A Seven-Membered-Ring Allene Dimer: Synthesis of 1,2-Benzo-1,3,4-cycloheptatriene and Attempted Synthesis of 1,2-Benzo-1,4,5-cycloheptatriene

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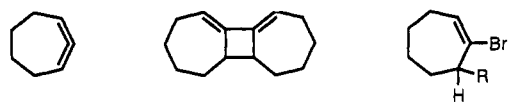
7,7-Dibromo-3,4-benzobicyclo[4.1.0]heptane (6) and 7,7-dibromo-2,3-benzobicyclo[4.1.0]heptane (14) have been synthesized and their silver ion-catalyzed reactions studied. Hydroxy alcohol **7a** was converted to the corresponding vinyl bromide **10**. Reaction of **10** with base gave the hydrocarbon **12**, instead of the expected allene **4**. Hydroxy alcohol **15a** was converted to the corresponding mesylate **20**, but all attempts to reduce **20** to the expected vinyl bromide **23** failed. Instead, unexpected ether **21** was obtained. Therefore, **15a** was treated with PBr_3 to give **22**, which upon treatment with $LiAlH_4$ gave the vinyl bromide **23**. Reaction of **23** with potassium *tert*-butoxide produced strained bicyclic allene **5**, which underwent a dimerization to give **24**. Addition of tetracyanoethylene to dimer **24** resulted in the formation of **26**, whose structure was investigated by X-ray crystallography.

Introduction

Favorski[1] reported the first attempts to synthesize strained cyclic allenes; however, the pioneering work on strained allenes, the generation of 1,2-cycloheptadiene **1**,



1 **2** **3**

3a R = H

3b R = D

was carried out by Ball and Landor,[2] who employed a dehydrohalogenation route and isolated [2 + 2] dimer **2**. Further work on **1** showed that it is too reactive to be isolated or observed spectroscopically.[3]

An allene unit in a six- or seven-membered ring is bent and twisted away from its optimum geometry.[4] Evidence for the chirality of **1** was provided by Balci and Jones.[5] They treated optically active bromide **3b** with potassium *tert*-butoxide and generated and trapped a chiral intermediate presumed to be **1**. Optically active products were also isolated when racemic **3a** was treated with optically active sodium menthoxide. The effect of temperature on the optical activity was also instructive. In the case of 1-bromocycloheptene (**3a**), the optical activity dropped off when the temperature was increased. The drop in optical activity was attributed to the isomerization of **1** being competitive with the trapping rate. Ab initio MCSCF calculations[6] on 1,2-cyclohexadiene support a strongly bent allene that interconverts easily to its enantiomer via the diradical.

It is well established that additional unsaturation in the ring system increases the ring strain.[7] In order to determine the effect of benzannelation on **1**, we investigated methods for the synthesis of **4** and **5**. (Some derivatives of **5** have previously been reported in the literature.[8,9])

4 **5**

In the past, several methods have been used to generate cyclic allenes: zinc elimination of dihalides,[10] base-catalyzed elimination[3a,11] of HX from cycloalkenes, photolysis of halocycloalkenes,[12] and the Doering–Moore–Skatebol approach.[13] The last method fails, somewhat inexplicably, for most 1,2-cycloheptadienes. Therefore, we have investigated a base-catalyzed elimination method using the appropriate vinylcycloalkenes, which gives us the ability to generate racemic and chiral allenes.

Results and Discussion

Dibromocyclopropane compound **6**,[14] the starting material for the synthesis of **4**, was prepared by the addition

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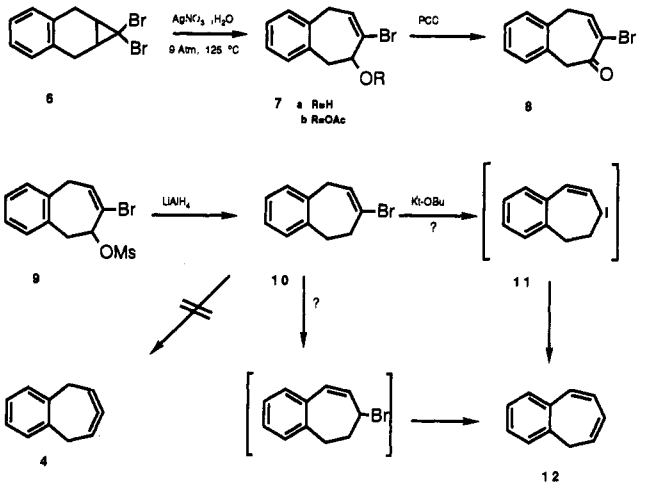
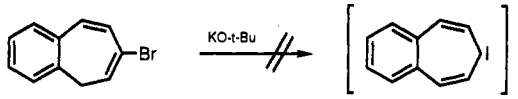
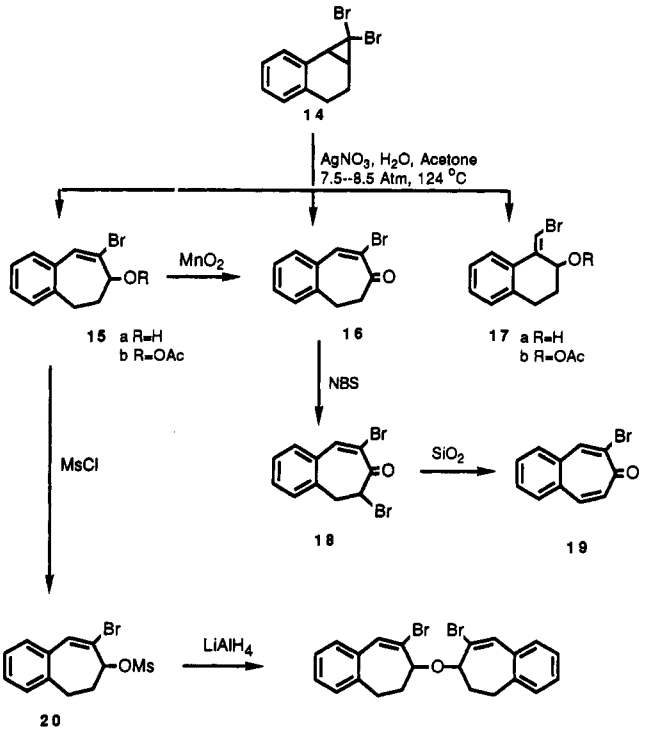
Scheme I



Scheme II



Scheme III



of dibromocarbene to 1,4-dihydronaphthalene under phase-transfer catalysis conditions. The electrophilic rearrangement of **6** was carried out with silver nitrate in aqueous acetone in an autoclave (9 atm, 125 °C, 30 min) to give bromo alcohol **7a** as the sole isolable product in a yield of 32%. Compound **7a** was characterized by spectroscopic methods and by chemical transformations. Pyridinium chlorochromate (PCC) oxidized **7a** smoothly to bromo ketone **8**. Reaction of **7a** with acetic anhydride in pyridine resulted in the formation of the corresponding acetate **7b** (Scheme I).

Bromo alcohol **7a** was converted to mesylate **9**, and $LiAlH_4$ reduction of mesylate **9** gave the desired starting material **10**. Spectroscopic data and elemental analysis of **10** were consistent with the structural assignment. Vinyl bromide **10** was submitted to dehydrobromination with potassium *tert*-butoxide in refluxing THF. To our surprise, we isolated 5*H*-benzocycloheptene (**12**) instead of an allene dimer (Scheme I). The base apparently preferentially attacks the doubly activated methylene group because it has both allylic and benzylic character. Dehydrobromination then results in the formation of carbene **11**, which rearranges easily to the 5*H*-benzocycloheptene by α-insertion. A second possible mechanism to explain the formation of **12** is double bond isomerization in **10** followed by rapid β-elimination. Jones and Mayor[15] reported that **13** was unaffected by potassium *tert*-butoxide even at 150 °C in diglyme (Scheme II). Comparison of these results with ours indicates that the second mechanism is probably operating.

The attempt to prepare **4** via **10** by means of the dehydrobromination route was abandoned.

A similar route for the preparation of **5**, starting with isomeric dibromo compound **14**, was investigated (Scheme III). Silver ion-catalyzed hydrolysis of **14** in aqueous acetone (autoclave, 7.5–8.5 atm, 120–124 °C) gave three products. The structure of the major product (53%) was shown by spectroscopic methods to be **15a**. The minor products, **16** and **17a**, were isolated in 3% and 8% yield, respectively. MnO_2-oxidation of **15a** resulted in the formation of **16**. Compound **16** was converted to the corresponding bromobenzotropone **19** by allylic bromination of **16** with *N*-bromosuccinimide followed by dehydrobromination with silica gel. Bromomethylene compound **17a** was converted to its acetate **17b** for further characterization.[16] Subsequent reaction of **15a** with mesyl chloride afforded mesylate **20** in 75% yield. All attempts to reduce **20** to the corresponding vinyl bromide **23** failed, and unexpected ether compound **21** was obtained. The mechanism for the formation of **21** is currently under investigation.[17] Desired compound **23** was prepared by the following route: alcohol **15a** was first converted to the corresponding dibromide **22** by reaction with PBr_3 in pyridine (yield 56%, Scheme IV). Dibromide **22** was treated with $LiAlH_4$ to give vinyl bromide **23**[18] in a yield of 70%. Vinyl bromide **23** was subjected to dehydrobromination with potassium *tert*-butoxide, and, after column chromatography, a colorless product whose spectral data were completely in agreement with the proposed structure **24** (yield 20%) was isolated. Initially, we could not distinguish between structure **24** (head-to-head dimer) and

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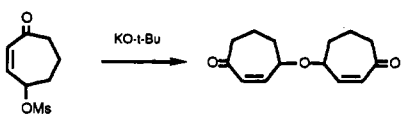
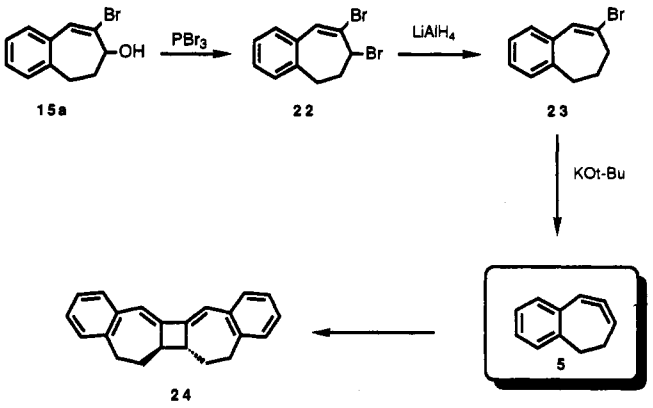
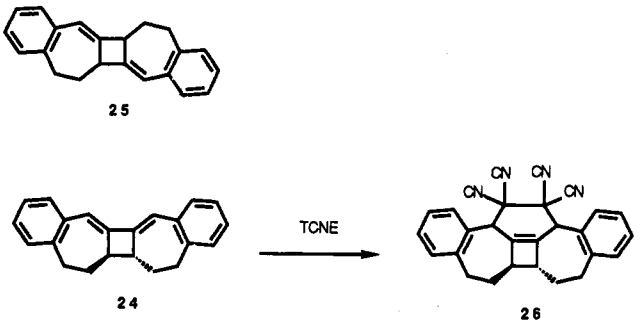


(18) This compound has recently been synthesized by an independent route starting from the corresponding ketone: Paquette, L. A.; Dahnke, K.; Doyon, J.; He, W.; Wyant, K.; Friedrich, D. *J. Org. Chem.* **1991**, *56*, 6199.

Scheme IV



Scheme V



the other possible dimerization product **25** (head-to-tail dimer). The NMR spectra were in complete agreement with both structures. The exact stereochemistry of the four-membered ring could not be established. To solve this stereochemical problem, dimer **24** was allowed to react with tetracyanoethylene at room temperature, and Diels–Alder adduct **26** was obtained as the sole product (Scheme V). The adduct was characterized by spectroscopic methods, and the formation of a [2 + 4] addition product demonstrates clearly that **24** is a head-to-head dimer. The ^{1}H- and ^{13}C-NMR spectra of **26** (28-line ^{13}C-NMR) were in agreement with the trans-configuration of the four-membered ring, and X-ray analysis of **26** confirmed unequivocally the proposed structure.[20] We conclude that the formation of **24** is most reasonably explained by the formation of the intermediate strained conjugated-allene.

Experimental Section

General Methods. Infrared spectra of liquids were obtained as films on NaCl plates, and spectra of solids were obtained from solution in 0.1-mm cells or KBr pellets on an infrared recording spectrophotometer. The ^{1}H-NMR spectra were recorded on 60-, 300-, 360-, and 400-MHz spectrometers and are reported in δ units with TMS as internal standard. Apparent splittings are given in all cases. Mass spectra were recorded at an ionizing voltage 70 eV. All column chromatography was performed on silica gel (60-mesh). TLC was carried out on 0.2-mm silica gel 60 F_{254} analytical alumina plates.

1-Bromo-4,5-benzo-7-hydroxy-1,4-cycloheptadiene (7a). To a solution of dibromocarbene adduct **6** (3 g, 9.9 mmol) in 15 mL of water and 30 mL of acetone was added silver nitrate (1.69 g, 9.9 mmol). The resulting mixture was heated in an autoclave under 8–9 atm of pressure at 124–126 °C and stirred for 30 min. After the mixture was cooled to rt, 50 mL of water and 250 mL of CH_2Cl_2 were added. The precipitate formed (AgBr) was filtered. The aqueous phase was extracted with CH_2Cl_2 (2 × 50 mL), and the combined organic extracts were dried (Na_2SO_4) and concentrated. The residue was chromatographed on silica gel (100 g) with $CHCl_3$/petroleum ether (1:5). The compound was crystallized from CCl_4: colorless crystalline solid; mp 64–65 °C; yield 0.76 g (32%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.21 (m, 4H), 6.4 (dd, J = 7.1 and 5.4 Hz 1H), 4.39 (dd, J = 3.3 and 6.4 Hz, 1H), 3.43 (dd, AB-system, J = 16.7 and 5.4 Hz, 1H), 3.33 (dd, AB-system, J = 16.7 and 7.1 Hz, 1H), 3.30 (dd, AB-system, J = 14.2 and 3.3 Hz, 1H), 3.12 (dd, AB-system, J = 14.2 and 6.4 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 140.9, 135.2, 131.6, 130.9, 129, 128.2, 127.2, 127.2, 72.4, 39.2, 34.1; MS m/z 240/238 (M^+, 20), 222/220 (33), 159 (10), 141 (100). Anal. Calcd for $C_{11}H_{11}BrO$: C, 55.25; H, 4.64. Found: C, 55.18; H, 4.56.

1-Bromo-4,5-benzo-1,4-cycloheptadienyl 7-Acetate (7b). To a stirring solution of **7a** (1 g, 4.18 mmol) in 10 mL of pyridine was added acetic anhydride (2 g, 19.6 mmol). The reaction mixture was stirred at rt for 12 h and then cooled to 0 °C; 40 mL of 2 N HCl solution was added, and the mixture was extracted with ether (3 × 70 mL). The combined organic extracts were washed with $NaHCO_3$ solution (3 × 10 mL) and water (3 × 10 mL) and then dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was filtered through a silica gel (10 g) column with CCl_4 to give the acetate: colorless wax; 890 mg (72%); ^{1}H-NMR (60 MHz, CCl_4) δ 7.15 (m, 4H), 6.55 (t, 1H), 5.48 (br d, 1H), 3.40 (br d, 2H), 3.15 (d, 2H), 1.95 (s, 3H); IR (KBr) 3020, 2925, 1735, 1675, 1640, 1610, 1490, 1440, 1370, 1310, 1230, 1105 cm^{-1}.

2-Bromo-5,6-benzo-2,5-cycloheptadien-1-one (8). To a solution of bromo alcohol **7a** (0.5 g, 2.1 mmol) in 20 mL of CH_2Cl_2 at 0 °C was added pyridinium chlorochromate (0.6 g, 2.6 mmol). The reaction mixture was stirred at room temperature for 10 h and filtered through a short silica gel column (20 g) with CH_2Cl_2 to give pure ketone **8** (liquid): ^{1}H-NMR (60 MHz, CCl_4) δ 7.50 (t, 1H), 7.15 (m, 4H), 3.95 (s, 2H), 3.64 (d, 2H); IR (NaCl, film) 3040, 2920, 1685, 1510, 1445, 1350, 1220, 1165, 880 cm^{-1}.

1-Bromo-4,5-benzo-1,4-cycloheptadienyl 7-Mesylate (9). To a stirring solution of **7a** (1 g, 4.18 mmol) in 20 mL of CH_2Cl_2 was added NEt_3 (0.43 mg, 4.24 mmol). The reaction mixture was cooled to −4 °C, and a solution of methanesulfonyl chloride (0.48 mg, 4.19 mmol) in 5 mL of CH_2Cl_2 was added over a period of 30 min with stirring. The reaction mixture was stirred for an additional 2 h at the same temperature. Triethylammonium chloride was removed by filtration. The solvent was evaporated under reduced pressure, and the residue was chromatographed through a short silica gel column eluting with CCl_4: colorless crystals from CCl_4; mp 92–94 °C; yield 0.83 g (63%); ^{1}H-NMR (60 MHz, CCl_4) δ 7.02 (m, 4H), 6.47 (t, 1H), 5.22 (dd, 1H), 3.35 (m, 4H), 3.01 (s, 3H); IR (KBr) 3080, 3050, 2660, 1640, 1490, 1450, 1420, 1340, 1170, 900 cm^{-1}.

1-Bromo-4,5-benzo-1,4-cycloheptadiene (10). A stirring suspension of $LiAlH_4$ (0.12 g, 3.15 mmol) in 30 mL of dry ether was cooled to −4 °C. A solution of **9** (1 g, 3.15 mmol) in 30 mL of dry ether was added to the resulting suspension over a period of 1 h, and the reaction mixture was refluxed for 2 h. After the reaction mixture was cooled to room temperature, 1 mL of water was added, and the precipitate formed was removed by filtration. The precipitate was extracted with ether (2 × 50 mL), and the combined organic extracts were dried ($CaCl_2$). Evaporation of the solvent and crystallization of the residue from *n*-hexane gave bromohydrocarbon **10**: colorless crystals; mp 54–55 °C; yield 0.52 g (74%); ^{1}H-NMR (60 MHz, CCl_4) δ 7.07 (m, 4H), 6.24 (t, 1H), 3.30 (d, 2H), 2.94 (AA′BB′-system, 4H); IR (KBr) 3050, 2950, 1665, 1500, 1470, 1440, 1340, 1320, 1235, 1180 cm^{-1}. Anal. Calcd for $C_{11}H_{11}Br$: C, 59.22; H, 4.97. Found: C, 58.93; H, 4.82.

Reaction of 10 with Potassium *tert*-Butoxide. Synthesis of 12. To a suspension of potassium *tert*-butoxide (100 mg, 0.9 mmol) in 30 mL of freshly distilled THF was added a solution of **10** in 10 mL of THF over 1 h at rt. The resulting reaction mixture was refluxed for 2 h. The reaction mixture was cooled to room temperature, and 20 mL of water was added. The solvent was evaporated, and the residue was extracted with hexane (2 × 50 mL). The combined organic extracts were dried ($CaCl_2$). Evaporation of the solvent and distillation of the residue (20 mmHg, 115–120 °C) afforded 7*H*-benzocycloheptene (**12**)[19] (95

(19) Wittig, G.; Eggers, H.; Duffner, P. *Liebigs Ann. Chem.* **1958**, *619*, 10.

mg, 74%): ^{1}H-NMR (60 MHz, CCl_4) δ 6.8–7.3 (m, 4H), 5.3–6.5 (m, 2H), 3.0 (d, 2H).

Silver Ion-Catalyzed Reaction of 7,7-Dibromo-2,3-benzobicyclo[4.1.0]heptene (14). For the silver-ion catalyzed reaction, the reaction procedure described for the synthesis of **7a** was used. Dibromo compound **14** (6 g, 19.0 mmol) was hydrolyzed for 2 h. The residue was chromatographed on a silica gel column with CH_2Cl_2/petroleum ether (1:5) as eluant. Compound **15a** was isolated as the first fraction.

1-Bromo-3,4-benzo-7-hydroxy-1,3-cycloheptadiene (15a): yield 2.52 g (53%); colorless crystals from CCl_4; mp 77–78 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.16 (m, 4H), 7.04 (s, 1H), 4.47 (t, 1H), 3.43 (dd, AB-system, 1H), 3.33 (dd, AB-system, 1H), 3.30 (AB-system, 1H), 3.12 (AB-system); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 121.4, 116.1, 115.3, 114.3, 113.5, 112.5, 111.9, 110.6, 75.2, 46.7, 44.1; MS *m/z* 240/238 (M^+, 20), 222/220 (33), 159 (10), 141 (100). Anal. Calcd for $C_{11}H_{11}BrO$: C, 55.25; H, 4.64. Found: C, 55.18; H, 4.56. Compound **16** was isolated as the second fraction.

2-Bromo-4,5-benzo-2,4-cycloheptadien-1-one (16): pale yellow liquid: 194 mg (3%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.80 (s, olefinic, 1H), 7.28 (m, 4H), 3.00 (AA'BB'-system, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.2, 136.6, 131.8. 131.48, 130.4, 130.3, 128.1, 127.5, 27.7, 22.1; IR (KBr) 3070, 2930, 2860, 1680, 1590, 1565, 1440, 1375, 1280 cm^{-1}.

Compound **16** was also synthesized by PCC oxidation starting from **15a** in a yield of 85% as described for the synthesis of **8**.

Compound **17a** was isolated as the third fraction.

1-(Bromomethylene)-2-hydroxy-1,2,3,4-tetrahydronaphthalene (17a): colorless crystals from CCl_4; mp 64–66 °C; 380 mg (8%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.28 (m, 4H), 5.13 (dd, 1H), 3.30 (dd, methylenic, 1H), 2.82 (dd, 1H), 2.38 (ddd, 1H), 1.75 (dt,); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 157.4, 145.9, 136.1, 136.1, 131.9, 129.2, 128.9, 126.9, 65.9, 29.9, 28.4; IR (KBr) 3450, 3090, 3030, 2940, 2880, 1740, 1650, 1605, 1580, 1535, 1450, 1340, 1240 cm^{-1}. MS *m/z* 240/238 (M^+, 30.3), 222/220 (10), 203/201 (20), 170 (100), 160 (99), 142 (99).

1-Bromo-3,4-benzo-1,3-cycloheptadienyl 7-Acetate (15b). The acetate **15b** was synthesized as described for the synthesis of **7b**: colorless liquid; yield 80%; ^{1}H-NMR (60 MHz, CCl_4) δ 7.35 (s, 1H), 7.20 (m, 4H), 4.70 (br t, 1H), 2.70 (m, 4H), 2.10 (s, 3H); IR ($CHCl_3$) 3060, 2950, 2910, 1760, 1648, 1540, 1440, 1430, 1370, 1240, 1110 cm^{-1}.

1-(Bromomethylene)-2-acetoxy-1,2,3,4-tetrahydronaphthalene (17b): yield 74%; ^{1}H-NMR (60 MHz, CCl_4) δ 8.20 (s, 1H), 7.30 (m, 4H), 6.35 (t, 1H), 2.85 (m, 4H), 2.20 (s, 3H); IR ($CHCl_3$) 3020, 2935, 2840, 1740, 1625, 1490, 1440, 1370, 1230, 1110, 1025, 1010, 940 cm^{-1}.

2-Bromo-4,5-benzotropone (19). To a solution of bromo ketone **16** (300 mg, 1.27 mmol) in 30 mL of CCl_4 was added *N*-bromosuccinimide (210 mg, 1.28 mmol) and diazoisobutyronitrile (20 mg). The resulting solution was refluxed for 2 h. The reaction mixture was chromatographed on silica gel with carbon tetrachloride as eluant to give **19** in a yield of 80% (240 mg): ^{1}H-NMR (60 MHz, CCl_4) δ 8.2 (s, 1H), 7.55 (s, 4H), 7.3 (AB-system, 1H), 6.85 (AB-system, 1H); IR (KBr) 3030, 1620, 1600, 1540, 1340, 1285, 1190, 995 cm^{-1}. Anal. Calcd for $C_{11}H_7BrO$: C, 56.20; H, 3.00. Found: C, 56.01; H, 2.86.

1-Bromo-3,4-benzo-1,3-cycloheptadienyl 7-Mesylate (20). To a solution of **15a** (2 g, 8.36 mmol) in 20 mL of pyridine at 0 °C was added methanesulfonyl chloride (1 g, 8.7 mmol). The reaction mixture was stirred for 6 h at room temperature. Then, 30 mL of water was added, and the reaction mixture was extracted with methylene chloride (3 × 50 mL). The combined extracts were washed with water (3 × 50 mL) and dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was filtered through silica gel (10 g) with carbon tetrachloride: 2.03 g (colorless liquid, 75%); ^{1}H-NMR (60 MHz, CCl_4) δ 7.11 (m, 4H), 6.94 (s, 1H), 4.95 (t, 1H), 3.55 (s, 3H), 2.0–3.74 (m, 4H).

Reaction of 20 with $LiAlH_4$: Formation of 21. To a stirring suspension of $LiAlH_4$ (120 mg, 3.15 mmol) in 30 mL of dry hexane at −4 °C was added a solution of **20** (1 g, 3.15 mmol) over a period of 1 h. The reaction mixture was refluxed for 2 h. After the reaction mixture cooled to rt, 1 mL of water was added, and the precipitate formed was removed by filtration. The organic phase was washed with water (2 × 10 mL) and dried ($CaCl_2$). After evaporation of the solvent, the residue was filtered through a silica gel (30 g) column with hexane to give pure ether (colorless liquid, 0.56 g, 77%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.20 (m, 4H), 6.98 (s, 1H), 4.97 (t, 1H), 3.32 (dd, 1H), 2.83 (dd, methylenic proton, 1H), 2.47 (ddd, 1H), 2.30 (ddd, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 142, 137.3, 133, 132.8, 129.6, 129, 126.7, 125.4, 66.7, 33.6, 29.6; MS *m/z* 460 (M^+, 0.3), 220 (67), 221 (3), 220 (100), 223 (92), 224 (89), 196 (13), 194 (15), 143 (35), 142 (50), 141 (100), 139 (100), 138 (68), 137 (40); IR (KBr) 3060, 3020, 2940, 1600, 1490, 1450, 1400, 1380, 1200, 1110, 980, 890 cm^{-1}. Anal. Calcd for $C_{22}H_{20}Br_2O$: C, 57.42; H, 4.38. Found: C, 57.11; H, 4.54.

1,7-Dibromo-3,4-benzocycloheptadiene (22). To a stirring solution of alcohol **15a** (2.39 g, 10 mmol) in 30 mL of absolute benzene at −5 °C was added pyridine (1.58 g, 20 mmol) and phosphorus tribromide (5.42 g, 20 mmol). The reaction mixture was stirred at rt for 12 h. The mixture was cooled to 0 °C, and 30 mL of water was added. The aqueous phase was extracted with $CHCl_3$ (3 × 50 mL) and dried (Na_2SO_4). Removal of the solvent under reduced pressure gave dibromide **22** (colorless liquid, 56%): ^{1}H-NMR (60 MHz, CCl_4) δ 7.18 (m, 4H), 6.95 (s, 1H), 5.15 (t, 1H), 2.20–3.80 (m, 4H); IR (KBr) 3055, 2940, 1608, 1567, 1513, 1440, 1345, 1295, 1273, 1209, 1158, 1109, 1055, 1000, 976, 943, 774, 740, 650 cm^{-1}.

1-Bromo-3,4-benzocycloheptadiene (23). To a suspension of $LiAlH_4$ (140 mg, 368 mmol) in 30 mL of THF was added dibromide **22** (1 g, 3.3 mmol) in 30 mL of THF over a period of 1 h. The reaction mixture was stirred at 40–45 °C for 2 h. The reaction mixture was cooled to 0 °C, and 10 mL of water was added. After the precipitate was filtered, the organic layer was extracted with $CHCl_3$ (2 × 50 mL) and dried ($CaCl_2$). The solvent was removed under reduced pressure. Chromatography of the residue on 40 g of silica gel with petroleum ether gave vinyl bromide **23** (85%, colorless liquid): ^{1}H-NMR (60 MHz, CCl_4) δ 7.1 (m, aromatic, 4H), 6.95 (s, olefinic, 1H), 2.90 (m, 4H), 2.00 (m, 2H); IR (NaCl) 3050, 3020, 2930, 2860, 1630, 1490, 1440, 1420, 940, 750 cm^{-1}.

Allene Dimer 24. To a solution of vinyl bromide (1 g, 4.5 mmol) in 30 mL of THF was added potassium *tert*-butoxide (0.56 g, 4.95 mmol) in 30 mL of THF over a period of 30 min. The reaction mixture was stirred for 2 h at 60 °C. The reaction mixture was cooled to room temperature, and 50 mL of water was added. The mixture was extracted with methylene chloride (2 × 50 mL), and the extracts were dried ($CaCl_2$). Removal of the solvent under reduced pressure and chromatographic separation of the residue over Al_2O_3 with *n*-hexane/chloroform (19:1) afforded 20% of pure dimer **24**: colorless crystals from chloroform/hexane; mp 121–122 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.15 (m, 8H), 6.55 (d, J = 1.47 Hz, 2H), 2.90 (m, 6H), 2.30 (m, 2H), 1.95 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 146.5, 140.3, 136.5, 130.7, 130.4, 126.2, 126.1, 118.1, 48.53, 35.6, 32.3; MS *m/z* 284 (100), 269 (10), 255 (10), 240 (40), 228 (8), 197 (58); IR (KBr) 3095, 2925, 1635, 1480, 1439, 1304, 1270, 1232, 1163, 1105, 1052, 943, 887, 853, 819, 753 cm^{-1}. Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.71; H, 7.22.

Tetracyanoethylene Adduct 26. To a solution of dimer **24** (150 mg, 0.528 mmol) in 20 mL of chloroform was added tetracyanoethylene (68 mg, 8.5 mmol). The reaction mixture was stirred at room temperature for 3 days. Removal of the solvent at reduced pressure and crystallization of the residue from chloroform/ether (4:1) afforded TCN adduct **26** as colorless crystals: mp 145–146 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.52 (m, 2H), 7.39 (m, 5H), 7.10 (m, 1H), 4.79 (br s, 1H), 4.68 (br s, 1H), 3.11 (m, 1H), 2.86 (m, 3H), 2.40 (m, 2H), 2.03 (m, 3H), 1.70 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 144.6, 139.6, 139.5, 139.38, 137.9, 133.8, 132.8, 131.7, 130.9, 130.3, 128.8, 128.7, 127.5, 126.8, 126.7, 123.86, 112.4, 111.6, 51.7, 49.1, 48.4, 45.5, 44.6, 39.7, 33.2, 30.9, 29.8; MS *m/z* 412 (7), 284 (100), 269 (7), 228 (5); IR (KBr) 3095, 2930, 2327, 2200, 1623, 1480, 1446, 1346, 1316, 1102, 872, 792, 761, 735 cm^{-1}. Anal. Calcd for $C_{28}H_{20}N_4$: C, 81.53; H, 4.89. Found: C, 81.40; H, 4.71.

(20) The author has deposited atomic coordinates for **26** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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Supplementary Material Available: ^{1}H NMR spectra of **7b**, **8**, **9**, **16**, **17a**, **17b**, and **22**, ^{13}C NMR spectra of **16** and **17a**, and X-ray ORTEP diagram of **26** (10 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.