Tetrahedron Letters No.45, pp. 4695-4698, 1968. Pergamon Press. Printed in Great Britain.

A RIGID CYCLOPROPYLCARBINYL SYSTEM.
THE 2-BICYCLO[3.1.0]HEXYL CATION

George H. Schmid and Allister Brown*
Department of Chemistry, University of Toronto
Toronto 5, Ontario, Canada

(Received in USA 17 June 1968; received in UK for publication 9 August 1968)

A recent report (1) describing the nature of the 2-bicyclo[3.1.0]-hexyl cation formed in the solvolysis of epimeric 2-chlorobicyclo[3.1.0]-hexanes prompts us to report our work on this system which provides an explanation for the small difference in rate between endo- and exo-isomers.

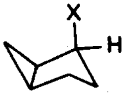
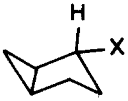
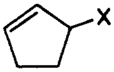
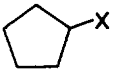
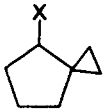
Endo- (Ib) and exo-bicyclo[3.1.0]hexan-2-ol (IIb) were prepared by the method of Dauben (2) and their N-methyl 4-alkoxypyridinium (Ia, IIa) iodides were prepared by the method of Roberts (3). The rates of solvolysis were followed at 86° in 80% aqueous ethanol by titrametric analysis using the ampoule technique. The data are given in Table 1. Also included in Table 1 for comparison are the rates of solvolysis of N-methyl 4-(cyclopentanoxy)pyridinium iodide (IVa) N-methyl 4-(cyclopent-2-enoxy)pyridinium iodide (IIIa) and N-methyl 4-(4-spiro-[2.4]heptanoxy)pyridinium iodide (Va).

Product compositions were determined in 80% aqueous ethanol at 86° in the presence of calcium carbonate. The compounds were analyzed by a combination of n.m.r. and v.p.c. and the results are summarized in Table 2.

---

*Holder of a National Research Council of Canada Studentship 1966-1968.

TABLE 1

Compound$^+$	 I	 II	 III	 IV	 V
k x 10^4/sec	2.20	1.71	0.354	0.000152	137
k_{rel}	14.5 x 10^3	11.3 x 10^3	2.33 x 10^3		90 x 10^4

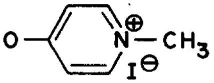
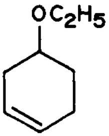
$^+$a, X=  b, X=OH c, X=OC_2H_5

TABLE 2

Product Composition %

Starting Material	Ib (endo)	IIb (exo)	Ic (endo)	IIc (exo)	
Ia (endo)	18	23	24†	26	9
IIa (exo)	20	24	23†	27	6

†Mixture of Ic and cyclohexene-4-ol

N-methyl oxopyridinium iodide was chosen as the leaving group to avoid complications of internal return. As a result the rates in Table 1 are true rates of ionization. The data in Table 1 clearly show that the cyclopropyl group of Ia and IIa has a rate enhancing effect relative to that for IVa even though the cyclopropyl group is not in the preferred bisected conformation (4). Placing the cyclopropyl group in this preferred conformation as in Va causes a further rate increase of a factor of 80 relative to that of IIa. Contrary to the results of Brook (1), our data show that the cyclopropyl group in Ia and IIa is slightly more effective than a double bond in activating an adjacent group in accord with previous findings on the solvolysis of cyclopropylcarbinyl derivatives (5). This difference is probably due to the lack of internal return in our system.

The low k_{endo}/k_{exo} ratio (1.29) is in agreement with that found by Brook (1.52). This small difference in rate (corresponding to $\Delta\Delta G^{*} = 180$ cal) is the same as the difference in the ground state energy of Ib and IIb (ΔG = 260 cal). This value of ΔG was obtained by equilibration of the two alcohols according to the method of Eliel (6). This indicates that the difference in rates of Ia and IIa is <u>due primarily to the difference in their ground states</u> and that both solvolyze by transition states which are of similar energy. Thus there is no rate enhancement due to stereoelectronic effects which indicate that considerable bond breaking has occurred in the transition state.

The ability of a cyclopropane ring to conjugate with an adjacent carbonium ion is accounted for on the basis of three different structures for the cyclopropylcarbonium ion (4). These are: (i) the homoallylic cation, (ii) the unsymmetrical bicyclobutonium ion and (iii) a symmetrical bisected form (bishomoallylic ion). In systems of rigid geometry, the indications are that for stabilization by an adjacent cyclopropane ring to occur, the leaving group and the cyclopropane ring must be in a particular geometry (7,8) favourable for orbital overlap. Stabilization of the intermediate by means of a bicyclobutonium ion is ruled out because of the geometry of the system, while stabilization by means of a symmetrical bishomoallylic or homoallyl ion would be expected to result in a stereospecific product (7,8,9).

Such is not the case in this system. The product composition of the solvolysis of Ia and IIa consists of both <u>endo</u>- and <u>exo</u>-alcohols and ethers indicating that there is little preferred attack by the nucleophile. Furthermore the product composition is identical indicating that the intermediate ion or series of ions which gives rise to products is the same for Ia and IIa. These results are inconsistent with the bishomoallylic structure of the 2-bicyclo[3.1.0]hexyl carbonium ion proposed by Brook.

Whatever the nature and extent of the charge delocalization from the carbinyl carbon to the cyclopropane ring in this system, it seems to be independent of the relative geometries of the cyclopropane ring and the leaving group.

ACKNOWLEDGEMENT: Financial support by the National Research Council of Canada is gratefully acknowledged.

REFERENCES

1. P. R. Brook, R. M. Ellam and A. S. Bloss, Chem. Comm., 425 (1968).
2. W. G. Dauben and G. H. Berezen, J. Am. Chem. Soc., 85, 468 (1963).
3. M. Vogel and J. D. Roberts, J. Am. Chem. Soc., 88, 2262 (1966).
4. P. von R. Schleyer and G. W. Van Dine, J. Am. Chem. Soc., 88, 2321 (1966).
5. J. D. Roberts and R. H. Mazur, J. Am. Chem. Soc., 73, 2509 (1951).
6. E. L. Elliel and R. S. Ro, J. Am. Chem. Soc., 79, 5992 (1951).
7. L. Birladeanu, T. Hanafusa, B. Johnson and S. Winstein, J. Am. Chem. Soc., 88, 2317 (1966).
8. S. Winstein and E. M. Kosower, J. Am. Chem. Soc., 81, 4399 (1959).
9. W. G. Dauben and Louis E. Friedrich, Tetrahedron Letters, 1735 (1967).