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ACETOLYSIS OF Δ^4-CYCLOOCTENYL CARBINYL BROSYLATE AND ENDO 2-BICYCLO[3.3.1]NONYL BROSYLATE

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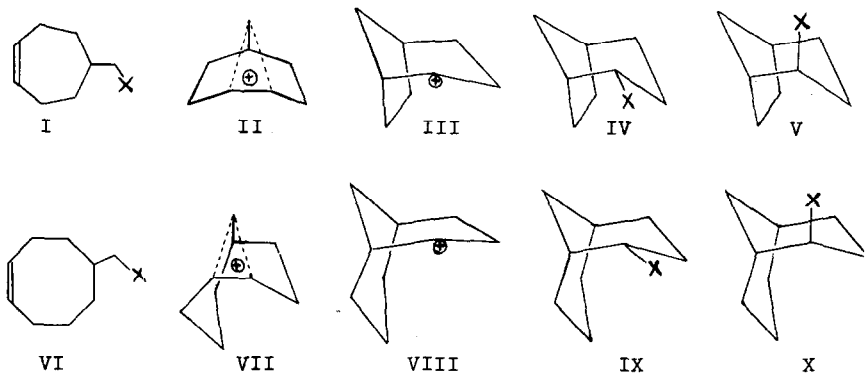
Cationic cyclisations involving double bonds are often concer-ed processes, and, in suitable systems, the double bond can pro-ide substantial driving force (1). Hanack and Kaiser (2), in n ingenious generalisation of earlier work on the next lower omologue I (X = OBs) (3), have observed that the acetolysis of ^{4}-cyclooctenyl carbinyl tosylate VI (X = OTs) at 60° is 50 times aster than that of the corresponding saturated compound and ffords essentially a 2-bicyclo[3.3.1]nonyl acetate which, on echanistic grounds, is obviously the endo acetate IX (X = OAc). n an important recent paper, Cope, Nealy, Scheiner and Wood 4) have shown that, perhaps not unexpectedly, acetolysis of the orresponding brosylate VI (X = OBs) also leads mainly to the ndo acetate IX (X = OAc).

Our own results with this brosylate are also in fair agree-

ment with those mentioned above: it is acetolysed (in AcOH-AcO⁻ at 80°) 70 times faster than the corresponding saturated compound and 346 times faster than isobutyl brosylate (5), and the acetate fraction* is composed mainly (91%) of the endo acetate IX (X = OAc), the remainder being exo acetate X (X = OAc) (8%) and 1% of another acetate**.



These results are very similar to those obtained previously with the lower homologue I (X = OBs) (3, 5), the acetolysis of which (under the same conditions) is 62 times faster than

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* The acetate fraction compositions mentioned in this paper were deduced from the compositions of the corresponding alcohol fractions obtained by treatment of the acetolysis products with lithium aluminium hydride. These alcohol fractions were analysed by gas chromatography on diglycerol, and their constituents were identified by their retention times and, in the case of the major (>10%) constituents, by comparison (IR) with authentic sample

** This may be a 2-bicyclo[4.2.1]nonyl acetate (2, 4).

that of the corresponding saturated compound and 251 times faster than that of isobutyl brosylate, and affords an acetate fraction composed mainly (93%) of the endo acetate IV (X = OAc), the remainder being exo acetate V (X = OAc) (4%) and an acetate which can safely be assumed to be 2-bicyclo[2.2.2]octyl acetate (3%). The major product-forming intermediate* in this reaction is probably the bridged, non-classical, ion II (3, 6), and this ion is probably also the intermediate in the acetolysis of the bicyclic brosylate IV (X = OBs), which has been shown to lead exclusively to the endo acetate IV (X = OAc) (6, 7).

Cope, Nealy, Scheiner and Wood (4) have made the interesting suggestion that the homologous bridged ion VII is the product-forming intermediate in the acetolysis of VI (X = OBs). If this were so, then the acetolysis of the bicyclic brosylate IX (X = OBs) would be expected to proceed via the same intermediate and hence to afford predominantly the same acetate IX (X = OAc), just as the lower homologues I and IV (X = OBs) afford upon acetolysis the same acetate IV (X = OAc).

We have found that the composition of the acetate fraction obtained (under the same conditions) from IX (X = OBs) is, in fact, strikingly different: only 45% of the endo acetate IX (X = OAc) is present, and this is accompanied by 46% of the exo epimer X (X = OAc); two other acetates (8% and 1%) are

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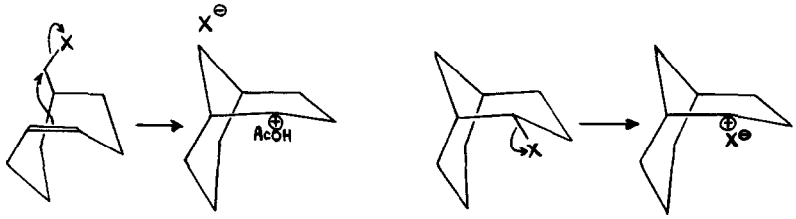
* The fact that the endo acetate IV (X = OAc) is not the only acetate formed from I (X = OBs) indicates that the bridged ion II cannot be the only intermediate, and it is now apparent from Berson's work (8) that systems involving bicyclooctyl cations are much more complex than was originally suspected.

also formed. In other words, whereas the ratio [endo acetate IX (X = OAc)]/[other acetates] is greater than ten in the product from the olefinic brosylate VI (X = OBs), it is only about one in the product from the bicyclic brosylate IX (X = OBs); this appears to preclude the bridged ion VII as an important intermediate in the acetolysis of IX (X = OBs), and casts some doubt upon its rôle in the acetolysis of VI (X = OBs).

Apart from rather superficial analogies with the endo 2-bicyclo[3.2.1]octyl system, there seems to us to be no reason for supposing that the bridged, non-classical, ion VII is more stable, or more readily formed, than the classical 2-bicyclo [3.3.1]nonyl cation VIII. The double chair conformation (cf.IX) has been shown to be the preferred conformation of the bicyclo[3.3.1]nonane system (9); the system is not strain-free on account of the close proximity between carbons 3 and 7, and both the chairs are flatter than in cyclohexane. In the classical cation VIII, the ring with the trigonal carbon must be flatter still, thus relieving the strain between carbons 3 and 7 and at the same time allowing the other six-membered ring to adopt a more perfectly staggered conformation; in the bridged ion VII, on the other hand, although the strain between carbons 3 and 7 is relieved, both the six-membered rings are distorted. It will be observed that the situation is the reverse in the 2-bicyclo[3.2.1]octyl system: strain between the eclipsed hydrogens on carbons 6 and 7 in the classical cation III is relieved on going to the bridged ion II. Berson (8) has shown, however, that, despite this, the stability of the classical endo 2-bicyclo[3.2.1]octyl cation III is not significantly lower than that of the bridged ion II. It follows that the stability

of the classical 2-bicyclo[3.3.1]nonyl cation VIII (which is less strained) is in fact expected to be significantly higher than that of the bridged ion VII.

Furthermore, the acetates formed from both VI (X = OBs) and IX (X = OBs) can be accounted for as follows on the basis of the classical cation VIII as the major product-forming intermediate in both reactions. When this ion is formed (with double bond participation) from the unsaturated brosylate VI (X = OBs), it is not protected on the endo side by the departing anion, and this side is open to preferential solvation (VIIIa);



VI VIIIa IX VIIIb

this leads essentially to the endo acetate IX (X = OAc). When the same ion is formed from the endo bicyclic brosylate IX (X = OBs), however, the endo side is protected to some extent by the departing anion (VIIIb), and a large proportion of exo acetate X (X = OAc) is formed*.

The present data do not, of course, prove that the bridged ion VII is not involved at all in the reactions discussed, but they do suggest that with the 2-bicyclo[3.3.1]octyl system we are approaching the end of a graded series (8) of bicyclic car-

* A somewhat similar reasoning has already been used in a somewhat similar case (10).

bonium ion behaviour.

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