Alternative Routes to Hexahydro[2.2]paracyclophane and Related Hydrocarbons[1]

Henning Hopf* and Rainer Savinsky

Institut für Organische Chemie, Technische Universität Braunschweig, Hagenring 30, D-38106 Braunschweig, Germany

Bernd Diesselkämper, Rhys G. Daniels, and Armin de Meijere*

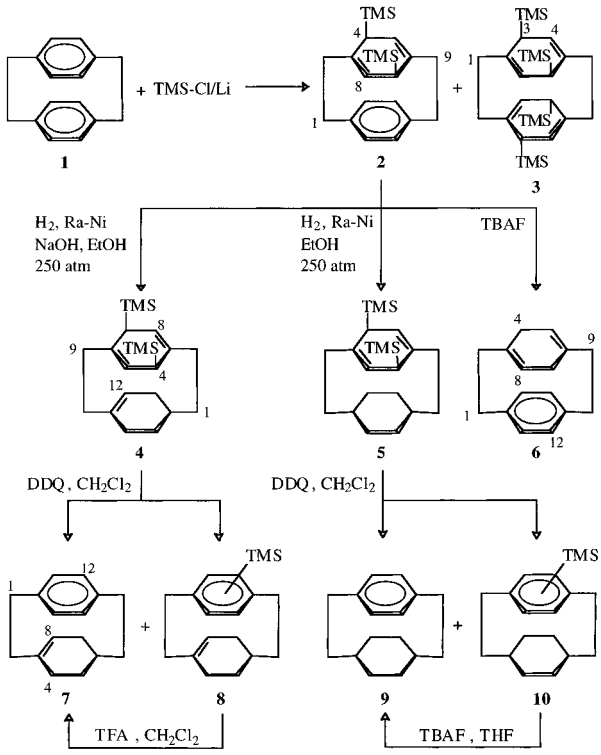
Institut für Organische Chemie, Georg-August-Universität Göttingen, Tammanstrasse 2, D-37077 Göttingen, Germany

Received July 15, 1997

Cyclophanes in which the aromatic subunit is bridged by an alicyclic or polycyclic moiety, the so-called araliphanes,[2] are of current interest because of their high inherent strain and the enhanced reactivity caused by it. An important member of this class of compounds is hexahydro[2.2]paracylophane (**9**) for which Yang and Lin published the first synthesis in this Journal last year,[3] previous attempts to obtain this hydrocarbon evidently having been unsuccessful.[4] The reported synthesis of **9** featured a sulfone pyrolysis of dithiahexahydro[3.3]paracyclophane tetraoxide which had been assembled from smaller building blocks employing classical methods of cyclophane synthesis.[2] We have also been interested in **9** and related partially hydrogenated [2.2]paracylophanes for some time[5] and report on an alternate route to **9** as well as to the di- and tetrahydro[2.2]paracyclophanes **6** and **7** in this Note (Scheme 1).

As Scheme 1 shows these three hydrocarbons may be prepared selectively from one common precursor: 4,7-bis(trimethylsilyl)-4,7-dihydro[2.2]paracyclophane (**2**). This compound is easily obtained in 53% yield in multigram amounts when [2.2]paracyclophane (**1**) is subjected to reductive silylation[6] with excess trimethylsilyl chloride and lithium powder. The tetrasilylated tetrahydro derivative **3** (11%) and the starting material **1** (22%) were also isolated from the product mixture. Compound **3** is formed from **2** by overreduction as was demonstrated in an experiment in which lithium was added successively until **2** had been completely consumed; under these conditions **3** is formed exclusively. When **2** is subjected to catalytic reduction in ethanol in the presence of sodium hydroxide at 250 atm and 40 °C, its aromatic ring is reduced partially and **4** is obtained; repeating the hydrogenation in the absence of base yields a mixture of **4** and **5**, i.e., a compound with a fully hydrogenated benzene ring as well. It is obvious that the bulky trimethylsilyl groups of **2** function as protective groups for the double

Scheme 1: Novel Routes to Partially Hydrogenated [2.2]Paracyclophanes



bonds of the ring to which they are attached, causing the remarkable result that a benzene ring is hydrogenated exclusively in a molecule which also contains olefinic double bonds. Both **4** and **5** are air sensitive oils, and although a small sample of the former was isolated by chromatography from the hydrogenation mixture for analytical purposes (see its spectroscopic data in the Experimental Section) normally the hydrogenation mixtures were used as obtained for the next reaction step (see below). As expected, compound **2** is desilylated on treatment with tetrabutylammonium fluoride (TBAF) in tetrahydrofuran and 4,7-dihydro[2.2]paracyclophane (**6**) is obtained in quantitative yield. Although this diene has previously been prepared by reduction of **1** with sodium in liquid ammonia,[7] the current synthesis gives better overall yields and makes **6** available in gram amounts for further transformations, e.g., ring expansion reactions via its olefinic double bonds. Oxidation of **4** with DDQ in dichloromethane at 0 °C leads to rearomatization of the substituted ring and provides a product mixture consisting of the monoolefin **7** and its monosilylated derivative **8** in a ratio of 4:1. Although the exact position of the substituent in **8** could not be determined spectroscopically, its removal with trifluoracetic acid (TFA) in dichloromethane took place readily, increasing the amount of ultimately isolated **7**. Taking 10 g of the starting material **1** through the whole sequence yields 5.3 g of **7** (52% total yield). Analogously, the oxidation of **5** with DDQ yields the title compound **9**, identical in its analytical and spectroscopic data with those reported,[2] and the trimethylsilyl derivative **10**. Removal of the trimethylsilyl substituent in this case was achieved with TBAF in tetrahydrofuran. Although the overall yield of the **1** → **9** reduction was only 7%, enough material was obtained for further experimentation (see below).

(1) This is part 43 of our cyclophane series. For part 42, see: Ernst, L.; Hopf, H.; Savinsky, R. *Liebigs Ann./Recueil* **1997**, 1499−1504.

(2) Vögtle F., *Cyclophan-Chemie*; Teubner Verlag: Stuttgart, 1990; p 449.

(3) Yang, F.-Z.; Lin, S.-T. *J. Org. Chem.* **1997**, *62*, 2727−2731.

(4) (a) Swepston, S.-T.; Lin, S.-T.; Hawkins, A.; Humphrey, S.; Siegel, S.; Cordes, A. W. *J. Org. Chem.* **1981**, 46, 3754−3758. (b) Cordes, A. W.; Lin, S.-T.; Lin, L.-H. *Acta Crystallogr.* **1990**, *C46*, 170−172.

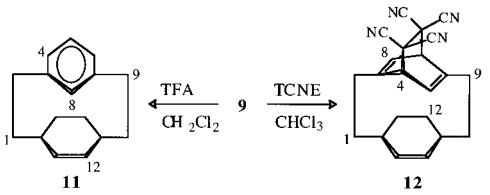
(5) (a) Hopf, H.; Savinsky, R.; Jones, P. G.; Dix, I.; Ahrens, B. *Liebigs Ann./Recueil* **1997**, 1499−1504. (b) Savinsky, R. Dissertation, Technische Universität Braunschweig, 1996.

(6) (a) Weyenberg, D. R.; Toporcer, L. H. *J. Am. Chem. Soc.* **1962**, *84*, 2843−2844. (b) Laguerre, M.; Dunogues, J.; Calas, R.; Duffaut, N. *J. Organomet. Chem.* **1976**, *112*, 49−59. (c) Laguerre, M.; Dunogues, J.; Calas, R. Duffaut, N. *J. Organomet. Chem.* **1975**, *93*, C17−C19. (d) Barrett, A. G. M.; O'Neil, I. A. *J. Org. Chem.* **1988**, *53*, 1815−1817.

(7) Jenny, W.; Reiner, J. *Chimia* **1970**, *24*, 69−71.

S0022-3263(97)01278-4 CCC: $14.00

Scheme 2: Some Reactions of Hexahydro[2.2]paracyclophane (9)



High strain in cyclophanes often manifests itself in an enhanced propensity of these compounds to undergo isomerization and addition reactions,[8] and **9** is no exception from this rule. Thus, it isomerizes in 92% yield to the metaparacyclophane **11**, and Diels−Alder addition[9] of tetracyanoethylene (TCNE) sets in at room temperature already. At 50 °C it is complete within 1 h, furnishing the [2 + 4] adduct **12** in 93% yield (Scheme 2).

Further investigations on the preparation and reactivity of partially hydrogenated [2.2]paracyclophanes are underway, and their results will be reported in due course.

Experimental Section

General. ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 and 100.6 MHz, respectively. Spin multiplicities were determined by the DEPT technique. Column chromatography was performed on Merck silica gel 60 (70−230 mesh), and for the gas chromatographic analyses (FID), a Dani 3800 HR gas chromatograph with a 50 m OV-1 capillary column was employed.

Reductive Silylation of [2.2]Paracyclophane (1). A 250 mL three-necked flask, equipped with a mechanical stirrer, charged with a suspension of 5 g (24 mmol) of [2.2]paracyclophane (**1**) in 100 mL of anhydrous THF and 30 mL (0.24 mol) of trimethylsilyl chloride is placed in an ultrasonic bath. After starting the stirrer and sonofication are started, 1 g (0.14 mol) of lithium powder is added in small portions under nitrogen during a 9 h period while the temperature is kept at 20 °C. When the lithium addition has been completed, the solvent is removed in vacuo and the remaining solid is dissolved in dichloromethane. The organic phase is washed with water twice and dried over sodium sulfate. Alumina (20 g) is added, the solvent is evaporated, and the reduction mixture is separated on alumina using petroleum ether as solvent. Fraction 1: R_f = 0.79; 4,7,13,16-tetrakis(trimethylsilyl)-4,7,13,16-tetrahydro[2.2]paracyclophane (**3**), 1.3 g (11%), colorless crystals (2-propanol), mp 187 °C. Fraction 2: R_f = 0.48; 4,7-bis(trimethylsilyl)-4,7-dihydro-[2.2]paracyclophane (**2**), 4.5 g (53%), colorless crystals (2-propanol), mp 69 °C. Fraction 3: R_f = 0.19; [2.2]paracyclophane (**1**), 1.1 g (22%).

Spectroscopic and Analytical Data of 2. ^{1}H NMR (400.1 MHz, $CDCl_3$/TMS): δ 6.91 (dd, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 2H); 6.80 (dd, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 2H) (aromat.-H); 4.44 (dd, $^3J_{4,5}$ = 5.2 Hz, ^4J = 1.7 Hz, 2H, 5-H, 8-H); 3.04 (ddd, ^2J = 13.2 Hz, ^3J = 7.9 Hz, ^3J = 3.1 Hz, 2H, 1-H, 10-H), 2.77 (dt, ^2J = 13.3 Hz, ^3J = 8.7 Hz, 2H, 1-H, 10-H); 2.29−2.19 (m, 4H, 2-H, 9-H); 1.68 (dd, $^3J_{4,5}$ = 5.1 Hz, ^3J = 2.0 Hz, 2H, 4-H, 7-H); 0.00 (s, 18H, TMS−H). ^{13}C NMR (100.6 MHz, $CDCl_3$ /TMS): δ 138.1, 131.0 (s, C-3, C-6, C-11, C-14); 130.1, 129.1, 127.3 (d, C-5, C-8, C-12, C-13, C-15, C-16); 35.5 (d, C-4, C-7); 36.8, 34.2 (t, C-1, C-2, C-9, C-10), −0.5 (q, C-TMS). IR (FT-IR, KBr): $\bar{\nu}$ = 2945 (s); 2927 (s); 2914 (s); 1502 (w); 1436 (m); 1409 (w); 1246 (s); 1177 (w); 1112 (m); 1027 (m); 896 (s); 873 (s); 833 (vs); 816 (s); 755 (m); 639 (m); 630 (m); 502 cm^{-1} (m). UV (*n*-hexane): λ_{max} (log ϵ) = 198 (4.48); 212 (4.27); 236 (3.92); 256 nm (s, 3.32). MS (70 eV): *m*/*z* (%) = 354 (4, M^+); 281 (30); 177 (8); 161 (10); 104 (40); 73 (100). Anal. Calcd for $C_{22}H_{34}Si_2$: C, 74.50; H, 9.66. Found: C, 74.41; H, 9.83.

Spectroscopic and Analytical Data of 3. ^{1}H NMR (400.1 MHz, $CDCl_3$/TMS): δ 5.08 (d, $^3J_{3,4}$ = 7.8 Hz, 4H, 4-H); 2.48 (d, $^3J_{3,4}$ = 7.8 Hz, 4H, 3-H); 2.40−2.31 (m, 4H), 2.20−2.12 (m, 4H, 1-H); 0.00 (s, 36H, TMS−H). ^{13}C NMR (100.6 MHz, $CDCl_3$/TMS): δ 132.4 (s, C-2); 125.4 (d, C-4); 36.1 (d, C-3); 34.8 (t, C-1); − 0.2 (q, C-TMS). IR (FT-IR, KBr): $\bar{\nu}$ = 3029 (w); 2984 (m); 2951 (s); 2935 (m); 2901 (m); 2844 (m); 1619 (w); 1435 (m); 1409 (w); 1363 (w); 1245 (vs); 1184 (w); 1162 (w); 1119 (w); 1060 (w); 997 (w); 965 (w); 917 (w); 899 (s); 876 (s); 831 (vs); 755 (s); 705 (w); 690 (m); 641 (m); 440 cm^{-1} (w). UV (*n*-hexane): λ_{max} (log ϵ) = 192 (4.54); 224 (4.15); 250 nm (s, 3.28). MS (70 eV): *m*/*z* (%) = 500 (12, M^+); 339 (10); 251 (24); 235 (18); 177 (10); 161 (14); 147 (46); 104 (12); 73 (100). Anal. Calcd for $C_{28}H_{52}Si_4$: C, 67.12; H, 10.46; Si, 22.42. Found: C, 67.14; H, 10.44; Si, 22.45.

When the reductive silylation is repeated with addition of 2 g (0.29 mol) of lithium, only **3** is formed.

Catalytic Hydrogenation of 2: (a) Under Basic Conditions. The product mixture obtained from the reductive silylation of 10 g of [2.2]paracyclophane as described above, dissolved in 500 mL of ethanol, is placed in a 1 L autoclave, and freshly prepared Raney nickel (from 15 g of Al/Ni alloy) and 4 g of sodium hydroxide are added. After 3 d at 40 °C and a hydrogen pressure of 250 atm, the hydrogenation is terminated and the reaction mixture is decanted from the catalyst. The mixture is filtered through a pad of silica gel, most of the solvent is removed in vacuo, water (500 mL) is added, and after repeated extraction with dichloromethane the organic phase is dried (Na_2SO_4). GC analysis shows that **2** has been converted completely to **4** as well as the presence of unreduced **3** and several (unidentified) hydrogenation products of **1**. This raw mixture can be used directly for the DDQ oxidation described below. For analytical purposes a small sample of **4** (a viscous oil) is isolated by column chromatography on alumina with petroleum ether as the eluent.

Spectroscopic Data of 4. ^{1}H NMR (400.1 MHz, $CDCl_3$/TMS): δ 5.29 (d, $^3J_{5,4}$ = 7.9 Hz, 1H, 5-H); 5.22−5.20 (m, 1H, 12-H); 5.16 (d, $^3J_{8,7}$ = 7.3 Hz, 1H, 8-H); 2.64 (d, $^3J_{4,5}$ = 7.8 Hz, 1H, 4-H); 2.60 (d, $^3J_{7,8}$ = 7.4 Hz, 1H, 7-H); 2.46−1.78 (m, 11H, 2-H, 9-H, 10-H, 13-H, 14-H, 16-H); 1.59−1.25 (m, 4H, 1-H, 15-H); 0.03 (s, 9H), and 0.02 (s, 9H, TMS-groups). To determine the relative position of the double bonds, an NOE experiment was carried out, in which the olefinic cyclohexene proton was irradiated.

irradiation frequency, δ	NOE, δ
5.21 (12-H)	only 2.60 (7-H) signal enhancement observed

^{13}C NMR (100.6 MHz, $CDCl_3$/TMS): δ 135.4, 134.9, 134.7 (s, 3-C, 6-C, 11-C); 127.9, 125.7, 124.3 (d, 5-C, 8-C, 12-C); 38.1, 36.4 (d, 4-C, 7-C); 36.9, 34.8, 33.2, 30.1, 28.9, 25.3, 23.4 (t, 1-C, 2-C, 9-C, 10-C, 13-C, 15-C, 16-C); 26.6 (d, 14-C); 0.00, 0.01 (q, TMS-groups). IR (FT-IR, KBr): $\bar{\nu}$ = 2950 (s); 2920 (s); 2849 (s); 1655 (w); 1449 (m); 1438 (m); 1420 (w); 1407 (w); 1247 (s); 1190 (w); 963 (w); 957 (w); 907 (m); 896 (m); 872 (s); 860 (s); 835 (vs); 757 (m); 688 (m); 630 cm^{-1} (m). UV (*n*-hexane): λ_{max} (log ϵ) = 194 (4.22); 214 (4.08); 230 (3.82); 262 nm (2.71). MS (70 eV): *m*/*z* (%) = 358 (4, M^+); 343 (1.5); 285 (4); 270 (5); 236 (10); 211 (11); 148 (20); 73 (100). HRMS: calcd for $C_{22}H_{38}Si_2$ 358.251208, found 358.2512 ± 3 ppm.

(b) Under Neutral Conditions. The experiment was repeated as described above but in the absence of sodium hydroxide and extending the reaction time to 7 d. GC analysis of the hydrogenation mixture showed the presence of the products described above plus the formation of a compound having a molecular mass of 360. This finding and the transformations described below suggest structure **5** for this compound; no attempt was made to purify the unstable oil. MS of **5**: *m*/*z* (%) = 360 (1, M^+); 286 (1); 272 (2); 244 (6); 213 (12); 161 (20); 148 (16); 73 (100).

Desilylation of 2 with Tetrabutylammonium Fluoride (TBAF). The product mixture obtained from the reductive

(8) For a review, see: Hopf, H.; Marquard, C. In *Strain and its Implications in Organic Chemistry*; de Meijere, A., Blechert, S., Eds.; NATO ASI Series C, Vol. 273; Kluwer Academic Publ., Dordrecht, 1989; pp 297−332.

(9) Hopf, H.; Mourad, A. F.; Kleinschroth, J. *Angew. Chem.* **1980**, *92*, 388−389; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 389−390.

silylation of 10 g (48.1 mmol) of [2.2]paracyclophane (**1**) as described above is completey liberated from its solvent and the remaining oil is taken up in 150 mL of anhydrous THF. After the solution is cooled to 0 °C, 1 g (1.25 mmol) of TBAF·30H_2O and 15.2 g (48.2 mmol) of TBAF·3H_2O are added, and the mixture is stirred under nitrogen for 2 h and subsequently for 15 h at room temperature. Most of the solvent is removed in vacuo, dichloromethane is added, and the organic phase is extracted thoroughly with water. After drying (Na_2SO_4), the solvent is removed by rotary evaporation, and the remaining oil is purified by column chromatography on silica gel with petroleoum ether as the eluent, yielding 5.1 g (51%) of 4,7-dihydro[2.2]paracyclophane (**6**). Although this is a known compound[6] its spectroscopic data, obtained with more modern spectrometers, are repeated here. ^{1}H NMR (400.1 MHz, $CDCl_3$/TMS): δ 6.88−6.82 (m, 4H, 12-H, 13-H, 15-H, 16-H); 4.87−4.85 (m, 2H, 5-H, 8-H); 3.08−3.02 (m, 2H), 2.80−2.72 (m, 2H, 1-H, 10-H); 2.37−2.28 (m, 4H, 2-H, 9-H); 2.17−2.08 (m, 2H), 1.94−1.84 (m, 2H, 4-H, 7-H). ^{13}C NMR (100.6 MHz, $CDCl_3$/TMS): δ 138.4 (s, C-11, C-14); 134.0 (s, C-3, C-6); 131.1, 129.9 (d, C-12, C-13, C-15, C-16); 129.0 (d, C-5, C-8); 35.9 (t, C-2, C-9); 33.6 (t, C-1, C-10); 29.8 (t, C-4, C-7). IR (FT-IR, KBr): $\bar{\nu}$ = 3034 (w); 3009 (w); 2947 (w); 2913 (s); 2891 (s); 2850 (s); 2811 (s); 1672 (w); 1638 (w); 1594 (w); 1499 (w); 1437 (w); 1421 (m); 1178 (w); 1019 (w); 932 (w); 879 (m); 802 (s); 717 (m); 619 (m); 565 (w); 485 (m); 437 cm^{-1} (w). UV (*n*-hexane): λ_{max} (log ϵ) = 194 (4.34); 198 (4.31); 218 (4.07); 238 (3.64); 284 nm (2.53). MS (70 eV): *m*/*z* (%) = 210 (60, M^+); 195 (18); 181 (12); 154 (16); 118 (20); 117 (22); 105 (30); 104 (100) 91 (46). Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.24; H, 8.72.

Oxidation of 4 to 4,5,6,7-Tetrahydro[2.2]paracyclophane (7). The hydrogenation mixture obtained from 10 g (48.1 mmol) of **1** under basic conditions (vide supra) is dissolved in 250 mL of dichloromethane, the solution is cooled to 0 °C, and dichlorodicyano-*p*-benzoquinone (DDQ) is added in small portions until a black color persists. The oxidation mixture is extracted four times with 50 mL portions of 10% aqueous sodium hydroxide solution, the aqueous phases are combined and acidified, and the precipitate formed is removed by filtration. The organic phase is dried (Na_2SO_4) and filtered through a short column of silica gel. GC/MS analysis of the product mixture shows the presence of two components formed in a ratio of 4:1, the desired monolefin **7** and a monosilylated derivative to which we assign structure **8**. MS of **8**: *m*/*z* (%) = 284 (14, M^+); 269 (4); 229 (6); 210 (6); 189 (8); 176 (34); 161 (54); 73 (100). Rather than attempting to separate these two compounds, the solution is concentrated to ca. 100 mL, and 5 mL of 80% trifluoroacetic acid is added. After 4 h no more **8** can be detected by GC analysis, and the mixture is neutralized and dried (Na_2SO_4). Column chromatogpahy on silica gel with petroleum ether provides 5.3 g (52%) of **7**, mp 153 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$/TMS): δ 7.13−7.08 (m, 3H); 6.88 (d, *J* = 7.2 Hz, 1H) (12-H, 13-H, 15-H, 16-H); 4.46−4.45 (m, 1H, 8-H); 3.08−3.02 (m, 1H, 1-H); 2.91−2.87 (m, 1H, 10-H); 2.77−2.70 (m, 1H, 1-H); 2.50−2.43 (m, 1H, 10-H); 2.34−2.28 (m, 1H, 2-H); 2.17−2.08 (m, 1H, 9-H); 2.02−1.95 (m, 1H, 6-H); 1.92−1.76 (m, 3H, 2-H, 7-H(2H)); 1.77−1.69 (m, 1H, 4-H); 1.35−1.26 (m, 1H, 5-H); 1.24−1.15 (m, 3H, 4-H, 5-H, 9-H). ^{13}C NMR (100.6 MHz, $CDCl_3$/TMS): δ 141.5, 140.5, 131.66 (s, C-3, C-11, C-14); 131.71, 130.8, 130.3, 129.31 (d, C-12, C-13, C-15, C-16); 129.34 (d, C-8); 36.61 (t, C-9); 36.56 (t, C-2); 33.8 (t, C-1); 31.6 (t, C-10); 30.2 (t, C-4); 26.1 (t, C-5); 25.9 (d, C-6); 24.7 (t, C-7). IR (FT-IR, KBr): $\bar{\nu}$ = 3031 (w); 3004 (w); 2887 (s); 2842 (s); 2827 (s); 1884 (w); 1663 (w); 1596 (m); 1566 (w); 1501 (m); 1445 (s); 1428 (m); 1410 (m); 1359 (w); 1307 (w); 1246 (w); 1231 (w); 1208 (w); 1194 (w); 1174 (w); 1161 (w); 1099 (m); 1040 (w); 1012 (w); 984 (w); 968 (w); 934 (w); 914 (m); 887 (w); 865 (m); 825 (m); 803 (s); 791 (m); 753 (w); 721 (m); 695 (w); 595 (w); 564 (w); 520 (w); 465 cm^{-1} (w). UV (*n*-hexane): λ_{max} (log ϵ) = 202 (4.35); 222 (3.86); 240 (3.76); 246 (3.70); 260 (2.96); 288 nm (2.56). MS (70 eV): *m*/*z* (%) = 212 (30, M^+); 197 (4); 156 (10); 117 (14); 104 (100); 91 (10). Anal. Calcd for $C_{22}H_{38}Si_2$: C, 90.51; H, 9.49. Found: C, 90.27; H, 9.71.

Oxidation of 5 to 3,4,5,6,7,8-Hexahydro[2.2]paracyclophane (9). The hydrogenation mixture obtianed from 10 g (48.1 mmol) of **1** under neutral conditions (vide supra) is oxidized with DDQ as described above for the conversion of **4** → **7**. GC/MS analysis of the raw product mixture shows the presence of **9**. The dichloromethane is removed in vacuo, and the resulting oil is taken up in 100 mL of anhydrous THF. After 4 g of TBAF·3H_2O is added to the solution, it is stirred for 8 h under nitrogen. Dichloromethane is added to the reaction mixture, which is thoroughly washed with water and dried (Na_2SO_4). Column chromatography on silica gel with petroleum ether as the eluent provides 0.73 g (7%) of the 1,4-cyclohexanoparacyclophane **9**. ^{1}H NMR (400.1 MHz, $CDCl_3$/TMS): δ 7.29 (s, 4H, 12-H, 13-H, 15-H, 16-H); 2.75 (t, *J* = 6.4 Hz, 4H, 1-H, 10-H); 1.70−1.59 (m, 6H, 2-H, 3-H, 6-H, 9-H); 1.06−0.87 (m, 8H, 4-H, 5-H, 7-H, 8-H). ^{13}C NMR (100.6 MHz, $CDCl_3$/TMS): δ 141.4 (s, C-11, C-14); 131.8 (d, C-12, C-13, C-15, C-16); 35.6 (t), 32.2 (t) (C-1, C-2, C-9, C-10); 30.2 (d, C-3, C-6); 26.2 (t, C-4, C-5, C-7, C-8). IR (FT-IR, KBr): $\bar{\nu}$ = 3025 (w); 3004 (w); 2913 (vs); 2895 (s); 2857 (s); 2841 (s); 2711 (w); 2668 (w); 1586 (m); 1499 (m); 1446 (s); 1404 (w); 1355 (w); 1193 (w); 911 (m); 847 (m); 830 (s); 793 (s); 710 (s); 593 (m); 552 (m); 506 cm^{-1} (w). UV (*n*-hexane): λ_{max} (log ϵ) = 206 (4.18); 214 (4.27); 248 (3.80); 294 nm (2.50). MS (70 eV): *m*/*z* (%) = 214 (5, M^+); 117 (15); 104 (100); 91 (10). Anal. Calcd for $C_{16}H_{22}$: C, 89.66; H; 10.34. Found: C, 89.56; H, 10.53. Mp: 158 °C. These data agree with those published in ref 2.

Acid-Catalyzed Isomerization of 9 to 11,12,13,14,15,16-Hexahydro[2.2]parametacyclo-phane (11). To a solution of 200 mg (0.93 mmol) of **9** in 30 mL of anhydrous dichloromethane is added 1 mL of trifluoroacetic acid and the mixture is stirred for 4 h at room temperature. After washing with water, neutralization with sodium bicarbonate solution, and additional washing, the solution is dried (Na_2SO_4) and filtered through a short column of silica gel. Removal of the solvent affords 183 mg (92%) of **11** as a viscous oil. ^{1}H NMR (400.1 MHz, $CDCl_3$/TMS): δ 7.65 (s, 1H, 8-H); 7.11 (t, ^3J = 7.4 Hz, 1H, 5-H); 6.91 (dd, ^3J = 7.4 Hz, ^4J = 1.3 Hz, 2H, 4-H, 6-H); 2.80−2.76 (m, 4H, 2-H, 9-H); 1.77−1.73(m, 6H, 1-H, 10-H, 11-H, 14-H); 1.05−0.99 (m, 4H, 12-H, 13-H); 0.69−0.67 (m, 4H, 15-H, 16-H). ^{13}C NMR (100.6 MHz, $CDCl_3$/TMS): δ = 142.9 (s, C-3, C-7); 133.3, 129.1, 125.6 (d, C-4, C-5, C-6, C-8); 32.9, 31.5 (t, C-1, C-2, C-9, C-10); 28.6 (d, C-11, C-14); 24.6 (t, C-12, C-13, C-15, C-16). Low-temperature NMR at -94 °C (CH_2Cl_2): δ = 7.58 (s); 7.06 (t, ^3J = 7.4 Hz); 6.91 (d, ^3J = 6.4 Hz); 6.85 (d, ^3J = 6.8 Hz); 2.96−2.92 (m); 2.79−2.76 (m); 2.68−2.64 (m); 2.38−2.35 (m); 2.10−194 (m); 1.68−1.43 (m); 1.23−0.96 (m); 0.18−0.17 (m); −1.35−1.43(m). IR (FT-IR, KBr): $\bar{\nu}$ = 2922 (vs); 2899 (vs); 1605 (w); 1466 (s); 1449 (m); 926 (w); 776 (m); 703 cm^{-1} (m). UV (*n*-hexane): λ_{max} (log ϵ) = 204 nm (4.47); 222 (3.91); 270 (2.43). MS (70 eV): *m*/*z* (%) = 114 (100, M^+); 199 (18); 183 (20); 143 (26); 118 (42); 117 (50); 104 (64); 91 (40). Anal. Calcd for $C_{16}H_{22}$: C, 89.66; H, 10.34. Found: C, 89.56; H, 10.26.

Diels−Alder Addition of 9 with Tetracyanoethene (TCNE). To a solution of 180 mg (0.84 mmol) of **9** in 30 mL of chloroform is added 200 mg (1.56 mmol) of TNCE. The solution turns deep red. After 1 h at 50 °C the color has faded and the solvent is removed in vacuo. Column chromatography on silica gel with dichloromethane/petroleum ether (1:3, v/v) provides 267 mg (93%) of **12**, mp 190 °C (dec). ^{1}H NMR (400.1 MHz, acetone-d_6/TMS): δ 6.61 (dd, $^3J_{8,7/5,4}$ = 6.5 Hz, $^4J_{8,2/5,9}$ = 1.3 Hz, 2H, 5-H, 8-H); 4.69 (dd, $^3J_{7,8/4,5}$ = 1.8 Hz, $^4J_{4,2/7,9}$ = 6.5 Hz, 2H, 4-H, 7-H); 2.78−2.69 (m, 2H, 2-H,9-H); 2.41−2.34 (m, 2H, 2-H, 9-H); 1.90−1.70 (m, 6H), 1.63−1.55 (m, 2H), 1.36−1.26 (m, 4H), 1.12−1.03 (m, 2H) (1-H, 10-H, 11-H, 12-H, 13 −H, 14-H, 15-H, 16-H). ^{13}C NMR (100.6 MHz, acetone-d_6/TMS): δ 154.3 (s, C-3, C-6); 127.7 (d, C-5, C-8); 113.8, 113.7 (s, C-19/C-21, C-20/C-22); 52.7 (d, C-4, C-7); 45.6 (s, C-17, C-18); 31.1 (d, C-11, C-14); 31.2, 30.6, 29.3, 27.9 (t, C-1, C-2, C-9, C-10, C-12, C-13, C-15, C-16). IR (FT-IR,KBr): $\bar{\nu}$ = 3053 cm^{-1} (w); 3010 (m); 2923 (s); 2895 (s); 2857 (s); 2250 (w); 1656 (w); 1628 (w); 1444 (s); 1305 (w); 1272 (w); 1227 (m); 1071 (w); 1032 (w); 1019 (w); 1004 (w); 927 (m); 891 (w); 869 (m); 834 (w); 805 (m); 674 (w); 654 (w); 581 (w). UV (acetonitrile): λ_{max} (log ϵ) = 212 nm (3.61); 240 (2.93). MS (70 eV): *m*/*z* (%) = 342 (3, M^+); 214 (6); 128 (14); 117 (20); 104 (100); 91 (18); 76 (16). Anal. Calcd for $C_{22}H_{22}N_4$: C, 77.16; H, 6.48; N, 16.36. Found: C, 77.17; H; 6.50; N, 16.30.

JO971278L