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TETRAHEDRON

Trapping of 1,2-Benzo-1,3,4-Cycloheptatriene as Evidence for A Strained Cyclic Allene Structure

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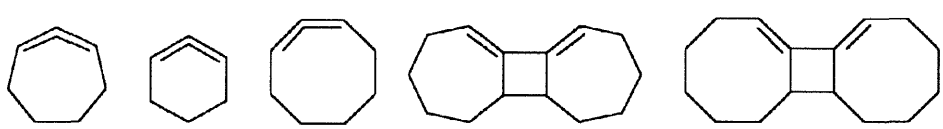
Abstract: 8-bromo-6,7-dihydrobenzocycloheptene **16** and 9-bromo-6,7-benzocycloheptadiene **17** have been synthesized *via* a new and simple method, and their allene reactions were studied. Treatment of **16** with a base in the presence of DPIBF (diphenylisobenzofuran) gave the strained bicyclic allene **9**, which underwent a cycloaddition reaction to yield **25** and **26**. On the other hand, the reaction of the vinyl bromide **17** with a base, either in the presence or absence of DPIBF, resulted in the formation of *7H*-benzocycloheptadiene **21**, rather than the alkyne **22**.

Over the past thirty years, the synthesis and isolation of highly strained molecules such as cyclic allenes have been the subject of extensive research.[1] The first attempt to generate a cyclic allene, which dates back to the mid 1930s, was reported by Favorski. Although the structure of the product was erroneously disclosed as **1**,[2] it remained unchallenged for 25 years. Later, one of Favorski's students, Domnin, reported unsuccessful attempts to isolate 1,2-cyclohexadiene **2**.[3] The next pioneering work on strained allenes was reported by Ball and Landor, who appear to be the first to make 1,2-cycloheptadiene **1** and 1,2-cyclooctadiene **3** successfully, both of which could only be isolated as their dimers **4** and **5**, respectively.[4]



1 **2** **3** **4** **5**

Undoubtedly, the facile dimerization of strained allenes such as **3** results from a two-fold strain on C-2. The first attempt to isolate an allene by employing a trapping agent, 1,3-diphenylisobenzofuran, was made by Wittig, who achieved trapping of **3** successfully.[5] Studies on **1** indicated that it is too reactive to isolate, however it could be observed spectroscopically by NMR and IR, at low temperatures.[6] Further studies by Balci and Jones provided evidence for the chirality of **1**.[7] They trapped a chiral intermediate, presumed to be **1**, generated by treatment of the optically active bromide **6b** with potassium *tert*-butoxide. When the achiral **6a** was treated with optically active sodium menthoxide, optically active products were also isolated. Observation

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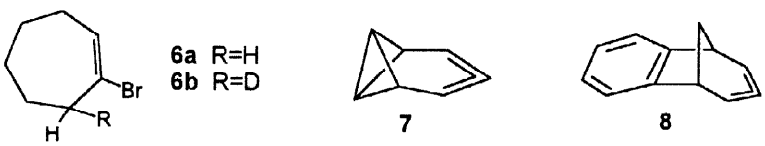
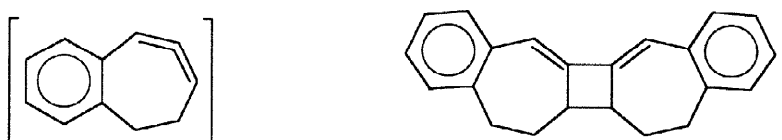
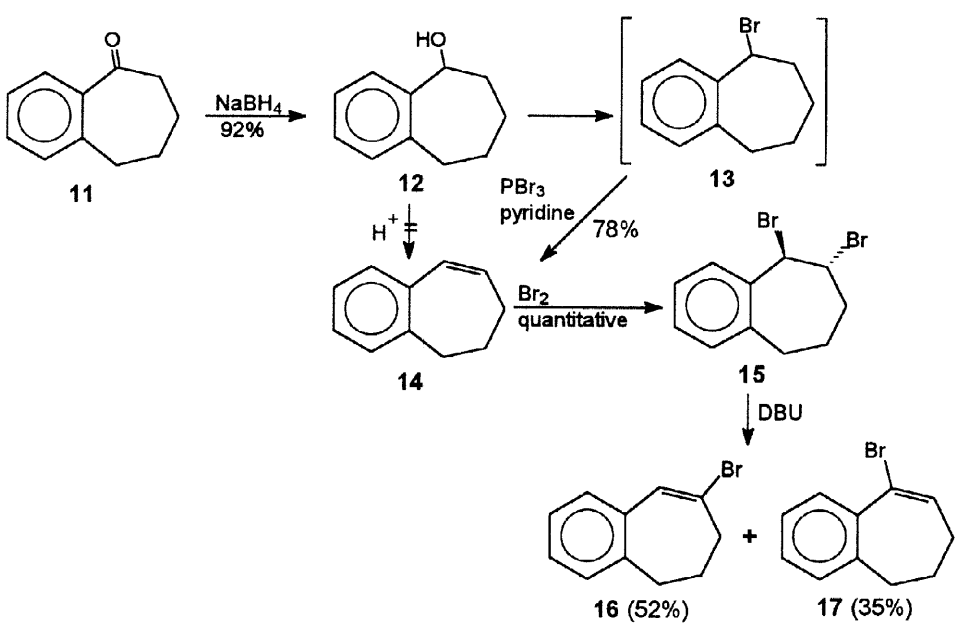
was treated with optically active sodium menthoxide, optically active products were also isolated. Observation of a drop in the optical activity of **6a**, as the temperature was increased, was attributed to the isomerisation of **1** being competitive with the trapping rate. Semi empirical and *ab initio* molecular orbital calculations[8] on 1,2-cyclohexadiene **2** support a strongly bent allene structure, which easily interconverts to its enantiomer *via* a diradical.



In the past, several methods[9] have been employed to generate cyclic allenes including some unusual example such as **7** prepared from benzvalene incorporating two highly strained functionalities.[10] Another approach to highly strained bicyclic allenes such as **8** was developed by Balci and Harmandar.[11] Trapping **8** with 1,3-diphenylisobenzofuran gave five isomeric cycloadducts.



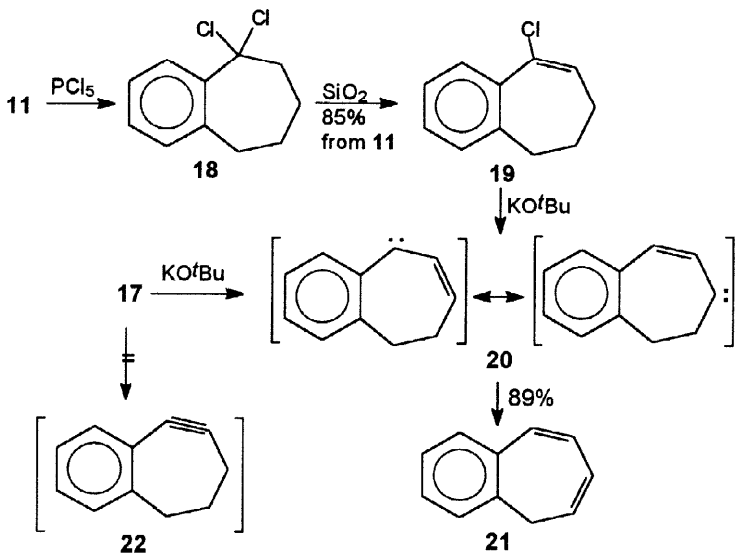
Recently reported evidence by our group has led us to the conclusion that benzannulation, which imparts additional strain on a thermally unstable allene, does not preclude the formation of 1,2-benzo-1,3,4-cycloheptetriene **9**.[12] It is well known that benzannulation is a significant obstacle for the formation of the allene



Scheme 1

9 through the traditional dehydrohalogenation route, and it could only be obtained as the dimer 10. Similar results were reported by Tochtermann *et al.*[12c, 13] We report here a convenient route to the synthesis of the highly strained bicyclic allene 9, which was subsequently trapped with 1,3-diphenylisobenzofuran.

An easy and simple method for the synthesis of the vinyl bromides 16 and 17 has been developed starting from the ketone 11. Reduction of 1-benzsuberone 11 with $NaBH_4$ in aqueous methanol yielded the corresponding alcohol 12[13a] in 92% (Scheme 1). Surprisingly, attempts to convert 12 to the alkene 14 in acid, with or without reflux, failed. Only a polymeric material was isolated. Consequently, treatment of the alcohol 12 with PBr_3 in pyridine furnished the desired olefine 14 in one pot through the intermediate 13 in 78%, the structure of which was confirmed by comparison with literature data.[14] Addition of bromine to the alkene 14 in CCl_4 gave racemic dibromide 15 in quantitative yield. Hydrogen bromide elimination from 15 was performed by treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU),[13b] which resulted in the formation of the desired vinylbromides 16 and 17 in 52 and 35% yields, respectively. A successful separation of the isomers was achieved by thin layer chromatography. The structure of the major product 16 was determined by comparison with literature data,[15] and the minor product was characterized by spectroscopic methods and chemical transformations.

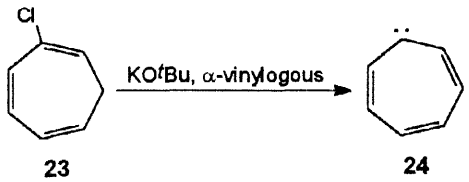


Scheme 2

The vinyl chloride 19 was synthesized through the intermediate 18 as a sole product from 1-benzsuberone 11 in two steps in overall 85% yield (Scheme 2), i) treatment of 11 with PCl_5[16] to give 18 and ii) elimination[17] of HCl over SiO_2. When both 17 and 19 were subjected to dehydrohalogenation using potassium *t*-butoxide in refluxing THF, *7H*-benzocycloheptene 21, rather than the alkyne 22 was obtained. Apparently, the base preferentially attacks the activated methylene hydrogen rather than the hydrogen attached to the vinylic carbon, and subsequent dehydrohalogenation results in the formation of the carbene 20, which easily rearranges to *7H*-

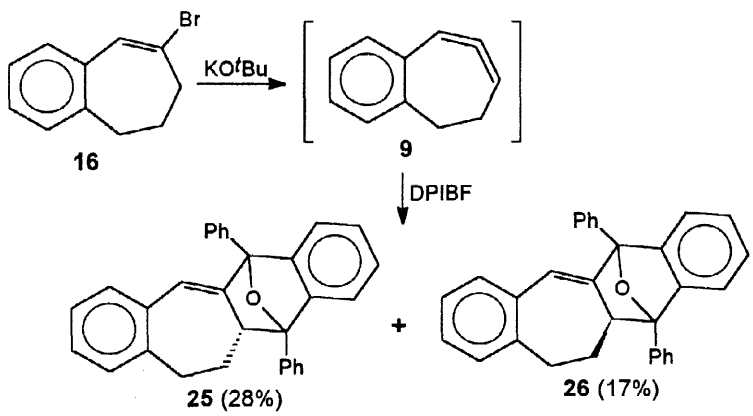
benzocycloheptene **21** *via* an α-insertion mechanism. It was reported that when the vinyl chloride **23** was reacted with potassium *t*-butoxide, a vinylic α-elimination takes place to give the carbene **24** (Scheme 3).[17, 18] This similar system to ours could also be evidence that **20** is an intermediate in the formation of **21**.

At this point, considering the α-elimination behavior of **17**, the isomer **16** was subjected to the hydrogen bromide elimination employing the same base, potassium *t*-butoxide, in the presence of DPIBF diphenylisobenzofuran), which yielded **25** and **26** in 28% and 17%, respectively, after column chromatography (Scheme 4). Formation of the cycloaddition products **25** and **26** can only be explained by the strained allene intermediate **9**.[19] Although the intermediate **9** has two active sides for the cycloaddition reaction, the exclusive formation of **25** and **26** shows that the trapping occurs with a high degree of regioselectivity.



Scheme 3

In conclusion, dehydrobromination of the two isomers, **16** and **17**, gave two separate products through two different intermediates, **9** and **20**, respectively. Treatment of **16** with a base led to the formation of the strained cyclic allene **9** as an intermediate, rather than a carbene. On the other hand, a carbene rather than an alkyne formed when the other isomer **17** was treated with the same base. It seems obvious that, in such a system, the presence of an acidic proton and the location of the leaving group are key factors in determination of the reaction pathway.



Scheme 4

EXPERIMENTAL

Infrared spectra were recorded on a Perkin Elmer 983 IR machine as liquid films, KBr pellets or solutions in 0.1 mm cells. NMR spectra were measured on a Bruker AC 200L and JEOL GX 270 machines at 60, 200 and 270 MHz for ^{1}H and at 67.8 MHz for ^{13}C NMR using $CDCl_3$ as solvent and tetramethylsilane (TMS) as an internal standard, and measured in ppm downfield from TMS, unless otherwise stated. Coupling constants (*J*) are given in Hz. Mass spectra were recorded on a Micromass LTD Labzabspec machine at an ionizing voltage of 70 eV. Flash chromatography was performed on 40-60 mesh silica gel (Merck) and TLC was carried out on 0.2 mm silica gel plates.

6,7,8,9-Tetrahydro-5*H*-benzo[*a*]cyclohepten-5-ol (12). To a solution of 1-benzsuberon **11** (7 g, 43.75 mmol) in aqueous methanol (50 ml) was added $NaBH_4$ (1.82g, 48.13 mol) portionwise as the temperature of the solution was kept at -10°C. The mixture was left stirring at room temperature for 6 h. It was then cooled to 0°C and water (50 ml) was added. The mixture was extracted with CH_2Cl_2 (3x50 ml). The organic layer was dried over $CaCl_2$, filtered and the solvent was evaporated. The residue was separated by column chromatography eluting with petrol ether/CH_2Cl_2 (10:1) to give **12** (6.52g, 92%), which was recrystallized from CH_2Cl_2/petrol ether, colorless crystals mp 96-98°C; [Found: C, 81.52; H, 8.83. $C_{11}H_{14}O$ requires C, 81.43; H, 8.70%]; ν_{max} (KBr) 3285, 3015, 2930, 2860, 1558, 1546, 1540, 1335, 1300, 1100, 1040, 935, 900, 758, 730 cm^{-1}; δ_H (200 MHz, $CDCl_3$) δ 7.43 (1H, m, Ph), 7.16 (3H, m, Ph), 4.92 (1H, dd, *J* 7.0, 2.2 Hz, C<u>H</u>OH), 2.82 (2H, m, PhC<u>H</u>$_2$), 2.02 (2H, m, HOCHC<u>H</u>$_2$),1.78 (3H, m, C<u>H</u>$_2$C<u>H</u>$_a$H$_b$), 1.48 (1H, m, CH$_2$C<u>H</u>$_a$H$_b$).

6,7-Dihydro-5*H*-benzo[*a*]cycloheptene (14). To a stirred solution of the alcohol **12** (3.24 g, 20 mmol) in dry benzene at -10°C was subsequently added pyridine (2.37 g, 30 mmol) and phosphorus tribromide (8.13 g, 30 mmol). The reaction mixture was left stirring at room temperature for 8 h. It was then cooled to -10°C and water was added (50 ml). The mixture was extracted with petroleum ether (3x50 ml), dried over Na_2SO_4 and the solvent was evaporated. The residue was separated by column chromatography eluting with petroleum ether to give the pure alkene **14**[14,15] as a colorless liquid (2.24 g, 78%); [Found; C, 92.12; H, 7.91. $C_{11}H_{12}$ requires C, 91.66; H, 8.3%]; ν_{max} (liquid film) 2920, 1950, 1915, 1690, 1640, 1600, 1575, 1480, 1425, 1345, 1035, 940 cm^{-1}; δ_H (200 MHz, $CDCl_3$) δ 7.10 (4H, m, Ph), 6.40 (1H, d, *J* 12.7 Hz, PhC<u>H</u>=CH), 6.15 (1H, dt, *J* 12.7, 3.2 Hz, PhCH=C<u>H</u>), 2.85 (2H, m, PhC<u>H</u>$_2$), 2.35 (2H, m, =CHC<u>H</u>$_2$CH$_2$), 1.95 (2H, m, =CHCH$_2$C<u>H</u>$_2$).

(5*R(S)*,6*R(S)*)-5,6-Dibromo-6,7,8,9-tetrahydro-5*H*-benzo[*a*]cycloheptene (15). A solution of bromine (1.11 g, 6.99 mmol) in CCl_4 (25 ml) was added over a period of 30 min to a stirred solution of **14** (1.00g, 6.99 mmol) in dry CCl_4 (30 ml). The reaction mixture was stirred for an additional 2 h, and then the solvent was evaporated under reduced pressure. The residue was chromatographed through a short silica gel column eluting with CCl_4 to give the pure dibromo compound **15** as a colorless liquid (2.11g, quantitative); [Found; C, 58.84;

H, 5.48. $C_{11}H_{12}Br_2$ requires C, 58.95; H, 5.4%]; ν_{max} (nujol) 3050, 3020, 2925, 2850, 1600, 1495, 1455, 1430, 1302, 1165, 1142, 925, 745 cm^{-1}; δ_H (200 MHz, $CDCl_3$) δ 7.24 (4H, m, Ph), 5.58 (1H, d, *J* 4.1 Hz, PhC<u>H</u>Br), 4.95 (1H, m, Hz, PhCHBrC<u>H</u>Br), 3.32 (1H, m, PhC<u>H</u>$_a$H$_b$), 3.02 (1H, m, PhC<u>H</u>$_a$H$_b$), 2.82 (1H, m, CHBrC<u>H</u>$_a$H$_b$), 2.32 (1H, m, CHBrC<u>H</u>$_a$H$_b$), 2.00 (2H, m, PhCH$_2$C<u>H</u>$_2$).

8-Bromo-6,7-dihydro-5*H*-benzo[*a*]cycloheptene (16) and 9-bromo-6,7-dihydro-5*H*-benzo[*a*]cycloheptene (17). The vinyl bromides **16** and **17** were synthesized as described for the synthesis of **14**. The residue was chromatographed on a silica gel TLC plate using CH_2Cl_2/hexane (1:9) solvent combination as a mobile phase to give **16** in 52% (388 mg) and **17** in 35% (256 mg) yields. *8-bromo-6,7-dihydro-5H-benzo[a]cycloheptene* **16**; [Found: C, 59.34; H, 4.39. $C_{11}H_{11}Br$ requires C, 59.22; H, 4.97%]; ν_{max} (liquid film) 3050, 3020, 2930, 2860, 1630, 1490, 1440, 1420, 940, 750 cm^{-1}; δ_H (60 MHz, $CDCl_3$) 7.01 (4H, m, Ph), 6.95 (1H, s, C<u>H</u>=CBr), 2.90 (4H, m, =CBrC<u>H</u>$_2$ and PhCH$_2$), 2.00 (2H, m, CH$_2$C<u>H</u>$_2$CH$_2$); *9-bromo-6,7-dihydro-5H-benzo[a]cycloheptene* **17** [Found: C, 59.41; H, 5.06. $C_{11}H_{11}Br$ requires C, 59.22; H, 4.97%]; ν_{max} (liquid film) 3055, 3010, 2930, 2855, 1615, 1580, 1450, 900, 830, 765, 745 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.46 (1H, m, Ph), 7.17 (3H, m, Ph), 6.57 (1H, t, *J* 4.5 Hz, CBr=C<u>H</u>), 2.70 (2H, t, *J*=3.2, PhCH$_2$), 2.41 (2H, m, =CHC<u>H</u>$_2$); 2.12 (2H, m, CH$_2$)

9-Chloro-6,7-dihydro-5*H*-benzo[*a*]cycloheptene (19). To a solution of the ketone **11** (2 g, 12.5 mmol) in dry benzene (30 ml) was added PCl_5 (2.60g, 12.5 mmol). The reaction mixture was refluxed for 8 h. It was then cooled to -10°C and water (30 ml) was added. The mixture was extracted with CH_2Cl_2 (3x50 ml), dried over $CaCl_2$ and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography eluting with *n*-hexane to give **19** as the sole product (2.23 g, 85%), colorless liquid; [Found: C, 73.86; H, 6.13. $C_{11}H_{11}Cl$ requires C, 73.95; H, 6.20%]; ν_{max} (KBr) 3050, 3010, 2970, 2850, 1690, 1620, 1480, 1440, 1345, 1305, 1200, 1160, 1105, 980, 915, 820, 770, 740 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.62 (1H, m, Ph), 7.24 (3H, m, Ph), 6.45 (1H, t, *J* 6.45 Hz, CCl=C<u>H</u>CH$_2$), 2.71 (2H, t, *J* 6.45 Hz, PhC<u>H</u>$_2$), 2.10 (2H, dt, *J* 6.45, 3.2 Hz, CHCl=CHC<u>H</u>$_2$), 1.95 (2H, m, =CHCH$_2$C<u>H</u>$_2$).

(12*R*)-20-Oxapentacyclo[11.6.1.0^{2,12}.0^{4,9}.0^{14,19}]icosa-2,4,6,8,14,16,18-heptaene (25) and (12*S*)-20-oxapentacyclo[11.6.1.0^{2,12}.0^{4,9}.0^{14,19}]icosa-2,4,6,8,14,16,18-heptaene (26). Potassium *tert*-butoxide (138 mg, 1.23 mmol) in 30 ml THF was added to a solution of DPIBF (diphenylisobenzofuran) (303 mg, 1.12 mmol) and bromocycloalkene **16** (250 mg, 1.12 mmol) in 25 ml dry THF over a period of 30 min whilst maintaining reflux. The mixture was refluxed until the reaction was complete on TLC. The reaction mixture was then cooled to room temperature and water (60 ml) was added. After the extraction with CH_2Cl_2 (3 x50 ml), the excess diphenylbenzo[c]furan was destroyed with maleic anhydride. The organic layer was dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography eluting with *n*-hexane/CH_2Cl_2 (95/5) to give **25**, which was recrystallized from CH_2Cl_2/petrol ether, colorless crystals; mp 215-217°C; yield 128.8 mg (28%) and **26,** which was recrystallized from CH_2Cl_2/petrol ether,

colorless crystals; mp 165-167°C; yield 78.2 mg (17%). **25** [Found: C, 90.06; H, 5.71. $C_{31}H_{24}O$ requires C,90.25; H, 5.86%]; R_f (5% CH_2Cl_2/*n*-hexane) 0.42; ν_{max} (KBr) 3085, 2920, 2840, 1600, 1495, 1445, 1355, 1300, 1260, 1020, 985, 745, 700 cm^{-1}. δ_H (200 MHz, $CDCl_3$) 8.05 (2H, m, Ph), 7.30 (16H, m, Ph), 6.55 (1H, d, *J* 3.1 Hz, =C<u>H</u>), 3.75 (1H, m, =CRC<u>H</u>R'R"), 2.65 (2H, m, PhC<u>H</u>$_2$CH$_2$), 2.17 (1H, m, PhCH$_2$C<u>H$_a$</u>H$_b$), 1.90 (1H, m, PhCH$_2$C<u>H$_a$</u>H$_b$); δ_C (67.5 MHz, $CDCl_3$) 149.07, 149.03, 145.12, 140.15, 139.50, 136.82, 129.53, 128.95, 128.54, 128.51, 128.46, 128.30, 128.17, 128.07, 127.78, 127.75, 127.60, 126.86, 126.55, 126.41, 126.10, 125.84, 125.83, 125.81, 121.48, 119.62, 90.02, 89.97, 47.19, 38.52, 33.13; *m/z* (CI, *iso*-butane) 412.2(49), 394.2(39), 317.1(12), 307.1(100), 270.1(22), 241.1(11), 229.1(35), 215.1(32); **26** [Found: C, 90.11; H, 5.68. $C_{31}H_{24}O$ requires C,90.25; H, 5.86%]; R_f (5% CH_2Cl_2/*n*-hexane) 0.38; ν_{max} (KBr) 3070, 2950, 2920, 1965, 1750, 1660, 1600, 1495, 1445, 1310, 1265, 1050, 980, 745, 700 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.90 (2H, m, Ph), 7.30 (16H, m, Ph), 6.48 (1H, d, *J* 3.1Hz, =C<u>H</u>), 3.52 (1H, dd, *J* 3.0 2.2 Hz, =CRC<u>H</u>R'R"), 2.65 (1H, m, PhC<u>H$_a$</u>H$_b$), 2.35 (2H, m, PhC<u>H$_a$</u>H$_b$ and PhCH$_2$C<u>H$_a$</u>H$_b$), 1.62 (1H, m, PhCH$_2$C<u>H$_a$</u>H$_b$); δ_C (67.5 MHz, $CDCl_3$) 149.22, 146.45, 140.10, 139.37, 136.81, 136.53, 129.64, 128.47, 128.40, 128.27, 128.15, 128.08, 127.98, 127.76, 127.59, 127.25, 127.19, 127.12, 126.38, 126.30, 125.96, 125.50, 122.03, 120.87, 119.44, 119.40, 90.79, 90.49, 47.85, 35.52, 33.93; *m/z* (CI, *iso*-butane) 412.2(24), 394.2(64), 317.1(22), 307.1(100), 291.1(21), 270.1(29), 241.1(11), 229.1(31), 215.1(35), 202.1(9), 179.1(10), 149.0(30).

5*H*-Benzo[*a*]cycloheptene (21). A solution of **17** in dry THF (20 ml) was added to a suspension of potassium *tert*-butoxide (200 mg, 1.8 mmol) in 30 ml of dry THF over a period of 1h. The reaction mixture was cooled to room temperature and water (20 ml) was added. THF was evaporated under reduced pressure and the remaining residue was extracted with hexane (3x50 ml). The combined organic extracts were dried over $CaCl_2$, filtered and the solvent was evaporated. The residue was then distilled (20 mmHg, 115-120°C) to obtain *7H*-benzocycloheptene **21**[19] (225 mg, 89%). δ_H (200 MHz, $CDCl_3$) 7.24 (5H, m, Ph and PhC<u>H</u>), 6.48 (1H, dd, *J* 4.8, 4.2 Hz, =C<u>H</u>), 6.15 (1H, dd, *J* 4.8, 4.2 Hz, =C<u>H</u>), 5.90 (1H, m, =C<u>H</u>), 3.02 (2H, d, *J* 4.8 Hz, PhC<u>H$_2$</u>). Compound **21** was also synthesized, employing the same reaction conditions, from 2-chloro-3,4-benzo-1,3-cycloheptadien **19** in 83% yield.

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