Bromination of isomeric 7,8-dibromobenzobicyclo[2.2.2]octa-2,5-dienes: neighbouring group effect on bromination

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The bromination reactions of isomeric 7,8-dibromobenzobicyclo[2.2.2]octa-2,5-dienes were studied and the possible role of neighbouring groups in rearrangements was investigated. Bromination of *endo-cis* dibromide **9** gives only the rearranged product **14** while the reaction of the *exo-cis*-dibromide **11** under the same conditions gives only *non*-rearranged products **15**, **16** and **19**. The possible role of substituents in the rearrangements was discussed.

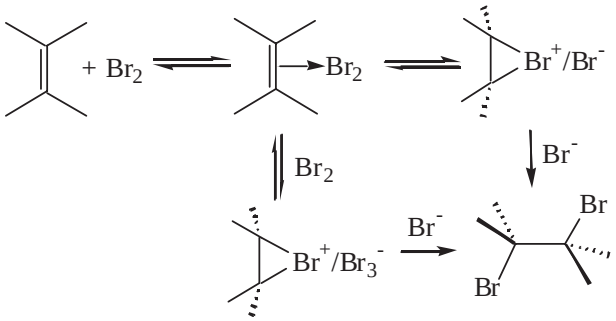
Keywords: bromination, Wagner–Meerwein rearrangement, neighbouring group effect, polybromides

The electrophilic bromination of an alkene is probably the quintessential reaction of the double bond and is portrayed in undergraduate textbooks as being a well understood process adhering to the generalised mechanism depicted in Scheme 1.[1] Formation of the three-membered bromonium intermediate has been proven by the crystal structure of the salt formed by bromination of adamantylideneadamantane.[2]

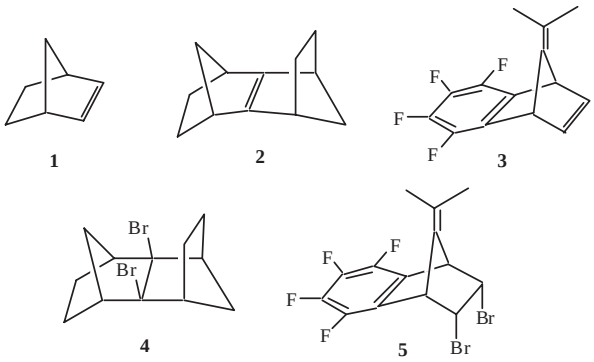
Although the addition of bromine to the carbon–carbon double bond by molecular bromine is formally one of the simplest reactions typical of unsaturated compounds, the bromination of unsaturated bicyclic systems with molecular bromine generally leads to rearrangements of the molecular skeleton. For example, the addition of bromine or other electrophilic reagents to benzobarrelene and derivatives generally results in formation of several rearranged products.[3] In addition to this, we have shown previously that high temperature bromination of bicyclic systems gives mainly *non*-rearranged products.[4]

As well as temperature,[4] light,[5] and concentration,[3f] neighbouring group participation and steric factors affect the structures of products in the bromination reaction. For example, the reaction of *anti*-sesquinorbornene **2** with bromine results in the formation of the corresponding *cis*-dibromide **4**.[1d,6] This reaction is an interesting one since it lacks the proclivity of its parent, norbornene **1**, to undergo extensive rearrangement, and its structure allows only the formation of *cis* adducts. This unusual *cis* addition is explained by the formation of a classical carbocation.[1d,6] The bromination of benzonorbornadiene derivative **3** results in formation of the *non*-rearranged *cis* addition product **5**.[7] The unusual behaviour of these compounds is associated with neighbouring group effects.

In addition to this, Caple and co-workers showed that bromination of 7-bromobenzonorbornadiene **6** gives tribromide **8** in quantitative yield[8] (Scheme 3). The exclusive formation of the *cis-exo*-tribromide **8** can be explained only by the Wagner Meerwein rearrangement where the symmetrical *non*-classical carbocation **7** is involved as the intermediate. This reaction clearly demonstrates that even in a case where a bulky group such as a bromine atom is located in the *anti*-face



Scheme 1



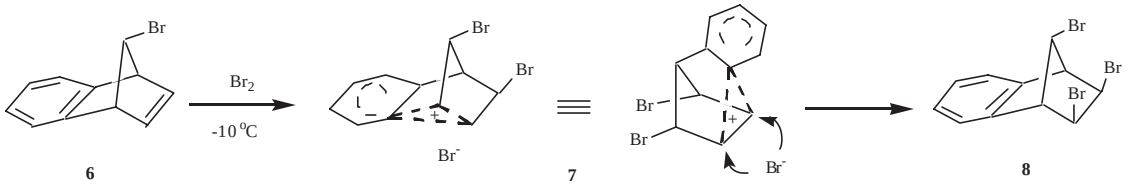
Scheme 2

of the molecule **6**, the *exo*-selectivity of the electrophile is not affected during the addition of bromine.

Results and discussion

In the present work, we describe the bromination of 7,8-dibromobenzobicyclo[2.2.2]octa-2,5-dienes in order to investigate the effects of neighbouring groups in the bromination of these systems. [see Caution in the Experimental section].

Starting materials **9**, **10** and **11** were synthesised by the procedure described in the literature.[3h] Firstly, bromination of dibromide **9** in $CHCl_3$ at –45±5 °C was investigated and



Scheme 3

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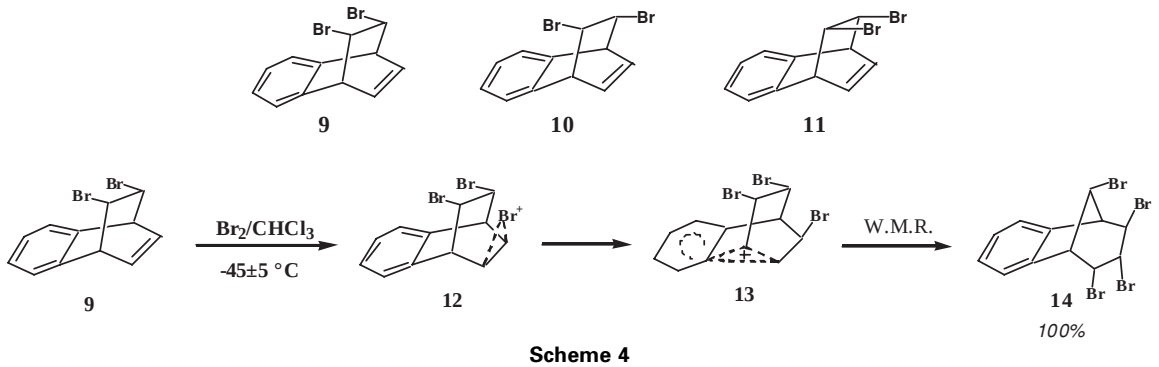
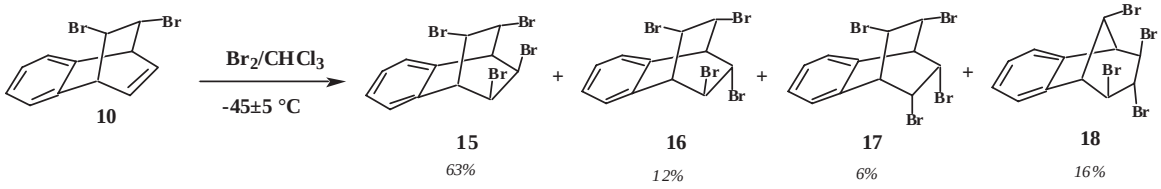


Scheme 4



Scheme 5

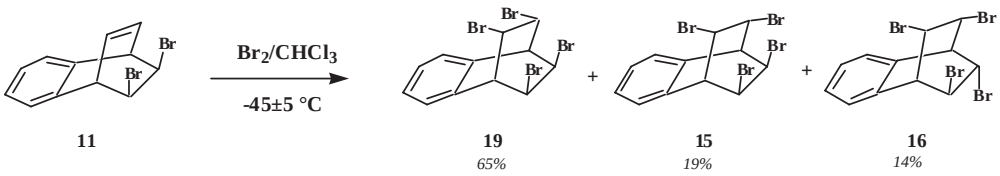
only the rearranged product **14** was obtained, formed by Wagner–Meerwein rearrangement via the *exo*-bromonium ion **12** (Scheme 4).

Bromination of the isomeric *trans*-dibromide **10** under the same reaction conditions gives mainly *non*-rearranged products **15**, **16** and **17** (Scheme 5). From this reaction, the expected rearranged product **18** was observed in low yield (16%). This result was initially unexpected, since benzobicyclic systems are prone to Wagner–Meerwein rearrangement.[3] This shows that the *trans* analogue of **9** behaves differently in ionic additions. During the bromination of **9**, the *exo* bromonium ion **12** was formed and this ion is eligible for aryl migration. But in molecule **10**, the *exo* bromine atom at C_7 partly hindered the formation of the *exo*-bromonium ion **20** and favoured the *endo* bromonium ion **22** which is responsible for the formation of *non*-rearranged products.

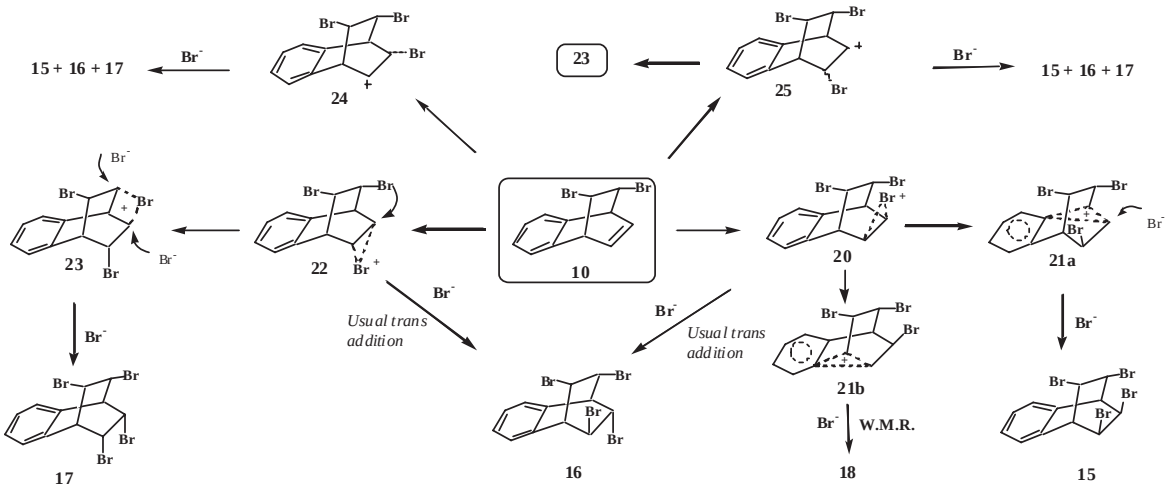
The bromination of *exo*-*cis* dibromide **11** gives only skeletally *non*-rearranged products **15**, **16** and **19**. This supports above postulate *i.e.* steric hindrance by the two bromine atoms at C_7 and C_8 prevents the formation of an *exo*-bromonium ion and therefore rearranged products were not observed at all (Scheme 6).

In addition to this, the products **15** and **17** that were formed from bromination of **10** and the products **16** and **19** formed from the bromination of **11** are unexpected because the addition of bromine to a double bond under ionic conditions generally gives *trans* dibromides. It is not possible to explain the formation of these *cis* products by classical addition of bromine to a double bond. The formation of all-*trans* isomer **16** (from the bromination of **11**) is interesting since the two bromine atoms in the starting material are *exo*-*cis*. These products can not be secondary products, formed by isomerisation of the primary product, because all products are stable under the reaction conditions. This unusual stereochemistry of the addition of bromine can be understood from neighbouring group participation and *non*-classical carbocation formation. In our opinion, these results can be explained in the following way. The formation of aryl shift product **18** can be explained in terms of the formation of *n*on-classical ion **21b** formed by *exo*-attack of bromine on **10**. The *exo*-configuration of the bromine atom at the bridge carbon is also in agreement with *exo*-attack of bromine on the double bond. The *cis* addition product **15** can be formed via *non*-classical carbonium **21a** by *exo* attack of bromine on ion **21a**. In the *endo* attack of bromine on the double bond, the *endo* bromonium ion **22** formed is rapidly converted into ion **23**.[9] This makes the approach of Br^- from the *endo* side more favourable and the *cis* addition product **17** is formed (Scheme 7). The formation of all *trans* tetrabromide **16** can be explained by usual *trans* attack of Br^- ion on **20** and/or **22**. In addition to the given mechanisms, the formation of the products can be explained as described in the literature for strained olefin as occurring via classical carbocations **24** and **25** as given in Scheme 7. However, rather than unpreferred *exo* bromonium ion **20**, the intermediates **24** and **25** are more likely to be responsible for the formation of major product **15** from **10**.

The formation of the unexpected products **15** and **19** from the reaction of **11** can be explained a similar way. We assume that the first formed *endo* bromonium ion **26** is converted into the ion **27** which is responsible for the formation of the unexpected products **16** and **19**. This explains why all the *trans* tetrabromide **16** and all the *cis* tetrabromide **19** is formed by the bromination of *exo*-*cis* dibromide **11**. The formation of the tetrabromide **15** can be explained by the usual *trans* attack of Br^- on *endo* bromonium ion **26**. In addition to this assumption, formation of the *cis* addition products can be explained via classical carbocations **28** and **29**. Even so, the formation of **16** from **11** can be only explained as proceeding via **27**, since, in



Scheme 6



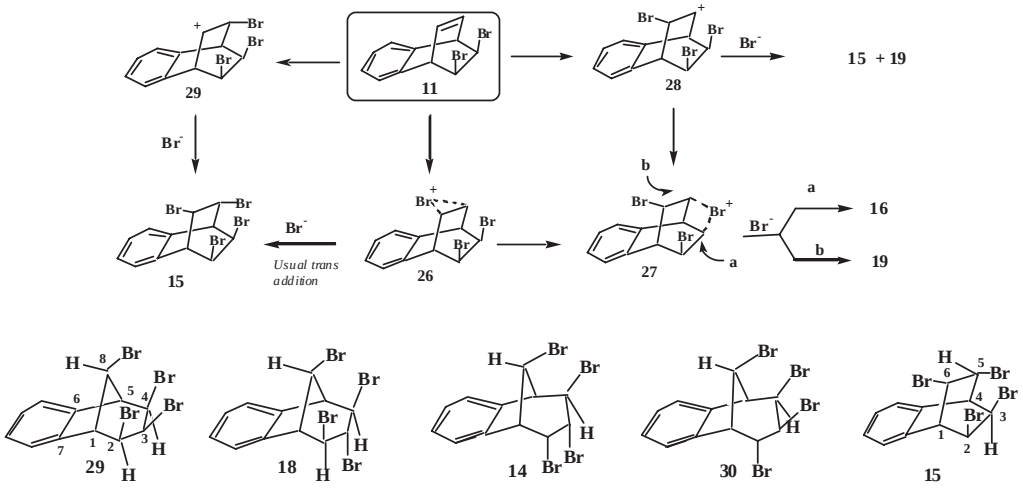
Scheme 7

addition to *cis* addition there is also an inversion in the other ethano bridge in this reaction (Scheme 8).

NMR spectral studies and configurational assignments

The structures of the compounds have been elucidated on the basis of ^{1}H and ^{13}C NMR spectroscopic data, extensive double resonance experiments and by comparison with some spectroscopic data of similar compounds and related systems reported in the literature.[3b,3f,10] In a previous study,[10] the tetrabromides **14**, **15**, **16** and **18** were obtained by a different route during the bromination of the isomeric 4,8-dibromo-6,7-benzobicyclo[3.2.1]octa-2,6-dienes and they were well characterised.

We have mainly used the coupling constants between the relevant protons to assign the correct configurations of the bromine atoms. For tetrabromide **14** and **18**, [3.2.1]octene systems, the coupling patterns that are important for stereochemical characterisation of the bromine atom at the C_8 carbon are the coupling constants between the bridge proton H_8 and the bridgehead protons H_1 and H_5 ($J_{1,8syn}$, $J_{5,8syn}$). As a consequence of the rigid geometries and reliability of the Karplus rule[11] in [3.2.1]octene systems,[3b,3f,10] the dihedral relationship of the H_1 proton to H_{8anti} (~40°), and to H_{8syn} (~80°) is sufficiently distinctive to be revealed by the magnitude of the spin-spin interaction. Thus, the high value of $J_{1(5)8anti}$ (J=4.0–5.0 Hz) is uniquely accommodated by the *syn*-orientation of the bromine atom bonded to the bridge carbon. Furthermore, the formation mechanism of this product requires the *syn*-orientation of the bromine atom at C_8. After determining the orientation of the bromine atom at the C_8 carbon, we turned our attention to the exact configuration of the remaining three bromine atoms in **14** and **18**. In the bicyclic systems, if the bonding arrangement of the protons meets the **W** or **M** criterion (as in the case of H_{8anti} and H_{2endo} and H_{4endo}) long-range couplings of a value of J=0.9–1.3 Hz are observed. The bridge proton H_8 in **18** resonates at 4.59 ppm as a triplet of triplets (J=4.2 and 1.1 Hz). The large coupling constant arises from the coupling with the vicinal bridgehead protons, whereas the smaller coupling (J=1.1 Hz) was assigned unambiguously to the long-range coupling with the protons H_2 and H_4 indicating the *exo* orientation of the bromine atoms in compound **18**. On the other hand, the existence of coupling between the H_4 and H_8 protons and the absence of any coupling between the H_2 and H_8 protons in compound **14** confirm the orientation of the protons at C_2 and C_4. In addition to this, compound **14** is asymmetric which gives 12 lines in ^{13}C NMR, whereas compound **18** is symmetric giving seven lines. There is one other possibility in each case (symmetric compound **29** and asymmetric compound **30**) matching these criteria. The symmetric isomer **29** may be eliminated immediately because of the *syn* orientation of the bulky bromine atoms. Furthermore, the observed large coupling, J=8.6 Hz between the protons H_2 and H_3, as well as between H_3 and H_4 in **18** is in complete agreement with



Scheme 8

the calculated dihedral angle of 152.25°.[10] The lack of vicinal coupling between the bridgehead protons (H_1 and H_5) and H_2 and H_4 is also in agreement with the calculated dihedral angle of 92.57°.[10] The observed coupling constants between related protons in asymmetric tetrabromide **14** also are in agreement with the calculated dihedral angles between the appropriate protons and exclude the other asymmetric tetrabromide **30**.[10]

For [2.2.2]octene systems symmetry elements and coupling constants are quite informative for determining the constitutions and conformations of compounds. Asymmetric tetrabromides **15** and **17** each give 12 lines in ^{13}C NMR whereas the tetrabromides **16** and **19** are symmetric and each give six lines.

The structural assignments of asymmetric tetrabromides **15** and **17** are accomplished by using coupling constants. The long distance coupling constant ($J_{3,5}$=1.8 Hz) in molecule **15** (**M** or **W** orientation) supports the tri *exo* structure **15**, whereas there are no long range couplings in the tri-*endo* structure **17**. In addition to these, in a [2.2.2] system typical[3f,3j] *cis* coupling constants (J=8.8±0.8) and *trans* coupling constants (J=4.5±0.9) are in agreement with proposed structures.

Characterisations of the symmetric tetrabromides **16** and **19** are possible by use of double resonance experiments. Irradiation of bridgehead protons converted the signals of CHBr protons into a singlet in tetrabromide **19**, whereas CHBr protons in compound **16** appear as a doublet after the irradiation of the bridgehead CH protons. *Cis* and *trans* coupling constants between CHBr protons are also in full agreement with proposed structures.

Conclusions

These results show that benzobarrelene systems tend to undergo skeletal rearrangements in bromination reactions. In addition to this, contrary to benzonorbornadiene systems such as **6** which forms only rearranged products, despite the bromine atom at 7-*anti* position, the steric effect of the *anti* substituent at the etheno bridge on benzobicyclo[2.2.2]octa-2,5-diene systems determines the reaction pathway. Skeletal rearrangement in bromination reactions is determined by the configuration of the initially formed bromonium ion. *exo* Bromonium ions are eligible for rearrangements by aryl shifts whereas *endo* bromonium ions give addition products without skeletal rearrangement. Steric hindrance at C_7 and/or C_8 carbons supports predominantly the formation of *endo* bromonium ions. In addition to this, the formation of unexpected products can be also explained by the formation of classical carbocations. The stereochemistry of bromine atoms in non-rearranged products is also controlled by neighbouring group effects in the bromination of benzobicyclo[2.2.2]octa-2,5-dienes systems.

Experimental

General: Melting points are uncorrected. Infrared spectra were obtained from solution in 0.1 mm cells or KBr pellets on a regular instrument. The ^1H and ^{13}C NMR spectra were recorded on 200 (50) MHz spectrometers. Apparent splitting is given in all cases. Column chromatography was performed on silica gel (60-mesh, Merck). TLC was carried out on Merck 0.2 mm silica gel 60 F_{254} analytical aluminum plates. All substances reported in this paper are in their racemic form.

CAUTION: It has been reported[12] that of three laboratory workers who have used dibromides and a bromohydrin derived from norbornadiene, two later developed similar pulmonary disorders, which contributed to their subsequent deaths. The third exhibited minor skin sensitivity reactions. In the case of dibromides derived from benzonorbornadiene there is no report in the literature about the toxicological effects. However, we recommend that the compounds must be handled only with extreme caution.

Bromination of endo,endo-7,8-dibromo-5,6-benzobicyclo[2.2.2]octa-2,5-diene **(9)**: To a magnetically stirred solution of **9** (314 mg, 1 mmol) in dry $CHCl_3$ (15 ml) at –45±5 °C was added dropwise a cold solution of bromine (165 mg, 1.03 mmol) in $CHCl_3$ (2 ml). The reaction temperature was continuously checked by an internal thermometer. After 30 min at –45±5 °C, the solvent was evaporated and tetrabromide **14**[10] was obtained as sole product. *2,3-diendo-4-exo-8-syn-tetrabromo-6,7-benzobicyclo[3.2.1] oct-6-ene* **(14)**[10]: (474 mg, 100%, m.p. 145–146 °C, colourless crystals from methylene chloride/ *n*-hexane (1:1) lit.[10] m.p. 145–146 °C. IR (KBr, cm^{-1}): 3076, 2974, 2962, 1458, 1302, 1250, 1218, 1208, 1175, 1153, 890, 779. ^1H NMR (200 MHz, $CDCl_3$): 7.49–7.30 (m, 4 H-aryl), 5.39 (bdd, $J_{2,3}$=5.6 Hz, $J_{1,2}$=2.0 Hz, 1H, 1 H-C(2)), 5.05 (m, 1 H-(C4)), 4.85 (bd, $J_{2,3}$=5.6 Hz, 1 H-(C3)), 4.72 (dt, $J_{1,8}$=$J_{5,8}$=4.6 Hz, $J_{4,8}$=1.4 Hz, 1 H-(C8)), 3.75 (dd, $J_{5,8}$=4.6 Hz, $J_{4,5}$=2.6 Hz, 1 H-(C5)), 3.61(dd, $J_{1,8}$=4.6 Hz, $J_{1,2}$=2.0 Hz, 1 H-(C1)). ^{13}C NMR (50 MHz, $CDCl_3$): 142.01, 139.50, 129.72, 129.63, 126.38, 124.21, 53.81, 52.45, 52.31, 49.28, 48.67, 45.90. [Found: C, 30.6; H, 2.15 $C_{12}H_{10}Br_4$ requires C, 30.4; H, 2.1 %].

Bromination of exo,endo-7,8-dibromo-5,6-benzobicyclo[2.2.2]oct-2,5-diene (**10**): The reaction was carried out as described according to general procedure by using dibromide **10** (314 mg, 1 mmol) and $CHCl_3$ (17 ml). The solvent was evaporated and the residue was subjected to silica gel (90 g) chromatography eluting with *n*-hexane.

The first fraction: *2,5-diexo-3,6-diendo-tetrabromo-7,8-benzobicyclo[2.2.2]oct-7-ene* (**16**)[10]: (57 mg, 12%, m.p. 132–133 °C, colourless crystals from methylene chloride/ *n*-hexane (1:1) lit.[10] m.p. 132–133 °C. IR (KBr, cm^{-1}): 3062, 3040, 2972, 1480, 1460, 1450, 1330, 1310, 1270, 1230, 1182, 1152, 930, 813. ^1H NMR 7.46–7.27 (AA'BB' system, 4 H-aryl), 4.98 (dd, $J_{2,3}$=$J_{5,6}$=4.4 Hz, $J_{1,2}$=$J_{4,5}$=2.3 Hz, 2 H-(C2) and H-(C5)), 4.21 (dd, $J_{2,3}$=$J_{5,6}$=4.4 Hz, $J_{3,4}$=$J_{1,6}$=3.1 Hz, 2 H-(C3) and H-(C6)), 3.44 (dd, $J_{3,4}$=$J_{1,6}$=3.1 Hz, $J_{1,2}$=$J_{4,5}$=2.3 Hz, 2 H-(C1) and H-(C6)). ^{13}C NMR (50 MHz, $CDCl_3$): 135.10, 129.51, 127.16, 56.56, 53.28, 50.44. [Found: C, 30.3; H, 2.1 $C_{12}H_{10}Br_4$ requires C, 30.4; H, 2.1 %].

The second fraction: *2,4-diexo-3-endo-8-syn-tetrabromo-6,7-benzobicyclo[3.2.1]oct-6-ene* **(18)**[10]: (76 mg, 16%, m.p. 195–196 °C, colourless crystals from chloroform/*n*-hexane (1:2). lit.[10] m.p. 195–196 °C. IR (KBr, cm^{-1}): 3043, 3004, 2977, 1471, 1465, 1330, 1251, 1151, 1059, 1041, 863, 839, 775, 731. ^1H NMR (200 MHz, $CDCl_3$): 7.33–7.27 (AA'BB' system, 4 H-aryl), 5.56 (t, $J_{2,3}$=$J_{3,4}$=8.6 Hz, 1 H-(C3)), 4.59 (tt, $J_{1,8}$=$J_{5,8}$=4.2 Hz, $J_{2,8}$=$J_{4,8}$=1.1 Hz, 1 H-(C8)), 4.32 (dd, $J_{2,3}$=$J_{3,4}$=8.6 Hz, $J_{2,8}$=$J_{4,8}$=1.1 Hz, H-(C2) and H-(C4)), 4.32 (d, $J_{1,8}$=$J_{5,8}$=4.2 Hz, 2 H-(C1) and H-(C5)). ^{13}C NMR (50 MHz, $CDCl_3$): 143.50, 130.25, 123.94, 58.23, 54.05, 52.93, 45.33. [Found: C, 30.5; H, 2.15 $C_{12}H_{10}Br_4$ requires C, 30.4; H, 2.1 %].

The third fraction: *2,3,5-triexo-6-endo-tetrabromo-7,8-benzobicyclo[2.2.2]oct-7-ene* **(15)**[10]: (300 mg, 63%, m.p. 133–134 °C, colourless crystals from methylene chloride/ *n*-hexane (1:1) lit.[10] m.p. 133–134 °C. IR (KBr, cm^{-1}): 3070, 3042, 3025, 2982, 2945, 1477, 1460, 1288, 1257, 1245, 1181, 1100, 1019, 950, 856, 849, 758, 750. ^1H NMR (200 MHz, $CDCl_3$)**:** 7.40–7.19 (m, 4H, H-aryl), 5.25 (dd, $J_{5,6}$=5.4 Hz, $J_{1,6}$=2.1 Hz, 1 H-(C6)), 4.64 (dd, A part of AB system, $J_{2,3}$=9.6 Hz, $J_{1,2}$=2.9 Hz, 1 H-(C2)), 4.46 (dt, B part of AB system, $J_{2,3}$=9.6 Hz, $J_{3,4}$=$J_{3,5}$=1.8 Hz, 1 H-(C3)), 4.12 (bd, $J_{5,6}$=5.4 Hz, 1 H-(C5)), 3.68 (m, 2 H-(C1) and H-(C4)).^{13}C NMR (50 MHz, $CDCl_3$): 139.82, 135.17, 129.64, 129.54, 127.92, 124.34, 53.19, 52.93, 52.54, 51.59, 50.08, 45.92. [Found: C, 30.2; H, 2.1 $C_{12}H_{10}Br_4$ requires C, 30.4; H, 2.1 %].

The fourth fraction: *2,3,6-triendo-5-exo-tetrabromo-7,8-benzobicyclo[2.2.2]oct-7-ene* **(17)**: (28 mg, 6%, m.p. 176–176.5 °C, colourless crystals from chloroform/*n*-hexane (1:1); IR (KBr, cm^{-1}): 3040, 3005, 2960, 1445, 1320, 1235, 1148, 850, 715. ^1H NMR (200 MHz, $CDCl_3$): 7.48–7.28 (m, 4 H-aryl), 5.18 (dd, A part of AB system, $J_{2,3}$=8.5, $J_{3,4}$=2.2, 1 H-C(3)), 4.78 (dd, B part of AB system, $J_{2,3}$=8.5, $J_{1,2}$=2.4, 1 H-C(2)), 4.46 (dd, $J_{5,6}$=3.8, $J_{1,6}$=2.4, 1 H-C(6)), 4.19 (dd, $J_{5,6}$=3.8, $J_{4,5}$=2.8, 1 H-C(5)), 3.64 (dd, $J_{4,5}$=2.8, $J_{3,4}$=2.2, 1 H-C(4)), 3.62 (t, $J_{1,2}$= $J_{1,6}$=2.4, 1 H-C(1)).^{13}C NMR (50 MHz, $CDCl_3$): 135.2, 133.3, 129.2, 129.1, 129.0, 127.2, 55.8, 53.1, 52.7, 52.6, 49.6, 47.4. [Found: C, 30.5; H, 2.2 $C_{12}H_{10}Br_4$ requires C, 30.4; H, 2.1 %].

Bromination of exo,exo-7,8-dibromo-5,6-benzobicyclo[2.2.2]oct-2,5-diene **(11)**: The reaction was carried out as described according to general procedure by using 314 mg (1 mmol) of dibromide **11** and $CHCl_3$ (17 ml) for 50 min. The solvent was evaporated and the residue was subjected to silica gel (90 g) chromatography eluting with *n*-hexane.

The first fraction: 2,5-diexo-3,6-diendo-tetrabromo-7,8-benzobicyclo[2.2.2]oct-7-ene **(16)**[10]: (66 mg, 14%).

The second fraction: 2,3,5-triexo-6-endo-tetrabromo-7,8-benzo-bicyclo[2.2.2]oct-7-ene **(15)**[10]: (90 mg, 19%).

The third fraction: *2,3-diexo-5,6-diendo-tetrabromo-7,8-benzo-bicyclo[2.2.2]oct-7-ene* **(19)**: (308 mg, 65%, m.p. 243–245 °C, colourless crystals from chloroform/*n*-hexane (1:1); IR (KBr, cm^{-1}): 3060, 3036, 3016, 2973, 2957, 1466, 1458, 1234, 1198, 765.; ^{1}H NMR (200 MHz, $CDCl_3$): 7.43–7.28 (AA'BB' system, 4H, aryl), 5.31 (m, 2 H-C(5)) and H-C(6)), 4.44 (m, 2 H-C(2)) and H-C(3)), 3.70 (m, 2 H-C(1)) and H-(C4)). ^{13}C NMR (50 MHz, $CDCl_3$): 136.2, 129.2, 127.5, 53.1, 51.4, 48.6. [Found: C, 30.3; H, 2.1 $C_{12}H_{10}Br_4$ requires C, 30.4; H, 2.1 %].

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