EFFICIENCY OF CARBON-CARBON DOUBLE BOND PARTICIPATION IN ACETOLYSIS

OF cis-5-CYCLOOCTENE-1,2-DIOL DIBROSYLATES[1]

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The efficiency with which a neighboring π-bond will displace one of a pair of

vicinal sulfonyloxy groups has recently become an important question. Lambert and Holcomb

suggested that the high solvolytic reactivity of exo-cis-5-norbornene-2,3-ditosylate (I)

relative to that of its saturated analog, II, (k_I/k_{II} = 500) might be explained by concerted,

or near-concerted, loss of both tosylates to form a resonance stabilized dication III,[3] but

Tanida and Tsushima's observations that the benznorbornene
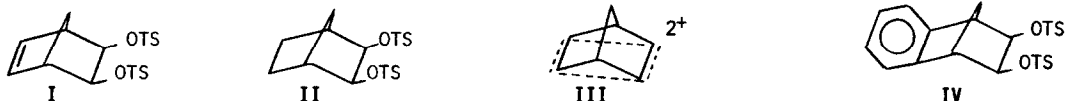
derivative IV also has a relatively high acetolysis rate (k_{IV}/k_{II} = 19.6), yet clearly

solvolyzes by a step-wise mechanism, throws this interpretation in doubt.[4] An alternative

explanation advanced by Lambert and Holcomb, that neighboring group displacement by a π-bond

may be better at removing positive charge from the vicinity of the remaining tosylate than

are other forms of ionization[3] now seems more attractive. We have therefore examined the

acetolyses of the cyclooctane- and cis-5-cyclooctene-1,2-dibrosylates (V and VI, respectively)

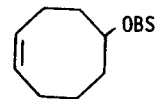in an effort to answer this question.
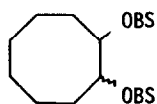
V, a = <u>cis</u>   VI, a = <u>cis</u>   VII   VIII
   b = <u>trans</u>   b = <u>trans</u>
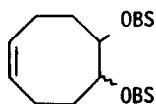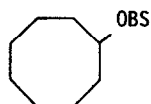
In Table I are presented the rates of acetolysis of these dibrosylates as well as
those of the monobrosylate analogs VII and VIII. All of the dibrosylates solvolyzed with
excellent first-order kinetics and the solvolysis equivalents of all but VI a were within
1% of theory.[5] Acetolysis of VI a was not followed to completion owing to its slowness and
discoloration of solution, but its rate was unchanged over 80% of reaction. The nmr spectra
of the dibrosylates were in complete agreement with their proposed structures. The products
from VI a and VI b were complex mixtures consisting of hydrocarbons, monoacetates, and
diacetates. For VI a these fractions constituted 17.5%, 55.5%, and 27% of the product
mixture, respectively. For VI b they were 26%, 61%, and 13%. After hydrogenation (Pt,
acetic acid) neither product mixture showed the presence of cyclooctane, and the monoacetate
fractions, after LiAlH$_4$ reduction to alcohols, were found to be almost entirely composed of
<u>exo-</u> and <u>endo-cis</u>-bicyclo[3.3.0]octan-2-ols(IX), identified by comparison of gc retention
times with those of authentic samples on several different columns. For VI a, the monosub-
stituted fraction, after reduction, consisted of 17% <u>endo</u> and 77% <u>exo</u> IX; for VI b, 36% <u>endo</u>
and 61% <u>exo</u>. The remainder in each case was a single component, not yet identified. The
diacetate fractions have not been identified but are probably mainly bicyclo[3.3.0] octanediol
derivatives. The retention times of the gc peaks corresponding to these fractions did not
change after hydrogenation. Clearly, the bulk of the acetolysis products arise by ring
closure at some stage of reaction. The acetolysis products of the saturated ditosylates
corresponding to V have been reported by Cope, <u>et al</u>.[7]
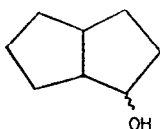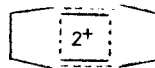
IX   X

The saturated systems, V, are known to ionize with almost exclusive transannular hydride shift,[7] and this apparently represents an efficient process for removal of positive charge from the vicinity of the second brosylate. The rate retardations observed here (relative to VII) are only 1.7×10^3-fold for V a and 4×10^2-fold for V b as opposed to the factor of 10^4 observed in the cyclohexane system[8] and the 3.5×10^5-fold factor observed between II and exo-2-norbornyl tosylate.[3] Introduction of the double bond in VIII results in a 40-fold deceleration, primarily through relief of steric compressions,[9] and participation of the double bond has only a modest kinetic effect since the rate of acetolysis of VIII is not significantly greater than that of a normal secondary brosylate.[9,10] Therefore, it is striking that introduction of a second brosylate in VIII, β- to the first, results in deceleration that is only moderate (7×10^2-fold) for the cis isomer, VI a, and quite small (60-fold) for the trans compound, VI b. It should be emphasized that VI b would have great steric difficulties in forming a cyclobutadiene dication-like species (X) in any concerted fashion because of the trans relationship of the brosylate groups, and its mechanism of acetolysis must almost certainly be step-wise. (If ring closure occurs in the first step, ionization of the second brosylate should be only a little slower than those of saturated bicyclo[3.3.0]oct-2-yl brosylates[10] and therefore considerably faster than the initial step.) Clearly, the double bond in these systems must be quite efficient at removing positive charge from the vicinity of the second brosylate in the transition state, or possibly, not much charge is developed in the transition state of these π-route reactions.[11]

While extrapolation from these conformationally mobile systems to the rigid norbornane ring system may be hazardous, it is interesting that the deceleration of acetolysis rate in I, attributable to introduction of the second tosylate, is 200-fold,[3] nicely bracketed by those of VI a and VI b.

Table I

Rates of Acetolysis of Cyclooctane Derivatives at 90°[a]

Compound	$10^5 k$, sec^{-1}	relative rates	
V a	5.35 ± 0.02	0.0255	1
V b	22.1 ± 0.1	0.105	4.1
VI a	0.31. ± 0.02	0.0015	0.058
VI b	3.49 ± 0.01	0.017	0.65
VII[b]	89×10^2	42	1700
VIII[b]	2.1×10^2	1	39

[a]Solutions were 0.01 M in dibrosylate and 0.036 M in sodium acetate.

[b]Extrapolated from the data of ref. 9.

References

1.   Supported in part by the Alfred P. Sloan Foundation.

2.   Alfred P. Sloan Research Fellow, 1968-70.

3.   J. B. Lambert and A. G. Holcomb, J. Amer. Chem. Soc., 91, 1572 (1969).

4.   H. Tanida and T. Tsushima, Tetrahedron Letters, 3647 (1969).

5.   The dibrosylates were prepared from the corresponding diols. The saturated diols were prepared in the manner of Traynham and Greene.[6] The unsaturated diols were prepared from cis,cis-1,5-cyclooctadiene in analogous fashion. The m.p.'s of the dibrosylates were: V a, 115.5-116.5°, V b, 125.5-126°; VI a, 146-147°; VI b, 132.5-133.5°. Anal. of VI a: Calcd. for $C_{20}H_{20}O_6Br_2S_2$: C, 41.39; H, 3.47. Found: C, 41.22; H, 3.45.

6.   J. G. Traynham and P. M. Greene, J. Amer. Chem. Soc., 86, 2657 (1964).

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