

SOLVOLYSIS OF EXO AND ENDO-CIS-BICYCLO[3.3.0]OCT-2-YL

AND CIS-4-CYCLOOCTEN-1-YL TOLUENESULFONATES^{1a}

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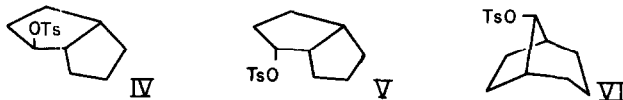
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The bicyclo[3.3.0]-[3.2.1]octyl carbonium ion system (structures I, II and III where each structure may represent a metastable ion, canonical form, or transition state) has been the subject of considerable interest.^{2,3,4} Evidence that bridged ion II is a meta-



stable form has been advanced,³ but formation of both exo and endo-bicyclo[3.3.0]oct-2-yl product on solvolysis of several suitable systems has been interpreted as evidence that classical ion I is probably in equilibrium with it.^{3,4} If so, one would expect that precursors close to I in structure should show no rate enhancement and in particular that exo and endo-bicyclo[3.3.0]oct-2-yl tosylates (IV and V) should have very similar rates of acetolysis. Rates of solvolysis of IV and V have been measured (Table I) and the exo/endo rate ratio is about 1.3 in acetic acid and 0.8 in ethanol. Estimation of the unenhanced

acetolysis rate for the [3.3.0] system by means of the Foote-Schleyer



relationships⁵ indicates that the observed rates for IV and V are consistent with little or no anchimeric assistance.⁶ Overall, it appears that the [3.3.0]-[3.2.1] system is similar to the bicyclo-[3.2.1]-[2.2.2]octyl carbonium ion systems⁷ in that bridged ions are often of about the same stability as some of the related classical ions.

TABLE I
Rates of Solvolysis of Alkyl Tosylates at 75°

Tosylate	Solvent	$10^5 k, \text{sec.}^{-1}$
<u>exo-cis</u> -Bicyclo[3.3.0]oct-2-yl, (IV) ^a	Acetic Acid ^c	11.6 ± 0.8^e
	Ethanol	5.0 ± 0.8^d
<u>endo-cis</u> -Bicyclo[3.3.0]oct-2-yl, (V) ^a	Acetic Acid ^c	8.73 ± 0.02
	Ethanol	6.5 ± 0.8^d
<u>cis</u> -4-Cycloocten-1-yl, (VII) ^b	Acetic Acid ^c	9.50 ± 0.18

^aTosylates IV and V were oils but yielded within 2% of the theoretical amount of acid on acetolysis. ^bTosylate VII had m.p. 47-48°, Anal.

Calcd. for $C_{15}H_{20}SO_3$: C, 64.24; H, 7.20. Found: C, 64.12; H, 7.22.

^cSolutions were 0.030 M in tosylate and 0.036 M in sodium acetate.

^dDetermined conductometrically. ^eDetermined as indicated in text.

While the endo tosylate (V) solvolyzes with good first-order kinetics, the acetolysis of IV is accompanied by internal return to

exo-bicyclo[3.2.1]oct-8-yl tosylate, (VI). In order to obtain the true acetolysis rate of IV (k_{IV}) the data shown in Table II were compiled by isolating unreacted tosylate after partial acetolysis, cleavage to the alcohol⁸ and gas chromatographic analysis. Using eq. (1)⁹ k_{IV} can be estimated and from the acetolysis rate of the steady-state mixture

$$\text{Mole fraction IV} = (k_{\text{obs}} - k_{\text{VI}})/(k_{\text{IV}} - k_{\text{VI}}) \quad (1)$$

$(3.16 \times 10^{-5} \text{ sec.}^{-1} \text{ at } 75^\circ)^3$ the mole fraction of IV present at equilibrium can be shown to be about 0.2.

TABLE II

Ion Pair Return in Acetolysis of

exo-cis-Bicyclo[3.3.0]oct-2-yl Tosylate at 75°

t, Ksec.	% Reaction	$10^5 k, \text{ sec.}^{-1} \text{ }^a$	% IV	% IV
0	0	∞	100	0
0.90	10	10.5	95.5	4.5
2.70	25	9.67	87	13
5.70	50	9.08	77	23

^aInstantaneous rate constant determined graphically from a plot of $\log [\text{ROTs}]$ vs. time.

Using the same analytical technique, it was possible to show that internal return also accompanies acetolysis of cis-4-cycloocten-1-yl tosylate (VII). After 50% reaction, 6% rearranged tosylate was present and after 75% reaction about 12%. The rearranged tosylate was a mixture of about 75% IV and 25% VI. Since this is far from the steady-



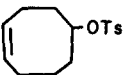
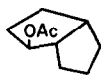
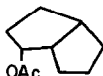



state ratio of IV and VI it is probable that IV is the initial product of internal return and VI is formed from it. If so, the conversion of VII to IV by ion-pair return is remarkably similar in stereochemistry to those rearrangements previously observed in the cis and trans-5-cyclodecen-1-yl systems.¹⁰ Kinetic detection of this rearrangement is



also possible, a definite downward drift in reaction rate (due to buildup of VI) becoming detectable after about 80% acetolysis.

The acetolysis products of IV, V and VII (Table III) are quite interesting. The products from VII are somewhat different from those reported previously for the corresponding brosylate² and are more in keeping with the observed isomerization of VII. The substitution products from IV and V are remarkably different, no endo-bicyclo[3.3.0]oct-2-yl or exo-bicyclo[3.2.1]oct-8-yl acetate being formed from V. (Detection of 0.5% of these acetates would have been possible.) Assuming classical ion I is the initial intermediate in both cases, the major cause of divergence in the product-forming step must be orientation of the counter ion. (If exo tosylate ionizes competitively to both I and II the conclusions remain the same.) Since the exo side of I appears most open to solvent attack,² temporary shielding of the endo side by the counter ion, as in the ion pair initially derived from V, may be sufficient to divert all product to exo [3.3.0] acetate. Whether, in the case of V, the Wagner-Meerwein shift cannot compete with the rapid exo attack of solvent or whether it is physically "blocked" by the

Table III
Products of Acetolysis^a

Product	% Yield from			
		IV	V	VII ^b
		24.6	51.3	26
		14.7	0	41.3
		0.9	1.7	1.2
		7.9	0	5
		52	47	26

^aAcetolyses were carried out at 95°; solutions were 0.030 M in tosylate and 0.036 M in sodium acetate; analyses done by gas chromatography. ^bPer cent of total bicyclic product. Monocyclic product (ca. 20%) was about half cyclooctenyl acetate and half a mixture of cyclooctadienes.

endo anion remains an interesting question.

References

- 1.a. Supported in part by the National Science Foundation and by the Petroleum Research Fund, administered by the American Chemical Society.
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