

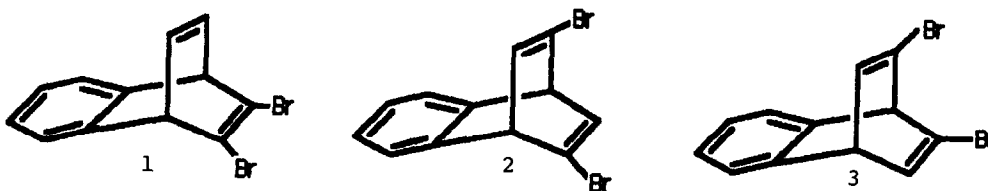
Synthesis of 2,3-, 2,5-, and 2,6-Dibromobenzobarrelenes High Temperature Bromination 1

*Osman Çakmak and Metin Balcı**

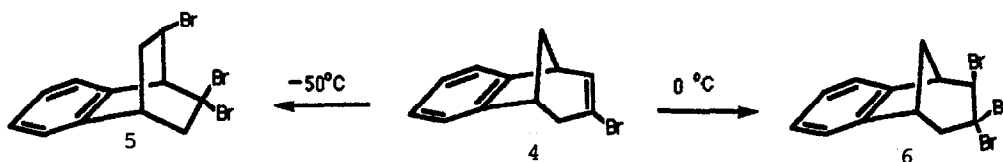
Atatürk University, Department of Chemistry, Faculty of Science, Erzurum Turkey

Abstract: 2-Bromobenzobarrelene **7** has been brominated at 78 °C. Four bromine addition products **8**, **9**, **10**, **11** with bicyclo [2.2.2] skeleton have been isolated whose structures were established on the basis of the ¹H- and ¹³C-NMR spectral measurements. The dehydrobromination of **8**, **9**, **10**, and **11** was achieved using potassium tert.-Butoxide and sodium methoxide to give 2,3-, 2,4-, and 2,5-dibromobenzobarrelenes, respectively.

Interest in our laboratory has been heavily focused on synthesis of disubstituted benzobarrelene derivatives **1**, **2**, and **3**, in order to study the effect of the different substituents¹ in the same molecule on the course of the di- π -methane rearrangement². For this reason we treat 2-bromobenzobarrelene^{1c,3} with bromine at 0 °C⁴ and obtained instead of the desired nonrearranged products only products with skeleton rearrangement.

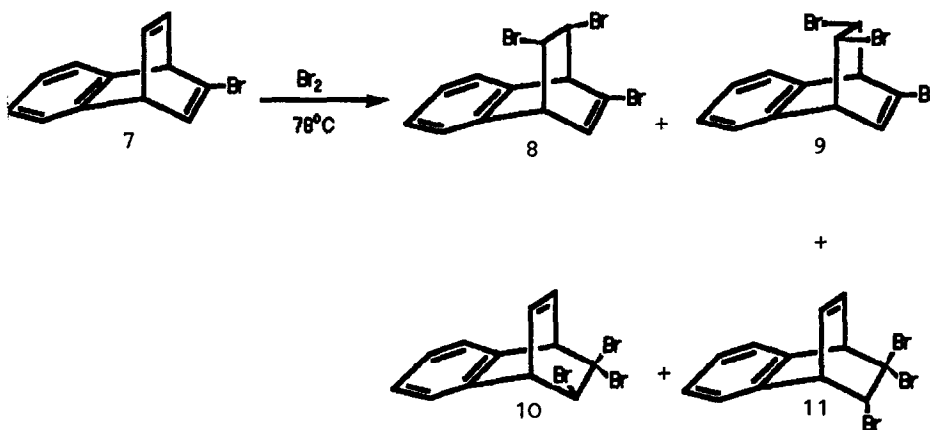


In the course of bromination⁵ of 3-bromo-6,7-benzobicyclo[3.2.1]octa-2,6-diene, we noticed that the reaction temperature has a dramatic influence on the product distribution. The bromination of **4** at -50 °C has been found to give only rearranged product, the tribromide **5** via Wagner-Meerwein rearrangement with accompanying aryl migration. The bromination at 0 °C produced nonrearranged tribromides besides the rearranged product (Scheme 1). In the light of this observation we treated **7** with bromine at high temperature (78 °C). In this paper we describe our results.



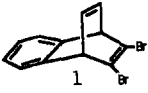
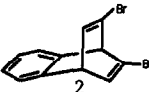
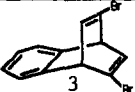
Scheme 1

To a refluxing solution of **7** in CCl_4 was added a hot solution of bromine in CCl_4 in one portion. The colour of the bromine disappeared immediately. After silica gel chromatography followed by fractional crystallization we isolated four products **8**, **9**, **10**, and **11** with non-rearranged skeleton (Scheme 2). ^1H - and ^{13}C -NMR studies have permitted structural assignments⁶. Furthermore, product analysis has indicated clearly that bromine has added to the both double bond in a ratio of approximately 1:1. By the addition of bromine to **7** at 0°C we observed completely regioselectivity. However, by the reaction at 78°C we can not see any regio- and stereo-selectivity. The formation of both stereoisomers **8** and **9** (**10** and **11**) does not give any indication of which of the two competing modes of endo- and exo-attack is preferred, since both isomers can be formed from endo-attack as well as from exo-attack. The different product distribution at 0°C and 78°C results from the life-time of the first formed intermediate, the bromonium ion. At 0°C the life time of the intermediate is increased so that the rearrangement can take place completely. However at 78°C bromide ion can attack the intermediate before rearrangement since the life-time of the intermediate is decreased.

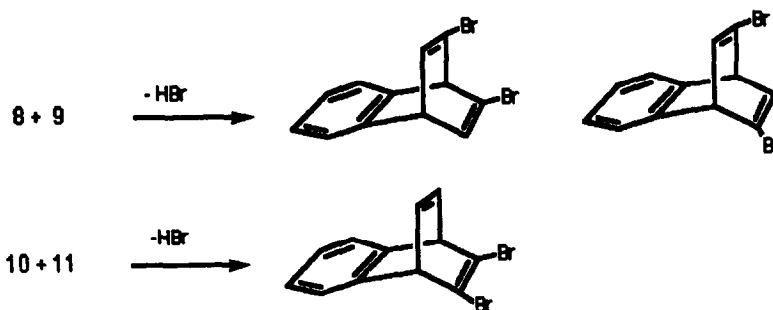


Scheme 2

Table 1. Selected Physical data of 1, 2, and 3.

	$^1\text{H-NMR}$	$^{13}\text{C-NMR}$	IR
	6.96-7.22 AA'BB'-system (4H, aromatic), 6.93 AA'-part, 4.95, BB'-part	144.54, 138.69, 129.41 124.58, 122.61, 58.56	1610, 1460, 1450, 1310 1260, 1215, 1185, 1060 980, 910
	6.94-7.3 m, (4H, arom.) 6.84 dd, 4.76, s, 4.75 dd	144.60, 144.41, 136.80 130.98, 125.13, 124.17 123.15, 122.39, 66.28 51.27	3070, 2980, 1580, 1460 1450, 1260, 1200, 1190 1130, 1090, 985
	6,91-7,16 AA'BB'-system (4H, aromatic), 6.83 AA'XX' system 4.63	144.48, 136.30, 132.44 124.67, 122.77, 59.2	3010, 2980, 1610, 1460 1450, 1260, 1250, 1240 1130

In the final step, the double dehydrobromination of a mixture consisting of 8 and 9 (or pure 8 and 9) was achieved with efficiency by using potassium tert.-butoxide. With 2 mol of potassium tert.-butoxide we isolated a mixture of dibromobenzobarrelenes 2 and 3 in a yield of 80% in a ratio of 1:1 which was separated by fractional crystallization (Scheme 3). The proton and carbon NMR spectra of 3 showed the expected symmetry in the molecule. The $^1\text{H-NMR}$ spectrum consists of an AA'BB' system (aromatic protons) and AA'XX' system arising from the bridgehead and the double bond protons. A six-line $^{13}\text{C-NMR}$ spectrum is in good agreement with the structure 3. The $^1\text{H-NMR}$ spectrum of 2 was also in agreement with the expected structure. Especially, a ten-line $^{13}\text{C-NMR}$ spectrum is also completely in agreement with the symmetry in the molecule. Dehydrobromination of 10 and 11 with sodium methoxide provided 1 in a yield of 98%.



Scheme 3

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