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THE SYNTHESIS OF PRESUMABLY PLANAR CONJUGATED 8-MEMBERED RING COMPOUNDS[1,2]

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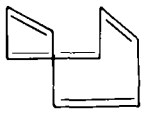
Abstract—Using mainly base dehydrobromination reactions of carbocyclic 8-membered bromides, a variety of acetylenic and cumulenic compounds were isolated or postulated as transient intermediates. The physical and chemical properties of the isolable presumably planar 8-membered ring compounds were investigated. Trapping experiments were used to confirm the transitory existence of the unstable intermediates.

It is now unanimously accepted[5] that the structure of cyclooctatetraene (1) is best represented by the "tub" or "boat" conformation, which belongs to the D_{2d} symmetry point group. Such a formulation will be strainless, and the adjacent π bonds will not be able to overlap effectively since they are at right angles to each other. Cyclooctatetraene (1) is therefore a normal cyclic



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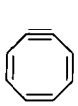
polyene with no electron delocalization between its double bonds. The consequence of this is the absence of a paramagnetic ring current in the 8-membered ring, thus leaving a gap in the presumably paratropic noncharged $4n\pi$ annulene series.

There are only very few examples in the literature of noncharged fully conjugated planar 8-membered ring compounds. The work of Krebs[6] provided the first example. By treatment of bromocyclooctatetraene with potassium t-butoxide (KO'Bu), Krebs showed that cyclooctatrienyne (2) appeared to be an intermediate, which can be trapped with various reagents. It was impossible to isolate 2 because it was not actually stable.



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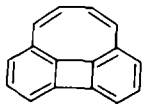

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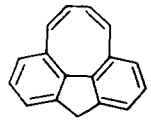

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Wilcox, Jr. *et al.*[7] synthesized cycloocta[*def*]biphenylene (3), and suggested that the 8-membered ring was planar by examination of its NMR spectrum. Similarly, Rabinovitz[8] prepared cycloocta[*def*]fluorene (4). The compound 4 was presumably planar because the 8-membered ring was shown to possess paratropic property.

It was our aim to synthesize stable noncharged fully conjugated planar 8-membered ring compounds, in order to investigate some of their extraordinary physical and chemical properties, which may result due to the planarity of the rings. Our method is to introduce one or two triple bonds into a fully conjugated 8-membered ring. This will provide a strained sp–sp hybrid bond, which is expected to contribute structurally to the planarity of a fully conjugated 8-membered carbocycle.

RESULTS AND DISCUSSION

5,6,9,10-*Tetrahydrobenzocyclooctene* (6). The role of fused benzo groups in the stabilization of unstable systems is being increasingly understood.[9] It was expected that cycloocta-1,5-diene-3,7-diyne (5) would be stabilized

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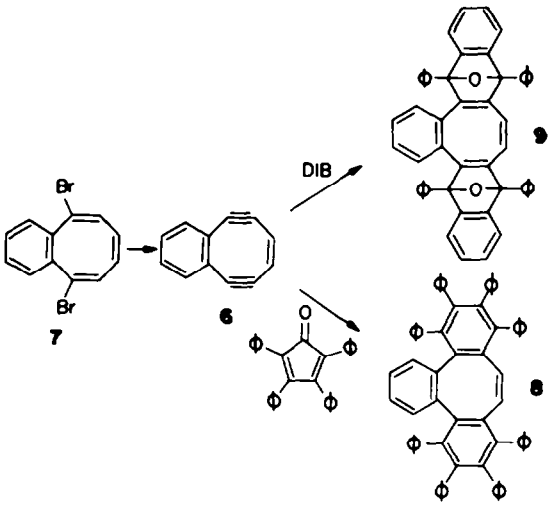
when fused to a benzo group, and it might therefore be possible to isolate such a compound.

Although the diacetylene 6 has not been isolated previously, it may have been an intermediate in the dehydrobromination of 5,10-dibromobenzocyclooctene (7) with KO'Bu in the presence of 2,3,4,5-tetraphenylcyclopentadienone (TC) to give 1,2,3,4,9,10,11,12-octaphenyltribenzo[*a*, *c*, *e*]cyclooctene (8).[10] It was desirable to isolate 6 in order to study its physical as well as chemical properties, and the dehydrobromination of 7 was therefore repeated in the absence of TC.

5,10-Dibromobenzocyclooctene (7) was prepared by the photo induced bromination of biphenylene in CCl_4 (500 W clear lamp) for 30 min. The resulting mixture of tetra- and hexabromides[11] were separated from other products by preparative layer chromatography (PLC) and treated with an excess of NaI in DMF at 50° for 4 hr.[11] The dibromide 7 was then obtained by chromatography in 10% overall yield, m.p. 89–91°.

The dibromide 7 was treated with an excess of KO'Bu

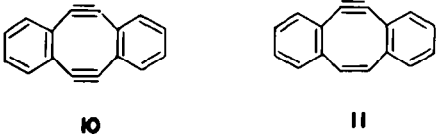


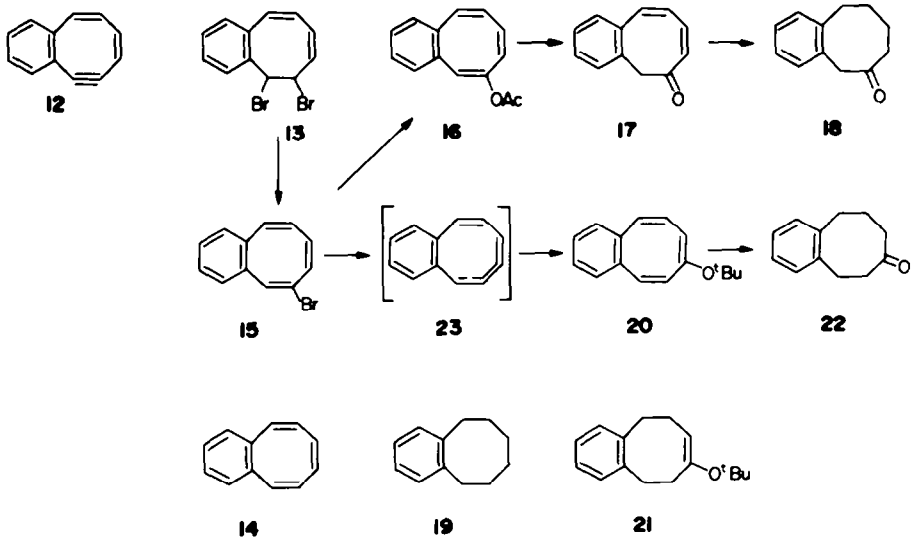
in THF for 30 sec at room temperature, followed by isolation with ether and chromatography. The diacetylene **6** was isolated as a yellow oil, which decomposed very rapidly even at 0°. The work-up procedure and the chromatography must be carried out as quickly as possible. The diacetylene **6** was quite unstable even in solution, and this instability seriously hampered efforts to obtain a satisfactory mass spectrum or elemental analysis, or to estimate the chemical yield. However, the IR spectrum of **6** exhibited a weak triple bond stretching band at ca 2100 cm^{-1}. The NMR spectrum (−20°) showed a sharp olefinic singlet at τ 5.07 (which gradually disappeared on standing), but the exact location of the benzenoid multiplet was obscured by the appearance of bands due to decomposition products. The UV spectrum of **6** was rather similar to its dibenzoannulated counterpart **10** and **11**,[12] showing rather complex absorption maxima. The major band at 257 mμ (ϵ 71,900) suggested that there were bathochromic shifts as well as a hyperchromic effect when compared with the nonplanar analogue **14** [UV: 234 mμ (ϵ 21,600)]. The presence of these effects in **6** could only be explained by a fully conjugated 8-membered ring. Such a planar $4n\pi$ system in **6** should also be capable of sustaining paramagnetic ring currents in an applied magnetic field. Indeed, the diacetylene **6** was proved to be paratropic, as vindicated by the high-field resonance (τ 5.07) of the olefinic protons in the NMR spectrum.

The strained diacetylene **6** readily underwent cycloaddition with reactive dienes. Thus, treatment of a freshly prepared sample of **6** with excess of TC in pentane–ether at 40° yielded the previously described substance **8**, which formed colorless crystals, m.p. 305–307° (lit.[10] 308–312°); Mass spectrum *m/e* 862. Further structure proof of **6** was obtained by treatment of **6** with 1,3-diphenylisobenzofuran (DIB) in pentane–ether at room temperature. 2,3 : 10,11 - dibenzo - 1,4 : 9,12 - diepoxy - 1,4 : 9,12 - dihydro - 1,4 : 9,12 - diphenyltribenzo[*a*, *c*, *e*]cyclooctene (**9**) was obtained as colorless crystals, m.p. 208–209°; Mass spectrum *m/e* 690.

6,7-*Didehydrobenzocyclooctene* (**23**). The existence of 5,6,9,10 - tetradehydrobenzocyclooctene (**6**) has been demonstrated. It was of interest to prepare the related 5,6 - didehydrobenzocyclooctene (**12**), for which 5,6 - dibromo - 5,6 - dihydrobenzocyclooctene (**13**) seemed to be a suitable precursor.

The dibromide **13** was prepared from benzocyclooctene (**14**).[13] Bromination[14] of **14** was accomplished at −70° to afford the di-bromide **13** in 40% yield, m.p. 67–70°. Treatment of the dibromide **13** with 1.3 molar equivalents of KO^{t}Bu in dry THF at room temperature led to the yellow liquid 6-bromobenzocyclooctene (**15**). The structure of **15** was confirmed by treatment of **15** with freshly prepared silver acetate (1.1 molar equivs) in glacial acetic acid[15] at 100° for 22 hr. This reaction led to the crude acetate **16**, which was hydrolyzed directly with 60% H_2SO_4 in boiling THF for 30 min. The unsaturated ketone **17** was obtained as a yellow oil, IR 1670 cm^{-1}. The ketone **17** was hydrogenated catalytically in ethyl acetate over 10% Pd–C to give 7,8,9,10-tetrahydro-6(5H)-benzocyclooctenone (**18**) as a colorless oil in 90% yield. The oxime of **18** was prepared,[16] m.p. 130–131°. The





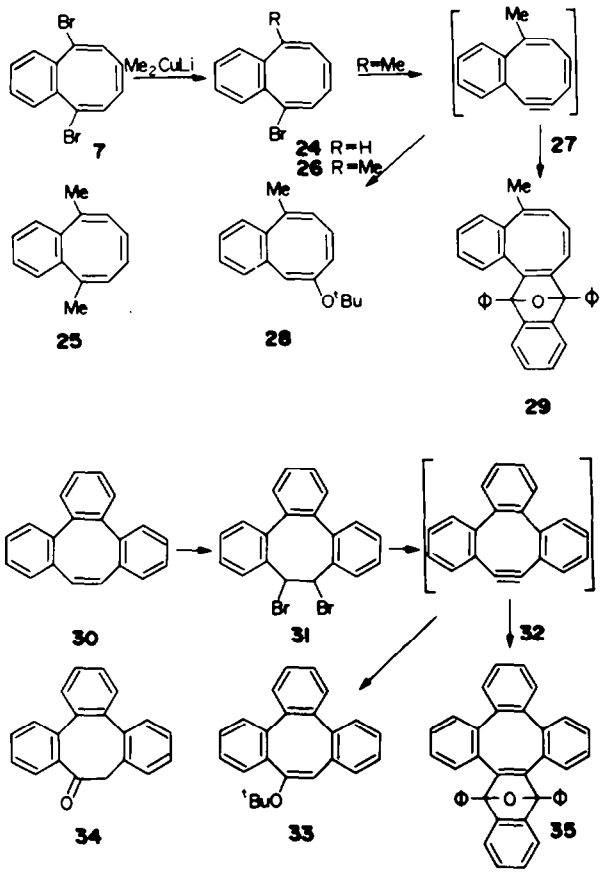
carbon skeleton of **18** was confirmed by the Kishner-Wolff reduction to the known 5,6,7,8,9,10 - hexahydrobenzocyclooctene (**19**), which was identical in all aspects to an authentic sample.

Treatment of the bromide **15** with a large excess of KO'Bu (10 molar equivs) in dry THF at room temperature led to 7-t-butoxybenzocyclooctene (**20**) as the sole isolable product. The structure of **20** was confirmed through catalytic hydrogenation of the two less hindered double bonds to the t-butyl enol ether **21**. Hydrolysis of **21** with conc H_2SO_4 in dioxane led to 5,6,9,10 - tetrahydro - 7(8H) - benzocyclooctenone (**22**), m.p. 49–51° (lit.[17] 48.5–50.5°). The oxime of **22** showed m.p. 108–110° (lit.[17] 112.5–114°).

It is conceivable that the conversion of **15** to **20** may involve the cyclic cumulenic intermediate, namely, 6,7 - didehydrobenzocyclooctene (**23**). The cumulene **23** proved too unstable for isolation to be possible, therefore, no physical data could be obtained.

5,6-*Didehydro*-10-*methylbenzocyclooctene* (**27**). It has been shown that dehydrobromination of 6-bromobenzocyclooctene (**15**) did not proceed via the desirable acetylenic intermediate **12**. It therefore appears that 5-bromobenzocyclooctene (**24**) should be more suitable precursor, since the primary dehydrobromination product must be 5,6-didehydrobenzocyclooctene (**12**). We decided to use 5-bromo-10-methylbenzocyclooctene (**26**) because it was easily accessible and the presence of a Me group would serve as a probe for the recognition of the paratropic properties which would result in its presumable planar dehydrobromination product. Treatment of the dibromide **7** with one molar equivalent of lithium dimethyl cuprate in ether led to the monobromide **26** as well as small amounts of recovered starting material **7** and 5,10-dimiethylbenzocyclooctene **25**. dehydrobromination of the bromide **26** with one molar equivalent of KO'Bu in dry THF gave 5 - methyl - 9 - t - butoxybenzocyclooctene (**28**) as the only product. It then appears that 5,6 - didehydro - 10 - methylbenzocyclooctene (**27**) was a transient intermediate in the reaction. Trapping of the intermediate **27** was successful by using DIB as an reactive diene, in which the Diels–Alder adduct **29** was isolated. The acetylene **27** was proved to be too unstable for isolation under the reaction condition used. The instability of the acetylene **27** and the relative stability of the diacetylene **6** were in keeping with the results reported in the literature.[12,18–19]

13,14-*Didehydrotribenzo*[a, c, e]*cyclooctene* (**32**). The suitable precursor for the preparation of 13,14 - didehydrotribenzo[*a, c, e*]cyclooctene (**32**) seemed to be 13,14 - dibromo - 13,14 - dihydrotribenzo[*a, c, e*]cyclooctene (**31**), which has been obtained by bromination[20] of tribenzo[*a, c, e*]cyclooctene (**30**). The compound **30** has been prepared by two independent methods.[20,21] However, we have developed two more superior and simpler methods to prepare **30** in good yields.[22,23] Treatment of the compound **30** with one molar equivalent of bromine in boiling CCl_4 followed by direct crystallization, yielded the dibromide **31** as colorless crystals. Dehydrobromination of the dibromide **31** with an excess of KO'Bu in THF at room temperature, afforded 13 - t - butoxytribenzo[*a, c, e*]cyclooctene (**33**) as well as 13(14H) - tribenzo[*a, c, e*]cyclooctenone (**34**) after acid work-up. Despite very careful extraction and low temperature chromatography, no sign of the expected 13,14 - didehydrotribenzo[*a, c, e*]cyclooctene (**32**)



was observed. The findings of Gugel and Meier[21] are in full accord with our results. The data obtained so far suggest that the acetylene **32** is very reactive and it undergoes subsequent nucleophilic addition with t-BuO group. The transient existence of **32** could be confirmed by carrying out the dehydrobromination reaction in the presence of DIB. The adduct **35** was obtained in 26% yield as colorless crystals.

The instability of the acetylene **32** is not a surprising result. Inspection of a molecular model of **32** reveals that the neighboring protons on the three fused benzene rings will suffer severe H–H nonbonded interactions if a planar geometry of the 8-membered ring is to be attained.

EXPERIMENTAL

Microanalysis was carried out by the microanalytical section of the Chemistry Department, University College London. M.ps were determined on a Kofler hot-stage microscope and are uncorrected. The electronic spectra were determined on a Unicam SP 800 recording spectrophotometer. The abbreviation "sh" is used to indicate a shoulder in a spectrum. The IR spectra were recorded on a Unicam SP 200 spectrophotometer or a Perkin–Elmer 177 spectrophotometer. The ^{1}H NMR spectra were recorded on a Varian T-60 spectrometer (60 MHz) or a Varian HA-100 spectrometer (100 MHz) in $CDCl_3$ unless stated otherwise, and are reported in τ units relative to TMS as internal standard. The mass spectra were recorded on A.E.I. MS 9 (high resolution) or A.E.I. MS 12 (low resolution) mass spectrometers at 70 eV. Thin layer chromatographic plates were prepared by using Merck Kieselgel HF_{254}, or purchased from commercially available pre-coated Merck Kieselgel 60 F_{254} plates (layer thickness 0.25 mm). KO^{t}Bu was obtained from Fluka Chemical Ltd., and was used after purification by sublimation at high vacuum. Solvents were purified and dried by standard methods.

5,10-*Dibromobenzocyclooctene* (**7**). Biphenylene (1.6 g, 10.52 mmol) in CCl_4 (100 ml) was treated with Br_2 (1.2 ml) and irradiated (500 W clear lamp) for 30 min until the soln became pale yellow. The mixture was then washed by water and the organic layer was dried over $MgSO_4$. The residue, after removal of the solvent, was chromatographed on Merck Kieselgel $PF_{254-366}$ thick plates (pentane–ether 9 : 1) to give four zones, the most nonpolar fraction was confirmed to be a mixture of biphenylene and monobromobiphenylene (yield 0.81 g) by MS and ^{1}H NMR. The remaining fractions were dissolved in DMF (50 ml). NaI (6 g) was added, the mixture was heated to 50° for 4 hr, then poured into water (*ca* 200 ml) and extracted by ether (*ca* 500 ml). The ethereal extract was washed with water, separated and dried over $MgSO_4$. The residue, after removal of the ether, was subjected to PLC on Merck Kieselgel $PF_{254+366}$ (pentane) to give two fractions. The less polar fraction failed to crystallize from pentane and was not identified, whereas the more polar fraction crystallized from pentane to give 325 mg (10% overall yield from biphenylene) of **7**, m.p. 89–91° (lit.[11] 93–94°); ^{1}H NMR 2.66 (4H, s), 3.43 (dd, J = 1, 5 Hz, 0.75 Hz, 2H), 4.25 (dd, J = 1.5 Hz, 0.75 Hz, 2H).

5,6,9,10-*Tetradehydrobenzocyclooctene* (**6**). The dibromide **7** (50 mg, 0.16 mmol) in THF (3 ml) was added dropwise over 30 sec to a stirred soln of KO^{t}Bu (110 mg, 0.98 mmol) in THF (7 ml) at room temp under N_2. 2N HCl was added immediately and ether extraction was followed by washing with water and drying over Na_2SO_4. After removal of the ether at 0° under reduced pressure, the residue was chromatographed on an alumina column (Woelm, pentane) to yield **6** as a yellow oil, which decomposed within a few min at 0°. The isolation and chromatography were carried out within *ca* 15 min, in view of the instability of **6**: ^{1}H NMR (−20°) 5.07 (s), the benzenoid resonances were obscured by decomposition products; UV (pentane) λ 228 (ϵ 23,700), 233 (23,300), 238sh (27,000), 244 (46,600), 249 (40,700), 257 (71,900), 327 (580), 332 (590), 341 (750), 345 (820), 361 (890), 366 mμ (750); IR (CCl_4) 2100 cm^{-1}.

1,2,3,4,9,10,11,12 - *Octaphenyltribenzo*[a, c, e]*cyclooctene* (**8**). The diacetylene **6** was obtained from **7** (100 mg, 0.32 mmol) as described. The pentane eluent from the column was concentrated at 0° under reduced pressure, ether (5 ml) was added and this soln of **6** was added rapidly to a stirred and boiling soln of TC (50 mg) in ether (20 ml) under N_2. The stirred mixture was boiled under reflux for 4 hr, and was then allowed to cool to room temp. Removal of the solvents followed by PLC of the residue on Merck Kieselgel 60 PF_{254} (pentane–ether 9 : 3) afforded 14 mg (5%) of **8**, m.p. 305° (MeOH–benzene): ^{1}H NMR 2.50–3.50 (m, 44H), 3.80 (s, 2H); MS *m/e* 862 (M^+).

2,3 : 10,11 - *Dibenzo* - 1,4 : 9,12 - *diepoxy* - 1,4 : 9,12 - *dihydro* - 1,4 : 9,12 - *diphenyltribenzo*[a, c, e]*cyclooctene* (**9**). The diacetylene **6** was obtained from **7** (50 mg, 0.16 mmol) as described. The pentane eluent from the column was concentrated at 0° under reduced pressure, ether (10 ml) was added to the concentrated pentane soln to make up the volume to *ca* 15 ml. This ether–pentane soln of **6** was then added rapidly to a stirred soln of DIB (25 mg, 0.09 mmol) in ether (8 ml) at room temp. The mixture was stirred for 48 hr at room temp. Removal of the solvents, followed by PLC of the residue on Merck Kieselgel 60 PF_{254} (pentane–ether 9 : 1) afforded 6.75 mg (6%) of **9** as colorless crystals, m.p. 208–209° (dec) (from ether–EtOH): ^{1}H NMR (CCl_4) 2.00–2.30 (m, 8H), 2.40–2.70 (m, 12H), 2.75–3.05 (m, 14H); MS M^- measured 690.2518, Calc. for $C_{52}H_{34}O_2$: 690.2559. Calc. for $C_{52}H_{34}O_2$: C, 90.43; H, 4.93%). (Found: C, 90.18; H, 4.82.

6-*Bromobenzocyclooctene* (**15**). A soln of Br_2 (310 mg, 1.94 mmol) in dry CH_2Cl_2 (4 ml) was added dropwise over 5 min to a stirred soln of **14**[13] (310 mg, 2.01 mmol) in CH_2Cl_2 (6 ml) at −70°. After further stirring at this temp for additional 10 min, the soln was brought to room temp. Removal of the solvent under reduced pressure gave essentially quantitative yield of crude **13**, which was dissolved in dry THF (10 ml). A soln of KO^{t}Bu (300 mg, 2.65 mmol) in dry THF (6 ml) was added dropwise over 5 min into the **13** soln. After the resultant mixture had been stirred for 1 hr at room temp, 10% HCl aq (25 ml) was added. The aq suspension was extracted with CH_2Cl_2 and the combined extracts were washed with water and dried over Na_2SO_4. The residue obtained on solvent removal was taken up in a small amount of benzene and poured onto a Merck Kieselgel column. Elution with petroleum ether (< 40°) gave 310 mg (66%), based on **14**, of the monobromide **15** as clear yellow oil: ^{1}H NMR 2.20–3.12 (m, 7H), 3.12–3.67 (m, 1H), 3.67–4.30 (m, 1H); MS M^+ measured 231.9892, Calc. for $C_{12}H_9{}^{79}Br$: 231.9888. (Found: C, 61.89; H, 3.94; Br, 34.56. Calc. for $C_{12}H_9Br$: C, 61.80; H, 3.86; Br 34.33%).

7-*t-Butoxybenzocyclooctene* (**20**). The dibromide **13** (75 mg, 0.24 mmol) in THF (3 ml) was added dropwise to a stirred soln of KO^{t}Bu (300 mg, 2.67 mmol) in THF (15 ml) at room temp under N_2. The mixture was stirred for 1 hr, and 2N HCl and ether were then added. The ethereal extract was washed with water and dried over Na_2SO_4. Removal of the ether followed by PLC of the residue on Merck Kieselgel 60 PF_{254} (pentane–ether 8 : 1) gave two components. The less polar compound, a pale yellow oil, was **15**, the yield was 10.6 mg (19%) and it was identical in all aspects to an authentic sample. The more polar compound, a pale yellow oil, was **20**, the yield was 36.4 mg (67%): ^{1}H NMR 2.60–3.10 (m, 4H), 3.20–4.08 (m, 5H), 8.64 (s, 9H); MS M^+ measured 226.1347, Calc. for $C_{16}H_{18}O$: 226.1358.

Dehydrobromination of 6-*bromobenzocyclooctene* (**15**). The bromide **15** (35 mg, 0.15 mmol) in THF (1 ml) was added dropwise to a stirred soln of KO^{t}Bu (90 mg, 0.80 mmol) in THF (5 ml) at room temp under N_2. The mixture was stirred for 30 min. 2N HCl and ether were added, the extract was washed with water and dried over Na_2SO_4. Removal of the solvent, followed by PLC of the residue on Merck Kieselgel 60 PF_{254} (pentane–ether 8 : 1) yielded two compounds. The less polar compound (14.8 mg, 42%) was the starting material **15**. The more polar compound (9.05 mg, 43%) was **20**.

Catalytic hydrogenation of 6-*bromobenzocyclooctene* (**15**). The bromide **15** (46.9 mg, 0.20 mmol) in EtOH (13 ml) was hydrogenated over 10% Pd–C (10 mg) at room temp and atmospheric pressure. Removal of the catalyst and evaporation, followed by PLC of the residue on Merck Kieselgel 60 PF_{254} (pentane) afforded two compounds. The less polar compound (5.2 mg, 33.5%) was **19**: ^{1}H NMR 2.87 (s, 4H), 7.10–7.35 (m, 4H),

8.10–8.80 (m, 8H). The more polar compound (24.4 mg, 52%) was the starting material **15**.

Catalytic hydrogenation of benzocyclooctene (**14**). **14** (9.6 mg, 0.06 mmol) in EtOAc (15 ml) was hydrogenated over 10% Pd–C (5 mg) at room temp and atmospheric pressure. The uptake of H_2 was 5 ml (*ca* 0.23 mmol). The catalyst was removed by filtration. Removal of EtOAc, followed by PLC of the residue on Merck Kieselgel 60 PF_{254} (pentane) yielded **19** as a colorless oil: ^{1}H NMR 2.87 (s, 4H), 7.10–7.35 (m, 4H), 8.10–8.80 (m, 8H).

6(5H)-*Benzocyclooctenone* (**17**) *from the monobromide* **15** *via* 6-*acetoxybenzocyclooctene* (**16**). A mixture of **15** (233 mg, 1.0 mmol), freshly prepared (AgOAc (181 mg, 1.1 mmol) and glacial AcOH(10 ml) was heated at 100° for 22 hr. The mixture was filtered and the insoluble inorganic substance was washed with fresh AcOH. Neutralization with cold dil NaOH aq was followed by extraction with ether. The combined ethereal extracts were washed with water and evaporated under reduced pressure. The residue which contained mainly **16** was hydrolyzed without purification in refluxing soln containing THF (10 ml), H_2O (1 ml), and conc H_2SO_4 (1.5 ml). Workup of the hydrolysis product by addition of water and extraction with CH_2Cl_2 gave 205 mg of a crude mixture which was subjected to column chromatography over alumina (Woelm). Elution with petroleum ether (< 40°)-EtOAc (10 : 1) gave 25 mg of the unreacted **15**. Further elution with petroleum ether (< 40°)-EtOAc (5 : 1) afforded essentially pure **17** (95 mg, 63% based on reacted **15**) as a clear yellow oil: ^{1}H NMR 2.65 (m, 4H), 2.85–3.75 (m, 4H), 6.38 (s, 2H); IR 1670 cm^{-1}; (Found: C, 84.64; H, 5.97. Calc. for $C_{12}H_{10}O$: C, 84.68; H, 5.92%).

2,4-*Dinitrophenylhydrazone of* 6(5H)-*benzocyclooctenone* (**17**). To a soln of **17** (30 mg, 0.176 mmol) in MeOH (1.5 ml) was added 1 ml of the reagent prepared by dissolving 2,4-dinitrophenylhydrazine (250 mg) in MeOH (5 ml) containing conc H_2SO_4 (0.5 ml). The ppt was collected by filtration and washed with water. Recrystallization from MeOH gave 53 mg (91%) of the hydrazone as crimson needles, m.p. 176–178°; (Found: C, 61.65; H, 4.05; N, 15.91. Calc. for $C_{18}H_{14}N_4O_4$: C, 61.71; H, 4.03; N, 16.00%).

7,8,9,10 - *Tetrahydro* - 6(5H) - *benzocyclooctene* (**18**). A soln of **17** (55 mg, 0.323 mmol) in EtOAc (10 ml) was hydrogenated over 10% Pd–C (10 mg) at room temp and atmospheric pressure until the calculated amount of H_2 had been absorbed. Removal of the catalyst followed by solvent evaporation afforded pure **18** (51 mg, 90%) as colorless oil: ^{1}H NMR 2.75 (m, 4H), 6.18 (s, 2H), 7.20 (m, 2H), 7.60 (m, 2H), 8.20 (m, 4H); IR 1710 cm^{-1}.

The oxime of 7,8,9,10 - *tetrahydro* - 6(5H) - *benzocyclooctenone* (**18**). A mixture of **18** (32 mg, 0.18 mmol) and hydroxylamine hydrochloride (26 mg, 0.37 mmol) in 5% KOH aq (5 ml) was allowed to stand at room temp overnight. The white ppt was collected, washed with water and air-dried. Recrystallization from petroleum ether (40–60°) gave 18 mg (53%) of the oxime as colorless prisms, m.p. 130–131° (lit.[16] 129.5–130°). An analytical sample was obtained by additional recrystallization from cyclohexane (Found: C, 75.82; H, 8.20; N, 7.72. Calc. for $C_{12}H_{15}NO$: C, 76.15; H, 7.99; N, 7.40%).

Kischner-Wolff reduction of 7,8,9,10 - *tetrahydro* - 6(5H) - *benzocyclooctenone* (**18**). A mixture of **18** (60 mg, 0.345 mmol), hydrazine hydrate (120 mg, excess), powdered KOH (160 mg, excess), and ethylene glycol (10 ml) was heated under reflux for 1 hr after which period the apparatus were rearranged for distillation. Slow heating was resumed until the internal temp reached 170°. After further refluxing for 2 hr; water was added to the dark syrupy mixture. The aq solution was repeatedly extracted with petroleum ether (< 40°) and the extracts were combined with the rinse obtained from washing with the same solvent the condensers used at various stages during this operation. The organic phase was washed with water and dried over Na_2SO_4. Removal of solvent left a brown residue which was subjected to column chromatography over Merck Kieselgel. Elution with petroleum ether (< 40°) gave **19** (22 mg, 40%) as a colorless oil. The ^{1}H NMR of this substance was identical with that of an authentic sample obtained in the previous experiment.

5,6,9,10 - *Tetrahydro* - 7(8H) - *benzocyclooctenone* (**22**). **20** (24 mg, 0.11 mmol) in EtOAc (13 ml) was hydrogenated over 10% Pd–C (10 mg) at room temp and atmospheric pressure. The hydrogenation was terminated when *ca* 5 ml (0.23 mmol) of H_2 had been absorbed. The catalyst was removed by filtration and the solvent was evaporated. The residue was dissolved in dioxane (6 ml) and conc H_2SO_4 (2 ml) was added dropwise. The soln was stirred for 15 min, and water (100 ml) was then added. Ether (200 ml) extraction was followed by washing with water and dried over Na_2SO_4. Removal of the ether, followed by PLC of the residue on Merck Kieselgel 60 PF_{254} (pentane–ether 7 : 1) yielded 4.8 mg (26%) of **22** as a colorless oil, which crystallized readily on standing to colorless needles, m.p. 49–51° (lit.[17] 48.5–50.5°), ^{1}H NMR 2.80 (s, 4H), 6.72–7.48 (m, 10H); MS M$^+$ at *m/e* 174.

5-*Bromo*-10-*methylbenzocyclooctene* (**26**). To **7** (50 mg, 0.16 mmol) in ether (10 ml) was added a soln of Me_2CuLi (0.16 mmol) in ether (10 ml). The mixture was stirred at room temp for 1 hr and decomposed with NH_4OH and extracted with ether. Use of HPLC (SiO_2, pentane) separated **26** (10.7 mg, 27%): ^{1}H NMR 2.58–2.93 (m, 4H), 3.38–3.49 (m, 1H), 4.00–4.30 (m, 3H), 7.79 (d, 3H, J = 1.2 Hz); MS: M$^-$ measured 246.0046, calc. for $C_{13}H_{11}{}^{79}Br$ 246.0045; from small amounts of unchanged **7**, and **25**: ^{1}H NMR 2.70–2.90 (m, 4H), 4.00–4.23 (m, 4H), 7.85 (s, 6H); MS: M$^+$ measured 182.1091, Calc. for $C_{14}H_{14}$ 182.1095.

5-*Methyl*-9-*t*-*butoxybenzocyclooctene* (**28**). The bromide **26** (30 mg, 0.12 mmol) in THF (1 ml) was added dropwise to a soln of KO^{t}Bu (13.4 mg, 0.119 mmol) in THF (5 ml) under N_2. The mixture was stirred for 5 min. It was then decomposed with 2N HCl and extracted with water. Evaporation and PLC on Merck Kieselgel 60 PF_{254} (pentane–ether 10 : 1) yielded **28**: ^{1}H NMR 2.70–3.00 (m, 4H), 3.75 (s, 1H), 3.98–4.25 (m, 3H), 7.89 (d, 3H, J = 0.5 Hz), 8.65 (s, 9H): MS: M$^+$ measured 240.1514, Calc. for $C_{17}H_{20}O$: 240.1514.

5,6-*Didehydro*-10-*methylbenzocyclooctene DIB adduct* (**29**). The bromide **26** (30 mg, 0.12 mmol) in THF (1 ml) was added dropwise to a soln of KO^{t}Bu (13.5 mg, 0.12 mmol) and excess of DIB in THF (10 ml). The mixture was stirred for 48 hr, decomposed with 2N HCl. Extraction with CH_2Cl_2, drying over $MgSO_4$, evaporation and PLC om Merck Kieselgel 60 PF_{254} (pentane–ether 5 : 1) yielded **29** as a colorless solid (9 mg, 17%) m.p. 75–79°, ^{1}H NMR 2.00–2.90 (m, 21H), 8.55 (s, 3H); MS: M$^+$ measured 436.1750, Calc. for $C_{33}H_{24}O$: 436.1830.

13,14-*Dibromo*-13,14-*dihydrotribenzo*[a, c, e]*cyclooctene* (**31**). Br_2 (25 mg, 0.16 mmol) in CCl_4 (3 ml) was added dropwise to **30** (37 mg, 0.15 mmol) in CCl_4 (5 ml) at room temp. The soln was then boiled under reflux for 1 hr and allowed to cool to room temp. Evaporation of the solvent and crystallization of the residue from absolute ether yielded 36 mg (59%) of **31**, m.p. 153–154° (lit.[20] 155–156°), ^{1}H NMR 2.38–3.18 (m, 12H), 4.55 (d, J = 2 Hz, 2H); MS: M$^-$ measured 411.9449, Calc. for $C_{20}H_{14}{}^{79}Br_2$: 411.9460.

Dehydrobromination of 13,14-*dibromo* - 13,14 - *dihydrotribenzo*[a, c, e]*cyclooctene* (**31**). The dibromide **31** (36 mg, 0.09 mmol) in THF (3 ml) was added dropwise to a stirred soln of KO^{t}Bu (2 g, 17.8 mmol) in THF (10 ml) under N_2. The soln was then stirred for a further 1 hr and 2N HCl and ether were added. The ethereal extract was washed with water, dried over $MgSO_4$ and evaporated. PLC of the residue on Merck Kieselgel 60 PF_{254} (pentane–ether 10 : 1) gave two products. The less polar compound was **33**, which on crystallization from absolute EtOH afforded 12.5 mg (44%) of colorless crystals, m.p. 158–159°, ^{1}H NMR 2.56–3.00 (m, 12H), 3.66 (s, 1H), 9.03 (s, 9H); MS: M$^+$ measured 326.1688, Calc. for $C_{24}H_{22}O$: 326.1671. The more polar compound was **34**, which on crystallization from hexane yielded 3.5 mg (15%) of colorless crystals, m.p. 157–158°, ^{1}H NMR 2.60–2.89 (m, 12H), 6.22 (s, 2H); MS: M$^+$ measured 270.1045, Calc. for $C_{20}H_{14}O$: 270.1045; IR ($CHCl_3$): 1680 cm^{-1}.

6,7,8,9,10,11 - *Tribenzo* - 5,12 - *diphenyl* - 5,12 - *dihydro* - 5,12 - *epoxycycloocta*[b]*naphthalene* (**35**). The dibromide **31** (20 mg, 0.05 mmol), DIB (15 mg, 0.06 mmol), KO^{t}Bu (150 mg, 1.34 mmol) in ether (5 ml) were stirred for 72 hr. Water was then added, the ppt was collected by filtration and combined with the residue from the Na_2SO_4 dried ethereal layer after removal of ether. The combined solids were subjected to PLC on Merck Kieselgel 60 PF_{254} (pentane–ether 10 : 1), which yielded 5.2 mg (26%) of **35** as colorless crystals, m.p. 295° (ether–EtOH), ^{1}H NMR 2.60 (s,

10H), 2.70–3.70 (m, 16H); MS: M^+ measured 522.2013, Calc. for $C_{40}H_{26}O$: 522.1983.

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