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Bromination of 2-Bromobenzobarrelene

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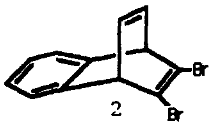
Abstract: Bromination of 2-bromobenzobarrelene **1** has been studied. Five bromine addition products **5**, **6**, **7**, **8**, and **9** have been isolated whose structural assignments were made on the basis of ^{1}H-, ^{13}C-NMR spectral data and X-ray structural analysis. The formation of the rearranged product has been discussed in terms of Wagner-Meerwein rearrangement.

Benzobarrelene is an intriguing compound in view of the di-π-methane rearrangement[2] which it undergoes. Triplet sensitized photolysis of benzobarrelene leads to semibulvalene. Di-π-methane rearrangement may occur by vinyl-vinyl or vinyl-benzo bridging[3]. However, deuterium labeling studies shows that the vinyl-vinyl bridging is mainly utilized by benzonorbornadiene[4]. Therefore, we are interested in disubstituted benzobarrelene derivatives **2**, **3**, and **4** which are intermediates for the synthesis of other benzobarrelene derivatives.

1



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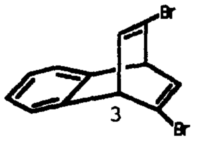

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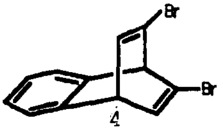

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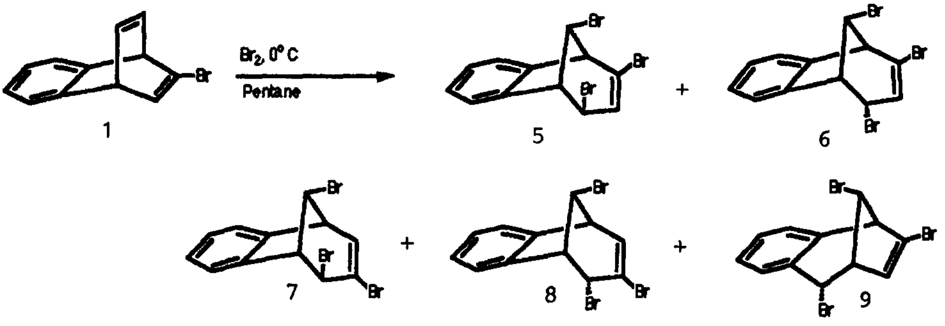
More recently, we succeeded in the synthesis of mono-[5] **1** and 2,3-disubstituted benzobarrelenes[6] **2**. As an extension of this work, we planned to synthesize benzobarrelene derivatives **3** and **4** in order to study the effect of different substituents in the same molecule on the mechanism of the di-π-methane rearrangement.



Scheme 1

Addition of bromine to the unsubstituted double bond in, if **1** giving unrearranged products, followed by HBr elimination should give a mixture of **3** and **4**. For this reason we reacted **1** with bromine. In this paper we describe our results.

The starting material **1** was prepared by our published method[5] starting from benzonorbornadiene and was subjected in pentane at 0 °C to bromination. The ^{1}H-NMR studies revealed that the reaction mixture was very complex and consisted of five products. As the major product formed, **5** was isolated by crystallization of the reaction mixture from pentane in a yield of 58%. The rest was subjected to repeated column chromatography and we isolated 4 additional products **6, 7, 8,** and **9** in a yield of 19, 3, 6, and 9%, respectively (Scheme 1). The structural assignments followed mainly from ^{1}H-NMR and ^{13}C-NMR spectral data[7]. The exo-configuration of bromine at C_8 in **5, 6, 7,** and **8** was determined on the basis of coupling constants between bridge proton H_8 and bridge head protons H_1 and H_5. As a consequence of the rigid geometries and the reliability of the Karplus rule[8] in bicyclo [3.2.1]octane systems[9], the dihedral relationship of the C-5-H (C-1-H) bond to an endo- (20°) to an exo-proton (90°) are sufficiently distinctive to be revealed by the magnitude of the spin-spin-interactions. Thus, the high value of the J_{18} and J_{58} in **5, 6, 7,** and **8** (J= 4.0-4.2 Hz) is uniquely accomodated by the exo-orientation (endo-configuration of bromine) of H_8. The configuration of the bromine at C_4 (in **5** and **6**) and C_2 (in **7** and **8**) was also determined from the coupling constatnts J_{45} (in **5** and **6**) and J_{12} (in **7** and **8**), respectively. We observe a large coupling constant (J = 4.6 and J=5.0 Hz for 6 and 8) in the case of endo-orientation of bromine and a small coupling for exo-orientation (J =1.2 and J< 0.7 Hz for **5** and **6**).

Finally, X-ray structure analysis of **5** and **7** (Figure 1) confirm these structural findings[10]. On the basis of these analysis we established also the correct structures of the other isomers **6** and **8**. We have isolated among the compounds an alkyl shift product **9** whose ^{1}H-NMR and ^{13}C-NMR spectra indicated the structure **9**. We were not able to isolate any trace of the desired nonrearranged products which could be precursors for **3** and **4**.

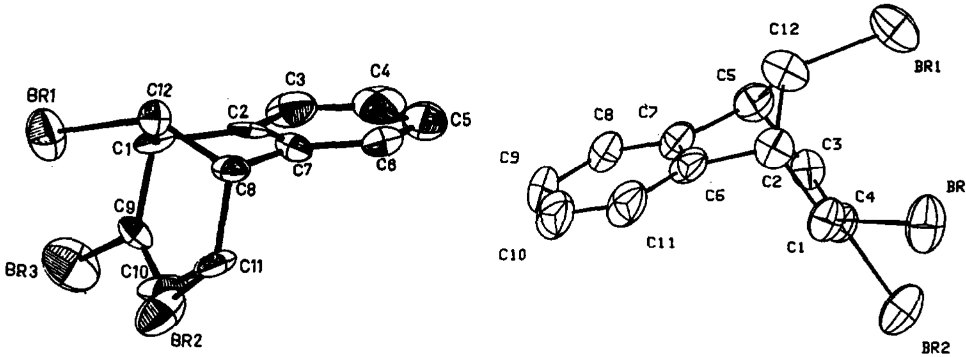
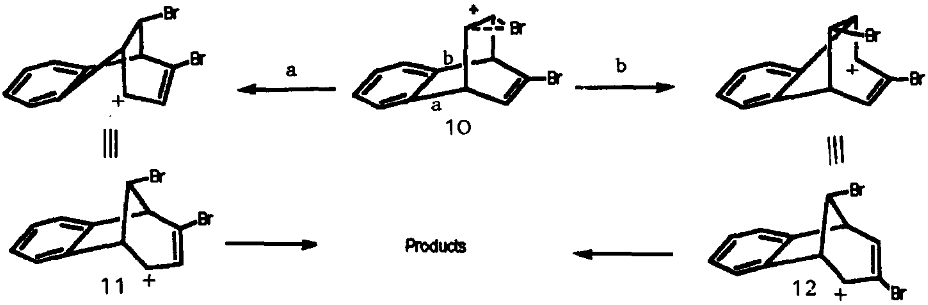


Figure 1. X-Ray crystal structures for **5** and **7**.

Electrophilic addition of bromine leads to a multiplicity of products as shown in scheme 1. Product analysis indicates clearly that bromine has added only to the unsubstituted double bond. It is known that bromine decreases the reactivity of a double bond towards electrophiles. Therefore, it is not suprising that we have isolated only addition products arising from the attack to the unsubstituted double bond. On the other hand, attack at the double bond may be endo or exo. Again, structural analysis shows undoubtedly that the main attack is from the exo face of the molecule giving the bromonium ion **10** which leads only to aryl shift products as **5**, **6**, **7**, and **8**. Only **9** arises from endo-attack. Since the exo-attack intermediate 10 is unsymmetrical, there are two possible aryl shifts involving aryl bonds "a" and "b". The fact that **5** was formed as the major product indicates clearly that the shift of the aryl bond "a" is predominating which can be explained in turns of mesomeric effect of the bromine atom which increases the stability of the cation **11** over **12**.



Scheme 2

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