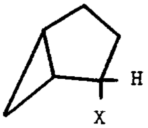
Tetrahedron Letters No.18, pp. 1373-1376, 1971. Pergamon Press. Printed in Great Britain.

THE NATURE OF THE ACTIVATED COMPLEXES AND INTERMEDIATES INVOLVED IN SOLVOLYSIS OF THE *ENDO*-AND *EXO*-2-BICYCLO[3.1.0]HEXYL 3,5-DINITROBENZOATES

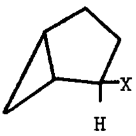
Edwin C. Friedrich and Mahmoud A. Saleh
Department of Chemistry, University of California
Davis, California 95616

(Received in USA 22 March 1971; received in UK for publication 30 March 1971)

Several years ago, in connection with other investigations[1] involving the nature and behavior of the unsubstituted trishomocyclopropenyl cation, one of us (E.C.F) carried out an exploratory investigation of the kinetics for formation of the 2-bicyclo[3.1.0]hexyl cation and the nature of its solvolysis products. This was done by means of acetolysis studies using the *endo*-and *exo*-2-bicyclo[3.1.0]hexyl *p*-toluenesulfonate derivatives 1-OTs and 2-OTs. Both isomeric *p*-toluenesulfonates were found to exhibit the high reactivity in acetolysis expected for a system reacting *via* formation of a non-classical cyclopropylcarbinyl cation intermediate. However, we were surprised to observe that in acetolysis at 25° both 1-OTs and 2-OTs reacted at approximately the same rates and gave nearly identical product mixtures consisting of 1-OAc, 2-OAc and 3-OAc.[2]



1



2

3

Because of the above unexpected[3] observations, we became interested in carrying out a more detailed examination of the nature and behavior of the activated complexes and intermediates involved in the solvolytic reactions of *endo*-and *exo*-2-bicyclo[3.1.0]hexyl derivatives. In this work we chose to use 3,5-dinitrobenzoate ester derivatives rather than the *p*-toluenesulfonates 1-OTs and 2-OTs. This is because of the difficulties of preparation and instability of the *p*-toluenesulfonates, and because their rates of reaction were too rapid for highly accurate measurements. The 3,5-dinitrobenzoates 1-ODNB and 2-ODNB were prepared by the usual methods[4] from the corresponding alcohols.

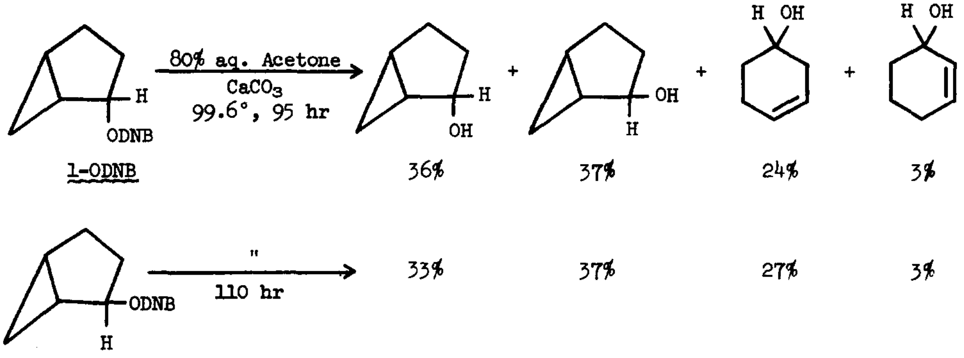
The kinetics for hydrolysis of 1-ODNB and 2-ODNB were measured in 80% aqueous acetone at 80° and 100°, and the results are shown in Table I. The reactions of both esters followed good first-order kinetics, with the *endo*-isomer (1-ODNB) being slightly faster than the *exo*-isomer (2-ODNB), and gave nearly theoretical production of acid at 10 half-lives. The

Table I

Rates of Hydrolysis in 80% Aqueous Acetone

3,5-Dinitrobenzoate	Temp., °C	$10^6 k_1$, sec^{-1}	$\Delta H^{\ddagger}$ kcal/mole	$\Delta S^{\ddagger}$ e.u.
endo(1-ODNB)	100.0	12.4	24.2	-16
	80.0	1.84		
exo(2-ODNB)	100.0	11.5	26.1	-12
	80.0	1.52		

products obtained from hydrolysis in 80% aqueous acetone at 99.6° in the presence of a $CaCO_3$ buffer after about 5 half-lives for reaction were measured using glpc techniques and are summarized below. No olefinic products were observed, and controls showed that all of the product



1-ODNB

2-ODNB

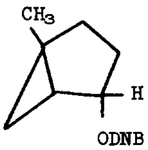
alcohols are stable under the reaction conditions.[5] Thus, within experimental error, both isomeric 2-bicyclo[3.1.0]hexyl 3,5-dinitrobenzoates gave identical product mixtures.[6]

All of the available evidence therefore seemed to indicate that the natures of the activated complexes involved in ionization and intermediates involved in product formation for solvolysis of both 1-ODNB and 2-ODNB must be very similar, or identical. However, to employ even more sensitive tests than those used above for proving the similarity or dissimilarity of the activated complexes and intermediates, the following further studies were carried out.

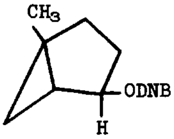
Friedrich and Wight[7] have recently observed in hydrolysis of the 2-deutero-endo- and exo-2-bicyclo[5.1.0]octyl 3,5-dinitrobenzoates that completely different deuterium scrambling results are obtained for each isomer even though both give similar hydrolysis product mixtures. After 81% reaction the alcoholic products from the endo-isomer retained unscrambled deuterium atoms. However, after 93% reaction the deuterium in the alcoholic products from the exo-isomer was found to be greater than 90% scrambled. Thus, samples of 1-ODNB and 2-ODNB labeled with deuterium at their 2-positions were prepared,[8] hydrolyzed in 80% aq. acetone at 100°, and the alcohol products were examined for deuterium scrambling using nmr and mass spectral techniques.

Within experimental error no deuterium scrambling such as might result from a degenerate cyclopropylcarbinyl cation rearrangement was observed in any of the alcohol products (1-OH, 2-OH or 3-OH) obtained from either isomer.

To study more closely the natures of the activated complexes involved in ionization of the endo- and exo-2-bicyclo[3.1.0]hexyl derivatives, samples of the endo- and exo-5-methyl-2-bicyclo-[3.1.0]hexyl 3,5-dinitrobenzoates 4 and 5 were prepared[8] and their kinetics of hydrolysis in 80% aqueous acetone were measured. It was anticipated from examination of models that if the type of delocalization involved in ionization utilizes only one bond of the cyclopropane ring (i.e., as in bicyclobutonium or homoallyl cation species), introduction of the 5-methyl substituent should result in rate acceleration in hydrolysis of the endo-isomer but have little or no effect in the exo-isomer. The results, which are shown in Table II, indicate that introduction of the 5-methyl substituent produces a similar large acceleration of about 20 in the rates of reaction of both isomeric 2-bicyclo[3.1.0]hexyl 3,5-dinitrobenzoates.[9]



4



5

Table II

Rates of Hydrolysis in 80% Aqueous Acetone

3,5-Dinitrobenzoate	Temp., °C	$10^6 k_1$, sec^{-1}	$\Delta H^{\ddagger}$ kcal/mole	$\Delta S^{\ddagger}$ e.u.
4	80.0	40.4	29.5	4
	60.0	3.22		
5	80.0	26.9	27.7	-1
	60.0	2.40		

Thus, the evidence seems to indicate clearly that the type of delocalization involved in ionization and in the intermediates involved in product formation in the 2-bicyclo[3.1.0]hexyl system is independent of the geometric relationship of the leaving group and the cyclopropane ring. It is proposed that these results can best be explained by intervention of a bisected bishomoallylic[10] intermediate 6 in product formation, and bisected bishomoallylic type activated complexes in ionization.

6

Acknowledgement: This research was supported in part by a grant from the Petroleum Research Fund, administered by the American Chemical Society, and by the Academic Senate Committee on Research of the University of California, Davis.

References

1. S. Winstein, E. C. Friedrich, R. Baker, and Yang-I Lin, *Tetrahedron*, **Suppl 8, Part II**, 621 (1966).
2. Unpublished work of E. C. Friedrich and S. Winstein. A portion of the results obtained in this work has been quoted by K. B. Wiberg, R. A. Fenoglio, V. Z. Williams and R. W. Urbersax, *J. Amer. Chem. Soc.*, **92**, 568 (1970).
3. S. Winstein and E. M. Kosower, *J. Amer. Chem. Soc.*, **81**, 4399 (1959).
4. M. Hanack and H. Allmendinger, *Chem. Ber.*, **97**, 1669 (1964).
5. Controls were also run which demonstrated that neither **1-ODNB** or **2-ODNB** undergoes isomerization or interconversion *via* ion-pair return during the course of the reaction. Isolation of unreacted dinitrobenzoate after a period of time sufficient for approximately 65% acid production yielded material with an identical melting point and nmr spectrum as that of the starting material.
6. After the kinetic and product studies reported above were essentially complete, P. R. Brook, R. M. Ellam and A. S. Bloss, *Chem. Commun.*, 425 (1968), and G. H. Schmid and A. Brown, *Tetrahedron Lett.*, 4695 (1968), reported similar kinetic and product results from hydrolysis of the *endo*- and *exo*-2-bicyclo[3.1.0]hexyl chlorides and N-methyl oxopyridinium iodides, respectively.
7. L. E. Friedrich and F. R. Wight, *J. Amer. Chem. Soc.*, **92**, 1807 (1970).
8. All new compounds reported had satisfactory analyses and spectra.
9. P. von R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, **88**, 232 (1966).
10. L. Birladeanu, T. Hanafusa, B. Johnson and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 2316 (1966).