Enhanced Solvolytic Reactivity of 1-Bromobicyclo[3.1.1]heptane: Intermediacy of a Stabilised Bridgehead Carbenium Ion

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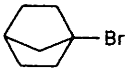
1-Bromobicyclo[3.1.1]heptane displays greater solvolytic reactivity than t-butyl bromide and produces a bridgehead carbenium ion which appears to be stabilised by transannular orbital interactions.

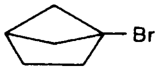
Previous workers have demonstrated the extreme reluctance of 1-bromobicyclo[2.2.1]heptane (**1**)[1] and, to a lesser extent, 1-bromobicyclo[2.1.1]hexane (**2**)[2] to ionise under solvolytic conditions. The former is essentially inert to hydroxylic solvents, and this has been attributed to the difficulty of generating a carbocationic centre at the bridgehead position because of geometric constraints. The lower homologue (**2**), while somewhat more reactive, undergoes solvolysis slowly in hot aqueous ethanol giving dienes, such as (**3**), which arise *via* a ring-opening process.

We now report that, in contrast with those observations, 1-bromobicyclo[3.1.1]heptane (**4**) is extraordinarily reactive under even mild solvolytic conditions; for example, when dissolved in methanol (**4**) is consumed rapidly at ambient temperatures ($T_{\frac{1}{2}}$ ~ 30 min at 25 °C). As a guide to its reactivity, we have found the bromide (**4**) to be at least 8 times more reactive than t-butyl bromide. The other interesting feature concerning the solvolytic behaviour of (**4**) is the observation that the product consists of a mixture (79% yield) of the isomeric ethers† (**5**), (**6**), and (**7**) in the ratio 3:4:2; dienes, such as (**8**), were not detected.

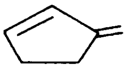
Formation of 1-methoxybicyclo[3.1.1]heptane (**5**) is quite remarkable because it requires the intermediacy of the bridgehead carbenium ion (**9**). Unlike the case of related species such as the 1-bicyclo[2.2.2]octyl cation (**10**) and the 1-adamantyl cation (**11**) which can accommodate positive charge at the bridgehead by relatively facile molecular distortion, geometrical modification of the more rigid 1-bicyclo[3.1.1]heptyl system (**9**) towards planarity at the bridgehead position is much more difficult. Indeed, as observed in the analogous 1-bicyclo[2.2.1]heptyl and 1-bicyclo[2.1.1]hexyl systems, the expectation was that production of the carbenium ion (**9**) from solvent-assisted ionisation of the bromide (**4**) would be energetically unfavourable. The unexpected enhancement in the stability of (**9**) may be attributed to the fact that it is a cyclobutyl carbenium ion and hence is likely to possess partial cyclopropylmethyl carbenium ion character [*e.g.* as in (**14**)]. Similar remarks would apply to the bicyclo[2.1.1]hexyl cation (**12**), however. An alternative explanation, which we prefer, is that the destabilising steric forces in (**9**) are counterbalanced by a favourable interaction, essentially one of homohyperconjugation, involving overlap



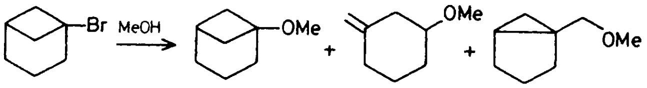
(**1**)



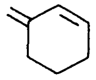
(**2**)



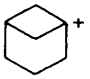
(**3**)



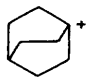
(**4**) (**5**) (**6**) (**7**)



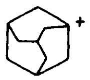
(**8**)



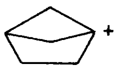
(**9**)



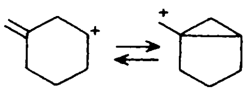
(**10**)



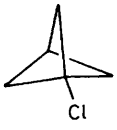
(**11**)



(**12**)



(**13**) (**14**)



(**15**)

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† All new compounds were characterised by elemental and spectral analyses, and the properties of known compounds were consistent with those reported.

of one lobe of the vacant orbital of the α-carbon with the back-lobe of the other bridgehead carbon–hydrogen bonding orbital. There does appear to be a delicate balance between these opposing effects because while the same kind of intra-annular orbital overlap is available to the bicyclo[2.1.1]hexyl cation (**12**) it does not appear to be powerful enough to overcome the greater strain inherent in the smaller system. It is noteworthy that although homohyperconjugation was suggested[3] to contribute to the stability of the 1-adamantyl cation (**11**), this view has met with some opposition.[4]

In view of the greatly increased stability of the cation (**9**) we speculate that it is the primary intermediate in the solvolysis of (**4**), and accordingly it is the precursor to the isomeric ethers (**6**) and (**7**) *via* the ring-opened species (**13**) and (**14**), respectively. Interestingly, the observed products of solvolysis are precisely those obtained (albeit in low yield) from methanolysis of [3.1.1]propellane.[5] However, by employing CD_3OD as solvent, we have shown by ^1H and ^2H n.m.r. analysis of the product that the propellane is not an intermediate in the solvolysis of (**4**); under these conditions the only point of incorporation of deuterium in (**5**), (**6**), and (**7**) was found to be at the methyl group. Had [3.1.1]propellane been a precursor to (**9**), and hence (**13**) and (**14**) also, deuterium would have been detected at C-5 in the ethers (**5**) and (**7**), and at C-1 in (**6**).

Finally, it is significant that some time ago Wiberg and Williams[6] observed that 1-chlorobicyclo[1.1.1]pentane (**15**) underwent rapid solvolysis in 80% ethanol. They attributed the enhanced solvolytic reactivity of (**15**) to the operation of a favourable interaction between the bridgehead carbon orbitals. Additionally, transannular interactions of this kind have been shown[7] to be important in determining the magnitude of nuclear spin–spin coupling constants in various derivatives of the bicyclo[*n*.1.1]alkanes.

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