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SOLVOLYTIC REACTIONS OF BICYCLO[3.1.0]HEXANE-6-METHANOL (1)

Kenneth B. Wiberg and Arthur J. Ashe III (2)

Department of Chemistry, Yale University

New Haven, Connecticut

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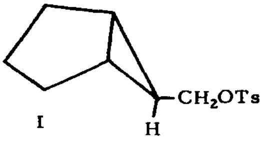
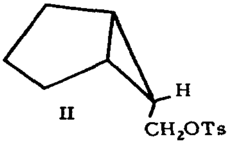
In connection with our interest in the participation of bicyclobutonium type ions in solvolytic reactions, and more specifically in the solvolysis of bicyclo[2.1.0]pentane-5-methanol derivatives, we have examined the reactions of the exo- and endo-bicyclo[3.1.0]hexane-6-methyl tosylates (I and II). The alcohols required for the preparation of

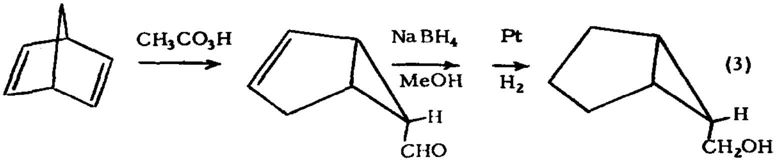


I

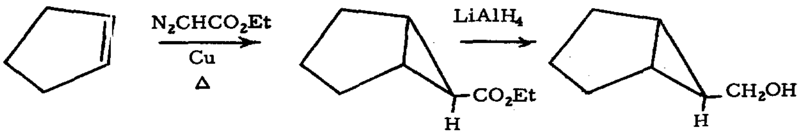


II

I and II were obtained as shown below:

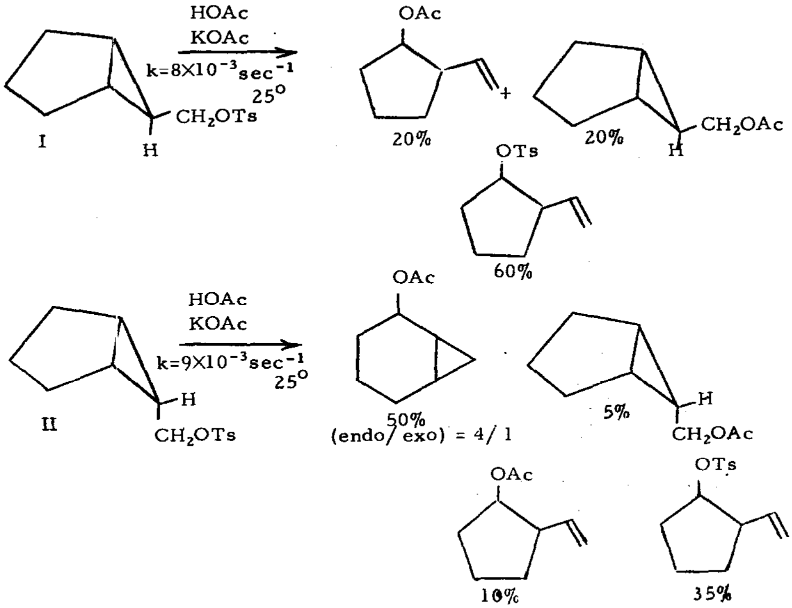


(3)



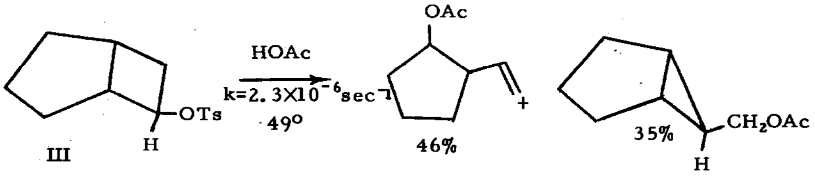
The reaction of cyclopentene with diazoacetic ester gave largely the *exo*-ester (exo/endo = 4 : 1). The *two* alcohols formed by reduction of the ester could be separated by gas chromatography and the one formed in smaller amount was found to be identical with that obtained in the sequence starting with norbornadiene.

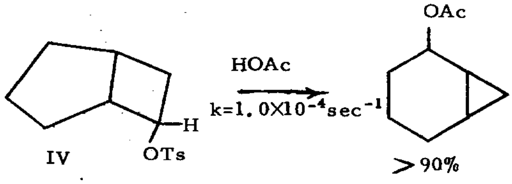
The tosylates were formed via the treatment of the corresponding alkoxide with *p*-toluenesulfonyl chloride. The rates of solvolysis and the products formed are indicated below:



It is interesting to note that whereas the rate constants are essentially the same for the two isomers, the products are quite different. Clearly, the course of the reaction is different for the two, whereas this might not have been expected.

It is interesting to compare the above results with those of Goering and Nelson (4) on the isomeric bicyclo[3. 2. 0]heptyl-6 derivatives. Their results are summarized below:



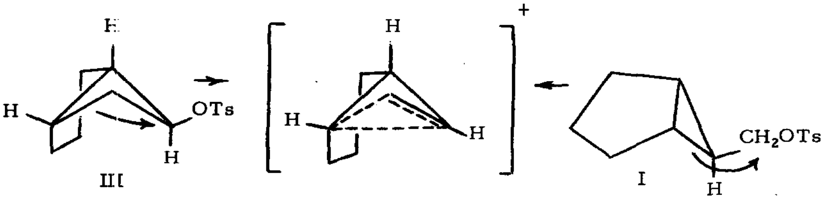


Except for the amount of internal return, the products derived from I and III are the same. The 2-vinylcyclopentyl tosylate undergoes solvolysis at a rate slightly greater than that of III. If it were formed in the solvolysis of the latter, it would not be observed in the products. Thus, it appears likely that the reactions of I and III proceed via the same ion.

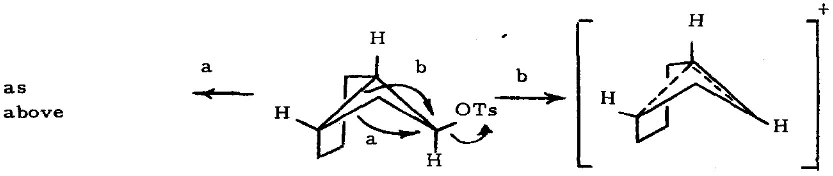
It is known that both cyclobutane (5) and cyclopentane (6) rings are normally puckered; therefore, the bicyclic structure should also be puckered. The cyclobutane ring will have pseudo-<u>axial</u> and pseudo-

equatorial positions. For a *cis*-ring fusion, one carbon of the cyclopentane ring must occupy an axial position and another an equatorial position. Thus, the tosyloxy group should control the conformation, and would probably be in the pseudo-equatorial position. We have previously shown that bicyclobutonium ion participation has a strong preference for a pseudo-equatorial tosyloxy group (7). Consequently, the preferred conformation is the one best suited for this type of participation.

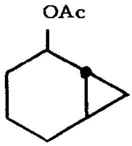
As shown below, both I and III could easily give the same bicyclobutonium type ion:



Whereas the symmetry of the cyclopropylcarbinyl compounds is such that only one possibility for forming a bicyclobutonium ion exists, the unsymmetrically substituted cyclobutanes may undergo reaction in either one of two ways as in the case of the isomer III

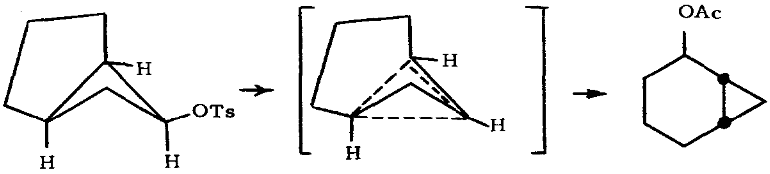


Ordinarily, reaction via path b might be expected to predominate since it leads to more highly alkyl substituted ion. However, in this case it leads to a badly strained structure, the trans-fused (2) norcaranyl acetate: (8)



Thus, path a predominates. This factor probably accounts for most, if not all of the rate difference between III and IV (note that III is only slightly less reactive than cyclobutyl tosylate).

The tosylates II and IV must, at least at first, lead to different ions. The reaction of IV, viewed in the terms described above, is quite normal with the intraannular bond participating in the ionization step. The ion thus formed is relatively strain free and leads to the cis-fused 2-norcaranyl acetate:



IV

It might be noted that the norcaranyl acetate may also be obtained from the corresponding homoallylic brosylate, cyclohepten-3-yl-1 brosylate (9). The difference between III and IV described above will also account for the difference in rate of solvolysis.

It is not possible for II to give directly the ion derived from IV.

It appears that II is one of a group of unique cyclopropyl carbinyl systems for which there is no corresponding cyclobutyl and homoallylic counterparts. The ion formed directly from II is sterically crowded, and apparently undergoes a fairly facile isomerization to the ion derived from IV. The tosylate II is also somewhat sterically crowded. It appears that this compensates for the crowding in the activated complex, leading to about the same rate of solvolysis for I and II.

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