Bromination of tricyclo[6.3.1.0^{2,7}]dodeca-2,4,6,10-tetraene derivatives: electronic and neighbouring group effects on bromination

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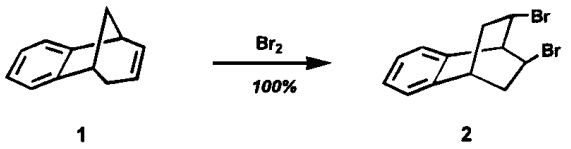
J. Chem. Research (S), 2002, 591–592
J. Chem. Research (M), 2002, 1233–1242

The bromination reactions of tricyclo[6.3.1.0^{2,7}]dodeca-2,4,6,10-tetraene derivatives have been studied and the possible role of a substituent in rearrangements was investigated.

Keywords: bromination, halogenation, Wagner-Meerwein rearrangement, neighbouring group effect, polybromides

Skeletal rearrangements in the reactions of benzocyclooctene systems have attracted a great deal of attention, particularly in relation to discussions about nonclassical carbonium ions.[2–12]

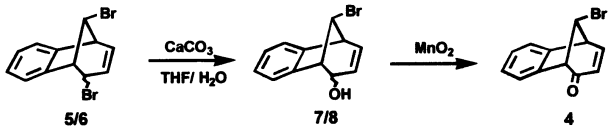
Earlier, Jefford and coworkers[13] showed that, during the bromination of homobenzonorbornadiene **(1)**, rearrangement of the skeleton was observed, and only dibromide **2** was formed. Later we also showed that bromination of **1** at 150°C in decalin gives mainly *non*-rearranged products.[10]



Scheme 1

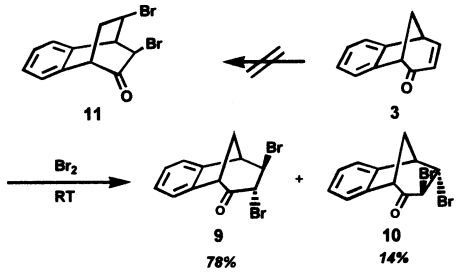
In the present work, we are interested in the bromination of ketone **3** and its monobromo derivative **4** in order to investigate the behaviour of electronic and neighbouring group effects on bromination in tricyclo[6.3.1.0^{2,7}]dodeca-2,4,6,10-tetraene systems.

Starting material **3** was synthesised by the procedure described in the literature.[14] The monobromoketone **4** was obtained by hydrolysis of dibromides **5/6**[8] and subsequent oxidation of the hydroxy bromides **7/8**[8] with MnO_2.



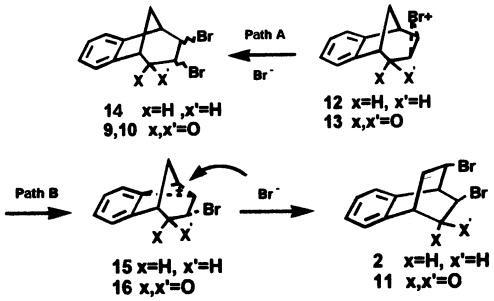
Scheme 2

Firstly, bromination of dibromide **3** in CCl_4 at RT was investigated and only *non*-rearranged products **9/10** were obtained.



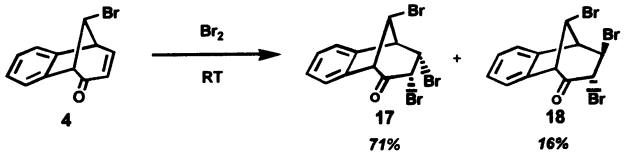
Scheme 3

From this reaction, the expected product **11** was not obtained. This result is, at first glance, surprising, since benzobicyclic systems are quite liable to Wagner-Meerwein rearrangement. This shows that the oxo analogue of **1** behaves differently in ionic additions. During the bromination of **1**, the *exo* bromonium ion **12** is formed. Opening of the halogenonium ion only takes place with the participation of the benzo-bromonium ion to form *non*-classical ion **15**, which is attacked stereospecifically from the *exo* side at C_1 (scheme 4). Opening of the ion **12** with the assistance of the attacking nucleophile (path A) to form a classical carbonium ion does not occur to any appreciable degree, since this would lead to the formation of a *trans*-dibromide with the same skeleton (*i.e.*, for **1**, path B favourable to path A). However, ketone **3** behaves differently in bromination reactions. This compound gives only *non*-rearranged products unlike **1**. The different product distribution in molecule **3** may be the result of the lifetime of the first formed intermediate, the bromonium ion **13**. In molecule **1**, the lifetime of the intermediate (**12**) is increased so that the rearrangement can take place completely. However, in molecule **3**, the bromide ion may attack the intermediate **13** before rearrangement, since the lifetime of the intermediate is decreased because of the electronegative oxygen atom (i.e., for **3**, path A favourable to path B).



Scheme 4

The bromination reaction of mono bromide **4**, which has an *anti* bromine atom at C_{12} carbon, was also studied in order to investigate the steric effect of *anti* substituent at C_{12} carbon on bromination in the tricyclo[6.3.1.0^{2,7}]dodeca-2,4,6,10-tetraene system. Bromination of compound **4** with molecular bromine in chloroform at RT leads to a reaction mixture consisting of two compounds (**17**/**18**). After crystallisation, we were able to separate the two compounds (Scheme 5).



Scheme 5

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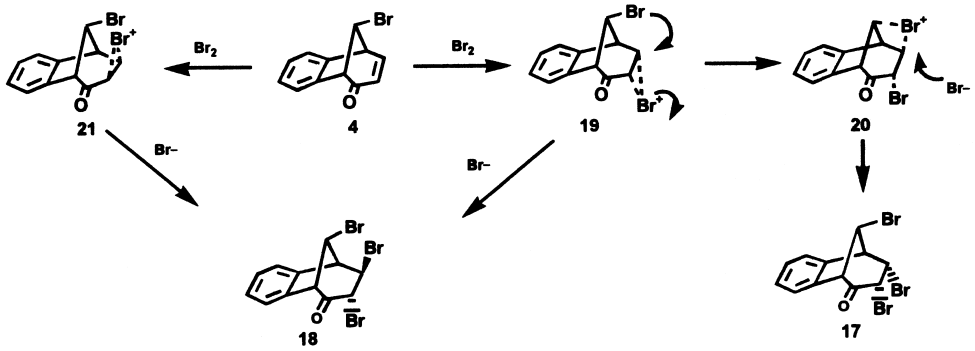

Scheme 6

The fact that the addition of bromine to the double bond in molecule **4** takes place exclusively from the *endo* side is extremely interesting. It is not possible to explain the formation of *endo-cis* tribromide **17** by the classical addition of bromine to the double bond. This unusual stereochemistry of the addition of bromine may be connected to steric hindrance from the side of the bromine atom at C_{12}, since neither **1** nor **3** gives a similar product. In our opinion, these results may be explained in the following way. In the *endo* attack of bromine on the double bond, the *endo* bromonium ion **19** formed is rapidly converted into ion **20**. This makes the approach of Br^- from the *endo* side more favourable. (Scheme 6).

In conclusion, the results of the present work demonstrate that benzobicyclo[3.21]octadienone systems do not tend to undergo skeletal rearrangement in bromination reactions, unlike other benzobycyclo systems. The electronic effects of the substituent cause this effect. Steric hindrance at C_{12} carbons also affects the stereochemistry of the products.

Caution: It has been reported[25] that of three laboratory workers who have used dibromides and a bromohydrin derived from norbornadiene, two later developed similar pulmonary disorders, which contributed to their subsequent 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.

The author is indebted to the Turkish Academy of Science (TÜBA) for financial support of this work (TÜBA-GEBİP) and assistant Dr Lokman Torun for providing necessary documents.

Received 20 March 2002; accepted 17 June 2002
Paper 02/1300

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