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A CLASSICAL NORBORNYL CATION

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The overwhelming predominance of exo substitution, which occurs in solvolysis reactions of norbornyl tosylates, has been a topic of considerable importance in discussions (1-3) of the classical versus non-classical norbornyl cation. In considering the products of solvolysis of norbornyl tosylates, Berson (1) and Winstein (2) have used the exclusive exo substitution, which occurs even in norbornyl derivatives containing gem-dimethyl groups in the 7-position, as evidence for the existence of a delocalized ion which shields the endo side of the molecule from nucleophilic addition of solvent. Alternatively, Brown (3) has used the exclusive exo addition of solvent to certain tertiary norbornyl cations, which he presumes to be classical in nature, as a basis for questioning the use of product stereochemistry as evidence for the intermediacy of non-classical carbonium ions in the solvolysis of bicyclo[2.2.1]heptyl tosylates.

In view of the prominent position afforded to discussions of product stereochemistry, we wish to report on the composition of products obtained from the acetolysis of 2-exo-hydroxybicyclo[2.2.1]heptan-7-one tosylate (I) and 2-endo-hydroxybicyclo[2.2.1]heptan-7-one tosylate (II). Since I solvolyzes more slowly than II, it is probable that both tosylates

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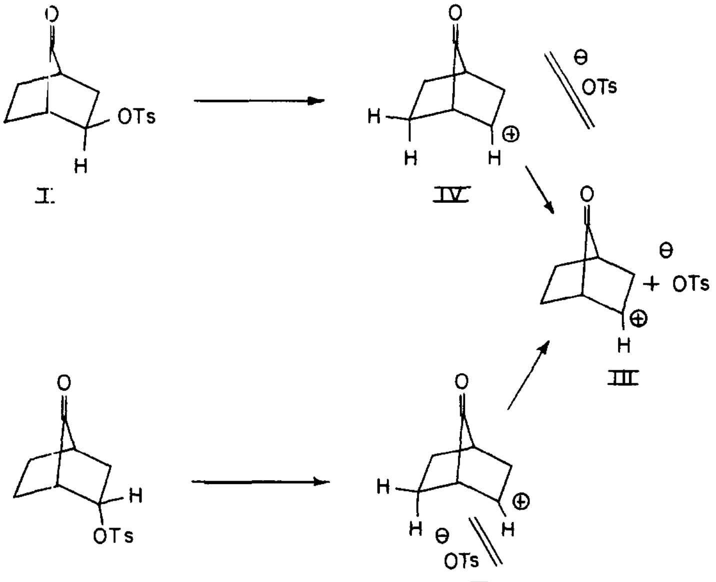
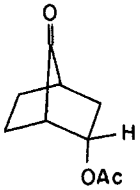
solvolyze to a classical carbonium ion (4). Thus the products resulting from the acetolyses of I and II should be those produced by the addition of acetic acid to the classical secondary carbonium ion, III, or to the solvent separated ion pairs IV and V, respectively.



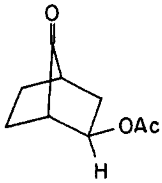
I IV III II V

When the product analyses were carried out by vapor phase chromatography of the crude solvolysis mixtures, the only detectable products were 2-*endo*-acetoxybicyclo[2.2.1]heptan-7-one (VI) and 2-*exo*-acetoxybicyclo[2.2.1]heptan-7-one (VII). The nature of these products was established by comparison of v.p.c. retention times on three columns and by comparison of infrared spectra of samples isolated by preparative v.p.c. with the infrared spectra of authentic samples of VI and VII.

The exact yields and product ratios were very difficult to assess due to the sensitivity of VI to heat, acid and base. Vapor phase chromatography of the crude acetolysis mixture resulting from I showed only VI and



VI



VII

VII in the ratio of 2:3. The presence of 40% *endo*-acetate is probably a minimal value due to the thermal instability of VI. When the acetolysis mixture was neutralized with base and the solvolysis products were isolated and distilled, a 71% yield of mixed products was obtained. This material consisted of 65% *exo*-acetate and 20% *endo*-acetate. Five minor components, which were not identified, constituted the remaining 15%. The relatively low yield (71%) and reduced ratio of *endo* and *exo* products of the isolated solvolysis mixture from I can be attributed to the extreme sensitivity of VI to base. It has been shown by DePuy and Story (5) that VI ''hydrolyzed completely in a few minutes at room temperature with dilute base.'' DePuy and Story did not characterize the products which resulted from base hydrolysis of VI. It is possible that the minor components observed in the isolated product mixture are a result of the reaction of VI with base in the neutralization of the acetic acid, since these impurities were not detected in the v.p.c. of the crude product.

To our knowledge this is the first case of an *exo*-tosylate solvolysis in a bicyclo[2.2.1]heptyl system which yielded a large proportion of *endo* product (6).

Analysis of the crude products from the acetolysis of II also showed a mixture of VI and VII. In this case the reaction mixture gave VI and VII in the ratio of 1.7 : 98.3 (7). Although *endo* product was observed in this solvolysis, the drastic change in product ratio, as compared to the product ratio from I, deserves consideration.

It appears that the products obtained from I and II are not arising from a carbonium ion such as III in which the tosylate moiety is completely divorced from the carbonium ion since this would require I and II to yield identical proportions of exo- and endo-acetate. An attractive explanation for the observed products is that the carbonium ions formed are highly reactive since they lack the stabilization normally derived from non-classical ion formation. As a result both I and II may be yielding products at the solvent separated ion-pair stage represented by IV and V, respectively.

The ion-pair, IV, would be hindered on the bottom side by the endo-hydrogen at C-6 and on the top side by the leaving tosylate ion. By comparison the ion-pair, V, would have both the C-6 endo-hydrogen and the leaving tosylate ion hindering endo substitution while the exo side would be relatively available for solvent addition.

What part, if any, is played by the carbonyl dipole in controlling the stereochemistry of the products is difficult to evaluate. Since the carbonyl dipole should attract solvent it might be anticipated that such a dipole-solvent interaction would hold the solvent tightly on the exo side of molecule and thus facilitate the formation of exo product. This could be a significant factor in the high exo/endo product ratio observed in the solvolysis of II.

In view of this data, the question of why the ''presumably classical'' (6) tertiary norbornyl cations yield only exo products merits comment. If a classical secondary norbornyl cation yields both exo and endo products, it would seem that a tertiary norbornyl cation, if classical in nature, should also yield a mixture of endo and exo products. The exclusive formation of exo products from tertiary norbornyl cations casts doubt on the classical nature of these ions (8). Clearly, it is necessary to give careful consideration to the question of whether the *endo* side of tertiary norbornyl cations is blocked by either a rapidly equilibrating pair of classical ions or by a delocalized ''non-classical'' carbonium ion.

Acknowledgment

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6. H. M. Bell and H. C. Brown, *J. Am. Chem. Soc.*, **86**, 5007 (1964) report an 87:13 *exo:endo* product ratio in the reaction of sodium borohydride with 1-(*p*-anisyl)camphene hydrochloride in aqueous diglyme. However, in the absence of sodium borohydride, these same authors found no trace of *endo* products in the closely related solvolyses of either 2,7,7-trimethylnorbornyl chloride (α-fenchene hydrochloride) or *exo*-fenchyl tosylate [H. C. Brown and H. M. Bell, *J. Am. Chem. Soc.*, **86**, 5006 (1964)].
7. A 59% yield was obtained when the acetic acid solvent was neutralized and the product isolated and distilled. Control experiment showed that no isomerization of *exo*- to *endo*-acetate occurred during the analyses by v.p.c.
8. S. Winstein, *J. Am. Chem. Soc.*, **87**, 381 (1965) also discusses the possibility that evidence seems ''to favor preferred bridged structures for typical secondary and tertiary norbornyl cations.''