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High Temperature Bromination VIII[1]: Bromination of Homobenzonorbornadiene

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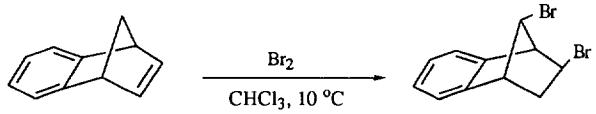
Abstract: The electrophilic addition of bromine to homobenzonorbornadiene (**3**) at 10 °C led in quantitative yield to the formation of di-*anti*-bromo adduct **4**. However, high-temperature bromination of **3** in decalin at 150 °C followed by repeated chromatography combined with fractional crystallization gave us 13 products. Non-rearranged products **5** and **6** have been isolated in 34% yield. The formation of allylic brominated products **8**, **9** and **13** (33%) at high temperature have been discussed in terms of free radical mechanism. **14** and **15** are alcohol compounds which arise from hydrolysis of **8**, **9**, and **13**, respectively. All compounds have been characterized properly, especially by 200 MHz ^{1}H NMR and 50 MHz ^{13}C NMR and by chemical transformations. 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[2]. 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)[3,4a]. This compound is formed as a result of Wagner-Meerwein rearrangement.



1 **2** (1)

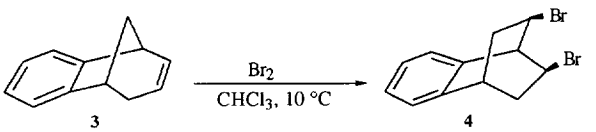
In the course of studying the bromination reactions of the unsaturated bicyclic systems we noticed that the reaction temperature has a dramatic influence on product distribution. Bromination at room and lower

temperatures give rearranged products via Wagner-Meerwein rearrangement with accompanying alkyl and aryl (in the case of benzannelated systems) migration. However, the bromination of these hydrocarbons at higher temperatures (80-150 °C) resulted partly or completely in the formation of non-rearranged products[4]. High temperature bromination prevent skeletal rearrangement.

In connection with our continuing work in the temperature bromination reactions[4] we have been interested in the bromination reaction of homobenzonorbornadiene at room and high temperature in order to see the effect of the temperature on skeletal rearrangement.

Results and Discussion

The electrophilic addition of bromine to homobenzonorbornadiene (**3**) was first reported by Jefford et al.[5] to yield a dibromide **4** in essentially quantitative yield. We also reacted homobenzonorbornadiene (**3**) with bromine in chloroform solution at room temperature and isolated the di-*anti*-bromo adduct **4** in quantitative yield as reported in the literature[5] (Eq. 2).

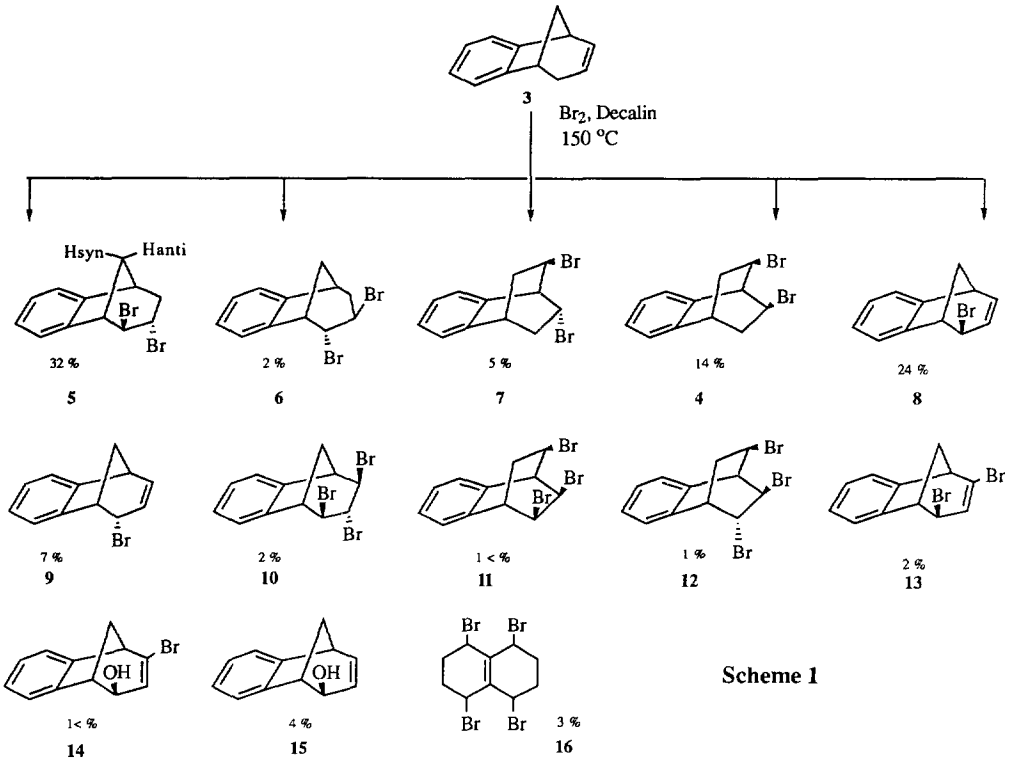


3 4 (2)

Furthermore, we studied high temperature bromination of homobenzonorbornadiene (**3**) at 150 °C. For this purpose bromine was directly distilled into a hot solution of **3** in decalin at 150 °C. NMR analysis of crude product indicated that the reaction mixture was very complex. After repeated column chromatography combined with fractional crystallization we have been able to separate 13 compounds (Scheme 1). The structures of the products have been elucidated on the basis of ^1H, and ^{13}C NMR data and chemical transformations (Table 1).

As the major products we isolated two non-rearranged *trans*-addition products **5** and **6** (34%) which were not formed by the reaction at 10 °C. NMR analysis indicated that the other possible *cis*-non-rearranged compounds with the *exo-exo* or *endo-endo* configuration were not among the products. The Wagner-Meerwein rearranged product **4** was also formed in a yield of 14%. The formation of tetrabromo compound **16** which is derived from solvent (decalin) has been described in our earlier works[4a,4b].

The structures of **5** and **6** have been elucidated on the basis of the spectral data obtained by ^1H NMR and ^{13}C NMR experiments (Table 1) and chemical transformations. ^{13}C NMR spectra of **5** and **6** are completely in agreement with these unsymmetrically structures. However, ^{13}C NMR does not give any indication about the stereochemistry of the bromine atom at the C_2 and C_3 carbon atoms in **5** and **6**. The configuration of bromine at the C_2 carbon in both isomers has been established by analysis of the AB system arising from the bridge methylene protons H_{8anti} and H_{8syn}[6]. B parts of these AB systems (H_{8anti}) show in both cases a doublet. H_{8anti} in **5** resonates at lower field (2.54 ppm) compared to the H_{8anti} (1.98 ppm) in **6**. This fact can be explained on the basis of strong steric repulsion between H_{8anti} in **5** and neighboring bromine in the *exo* position. Any steric repulsion between H_{8anti} and bromine atom at the C_3 carbon atom is out of the question due to the chair conformation of the cyclohexane ring. It is well known that interactions related to the van der Waals effect cause a paramagnetic contribution to the shielding constants, which results in a shift to lower field[7].



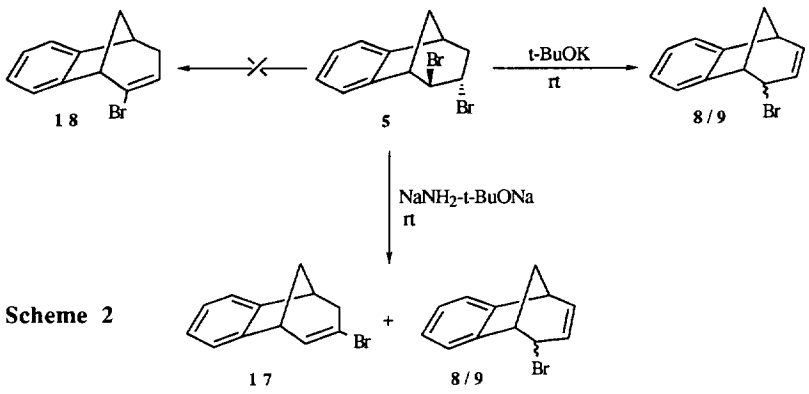
Scheme 1

This configurational finding was also supported by ^{13}C NMR chemical shifts of the methylene carbons (C_8). Downfield chemical shift of the methylene carbon in **6** compared to the chemical shift of the methylene carbon in **5** is associated with the *endo* configuration of the C_2-bromine atom in **6** (See Table 1).

The configuration of bromine atom at C_3 atom was determined from the coupling constants J_{23}. We observe large coupling constants of J=9.9 Hz in the case of *exo*-orientation of bromine (*endo*-proton) in **6** and J≤1 Hz in tha case of *endo*-orientation of bromine (*exo*-proton) in **5**.

These observations are in accordance with results obtained by Smith[8] and Barkhash[9]. Barkhash et al.[9] have reported similar coupling constants with values of J_{ee}=0-1 Hz, J_{aa}=9-10 Hz, and J_{ae}=4-5 Hz for this kind of systems. Differential ^1H NMR-NOE measurements support also the proposed structure for **5**. Irradiation at the resonance frequency at δ 4.63 (H_3 proton) caused enhancement of the signals for H_{4exo} at δ 2.76 and H_{4endo} at δ 2.26. However, higher enhancement of the H_{4exo} proton signal revealed exactly the *exo*-orientation of H_3 proton which clearly indicates the *trans*-configuration of bromine atoms in **5**.

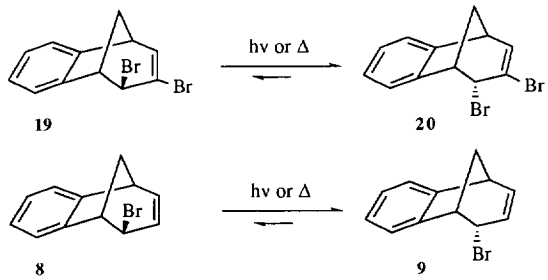
The structure of **5** was also supported by chemical transformation. When pure **5** was subjected to dehydrobromination by potassium *tert*-butoxide, allylic bromides **8** and **9** were obtained in high yield as an isomeric mixture (79:21) (Scheme 2). Treatment of **5** with $NaNH_2$/t-BuONa complex base[10] resulted in the formation of the known bromo compound **17**[11] and a mixture of **8** and **9**. Any trace of the other vinylic isomer **18** was not detected among the products (Scheme 2). These observations indicate that the original skeletal structure of homobenzonorbornadiene was retained by addition of bromine. The structures of isomers **8** and **9**



Scheme 2

were determined on the basis of spectral data[12] and chemical transformations. The configuration of bromine atoms (*exo* or *endo*) was made by comparison of their ^{1}H NMR spectra of their 2,3-dibromo analogues (**19** and **20**) whose structures were previously established[13].

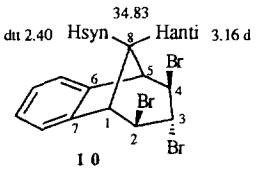
Because of the *exo* configuration of bromine at C_2 carbon atom in **5** it is expected only the formation of allylic bromide **8** with *exo* configuration during dehydrobromination reaction. Recently, we have discovered that the configuration isomerization of bromine[13] in the bicyclo[3.2.1]system can be catalyzed by light or by heat. Irradiation or heating of the pure *exo* dibromide **19** (or *endo* isomer **20**) resulted in the formation of an equilibrium mixture consisting from *exo* and *endo* dibromides **19** and **20** (86:14) (Scheme 3). In analogy to this reaction pure **8** or **9** were each subjected to direct irradiation with a sun lamp (250 W) or day light; a mixture of **8** and **9** in which the first predominated (79:21) was formed. A similar product distribution was also observed by heating of pure samples **8** and **9**. Therefore, we assume that the formed *endo* bromide **9** is secondary product during high temperature bromination of homobenzonorbornadiene.



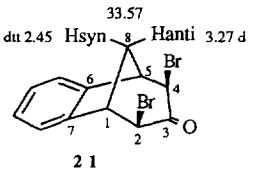
Scheme 3

Additionally, we isolated six products (**8-10, 13-15**) with the benzobicyclo[3.2.1]octane skeleton besides *trans*-adducts (**5** and **6**) at high temperature bromination of **3** (Scheme 1). Two of them were alcohol compounds **14** and **15**. Compound **8, 9**, and **13** contain allylic bromine atom which can be hydrolyzed easily on column material to the corresponding alcohols. Therefore, we assume that the primarily formed isomeric allylic bromides (**8, 9**) and dibromide **13** partly hydrolyze to the known *exo* alcohol **15**[14] and **14**, respectively. The structure of **13** was established unambiguously by ^{1}H and ^{13}C NMR spectra. Asymmetry in the molecule is supported by its 12-line ^{13}C NMR spectrum. The ^{1}H NMR and ^{13}C NMR spectra of **10** were highly characteristic. Analysis of the AB system arising from the bridge methylene protons show that the high field part

(2.40 ppm, H_{8syn}) is split into doublets of triplets of triplets (J=12.1, 5.2, 1.5 Hz). The second triplet splitting is reconcilable only with an *exo-exo* arrangement of the bromines at C_2 and C_4 carbon atom.[13]C NMR chemical shifts (seven-line) in **10** were also completely in agreement with the structure and results obtained by [13]C NMR spectra of dibromo ketone **21**[6a].

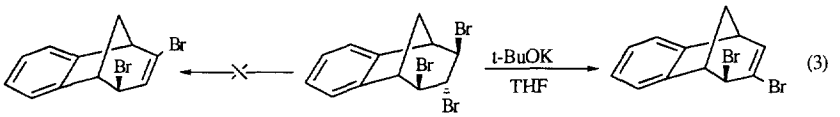


10



21

For further characterization we converted the tribromide **10** into the known compound **19**[11] by using the classical method of potassium *tert*-butoxide in tetrahydrofurane (Eq. 3). The other expected elimination product **13** was not formed in this reaction.

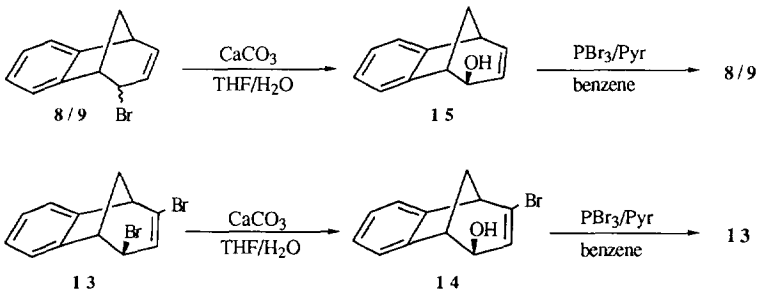


(3)

13 **10** **19**

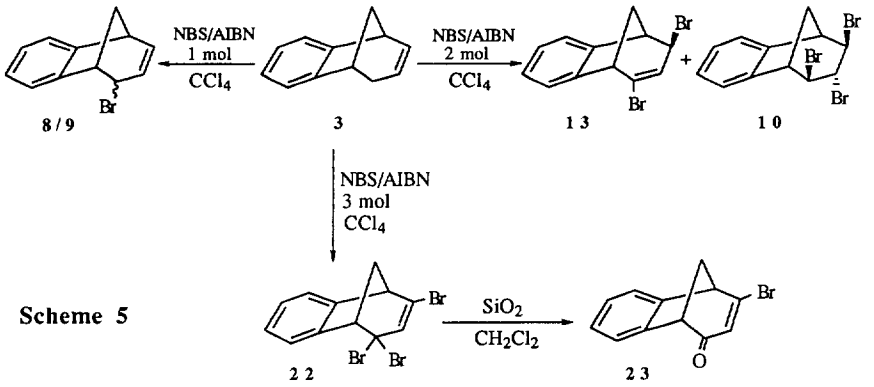
Independently, an isomeric mixture of allylic bromides (**8**, **9**) and dibromide **13**, separately, were hydrolyzed to the corresponding alcohols **15** and **14** by using the procedure of Kitahonoki and co-Workers[11] (Scheme 4). With this reaction we established the origin of alcohols **14** and **15**. For further support of the structures **14** and **15**, pure alcohols were treated with phosphorous tribromide to provide dibromide **13** and a mixture of **8/9** (ratio 79:21) in high yield.

Allylic bromides (**8**, **9**) were also obtained by an independent reaction. Treatment of **3** and one mol of N-bromosuccinimide (NBS) and catalytic amount of AIBN in refluxing CCl_4 afforded a mixture of **8** and **9** (in a ratio of 78:22) in high yield (91%) (Scheme 5). The isomeric monobromides (**8**, **9**) were separated by low temperature column chromatography. We have shown that the dibromide **13** is formed by the reaction of **3** with 2 mol of NBS under the same reaction conditions. Tribromide **10** was also obtained from this reaction in a yield of 15%. Furthermore, treatment of **3** with 3 mol of NBS gave tribromide **22** which hydrolyzed to the corresponding unsaturated ketone **23** on column material (Scheme 5).



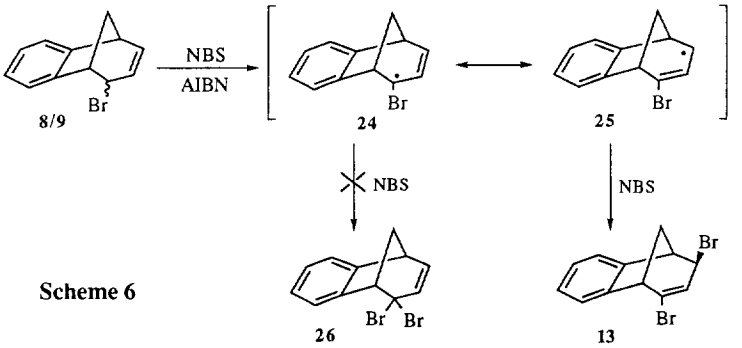
Scheme 4

Allylic bromo compounds **8** and **9** were the expected products in this reaction, but **13** and **10** are not. The unusual conversion of **3** to **13** where a vinylic bromination takes place can be reasonably explained by the following mechanism involving the allylic radicals **24** and **25** (Scheme 6).



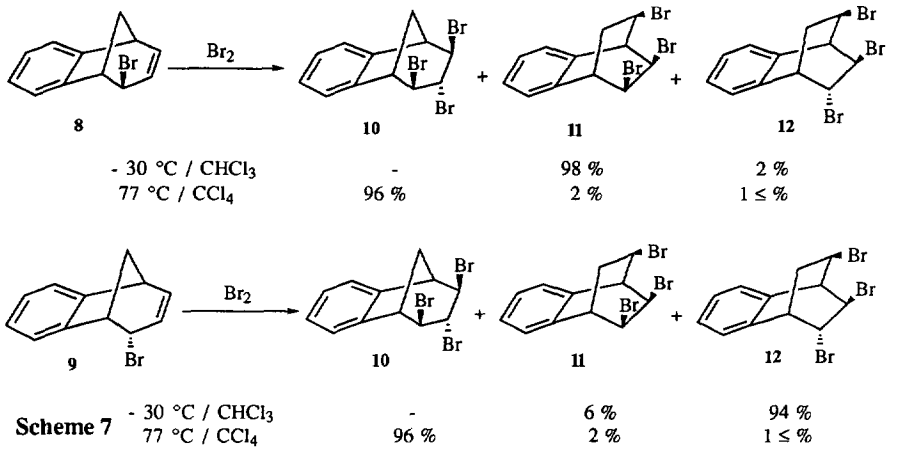
Scheme 5

We assume that the primarily formed allylic radical **24** completely rearranges to **25** before recombination with NBS to give dibromide **13**. Recently, we have observed similar allylic rearrangement in these systems and confirmed this observation by deuterium labeling studies[13,15]. Paquette et al.[16] have also observed similar results in cyclooctadiene systems.



Scheme 6

In the light of above mentioned reactions we believe that radical mechanism is responsible for the formation of **8**, **9**, and **13** at high temperature bromination of homobenzonorbornadiene **3**. There are two possible explanation for the formation of tribromide **10** at high temperature bromination of **3**. One of them *cis*-addition of HBr to double bond of **13**, the other possible mechanism involves addition of bromine to double bonds of allylic bromides **8** and **9** under reaction conditions. In order to determine which of these possible mechanism is operating, the reaction of allylic bromides **8** and **9** with bromine at different temperatures was studied (Scheme 7). For this, pure isomers (**8**, **9**) were treated with bromine. From the reaction at -30 °C we isolated only Wagner-Meerwein rearrangement products **11** and **12** with accompanying aryl migration in quantitative yield. At high temperature (77 °C) non-rearranged addition product, the tribromide **10**, was the major compound (96%). With these reactions we established also the origin of rearranged-products **11** and **12**.

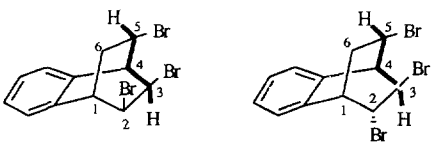


Scheme 7

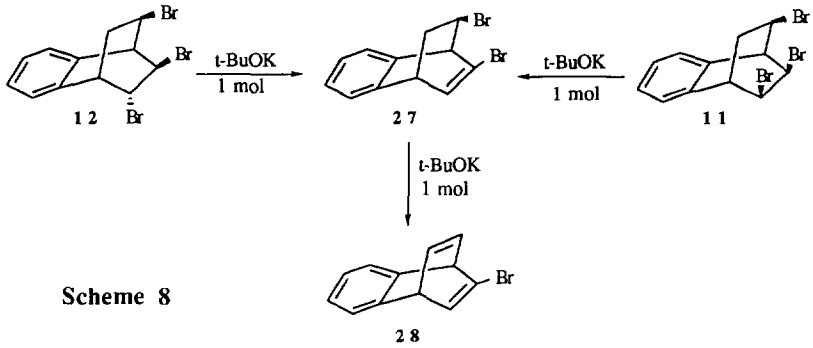
On the basis of these results, we can conclude that bromine addition mechanism to double bond of **8/9** is favored. In this case, we assume that the high-temperature bromination is occurring by a free-radical mechanism. Radical intermediates are much less likely to rearrange. Conducting the bromination reaction of benzonorbornadiene (**1**) in the presence of free radical inhibitors like 2,4,6-tri-*tert* -butylphenol suppressed the formation of the non-rearranged products[4a]. This supports very strongly that there is a competition between radical and ionic mechanism.

The structures of rearranged products **11** and **12** were determined on the basis of spectral data and especially by chemical transformations. The correct stereochemical assignments to **11** and **12** were made by proton NMR spectroscopy. The *anti* configuration of bromines at C_3 and C_5 carbon atoms in both isomers has been established by means of long-range (^4J) coupling between H_3 and H_5. In the case of ^4J in the bicyclic systems one speaks of the **M** or **W** arrangement. The bonding arrangement of the coupled protons H_3 and H_5 in both isomers meets the **M** criterion. The fact that there is any coupling between H_3 and H_5 ($^4J_{35}$=2.0 Hz in **11** and $^4J_{35}$=2.3 Hz in **12**) is an indication for the *anti* configuration of the bromine atoms at C_3 and C_5.

Furthermore, the configuration of vicinally located bromine atoms at C_2 and C_3 carbon atoms was determined from the coupling constants J_{23}. J_{cis} coupling was measured approximately 9-10.5 Hz while J_{trans}=4-6 Hz for this kind of systems[5,17]. We observed large coupling constants of J_{23}=9.9 Hz in the case of **11** and J_{23}=5.0 Hz in the case of **12** which clearly indicates that bromines are *cis* located in **11** and *trans* in **12**.

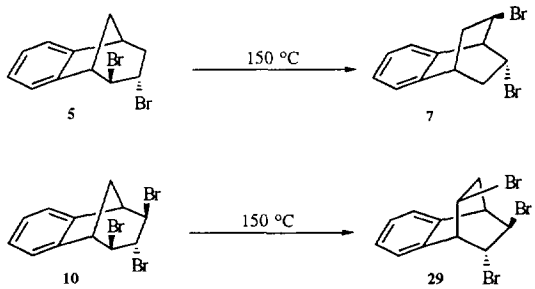


The position of the bromine atoms at ethano bridge in both isomers (**11,12**) has also been established by means of chemical reactions. Treatment of both **11** and **12** with one mol of potassium *tert*-butoxide gave the known dibromo alkene **27**[4e]. With two mol of potassium *tert*-butoxide we isolated the 2-bromobenzobarralene **28**[4e] (Scheme 8). This reaction shows exactly that the bromine atoms at ethano bridge in both isomers has to be in *anti* position.



Scheme 8

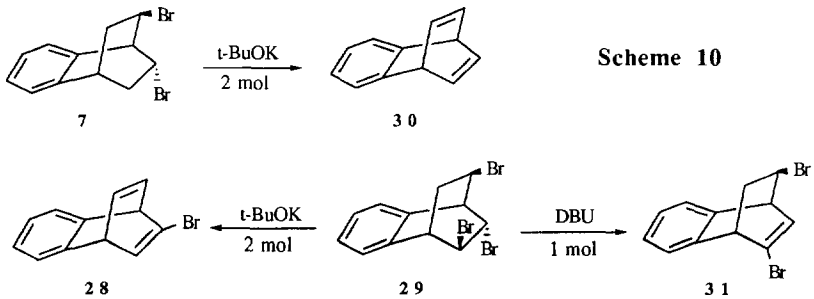
From the high temperature bromination reaction we encountered also the rearranged product **7** (Scheme 1). Low-temperature bromination reaction of **3** resulted in the formation of only Wagner-Meerwein rearranged product **4** via ionic mechanism (Eq. 2). Dibromo compound **7** was not observed at low temperature. In order to shed light into the formation mechanism of **7**, we studied the chemical behavior and stability of all isolated products under the applied reaction conditions and noticed that prolonged heating of **5** and **10** at 150 °C provided **7** and **29**, respectively (Scheme 9).



Scheme 9

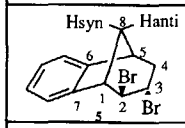
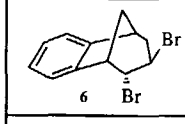
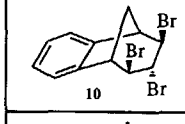
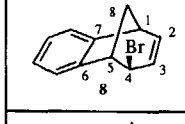
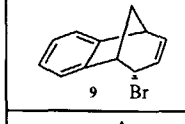
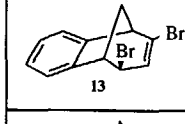
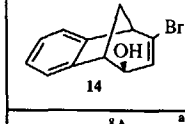
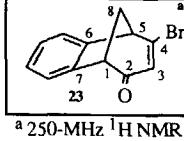
The structures of **7** was determined by NMR spectral data and extensive double resonance experiments. ^{13}C NMR data was consistent with the proposed structure showing 6 aliphatic and 6 aromatic carbons. A chemical proof for the structure was obtained by treatment of **7** with potassium *tert*-butoxide to give benzobarralene **30**[5] (Scheme 10).

The structures of **29** which was obtained by thermal rearrangement of **10** was determined by NMR spectral data. A twelve-line ^{13}C NMR spectrum is in good agreement with the proposed structure. The structure



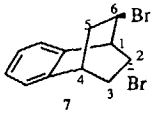
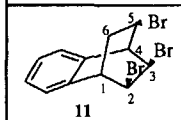
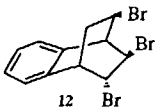
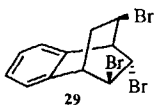
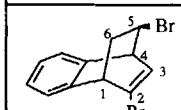
Scheme 10

Table 1 ^{1}H and ^{13}C Spectral Data of the Compound **5**, **6**, **10**, **8**, **9**, **13**, **14** and **23** Downfield from Internal Me_4Si in $CDCl_3$ Solutions

Compound	Chemical Schifts (C/H) (ppm) 1	2	3	4	5	8	H_{aryl}	Other ^{13}C value	Coupling constants (Hz)
 Hsyn Hanti	3.55 dd	4.87 m 56.28	4.63 b d 48.51	Hexo Hendo 2.76 2.26 ddd b d	3.30 m	Hanti Hsyn 2.54 2.40 d m 35.29	7.32-7.22 m	146.27, 144.09, 128.77, 127.83, 124.56, 124.49, 46.84, 40.08, 39.37	$J_{4endo4exo}$=15.7, J_{34endo}=0 $J_{8syn8anti}$=11.4, J_{34exo}=6.2 J_{54exo}=2.8, J_{18syn}=4.7 J_{12}=3.1, $J_{23}\leq 1$
 **6**	3.62 dd	4.44 dd 60.58	3.34 m 54.00	Hexo Hendo 2.37 2.26 m b dd	3.22 m	Hanti Hsyn 1.96 2.43 d m 42.67	7.42-7.18 m	145.17, 141.07, 128.66, 127.43, 125.74, 122.94, 51.26, 45.56, 43.40,	$J_{4endo4exo}$=12.9, J_{23}=9.9 $J_{8syn8anti}$=11.3, J_{18syn}=5.2 J_{54endo}=2.5, J_{12}=2.8
 **10**	3.62 dd 48.28	4.76 dd 52.73	4.90 b s 49.75	4.76 dd 52.73	3.62 dd 48.28	Hanti Hsyn 3.16 2.40 d dtt. 34.83	7.35-7.26 AA'BB' System	144.15, 129.12, 124.96	$J_{8syn8anti}$=12.1 $J_{18syn}=J_{58syn}$=5.2 $J_{12}=J_{45}$=2.8, $J_{23}=J_{34}<1$ $J_{28syn}=J_{48syn}$=1.5
 **8**	3.41 dd 49.78	6.35 ddt	5.45 ddd	4.80 m 51.52	3.72 b d 41.23	Hanti Hsyn 2.66 2.49 d b dt. 38.83	7.43-7.15 m	153.82, 142.65, 138.57, 127.42, 127.09, 125.87, 125.65, 121.91	$J_{8syn8anti}$=10.7, J_{23}=9.4 J_{18syn}=4.3, J_{58syn}=4.8 J_{12}=6.5, J_{34}=3.7, J_{35}=1.6 $J_{28syn}=J_{24}$=0.9
 **9**	3.31 dd 49.22	6.27 ddt	5.33 m	5.32 m 52.06	3.64 t 40.72	Hanti Hsyn 2.29 2.51 d ddt 45.93	7.50-7.14 m	151.58, 141.86, 137.02, 127.78, 127.57, 126.29, 125.73, 121.40	$J_{8syn8anti}$=10.7, J_{23}=9.3 $J_{18syn}=J_{58syn}$=4.7, J_{12}=6.4 J_{45}=5.0, $J_{28syn}=J_{24}$=1.6
 **13**	3.62 b d	- 133.18	5.69 dt	4.68 m	3.67 b d	Hanti Hsyn 2.78 2.46 d b dt 38.81	7.40-7.15 m	151.01, 142.07, 127.98, 127.84, 125.46(2x), 122.19, 51.80, 51.00, 48.42	$J_{8syn8anti}$=11.0 $J_{18syn}=J_{58syn}$=4.5 J_{34}=4.3, $J_{35}=J_{13}$=1.2
 **14**	3.62 b d	- 134.40	5.61 dd	4.12 dd 71.45	3.36 b d	Hanti Hsyn 2.49 2.32 d b dt 39.41	7.40-7.12 m	150.07, 143.21, 127.53, 127.30, 125.63, 125.23, 122.21, 52.51, 47.31	$J_{8syn8anti}$=10.7 $J_{18syn}=J_{58syn}$=4.5 J_{34}=4.2, J_{45}=2.1, J_{35}=1.3
 **23**	3.85 dd	- 194.99	5.81 t	-	4.02 dd	Hanti Hsyn 2.84 2.67 d dt 49.48	7.42-7.20 m	154.08, 146.21, 140.54, 127.62, 127.51, 125.50, 125.25, 123.13, 56.56, 54.34	$J_{8syn8anti}$=10.0 $J_{18syn}=J_{58syn}$=3.6 $J_{13}=J_{35}$=1.2

[a] 250-MHz ^{1}H NMR, 63-MHz ^{13}CNMR

Table 1 (Continued) ^{1}H and ^{13}C Spectral Data of the Compound **7, 11, 12, 29** and **31** Downfield from Internal Me_4Si in $CDCl_3$ Solutions

Compound	Chemical Schifts (C/H) (ppm) 1	2	3	4	5	6	Haryl	Other ^{13}C value	Coupling constants (Hz)
 **7**	3.60 t	4.19 ddd	H_{endo} 2.27 ddt H_{exo} 2.05 m	3.00 p	H_{endo} 1.92 m H_{exo} 2.75 ddd	5.10 ddd	7.37-7.18 m	141.08, 137.69, 128.56, 127.34, 126.27, 124.28, 51.44, 49.23, 45.39, 40.16, 37.49, 35.66	$J_{3endo3exo}$=15.0, J_{23exo}=4.8 $J_{5endo5exo}$=14.5, J_{65exo}=9.4 J_{23endo}=9.6, J_{65endo}=4.1 J_{16}=2.7, J_{12}=2.9, J_{43endo}=J_{45endo}=3.0,J_{43exo} = J_{45exo}=2.8, $J_{3endo5endo}$=3.0
 **11**	3.39 m	4.58 dt	4.47 dt	3.70 t	4.09 ddt	H_{endo} 2.36 ddt H_{exo} 3.05 ddd 32.47	7.33-7.13 m	141.17, 138.70, 129.12, 128.70, 125.88, 124.46, 53.34, 49.33, 48.02, 44.66, 43.67	$J_{6endo6exo}$=14.5, J_{56exo}=6.3 J_{56endo}=10.7, J_{23}=9.9 J_{12}=J_{26endo}=J_{16endo}=2.3 J_{45}=J_{35}=J_{34}=J_{16exo}=2.0
 **12**	3.32 dt	4.73 dd	4.17 dt	3.68 t	4.09 ddt	H_{endo} 2.60 ddd H_{exo} 2.52 ddd 39.60	7.36-7.17 m	140.07, 136.16, 129.07, 128.62, 127.40, 124.29, 56.84, 54.13, 49.77, 45.21, 42.29	$J_{6endo6exo}$=14.7, J_{56exo}=5.9 J_{56endo}=9.9, J_{16endo}=4.0 J_{16exo}=J_{34}=J_{12}=J_{35}=J_{45}= 2.3 , J_{23}=5.0
 **29**	3.18 q	4.18 m	5.08 dd	3.49 t	4.13 m	H_{endo} 2.28 dddd H_{exo} 2.72 ddd 31.57	7.39-7.18 m	138.64, 136.37, 129.14, 128.61, 127.25, 125.07, 58.66, 52.87, 52.73, 48.07, 44.79	$J_{6endo6exo}$=14.8, J_{56exo}=5.2 J_{56endo}=10.2, J_{26endo}=2.2 J_{16endo}=J_{16exo}=J_{12}=2.8 J_{23}=4.3, J_{34}=J_{45}=2.3
 **31**	4.02 m	- 126.37	6.67 dd	4.33 dd	4.02 m	H_{endo} 2.36 H_{exo} 2.16 m 38.99	7.35-7.15 m	141.82, 140.41, 132.48, 127.14, 127.05, 124.40, 123.87, 51.45, 50.98, 47.24.	$J_{6endo6exo}$=14.3 J_{34}=6.3 J_{45}=2.6 J_{13}=1.9

of **29** was also supported by chemical transformation. When **29** was subjected to dehydrobromination by 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), dibromoalkene **31** with *anti* configuration was obtained in a yield of 85% (Scheme 10). For further characterization we converted the tribromide **29** into the known compound **28**[4e] by using two mol of potassium *tert*-butoxide (yield 90-93%). Dehydrobromination of **31** with one mol of potassium *tert*-butoxide gave also compound **28**.

Finally, we conclude that bromination of homobenzonorbornadiene at 10 °C gives only rearranged product (**4**) via Wagner-Meerwein rearrangement. However, bromination at high temperature results mostly in the formation of non-rearranged products (**5**, **6**) (34%). Free radical mechanism is responsible for the formation of allylic brominated products **8**, **9**, and **13** which are isolated in a 33% total yield. The formation of allylic brominated products at high temperature is probably due to the involvement of a highly reactive allylic system of homobenzonorbornadiene. On the other hand, the formation of rearranged product (**4**) in a yield of 14% at high temperature shows that there is a competition between radical and ionic mechanism.

Experimental Section

General. Melting points are uncorrected. Infrared spectra were obtained from films on NaCl plates for liquids or from solution in 0.1 mm cells or KBr pellets for solids on a regular instrument. The ^{1}H and ^{13}C NMR spectra were recorded on 200 (50)-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[18] 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 Homobenzonorbornadiene 3 at 10 °C. To a magnetically stirred solution of homobenzonorbornadiene **3**[5] (2.0 g, 12.82 mmol) in 20 mL dry chloroform cooled to 10 °C was added dropwise a solution of bromine (2.49 g, 15.38 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. The oily residue was crystallized from chloroform/hexane (1/3) to give 4.01 g (100%) of rearranged dibromide **4**[5]. mp 133-134 °C (Lit.[5] 133.5-134.5 °C), colorless crystals from chloroform/hexane (1/3).

Bromination of Homobenzonorbornadiene 3 at 150 °C. Homobenzonorbornadiene (**3**) 3.35 g (21.47 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 3.61 g (22.56 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. The oily residue was chromatographed on silica gel (130 g) eluting with hexane.

The first fraction consisted of a mixture of compounds **13**, **5** and **16**. This mixture was submitted to fractional crystallization from hexane/ethyl acetate (2/1), to give 60 mg (3%) of tetrabromide **16**[4a,4b].

After filtration of tetrabromide **16**, the organic solvent was evaporated and the oily residue was recrystallized from ethanol/hexane (1/2) to give dibromide **13**.

***exo*-2,4-Dibromo-6,7-benzobicyclo[3.2.1]octa-2,6-diene 13** (134 mg, 2%): mp 71-72 °C, colorless crystals from carbon tetrachloride. IR (KBr, cm^{-1}) 3065-3010, 2960, 2860, 1610, 1480. Anal. Calcd for $C_{12}H_{10}Br_2$: C, 45.90; H, 3.21; Found: C, 46.12; H, 3.08.

After filtration of dibromide **13**, the organic solvent was evaporated and the residue was dissolved in THF (15 mL) and H_20 (5 mL). 200 mg (2.0 mmol) of $CaCO_3$ was added to the solution. The suspension was heated at 40-45 °C overnight. After the reaction mixture was cooled to room temperature, the insoluble materials were separated by filtration. The filtrate was extracted with ether, washed with water, and dried over $MgSO_4$. Thus allylic bromides **13** and **16** which are found in the mixture in small quantity , were hydrolyzed to the corresponding alcohols. After removal of the solvent, the oily residue was chromatographed over silica gel (20 g) with hexane as the eluent, to give 2.18 g (32%) of dibromide **5** as a pale yellow viscous oil.

***exo,endo*-2,3-Dibromo-6,7-benzobicyclo[3.2.1]octa-6-ene 5.** IR (NaCl, film, cm^{-1}) 3070, 3042, 3020, 2948, 2892, 1471, 1460, 1430, 1331, 1231, 1171, 1026, 973, 754. Anal. Calcd for $C_{12}H_{12}Br_2$: C, 45.60; H, 3.83; Found: C, 45.83; H, 3.61.

The second fraction consisted of a mixture of compounds **10** and **8**. This mixture was crystallyzed from ethanol/hexane (1/1). The solution was allowed to stand for a while in refrigerator. The formed crystals were identified as

***exo,endo,exo*-2,3,4-Tribromo-6,7-benzobicyclo[3.2.1]octa-6-ene 10** (170 mg, 2%): mp 111-112 °C, colorless crystals, recrystallized from methylene chloride/hexane (1/3). IR (KBr, cm^{-1}) 3060, 3040, 3020, 2960, 1470, 1400, 1330, 1242, 1160, 1015. Anal. Calcd for $C_{12}H_{11}Br_3$: C, 36.49; H, 2.81; Found: C, 36.12; H, 2.42.

After filtration of tribromide **10** the solvent was evaporated and the residue was identified as

***exo*-4-Bromo-6,7-benzobicyclo[3.2.1]octa-2,6-diene 8** (1.41 g, 24%): pale yellow oil. IR (NaCl, film, cm^{-1}) 3065, 3038, 2940, 2860, 1460, 1363, 1225, 1160, 1150, 1125, 1025.

The third fraction: ***exo,endo*-2,6-Dibromo-7,8-benzobicyclo[2.2.2]octa-7-ene 7** (340 mg, 5%): pale yellow oil. IR (NaCl, film, cm^{-1}) 3076, 3050, 3023, 2862, 1483, 1462, 1252, 1230, 1153, 1009, 848,761.

The fourth fraction: ***endo*-4-Bromo-6,7-benzobicyclo[3.2.1]octa-2,6-diene 9** (353 mg, 7%): pale yellow oil. IR (NaCl, film, cm^{-1}) 3065, 3038, 2940, 2860, 1465, 1180, 1148, 1150, 1015.

The fifth fraction: ***endo,exo*-2,3-Dibromo-6,7-benzobicyclo[3.2.1]octa-6-ene 6** (136 mg, 2%): mp 123-124 °C, colorless crystals from methylene chloride/hexane (1/4). IR (KBr, cm^{-1}) 3060, 3010, 2920, 1460, 1450, 1315, 1300, 1290, 1240, 1205, 1160, 820, 750. Anal. Calcd for $C_{12}H_{12}Br_2$: C, 45.60; H, 3.83; Found: C, 45.89; H, 3.65.

The sixth fraction: ***exo,exo*-2,6-Dibromo-7,8-benzobicyclo[2.2.2]octa-7-ene 4**[5] (950 mg, 14%).

The seventh fraction: ***endo,exo,exo*-2,3,5-Tribromo-7,8-benzobicyclo[2.2.2]octa-7-ene 12** (85 mg, 1%): mp 127-128 °C, colorless crystals from methylene chloride/hexane. IR (KBr, cm^{-1}) 3018, 2983, 2960, 1463, 1460, 1440, 1335, 1258, 1240, 1231, 1175, 941, 845. Anal. Calcd for $C_{12}H_{11}Br_3$: C, 36.49; H, 2.81; Found: C, 36.62; H, 2.62.

The eigth tractıon: ***exo,exo,exo*-2,3,5-Tribromo-7,8-benzobicyclo[2.2.2]octa-7-ene 11** (30 mg, 1<%): mp 147 °C, colorless crystals from methylene chloride/hexane. IR (KBr, cm^{-1}) 3067, 3039, 2962, 2942, 1475, 1460, 1440, 1341, 1338, 1298, 1268, 1234, 1200, 1148, 1102, 948. Anal. Calcd for $C_{12}H_{11}Br_3$: C, 36.49; H, 2.81; Found: C, 36.23; H, 2.55.

Then the column was eluted with hexane/ethyl acetate (95:5).

The ninth fraction: ***exo*-2-Bromo-4-hydroxy-6,7-benzobicyclo[3.2.1]octa-2,6-diene 14** (28 mg, 1<%): mp 105-107 °C, colorless crystals from chloroform/hexane (1/3). IR (KBr, cm^{-1}) 3260, 2960, 2940, 2870, 1620, 1463, 1400, 1315, 1240, 1010, 990.

The tenth fraction: ***exo*-4-Hydroxy-6,7-benzobicyclo[3.2.1]octa-2,6-diene 15**[13] (88 mg, 4%): pale yellow oil.

Bromination of 8 at -30 °C. To a magnetically stirred solution of monobromide **8** (0.5 g, 2.13 mmol) in 15 mL of dry chloroform cooled to -30 °C was added dropwise a cooled solution of bromine (357 mg, 2.23 mmol) in 3 mL of chloroform during 5 min. After stirring for 30 min at -30 °C, the solution was slowly warmed to room temperature. The solvent was removed under reduced pressure and the crude product was crystallyzed from methylene chloride/hexane (1/3). 672 mg of tribromide **11** crystallized. After filtration of **11**, the organic solvent was evaporated and the oily residue was chromatographed on silica gel (30 g) eluting with hexane. The first fraction consisted of the tribromide **12** which was crystallyzed from methylene chloride/hexane (1/3) to give 17 mg (2%) of tribromide **12**. From the second fraction we isolated 152 mg (total yield 98%) of pure crystalline tribromide **11**.

Bromination of 9 at -30 °C. The reaction was carried out as described above by using 300 mg (1.28 mmol) of monobromide **9** and obtained 504 mg of crude tribromides **12** and **11** in a ratio of 94:6 (by NMR).

Bromination of 8 at 77 °C. 0.5 g (2.13 mmol) of monobromide **8** was dissolved in 15 mL of carbon tetrachloride in a 50 mL flask which was equipped with reflux condenser. The solution was heated until carbon tetrachloride started to reflux while stirring magnetically. To the refluxing solution was added dropwise a hot solution of bromine (357 mg, 2.23 mmol) in 3 mL of carbon tetrachloride during 5 min. The resulting reaction mixture was heated for 15 min at reflux temperature. After being cooled to room temperature the solvent was evaporated. The crude product was crystallized from methylene chloride/hexane (1/3) and 690 mg of tribromide **10** crystallized as the sole material.

After filtration of **10**, the residue was analyzed by NMR spectral measurements.

Tribromide	**10**	100 mg	total yield 96%
Tribromide	**11**	17 mg	2%
Tribromide	**12**	7-8 mg	1<%

Bromination of 9 at 77 °C. 300 mg (1.28 mmol) of monobromide **9** was reacted with 1 mol of bromine and the same reaction mixture was obtained as described by the reaction of monobromide **8** at 77 °C.

Thermal Reaction of 8 and 9. An 100 mg (0.42 mmol) sample of **8** (or **9**) was heated at 150 °C in a sealed tube (without solvent) for 2 h. The ^1H NMR analysis of the mixture indicated the formation of equilibrium mixture consisting of **8** and **9** in ratio of 79:21.

Direct Irradiation of 9 in $CDCl_3$. A solution of 100 mg (0.42 mmol) of **9** in 0.5 mL of $CDCl_3$ was placed into a NMR tube. Deoxygenation was followed by irradiation by a 150-W projector lamp for 5 h. The ^1H NMR analysis indicated the formation of the equilibrium mixture consisting of **8** and **9** in a ratio of 79:21.

Prolonged irradiation did not change this ratio. The same equilibrium mixture was also obtained starting from pure **8**.

Thermal Rearrangement of Dibromide 5. 100 mg (0.32 mmol) of dibromide **5** was heated at 150 °C in a sealed tube (without solvent) for 8 h. The oily residue was chromatographed on silica gel (10 g) eluting with hexane, 88 mg (88%) of dibromide **7** was isolated as the sole product.

Thermal Rearrangement of Tribromide 10. 200 mg (0.51 mmol) of tribromide **10** was heated at 150 °C in a sealed tube (without solvent) for 15 h. The residue was filtered on a short silica gel column (10 g) eluting with hexane. After evaporation of the solvent the crude product was crystallized from methylene chloride/hexane (2/5) to give 162 mg (81%) of tribromide **29**.

***exo,endo,exo*-2,3,5-Tribromo-7,8-benzobicyclo[2.2.2]octa-7-ene 29**: mp 80-81 °C, colorless crystals. IR (KBr, cm^{-1}) 3068, 3043, 3021, 2978, 2940, 1479, 1460, 1446, 1259, 1251, 1190, 981, 849, 819, 769, 731. Anal. Calcd for $C_{12}H_{11}Br_3$: C, 36.49; H, 2.81; Found: C, 36.15; H, 2.45.

Elimination of Tribromide 10. To a stirred solution of tribromide **10** (200 mg, 0.51 mmol) in dry and freshly distilled THF (20 mL) was added 59 mg (0.51 mmol) of potassium *tert*-butoxide. The resulting reaction mixture was stirred overnight at room temperature. The mixture was diluted with water and the aqueous solution was extracted with ether (3x50 mL), washed with water, and dried over $MgSO_4$. After removal of the solvent, the residue was filtered on a short silica gel column (10 g) eluted with hexane to give 138 mg (87%) of dibromide **19**[11] as the sole product.

Elimination of Dibromide 7. The reaction was carried out as described above by using 200 mg (0.63 mmol) of dibromide **7** and 213 mg (1.90 mmol) of potassium *tert*-butoxide and obtained 90 mg (91%) of benzobarralene **30**[5].

Elimination of Tribromide 11. The reaction was carried out as described above by using 250 mg (0.63 mmol) of tribromide **11** and 70 mg (0.63 mmol) of potassium *tert*-butoxide and obtained 181 mg (91%) of dibromo alkene **27**[4e]. mp 80-81 °C, colorless crystals from hexane/methylene chloride (5/1).

Elimination of Tribromide 12. The reaction was carried out as described above by using 200 mg (0.51 mmol) of tribromide **12** and 57 mg (0.51 mmol) of potassium *tert*-butoxide and obtained 146 mg (91%) of dibromo alkene **27**[4e].

From the reaction of **12** with 2 mol or **27** with 1 mol of potassium *tert*-butoxide we isolated monobromo benzobarralene **28**[4e] as the sole product.

Elimination of Tribromide 29. To a stirred solution of tribromide **29** (200 mg, 0.51 mmol) in 15 mL of absolute benzene was added 78 mg (0.51 mmol) of DBU. The resulting reaction mixture was heated at reflux temperature for 10 h and then cooled to room temperature. The mixture was diluted with water and the aqueous solution was extracted with ether (3x60 mL), washed with water, and dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel (30 g). Eluting with hexane gave 135 mg (85%) of dibromide **31** as a pale yellow viscous material.

***exo*-2,5-Dibromo-7,8-benzobicyclo[2.2.2]octa-2,7-diene 31.** IR (NaCl, film, cm^{-1}) 3077, 3022, 2967, 2938, 1608, 1470, 1458, 1320, 1270, 1020, 985.

Reaction of tribromide **29** with 2 mol or **31** with 1 mol of potassium *tert*-butoxide at the same reaction conditions as described above gave monobromo benzobarralene **28**[4e] in a yield of 90-93%.

Reaction of Alcohol 15 with PBr_3. A solution of phosphorous tribromide (2.08 g, 7.68 mmol) in 10 ml of absolute benzene was added dropwise to a stirred solution of alcohol **15** (1.2 g, 6.98 mmol) and

pyridine (607 mg, 7.68 mmol) in 20 mL of absolute benzene over 20 min at 5-10 °C. The reaction mixture was stirred overnight at room temperature. The mixture was cooled to 0 °C and added dropwise 100 mL of water. The aqueous phase was extracted with ether (3x50 mL). The combined ether layers were washed successively with 10% HCl, saturated $NaHCO_3$ solution, water and dried over $MgSO_4$. Evaporation of the solvent left a viscous oil whose ^1H NMR spectrum indicated a mixture (1.3 g, 79%) of **8** and **9** in a ratio of 79:21.

Reaction of Hydroxybromide 14 with PBr_3. 300 mg (1.20 mmol) of alcohol **14** was reacted with 1 mol of phosphorous tribromide in the presence of pyridine (1 mol) at the same reaction conditions as described above and obtained 281 mg (75%) of dibromide **13** as the sole product.

Reaction of Dibromide 5 with Potassium *tert*-Butoxide. To a stirred solution of dibromide **5** (400 mg, 1.27 mmol) in 15 mL of dry and freshly distilled THF was added 144 mg (1.28 mmol) of potassium *tert*-butoxide. The reaction mixture was stirred overnight at room temperature. The mixture was diluted with water and the aqueous solution was extracted with ether, washed with water, and dried over $MgSO_4$. After removal of the solvent, the residue was filtered on a short silica gel column (10 g) eluted with hexane to give a mixture of monobromides **8** and **9** (241 mg, 81%) in a ratio of 79:21.

Reaction of Dibromide 5 with $NaNH_2$/t-BuONa Complex Base. A solution of *tert*-BuOH (95 mg, 1.28 mmol) and $NaNH_2$ (100 mg, 2.56 mmol) in 5 mL of dry THF was added dropwise to a stirred solution of dibromide **5** (400 mg, 1.27 mmol) in 15 mL of THF over 10 min at room temperature. The resulting reaction mixture was stirred overnight at room temperature. The mixture was diluted with water and the aqueous solution was extracted with ether (3x50 mL), washed with water, and dried over $MgSO_4$. The solvent was evaporated at reduced pressure. The ^1H NMR analysis of the residue (268 mg, 90%) indicated the formation of vinylic monobromide **17**[11] (59%) and allylic monobromides **8** and **9** (41%) as a mixture.

Reaction of Homobenzonorbornadiene 3 with 1 mol of N-Bromosuccinimide[12]**.** A mixture of **3**[5] (2.0 g, 12.82 mmol), N-bromosuccinimide (2.32 g, 12.95 mmol), AIBN (10 mg), and CCl_4 (80 mL) was heated at reflux temperature for 1 h, cooled, and filtered to remove succinimide. After the solvent was removed, the residue was purified on a short silica gel column eluted with hexane to give 2.74 g (91%) of pure crude product. The ^1H NMR analysis of the crude product indicated the formation of a mixture consisting of **8** and **9** in a ratio of 78:22. The crude product was subjected to a cooled silica gel column (30 g). Elution with hexane gave as the first fraction the *exo* bromide **8** (1.75 g, 58%) as a pale yellow oil. Continued elution with the same solvent afforded the *endo* bromide **9** (140 mg, 4.7%) as a pale yellow oil.

Reaction of Homobenzonorbornadiene 3 with 2 mol of N-Bromosuccinimide. A mixture of **3** (2.95 g, 18.91 mmol), N-bromosuccinimide (6.73 g, 37.80 mmol), AIBN (10 mg), and CCl_4 (60 mL) was heated at reflux temperature for 6.5 h, cooled, and filtered to remove succinimide. After the solvent was removed, the residue was chromatographed on silica gel (30 g). Eluting with hexane gave as the first fraction the dibromide **13** (3.26 g, 55%) as a colorless crystals from carbon tetrachloride .

As the second fraction we isolated the tribromide **10** (1.12 g, 15%) as a colorless crystals from methylene chloride/hexane (1/3).

Reaction of Homobenzonorbornadiene 3 with 3 mol of N-Bromosuccinimide. A mixture of **3** (0.5 g, 3.2 mmol), N-bromosuccinimide (2.4 g, 13.48 mmol), AIBN (10 mg), and CCl_4 (20 mL) was heated at reflux temperature for 12 h, cooled, and filtered to remove succinimide. The solvent was evaporated and the oily residue (1.12 g) was dissolved in 20 mL of methylene chloride. 5 g of silica gel and 1-2 mL of water was added to the solution. The resulting reaction mixture was stirred at room temperature for 24 h, filtered and the

filtercake washed thoroughly with methylene chloride. After removing of the solvent the oily residue was crystallized from methylene chloride/hexane (1/3) to give unsaturated ketone **23**.

4-Bromo-6,7-benzobicyclo[3.2.1]octa-3,6-dien-2-one 23 (0.52 g, 65.8%): mp 96-97 °C, colorless crystals. IR (KBr, cm^{-1}) 3060, 2960, 2940, 2880, 1665, 1585, 1450, 1310, 1285, 1245, 1220, 1120, 1030, 995, 880, 770. MS, m/e 169 (M^+-Br), 141 (M^+-Br, -CO).

Hydrolysis of 8 and 9 to the Alcohol 15. A suspension of **8** and **9** (1.0 g, 4.2 mmol) and $CaCO_3$ (1.2 g, 12 mmol) in THF (25 mL) and H_2O (5 mL) was refluxed for 4 h. After the reaction mixture was cooled to room temperature, the insoluble materials were separated by filtration. The filtrate was extracted with chloroform (2x50 mL), washed with water, and dried over $MgSO_4$. The residue after removal of solvent was purified on a short silica gel column with chloroform/hexane (1/4) as the eluent, to give 0.51 g (69.5%) of *exo* alcohol **15**[14] as a pale yellow oil.

Hydrolysis of Dibromide 13 to the Alcohol 14. A suspension of **13** (300 mg, 0.95 mmol) and $CaCO_3$ (0.28 g, 2.85 mmol) in THF (15 mL) and H_2O (5 mL) was refluxed for 20 h. Same workup was done as described above and obtained 190 mg (79.5%) of alcohol **14**.

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