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ON THE ACETOLYSIS OF EXO - AND ENDO-BICYCLO[2.1.1] - HEXYL-5 TOSYLATES

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Although good evidence has been found for anchimeric assistance in the solvolytic reactions of unsaturated systems such as the 2-norbornenyl tosylates ($k_{exo}/k_{endo} = 8 \times 10^3$)[1] and the 7-isopropylidene 5-norbornen-2-yl tosylates[2], the smaller rate factor observed with saturated systems such as the 2-norbornyl tosylates ($k_{exo}/k_{endo} = 350$)[3] lends an element of uncertainty in the interpretation of the results.[4]

We have observed that the bicyclo[2.1.1]hexyl-5 tosylates[5]

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(1) S. Winstein and M. Shatavsky, J. Am. Chem. Soc. 78, 592 (1956); S. Winstein, H. M. Walborsky and K. Schreiber, J. Am. Chem. Soc. 72, 5795 (1950).

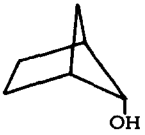
(2) C. H. DePuy, L. A. Ogawa and J. C. McDaniels, J. Am. Chem. Soc. 82, 2397 (1960).

(3) S. Winstein and D. Trifan, J. Am. Chem. Soc. 74, 1147, 1154 (1952).

(4) H. C. Brown in The Transition State, Chemical Soc. Special Pub. No. 16, 140 (1962).

(5) K. B. Wiberg, B. R. Lowry and T. H. Colby, J. Am. Chem. Soc. 83, 3998 (1961).

give a remarkably large rate difference in acetolysis. The more reactive *endo*-isomer (I) gave a rate constant of 2.79×10^{-3} sec^{-1} at 25°, whereas the *exo*-isomer (II) gave a rate constant of 5.82×10^{-4} sec^{-1} at 164.2°. The latter value corresponds to a rate constant at 25° of about 9×10^{-10} sec^{-1} giving $k_{endo}/k_{exo} = 3 \times 10^6$. The acetolysis of I led to 80% ion-pair return to 4-cyclohexenyl tosylate, 8% 4-cyclohexenyl acetate and 8% bicyclo[3.1.0]hexyl-2 acetate, plus some minor components. A complete product study of the acetolysis of II has not as yet been made, but a major product is 4-cyclohexenyl acetate.



I

II

The structure of I is similar to that of cyclobutyl tosylate, and has the possibility of an anchimeric participation leading to a "bicyclobutonium" type ion.[6] The products of the reaction are those expected from this type of participation: cyclobutyl tosylate gave cyclopropylcarbinyl acetate, cyclobutyl acetate, allylcarbinyl acetate and allylcarbinyl tosylate.[6] The product corresponding to cyclobutyl acetate was not observed in the acetolysis of I, but it was obtained in the reaction in acetone in the presence of halide ion.[5] The rate constant for the acetolysis

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(6) J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.* **73**, 5034 (1951).

of cyclobutyl tosylate at 25° is about 3×10^{-6} sec $^{-1}$, [6,7] or about 10^3 lower than that for I. Thus, the extra bond angle deformation in I results in an accentuated rate of reactions.

The structure, II, is quite similar to that of 7-norbornyl tosylate (III), the acetolysis of which is characterized by the rate constant 6.4×10^{-15} at 25°.[8] The acetolysis of II is nearly 10^5 faster than that of III. The low rate of solvolysis of III is attributed to the bond angle deformation at the 7 position, which would be accentuated in the activated complex in which C_7 approaches a trigonal configuration.[8] This factor should be even more important in the reaction of II because of the smaller bridge involved. Thus, the higher rate of reaction of II suggests that here also, participation may be involved in the formation of the acetolysis activated complex.

The further details of the solvolytic reactions of I and II are presently under investigation. This work was supported by the U. S. Army Research Office, Durham, to whom we express our appreciation.

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(7) H. C. Brown and G. Ham, J. Am. Chem. Soc. 78, 2735 (1956).

(8) S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, J. Am. Chem. Soc. 77, 4183 (1955).