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SOLVOLYSIS OF EXO-TETRACYCLO$[4.3.1.0^{3,8}.0^{7,9}]$DEC-2-YL DERIVATIVES; A REFERENCE SYSTEM FOR THE ASSESSMENT OF ANCHIMERIC ASSISTANCE BY REMOTE CYCLOPROPANE RINGS[1]

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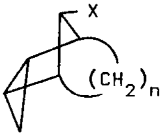
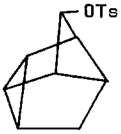
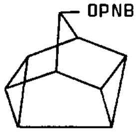
Only few bridged systems (I[2], II[3], III[4]) that can lead to trishomocyclopropenyl cations have been studied. They exhibit extraordinarily high solvolytic reactivities.



I (n = 1,2)



II



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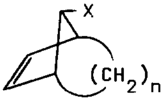
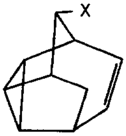
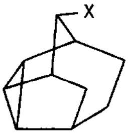


IV (n = 1-4)

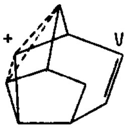
Since systems I solvolyze with rearrangement to less strained structures, relief of strain contributes an as yet unknown amount of driving-force not present in their olefinic counterparts IV[5]. Comparison of the reactivities of I and IV therefore cannot yield an answer to the question, which one, a cyclopropane ring or a double bond, is, intrinsically, the more effective participating group in such molecules[6]. We now report on the solvolyses of the tosylates Va and VIa, which are not accompanied by rearrangement and where additional complications arising from distortion of the carbon skeleton probably play a less important role[7].



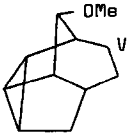
V
a: X = OTs
b: X = OH
c: X = OAc



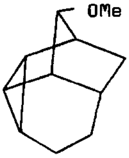
VI
a: X = OTs
b: X = OH
c: X = OMe



VII



VIII



IX

Tosylates Va and VIa were obtained from the alcohol Vb[8] by standard methods. Buffered acetolysis of Va and hydrolysis of Va and VIa yielded only unrearranged acetate Vc and alcohols Vb and VIb, respectively. The high rates (table 1) as well as the retention of configuration observed in all products are in accord with the assumption that these ionizations occur with participation of the cyclopropane rings and lead to the trishomocyclopropenyl cations VII and VII-H_2.

Table 1. Kinetic data for solvolyses of Va and VIa at 25°[a]

		k (sec^{-1})	$\Delta H^{\neq}$ (kcal/mole)	$\Delta S^{\neq}$ (e.u.)
Hydrolysis (60/40 v/v acetone-H_2O)[b]	Va	3.38×10^{-4}	20.7 ± 0.2	-5.0 ± 0.5
	VIa	3.12×10^{-2}[c]	17.2 ± 0.5	-7.8 ± 1.6
Acetolysis (0.01 M NaOAc)[d]	Va	1.32×10^{-5}[e]	23.3 ± 0.2	-2.9 ± 0.6
	VIa	1.2×10^{-3}[f]		

a) All reactions were first order; infinity titers were about 95%.

b) Hydrolyses were carried out at constant pH = 7 by continuously following the reactions using a Metrohm Combititrator 3D[9].

c) Value obtained by extrapolation from lower temperatures.

d) Acetolyses were carried out by the sealed ampoules technique.

e) Value obtained by extrapolation from higher temperatures.

f) Value obtained by assuming that the ratio $k_{\text{hydrolysis, 60\% acetone}} : k_{\text{acetolysis}}$ (at 25°) has about the same value (ca. 25) for Va and VIa[10].

Additional evidence for the intermediacy of delocalized ions comes from the low value of ca. 0.6 of the Winstein-Grunwald m-parameter of Va and from the methanolysis of VIa in the presence of $NaOCH_3$ (4 M), which resulted in the formation of three isomeric methyl ethers. The two main products were shown to be VIc (83%) and VIII (15%) by comparison with authentic samples. The third ether (2%) is assumed to be IX, however lack of material prevented further investigation of this product. These structures are the ones expected from a tridentate cation VII-H_2. Methanolysis of VIa in the absence of $NaOCH_3$ gave only VIc. A Foote-Schleyer analysis[11] of the reactivities of Va and VIa is given below.

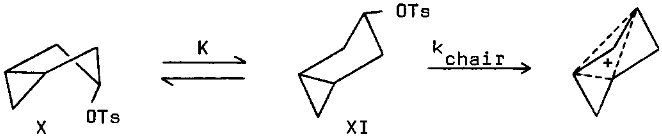
	lg k_{rel}	$\frac{(1715-\nu_{CO})}{8}$	$1.32\sum_i(1+\cos 3\phi_i)$	$\frac{(\text{GS-TS strain})}{1.36}$	inductive term	lg anch.ass.
Va	2.43	-4.13[a]	2.6	0.3	-1.4	5
VIa	4.40	-3.75	2.6	1.0	-0.5	5

a) The value of 1748 cm^{-1} used is the weighted average of bands at 1738 and 1755 cm^{-1}.

Since no change of the σ-skeletons occurs the total amount of the anchimeric assistance calculated is attributed to the electronic effect of the cyclopropane rings.

Dreiding models show that in VIa the degree of puckering of the five-membered ring carrying the leaving group must be very similar to that in IV (n = 4, X = OTs)[12] which is assumed to yield a bishomocyclopropenyl cation upon ionization. The relative reactivities of VIa and IV (n = 4, X = OTs) can therefore give information about the intrinsic propensities for participation of a cyclopropane ring and of a double bond, respectively. Although lack of data prevents an assessment of anchimeric assistance in the acetolysis of IV (n = 4, X = OTs) it can be concluded from its very low reactivity [$k_{125} = 7.5 \times 10^{-6}$ sec^{-1}, this is only twice as fast as H_2-IV (n = 4, X = OTs) reacts at this temperature] that in a conformation as in VIa a cyclopropane ring exerts more stabilization towards a developing positive center than a double bond[13].

Our analysis of the reactivity of VIa also sheds light upon another problem in nonclassical carbonium ion chemistry: Much evidence has been adduced by Winstein to support the notion that the nonclassical trishomocyclopropenyl cation is formed by anchimerically assisted ionization of cis-3-bicyclo[3.1.0]hexyl tosylate ($X \leftrightarrows XI$). However lg anch.ass. calculated for $X \leftrightarrows XI$ is rather low compared to values of other nonclassical systems[11,14]. This can be explained by the very small equilibrium constant ($K < 1$) of the boat-to-chair equilibrium of bicyclo[3.1.0]hexyl systems, which causes observed rates of chair forms ($k_{obs.}$) to be much less than their actual rates (k_{chair}):



$k_{obs.} = (K/1+K)k_{chair} \approx Kk_{chair}$ and $\lg(\text{anch.ass.})_{obs.} = \lg(\text{anch.ass.})_{chair} + \lg K$.
A recent review concludes: "Obviously it would be very valuable to know the value of K"[14]. From the difference of 3.5 between $\lg(\text{anch.ass.})_{obs.}$ of $X \leftrightarrows XI$ (1.5) and lg anch. ass. of Va and VIa - whose cis-3-tosyloxybicyclo[3.1.0]hexyl moieties have nearly the same conformation as XI - we derive $K \approx 10^{-3.5}$.

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1 a. Taken from the dissertation of G. Ellen, Vrije Universiteit, Amsterdam, 1974.

b. Presented at the IInd IUPAC Conference on Physical Organic Chemistry, Noordwijkerhout, The Netherlands, April, 1974.

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14 Cf. P.R. Story and B.C. Clark, Jr., in Carbonium Ions, G.A. Olah and P.v.R. Schleyer, Ed., Wiley-Interscience, Vol. III, 1007 (1972).