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Bromination of 2,3-dihydrobenzobarrelene and synthesis of its mono- and dibromide derivatives: unexpected Wagner-Meerwein rearrangement on silica gel

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The bromination reaction of dihydrobenzobarrelene under different conditions was studied. The bromination reaction of dihydrobenzobarrelene with molecular bromine gave only a Wagner-Meerwein rearrangement product by aryl and alkyl migration. Its high-temperature bromination reaction resulted in the formation of normal addition products besides rearrangement products. The bromination reaction of the alkene with 1,2-dibromotetrachloroethane (DBTCE) gave a *non*-rearrangement product as the sole product. The synthesis and bromination reaction of 2-bromodihydrobenzobarrelene was also studied. An unexpected Wagner-Meerwein rearrangement was observed on silica gel during the column chromatography of isomeric tribromides. Herein, we report the results of the synthesis, and the X-ray crystal structures and the possible mechanism of processes are discussed.

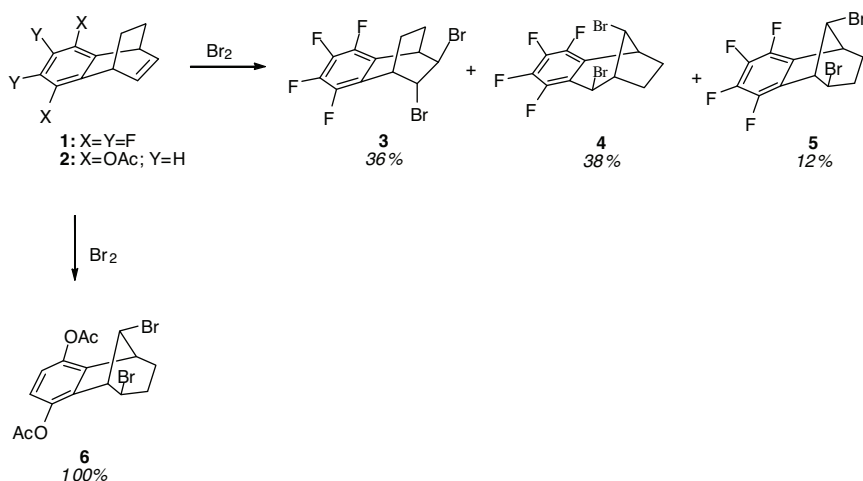
Key Words: Bromination, benzobarrelene, Wagner-Meerwein rearrangement

Introduction

The transformation of alkyl halides into valuable products is often utilized in organic syntheses. Alkyl chlorides are often used since they are easily prepared using many reagents. However, alkyl chlorides are less reactive than alkyl bromides or iodides. Thus, an efficient and practical protocol for the preparation of alkyl bromides would be valuable.¹ Vinylic dibromides derived from bicyclic systems are used as key compounds to obtain cyclotrimers,^{2–15} dioxetanes,^{16–18} alkynes,^{19–20} etc. Therefore, effective synthesis of this kind of product is important.

*Corresponding authors

The addition of bromine to the carbon-carbon double bond is formally one of the simple reactions typical of unsaturated compounds.²¹ However, bromination of unsaturated bicyclic systems results in Wagner-Meerwein rearrangement.^{22–27} For example, Smith²⁸ reported the bromination of diacetoxy dihydrobenzobarrelene **2** and found that a single stereo, specifically dibromide **6**, was formed. Povolotskaya et al.²⁹ reported the bromination of tetrafluorodihydrobenzobarrelene **1** and isolated *non*-rearranged product **3** besides rearranged products **4** and **5** (Scheme 1). The single product formed by aryl migration in diacetoxy compounds is minor in the tetrafluoro derivative. These results show that functional groups determine the outcome of the reaction. Surprisingly, there is no report in the literature on the bromination of parent compound **11**.

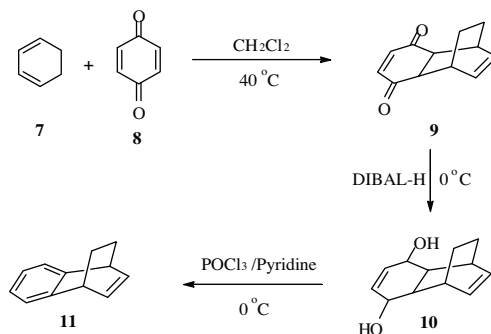


Scheme 1.

Results and discussion

Synthesis of 2,3-dihydrobenzobarrelene

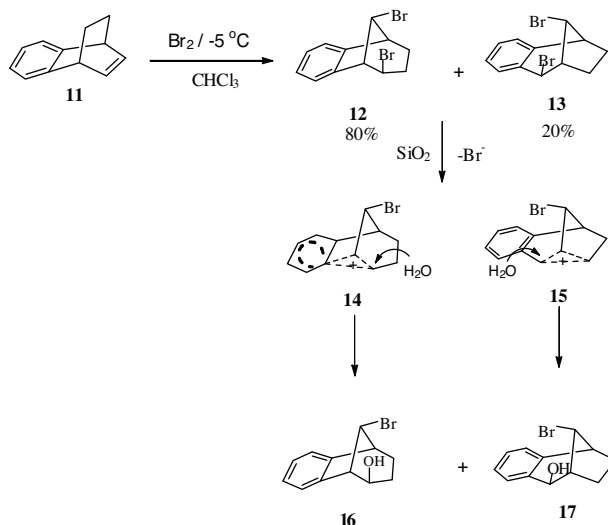
The starting material, 2,3-dihydrobenzobarrelene (**11**), was synthesized using a procedure described in the literature³⁰ (Scheme 2). Adduct **9** was obtained from the Diels-Alder reaction of cyclohexa-1,3-diene (**7**) with 1,4-benzoquinone (**8**). Selective reduction of **9** with diisobutylaluminum hydride, followed by reaction of the formed diol **10** with phosphorous oxychloride in pyridine, resulted in the formation of **11**.



Scheme 2.

Bromination of **11** at low temperature

The electrophilic addition of bromine to **11** was carried out in a chloroform solution at $-5\text{ }^{\circ}\text{C}$. The $^1\text{H-NMR}$ spectral studies of the crude product revealed the formation of 2 isomeric rearranged products, **12** and **13**, in quantitative yields by aryl and alkyl migration in a ratio of 4:1, respectively. During the separation of the mixture, we observed that dibromides **12** and **13** hydrolyzed to the corresponding hydroxy bromides **16** and **17**. The retention of the configuration on the reaction center was attributed the formation of *non*-classical ions **14** and **15** during hydrolysis reactions, as described in Scheme 3.



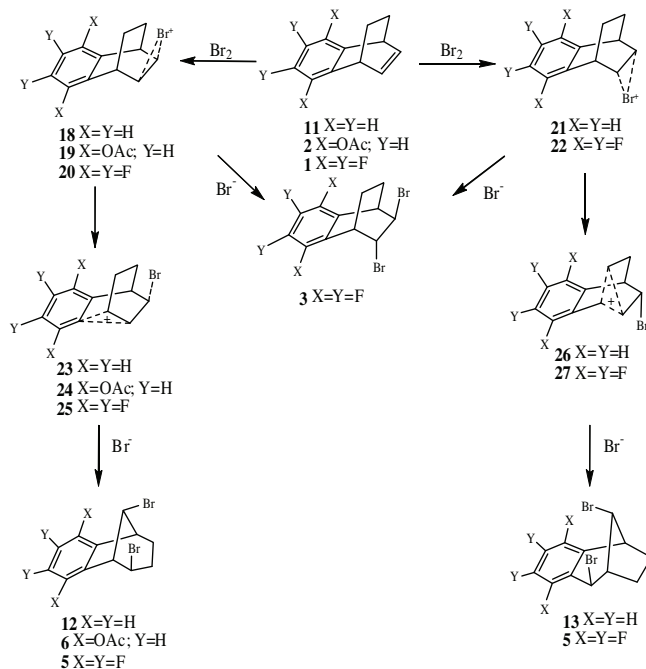
Scheme 3.

In the bromination of 5,8-diacetoxy dihydrobenzobarrelene (**2**), Smith observed that only *exo*-bromonium ion **19** formed²⁸ (Scheme 4). This is evidently due to the higher rate of the formation of ion **19**, which is stabilized on account of the π -participation of the electron-rich aromatic ring (ion **24**). Because 2 acetoxy groups enhance the electron density in the aromatic ring, formation of *non*-classical ion **24** is favored. In contrast to **2**, in the bromination of tetrafluorodihydrobenzobarrelene (**1**),²⁹ the aromatic ring is electron-poor and the *non*-classical ion is not supported by the π -participation of the aromatic ring. Thus, formation of *exo*-bromination ion **20** and *non*-classical ion **25** is not favored. Ion **22** is responsible for *non*-rearranged product **3** and rearranged product **5**. In the case of **11**, we found that the ratio of **12**, formed from *exo*-ion **18**, to **13**, formed from *endo*-ion **21**, was 4:1. This shows that in the nonsubstituted aromatic ring, aryl migration is favorable to alkyl migration.

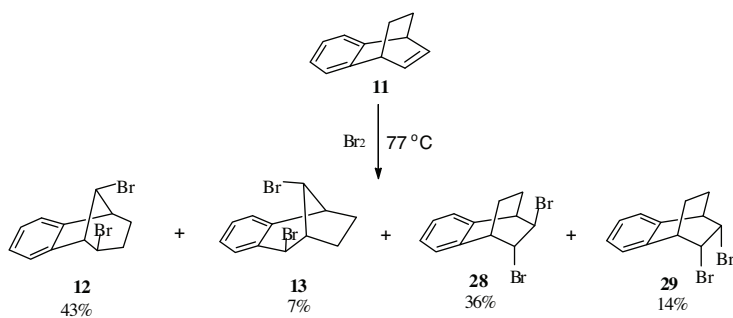
Bromination of **9** at high temperature

At room temperature, the reaction of **11** with bromine gives Wagner-Meerwein rearrangement products **12** and **13**. 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.^{23–27} Thus, we were encouraged to further increase the bromination temperature in order to obtain the *non*-rearranged bromination products derived from **11**. For the high-temperature bromination reaction, a hot solution of bromine in CCl_4

was added directly to a refluxing solution of **11** in CCl_4 . The NMR analysis of the crude product indicated that the reaction mixture consisted mainly of 4 products: *non*-rearranged dibromides **28** (36%) and **29** (14%), and rearranged dibromides **12** (43%) and **13** (7%) (Scheme 5). During the column chromatography, we observed that the initially formed dibromides, **12** and **13**, hydrolyzed to corresponding hydroxy bromides **16** and **17**.



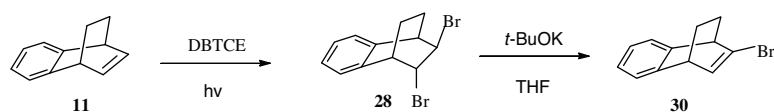
Scheme 4.



Scheme 5.

Bromination of **9** with DBTCE

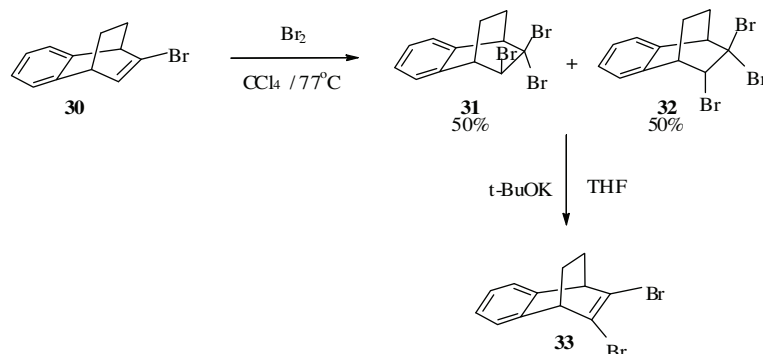
1,2-Dibromotetrachloroethane (DBTCE) is a mild bromination reagent, and the reaction of alkene with this reagent proceeds via radical intermediates.³¹ The bromination reaction of strained olefins with this reagent generally gives *non*-rearrangement products.³¹ The bromination of **11** with DBTCE in CCl_4 gave a sole product, *trans*-dibromide **28** (Scheme 6). Reaction of **28** with potassium *t*-butylate (*t*-BuOK) allowed us the first effective synthesis of 2-bromo-9,10-dihydrobenzobarrelene (**30**).



Scheme 6.

Bromination of monobromide **30** at high temperature and synthesis of dibromide **33**

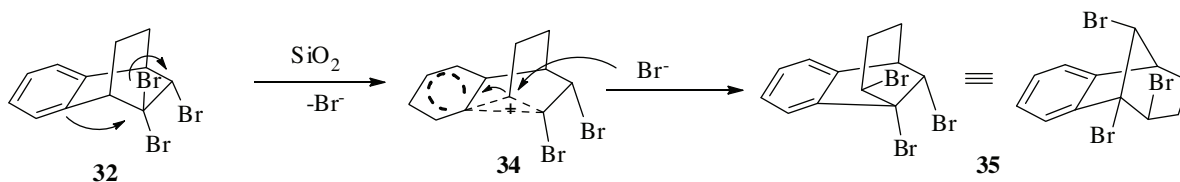
High-temperature bromination of **30** at 77 °C in CCl₄ yielded only *non*-rearranged products **31** and **32** in a nearly quantitative yield. This observation indicates that bromo analog **30** of alkene **11** is less prone to rearrangement. Treatment of tribromides **31** and **32** with *t*-BuOK in ether at room temperature gave a mixture of target compound **33** (Scheme 7).



Scheme 7.

Reaction of tribromide **32** with silica gel

During the separation of tribromides **31** and **32** on silica gel, we also observed a secondary product, **35** (Scheme 8). For this reason, we treated pure tribromides **31** and **32** with silica gel and confirmed that **32** was responsible for the formation of rearranged product **35**. The treating of tribromide **32** with SiO₂ in methylene chloride at room temperature for 15 days cleanly gave tribromide **35**. We also determined that when the reaction temperature was raised to 65 °C in a sealed tube, the rearrangement was completed in 4 days. For the formation of rearranged product **35**, the following reaction mechanism is proposed (Scheme 8). After the Lewis acid (SiO₂) catalyzes, leaving the bromine atom from tribromide **32**, the *non*-classical carbocation **34**, which is stabilized on account of the π -participation of the aromatic rings, is formed. After the attaching of the bromide ion to the carbocation center, a Wagner-Meerwein rearrangement occurs and tribromide **35** is formed.



Scheme 8.

The structures of the compounds were elucidated on the basis of ^1H - and ^{13}C -NMR spectroscopic data, extensive double resonance experiments, and comparison with some spectroscopic data of similar compounds and related systems reported in the literature.^{25–29,31} To confirm the structural assignment, the single-crystal X-ray structures of **31** and **35** were analyzed and are shown in Figures 1 and 2. The resulting compounds, **31** and **35**, crystallized in the triclinic space group $P-1$ ($Z = 2$) and the orthorhombic space group $Pbca$ ($Z = 8$), respectively. The Figures clearly show the *exo* and *endo* (or *syn* and *anti*, with respect to the benzene ring) stereochemistry of the bromides. C-Br bond lengths were within the expected range [1.940(3)-1.969(3) Å]. On the other hand, these lengths are longer than those of aromatic bromine compounds.

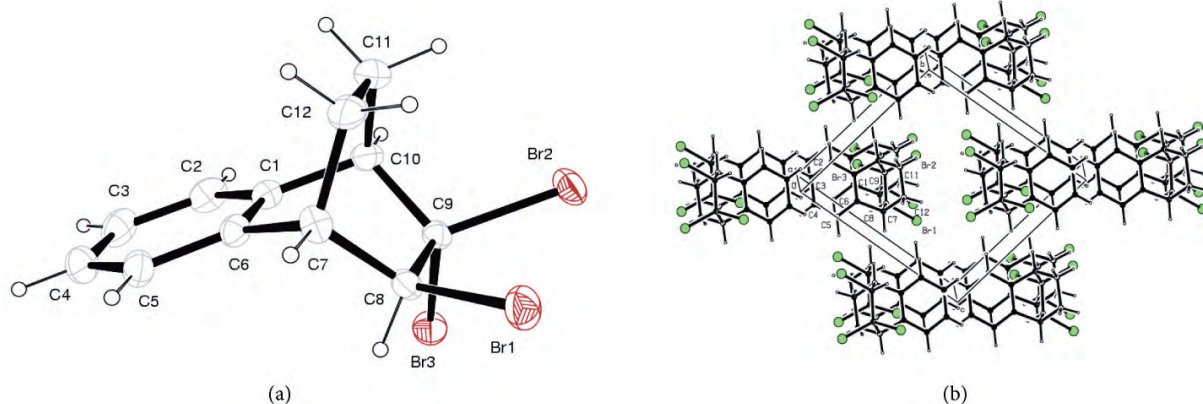


Figure 1. a) The molecular structure of compound **31**, showing the atom numbering scheme, with thermal ellipsoids drawn at the 40% probability level; b) packing diagram along the *c*-axis.

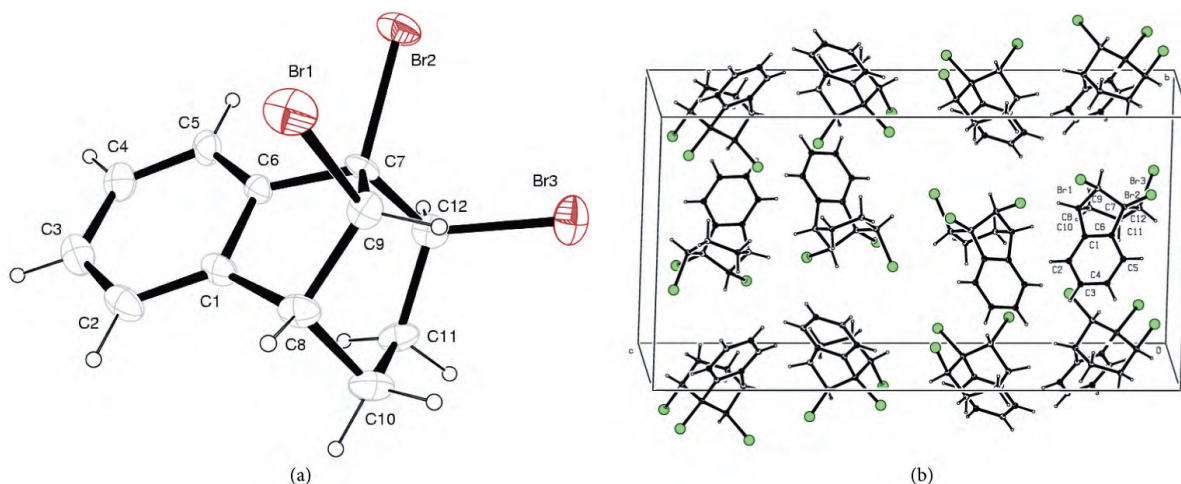


Figure 2. a) The molecular structure of compound **35**, showing the atom numbering scheme, with thermal ellipsoids drawn at the 40% probability level; b) packing diagram along the *a*-axis.

Experimental

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 a 400 (100) MHz spectrometer. 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 F₂₅₄ analytical aluminum plates. All substances reported in this paper are in their racemic forms.

Caution: It has been reported³² that of 3 laboratory workers who used dibromides and a bromohydrin derived from norbornadiene, 2 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 effects. However, we recommend that the compounds only be handled with extreme caution.

General procedure for the elimination of bromides

A solution of bromide (3.0 mmol) in dry ether (20 mL) was added to potassium *tert*-butoxide (405 mg, 3.6 mmol). The resulting reaction mixture was stirred for 12 h. 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 Na_2SO_4 , and concentrated. The residue was filtered on a short silica gel column (10 g), eluting with *n*-hexane to give the olefin product.

Synthesis of 2,3-dihydrobenzobarrelene (11)

The starting material, **11**, was synthesized using a procedure described in the literature.³⁰ First, a solution of 1,4-benzoquinone (**8**) (21.62 g, 0.20 mol) and cyclohexa-1,3-diene (**7**) (17.63 g, 0.22 mol) in 50 mL of methylene chloride was refluxed for 48 h. The solvent was evaporated and product **9** was crystallized from methylene chloride/*n*-hexane (1:1) (72%, 27.10 g). Then, to a magnetically stirred solution of **9** (9.41 g, 0.05 mol) in 500 mL of toluene cooled to 0 °C, was added, dropwise, a solution of DIBAL-H, 18 mL in 20 mL of toluene, over the course of 15 min. This solution was stirred for 1 h at room temperature. The mixture was quenched with a NaOH solution (30%) and the solvent was evaporated. The aqueous solution was extracted with ether (3 × 50 mL). Combined organic layers were washed with water, dried over Na_2SO_4 , and concentrated. Product **10** was crystallized from methylene chloride/*n*-hexane (1:1) (69%, 6.63 g). Next, to a magnetically stirred solution of **10** (13.46 g, 0.07 mol) in 90 mL of pyridine cooled to 0 °C, POCl_3 was added dropwise, 15 mL over the course of 15 min. The reaction mixture was stirred for 24 h at room temperature and for an additional 1 h in a steam bath. The solvent was evaporated, 100 mL of ether was added to the residue, and the solution was washed with a 15% HCl (100 mL) solution and water and dried over Na_2SO_4 . After removal of the solvent, the residue was filtered on a short silica gel column (10 g), eluting with *n*-hexane/ethyl acetate (9:1) to give starting material **11** (63%, 6.88 g). ^1H -NMR (400 MHz, CDCl_3): δ = 7.26-7.15 (AA'BB' system, 4H, H_{aryl}), 6.59 (m, 2H), 4.03 (m, 2H), 1.64 (m, 2H), 1.53 (m, 2H). ^{13}C -NMR (100 MHz, CDCl_3): δ = 144.65, 135.36, 125.23, 122.86, 40.55, 26.08.

Bromination of **11** at low temperature

To a magnetically stirred solution of **11** (625 mg, 4.0 mmol) in chloroform (10 mL) at $-5\text{ }^{\circ}\text{C}$ was added, dropwise, a solution of bromine (656 mg, 4.1 mmol) in chloroform (2 mL) over the course of 5 min. After stirring for 10 min at the same temperature, the solvent was evaporated and the crude product, 500 mg of dibromide **12**, was crystallized from ether/*n*-hexane (1:1). The residue was chromatographed on silica gel (25 g), eluting with *n*-hexane.

The first fraction was (5*S*(*R*),6*R*(*S*),9*S*(*R*),10*S*(*R*))-6,10-dibromo-6,7,8,9-tetrahydro-5*H*-5,9-methanobenzo[*a*][7]annulene (**12**) (500 mg from crystal, 200 mg from column, total 700 mg, 55%): colorless crystals, mp 95-96 $^{\circ}\text{C}$ (ether/*n*-hexane 1:1). $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 7.29\text{--}7.18$ (m, 4H), 4.60 (t, $J = 4.4$ Hz, 1H), 4.31 (dd, $J = 6.4$ Hz, $J = 2.7$ Hz, 1H), 3.61 (m, 1H), 3.23 (m, 1H), 2.65 (m, 1H), 1.96 (bdd, $J = 15.9$ Hz, $J = 5.6$ Hz, 1H), 1.72 (m, 1H), 1.56 (m, 1H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): $\delta = 143.20, 142.52, 128.80, 127.97, 123.63, 123.01, 52.13, 50.03, 46.48, 44.69, 28.17, 20.83$. IR (KBr, cm^{-1}): 3069, 3041, 3021, 2951, 2860, 1460, 1435, 1308, 1287, 1253, 1233, 1207, 1169, 1154, 968, 835, 758, 719. Found: C 45.81%, H 3.72%; required for $\text{C}_{12}\text{H}_{12}\text{Br}_2$: C 45.61%, H 3.83%. MS (EI, 70 eV): m/z 318/316/314 (M^+ , 1), 237/235 (M^+ , -Br, 54), 155 (M^+ , -2Br, 97), 128(100), 115(50), 76(71), 64(20).

The second fraction was (5*S*(*R*),6*R*(*S*),9*S*(*R*),10*S*(*R*))-10-bromo-6,7,8,9-tetrahydro-5*H*-5,9-methanobenzo[*a*][7]annulene-6-ol (**16**) (245 mg, 24%): colorless crystals, mp 108-109 $^{\circ}\text{C}$ (methylene chloride/*n*-hexane 1:1). $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 7.24\text{--}7.15$ (m, 4H), 4.61 (t, $J = 4.2$ Hz, 1H), 3.89 (m, 1H), 3.44 (m, 1H), 3.30 (m, OH, 1H), 3.26 (m, 1H), 2.51 (m, 1H), 1.60-1.54 (m, 2H), 1.34 (m, 1H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): $\delta = 142.65, 142.55, 128.25, 127.77, 123.58, 122.87, 70.30, 54.28, 49.70, 45.17, 26.71, 21.02$. IR (KBr, cm^{-1}): 3681, 3286, 3220, 2938, 1457, 1446, 1350, 1268, 1254, 1067, 992, 883, 751, 722. Found: C 56.90%, H 5.02%; required for $\text{C}_{12}\text{H}_{13}\text{BrO}$: C 56.94%, H 5.18%. MS (EI, 70 eV): m/z 254/252 (M^+ , 1), 234/232 (M^+ , $-\text{H}_2\text{O}$, 1), 172 (M^+ , -Br, 13), 128(100), 115(41).

The third fraction was (5*R*(*S*),8*S*(*R*),9*S*(*R*),10*S*(*R*))-10-bromodecahydro-1*H*-5,8-methanobenzo[*a*][7]annulene-9-ol (**17**) (200 mg, 20%): colorless crystals, mp 89-90 $^{\circ}\text{C}$ (methylene chloride/*n*-hexane 1:1). $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 7.56\text{--}7.06$ (m, 4H), 4.42 (d, $J = 11.8$ Hz, 1H), 4.36 (dd, $J = 4.7$ Hz, $J = 4.1$ Hz, 1H), 3.32 (m, 1H), 3.15 (d, $J = 11.8$ Hz, 1H), 2.87 (m, 1H), 2.10-1.94 (m, 2H), 1.72 (m, 1H), 1.38 (m, 1H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): $\delta = 139.60, 135.34, 130.67, 128.53, 127.68, 127.63, 75.01, 50.92, 47.33, 44.51, 30.56, 25.60$. IR (KBr, cm^{-1}): 3555, 3449, 3063, 3022, 2952, 2909, 2872, 1487, 1455, 1400, 1216, 1039, 978, 763. Found: C 57.08%, H 5.20%; required for $\text{C}_{12}\text{H}_{13}\text{BrO}$: C 56.94%, H 5.18%. MS (EI, 70 eV): m/z 254/252 (M^+ , 11), 235/233 (M^+ , $-\text{H}_2\text{O}$, 1), 173 (M^+ , -Br, 48), 156(100), 144(46), 129(62), 115(61), 105(42), 77(45).

Bromination of **11** at high temperature

Alkene **11** (625 mg 4.0 mmol) was dissolved in CCl_4 (10 mL) in a 25-mL flask equipped with a reflux condenser. The solution was heated until the solvent started to reflux, while being stirred magnetically. To the refluxing solution was added, dropwise, a hot solution of bromine (656 mg, 4.1 mmol) in CCl_4 (2 mL) for 5 min. After being cooled to room temperature, the solvent was evaporated and the residue was chromatographed on silica gel (50 g), eluting with *n*-hexane.

The first fraction was (1*R*(*S*),2*R*(*S*),3*R*(*S*),4*S*(*R*))-2,3-dibromo-1,2,3,4-tetrahydro-1,4-ethanonaphtha-

lene (**28**) (450 mg, 36%): white solid, mp 65-66 °C (methylene chloride/*n*-hexane 1:2). ¹H-NMR (400 MHz, CDCl₃): δ = 7.32-7.19 (m, 4H), 4.48 (dd, *J* = 3.8 Hz, *J* = 2.6 Hz, 1H), 4.21 (m, 1H), 3.26 (m, 2H), 2.35 (m, 1H), 2.04 (m, 1H), 1.66 (m, 1H), 1.44 (m, 1H). ¹³C-NMR (100 MHz, CDCl₃): δ = 139.97, 138.20, 127.69, 127.66, 126.30, 124.50, 59.28, 58.00, 44.23, 43.66, 26.33, 19.15. IR (KBr, cm⁻¹): 3070, 3025, 2948, 2902, 2869, 1482, 1462, 1251, 1217, 1171, 982, 948, 805, 756, 730. Found: C 45.43%, H 3.82%; required for C₁₂H₁₂Br₂: C 45.61%, H 3.83%. MS (EI, 70 eV): *m/z* 319/315/312 (M⁺, 3), 237/235 (M⁺, -Br, 32), 156 (M⁺, -2Br, 66), 129(100), 115(34), 76(46).

The second fraction was (1*R*(*S*),2*R*(*S*),3*S*(*R*),4*S*(*R*))-2,3-dibromo-1,2,3,4-tetrahydro-1,4-ethanonaphthalene (**29**) (175 mg, 14%): colorless crystals, mp 204-205 °C (methylene chloride/*n*-hexane 1:1). ¹H-NMR (400 MHz, CDCl₃): δ = 7.34-7.25 (AA'BB' system, 4H), 4.68 (m, 2H), 3.45 (m, 2H), 1.90 (m, 2H), 1.59 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃): δ = 138.12, 127.32, 126.31, 53.84, 44.52, 25.33. IR (KBr, cm⁻¹): 3029, 2955, 2905, 2850, 1642, 1557, 1437, 1270, 1215, 1111, 1045, 996, 965, 913, 881, 846. Found: C 45.91%, H 3.85%; required for C₁₂H₁₂Br₂: C 45.61%, H 3.83%. MS (EI, 70 eV): *m/z* 318/316/314 (M⁺, 3), 238/236 (M⁺, -Br, 16), 156 (M⁺, -2Br, 57), 128(100), 115(31), 77(39).

The third fraction was **16** (430 mg, 42%).

The fourth fraction was **17** (70 mg, 7%).

Bromination of **11** with DBTCE

A solution of **11** (2.50 g, 16.0 mmol), 5.28 g (16.5 mmol) of DBTCE, and AIBN (catalytic) in CCl₄ (20 mL) was irradiated with a 500-W lamp at reflux temperature in a 100-mL flask equipped with a reflux condenser for 24 h. The solvent and tetrachloroethylene formed during reaction were evaporated. The residue product was purified by a silica gel (20 g) column with *n*-hexane, and dibromide **28** (5.0 g, 99%) was obtained as a white solid.

Synthesis of monobromide **30**

The reaction was carried out by the general procedure described in 3.2., using dibromide **28** (950 mg, 3.0 mmol), potassium *t*-butoxide (405 mg, 3.6 mmol), and ether (20 mL). Monobromide **30** (640 mg, 91%) was obtained as the sole product. (1*R*(*S*),4*R*(*S*))-2-bromo-1,4-dihydro-1,4-ethanonaphthalene (**30**): colorless liquid at room temperature. ¹H-NMR (400 MHz, CDCl₃): δ = 7.25-7.13 (m, 4H), 6.61 (dd, *J* = 6.7 Hz, *J* = 2.3 Hz, 1H), 4.09 (m, 1H), 4.00 (dt, *J* = 6.7 Hz, *J* = 2.3 Hz, 1H), 1.87 (m, 1H), 1.71 (m, 1H), 1.53-1.49 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃): δ = 143.01, 142.90, 134.29, 126.05, 125.79, 125.57, 123.14, 122.85, 50.59, 43.02, 26.40, 26.25. IR (KBr, cm⁻¹): 3066, 3022, 2959, 2869, 1609, 1474, 1458, 1306, 1138, 999, 852, 753. MS (EI, 70 eV): *m/z* 237/235 (M⁺, 3), 208/206 (M⁺, -C₂H₄, 100), 156 (M⁺, -Br, 31), 127(60), 77/76(56), 63(24).

Bromination of monobromide **30** at high temperature

Monobromide **30** (705 mg, 3.0 mmol) was dissolved in CCl₄ (10 mL) in a 25-mL flask equipped with a reflux condenser. To the refluxing solution was added, dropwise, a hot solution of bromine (496 mg, 3.1 mmol) in CCl₄ (2 mL) for 5 min. After being cooled to room temperature, the solvent was evaporated and the residue was chromatographed on silica gel (50 g), eluting with *n*-hexane.

The first fraction was (1*R*(*S*),3*S*(*R*),4*S*(*R*))-2,2,3-tribromo-1,2,3,4-tetrahydro-1,4-ethanonaphthalene (**31**) (590 mg, 50%): colorless crystals, mp 85-86 °C (ether/*n*-hexane 1:1). ¹H-NMR (400 MHz, CDCl₃): δ = 7.33-7.16 (m, 4H), 4.86 (t, *J* = 2.2 Hz, 1H), 3.89 (t, *J* = 2.9 Hz, 1H), 3.23 (dt, *J* = 3.6 Hz, *J* = 2.2 Hz, 1H), 2.65 (m, 1H), 2.29 (m, 1H), 1.53 (m, 1H), 1.42 (m, 1H). ¹³C-NMR (100 MHz, CDCl₃): δ = 139.47, 139.43, 128.11, 127.89, 126.15, 124.32, 71.07, 65.74, 55.23, 45.76, 26.12, 16.95. IR (KBr, cm⁻¹): 3070, 3025, 2948, 2872, 1482, 1460, 1223, 1172, 1110, 996, 950, 908, 874, 826, 813, 755. Found: C 36.08%, H 2.76%; required for C₁₂H₁₁Br₃: C 36.49%, H 2.81%. MS (EI, 70 eV): *m/z* 398/397/395/393/391 (M⁺, 1), 318/316/314 (M⁺, -Br, 53), 235/233 (M⁺, -2Br, 29), 208/206 (M⁺, -C₂H₄, 64), 154 (M⁺, -3Br, 87), 127(78), 115(19), 76(100), 63(37).

The second fraction was (1*R*(*S*),3*R*(*S*),4*S*(*R*))-2,2,3-tribromo-1,2,3,4-tetrahydro-1,4-ethanonaphthalene (**32**) (600 mg, 50%): colorless crystals, mp 104-105 °C (ether/*n*-hexane 1:1). ¹H-NMR (400 MHz, CDCl₃): δ = 7.36-7.22 (m, 4H), 5.09 (d, *J* = 2.0 Hz, 1H), 3.95 (t, *J* = 2.6 Hz, 1H), 3.30 (m, 1H), 2.63 (m, 1H), 2.08 (m, 1H), 1.64-1.54 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃): δ = 138.93, 135.82, 127.95, 127.67, 126.41, 126.23, 72.58, 65.17, 55.69, 46.59, 26.15, 23.53. IR (KBr, cm⁻¹): 3025, 2950, 2868, 1482, 1461, 1190, 949, 825, 755. Found: C 36.09%, H 2.75%; required for C₁₂H₁₁Br₃: C 36.49%, H 2.81%. MS (EI, 70 eV): *m/z* 398/397/395/393/391 (M⁺, 6), 317/315/313 (M⁺, -Br, 65), 235/233 (M⁺, -2Br, 22), 208/206 (M⁺, -C₂H₄, 84), 155/154 (M⁺, -3Br, 83), 127(100), 115(20), 76(81).

Elimination of tribromides 31-32 and synthesis of dibromide 33

The reaction was carried out by the general procedure described in 3.2., using a mixture of dibromides **31** and **32** (1.2 g, 3.0 mmol), potassium *t*-butoxide (405 mg, 3.6 mmol), and ether (20 mL). Dibromide **33** (870 mg, 92%) was obtained as the sole product. (1*R*(*S*),4*S*(*R*))-2,3-dibromo-1,4-dihydro-1,4-ethanonaphthalene (**33**): colorless crystals, mp 128-129 °C (ether/*n*-hexane 1:1). ¹H-NMR (400 MHz, CDCl₃): δ = 7.24-7.14 (AA'BB' system, 4H, *H_{aryl}*), 4.22 (m, 2H), 1.93 (m, 2H), 1.52 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃): δ = 141.65, 126.33, 124.71, 123.07, 52.36, 26.64. IR (KBr, cm⁻¹): 3066, 3036, 2959, 2921, 2890, 2855, 1447, 1376, 1308, 1283, 1236, 1200, 1076, 1039, 1019, 987. Found: C 45.22%, H 3.20%; required for C₁₂H₁₀Br₂: C 45.90%, H 3.21%. MS (EI, 70 eV): *m/z* 316/314/312 (M⁺, 2), 289/287/285 (M⁺, -C₂H₄, 26), 207/205 (5), 154/152 (M⁺, -2Br, 27), 126(73), 76(100), 63(51).

Reaction of tribromide 32 with silica gel

Tribromide **32** (100 mg, 25 mmol) was dissolved in 1 mL of methylene chloride and added to a silica gel (50 g) column. After 15 days, the column was eluted with ethyl acetate. The solvent was evaporated and ¹H-NMR analysis of the residue showed the formation of tribromide **35** in 100% yield. The mixture was crystallized from ether/*n*-hexane (1:2) and product **35** was obtained. The same procedure was repeated at 65 °C, and after 4 days, tribromide was obtained as the sole product. (6*S*(*R*),9*R*(*S*),10*S*(*R*))-5,6,10-tribromo-6,7,8,9-tetrahydro-5*H*-5,9-methanobenzo[*a*][7]annulene (**35**): colorless crystals, mp 113-114 °C. ¹H-NMR (400 MHz, CDCl₃): δ = 7.53-7.23 (m, 4H), 5.34 (s, 1H), 4.71 (bd, *J* = 4.8 Hz, 1H), 3.74 (dd, *J* = 4.1 Hz, *J* = 1.5 Hz, 1H), 2.32 (m, 1H), 1.98 (dd, *J* = 15.4 Hz, *J* = 5.2 Hz, 1H), 1.65 (m, 1H), 1.46 (m, 1H). ¹³C-NMR (100 MHz, CDCl₃): δ =

141.17, 140.80, 130.31, 128.59, 124.93, 124.26, 75.10, 68.18, 61.15, 52.06, 30.88, 26.23. IR (KBr, cm^{-1}): 3070, 3042, 2952, 2925, 2852, 1463, 1435, 1290, 1212, 961, 880, 855, 820. Found: C 36.25%, H 2.72%; required for $\text{C}_{12}\text{H}_{11}\text{Br}_3$: C 36.49%, H 2.81%. MS (EI, 70 eV): m/z 298/297/395/393/391 (M^+ , 10), 317/315/313 (M^+ , -Br, 100), 235/233 (M^+ , -2Br, 35), 207/205(64), 153 (M^+ , -3Br, 79), 128(33), 111(41), 76(100), 63(24).

The same procedure was followed for tribromide **32**. After 6 days, $^1\text{H-NMR}$ analysis of the residue showed the formation of tribromide **35** in 75% yield and tribromide **31** in 22% yield, besides the unchanged starting material (**32**, 3%).

Crystal structure analysis

For the crystal structure determination, the single crystals of tribromides **31** and **35** were used for data collection on a 4-circle Rigaku R-AXIS RAPID-S diffractometer (equipped with a 2-dimensional area IP detector). The graphite-monochromatized Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$) and oscillation scan technique with $\Delta\omega = 5^\circ$ 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 were performed using CrystalClear (Rigaku/MSI Inc., 2005) software.³³ The structures were solved by direct methods using SHELXS-97³⁴ and refined by a full-matrix least-squares procedure using SHELXL-97.³⁴ 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 **31**: $\text{C}_{12}\text{H}_{11}\text{Br}_3$, crystal system, space group: triclinic, $P-1$; (no:2); unit cell dimensions: $a = 7.0637(3)$, $b = 9.3461(4)$, $c = 10.5087(5) \text{ \AA}$, $\alpha = 72.85(2)$, $\beta = 74.51(3)$, $\gamma = 71.92(2)^\circ$; volume: $618.32(6) \text{ \AA}^3$; $Z = 2$; calculated density: 2.12 mg/m^3 ; absorption coefficient: 9.750 mm^{-1} ; $F(000)$: 376; θ -range for data collection: $2.8\text{--}26.4^\circ$; refinement method: full-matrix least-square on F^2 ; data/parameters: 2138/137; goodness-of-fit on F^2 : 1.232; final R indices [$I > 2\sigma(I)$]: $R_1 = 0.055$, $wR_2 = 0.108$; R indices (all data): $R_1 = 0.069$, $wR_2 = 0.114$; largest diff. peak and hole: 0.763 and $-0.556 \text{ e \AA}^{-3}$. Crystal data for **35**: $\text{C}_{12}\text{H}_{11}\text{Br}_3$, crystal system, space group: orthorhombic, $Pbca$; (no:61); unit cell dimensions: $a = 7.4259(4)$, $b = 13.4946(5)$, $c = 25.1075(8) \text{ \AA}$, $\alpha = 90$, $\beta = 90$, $\gamma = 90^\circ$; volume: $2516.01(8) \text{ \AA}^3$; $Z = 8$; calculated density: 2.08 mg/m^3 ; absorption coefficient: 9.584 mm^{-1} ; $F(000)$: 1504; θ -range for data collection: $3.0\text{--}26.4^\circ$; refinement method: full-matrix least-square on F^2 ; data/parameters: 2428/137; goodness-of-fit on F^2 : 1.61; final R indices [$I > 2\sigma(I)$]: $R_1 = 0.089$, $wR_2 = 0.193$; R indices (all data): $R_1 = 0.148$, $wR_2 = 0.196$; largest diff. peak and hole: 0.620 and $-0.518 \text{ e \AA}^{-3}$. The crystallographic data were deposited with the Cambridge Crystallographic Data Centre (deposition numbers CCDC 798551 and 799311 for **31** and **35**, respectively) and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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