Y-ribose bond by acid can be accounted for by participation of the protonated canonical structure **14**, which leads to irreversible liberation of the Y base.

The proposed structure of Y base represents the most complex modified base that has been found thus far in any RNA molecule. This unusual degree of modification may be necessary to stabilize the relatively weak codon–anticodon interaction expected for phenylalanine.

Acknowledgments. We are grateful to Professor C. R. Cantor, Department of Chemistry, for bringing this problem to our attention and stimulating discussions, and to Dr. S. Fujimura, Institute of Cancer Research, for valuable advice. We also thank Professor H. G. Zachau, University of Munich, for his interest in our studies. The work was supported by Grants No. CA-11572 and CA-02332 from the U. S. Public Health Service, and by the Hoffmann-La Roche Company.

(21) Isolation of Y nucleoside by enzymatic cleavage and direct structural studies of the nucleoside are essential for establishment of the nucleoside structure.

(22) Career Scientist of the Health Research Council of the City of New York (I-190).

* Address correspondence to this author.

Koji Nakanishi,* Nobuo Furutachi, Makoto Funamizu
Department of Chemistry, Columbia University
New York, New York 10027

Dezider Grunberger, I. Bernard Weinstein[22]
Institute of Cancer Research and Department of Medicine
College of Physicians and Surgeons
New York, New York 10032

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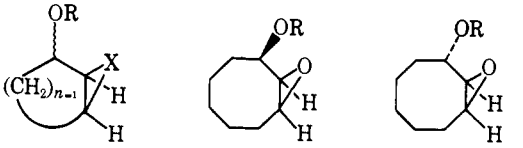
Solvolysis of *syn*- and *anti*-9-Oxabicyclo[6.1.0]non-2-yl *p*-Bromobenzenesulfonates

Sir:

The solvolytic reactions of *syn*- and *anti*-2-bicyclo[*n*.1.0]alkyl systems Ia have recently been the subject of extensive research.[1] The important effect that the stereochemistry of the leaving group has upon the product distributions is of particular interest. Whereas the solvolytic reaction products of Ia, with n = 2–5,[1a-e] have been shown to be independent of the orientation of the leaving group relative to the cyclopropane ring, other larger medium-ring cyclopropylcarbinyl systems yield one product mixture when the leaving group is syn to the cyclopropane ring, and a completely different product mixture when the leaving group is anti to the cyclopropane ring.[1f-h] We have therefore undertaken a study of the structurally related *syn*- and *anti*-oxabicyclo[*n*.1.0]alkyl systems Ib to make a comparison between the chemical reactivities of epoxycarbinyl and cyclopropylcarbinyl derivatives. We wish to report that this study has revealed a large syn:anti rate ratio and distinctly different product distributions for the solvolyses of *syn*- and *anti*-9-oxabicyclo[6.1.0]non-2-yl *p*-bromobenzenesulfonates (IIb[2] and IIIb[3]).



Ia, X = CH_2 b, X = O IIa, R = H b, R = Bs IIIa, R = H b, R = Bs

Products from hydrolysis of IIb and IIIb in 80% acetone–water are summarized in Table I. Of significance is the fact that the major products from hydrolysis of IIIb (namely IIIa, VI, and VIII[4]) are formed in only trace amounts from IIb. Also, the major products from IIb are isolated as relatively minor products from IIIb. The very different product distributions require that IIb and IIIb solvolyze through distinctly different mechanistic pathways, with a maximum of 1–2% crossover between pathways.

syn-*p*-Bromobenzenesulfonate IIb solvolyzed 259 times faster than IIIb at 25° (Table II), and yielded mainly suberaldehyde (V). A plausible mechanism that might account in part for the syn:anti rate ratio and large amount of V produced from IIb involves a competition between backside participation by the C–C bond of the oxirane ring (Scheme I) and solvent-assisted ionization. Such assistance of the oxirane ring would lead to oxonium ion XII, perhaps *via* an intermediate ion XI.[5]

Table I. Product Distributions from Hydrolysis of IIb and IIIb in 80% Acetone–Water[a]

Product	IIa	IIIa	V	VI	VII	VIII	IX
			$HC(=O)(CH_2)_3C(=O)H$	CHO	HO O	HO O	O
% from IIb	9.1	1.5	52.4	2.8	2.5[b]	~0[b]	28.3
% from IIIb	5.1	36.0	1.9	17.4[c]	~0[b]	28.9[b]	4.9

[a] Triethylamine was used as a buffer. [b] Epimers VII and VIII could not be separated on glpc. However, analysis of the ir spectra of the solvolysis compounds indicated the lack of contamination ($\lesssim$5%) of the other epimer.

(1) (a) K. Wiberg, V. Williams, Jr., and L. Friedrich, *J. Amer. Chem. Soc.*, 90, 5338 (1968); (b) E. C. Friedrich and S. Winstein, unpublished work; (c) H. L. Goering and K. E. Rubenstein, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 28–31, 1966, p 5K; (d) A. C. Cope and P. E. Peterson, *J. Amer. Chem. Soc.*, 81, 1643 (1959); (e) A. C. Cope, S. Moon, and P. E. Peterson, *ibid.*, 84, 1935 (1962); (f) M. Gasic, D. Whalen, B. Johnson, and S. Winstein, *ibid.*, 89, 6382 (1967); (g) D. Whalen, M. Gasic, B. Johnson, H. Jones, and S. Winstein, *ibid.*, 89, 6384 (1967); (h) C. D. Poulter and S. Winstein, *ibid.*, 92, 4274, 4282 (1970).

(2) Appropriate spectral data and elemental analyses were obtained: mp of IIb, 117.5–118.5°; mp of IIIb, 85.5–86.5°. *syn*-Alcohol IIa, mp 89.5–91.0°, was prepared by sodium borohydride reduction (99% stereospecificity) of 9-oxabicyclo[6.1.0]nonan-2-one.[3]

(3) A. C. Cope, A. Keough, P. Peterson, H. E. Simmons, Jr., and G. Wood, *J. Amer. Chem. Soc.*, 79, 3900 (1957).

(4) Compounds VII and VIII were oxidized with Jones reagent to 9-oxabicyclo[6.1.0]nonan-3-one; ir (CCl_4) 1705 cm^{-1}.

(5) The reaction of X → XI is related to the cyclopropylcarbinyl–homoallyl rearrangement. The net retention of stereochemistry at C-2 might be explained by ion XI; see ref 1f and g.

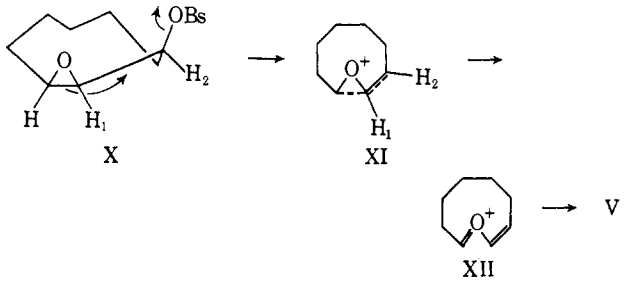
Table II. First-Order Rate Constants[a] and Activation Parameters[a] for Solvolysis of IIb and IIIb in 80% Ethanol–Water

Compd	Temp, °C	10^5k, sec^{-1}	$\Delta H^{\pm}$, kcal/mol	$\Delta S^{\pm}$, kcal/mol
IIb	59.8	22.7 ± 0.5	25.3 ± 0.4	0.7 ± 1.3
	49.8	6.64 ± 0.26		
	40.1	1.82 ± 0.07		
	25.0	0.23[b]		
IIIb[c]	100.3	12.2 ± 0.18	27.3 ± 0.1	−3.7 ± 0.4
	90.2	4.26 ± 0.004		
	80.1	1.40 ± 0.003		
	25.0	0.00089[b]		

[a] Calculated by nonlinear regression analysis. The reactions were monitored spectrophotometrically. [b] Extrapolated from data at higher temperatures. [c] Triethylamine was used as a buffer.

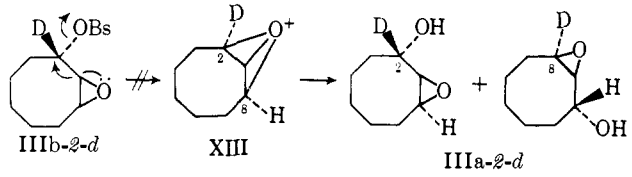
The mechanism by which IIIb solvolyzed to yield IIIa was investigated by solvolyzing IIIb-*2-d*.[6] The major

Scheme I



product possessed identical infrared and nmr spectra as IIIa-*2-d*. Therefore, participation by the nonbonding electrons of oxygen in the solvolysis of IIIb, which would lead to oxabicyclobutonium ion XIII, was ruled out as a major solvolytic pathway.[7] Intermediate XIII, if formed, would lead to scrambling of deuterium between C-2 and C-8 of the product IIIa because of the chemical equivalency of C-2 and C-8 in XIII (Scheme II).

Scheme II

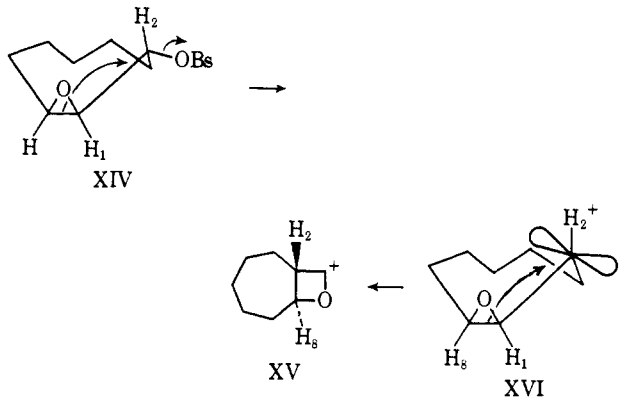


A plausible intermediate in the formation of 17% of cycloheptenecarboxaldehyde (VI) from IIIb is the trans-fused bicyclic oxonium ion XV, formed either by concurrent ionization-bond migration or ionization followed by migration of the C–C bond of the oxirane ring to the backside of the vacant p orbital at C_2 (Scheme III).[8] The low reactivity of IIIb and formation of significant amounts of retained, inverted, and hydride-shift alcohols from IIIb indicate that anchimeric assistance to ionization by the oxirane ring is at best a minor

(6) *anti*-Alcohol IIIa-*2-d* was prepared by sodium borodeuteride reduction of 2-cyclooctenone, followed by epoxidation of 2-cyclooctenol-*1-d* with *m*-chloroperbenzoic acid.

(7) Oxabicyclobutonium ions have been proposed as intermediates in the solvolysis of several simple epoxycarbinyl derivatives: H. Morita and S. Oae, *Tetrahedron Lett.*, 1347 (1969); H. G. Richey, Jr. and D. V. Kinsman, *ibid.*, 2505 (1969).

Scheme III



reaction pathway, and that an intermediate with charge residing mainly on C-2 must exist.

The solvolytic reactivity of 9-oxabicyclo[6.1.0]non-2-yl system Ib (n = 6) can be estimated to be a factor of *ca.* 10^6–10^7 less than the corresponding bicyclo[6.1.0]-non-2-yl system Ia (n = 6).[9] These data indicate that oxirane rings, in the absence of participation by the nonbonding electrons on oxygen, are not nearly as effective as cyclopropane rings in stabilizing developing positive charge on adjacent carbon atoms. In the solvolysis of IIIb, where only 17% of VI is formed, the product distribution indicates that the oxirane ring exhibits a destabilizing effect.

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(8) Stereospecific bond migration in *anti*-2-bicyclo[6.1.0]nonyl *p*-nitrobenzoate solvolysis leads to a trans-fused cyclobutane ring.[1h]

(9) The solvolytic reactivity of 2-bicyclo[*n*.1.0]alkyl brosylates was estimated to be *ca.* 10^9 times greater than that of 2-bicyclo[*n*.1.0]alkyl *p*-nitrobenzoates.[1b] The rates of solvolyses of IIb, IIIb, and Ia (n = 6) were extrapolated to common solvents and temperature.

Dale L. Whalen
Department of Chemistry
University of Maryland, Baltimore County
Baltimore, Maryland 21228
Received September 3, 1970

Establishment of Absolute Configuration in Tris-β-diketonate–Chelate Complexes by X-Ray Methods. The Structure of Λ(+)$_{589}$-*trans*-Tris[(+)-3-acetylcamphorato]chromium(III)

Sir:

Of chiral coordination compounds, tris complexes of bidentate ligands comprise an important and much studied subclass. Despite considerable interest in this area, only a small number of absolute configurations have been put on a firm basis *via* X-ray analysis.[1] Surprisingly, tris-β-diketonate complexes, which have occupied a prominent position in the development of coordination chemistry, are among the types of complex for which absolute configurations have not been

(1) For a recent review, see R. D. Gillard and P. R. Mitchell, *Struct. Bonding (Berlin)*, 7, 46 (1970).