl benzenesulfonate, tetrakis(trifluoroethyl)thiophenylphosphorane was isolated. When the other tricoordinated phosphorus compounds were allowed to react with 1 mol of trifluoroethyl benzenesulfonate, only recovered starting material and the pentacoordinated phosphorus compounds formed by the addition of two trifluoroethoxy groups were found in the reaction mixtures. All of the trifluoroethoxy-containing phosphoranes except for bis(trifluoroethoxy)triphenylphosphorane reacted with trifluoroethoxide ion to give hexacoordinated phosphorus compounds. Tris(trifluoroethoxy)diphenylphosphorane reacts with trifluoroethoxide ion to give the hexacoordinated compound in which the phenyl groups are *cis* to each other. This material rapidly isomerizes to a mixture of *trans* (82%) and *cis* (18%). Treatment of pentakis(trifluoroethoxy)phosphorane with 1 and 2 mol of ethylene glycol yielded new phosphoranes containing one and two five-membered rings, respectively. Both reacted with trifluoroethoxide ion to give hexacoordinated phosphorus compounds. In the case of the compound containing two five-membered rings, both *cis* and *trans* isomers were detected in the ratio of 2:1 at equilibrium.

The chemistry of pentacoordinated phosphorus compounds has received much attention during the last two decades, and many important questions concerning these molecules have been answered.<sup>1</sup> There remain several areas of interest within the chemistry of these substances. In particular, an understanding of steric effects in governing stability and structure remains to be delineated. The factors which govern intermolecular and intramolecular ligand reorganization reactions have received much attention. Attempts to generalize rules purported to govern these processes have met with some success, but important exceptions have been noted. The structures of these materials in the crystalline state have been shown to vary from trigonal bipyramidal (TBP) to square or rectangular pyramidal (SP or RP).<sup>2</sup> Interestingly, the structures of many of these substances in solution are not known. Considerable effort has been expended in developing an

apicophilicity series, i.e., within a TBP which ligands will prefer the apical positions, and certainly progress has been made in this area. Most of these studies have involved phosphoranes with halogen, oxygen, and to a lesser degree carbon and nitrogen bonded to phosphorus, and thus there is potentially a vast unknown area for further exploration.

The chemistry of hexacoordinated phosphorus compounds has received much less attention than that of the pentacoordinated materials. Muetterties and Mahler<sup>3</sup> showed that electronegative elements, in particular fluorine, stabilize the hexacoordinated state. Somewhat later Ramirez<sup>4</sup> and others suggested that hexacoordinated phosphorus compounds are formed during nucleophilic displacement reactions on pentacoordinated phosphorus com-

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