Tetrahedron Letters No.20, pp. 2433-2436, 1968. Pergamon Press. Printed in Great Britain.

# ACETOLYSIS OF 7,7-DIMETHOXYBICYCLO[2.2.1]HEPTAN-exo-2-YL p-TOLUENESULFONATE

Paul G. Gassman[a] and James L. Marshall[b]

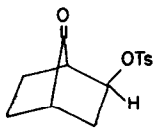
Department of Chemistry

The Ohio State University

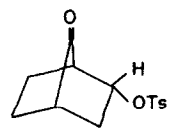
Columbus, Ohio 43210

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

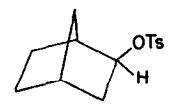
The recent observation of the formation of both exo and endo substitution products in the acetolyses of the epimeric 2-hydroxybicyclo[2.2.1]heptan-7-one p-toluenesulfonates (1 and 2) has provided one of the first examples of a norbornane derivative which did not give exclusive exo substitution on solvolysis.[1] It was suggested[1] that 1 and 2 yielded products




1




2




3

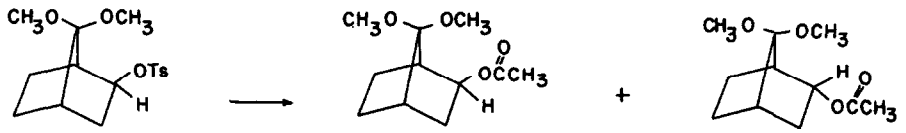
which were not derived via an intermediate nonclassical ion, whereas the formation of only exo product in the solvolysis of 3 probably was due to the formation of a delocalized cation. Two distracting features of this comparison between 1, 2, and 3 were the questionable effect of the difference in hybridization between 1, 2, and 3 and the possible intermediacy of a hemiketal in the solvolysis of 1 and 2. We now wish to report the results of the acetolysis of 7,7-dimethoxybicyclo[2.2.1]heptan-exo-2-yl p-toluenesulfonate (4),[2] a molecule more analogous to 3 than to 1, since it is $sp^3$ hybridized at C-7.

---

a) Alfred P. Sloan Research Fellow, 1967-1969.

b) National Science Foundation Cooperative Predoctoral Fellow, 1962-1963, 1964-1966.

When 4 was solvolyzed in anhydrous acetic acid buffered with anhydrous sodium acetate, a 66% yield of 5 and 6 was obtained. This mixture consisted of 95.5% of 5 and 4.5% of 6.



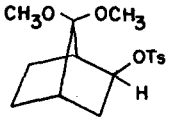
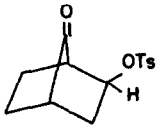
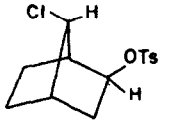
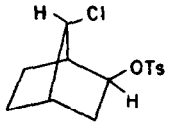
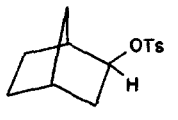
4 5 6

These solvolytic results are to be contrasted with the acetolysis of 7,7-dimethoxybicyclo-[2.2.1]heptan-endo-2-yl p-toluenesulfonate (7) which yields only ketonic products via MeO-4 neighboring group participation.[3] Since methoxyl participation in the acetolysis of 7 resulted in the loss of the ketal function and since no endo products were observed in the acetolysis of 7, it is apparent that the products obtained in the acetolysis of 4 cannot arise via participation of a C-7 methoxyl. Hence the formation of 5 and 6 must result from the incorporation of acetic acid at the solvent separated ion pair stage in a manner very similar to that suggested[1] for the formation of exo and endo products from 1 and 2. In addition, since both exo and endo products are formed from 1, 2, and 4, the formation of these products cannot be a function of the $sp^2$ hybridization at C-7 in 1 and 2 because 4 is not $sp^2$ hybridized at C-7. Thus, the formation of 5 and 6 in the acetolysis of 4 removes the two major points of concern connected with the solvolysis of 1 and 2 to yield both exo and endo products. This lends further support to the theory that a delocalized carbonium ion is an intermediate in the formation of only exo acetate in the acetolysis of 3.

An additional point of interest, connected with the rates of solvolysis of norbornyl systems with electron-withdrawing groups at C-7, is a comparison of the rates of acetolysis of 1, 4, 8,[4] and 9[4] with 3[5] as shown in Table 1. It should be noted that 1, 4, 8, and 9 solvolyze at very similar rates, whereas 3 undergoes acetolysis at a much faster rate. This difference in rate can be readily rationalized by a combination of inductive effects and the lack of anchimeric assistance in the solvolysis of 1, 4, 8, and 9.[6] The detection of both exo and endo products from 1 and 4 is consistent with the rate data[7] in that the more unreactive exo-p-toluenesulfonates produced endo products. In comparing the exo/endo product ratios from the acetolysis of 1 and 4, it should be noted that the more reactive 4 gives the larger exo/endo product ratio. Indeed, our findings give credence to Brown's hypothesis that

Table 1

Acetolysis Rates of Norbornyl p-Toluenesulfonates

| Compound | Ref. | Temp. °C. | Rate (sec.$^{-1}$) | $k_{rel.}$ |
|---|---|---|---|---|
|  4 | | 100.00 ± 0.02 | (1.07 ± 0.04) x $10^{-3}$ | |
| | | 90.00 ± 0.02 | (3.58 ± 0.13) x $10^{-4}$ | |
| | | 75.85 ± 0.02 | (8.12 ± 0.03) x $10^{-5}$ | |
| | | (25)[a] | 9.53 x $10^{-8}$ | 7 |
|  1 | 1 | (25)[a] | 1.44 x $10^{-8}$ | 1 |
|  8 | 4 | (25)[a] | 6 x $10^{-8}$ | 4 |
|  9 | 4 | (25)[a] | 1 x $10^{-7}$ | 7 |
|  3 | 5 | (25)[a] | 2.33 x $10^{-5}$ | 1620 |

a) rate constants extrapolated from higher temperatures

a spectrum of ions should exist, with "a gradual transition between static classical, equilibrating classical, equilibrating π bridged, and static bridged cations."[8]

## References


1. P. G. Gassman and J. L. Marshall, J. Am. Chem. Soc., 88, 2822 (1966).

2. For the preparation of 7,7-dimethoxybicyclo[2.2.1]heptan-exo-2-ol see reference 1. Satisfactory elemental analyses have been obtained for all new compounds.

3. For a discussion of this example of MeO-4 neighboring group participation see the preceeding communication.

4. W. G. Woods, R. A. Carboni, and J. D. Roberts, J. Am. Chem. Soc., 78, 5653 (1956).

5. P. von Schleyer, M. M. Donaldson, and W. E. Watts, J. Am. Chem. Soc., 87, 375 (1965).

6. The change in bond angles resulting from the $sp^2$ hybridization of 1 must be considered. This factor has previously been discussed.[1]

7. The product analysis of the solvolysis products from 8 and 9 were determined from the infrared spectra of "mixtures".[4] The presence of endo products could have been overlooked by this method of analysis. We are presently reinvestigating the acetolysis of 8 and 9 in order to determine if endo products were formed during acetolysis.

8. H. C. Brown, Chem. and Eng. News, Feb. 13, 1967, pp. 87-97.