Bromination of 2,3-dibromobenzobarrelene: a new and efficient synthesis of 2,3,5-tribromobenzobarrelene

Arif Dastan*

Department of Chemistry, Atatürk University, 25240 Erzurum, Turkey

J. Chem. Research (S), 2001, 463–464
J. Chem. Research (M), 2001, 1172–1179

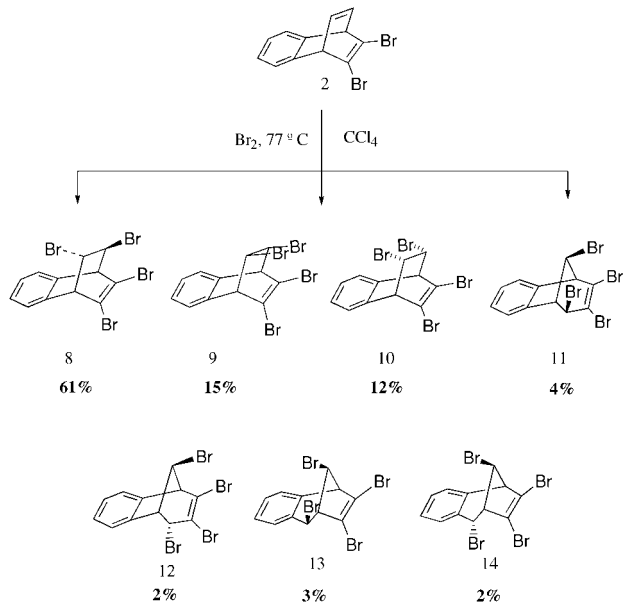
Bromination of 2,3-dibromobenzobarrelene at 77 °C was studied and 2,3,5-tribromobenzobarrelene was obtained in high yield. All compounds were characterised properly, especially by NMR spectra.

Keywords: bromination, benzobarrelene, tetrabromides

Benzobarrelene systems afford the possibility of several mechanistically interesting investigations. These compounds are intriguing in view of the di-π-methane rearrangement,[1-2] solvolytic reactivity[3-4] and versatile purposes.[5-8] In view of this aspect substituted benzobarrelene derivatives are important compounds that can provide information about how substituents present will influence the reaction modes.[9]

Therefore, short and efficient syntheses of these compounds are important. In this paper, bromination of 2,3-dibromobenzobarrelene **(2)** was investigated and a new and efficient synthesis for the preparation of 2,3,5-tribroromobenzobarrelene (**3**), which is a synthon for the synthesis of other tri- substituted benzobarrelenes and 2,3,5,6-tetrabromobenzobarrelene **(4)**, is reported.

The starting material 2,3-dibromobenzobarrelene **(2)** was prepared by published methods.[10-14] Bromination of 2,3-dibromobenzobarrelene **(2)** at low temperature gives[18] only rearranged products (**11–14**) via ionic intermediates. In the course of studying the bromination reaction it was noticed that the reaction temperature has a dramatic influence on the product distribution. Increasing the temperature gives non-rearranged reaction products.[19-24] This factor encouraged us take the bromination temperature higher in order to obtain the non-rearranged bromination products derived from **2**. For this reason, bromination of 2,3-dibromobenzobarrelene **(2)** at 77 °C in CCl_4 was studied. After column chromatography combined with crystallisation it was possible to separate seven compounds (Scheme 2). At higher temperature, the formation of non-rearranged addition products, which were not formed by the reaction at low temperature, was expected. NMR analysis indicated that all possible non-rearranged addition compounds **8–10** were formed as the major products.



Scheme 2

Bromination of bicyclic alkenes at low temperature gives only rearranged products.[3,19-23] Earlier we showed that bromination of these compounds at higher temperature gives mainly non-rearranged and a trace of rearranged products.[19-23] The formation of non-rearranged products at high temperature is explained by a radical mechanism. This could also explain our stereochemical results, including the formation of *cis* addition products. We also showed that there is a competition between a radical and ionic mechanism at high temperature.[19-20] In the light of these observations, we suggest that the non-rearranged products, **8–10**, are formed by a radical mechanism while the rearranged products, **11–14**, are formed by ionic intermediates at high temperature.

The structures of these compounds have been elucidated on the basis of ^1H and ^{13}C NMR data and extensive double resonance experiments and by comparison with some spectral data of related systems reported in the literature. A summary of the proton coupling constants exhibited by the closely related [3.2.1]octadienes is given in the experimental section.

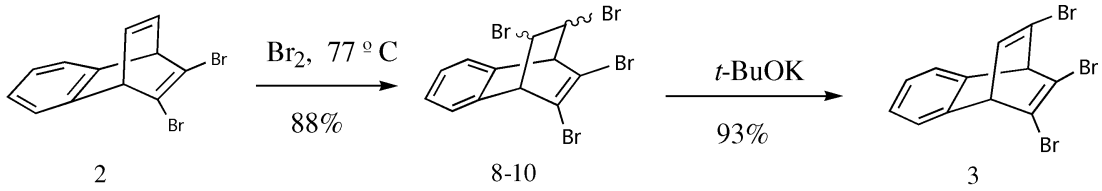
Both for the further support of the structures **8–10** and for the synthesis of 2,3,5-tribromobenzobarrelene **(3)**, either pure isomers or a mixture consisting of **8–10** were treated with potassium-*tert*-butoxide.[27] Compound **3** was obtained as a sole product in high yield (Scheme 3). This observation indicates that the original skeletal structure of 2,3-dibromobenzobarrelene was retained on addition of bromine. Also, this transformation affords us a new, shorter and efficient synthesis of 2,3,5-tribromobenzobarrelene **(3)**.

In summary, a new and effective synthetic methodology for the preparation of 2,3,5-tribromobenzobarrelene **(3)**, which can be further transformed into various tri-substituted benzobarrelenes and 2,3,5,6-tetrabromobenzobarrelene **(4)**,[14] has been developed. Further investigation of these types of reactions is currently under progress.

Caution: It has been reported[28] that of three laboratory workers who have used dibromides and a bromohydrin derived from norbornadiene, two later developed similar pulmonary disorders that contributed to their 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 must be handled only with extreme caution.

Received 25 May 2001; accepted 16 August 2001
Paper 01/895

* To receive any correspondence. E-mail: adastan@atauni.edu.tr



Scheme 3

References cited in synopsis

1 H.E. Zimmerman, *Rearrangements in Ground and Excited States*, ed. de Mayo, P. Academic Press, New York; 1980, Vol.3, Essay 16, pp. 131–164.
2 H.E. Zimmerman, R.S. Givens and R.M. Pagni, *J. Am. Chem. Soc*., 1968, **90**, 6096.
3 V.A. Barkhash, *Topp. Cur. Chem*., 1984, **115–117**, 1–265.
4 A. Menzek, *Tetrahedron*, 2000, **56**, 8505.
5 W. Adam, O. De Lucchi and I. Erden, *J. Am. Chem. Soc*., 1980, **102**, 4806.
6 I. Erden and A. de Meijere, *Tetrahedron Lett*., 1983, **24**, 3811.
7 N.J. Hales, H. Heaney and J.H. Hollinshead, *Tetrahedron*, 1995, **51**, 7411.
8 L.A. Paquette and W.E. Volz, *J. Am. Chem. Soc*., 1976, **98**, 2910.
9 R. Altundas and M. Balci, *Aust. J. Chem*., 1997, **50**, 787.
10 M. Balci, O. Cakmak and M. Harmandar, *Tetrahedron Lett*., 1985, **44**, 5469.
11 O. Cakmak and M. Balci, *J. Org. Chem*., 1989, **54**, 181.
12 O. Cakmak and M. Balci, *Tetrahedron Lett*., 1990, **31**, 2349.
13 M. Balci, O. Cakmak and T. Hökelek, *Tetrahedron* 1992, **48**, 3163.
14 M. Balci, O. Cakmak and T. Hökelek, *J. Org. Chem*. 1992, **57**, 6640.
18 A. Dastan, *Unpublished results.*
19 A. Dastan, M. Balci, T. Hökelek, D. Ülkü and O. Büyükgüngör, *Tetrahedron*, 1994, **50**, 10555.
20 A. Dastan, Ü. Demir and M. Balci, *J. Org. Chem*., 1994, **59**, 6534.
21 A. Dastan, Y. Taskesenligil, F. Tümer and M. Balci, *Tetrahedron*, 1996, **52**, 14005.
22 A. Tutar, Y. Taskesenligil, O. Cakmak, R. Abbasoglu and M. Balci, *J. Org. Chem*., 1996, **61**, 8297.
23 A. Menzek, N. Saracoglu, A. Dastan, M. Balci, and R. Abbasoglu, *Tetrahedron*, 1997, **53**, 14451.
24 A. Altundas, A. Dastan, M.M. McKe and M. Balci, *Tetrahedron*, 2000, **56**, 6115.
27 HBr elimination takes place via *syn*-elimination in molecule **34**. Gronert explained that *cis*-elimination could occur more readily than *trans*-elimination in bicyclic systems; S. Gronert. *J. Org. Chem*. 1994, **59**, 7046.
28 S. Winstein, *J. Am. Chem. Soc*., 1961, **83**, 1516.