Nickel-Mediated Cyclobutabenzene Syntheses. *trans*-7,8-Dibromocyclobutabenzenes:[1] Their One-Pot Preparation, X-ray Structure, and Diels−Alder Reactions

Amnon Stanger,*[,2a] Nissan Ashkenazi,[2a] Alona Shachter,[2a] Dieter Bläser,[2b] Peter Stellberg,[2b] and Roland Boese*[,2b]

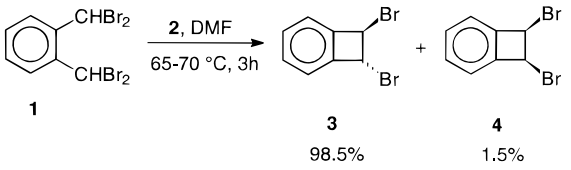
Department of Chemistry, Technion−Israel Institute of Technology, Haifa 32000, Israel, and Institut für Anorganische Chemie der Universität-GH Essen, Universitätsstrasse 5-7, D-45117, Essen, Germany

Received January 24, 1996

Cyclobutabenzenes are of considerable interest, both from a synthetic point of view, being synthons for *o*-xylylenes,[3,4] and from that of theory, as they are key compounds for the study of the Mills Nixon effect.[5] However, the number of methods for their preparation is limited. Cyclobutabenzene is usually prepared in moderate yields from NaI/KI-mediated cyclization of α,α,α′,α′-tetrabromo-*o*-xylene (**1**).[6] This reaction yields dibromo- and diiodocyclobutabenzenes, each as a mixture of *cis* and *trans* isomers.[7] Thus, the method's only practical use is for the preparation of unsubstituted cyclobutabenzene (after a medium yield reduction of the halogen atoms)[8] or as precursors for the preparation of systems in which the stereochemistry is unimportant.[9] Another synthetic method for the preparation of cyclobutabenzenes is based on the $CpCoL_2$ (L = CO, ethene)-mediated [2 + 2 + 2] cyclization between 1,5-hexadiyne and an alkyne.[10] This method, however, yields cyclobutabenzenes that are disubstituted in the aromatic ring, whereas the four-membered ring is not functionalized.[11] We report here a simple, single-step, and high-yield preparation of the title compounds, the X-ray structure of the parent system, and preliminary results concerning their Diels−Alder reactivity.

Nickel-mediated coupling of RX (where R is aryl, benzyl, ethenyl, allyl and X = Br, I) is a well-known and widely used synthetic method.[12] In all cases of which we are aware, this method have been used for bimolecular coupling, except for Semmelhack's work[12a] in which he reports intramolecular ring formation (where the ring sizes are equal or larger than six) by the Ni(0) coupling of the respective bis(iodoaryls). We intended to use the Ni-mediated coupling reaction intramolecularly to form a four-membered ring. In order to enable better control of the reaction, we decided to use defined Ni(0) complexes instead of the usual *in-situ* prepared cyclization mediators, formed from Ni(II), phosphines, and a reducing agent. We did this because in several of the reported cases the product may have resulted from a reaction mediated by the reducing agent (e.g., Zn) rather than from the Ni-mediated reaction. Thus, when a solution of α,α,α′,α′-tetrabromo-*o*-xylene was stirred with Zn in DMF, with or without the presence of ca. 10% $(Bu_3P)_2$-Ni(COD) (COD = 1,5-cyclooctadiene), identical product mixtures were obtained. We have therefore used definite Ni(0) complexes: $(Bu_3P)_2NiL$ (L = anthracene, COD, **2a** and **2b**,[13] respectively).[14]

The initial attempts to close a four-membered ring were focused on α,α′-dibromo-*o*-xylene, but the only reaction products were dimers, mainly 1,5-dibenzocyclooctadiene. Under no conditions (including addition of reagents by a syringe pump) could we obtain the intramolecular ring-closure product.[15] Thus, as the intermolecular coupling is extremely facile, it was necessary to decrease the rate of the bimolecular coupling and/or increase the rate of the intramolecular coupling in order to force the reaction to proceed via the intramolecular pathway. Steric congestion near the reaction center(s) was thought to retard the bimolecular coupling, since it should prevent close contact between the reacting molecules. The intramolecular reaction should be enhanced by stabilization of the intermediate in order to prolong its lifetime and thus let the entropy (which favors the intramolecular ring closure) play a more important role in the determination of the reaction rate. In case of the nickel-mediated coupling, one of the key intermediates is probably an insertion product of Ni into a C−X bond;[16] thus, an electronegative substituent on the reacting carbon atom should stabilize it. A substituent that fulfills both demands is Br; therefore, we have reacted α,α,α′,α′-tetrabromo-*o*-xylene (**1**) with a Ni(0) complex (**2a** or **2b**) under cyclization conditions. The reaction is described in eq 1. The products were assigned by ^1H



(1)

1 **3** 98.5% **4** 1.5%

NMR,[17] and the X-ray structure of the major product (shown in Figure 1, see below) shows that the tentative assignments of the NMR signals of **3** and **4** were correct. When the reaction is carried out in an NMR tube the convergence of **1** to **3** and **4** is quantitative and no side products are observed. The yield of the mixture (after

(1) Alternative name: *trans*-1,2-dibromobenzocyclobutene.
(2) (a) Technion. (b) Essen.
(3) Alternative name: *o*-quinodimethanes.
(4) Oppolzer, W. *Synthesis* **1978**, 793.
(5) (a) Boese, R.; Bläser, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 304. (b) Boese, R.; Bläser, D.; Billups, W. E.; Haley, M. M.; Maulitz, A. H.; Mohler, D. L.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 313. (c) Stanger, A. *J. Am. Chem. Soc.* **1991**, *113*, 8277 and references therein. (d) Siegel, J. S. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1721.
(6) Cava, M. P.; Napier, D. R. *J. Am. Chem. Soc.* **1956**, *78*, 500
(7) In a control experiment using Cava's procedure we obtained *trans*- and *cis*-dibromo and diiodocyclobutabenzene in a ratio of 63:19:12:6, respectively. The yield of pure **3** obtained from this procedure (mp = 52.4−52.8 °C) after repeated recrystallization is 4.8%. See: Cava, M. P.; Napier, D. R. *J. Am. Chem. Soc.* **1957**, *79*, 1701.
(8) (a) Sanders, A.; Giering, W. P. *J. Org. Chem.* **1973**, *38*, 3055. (b) Cava, M. P.; Napier, D. R. *J. Am. Chem. Soc.* **1958**, *80*, 2255.
(9) Cava, M. P.; Deana, A. A.; Muth, K. *J. Am. Chem. Soc.* **1959**, *81*, 6458.
(10) Funk, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1976**, *98*, 6755.
(11) Another drawback is the necessity to prepare the diyne that is not commercially available.
(12) (a) Semmelhack, M. F.; Helquist, P. M.; Jones, D. *J. Am. Chem. Soc.* **1971**, *93*, 5908. (b) Semmelhack, M. F.; Ryono, L. S. *J. Am. Chem. Soc.* **1975**, *97*, 3873. (c) Kende, A. S.; Liebeoking, L. S.; Braitsch, D. M. *Tetrahedron Lett.* **1975**, 3375. (d) Zembayashi, M.; Tameo, K.; Yoshida, J.; Kumada, M. *Tetrahedron Lett.* **1977**, 4089. (e) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 7549. (f) Semmelhack, M. K.; Helquist, P.; Jones, L. D.; Keller, L.; Mendelson, L.; Ryono, L. S.; Smith, J. G.; Stauffer, R. D. *J. Am. Chem. Soc.* **1981**, *103*, 6460.
(13) Stanger, A.; Shazar, A. *J. Organomet. Chem.* **1993**, *458*, 233.
(14) It is unimportant which L is used as the $(Bu_3P)_2Ni$ ligand, because the reaction solvent (DMF) replaces L after a few minutes and the mediator is actually $(Bu_3P)_2Ni(DMF)_n$.

0022-3263/96/1961-2549$12.00/0

chromatography) is 83%, and the isolated yield of **3** (after crystallization) is 70%.[18]

Attempts to carry out the reaction catalytically, using a catalytic amount of Ni(0) complex and a reducing agent (Zn, Mg, Na−ascorbate) were unsuccessful. The maximum yield of **3** and **4** obtained was the same as the molar percentage of the Ni complex.[19] It occurred to us that nickel powder should serve as a good reducing agent. Being a solid heterophase, its chemical potential is 1, whereas the concentration of the $(Bu_3P)_2Ni(II)$ species in solution is small. Therefore, the reduction of the dissolved Ni(II) species by the solid Ni powder should be thermodynamically favorable. This reasoning also holds for the other reducing agents that we have tried to utilize, but Ni powder does not introduce any other metal (and therefore different chemistry) to the reaction mixture. This, indeed, seemed to be a correct approach because relatively high yields of dibromocyclobutabenzene were obtained from the reaction containing **1**, 5 mol % of $(Bu_3P)_2Ni(COD)$, and Ni powder. However, in a control experiment, it was found that nickel powder can mediate ring closure in the absence of **2**. The drawbacks, relative to the $(Bu_3P)_2Ni(COD)$-mediated reaction, are the lower total yield (81%) and a lower **3**:**4** ratio (ca. 90:10). The advantages, however, are that the nickel powder is much easier to handle, the reaction can be carried out under air, and the process is much less expensive than the Ni(0) complex-mediated reaction. This process can also be utilized for substituted systems (see below).

The X-ray structure of **3**[20] (Figure 1 and Table 1) shows that the substitution of C(1) and C(2) by Br does not alter the structure of the carbon skeleton substantially, and the major geometrical parameters are the same for **3** as for the nonsubstituted cyclobutabenzene.[5a] There is no evidence for bond alternation in the benzene ring, and the C(1)−C(2)−C(3) angle (114.9°) is significantly decreased (relative to benzene) due to the strain implied onto the benzene ring.

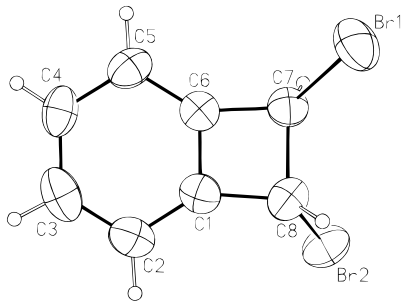


Figure 1. X-ray structure of **3**. See ref 20 for details. The ellipsoids correspond to 50% probability of electron distribution. Distances (Å) and angles (deg) (standard deviations in parentheses): C1−C2 1.375(7), C2−C3 1.391(7), C3−C4 1.407(8), C4−C5 1.393(7), C5−C6 1.398(6), C6−C7 1.507(6), C7−C8 1.571(8), C7−Br1 1.964(6), C8−Br2 1.951(5), C1−C2−C3 114.9(5), C2−C3−C4 122.4(5), C3−C4−C5 122.3(4), C4−C5−C6 114.8(5), C1−C6−C5 122.1(4), C2−C1−C6 123.4(4), C6−C1−C8 93.2(4), C1−C8−C7 86.2(3), C6−C7−C8 87.1(4), C1−C6−C7 93.3(4) Br1−C7−C8 114.0(3), Br2−C8−C7 115.2(3).

Table 1. Some Details of the Structure Determination of 3

chem formula $C_8H_6Br_2$	fw 261.94	space group $P2_1/c$ (No. 14)
$\lambda = 0.710\ 69$ Å	$\mu = 9.59\ mm^{-1}$	$Z = 4$
$T = 125$ K		
$a = 7.488(2)$ Å	$b = 14.980(4)$ Å	$c = 8.316(2)$ Å
$\alpha = 90°$	$\beta = 116.07(2)°$	$\gamma = 90°$
$V = 837.9(3)$ Å^3	$\rho_{calcd} = 2.076\ g\ cm^{-3}$	
$R = 0.0451$	$R_w = 0.0473$	$w^{-1} = (\sigma 2(F_o)+0.0015F_o^2)$

The fact that **3** (the *trans* isomer) can be prepared easily in high yield makes it a potential starting material for the syntheses of organic systems on the basis of its Diels−Alder reactivity. There are two stereoselective requirements for making this reaction useful: the opening of **3** to the *o*-xylylene and its addition to a dienophile. In order to check this **3** was reacted with several dienophiles (Scheme 1). Two of the products clearly indicate that the opening of **3** is conrotatory, leading only to **5** as an intermediate, and that the Diels−Alder addition is exclusively *endo*. Thus, **6**[21] is the only product obtained from the reaction of **3** with maleic anhydride (Scheme 1, i). The reaction of **3** with styrene (Scheme 1, iv) leads directly to the elimination product **9**. The reaction conditions (benzene as a solvent with no additional base except the reactants) suggest that the elimination of two HBr molecules is very facile, indicating that the hydrogen and bromine atoms are antiperiplanar. This arrangement is possible only if the styrene adds *endo* to **5**. The reaction of **3** with tetracyanoethylene and phenylacetylene (Scheme 1, ii and iii, respectively) yields only one product in each case, tentatively assigned as **7** and **8**, respectively. Attempts to measure NOE enhancement between H(1) and H(4) of the newly formed six-membered ring in **8** failed. However, molecular modeling at the PM3 level suggests that the distance between these protons is 4.857 Å (4.738 Å at a force field level); thus, the absence of NOE enhancement is not proof for the *trans* arrangement of these protons. We are currently trying to crystallize the product and obtain its stereochemistry from X-ray analysis.

We have investigated the scope of the nickel-mediated cyclization method in two directions. One is the pos-

(15) If (Bipy)Ni(COD) is used instead of $(Bu_3P)_2Ni(COD)$ the benzonickelacyclopentane can be isolated instead of the dimer. However, this nickelacycle does not yield the cyclobutabenzene upon reductive elimination. See: Matsunaga, P. T.; Mavropoulos, J. C.; Hillhouse, G. L. *Polyhedron* **1995**, *14*, 175. See also: Khomik, L. I. *Deposited Doc.* **1981**, *SPSTL 836*, khp-D81; *Izv. Vyssh. Uchebn. Zaved. Kim. Kim. Tekhnol.* **1983**, *26*, 664. We have tried to mediate the reaction by using (Depe)Ni(anthracene) instead of $(Bu_3P)_2NiL$ (L = COD, anthracene), but only starting materials were isolated. Thus, no coupling is observed when a bidentate ligand is used, and a bisphosphine leads only to dimerization.

(16) Yamamoto, T.; Wakabayashi, S.; Osakada, K. J. *J. Organomet. Chem.* **1992**, *428*, 223.

(17) ^{1}H NMR: **3**, 7.39, 7.19 (AA′BB′, 4H), 5.41 (s, 2H, C*H*Br); **4**, 7.43, 7.26 (AA′BB′, 4H), 5.81 (s, 2H, C*H*Br). See Fraenkel, G.; Asahi, Y.; Mitchell, M. J.; Cava, M. P. *Tetrahedron* **1964**, *20*, 1179.

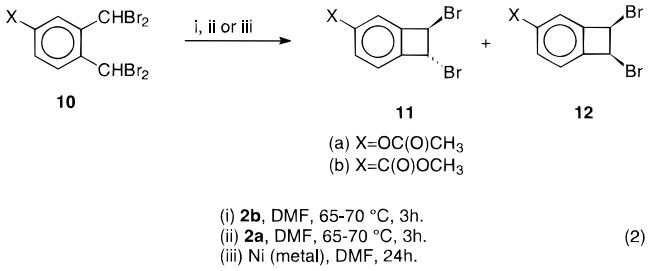
(18) Mp 52.7−52.8 °C (uncorrected) and GC analysis of the crystals show that they contain 99.7% **3** and 0.3% **4**.

(19) No starting material, however, was recovered, and most products were Wurtz type.

(20) A crystal of approximately 0.33 × 0.27 × 0.17 mm^3 was measured on a Nicolet R3m/V four circle diffractometer with Mo Kα-radiation (graphite monochromator). The crystal system is monoclinic and the cell dimensions are refined from the diffractometer angles of 50 centered reflections in the 2Θ-range of 20−25°. Extinction correction ($F^* = F_c/[(1 + 0.002xF^2_c)/\sin 2\Theta]^{0.25}$; $x = 0.000\ 59$) and empirical absorption correction in the 2Θ-range of 3−35° has been performed (max/min transmission: 0.29/0.86, R_{merg} before/after correction: 0.199/0.036). The maximum scan angle in 2Θ was 80°, which led to 2444 unique intensities (R_{merg} 0.0329) and 1733 observed intensities ($F_o \geq 4\sigma(F_o)$). The structure solution with direct methods and the refinement with full-matrix least-squares was performed with the SHELXTL-Plus program package (Vers.4.11/V). One hundred sixteen parameters were refined with anisotropic displacement parameters for C and Br, hydrogen atoms, located from a difference map and refined without any constraints, with isotropic displacement parameters. The maximum residual electron density is 1.32 eÅ^{-3}. Further details are given in Table 1.

(21) (a) Mueller, P.; Rey, M. *Helv. Chim. Acta* **1981**, *64*, 354. (b) Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1982**, *104*, 7609.

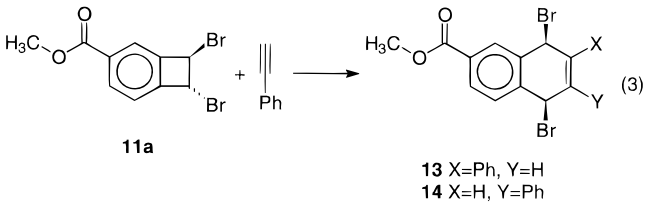
sibility to close more than one four-membered ring in a "one pot" fashion. Indeed, hexabromotricyclobutabenzene can be prepared in high yield in a single reaction.[22] The second is a study of the generality of the ring closure in substituted **1**. We have attempted few of these reactions; those reported here are our preliminary results. Equation 2 describes two examples of substituted systems (**10**)



(2)

reacting with a Ni(0) complex or Ni metal to form the respective dibromocyclobutabenzenes **11** and **12**. In all cases, the nickel-mediated cyclizations yielded the expected products. For example, when **10a** or **10b** was subjected to cyclization conditions, the total isolated yield was only ca. 25%, with an **11**:**12** ratio of 8:1. However, when **10b** was reacted with $(Bu_3P)_2Ni$(anthracene) the yield was 80%, and **11a** was shown by NMR to be the sole product. Metallic nickel cyclizes **10a** to **11a** and **12a** with a total yield of 38%. The solvent employed is of prime importance: When the cyclization of **10a** is carried out in THF with metallic nickel and stoichiometric amount of DMF the yield is only 38% but the only product is **11a**.

Preliminary results suggest that **11** undergoes regiospecific Diels–Alder cyclization (eq 3), where only one of the two possible products (**13** or **14**) is obtained. Under



(3)

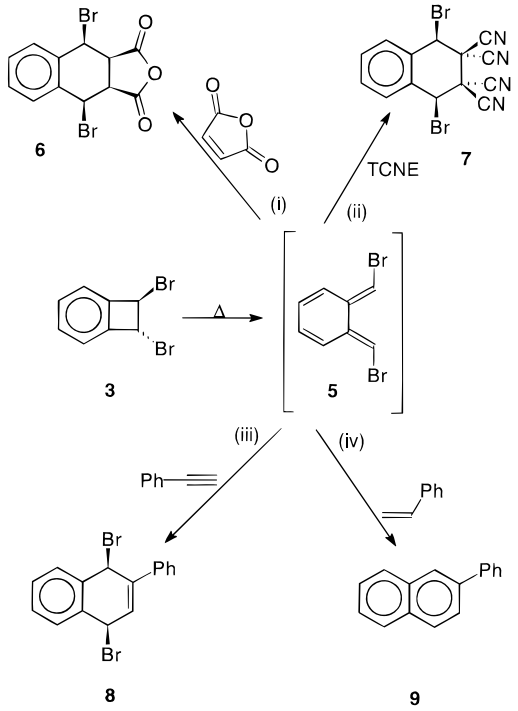
Diels–Alder conditions, **12a** is completely unreactive and is fully recovered. We are currently optimizing the cyclization conditions and investigating the Diels–Alder reactivity of **11** and **12**. Note that **11** and **12** are chiral, so enatioselective closure of the four-membered ring using chiral phosphines as ligands to nickel is also under investigation.

Experimental Section

General. All solid starting materials were recrystallized prior to use. THF and DMF were freshly distilled from potassium–benzophenone ketyl and CaH_2, respectively, prior to use. C_6D_6 and CD_2Cl_2 were dried and kept on molecular sieves 4A and vacuum transferred to the NMR tubes which were fire-sealed. Metallic nickel was Nickel sponge gd.II b2152 (Johnson, Matthey and Co. Ltd.) used without any treatment. Alumina and florisil used for chromatography were Merck neutral alumina activity I and Riedel-de Haën Florisil, respectively. Elemental analyses were performed in the Hebrew university microanalysis laboratory. NMR spectra were recorded on a 400 MHz spectrometer (100.8 MHz for ^{13}C) in $CDCl_3$ unless otherwise noted. Reported melting points are uncorrected.

(22) Stanger, A; Ashkenazi, N.; Bläser, D.; Stellberg, P.; Mauliz, A.; Boese, R. manuscript in preparation.

Scheme 1



3,4-Dimethylphenyl Acetate. Acetyl chloride (8.5 mL, 0.12 mol) was added dropwise to a cold (0 °C) solution of 3,4-dimethylphenol (10 g, 0.082 mol) and Et_3N (20 mL) in CH_2Cl_2 (150 mL). The reaction was stirred at rt for 4 h. Water (100 mL) was added, the organic phase separated, washed with HCl 2 M, NaOH 2 M, and water, and dried over $MgSO_4$, and the solvent removed under reduced pressure. The product was purified over a Florisil column (hexane) to give 3,4-dimethylphenyl acetate as a light yellow oil (11.0 g, 82%). NMR: ^1H δ 7.14 (d, ^3J = 8.4 Hz, 1H), 6.93 (s, 1H), 6.89 (d, ^3J = 8.4 Hz, 1H), 2.30 (s, 3H), 2.28 (s, 6H); ^{13}C (50.4 MHz) δ 169.57, 148.64, 137.74, 133.97, 130.24, 122.40, 118.53, 20.94, 19.70, 19.01.

Methyl 3,4-Dimethylbenzoate. Five equiv of diazomethane in dry ether was added dropwise to a cold (0 °C) solution of 3,4-dimethylbenzoic acid in dry CH_2Cl_2 (40 mL). The reaction was stirred overnight at rt. The crude product was washed with NaOH 2 M and water and dried over $MgSO_4$, and the solvent was removed under reduced pressure to yield the product (a light yellow oil) which was used as is in the subsequent bromination. NMR: ^1H δ 7.74 (s, 1H), 7.70 (d, ^3J = 8.0 Hz, 1H), 7.08 (d, ^3J = 8.0 Hz, 1H), 3.61 (s, 3H), 2.20 (s, 6H); ^{13}C (50.4 MHz) δ 167.17, 142.02, 136.52, 130.53, 129.52, 127.71, 127.05, 51.66, 19.76, 19.45.

3,4-Bis(dibromomethyl)phenyl Acetate (10a). A solution of Br_2 (6.6 mL, 0.13 mol) in CCl_4 (30 mL) was added to an irradiated refluxing solution (using a 375W sun-light lamp as the light and heat sources) of (3,4-Dimethyl)phenyl acetate (5 g 30 mmol) in CCl_4 (70 mL) during 24h. The reaction mixture was cooled, washed with 10% $Na_2S_2O_3$, water, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The product was filtered on a florisil column (hexane:CH_2Cl_2 3:1) to give **10a** (8 g, 62%). Mp: 109 °C. NMR: ^1H δ 7.64 (d, ^3J = 8.4 Hz, 1H), 7.43 (s, 1H), 7.11 (dd, ^3J = 8.7, 2.2 Hz, 1H), 7.06 (s, 1H), 7.04 (s, 1H), 2.31 (s, 3H); ^{13}C δ 168.40, 151.45, 138.96, 134.56, 130.58, 123.53, 122.48, 35.38, 35.31, 21.02. Anal. Calcd for $C_{10}H_8Br_4O_2$: C, 25.03; H, 1.68. Found: C, 25.35; H, 1.72.

Methyl 3,4-Bis(dibromomethyl)benzoate (10b). The compound was prepared using the same procedure that was used for the preparation of **10a** with similar yields. Mp: 96.2 °C. NMR: ^1H δ 8.26 (s, 1H), 7.99 (d, ^3J = 8.1 Hz, 1H), 7.78 (s, 1H), 7.15 (s, 1H), 7.06 (s, 1H), 3.93 (s, 3H); ^{13}C δ 165.07, 141.85, 137.54, 131.82, 131.16, 130.72, 130.18, 52.54, 35.45, 35.29. Anal. Calcd for $C_{10}H_8Br_4O_2$: C, 25.03; H, 1.68. Found: C, 25.31; H, 1.65.

***trans*-7,8-Dibromocyclobutabenzene (3). (A) Under 2b/DMF Cyclization Conditions.** A solution of **1** (153 mg, 0.36

mmol) in dry and degassed DMF (25 mL) was cannulated under argon into a Schlenk flask containing **2b** (225 mg, 0.39 mmol). The reaction was stirred at 70 °C for 3 h. The volatiles were removed under vacuum, and the residue was extracted with $CHCl_3$, washed with water, dried over $MgSO_4$, and the solvent was removed under reduced pressure. Filtration on alumina (hexane:$CHCl_3$ 1:1) gave a mixture of **3** and **4** (78.4 mg, 83% yield) in a ratio of 98.5:1.5. Recrystallization from hexane at −85 °C gave pure **3** (66 mg, 70% yield).[18] **(B) Under Metallic Nickel/DMF Cyclization Conditions.** Nickel (0.3 g, 5.11 mmol) and **1** (490.4 mg, 1.16 mmol) in DMF (25 mL) were stirred at 85−90 °C for 24 h. The workup was identical to that used for the **2b**-mediated reaction. Obtained were **3** and **4** (246 mg, 81% yield) in a 9:1 ratio. Recrystallization from hexane at −85 °C yielded pure **3** (197 mg, 65% yield). ^{1}H NMR for **3** and **4** are identical to that reported in ref 17. **3**. ^{13}C NMR: δ 142.4, 131.5, 123.1, 49.8. MS: 262 (20), 181 (68), 102 (100). **4**. ^{13}C NMR: δ 133.9, 128.2, 51.3 (the quaternary carbon was not detected). MS: 262 (10), 181 (40), 102 (100).

***trans*-7,8-dibromo-cyclobuta[3,4]phenyl Acetate (11a) and methyl *trans*-7,8-dibromocyclobuta[3,4])benzoate (11b)** were prepared using the same procedures that were used for the preparation of **3**.

***trans*-7,8-Dibromocyclobuta[3,4]phenyl Acetate (11a). (A) Under 2b/DMF Cyclization Conditions. 10a** (170 mg, 0.354 mmol), **2b** (200 mg, 0.35 mmol), DMF (25 mL). **11a** (30 mg, 26% yield) was obtained as a light yellow oil. **(B) Under Metallic Nickel/DMF Cyclization Conditions. 10a** (0.6 g, 1.25 mmol), nickel (0.3 g, 5.11 mmol), DMF (25 mL). **11a** and **12a** (120 mg, 30%) were obtained. NMR: ^{1}H δ 7.22 (d, ^3J = 8.3 Hz, 1H), 7.11 (d, ^3J = Hz, 1H), 6.98 (s, 1H), 5.75 (*cis*-dibromo, s, 2H), 5.37 (*trans*-dibromo, s, 2H), 2.29 (s, 3H); ^{13}C δ 168.99, 153.04, 143.00, 139.33, 125.65, 124.68, 116.89, 48.91, 48.69, 21.06. FTIR (neat): 1772 cm^{-1}. HRMS: calcd for $C_{10}H_8O_2Br_2$ 317.8891/319.8870/321.8850, found 317.8898/319.8874/321.8847. Anal. Calcd for $C_{10}H_8Br_2O_2$: C, 37.54; H, 2.52. Found: C, 37.84; H, 2.60.

Methyl *trans*-7,8-Dibromocyclobuta[3,4]benzoate (11b). (A) Under 2b/DMF Cyclization Conditions. 10b (182 mg, 0.379 mmol), **2b** (330 mg, 0.577 mmol), DMF (10 mL). **11b** was obtained as a light yellow oil (24 mg, 20%). **(B) Under Metallic Ni/THF Cyclization Conditions.** A solution of **10b** (5 g, 10 mmol) and DMF (3 mL) in THF (150 mL) was refluxed for 5 days with metallic nickel (2.5 g, 40 mmol) under Ar. Water (70 mL) was added, and the THF was removed under reduced pressure. The crude product was extracted with $CHCl_3$, washed with water, and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The product was purified using an alumina column (hexane:$CHCl_3$ 1:1) to give pure **11b** (900 mg, 30% yield). **(C) Under 2a/DMF Cyclization Conditions.** A solution of **10b** (175 mg, 0.365 mmol) and **2a** (295 mg, 0.460 mmol) in DMF (10 mL) was stirred overnight at 65 °C. The volatiles were removed in vacuo, and the residue was extracted with $CHCl_3$. NMR of the crude shows 80% yield (relative to anthracene). The reaction was not treated further. NMR: ^{1}H δ 8.11 (d, ^3J= 8.0 Hz, 1H), 7.86 (s, 1H), 7.26 (d, ^3J=8.0 Hz, 1H), 5.39 (s, 2H), 3.89 (s, 3H); ^{13}C δ 166.07, 147.00, 142.48, 133.32, 132.95, 124.68, 123.22, 52.43, 48.76, 48.64. FTIR (neat): 1730 cm^{-1}. HRMS: calcd for $C_{10}H_8O_2Br_2$ 317.8891/319.8870/321.8850, found 317.8862/319.8883/321.8862.

Methyl *cis*-7,8-Dibromocyclobuta[3,4]benzoate (12b). Crystallization of a crude reaction product described above (containing **11b** and **12b**) from ethanol gave pure **12b**. Mp: 131−2 °C. NMR: ^{1}H δ 8.10 (d, ^3J = 8.0 Hz, 1H), 7.87 (s, 1H), 7.27 (d, ^3J = 9.0 Hz, 1H), 5.79 (s, 2H), 3.90 (s, 3H); ^{13}C δ 166.42, 148.02, 143.42, 133.24, 132.97, 124.85, 123.45, 52.70, 50.47, 50.41. HRMS: calcd for $C_{10}H_8O_2Br_2$ 317.8891/319.8870/321.8850, found 317.8957/319.8903/321.8781.

Reaction of *trans*-7,8-Dibromocyclobutabenzene (3) with Maleic Anhydride. A solution of **3** (14 mg, 0.05 mmol) and maleic anhydride (5.3 mg, 0.05 mmol) in benzene-d_6 (0.4 mL) was fire-sealed in an NMR tube under vacuum (10^{-2} mbar). The tube was allowed to stand at 155 °C for 72 h and the reaction monitored by ^{1}H-NMR spectroscopy. The sole product was **6** when **3** had completely reacted.[21] NMR: ^{1}H (200 MHz, C_6D_6) δ 6.82 (AA′BB′, 2H), 6.70 (AA′BB′, 2H), 5.22 (d, ^3J = 6.0 Hz, 2H), 3.85 (d, ^3J = 6.0 Hz, 2H); ^{13}C (50.4 MHz, C_6D_6) δ 170.21, 130.16, 128.19, 123.13, 49.94, 29.82. Upon exposure to air **6** is decomposed to 2,3-naphthalic anhydride.[23]

Reaction of *trans*-7,8-Dibromocyclobutabenzene (3) with Tetracyanoethylene. A fire-sealed NMR tube containing **3** (36.5 mg, 0.14 mmol), tetracyanoethylene (19 mg, 0.14 mmol), and benzene-d_6 (0.4 mL) was prepared as described above. The mixture was allowed to react at 185 °C for 1 h until complete disappearance of **3** to give **7** as the only observed product. The NMR tube was opened and the reaction mixture stirred over active charcoal. Solvent evaporation and crystallization from CH_2Cl_2/hexane at −85 °C yielded **7** (35 mg, 64% yield). Mp 133−135 °C sub. NMR: ^{1}H (200 MHz, C_6D_6) δ 6.75 (AA′BB′, 2H), 6.62 (AA′BB′, 2H), 4.64 (s, 2H). ^{1}H (200 MHz, $CDCl_3$) δ 7.67 (AA′BB′, 2H), 7.55 (AA′BB′, 2H), 5.86 (s, 2H); ^{13}C (C_6D_6) δ 131.08, 130.85, 127.24, 110.04, 109.01, 45.13, 43.01. FTIR (neat): 2196, 2240 cm^{-1}. HRMS: calcd for $C_{14}H_6N_4Br_2$ 387.8959/389.8939/391.8918, found 387.8952/389.8927/391.8896.

Reaction of *trans*-7,8-Dibromocyclobutabenzene (3) with Phenylacetylene. A fire-sealed NMR tube that had been prepared as described above, containing **3** (17 mg, 0.06 mmol), phenylacetylene (7 mg, 0.06 mmol), and benzene-d_6 (0.4 mL), was allowed to react at 155 °C for 27 days. The only observed product was **8**. NMR: ^{1}H (200 MHz, C_6D_6) δ 7.38 (m, 2H), 6.97 (m, 1H), 6.94 (m, 2H), 6.84 (AA′BB′, 2H), 6.68 (AA′BB′, 2H), 5.68 (d, ^3J = 2.0 Hz, 1H), 5.51 (d, ^3J = 2.0 Hz, 1H), 5.12 (s, 1H); ^{1}H (200 MHz, CD_2Cl_2) δ 7.46 (m, 5H), 7.33 (AA′BB′, 2H), 7.24 (AA′BB′, 2H), 6.14 (d, ^3J = 2.0 Hz, 1H), 5.86 (s, 1H), 5.79 (d, ^3J = 2.0 Hz, 1H); ^{13}C (50.4 MHz, C_6D_6) δ 132.35, 131.32, 129.12, 128.80,[24] 128.73, 128.29, 127.85,[24] 127.80, 127.27,[24] 126.76, 123.12, 117.64, 77.69, 44.94. Under air **8** slowly decomposes to **9**.[25]

Reaction of *trans*-7,8-Dibromocyclobutabenzene (3) with Styrene. A fire-sealed NMR tube that had been prepared as described above containing **3** (22 mg, 0.08 mmol), styrene (9 mg, 0.08 mmol), and benzene-d_6 (0.4 mL) was reacted for 31 days at 155 °C. **9** was the only observed product after **3** had completely reacted.[25]

Acknowledgment. We thank Volkswagen Stiftung, the basic research fund administrated by the Israeli Academy for Sciences and Humanities, the fund for promotion of research at the Technion and the Fonds der Chemischen Industrie, for financial support.

Supporting Information Available: ^{1}H NMR spectra of 3,4-dimethylphenyl acetate, methyl 3,4-dimethylbenzoate, **11b**, **12b**, and **7** and ^{13}C spectrum of **7** are available (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9516852

(23) Cava, M. P.; Van Meter, J. P. *J. Org. Chem.* **1969**, *34*, 538.

(24) These signals were obtained by subtracting the C_6D_6 spectrum from the spectrum of **8** in C_6D_6.

(25) (a) Guyot, M.; Mentzer, C. *Bull. Soc. Chem. Fr.* **1967**, 1843. (b) Wenkert, E.; Michelotti, E. L.; Swindel, C. S.; Tingoli, M. *J. Org. Chem.* **1984**, *49*, 4894.