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High Temperature Bromination VI[1]: Bromination of Benzobarrelene

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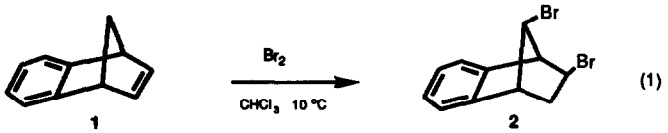
Abstract: The electrophilic addition of bromine to benzobarrelene in chloroform at 10° C followed by repeated chromatography combined with fractional crystallization allowed us to isolate ten products **12-21** Structural determination of these compounds revealed that the barrelene skeleton was rearranged completely. **18-21** are alcohol compounds which arise from hydrolysis of **12, 13, 14,** and**15**, respectively. High temperature bromination of benzobarrelene in decalin at 150 °C followed by repeated chromatography combined with fractional crystallization gave us 18 products. Nonrearranged products **24, 25,** and **26** have been isolated in 50% yield. All compounds have been characterized properly, especially by 200 MHz ^{1}H NMR and 50 MHz ^{13}C NMR spectra. Furthermore, it has been concluded that high temperature bromination of bicyclic systems gives more non-rearranged products. If the molecule is more strained, the tendency to rearrange decreases as in the case of benzonorbornadiene.

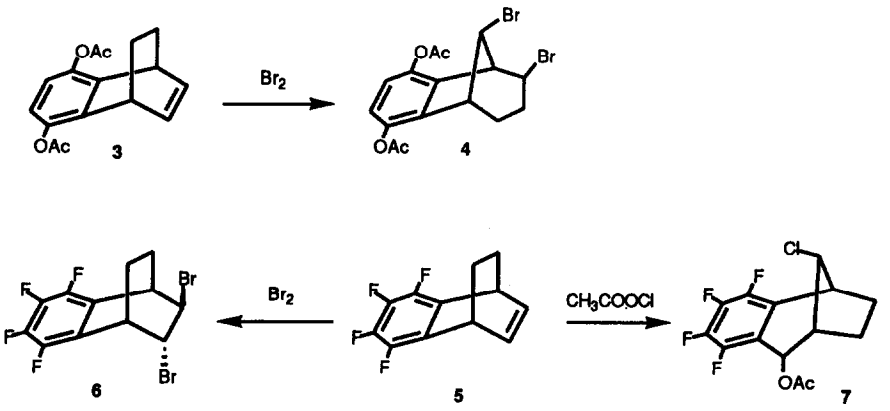
Introduction

The addition of bromine to the carbon-carbon double bond is formally one of the simplest reactions typical of unsaturated compounds. The nature of the intermediates of the addition depends on the structure of the substrate and on the reaction medium. The intermediates, strongly bridged bromonium ions, are involved in the bromination of nonconjugated olefins which give *anti*-adducts[4]. However, bromination of unsaturated bicyclic systems leads to rearrangements of the molecular skeleton. For example, the electrophilic addition of bromine to benzonorbornadiene leads to the formation of rearranged product 2 in high yield (Eq. 1)[1,5]. This compound is formed as a result of Wagner-Meerwein rearrangement.



(1)

In the course of studying the bromination reactions of the unsaturated bicyclic systems we noticed that the reaction temperature has a dramatic influence on product distribution. Bromination at room and lower temperatures give rearranged products via Wagner-Meerwein rearrangement with accompanying aryl and alkyl migration. However, the bromination of these hydrocarbons at higher temperatures (80-150° C) resulted in the formation of non-rearranged products[6]. High temperature bromination prevents skeletal rearrangement.

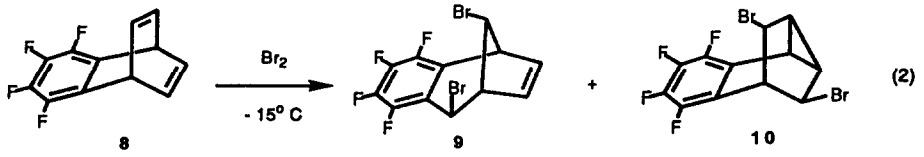


Scheme 1

The chemistry of benzobicyclo[2.2.2]octadienes can become plagued by skeletal rearrangements especially as the lifetimes of the intermediates cations are increased. The bromination of diacetoxy-dihydro-benzobarrelene **3** has been found to give only one product, dibromide **4** produced via a Wagner-Meerwein rearrangement with accompanying aryl migration[7]. On the other hand, in earlier work by Barkhash's group, who has examined selective ionic additions to tetrafluoro derivative **5**. Reaction with bromine was found to proceed without rearrangement to give **6**[8]. However, the reaction of **5** with acetyl hypochlorite contrasts markedly with bromine. In this instance, complete isomerization to **7** is observed[9]. These examples show the propensity for skeletal rearrangement expectedly increases as the migration ability of the aromatic moeity is enhanced such as in **3** and also electronic nature of the electrophiles determines the course of the reaction[10].

Barkhash et al.[11] have reported previously bromination of tetrafluorobenzobarrelene **8** and isolated only two compounds **9** and **10**. Surprisingly, there is no report in the literature on bromination of benzobarrelene.

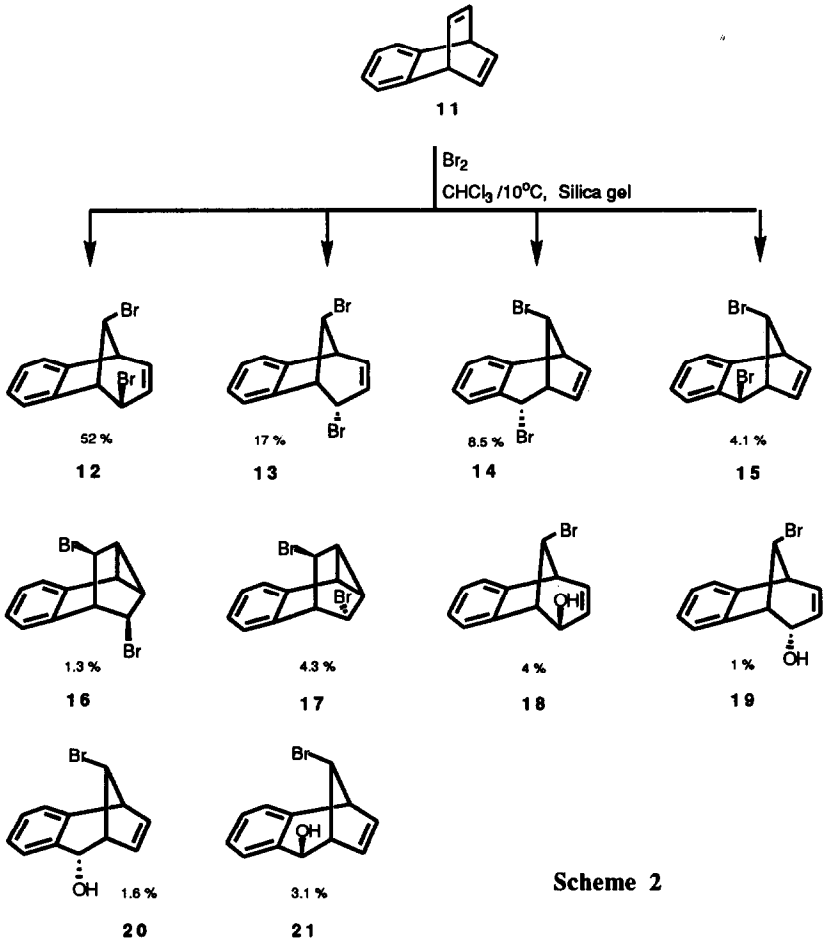
In connection with our continuing work in the temperature bromination reactions we have been interested in the bromination reaction of benzobarrelene at room and at high temperature in order to see the effect of the temperature on skeletal rearrangement[12].



(2)

Results and Discussions

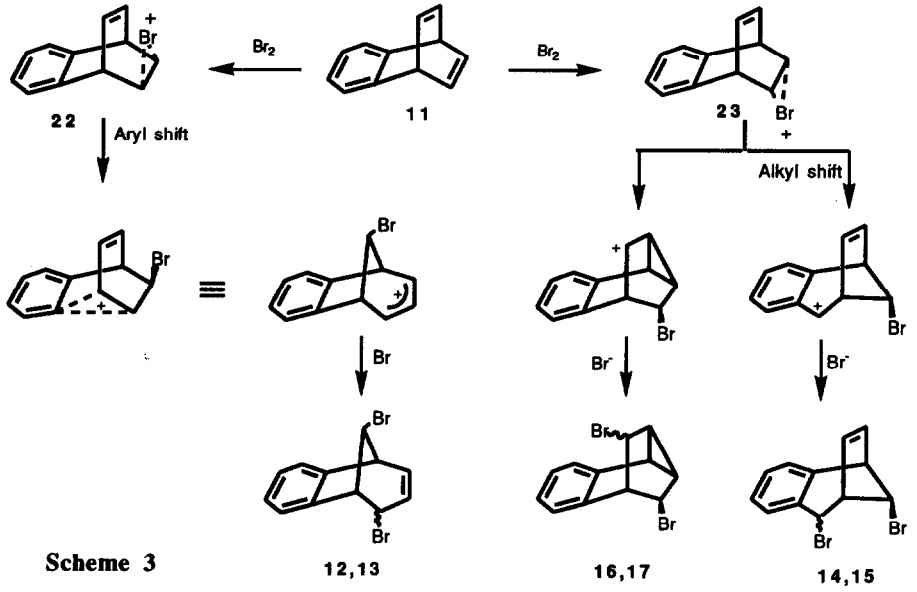
In the present work we investigated the reaction of **11** with bromine in chloroform at 10° C. We expected the addition of two molecules of bromine with formation of tetrabromides. However, **11** reacted quantitatively only with one molecule of bromine. ^{1}H NMR studies have revealed that the reaction mixture was very complex and consisted of six products. This mixture was submitted to silica gel column chromatography. Careful repeated chromatography followed by fractional crystallization allowed us to isolate ten products. According to elemental analysis and mass spectral studies six of these were isomeric dibromides. IR analysis indicated that a hydroxyl group was incorporated in compounds **18-21.** Therefore, we assume that this products have been formed by



Scheme 2

partial hydrolysis of compounds **12-15**. Structural determination of compounds **12-21** has revealed that the barrelene skeleton was rearranged completely.

For the formation of the rearranged products we propose following reaction mechanism. Generally a positive charge when placed on the double bond of **11** induces a Wagner-Meerwein rearrangement and



Scheme 3

transforms the [2.2.2] ring system into the [3.2.1] ring system which then reacts with bromide ion to give the products. It is evident from the bromine configuration at bridge carbon in major products **12** and **13** that initial attack by the bromine has occured from the *exo*-face of the π-system (Scheme 3). Most reasonably, the driving force of this mode of addition is supplied by the formation of aryl bridged intermediate. The formation of alkyl shift products **14** and **15** can be explained in terms of the formation of *endo*-intermediate **23** formed by *endo*-attack of bromine to **11** (Scheme 3). *endo*-Configuration of the bromine atom at the bridge carbon is also in agreement with *endo*-attack of bromine to double bond. The compounds **16** and **17** do not contain a double bond; since the addition of one molecule of bromine to **11** was accompanied by the disappearance of two double bonds, we must supposed that, in comparison with other products, another ring is formed. On the basis of NMR data we established that the compounds **16** and **17** contain cyclopropane units.

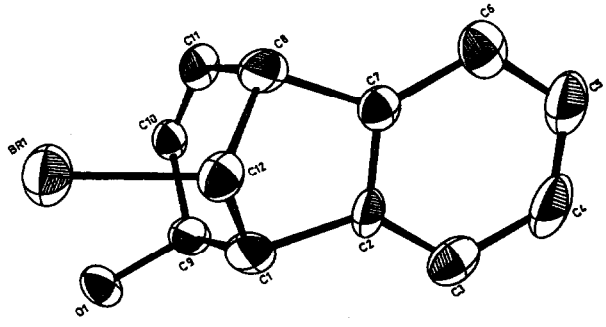
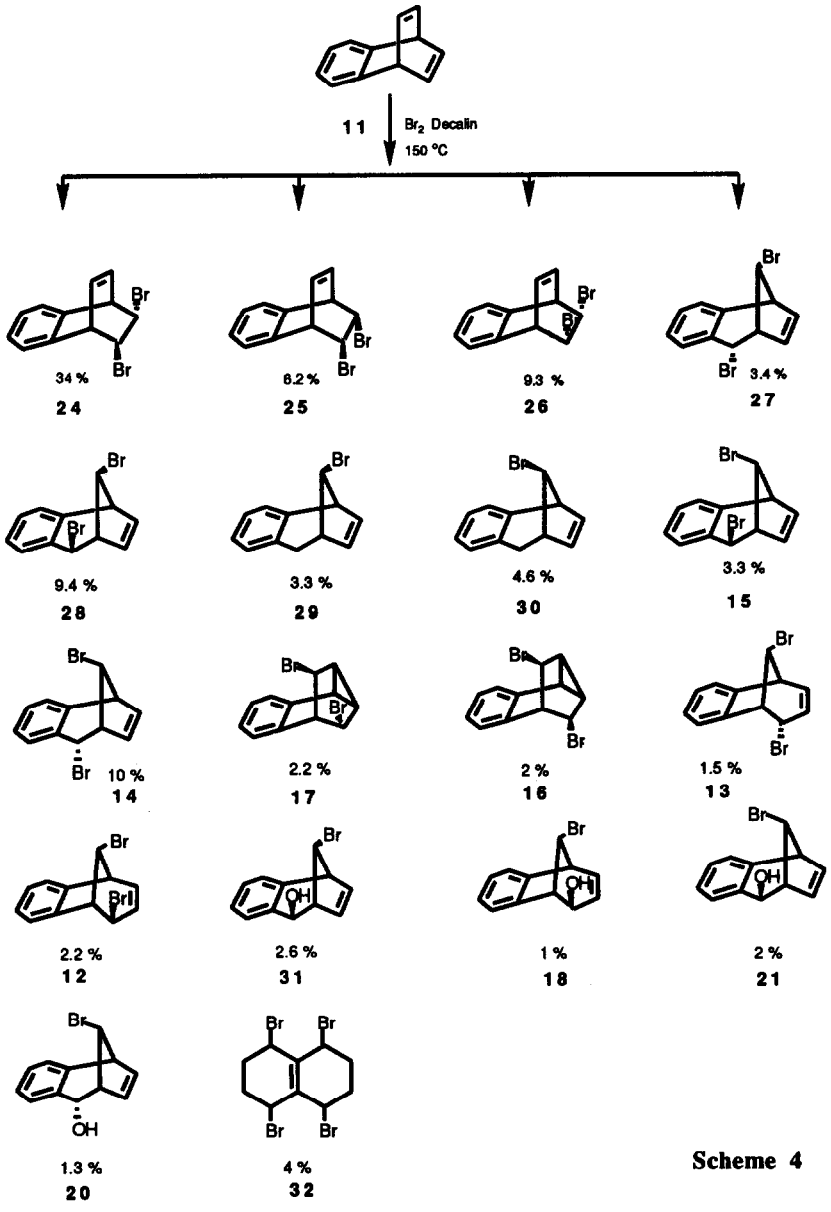


Figure 1. X-ray Crystal Structure of **18**

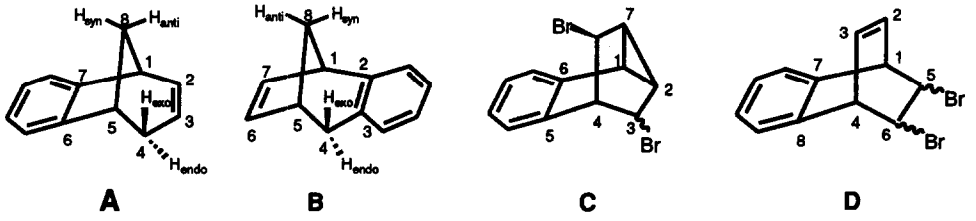
Finally, from the reaction mixture we isolated in 10 % isomeric alcohol's having the $C_{12}H_{10}BrO$ composition. Aryl and alkyl shift products **12-15** contain benzylic and allylic bromine atoms which can be hydrolyzed easily on column material to the corresponding bromoalcohols **18-21.** Because of the very close structural similarity we were not able to make clear-cut differentiation between the isomers. Therefore, we carried out X-ray crystal analysis of one of these alcohol's and assigned the correct configuration to **18** (Figure 1). Comparison of the NMR spectra of these alcohol's with the corresponding bromo compounds made it possible to analyze the spectra and assign the other alcohol's the correct structures.



Scheme 4

Next we studied high temperature bromination of benzobarrelene **11** at 150° C. For this reason bromine was directly distilled into a hot solution of **11** in decalin at 150° C. NMR analysis indicated that the reaction mixture was very complex and consisted of at least ten products. After repeated column chromatography combined with fractional crystallization we have been able to separate 18 compounds (Scheme 4). Four of them were bromo alcohol compounds **18, 20, 21,** and **31**. In high temperature reaction we expected especially the formation of non-rearranged addition products which were not formed by the reaction at 10° C. NMR analysis indicated that all possible non-rearranged addition compounds **24-26** were among the products and formed as the major products.

NMR Spectral Studies and Configurational Assignments: The structures of these compounds have been 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 snopsis of the proton coupling constants exhibited by these closely related [3.2.1]octadienes (Structure A and B) is given in Table 1.



**syn* and *anti* refer to benzene ring.

The coupling pattern which are important for stereochemical characterization of this triad are J_{58syn}, J_{58anti}, J_{54endo}, and J_{54exo}. As a consequence of the rigid geometry's and reliability of the Karplus rule[13] in [3.2.1.]octane systems[14], the dihedral relationship of the H_5 proton to H_{8anti} in **A** and H_5proton to H_{8syn} in **B** (20°), and to H_{8syn} in **A** and to H_{8anti} in **B** (80°) are sufficiently distinctive to be revealed by the magnitude of the spin-spin interaction. Thus the high value of J_{5Hsyn} in **A** and J_{5Hanti} in **B** (J = 4,0-5.0 Hz) is uniquely accommodated by the *anti*-orientation of bromine atom in **A** (*syn*-orientation of bromine in **B**) bonded to bridge atom. H_{8anti} in **A** and H_{8syn} in **B** give a singlet with line-broadening (J ≤ 1 Hz). Furthermore, the configuration of bromine atom at C_8 atom in **A** and **B** was also determined by measuring of long-range coupling constants between H_{syn}- H_2 in **A** and H_{syn} - $H_{6(7)}$ in **B**. In the case of ^{4}J in the bicyclic systems one speaks of the **M** or **W** arrangement. If the bonding arrangement of the coupled protons meets **M** criterion (as in the case of H_{syn}- H_2 in **A** and H_{syn} - $H_{6(7)}$ in **B**) we observe a coupling of a value J =0.9-1.3 Hz. In the case of *syn*-orientation of bromine in **A** and **B** there is no measurable coupling constant.

The configuration of bromine atom at C_4 atom was determined from the coupling constants J_{45}. Inspection of Dreidings models indicates that the dihedral angle between H_5 and H_{4exo} proton is approximately 40° whereas dihedral angle between H_5 and H_{4endo} proton is 60°. We observe large coupling constants of J = 4.0-5.0 Hz 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 **A** and alkyl shifts product type **B** can also be easily distinguished on the pattern of aromatic resonances (See Figure 3-6).

Table 1 ^{1}H and ^{13}C Spectral Data of the Compound **12**, **13**, **16**, **17**, **18**, **24**, **25**, and **26** Downfield from Internal Me_4Si in $CDCl_3$ Solutions

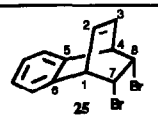
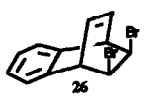
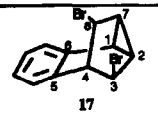
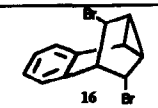
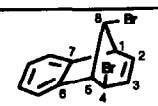
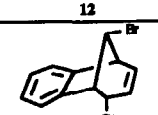
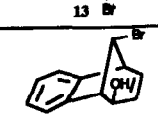
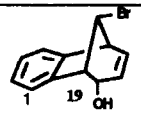
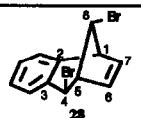
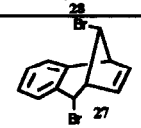
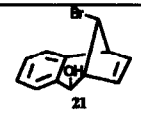
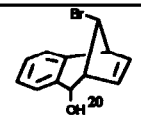
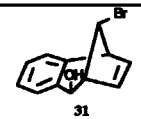
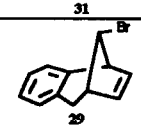
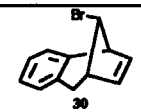
Compund	Chemical Schifts (C/H) (ppm) 1	2	3	4	5	6	7	8	H_{aryl}	Other ^{13}C value	Coupling constants (Hz)
 25	4.24 ddd 49.62	6.55 dd	6.55 dd	4.24 ddd 49.62	- 138.75	- 138.75	4.43 d 51.32	4.43 d 51.32	7.32-7.21 AA'BB' System	136.29, 126.72, 126.50	$J_{12}=J_{34}=4.4$ $J_{13}=J_{24}=3.1$ $J_{17}=J_{48}=1.5$
 26	4.39 dd 49.78	6.70 dd	6.70 dd	4.39 dd 49.78	- 141.30	- 141.30	4.24 s 51.68	4.24 s 51.68	7.32-7.21 AA'BB' System	134.14, 127.37, 124.40	$J_{12}=J_{34}=4.3$ $J_{13}=J_{24}=3.0$
 24	4.25 ddd	6.65-6.71 m		4.12 ddd	-	-	4.05 dd	4.31 dd	7.33-7.21 m	140.30,138.92,135.01 134.53,127.25,127.13, 126.60, 124.30, 55.63, 55.58,49.31,49.09	$J_{78}=J_{48}=2.9$ $J_{12}=J_{34}=7.3$ $J_{24}=J_{13}=2.6$ $J_{17}=2.7$
 17	2.56 t 27.09	2.17 dd	3.85 s	3.54 d 48.33	- 135.13	- 131.94	2.32 ddd	5.12 dd	7.34-7.06 m	128.61,128.85, 126.51 126.13, 52.73, 52.23, 25.22, 24.13	$J_{48}=4.7$ $J_{78}=2.9$ $J_{12}=J_{17}=7.2$ $J_{27}=5.2$
 16	2.72 t 22.71	2.20 dd 25.89	4.58 dd 46.33	3.58 t 48.64	- 134.07	- 130.85	2.20 dd 25.89	4.58 dd 46.33	7.43-7.13 m	128.45,127.74,126.82, 125.94	$J_{48}=J_{34}=4.8$ $J_{23}=J_{78}=1.6$ $J_{12}=J_{17}=7.0$
 12	3.61 dd	6.20 dddd	5.66 ddd	4.66 ddd	3.76 m	-	-	4.79 dt	7.38-7.13 m	149.35,141.06,133.06, 128.40,128.04,126.61, 124.96,122.17, 50.73, 48.02, 46.53, 45.35	$J_{23}=9.6$ $J_{35}=1.6$ $J_{28}=1.2$ $J_{12}=6.6$ $J_{45}\leq 1$ $J_{34}=3.3$ $J_{24}=1.5$ $J_{58}=J_{18}=4.1$
 13	3.48 dd	6.16 bd	5.52 dd	5.36 ddd	3.59 dd	-	-	4.72 dt	7.47-7.16 m	148.81, 139.20, 131.82, 128.55, 127.88, 127.31 126.45, 121.63, 55.07, 52.20, 48.24, 46.09	$J_{23}=9.6$ $J_{58}=J_{18}=4.1$ $J_{12}=6.0$ $J_{28}=1.2$ $J_{34}=2.1$ $J_{45}=3.3$
 18	3.59 m	6.16 ddd	5.63 ddd	4.02 m	3.59 m	-	-	4.80 dt	7.35-7.10 m	148.84, 141.37, 131.96, 127.90, 127.80, 127.31, 124.92, 122.07, 69.82, 51.60, 51.18, 47.09	$J_{23}=9.8$ $J_{12}=6.4$ $J_{28}=1.0$ $J_{58}=J_{18}=4.2$ $J_{35}=1.7$ $J_{34}=3.3$

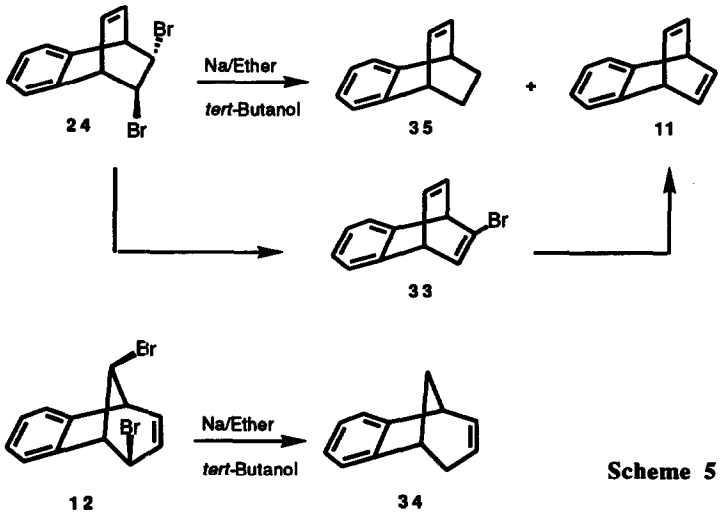
Table 1 (Continued) ^{1}H and ^{13}C Spectral Data of the Compund **19**, **20**, **21**, **26**, **27**, **29**, **30**, and **31** Downfield from Internal Me_4Si in $CDCl_3$ Solution

Compund	Chemical Schifts (C/H) (ppm) 1	2	3	4	5	6	7	8	H_{aryl}	Other ^{13}C value	Coupling constants (Hz)
	3.44 dd	6.12 ddd	5.42 dt	4.66 m	3.57 ddd	-	-	4.80 dt	7.36-7.19 m	150.91,138.52,132.17, 128.33,127.69,127.69, 126.81,122.07, 66.54, 56.14, 51.97, 46.67	J_{23}=9.4 J_{12}=6.3 J_{45}=5.1 J_{18}=J_{58}=4.0 J_{28}=1.3 J_{34}=J_{35}=2.1
	3.70 d	-	-	5.26 d	3.59 dd	5.82 ddd	6.56 ddd	5.14 t	7.36-6.95 m	134.13,133.66,128.69 128.46,126.99,126.31 59.15,58.50,55.10, 49.35	J_{67}=5.6 J_{17}=J_{56}=2.9 J_{68}=J_{78}=1.0 J_{45}=2.1
		144.12	141.97								
	3.45 dd	-	-	5.68 d	3.33 ddd	6.03 dd	6.53 dd	4.73 t	7.57-6.95 m	141.96,139.04,134.38, 132.73,131.97,128.61, 128.51,127.15,55.43, 50.82,50.63,48.74	J_{67}=6.2 J_{17}=3.2 J_{56}=3.0 J_{45}=5.1 J_{58}=J_{18}=4.6
	3.52 dd	-	-	4.49 m	3.15 m	5.97 dd	6.45 dd	4.87 t	7.57-7.01 m	142.77,138.24,137.05, 131.85,131.13,128.63, 127.93,126.88,50.80, 49.96	J_{67}=6.1 J_{45}=2.2 J_{17}=3.2 J_{56}=3.3 J_{58}=J_{18}=4.4
				67.93				52.62			
	3.42 dd	-	-	5.01 d	3.29 ddd	5.89 dd	6.61 dd	4.80 t	7.51-7.00 m	144.89,130.33,129.87, 128.51,127.87,126.87, 50.95,49.78	J_{67}=6.2 J_{45}=5.2 J_{17}=3.2 J_{56}=3.1 J_{58}=J_{18}=4.8
		137.18	138.66	67.48				58.21			
	3.70 d	-	-	4.66 d	3.27 dd	5.89 ddd	6.48 ddd	4.91 t	7.35-6.99 m	142.60,131.09,128.67, 128.27,128.21,128.15 126.13,59.25,57.93, 55.55	J_{67}=5.7 J_{45}=2.2 J_{17}=J_{56}=2.9 J_{68}=J_{78}=0.9
		135.64	142.19	70.29				59.25			
	3.66 d	-	-	3.16 2.71 dd d H_{ex} H_{en}	3.25 m	5.81 ddd	6.27 ddd	4.61 t	7.27-6.97 m	141.02,137.80,132.95, 130.73,128.77,127.87 126.43, 126.14, 62.21, 55.13, 49.40	$J_{4endo4exo}$=17.0 J_{67}=5.7 J_{4exo5}=5.2 J_{17}=J_{56}=2.7 J_{68}=J_{78}=0,9
				32.06							
	3.43 dd	-	-	3.23 2.63 dd d H_{ex} H_{en}	2.90 m	5.86 dd	6.33 dd	4.74 t	7.27-6.98 m	140.24,138.47,134.15, 131.13,130.35,127.72, 127.48,126.05,54.20, 50.40,42.87	$J_{4endo4exo}$=17.2 J_{67}=6.2 J_{4exo5}=4.9 J_{18}=J_{58}=4.7 J_{56}=J_{17}=3.1
				27.45							

The constitution of **16** and **17** has been determined by ^{1}H and ^{13}C NMR chemical shifts especially by analysis of cyclopropane J_{C13H} coupling constants (168 and 181 Hz). The configuration of bromine atoms was established by the observed symmetry element. A ten-line ^{13}C NMR is in agreement with symmetrical structure **16**. However, **17** gave twelve-line ^{13}C NMR spectrum as expected. ^{1}H NMR supports also this assignment. The correct configuration of bromine atoms in **16** follows from the coupling constants $J_{48}=J_{34}=4.8$ Hz where the coupling constant J_{34} in **17** is less than 1.0 Hz.

Non-rearranged dibromides **24-26** were distinguished easily. The ^{1}H NMR spectrum of this isomers reveal sufficient information for tentative assignments to be made. Dibromide **25** and **26** exhibit AA'BB' and AA'XX' systems arising from the aromatic bridgehead and C*H*Br protons which indicate clearly symmetrical structure and *syn*-addition of bromine. The *endo*-configuration of bromine atoms in **25** was determined by X-ray structural analysis. The other isomer **26** exhibiting a six-line ^{13}C NMR spectrum was assigned *exo-exo* configuration. *trans*-Addition product **24** showed a twelve-line ^{13}C NMR which is completely in agreement with the proposed structure.

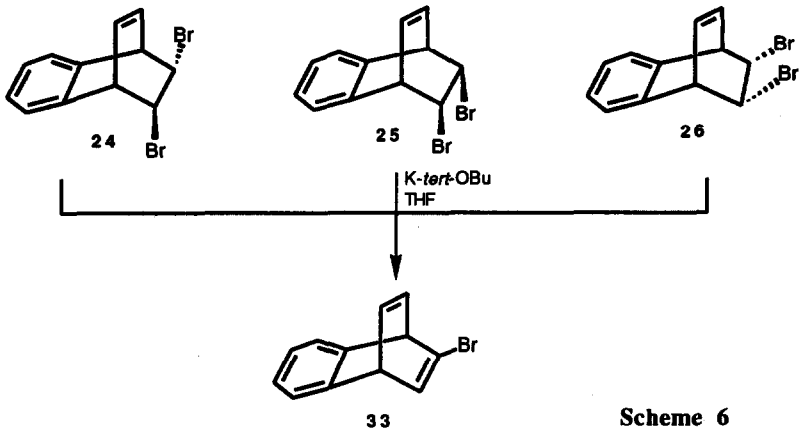
Reductive Dehalogenation: For further supporting of the proposed structures we carried out some reactions. For example, reductive elimination of bromine atoms in **24** with sodium in ether provided a mixture of **35** and **11.** Application of the same reaction to **12** gave the reduced hydrocarbon **34**[15] with the retained skeleton (Scheme 5).



Scheme 5

Usually, treatment of dibromides of these systems gives significant amount of returned starting material. Barkhash group[8,16] observed that the rearranged dibromide, 2-*exo*-7-*anti*-dibromotetrafluorobenzonorborn-5-ene, when treated with magnesium in tetrahydro gave back tetrafluorobenzonorbornene from which the dibromide had originated.

For further support of the structures **24-26**, either pure isomers or a mixture consisting of **24-26** was treated with potassium-*tert*-butoxide to provide only **33** in high yield (Scheme 6). This observation indicates that the original skeletal structure of benzobarrelene was retained by addition of bromine.



Scheme 6

X-Ray Structural Determination[17]: In order to distunguish between the symmetrical structures **25** and **26** we have carried out from one of these isomers single crystal x-ray analysis and determined the correct *endo*/*endo*-configuration of bromine atoms in **25** (Figure 2). The exact stereochemistry of alkyl-shift product **28** was established by single crystal analysis (Figude 2).

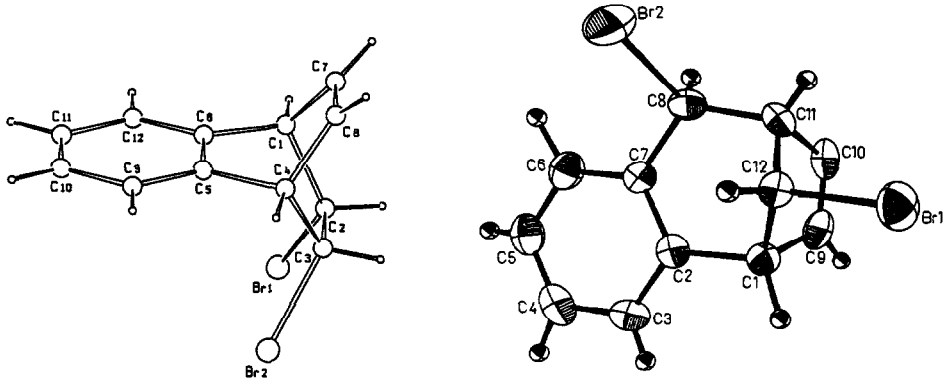
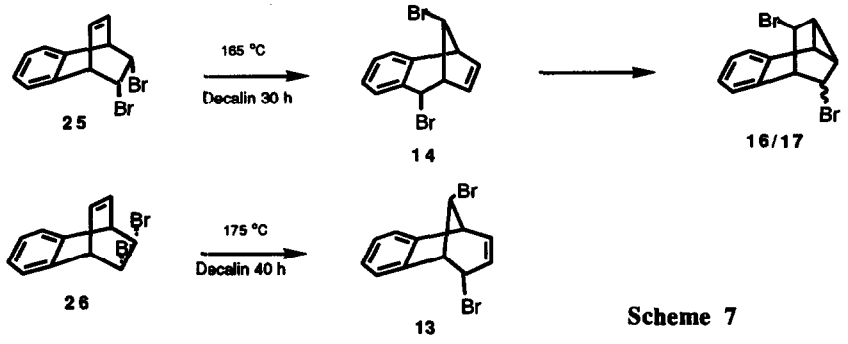


Figure 2. X-ray Crystal Structures of **25** and **28**

Studies concerning the mechanism of *syn*-addition show that the *syn*-adduct can arise either from direct *syn*-collapse of an ion pair or from rotation followed by *anti*-collapse.[18] Because of the rigid skeleton in **11**, a bond rotation is out of the question. In this case, we assume that the high temperature bromination is occurring by a free radical mechanism. Radical intermediates are much less likely to rearrange. This could explain also our stereochemical results. Conducting the bromination reaction in the presence of free radical inhibitors like 2,4,6-tri-*tert*-butylphenol suppressed the formation of the non-rearranged products. This very strongly supports the assumption that there is a competition between radical and ionic reactions.

In order to test whether the isolated non-rearranged product **24-26** and other products formed by high temperature bromination are primary or secondary products, we reacted them under the given reaction conditions and observed that all products are stable so we can conclude that all formed compounds beside the oxygenated products are primary formed. However, prolonged heating of **25** resulted in the formation of a mixture **16/17**. NMR controls indicated that **14** was formed at first which was then transfered into **16** and **17** (Scheme 7). On the other hand, *exo*/*exo*-isomer **26** rearranged upon prolonged heating (165 °C, 30 h) to alkyl shifts products **13**.



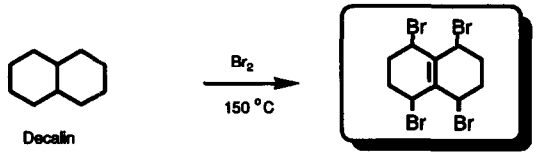
25 14 16/17

26 13

Scheme 7

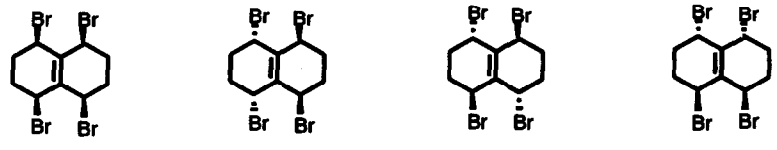
From the high temperature bromination reaction we encountered two HBr-addition products **29/30** and two bromine addition products **27/28** for their formation ionic addition mechanism can not be responsible. At first, we assumed that HBr-addition products have been formed by HBr-addition to **11**. However, treatment of **11** with HBr did not provide **29** and **30**. For the formation mechanism of these compounds, we propose that bromine radical firstly adds to double bond of benzobarrelene **11** and then rearranges to stable benzyl radical, which can abstract a hydrogen atom from solvent molecule to form **29** and **30**. We assume that radical mechanism is also responsible for the formation of **27/28**. *anti*-Configuration of bromine in **27, 28,** and, **29** can be explained only by radical mechanism where in most cases stereochemical control of configuration can not be achieved.

Lastly, we isolated a tetrabromo compound **32**[19] highly symmetrical compound whose exact configuration could not be determined on the basis of NMR spectral data. Possible configurations are given on Scheme **8**. On an independent reaction we treated decalin with bromine at high temperature and obtained **32** in high yield[20]. The formation of **32** indicates that decalin is proton source for **29** and **30**.



Decalin **32**

Scheme 8



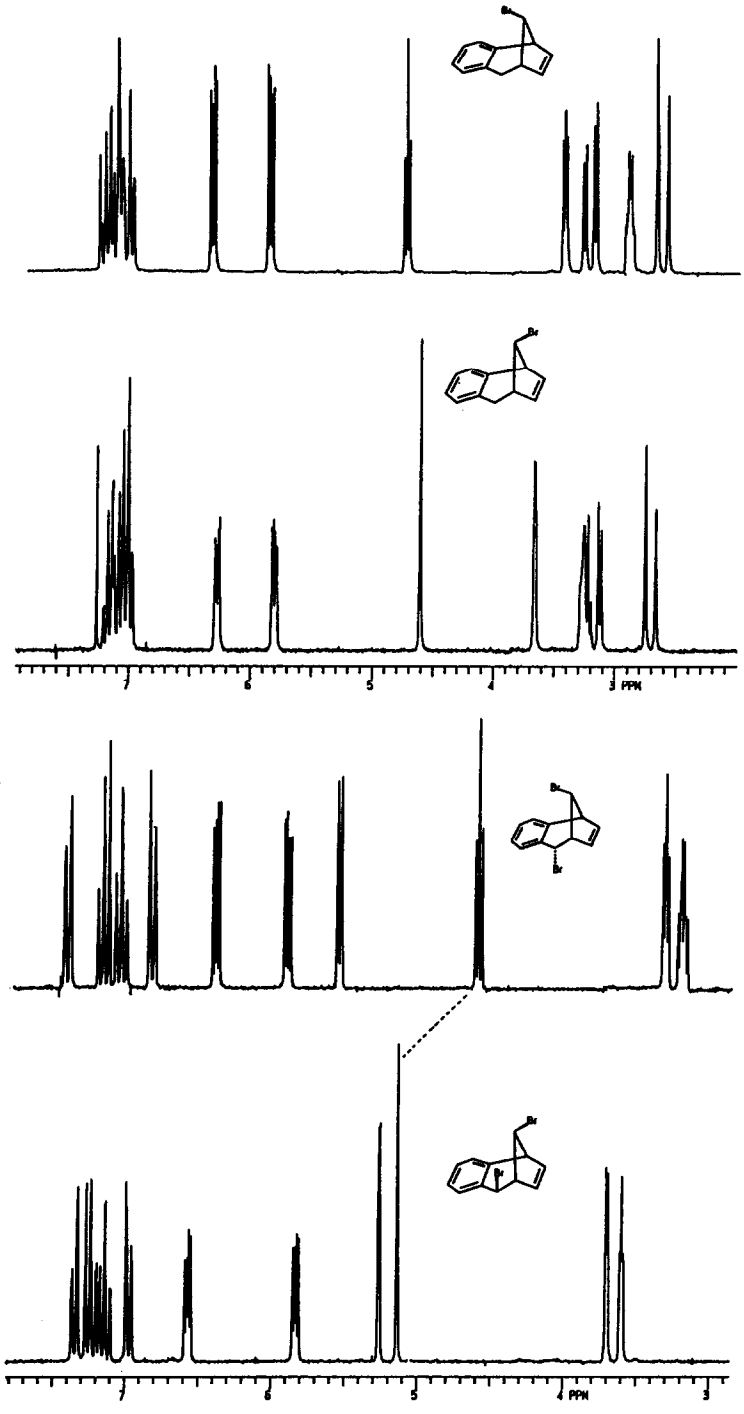


Figure 3. 200 MHz ^{1}H NMR Spectra of the Compounds **14, 27, 29** and **30.**

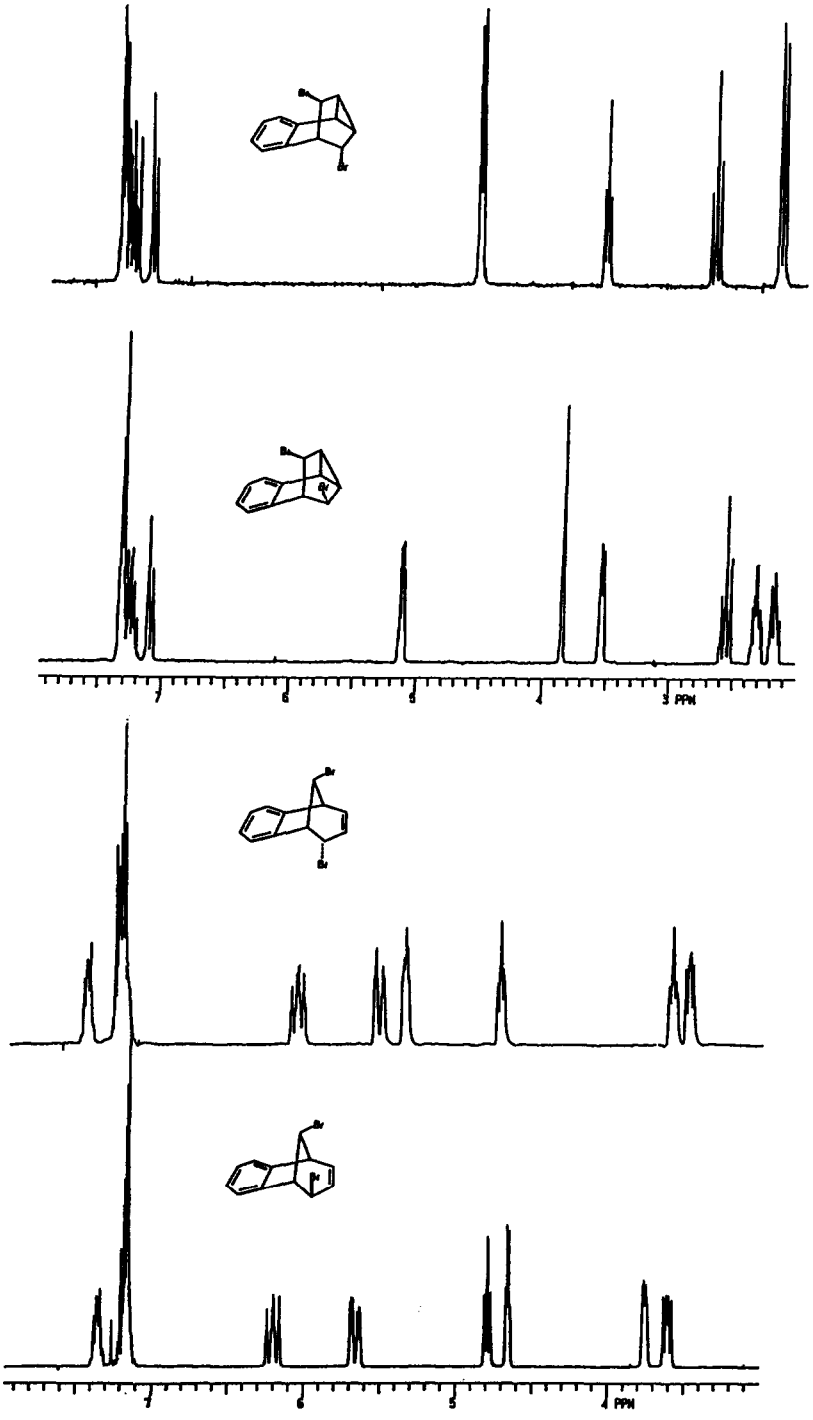


Figure 4. 200 MHz ^{1}H NMR Spectra of the Compounds **16, 17, 12** and **13.**

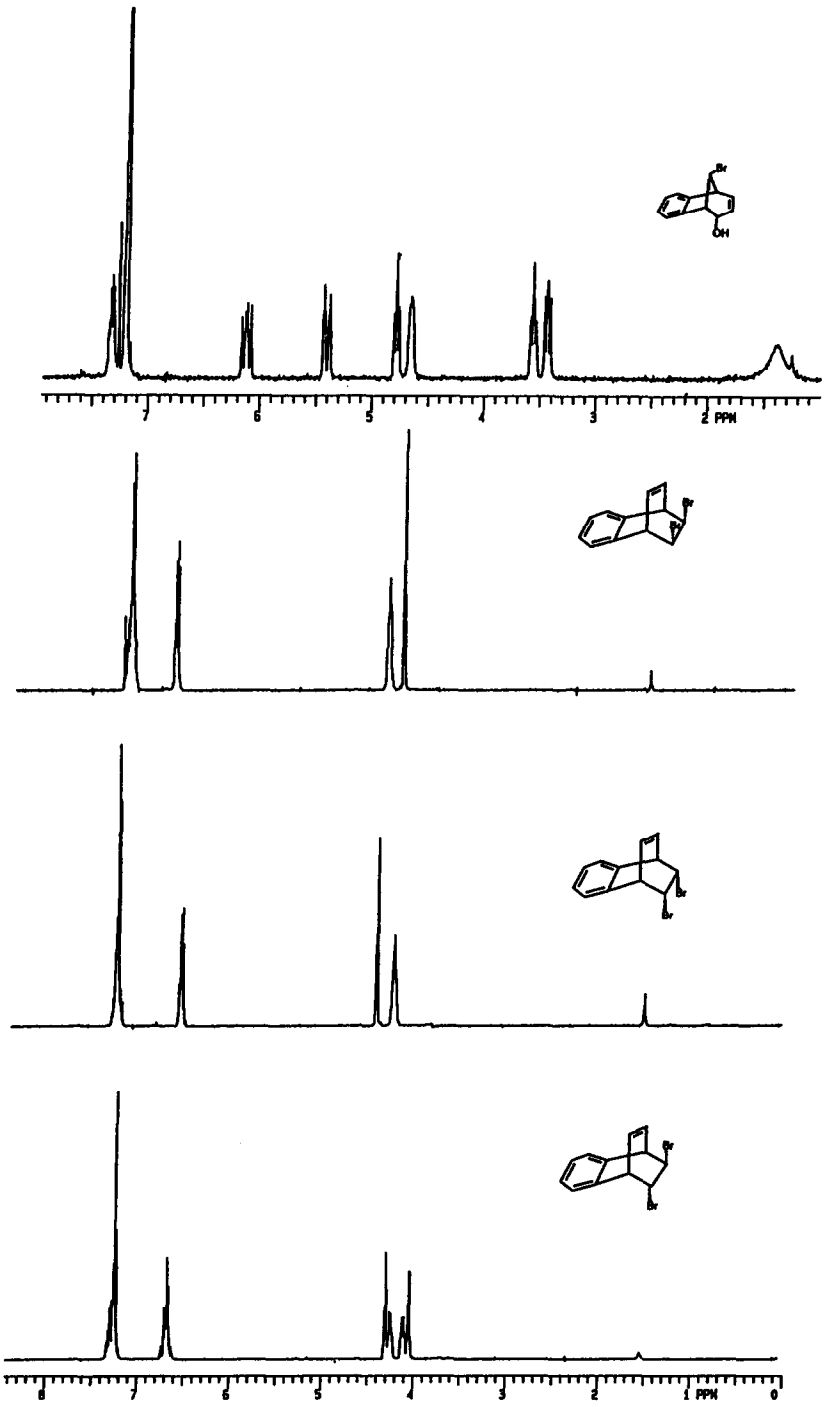


Figure 5. 200 MHz ^{1}H NMR Spectra of the Compounds **19**, **24**, **25** and **26**.

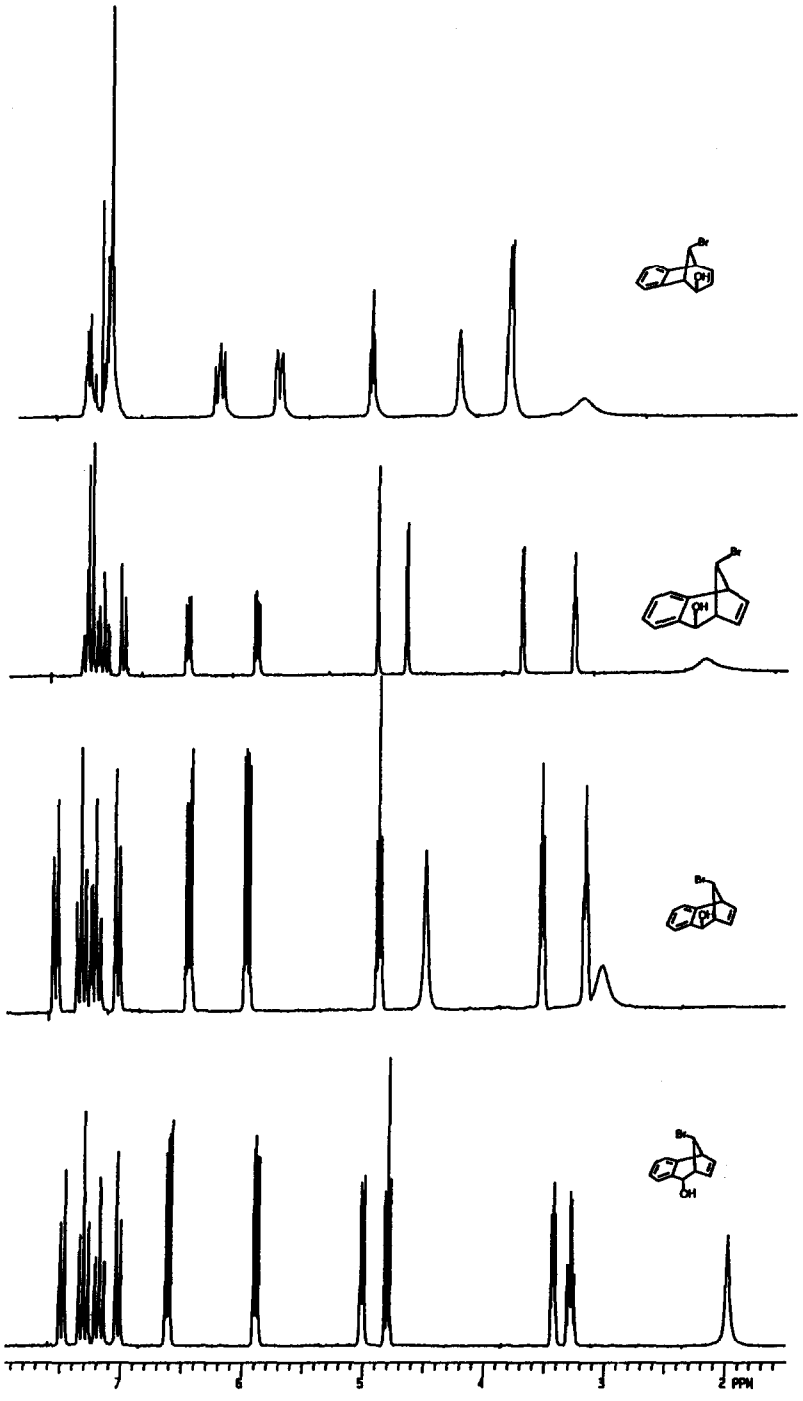


Figure 6. 200 MHz ^{1}H NMR Spectra of the Compounds **18, 20, 21** and **31.**

Finally, we would like to conclude that bromination of benzobarrelene at 10° C give 100% rearranged products arising from the formation of *endo*- and *exo*-intermediates **22** and **23** where aryl and alkyl shifts via Wagner-Meerwein rearrangement are involved. However, bromination at high temperature gives rearranged and non-rearranged products in a ratio of 1:1. At higher temperatures there is a competition between radical and ionic mechanism. If we compare these results with high temperature bromination of benzonorbornadiene we notice that molecular rearrangement is getting suppressed by going from benzobarrelene to benzonorbornadiene (Benzonorbornadiene provides 80% non-rearranged products by 150° C bromination). We assume that the strain in the molecule is responsible for the product distribution in high temperature bromination. In order to test this strain effect, further works are in progress. Furthermore, comparison of high temperature bromination results of benzobarrelene with those of substituted benzobarrelene derivatives, indicates substituents at double bond of benzobarrelene retards also rearrangement[6b].

Experimental Section

General. Melting points are uncorrected. Infrared spectra were obtained from films on NaCl plates for liquids or from solution in 0.1mm cells or KBr pellets for solids on a regular instrument. The ^{1}H and ^{13}C NMR spectra were recorded on 200 (50)- and 60-MHz spectrometers. Apparent splitting are given in all cases. Mass spectra (electron impact) were recorded at 70 eV as *m/z*. 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.

Caution: It has been reported[21] that of three laboratory workers who has used dibromides and bromohydrin derived from norbornadiene, two later developed similar pulmonary disorders which contributed to their subsequent deaths. The third exhibited minor skin sensitivity reactions. In the case of dibromide derived from benzonorbornadiene there is no report in the literature about the toxicological effect. However, we recommend that the compounds be handled only with extreme caution.

Bromination of Benzobarrelene 11 at 10 °C. To a magnetically stirred solution of benzobarrelene[22] **11** (2 g,12.99 mmol) in 15 mL dry chloroform cooled to 10° C was added dropwise a solution of bromine (2.08 g, 12.99 mmol) in 5 mL chloroform during 10 min. After completion of the addition, the solution was allowed to warm to 20 °C. The solvent was removed under reduced pressure. Oily residue was chromatographed on silica gel (130 g) eluting with hexane.

The first fraction (0.85 g) consisted of a mixture of compounds **13, 14** and **15**. This mixture was submitted to fractional crystallization from methylene chloride/hexane (1:3), to give dibromide **13.**

***endo,anti*-4,8-Dibromo-6,7-benzobicyclo[3.2.1]octa-2,6-diene 13** (693 mg, 17 %) mp 79-80 °C. IR (KBr, cm^{-1}): 3080, 3040, 2980, 1460, 1245, 1170, 1150, 960, 810, 740. Anal. Calcd for $C_{12}H_{10}Br_2$: C, 45.90; H, 3.21. Found: C, 46.04, H, 3.28.

After filtration of tribromide **13**, the organic solvent was evaporated and the oily residue was recrystallized from ethanol/hexane (2/1). The mixture was allowed to stand for several days in refrigerator to give dibromide **14.**

***endo,syn*-4,8-Dibromo-2,3-benzobicyclo[3.2.1]octa-2,6-diene 14** (60 mg pure crystals and 286 mg mixture, total yield 8.5 %): mp 65-66 °C. IR (KBr, cm^{-1}): 3060, 3020, 2950, 1480, 1450, 1310, 1260,

1240, 1170, 1150, 908, 883, 740. MS (m/e, %) 316/314/312 (M^+, 4), 235/233 (M^+-Br, 58), 154 (M^+-2Br, 100), 128 (M^+-2Br-acetylene, naphthalene, 20).

NMR spectral studies indicated the formation of **15** which could not be isolated in pure state because of the tendency of these molecule to undergo easily either configuration isomerization and hydrolysis on column material to form **14, 20,** and **21,** respectively.

The second fraction: ***exo,endo*-3,8-Dibromo-5,6-benzotricyclo[2.2.2.$0^{2,7}$]octa-5-ene 17** (175 mg 4.3 %): mp 94-95 °C, colorless crystals from ethanol/hexane (2/1). IR(KBr, cm^{-1}): 3060, 3030, 2970, 1600, 1480, 1460, 1310, 1209, 1010, 850, 755. MS (m/e, %) 316/314/312 (M^+, 35), 235/233 (M^+-Br, 94), 154 (M^+-2Br, 100), 128 (M^+-2Br-acetylene, naphthalene, 20). Anal. Calcd for $C_{12}H_{10}Br_2$: C, 45.90; H, 3.21. Found: C, 46.04, H, 3.28.

The third fraction: ***exo,anti*-4,8-Dibromo-6,7-benzobicyclo[3.2.1]octa-2,6-diene 12** (2.14 g 52 %): mp 96 °C colorless crystals from methylene chloride/hexane (1/3) IR(KBr, cm^{-1}): 3042, 3020, 2990, 1462, 1380, 1242, 857, 740. MS (m/e, %) 316/314/312 (M^+, 5), 235/233 (M^+-Br, 62), 154 (M^+-2Br, 100), 128 (M^+-2Br-acetylene, naphthalene, 15). Anal. Calcd for $C_{12}H_{10}Br_2$: C, 45.90; H, 3.21. Found: C, 45.67, H, 3.0.

The fourth fraction: ***endo,endo*-3,8-Dibromo-5,6-benzotricyclo[2.2.2.$0^{2,7}$]octa-5-ene 16** (53 mg 1.3 %): mp 155-156°C, colorless crystals from ethanol/hexane (2/1). IR (KBr, cm^{-1}): 3070, 3050, 2980, 2975, 1490, 1470, 1330, 1310, 1200, 1035, 900, 880, 705.

Then the column was eluted with hexane/ethyl acetate (97:3) As the fifth fraction we isolated ***exo,anti*-4-hydroxy-8-bromo-6,7-benzobicyclo[3.2.1]octa-2,6-diene 18** (163 mg 4 %): mp 88 °C colorless crystals from methanol IR (KBr, cm^{-1}): 3410, 3063, 3038, 3020, 2980, 1468, 1428, 1370, 1305, 1305, 1291, 1242, 1032, 773, 732. MS (m/e, %) 252/251(M^+, 3), 171(M^+-Br, 62), 154 (M^+-Br-H_2O, 33), 128 (M^+-Br-H_2O-acetylene, naphthalene, 27). Anal. Calcd for $C_{12}H_{11}BrO$: C, 57.40; H, 4.42. Found: C, 57.75, H, 4.56

The sixth fraction: ***exo,syn*-4-Hydroxy-8-bromo-2,3-benzobicyclo[3.2.1]octa-2,6-diene 21** (126 mg 3.1 %): mp 101-102 °C colorless crystals from methanol, IR (KBr, cm^{-1}): 3540, 3480, 3020, 2980, 2942, 2900, 2835, 1485, 1453, 1395, 1318, 1230, 1205, 990, 810. Anal. Calcd for $C_{12}H_{11}BrO$: C, 57.40; H, 4.42. Found: C, 57.05, H, 4.42

The seventh fraction: ***endo,anti*-4-Hydroxy-8-bromo-6,7-benzobicyclo[3.2.1]octa-2,6-diene 19** (41mg 1 %): mp 102-103 °C colorless crystals from methanol, IR (KBr, cm^{-1}): 3140, 3070, 3040, 2965, 1469, 1458, 1370, 1295, 1242, 1230, 1050, 870, 765.

The eighth fraction: ***exo,syn*-4-Hydroxy-8-bromo-2,3-benzobicyclo[3.2.1]octa-2,6-diene 20** (65 mg 1.6 %): mp 98-99 °C colorless crystals from methanol, IR (KBr, cm^{-1}): 3340, 3060, 3020, 2940, 2880, 1482, 1452, 1310, 1240, 1032, 843.

Bromination of Benzobarrelene 11 at 150 °C. Benzobarrelene **11** 2 g (12.99 mmol) was dissolved in 25 mL of decalin in a 50 mL two necked flask equipped with reflux condenser and an inlet glass tube touching the bottom of the reaction flask. The inlet glass-tube was connected to a 2 mL of round-bottom flask which contains 2.08 g (12.99 mmol) of bromine. Bromine vapors obtained by heating of the flask to 100 °C, was transferred directly to decalin solution having a temperature of 150 °C, in 5 min. while stirring

magnetically. The color of bromine was disappeared immediately. The solvent was removed under reduced pressure. Oily residue was chromatographed on silica gel (130 g) eluting with hexane.

The first fraction : **1,4,5,8-Tetrabromo-1,2,3,4,5,6,7,8-octahydronaphthalene 32** (156 mg, 4 %),: Colorless crystals, mp 185.5-186 °C from chloroform/n-hexane 1:2 (Lit. 188-189 °C[19]); ^{1}H NMR (200 MHz, $CDCl_3$) d 5.16 (d, J=2.7 Hz, 4H, H_1,H_4,H_5 and H_8), 2.10- 2.60 (AA'BB' system, 8H, H_2,H_3,H_6 and H_7); ^{13}C NMR (50 MHz, $CDCl_3$) δ 135.5, 49.5, 28; MS (70 eV) *m/z* 375/373/372/371 (M^+-Br,8), 292/291/289 (M^+-2Br, 8), 213/211 (M^+-3Br, 27), 131/129/128 (M^+- 4Br, naphthalene, 100); IR (KBr, cm^{-1}) 2955, 2905, 2835, 1423, 1335, 1200, 1170, 1000, 895, 743.

As the second fraction we isolated the starting material benzobarrelene **11** (120 mg) and the third fraction (306 mg) consisted of a mixture of monobromides **29** and **30**. This mixture has been separated on 65 g Al_2O_3 (basic, activity 1) column eluting with hexane. The first component was ***syn*-8-bromo-2,3-benzobicyclo[3.2.1]octa-2,6-diene 30** (178 mg 4.6 %): mp 88 °C from methylene cloride/hexane (1/3) IR (KBr, cm^{-1}): 3063, 3000, 2942, 2905, 1485, 1452, 1420, 1315, 1232, 1205, 1110, 1010, 885, 810, 760.
The second component was identified as ***anti*-8-bromo-2,3-benzobicyclo[3.2.1]-octa-2,6-diene 29** (128 mg 3.3 %): mp 69-70 °C from methylene cloride/hexane (1/3) IR (KBr, cm^{-1}): 3060, 3020, 2955, 2900, 1480, 1455, 1350, 1320, 1235, 980, 898, 810, 770, 725. Anal. Calcd for $C_{12}H_{11}Br$: C, 61.30 H, 4.72. Found: C, 61.25, H, 4.82.

Fourth fraction (from silica gel column) consisted of a mixture of dibromides **13, 14, 15, 24, 27** and **28**. This mixture was crystallized from 25 mL of ethanol/hexane (2/1). The solution was allowed to stand for a while in refrigerator. The formed crystals were identified as

***exo,endo*-7,8-dibromo-5,6-benzobicyclo[2.2.2]-octa-2,5-ene 24** (1.1 g pure crystals, 0.216 g mixture, total yield 34 %) : mp 97-98 °C. IR (KBr, cm^{-1}): 3070, 3040, 2980, 1460, 1340, 1307, 1251, 1162, 998, 805, 760. MS (m/e, %) 316/314/312 (M^+ 3), 235/233 (M^+-Br, 7), 154 (M^+-2Br, 21), 128 (M^+-2Br-acetylene, naphthalene, 100). Anal. Calcd for $C_{12}H_{10}Br_2$: C, 45.90; H, 3.21. Found: C, 45.97, H, 3.15.

After filtration of **24** the solvent was evaporated and the oily residue was crystallized from 15 mL of ethanol/hexane (2/1). The mixture was allowed to stand for several days in refrigerator and dibromide **28** crystallized as the sole material.

***exo,anti*-4,8-Dibromo-2,3-benzobicyclo[3.2.1]octa-2,6-diene 28** (290 mg pure crystals, and 82 mg mixture, total yield 9.4 %) : mp 144-144.5 °C. IR (KBr, cm^{-1}): 3065, 3025, 2978, 1480, 1320, 1265, 1230, 1145, 910, 790, 765, 710 Anal. Calcd for $C_{12}H_{10}Br_2$: C, 45.90; H, 3.21. Found: C, 45.69, H, 3.04.

After filtration of **28,** the residue was analyzed by NMR spectral measurements. For separation of **13, 14,** and **15** see room temperature bromination. By standing of this mixture at room teemperature we observed that dibromide **27** was converted completely to dibromide **28.**

Dibromide **13**	58 mg	1.5 %
Dibromide **14**	386 mg	10 %
Dibromide **15**	128 mg	3.3 %
Dibromide **27**	132 mg	3.4 %

Fifth fraction (from silica gel column):***exo,endo*-3,8-Dibromo-5,6-benzotricyclo[2.2.2.0^{2,7}]octa-5-ene 17** (85 mg 2.2 %): mp 94-95 °C, colorless crystals from ethanol/hexane (2/1).

The sixth fraction: ***exo,exo*-7,8-Dibromo-5,6-benzobicyclo[2.2.2]octa-2,5-ene 26** (360 mg 9.3 %) : mp 126-127°C. IR(KBr, cm^{-1}): 3060, 3020, 2980, 1470, 1460, 1342, 1300, 1202, 982, 800, 760. Anal. Calcd for $C_{12}H_{10}Br_2$: C, 45.90; H, 3.21. Found: C, 45.54, H, 3.24.

Seventh fraction: ***exo,anti*-4,8-Dibromo-6,7-benzobicyclo[3.2.1]octa-2,6-diene 12** (77 mg 2 %): mp 96 °C colorless crystals from methylene chloride/hexane (1/3).

The eighth fraction: ***endo,endo*-7,8-Dibromo-5,6-benzobicyclo[2.2.2]octa-2,5-ene 25** (246 mg 6.2 %) : mp 146-146.5 °C. IR (KBr, cm^{-1}): 3060, 3040, 2960, 1470, 1460, 1458, 1340, 1250, 1245, 1195, 1185, 860, 780, 710. MS (m/e, %) 316/314/312 (M^+, 6), 235/233 (M^+-Br, 4), 154 (M^+-2Br, 31), 128 (M^+-2Br-acetylene, naphthalene, 100).

The ninth fraction: ***endo,endo*-3,8-Dibromo-5,6-benzotricylo[2.2.2.$0^{2,7}$]octa-5-ene 16** (77 mg 2 %): mp 155-156°C, colorless crystals from ethanol/hexane (2/1).

Then the column was eluted with hexane/ethyl acetate (97:3)

The tenth fraction: ***exo,anti*-4-Hydroxy-8-bromo-6,7-benzobicylo[3.2.1]octa-2,6-diene 18** (35 mg 1≤ %): mp 88 °C colorless crystals from methanol.

The eleventh fraction: ***exo,syn*-4-Hydroxy-8-bromo-2,3-benzobicylo[3.2.1]octa-2,6-diene 21** (77 mg 2 %); mp 101-102 °C colorless crystals from methanol.

The twelfth fraction: ***exo,anti*-4-Hydroxy-8-bromo-2,3-benzobicylo[3.2.1]octa-2,6-diene 31** (101 mg 2.6 %): mp 122-123 °C colorless crystals from methanol. IR (KBr, cm^{-1}): 3280, 3070, 2980, 2960, 2880, 1487, 1460, 1318, 1280, 1235, 1020, 910, 800, 760. MS (m/e, %) 252/251(M^+, 1), 171(M^+-Br, 100), 153 (M^+-Br-H_2O, 40), 128 (M^+-Br-H_2O-acetylene, naphthalene, 19).

The thirteenth fraction: ***endo,syn*-4-Hydroxy-8-bromo-2,3-benzobicylo[3.2.1]-octa-2,6-diene 20** (50 mg 1.3 %): mp 98-99 °C colorless crystals from methanol.

Thermal Rearrangement of *endo,endo*-Dibromide 25 100 mg of *endo,endo*-dibromide **25** was heated at 165 °C in a sealed tube (without solvent) for 30 h. ^1H NMR analysis of the residue has revealed the exclusively formation of dibromides **16, 17** in a ratio of 5/2 and in 95 % yield. By heating for shorter periods we observed the primary formation of alkyl shifts products **14** and **15** as the intermediates. By an independent reaction we have converted pure sample of **14** completely to **16** and **17** by heating in a sealed tube at 165 °C in 30 h.

Thermal Rearrangement of *exo,exo*-Dibromide 26. 100 mg (0.32 mmol) *exo*,exo-dibromide **26** was heated at 175 °C in sealed tube (without solvent) for 40 h. The oily residue was chromatographed on silica gel (10 g) eluting with hexane. Dibromide **13** was formed as the sole product in 65 % yield.

Reduction of Dibromide 12. 100 mg (0.32 mmol) dibromide **12** and 190 mg of *tert-s*BuOH were dissolved in 10 mL of ether. 74 mg (3.2 mmol) of metallic sodium of small pieces were added during 15 min. After stirring at reflux temperature of the solvent for 12 h, the reaction mixture was cooled and methanol was added carefully to destroy unreacted sodium. The resulting mixture was poured into 100 mL water and extracted with ether. The combined organic layers were washed with water, dried ($MgSO_4$). The solvent was removed at reduced pressure yielding 42 mg (85 %) of olefin **34**[15].

Reduction of Dibromide 24. 100 mg (0.32 mmol) of dibromide **24** was reduced as described above. According to the NMR spectrum, the reaction mixture consisted a mixture of benzobarrelene **11** (61 %) and dihydrobenzobarrelene **35**[23] (21 %).

Elimination of Dibromides 24, 25, and 26. A solution of a mixture consisting of dibromides **24, 25,** and **26** (100 mg, 0.32 mmol) in 10 mL of dry tetrahydrofuran was added dropwise to a stirring solution of potassium-*tert*-butoxide (0.5 mmol) in 5 mL of tetrahydrofuran during 5 min. The mixture was stirred overnight and quenched with water. The mixture was extracted with ether, dried ($MgSO_4$), and concentrated at reduced pressure to afford monobrombenzobarrelene **33**[24], 68 mg (91 %).

Table 2. X-ray data of compund **28**

Bond lengths Å angles (o) and torsion angles (o) with e.s.d.'s in parentheses.

Br1 - C12	1.960 (5)	C4 - C5	1.371 (8)	C1 - C12	1.533 (7)	C8 - C11	1.538 (7)
Br2 - C8	2.000 (5)	C5 - C6	1.391 (8)	C2 - C3	1.390 (7)	C9 - C10	1.296 (9)
C1 - C2	1.522 (7)	C6 - C7	1.388 (7)	C2 - C7	1.399 (7)	C10 - C11	1.535 (7)
C1 - C9	1.531 (8)	C7 - C8	1.505 (7)	C3 - C4	1.379 (8)	C11 - C12	1.515 (7)

C1 - C12 - Br1	110.9 (3)	C7 - C2 - C1	119.0(4)	C12 - C11 - C10	107.8 (4)	C7 - C8 - Br2	109.1 (4)
C11 - C12 - C1	100.8 (4)	C7 - C2 - C3	119.2 (5)	C11 - C10 - C9	109.3 (5)	C7 - C7 - C2	120.1 (4)
C11 - C12 - Br1	112.6 (3)	C4 - C3 - C2	120.8 (5)	C9 - C1 - C2	106.4 (4)	C8 - C7 - C6	120.1 (5)
C12 - C11 - C8	107.1 (4)	C11 - C8 - Br2	108.2 (3)	C10 - C9 - C1	110.9(5)	C6 - C7 - C2	119.8 (5)
C12 - C1 - C2	106.9 (4)	C6 - C5 - C4	120.8 (5)	C3 - C2 - C1	121.7 (5)	C5 - C4 - C3	119.7 (6)
C12 - C1 - C9	100.4 (4)	C7 - C6 - C5	119.6 (5)				

C3 - C2 - C7 - C8	178.7 (5)	C6 - C7 - C2 - C1	-175.4 (5)
C7 - C8 - C11 - C10	-78.1 (4)	C2 - C1 - C9 - C10	-85.5 (6)
Br1 - C12 - C1 - C2	-168.1 (3)	Br1 - C12 - C1 - C9	81.0 (4)
Br1 - C12 - C11 - C8	171.5 (3)	Br1 - C12 - C11 - C10	- 93.2 (4)

Bond lengths Å, angles (o) and angles (o) of hydrogen atoms with e.s.d.'s in parentheses.

H1 · C1 · C12	112.8(2.7)	H8 · C8 · Br2	104.1(3.0)	C1 · H1	1.053(51)	C8 · H8	.909(51)
H3 · C3 · C2	120.3(2.8)	H8 · C8 · C7	109.7(3.2)	C3 · H3	.825(39)	C9 · H9	.921(60)
H3 · C3 · C4	118.6(2.7)	H8 · C8 · C11	110.8(3.1)	C4 · H4	.988(67)	C11 · H11	.849(46)
H4 · C4 · C3	111.8(3.5)	H9 · C9 · C1	121.4(3.6)	C5 · H5	.854(52)	C12 · H12	.903(46)
H4 · C4 · C5	128.3(3.5)	H9 · C9 · C10	127.5(3.6)	C6 · H6	1.043(57)		

H5 · C5 · C4	119.5(3.7)	H11 · C11 · C8	114.4(3.3)	H1 · C1 · C9	115.5(2.6)		
H5 · C5 · C6	119.5(3.7)	H11 · C11 · C10	107.4(3.3)	H12 · C12 · C11	118.7(3.0)		
H6 · C6 · C5	120.4(3.5)	H11 · C11 · C12	117.3(3.3)	H1 · C1 · C2	113.7(3.0)		
H6 · C6 · C7	119.4(3.5)	H12 · C12 · Br1	104.3(3.1)	H1 · C1 · C9	115.5(2.6)		

Table 3. X-ray data of compund **18**

Bond lengths Å, angles (o) and torsion angles (o) with e.s.d.'s in parentheses.

Molecule (a)		Molecule (b)		Molecule (c)	
C12 · Br1	1.983(12)	C12 · Br1	1.969(12)	C12 · Br1	1.978(11)
C12 · C1	1.493(19)	C12 · C1	1.524(17)	C12 · C1	1.536(16)
C12 · C8	1.517(16)	C12 · C8	1.551(16)	C12 · C8	1.545(19)
C11 · C8	1.521(16)	C11 · C8	1.541(17)	C11 · C8	1.505(17)
C10 · C11	1.318(17)	C10 · C11	1.330(18)	C10 · C11	1.366(17)
C10 · C9	1.509(16)	C10 · C9	1.511(16)	C10 · C9	1.487(17)

C9 · C1	1.544(17)	C9 · C1	1.545(17)	C9 · C1	1.535(16)
C9 · O1	1.428(14)	C9 · O1	1.404(15)	C9 · O1	1.449(15)
C8 · C7	1.533(17)	C8 · C7	1.534(17)	C8 · C7	1.530(16)
C7 · C6	1.421(17)	C7 · C6	1.337(18)	C7 · C6	1.360(19)
C7 · C2	1.384(16)	C7 · C2	1.382(17)	C7 · C2	1.405(17)
C6 · C6	1.354(20)	C6 · C5	1.416(18)	C6 · C5	1.414(18)
C5 · C4	1.385(21)	C5 · C4	1.392(20)	C5 · C4	1.426(21)
C4 · C3	1.405(19)	C4 · C3	1.341(20)	C4 · C3	1.324(21)
C3 · C2	1.386(18)	C3 · C2	1.399(16)	C3 · C2	1.404(16)
C2 · C1	1.530(16)	C2 · C1	1.507(18)	C2 · C1	1.535(17)

Molecule (a)

C1 · C12 · Br1	116.7(8)	C8 · C7 · C6	130.9(1.1)	C7 · C8 · C12	96.3(9)
C8 · C12 · Br1	112.1(8)	C8 · C7 · C2	108.6(9)	C1 · C8 · C12	107.7(9)
C8 · C12 · C2O	104.6(1.0)	C7 · C6 · C5	118.3(1.2)	C1 · C8 · C7	107.0(1.0)
C10 · C11 · C8	122.1(1.0)	C6 · C5 · C4	122.1(1.2)	C2 · C7 · C6	120.4(1.1)
C9 · C10 · C11	122.9(1.1)	C5 · C4 · C3	119.9(1.3)	C1 · C2 · C7	109.4(1.0)
C10 · C9 · C1	111.0(1.0)	C2 · C3 · C4	118.7(1.3)	C9 · C1 · C12	113.2(1.0)
O1 · C9 · C1	112.2(1.0)	C7 · C2 · C3	120.5(1.1)	C2 · C1 · C12	96.9(9)
O1 · C9 · C10	108.8(9)	C1 · C2 · C3	130.0(1.2)	C9 · C1 · C2	107.9(1.0)

C3 · C2 · C7 · C8	107.4(1.3)	C6 · C7 · C2 · C1	178.5(1.3)
C7 · C8 · C11 · C10	71.5(1.8)	C2 · C1 · C9 · C10	73.0(1.5)
O1 · C9 · C1 · C12	88.8(1.5)	O1 · C9 · C10 · C11	127.1(1.5)
Br1 · C12 · C1 · C2	170.7(1.0)	Br1 · C12 · C1 · C9	-57.7(1.5)
Br1 · C12 · C8 · C7	74.5(19)	Br1 · C12 · C8 · C11	64.3(1.3)

Molecule (b)

C8 · C12 · Br1	113.3(7)	C2 · C7 · C8	108.7(1.0)	C11 · C8 · C7	108.0(9)
C1 · C12 · Br1	117.4(9)	C2 · C7 · C6	121.1(1.1)	C12 · C8 · C7	98.6(9)
C1 · C12 · C8	102.1(9)	C7 · C6 · C5	120.1(1.3)	C12 · C8 · C11	107.1(1.1)
C9 · C10 · C11	122.9(1.1)	C5 · C4 · C3	119.9(1.3)	C1 · C2 · C7	110.1(1.0)
C10 · C11 · C8	121.4(1.1)	C4 · C5 · C6	118.0(1.3)	C6 · C7 · C8	130.0(1.1)
C9 · C10 · C11	123.6(1.1)	C3 · C4 · C5	121.7(1.2)	C1 · C2 · C7	110.1(1.0)
C1 · C9 · C10	110.8(1.0)	C2 · C3 · C4	119.5(1.3)	C12 · C1 · C2	98.3(1.0)
O1 · C9 · C10	108.8(1.0)	C7 · C2 · C3	119.5(1.2)	C12 · C1 · C9	112.7(9)
O1 · C9 · C1	114.1(9)	C1 · C2 · C3	130.3(1.2)	C9 · C1 · C2	109.4(9)

C3 · C2 · C7 · C8	-175.6 (1.3)	C6 · C7 · C2 · C1	177.6 (1.4)
C7 · C8 · C11 · C10	-68.3 (1.8)	C2 · C1 · C9 · C10	71.3(1.5)
O1 · C9 · C1 · C12	86.4 (1.5)	O1 · C9 · C10 · C11	125.8(1.5)
Br1 · C12 · C1 · C2	-168.2 (1.0)	Br1 · C12 · C1 · C9	56.3 (1.5)
Br1 · C12 · C8 · C7	173.6 (9)	Br1 · C12 · C8 · C11	62.3 (1.3)

Molecule(c)

C11 · C8 · C7	107.6(1.0)	C1 · C2 · C7	110.3(9)	C2 · C7 · C8	107.2(1.0)
C12 · C8 · C7	97.8(9)	C10 · C11 · C8	120.8(1.1)	C2 · 7 · C6	120.8(1.1)
C12 · C8 · C11	109.8(1.0)	C9 · C10 · C11	122.5(1.1)	C7 · C2 · C3	120.0(1.2)
C7 · C6 · C5	119.9(1.2)	C1 · C9 · C10	112.4(9)	C1 · C2 · C3	129.6(1.1)
C4 · C5 · C6	116.9(1.3)	O1 · C9 · C10	107.6(9)	C12 · C1 · C9	114.2(9)
C3 · C4 · C5	123.6(1.2)	O1 · C9 · C1	111.9(1.0)	C8 · C12 · Br1	111.9(8)
C2 · C3 · C4	118.6(1.3)	C9 · C1 · C2	106.8(1.0)	C1 · C12 · Br1	115.4(8)
C6 · C7 · C8	132.0(1.1)	C12 · C1 · C2	96.8(9)	C1 · C12 · C8	101.1(1.0)

C3 · C2 · C7 · C8	-176.3 (1.3)	C6 · C7 · C2 · C1	-178.9(1.4)
C7 · C8 · C1 · C10	-72.1 (1.7)	C2 · C1 · C9 · C10	72.9(1.4)
O1 · C9 · C1 · C12	88.4 (1.4)	O1 · C9 · C10 · C11	-56.3 (1.5)
Br1 · C12 · C1 · C2	-168.2 (1.0)	Br1 · C12 · C1 · C9	-127.3(1.4)
Br1 · C12 · C8 · C7	172.6 (1.0)	Br1 · C12 · C8 · C11	60.7 (1.4)

Bond angles of hydrogen atoms with e.s.d.'sin parentheses.

Molecule(a)

H12	C12	Br1	99.8 (8)	H6	C6	C5	120.7 (1.2)	O1	C9	H9	108.9(1.0)
C1	C12	C12	108.2(1.0)	C7	C6	H6	121.6 (1.3)	H9	C9	C1	108.0(1.0)
C8	C12	H12	115.8(1.0)	H5	C5	C4	116.6 (1.4)	H8	C8	C12	119.0(1.1)
H11	C11	C8	132.6(1.1)	C6	C5	H5	121.3 (1.4)	H8	C8	C7	116.7(1.0)
C10	C11	H11	104.7(1.0)	H4	C4	C3	118.8 (1.5)	C11	C8	H8	109.0(9)
H10	C10	C11	78.5(9)	C5	C4	H4	121.1 (1.3)	H1	C1	C12	111.9 (1.1)
C9	C10	H10	152.7(1.3)	C4	C3	H3	121.1 (1.3)	H1	C1	C2	119.8 (1.0)
H9	C9	10	108.0(1.0)	C2	C3	H3	120.1 (1.2)	C9	C1	H1	107.1 (1.0)
H	O1	C9	168.1 (1.0)								

Molecule (b)

H12	C12	Br1	98.9 (7)	C7	C8	H8	117.6 (1.1)	C1	C9	H9	106.9(1.0)
H12	C12	C8	113.0 (1.2)	C7	C6	H6	120.9 (1.2)	O1	C9	H9	106.0 (1.0)
H12	C12	C1	112.6 (9)	H5	C5	C6	121.0 (1.4)	C11	C8	H8	1 08.8 (1.0)
H	O1	C9	168.1 (9)	C4	C5	H5	121.1 (1.3)	C12	C8	H8	117.6 (1.0)
C10	C11	H11	97.1 (1.1)	H4	C4	C5	116.8 (1.3)	H1	C1	C2	118.5 (1.0)
H11	C11	C8	160.3 (1.0)	C3	C4	H4	121.5 (1.4)	H1	C1	C9	103.4. (1.1)
H10	C10	C11	78.2 (9)	H3	C3	C4	119.8 (1.2)	C12	C1	H1	114.9 (1.0)
C9	C10	H10	153.2(1.2)	C5	C6	H6	119.0 (1.3)	H	O1	C9	168.1 (9)
H9	C9	C10	110.1 (1.0)	C2	C3	H3	120.7 (1.3)				

Molecule (c)

H12	C12	Br1	103.5 (9)	C7	C8	H8	119.7 (1.0)	C1	C9	H9	105.7 (9)
H12	C12	C8	110.5 (1.0)	C11	C8	H8	107.7 (9)	O1	C9	H9	109.3 (9)
H12	C12	C1	113.9 (1.0)	C12	C8	H8	113.7 (1.1)	C4	C5	H5	121.3 (1.2)
H11	C11	C8	134.2 (1.2)	C5	C6	H6	120.2 (1.3)	H4	C4	C5	115.7 (1.4)
C10	C11	H11	104.0 (1.0)	C7	C6	H6	119.8 (1.2)	C3	C4	H4	120.6 (1.5)
C8	C12	H12	115.8 (1.0)	H5	C5	C4	116.6 (1.4)	H1	C1	C9	104.3 (9)
H10	C10	C11	78.8 (9)	H5	C5	C6	121.7 (1.3)	C12	C1	H1	113.8 (1.1)
C9	C10	H10	152.7 (1.2)	H3	C3	C4	120.7 (1.2)	H	O1	C9	167.8 (9)
H9	C9	C10	110.0 (1.1)	C2	C3	H3	120.6 (1.3)	H1	C1	C2	121.1(1.0)

Table 4. X-ray data of compund **25**

Bond lengths Å

Br1	C2	1.957 (6)	Br2	C3	1.965 (6)	C3	H3	1.00 (7)
C1	C2	1.56 (1)	C1	C6	1.51 (1)	C7	H7	0.96 (6)
C1	C7	1.522 (9)	C2	C3	1.556 (9)	C9	H9	0.96 (7)
C3	C4	1.57 (1)	C4	C5	1.523 (9)	C11	H11	0.97(8)
C4	C8	1.526 (9)	C5	C6	1.397 (9)	C4	H4	1.07 (6)
C5	C9	1.38 (1)	C6	C12	1.392 (9)	C8	H8	1.05 (7)
C7	C8	1.33 (1)	C9	C10	1.38 (1)	C10	H10	1.00 (7)
C10	C11	1.40 (1)	C11	C12	1.39 (1)	C12	H12	0.95 (6)
C1	H1	1.06 (5)	C2	H2	1.01 (7)			

Bond Angles(deg)

C2	C1	C6	108.1 (5)	C2	C1	C7	104.1 (5)	C1	C6	C12	126.7 (6)
C6	C1	C7	108.8 (6)	Br1	C2	C1	109.7 (4)	C1	C7	C8	113.9 (6)
Br1	C2	C3	116.7 (4)	C1	C2	C3	108.9 (6)	C5	C9	C10	119.3 (6)
Br2	C3	C2	116.4 (4)	Br2	C3	C4	108.5 (5)	C10	C11	C12	121.0 (7)
C2	C3	C4	109.3 (5)	C3	C4	C5	106.0 (5)	C5	C6	C12	120.1 (6)
C3	C4	C8	103.8 (6)	C5	C4	C8	109.1 (5)	C4	C8	C7	114.5 (6)
C4	C5	C6	112.9 (6)	C4	C5	C9	126.2 (6)	C9	C10	C11	120.0 (8)
C6	C5	C9	120.9 (6)	C1	C6	C5	113.0(5)	C6	C12	C11	118.7 (6)

For molecule **18** Crystals from Methanol Crystal size 0.17x0.35x0.65 mm ; Triclilic ; Z=2; a=7.946 (3) Å, b=15.192(4) Å, c=15.192 (2) Å; v=1539.78 (1.09) Å^c; D_X=1.624 mg. m^{-3}; Ømax=26 °,(M_oKa , l=0.71069 Å, Huber four circle diffractometer, w/2ø-scans, T=293 °K) , 4049 indepented, 3279 observed [I ≥ 3 s (I)] ; R=0.032.

For molecule **25** Crystals from Methylene chloride/hexane (1/3). Orthorhombic; Z=8; a=11.481 (5) Å, b=7.953(3) Å, c=22.977 (8) Å; v=2098 Å^c; T=235 °K) R=0.0462, R_w=0.0366.

For molecule **28** Crystals from Ethylalcohol/hexane (2/1). Crystal size 0.35x0.30x0.50 mm ; Orthorhombic; Z=8; a=8.409(3)Å b=23.124(2) Å, c=10.969(2) Å; v=2132.9 (9) Å^c; D_X=1.949 mg. m^{-3}; Ømax=26 °,(M_oKa , l=0.71069 Å, Huber four circle diffractometer, w/2ø-scans, T=293 °K) , 2445 indepented, 1288 observed [I ≥ 3 s (I)] ; R=0.032, R_w=0.037.

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