Bromination of *endo*- and *exo*-benzocyclobutenonorbornene derivatives: neighbour group effect on bromination

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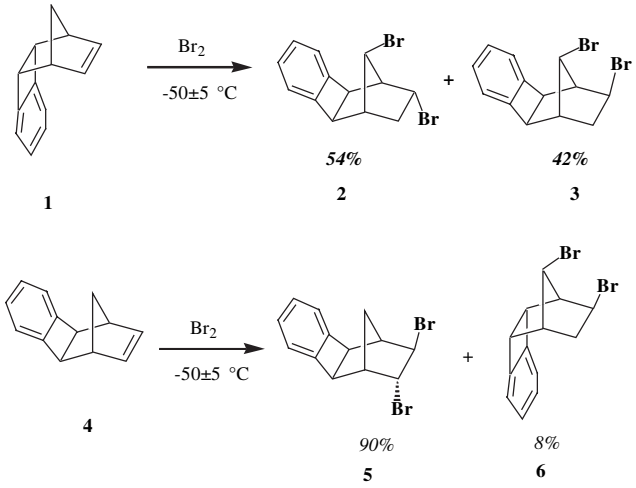
The electrophilic addition of bromine to 13-*anti*-bromo-*endo*-benzocyclobutenonorbornene **7** at –50 ± 5 °C has led in high yield to the formation of the rearranged dibromides **9**, **10** and **11**. In addition to this, bromination of *exo* isomer **8** results in formation of rearranged **9** and *non* rearranged product **10**. However, high-temperature bromination of *endo* **7** and *exo* isomer **8** at 77 °C gave only *non*-rearranged products. The possible role of a substituent in rearrangements is discussed in these systems.

Keywords*:* bromination, benzocyclobutene, Wagner-Meerwein rearrangement, norbornene, neighbour group effect

In addition to synthetic aspects, bromination of bicyclic olefins is a process of considerable potential mechanistic interest. Electrophilic bromination of simple olefins almost invariably yields *trans*-1,2-dibromides.[1,2] In addition to this, the nature of the intermediates of the addition depends on temperature, steric factors, torsional effects, π- and σ-participation in the transition state and the formation of *non*-classical ions or a fast equilibrium of classical ions. The bromination of unsaturated bicyclic systems with molecular bromine leads to rearrangements of the molecular skeleton.[3] Earlier, we showed that[4] bromination of *endo*-benzocyclobutenonorbornene **1** at –50 ± 5 °C led in high yield to the formation of the rearranged dibromides **2** and **3**. However, bromination of *exo* isomer **4** at the same reaction condition gave mainly non-rearranged product **5** (90%) and rearranged product **6** (8%)[5] (Scheme 1).

In this work, we studied the bromination of 13-*anti* bromo derivatives of *endo*- and *exo*- benzocyclobutenonorbornene (**7**/**8**) in order to investigate the behaviour of neighbouring group effects on the product distribution at low- and high-temperature bromination in benzocyclobutenonorbornene systems.



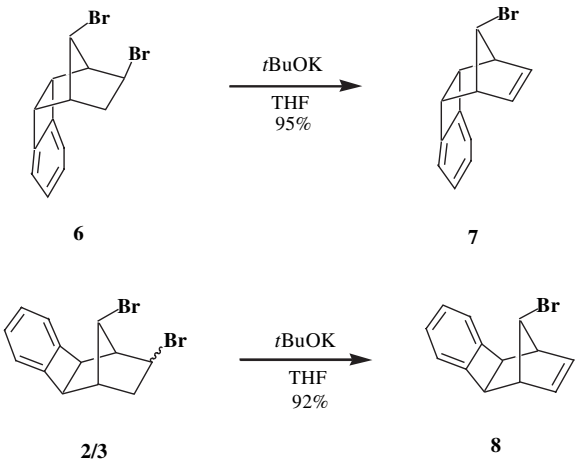
Scheme 1

Results and discussions

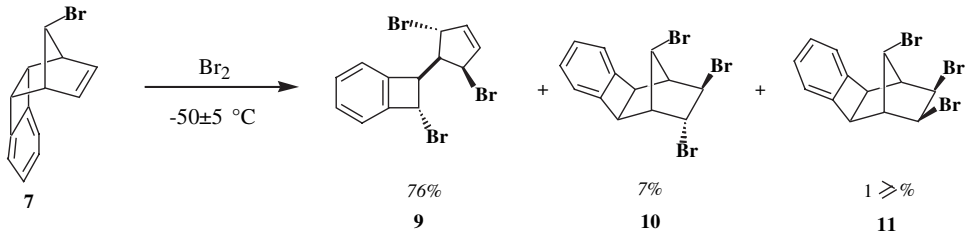
One of the starting materials **8** was synthesised by elimination of dibromides **2** and **3** described in the literature.[6] The other, new isomer **7** was obtained by similar way using dibromide **6** (Scheme 2).

Firstly, the bromination of *endo* isomer **7** at –50 ± 5 °C was investigated. ^{1}H NMR spectroscopic studies revealed that the reaction mixture consisted of three products; one of them is ring opened product **9** (76%), the others Wagner–Meerwein Rearrangement products **10** (7%) and **11** (1 ≥%) (Scheme 3).

The electrophilic addition of bromine to *exo*-isomer 8 was first reported by Dinilescu *et al.*[6] They mention only the formation of tribromide 10 (20%) and there is no information about the remaining products. To update the literature data, we also reacted **8** with bromine in chloroform solution at –50 ± 5 °C and isolated two product: one is ring opened product



Scheme 2



Scheme 3

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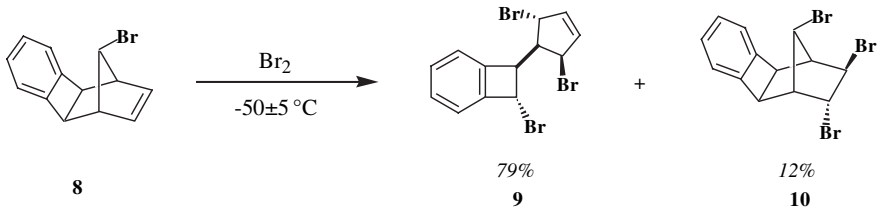
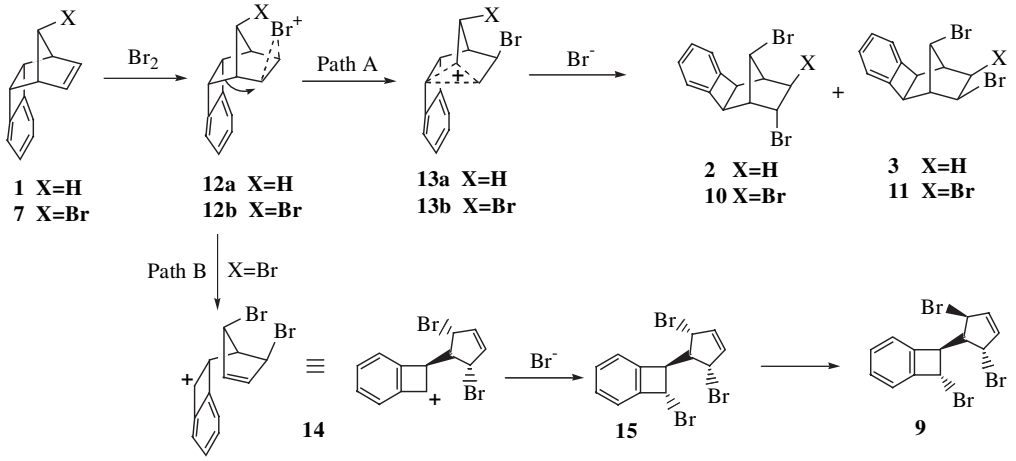


Scheme 4



Scheme 5

9 (79%) and the other is non-rearranged tribromide **10** (12%) (Scheme 4).

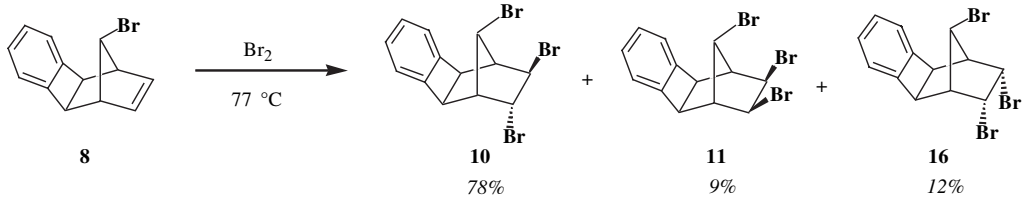
The reaction of parent molecules **1** and **4** does not give ring-opened molecules. For the different behaviour of bromine-substitued derivatives, the following general reaction mechanism is proposed (Scheme 5). The initially formed bromonium ion **12** may form either non-classical ion **13** (path A) to form **10** and **11** or it can rearrange to benzyl cation intermediate **14** to give **9** (path B). Bromination of **1** and **4** follows the single route (path A), but monobromides **7** and **8** behave differently, namely it follows two different routes (path A and path B). The observed different behaviour in molecules **7** and **8** may be attributed to the stability of the intermediates. We assume that the formation of non-classical ion **13b** is destabilised because of the electron-withdrawing substituent and steric effect caused by bromine atom. The formation of the stable benzyl cation **14** is partially favourable (path B) in molecules **7** and **8**. The production of **10** formed by bromination of *exo* isomer **8** can be explained by typical *trans* addition of bromine to the double bond.

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 the non-rearranged reaction products.[7-16] This factor encouraged us to raise the bromination temperature in order to obtain the *non*-rearranged bromination products derived from **8**. For the high-temperature bromination reaction, a hot solution of bromine in CCl_4 was added directly to the refluxing solution of **8** in CCl_4. NMR analysis of the crude product indicated that the reaction mixture consisted mainly of three products. After column chromatography, three isomeric non-rearranged dibromides **10** (78%), **11** (9%) and **16** (12%) were isolated (Scheme 6). At this temperature, the ring opened products and Wagner–Meerwein rearrangements products were not detected in any trace because brominations at high temperature take place especially via radical intermediates rather than ionic intermediates.[7-16] Contrary to cationic intermediates, radical intermediates are not prone to rearrangement except for the specific situation such as in homo allylic radicals.[17]

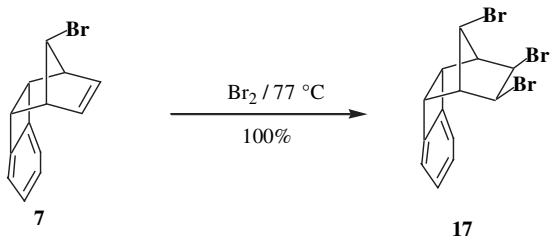
The bromination of *endo* isomer **7** at 77 °C gives only *exo-cis* tribromide **17**. The *endo* face of the double bond in monobromide **7** is hindered by the *endo* fused benzocyclobuteno group and so, the reaction result in *exo syn* addition of bromine atoms to double bond. *Trans* and *endo-cis* addition products were not obtained in any trace.

NMR spectral studies and configurational assignments: The structures of these compounds have been elucidated on the basis of ^1H and ^{13}C NMR spectral data and extensive double resonance experiments.

Structural analysis of the compounds having norbornane skeletal[4,8,11,18] was achieved with the help of the coupling constants. The configuration of the benzocyclobutene moiety was determined by measuring the coupling constants between H_1 (H_{10}) and H_2 (H_9). In the case of monobromide



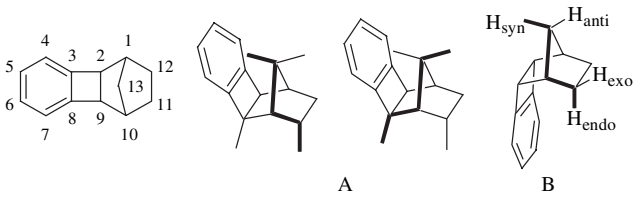
Scheme 6



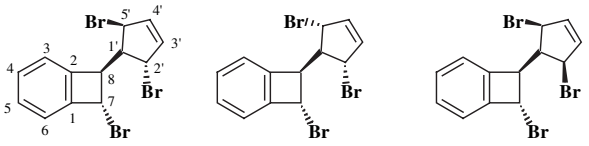
Scheme 7

7 and tribromide **17** (B-type), the coupling constants between H_1 (H_{10}) and H_2 (H_9) protons indicate the *endo* orientation of the benzocyclobutene moiety, whereas, in the case of monobromide **8** and tribromides **10**, **11** and **16** (A-type), the absence of the coupling constant between related protons confirm the *exo* orientation of the benzocyclobutene moiety. In addition to this, for the type B products, there is no measurable coupling constant between H_2 (H_9) and H_{13anti} proton. However, the existence of long range coupling constants (M or W orientation) between related protons in the compounds of A-type indicate *exo* orientation of the benzocyclobutene moiety (Scheme 8). Similarly, the configuration of the bromine atoms at C_{11}, C_{12} and C_{13} carbon atoms can be determined by measuring of the corresponding coupling constants between the protons $H_{11}(H_{12})$ – $H_{10}(H_1)$ and the protons $H_{11}(H_{12})$ – H_{13syn}. Tribromides **11**, **16** and **17** exhibit an AA'BB' for the aromatic protons which supports the symmetrical structure and *syn*-addition of bromine to the double bond. Furthermore, seven-lines ^{13}C NMR are also in agreement with the proposed structure. The existence of a coupling between CHBr protons and the bridge proton H_{13syn} (W or M arrangement of the coupled protons) and the lack of a coupling between CHBr protons and H_1 (H_{10}) supports the *exo* stereochemical arrangement of the bromine atoms in dibromides **11** and **17**. The structure of the tribromide **9** was ascribed on the basis of their NMR spectra. The coupling constant (J=1.9) between the cyclobutene moiety protons H_7 and H_8 show that the protons are *trans* configuration. The 13 lines in ^{13}C NMR exclude all *trans* **15** and all *cis* **18** structures in cycopentene ring. If we have these molecules, one would expect 11 lines in ^{13}C NMR because of symmetry in cyclopentene ring in these molecules (Scheme 9).

In conclusion, the results of the present work demonstrate that monobromo derivatives of benzocyclobutenonorbornene systems behave differently skeletal rearrangement in bromination reactions, unlike parent molecules. The electronic and steric effects of the substituent orientate the reaction tendency. In addition to this, bromination of these molecules at higher temperature prevents rearrangement.



Scheme 8



Scheme 9

Experimental

General: Melting points are uncorrected. IR 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-MHz spectrometers. The apparent splitting is given in all cases. Elemental analyses were recorded on Leco-CHNS-932 model spectrometer. Column chromatography (CC) was performed on silica gel (60-mesh, Merck). All substances reported in this paper are in their racemic form.

Caution: It has been reported[19] 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 deaths. The third exhibited minor skin sensitivity reactions. In the case of dibromide derived from benzonorbornadiene there is no literature report about the toxicological effect. However, we recommend that the compounds be handled only with extreme caution.

Synthesis of monobromide **7***:* To a stirred solution of dibromide **6**[5] (0.50 g, 1.52 mmol) in dry and freshly distilled THF (20 ml) was added 0.26 g (2.28 mmol) of potassium *tert*-butoxide solution in THF (5 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 filtered on a short silica gel column (10 g) eluted with *n*-hexane to give 358 mg (95%) of **7** as the sole product.

(1R(S),2R(S),9S(R),10S(R))-13-anti-bromotetracyclo[*8.2.1.0*^{2,9}*.0*^{3,8}] *trideca-3,5,7,11-tetraene* (**7**)*:* Colourless crystals from methylenchloride/*n*-hexane (1:3). m.p. 136-137 °C; ^1H NMR (200 MHz, $CDCl_3$): δ 7.26–6.92 (AA'BB' system, 4H, H_{aryl}); 5.65 (m, 2H, H_{11} and H_{12}); 4.07 (m, 1H, H_{13}); 3.77 (m, 2H, H_2 and H_9); 3.29 (m, 2H, H_1 and H_{10}). ^{13}C NMR (50 MHz, $CDCl_3$): δ 148.58, 132.23, 129.29, 124.40, 68.52, 53.37, 44.29. IR (KBr, cm^{-1}): 3056, 2998, 2960, 1451, 1343, 1293, 1254, 1181, 946, 850, 727. Anal. Calc. for $C_{13}H_{11}Br$: C, 63.18; H, 4.49 found: C, 63.08; H, 4.53. MS (EI, 70 eV) *m/z* 247/246 (M^+, 3); 167 (M^+-Br, 100); 152 (51); 115 (10); 102 (45); 83 (17%).

Synthesis of monobromide **8**: The reaction was carried out according to above procedure using a mixture of dibromides (2/3) (0.5 g, 1.52 mmol) and monobromide **8** was obtained as a sole product (346 mg, 92%).

(1R(S),2S(R),9R(S),10S(R))-13-anti-bromotetracyclo[*8.2.1.0*^{2,9}*.0*^{3,8}] *trideca-3,5,7,11-tetraene* (**8**)*:* Colourless crystals from methylenchloride/*n*-hexane (1:5). m.p. 91 °C; lit[6] m.p. 93–93.5 °C (from methanol) ^1H NMR (200 MHz, $CDCl_3$): δ 7.27–7.01 (AA'BB' system, 4H, H_{aryl}); 6.25 (m, 2H, H_{11} and H_{12}); 3.64 (m, 1H, H_{13}); 3.30 (m, 2H, H_2 and H_9); 3.09 (m, 2H, H_1 and H_{10}). ^{13}C NMR (50 MHz, $CDCl_3$): δ 145.88, 136.53, 129.89, 124.17, 65.69, 51.55, 48.98. IR (KBr, cm^{-1}): 3063, 2998, 2954, 1452, 1330, 1266, 1189, 1157, 836, 791, 701. Anal. Calc. for $C_{13}H_{11}Br$: C, 63.18; H, 4.49 found: C, 63.33; H, 4.46. MS (EI, 70 eV) *m/z* 247/246 (M^+, 6); 167 (M^+-Br, 100); 152 (49); 115 (10); 102 (55); 82 (35%).

Bromination of (1R(S),2R(S),9S(R),10S(R))-13-anti-bromotetracyclo[*8.2.1.0*^{2,9}*.0*^{3,8}]*trideca-3,5,7,11-tetraene* (**7**) *at –50±5 °C:* To a magnetically stirred solution of **7** (0.5 g, 2.02 mmol) in 10 ml dry $CHCl_3$ at –50±5 °C was added dropwise a solution of bromine (356 mg, 2.22 mmol) in 2 ml $CHCl_3$ over 5 min. After 30 min, the solvent was evaporated. The residue was treated with 5 ml methylenechloride/*n*-hexane (1:5) and allowed to stand one day in refrigerator. Pure tribromide **9** was obtained (580 mg). After filtration of **9**, the residue was analysed by NMR spectroscopy. Tribromide **9** (580 mg crystal, 46 mg mixture, total 76%), tribromide **10** (58 mg, 7%) and tribromide **11** (7–8 mg, 1≥%).

(7S(R),8R(S))-7-bromo-8-(2R(S),5R(S))-2,5-dibromocyclopent-3-en-1-ylbicyclo[*4.2.0*]*octa-1,3,5-triene* (**9**)*:* Colourless crystals m.p. 77–78 °C ^1H NMR (200 MHz, $CDCl_3$): δ 7.41–7.15 (m, 4H, H_{aryl}); 6.11 (m, 2H, $H_{3'}$ and $H_{4'}$); 5.28 (d, $J_{7,8}$=1.9 Hz, 1H, H_7) 4.92 (m, 2H, $H_{2'}$ and $H_{5'}$); 3.78 (dd, A part of AB system, $J_{8,1'}$=9.2 Hz, $J_{7,8}$=1,9 Hz, 1H, H_8); 3.47 (dt, B part of AB system, $J_{1',8}$=9.2 Hz, $J_{1',2'}$=$J_{1',5'}$=2.3 Hz, 1H, $H_{1'}$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 145.30, 143.76, 137.32, 137.28, 132.57, 131.59, 125.00, 124.95, 63.01, 60.61, 54.04, 53.95, 45.80. IR (KBr, cm^{-1}): 3068, 3037, 2960, 2921, 1451, 1351, 1235, 1197, 1085, 927, 881, 792. Anal. Calc. for $C_{13}H_{11}Br_3$: C, 38.37; H, 2.72; found: C, 37.79; H, 2.69. MS (EI, 70 eV) *m/z*

410/408/406/404 (M^+, 1); 329/327/325 (M^+-Br, 4); 247/245 (M^+-2Br, 19); 181 (15); 166 (M^+-3Br, 100); 152 (24); 102 (32); 82 (39%).

Bromination of (1R(S),2S(R),9R(S),10S(R))-13-anti-bromotetracyclo[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7,11-tetraene (**8**) *at –50±5 °C:* The reaction was carried out according to above procedure using monobromide **8** (0.5 g, 2.02 mmol) After reaction, the residue was analysed by NMR spectroscopy. Tribromide **9** (650 mg, 79%), tribromide **10** (107 mg, 7%).

Bromination of (1R(S),2S(R),9R(S),10S(R))-13-anti-bromotetracyclo[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7,11-tetraene (**8**) *at 77* °C: 0.5 g (2.02 mmol) of alkene **8** 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 (0.42 g, 2.63 mmol) in 2 ml of carbon tetrachloride during 5 min. The resulting reaction mixture was heated for 5 min 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 hexane.

The first fraction: *13-anti-(1R(S),2S(R),9R(S),10S(R),11S(R),12R(S))-11,12,13-tribromotetracyclo[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7-triene* (**16**): (100 mg, 12%) Colourless crystals from methylenchloride/*n*-hexane (1:3). m.p. 169 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.32–7.00 (AA'BB' system, 4H, H_{aryl}); 5.11 (AA' part of AA'XX' system, 2H, H_{11} and H_{12}); 4.08 (s, 2H, H_2 and H_9); 3.69 (t, $J_{1,13}$= $J_{10,13}$=1.7 Hz, 1H, H_{13}); 2.73 (XX' part of AA'XX' system, 2H, H_1 and H_{10}). ^{13}C NMR (50 MHz, $CDCl_3$): δ 145.83, 130.70, 124.71, 56.05, 55.61, 51.46, 46.86. IR (KBr, cm^{-1}): 3064, 2979, 2948, 1447, 1351, 1316, 1254, 1150, 1085, 977. Anal. Calc. for $C_{13}H_{11}Br_3$: C, 38.37; H, 2.72; found: C, 39.02; H, 2.65. MS (EI, 70 eV) *m/z* 410/408/406/404 (M^+, 5); 329/327/325 (M^+-Br, 1); 247/245 (M^+-2Br, 30); 199 (41); 166 (M^+-3Br, 100); 141 (73); 102 (27); 82 (43%).

The second fraction: 13-anti-*(1R(S),2S(R),9R(S),10S(R),11R(S),12R(S))-11,12,13-tribromotetracyclo[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7-trien* (**10**): (642 mg, 78%) Colourless crystals from methylenchloride/*n*-hexane (1:3). m.p. 152 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.33–7.29 (m, 2H, H_{aryl}); 7.11–7.05 (m, 2H, H_{aryl}); 5.13 (t, $J_{11,12}$= $J_{1,12}$=4.6 Hz, 1H, H_{12}); 4.08 (bd, A part of AB system, $J_{2,9}$=4.4 Hz, 1H, H_2 or H_9); 3.85 (dd, $J_{11,12}$=4.6 Hz, $J_{11,13}$=2.3 Hz, 1H, H_{11}); 3.68 (m, 1H, H_{13}); 3.47 (bd, B part of AB system, $J_{2,9}$=4.4 Hz, 1H, H_2 or H_9); 2.87 (m, 1H, 10-H); 2.76 (m, 1H, H_1). ^{13}C NMR (50 MHz, $CDCl_3$): δ 145.50, 144.49, 131.06, 130.82, 124.85, 124.73, 61.18, 56.34, 53.61, 53.30, 53.02, 50.92, 46.40. IR (KBr, cm^{-1}): 3068, 2971, 1451, 1351, 1293, 1189, 1081, 919, 823, 754. Anal. Calc. for $C_{13}H_{11}Br_3$: C, 38.37; H, 2.72; found: C, 38.05; H, 2.70. MS (EI, 70 eV) *m/z* 410/408/406/404 (M^+, 5); 329/327/325 (M^+-Br, 5); 247/245 (M^+-2Br, 27); 199 (29); 166 (M^+-3Br, 100); 141 (27); 82 (43%).

The third fraction: *13-anti-(1R(S),2S(R),9R(S),10S(R),11R(S),12S(R))-11,12,13-tribromotetracyclo[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7-trien* (**11**): (74 mg, 9%) Colourless crystals from methylenchloride/*n*-hexane (1:3). m.p. 236–237 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.32–7.04 (AA'BB' system, 4H, H_{aryl}); 4.20 (d, $J_{11,13}$= $J_{12,13}$=1.3 Hz 2H, H_{11} and H_{12}); 3.70 (m, 1H, H_{13}); 3.39 (m, 2H, H_2 and H_9); 3.03 (m, 2H, H_1 and H_{10}). ^{13}C NMR (50 MHz, $CDCl_3$): δ 144.76, 131.00, 124.77, 54.45, 53.54, 50.40, 50.27. IR (KBr, cm^{-1}): 3430, 1643, 1451, 1285, 1235, 1200, 1139, 985. Anal. Calc. for $C_{13}H_{11}Br_3$: C, 38.37; H, 2.72; found: C, 37.99; H, 2.75. MS (EI, 70 eV) *m/z* 410/408/406/404 (M^+, 5); 329/327/325 (M^+-Br, 3); 247/245 (M^+-2Br, 12); 199 (15); 166 (M^+-3Br, 100); 141 (36); 102 (23); 82 (35%).

Bromination of (1R(S),2R(S),9S(R),10S(R))-13-anti-bromotetracyclo[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7,11-tetraene (**7**) *at 77 °C:* The reaction was carried out according to above procedure using monobromide **7** (0.5 g, 2.02 mmol). After reaction, tribromide **17** was obtained as a sole product.

13-anti-(1R(S),2R(S),9S(R),10S(R),11R(S),12S(R))-11,12,13-tribromotetracyclo[8.2.1.0^{2,9}.0^{3,8}]-trideca-3,5,7-triene (**17**): Colourless crystals from methylenchloride m.p. 212–213 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.32–7.16 (AA'BB' system, 4H, H_{aryl}); 4.16 (m, 1H, H_{13}); 3.94 (d, $J_{11,13}$=$J_{12,13}$=1.4 Hz, 2H, H_{11} and H_{12}); 3.74 (AA' part of AA'XX' system, 2H, H_2 and H_9); 3.24 (XX' part of AA'XX' system, 2H, H_1 and H_{10}). ^{13}C NMR (50 MHz, $CDCl_3$): δ 146.74, 130.64, 126.80, 56.81, 53.01, 52.86, 49.74. IR (KBr, cm^{-1}): 3064, 3029, 2948, 1447, 1285, 1239, 1189, 1143, 1027, 977, 862, 754. Anal. Calc. for $C_{13}H_{11}Br_3$: C, 38.37; H, 2.72; found: C, 39.01; H, 2.68. MS (EI, 70 eV) *m/z* 410/408/406/404 (M^+, 2); 329/327/325 (M^+-Br, 5); 247/245 (M^+-2Br, 15); 199 (18); 166 (M^+-3Br, 100); 141 (32); 102 (20); 82 (34%).

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