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Bromination of Benzhomobarrelene Derivatives: 10. High Temperature Bromination[1]

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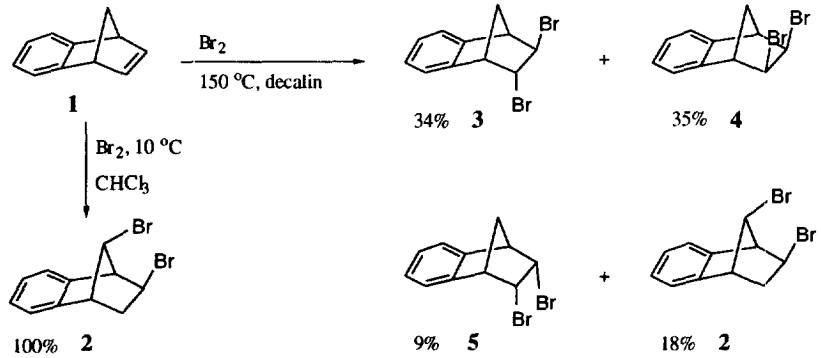
Abstract: The electrophilic addition of bromine to benzhomobarrelene derivatives **18a** and **18b** in CCl_4 at low temperatures (0 °C) followed by repeated chromatography combined with fractional crystallization allowed us to isolate seven (**19a-25a**) and five products (**19b-23b**), respectively. Structural determinations of these compounds revealed that the barrelene skeleton was mainly rearranged. Alcohol **24a** and ketone **25a** are secondary products and arise from **21a** and **22a**. However, high temperature (77 °C) bromination of compounds **18a** and **18b** gave only nonrearranged products **19** and **20** whose barrelene skeletons were preserved. It is our conclusion that the low temperature reaction is ionic, where in the high temperature reaction radical intermediates are involved. The mechanism for the formation of the products is discussed and is supported by computational calculations. The structures of **21**, **22** and **23** revealed that bromine approachs the double bond from the *endo*-face of the π-system. The reaction of **18a** with *m*-chloroperbenzoic acid gave only *endo*-epoxide **40**, which in turn supports also the *endo*-selectivity of the double bond in **18a** and **18b**. © 1997 Elsevier Science Ltd.

Introduction

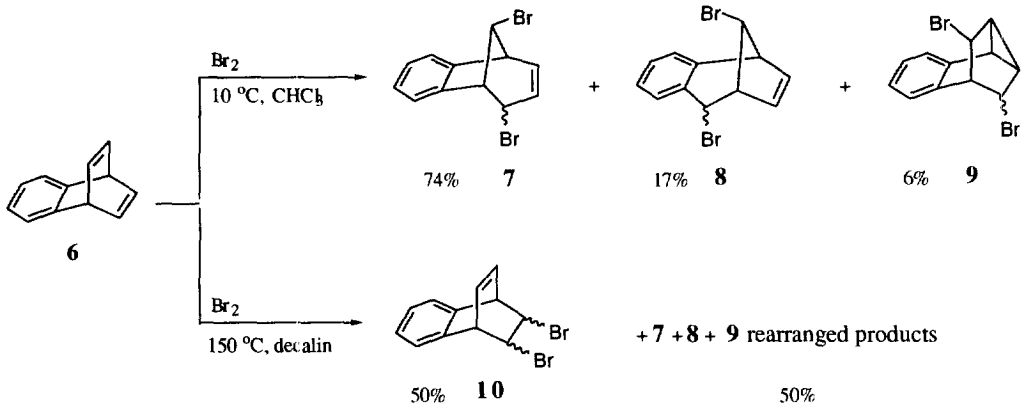
In connection with our continuing interest in high temperature bromination reactions of unsaturated bicyclic systems we recently noticed that the reaction temperature has a dramatic influence on the product distribution.[2]



Scheme 1

Bromination at room temperature or lower gave only rearranged products via Wagner-Meerwein rearrangement. However, bromination of these hydrocarbons at higher temperatures (80-150 °C), resulted in the formation of non-rearranged products. High temperature bromination seems to prevent skeletal rearrangement.

For example, the electrophilic addition of benzonorbornadiene (**1**)[3] at 10 °C gives **2** in almost quantitative yield . However, high temperature bromination at 150 °C, resulted in the formation of non-rearranged products **3-5** and rearranged product **2** in a ratio of 4:1 (Scheme 1).



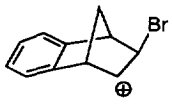
6

Scheme 2

Bromination of benzobarrelene[4,5] (**6**) at 10 °C provided six isomeric (*endo, exo*) dibromides **7-9** with rearranged skeleton. On the other hand, high temperature bromination provided 13 isomeric dibromides where the ratio of the rearranged and non-rearranged products was 1:1. Conducting the bromination reaction in the presence of free radical inhibitors suppressed the formation of the non-rearranged products.[3,4] This strongly supports the assumption that there is a competition between the radical and ionic mechanisms and that high temperature bromination is occurring by a free radical mechanism. Since radical intermediates are much less likely to rearrange, at higher temperatures we obtained more non-rearranged products. To explore why benzonorbornadiene gave more non-rearranged products (80%) in comparison to benzobarrelene (50%) when brominated at 150 °C, we have conducted AM1 calculations on the possible intermediates formed during bromination of **2** and **6**. Furthermore, we studied the bromination of homobenzobarrelene systems **18a** and **18b**, which contain barrelene skeletons where the double bond is blocked by a cyclopropane ring. The interesting feature of these compounds is that the cyclopropane ring will prevent the attack of bromine from the *exo*-face of the molecule, therefore this molecule can only be attacked from the *endo*-face of the π-system.

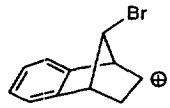
Results and Discussion

The bromonium ion **11** resulting from reaction of **1** with bromine (Scheme 1) undergoes Wagner-Meerwein migration of the benzyl group to form the rearranged cation **12**, which can be easily trapped by a bromide anion. AM1 calculations[6] show that the rearranged isomer **12** has a lower heat of formation (260.32 kcal/mol) than the primarily formed bromonium ion **11** (263.57 kcal/mol). This energy difference (ΔE = 3.3 kcal/mol) is most likely the driving force of the Wagner-Meerwein rearrangement. In the case of high temperature



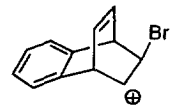
11

ΔH_f = 263.57 kcal/mol



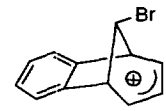
12

ΔH_f = 260.82 kcal/mol



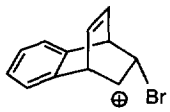
13

ΔH_f = 268.28 kcal/mol



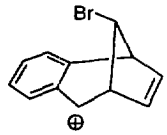
14

ΔH_f = 253.67 kcal/mol



16

ΔH_f = 268.60 kcal/mol



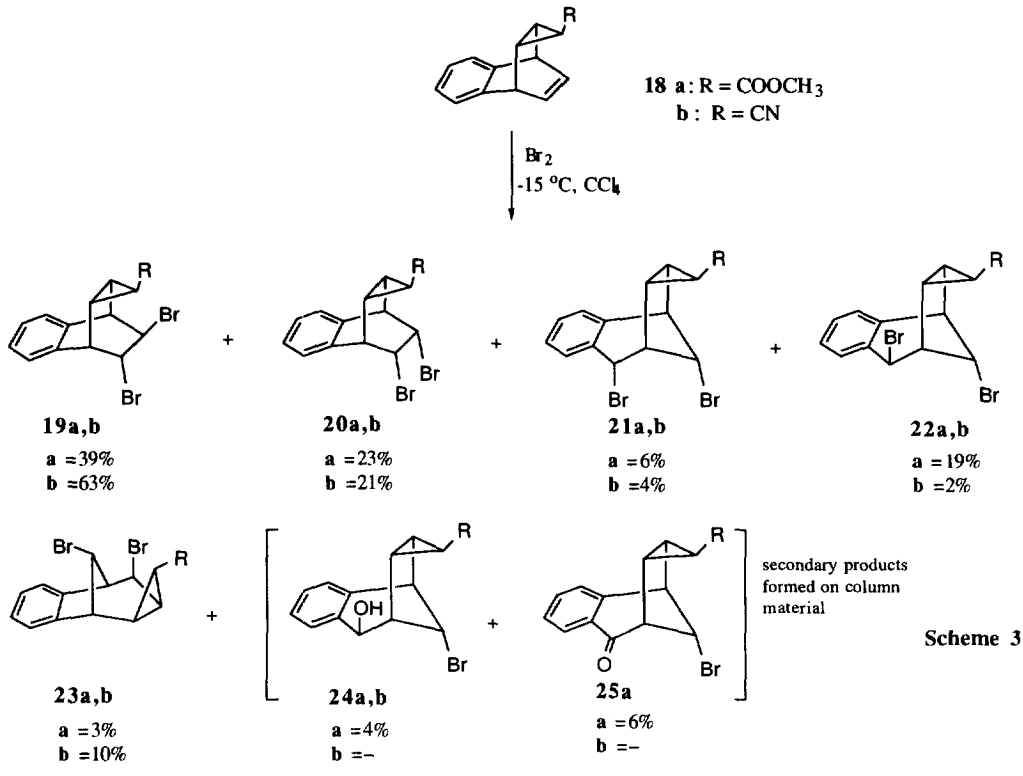
17

ΔH_f = 250.57 kcal/mol

bromination, we have established that the reaction goes primarily through radical intermediates.[1,3,4] Rearrangements are much less prevalent in radical chemistry than in the chemistry of cations.[7] Therefore, we assume that the change in the mechanism is responsible for the experimental outcome whereby high temperature bromination affords mostly nonrearranged products (80%).

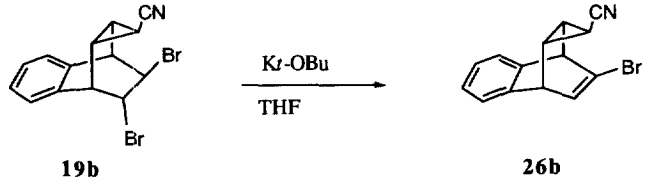
Once again the semi-empirical AM1 calculations were carried out with the benzobarrelene system. Comparison of heats of formation of the cation **13** (268.28 kcal/mol) with that of **14** (253.67 kcal/mol) shows that **14** is 14.6 kcal/mol more stable than **13**. This large energy gap can be explained by the formation of the stable allylic cation **14**. This energy difference is responsible for the fact that the bromination of **6** at higher temperatures can not completely suppress the formation of the rearranged products since there is a competition between ionic and radical reactions. The isomeric dibromides **8** can only be formed by *endo*-attack of bromine on **6**, followed by alkyl shift. The AM1 calculations indicate that **17** is 18 kcal/mol more stable than **16** because of the formation of a benzyl cation which increases the tendency of benzobarrelene system to undergo rearrangement.

In order to test the effect of the cyclopropyl group on the product distribution (the ratio of rearranged and non-rearranged products) we have studied bromination reactions of **18** at 0 °C and 77 °C. The homobenzobarrelene derivatives **18a** and **18b** were synthesized as described in the literature.[8] The reaction of **18** with bromine was carried out in carbon tetrachloride at 0 °C. The ^{1}H-NMR studies of the reaction mixture revealed that in both cases five products were formed (**24** and **25** were formed on column material). Carefully repeated fractional crystallizations combined with column chromatography allowed us to isolate all the formed products. According to the elemental analyses and mass spectral studies, they were isomeric dibromides **19-23**. IR analysis indicated that a hydroxyl group and a carbonyl group were present in compounds **24** and **25**, respectively. The exact configuration of these compounds (**19-25**) has been elucidated on the basis of their ^{1}H, ^{13}C NMR spectra, extensive double resonance experiments and by comparison of some spectral data of related systems reported in the literature.[4,9] Only isomer **20** had a symmetrical structure and exhibited an AA'BB'

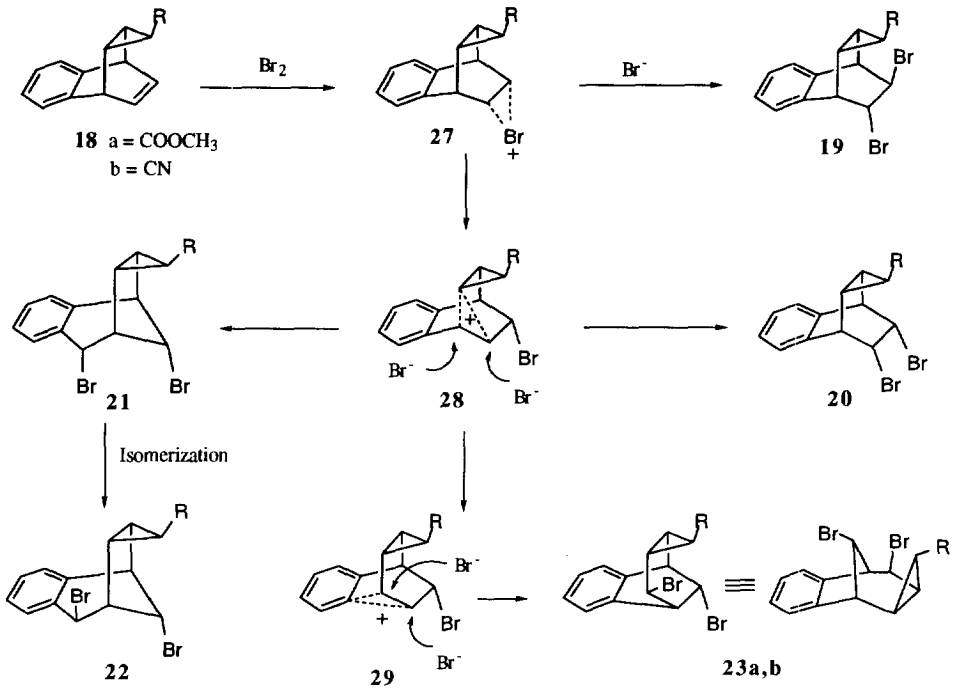


Scheme 3

system for the aromatic protons, which clearly indicates *syn*-addition of bromine. The configuration of bromine atoms (*exo* or *endo*) has been confirmed by differential ^{1}H-NMR Nuclear Overhauser Enhancement (NOE) studies. Irradiation of the cyclopropane proton HCCN at δ =1.99 caused enhancement of the HCBr proton resonances which is in complete agreement with the *endo*-orientation of bromine atoms. The *trans*-dibromide **19** was formed as the major product and whose spectral data supports the proposed structure. Furthermore, the structural assignment of compound **19** has been further confirmed by the *cis* elimination of HBr from **19b** using potassium *tert*-butoxide to give **26**. Gronert explained that *cis*-elimination could occur more readily than *trans*-elimination in the bicyclic systems.[10] This observation indicates that the original skeletal structure of benzobarrelene was retained following addition of bromine.



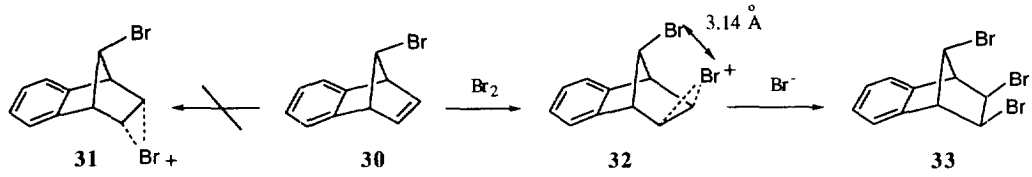
19b **26b** **Eq. 1**



Scheme 4

To rationalize the formation of these products, we propose the following reaction mechanism. The intermediates, strongly bridged bromonium ions, are involved in the bromination of nonconjugated olefins which usually give *anti* - adducts.[11] Bromine can attack the double bond in **18** from both the *endo*- and *exo* -face; however, the cyclopropane ring will prevent any approach from the *exo*-face. It is evident from the bromine configuration at the bridge in the rearranged products **21**, **22**, and the *endo,endo*-configuration of the bromines in **20** that the initial attack by bromine has occurred from the *endo*-face of the π-systems to give **27**. The most reasonable driving force for this mode of addition is due to the steric hindrance caused by the cyclopropane ring and by formation of alkyl bridged intermediate **28**. Bromide ions can then attack the intermediates **28** at two different positions to afford **20** and **21**, respectively. Furthermore, we found that dibromide **21** isomerizes during column chromatography to form the thermodynamically more favored isomer **22**. Therefore we can assume **22** is not a primary product formed during the actual bromination reaction. Dibromide **23** could arise from the *exo*-attack of bromine to **18** where an aryl shift *via* Wagner-Meerwein rearrangement is involved. Computational calculations disfavored the formation of an *exo*-bromoniumion **35** by 7-9 kcal/mol compared to *endo*-isomer **34** (Table 1). On the other hand, the configuration of the bromine atom at the bridge in **23** can not be in agreement with the initial formation of an *exo*-bromonium ion; in this case, the configuration should be reversed.

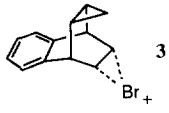
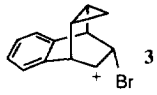
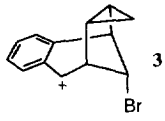
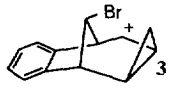
To elucidate the steric factors in halogen addition, Caple[12] studied the bromination reaction of 7-*anti*-bromobenzonorbornadiene. The bulky substituent at C-7 favors an *endo*-attack on C-5 and C-6. We have carried



Scheme 5

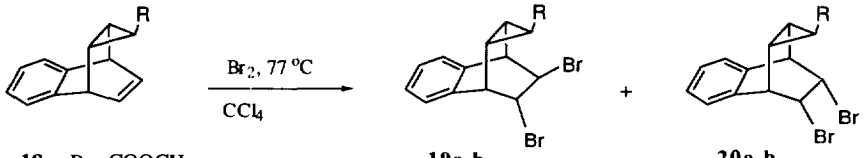
out AM1 calculations on both possible bromonium intermediates an found that the difference between heats of formations of *exo and endo*-intermediates was only 0.8 kcal (compared to **34/35** where it is 9 kcal/mol by AM1), which can explain the exclusive *exo*-attack. Therefore, we assume that this product has been formed by rearrangement of the *endo*-bromonium ion **28** to form the classical bromonium ion **29**, which then can undergo Wagner-Meerwein rearrangement where an aryl shift is involved. Subsequent capture of this cation **29** by bromide then provides dibromide **23**.

Table 1 Calculated total and formation energies of the intermediates **34-38**

Cations[13]	E_{tot} (kcal/mol)		ΔH_f (kcal/mol)	
	MNDO	MP2/STO-3G	MNDO	AM1
 **34**	-50008.262	-1906649.226	280.21	275.25
 **35**	-50000.766	-1906639.229	287.71	286.24
 **36**	-50009.862	-1906625.999	273.61	275.56
 **37**	-50039.183	-1906664.501	249.29	253.41
 **38**	-50025.554	-1906646.042	262.92	268.61

High Temperature Bromination: Finally, benzhomobarrelene derivatives were submitted to high temperature bromination. To a refluxing solution of benzhomobarrelenes **18a** and **18b** in carbon tetrachloride

was added a hot solution of bromine in carbon tetrachloride. In contrast to the reaction at 0 °C, it went to completion in 30 min. ^{1}H NMR analysis of the reaction mixture indicated the formation of the non-rearranged products **19** and **20** in a ratio of approximatel 3:2 (Eq 2).



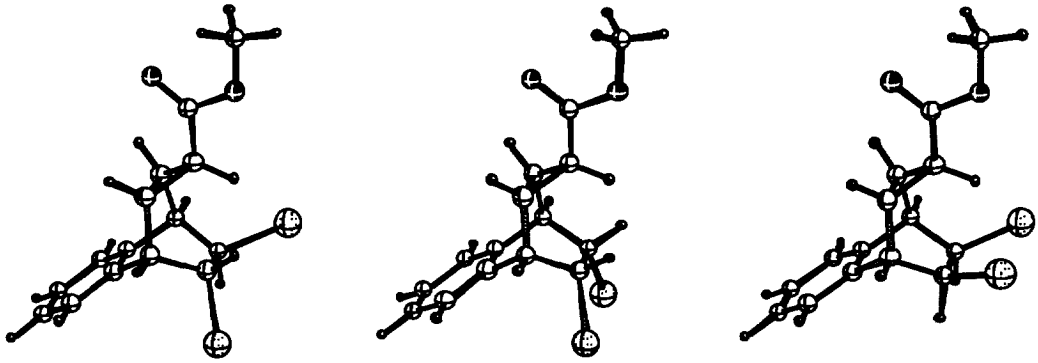
Eq. 2

18 a R = $COOCH_3$
b: R = CN

19a,b
a = 65%
b = 70%

20a,b
a = 35%
b = 30%

We assume that these dibromides are formed by a radical mechanism. Studies concerning the mechanism of *syn*-addition in bicyclic systems show that the *syn*-adduct can arise from direct collapse.[14] The fact that we do not observe any trace of Wagner-Meerwein rearranged products indicates that the *trans*-addition product **19** can also originate from the radical intermediates. The AM1 calculations and geometry optimizations on three possible isomers **19a, 20a** and **39a** indicate that the *exo,exo*-isomer **39** has the less stable structure (ΔH_f = -15.26 kcal/mol) whereas the other isomers *endo,exo*- **19a** and *endo-endo* **20a** have almost the same energies (-17.7 kcal/mol and -17.8 kcal/mol) (Figure 1). These results are well in agreement with the formation of **19** and **20.** It is not surprising therefore that *endo-exo* isomer **19** is the major product. Dipole-dipole interactions often force bromines to be as far apart as possible; for example, 1,2-dibromocyclohexane is more stable in the diaxial than in the diequatorial conformation.[15] In the case of the *endo-exo* orientation of the bromine atoms, the cyclopropane proton causes steric interaction with the *exo*-bromine atom.



19a
ΔH_{rel} = 0.0 kcal

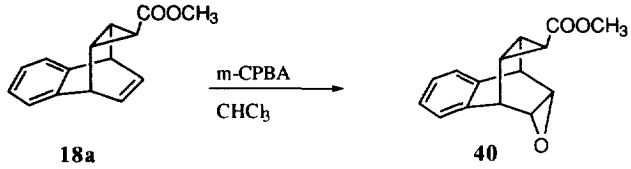
20a
ΔH_{rel} = 0.1 kcal

39
ΔH_{rel} = 2.6 kcal

Figure 1. AM1 optimized geometries and relative heats of formation of the three diastereomeric dibromides **19a**, **20a**, and **39**.

Epoxidation of compound 18a: To test the *endo*- and *exo*-selectivity of benzhomobarrelene derivatives[16] against other electrophiles, **18a** was reacted with *m*-chloroperbenzoic acid and dimethyldioxirane.[17] In both cases

we obtained only one epoxide, isomer **40**, whose configuration was established unambiguously by NOE-measurements. Irradiation of the cyclopropane proton at $\delta = 2.77$ caused an enhancement of the epoxide protons, which is only in agreement with an *endo*-orientation of epoxide rings. This finding also supports that attack by bromine to the double bond can occur only from the *endo*-face.



18a **40** Eq. 3

Conclusion

These experiments demonstrate that brominations carried out at high temperatures can occur with remarkable regiospecifity. Bromination of benzonorbornadiene (**1**) at 0 °C gives only one rearranged product. However bromination at 150 °C suppresses the formation of rearranged products and provides 80% nonrearranged products. Benzobarrelene also gives only rearranged products at 0 °C. High temperature reactions only partially suppress the skeletal rearrangement. Mechanistic studies[1,3,4] clearly indicate that there is competition between ionic and radical reactions at higher temperatures. In both cases, bromine attack to the double bond from the *exo*-face and gives aryl shift products. Calculations indicate that the energy difference in the benzobarrelene system by rearrangement (transformation of the [2.2.2] ring system into the [3.2.1] ring system) is much higher ($\Delta H_f = 14.6$ kcal/mol) than those in the case of benzonorbornadiene system since an allylic cation is formed. However, when benzonorbornadiene undergoes Wagner-Meerwein rearrangement whit the accompanying aryl shift, the [2.2.1] ring system is preserved and the cation formed is stabilized by only 2.6 kcal/mol. Therefore the tendency of benzobarrelene to undergo rearrangement is much higher than that of the benzonorbornadiene system. Blocking one of the double bonds in benzobarrelene by cyclopropanation in *exo*-position (**18a,b**) will not allow for the formation of an allylic cation, which is the driving force of the reaction. On the other hand, steric hindrance of the cyclopropane ring prevents *exo*-attack of bromine to the double bond (as established by epoxidation reactions). Therefore the probability for an Wagner-Meerwein rearrangement where an aryl shift is involved is minimized, especially at high temperatures where the reaction goes primarily by radical mechanism. However, at higher temperatures *endo*-orientation of the cyclopropane ring in **18** can eventually change the product distribution remarkably.

Experimental Section

General Methods: Melting points were determined on a Thomas-Hoover capillary melting point apparatus. Solvents were concentrated at reduced pressure. Infrared spectra were obtained from KBr pellets or from solution in 0.1 mm cells on Perkin-Elmer 337 Infrared recording spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on 200 (50) MHz Varian spectrometer and are reported in δ units with TMS as an internal standard. All column chromatography's were performed on silica gel (60-Mesh, Merck).

Bromination of 19a : To a solution of 680 mg (3.01 mmol) of **19a** in 40 mL of CCl_4 was added dropwise, over a period of 10 min, with stirring, a solution of excess bromine in 10 mL of CCl_4 at 0±2 °C. After stirring at the same temperature for 20 min.. the reaction mixture was allowed to stand for 20 h at -15±5 °C and the solvent was removed by rotoevaporation. The ^{1}H-NMR of the crude material indicated the existence of a complex mixture. The crystallization of the residue from $CHCl_3$/hexane gave **22a** (330 mg, 28%)[18]. The remaining crude product was chromatographed on silica gel (30 g) by eluting with hexane/ether (95:5).

1. fraction : ***trans*-Dibromide 19a:** (128 mg, 11 %) colorless crystals, mp 109-111 °C from $CHCl_3$/hexane; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.36-7.21 (AA'BB'-system, aromatic, 4H), 4.39 (m, *exo*-CHBr, 1H), 3,91 (m, *endo*-CHBr, 1H), 3.71 (s, OCH_3, 3H), 3.66 (m, bridgehead, 2H), 3.17 (t, 3.16 Hz, cyclopropane, 1H), 2.01-1.82 (m, cyclopropane, 2H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ = 172.19 (CO), 142.64 (C), 139.41 (C), 128.05 (CH), 128.00 (CH), 127.59 (CH), 124.66 (CH), 56.12 (CH), 53.07 (CH), 52.58 (CH_3), 45.05 (CH), 44.07 (CH), 31.82 (CH), 29.79 (CH), 26.36 (CH); (KBr, cm^{-1}) 3020, 3000, 2940, 1735, 1430, 1310, 1210, 1200, 1180, 1170, 935; Anal. Calcd.for $C_{15}H_{14}O_2Br_2$: C, 46.67; H, 3.66; Found: C, 46.65; H, 3.71.

2. fraction: **22a**: (220 mg, total 47%) mp 187-189 °C colorless crystals from $CHCl_3$/hexane; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.67-6.95 (m, aromatic, 4H), 5.89 (d, *J* = 4.7 Hz, *exo*-CHBr, 1H), 4.10 (t, 4.72 Hz, bridge, 1H), 3.67 (s, OCH_3, 3H), 3.25 (d, 4.32 Hz, bridgehead, 1H), 2.93 (t, *J* = 4.7 Hz, bridgehead, 1H), 2.50 (dd, A part of AB-system, *J* = 7.3, 3.1 Hz, cyclopropane, 1H), 2.18-2.12 (m, cyclopropane, 2H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 172.67 (CO), 140.63 (C), 134.44 (C), 132.04 (CH), 128.69 (CH), 128.56 (CH), 127.43 (CH), 54.85 (CH), 52.53 (CH_3), 49.70 (CH), 46.72 (CH), 46.13 (CH), 33.86 (CH), 25.91 (CH), 21.91 (CH); (KBr, cm^{-1}) 3060, 3000, 1750, 1470, 1440, 1330, 1285, 1230, 1200, 870, 830; Anal. Calcd. for $C_{15}H_{14}O_2Br_2$: C,46.67; H, 3.66; Found: C, 46.40; H, 3.56.

3. fraction : a mixture of **22a** and **23a** (20 mg, 1:1)

4. fraction: ***endo,endo*-Dibromide 20a** (70 mg, 6 %) mp 186-188 °C colorless crystals from $CHCl_3$/hexane; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.33 (s, aromatic, 4H), 4.52 (m, CHBr, 2H), 3.78-3.74 (m, bridgehead, 2H), 3.68 (s, OCH_3, 3H), 2.74 (t, *J* = 3.0 Hz, cyclopropane, 1H), 1.90 (m, cyclopropane, 2H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 171.76 (CO), 139.66 (C), 127.62 (CH), 127.42 (CH), 52.61 (CH_3), 50.09 (CH), 44.40 (CH), 29.85 (CH), 27.80 (CH); (KBr, cm^{-1}) 3020, 2955, 1740, 1435, 1320, 1220, 1190, 930, 865, 760, 700; Anal. Calcd.for $C_{15}H_{14}O_2Br_2$: C, 46.67; H, 3.66; Found: C, 46.65; H, 3.72.

Further elution with hexane/ether (85:15) furnished the ketone **25a:** (45 mg, 3 %) mp 137-138 °C colorless crystals from CCl_4; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 8.10-7.26 (m, aromatic, 4H), 4,25 (t, *J* = 4.5 Hz, bridge proton, 1H), 3.66 (s, OCH_3, 3H), 3.60 (d, *J* = 4.5 Hz, bridgehead, 1H), 3.38 (d, *J* = 4.5 Hz, bridgehead, 1H), 2.58 (t, *J* = 2.7 Hz, cyclopropane, 1H), 2.22 (dd, A part of AB-system, *J* = 7.3, 2.7 Hz, cyclopropane, 1H), 1.90 (dd, B part of AB-system, *J* = 7.3, 2.7 Hz cyclopropane, 1H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 194.67 (CO), 171.60 (CO), 145.37 (C), 134.38 (C), 131.22 (CH), 128.67 (CH), 128.60 (CH), 127.47 (CH), 55.70 (CH), 52.67 (CH_3), 48.31 (CH), 47.33 (CH), 34.81 (CH), 27.74 (CH), 26.52 (CH). (KBr, cm^{-1}) 3040, 2960, 1715, 1690, 1600, 1450, 1400, 1300, 1285, 1250, 1210, 1170, 850, 800, 755, 700, 560, 540; MS (m/z) 322/320 (M^+), 243/242/241 (3/10/62), 213/210/209 (3/8/60), 182/181 (100/21), 153/152 (39/39), 77/76 (26/54); Anal. Calcd. for $C_{15}H_{14}O_3Br$: C, 56.10; H, 4.08; Found: C, 55.76; H, 3,96.

Finally, elution with hexane/ether (70:30) gave the alcohol **24a** (60 mg, 4 %) pale yellow oil; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.61-7.05 (m, aromatic, 4H), 4.63 (bd, J = 12.1 Hz, OCH, 1H), 4.13 (t, 4.42 Hz, bridge, 1H), 3.67 (s, OCH_3, 3H), 3.31 (d, J = 4.4 Hz, bridgehead, 1H), 3.00 (bd, J = 12.1 Hz, OH, 1H), 2.91 (d, J = 4.4 Hz, bridgehead, 1H), 2.17 (t, J = 2.7 Hz, cyclopropane, 1H), 2.03 (dd, A part of AB-system, J = 7.5, 2.7 Hz, cyclopropane, 1H), 1,66 (dd, B part of AB-system, J = 7.54, 2.70 Hz, cyclopropane, 1H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 172.40 (CO), 139,02 (C), 136.95 (C), 131.15 (CH), 128.62 (CH), 128.38 (CH), 127.41 (CH), 72.81 (OCH), 52.67 (CH), 52.51 (CH_3), 46.55 (CH), 45.05 (CH), 33.98 (CH), 27.08 (CH). 24.76 (CH).

The initially formed isomer **21a** could not be isolated in a pure state because of its tendency to readily undergo isomerization to **22a**, and to hydrolysis on column material to form **24a**. However we were able to extract its NMR data from the mixture. **21a**; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.40-7.05 (m, aromatic, 4H), 5.43 (br s, endo, CHBr, 1H), 4.10 (t, J = 4.1 Hz, bridge, 1H), 3.9 (d, J = 4.1 Hz, bridgehead, 1H), 3.74 (s, OCH_3, 3H), 3.23 (d, 4.08 Hz, bridgehead, 1H), 2.32 (t, 2.85 Hz, cyclopropane, 1H), 2.08 (dd, A part of AB-system, J = 7.1, 2.9 Hz, cyclopropane, 1H), 1.93 (dd, B part of AB-system, 7.10, 2.85 Hz, cyclopropane, 1H).

Bromination of 18b: To a solution of 1.2 g (6.22 mmol) of **18b** in 30 mL of CCl_4 was added dropwise, over a period of 0.5 h, with stirring, a solution of 1.35 g (8.44 mmol) bromine in 10 mL of CCl_4 at 0±2 °C. The reaction mixture was allowed to stand for 20 h at -15±5°C and the solvent was evaporated. The ^{1}H-NMR spectrum of the crude material indicated the existence of a complex mixture. The crude material was filtered through a short silica gel (5 g) column. The crystallization of the mixture from $CHCl_3$/ether gave **19b** (760 mg). The residue was submitted to column chromatography (silica gel, 30 g) eluting with hexane/ether (90/10).

1. Fraction **19b** (50 mg, total 37 %); 2. Fraction **22b** (70 mg, 3 %); 3. Fraction **23b** (50 mg, 2 %) and **20b** (220 mg, 10 %).

***trans*-Dibromide 19b**; mp 205-207 °C colorless crystals from $CHCl_3$/ether; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.37-7.23 (m, aromatic, 4H), 4.28 (dd, A part of AB-system, J = 4.4, 2.6 Hz, *exo*-CHBr, 1H), 3.90 (ddd, B part of AB-system, J = 4.4, 3.0, 1.5 Hz, *endo*-CHBr, 1H), 3.70 (m, bridgehead, 2H), 2.97 (t, 3.52 Hz, cyclopropane, 1H), 2.07 (ddd, A part of AB-system, J = 9.8, 3.5, 5.3 Hz, cyclopropane, 1H), 1,94 (dddd, B part of AB-system, J = 9.8, 5.4, 3.5, 1.5, Hz, cyclopropane, 1H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 141.46 (C), 138.34 (C), 128.53 (CH), 128.49 (CH), 127.87 (CH), 124.94 (CH), 119.55 (CN), 55.14 (CH), 51.80 (CH), 44.48 (CH), 43.43 (CH), 30.43 (CH), 25.23 (CH), 13.54 (CH). (KBr, cm^{-1}) 3040, 2975, 2220, 1470, 1450, 1205, 1170, 1100, 995, 815, 755, 725, 565, 530; Anal. Calcd. for $C_{14}H_{11}NBr_2$: C, 47.63; H, 3.14; N, 3.97; Found: C, 47.32; H, 3.09; N, 3. 70.

***endo,endo*-Dibromide 20b**: mp 170-172 °C colorless crystals from $CHCl_3$/hexane; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.38-7.26 (AA'BB'-system, aromatic, 4H), 4.42 (m, CHBr, 2H), 3.81 (m, bridgehead, 2H), 1.99 (m, cyclopropane, 3H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 138.61 (C), 128.09 (CH), 127.68 (CH), 119.39 (CN), 49.00 (CH), 43.83 (CH), 27.80 (CH), 11.28 (CH); (KBr, cm^{-1}) 2940, 2220, 1430, 1410, 1275, 1100, 810, 700, 710, 500; Anal. Calcd.for $C_{14}H_{11}NBr_2$: C, 47,63; H, 3,14; N, 3.97; Found: C, 47,43; H, 3,25; N, 3,67.

22b : mp 156-158 °C colorless crystals from $CHCl_3$/hexane; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.65-7.00 (m, aromatic, 4H), 5.87 (d, J = 4.7 Hz, *exo*-CHBr, 1H), 3,97 (t, J = 4.7 Hz, bridge, 1H), 3.31 (d, J = 3.4 Hz ,

bridgehead, adjacent to benzene, 1H), 2.97 (t, J = 4.7 Hz, bridgehead, adjacent to *exo*-CHBr, 1H), 2.65 (dd, A-part of AB-system, J = 7.4, 3.1 Hz, cyclopropane, 1H), 2.26 (dd, B part of AB-system, J = 7.4, 3.1 Hz, cyclopropane, 1H), 1.87 (t, 3.0 Hz, cyclopropane, 1H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 139.34 (C), 134.07 (C), 132.13 (CH), 129.05 (CH, 2x), 127.63 (CH), 119.72 (CN), 53.94 (CH), 47.64 (CH), 46.17 (CH), 45.63 (CH), 32.26 (CH), 25.11 (CH), 5.82 (CH). (KBr, cm^{-1}) 3035, 2240, 1450, 1250, 1090, 835, 790, 760, 645.

23b : mp 136-137 °C colorless crystals from $CHCl_3$/hexane; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.34 (br s, aromatic, 4H), 4.65 (dd, *endo*-CHBr, J = 8.00, 2.1 Hz, 1H), 4.44 (s, bridge, 1H), 3,79 (d, J = 3.0 Hz, bridgehead, adjacent to cyclopropane, 1H), 3.66 (d, 2.12 Hz, bridgehead, adjacent to benzene, 1H), 2,32 (ddd, A part of AB-system, J = 3.0, 4.9, 8.8 Hz, cyclopropane, 1H), 2.96 (t, J = 4.9 Hz, cyclopropane, 1 H), 1.83 (ddd, B part of AB-system, 8.0, 4.9, 8.8 Hz, cyclopropane, 1H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 145.96 (C), 139.74 (C), 129.45 (CH), 129.12 (CH), 126.25 (CH), 124.33 (CH), 119.68 (CN), 59.25 (CH), 42.50 (CH), 47.77 (CH), 47.18 (CH), 35.69 (CH), 23.32 (CH), 13.11 (CH). (KBr, cm^{-1}) 3180, 3120, 3040, 2320, 1520, 1510, 1460, 1320, 1200, 925, 735.

The reaction of 19b with potassium *tert*-butoxide: To a solution of 510 mg (1.45 mmol) **19b** in 25 mL of abs. THF was added potassium *tert*-butoxide (290 mg, 2.59 mmol) and the resulting mixture stirred at room temperature for 1 day. To the reaction mixture was then added water (600 mL) and the aqueous phase extracted with $CHCl_3$ (2 x 50 mL). The combined organic layers were washed with water, dried, filtered and evaporated. The crude product **26** (370 mg, 94 %) was crystallized from CCl_4 mp 91-93 °C, colorless crystals; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.32-7.09 (m, aromatic, 4H), 6.35 (dd, J = 6.9, 2.45 Hz, olefinic, 1H), 4.28 (dd, J = 2.45, 4.0 Hz, bridgehead, adjacent to CBr, 1H), 4.19 (dd, J = 6.9, 4.0 Hz, bridgehead, 1H), 2.08-1.92 (m, cyclopropane, 2H), 1.70 (t, J = 3.3 Hz, cyclopropane, 1H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 143.38 (C), 143.14 (C), 131.26 (CH), 126.80 (CH), 126.30 (CH), 124.55 (CH), 124.27 (CH), 122.49 (C), 119.90 (CN), 50.82 (CH), 42.67 (CH), 25.99 (CH), 25.06 (CH), 11.64 (CH); (KBr, cm^{-1}) 3040, 2980, 2220, 1590, 1455, 1445, 1305, 1290, 1200, 1140, 1110, 760; Anal. Calcd for $C_{14}H_{10}NBr$: C, 61.79; H, 3.70; N, 5.15; Found: C, 61.46; H, 3,82; N, 4.96.

Bromination of 18a and 18b at 77 °C: Compound **18a** (**18b**) (452 mg, 2 mmol) was dissolved in 25 mL of CCl_4. While stirring magnetically, the solution was heated until the carbon tetrachloride began to reflux . To the refluxing solution was then added a hot solution of bromine (400 mg, 2,5 mmol) in 20 mL of CCl_4, dropwise over a period of five min. After refluxing for 30 min, the reaction mixture was cooled to room temperature and the solvent evaporated. ^{1}H and ^{13}C-NMR spectral analysis of the products indicated the formation of only two isomers **19a** (**19b**) and **20a** (**20b**), respectively in a ratio of 1:1.

Epoxidation of 18a with m-CPBA: To a solution of **18a** (226 mg, 2 mmol) in 20 mL of $CHCl_3$ was added *m*-chloroperbenzoic acid (2 g,) and $NaHCO_3$ (1.0 g). The resulting mixture was refluxed for 3 days. The reaction mixture was cooled, washed with dilute NaOH (60 mL), water (150 mL) and dried. The solvent was removed under reduced pressure. The residue was chromatographed (40 g, silica gel). Elution with hexane/ether (9/1) afforded the epoxide **40** (145 mg, 60 %) which was crystallized from ether/$CHCl_3$. mp 117-119 °C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.27-7.14 (AA'BB'-system, aromatic, 4H), 3.79 (m, bridgehead, 2H), 3.68 (s, methoxy, 3H), 3.29 (m, epoxide. 2H), 2.77 (t, 3.12 Hz, cyclopropane, 1H), 1.82 (m, cyclopropane, 2H); ^{13}C-

NMR (50 MHz, $CDCl_3$) δ 172.74 (CO), 139.85 (C), 127.27 (CH), 124.87 (CH), 52.39 (CH_3), 46.52 (CH), 36.39 (CH), 27.53 (CH), 25.74 (CH); (KBr, cm^{-1}) 3020, 2960, 1735, 1440, 1400, 1370, 1305, 1240, 1210, 950, 915, 845, 760, 650, 575; Anal Calcd. for $C_{15}H_{14}O_3$:C, 74.37; H, 5.82; Found: C, 73.64; H, 5.77.

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18. Yields given on Scheme 3 are determined by analysis of the NMR spectrum of the reaction mixture.

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