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ACETOLYSIS OF EXO-BICYCLO[2.1.0]PENTANE-5-METHYL TOSYLATE; CYCLOPROPYLCARBINYL INTERMEDIATES IN SOLVOLYTIC REACTIONS[1]

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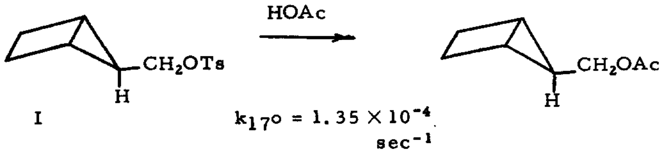
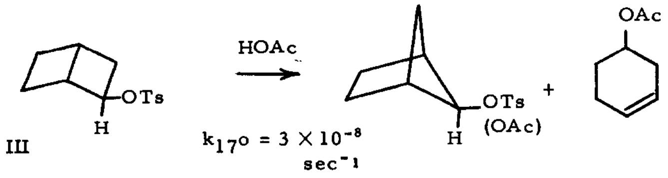
Among solvolytic reactions, those involving cyclobutyl, cyclopropylcarbinyl and allylcarbinyl derivatives lead to the largest degree of rate acceleration. This has been suggested to result from the intervention of a relatively stable "bicyclobutonium" ion intermediate.[2] In order to determine the structural requirements for the formation of this type of ion, we are examining two series of isomeric cyclobutyl, cyclopropanecarbinyl and allylcarbinyl compounds, having 6 and 7 carbons respectively. We[3,4] and others[5,6] have reported on the solvolytic reactivity of some of these compounds, and we now wish to present what we think is a particularly important observation concerning exo-bicyclo-[2.1.0]pentane-5-methyl tosylate (I).

The starting alcohol was prepared by the reaction of cyclobutene with diazoacetic ester, followed by lithium aluminum hydride reduction. The endo isomer was also formed, but could be separated by gas chromatography. The acetolysis result is:



Unlike the homologous exo-bicyclo[3. 1. 0]hexane-6-methyl tosylate (II)[4] little fragmentation to an allylcarbinyl derivative was noted. The rate of reaction is about one-fiftieth as fast as that of II, and 1.3 times as fast as that of cyclopropylcarbinyl tosylate.

McDonald and Reineke[5] have recently reported that exo-bicyclo[2. 2, hexyl-2 tosylate (III) on acetolysis gives largely bicyclo[2. 1. 1]-hexyl derivati



This is clearly a norbornyl type rearrangement, and cannot involve a bicyclobutonium type ion. The reason must be that the two four membered rings are forced to be essentially planar when fused to each other, preventing the formation of the bicyclobutonium ion. We believe this ion to have a geometry not unlike that of bicyclobutane, leading to approximately a 60° dihedral angle between the groups fused at adjacent carbons, and this appears to be supported b our data on compounds in which the cyclobutane ring is fused 1, 3 to another ri

The reaction of I cannot proceed via a bicyclobutonium ion since III does not find it possible to react via such an ion. The reaction of I is nevertheless accelerated, thus leading to the conclusion that a relatively stable cyclopropylcarbinyl cation is involved. Such an ion may be stabilized by the interaction of the empty p orbital at the carbinyl carbon with the bent ring orbitals. There is evidence supporting the view that this is the best geometry for interaction.[7,8] It is important to note that the cyclopropylcarbinyl cation requires a 0° dihedral angle between groups fused at adjacent carbons, leading to a much different structural requirement than the bicyclobutonium ion.

It has recently been shown that the dialkylcyclopropylcarbinyl cations are stable species in some solvents.[8] The present data show that the unsubstituted cyclopropylcarbinyl cations have at least a limited stability. This should have been anticipated from the several observations that cyclopropylcarbinyl derivatives are more reactive in solvolytic processes than are the corresponding cyclobutyl derivatives despite the fact that the latter are secondary whereas the former are primary. Since ring expansion from cyclopropyl to cyclobutyl provides little, if any, driving force for the reaction, some special feature of the cyclopropyl ring must be involved.

These conclusions also provide an explanation of the importance of the structures of the possible cyclopropylcarbinyl products[4] in the acetolysis of the bicyclo[3.2.0]heptyl-6 tosylates,[9] and for the observation that the norcaranyl acetate obtained from the above and from cycloheptenyl tosylate is a mixture of epimers.[4]

Several predictions may be made from the above conclusions. First, the fusion of a six membered ring 1,2- to a cyclobutane ring should favor the bicyclobutonium structure over the cyclopropylcarbinyl structure for the ion. Second, the *trans*- fusion of a five membered ring 1, 2- to a cyclobutane ring should favor the bicyclobutonium structure more than in the case of *cis*- fusion. These and related predictions are being tested.

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