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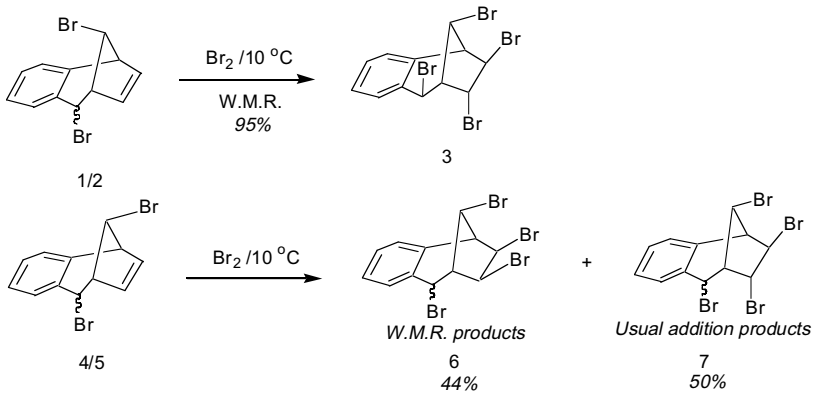
The bromination reaction of tricyclo[7.2.1.$0^{2,7}$]dodeca-2,4,6,10-tetraene derivatives was studied. The bromination of **9** gave only rearranged products **12** and **13**, while the bromination of **8** with molecular bromine formed both rearranged **12** and non-rearranged products **15** and **16**. The possible role of a substituent in the rearrangements was examined. All compounds were characterized properly, in particular by NMR spectra and chemical transformation.

Key Words: Bromination, Wagner-Meerwein Rearrangement (W.M.R.), Polybromides, Neighboring Group Effect

Introduction

Skeletal rearrangements in the reactions of benzocyclooctene systems have attracted a great deal of attention, particularly in relation to discussions about non-classical carbonium ions. Although the addition of bromine to the carbon-carbon double bond with molecular bromine is formally one of the simplest reactions typical of unsaturated compounds,[1] the bromination of unsaturated bicyclic systems with molecular bromine generally leads to rearrangements of the molecular skeleton.[2−11] The structure of the addition products 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[2−11] in these systems.

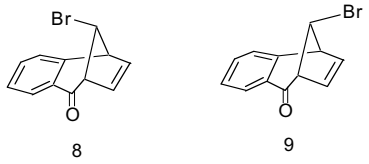
Earlier we showed that[12] the bromination of 12-*syn*-bromo tricyclo[7.2.1.$0^{2,7}$]dodeca-2,4,6,10-tetraene derivatives at 10 °C gives only rearranged products, whereas the bromination of *anti* isomers under the same reaction conditions forms both rearranged and non-rearranged products (Scheme 1). These differences were attributed to the neighboring group effect, i.e. an *anti* orientated bromine atom at C_{12} hinders the formation of an *exo* bromonium ion. The former is known to promote rearrangements.[12]



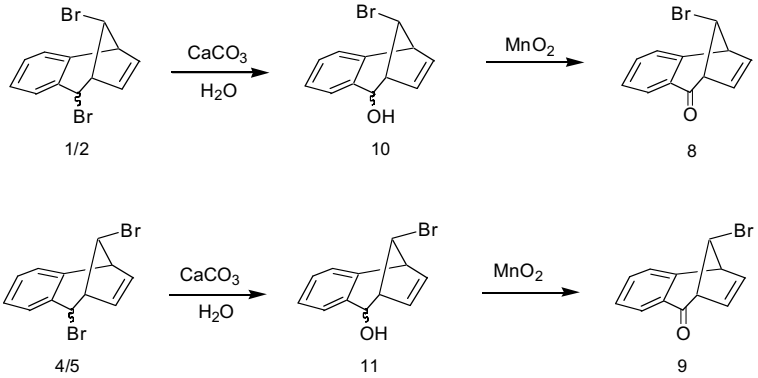
Scheme 1

Results and Discussion

In the present work, we are interested in the bromination of ketones **8** and **9** in order to investigate the electronic and neighboring group effects on bromination in tricyclo[7.2.1.0^{2,7}]dodeca-2,4,6,10-tetraene systems.

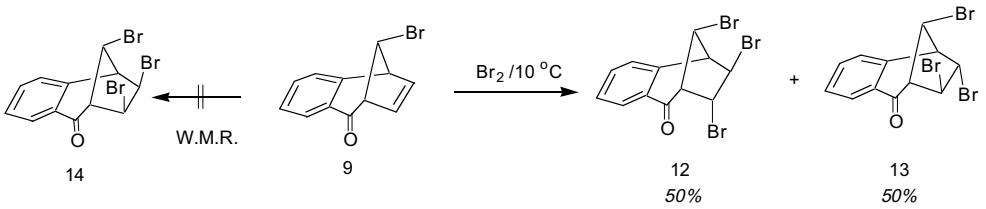


Starting materials **8** and **9** were obtained by hydrolysis of dibromides **1/2**[3] and **4/5**[3] and the oxidation of hydroxy bromides **10/11** with MnO_2(Scheme 2).



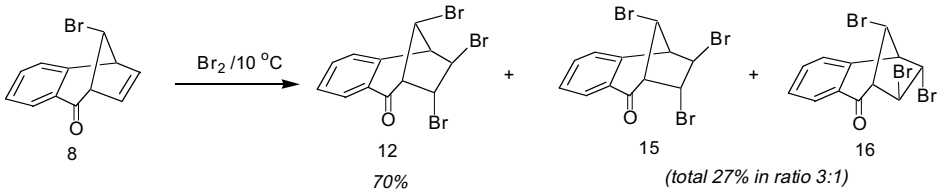
Scheme 2

Firstly, the bromination of **9** in $CHCl_3$ at RT was investigated, and only non−rearranged products **12** and **13** were obtained in a ratio of 1:1 (Scheme 3). From this reaction no trace of rearranged product **14** was observed, even though the presence of **14** was carefully checked by means of the NMR spectra of **14** obtained in a different way.



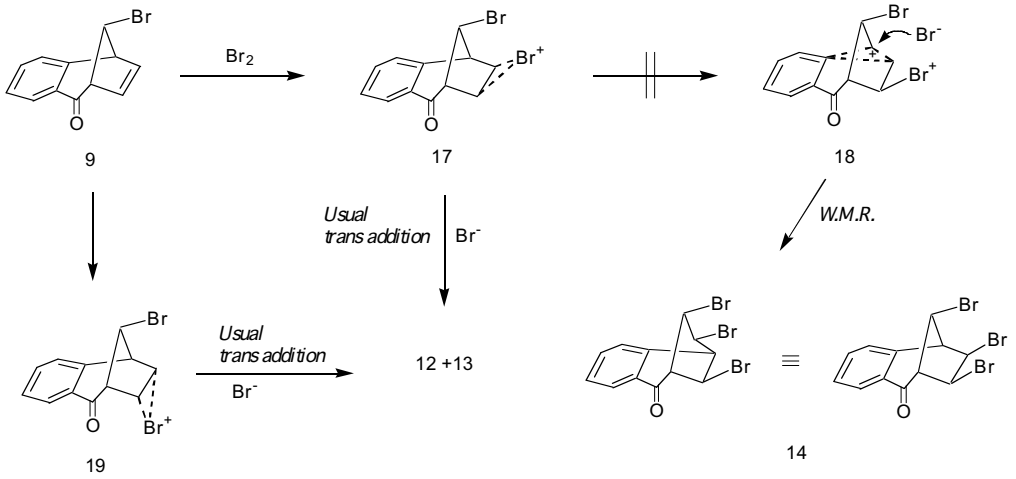
Scheme 3

The bromination of *syn*-isomer **8** in the same conditions gave mainly rearranged product **12** (70% yield) and non-rearranged products **15** and **16** (total 27% yield) (Scheme 4). From this reaction, the major product, tribromide **12** was isolated by crystalization. The remaining 2 isomeric compounds **15** and **16** could not be isolated. These inseparable isomers (total 27% yield, in a ratio of 3:1) are not the tribromides **13** and **14** because the NMR spectra of the mixture were compared to the NMR spectra of pure **13** and **14**. However, according to NMR analyses of the mixture, coupling constants ($J_{9,12}$=$J_{10,12}$=4.7-4.9 Hz) belonging to the triplets of each of the 2 isomers at δ=5.08 ppm and δ=4.95 ppm) strongly show that both of them are non-rearranged products because these coupling constants are typical[12] for H_{anti} proton at C_{12} atoms. If these protons were *syn*, one would expect no visible coupling constants between related protons. In addition, there are no other reasonable possibilities for the structures of these molecules because we have all the possible alternatives. In short, the bromination of *syn* isomer **8** gives rearranged product **12** (70%) and non-rearranged products **15**/**16** (27%), whereas the bromination of *anti* isomer **9** gives only non-rearranged products **12**/**13** (100%).

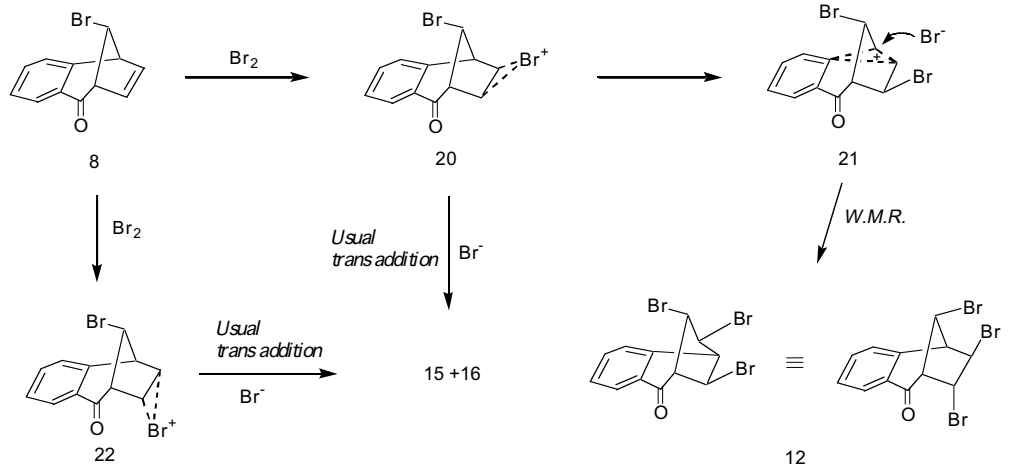


Scheme 4

This raises the question of how we can determine whether the formed products are non-rearranged or rearranged. This can be easily answered by the mechanism given in Schemes 5 and 6: in the case of rearrangement by aryl migration in *anti* isomer **9**, non-classical carbonium ion **18** is formed. In this way, the formation of *exo*-cis tribromide **14** by *exo* attachment of Br^- to a non-classical ion is expected. The formation of *trans* bromides **12**/**13** from **17** does not show rearrangement (Scheme 5). As for *syn* isomer **8**, whether there is a skeletal rearrangement or not can be easily determined by the orientation of the bromine atom at the C_{12} carbon. After rearrangement, the bromine atom at C_{12} will be *anti*, whereas the *syn* bromine atom at C_{12} shows the conservation of the skeleton (Scheme 6).



Scheme 5



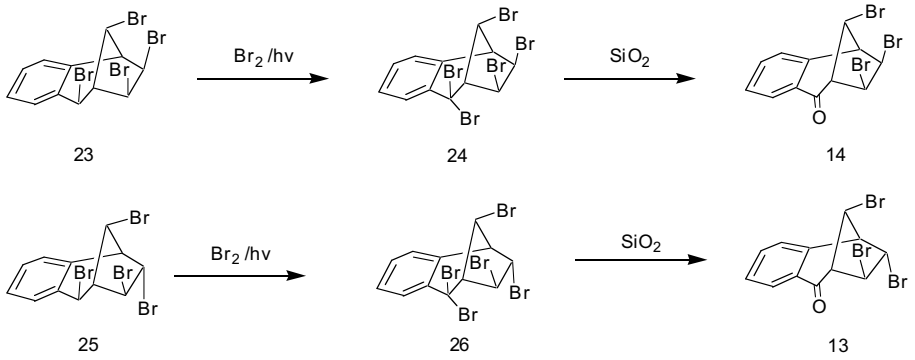
Scheme 6

As discussed in our similar studies previously,[12] a comparison of the results obtained during the halogenation of *syn* isomer **8** and *anti* isomer **9** shows that the bromine atom at C_{12anti} affects skeletal rearrangements. The steric hindrance of the bromine atom at C_{12} carbons comparatively prevents the formation of *exo* bromonium ion **17,** which is responsible for rearrangements, and supports the formation of *endo* bromonium ion **19**, which is open to the usual addition. However, it is also possible that *endo* bromonium ion **19** is stabilized by the through-space donation from the bromo group as described in the literature for 7-substituted bicycloheptadienes.[13]

A comparison of the results obtained during the halogenation[12] of dibromides **1/2/4/5** and monobromo ketones **8/9** also yields meaningful results showing that ketones **8/9** are less prone to rearrangement than dibromides **1/2/4/5**. These differences can be easily explained by electronic factors. It is clear that the benzene ring attached to the carbonyl group has a lower electron density in molecules **8** and **9**. In contrast to related compounds, this behavior of ketones shows that the positive charge in non-classical ions **18** and **21** is less stabilized by the electron-poor benzene ring and ketones **8** and **9** are less prone to rearrangement than the plain analogues.

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, and by comparison of some spectral data of similar compounds and related systems reported in the literature.[12,14−17] For all the compounds bearing the same skeletal systems, the structural analysis was achieved according to the coupling constants. The configurations of the bromine at C_{12} can be determined by the coupling constants between H_9 (or H_1) and H_{12} protons. As a consequence of the rigid geometry and reliability of the Karplus rule[19] in [3.2.1]octane systems,[12,14−18] the dihedral relationship of the H_9proton to H_{12anti} (in relation to the benzene ring) (∼40°), and to H_{12syn} (∼80°), is sufficiently distinctive to be revealed by the magnitude of the spin-spin interaction. Thus, the high value of J_{H12} (J=4.0-5.0 Hz) is uniquely accommodated by the *syn*-orientation of the bromine atom bonded to the bridge atom. H_{12syn} protons give no measurable coupling with the H_9(or H_1) protons (J≤1 Hz).[12,14−17] The configuration of bromine at the C_{10} and C_{11} atoms was determined from the coupling constants between $J_{1,11}$ and $J_{9,10}$. The coupling constants between H_1- H_{11exo} protons and H_9-H_{10exo} protons are 6.3 ± 0.5 Hz, whereas there is no measurable coupling constant between the protons H_1- H_{11endo} and H_9-H_{10endo} because the dihedral angles are close to 90° between related protons. In molecules **12**, **13** and **14**, the long range coupling constant ($J_{11,12}$ or $J_{10,12}$=1.2 ± 0.5 Hz, M or W orientation) also confirms the orientation of the protons at C_{12} and C_{10} and/or C_{11}. Similarly, the absence of any long range coupling between the protons at C_{12} and C_{10}/C_{11}gives information about their configurations. A typical spin-spin interaction in tricyclo[7.2.1.0^{2,7}]dodeca-2,4,6,10-tetraene systems is summarized in Table 1.

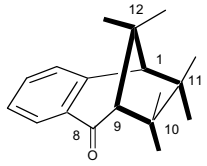
The structures of some of the molecules were also supported by chemical transformations. For example, when pure tetrabromides **23** and **25** were subjected to photo bromination with molecular bromine, pentabromides **24** and **26** were obtained in high yield (Scheme 7). Treatment of pentabromides **24** and **26** with silica gel resulted in the formation of the tribromo ketones **13** and **14**. These reactions also support the proposed structures.

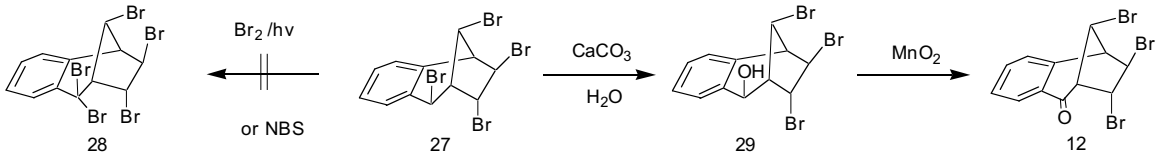


Scheme 7

Tribromide **27** could not be converted to the corresponding pentabromide **28** in a similar way, not even by bromination with NBS. This is evidently due to the steric compression of the *endo* bromine atom at C_{10} carbon. Therefore, in order to support the structure of **27**, other types of reaction were tried. Hydrolysis of **27** and later oxidation of **29** formed **12** in high yield. This reaction also supports the structure of **12** (Scheme 8).

Table. 1 Typical spin-spin interaction in tricyclo[7.2.1.$0^{2,7}$]dodeca-2,4,6,10-tetraene systems.

	$J_{1,11endo}=J_{9,10endo}$=0-<1 Hz	$J_{10endo,11endo}$=8.2 ± 0.4
	$J_{1,11exo}=J_{9,10exo}$=6.2 ± 0.6 Hz	$J_{10endo,11exo}=J_{10exo,11endo}$=5.5 ± 0.5 Hz
	$J_{1,12syn}=J_{9,12syn}$=0-<1 Hz	$J_{11endo,12}=J_{10endo,12}$=1.2 ± 0.5 Hz
	$J_{1,12anti}=J_{9,12anti}$=4.7 ± 0.3 Hz	$J_{1,9}$=2.1 ± 0.6 Hz



Scheme 8

Conclusions

The results of the present work demonstrate that tricyclo[7.2.1.$0^{2,7}$]dodeca-2,4,6,10-tetraene systems are prone to skeletal rearrangement in bromination reactions. Steric and electronic effects of the substituent also affect the reaction outcome. Skeletal rearrangement in the bromination reactions is determined by the configuration of the initially formed bromonium ion. An *exo* bromonium ion is eligible for rearrangement by aryl shifts. An *endo* bromonium ion gives addition products without skeletal rearrangement. Steric hindrance at C_{12} carbons and electron withdrawing groups condensed to the benzene ring supports predominantly the formation of *endo* bromonium ions. Consequently, we suggest that the most important influence on the stereochemistry of the electrophilic addition in tricyclo[7.2.1.$0^{2,7}$]dodeca-2,4,6,10-tetraene systems should be exerted by the factors π-delocalization in the transition ion and the possibility of the formation of non-classical ions as intermediate particles.

Experimental Section General: Melting points are uncorrected. Infrared spectra were obtained from solution in 0.1 mm cells or KBr pellets on a regular instrument. The ^{1}H and ^{13}C NMR spectra were recorded on 200 (50)-MHz spectrometers. Apparent splitting is given in all cases. Column chromatography was performed on silica gel (60-mesh, Merck). TLC was carried out on Merck 0.2 mm silica gel 60 F_{254} analytical aluminum plates. All substances reported in this paper are in their racemic form.

Caution: It has been reported[20] 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 dibromide derived from benzonorbornadiene, there is no report in the literature about the toxicological effects. However, we recommend that these compounds be handled only with extreme caution.

Synthesis of (1*S(R)*,9*R(S)*,12*R(S)*)-12-bromotricyclo[7.2.1.$0^{2,7}$]dodeca-2,4,6,10-tetraen-8-one (8):

a-) Hydrolysis of Dibromides **1/2**: A suspension of dibromides **1/2**[3] (0.7 g, 2.23 mmol) and $CaCO_3$ (0.78 g, 7.88 mmol) in THF (10 mL) and H_2O (20 mL) was refluxed for 30 h. After the reaction, the mixture

was cooled to room temperature and the insoluble materials were separated by filtration. The filtrate was extracted with chloroform (2 x 50 mL), washed with water, and dried over $MgSO_4$. After removal of solvent, the residue was purified on a short silica gel column with chloroform/*n*−hexane (1/4) as the eluent, to give 476 mg (85%) of hydroxy bromides **10**[3] as an isomeric mixture.

b-*Oxidation of Alcohols* **10**: A suspension of hydroxy bromides **10**[3] (476 mg, 1.90 mmol) and MnO_2 (3.31 g, 38 mmol) in chloroform (15 mL) was stirred for 30 h at room temperature. The reaction mixture was filtered and was purified on a short silica gel column with chloroform/*n*−hexane (1/4) as the eluent, to give 401 mg (85%) of ketone **8**. It was crystalized from chloroform/*n*−hexane (colorless crystals mp 143-145 °C).

(1*S(R)*,9*R(S)*,12*R(S)*)-12-bromotricyclo[7.2.1.0^{2,7}]dodeca-2,4,6,10-tetraen-8-one (8): ^{1}H-NMR (200 MHz, $CDCl_3$): 7.97 (m, 1H, aryl), 7.94-7.14 (m, 3H, aryl), 6.80 (dd, $J_{10,11}$=5.9 Hz, $J_{1,11}$=3.4 Hz, 1H, H_{11}), 6.15 (dd, $J_{10,11}$=5.9 Hz, $J_{9,10}$=3.4 Hz, 1H, H_{10}), 5.11 (t, $J_{1,12}$=$J_{9,12}$=4.6 Hz, 1H, H_{12}) 3.79 (dd, $J_{9,12}$=4.6 Hz, $J_{9,10}$=3.4 Hz, 1H, H_9), 3.60 (dd, $J_{1,12}$=4.6 Hz, $J_{1,11}$=3.4 Hz, 1H, H_1), ^{13}C-NMR (50 MHz, $CDCl_3$): 193.9, 147.1, 144.3, 135.2, 133.3, 131.1, 130.2, 130.0, 128.3, 62.7, 60.0, 53.8. IR (KBr, cm^{-1}): 3033, 2993, 2964, 1682, 1594, 1450, 1312, 1272, 1238, 1192.

Synthesis of (1*S(R)*,9*R(S)*,12*S(R)*)-12-bromotricyclo[7.2.1.0^{2,7}]dodeca-2,4,6,10-tetraen-8-one (9):

a-) Hydrolysis of Dibromides **4/5**: 251 mg (0.80 mmol) of dibromides **4/5**[3] was hydrolyzed as described above. According to the NMR spectrum, the reaction consisted of a mixture of hydroxy bromides **11** (177 mg, 88%).

b-) Oxidation of Alcohols **11**: 364 mg (1.45 mmol) of hydroxy bromide **11**[3] was oxidized as described above and ketone **9** was obtained as the sole product (325 mg, 90%). It was crystalized from chloroform/*n*−hexane (1:5) (Colorless crystals, mp 93-94 °C).

1*S(R)*,9*R(S)*,12*S(R)*)-12-bromotricyclo[7.2.1.0^{2,7}]dodeca-2,4,6,10-tetraen-8-one (9): ^{1}H-NMR (200 MHz, $CDCl_3$): 7.93 (m, 1H, aryl), 7.44-7.17 (m, 3H, aryl), 6.73 (dd, $J_{10,11}$=5.4 Hz, $J_{1,11}$=2.9 Hz, 1H, H_{11}), 6.11 (dd, $J_{10,11}$=5.4 Hz, $J_{9,10}$=2.7 Hz, 1H, H_{10}), 4.94 (s, 1H, H_{12}) 4.04 (d, $J_{9,10}$=2.7 Hz, 1H, H_9), 3.83 (d, $J_{1,11}$=2.9 Hz, 1H, H_1), ^{13}C-NMR (50 MHz, $CDCl_3$): 193.6, 146.6, 145.0, 135.5, 130.8, 130.6, 130.3(2C), 127.4, 67.6, 63.7, 59.0. IR (KBr, cm^{-1}): 3063, 2994, 2980, 1670, 1584, 1466, 1320, 1290, 1230, 1112, 1090, 1010, 900, 820.

Bromination of (1*S(R)*,9*R(S)*,12*S(R)*)-12-bromotricyclo[7.2.1.0^{2,7}]dodeca-2,4,6,10-tetraen-8-one (9):

To a magnetically stirred solution of **9** (200 mg, 0.80 mmol) in 10 mL of dry chloroform cooled to 10 °C was added dropwise a solution of bromine (141 mg, 0.88 mmol) in 2 mL of chloroform. The resulting solution was stirred for 30 min. The solvent was evaporated and the residue was subjected to silica gel (60 g) chromatography eluting with *n*−hexane/ ethyl acetate (95:5).

The first fraction: **(1S(R),9*R(S)*,10*S(R)*,11*S(R)*,12*S(R)*)-10,11,12-tribromotricyclo [7.2.1.0^{2,7}] dodeca-2,4,6-trien-8-one (13):** (164 mg, 50%, mp 165 °C, colorless crystals from methylene chloride/*n*−hexane (1:3), ^{1}H-NMR (200 MHz, $CDCl_3$): 8.03 (m, 1H, aryl), 7.67-7.31 (m, 3H, aryl), 5.36 (dd, $J_{1,11}$=5.9 Hz, $J_{10,11}$=5.5 Hz, 1H, H_{11}), 4.63 (m, 1H, H_{12}), 4.03 (bd, $J_{1,11}$=5.9 Hz, 1H, H_1), 3.80 (m, 1H, H_{10}), 3.77

(m, 1H, H_9), ^{13}C-NMR (50 MHz, $CDCl_3$): 194.8, 144.4, 136.5, 132.3, 131.4, 130.9, 130.4, 70.3, 60.0, 59.0, 51.2, 50.9. IR (KBr, cm^{-1}): 3081, 3055, 3030, 2979, 2953, 1677, 1574, 1548, 1447, 1294, 1268, 1243, 1217, 1140, 1089, 757.

The second fraction: **(1S(R),9*R(S)*,10*R(S)*,11*R(S)*,12*S(R)*)-10,11,12-tribromotricyclo [7.2.1.0^{2,7}]dodeca-2,4,6-trien-8-one (12):** (164 mg, 50%, mp 144-145 °C, colorless crystals from methylene chloride/*n*−hexane (1:2), ^{1}H-NMR (200 MHz, $CDCl_3$): 8.07 (m, 1H, aryl), 7.65-7.34 (m, 3H, aryl), 5.22 (dd, $J_{9,10}$=6.7 Hz, $J_{10,11}$=5.0 Hz, 1H, H_{10}), 4.59 (m, 1H, H_{12}), 4.19 (dd, $J_{10,11}$=5.0 Hz, $J_{11,12}$=1.6 Hz, 1H, H_{11}), 3.97 (d, $J_{1,9}$=2.1 Hz, 1H, H_1), 3.72 (dd, $J_{9,10}$=6.7 Hz, $J_{1,9}$=2.1 Hz, 1H, H_9), ^{13}C-NMR (50 MHz, $CDCl_3$): 194.3, 148.1, 137.3, 131.6, 131.3, 130.9, 128.3, 68.5, 62.2, 56.7, 52.4, 51.7. IR (KBr, cm^{-1}): 3081, 3055, 3030, 2979, 2953, 1702, 1600, 1574, 1294, 1268, 1217, 1191, 1013, 757.

Bromination of (1*S(R)*,9*R(S)*,12*R(S)*)-12-bromotricyclo[7.2.1.0^{2,7}]dodeca-2,4,6,10-tetraen-8-one (8):

The reaction was carried out as described according to the general procedure by using 200 mg (0.80 mmol) of ketone **8**. The solvent was evaporated and the residue was crystalized from choloroform/*n*−hexane (1/3). Tribromide **12** was isolated (160 mg crystals and 70 mg mixture, total 230 mg, 70% yield, for the spectral data see above). The other isomers, **15/16**, could not be isolated.

Photobromination of 23 at inert condition. A solution of **23** (200 mg, 0.42 mmol) and bromine (80 mg, 0.50 mmol) in 5 mL of CCl_4, under N_2, was irradiated with a sun lamp (150 W) at room temperature for 12 h. The ^{1}H NMR analysis of the crude product indicated the formation of pentabromide **24** as a sole product. It was crystalized from chloroform/*n*-hexane (1/2) (210 mg, 90%, colorless crystals, mp 142-143 °C).

(1S(R),9*R(S)*,10*S(R)*,11R(S),12*S(R)*)-8,8,10,11,12-pentabromotricyclo[7.2.1.0^{2,7}]dodeca-2,4,6-triene (24): ^{1}H-NMR (200 MHz, $CDCl_3$): 7.92 (m, 1H, aryl), 7.90-7.28 (m, 2H, aryl), 7.01 (m, 1H, aryl), 5.05 (m, 1H, H_{12}), 5.00 (dd, A part of AX system, $J_{10,11}$=8.0 Hz, $J_{11,12}$=0.7 Hz, 1H, H_{11}), 4.60 (dd, X part of AX system, $J_{10,11}$=8.0 Hz, $J_{10,12}$=0.7 Hz, 1H, H_{10}), 4.17 (bd, $J_{1,9}$=2.6 Hz, 1H, H_1), 3.89 (bd, $J_{1,9}$=2.6 Hz, 1H, H_9),^{13}C-NMR (50 MHz, $CDCl_3$): 138.6, 137.6, 134.6, 133.3, 131.9, 128.7, 75.8, 67.3, 60.4, 57.4, 51.6, 48.4. IR (KBr, cm^{-1}): 3055, 3030, 3004, 2979, 2953, 1472, 1447, 1421, 1319, 1293, 1268, 1243, 910, 834, 757.

From the bromination of **25** (100 mg, 0.21 mmol) under the same reaction conditions, the pentabromide **26** was also obtained as the sole product (105 mg 90%, colorless crystals from chloroform/*n*-hexane (1/3), mp 193 °C).

(1S(R),9*R(S)*,10*S(R)*,11S(R),12*S(R)*)-8,8,10,11,12-pentabromotricyclo[7.2.1.0^{2,7}]dodeca-2,4,6-triene (26): ^{1}H-NMR (200 MHz, $CDCl_3$): 7.94 (m, 1H, aryl), 7.50-7.29 (m, 2H, aryl), 6.97 (m, 1H, aryl), 5.37 (dd, $J_{1,11}$=6.8 Hz, $J_{10,11}$=5.1 Hz, 1H, H_{11}), 5.10 (m, 1H, H_{12}), 4.32 (bd, $J_{1,11}$=6.8 Hz, 1H, H_1), 3.98 (m, 1H, H_9), 3.48 (bd, $J_{10,11}$=5.1 Hz, 1H, H_{10}), ^{13}C-NMR (50 MHz, $CDCl_3$): 139.4, 134.0, 133.8, 132.0, 131.9, 131.9, 74.0, 67.4, 62.1, 58.0, 53.4, 49.8. IR (KBr, cm^{-1}): 3081, 3055, 3030, 2953, 2928, 1472, 1447, 1319, 1268, 1243, 1217, 782.

Hydrolysis of pentabromide 24 to the ketone 14: To a silica gel column (80 g) prepared with *n*−hexane was loaded pentabromide **24** (100 mg, 0.18 mmol) with 5 mL of $CHCl_3$and the faucet of the column

was closed for 10 h. The faucet of the column was opened and elution was continued with *n*−hexaneto give unreacted pentabromide **24**. Then the column was eluted with *n*−hexane/ethyl acetate (95:5) and ketone **14** was obtained as the sole product (64 mg) in 86% yield (colorless crystals from chloroform/*n*-hexane (1/3) mp 163-164 °C):

(1S(R),9*R(S)*,10*S(R)*,11R(S),12*S(R)*)-10,11,12-tribromotricyclo[7.2.1.0^{2,7}]dodeca-2,4,6-trien-8-one (14): ^{1}H-NMR (200 MHz, $CDCl_3$): 8.02 (m, 1H, aryl), 7.98-7.32 (m, 3H, aryl), 4.60 (m, 1H, H_{12}), 4.59 (bd, A part of AB system, $J_{10,11}$=8.6 Hz, 1H, H_{11}), 4.53 (bd, B part of AB system, $J_{10,11}$=8.6 Hz, 1H, H_{10}), 4.20 (bd, $J_{1,9}$=2.9 Hz, 1H, H_1), 3.96 (bd, $J_{1,9}$=2.9 Hz, 1H, H_9), ^{13}C-NMR (50 MHz, $CDCl_3$): 194.9, 147.6, 137.6, 131.4, 130.9, 129.9, 129.0, 71.7, 63.1, 55.1, 50.4, 49.6. IR (KBr, cm^{-1}): 3081, 3055, 3030, 3004, 2978, 1677, 1600, 1447, 1268, 1243, 1217, 1191.

From the hydrolysis of **26** (100 mg, 0.18 mmol) under the same reaction conditions, the tribromide **13** was also obtained as the sole product (66 mg 90%, for the spectral data see above).

Hydrolysis of tetrabromide (27): A suspension of tetrabromide **27** (0.5 g, 1.1 mmol) and $CaCO_3$ (330 mg, 3.3 mmol) in THF (7 mL) and H_2O (15 mL) was refluxed for 8 h. After the reaction mixture was cooled to room temperature, the insoluble materials were separated by filtration. The filtrate was extracted with chloroform (2 x 30 mL), washed with water, and dried over $MgSO_4$. After removal of the solvent, the residue was purified on a short silica gel column with chloroform/*n*−hexane (1/4) as the eluent, to give 369 mg (85%) of hydroxy bromide **29** as the sole product. It was crystalized from ether/*n*−hexane (3:1) (colorless crystals mp 80-82 °C).

(1S(R),8*R(S)*,9*R(S)*,10*R(S)*,11R(S),12*S(R)*)-10,11,12-tribromotricyclo[7.2.1.0^{2,7}]dodeca-2,4,6-trien-8-ol (29): ^{1}H-NMR (200 MHz, $CDCl_3$): 7.46-7.07 (m, 4H, aryl), 5.25 (d, $J_{8,9}$=2.2 Hz, 1H, H_8), 5.18 (dd, $J_{9,10}$=6.7 Hz, $J_{10,11}$=5.1 Hz, 1H, H_{10}), 4.75 (d, $J_{11,12}$=1.6 Hz, 1H, H_{12}), 4.05 (dd, $J_{10,11}$=5.1 Hz, $J_{11,12}$=1.6 Hz, 1H, H_{11}), 3.67 (bd, $J_{1,9}$=1.5 Hz, 1H, H_1), 3.09 (ddd, $J_{9,10}$=6.7 Hz, $J_{8,9}$=2.2 Hz, $J_{1,9}$=1.5 Hz, 1H, H_9).^{13}C-NMR (50 MHz, $CDCl_3$): 143.0, 135.8, 132.3, 131.5, 131.0, 128.2, 74.7, 60.7, 59.8, 58.5, 57.1, 51.7. IR (KBr, cm^{-1}): 3260, 3081, 3055, 3030, 2979, 2953, 2928, 1447, 1421, 1319, 1243, 1217, 1038, 1012, 936.

Oxidation of hydroxy bromide 29: A suspension of hydroxy bromide **29** (100 mg, 0.24 mmol) and MnO_2 (209 mg, 2.4 mmol) in chloroform (15 mL) was stirred for 30 h at room temperature. The reaction mixture was filtered and was purified on a short silica gel column with chloroform/*n*−hexane (1/4) as the eluent, to give 85 mg (85%) of ketone **12** (for the spectral data, see above).

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