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# Bromination of 2,3-Dibromobenzobarrelene at Different Conditions: Highly Brominated Benzobicyclic Systems

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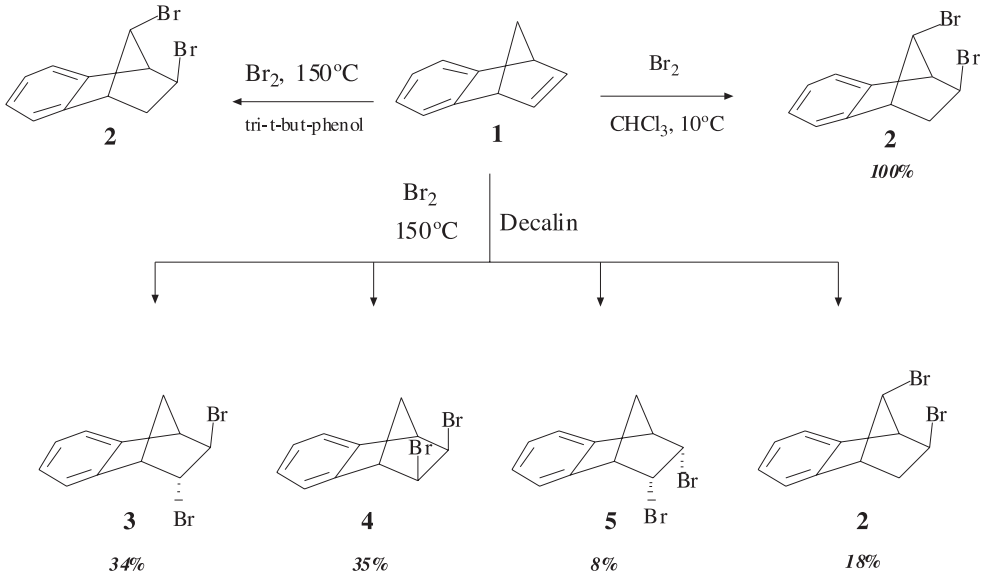
The electrophilic addition of bromine to 2,3-dibromobenzobarrelene at 10°C led to the formation of completely rearranged products in high yield. Bromination of 2,3-dibromobenzobarrelene with molecular bromine in decalin at 150°C and with DBTCE in $CCl_4$ at 77°C gave rearranged and *non*-rearranged products. The radical and ionic mechanism are discussed. All compounds were characterized properly, by NMR spectroscopy and chemical transformation.

**Key Words:** benzobarrelene, high temperature bromination, Wagner-Meerwein rearrangement and poly-bromides.

## Introduction

In addition to numerous industrial applications as pesticides, plastics, fire retardants and pharmaceutical chemicals, the halogen derivatives of a compound are valuable as a model for synthesizing other derivatives. Therefore, the halogenation of organic compounds is an important process. The addition of bromine to the carbon-carbon double bond with molecular bromine is formally one of the simplest typical reactions of unsaturated compounds.[1] The nature of the intermediates of the addition depends on temperature, steric factors, torsional effects, $\pi$- and $\sigma$-participation in the transition state and the formation of *non*-classical ions or a fast equilibrium of classical ions.[2]

The bromination of unsaturated bicyclic systems with molecular bromine leads to rearrangements of the molecular skeleton.[2,3] Furthermore, we have shown previously that high temperature bromination of bicylic system gives mainly *non*-rearranged products.[3] For example, bromination of benzonorbornadiene (**1**) at room temperature or lower gave only rearranged product **2** in almost quantitative yield.[3a] However, high temperature bromination of **1** at 150°C resulted in the formation of *non*-rearranged products **3**, **4** and **5** and rearranged product **2** in a ratio of 4:1 (Scheme 1). Conducting the bromination reaction with free radical inhibitors suppressed the formation of the *non*-rearranged products.[3a] This strongly supports the assumption that there is competition between the radical and ionic mechanism and that high temperature bromination occurb via a free radical mechanism. Since radical intermediates are much less likely to rearrange, at higher temperatures we obtained mostly *non*-rearranged products.

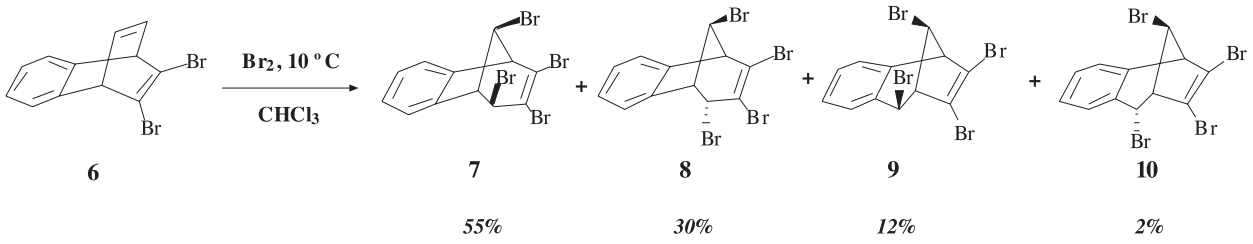



**Scheme 1**

In the present work, we investigated the behavior of 2,3-dibromobenzobarralene (**6**) in reaction with bromine and DBTCE under different conditions.

# Results and Discussion

Firstly, the starting material, 2,3-dibromobenzobarrelene **(6)** was prepared using methods described in the literature[4] and it was subjected to bromination in chloroform at 10°C. $^1$H NMR studies revealed that the reaction mixture consisted of four products. This mixture was submitted to silica gel column chromatography and four rearranged products **(7-10)** were isolated (Scheme 2).

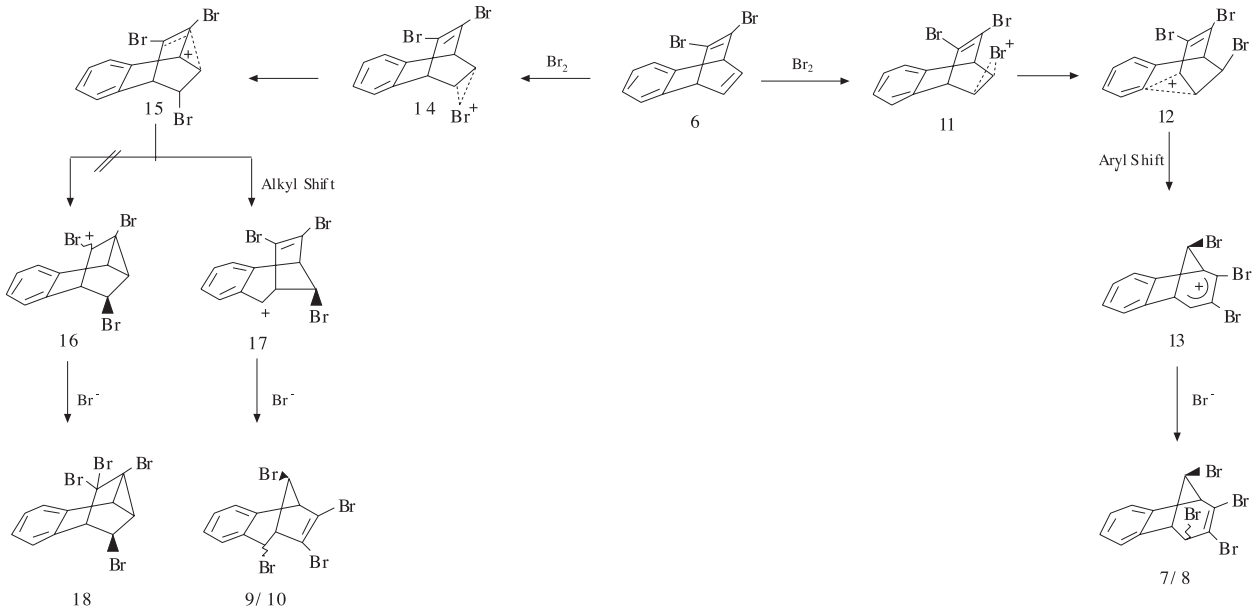



**Scheme 2**

## Mechanism for ionic bromination

For the formation of the rearranged products, the following reaction mechanism was proposed. Generally, when placed on the double bond of **6**, a positive charge induces a Wagner-Meerwein rearrangement and transforms the [2.2.2] ring system into the [3.2.1] ring system that then reacts with bromide ion to yield the products. It is evident from the bromine configuration at the bridge carbon in major products **7** and **8** that the initial attack by the bromine occurred from the *exo*-face of the $\pi$-system (**11**) (Scheme 3). Most probably, the driving force of this mode of addition is supplied by the formation of aryl-bridged intermediate **12**. The formation of alkyl shift products **9** and **10** can be explained in terms of the formation of *endo*-intermediate **14** of products **9** and **10**. *endo*-Configuration of the bromine atom at the bridge carbon is

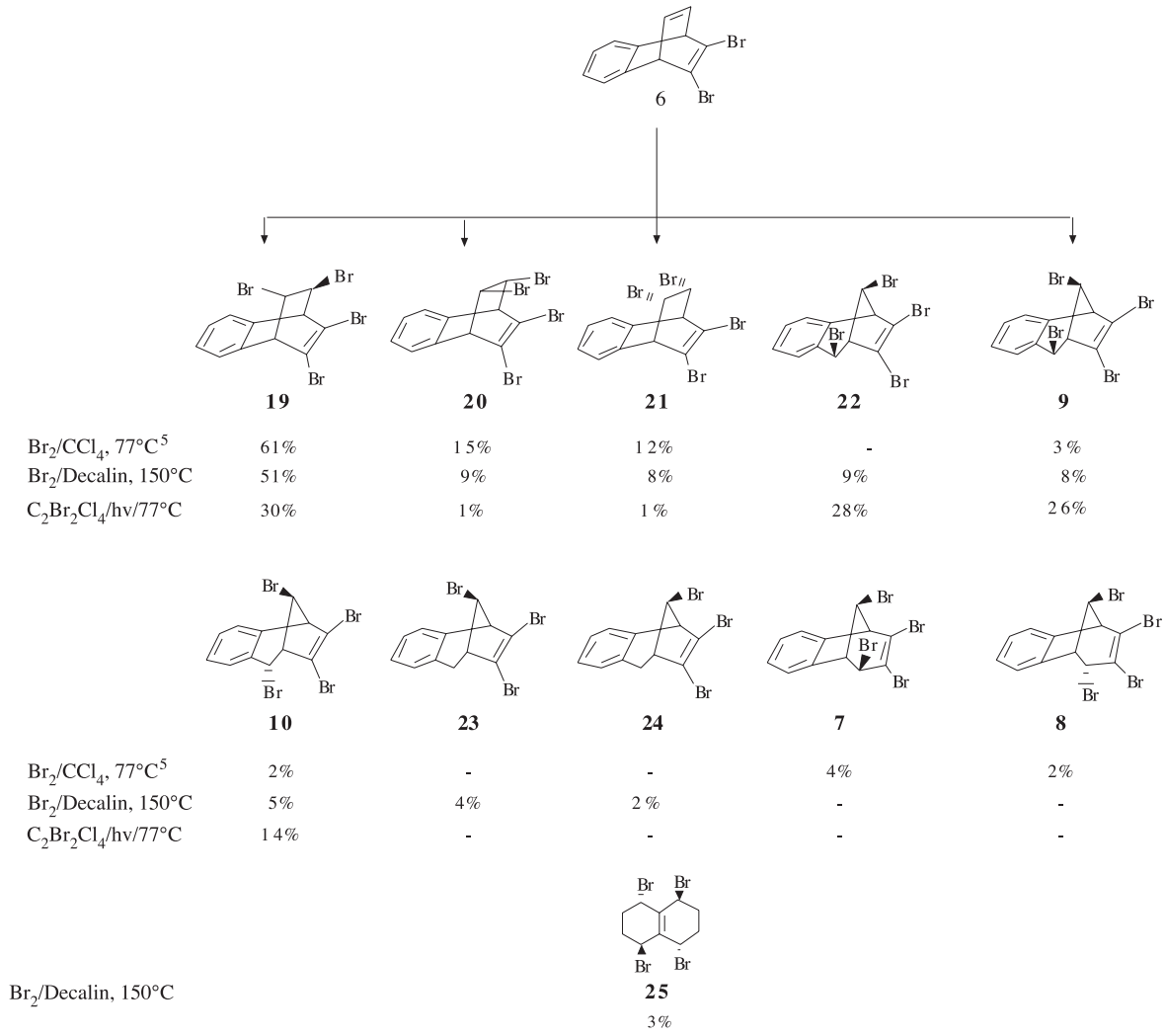
also in agreement with *endo*-attack of bromine on the double bond. The expected product **18** was not observed among the products. This example demonstrates that bromine atoms at the 9- and 10-positions in **6** probably prevent the formation of the cyclopropanoid-bridged intermediate **16**. In addition it was observed that the ratio of aryl shift products **(7/8)** formed from *exo* ion **11** and alkyl shift products **(9/10)** formed from *endo* ion **14** is almost ∼6:1. This is evidently due to the higher rate of the formation of ion **11**, which is stabilized on account of the $\pi$ participation of the aromatic ring (ion **12**). Such participation is significantly more effective[3b] than participation of the double bond, as in ion **15**. In the case of benzobarrelene, it was observed that the ratio of aryl shift products to alkyl shift product is approximately 4:1[3b]. These differences are due to fact that the intermediate **15** is less favorable because of the electronegative bromine atoms at the double bond in molecule **6**.




**Scheme 3**

In a previous report[5] we showed that the bromination of 2,3-dibromobenzobarralene (**6**) at 77°C in $CCl_4$ gave mainly *non*-rearranged products (88%) in addition to minor rearranged products (12%). In the present work, we are also interested in the bromination of **6** with molecular bromine at 150°C in decalin. For this purpose, bromine was directly distilled into a hot solution of **6** in decalin at 150°C. After repeated column chromatography combined with fractional crystallization, it was possible to separate nine products (**9**,**10**, **19-25**) (Scheme 4). Three of them, **22-24**, were not observed in the bromination of **6** at 10°C and 77°C. This experiment shows that the ratio of *non*-rearranged products depends on the reaction temperature. For the synthesis of *non*-rearranged products from **6**, bromination at 77°C is more convenient than bromination at 150°C because of rearrangement via radical intermediates at higher temperatures.

We are also interested in the bromination of **6** with 1,2-dibromotetracholoroethane (DBTCE), which is a mild brominating agent[6] for special products, at 77°C in $CCl_4$. From this reaction, rearranged (68%) and *non*-rearranged (32%) products were formed.




| | **19** | **20** | **21** | **22** | **9** |
|---|---|---|---|---|---|
| $Br_2/CCl_4$, 77°C[5] | 61% | 15% | 12% | - | 3% |
| $Br_2$/Decalin, 150°C | 51% | 9% | 8% | 9% | 8% |
| $C_2Br_2Cl_4$/hv/77°C | 30% | 1% | 1% | 28% | 26% |

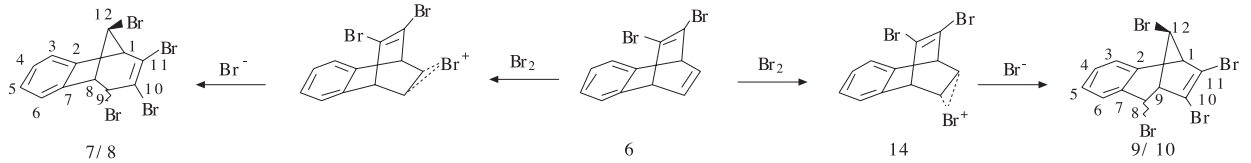
| | **10** | **23** | **24** | **7** | **8** |
|---|---|---|---|---|---|
| $Br_2/CCl_4$, 77°C[5] | 2% | - | - | 4% | 2% |
| $Br_2$/Decalin, 150°C | 5% | 4% | 2% | - | - |
| $C_2Br_2Cl_4$/hv/77°C | 14% | - | - | - | - |

| | **25** |
|---|---|
| $Br_2$/Decalin, 150°C | 3% |

**Scheme 4**

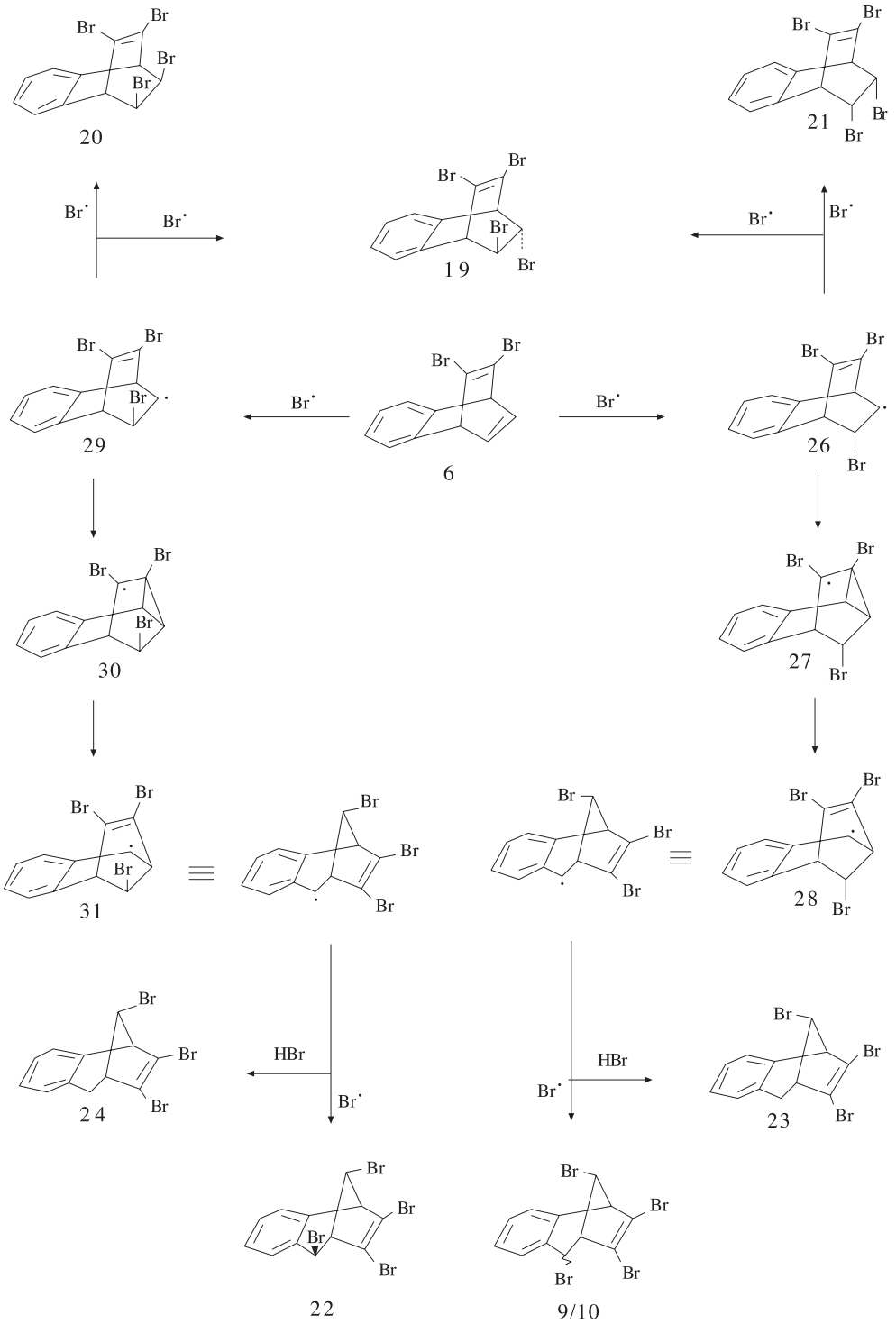
## Mechanism for radical bromination

It is clear that bromination of a bicylic system with molecular bromine at low temperature gives rearranged products via aryl and alkyl migration[3,4]. In these reactions, the addition of bromine to the double bond takes place stereoselectively.[2,3] For the products obtained by aryl migration, the bromine atom at $C_{12}$ carbon is absolutely *anti*, while for the products obtained by alkyl migration, the bromine atom at $C_{12}$ carbon is absolutely *syn* in respect of the benzene ring (Scheme 5).




**Scheme 5**

However, there is no stereoselectivity in the radical mechanism. It was observed that bromination of **6** with molecular bromine at high temperature and with DBTCE gave both *anti* and *syn* bromine atoms at

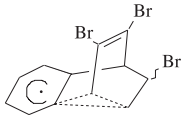



**Scheme 6**

$C_{12}$ carbon. The *anti*-configuration of the bromine in molecules (**22** and **24**) cannot be explained by an ionic mechanism. It can be explained only by a radical mechanism in which stereochemical control of configuration cannot be achieved in most cases. Therefore, for the formation of the rearranged products at radical conditions, the following general reaction mechanism is proposed (Scheme 6). The initially formed radicals **26** and **29** may either form *non*-rearranged products **19-21** or change radical-vinyl bridged intermediates

**27/30**. Radical-vinyl bridged intermediates **27/30** also open to the benzylic radicals **28/31**, which are then captured either by the bromine radical to form **9/10/22** or by the hydrogen radical to form **23/24** by means of HBr obtained during the bromination of solvent (decalin). The formation of tetrabromide **25**, which is derived from solvent (decalin), has been described in our earlier works.[7]

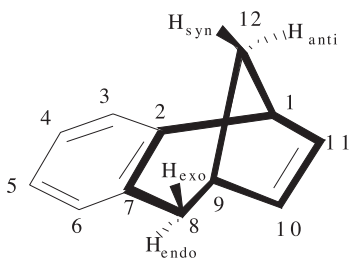
It was also assumed that, during the reaction, the radicals **26/29** were not able to turn into aryl-radical bridged intermediate **32**. If they had, it would have been necessary to obtain rearranged products like **7/8** during the bromination with DBTCE and bromine at 150°C. This also shows that benzo-vinyl bridging is not favorable. Therefore the bromination of benzonorbornadiene derivatives with DBTCE[6] gives only *non*-rearranged products because they cannot form benzo-vinyl bridging radicals like **33**. In contrast to norbornene and benzonorbornadiene derivatives, benzobarrelene derivatives, which are also eligible for vinyl-vinyl bridging (Scheme 6), give *non*-rearranged and rearranged products via radical intermediates.



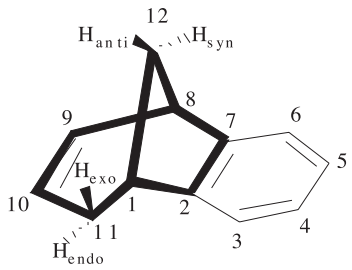

**32**


**33**

**NMR Spectral Studies and Configurational Assignments:** The structures of these compounds were elucidated on the basis of $^{1}H$ and $^{13}C$ NMR data and extensive double resonance experiments and by comparison of some spectral data of related systems reported in the literature. A summary of the proton coupling constants exhibited by these closely related [3.2.1]octadienes (Structures A and B) is given in the Experimental section.




A



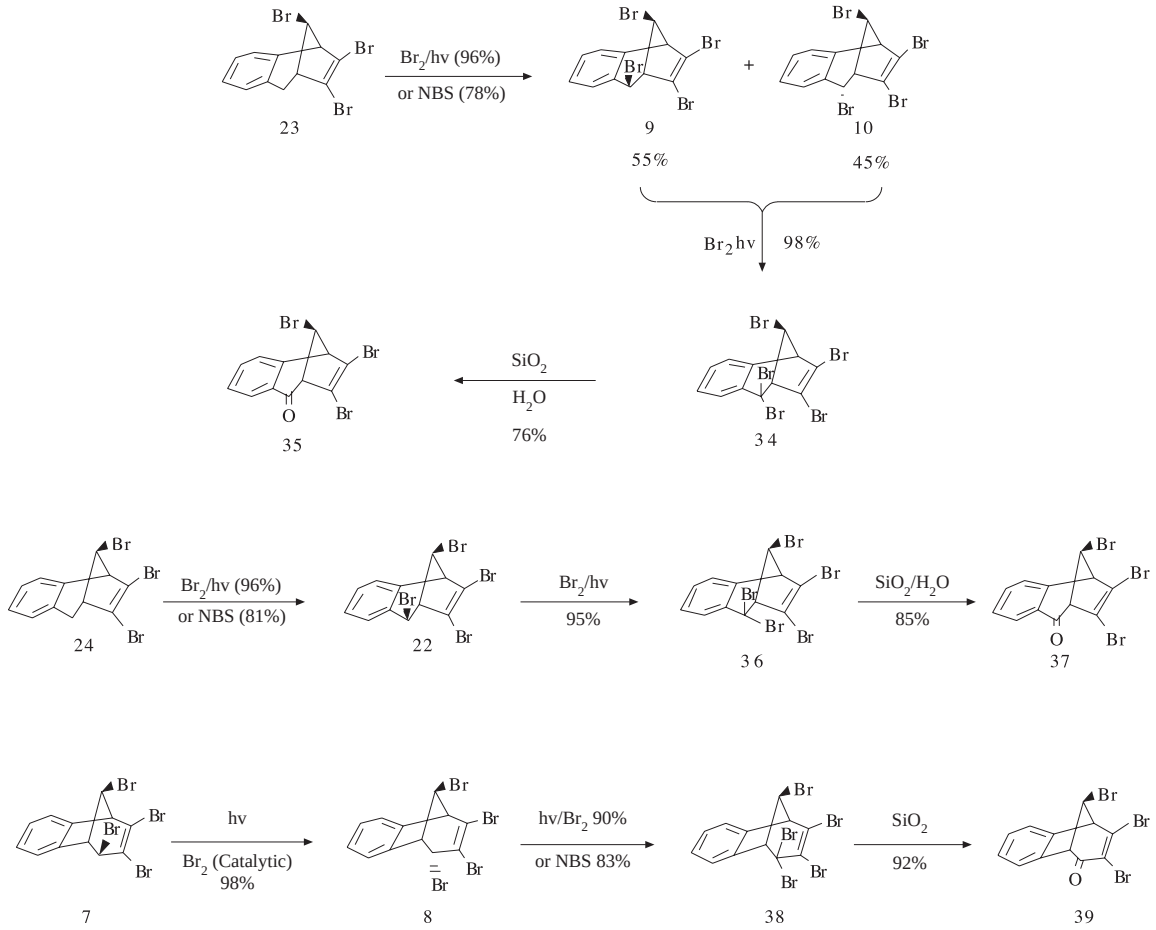

B

The coupling patterns that are important for stereo chemical characterization of this dual are $J_{9,12syn}$, $J_{9,12anti}$, $J_{9,8exo}$ and $J_{9,8endo}$ in A and $J_{1,12syn}$, $J_{1,12anti}$, $J_{1,11exo}$ and $J_{1,11endo}$ in B. As a consequence of the rigid geometries and reliability of the Karplus rule[8] in [3.2.1]octane systems,[9,3b,6a] the dihedral relationship of the $H_9$proton to $H_{12anti}$ in A and $H_1$ proton to $H_{12syn}$ in B (∼40°), and to $H_{12syn}$ in A and to $H_{12anti}$ in B (∼80°) is sufficiently distinctive to be revealed by the magnitude of the spin-spin interaction. Thus, the high value of $J_{H12anti}$ in A and $J_{H12syn}$in B (J=4.0-5.0) is uniquely accommodated by the *syn*-orientation of the bromine atom in A (*anti*-orientation of bromine in B) bonded to bridge atom. $H_{12syn}$ in A and $H_{12anti}$ in B give a singlet with line broadening (J≤1 Hz).

The configuration of bromine at the $C_8$ atom in A and at the $C_{11}$ atom in B was determined from the coupling constants $J_{8,9}$ (in A) and $J_{1,11}$ (in B). Inspection of Dreidings models indicates that the dihedral angle between protons $H_9$ ($H_1$ in B) and $H_{8exo}$ ($H_{11exo}$ in B) is approximately 40°, whereas the dihedral

angle between $H_9$ ($H_1$ in B) and $H_{8endo}$ ($H_{11endo}$ in B) is 60°. Large coupling constants of J=4.0-5.0 Hz are observed in the case of *endo*-orientation of bromine (*exo*-proton), and J=0.0-2.0 Hz in the case of *exo*-orientation of bromine (*endo*-proton). Aryl shift products type B and alkyl shifts products type A can also be easily distinguished in the typical pattern of aromatic resonance.[3b]

The structures of [3.2.1]octane systems were also supported by chemical transformation. These conversions both support the proposed structures and allow us to synthesize poly-brominated benzo biycyclic compounds that may have insecticide activity. For example, when pure HBr addition products **23/24** subjected to radicalic bromination by NBS or by photobromination with molecular bromine, tetrabromides **9**, **10** and **22** were obtained in high yield (Scheme 7). Further treatment of tetrabromides **9**, **10** and **22** with bromine resulted in the formation of the pentabromides **34/36**, which could be hydrolyzed to corresponding unsaturated ketone **35/37** on column material. The similar reaction of tetrabromide **8** gave pentabromide **38**, which could be converted to corresponding ketone **39**. In addition bromine catalyzed irradiation of **7** gave isomeric tetrabromide **8** in nearly quantitative yield (Scheme 7). These observations also support the proposed structures.




**Scheme 7**

## Conclusions

The results of the present work demonstrate that high temperature bromination is a useful synthetic method for generating *non*-rearranged bromine addition products in unsaturated bicyclic systems that have a great tendency to undergo Wagner-Meerwein rearrangement. Furthermore, it was observed that the tendency of the bromo functionalize benzobarrelene system to undergo Wagner-Meerwein rearrangement is less than that found in the unsubstituted benzobarrelene system. In the case of benzobarrelene, a much higher temperature (150°C) was applied to prevent the skeletal rearrangement.[3b] Even at this high temperature, ca. 50% of the rearranged products were formed. However, for the 2,3-dibromobenzobarrelene **(6)**, a temperature of 77°C was sufficient to prevent skeletal rearrangement. At this temperature, trace amount of the rearranged products were detected. From the bromination of benzobarrelene at 77°C, *non*-rearranged products were obtained only in 15% yields.[3b,10] It is assumed that the inductive effect of the substituted bromine atoms plays an important role in this case. Probably the tendency of the system to form the bridged carbocations **12/15** is retarded by the electronegative bromine atoms.

It was also shown that rearrangements occur via vinyl-vinyl bridging intermediates at radicalic conditions and benzo-vinyl bridging is not favorable. Therefore bromination of norbornene and benzonorbornadiene derivatives at radical conditions results in conservation of skeletal while bromination of benzobarrelene systems with the same conditions gives mainly rearranged products via vinyl-vinyl bridging intermediates.

### 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. Elemental analyses were performed with a Carlo Erba Model 1106 apparatus. Column chromatography was performed on silica gel (60-mesh, Merck). All substances reported in this paper are in their racemic form.

**Caution:** It has been reported[11] that of three laboratory workers who used dibromides and bromohydrin derived from norbornadiene, two later developed similar pulmonary disorders that 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, I recommend that the compounds only be handled with extreme caution.

**Bromination of 9,10-dibromotricyclo[6.2.2.0$^{2,7}$]dodeca-2,4,6,9,11-pentaene (6)[4] at 10°C.** To a magnetically stirred solution of **6**[4] (2.13 g, 6.83 mmol) in 25 mL of dry chloroform cooled to 10°C was added dropwise a solution of bromine (1.17 g, 7.33 mmol) in 5 mL of chloroform over 10 min. After stirring for 30 min at 10°C, the solution was allowed to warm to 20°C. The solvent was removed under reduced pressure. The oily residue was chromatographed on silica gel (90 g) eluting with hexane. Four compounds were isolated: **10**[5] (64 mg, 2%), **8**[5] (966 mg, 30%), **9**[5] (387 mg, 12%) and **7**[5] (1.77 g, 55%), in that order.

**Bromination of 9,10-dibromotricyclo[6.2.2.0$^{2,7}$]dodeca-2,4,6,9,11-pentaene (6) at 150°C.** Two grams (6.41 mmol) of **6** was dissolved in 60 mL of decalin in a 100 mL two-necked flask equipped with a reflux condenser and an inlet glass tube touching the bottom of the reaction flask. The inlet-glass tube was connected to a 2 mL round-bottom flask that contains 1.23 g (7.69 mmol) of bromine. Bromine vapors, obtained by heating the flask to 100°C, was transferred directly to decalin solution with a temperature of 150°C, over 5 min while stirring magnetically. The bromine immediately became colorless. The solvent was

removed under reduced pressure. The oily residue was chromatographed on silica gel (130 g) eluting with hexane. Nine compounds were isolated. The first fraction:

**(1*S(R)*,4*S(R)*,5*S(R)*,8*S(R)*)-1,4,5,8-tetrabromo-1,2,3,4,5,6,7,8-octahydronaphthalene (25)[7]:** (61 mg, 3%).

The second fraction: **(1*S(R)*,8*R(S)*,9*S(R)*,12*S(R)*)-8,10,11,12-tetrabromotricyclo[7.2.1.0$^{2,7}$] dodeca-2,4,6,10-tetraene (22):** (272 mg, 9%) colorless crystals, mp 120-121°C from methylene chloride/n-hexane 1:3. [Found: C, 30.94; H, 1.76 $C_{12}H_8Br_4$ requires C, 30.55; H, 1.71%]; $^1$H-NMR (200 MHz, $CDCl_3$) $\delta$ 7.42-7.03 (m, aromatic, 4H), 5.37 (d, $J_{8,9}$=2.0 Hz, $H_8$, 1H), 5.14 (s, $H_{12}$, 1H), 3.67 (m, $H_1$, 1H), 3.63 (m, $H_9$, 1H), $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 139.28, 137.04, 135.35, 135.24, 131.23, 130.43, 128.76, 121.42, 66.87, 63.31, 56.54, 47.29. IR (KBr, cm$^{-1}$) 3055, 3030, 2978, 1472, 1446, 1293, 1217, 1166, 1140, 885, 860, 782, 731.

The third fraction consisted of a mixture of compounds **19** and **23**. This mixture was submitted to fractional crystallization from methylene chloride/n-hexane (1:3) to give 1.04 g (0.5 g mixture, total 51%) of tetrabromide **19**.[5]

After filtration of tetrabromide **19**, the organic solvent was evaporated and the oily residue was recrystallized from methylene chloride/hexane (1/2) to give 61 mg (50 mg mixture, total 4%) of tribromide **23**:

**(1*S(R)*,9*R(S)*,12*S(R)*)-10,11,12-tribromotricyclo[7.2.1.0$^{2,7}$]dodeca-2,4,6,10-tetraene (23):** colorless crystals, mp 132°C from methylene chloride/n-hexane 1:3. [Found: C, 35.78; H, 2.27 $C_{12}H_9Br_3$ requires C, 36.68; H, 2.31%]; $^1$H-NMR (200 MHz, $CDCl_3$) $\delta$ 7.32-7.04 (m, aromatic, 4H), 4.94 (t, $J_{9,12}$= $J_{1,12}$=4.5 Hz, $H_{12}$, 1H), 3.51 (d, $J_{1,12}$=4.5 Hz, $H_1$, 1H), 3.12 (bd, A part of AB system, $J_{8endo,8exo}$=19.0 Hz, $H_{8exo}$, 1H), 3.10 (m, 1H, $H_9$), 2.85 (bd, B part of AB system, $J_{8endo,8exo}$=19.0 Hz, $H_{8endo}$, 1H), $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 136.14, 134.79, 132.16, 130.98, 130.27, 129.89, 128.08, 123.54, 59.03, 52.52, 51.34, 27.56. IR (KBr, cm$^{-1}$) 3055, 3030, 2953, 1472, 1446, 1421, 1242, 1064, 834, 757.

The fourth fraction: **(1*S(R)*,9*R(S)*,12*R(S)*)-10,11,12-tribromotricyclo[7.2.1.0$^{2,7}$]dodeca-2,4, 6,10-tetraene (24):** (50 mg, 2%) pale yellow viscous oil. [Found: C, 35.83; H, 2.28 $C_{12}H_9Br_3$ requires C, 36.68; H, 2.31%]; $^1$H-NMR (200 MHz, $CDCl_3$) $\delta$ 7.30-7.02 (m, aromatic, 4H), 4.61 (s, $H_{12}$, 1H), 3.63 (m, $H_1$, 1H), 3.33 (bd, $J_{8exo9}$=4.4 Hz $H_9$, 1H), 3.05 (bdd, A part of AB system, $J_{8endo,8exo}$=17.5 and $J_{8exo,9}$=4.4 Hz, $H_{8exo}$, 1H), 2.93 (bd, B part of AB system, $J_{8endo,8exo}$=17.5 Hz, $H_{8endo}$, 1H), $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 138.74, 133.69, 132.53, 130.58, 130.41, 128.84, 128.17, 123.13, 63.35, 59.52, 58.41, 31.99. IR (NaCl, cm$^{-1}$) 3055, 3030, 2979, 2953, 2928, 2902, 1600, 1472, 1447, 1294, 1268, 1166, 911, 757, 732.

From the elution of this last fraction, four compounds were isolated in the following order: **10**[5] (151 mg, 5%), **9**[5] (242 mg, 8%), **21**[5] (242 mg, 8%) and **20**[5] (272 mg, 9%).

**Bromination of 6 with DBTCE:** A solution of **6** (1.0 g, 3.21 mmol), DBTCE (1.2 g, 3.68 mmol), AIBN (catalytic) in $CCl_4$ was irradiated with a 150 W sun lamp at reflux temperature in a 50 mL flask equipped with a condenser. The progress of the reaction was monitored by $^1$H NMR spectra. After 4 d, the solvent and tetracholoroethylene formed during bromination were removed under reduced pressure. The product ratio was determined by $^1$H-NMR spectra: **19**[5] (30%) **22**[5] (28%), **9**[5] (26%), **10**[5] (14%), **20**[5] (1%) and **21**[5] (1%).

**Reaction of 23 with N-Bromosuccinimide.** A mixture of **23** (100 mg, 0.25 mmol), N-bromo-

succinimide (46 mg, 0.26 mmol), AIBN (10 mg), and $CCl_4$ (40 mL) was heated at reflux temperature for 12 h, cooled, and filtered to remove succinimide. After the solvent was removed, the residue was purified on a short silica gel column (5 g) eluted with hexane to give 94 mg (78%) of pure crude product. The $^1$H NMR analysis of the crude product indicated the formation of a mixture consisting of **9** and **10** in a ratio of 55:45.

**Photobromination of 23.** A solution of **23**(100 mg, 0.25 mmol) and bromine (41 mg, 0.26 mmol) in 5 mL of $CCl_4$ was subjected to direct irradiation with a sun lamp (150 W) at room temperature for 10 min. After the solvent was removed, the residue was filtered on a short silica gel column (5 g) eluted with $CCl_4$ to give 115 mg (96%) of pure crude product. The $^1$H NMR analysis of the crude product indicated the formation of a mixture consisting of **9** and **10** in a ratio of 55:45.

**Photobromination of 9 at inert conditions.** A solution of **9** (106 mg, 0.22 mmol) and bromine (36 mg, 0.23 mmol) in 5 mL of $CCl_4$, under $N_2$, was irradiated with a sun lamp (150 W) at room temperature for 4 h. The $^1$H NMR analysis of the crude product indicated the formation of pentabromide **34** as the sole product. From the bromination of **10** under the same reaction conditions, the pentabromide **34** was again obtained as the sole product. Due to fact that pentabromide **34** was unstable, it could not be crystallized.

**(1*S(R)*,9*R(S)*,12*R(S)*)-8,8,10,11,12-pentabromotricyclo[7.2.1.0$^{2,7}$]dodeca-2,4,6,10-tetraene (34):** $^1$H-NMR (200 MHz, $CDCl_3$) $\delta$ 8.05 (m, aromatic $H_6$, 1H), 7.51-6.97 (m, aromatic, 3H), 5.10 (t, $J_{1,12}$= $J_{9,12}$=4.3 Hz, $H_{12}$, 1H), 3.99 (dd, $J_{1,12}$=4.3, $J_{1,9}$=1.2 Hz, $H_1$, 1H), 3.57 (dd, $J_{9,12}$=4.3, $J_{1,9}$=1.2 Hz, $H_9$, 1H), $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 140.88, 135.75, 135.20, 133.30, 131.96, 131.63, 129.06, 126.68, 66.10, 60.03, 57.41, 49.51. IR (KBr, cm$^{-1}$) 3055, 3030, 2979, 2953, 1575, 1447, 936, 885, 834.

**Hydrolysis of pentabromide 34 to the ketone 35:** To a silica gel column (80 g) prepared with hexane, pentabromide **34** (100 mg, 0.18 mmol) loaded 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 hexaneto give unreacted pentabromide **34**. Then the column was eluted with hexane/ethyl acetate (95:5) and ketone **35** was obtained as the sole product (56 mg) in 76% yield.

**(1*S(R)*,9*R(S)*,12*R(S)*)-10,11,12-tribromotricyclo[7.2.1.0$^{2,7}$]dodeca-2,4,6,10-tetraen-8-one (35):** Colorless crystals, mp 156-157°C from methylene chloride/n-hexane 1:2. [Found: C, 34.89; H, 1.77 $C_{12}H_7Br_3O$ requires C, 35.42; H, 1.73%]; $^1$H-NMR (200 MHz, $CDCl_3$) $\delta$ 8.03 (m, aromatic $H_6$, 1H), 7.57-7.02 (m, aromatic, 3H), 5.33 (t, $J_{1,12}$= $J_{9,12}$=4.7 Hz, $H_{12}$, 1H), 3.83 (dd, $J_{1,12}$=4.7, $J_{1,9}$ ≤1.0 Hz, $H_1$, 1H), 3.71 (dd, $J_{9,12}$=4.7, $J_{1,9}$ ≤1.0 Hz, $H_9$, 1H), $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 189.84, 141.24, 136.60, 135.85, 131.26, 130.61, 130.54, 128.92, 123.35, 68.17, 60.60, 55.79, IR (KBr, cm$^{-1}$) 3081, 3055, 3030, 2978, 2953, 2928, 1702, 1600, 1293, 1217, 1063, 1012.

**Photobromination of 24.** The reaction was carried out as described above by using 50 mg (0.13 mmol) of tribromide **24** and 21 mg (0.13 mmol) of bromine and 58 mg (96%) of **22** was obtained as sole product.

**Reaction of 24 with N-Bromosuccinimide.** The reaction was carried out as described above by using a mixture of **24** (100 mg, 0.25 mmol), N-bromosuccinimide (46 mg, 0.26 mmol), AIBN (10 mg), and 98 mg (81%) of pure **22** was obtained.

**Photobromination of 22 at inert conditions.** The reaction was carried out as described above by using 106 mg (0.22 mmol) of tetrabromide **24** and 36 mg (0.23 mmol) of bromine, and pentabromide **36** was obtained as sole product. Due to fact that pentabromide **36** was unstable, it could not be crystallized.

**(1*S(R)*,9*R(S)*,12*S(R)*)-8,8,10,11,12-pentabromotricyclo[7.2.1.0$^{2,7}$]dodeca-2,4,6,10-tetraene (36):** $^1$H-NMR (200 MHz, $CDCl_3$) $\delta$ 7.99 (m, aromatic $H_6$, 1H), 7.46-6.95 (m, aromatic, 3H), 5.14 (s, $H_{12}$, 1H), 4.11 (m, $H_1$, 1H), 3.61 (m, $H_9$, 1H), $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 140.51, 137.52, 135.84, 135.58, 131.96, 131.67, 127.68, 123.24, 74.52, 62.88, 59.14, 57.84. IR (NaCl, cm$^{-1}$) 3080, 3055, 3030, 2978, 2954, 1575, 1447, 1243, 1217, 1140, 1089, 936.

**Hydrolysis of pentabromide 36 to the ketone 37:** The reaction was carried out as described above by using 100 mg (0.18 mmol) of pentabromide **36** and 63 mg (85%) of **37** was obtained as the sole product.

**(1*S(R)*,9*R(S)*,12*S(R)*)-10,11,12-tribromotricyclo[7.2.1.0$^{2,7}$]dodeca-2,4,6,10-tetraen-8-one (37):** Colorless crystals, mp 200-201°C from methylene chloride/n-hexane 1:2. [Found: C, 36.07; H, 1.69 $C_{12}H_7Br_3O$ requires C, 35.42; H, 1.73%]; $^1$H-NMR (200 MHz, $CDCl_3$) $\delta$ 7.99 (m, aromatic $H_6$, 1H), 7.56-7.26 (m, aromatic, 3H), 4.99 (bs, $H_{12}$, 1H), 3.95 (m, $H_1$, 1H), 3.85 (m, $H_9$, 1H), $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 189.59, 143.58, 136.26, 136.19, 131.41, 131.33, 130.25, 128.12, 122.47, 72.80, 65.21, 59.77. IR (KBr, cm$^{-1}$) 3004, 2978, 2953, 2928, 1677, 1600, 1472, 1242, 1217, 1038.

**Direct Irradiation of 7 in $CDCl_3$.** A solution of 100 mg (0.21 mmol) of **7** in 0.5 mL of $CDCl_3$ was placed into a NMR tube and irradiated by a 150-W projector lamp for 6 h. The $^1$H NMR analysis indicated the formation of **8** as the sole product.

**Reaction of 8 with N-Bromosuccinimide.** A mixture of **8** (300 mg, 0.64 mmol), N-bromosuccinimide (226 mg, 1.28 mmol), AIBN (10 mg), and $CCl_4$ (60 mL) was heated at reflux temperature, under $N_2$ for 14 h, cooled, and filtered to remove succinimide. After the solvent was removed at rt, the residue was crystallized from methylene chloride/n-hexane (1:1) to give 291 mg (83%) of pentabromide **38**.

**(1*R(S)*,8*S(R)*,12*S(R)*)-9,10,11,11,12-pentabromotricyclo[6.3.1.0$^{2,7}$]dodeca-2,4,6,9-tetraene (38):** Colorless crystals, mp 144°C from methylene chloride /n-hexane 1:1. [Found: C, 26.84; H, 1.33 $C_{12}H_7Br_5$ requires C, 26.17; H, 1.28%]; $^1$H-NMR (200 MHz, $CDCl_3$) $\delta$ 7.62 (m, aromatic $H_3$, 1H), 7.29 (m, aromatic, 3H), 4.74 (t, $J_{1,12}$= $J_{8,12}$=4.1 Hz, $H_{12}$, 1H), 4.48 (dd, $J_{1,12}$=4.1, $J_{1,8}$=1.0 Hz, $H_1$, 1H), 4.12 (dd, $J_{8,12}$=4.1, $J_{1,8}$=1.0 Hz, $H_1$, $H_8$, 1H), $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 145.41, 141.99, 131.16, 131.01, 130.72, 129.71, 128.39, 124.24, 64.25, 62.16, 60.98, 50.28, IR (KBr, cm$^{-1}$) 3055, 3030, 2979, 1574, 1549, 1447, 1243, 1217, 1140, 1114, 885, 834, 732.

**Photobromination of 8 at inert conditions.** The reaction was carried out as described above for 20 h by using 300 mg (0.64 mmol) of tetrabromide **8** and 123 mg (0.77 mmol) of bromine, and 315 mg (90%) of **38** was obtained as the sole product.

**Hydrolysis of pentabromide 38 to the ketone 39:** The reaction was carried out as described above by using 100 mg (0.18 mmol) of pentabromide **38**, and 61 mg (82%) of **39** was obtained as the sole product

**(1*S(R)*,8*S(R)*,12*R(S)*)-10,11,12-tribromotricyclo[6.3.1.0$^{2,7}$]dodeca-2,4,6,10-tetraen-9-one (39):** colorless crystals from methylene chloride/n-hexane (1:1), mp 147-148°C, [Found: C, 36.11; H, 1.67 $C_{12}H_7Br_3O$ requires C, 35.42; H, 1.73%]; $^1$H-NMR (200 MHz, $CDCl_3$) $\delta$ 7.48-7.25 (m, aromatic, 4H), 4.89 (t, $J_{1,12}$= $J_{8,12}$=4.4 Hz, $H_{12}$, 1H), 4.44 (dd, $J_{1,12}$=4.4, $J_{1,8}$ ≤1.0 Hz, $H_1$, 1H), 4.26 (dd, $J_{8,12}$=4.4, $J_{1,8}$ ≤1.0 Hz, $H_8$, 1H), $^{13}$C NMR (50 MHz, $CDCl_3$) 186.24, 150.00, 145.52, 139.33, 130.90, 127.63, 125.58, 123.66, 63.75, 62.80, 57.44, IR (KBr, cm$^{-1}$) 3008, 2988, 1696, 1566, 1460, 1260, 1225, 1201, 1177, 1142, 977.

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