

Preparation and Reduction of Hexahydro[2.2]paracyclophane

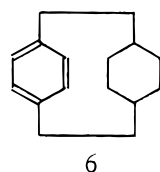
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Hexahydro[2.2]paracyclophane (**6**) and related compounds were prepared from the extrusion of sulfur dioxide from 2,11-dithia-4,5,6,7,8,9-hexahydro[3.3]paracyclophane 2,2,11,11-tetraoxide (**9**) by either the Ramberg–Backlund reaction or a flash pyrolysis. Compound **6** is the first cyclophane to contain both a benzene ring and a cyclohexane ring. Birch reduction of compound **6** gave a diene containing two double bonds in the same ring, which is different from the dienes obtained from the catalytic hydrogenation of [2.2]paracyclophane.

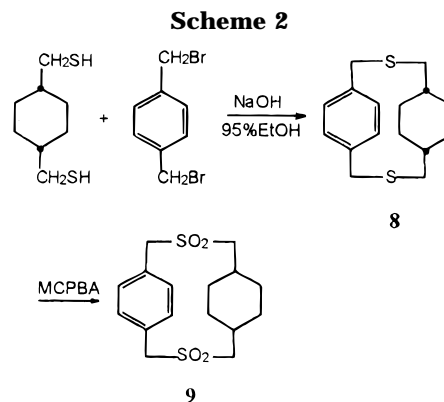
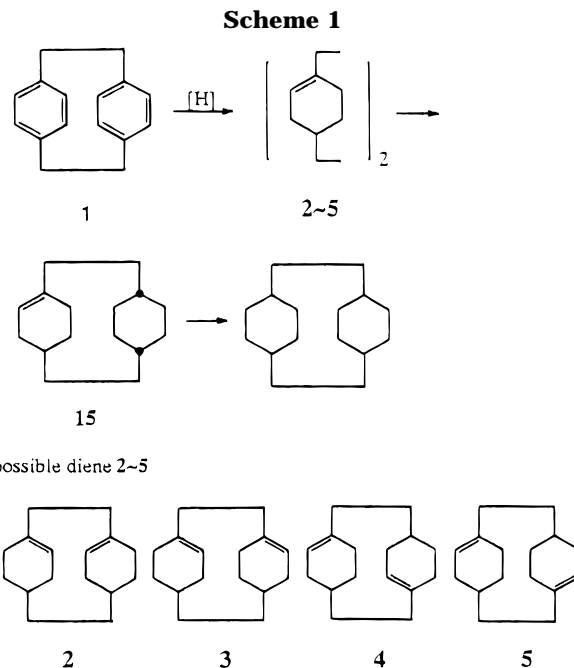
The unique structures of cyclophanes have inspired their use in the study of bent arene rings, transannular interactions between two rings, donor–acceptor properties, the formation of inclusion complexes, and chiral molecular recognition. Recent reviews have discussed the preparation and properties of cyclophanes, as well as their applications.¹ Most of the purely hydrocarbon cyclophanes which have been reported thus far contain two arene rings. The hydrogenation of [2.2]paracyclophane (**1**) over reduced platinum oxide has been reported to yield a diene in which both double bonds are in the same six-membered ring.² We repeated the hydrogenation of [2.2]paracyclophane under the conditions given by Cram and Allinger and have obtained three dienes.³ On the basis of their chemical and spectral properties and with the aid of various computations, we conclude that the double bonds of these dienes are in different rings (Scheme 1). We report here the preparation of 3,4,5,6,7,8-hexahydro[2.2]paracyclophane (**6**) followed by



Birch reduction to yield a diene **7**, which contains two double bonds in the same ring. In a comparison of this diene with those which had been isolated from the catalytic hydrogenation of [2.2]paracyclophane in our previous work, the 1,4-diene (**7**) differed markedly from the other dienes.

Results and Discussion

Dithiahexahydro[3.3]paracyclophane (**8**) was prepared by the addition of *cis*-1,4-bis(mercaptomethyl)cyclohexane in ethanol solution to α, α' -dibromo-*p*-xylene in ethanolic KOH solution, using the high-dilution technique described by Davis.⁴ Compound **8** was oxidized quantitatively to the corresponding sulfone **9** using *m*-chloroperbenzoic acid (MCPBA) as the oxidation agent (Scheme 2).⁵

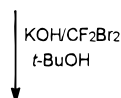
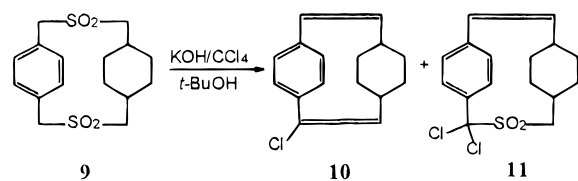


Several methods can be used for the extrusion of SO₂ along with the formation of either C–C or C=C bonds. In this study, we used the Ramberg–Backlund reaction⁶ and its modification⁷ as well as pyrolysis⁸ to remove sulfur dioxide from **9** for the formation of C–C bonds.

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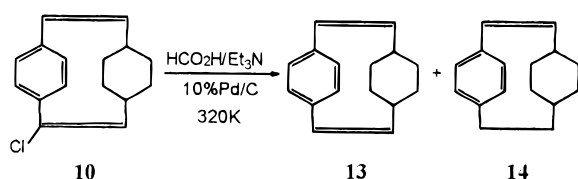
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Scheme 3



12

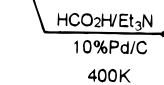
Scheme 4



10

13

14



15

The conventional Ramberg–Backlund reaction at 27 °C yields two products, (a) one with two double-bond bridges between the benzene and the cyclohexane ring (**10**, 8.4% yield) from the double extrusion of SO₂ and (b) a compound with only one double-bond bridge from the extrusion of a single SO₂ (**11**, 22.0% yield) in benzene extract (Scheme 3). Compound **10** (10.5% yield) was the only product in the benzene extract when the reaction was carried out at 80 °C. Therefore, compound **11** is presumably an intermediate which can be converted to compound **10** with either a longer reaction time or a higher reaction temperature. The Ramberg–Backlund reaction have recently been modified by mixing powdered KOH and Al₂O₃ to improve the yield of product from the extrusion of SO₂ of sulfones.⁷ The same process was used to form compound **10** in a yield of 16.8%. If CF₂Br₂ was used instead of CCl₄, a bromo analogue (**12**) was obtained as the only product in the benzene extract.⁸

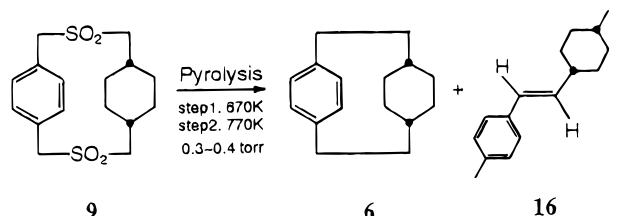
Compound **10** was reduced by catalytic hydrogen transfer in a mixture of formic acid and triethylamine with 10% Pd/C as a catalyst.⁹ At 50 °C, hydrodechlorination and reduction of a double bond from compound **10** took place to yield compounds **13** and **14** (Scheme 4). At a higher temperature (120 °C), this reaction gave only the monoene, decahydro[2.2]paracyclophane (**15**). Neither hexahydroparacyclophane **6** nor a diene **7** with both double bonds in the same ring was obtained during this process. Perhaps the high ring strain of compound **6** and

Table 1. Product Distribution from Birch Reduction of **6 under Various Conditions^a**

	time	temp, °C	ratio 15:7:6
Li/NH ₃	2 h	−53	94.7:1.1:4.2
Li/NH ₃ , EtOH	30 min	−73	60.6:2.7:36.7
Na/NH ₃ , EtOH	30 min	−73	29.8:0.7:69.5
Li/NH ₃	2 h	−83	88.9:10.2:0.9
Li/NH ₃	40 min	−83	80.5:6.1:13.4

^a The ratio were estimated according to the area ratio from HPLC analyses by using RP-18 as stationary phase and using UV detector at wavelength of 210 nm.

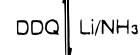
Scheme 5



9

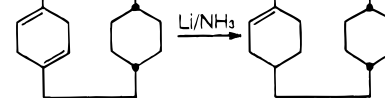
6

16



7

15



the possible diene intermediate direct the reduction to monoene **15**, one of “hyperstable olefins”.¹⁰

Pyrolysis is a valuable process for forming a C–C bond from a sulfone series or quaternary ammonium salt.⁸ In this work, compound **9** was pyrolyzed at 400 °C for 20 min and then at 500 °C for 30 min at 0.3–0.4 Torr. During this process, the products were trapped in a cold trap (−196 °C). The mixture obtained from the cold trap was separated chromatographically to yield 3,4,5,6,7,8-hexahydro[2.2]paracyclophane (**6**) as a minor (14.2%) product and a ring-opened compound, (*E*)-1-(*cis*-4-methylcyclohexyl)-2-(4-tolyl)ethylene (**16**) as a major product (48.0%) (Scheme 5). The structure of compound **16** was determined from its ¹H NMR spectrum. Two methyl resonances (a doublet at 0.93 ppm and a singlet at 2.32 ppm) suggested that **16** resulted from a ring-opening process. The large coupling constants for two vinyl protons (6.28 and 6.40 ppm with *J* = 16.0 Hz) indicated that this double bond has a *trans* configuration.

The reduction of compound **6** by Birch reduction gave monoene **15** as well as a diene **7**. The yields from the Birch reduction¹¹ under different conditions are summarized in Table 1. As shown, this system tends to form a monoene **15** as the major product even if the reduction is carried out at a relatively low temperature (−83 °C). We held the reaction temperature at −83 °C for 40 min to obtain the maximum amount of diene **7**. The ¹H and ¹³C NMR spectra of diene **7** are different from those of dienes obtained from the catalytic hydrogenation of [2.2]-paracyclophane.¹² The two sets of doublet signals for the

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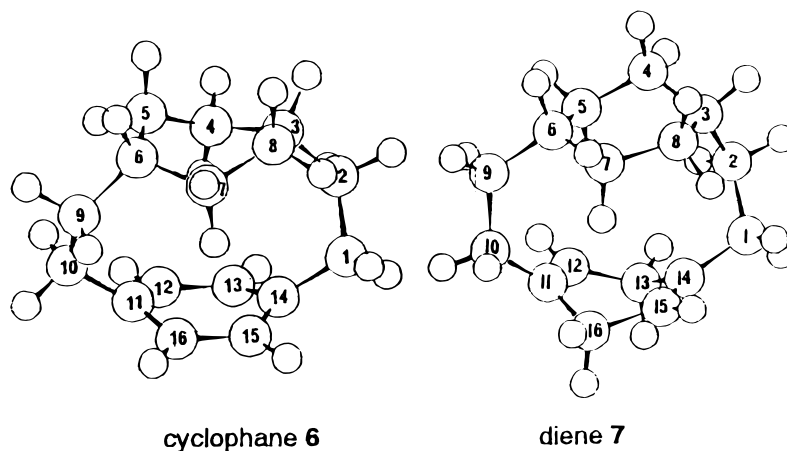


Figure 1. Lowest energy conformations of cyclophane **6** and diene **7** obtained from semiempirical calculation.

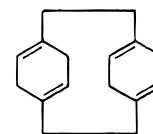
Table 2. Bond Lengths (Å) and Torsion Angles (deg) of Cyclophane **6** and Diene **7** Obtained from Semiempirical Calculation

parameter	methods					
	compound 6			compound 7		
	MNDO	AM1	PM3	MNDO	AM1	PM3
bond length						
C ₃ –C ₁₄	3.28	3.20	3.22	3.47	3.34	3.35
C ₄ –C ₁₃	3.44	3.22	3.21	4.64	4.40	4.30
C ₅ –C ₁₂	3.88	3.71	3.71	3.53	3.26	3.16
C ₆ –C ₁₁	3.29	3.19	3.19	3.25	3.14	3.15
C ₇ –C ₁₆	3.44	3.22	3.20	3.71	3.47	3.54
C ₈ –C ₁₅	3.83	3.78	3.81	3.63	3.41	3.56
torsion angle						
C ₁₄ –C ₁ –C ₂ –C ₃	47.37	52.19	52.33	75.23	76.27	77.50
C ₁₁ –C ₁₀ –C ₉ –C ₆	42.00	50.77	50.25	–23.16	–38.60	–38.71
ΔH _f ⁰ (kcal/mol)	32.96	13.96	22.26	20.30	–3.62	5.23

vinyl protons in the ¹H NMR spectrum and the chemical shifts of the carbons in the ¹³C NMR spectrum suggest that the structure of diene **7** must be either severely distorted to minimize its strain energy or the nature of hyperstable olefins resulted in the presence of two conformers.¹⁰

Calculations permit us to predict the structures of the compounds that are most likely present in the gas phase. While these simulated structures may vary somewhat from the actual structure, if the limit deviation can be obtained using a suitable method, the simulation results may still be useful for determining the unknown structure. Three methods (MNDO,¹³ AM1,¹⁴ and PM3¹⁵) were used to optimize the structures of cyclophane **6** and diene **7**. Some of the results are summarized in Table 2, and the possible conformations are shown in Figure 1. These results indicate that the distances between two corresponding carbons of the rings and the torsion angles of both bridging ethylene groups of diene **7** are substantially different using the three methods, while the results with cyclophane **6** varied only slightly. These computational results support the notion that diene **7** has an asymmetrical structure deduced on the basis of the different chemical shifts for each carbon.

DDQ (4,5-dichloro-3,6-dioxo-1,4-cyclohexadiene-1,2-dicarbonitrile) readily aromatizes tetrahydro[2.2]paracyclophane (**17**).¹⁶ Unlike the other three dienes (**2–5**) obtained by hydrogenation of [2.2]paracyclophane, treat-



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ment of the diene **7** with DDQ at room temperature for 1 h gave hexahydrocyclophane **6** in 89% yield. This verifies that the diene **7** is different from the other dienes and has its double bonds in the same ring.

Conclusion

A [2.2]paracyclophane which contains an arene ring and a cyclohexane was synthesized. The lower yield in the sulfur dioxide extrusion in this system than in the preparation of [2.2]paracyclophane using the same procedure is not only due to the flexibility and strain of the cyclohexane moiety but, more importantly, due to the lability of nonbenzyl radical intermediates. This flexibility of the cyclohexyl ring lowers the possibility of closure. Birch reduction of hexahydro[2.2]cyclophane gave diene **7**, which has two double bonds in the same ring. On the basis of a comparison of the spectral and chemical properties of **7** and the dienes obtained from the catalytic hydrogenation of [2.2]paracyclophane, we conclude that diene **7** is not a product of the catalytic hydrogenation of [2.2]paracyclophane.

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Experimental Section

General. ^1H NMR and ^{13}C NMR spectra were recorded at 250 and 62.86 MHz, respectively, at ambient temperature. Chemical shifts for samples in deuteriochloroform solution are reported in δ units relative to tetramethylsilane. Mass spectra were obtained on a JEOL JMS DX-300 double-focusing mass spectrometer at an ionization potential of 70 eV. Samples were introduced via a direct probe. Elemental analyses were performed at the Instrumental Analytic Center at National Chung Hsien University. HPLC analyses and preparative separation were conducted on a PC-controlled binary pump (Perkin-Elmer series 2001C pump) with UV detection at 210 nm (Perkin-Elmer diode array detector LC295 or a UV/vis detector 235C with a flow cell).

The calculations were carried out with the spin-unrestricted versions of the MNDO, AM1, and PM3 methods available in MOPAC 6.0¹⁷ on a Silicon Graphics workstation, Model 4D-20G. The geometries of the compounds were optimized through the eigenvector following (EF) routine incorporated into the MNDO, AM1, and PM3 programs. The distances of carbons and the torsion angles were obtained from output files which reflected the molecules at their lowest energy states.

2,11-Dithia-4,5,6,7,8,9-hexahydro[3.3]paracyclophane (8). This compound was prepared as described in the literature: mp 142–143 °C (lit.¹⁸ mp 140.0–141.5 °C); ^1H NMR δ 0.45 (br, 2H), 0.95–1.65 (m, 8H), 2.33 (d, $J = 20$ Hz, 4H), 3.58 (s, 4H), 6.96 (s, 4H).

2,11-Dithia-4,5,6,7,8,9-hexahydro[3.3]paracyclophane 2,2,11,11-Tetraoxide (9). A mixture of **8** (1.0 g, 3.48 mmole), *m*-chloroperbenzoic acid (MCPBA) (70% purity, 3.52 g, 14.3 mmol), and 20 mL of CHCl_3 was refluxed for 16 h. The solvent was removed by evacuation, and the remaining solid was stirred with saturated $\text{Na}_2\text{S}_2\text{O}_3$ (50 mL) for 10 min to quench the excess of MCPBA. The solid was collected by the filtration and washed with water (30 mL \times 3) and ether (30 mL \times 3) to give 1.20 g (yield 98.0%) of compound **9** as a white powder: mp 287–289 °C; IR (KBr) 1330, 1116 cm^{-1} (ν SO_2); MS (relative intensity) m/z 342 (M^+ , 1), 280 [($\text{M} - 2\text{SO}_2$)⁺, 16], 104 (100). Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{S}_2\text{O}_4$: C, 56.11; H, 6.47; S, 18.72. Found: C, 56.28; H, 6.60; S, 18.63.

Sulfur Dioxide Extrusion of Compound 9. Method A. Under a nitrogen atmosphere, a mixture of **9** (0.2 g, 0.59 mmol), KOH powder (2.0 g), *t*-BuOH (10 mL), and CCl_4 (10 mL) was stirred at room temperature for 13 h. After addition of H_2O (2.0 mL) and an additional 2 h of stirring, the solvent was removed under reduced pressure to give a viscous residue. The residue was extracted with benzene (3 \times 10 mL), dried over Na_2SO_4 , filtered, and vacuum evaporated to give a waxy residue. The residue was separated chromatographically on a silica gel column using hexane/ethyl acetate (from 10:0 to 10:1 v/v) as eluent to yield 1-chloro-3,4,5,6,7,8-hexahydro[2.2]-paracyclophane-1,9-diene (**10**) and 10-thia-11,11-dichloro-3,4,5,6,7,8-hexahydro[2.3]paracyclophane-1-ene 10,10-dioxide (**11**). Compound **10**: 12 mg (yield 8.4%); white solid; mp 69.8–70.2 °C; ^1H NMR δ 1.09 (m, 8H), 2.20 (br, 2H), 5.80 (dd, 1H, $J = 12.2$, 9.3 Hz), 6.04 (d, 1H, $J = 10.0$ Hz), 6.93 (d, 1H, $J = 12.2$ Hz), 7.30 (d, 2H, $J = 8.5$ Hz), 7.43 (d, 2H, $J = 8.5$ Hz); ^{13}C NMR δ 24.7, 25.3, 31.9, 32.5, 130.1, 130.6, 130.9, 131.4, 136.9, 138.9, 141.7, 142.1; MS (relative intensity) m/z 244 (M^+ , 56), 155 (100). Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{Cl}$: C, 78.51; H, 7.00. Found: C, 78.43; H, 7.15. Compound **11**: 46 mg (yield 22.3%); white solid; mp 164–166 °C; ^1H NMR δ 1.20 (m, 9H), 2.00 (d, 2H, $J = 7.90$ Hz), 2.30 (br, 1H), 6.08 (dd, 1H, $J = 8.6$, 12.2 Hz), 6.93 (d, 1H, $J = 12.2$ Hz), 7.42 (d, 2H, $J = 8.5$ Hz), 7.97 (d, 2H, $J = 8.5$ Hz); ^{13}C NMR δ 24.3, 27.8, 28.9, 35.4, 44.7, 109.6, 128.9, 130.7, 131.4, 132.3, 139.5, 144.4; IR 1332, 1138 cm^{-1} (ν SO_2); MS (relative intensity) m/z 358 (M^+ , –), 172 (172, 100). Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{Cl}_2\text{SO}_2$: C, 55.66; H, 5.25; S, 9.29. Found: C, 55.70; H, 5.21; S, 9.20.

Method B. The reaction conditions are the same as in method A except the reaction temperature was kept at 80 °C

for 5 h. Compound **10** (15 mg, yield 10.5%) was isolated as the only product.

Method C. A mixture of KOH (2.0 g) and Al_2O_3 (6.0 g, 70–230 mesh, neutral) in methanol (50 mL) was stirred and was dried under reduced pressure. To this mixture in *t*-BuOH (10 mL) and CCl_4 (10 mL) was added compound **9** (0.2 g, 0.59 mmol). After being stirred at 27 °C for 24 h, the mixture was treated as in method A to give compound **10** as the only product in 16.8% yield.

Method D. Same procedure as method C except for $\text{CF}_2\text{-Br}_2$ (2.09 mL, 10 mmol) was used instead for CCl_4 . After workup and chromatographic separation to give 1-bromo-3,4,5,6,7,8-hexahydro[2.2]paracyclophane-1,9-diene (**12**) was obtained as the only product (16 mg, 6.2% yield): mp 67.5–68.2 °C; white solid; ^1H NMR δ 1.03–1.25 (m, 8H), 2.24 (br, 2H), 5.82 (dd, 1H, $J = 12.5$, 9.3 Hz), 6.26 (d, 1H, $J = 9.9$ Hz), 6.93 (d, 1H, $J = 12.5$ Hz), 7.29 (d, 2H, $J = 7.8$ Hz), 7.42 (d, 2H, $J = 7.8$ Hz); ^{13}C NMR δ 24.7, 25.4, 32.0, 34.2, 119.2, 130.6, 131.3, 139.2, 141.7, 141.9, 142.1, 143.0; MS (relative intensity) m/z 288 (M^+ , 92), 141 (100). Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{Br}$: C, 66.45; H, 5.92. Found: C, 66.50; H, 6.12.

Catalytic Hydrogenation of Compound 10 via Hydrogen Transfer Process. Reaction A. A mixture of compound **10** (40 mg, 0.16 mmol), triethylamine (2 mL, 14.3 mmol), formic acid (0.5 mL, 8.9 mmol), and Pd/C (10%, 20 mg) was heated at 50 °C for 2 h. After the mixture was cooled to room temperature, H_2O (5 mL) was added to quench the reaction. The aqueous mixture was extracted with CH_2Cl_2 (3 \times 20 mL) and dried over MgSO_4 , and the organic phase was evaporated to give a white solid. The residue was separated by means of HPLC (20 mm o.d. \times 25 cm, RP-18) with $\text{MeOH}:\text{H}_2\text{O}$ (90:10, v/v) as the eluent to give 3,4,5,6,7,8-hexahydro[2.2]paracyclophane-1,9-diene (**13**) and 3,4,5,6,7,8-hexahydro[2.2]paracyclophane-1-ene (**14**). Compound **13**: mp 142.5–144.0 °C (subl); white solid; 3.1 mg, yield 9.0%; ^1H NMR δ 1.06–1.29 (m, 8H), 2.24 (br, 2H), 5.82 (dd, 2H, $J = 12.2$, 8.3 Hz), 6.93 (d, 2H, $J = 12.2$ Hz), 7.26 (s, 4H); ^{13}C NMR δ 25.5, 32.5, 131.1, 139.3, 142.0; MS (relative intensity) m/z 210 (M^+ , 43), 128 (100). Anal. Calcd for $\text{C}_{16}\text{H}_{18}$: C, 91.37; H, 8.63. Found: C, 91.30; H, 8.71. Compound **14**: mp 40.5–41.0 °C; white solid; 4.5 mg, yield 13.0%; ^1H NMR δ 0.85–1.28 (m, 8H), 1.68–2.03 (m, 4H), 2.75 (t, 2H, $J = 6.2$ Hz), 5.81 (dd, 1H, $J = 11.6$, 8.8 Hz), 6.91 (d, 1H, $J = 11.6$ Hz), 7.20 (d, 2H, $J = 8.2$ Hz), 7.33 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR δ 24.2, 26.9, 28.7, 32.2, 33.7, 36.2, 130.7, 131.2, 132.1, 137.2, 142.0, 143.9; MS (relative intensity) m/z 212 (M^+ , 14), 104 (100). Anal. Calcd for $\text{C}_{16}\text{H}_{20}$: C, 90.51; H, 9.49. Found: C, 90.44; H, 9.40.

Reaction B. Same procedure was used except the reaction was carried out at 127 °C for 3 h. After workup, 18 mg (51.0% yield) of decahydro[2.2]paracyclophane (**15**) was obtained as the only product. The identity of this waxy compound was confirmed by comparison of its ^1H NMR and ^{13}C NMR spectra as well as HPLC analysis by using RP-18 as stationary phase with those of an authentic sample.⁴

Pyrolysis of Compound 9. Compound **9** (0.8 g, 2.3 mmol) was placed in a quartz tube (2.5 cm o.d. \times 120 cm length) with a cold trap for pyrolysis. The pyrolysis system was preevacuated to a pressure of 0.3–0.4 Torr for 20 min, and then the cold trap was cooled by means of liquid nitrogen. During the pyrolysis, the temperature was held at 400 °C for 20 min and then at 500 °C for 30 min. After the trap was warmed to room temperature, the residue was dissolved in CH_2Cl_2 (3 \times 30 mL). A waxy material obtained from the CH_2Cl_2 solution was subjected to chromatographic separation on 20% AgNO_3 on Al_2O_3 (1.5 cm o.d. \times 30 cm length) with hexane as an eluent to give 3,4,5,6,7,8-hexahydro[2.2]paracyclophane (**6**) and (*E*)-1-(4-methylcyclohexyl)-2-(4-tolylethylene) (**16**). Compound **6**: mp 154–156 °C; white solid; 72.0 mg (14.2% yield); ^1H NMR δ 0.89–1.06 (m, 8H), 1.60–1.71 (m, 6H), 2.75 (t, 4H, $J = 6.3$ Hz), 7.29 (s, 4H); ^{13}C NMR δ 24.4, 30.2, 32.2, 35.6, 130.9, 141.4; MS (relative intensity) m/z 214 (M^+ , 3), 104 (100). Anal. Calcd for $\text{C}_{16}\text{H}_{22}$: C, 89.65; H, 10.35. Found: C, 89.63; H, 10.37. Compound **16**: viscous liquid; freezing point –41 °C; 240 mg (48% yield); ^1H NMR δ 0.93 (d, 3H, $J = 6.8$ Hz), 1.32–1.62 (m, 10H), 2.32 (s, 3H), 6.28 (dd, 1H, $J = 16.0$, 5.7 Hz), 6.40 (d, 1H, $J = 16.0$ Hz), 7.10 (d, 2H, $J = 7.8$ Hz), 7.25 (d,

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2H, $J = 7.8$ Hz); ^{13}C NMR δ 20.3, 21.0, 29.2, 30.1, 30.8, 38.2, 125.8, 127.9, 129.1, 134.5, 135.3, 136.4; MS (relative intensity) m/z 214 (M^+ , 74), 118 (100), 105 (89); HRMS calcd for $\text{C}_{16}\text{H}_{22}$ 214.1716, found 214.1722.

Birch Reduction of Compound 6. To a mixture of compound **6** (20.0 mg, 0.093 mmol) and THF (5.0 mL) at -83 °C was condensed NH_3 (about 5 mL) followed by addition of Li (2.5 mg, 0.37 mmol). After the reaction at that temperature for 2 h, NH_4Cl (5 mg) was added to protonate the dienyl anion. The reaction mixture was allowed to warm to room temperature followed by addition of H_2O (20 mL) and extraction with CHCl_3 (3×20 mL). The organic layer was dried over MgSO_4 and filtered, and the solvent was removed under reduced pressure to give a waxy residue, which was analyzed by means of HPLC using RP-18 as a stationary phase and MeOH as an eluent with UV detector at wavelength of 210 nm. The chromatograph indicated that the mixture consisted of compounds **6** (0.9%), diene **7** (10.2%), and monoene **15** (88.9%). The mixture was separated by using a HPLC preparative column (RP-18) with MeOH as an eluent. Compound **7**: viscous liquid; ^1H NMR δ 1.10–1.78 (m, 20H), 2.31–2.50 (m, 2H), 5.63 (dd, 1H, $J = 1.9, 10.4$ Hz), 5.87 (dd, 1H, $J = 1.8,$

10.6 Hz); ^{13}C NMR δ 21.8, 22.6, 23.3, 26.5, 28.1, 29.5, 29.7, 32.5, 34.0, 35.8, 36.5, 38.2, 128.3, 129.5, 130.9, 132.1; MS (relative intensity) m/z 216 (M, 16), 108 (100); HRMS calcd for $\text{C}_{16}\text{H}_{24}$ 216.1872, found 216.1879.

Dehydrogenation of Diene 7. A mixture of DDQ (12.7 mg, 0.06 mmol) and **7** (3.0 mg, 0.015 mmol) in 3 mL of toluene was stirred at room temperature for 1 h. The mixture was then passed through a short silica gel column using hexane as the eluent. The solvent was evaporated under reduced pressure to give 2.7 mg (89.0% yield) of a white solid. The compound was identified as 3,4,5,6,7,8-hexahydro[2.2]paracyclophane (**6**) by comparison of its ^1H NMR spectra and the retention time in HPLC with those of an authentic sample.

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