Solvolysis of 10,10-Dibromotricyclo[4,3,1,$0^{1,6}$]decane. Evidence for an Intermediate Bicyclo[4,3,1]dec-1(10)-ene Derivative

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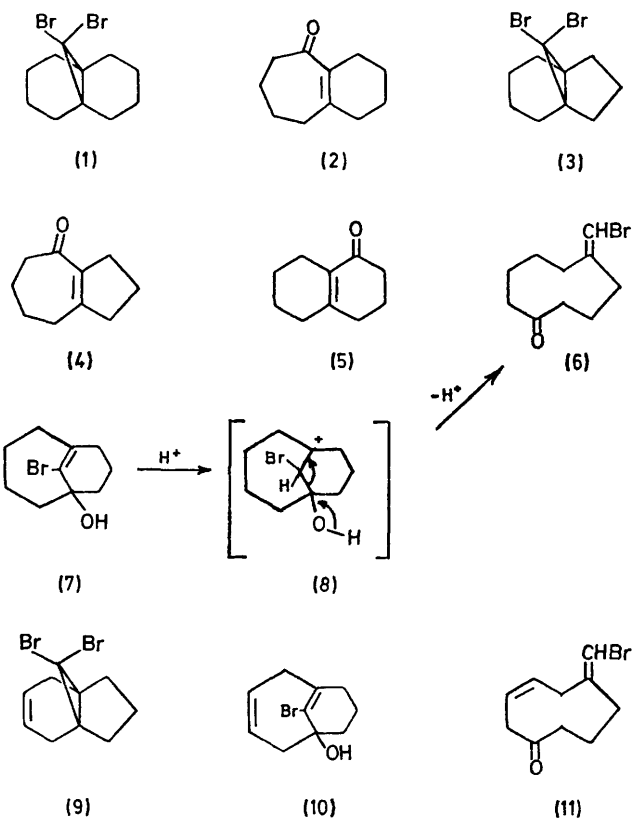
Summary Both (**3**) and (**9**) readily undergo Ag^+-promoted solvolysis in aqueous acetone solution to give monocyclic ketones [(**6**) and (**11**), respectively] as the major products; it seems likely that the latter compounds result from the fragmentation of highly-strained bicyclic intermediates [(**7**) and (**10**), respectively].

WE recently found[1] that (**1**) rapidly undergoes silver perchlorate promoted hydrolysis in aqueous acetone (5:95, v/v) solution at 20° to give (**2**) in good yield. This product (**2**), which has also been obtained[2] by treating (**1**) with silver nitrate in methanol solution, would appear to be formed by a mechanism involving a 1,2-alkyl shift. In order to ascertain whether a skeletal rearrangement occurs generally when the more usual ring-expansion reaction is unfavourable,[1] we have examined the solvolysis of 10,10-dibromotricyclo[4,3,1,$0^{1,6}$]decane (**3**).

When the latter compound (**3**), which was prepared in high yield by the catalytic hydrogenation of (**9**),[3] was subjected to Ag^+-promoted solvolysis under the conditions described above for the hydrolysis of (**1**), it was completely converted within 10 min into a mixture of 5-bromomethylenecyclononanone (**6**) (50%), bicyclo[5,3,0]dec-1(7)-en-2-one (**4**) (15%) and an unidentified product (<5%). The formation of (**4**), which was identified by comparison with authentic material,[4] is analogous to the formation of (**2**) from (**1**).† The major product was identified as (**6**) on the basis of its n.m.r. [τ ($CDCl_3$) 3·98 (1H, s), 7·5—8·3 (14H)], i.r. [ν_{max} (film) 1702s, 1618w cm^{-1}], and high resolution mass [Found: M^+ at m/e 230·0308. Calc. for $C_{10}H_{15}{}^{79}BrO$: 230·0307] spectra, and the elemental analysis of its 2,4,6-tri-isopropylbenzenesulphonylhydrazone,[5] m.p. 127—128° (decomp.).

It seems likely that (**6**) results from the fragmentation of a highly-strained intermediate, 10-bromobicyclo[4,3,1]dec-1(10)-en-6-ol (**7**), possibly *via* the carbonium ion (**8**). The intermediate (**7**) is the expected product of the normal Ag^+-promoted ring-expansion of (**3**) by a mechanism involving ionization of the bromine atom *endo* to the five-membered ring and concerted disrotatory opening of the resulting cyclopropyl cation in the allowed direction.[6] The instability of (**7**) can be explained in terms of its being a



† It is noteworthy that the isomeric ketone (**5**), which could have been formed from (**3**) by a mechanism involving the migration of the five-membered ring, was not detected in the products.

bridged *trans*-cycloheptene derivative rather than by invoking Bredt's rule.[7] It is especially noteworthy that the solvolysis of (**1**) does not lead to a similar fragmentation process. Attempts to trap (**7**) as a bicyclic adduct have so far been unsuccessful.

The Ag^+-promoted hydrolysis of (**9**) was also found to proceed rapidly at 20° under the above conditions and 6-bromomethylenecyclonon-3-en-1-one (**11**) (50%) was obtained as the major product. It seems likely that this reaction also proceeds *via* an intermediate bicyclo[4,3,1]-dec-1(10)-ene derivative (**10**). It would appear to follow from the sharpness of the bromomethylene proton resonances in their n.m.r. spectra that (**6**) and (**11**) are both pure geometrical isomers and thus that the fragmentation reaction is stereospecific.

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