

THE SOLVOLYSIS OF EXO 5-*p*-TOLUENESULFONYLOXYBICYCLO [2.2.2] OCT-2-ENE

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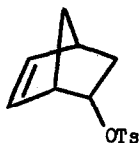
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THE effect of a neighbouring double bond in accelerating the solvolysis of halides and sulfonates in the bicyclo [2.2.1] heptane system is well known.² Its effect can be seen from a comparison of the results of acetolysis of the *p*-toluenesulfonates of *exo* and *endo* 5-hydroxybicyclo [2.2.1] hept-2-ene I and II. Compound I was found to react about 10⁴ times faster in acetic



I



II

acid at 25° C than compound II.³ The observed increase in rate was attributed to the fact that only in the *exo* isomer I was the β - γ double bond able to participate during the solvolysis; that is, only when the geometry of the compound allows the π orbital of the neighbouring double bond to interact from the rear with the developing carbonium ion is the energy of the transition state lowered and a rate enhancement observed.

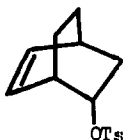
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² S. Winstein and C. Ordronneau, *J. Amer. Chem. Soc.* 82, 2084 (1960) and references therein.

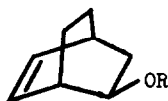
³ S. Winstein and M. Shatavsky, *J. Amer. Chem. Soc.* 78, 595 (1956).

Indeed, stabilization of a carbonium by a neighbouring double bond is sufficiently large in the case of the 7-norbornadienyl carbonium ion to have allowed proof of its existence as a stable entity in sulfur dioxide.⁴

Much recent work has been done on the bicyclo[2.2.2]oct-2-ene system^{5,6} although none of it provides evidence about direct participation of the double bond. Goering found that the double bond accelerated the rate of solvolysis of endo tosylate IV, presumably by aiding in the stabilization of the carbonium ion resulting from participation of the carbon-carbon σ bond. We wish to report evidence for the direct participation of the double bond obtained from a study of the solvolysis of the tosylate of exo 5-hydroxybicyclo[2.2.2]oct-2-ene Va.



IV



V

- a) R = H
- b) R = Ac
- c) R = Ts

Compound Va was prepared as follows. Reduction of bicyclo[2.2.2]oct-2-ene-5-one with lithium aluminum hydride gave a mixture of exo and endo alcohols in the proportion of 1:3. By using lithium tri-*t*-butoxyaluminum hydride as reducing agent the ratio of exo to endo was increased to 2:3. The mixture was then separated by vapour phase chromatography using a column of 20% Carbowax 20M on firebrick. The exo isomer was obtained as a solid m.p. 175-176° C (correct C & H analysis) which on hydrogenation gave the same product (by mixed m.p. and I.R.) as that obtained from hydrogenation

⁴ P. R. Story and M. Saunders, J. Amer. Chem. Soc. 82, 6199 (1960).

⁵ A. Gagneux and C. A. Grob, Helv. Chim. Acta 42, 1753 (1959).

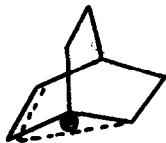
⁶ H. L. Goering and M. F. Sloan, J. Amer. Chem. Soc. 83, 1391, 1394, 1992 (1961).

of the corresponding endo alcohol. That the stereochemical assignment of exo to the minor component is correct is corroborated by a comparison of the N.M.R. spectra of the two isomers in the region of 6.3 τ . The proton on the carbon bearing the hydroxyl group occurs 8 c.p.s. to higher field in the exo isomer. This is in agreement with the observed effect of a neighboring double bond on chemical shifts in the bicyclo[2.2.1]hept-2-enes.⁷

The tosylate of Va was prepared and solvolysed at 18.2° C in 100% glacial acetic acid, the same conditions as Goering employed for the endo isomer.⁶ The reaction was followed titrimetrically and proceeded with excellent first order kinetics to >80% reaction. From two runs a rate constant of $2.4 \times 10^{-4} \text{ sec}^{-1}$ was obtained reproducibly. This is the largest rate constant observed in the 2.2.2 series. The product of solvolysis was shown to be 85% exo acetate Vb by comparison of its I.R. spectrum with that of the product of acetylation of exo alcohol Va. The limited supply of Va prevents determination of the nature of the minor solvolysis product. A comparison of the rate of solvolysis of tosylate Vc with its endo isomer IV and cyclohexyl tosylate shows their relative rates to be 10,000:300:1. Since the endo isomer is accelerated by carbon-carbon σ bond participation it is obvious from the rate comparison and also from the fact that the major solvolysis product is acetate of retained configuration, that the double bond does participate during solvolysis of tosylate Vc. Presumably the intermediate can be approximated in character by VI. This conclusion

⁷ R. R. Fraser, Can. J. Chem. 40, 78 (1962).

refutes an earlier proposal by Wildman and Saunders⁸ that direct participation of the double bond is absent in the bicyclo[2.2.2]octene system.



VI

Acknowledgement - This research was supported by the National Research Council of Canada.

⁸ W. C. Wildman and D. R. Saunders, J. Org. Chem. 19, 381 (1954).