Tetrahedron Letters No.20, pp. 2429-2431, 1968. Pergamon Press. Printed in Great Britain.

MeO-4 PARTICIPATION IN SOLVOLYSIS REACTIONS

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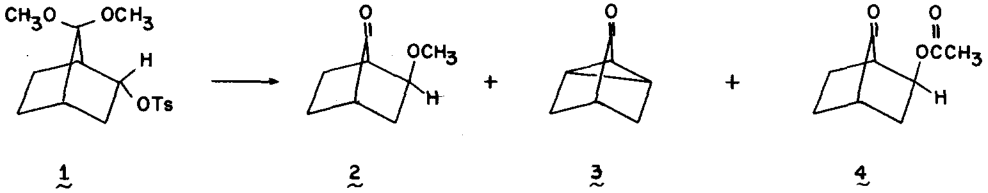
(Received in USA 18 January 1968; accepted for publication 14 February 1968)

Although examples of MeO-3, MeO-5, and MeO-6 neighboring group participation have been well established in the chemical literature,[1,2] instances of MeO-4 participation are conspicuous by their absence. We wish to report evidence for MeO-4 neighboring group participation in the acetolysis of 7,7-dimethoxybicyclo[2.2.1]heptan-endo-2-ol-p-toluenesulfonate (**1**).[3]

When **1** was solvolyzed in anhydrous acetic acid buffered with anhydrous sodium acetate, a three component product mixture was obtained in 70% isolated yield after distillation. This mixture consisted of 16% of exo-2-methoxybicyclo[2.2.1]heptan-7-one (**2**), 29% of nortricyclanone (**3**), and 55% of exo-2-acetoxybicyclo[2.2.1]heptan-7-one (**4**). These results are to



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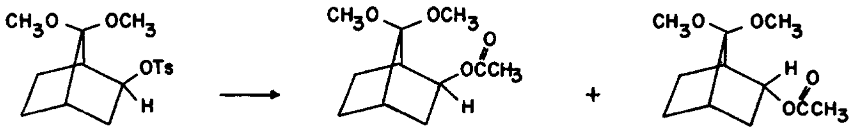
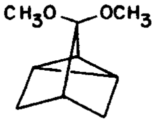
be contrasted with the acetolysis of 7,7-dimethoxybicyclo[2.2.1]heptan-*exo*-2-ol-*p*-toluenesulfonate (5) which gave 6 and 7.[4] In order to establish that 2, 3, and 4 were derived directly from the solvolysis of 1 certain control experiments were performed. Compounds 2, 3, and 4 were each subjected to approximately ten half-lives under solvolysis conditions. In each case the starting materials were recovered unchanged. Hence no interconversion of the reaction products was occurring. Next the ketals 6, 7, and 8 were treated under the reaction conditions. Again it was shown that these compounds could not have been responsible for the formation of the observed products from the acetolysis of 1.[5]



5 6 7



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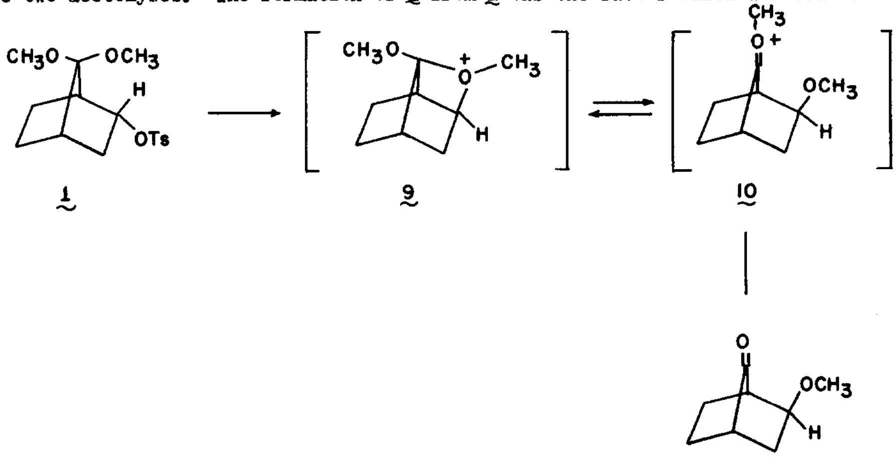
Since 1 yields only ketonic products, while the epimer, 5, under identical solvolytic conditions, produces only ketal type products, a basic difference must exist in the mechanism of these two acetolyses. The formation of 2 from 1 was the factor which allowed delineation



1 9 10

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of the mechanism of acetolysis of 1. This transformation of 1 into 2 is readily explained in terms of MeO-4 neighboring group participation. As the *p*-toluenesulfonate group leaves from the *endo* side of 1, the ideally situated *syn*-7-methoxy group participates to yield the ion 9 which could readily interconvert with ion 10. Transfer of a methyl group from 10 to the acetic acid solvent would lead directly to 2.

Numerous reaction paths can be written for the conversion of 1 into 3 and 4. However, the ketonic nature of 3 and 4 and the failure of 6, 7, and 8 to account for the presence of 3 and 4 require that the formation of 9 be the first step in any route to these ketonic products. In view of the many possible routes from 9 to 3 and 4 no specific mechanistic path can be recommended as being preferred.

Acknowledgment. The authors are indebted to the Petroleum Research Fund administered by the American Chemical Society for a grant in support of this study.

References

1. B. Capon, *Quart. Rev.*, **18**, 45 (1964) and references contained therein.
2. S. Winstein and E. L. Allred, *J. Am. Chem. Soc.*, **89**, 3991, 3998, 4012 (1967).
3. See P. G. Gassman and J. L. Marshall, *J. Am. Chem. Soc.*, **88**, 2822 (1966) for details of the synthesis of 7,7-dimethoxybicyclo[2.2.1]heptan-*endo*-2-ol. Satisfactory elemental analyses have been obtained for all new compounds.
4. For details of this solvolysis see the following communication.
5. Compounds 6 and 7 were stable to the reaction conditions. The ketal, 8, was completely reacted under the solvolytic conditions. Upon decomposition in anhydrous acetic acid (buffered with sodium acetate) 8 gave a very low yield of 3.