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THE SOLVOLYSES OF *exo*- AND *endo*-5-NORBORNEN-2-YL *p*-BROMOBENZENESULFONATES. A RE-INVESTIGATION USING DEUTERIUM NMR SPECTROSCOPY.

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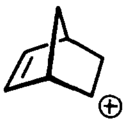
The solvolyses of 5-norbornen-2-yl esters have posed a considerable problem in interpretation, especially since there are divergences between the reported results.[1,2,3]

Recently, it has been suggested on the basis of a tritium labeling study that the process involves a pair of enantiomeric homoallylic cations (1 and 2) equilibrating by Wagner-Meerwein and *exo* 3,2 hydride shifts which can further eliminate to norbornadiene before capturing solvent.[3]

However, this interpretation seemed to us to be a special one for two reasons. Firstly, it is difficult to understand why 1 and 2 do not collapse to the more stable symmetrical cyclopropylcarbinyl cation 3.[4] Secondly, why should the norbornenyl system behave differently from other structurally similar homoallylic esters where species like 3 have been invoked to explain the kinetics and products.[1,5,6]


1

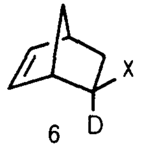
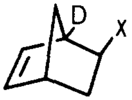
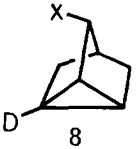
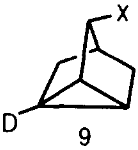
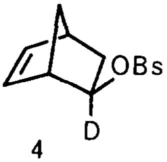
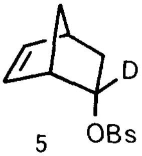

2


3

We now show that the solvolyses of these esters can be adequately explained in terms of 3.

We have carefully re-investigated the acetolysis[7] and trifluoroethanolysis in buffered medium of the deuterated *exo*- and *endo*-brosylates 4 and 5. The deuterium distribution in the products (Table) was determined unambiguously by ^{2}H-{^{1}H}-FT-NMR[8] and MS techniques.[2,9] In contradistinction to the previous methods,[3,5,7] we have succeeded in identifying each hydrogen and, consequently each deuterium atom in the products using Eu(fod)$_3$ shift reagent.

Table. Products and deuterium label distribution therein for the acetolysis and trifluoroethanolysis of 4 and 5[a]

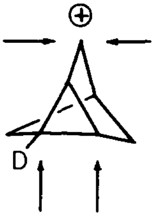
Starting Brosylates		 6	 7	 8	 9
 4	$\xrightarrow[(X = OAc)]{b}$	3.8%	3.8%	46.2%	46.2%
	$\xrightarrow[(X=OCH_2CF_3)]{c}$	3.15%	3.15%	46.85%	46.85%
 5	$\xrightarrow[(X = OAc)]{d}$	17.86%	5.34%	38.4%	38.4%
	$\xrightarrow[(X=OCH_2CF_3)]{e}$	4.74%	3.16%	46.05%	46.05%

[a] Less than 2% of norbornadiene also formed. Values are corrected for 98.5% deuteration of starting material. [b] At 25°C, in HOAc + 1.1 equiv. KOAc + 3% Ac$_2$O. [c] At 25°C in HOCH$_2$CF$_3$/CH$_2$Cl$_2$ 1:1 + 1.1 equiv. pyridine. [d] as [b] however at 80°C. [e] as [c] however at 80°C.

It is seen immediately that both acetolysis and trifluoroethanolysis of the *exo*-brosylate give essentially the same product pattern. Moreover, the distribution of deuterium label is exactly the same, within experimental error, ±2%, namely 50:50 in both the norbornenyl (6 and 7) and nortricyclic products (8 and 9).

Acetolysis of the *endo*-brosylate also gives exclusively *exo*-norbornenyl acetates, however with much less rearrangement occurring. Furthermore, nortricyclyl products are found to a lesser degree, but here deuterium label is evenly partitioned. Trifluoroethanolysis displays similar behaviour, but the equilibration between norbornenyl products is more advanced and there is correspondingly more nortricyclyl product, in which once again label has equally been distributed

These results can be conveniently rationalized in terms of the nortricyclyl cation 10.[10] *exo*-Brosylate 4 generates 10 or corresponding symmetrical ion-pair intermediates. Capture of solvent will occur at any of the four sites (Figure). Direct attack on the cationic centre yields the pair of nortricyclyl product 8 and 9, whereas attack on the cyclopropane moiety furnishes the pair of norbornenyl esters 6 and 7.



Figure

10

Clearly, the less reactive *endo*-brosylate 5 also gives 10 or corresponding symmetrical ion-pair intermediates [12], most probably in non-concerted fashion, as solvent participation (direct SN2 reaction), greater in acetic acid than in trifluoroethanol,[11] intervenes, thereby leading to less nortricyclyl product and less rearranged norbornenyl esters.

It seems to us that other explanations involving equilibrating homoallylic cations are unnecessary.

Details of these matters will be discussed in our full paper.

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12) We wish to point out that the solvolyses of 4 and 5 may generate different types of symmetrical ion-pairs leading to the products, e.g. :