High temperature bromination Part XXIII: Bromination of octahydro-1*H*-indene and octahydro-1*H*-4,7-methanoindene

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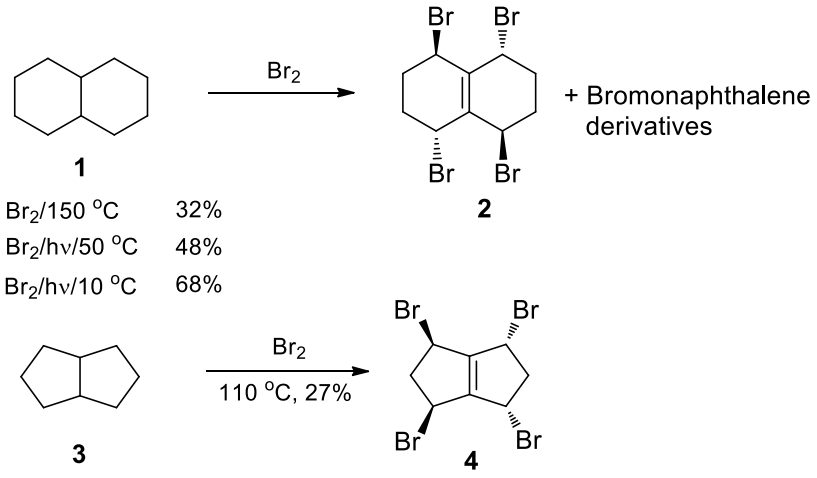
Abstract
Thermal and photobromination of octahydro-1*H*-indene and octahydro-1*H*-4,7-methanoindene were investigated. Three isomeric tetrabromides (1,3,4,7-tetrabromo-2,3,4,5,6,7-hexahydro-1*H*-indene) were formed along with a smaller amount of tribromoindane and a pentabromide by thermal bromination of octahydro-1*H*-indene. The thermodynamically most stable isomers were formed. Morover, thermal and photochemical bromination of octahydro-1*H*-4,7-methanoindene furnished bromides resulting regiospecifically from the allylic bromination of the five-membered ring. Furthermore, the double bond formed as the intermediate functional group was also brominated due to its pyramidalization. The mechanism proposed for the formation of product distribution was discussed.

Keywords: Bromination, high temperature bromination, hydrocarbons, substitution.

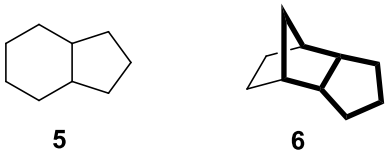
Introduction

The selective functionalization of hydrocarbons is a seminal and challenging process in organic synthesis and industrial chemistry.[2,3] Thus, a new chemical process for selective functionalization of alkanes to upgraded products is one of the most promising methods for future organic synthesis. In spite of decades of efforts by a plethora of research groups, only a small number of chemical systems have been described for the transformation of such substrates by metallic[4-9] and nonmetallic catalysts,[10-16] aerobic oxidation,[17] and photochemical oxidation.[18] Moreover, studies about the functionalization of rigid and strained bicyclic and tricyclic saturated hydrocarbons are rare in the literature. Recently, we showed that thermal and photobromination of decalin (**1**) gave *trans*,*trans*,*trans*-2,5,7,9-tetrabromooctalin (**2**) as the major product along with smaller amounts of bromonaphthalene derivatives (Scheme 1).[19-20] It was remarkable that the reaction proceeded with high regio- and stereoselectivity. Although the calculations demonstrated that the most stable tetrabromide, **2,** was formed exclusively, it may well be that this is also a kinetically controlled product. It was not surprising that this configuration is the most stable because dipole-dipole interactions between bromine atoms force each other to be as far apart as possible.



Scheme 1. Bromination of decalin **1** and octahydropentalene **2** at high temperatures.

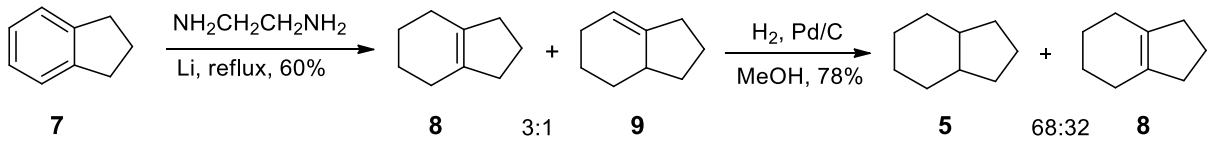
On the other hand, high temperature bromination[20-24] of octahydropentalene (**3**) provided *cis,trans,cis*-1,3,4,6-tetrabromo-1,2,3,4,5,6-hexahydropentalene (**4**) as the sole compound.[25] However, the formation of **4** among other possible isomers was kinetically favored in contrast to AM1 and MM+ molecular mechanics calculations.



Inspired by our encouraging results with decalin (**1**) and octahydropentalene (**3**) giving single products with completely different geometries, we decided to investigate the behavior of octahydro-1*H*-indene (**5**), which is formed of a fused five- and six-membered ring. Furthermore, we examined the bromination reaction of an octahydropentalene system **6**, where the six-membered ring is incorporated in a bicyclic system.

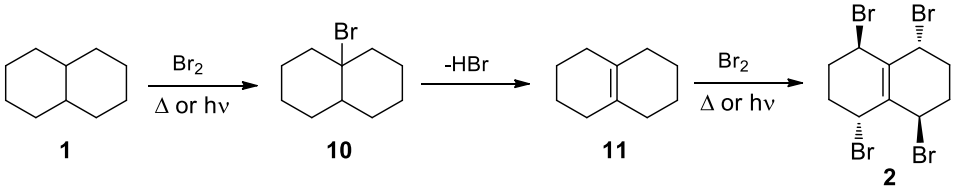
Results and Discussion

For the synthesis of octahydro-1*H*-indene (**5**), the Benkeser reduction reaction,[26-28] was used, which is a hydrogenation of aromatic hydrocarbons, using lithium or calcium metal and any of the primary amines as reductants. A modified tetraline reduction procedure[26] was applied to indane (**7**). Treatment of indane (**7**) with lithium in ethylenediamine gave a mixture of 2,3,4,7-tetrahydro-1*H*-indene (**8**) and 2,3,3a,4,5,6-hexahydro-1*H*-indene (**9**) in a ratio of 76:24 (60.0% yield) (Scheme 2). The hydrogenation of those isomers **8** and **9** over Pd/C in MeOH furnished the desired saturated hydrocarbon **5** along with a large amount of nonreduced compound **8** in a ratio of 68:32 (78.0%) as determined by the ^{1}H NMR spectrum.



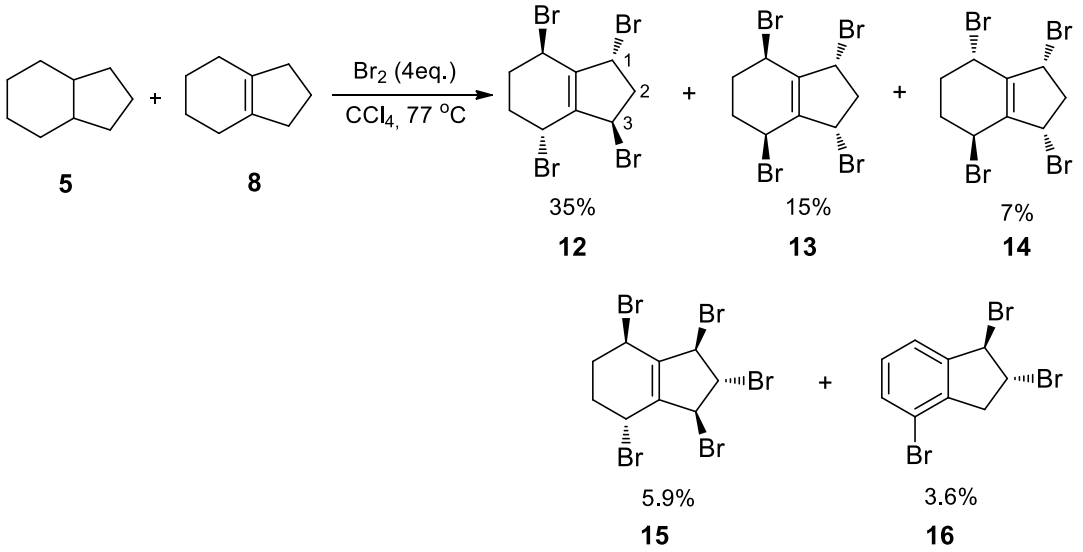
Scheme 2. Synthesis of octahydro-1*H*-indene (5).

During the mechanistic evaluation of the bromination of decalin, we showed that the reaction proceeds via the free radical bromination of **1** to give **10** followed by dehydrobromination to generate **11**. Subsequent allylic bromination of octalin (**11**) generated the tetrabromide **2** (Scheme 3).



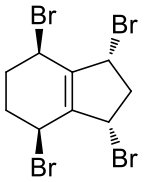
Scheme 3. Formation of tetrabromide **2** over octalin as the intermediate.

As we could not separate **5** and **8,** and possible bromination reaction of **5** will proceed via **8**, a mixture consisting of **5** and **8** was subjected to bromination reaction. The mixture of **5** and **8** was reacted with 4 equiv. of bromine at 77 °C in CCl_4 over 20 min. The ^{1}H-NMR spectral analysis of the reaction mixture indicated the formation of brominated compounds as well as the formation of some aromatic compounds. Column chromatographic separation provided **12**, **13**, **14**, **15**, and **16** in 35.0%, 15.0%, 7.0%, 5.9%, and 3.6% yields, respectively (Scheme 4).



Scheme 4. High temperature bromination of the mixture of **8** and **5**.

All structures were well characterized by ^{1}H-, ^{13}C-, and 2D-NMR experiments (DEPT, COSY, HMQC, HMBC). The dihedral angles between the methylenic protons of the five-membered ring and its neighboring protons were used to define the configuration of bromine atoms in the compounds **12-16**. The ^{13}C-NMR spectrum of **12** consisted of five distinct carbon resonances, indicating the high symmetry in the molecule. The methylene protons of the five-membered ring resonate as a triplet (*J* 5.6 Hz), indicating the equivalency of the methylene protons and the *trans*-configuration of the bromine atoms connected to the five-membered ring. Because of the observed symmetry in the molecule, the bromine atom at the six-membered ring must also have *trans*-configuration. Notably, the ^{1}H-NMR spectrum of **13** is quite different from that of **12**, whereas the ^{13}C-NMR spectrum consists of five distinct signals indicating the symmetry in the molecule. The methylene protons of the five-membered ring appear as an AB system as a doublet of triplets at 3.24 ppm (A-part of AB-system, ^{2}J 16.9 and ^{3}J 7.0 Hz) and as a doublet at 2.85 ppm (B-part of AB-system (^{2}J 16.9 Hz). These couplings clearly show the *cis*-configuration of the bromine atoms. The observed symmetry in the molecule was in agreement with the following structures **13** and **17**.



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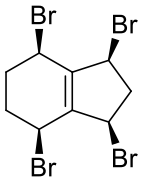
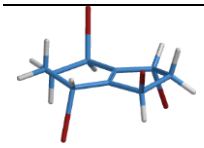
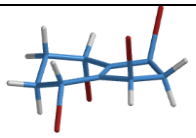
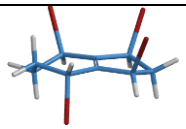
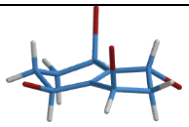
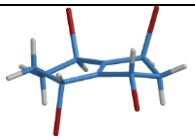
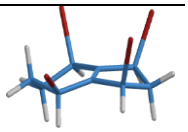


17

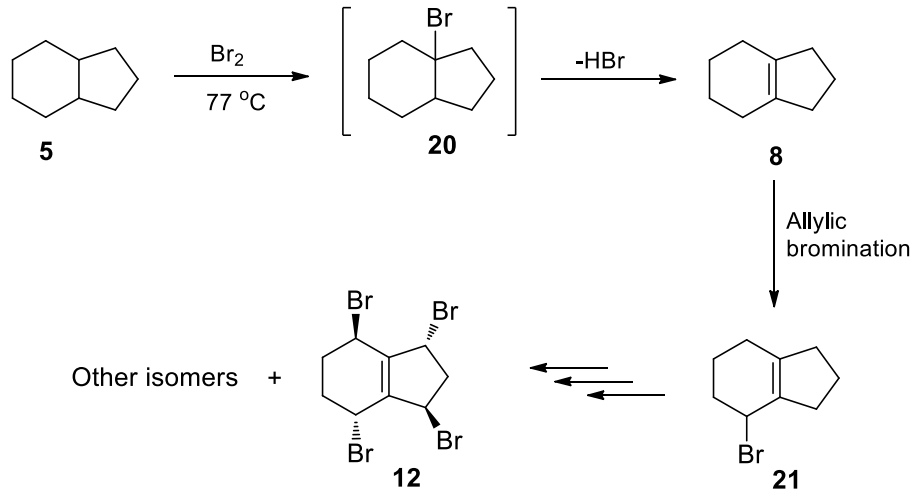
However, on the basis of NMR data alone, we were not able to distinguish between those structures. By considering the results obtained by bromination of **5** and steric effects associated with the adjacent bromine atoms in **17**, we assigned the structure **13** to this compound. Furthermore, we determined the relative energies of those isomers at RB3LYP (6-31G**) level using the SPARTAN'08 mechanic program, indicating that **13** is about 9.43 kcal/mol more stable than the isomer **17**. Therefore, we assume that **13** is a thermodynamically controlled product. The assignment of the structure **14** was also accomplished using ^{1}H- and ^{13}C-NMR spectral data. The 9-line ^{13}C-NMR spectrum supports the asymmetry in the molecule. Again, the methylene protons in the five-membered ring resonate as an AB-system as a doublet of doublet of doublets at 3.45 (A-part of AB-system, ^{2}J 18.3, ^{3}J 5.7 and 2.2 Hz) and as a doublet at 2.62 ppm (B-part of AB-system (^{2}J 18.3 Hz). The fact that one of these protons H-2_{cis} resonates as a doublet (arising from the geminal coupling) indicates again the *cis*-configuration of the bromine atoms as discussed above. The geometry optimized structure of **14** shows dihedral angles of 92.8° and 93.8° between the vicinal protons H-2_{cis} and the protons H-1 and H-3, which is in good agreement with a *cis*-configuration. The asymmetrical structure can be only in agreement with the *trans*-configuration of the bromine atoms in the six-membered ring.

Table 1. Relative energies of all possible 1,3,4,7-tetrabromo-2,3,4,5,6,7-hexahydro-1*H*-indene isomers **11-13** and **17-19** calculated at RB3LYP (6-31G**) level using the SPARTAN'08 mechanic program indicated

 **11**	 **12**	 **13**	 **18**	 **19**	 **17**
0.0 kcal/mol	1.55 kcal/mol	4.54 kcal/mol	6.39 kcal/mol	8.80 kcal/mol	10.98 kcal/mol
$J_{12} = J_{12'} = 5.6$ Hz $J_{32} = J_{32'} = 5.6$ Hz	$J_{2cis,2tr} = 16.8$ Hz $J_{12tr} = J_{32tr} = 7.0$ Hz $J_{12cis} = J_{32cis} = 0.0$ Hz	$J_{2cis,2tr} = 18.3.8$ Hz $J_{12tr} = 5.7$ Hz $J_{32tr} = 2.2$ Hz $J_{12cis} = J_{32cis} = 0.0$ Hz	Selected coupling constants in Hz		
	$H1C1C2H2_{cis} = 92.4°$ $H1C1C2H2_{tr} = 29.9°$	$H1C1C2H2_{cis} = 93.3°$ $H31C3C2H2_{cis} = 92.83$	Dihedral angles		

The nine-line ^{13}C-NMR spectrum of **15** also indicates the presence of an asymmetrical structure. The location of bromine atoms on the carbon skeletons was determined by COSY-spectrum. The protons H-1, H-2, and H-3 resonate at 5.11 (H-1) as a broad singlet, at 4.91 (H-3) as a singlet, and at 4.77 ppm (H-2) as a triplet with a coupling of *J*=1.0 Hz. This coupling mode can be explained only by *trans*-configuration of the bromine atoms, since the relevant dihedral angles were determined to be 87.8° and 90.0°. Then the configuration of the bromine atoms at the six-membered ring must be *trans* for an asymmetrical structure.[29] Finally, we identified as the last compound **16**, which was aromatized under the reaction conditions.

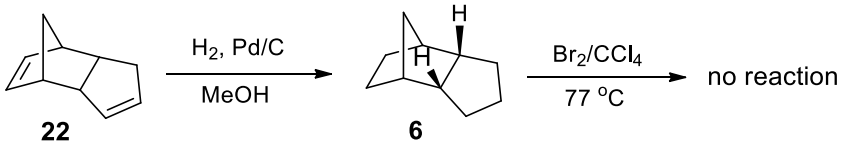
In order to evaluate the relative stabilities of all possible diasteromeric 1,3,4,7-tetrabromohexahydroindenes **11-13** and **17-19** we carried out DFT calculations. Our computational investigation of these substituted hexahydroindene derivatives shows that the isomers **11** and **12** are close in energy and they are approximately 4-11 kcal more stable than the other isomers **17-19**. In the case of *cis*-configuration of the substituents in the six- or five-membered rings the bromine atoms are far from each other. However, if the bromine atoms at 1,7 and 3,4 positions have the *cis*-configuration, there is a strong dipol-dipol interaction. This interaction increases the relative energy of the compounds. In the case of **18** and **19** the bromine atoms at 1,7 and 3,4 positions have the *cis*-configuration. Therefore, the energy of these isomers is much higher than that of other isomers.



Scheme 5. Suggested mechanism for the formation of the tetrabromides derived from **5**.

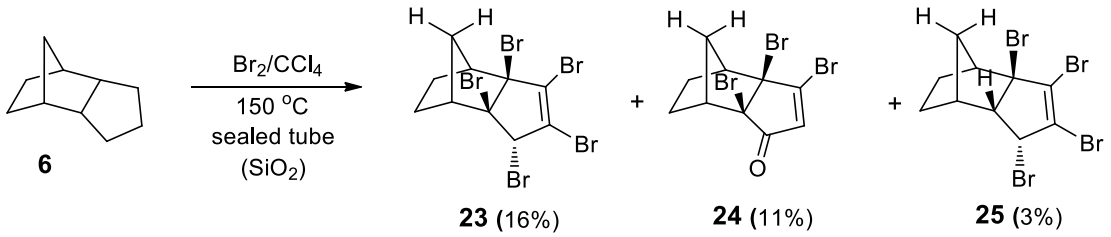
For the mechanism of formation of the products we propose that the reaction proceeds via the free radical bromination of **5** followed by dehydrobromination to form **8**. Subsequent allylic bromination of **8** generates the products **12-16**. Once the first bromine is placed at an allylic position, it may direct the second bromine *trans* to it three carbons removed. If this *trans*-directing effect continues, the isomer **12** with all bromine atoms *trans* will be formed (Scheme 5).

In order to clarify the remarkable stereospecificity observed in these tetrabromides **12-13** we incorporated the six-membered ring in a bicyclic system **6**, and studied the thermal bromination of compound **6**. Thermal bromination of rigid and more strained tricyclic structures are not described in literature.



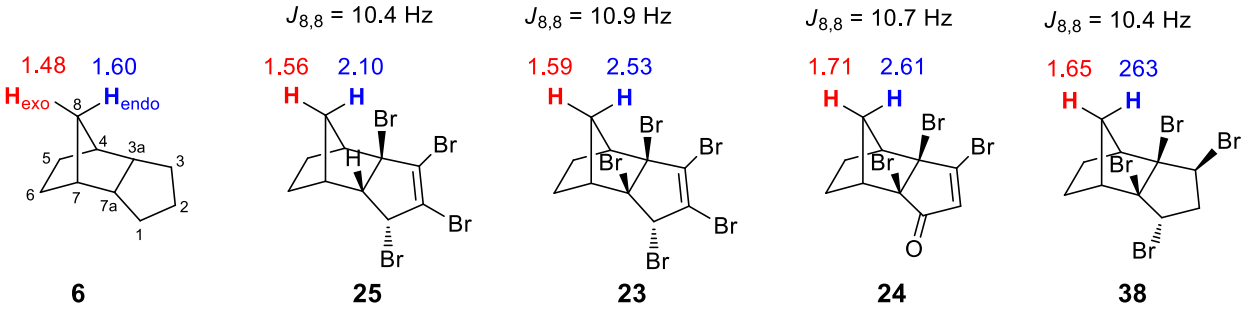
Scheme 6. Synthesis of the starting material 6 and its reaction with Br_2 at 77 °C.

Therefore, we aimed to investigate the bromination of tricyclic saturated hydrocarbon **6** obtained from the modified procedure about catalytic hydrogenation of **22** as reported in the literature (Scheme 6).[30-31] Bromination of octahydro-1*H*-4,7-methanoindene (**6**) at 77 °C in CCl_4 failed. To start the bromination reaction, first one of the tertiary protons in **6** should be abstracted. We assume that the methylene bridge protons hinder the approach of initially formed bromine radical to abstract one of the tertiary protons and probably the reaction temperature was not high enough to overcome the energy of the transition state for proton abstraction. Therefore, the reaction was carried out in a sealed tube at higher temperatures. Bromination of **6** in a sealed tube at 150 °C provided a mixture of three isolable brominated compounds, **23-25**, in 16.0%, 11.0%, and 3.0% yields, respectively (Scheme 7).



Scheme 7. Bromination of **6** at 150 °C.

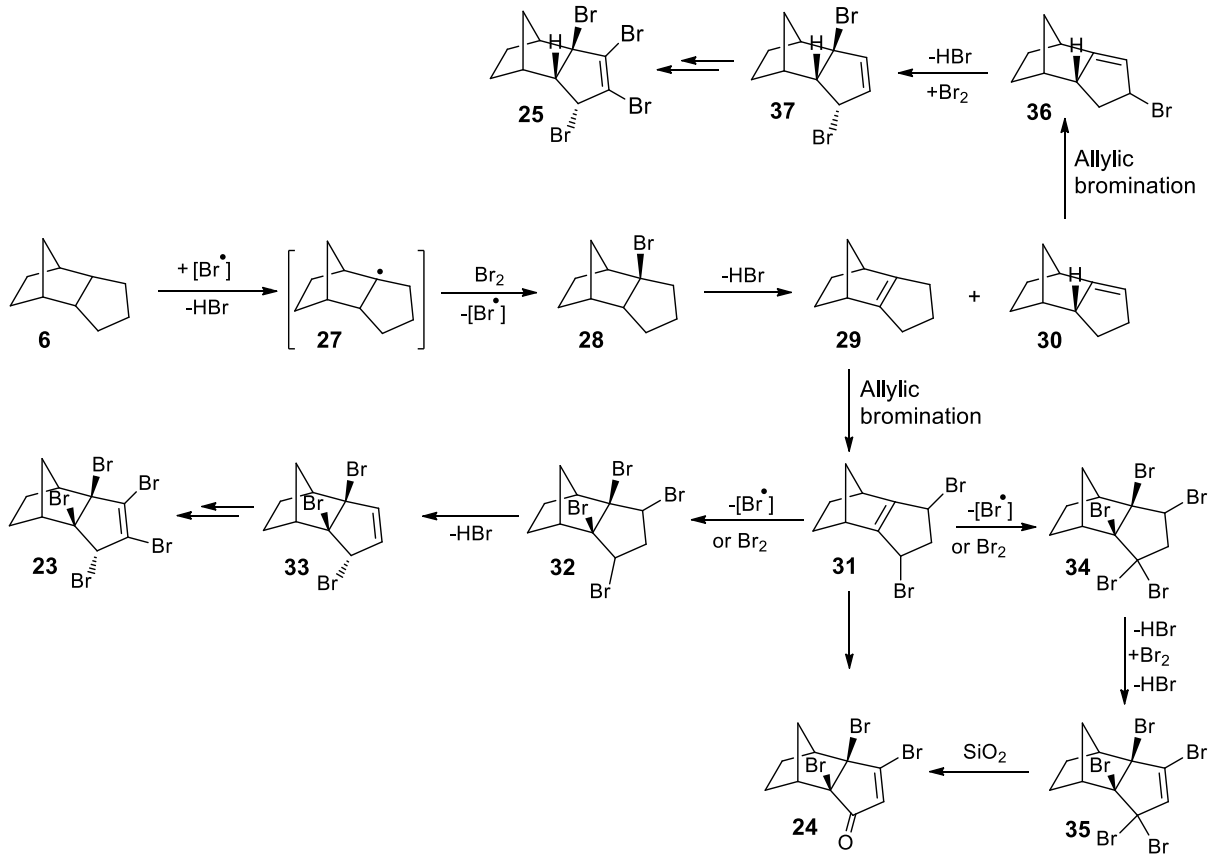
The products were separated by column chromatography and their structures were well characterized by 1D and 2D NMR experiments. First, the number and exact positions of the bromine atoms incorporated into the molecule were determined from MS and NMR spectra. The DEPT and 2D NMR (COSY, DEPT, HSQC, and HMBC) spectra of **23-25** showed the presence of three methylene groups located in the bicyclic part of the molecule. This clearly indicates that methylene groups in the five-membered ring were brominated. The presence of two carbon signals in the range of sp^2-hybridized carbon atoms indicated the presence of a tetrasubstituted carbon-carbon double bond substituted by bromine atoms.



The bridging methylene protons H_{8exo} and H_{8endo} resonate as an AB-system and the geminal coupling constants between those protons were found to be 10.4-10.9 Hz. It was notable that the chemical shifts of the H_{8exo} protons (1.56-1.71 ppm) in **23-25** are comparable with that of unsubstituted hydrocarbon **6** (1.48 ppm). However, the chemical shifts of the H_{8endo} protons are moved successively to lower field depending on the number of bromine atoms bonded to C_{3a} and C_{7a}. Recently, we showed that the interaction between the hydrogen and bromine atoms related to the van der Waals effect causes a paramagnetic contribution to the ^1H shielding constant, which results in a shift to lower field.[28-35] Insertion of one bromine atom at the C_{3a} position causes a remarkable lowfield shift of the proton H_{8endo} (2.10 ppm) due to the steric repulsion caused by bromine atoms. In the case of **23** and **24** there are two bromine atoms; the H_{8endo} proton resonances are shifted down to 2.53 and 2.61 ppm, respectively. The shift effect of the bromine atoms is additive. On the basis of these observations we assigned *exo*-configuration to the bromine atoms bonded to C_{3a} and C_{7a} carbons. Furthermore, the lack of coupling between the protons H_{8exo} and H_{7a} in **25** clearly indicated the *cis*-configuration of this proton (related to the adjacent bromine atom). In the case of a *trans*-configuration of this proton, as shown in **26**, a coupling between H_{8exo} and H_{7a} should be observed according to a "W" or "M" orientation

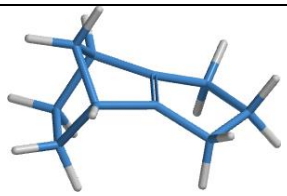
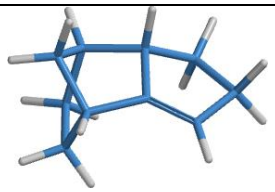
mechanism.[13c] The carbonyl carbon resonance in **24** appears at 195.9 ppm, showing conjugation with a double bond. The olefinic proton in **24** resonates at 6.48 ppm as a singlet, clearly indicating the β-position. Otherwise, this proton resonance should be shifted down to 7.50 ppm or lower.

To rationalize the formation of compounds **23-25** we propose the following mechanism. As discussed above, we assume that the reaction proceeds via the free radical bromination of **6**. First, a bromine radical initially formed abstracts one of the protons H_{3a} or H_{7a} forms **27**, which is then captured by bromine to give the monobromide **28** (Scheme 8). Dehydrobromination of **28** can generate two isomeric alkenes **29** and **30**. Successive allylic bromination followed by dehydrobromination of **29** and **30** through the intermediates **31-36** furnishes the products **23-25**. Contrary to the bromination reaction of **1** and **3**, in the case of **6** the double bond formed as an intermediate is also further brominated. To explain this outcome, we carried out some calculations on the possible olefins **29** and **30**.



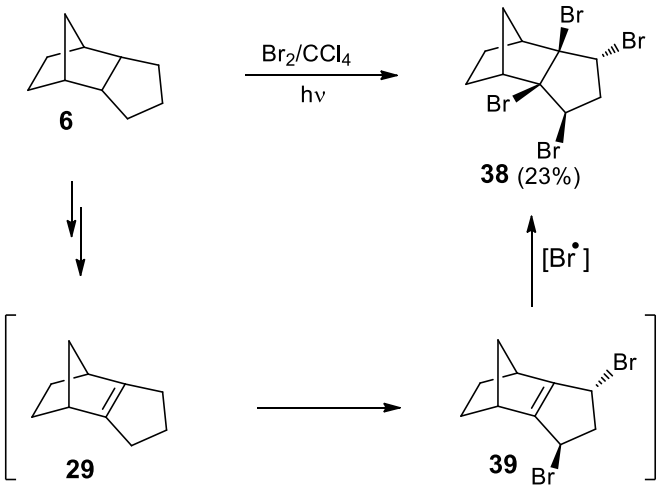
Scheme 8. Suggested mechanism for the formation of **23-25** derived from **6**.

Table 2. Relative energies of **29** and **30** calculated at RB3LYP (6-31G**) level using the SPARTAN'08 mechanic program indicated and the bending angles of the double bonds

Compounds	 **29**	 **30**
Relative energies	0.0 kcal/mol	0.26 kcal/mol
Dihedral angle	166.63°	160.46°
Butterfly bending angle/direction	13.37° *endo*	19.54° *endo*

The geometry optimization calculations (DFT, B3LYP at 6-311+G** level) carried out on **29** and **30** showed that **29** is about 0.26 kcal/mol more stable than the isomer **30** (Table 2). Therefore, we assume that these two isomers may be formed under the reaction conditions. The double bonds in **29** and **30** are pyramidalized[36-37] in the *endo* direction. Norbornene and norbornadiene exclusively undergo an *exo* attack upon treatment with electrophiles. This *exo* selectivity[38-40] is certainly not surprising since electronic factors favor attack on the convex face of the pyramidalized double bond.[41-43] Since the double bonds in **29** and **30** are pyramidalized, they will undergo an *exo*-attack by bromine radicals to form **32** and **37**, respectively. The formation of the final products can be rationalized by tandem HBr elimination followed by bromine addition as depicted in Scheme 8. The ketone **24** may be formed during chromatography of the reaction mixture on a silica gel column probably by hydrolysis of the corresponding geminal dibromide **34**.

Photobromination of 6. After bromination of **6** under very harsh conditions (150 °C) we have examined the photobromination reaction of **6** at room temperature in order to prevent eventually the dehydrobromination reaction of brominated intermediates that are initially formed. For this purpose, to a solution of **6** in CCl_4 was added 4 eqiv. of bromine and the resulting solution was irradiated for 72 h with 150-W projector lamp at room temperature (Scheme 9). The tetrabromide **38** was separated and characterized as the sole isolable compound. Again, the configuration of the bromine atoms connected to C_{3a} and C_{7a} was assigned as *exo* due to the lowfield shift (2.61 ppm) of the resonance frequency of the proton H_{8endo}.



Scheme 9. Photobromination of **6** at room temperature.

The methylenic H_2 and $H_{2'}$ protons give rise to an AB-system at 2.76 ppm (dd, A-part of AB-system $J_{22'(gem)}$ 15.2 Hz, J_{23} 7.6 Hz) and 2.60 ppm (ddd, B-part of AB-system $J_{2'2}$ 15.2 Hz, $J_{2'3}$ 13.2 Hz, $J_{2'1}$ 6.0 Hz). The correlations between the methylenic protons and H_3 and H_1 were clearly observed from the COSY spectrum of the compound. The formation of this tetrabromide can be explained first by the formation of the alkene **29**, followed by allylic bromination to give **39**, which can be transformed into the final product by addition of bromine radicals to the pyramidalized double bond. The isolation of this product **39** also supports the proposed mechanism shown in Scheme 8.

Conclusion

High temperature bromination of saturated bicyclic[4.3.0]system **5** carried out at high temperature results in the formation of three isomeric tetrabromides: **12**, **13**, and **14**. Pentabromide **15** and the aromatic tribromide **16** are formed by sequential HBr elimination followed by bromination reactions. Significantly, the regioselectivity of the high temperature bromination reaction is still preserved even though the stereoselectivity was diminished to a lesser extent in contrast to bromination of decalin (**1**) and octahydropentane (**3**). Calculation and product analysis indicate that the major factor contributing to this specificity is the thermodynamic stability of the formed products. Furthermore, the steric interaction between the bromine atoms connected to C-1 and C-7, and C-3 and C-4 dictates that products with these atoms as far apart as possible will predominate.

In the second part of this work, the allylic positions in the six-membered ring in **5** were bridged with a methylene group, so that this system would not allow the bromination reaction at the bridgehead. As expected, high temperature as well as photochemical bromination of **6** resulted in the formation of products arising from allylic bromination of the five-membered ring.

The fact that the double bond was also brominated can be attributed to the pyramidalization of the double bond, which increases the reactivity of the system.

Experimental Section

General. All comercially available compounds were purchased from the Company MERCK. NMR spectra were recorded on a Bruker Instrument Avance Series-Spectrospin DPX-400 Ultrashield instrument $CDCl_3$ with TMS as internal reference. Infrared spectra were recorded on a Matson 1000 FT-IR spectrometer and Vertex 70 series FT-IR spectrometer. Band positions were reported in reciprocal centimeters (cm^{-1}). Column chromatographic separations were performed by using Fluka Silica Gel 60 plates with a particle size of 0.063–0.200 mm. Thin layer chromatography (TLC) was performed by using 0.25 mm silica gel plates purchased from Fluka. Elemental analysis were carried out at Atatürk University, Department of Chemistry on a LECO CHNS-932 elemental analyzer.

Reduction of 2,3-dihydro-1*H*-indene (7). Anhydrous ethylene diamine was dried by heating with sodium for a few days before distilling. Indane (**7**) (23.6 g, 0.2 mole) and ethylene diamine (500 mL) were added into a three-necked round-bottom flask (1 L) equipped with a mechanical stirrer, a condenser and a dropping funnel. The mixture was heated up to 100-110 °C. Lithium (11.2 g, 1.6 mole) was then introduced into the flask in small portions about 1 h. The characteristic dark-blue color developed quickly. The solution was stirred for an additional 4 h. The reaction flask was cooled in an ice-bath and then water (150 mL) was added carefully to destroy excess of lithium. The resulting solution was extracted with pentane three times (3 × 100 mL) and combined pentane layers were dried over $MgSO_4$. Evaporation of the solvent gave a mixture consisting of **8** and **9** as a light yellow liquid (14.6 g, 60.0%) in a ratio of 3:1. 2,3,4,5,6,7-Hexahydro-1*H*-indene (**8**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24 (t, J_{12} J_{32} 7.4 Hz, 4H, H-1 and H-3), 1.96-1.94 (m, 4H, H-4 and H-7), 1.72 (qui, J_{12} J_{32} 7.4 Hz, 2H, H-2), 1.55-1.51 (m, 4H, H-5 and H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.7 (C-3a, C-7a), 36.3 (C-1, C-3), 26.0 (C-4, C-7), 23.4 (C-2), 21.9 (C-5, C-6); IR ($\nu_{max,}$ cm^{-1}) 2934, 2958, 1447, 1189, 1079.

Hydrogenation of (8) and (9). A mixture of **8** and **9** (1.0 g, 8.3 mmole) in methanol (20 mL) was placed in a 50 mL, two-necked, round-bottomed flask and Pd/C (100 mg, 10.0%) catalyst was added. One of the necks was attached to hydrogen gas with a three-way stopcock, the other neck was capped with a rubber septum. The reactants were degassed and flushed with hydrogen gas, while magnetically stirring. After 24 h, the solution was decanted from the catalyst and water was added. The aqueous phase was extracted with pentane (3 × 25 mL). Organic extracts were dired over $MgSO_4$. Evaporation of the solvent provided octahydro-1*H*-indene **5** (0.79 g, 6.5 mmol, 78.0%) and unreacted **8** as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.87-1.83 (m, 4H, H-1, H-3), 1.75-1.69 (m, 2H, H-3a and H-7a), 1.59-1.55 (m, 4H, H-4, H-7), 138-1.28 (m, 6H, H-2, H-5, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 46.7, 31.9, 31.3, 26.6, 21.6.

High Temperature Bromination of the mixture of 5 and 8 with 4 equiv Br_2. The mixture of 2,3,4,5,6,7-hexahydro-1*H*-indene (**5**) and octahydro-1*H*-indene (**8**) (1.0 g, 8.09 mmol (68:32) was placed into a two-necked, round-bottom flask and the solution was heated until carbon

tetrachloride began to reflux, while magnetically strirring. A solution of bromine (5.15 g, 32.2 mmol) in carbontetrachloride (20 mL) was added dropwise to the refluxing solution over a period of 15 min. After heating for 5 min at reflux temperature, the mixture was allowed to cool to room temperature. The excess bromine was quenched with saturated $Na_2S_2O_5$ solution and organic layer was seperated and dried over $MgSO_4$. After the evaporation of carbon tetrachloride, the residue was submitted to column chromatography on silica gel (80 g). Elution with hexane afforded five products in the following order: **16** (103 mg, 3.6%), **12** (1.236 g, 35.0%), **14** (248 mg, 7.0%), **13** (528 mg, 15.0%), and **15** (0.246 mg, 5.9%).

***rel-(1S,3S,4S,7S)*-1,3,4,7-Tetrabromo-2,3,4,5,6,7-hexahydro-1*H*-indene** (**12**)**.** White solid from EtOH, mp 79-81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.15 (t, J_{12} $J_{12'}$ J_{32} $J_{32'}$ 5.6 Hz, 2H, H-1 and H-3), 5.08-5.07 (m, 2H, H-4, H-7), 3.04 (t, J_{21} J_{23} 5.6 Hz, 2H, H-2, H-2′), 2.52-2.25 (AA′BB′-system, 4H, H-5, H-5′, H-6 and H-6′); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5 (C-3a, C-7a), 51.2 (C-1, C-3), 46.2 (C-2), 42.7 (C-4, C-7), 28.0 (C-5, C-6); IR (ν_{max}, cm^{-1}) 2958, 2917, 2848, 2360, 2341, 1458, 1430, 1386, 1299, 1260, 1170, 1082, 961, 881, 764, 729, 607. Anal. Calcd for $C_9H_{10}Br_4$: C, 24.69, H, 2.30. Found: C, 24.63, H, 2.25.

***(1R,3S,4S,7R)*-1,3,4,7-Tetrabromo-2,3,4,5,6,7-hexahydro-1*H*-indene** (**13**)**.** White solid mp 148-150 °C from EtOH. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.25 (d, J_{12tr} J_{32tr} 7.0 Hz, 2H, H-1, H-3), 4.99-4.94 (m, 2H, H-4, H-7), 3.24 (dt, A part of AB-system, $J_{22'}$ 16.9 Hz, J_{12tr} J_{32tr} 7.0 Hz, 1H, H-2), 2.85 (d, B part of AB-system, $J_{22'}$ 16.9 Hz, 1H, H-2′), 2.43-2.30 (m, 4H, H-5, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5 (C-3a, C-7a), 52.1 (C-1, C-3), 43.3 (C-2), 42.7 (C-4, C-7), 31.9 (C-5, C-6); IR (ν_{max}, cm^{-1}) 3003, 2992, 2954, 2912, 1428, 1272, 1199, 1162, 1140, 1128, 958, 758, 617; Anal. Calcd for $C_9H_{10}Br_4$: C, 24.69, H, 2.30. Found: C, 24.63, H, 2.36.

***rel-(1R,3S,4S,7S)*-1,3,4,7-Tetrabromo-2,3,4,5,6,7-hexahydro-*1H*-indene** (**14**)**.** Light yellow liquid. ^{1}H NMR 400 MHz, $CDCl_3$) δ 5.09 (br s, 1H, H-4 or H-7), 4.90-4.89 (m, 1H, H-1 or H-3), 4.80 (br s, 1H, H-4 or H-7), 4.58 (br d, J_{12} 5.7 Hz, H-1 or H-3), 3.48-3.42 (ddd, A-part of AB-system $J_{22'}$ 18.3 Hz, J_{21} 5.7 Hz, J_{23} 2.2 Hz, 1H, H-2′), 2.62 (d, B-part of AB-system, $J_{2'2}$ 18.3 Hz, 1H, H-2), 2.50-2.35 (m, 2H, H-5, H-6), 2.22-2.13 (m, 2H, H-5′, H-6′); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1 (C-3a), 138.4 (C-7a), 60.3 (C-3), 49.9 (C-1), 44.6 (C-4), 44.1 (C-2), 42.3(C-7), 28.3 (C-5), 27.8 (C-6); IR (ν_{max}, cm^{-1}) 3002, 2945, 2818, 2809, 2321, 2329, 1602, 1601, 1546, 1514, 1428, 1265, 1214, 1149, 1083, 1019, 887, 836, 712, 615. Anal. Calcd for $C_9H_{10}Br_4$: C, 24.69, H, 2.30. Found: C, 24.63, H, 2.25.

***rel-(1R,2R,3S,4R,7R)*-1,2,3,4,7-Pentabromo-2,3,4,5,6,7-hexahydro-1*H*-indene** (**15**)**.** White solid mp 165-168 ºC from CH_2Cl_2/*n*-hexane. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.11 (br s, 1H, H-3), 4.98 (dd, $J_{45'}$ 4.5 Hz, J_{45} 1.4 Hz, 1H, H-4), 4.91 (s, 1H, H-1), 4.77 (t, J_{13} J_{23} 1.0 Hz, H-2), 4.74-4.73 (m, 1H, H-7), 2.63 (dddd, $J_{55'}$ 15.0 Hz, $J_{56'}$ 13.0 Hz, J_{56} 4.5 Hz, $J_{54'}$ 1.5 Hz, 1H, H-5), 2.42 (dddd, $J_{6'6}$ 14.9 Hz, $J_{6'5}$ 13.0 Hz, $J_{6'5'}$ 3.9 Hz, $J_{6'7}$ 2.4 Hz, 1H, H-6), 2.26-2.21 (m, 1H, H-5′); 2.18-2.12 (m, 1H, H-6′); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7 (C-3a), 139.5 (C-7a), 55.3 (C-2), 54.5 (C-3), 54.2 (C-1), 42.9 (C-4), 40.9 (C-7), 29.3 (C-5), 28.2 (C-6); IR (ν_{max}, cm^{-1}) 3003, 2970, 2953, 2841, 1428, 1365, 1229, 1216, 1199, 1140, 957, 712, 616. Anal. Calcd for $C_9H_9Br_5$: C, 20.92; H, 1.76. Found: C, 21.07, H, 1.78.

***rel-(1R,2R)*-1,2,4-Tribromo-2,3-dihydro-1*H*-indene** (**16**)**.** Light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J_{56} 7.8 Hz, 1H, H-5), 7.40 (d, J_{76} 7.5 Hz, 1H, H-7), 7.19 (t, J_{56} J_{76} 7.8 Hz, 1H, H-6), 5.65 (bs, 1H, H-1), 4.84 (bd, J 5.3 Hz, 1H, H-2), 3.77 (dd, A-part of AB-system, $J_{33'}$

18.0 Hz, J_{32} 5.3 Hz, 1H, H-3), 3.35 (d, B-part of AB-system, $J_{3'3}$ 18.0 Hz, 1H, H-3′); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5 (C-4), 141.1 (C-5), 132.6 (C-7), 129.5 (C-6), 124.4 (C-3a), 120.0 (C-7a), 57.2 (C-1), 52.3 (C-2), 42.8 (C-3); IR (ν_{max}, cm^{-1}) 3005, 2918, 2849, 2352, 2318, 1571, 1556, 1456, 1376, 1275, 1212, 1111, 947, 885, 764, 750, 620; Anal. Calcd for $C_9H_7Br_3$: C, 30.46, H, 1.99. Found: C, 30.38, H, 2.02.

Hydrogenation of cyclopentadiene dimer (22). Into a 50 mL, two-necked, round-bottomed flask were placed Pd/C (10.0%) (100 mg) catalyst and of **22** (1.0 g, 7.56 mmol) in MeOH (20 mL). One of the necks was attached to hydrogen gas with a three-way stopcock, the other neck was capped with a rubber septum. The reactants were degassed and flushed with hydrogen gas, while stirring magnetically. After 24 h the solution was decanted from the catalyst, water was added, and the aqueous phase was extracted with pentane (3 × 20 mL). Organic extracts were dired over $MgSO_4$. Evaporation of the solvent provided (3a*R*,4*R*,7*S*,7a*S*)-octahydro-1*H*-4,7-methanoindene (**6**) (0.85 g, 6.23 mmol, 82.0%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27-2.22 (m, 2H, H-4 and H-7), 2.01-2.00 (m, 2H, H-3a and H-7a), 1.56-1.48 (m, 2H, H-8 and H-8′), 1.45-1.32 (m, 6H), 1.31-1.15 (m, 3H), 0.83-0.79 (t, *J* 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 45.5, 43.2, 41.5, 28.7, 26.9, 23.0. IR (ν_{max}, cm^{-1}) 2941, 2874, 1483, 1454, 1263, 741.

High temperature bromination of 6. Octahydro-1*H*-4,7-methanoindene (**22**) (2.0 g, 14.68 mmol) and bromine (11.7 g, 73.4 mmol) were dissolved in 30 mL of carbon tetrachloride in a sealed tube. The mixture was stirred at 150 °C over a period of 4 h. After being cooled to room temperature the solvent was evaporated. The residue was chromatographed on silica gel (100 g). Elution with hexane afforded three isolable products in the following order; **23** (1.24 g, 16.0%), **25** (726 mg, 11.0%). **24** (170 mg, 0.27 mmol, 3.0%),

***rel-(1R,3aR,7aS)*-1,2,3,3a,7a-Pentabromo-3a,4,5,6,7,7a-hexahydro-1*H*-4,7-methano-indene (23):** Colorless crystals mp 96-98 °C from *n*-hexane. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.47 (s, 1H, H-1), 3.02-3.01 (m, 1H, H-4), 2.95 (bd, 1H, H-7), 2.61 (bd, A-part of AB-system, $J_{88'}$ 10.9 Hz, 1H, H-8), 1.84-1.76 (m, 1H, H-6), 1.66 (dt, B part of AB-system, $J_{88'}$ 10.9, $J_{8'4}$ $J_{8'7}$ 1.6 Hz, 1H, H-8′), 1.63-1.42 (m, 4H H-5 and H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.2 (C-2), 125.1 (C-3), 80.7 (C-3a), 77.2 (C-7a), 62.7 (C-1), 55.7 (C-7), 54.3 (C-4), 37.5 (C-8), 26.2 (C-6), 23.6 (C-5); IR (ν_{max}, cm^{-1}) 3566, 3420, 2986, 2956, 2878, 1591, 1450, 1308, 1189, 1166, 1092, 933, 848, 723. Anal. Calcd for $C_{10}H_9Br_5$: C, 22.72, H, 1.72. Found: C, 22.67, H, 1.95.

***rel-(1S,3aR)*-1,2,3,3a-Tetrabromo-3a,4,5,6,7,7a-hexahydro-1*H*-4,7-methanoindene (25).** Colorless crystals, mp 130-133 °C from *n*-hexane/$CHCl_3$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.75 (d, J_{17a} 0.6 Hz, 1H, H-1), 3.61 (br d, J_{7a7} 4.0 Hz, 1H, H-7a), 2.73-2.72 (m, 1H, H-4), 2.65-2.63 (m, 1H, H-7), 2.12-2.07 (bd, A-part of AB-system, $J_{88'}$ 10.4 Hz, 1H, H-8), 1.56 (dt, B-part of AB-system, $J_{88'}$ 10.4 Hz, $J_{8'4}$ $J_{8'7}$ 1.4 Hz, 1H, H-8′), 1.45-1.18 (m, 3H, H-5, H-6), 1.02-0.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.3 (C-3), 125.5 (C-2), 77.2 (C-3a), 65.8 (C-7a), 54.0 (C-1), 51.1 (C-4), 41.8 (C-7), 38.7 (C-8), 22.6 (C-6), 20.8 (C-5). IR (ν_{max}, cm^{-1}) 2969, 2878, 2251, 1586, 1474, 1306, 1261, 1234, 1189, 1172, 905, 852, 729, 688. Anal. Calcd for $C_{10}H_{10}Br_4$: C, 26.70, H, 2.24. Found: C, 26.52, H, 2.57.

***rel-(3aS,7aS)*-3,3a,7a-Tribromo-3a,4,5,6,7,7a-hexahydro-1*H*-4,7-methanoinden-1one (24).** Colorless crystals 154-156 °C from *n*-hexane/CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.40 (s, 1H, H-2), 2.89-2.88 (m, 2H, H-7 and H-4); 2.63 (bd, A-part of AB-system, $J_{88'}$ 10.7 Hz, 1H, H-8), 1.70 (bd, B-part of AB-system, $J_{88'}$ 10.7 Hz, H-8′), 1.61-1.49 (m, 2H); 1.37-1.29 (m, 1H); 1.22-

1.15 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9 (C-1), 161.5 (C-3), 132.8 (C-2), 81.3 (C-3a), 74.1 (C-7a), 51.8 (C-4), 51.5 (C-7), 40.8 (C-8), 25.3 (C-6), 24.5 (C-5); IR (ν_{max}, cm^{-1}) 3004, 2955, 2918, 2849, 2351, 2339, 1866, 1770, 1714, 1682, 1651, 1634, 1556, 1504, 1424, 1275, 1204, 1149, 1093, 1009, 897, 826, 714, 619. Anal. Calcd for $C_{10}H_9Br_3$: C, 31.21, H, 2.36. Found: C, 31.37, H, 2.63.

Photochemical Bromination of 22. Octahydro-1*H*-4,7-methanoindene (**22**) **(**2.0 g, 14.68 mmol) and bromine (11.7 g, 73.4 mmol) were dissolved in 30 mL of carbon tetrachloride in a flask. The resulting solution was photolyzed with a 150 W sun lamp at room temperature for 7 h while magnetically stirring. After the excess bromine quenced with saturated $Na_2S_2O_5$ solution, the mixture was extracted with dichloromethane (3 × 25 mL). The organic phase was dried over $MgSO_4$ an solvent was evaporated. The residue was chromatographed on silica gel (100 g) eluting with *n*-hexane. The tetrabromide **38** was collected as the sole isolable compound (1.51 mg, 2.07 mmol, 23.0%).

***rel*-(1*R*,3*R*,3a*S*,7a*S*)-1,3,3a,7a-Tetrabromo-octahydro-1*H*-4,7-methanoindene** (**38**)**.** Colorless crystals mp 165-166 °C from *n*-hexane. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10 (dd, $J_{32'}$ 12.8 Hz, J_{32} 7.6 Hz, H, H-3), 4.83 (d, $J_{12'}$ 6.0 Hz, 1H, H-1), 3.15-3.14 (m, 1H, H-4), 2.90-2.89 (m, 1H, H-7), 2.76 (dd, A-part of AB-system, $J_{22'}$ 15.2 Hz, J_{23} 7.6 Hz, 1H, H-2); 2.60 (ddd, B-part of AB-system, $J_{22'}$ 15.2 Hz, $J_{2'3}$ 13.2 Hz, $J_{2'1}$ 6.0 Hz, 1H, H-2′); 2.62 (bd, A-part of AB-system, $J_{88'}$ 10.4 Hz, 1H, H-8), 2.13-2.05 (m, 1H, H-5 or H-6), 1.69-1.64 (bd, B-part of AB-system, $J_{88'}$ 10.4 Hz, 1H, H-8′), 1.62-1.47 (m, 3H, H-6 and H-5); ^{13}C NMR (100 MHz, $CDCl_3$) δ 82.4 (C-3a), 81.1 (C-7a), 58.2 (C-3), 57.9 (C-1), 56.5 (C-4), 55.6 (C-7), 45.8 (C-2), 42.3 (C-8), 24.9 (C-5), 24.0 (C-6); IR (ν_{max}, cm^{-1}) 2986, 2956, 2878, 1591, 1450, 1308, 1189, 1166, 1092, 933, 848, 723. Anal. Calcd for $C_{10}H_{12}Br_4$: C, 26.58, H, 2.68. Found: C, 26.53, H, 3.04. Colorless crystals mp 165-166 ^{o}C.

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Supplementary Material Available

These data include the ^{1}H and ^{13}C NMR spectra of following compounds: **12**-**16**, **23**-**25**, **38**.

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