High temperature bromination of benzobicyclo[2.2.2]octa-2,5-diene derivatives: alternative synthesis of di-, tri- and tetra-bromobenzobarrelenes

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The electrophilic bromination of benzobarrelene derivatives has been studied and alternative synthetic methods developed for, di-, tri- and tetrabromobenzobarrelenes.

Keywords: benzobarrelene, bromination, Wagner–Meerwein rearrangement and polybromides

Benzobarrelene systems afford the possibility of several mechanistically interesting investigations. These compounds are intriguing compounds in view of the di-π-methane rearrangement,[1,2] their solvolytic reactivity[3,4] and their versatile purposes.[5-8] In view of this aspect substituted benzobarrelene derivatives are important compounds that can provide information about how the substituents will influence reaction path ways.[9,10]

A halogen derivative of a compound is useful because it is a key for synthesising other derivatives. For example, *di-*, *tri-* and *tetra-* bromobenzobarrelenes (**1**, **2**, **3** and **4**) have been synthesised by Balci and coworkers,[11-15] and by us[16] and these compounds have been used for various purposes.[9,10,17-19] Therefore, short and efficient syntheses of these compounds are important. In this paper, the bromination of benzobarrelene derivatives was investigated and new synthetic methods for the preparation of 2,6-dibromobenzobarrelene (**1**), 2,5-dibromobenzobarrelene (**2**), 2,3,5-tribromobenzobarrelene (**3**) and 2,3,5,6-tetrabromobenzobarrelene (**4**), which are synthons for the synthesis of other derivatives, are reported.†

Results and discussion

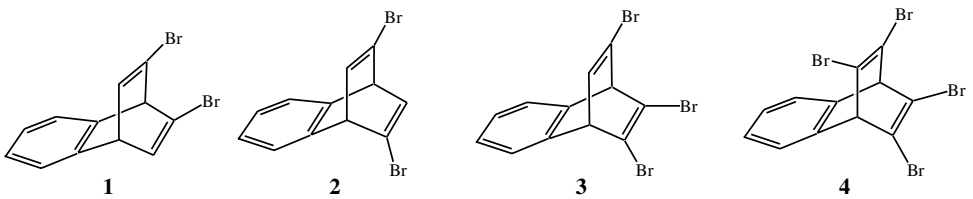
Previously, we showed that[20] the bromination of the *endo-cis* dibromide **5** at -45±5 °C results in the formation of only one rearranged product **6**. In the course of studying the bromination reaction it was noticed that the reaction temperature has a dramatic influence on the product distribution. Increasing the temperature gives *non*-rearranged reaction products.[21-28] This factor encouraged us to raise the bromination temperature higher in order to obtain the *non*-rearranged bromination products derived from **5**. For the high-temperature bromination reaction, a hot solution of bromine in CCl_4 was added directly to a refluxing solution of **5** in CCl_4. NMR analysis of the crude product indicated that the reaction mixture consisted mainly of four products. After column chromatography, three isomeric *non*-rearranged dibromides **7** (76%), **8** (10%), **9** (7%) and one rearranged product **6** (6%) were isolated (Scheme 2).

Bromination of *trans*-dibromide **10** at –45±5 °C in $CHCl_3$ gives rearranged **14** (16%) and *non*-rearranged products **7**, **11** and **13** (total 81%).[20] Formation of rearranged product **14** was not welcome because on the way to dibromobenzobarrelenes **1** and **2**, all steps were contaminated with this substance which was too similar to the products to be easily separated. In the experiments that followed, we aimed to minimise formation of **14**. For this reason, the reaction was carried out at a higher temperature and only the *non*-rearranged products **7**, **11** and **12** were obtained (Scheme 3).

Bromination of the *exo cis*-dibromide **15** at –45±5 °C gives only the desired *non*-rearranged products **8**, **11** and **13**.[20] However, we were also interested in high temperature bromination of **15** to compare the results obtained from the bromination of dibromides **5** and **10**. The reaction of **15** with bromine carried out at 77 °C in CCl_4 gave only two *non*-rearranged products **8** and **13**.

Comparing the result of the three isomeric compounds **5**, **10** and **15** both in low and high temperature bromination we can say that the *exo cis*-dibromide **15** does not have a tendency to rearrange because bromination of this compound even at –45±5 °C gives only the *non*-rearranged products **8**, **11** and **13**. Contrary to this isomer, *endo cis*-dibromide **5** behaves differently in the bromination reaction i.e bromination of **5** even at 77 °C did not completely prevent rearrangement and rearranged tetrabromide **6** was also formed. It is also clear that the behaviour of the *trans*-dibromide **10** towards to bromination is between the *exo* and *endo-cis* dibromides as described in Table 1.

We accomplished the syntheses of tetrabromides **7**, **8**, **9**, **11** and **13** with the [2.2.2] skeleton in high yield by using high temperature bromination of dibromides **5**, **10** and **15**. These compounds give us a new synthetic way for dibromobenzobarrelenes **1** and **2** by HBr elimination of a mixture of tetrabromides **7**, **8**, **9**, **11** and **13**. However, we also carried out the elimination of these compounds using pure samples to learn which isomer is suitable for the synthesis of which kind of dibromobenzobarrelenes **1** and **2**. Scheme **5** shows that tetrabromide **11** is suitable to obtain dibromides **1**, whereas the tetrabromide **8** is suitable for dibromide **2**. However, the formation of the mixtures from elimination reactions is not a serious problem because the mixture can be separated simply by way of fractional crystallisation as described in the literature.[14]



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

Scheme 1

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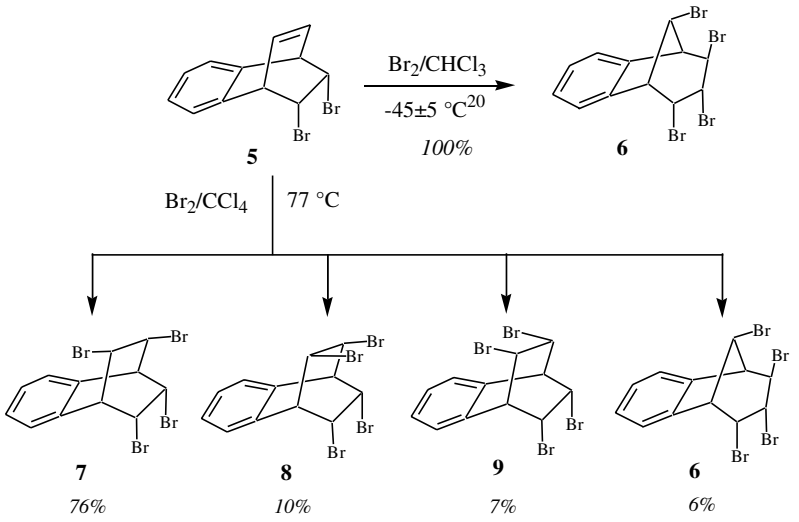
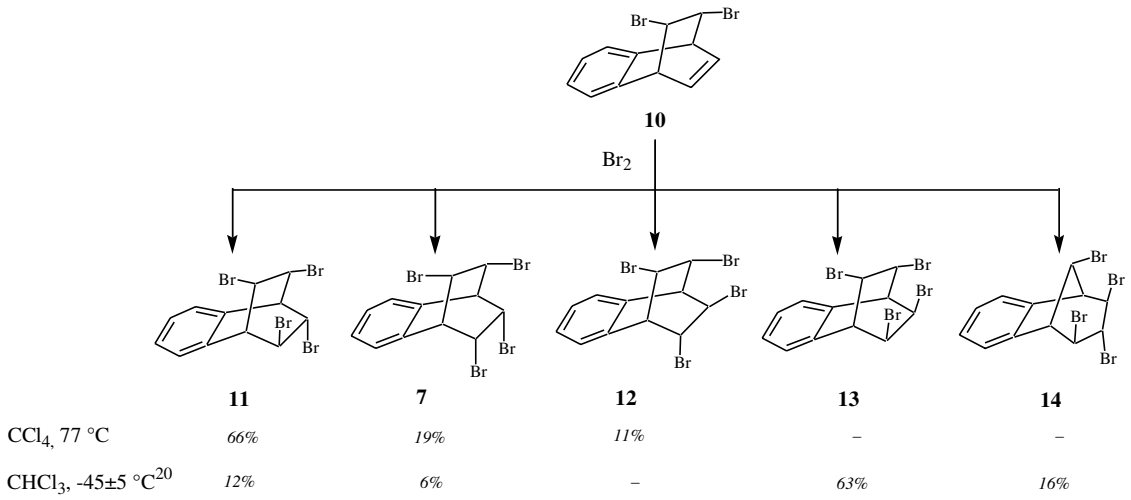
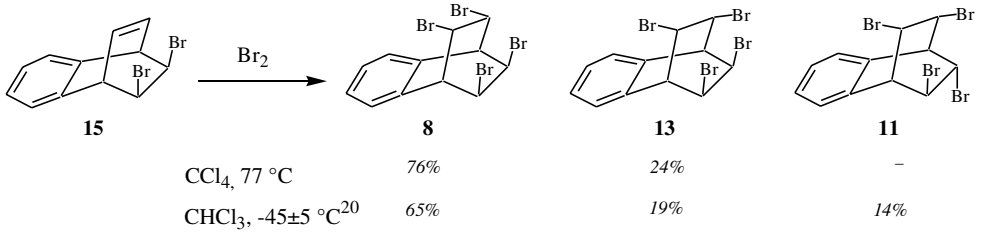
† See Caution in Experimental Section.



Scheme 2

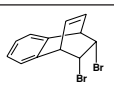
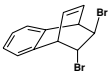
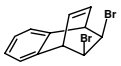


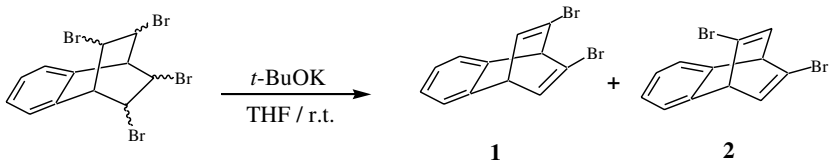
Scheme 3



Scheme 4

Table 1 Reaction conditions

$CHCl_3$, 44±5 °C		Molecules	CCl_4, 77 °C	
Amount of rearranged products/%	Amount of non -rearranged products/%		Amount of non-rearranged products/%	Amount of non-rearranged products/%
100	–		6	94
16	84		–	100
–	100		–	100



Tetrabromide	1	2
7	58%	34%
8	28%	66%
9	81%	12%
11	82%	9%
13	71%	22%

Scheme 5

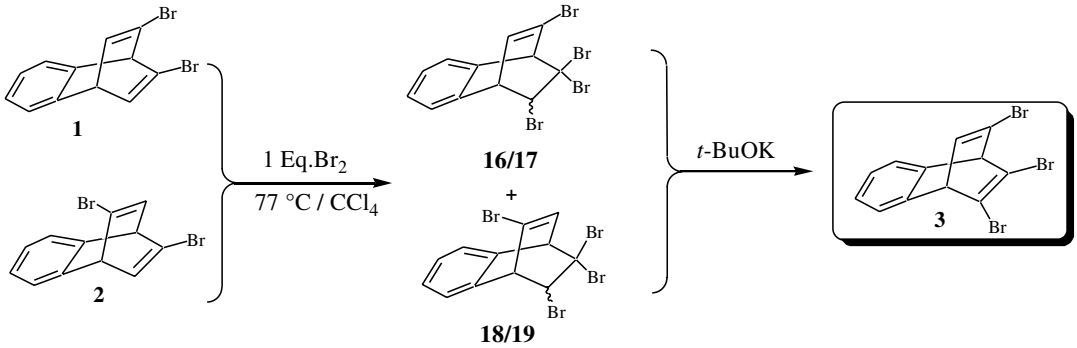
After obtaining dibromo benzobarrelenes **1** and **2**, we turned our direction to the synthesis of tribromobenzobarrelene **3** the chemistry of which is still unexplored. Reaction of the mixture of dibromides **1** and **2** with one equivalent of bromine at 77 °C gives *non*-rearranged products **16–19** in high yields. The mixture was not separated but directly underwent elimination.

From the elimination reaction of a mixture of **16–19** tribromobenzobarrelene **3** was obtained in high yield. These routes allow us an alternative synthetic pathway to tribromobenzobarrelene **3** which is open to several investigations and other trisubstituted benzobarrelenes. Independently, we also carried out the bromination of pure dibromide **1** to characterise two of the formed products. From this reaction tetrabromides **18** and **19** were isolated and characterised by spectroscopic methods.

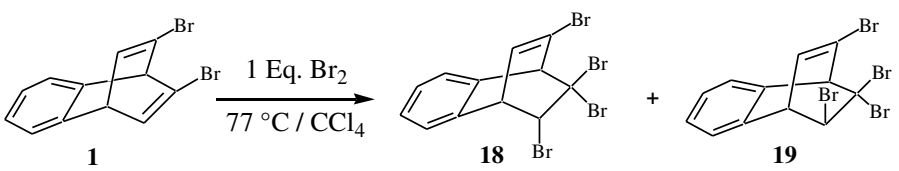
During the bromination of dibromobenzobarrelenes **1** and **2**, both at high temperature and at low temperature, the fact that only one mole of bromine is absorbed is advantageous because this allows us selectively to synthesise tribromobenzobarrelene **3**. In addition to this, as compounds **1** and **2** have two double bonds further or two equivalent bromination of these compounds is possible to obtain the starting material tetrabromobenzobarrelene **4**. To this end the reaction of dibromides **1** and **2** with two equivalents of bromine was also investigated. After a long time reaction followed by elimination of the product mixtures tetrabromide **4** was obtained in a moderate yield (for two step total yield is 58%). This reaction allows us an alternative synthetic way for tetrabromobenzobarrelene **4**. However, expected good yields could not be obtained from these reactions because of difficulties in the reaction of dibromides **1** and **2** with bromine. This difficulty was attributed to steric crowding in the products **20** and **21** (six bulky bromine atoms in the molecule) and decreasing reactivity of the double bonds in molecules **1** and **2** because of the electronegative bromine atoms. Instead of route A (overall yield 58%) we can say that route B (overall yield 81%), even though it has one more step, is preferred to form tetrabromide **4** (Scheme 8). Balci *et al.*[15] obtained the tetrabromide **4** from tribromide **3** in 90% yield.

NMR spectroscopic studies and configurational assignments on benzobicyclic [2.2.2]octene systems

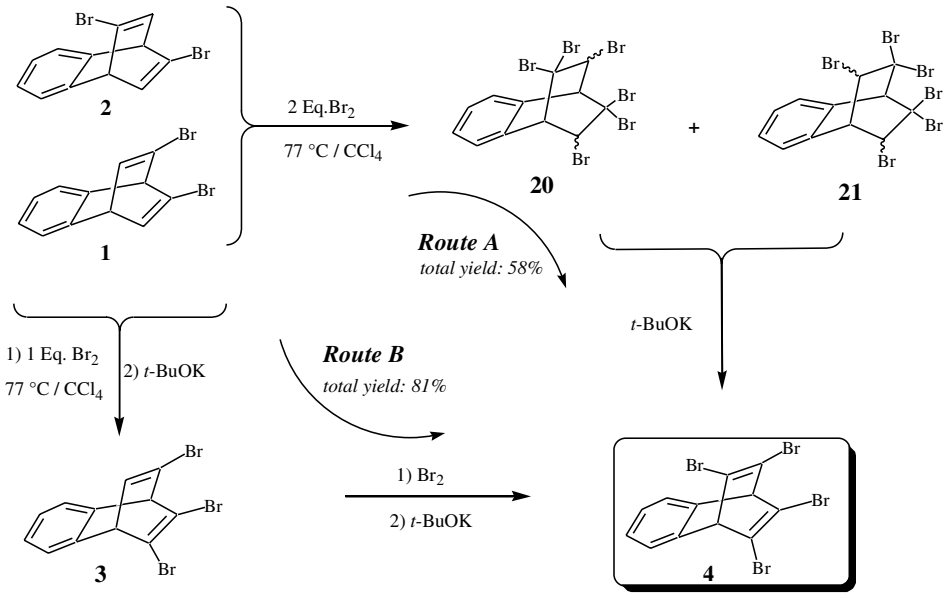
The structure of these compounds have been elucidated on the basis of ^{1}H and ^{13}C NMR spectroscopic data, extensive double resonance experiments and by comparison of some spectroscopic data of related systems reported in the literature.[28-31] ^{13}C NMR spectra of all the tetrabromides with a [2.2.2] skeleton, gives information about the structures. Five lines in the ^{13}C NMR spectra indicate only



Scheme 6



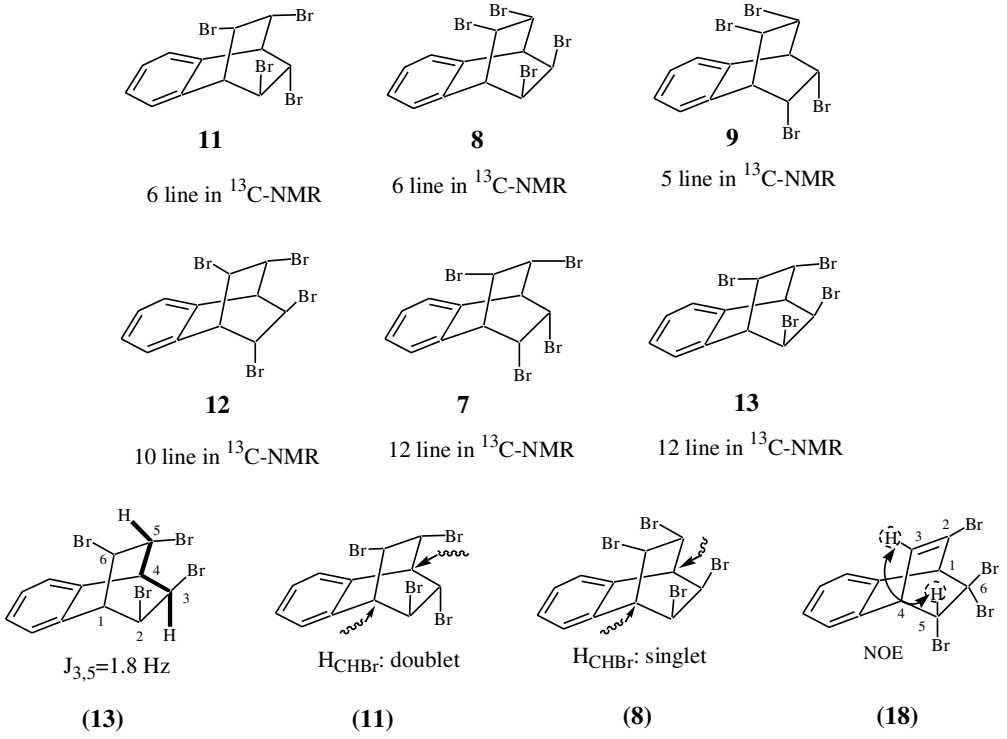
Scheme 7



Scheme 8

the fully symmetric tetrabromide **9**, and 10 lines in the ^{13}C NMR spectra indicate the structure of **12**. Asymmetric tetrabromides **7** and **13** give 12 lines in ^{13}C NMR. However, structural analyses of these compounds are accomplished by using ^{1}H NMR spectroscopy. The long distance coupling constant ($J_{3,5}$=1.8 Hz) in molecule **13** (M or W orientation) indicates the tri-*exo* structure **13**, whereas there are no long range couplings in the tri-*endo* structure **7**. Symmetric tetrabromides **8** and **11** also give 6 lines in ^{13}C NMR. Characterisations of these compounds are possible by using double resonance experiments. Irradiation of the bridgehead protons converted the signals of the CHBr protons into a singlet in tetrabromide **8**, whereas the CHBr protons in compound **11** appear as doublets after the irradiation of the CH protons. In addition to these, in a [2.2.2] system typical *cis* coupling constants[28,29] (J=8.8±0.8) and *trans* coupling constants (J=4.5±0.9) are in agreement with the proposed structures. Structural analyses of isomeric tetrabromides **18** and **19** were carried out by NOE-diff experiments. Differential ^{1}H NMR-NOE measurements support the orientation of the proton at C_3 atom in molecule **18**. Irradiation of the CHBr (H_5) proton caused enhancement of the signals of bridgehead proton (H_4) and double bond proton (H_3) in molecule **18**. The spectroscopic experiments are in agreement with the proposed structures (Scheme 9).

In summary, the electrophilic bromination of benzobarrelene derivatives was studied and alternative synthetic methodology for the preparation of di- **1/2**, tri- **3** and tetrabromo-**4** benzobarrelene has been developed.



Scheme 9

Experimental

General: Melting points are uncorrected. IR spectra were obtained from solution in 0.1 mm cells or KBr pellets on a standard 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[32] 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 dibromide derived from benzonorbornadiene there is no report in the literature about the toxicological effect. However, we recommend that the compounds must be handled only with extreme caution.

Carbon tetrachloride is also toxic and environmental unfriendly. Therefore, personal and environmental precautions must be taken.

Bromination of endo,endo-7,8-dibromo-5,6-benzobicyclo[2.2.2]octa-2,5-diene (**5**) *at 77 °C:* 314 mg (1.0 mmol) of dibromide **5** was dissolved in 15 ml of carbon tetrachloride in a 25 ml flask, which was equipped with a reflux condenser. The solution was heated until carbon tetrachloride started to reflux while stirring magnetically. To the refluxing solution was added dropwise a hot solution of bromine (165 mg, 1.03 mmol) in 5 ml of carbon tetrachloride during 3 min. The resulting reaction mixture was heated for 40 min at reflux temperature. After being cooled to room temperature the solvent was evaporated and the oily residue was chromatographed on silica gel (130 g) eluting with *n*-hexane to give four products. The first fraction was the mixture of tetrabromide **7** [20] (360 mg, 76%) and tetrabromide **6**[31] (28 mg, 6%). The second fraction was tetrabromide **8**[20] (47 mg, 10%). The last fraction was: *2,3,5,6-tetraendo-tetrabromo-7,8-benzobicyclo[2.2.2]oct-7-ene* (**9**): (33 mg, 7%), m.p. 214–215 °C, colourless crystals from chloroform ^1H NMR (200 MHz, $CDCl_3$): 7.33–7.20 (AA'BB' system, 4H, H_{aryl}), 4.57 (m, 4H, H_2, H_3, H_5 and H_6), 3.89 (m, 2H, H_1 and H_4). ^{13}C NMR (50 MHz, $CDCl_3$): 140.04, 129.54, 125.08, 49.42, 46.71. IR (KBr, cm^{-1}): 3075, 3008, 2984, 1458, 1286, 1259, 1250, 1216, 1270, 1010, 900, 838. [Found: C, 30.4; 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]octa-2,5-diene (**10**) *at 77 °C:* The reaction was carried out as described according to the general procedure by using 314 mg (1.0 mmol) of dibromide **10** and CCl_4 (20 ml). The solvent was evaporated and the residue was subjected to silica gel (90 g) chromatography eluting with *n*-hexane. The first fraction was tetrabromide **11** (313 mg 66%) and the second fraction was a mixture of tetrabromide **7** (90 mg, 19%) and the tetrabromide **12** (52 mg, 11%). The mixture was separated by fractional crystallisation. Firstly, tetrabromide **7**[20] was crystallised from methylene chloride/ *n*-hexane (1:1). After filtration of **7**, the solvent was evaporated and the residue was crystallised from methylene chloride/ *n*-hexane (1:4) in a refrigerator to give tetrabromide **12**.

2,6-diendo-3,5-diexo-tetrabromo-7,8-benzobicyclo[2.2.2]-oct-7-ene **(12):** (43 mg crystal, 9 mg, mixture, 11%, m.p. 138–139 °C, colourless crystals from methylene chloride/ *n*-hexane (1:4); ^1H NMR (200 MHz, $CDCl_3$): 7.45–7.20 (m, 4H, aryl), 4.68 (dd, $J_{2,3}$=$J_{5,6}$=4.6, $J_{1,2}$=$J_{1,6}$=2.3, 2H, H_2 and H_6), 4.12 (dd, $J_{2,3}$=$J_{5,6}$=4.6, $J_{3,4}$=$J_{4,5}$=2.4, 2H, H_3 and H_5) 3.66 (t, $J_{3,4}$=$J_{4,5}$=2.4, 1H, H_4) 3.57 (t, $J_{1,2}$=$J_{1,6}$=2.3, 1H, H_1). ^{13}C NMR (50 MHz, $CDCl_3$): 138.78, 132.47, 129.51(2C), 129.38, 124.10, 53.28 (2C), 51.55, 50.06. IR (NaCl film, cm^{-1}): 3021, 2953, 2922, 2857, 1698, 1480, 1460, 1452, 1301, 1268, 1241, 1171, 938, 756. [Found: C, 30.5; H, 2.1 $C_{12}H_{10}Br_4$ requires C, 30.4; H, 2.1 %].

Bromination of exo,exo-7,8-dibromo-5,6-benzobicyclo[2.2.2]octa-2,5-diene **(15)** *at 77 °C:* The reaction was carried out as described according to general procedure by using 314 mg (1.0 mmol) of dibromide **15** and CCl_4 (20 ml). The solvent was evaporated and ^1H NMR analyses of the residue showed that tetrabromide **8**[20] (360 mg, 76%) and tetrabromide **13**[31] (114 mg, 24%) were formed.

Tetrabromide	Products	
	2,6-dibromo-benzobarrelene (**1**)	2,5-dibromobenzo-barrelene (**2**)
7	58%	34%
8	28%	66%
9	81%	12%
11	82%	9%
13	71%	22%

General procedure for elimination of tetrabromides **7/8/9/11/13:** To a stirred solution of tetrabromides (either pure or mixture) (400 mg, 0.84 mmol) in dry and freshly distilled THF (20 ml) was added (196 mg 1.75 mmol) of potassium butoxide solution in THF (6 ml). The resulting reaction mixture was stirred overnight at r.t. The solvent was evaporated and the mixture was diluted with water and the aqueous solution was extracted with ether (3 × 50 ml), washed with water, and dried over $MgSO_4$. After removal of the solvent, the residue was separated by fractional crystallisation. Firstly, dibromide **2** was crystallised from methylene chloride/ *n*-hexane (1:4). After filtration of **2**, the solvent was evaporated and the residue was crystallised from methylene chloride/ *n*-pentane (1:6) in a refrigerator to give tetrabromide **1**. Yields were given below for each reaction.

2,5-dibromobenzobarrelene **(2)**: Colourless crystals from methylene chloride/ *n*-hexane (1:4). (m.p. 172 °C, lit.[14] m.p. 172–173 °C). ^1H NMR (200 MHz, $CDCl_3$): 7.28–6.98 (AA'BB'system, 4H, aryl), 6.92 (dd, $J_{3,4}$=$J_{1,6}$=6.3, $J_{1,3}$=$J_{4,6}$=2.4, 2H, H_3 and H_6), 4.77 (dd, $J_{3,4}$=$J_{1,6}$=6.3, $J_{1,3}$=$J_{4,6}$=2.4, 2H, H_1 and H_4). ^{13}C NMR (50 MHz, $CDCl_3$): 144.94, 136.75, 132.89, 125.12, 123.23, 59.65. IR (KBr, cm^{-1}): 3010, 2980, 1610, 1460, 1450, 1260, 1250, 1240, 1130.

2,6-dibromobenzobarrelene **(1):** Colourless crystals from methylene chloride/ *n*-pentane (1:6). (m.p. 105 °C, lit.[14] m.p. 101 °C). ^1H NMR (200 MHz, $CDCl_3$): 7.35–6.95 (m, 4H, aryl), 6.87 (dd $J_{3,4}$=$J_{4,5}$=6.3, $J_{1,3}$=$J_{1,5}$=2.1, 2H, H_3 and H_5), 4.80 (m, 2H, H_1 and H_4). ^{13}C NMR (50 MHz, $CDCl_3$): 145.06, 144.88, 137.28, 131.45, 125.59, 124.64, 123.63, 122.87, 66.74, 51.74. IR (KBr, cm^{-1}): 3070, 2980, 1580, 1460, 1450, 1260, 1200, 1190, 1130, 1090, 985.

Bromination of **1** *and* **2** *with 1 equivalent bromine and synthesis of 2,3,5-tribromobenzobarrelene* **(3):** A mixture of dibromides **1** and **2** (1.0 g (3.2 mmol) was dissolved in 15 ml of carbon tetrachloride in a 50 ml flask, which was equipped with a reflux condenser. The solution was heated until carbon tetrachloride started to reflux while stirring magnetically. To the refluxing solution was added dropwise a hot solution of bromine (589 mg, 3.68 mmol) in 5 ml of carbon tetrachloride during 5 min. The resulting reaction mixture was heated for 30 min at reflux temperature. After being cooled to room temperature the solvent was evaporated and the oily residue (1.51 g) was dissolved in dry and freshly distilled THF (20 ml). To this solution was added 540 mg (4,82 mmol) of potassium *tert*-butoxide solution in THF (6 ml). The resulting reaction mixture was stirred for overnight at r.t. The solvent was evaporated and the mixture was diluted with water and the aqueous solution was extracted with ether (3 × 50 ml), washed with water, and dried over $MgSO_4$. After removal of the solvent, the residue was filtered on a short silica gel column (10 g) eluted with *n*-hexane to give 1.16 g (93%) of tribromide **3** as the sole product.

2,3,5-tribromobenzobarrelene **(3):** Colourless crystals m.p. 178–179 °C from methylene chloride /*n*-hexane (1:2). (Lit.[15] m.p. 178–179 °C) ^1H NMR (200 MHz, $CDCl_3$) δ 7.37–7.03 (m, aromatic, 4H), 6.94 (dd, $J_{1,6}$=6.3, $J_{4,6}$=2.2 Hz, 1H, H_6), 4.92 (d, $J_{4,6}$=2.2 Hz, 1H, H_4), 4.91 (d, $J_{1,6}$=6.3 Hz, 1H, H_1), ^{13}C NMR (50 MHz, $CDCl_3$) 145.18, 145.12, 138.17, 132.91, 131.94, 130.32, 127.48, 126.99, 125.14, 124.74, 68.91, 61.65. IR (KBr, cm^{-1}): 3080, 3020, 1610, 1590, 1460, 1455, 1450, 1260, 1225, 1190, 1140, 1060, 980, 850, 977.

Bromination of **1** *at 77 °C:* The reaction was carried out as described according to general procedure by using 312 mg (1.0 mmol) of dibromide **1** and CCl_4 (15 ml). After 20 min, the solvent was evaporated and the oily residue was chromatographed on silica gel (60 g) eluting with *n*-hexane.

The first fraction: *exo-2,5,6,6-Tetrabromo-7,8-benzobicyclo-[2.2.2]octa-2,7-diene* **(19):** (241 mg, 51%, m.p. 81–82 °C, colourless crystals from methylene chloride/ *n*-hexane (1:4); ^1H NMR (200 MHz, $CDCl_3$): 7.42–7.17 (m, 4H, aryl), 6.78 (dd, $J_{3,4}$=6.5, $J_{1,3}$=1.8, 1H, H_3), 4.85 (d, $J_{1,3}$=1.8, 1H, H_1), 4.67 (d, $J_{4,5}$=2.1, 1H, H_5), 4.27 (dd, $J_{3,4}$=6.5, $J_{4,5}$=2.1, 1H, H_4). ^{13}C NMR (50 MHz, $CDCl_3$): 140.16, 133.30, 130.12, 129.21, 128.71, 127.07, 126.43, 70.05, 66.12, 62.88, 54.35. IR (NaCl film, cm^{-1}): 3018, 2940, 2918, 2853, 1604, 1471,

1458, 1258, 1215. [Found: C, 30.4; H, 1.7 $C_{12}H_{10}Br_4$ requires C, 30.55; H, 1.7 %].

The second fraction: *endo-2,5,6,6-Tetrabromo-7,8-benzobicyclo-[2.2.2]octa-2,7-diene* **(18):** (189 mg, 40%, m.p. 142–143 °C, colourless crystals from methylene chloride/ *n*-hexane (1:1); ^{1}H NMR (200 MHz, $CDCl_3$): 7.39–7.22 (m, 4H, aryl), 6.77 (dd, $J_{3,4}$=6.6, $J_{1,3}$=1.8, 1H, H_3), 5.06, (bd, $J_{4,5}$=1.8, 1H, H_5), 4.86 (d, $J_{1,3}$=1.8, 1H, H_1), 4.14, (dd, $J_{3,4}$=6.6, $J_{4,5}$=1.8, 1H, H_4). ^{13}C NMR (50 MHz, $CDCl_3$): 138.59, 135.20, 134.13, 128.17, 127.43, 127.16, 127.10, 126.59, 68.31, 64.29, 61.32, 52.54. IR (KBr, cm^{-1}): 3040, 3020, 2970, 1593, 1451, 1310, 1280, 1262, 1170, 1161, 1094, 1011, 978, 748. [Found: C, 30.5; H, 1.7 $C_{12}H_{10}Br_4$ requires C, 30.55; H, 1.7 %].

Bromination of **1** *and* **2** *with 2 equivalent bromine and synthesis of 2,3,5,6-tetrabromobenzobarrelene* **(4):** A mixture of dibromides **1** and **2** (0.5 g, 1.6 mmol) was dissolved in 10 ml of carbon tetrachloride in a 25 ml flask, which was equipped with a reflux condenser. The solution was heated until carbon tetrachloride started to reflux while stirring magnetically. To the refluxing solution was added dropwise a hot solution of bromine (589 mg, 3.68 mmol) in 5 ml of carbon tetrachloride during 5 min. The resulting reaction mixture was heated for 50 h at reflux temperature. After being cooled to room temperature the solvent was evaporated and the residue (1.12 g) was solved in dry and freshly distilled THF (15 ml). To this solution was added (540 mg, 4,82 mmol) of potassium butoxide solution in THF (6 ml). The resulting reaction mixture was stirred for overnight at r.t. The solvent was evaporated and the mixture was diluted with water and the aqueous solution was extracted with ether (3×50 ml), washed with water, and dried over $MgSO_4$. After removal of the solvent, the residue was filtered on a short silica gel column (10 g) eluted with *n*-hexane. After removing of solvent the residue was crystallised from chloroform/*n*-hexane (1:4) to give tetrabromide **4**. *2,3,5,6-tetrabromobenzobarrelene* **(4):** Colourless crystals (437 mg, 58%, m.p. 209–210 °C) (lit.[15] m.p. 208–210 °C). ^{1}H NMR (200 MHz, $CDCl_3$): 7.35–7.05 (AA'BB'system, 4H, aryl), 4.97 (s, 2H, H_1 and H_4). ^{13}C NMR (50 MHz, $CDCl_3$): 142.35, 128.91, 126.19, 123.49, 67.80. IR (KBr, cm^{-1}): 3080, 3020, 1590, 1460, 1450, 1190, 1140, 1060, 980, 850.

Bromination of 2,3,5-tribromobenzobarrelene **(3)** *and synthesis of 2,3,5,6-tetrabromobenzobarrelene* **(4):** The reaction was carried out as described according to procedure in the literature[15] and tetrabromide **4** was obtained by starting tribromide **3** in total 81% yields.

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