

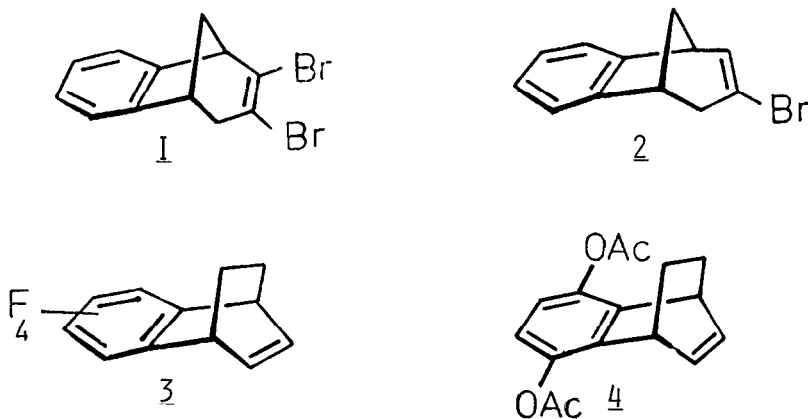
THE BROMINATION OF 3-BROMO-6,7-BENZOBICYCLO[3.2.1]OCTA-2,6-DIENE

Mansur Harmandar¹, Metin Balcı*

Faculty of Science, Department of Chemistry,
Atatürk University, Erzurum/TURKEY

Summary: The bromination of 3-bromo-6,7-benzobicyclo[3.2.1]octa-2,6-diene at -50°C has been found to give only one product, the tribromide(7) produced via Wagner-Meerwein rearrangement with accompanying aryl migration. The bromination at 0°C produced nonrearranged tribromides beside the rearranged product. The structures of the products were determined by means of spectral data. The addition mechanism is discussed in terms of exo- and endo-attack.

In connection with our studies on the bicyclic allenes and alkynes² we were interested in synthesis of (1). Therefore, we studied the bromination of 3-bromo-6,7-benzobicyclo[3.2.1]octa-2,6-diene (2).



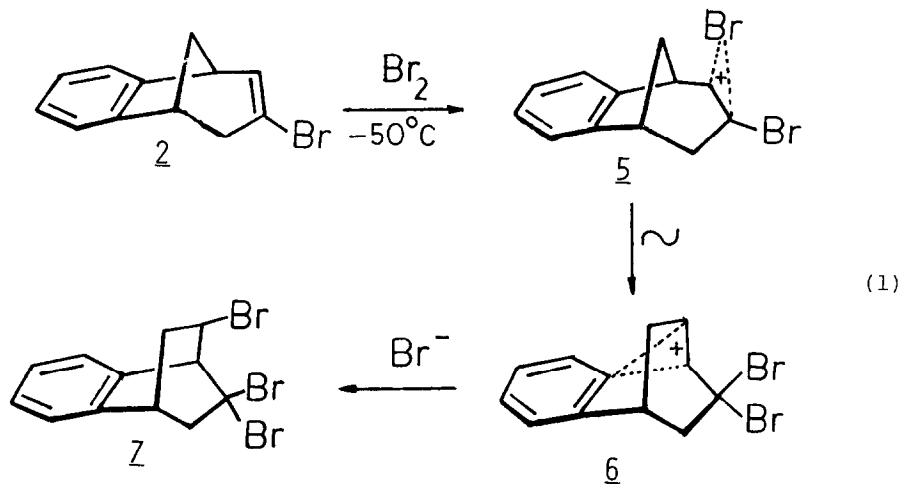
The addition of bromine to (2) may lead to a multiplicity of products. Attack on the double bond may be endo or exo. The intermediate may react with bromide ion to give nonrearranged product or undergo Wagner-Meerwein rearrangement involving either the aryl group or methano bridge before reacting to give rearranged tribromides.

In an earlier work, Barkhash et al. have examined the addition of bromine to tetrafluorobenzobicyclooctadiene (3) and the reaction was found to proceed without rearrangement³. However, the treatment of (3) with "acetyl chloride" (as tert.-butyl hypochlorite in acetic acid) gave completely isomerized product. More recently, Smith et al. have studied the addition of bromine to 5,8-diacetoxy-1,4-ethanonaphthalene (4) and obtained only one product, the bromide produced via a Wagner-Meerwein rearrangement with accompanying aryl migration⁴.

In the case of (2) one would not expect a competition between aryl and alkyl shift, since the later would produce a strained four-membered ring. On the other hand, the bromine does not allow analysis

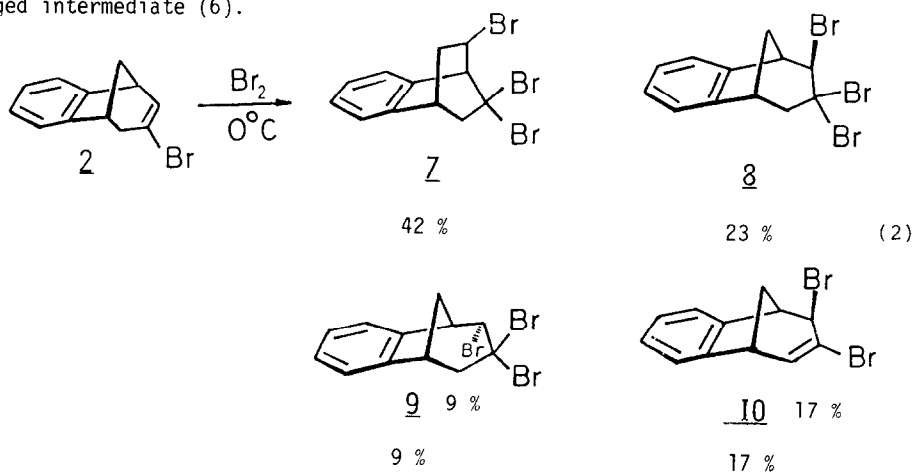
of which of the two competing modes of attack is preferred.

To this end, we prepared 3-bromo-6,7-benzobicyclo[3.2.1]octa-2,6-diene (2) by published method⁵ and subjected it in CHCl_3 to bromination at -50°C and 0°C . Surprisingly, we obtained completely different product distribution. From the reaction at -50°C we isolated a single tribromide (7) quantitatively.



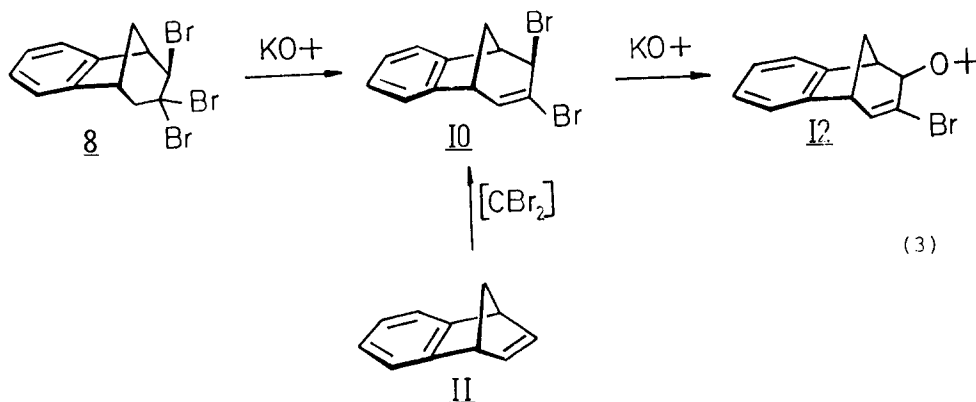
Assignment of the structure of the product was made by means of ^1H -, ^{13}C -NMR data and correct elemental analysis. A chemical proof for the structure was obtained by treatment of (7) with potassium tert.-butoxide to give 2-bromo-benzobarrelene⁶. Finally a single crystal X-ray analysis of (7) showed unambiguously its structure⁷.

It is evident from bromine configuration in (7) that initial attack by the bromine has occurred from the sterically least favored side of the π -system. There is no question that the hydrogen atom of the methano bridge can provide sufficient bulk to divert an incoming bromine preferentially away from the exo-face to the double bond. However, the fact that we obtained only the rearranged product shows this effect is clearly not overwhelming. Recent theoretical studies on the related systems revealed that electronic effects, like long-range homoconjugative stabilization⁸ and π/σ -interaction⁹ play an important role for determination of the origin of the exo-selectivity. Most reasonably the driving force for this mode of addition to exo-face is supplied by the formation of an arylbridged intermediate (6).

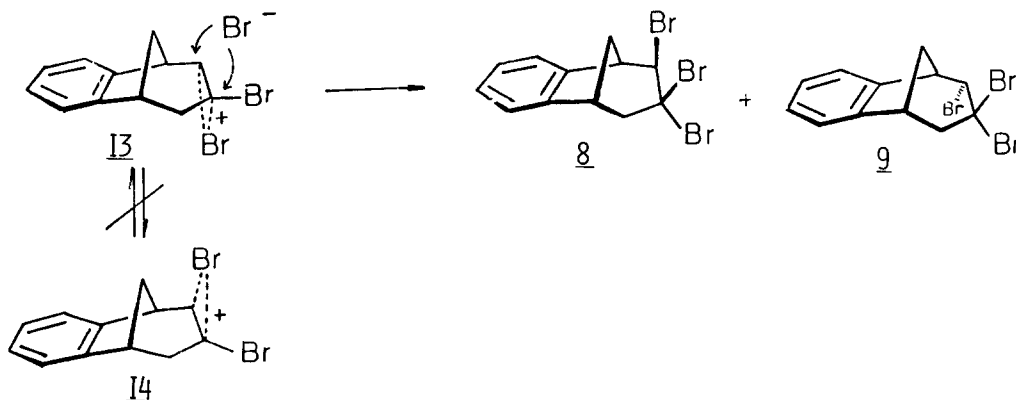


Surprisingly, the bromination of (2) was at 0°C. ¹H-NMR studies revealed that the reaction mixture was very complex. After repeated column chromatography we isolated four products. The identification of these products was no trivial task. As a major product we isolated (7) in a yield of 42%. The yields of the other products are given in Eq. 2. The structural assignments to (8) and (9) follow convincingly from their spectroscopic properties¹⁰. (10) was identified by comparison of the spectroscopic data with those of authentic sample⁵.

The position of the bromine in (8) could be established by means of chemical reactions. Treatment of (8) with one mol potassium tert.-butoxide gave the known exo-dibromide (10). With two mole potassium tert.-butoxide we isolated the ether (12) which is formed by displacement of bromine in exo-position. This reaction shows exactly that the third bromine in (8) has to be in exo-position.



There are two possible explanation for the reaction at 0°C. Bromine can attack the double bond from two sides. If exo-attack occurred predominately at 0°C to give a bromonium ion (5) that could rearrange by aryl-migration to give (6). In the case of endo-attack, the formed bromonium ion (13) can not rearrange, therefore can be opened by bromide ion to give (8) and (9). This would, of course, require bromonium ions that did not equilibrate as fast as rearrangement and intermolecular reaction with bromide.



An alternative way to explain this different product distribution at -50°C and 0°C is based on the exclusively formation of exo-bromonium ion. Since we increase the lifetime of the intermediate (5) at -50°C the rearrangement can take place completely. However, at 0°C the bromine can attack exo-intermediate (5) before rearrangement, since the lifetime of the intermediate is decreased.

A clear-cut differentiation between two possible mechanism can not be made at this stage. Further investigations are under way that might yield unequivocal evidence concerning the intermediate involved in the bromination reaction.

ACKNOWLEDGEMENT: The authors are indebted to the Department of Chemistry, Atatürk University for financial support of this work and wish to express their appreciation to Prof. E. Vogel, Dr. H. Schmickler (University of Cologne, W. Germany), Prof. H. Günther and Dr. J. Wessener (University of Siegen, W. Germany) for ^{13}C -NMR and Mass spectral measurements, and Prof. W. M. Jones and Prof. M. Battiste (University of Florida, USA) for helpful discussions.

REFERENCES

- 1) Department of Chemistry, Faculty of Education, Atatürk University, Erzurum.
- 2) a) M. Balcı, W.M. Jones, *J. Am. Chem. Soc.* 102, 7607, 1980.
b) M. Balcı, W.M. Jones, *J. Am. Chem. Soc.* 103, 2874, 1981
c) M. Balcı, M. Harmandar, *Tetrahedron Lett.* 25, 237, 1984.
- 3) N.N. Provolotskaya, T.I. Limasova, E.T. Berus, O. Exner, V.A. Barkhash, *J. Org. Chem. USSR (Engl. Transl.)* 39, 2264, 1969.
- 4) W.B. Smith, C. Saint, L. Johnson, *J. Org. Chem.* 49, 3771, 1984.
- 5) K. Kitahonoki, Y. Takano, A. Matsuura, K. Kotera, *Tetrahedron*, 25, 335, 1969.
- 6) M. Balcı, O. Çakmak, M. Harmandar, *Tetrahedron Lett.* following paper.
- 7) Ö. Ergin, M. Harmandar, M. Balcı, to be published.
- 8) a) L.A. Paquette, L.W. Hertel, R. Gleiter, M.C. Böhm, M.A. Beno, G.G. Christoph, *J. Am. Chem. Soc.* 103, 7106, 1981.
b) L.A. Paquette, F. Bellamy, G.J. Wells, M.C. Böhm, R. Gleiter, *J. Am. Chem. Soc.* 103, 7122, 1981.
- 9) a) R. Gleiter, M.C. Böhm, E. Vogel, *Angew. Chem.* 94, 925, 1982.
b) S. Inagaki, H. Fujimoto, K. Fukui, *J. Am. Chem. Soc.* 98, 4054, 1976.
c) L.A. Paquette, L.W. Hertel, R. Gleiter, M.C. Böhm, *J. Am. Chem. Soc.* 100, 6510, 1978.
d) K. Takahashi, K. Takase, T. Kagawa, *J. Am. Chem. Soc.* 103, 1186, 1981.
e) L.A. Paquette, P. Charumilind, *J. Am. Chem. Soc.* 104, 3749, 1982.
- 10) All new compounds were characterized by means of ^1H -, ^{13}C -NMR, mass spectral data and correct elemental analysis.

(Received in UK 24 July 1985)