Bromination of '*endo*-Benzocyclobutanorbornene': Synthesis of '*endo*-11,12-Dibromobenzocyclobutanorbornene': High-Temperature Bromination

Part XIV[1])

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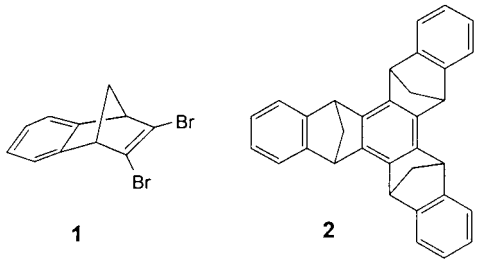
The electrophilic addition of Br to '*endo*-benzocyclobutanorbornene' **5** at −50° led in high yield to the formation of the rearranged dibromides **6** and **7**. However, high-temperature bromination of **5** in decalin at 150° gave exclusively nonrearranged product **8** in 98% yield. From the elimination of nonrearranged product **8**, '*endo*-bromobenzocyclobutanorbornene' **9** and '*endo*-benzocyclobutanorbornene' **5** were obtained. Similarly, bromination of monobromide **9** at 77° yielded the nonrearranged tribromide **12** in quantitative yield. The dehydrobromination of **12** provided the '*endo* 11,12-dibromobenzocyclobutanorbornene' **3** in high yield, which is a synthon for the trimerization reactions.

Introduction. – The recent discovery of fullerenes has spurred interest in the long-standing topic of aromaticity [2]. The mechanism of the formation and the reactivity of these molecules still awaits a convincing rationale, although many aspects are certainly related to the phenomenon of bond-length fixation of aromatic systems. 1-Bromo- and 1,2-dibromoethenyl derivatives of bicyclic systems are building blocks of fullerenes. For example, earlier [2a], we developed a high-yielding synthesis of **2**, which displays unusual geometric and electronic features, including bond-length fixation of the central benzene ring, using the dibromo derivative **1**.



1 **2**

In addition to synthetic aspects, bromination of bicyclic alkenes is a process of considerable potential mechanistic interest. Electrophilic bromination of simple cycloalkenes almost invariably yields *trans*-1,2-dibromo derivatives [3]. In addition to this, the nature of the intermediates of the addition reaction depends on

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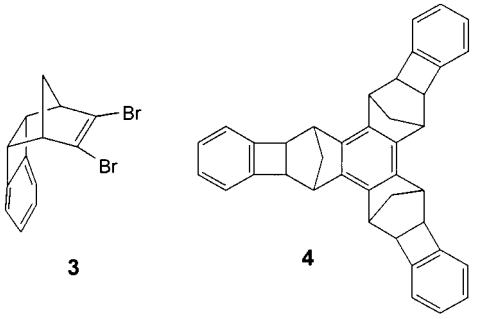
temperature, steric factors, torsional effects, π and σ participation in the transition state, and the formation of nonclassical ions or of classical ions in fast equilibrium. The bromination of unsaturated bicyclic systems with molecular Br_2 leads to rearrangements of the molecular skeleton [4]. Furthermore, we have shown previously that high-temperature bromination of bicyclic systems gives mainly *non*rearranged products [5].

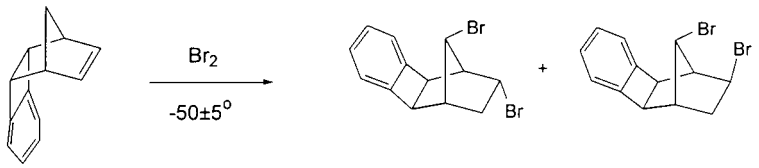
In this work, we were interested in the behavior of an *endo*-benzocyclobuta ring system fused to norbornene with respect to the product distribution in low- and high-temperature bromination reactions. Furthermore, we have directed our attention to the synthesis of '*endo*-dibromobenzocyclobutanorbornene' **3** that can serve as a building block for the construction of the basket-shaped fullerene cognate **4** in connection with our trimerization reaction [2a].



3 **4**

Results and Discussions. – First, '*endo*-benzocyclobutanorbornene' **5** was prepared according to published methods [6]. The electrophilic addition of Br_2 to **5** was first reported by *Nenitzescu* and co-workers [7]. For updating the literature data, we also reacted **5** with Br_2 in $CHCl_3$ solution at $-50 \pm 5^\circ$ and isolated the dibromo derivatives **6** and **7** in high yield as reported in the literature (*Scheme 1*).

Scheme 1

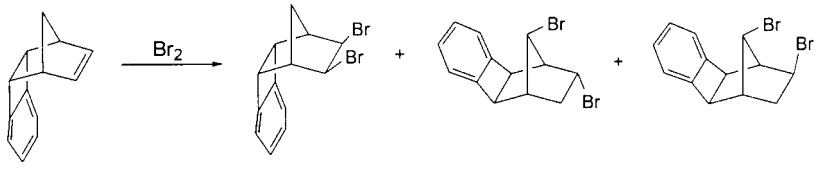


5 **6** (54%) **7** (42%)

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 nonrearranged reaction products [5]. This finding encouraged us to raise the bromination temperature in order to obtain the nonrearranged bromination products derived from **5**. For the high-temperature bromination reaction, a hot solution of Br_2 in CCl_4 was added directly to refluxing solution of **5** in CCl_4. NMR Analysis of the crude product indicated that the reaction mixture consisted mainly of three products. After column chromatography, three isomeric compounds, a nonrearranged dibromo derivative **8** (83%) and two rearranged dibromo derivatives **6** (7%) and **7**

(6%) were isolated (*Scheme 2*). The reaction temperature, 77°, was probably not sufficient to prevent the skeletal rearrangement completely. Therefore, we applied much higher temperature for the bromination of **5** in order to suppress the formation of the rearranged products. Bromination of **5** in decalin at 150° gave only nonrearranged product **8** beside of a trace of brominated decalin derivative (for bromination of decalin and derivatives, see [8]). At this temperature, the rearranged products **6** and **7** were not detected. Compound **8** exhibits an *AA′BB′* system arising from the aromatic H-atoms, which indicates clearly the symmetrical structure and the *syn* addition [9] of Br_2. Furthermore, a seven-line ^{13}C-NMR is also in agreement with the proposed structure.

Scheme 2



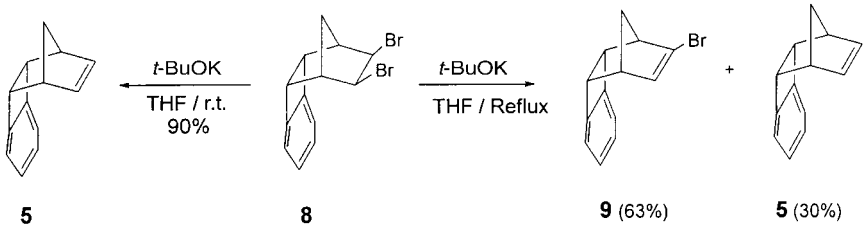
5	**8**	**6**	**7**
77° in CCl_4	83%	7%	6%
150° in Decalin	98%	-	-

In the case of high-temperature addition of Br_2, we assume that bromination is occurring mainly by a free-radical mechanism. Radical intermediates are much less prone to rearrange. The formation of rearranged products **6**/**7** and nonrearranged product **8** indicates that there is a competition between radical and ionic reactions. However, conducting the bromination reaction at high-temperature (150°), suppressed completely the formation of the rearranged products. This outcome supports the radical addition mechanism of Br_2 to the C=C bond in **5**.

Elimination Reaction with the Dibromo Derivative **8**: *Unusual Br_2 Elimination with* t-*BuOK*. Treatment of **8** with *t*-BuOK gave the *endo*-configured alkene **5** as the sole product in 90% yield (*Scheme 3*). This result is, at first glance, unexpected, since HBr elimination with a base is quite normal rather than Br_2 elimination. It has been well-documented that the activation barrier for *syn* elimination in five-membered rings is smaller than the barrier for the *anti* elimination [10]. Probably, the activation barrier of an *anti* HBr elimination in **8** is so high, that the HBr elimination did not take place at room temperature. However, the base can attack Br and perform a *syn* elimination of Br to give the alkene **5**. On the contrary, elimination of dibromide **8** in refluxing THF gave the expected monobromo compound **9** beside alkene **5** (*Scheme 3*). The mixture could be easily separated by vacuum distillation.

Bromination of the Monobromo Derivative **9**. Further bromination of **9** at $-50 \pm 5°$ gave mainly rearranged products **10**, **11**, **13**, and **14** beside nonrearranged product **12** (*Scheme 4*). The ^{1}H-NMR spectrum of the crude product indicated that the tribromo compounds **10**, **11**, **12**, and **13** were primary products. The bromo alcohols **15**/**16** were formed during column chromatography. The isomer **14** was formed by isomerization of **13**. The unchangeable ratio **13**/**14** shows that there is an equilibrium between **13** and **14**.

Scheme 3



Because of this equilibrium, tribromo compounds **13** and **14** could not be isolated as pure compounds. However, NMR analysis of a mixture provided us enough information for the configurational assignment to the proposed structures. For further support of the structures, bromo alcohols **15**/**16** were subjected to oxidation with MnO_2, and α,β-unsaturated ketones **17**/**18** were obtained in high yield. The chemical structures of these enones were determined by spectroscopic methods.

The formation of tribromo compounds **10** and **11** is straightforward because they are typical *Wagner-Meerwein* rearrangement products. However, the ring-opened isomers **13** and **14** were not expected from simple Br_2 addition to **9**. For the formation of the rearranged products **13**/**14**, a general reaction mechanism is proposed in *Scheme 5*. The initially formed bromonium ion **19** may form either nonclassical ion **20** (*Path A*) to form **6**/**7** and **10**/**11**, or it can rearrange to the benzyl cation intermediate **21** to give **13** (*Path B*). Bromination of **5** follows the single route (*Path A*), but **9** behaves differently, namely it follows two different routes (*Paths A* and *B*). The observed different behavior in molecule **9** may be attributed to the stability of the intermediates. We assume that the formation of nonclassical ion **20b** is destabilized because of the electron-withdrawing substituent and steric effect caused by Br-atom. The formation of the stable benzyl cation **21** is favorable (*Path B*) in molecule **9**.

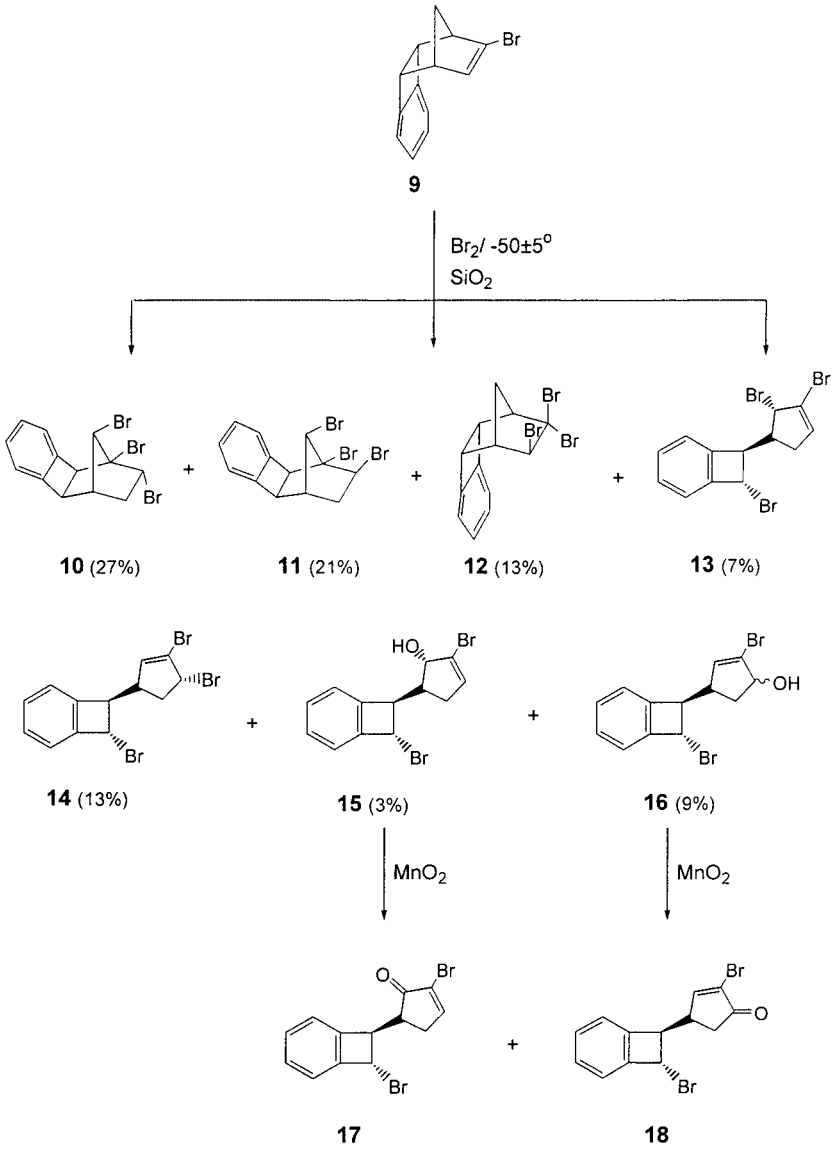
High-temperature bromination of **9** at 77° in CCl_4 yielded only nonrearranged product **12** in nearly quantitative yield (*Scheme 6*). This observation indicates that bromo analogue **9** of *endo*-alkene **5** is less prone to rearrangement.

Treatment of tribromo compound **12** in THF with *t*-BuOK at room temperature gave a mixture of the target compound **3** *via* HBr elimination and monobromo compound **9** *via* Br_2 elimination (*Scheme 7*). However, the dehydrobromination reaction of **12** at reflux temperature of THF resulted in the formation of **3** as the sole product in high yield. Comparison of this result with that from elimination of dibromo derivative **8** shows that tribromo compound **12** undergoes more easily HBr elimination (rather than Br_2 elimination) than **8**. This can be explained on the basis of **12** having a H-atom in the *syn* position relative to the Br-atom, which is not the case in **8**.

NMR-Spectral Studies and Configurational Assignments. The structures of these compounds have been elucidated on the basis of ^{1}H- and ^{13}C-NMR-spectral data and extensive double-resonance experiments.

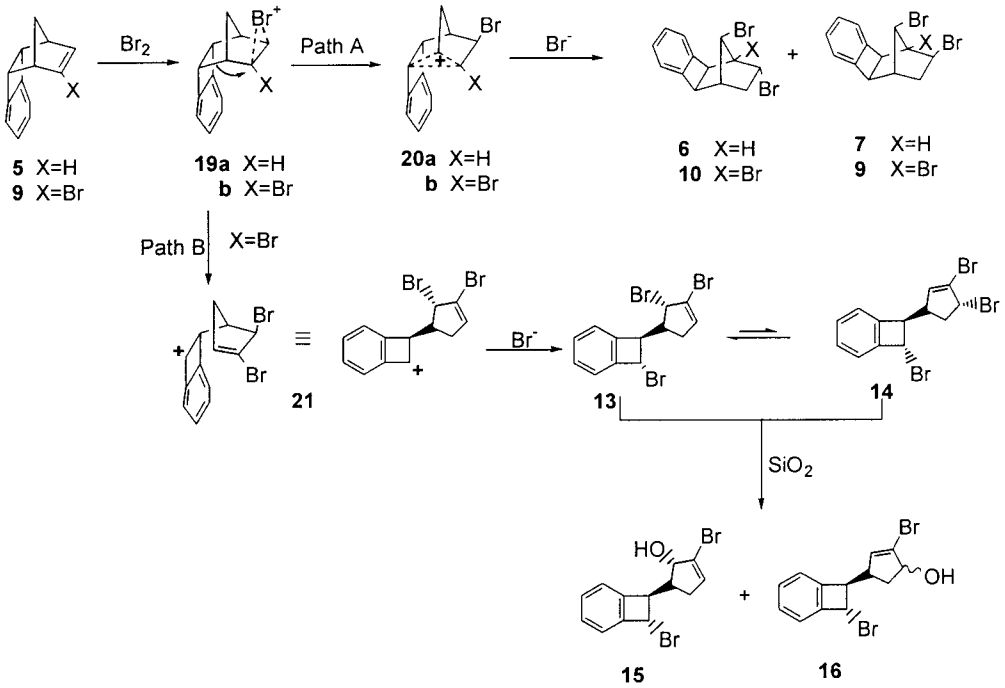
Structural analysis of the compounds with norbornane skeletons [5b][11] was achieved with the help of the coupling constants. The configuration of the benzocyclobuta moiety was determined by measuring the coupling constants between H–C(1), (H–C(10)) and H–C(2) (H–C(9)). In the case of dibromo compounds **3**

Scheme 4

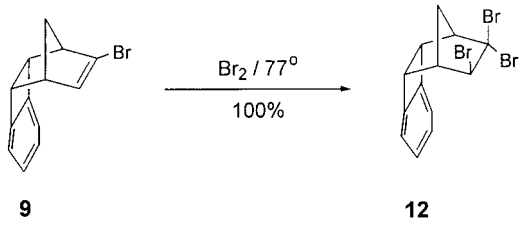


and **8**, monobromo compound **9**, and tribromo compound **12** (**B**-type; *Scheme 8*), the coupling constants between H–C(1) (H–C(10)) and H–C(2) (H–C(9)) ($J = 4.7$–5.5 Hz) indicate the *endo* orientation of the benzocyclobuta moiety, whereas, in the case of dibromo compounds **6**/**7** and tribromo derivatives **10**/**11** (**A**-type), the absence of the coupling constant between the corresponding H-atoms confirms the *exo* orientation of the benzocyclobuta moiety. In addition to this, for type **B** products, there

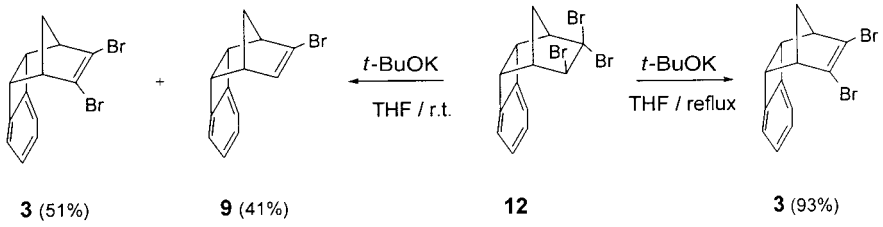
Scheme 5



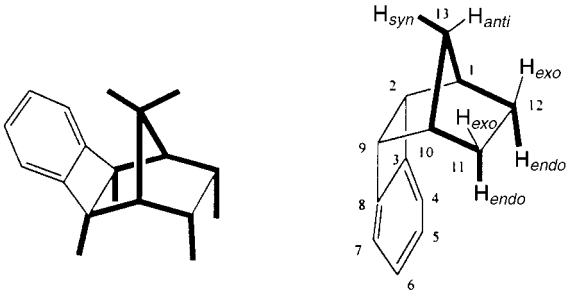
Scheme 6



Scheme 7



Scheme 8



A **B**

is no measurable coupling constant between H–C(2) (H–C(9)) and H_{anti}–C(13). However, the existence of long-range coupling constants (M or W orientation) between related H-atoms in the compounds of **A**-type indicate *exo* orientation of the benzocyclobuta moiety. Similarly, the spatial position of the Br atoms at C(11), C(12), and C(13) can be determined by measuring the corresponding coupling constants between H–C(11) (H–C(12)) and H–C(10) (H–C(1)), and H–C(11) (H–C(12)) and H_{syn}–C(13). Dibromo compound **8** exhibits an *AA′BB′* system for the aromatic H-atoms, which supports the symmetrical structure and *syn* addition of Br_2 to the C=C bond. Furthermore, a seven-line ^{13}C-NMR spectrum is also in agreement with the proposed structure. The existence of coupling between the H-atom of the CHBr moiety and the bridge H_{syn}–C(13) (W or M arrangement of the coupled H-atoms), and the lack of coupling between C*H*Br and H–C(1) (H–C(10)) supports the *exo*-orientation of the Br-atoms in **8**. The structures of the other molecules **13**–**16** were ascribed on the basis of their NMR spectra. The coupling constant between H-atoms H–C(7) and H–C(8) show that they are positioned *trans* relative to each other.

From these results, it can be concluded that the high-temperature bromination is a useful synthetic method to generate nonrearranged Br_2-addition products in the unsaturated bicyclic systems that exhibit a great tendency to undergo *Wagner-Meerwein* rearrangements. With this methodology, we have shown that the application of high-temperature bromination to '*endo*-benzocyclobutanorbornene' **5** provides an important synthetic tool for entry into the substituted '*endo*-benzocyclobutanorbornene' system. Furthermore, the synthesis of the dibromo compound **3** will serve as the key step for trimerization reactions.

Experimental Part

General. TLC: *Merck* 0.2-mm silica gel *60* F_{254} anal. aluminum plates. Column chromatography (CC): silica gel (60 mesh, *Merck*). M.p.: uncorrected. IR Spectra: from soln. in 0.1-mm cells or KBr pellets on a regular instrument, ^{1}H- and ^{13}C-NMR spectra: 400- and 200-MHz spectrometers; apparent splitting is given in all cases. All substances reported in this paper are racemates.

Caution: It has been reported [12] that of three laboratory workers who have used dibromides and a bromohydrin derived from norbornadiene, two later developed similar pulmonary disorders, which contributed to their subsequent deaths. The third exhibited minor skin sensitivity reactions. In the case of 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.

*Bromination of (1*SR,*2*SR,*9*RS,*10*SR*)-Tetracyclo[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7,11-tetraene* (**5**) *at* $-50 \pm 5°$: To a magnetically stirred soln. of **5** (0.5 g, 2.97 mmol) in 10 ml of dry $CHCl_3$ at $-50 \pm 5°$ was added dropwise a soln. of Br_2 (523 mg, 3.27 mmol) in 2 ml of $CHCl_3$ over 5 min. The color of Br_2 disappeared immediately. The solvent was evaporated. The residue was chromatographed on silica gel (100 g, hexane).

The first fraction provided *(1*RS,*2*SR,*9*RS,*10*RS,*11*RS,*13*RS*)-11,13-dibromotetracyclo[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7-triene* (**6**): 0.53 g (54%). Colorless crystals from CH_2Cl_2/hexane 1:3. M.p. 104–105° ([7]: 108°). IR: 3069*w*, 3024*w*, 2966*m*, 2934*m*, 2877*w*, 1459*s*, 1285*m*, 1247*m*, 1182*m*, 894*m*, 811*m*, 771*m*, 742*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.31–7.04 (*m*, 4 arom. H); 4.86 (*dt*, *J*(11,12*exo*) = 10.4, *J*(11,12*endo*) = *J*(10,11) = 4.2, 1 H–C(11)); 4.16 (*d*, *A* of *AX*, *J*(2,9) = 4.4, 1 H–C(9)); 3.61 (*m*, 1 H–C(13)); 3.48 (*d*, *X* of *AX*, *J*(2,9) = 4.4, 1 H–C(2)); 2.84 (*ddd*, *A* of *AX*, *J*(12*endo*,12*exo*) = 14.6, *J*(11,12*exo*) = 10.4, *J*(1,12*exo*) = 4.7, 1 H–C(12)); 2.69 (br. *d*, *J*(10,11) = 4.2, 1 H–C(10)); 2.47 (*d*, *J*(1,12*exo*) = 4.7, 1 H–C(1)); 1.60 (*ddd*, *X* of *AX*, *J*(12*endo*,12*exo*) = 14.6, *J*(11,12*endo*) = 4.2, *J*(12*endo*,13) = 2.4, 1 H–C(12)). ^{13}C-NMR (50 MHz, $CDCl_3$): 146.2; 146.1; 130.4; 130.3; 124.5; 124.3; 57.6; 52.3; 50.9 (2C); 47.9; 46.5; 40.1. Anal. calc. for $C_{13}H_{12}Br_2$: C 47.60, H 3.69; found: C 47.43, H 3.70.

The second fraction gave *(1*RS,*2*SR,*9*RS,*10*RS,*11*SR,*13*RS*)-11,13-dibromotetracyclo[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7-triene* (**7**): 0.41 g (42%). Colorless crystals from CH_2Cl_2/hexane 1:3. M.p. 99° ([7]: 76°). IR: 3063*w*, 2973*w*, 2947*m*, 2870*w*, 1452*m*, 1305*w*, 1240*m*, 1176*m*, 1138*m*, 926*m*, 894*m*, 823*m*, 778*m*, 752*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.30–7.04 (*m*, 4 arom. H); 3.90 (*ddd*, *J*(11,12*endo*) = 8.1, *J*(11,12*exo*) = 4.8, *J*(11,13) = 1.5, 1 H–C(11)); 3.68 (*m*, 1 H–C(13)); 3.37 (br. *d*, *A* of *AB*, *J*(2,9) = 4.8, 1 H–C(2)); 3.33 (br. *d*, *B* of *AB*, *J*(2,9) = 4.8, 1 H–C(9)); 2.91 (*m*, 1 H–C(10)); 2.74 (*dt*, *A* of *AB*, *J*(12*endo*,12*exo*) = 13.7, *J*(11,12*exo*) = *J*(1,12*exo*) = 4.8, 1 H–C(12)); 2.60 (br. *d*, *J*(1,12*exo*) = 4.8, 1 H–C(1)); 2.24 (*ddd*, *B* of *AB*, *J*(12*endo*,12*exo*) = 13.7, *J*(11,12*endo*) = 8.1, *J*(12*endo*,13) = 1.3, 1 H–C(12)). ^{13}C-NMR (50 MHz, $CDCl_3$): 146.2; 145.0; 130.6; 130.5; 124.5 (2C); 53.9; 52.5; 51.1; 49.7; 48.1; 47.5; 42.2. Anal. calc. for $C_{13}H_{12}Br_2$: C 47.60, H 3.69; found: C 47.38, H 3.73.

*Bromination of (1*RS,*2*SR,*9*RS,*10*SR*)-tetracyclo[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7,11-tetraene* (**5**) at 77°: 0.5 g (2.97 mmol) of alkene **5** was dissolved in 10 ml of CCl_4 in a 25-ml flask, which was equipped with a reflux condenser. The soln. was heated while stirring magnetically until CCl_4 started to reflux. To the refluxing soln. was added dropwise a hot soln. of Br_2 (0.57 g, 3.56 mmol) in 2 ml of CCl_4 during 5 min. The resulting mixture was heated for 1 min at reflux temp. After cooling to r.t., the solvent was evaporated, and the oily residue was crystallized from CH_2Cl_2/hexane 1:2. Compound **8** was obtained (695 mg of crystals and 115 mg of mixture, total 810 mg, 83% yield).

*(1*RS,*2*SR,*9*RS,*10*SR,*11*SR,*12*RS*)-11,12-Dibromotetracyclo[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7-triene* (**8**): Colorless crystals from CH_2Cl_2/hexane 1:2. M.p. 116–117°. IR: 3070*w*, 2966*m*, 2947*m*, 2870*w*, 1452*m*, 1271*w*, 1195*w*, 932*m*, 809*m*, 758*s*, 720*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.27–7.13 (*AA′BB′*, 4 arom. H); 3.90 (*d*, *J*(11,13*syn*) = *J*(12,13*syn*) = 2.0, 2 H–C(11), H–C(12)); 3.72 (*AA′* of *AA′XX′*, 2 H–C(2), H–C(9)); 2.92 (*XX′* of *AA′XX′*, 2 H–C(1), H–C(10)); 2.60 (br. *d*, *A* of *AB*, *J*(13*syn*,13*anti*) = 10.8, 1 H–C(13)); 1.83 (*dtt*, *B* of *AB*, *J*(13*syn*,13*anti*) = 10.8, *J*(11,13*syn*) = *J*(12,13*syn*) = 2.0, *J*(1,13*syn*) = *J*(10,13*syn*) = 1.4, 1 H–C(13)). ^{13}C-NMR (50 MHz, $CDCl_3$): 147.3; 129.8; 126.6; 56.7; 53.1; 51.8; 41.2. Anal. calc. for $C_{13}H_{12}Br_2$: C 47.60, H 3.69; found: C 47.91, H 3.71.

After filtration of **8**, the residue was chromatographed on silica gel (50 g) with hexane. Three compounds were isolated in the following order: **6** (68 mg, 7%), **8** (115 mg from column and 695 mg of crystals, total 810 mg, 83%), and **7** (59 mg, 6%).

*Bromination of (1*RS,*2*SR,*9*RS,*10*SR*)-Tetracyclo[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7,11-tetraene* (**5**) *at 150°*. Compound **5** (3.6 g, 21.42 mmol) was dissolved in 20 ml of decalin in a 50-ml two-necked flask equipped with reflux condenser and an inlet glass tube touching the bottom of the reaction flask. The inlet-glass tube was connected to a 2-ml of round-bottom flask containing 4.16 g (26.03 mmol) of Br_2. Br_2 Vapors obtained by heating the flask to 100°, were transferred directly to the decalin soln. at 150° in 5 min while stirring magnetically. The color of Br_2 disappeared immediately. The solvent was removed under reduced pressure. The oily residue was filtered on a short silica-gel column (10 g) eluting with hexane. Crystallization of residue gave pure **8** (6.9 g, 98%).

Elimination Reaction with **8**. To a stirred soln. of **8** (0.50 g, 1.52 mmol) in dry and freshly distilled THF (20 ml) *t*-BuOK (1.71 g, 15.20 mmol) in THF (5 ml) was added. The resulting mixture was stirred for 4 d at r.t. The solvent was evaporated, and the mixture was diluted with H_2O and the aq. soln. was extracted with Et_2O (3×50 ml), washed with H_2O, and dried ($MgSO_4$). After removal of the solvent, the residue was filtered on a short silica-gel column (10 g) eluted with hexane to give 231 mg (90%) of **5** as the sole product.

Elimination Reaction with **8** *in Refluxing THF*. To a stirred soln. of **8** (5.0 g, 15.24 mmol) in dry and freshly distilled THF (80 ml), *t*-BuOK (5.6 g, 5.00 mmol) in THF (15 ml) was added at r.t. The reaction mixture was

refluxed for 2 d. The solvent was evaporated, and the mixture was diluted with H_2O, and the aq. soln. was extracted with Et_2O (3×50 ml), washed with H_2O, and dried ($MgSO_4$). After removal of the solvent, ^{1}H-NMR shows that the mixture consists of **9** and **5** in a ratio of 2:1. The alkene **5** was separated from mixture by vacuum distillation (0.77 g, 30%). The residue was **9** (2.46 g, 63% yield).

*(1*SR*,2*SR*,9*SR*,10*RS*)-11-Bromotetracyclo[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7,11-tetraene* (**9**): Colorless crystals from hexane. M.p. 51°. IR: 3063*m*, 2986*m*, 2940*m*, 2870*m*, 1587*m*, 1452*m*, 1317*m*, 1279*m*, 1247*m*, 1138*m*, 1003*m*, 933*m*, 817*m*, 759*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.19–6.94 (*m*, 4 arom. H); 5.73 (*d*, *J*(1,12) = 3.1, 1 H–C(12)); 3.91 (*t*, *J*(2,9) = *J*(9,10) = 4.7, 1 H–C(9)); 3.74 (*t*, *J*(2,9) = *J*(1,2) = 4.7, 1 H–C(2)); 3.10 (br. *d*, *J*(9,10) = 4.7, 1 H–C(10)); 3.00 (*m*, 1 H–C(1)); 2.22 (br. *d*, *A* of *AB*, *J*(13*syn*,13*anti*) = 8.5, 1 H–C(13)); 1.70 (br. *d*, *J*(13*syn*,13*anti*) = 8.5, 1 H–C(13)). ^{13}C-NMR (50 MHz, $CDCl_3$): 149.0; 148.4; 134.2; 129.0; 128.6; 125.7; 124.5; 124.2; 56.3; 54.1; 49.1; 47.9; 46.8. Anal. calc. for $C_{13}H_{11}Br$: C 63.18, H 4.49; found: C 63.28, H 4.51.

Bromination of **9** *at* $-50 \pm 5°$. To a magnetically stirred soln. of **9** (1.5 g, 6.07 mmol) in 20 ml dry $CHCl_3$ at $-50 \pm 5°$, a soln. of Br_2 (1.0 g, 6.25 mmol) in 5 ml $CHCl_3$ was added dropwise over 10 min. The color of Br_2 disappeared immediately. The solvent was evaporated. The residue was chromatographed on silica gel (100 g) with hexane.

The first fraction yielded *(1*SR*,2*SR*,9*RS*,10*RS*,12*RS*,13*RS*)-1,12,13-tribromotetracyclo[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7-triene* (**10**): 667 mg (27%). Colorless crystals from CH_2Cl_2/hexane 1:4. M.p. 68°. IR: 3063*w*, 3012*m*, 2973*m*, 2947*m*, 2864*w*, 1452*m*, 1285*m*, 1240*s*, 1182*m*, 1144*m*, 933*m*, 803*s*, 752*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.39–7.07 (*m*, 4 arom. H); 4.81 (*dd*, *J*(11*exo*,12) = 10.7, *J*(11*endo*,12) = 4.3, 1 H–C(12)); 4.40 (*d*, *A* of *AX*, *J*(2,9) = 4.4, 1 H–C(2)); 3.74 (*dd*, *J*(11*endo*,13*syn*) = 2.4, *J*(10,13) = 1.7, 1 H–C(13)); 3.66 (br. *d*, *X* of *AX*, *J*(2,9) = 4.4, 1 H–C(9)); 3.06 (*ddd*, *A* of *AX*, *J*(11*endo*,11*exo*) = 13.5, *J*(11*exo*,12) = 10.7, *J*(10,11*exo*) = 4.9, 1 H–C(11)); 2.49 (br. *d*, *J*(10,11*exo*) = 4.9, 1 H–C(10)); 1.86 (*ddd*, *X* of *AX*, *J*(11*endo*,11*exo*) = 13.5, *J*(11*endo*,12) = 4.3, *J*(11*endo*,13*syn*) = 2.4, 1 H–C(11)). ^{13}C-NMR (50 MHz, $CDCl_3$): 145.4; 144.6; 131.2; 130.8; 125.2; 124.2; 68.6; 62.5; 58.9; 52.6; 52.0; 45.4; 41.8. Anal. calc. for $C_{13}H_{11}Br_3$: C 38.37, H 2.72; found: C 38.94, H 2.71.

The second fraction gave *(1*SR*,2*RS*,9*SR*,10*RS*,12*SR*)-11,11,12-tribromotetracyclo[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7-triene* (**12**): 321 mg (13%). Colorless crystals from CH_2Cl_2/hexane, 1:3). M.p. 137° IR: 3061*m*, 2992*s*, 2947*m*, 1461*m*, 1346*w*, 1269*m*, 1115*w*, 1000*s*, 930*m*, 807*m*, 753*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.30–7.11 (*m*, 4 arom. H); 4.19 (*d*, *J*(12,13*syn*) = 2.4, 1 H–C(12)); 3.83 (*dd*, *A* of *AB*, *J*(2,9) = 6.0, *J*(9,10) = 5.5, 1 H–C(9)); 3.67 (*dd*, *B* of *AB*, *J*(2,9) = 6.0, *J*(1,2) = 5.2, 1 H–C(2)); 3.51 (br. *d*, *J*(9,10) = 5.5, 1 H–C(10)); 2.93 (br. *d*, *A* of *AB*, *J*(13*syn*,13*anti*) = 11.1, 1 H–C(13)); 2.83 (br. *d*, *J*(1,2) = 5.2, 1 H–C(1)); 1.74 (*ddt*, *J*(13*syn*,13*anti*) = 11.1, *J*(12,13*syn*) = 2.4, *J*(1,13*syn*) = *J*(10,13*syn*) = 1.5, 1 H–C(13)). ^{13}C-NMR (50 MHz, $CDCl_3$): 147.38; 145.45; 129.91 (2 C); 129.67; 125.96; 74.44; 63.41; 61.88; 54.23; 53.49; 51.30; 43.44. Anal. calc. for $C_{13}H_{11}Br_3$: C 38.37, H 2.72; found: C 38.60, H 2.67.

The third fraction consisted of a mixture of **13** and **14** (494 mg, in ratio of 65:35, resp.), which could not be isolated in pure state because of the tendency of these molecules to undergo easily configuration isomerization and hydrolysis on the column material to form dibromo alcohols **15** and **16**. The structures of **13** and **14** were fully characterized by NMR of the mixture.

*(7*SR*,8*RS*)-7-Bromo-8-[(1*SR*,2*SR*)-2,3-dibromocyclopent-3-en-1-yl]bicyclo[4.2.0]octa-1,3,5-triene* (**13**): ^{1}H-NMR (400 MHz, $CDCl_3$): 7.33–7.10 (*m*, 4 arom. H); 6.02 (*t*, *J*(4,5a) = *J*(4,5b) = 2.5, 1 H–C(4)); 5.07 (*d*, *J*(7,8) = 1.5, 1 H–C(7)); 4.73 (*m*, 1 H–C(2)); 3.72 (*dd*, *J*(1,8) = 7.8, *J*(7,8) = 1.5, 1 H–C(8)); 3.12 (*m*, 1 H–C(1)); 2.78 (*ddt*, *A* of *AB*, *J*(5a,5b) = 17.0, *J*(5a,1) = 7.4, *J*(5a,4) = *J*(5a,2) = 2.5, 1 H–C(5)); 2.18 (*dt*, *B* of *AB*, *J*(5a,5b) = 17.0, *J*(4,5b) = *J*(1,5b) = 2.5, 1 H–C(5)).

*(7*SR*,8*RS*)-7-Bromo-8-[(1*SR*,4*RS*)-3,4-dibromocyclopent-2-en-1-yl]bicyclo[4.2.0]octa-1,3,5-triene* (**14**): ^{1}H-NMR (400 MHz, $CDCl_3$): 7.33–6.97 (*m*, 4 arom. H); 5.95 (*d*, *J*(1,2) = 1.7, 1 H–C(2)); 4.94 (*d*, *J*(7,8) = 1.6, 1 H–C(7)); 4.82 (br. *d*, *J*(4,5b) = 7.1, 1 H–C(4)); 3.73 (br. *d*, *J*(1,8) = 6.1, 1 H–C(8)); 3.38 (*m*, 1 H–C(1)); 2.62 (*dd*, *A* of *AB*, *J*(5a,5b) = 14.4, *J*(5a,1) = 6.7, *J*(5a,4) = 0, 1 H–C(5)); 2.27 (*dd*, *B* of *AB*, *J*(5a,5b) = 14.4, *J*(4,5b) = 7.1, *J*(5b,1) = 0, 1 H–C(5)).

The fourth fraction was *(1*SR*,2*SR*,9*RS*,10RS,12*SR*,13*RS*)-1,12,13-tribromotetracyclo[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7-triene* (**11**): 519 mg (21%). Colorless crystals from CH_2Cl_2/hexane 1:4. M.p. 85–86°. IR: 3075*w*, 2992*w*, 2947*m*, 2864*w*, 1445*m*, 1298*s*, 1240*m*, 1182*m*, 1138*m*, 1028*m*, 971*m*, 933*m*, 829*s*, 765*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.37–7.07 (*m*, 4 arom. H); 4.17 (*ddd*, *J*(11*endo*,12) = 8.0, *J*(11*exo*,12) = 4.9, *J*(12,13) = 1.5, 1 H–C(12)); 3.76 (*m*, 1 H–C(13)); 3.60 (*m*, 2 H–C(2), H–C(9)); 3.02 (*dt*, *A* of *AB*, *J*(11*endo*,11*exo*) = 13.9, *J*(11*exo*,12) = *J*(10,11*exo*) = 4.9, 1 H–C(11)); 2.57 (br. *d*, *J*(10,11*exo*) = 4.9, 1 H–C(10)); 2.50 (*ddd*, *B* of *AB*, *J*(11*endo*,11*exo*) = 13.9, *J*(11*endo*,12) = 8.0, *J*(11*endo*,13) = 1.4, 1 H–C(11)). ^{13}C-NMR (50 MHz, $CDCl_3$):

145.6; 144.2; 131.5; 130.8; 125.2; 124.4; 67.6; 60.1; 56.6; 54.3; 51.5; 46.7; 43.6. Anal. calc. for $C_{13}H_{11}Br_3$: C 38.37, H 2.72; found: C 38.96, H 2.74.

Then the column was eluted with hexane/AcOEt 97:3. The fifth fraction was *(1*SR,*5*SR*)-2-bromo-5-[(7*RS,*8*SR*)-8-bromobicyclo[4.2.0]octa-1,3,5-trien-7-yl]cyclopent-2-en-1-ol* (**15**): 63 mg (3%). Pale yellow oil. IR: 3397*m*, 3070*w*, 3020*w*, 2915*w*, 2852*w*, 1457*m*, 1218*m*, 1197*m*, 1081*w*, 1002*w*, 800*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.23–6.88 (*m*, 4 arom. H); 5.83 (br. *t*, *J*(3,4a) = *J*(3,4b) = 2.6, 1 H–C(3)); 5.04 (*d*, *J*(7,8) = 1.5, 1 H–C(8)); 4.41 (br. *d*, *J*(1,4a) = 2.6, 1 H–C(1)); 3.69 (*dd*, *J*(5,7) = 8.0, *J*(7,8) = 1.5, 1 H–C(7)); 2.52 (*ddt*, *A* of *AB*, *J*(4a,4b) = 18.7, *J*(4a,5) = 8.5, *J*(3,4a) = *J*(1,4a) = 2.6, 1 H–C(4)); 2.40 (*m*, 1 H–C(5)); 2.05 (*m*, OH); 2.00 (br. *d*, *B* of *AB*, *J*(4a,4b) = 18.7, 1 H–C(4)). ^{13}C-NMR (APT, 50 MHz, $CDCl_3$): 145.7; 145.6; 134.5 (–); 132.1 (–); 131.0 (–); 126.8; 124.9 (–); 124.5 (–); 84.2 (–); 62.3 (–); 50.6 (–); 46.4 (–); 36.5. Anal. calc. for $C_{13}H_{12}Br_2O$: C 45.38, H 3.52; found: C 45.20, H 3.49.

The sixth fraction was *(4*SR*)-2-bromo-4-(7*RS,*8*SR*)-8-bromobicyclo[4.2.0]octa-1,3,5-trien-7-yl]cyclopent-2-en-1-ol* (**16**): 188 mg (9%). Pale yellow oil. IR: 3378*m*, 3072*w*, 3014*w*, 2966*w*, 2927*w*, 1616*w*, 1457*m*, 1216*m*, 1193*m*, 1083*m*, 1068*m*, 1045*m*, 755*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.27–6.96 (*m*, 4 arom. H); 5.92 (*d*, *J*(3,4) = 2.1, 1 H–C(3)); 4.91 (*d*, *J*(7,8) = 1.5, 1 H–C(8)); 4.55 (*m*, 1 H–C(1)); 3.68 (*dd*, *J*(4,7) = 6.1, *J*(7,8) = 1.5, 1 H–C(7)); 3.27 (*m*, 1 H–C(4)); 2.08 (*m*, OH); 2.09–1.95 (*m*, 2 H–C(5)). ^{13}C-NMR (APT, 50 MHz, $CDCl_3$): 145.6; 145.2; 137.1 (–); 132.3 (–); 131.1 (–); 129.3; 124.9 (–); 124.5 (–); 81.1 (–); 62.4 (–); 47.7 (–); 45.8 (–); 37.8. Anal. calc. for $C_{13}H_{12}Br_2O$: C 45.38, H 3.52; found: C 45.27, H 3.53.

Oxidation of **16**. A suspension of **16** (100 mg, 0.29 mmol) and MnO_2 (253 mg, 2.9 mmol) in $CHCl_3$ (15 ml) was stirred for 30 h at r.t. The mixture was filtered and purified on a short silica-gel column (10 g) with $CHCl_3$/hexane 1:4 to give *(4*SR*)-2-bromo-4-[(7*SR,*8*RS*)-8-bromobicyclo[4.2.0]octa-1,3,5-trien-7-yl]cyclopent-2-en-1-one* (**18**): 83 mg (83%). Pale yellow oil. IR: 3066*w*, 3018*w*, 2960*w*, 2925*w*, 2859*w*, 1722*s*, 1589*w*, 1284*w*, 1216*m*, 1197*m*, 1162*m*, 925*m*, 887*w*, 755*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.70 (*d*, *J*(3,4) = 2.9, 1 H–C(3)); 7.36–7.00 (*m*, 4 arom. H); 5.05 (*d*, *J*(7,8) = 1.5, 1 H–C(8)); 3.91 (*dd*, *J*(4,7) = 6.1, *J*(7,8) = 1.5, 1 H–C(7)); 3.45 (*dddd*, *J*(4,5a) = 6.5, *J*(4,7) = 6.1, *J*(3,4) = 2.9, *J*(4,5b) = 2.1, 1 H–C(4)); 2.70 (*dd*, *A* of *AB*, *J*(5a,5b) = 18.9, *J*(4,5a) = 6.5, 1 H–C(5)); 2.21 (*dd*, *B* of *AB*, *J*(5a,5b) = 18.9, *J*(4,5b) = 2.1, 1 H–C(5)). ^{13}C-NMR (50 MHz, $CDCl_3$): 201.2; 162.9; 145.3; 143.4; 132.6; 131.7; 129.7; 125.1; 124.5; 61.0; 45.1; 44.0; 37.9. Anal. calc. for $C_{13}H_{10}Br_2O$: C 45.65, H 2.95; found: C 45.27, H 2.87.

Oxidation of **15**: The reaction was carried out as described above with 100 mg (0.29 mmol) of **15** and 253 mg (2.91 mmol) of MnO_2 in $CHCl_3$ (15 ml). After the filtration, *(5*RS*)-2-bromo-5-[(7*SR,*8*RS*)-8-bromobicyclo[4.2.0]octa-1,3,5-trien-7-yl]cyclopent-2-en-1-one* (**17**): (83 mg, 83%) was obtained. Pale yellow oil. IR: 3077*m*, 2935*s*, 2858*m*, 1720*s*, 1592*s*, 1457*m*, 1353*m*, 1292*m*, 1187*m*, 917*m*, 910*m*, 744*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.73 (*t*, *J*(3,4a) = *J*(3,4b) = 3.0, 1 H–C(3)); 7.39–6.88 (*m*, 4 arom. H); 5.24 (*d*, *J*(7,8) = 1.5, 1 H–C(8)); 4.13 (*dd*, *J*(5,7) = 6.6, *J*(7,8) = 1.5, 1 H–C(7)); 3.05 (*dt*, *J*(5,7) = *J*(4a,5) = 6.6, *J*(4b,5) = 2.1, 1 H–C(5)); 2.83 (*ddd*, *A* of *AB*, *J*(4a,4b) = 18.9, *J*(4a,5) = 6.6, *J*(3,4a) = 3.0, 1 H–C(4)); 2.30 (*ddd*, *B* of *AB*, *J*(4a,4b) = 18.9, *J*(3,4b) = 3.0, *J*(4b,5) = 2.1, 1 H–C(4)). ^{13}C-NMR (50 MHz, $CDCl_3$): 202.5; 162.4; 145.8; 143.5; 132.3; 131.4; 127.8; 124.9; 124.6; 59.0; 46.6; 46.0; 33.2. Anal. calc. for $C_{13}H_{10}Br_2O$: C 45.65, H 2.95; found: C 46.07, H 2.99.

Bromination of **9** *at 77°*. The reaction was carried out according to the general high-temperature bromination procedure described above with 200 mg (0.81 mmol) of **9** in CCl_4 (10 ml) and 168 mg (1.05 mmol) of Br_2 in CCl_4 (2 ml). After completion of the reaction, the solvent was evaporated, and **12** was obtained as the sole product (329 mg, 100%).

Elimination Reaction with **12** *at room Temp.* The reaction was carried out as described above with 1.0 g (2.46 mmol) of **12** and 0.83 g (7.41 mmol) of *t*-BuOK in freshly distilled THF (20 ml). The resulting mixture was stirred for 2 d at r.t. After completion of the reaction, the ^{1}H-NMR spectrum of residue was recorded, which showed a mixture consisting of two products: **3** and **9** in ratio of 55:45. The residue was crystallized, and **3** was obtained (0.30 g of crystals and 0.11 g of mixture, total yield 51%).

*(1*RS,*2*SR,*9*RS,*10*SR*)-11,12-Dibromotetracyclo[8.2.1.0^{2,9}.0^{3,8}]trideca-3,5,7,11-tetraene* (**3**): Colorless crystals from CH_2Cl_2/hexane 1:1. M.p. 95–96°. IR: 3070*m*, 2966*s*, 2910*s*, 2870*m*, 1588*m*, 1449*m*, 1299*m*, 1272*m*, 1177*m*, 1063*m*, 771*s*, 736*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.18–7.01 (*AA′BB′*, 4 arom. H); 3.86 (*AA′* of *AA′XX′*, H–C(2), H–C(9)); 3.18 (*XX′* of *AA′XX′*, H–C(1), H–C(10)); 2.39 (*dt*, *A* of *AB*, *J*(13*syn*,13*anti*) = 8.6, *J*(1,13*anti*) = *J*(10,13*anti*) = 1.8, 1 H–C(13)); 1.77 (*dt*, *B* of *AB*, *J*(13*syn*,13*anti*) = 8.6, *J*(1,13*syn*) = *J*(10,13*syn*) = 1.8, 1 H–C(13)). ^{13}C-NMR (50 MHz, $CDCl_3$): 147.4; 130.0; 125.4; 125.1; 55.2; 54.2; 49.1. Anal. calc. for $C_{13}H_{10}Br_2$: C 47.89, H 3.09; found: C 47.91, H 3.16.

Elimination Reaction with **12** *in Refluxing THF*. The reaction was carried out as described above with 1.0 g (2.46 mmol) of **12** and 0.83 g (7.41 mmol) of *t*-BuOK in freshly distilled THF (20 ml) at reflux temp. After the

extraction, **3** was obtained as the sole product. It was crystallized from CH_2Cl_2/hexane 1:1, to give **3** (0.75 g, 93%).

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