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The first and efficient synthesis of some of the polyhalogenated benzobarrelenes: unusual formation of a benzosemibullvalene derivative

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ABSTRACT

New polyhalogenated benzobarrelenes were synthesized in good yields. The bromination reaction of benzobarrelenes at high temperature gives *non*-rearranged products. Dehydrobromination of the formed products with *t*-BuOK yielded the desired polyhalogenated benzobarrelenes. The elimination reaction of cyclopropanoid dibromide with a base unusually resulted in the formation of a benzosemibullvalene derivative.

1. Introduction

In general, the class of molecules led by barrelene and including its benzo derivatives offers the possibility of several mechanistically interesting investigations. For example, these compounds exhibit a unique behaviour in the photochemical di-π-methane rearrangement[1–4] and in the cationic Wagner–Meerwein rearrangement,[5–10] as well as in other instances.[11–16] Thus, substituted benzobarrelene derivatives are important compounds that can provide information about how the substituents will influence reaction pathways.[3,4,17–19] A halogen derivative of a compound is useful as it is a key to synthesize other derivatives. For instance, mono-, di-, tri- and tetra-bromobenzobarrelenes (**1**, **2**, **3**, **4**, **5** and **6**) have been synthesized by Balci and co-workers,[20–24] and by the present authors[25,26] and these compounds have been used for various purposes[3,4,11,19,27–29] (Fig. 1). Therefore, a quick and efficient synthesis of these compounds is important. In this paper, we report the first and effective synthetic methods for the preparation of halogenated benzobarrelenes **7**–**12**, which are precursors for the synthesis of other derivatives.

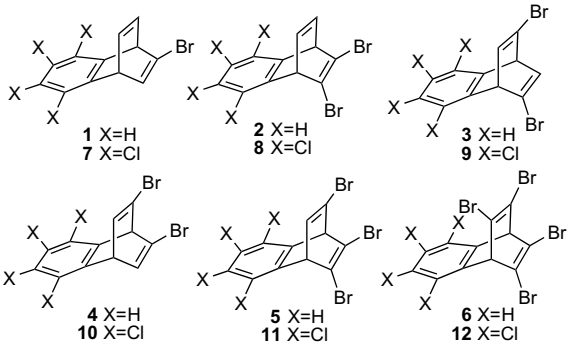

Figure 1.

2. Results and discussion

2.1. Synthesis of monobromide

Previously, we showed that[30] the bromination of **13** at 10 °C results in the formation of rearranged products. A reaction at 77 °C mainly gave *non*-rearranged reaction products **14**–**16** in 83% yield. This mixture was used in the next step without further purification. The elimination reaction of a mixture of dibromides **14**–**16** with potassium *tert*-butoxide allowed us the first synthesis of monobromide **7** (Scheme 1).

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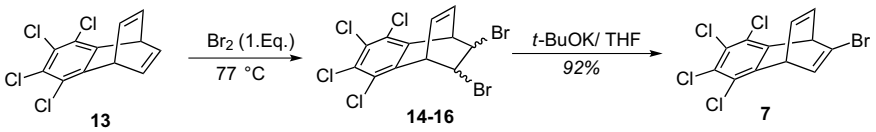
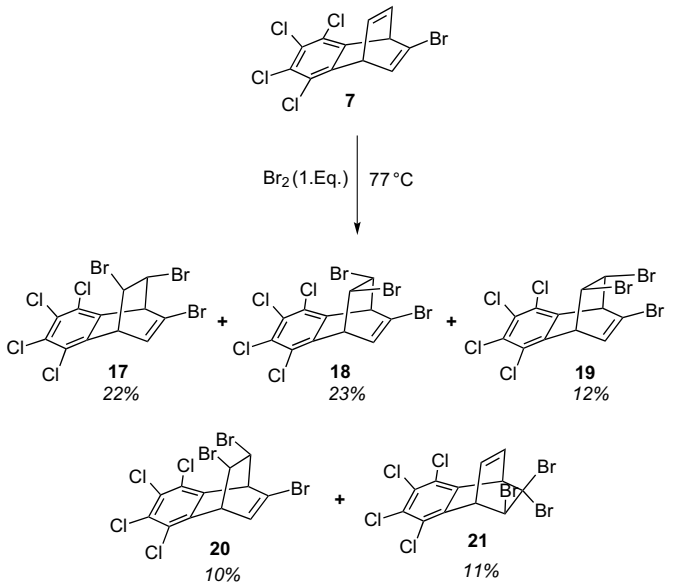


Scheme 1.

2.2. Bromination of 7 with 1 equiv of bromine at 77 °C

At room temperature, the reaction of **7** with bromine gives mainly the products of Wagner–Meerwein rearrangement. In our previous studies, we determined that the reaction temperature has a dramatic influence on the product distribution. Increasing the temperature gives *non*-rearranged reaction products.[31–37] Thus, we were encouraged to further increase the bromination temperature in order to obtain the *non*-rearranged bromination products derived from **7**. For the high-temperature bromination reaction, a hot solution of bromine in CCl_4 was added directly into a refluxing solution of **7** in CCl_4. The NMR analysis of the crude product indicated that the reaction mixture consisted mainly of six products. After column chromatography, isomeric *non*-rearranged tribromides **17** (22%), **18** (23%), **19** (12%), **20** (10%) and **21** (11%) were isolated (Scheme 2).



Scheme 2.

2.3. Dehydrobromination of tribromides 17–21 and synthesis of isomeric dibromides 8–10

After a successful isolation of these desired isomers **17**–**21**, tribromide **21** and a mixture of tribromides **17**–**20** were submitted to a dehydrobromination reaction with 1 equiv of potassium *tert*-butoxide. The elimination reaction of **21** gave dibromide **8** and the dehydrobromination of a mixture of **17**–**20** gave a mixture of **9** and **10** (Scheme 3).

2.4. Bromination of 13 with 2 equiv of bromine at 77 °C and an alternative synthetic way for 9 and 10

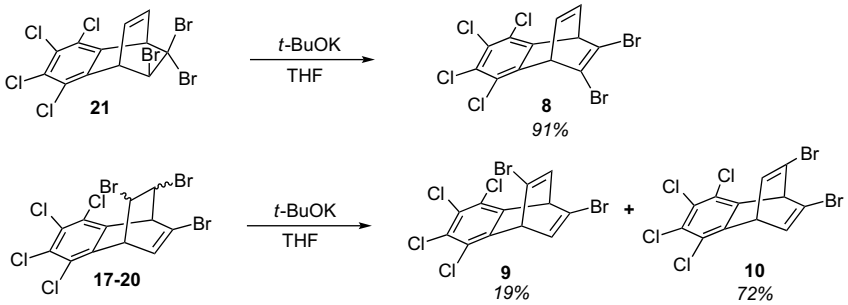
The synthetic method for **9** and **10** as described in Schemes 2 and 3 needs chromatography because on the way to dibromobenzobarrelenes **9** and **10**, the first steps were contaminated with **21**, which were too similar to the products to be easily separated. In the experiments that followed, we aimed to develop a simple synthetic procedure. For this reason, bromination of **13** with 2 equiv of bromine was carried out at a higher temperature and the *non*-rearranged products **22** were obtained in high yield (Scheme 4). The mixture was not separated but directly underwent elimination and from the elimination reaction of a mixture of isomeric tetrabromides **22**, dibromobenzobarrelenes **9** and **10** were obtained in high yield. The mixture can be separated simply by way of fractional crystallization. These methods allow us to discover an alternative and easier synthetic pathway to dibromobenzobarrelenes **9** and **10**.

2.5. Synthesis of tribromide 11

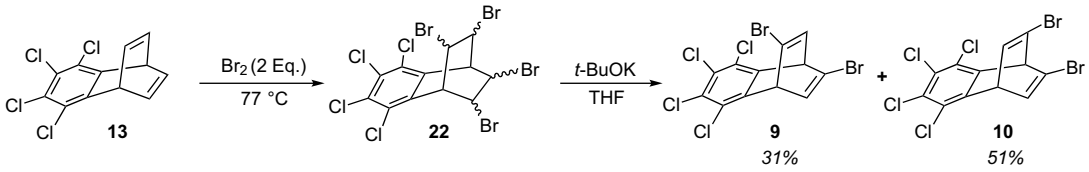
Reaction of **7** with 2 equiv of bromine at 77 °C gives mainly *non*-rearranged products **23**. The mixture was not separated but directly underwent elimination and tribromide **11** was obtained in 52% yield (Scheme 5). Alternatively, bromination of a mixture of dibromides **9** and **10**, which was easily obtained as seen in Scheme 4, with 1 equiv of bromine at 77 °C resulted in formation of *non*-rearranged products **24** and **25**. Dehydrobromination reaction of the products gives us tribromide **11** in 68% yield (Scheme 6).

2.6. Synthesis of tetrabromide

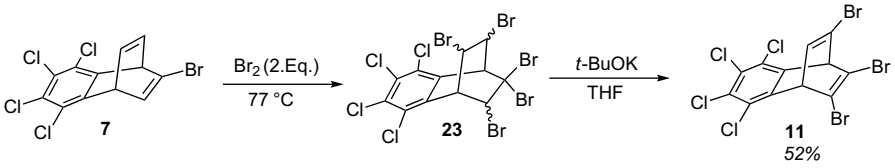
During the bromination of dibromobenzobarrelenes **9** and **10**, the absorption of only 1 mol of bromine is advantageous because



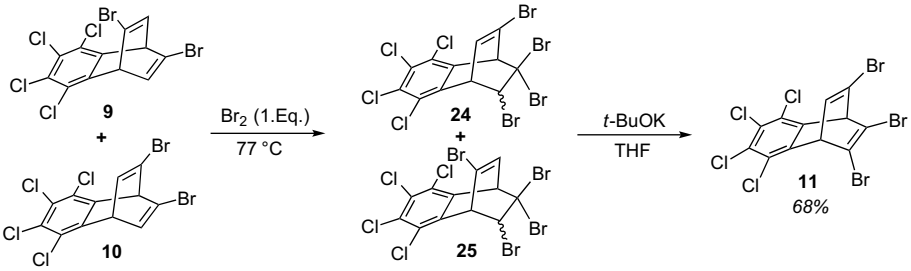
Scheme 3.



Scheme 4.



Scheme 5.

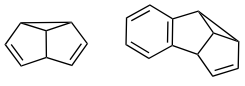


Scheme 6.

this allows us the selective synthesis of tribromobenzobarrelene **11**. In addition, as compounds **9** and **10** have two double bonds, through the reaction of these compounds with 2 equiv of bromine, it is possible to obtain the starting materials for tetrabromobenzobarrelene **12**. The reaction of dibromides **9** and **10** with 2 equiv of bromine was also investigated. After a lengthy bromination reaction for 1 h at 77 °C and 24 h at rt followed by the elimination of the mixture of hexabromides **26** and **27**, tetrabromide **12** was obtained in a moderate yield (for two steps, the total yield is 40%) (Scheme 7). This reaction allowed us to discover the first synthetic method for tetrabromobenzobarrelene **12**. However, the expected good yields could not be obtained from these reactions due to the difficulties in the reaction of dibromides **9** and **10** with bromine. Alternatively, bromination of tribromide **11** was studied and we observed that tetrabromides **28** and **29** gave only *non*-rearranged products even with bromination at room temperature. Dehydrobromination of the mixture of **28** and **29** gave us tetrabromide **12** in 92% yield (Scheme 8).

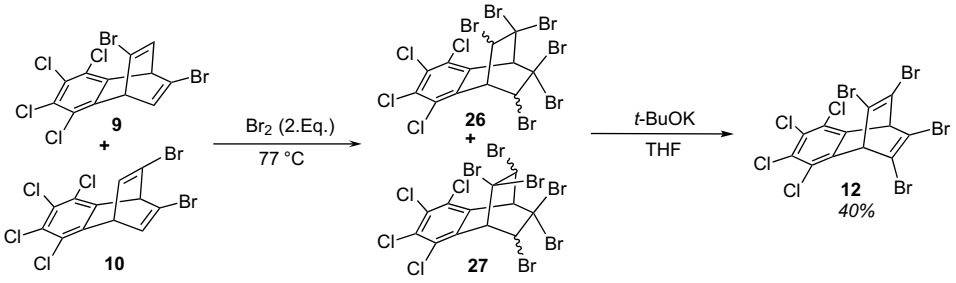
2.7. Reaction of dibromide 32 with potassium *tert*-butoxide: unusual formation of benzosemibullvalene derivative 33

Semibullvalene (**30**) is a hydrocarbon discovered by Zimmerman and Grunewald,[38] which is remarkable for undergoing a rapid degenerate Cope rearrangement even at −150 °C. Since that time, six additional syntheses of semibullvalene have been reported.[39] The benzo analogue of **30**, which is called benzo semibullvalene (**31**), is a product formed by the sensitized irradiation of benzobarrelene.[1–4] To our knowledge, no alternative preparation methods for benzosemibullvalene have been reported.

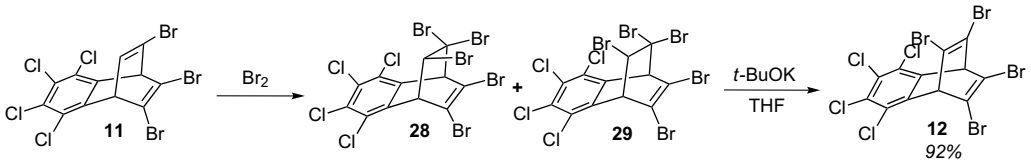


30 **31**

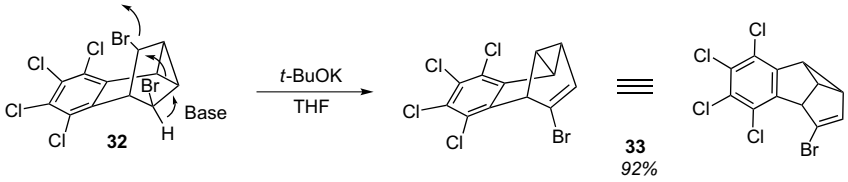
Dibromide **32** is a product formed by the bromination of benzobarrelene derivative **13** at 10 °C in 38% yield.[30] In relation to the synthesis of halobenzobarrelenes, we performed the elimination



Scheme 7.



Scheme 8.

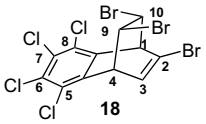


Scheme 9.

reaction of **32** with *t*-BuOK and observed the formation of **33** in a nearly quantitative yield according to the mechanism given in Scheme 9.

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.[6–9,24,25] In the ^{1}H NMR spectrum of tribromide **18**, olefinic proton (H_3) resonate at δ=6.77 ppm as doublet of doublet. The doublet of doublet splitting (J=6.3 Hz and J=1.6 Hz) originates from coupling of H_3 with bridgehead protons (H_4 and H_1). Bridgehead protons appear at δ=4.78 ppm as doublet of doublet ($J_{1,10}$=2.9 Hz, $J_{1,3}$=1.6 Hz, H_1) and at δ=4.75 ppm as doublet of doublet (dd, $J_{3,4}$=6.3 Hz, $J_{4,9}$=2.6 Hz, H_4). CHBr protons are resonating at δ=4.40 ppm as triplet ($J_{9,10}$=$J_{1,10}$=2.9 Hz, H_{10}) and δ=3.98 ppm as doublet of doublet ($J_{9,10}$=2.9 Hz, $J_{4,9}$=2.6 Hz, H_9). Irradiation of the resonances at δ=3.98 ppm converted each of the signal at δ=4.75 ppm and at δ=4.40 ppm doublets. Therefore, this signal at δ=3.98 ppm was assigned to the bridgehead proton H_9. Similarly irradiation of olefinic proton (H_3) converted the signals of H_4 and H_1 into doublet in tribromide **18**.

As a consequence of the rigid geometries in [2.2.2]octene systems, the configuration of vicinally located bromine atoms at C_9 and C_{10} carbon atoms is determined from the coupling constants $J_{9,10}$. Typical J_{cis} coupling is measured approximately J=8.5±1 Hz while J_{trans}=4±1 Hz.[8,9,23–25] We observed large coupling constants of $J_{9,10}$=7.7 Hz in the case of **19** and $J_{9,10}$=8.3 Hz in the case of **20** while $J_{9,10}$=3.0 Hz and 2.9 Hz in the case of **17** and **18**, respectively, which clearly indicates that bromines are cis located in **19** and **20** while trans in **17** and **18**.



The chemical shifts of the signals for CHBr protons at C_9 and C_{10} carbon also gives information about orientation of the bromine atoms at C_9 and C_{10}.[8,9,23–25] In the case of *exo* arrangement of bromine atoms, *endo* protons are shielded by the benzene ring and resonates at a high field in comparison to H_{exo} protons at C_9 and C_{10} carbons.[6,23,24] Differential ^{1}H NMR-NOE measurements also supports the orientation of the protons at C_9 and C_{10} atom. For example irritation of olefinic proton (H_3) in molecule **17** caused enhancement of the signals of bridgehead proton H_4 and H_9 proton. The same experiments in isomeric compound **18** don't change appearance of H_9 proton signal.

Structural assignments to dibromides **9** and **10** were achieved by means of proton and carbon NMR data. The ^{1}H and ^{13}C NMR spectra of **9** are agreement with the symmetry in the molecule. The ^{1}H NMR spectrums consist of two doublets of doublet arising from the bridgehead and double bond protons. A six line in ^{13}C NMR spectrum is in good agreement with the proposed structure. The spectral data of **10** are straightforward for this structure. In the ^{1}H

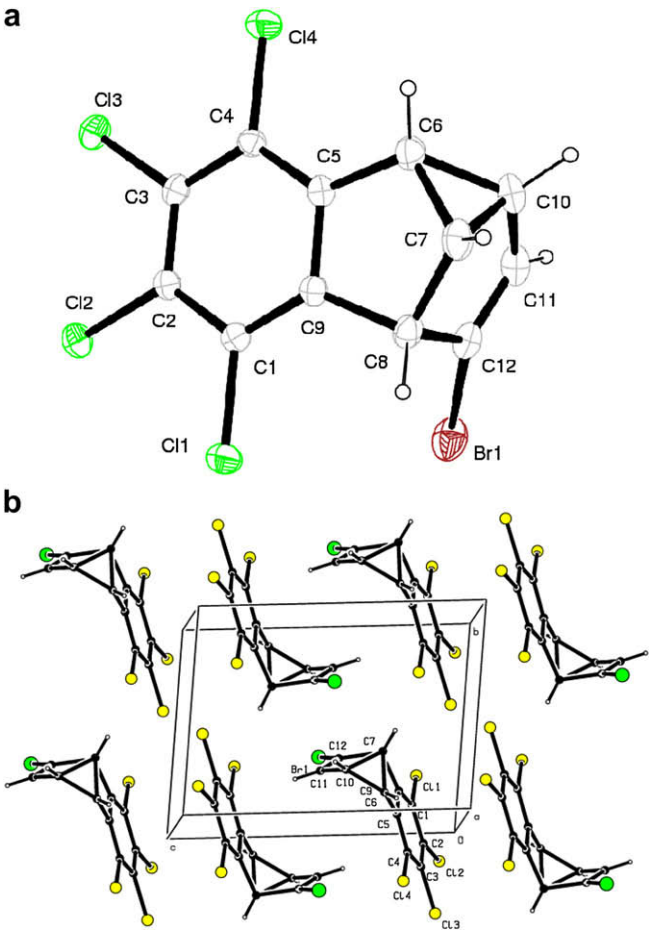


Figure 2. (a) The molecular structure of compound **33** showing the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level, (b) packing diagram along the *c*-axis.

NMR spectrum of dibromide **10**, olefinic protons (H_3 and H_9) resonate at δ=6.91 ppm as doublet of doublet. Bridgehead protons H_1 and H_4 appear at δ=5.34 ppm and δ=5.30 ppm, respectively, as triplet. Especially a ten-line ^{13}C NMR spectrum supports strongly the structure.

An X-ray diffraction analysis of **33** was undertaken. The results of this study confirmed unambiguously the proposed structure (Fig. 2a). The compound crystallizes in the triclinic space group *P*-1, with two molecules in the unit cell (Fig. 2b). Cl–C bond lengths are within the expected range (1.720–1.729 Å). Br–C bond length is 1.883(4) Å. Owing to the formation of C–C (C6–C10=1.564(4) Å) single bond, the most favourable conformation of the 1,3a,6,6a-tetrahydro-pentalene bicycle is fairly stretched out to avoid steric hindrances. Mutually, this bond is considerably lengthened. An interesting feature of the structure of **33** is the presence of weak π–π stacking interaction (along the [001] axis) between the almost parallel [inclined at 1.25(8)°] benzene rings of adjacent molecules oriented in opposite directions [distance between ring centroids $C_g(1)$–$C_g(2)^i$=3.744(2) Å, symmetry code: (i) 1−*x*, −*y*, −*z*]. The perpendicular distance between the ring centroid is 3.529(3) Å (Fig. 2b).

Crystallographic data (excluding structure factors) for the structure **33** in this letter have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 712108. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

3. Experimental

3.1. General

Melting points were determined on a Büchi model 530 apparatus and are uncorrected. Infrared spectra were recorded on a Mattson model 1000 FT-IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on 200(50) and 400(100) MHz spectrometers. Mass spectra (EI) were recorded at 70 eV as *m*/*z*. All solvents were dried and distilled before use. Column chromatography was performed on silica gel 60 (70–230 mesh, Merck). TLC was carried out on Merck 0.2 mm silica gel 60 F_{254} analytical aluminium plates. All substances reported in this paper are in their racemic form.

Caution. It has been reported[40] 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 bromides derived from norbornene there is no report in the literature about the toxicological effect. However, we recommend that the compounds must be handled only with extreme caution.

3.2. General procedure for the elimination of bromides

To a refluxing solution of the bromide (3.0 mmol) in dry THF (20 mL) was added a solution of potassium *tert*-butoxide (405 mg, 3.6 mmol, in the case of 2 mol HBr elimination, 810 mg, 7.2 mmol) in dry THF (5 mL). The resulting reaction mixture was refluxed for 3 h. The solvent was evaporated, the mixture was diluted with water and the aqueous solution was extracted with ether (3×50 mL). Combined organic layers were washed with water, dried over $MgSO_4$ and concentrated. The residue was filtered on a short silica gel column (10 g) eluting with *n*-hexane to give the olefin product.

3.3. General procedure for bromination of olefins at 77 °C

To a magnetically stirred solution of alkene (3.0 mmol) in refluxed CCl_4 (20 mL) was added dropwise to a hot solution of bromine (0.51 g, 3.2 mmol, in the case of two double bond bromination; 1.02 g, 6.4 mmol) in hot CCl_4 (2 mL) for 5 min. The resulting reaction mixture was heated at reflux temperature. After being cooled to room temperature, the solvent was evaporated and the residue was chromatographed on silica gel (100 g) eluting with *n*-hexane.

3.4. Elimination of the mixture of dibromides 14–16 and synthesis of monobromide 7

The reaction was carried out by the general procedure using the mixture of dibromides **14**–**16**[30] (4.52 g, 10 mmol), potassium *tert*-butoxide (1.35 g, 12 mmol) and THF (80 mL). The monobromide **7** (3.41 g, 92%) was obtained as the sole product. *(1R(S),4R(S))-2-Bromo-5,6,7,8-tetrachloro-1,4-dihydro-1,4-ethenonaphthalene* (***7***): colourless crystals from CH_2Cl_2/*n*-hexane (1:2). mp 149–151 °C. ^1H NMR (400 MHz, $CDCl_3$): 7.02–6.99 (m, H_9), 6.95–6.92 (m, 1H, H_{10}), 6.89–6.87 (dd, $J_{3,4}$=6.9 Hz, $J_{1,3}$=1.8 Hz, 1H, H_3), 5.39–5.34 (m, 2H, H_1 and H_4). ^{13}C NMR (100 MHz, $CDCl_3$): 145.13, 144.97, 139.52, 139.36, 136.82, 132.21, 129.07, 128.69, 126.98, 126.72, 55.96, 48.56. IR (KBr, cm^{-1}): 3070, 3003, 2924, 1366, 1203, 1134, 1016, 815, 733. Found: C, 38.55; H, 1.37; required for $C_{12}H_5BrCl_4$: C, 38.86; H, 1.36%. MS (EI, 70 eV): *m*/*z* 372/370 (M^+, 3), 291 (M^+−Br, 45), 254 (100), 218 (21), 184 (33), 145 (19), 109 (14), 104 (15%).

3.5. Bromination of 7 at 77 °C

The reaction was carried out by the general procedure using monobromide **7** (3.41 g, 9.2 mmol), bromine (1.69 g, 9.7 mmol) and CCl_4 (22 mL). After 5 min, the solvent was evaporated and the residue was purified by column chromatography on silica gel (100 g) using *n*-hexane as eluent. The first fraction was *(1S(R),4R(S),9R(S),10R(S))-2,9,10-tribromo-5,6,7,8-tetrachloro-1,4-dihydro-1,4-ethanonapthalene* (***18***): 1.16 g, 23%, colourless crystals, mp=125–126 °C (methylene chloride/*n*-hexane 1:2). ^1H NMR (400 MHz, $CDCl_3$): 6.77 (dd, $J_{3,4}$=6.3 Hz, $J_{1,3}$=1.6 Hz, 1H, H_3), 4.78 (dd, $J_{1,10}$=2.9 Hz, $J_{1,3}$=1.6 Hz, 1H, H_1), 4.75 (dd, $J_{3,4}$=6.3 Hz, $J_{4,9}$=2.6 Hz, 1H, H_4), 4.40 (t, $J_{9,10}$=$J_{1,10}$=2.9 Hz, 1H, H_{10}), 3.98 (dd, $J_{9,10}$=2.9 Hz, $J_{4,9}$=2.6 Hz, 1H, H_9). ^{13}C NMR (100 MHz, $CDCl_3$): 136.93, 136.84, 133.48, 132.34, 132.18, 130.68, 128.14, 124.12, 56.10, 51.71, 51.39, 48.48. IR (KBr, cm^{-1}): 3083, 3049, 3007, 2991, 1611, 1379, 1267, 1220, 1025, 953, 740. Found: C, 26.85; H, 1.01; required for $C_{12}H_5Br_3Cl_4$: C, 27.16; H, 0.95%.

The second fraction was *(1S(R),4R(S),9S(R),10S(R))-2,9,10-tribromo-5,6,7,8-tetrachloro-1,4-dihydro-1,4-ethanonaphthalene* (***17***): 1.11 g (22%), colourless crystals, mp=172–174 °C (methylene chloride/*n*-hexane 1:2). ^1H NMR (400 MHz, $CDCl_3$): 6.79 (dd, $J_{3,4}$=6.8 Hz, $J_{1,3}$=1.9 Hz, 1H, H_3), 4.80 (dd, $J_{1,10}$=2.5 Hz, $J_{1,3}$=1.9 Hz, 1H, H_1), 4.70 (dd, $J_{3,4}$=6.8 Hz, $J_{4,9}$=2.6 Hz, 1H, H_4), 4.33 (dd, $J_{9,10}$=3.0 Hz, $J_{4,9}$=2.6 Hz, 1H, H_9), 4.07 (dd, $J_{9,10}$=3.0 Hz, $J_{1,10}$=2.5 Hz, 1H, H_{10}). ^{13}C NMR (100 MHz, $CDCl_3$): 137.05, 136.99, 132.56, 132.23, 131.93, 130.47, 128.34, 126.82, 54.99, 51.41, 51.03, 48.94. IR (KBr, cm^{-1}): 3083, 3004, 2924, 2851, 1380, 1266, 1220, 1027, 932, 813, 756. Found: C, 27.23; H, 1.11; required for $C_{12}H_5Br_3Cl_4$: C, 27.16; H, 0.95%.

The third fraction was *(1R(S),4S(R),10R(S))-9,9,10-tribromo-5,6,7,8-tetrachloro-1,4-dihydro-1,4-ethanonaphthalene* (***21***): 557 mg (11%), mp=188–189 °C, colourless crystals (methylene chloride/*n*-hexane 1:2). ^1H NMR (400 MHz, $CDCl_3$): 6.72–6.65 (m, 2H, H_2 and H_3), 5.41 (dd, $J_{3,4}$=5.3 Hz, $J_{2,4}$=2.0 Hz, 1H, H_4), 4.88 (d, $J_{1,10}$=2.4 Hz, 1H, H_{10}), 4.77 (ddd, $J_{1,2}$=5.3 Hz, $J_{1,10}$=2.4 Hz, $J_{1,3}$=2.0 Hz, 1H, H_1). ^{13}C NMR (100 MHz, $CDCl_3$): 138.49, 135.83, 135.45, 134.60, 132.04, 131.84, 130.22, 129.98, 63.18, 59.83, 57.07, 48.57. IR (KBr, cm^{-1}): 2997, 2918, 2851, 1381, 1251, 1220, 892, 826, 713. Found: C, 27.05; H, 1.09; required for $C_{12}H_5Br_3Cl_4$: C, 27.16; H, 0.95%.

The fourth fraction was *(1S(R),4R(S),9S(R),10R(S))-2,9,10-tribromo-5,6,7,8-tetrachloro-1,4-dihydro-1,4-ethanonaphthalene* (***19***): 607 mg (12%), colourless crystals, mp=196–197 °C (methylene chloride/*n*-hexane 1:2). ^1H NMR (400 MHz, $CDCl_3$): 6.82 (dd, $J_{3,4}$=6.6 Hz, $J_{1,3}$=1.7 Hz, 1H, H_3), 4.92 (dd, $J_{1,10}$=2.5 Hz, $J_{1,3}$=1.7 Hz,

1H, H_1), 4.89 (dd, $J_{3,4}$=6.6 Hz, $J_{4,9}$=2.3 Hz, 1H, H_4), 4.27 (dd, A part of AB system, $J_{9,10}$=7.7 Hz, $J_{1,10}$=2.5 Hz, 1H, H_{10}), 4.19 (dd, B part of AB system, $J_{9,10}$=7.7 Hz, $J_{4,9}$=2.3 Hz, 1H, H_9). ^{13}C NMR (100 MHz, $CDCl_3$): 138.19, 138.07, 132.54, 132.16, 132.13, 128.49, 128.32, 124.84, 55.87, 49.54, 48.04, 47.90. IR (KBr, cm^{-1}): 3082, 2923, 2851, 1377, 1347, 1226, 1160, 820, 757. Found: C, 26.97; H, 1.19; required for $C_{12}H_5Br_3Cl_4$: C, 27.16; H, 0.95%.

The fifth fraction was *(1S(R),4R(S),9R(S),10S(R))-2,9,10-tribromo-5,6,7,8-tetrachloro-1,4-dihydro-1,4-ethanonaphthalene (**20**)*: 506 mg (10%), colourless crystals, mp=154–155 °C (methylene chloride/*n*-hexane 1:2). ^{1}H NMR (400 MHz, $CDCl_3$): 6.66 (dd, $J_{3,4}$=6.8 Hz, $J_{1,3}$=2.1 Hz, 1H, H_3), 4.93 (dd, $J_{1,10}$=2.6 Hz, $J_{1,3}$=2.1 Hz, 1H, H_1), 4.88 (dd, $J_{3,4}$=6.8 Hz, $J_{4,9}$=2.6 Hz, 1H, H_4), 4.56 (dd, A part of AB system, $J_{9,10}$=8.3 Hz, $J_{1,10}$=2.6 Hz, 1H, H_{10}), 4.46 (dd, B part of AB system, $J_{9,10}$=8.3 Hz, $J_{4,9}$=2.6 Hz, 1H, H_9). ^{13}C NMR (100 MHz, $CDCl_3$): 136.58, 136.56, 134.09, 132.19, 131.80, 130.35, 130.16, 126.46, 55.99, 48.93, 47.95, 47.85. IR (KBr, cm^{-1}): 2924, 2885, 2851, 1635, 1382, 1226, 1035, 820, 759. Found: C, 27.41; H, 1.10; required for $C_{12}H_5Br_3Cl_4$: C, 27.16; H, 0.95%.

3.6. Elimination of tribromide 21

The reaction was carried out by the general procedure using tribromide **21** (160 mg, 0.30 mmol), potassium *tert*-butoxide (41 mg, 0.36 mmol) and THF (5 mL). After the usual work up and crystallization, the dibromide **8** was obtained (123 mg, 91%). *(1R(S),4S(R))-2,3-dibromo-5,6,7,8-tetrachloro-1,4-dihydro-1,4-ethenonanaphthalene (**8**)*: colourless crystals, mp=192–193 °C (methylene chloride/*n*-hexane 1:2). ^{1}H NMR (400 MHz, $CDCl_3$): 7.01 (AA′ part of AA′XX′ system, 2H, H_9 and H_{10}), 5.49 (XX′ part of AA′XX′ system, 2H, H_1 and H_4). ^{13}C NMR (50 MHz, $CDCl_3$): 145.48, 140.72, 131.41, 131.09, 128.86, 58.54. Found: C, 31.91; H, 0.98; required for $C_{12}H_4Br_2Cl_4$: C, 32.04; H, 0.90%.

3.7. Elimination of tribromides 17–20

The reaction was carried out by the general procedure using a mixture of tribromides **17**, **18**, **19** and **20** (2.66 g, 5.0 mmol), potassium *tert*-butoxide (675 mg, 6.0 mmol) and THF (40 mL). After the usual workup, the residue was separated by fractional crystallization. Firstly, dibromide **9** was crystallized from methylene chloride/*n*-hexane (1:3) (430 mg, 19%). After filtration of **9**, the solvent was evaporated and the residue was crystallized from methylene chloride/*n*-hexane (1:4) in the refrigerator to give dibromide **10** (1.63 g, 72%).

*(1R(S),4R(S))-2,9-Dibromo-5,6,7,8-tetrachloro-1,4-dihydro-1,4-ethanonaphthalene (**9**)*: colourless crystals, mp=185–186 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 6.96 (dd, $J_{3,4}$=$J_{1,10}$=6.4 Hz, $J_{1,3}$=$J_{4,10}$=1.8 Hz, 2H, H_3 and H_{10}), 5.29 (dd, $J_{3,4}$=$J_{1,10}$=6.4 Hz, $J_{1,3}$=$J_{4,10}$=1.8 Hz, 2H, H_1 and H_4). ^{13}C NMR (100 MHz, $CDCl_3$): 143.60, 136.27, 132.27, 129.69, 127.17, 57.39. IR (KBr, cm^{-1}): 3082, 3014, 2975, 1367, 1225, 1198, 1017, 912, 834. Found: C, 32.21; H, 1.03; required for $C_{12}H_4Br_2Cl_4$: C, 32.04; H, 0.90%.

*2,10-Dibromo-5,6,7,8-tetrachloro-1,4-dihydro-1,4-ethanonaphthalene (**10**)*: colourless crystals, mp=179–180 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 6.91 (dd, $J_{3,4}$=$J_{4,9}$=6.3 Hz, $J_{1,3}$=$J_{1,9}$=1.9 Hz, 2H, H_3 and H_9), 5.34 (t, $J_{1,3}$=$J_{1,9}$=1.9 Hz 1H, H_1), 5.30 (t, $J_{3,4}$=$J_{4,9}$=6.3 Hz, 1H, H_4). ^{13}C NMR (100 MHz, $CDCl_3$): 143.82, 143.45, 136.67, 130.95, 130.08, 129.30, 127.47, 126.88, 64.24, 49.76. IR (KBr, cm^{-1}): 3081, 3008, 2930, 1366, 1249, 1133, 1034, 957, 782. Found: C, 32.19; H, 0.88; required for $C_{12}H_4Br_2Cl_4$: C, 32.04; H, 0.90%.

3.8. Bromination of 13 with 2 equiv of bromine and synthesis of 2,5- and 2,6-dibromobenzobarrelenes (9 and 10)

The reaction was carried out by the general procedure using alkene **13** (500 mg, 1.71 mmol), bromine (603 mg, 3.76 mmol) and CCl_4 (30 mL). The reaction mixture was refluxed for 30 min. After removal of the solvent by evaporation, the mixture was used in the next step without purification. To achieve this aim, the formed products were subjected to elimination by the general procedure using potassium *tert*-butoxide (770 mg, 6.84 mmol) and THF (80 mL). The crude was filtered on a short silica gel (10 g) column using *n*-hexane as eluent. A mixture of dibromides **9** and **10** was obtained (631 mg, 82% yield in a ratio 3:5, respectively).

3.9. Bromination of 7 with 2 equiv of bromine and synthesis of 2,3,5-tribromobenzobarrelene (11)

The reaction was carried out by the general procedure using monobromide **7** (500 mg, 1.35 mmol), bromine (1.08 g, 6.74 mmol) and CCl_4 (30 mL). The reaction mixture was refluxed for 1 h and stirred at rt for 48 h. After removal of the solvent by evaporation, the formed products were subjected to elimination reaction by the general procedure using potassium *tert*-butoxide (1.35 g, 12 mmol) and THF (80 mL). The crude was filtered on a short silica gel (10 g) column using *n*-hexane as eluent. The residue was crystallized from methylene chloride/*n*-hexane (1:4) in the refrigerator to give tribromide **11** (371 mg, 52%). *(1S(R),4S(R))-2,3,9-tribromo-5,6,7,8-tetrachloro-1,4-dihydro-1,4-ethenonaphthalene (**11**)*: colourless crystals, mp=144–145 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 6.97 (dd, $J_{1,10}$=6.4 Hz, $J_{4,10}$=1.8 Hz, 1H, H_{10}), 5.41 (d, $J_{4,10}$=1.8 Hz, 1H, H_4), 5.39 (d, $J_{1,10}$=6.4 Hz, 1H, H_1). ^{13}C NMR (100 MHz, $CDCl_3$): 142.41, 142.24, 136.06, 130.81, 130.55, 130.14, 129.62, 128.16, 127.53, 127.22, 64.96, 57.95. IR (KBr, cm^{-1}): 3087, 3019, 2925, 2853, 1368, 1359, 1208, 1063, 749. Found: C, 26.64; H, 0.74; required for $C_{12}H_3Br_3Cl_4$: C, 27.26; H, 0.57%. MS (EI, 70 eV): *m/z* 532/530/528/526 (M^+, 2), 451/449/447 (M^+-Br, 6), 370/368 (M^+-2Br, 100), 288 (M^+-3Br, 10), 252 (64), 228 (10), 184 (100), 149 (45), 126 (37), 109 (30), 106 (20), 73 (14%).

3.10. Bromination of 9 and 10 with 1 equiv of bromine and synthesis of 2,3,5-tribromobenzobarrelene (11)

The reaction was carried out by the general procedure using a mixture of dibromides **9** and **10** (2.25 g, 5.0 mmol, in a ratio 1:3, respectively), bromine (880 mg, 5.5 mmol) and CCl_4 (50 mL). The reaction mixture was refluxed 1 h. After evaporation of the solvent, the formed products were subjected to elimination reaction by the general procedure using potassium *tert*-butoxide (1.35 g, 12 mmol) and THF (80 mL). After usual workup the solvent was evaporated and the residue was filtered on a short silica gel (10 g) column using *n*-hexane as eluent. The residue was crystallized from methylene chloride/*n*-hexane (1:4) in the refrigerator and tribromide **11** was obtained (1.8 g 68%).

3.11. Bromination of 9 and 10 with 2 equiv of bromine and synthesis of 2,3,5,6-tetrabromobenzobarrelene (12)

The reaction was carried out by the general procedure using a mixture of dibromides **9** and **10** (2.25 g, 5.0 mmol, in a ratio 1:3, respectively), bromine (1.76 g, 11 mmol) and CCl_4 (50 mL). The reaction mixture was refluxed for 1 h and stirred at rt for 24 h. After evaporation of the solvent, the formed products were subjected to elimination reaction by the general procedure using potassium *tert*-butoxide (1.35 g, 12 mmol) and THF (80 mL). After usual workup the solvent was evaporated and the residue was filtered on a short silica gel (10 g) column using *n*-hexane as eluent. The residue was crystallized from methylene chloride/*n*-hexane (1:1) and tetrabromide **12** was obtained as colourless crystals (1.22 g, 40%).

*2,3,9,10-Tetrabromo-5,6,7,8-tetrachloro-1,4-dihydro-1,4-ethenonaphthalene (**12**)*: colourless crystals, mp=277–278 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 5.48 (s). ^{13}C NMR (100 MHz, $CDCl_3$): 141.12,

130.99, 128.23, 127.57, 65.53. IR (KBr, cm^{-1}): 3014, 2958, 1362, 1259, 1206, 1138, 1064, 800. Found: C, 23.64; H, 0.54; required for $C_{12}H_2Br_4Cl_4$: C, 23.72; H, 0.33%. MS (EI, 70 eV): m/z 599 (M^+, 2), 525 (M^+-Br, 2), 447 (M^+-2Br, 43), 375 (M^+-3Br, 2), 331(6), 289 (M^+-4Br, 10), 264 (16), 223 (49), 166 (45), 144 (100), 109/108 (94), 106 (20), 73 (99%).

3.12. Bromination of tribromide 11 and synthesis of tetrabromide (12)

To a magnetically stirred solution of **11** (1.9 g, 3.59 mmol) in dry CCl_4 (40 mL) at rt, a solution of bromine (443 mg, 5.5 mmol) in CCl_4 (2 mL) was added, dropwise. The reaction mixture was stirred for 25 min at rt. The solvent was evaporated. The ^1H NMR spectrum of the residue showed the formation of only non-rearranged products **28** and **29**. This mixture was used in the next step without purification. The crude was subjected to elimination by the general procedure using potassium *tert*-butoxide (606 mg, 5.4 mmol) and THF (50 mL). After the usual workup the solvent was evaporated and the residue was filtered on a short silica gel (10 g) column using *n*-hexane as eluent. The residue was crystallized from methylene chloride/*n*-hexane (1:4) in refrigerator and tetrabromide **12** was obtained (2.0 g, 92%).

3.13. Elimination reaction of dibromide 32

The reaction was carried out by the general procedure using dibromide **32** (452 mg, 1.0 mmol), potassium *tert*-butoxide (135 mg, 1.2 mmol) and THF (10 mL). After the usual workup, the residue was crystallized from methylene chloride/*n*-hexane (1:3) to give monobromide **33** (341 mg, 92%).

(2aS(R),2bR(S),6bS(R),6cR(S))-1-Bromo-3,4,5,6-tetrachloro-2a,2b, 6b,6c-tetrahydrobenzo[a]cyclopropa[cd]pentalene (***33***): mp=158–159 °C. ^1H NMR (400 MHz, $CDCl_3$): 5.59 (d, $J_{6b,6c}$=6.6 Hz, 1H, H_2),4.23 (d, $J_{6b,6c}$=6.6 Hz, H_{6b}), 3.46 (q, $J_{6c,6a}=J_{6c,2a}=J_{6c,2b}$=6.6 Hz, H_{6c}), 3.23 (t, $J_{2b,2a}=J_{2b,6c}$=6.6 Hz, H_{2b}), 2.83 (dt, $J_{2a,6c}=J_{2a,2b}=J_{2a,2b}$=6.6, $J_{2,2a}$=2.8 Hz, 1H, H_{2a}). ^{13}C NMR (100 MHz, $CDCl_3$): 148.12, 138.09, 131.51, 130.51, 129.83, 126.56, 126.13, 123.35, 59.67, 49.10, 39.77, 37.57. IR (KBr, cm^{-1}): 3048, 2969, 2919, 2852, 1390, 1367, 1281, 1259, 1217, 1155, 844. Found: C, 38.66; H, 1.38; required for $C_{12}H_5BrCl_4$: C, 38.86; H, 1.40%.

3.14. X-ray structure determination

For the crystal structure determination, the single-crystal of the compound **33** was used for data collection on a four-circle Rigaku R-AXIS RAPID-S diffractometer (equipped with a two-dimensional area IP detector). The graphite-monochromatized Mo Kα radiation (λ=0.71073 Å) and oscillation scans technique with $\Delta\omega$=5° for one image were used for data collection. The lattice parameters were determined by the least-squares methods on the basis of all reflections with $F^2>2\sigma(F^2)$. Integration of the intensities, correction for Lorentz and polarization effects and cell refinement was performed using CrystalClear (Rigaku/MSC Inc., 2005) software.[41] The structures were solved by direct methods using SHELXS-97[42] and refined by a full-matrix least-squares procedure using the program SHELXL-97.[42] H atoms were positioned geometrically and refined using a riding model. The final difference Fourier maps showed no peaks of chemical significance. *Crystal data for* ***33***: $C_{12}H_5Cl_4Br$, crystal system, space group: triclinic, *P*-1 (no:2); unit cell dimensions: a=8.0854(3), b=8.7188(4), c=10.1426(5) Å, α=91.04(4)°, β=100.80(3)°, γ=116.32(4)°; volume: 625.4(1) $Å^3$; Z=2; calculated density: 1.97 mg/m^3; absorption coefficient: 4.111 mm^{-1}; F(000): 360; θ range for data collection 2.6–30.5°; refinement method: full-matrix least-square on F^2; data/parameters: 3812/155; goodness-of-fit on F^2: 1.206; final R indices [$I>2\sigma(I)$]: R_1=0.076, wR_2=0.126; R indices (all data): R_1=0.099, wR_2=0.133; largest diff. peak and hole: 0.441 and −0.512 e $Å^{-3}$; CCDC-712108.

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