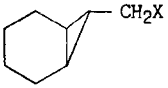
Tetrahedron Letters No.48, pp. 4255-4258, 1965. Pergamon Press Ltd.
Printed in Great Britain.

SOLVOLYSIS OF FUSED RING CYCLOPROPYLCARBINYL SYSTEMS

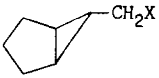
F. Thomas Bond and Louis Scerbo
Department of Chemistry, Oregon State University
Corvallis, Oregon

(Received 3 September 1965)

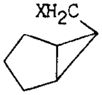
The nature of substituent effects on the solvolysis of substituted cyclopropylcarbinyl systems has been carefully examined by Roberts and co-workers (1). Extension of such studies to fused ring systems has been reported recently by Wiberg and Ashe (2), who studied the acetolysis of IIa and IIIa. We wish to report similar studies, in particular amine deaminations, in the 7 substituted bicyclo (4.1.0) heptane system I, and the two 6 substituted bicyclo (3.1.0) hexanes II and III. The preparation of these compounds followed standard routes from the corresponding acids (2-6).



I



II

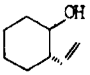
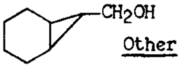
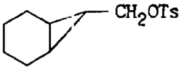
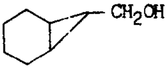
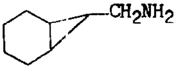
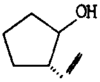
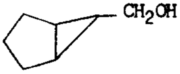
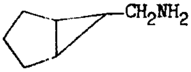
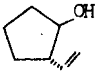
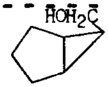
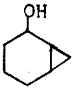
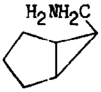


III

a, X = OTs
b, X = NH_2
c, X = OH
d, X = Cl

The conditions employed and the products from the various solvolyses are summarized in Table I. The products from tosylate Ia are analogous to those reported for IIa. The preponderance of trans-2-vinylcyclohexanol,

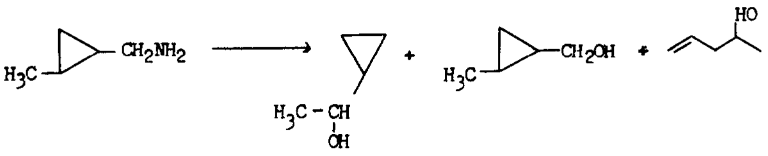
TABLE I

Reactant	Conditions	Products		
		 IVc	 Ic	Other
 Ia	HCOOH, a	72%	0%	Unidentified
	HOAc, b	65%	22%	Unidentified
 Ic	10% HCl, c	81%	0%	19% IVd
 Ib	HNO_2, d	30%	67%	Olefins
	HNO_2, e	60%	34%	Olefins
		 V	 IIc	
 IIb	HNO_2, e	16%	69%	Olefins
		 V	 IIIc	 VI
 IIIb	HNO_2, e	12%	70%	11%
			plus olefins	

Conditions: All data from corrected GLC analyses after LAH reduction

a. Buffered solution, 50°, 24 hours (7)
b. Buffered solution, 25°, 24 hours (2)
c. Room temperature, 24 hours (8)
d. 10% acetic acid, 50°, 24 hours (9)
e. 100% acetic acid, buffered solution, 50°, 24 hours

IVc, was expected on the basis of formation of this system in the addition of formic acid to 1,5-cyclooctadiene (10). The greater stability of this allylcarbinyl system is also indicated by the HCl isomerization of Ic to IV under conditions (8) which transform cyclopropylcarbinol into practically pure cyclobutanol. The deamination products from *exo* amines Ib and IIb are comparable with those reported for VII (1), only when it is realized that participation of the bond



VII VIII 51% 13% 35%

common to both rings, which would give a product analogous to VIII, is geometrically impossible as a *trans* fused cyclopropane ring would result.

The most interesting feature of the deaminations is the large amount of unrearranged alcohol that is produced. This is especially true of IIIb where the corresponding tosylate gave only 5% unrearranged product (2). Although direct nucleophilic displacement on the diazonium ion can be invoked to explain the results with the *exo* amines, this seems highly unlikely for the more hindered *endo* amine IIIb. Possibly in this case the initially formed cyclopropylcarbinyl cation is largely trapped by solvent before it can isomerize to an ion capable of forming VI. In this regard it is interesting that the ratio of V to VI is about the same as that found in the solvolysis of IIIa (2). The greater amount of rearrangement from the (4.1.0) amine Ib when compared with IIb is likely a reflection of the greater strain involved in fusing a three membered ring to cyclohexane.

Acknowledgement. This work was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgement is made to the donors of said fund.

REFERENCES

1. M. S. Silver, M. C. Caserio, H. E. Rice, and J. D. Roberts, *J. Am. Chem. Soc*., **83**, 3671 (1961).
2. K. B. Wiberg and A. J. Ashe III, *Tetrahedron Letters*, 1553 (1965).
3. P. S. Shell and R. M. Etter, *Proc. Chem. Soc*., 443 (1961).
4. J. Meinwald, S. K. Labana, and M. S. Chadha, *J. Am. Chem. Soc*., **85**, 582 (1963).
5. In an attempt to prepare *endo*-bicyclo (4.1.0) heptane-7-carboxylic acid using the procedure of Musso and Biethan[6] on cyclohexene, we obtained the lactone of 2-hydroxycyclohexyl acetic acid which results from acid catalyzed addition of water to the *endo* acid.
6. H. Musso and W. Biethan, *Chem. Ber*., **97**, 2282 (1964).
7. K. L. Servis and J. D. Roberts, *ibid*., **86**, 3373 (1964).
8. M. C. Caserio, J. D. Roberts, and W. H. Graham, *Tetrahedron*, **11**, 171 (1960).
9. M. Hanack and H. J. Schneider, *ibid*., **20**, 1863 (1964).
10. A. C. Cope and P. E. Peterson, *J. Am. Chem. Soc*., **81**, 1643 (1959).