Clark, *et al.*,[3] have found that in the breakdown of 2-methylnaphthalenediol 1,4-diphosphate[1] (Synkavit, V) under similar conditions, the product contains 50% orthophosphate, 15% pyrophosphate, and 35% trimetaphosphate. We have found in the presence of added phosphate in DMF solution that Synkavit (V) gives only phosphate and pyrophosphate (see Table I). It has also been reported[6] that when a quinol phosphate reacts in the presence of P^{32}-labeled inorganic phosphate, no radioactivity is detectable in the pyrophosphate, and that this observation rules out any simple nucleophilic attack by inorganic phosphate on metaphosphate. We have run the same reaction with both quinol monophosphate (I) and diphosphate (V) in the presence of O^{18}-labeled tetrabutylammonium phosphate and found that O^{18}-labeled pyrophosphate is formed in good yield.

These results are presented in Table II.

TABLE II

O^{18} IN PHOSPHATE AND PYROPHOSPHATE FROM OXIDATIVE HYDROLYSIS OF QUINOL PHOSPHATE IN DRY DMF[a]

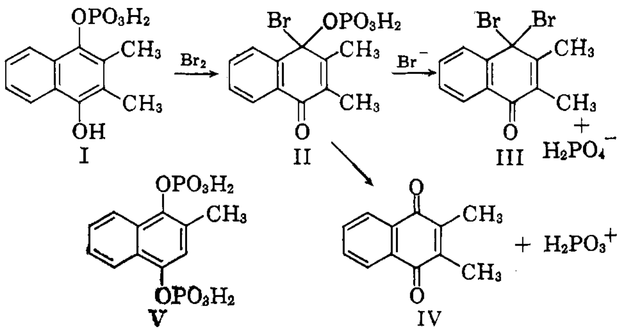
Quinol phosphate	Atom % excess O^{18} in added phosphate	Atom % excess O^{18} in product phosphate	Atom % excess O^{18} in product pyrophosphate[b]
I	11.1	5.1	3.9
V	21.4	12.8	8.0

[a] Conditions as in Table I. [b] Pyrophosphate isolated as zinc salt at pH 3–4. Oxygen isotopic analyses of phosphate and pyrophosphate by method of Anbar and Guttmann.[7]

It is apparent from Table II that O^{18} enrichment of the phosphate at the end of the reaction is considerably lower than at the start, indicating dilution by unlabeled inorganic phosphate. This phosphate must be formed in the course of the reaction, by C–O bond fission.

The O^{18}-enriched pyrophosphate in the product must be formed by phosphorylation of the total amount of inorganic phosphate by a "metaphosphate" intermediate formed by P–O bond fission. There appear, therefore, to be two parallel reaction pathways for the breakdown of a quinol phosphate in the presence of bromine in DMF solution, each involving bond fission in a different position.

The following tentative mechanism is suggested for the reactions of the monophosphate.



The quinonoid intermediate II which has not been isolated is similar to those suggested[8] for the bromination of phenols. The step converting II to III is a halide ion cleavage of an alkyl ester phosphate with attack on carbon similar to those found[9] for certain secondary and tertiary alkyl phosphates. Intermediate III has not been isolated since it is converted to the quinone IV on work-up. A quinonoid intermediate, the dimethyl ketal of *p*-benzoquinone, has been isolated by Durckheimer and Cohen[10] from the breakdown of hydroquinone phosphate in methanol solution, using ceric ammonium nitrate as oxidizer. In DMF solution the "metaphosphate" intermediate formed by P–O bond fission may be transiently bound to the solvent as an imidoyl phosphate. Enol phosphates of acid amides of this type have been prepared by Cramer.[11]

From the amount of pyrophosphate produced (see Table I) in the breakdown of compounds I and V, it appears that in DMF solution, the extent of P–O bond fission is about 30%. This is of the same order as the P–O bond fission of I in water.[4]

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THE ISOTOPE DEPARTMENT
WEIZMANN INSTITUTE OF SCIENCE
REHOVOTH, ISRAEL

AVIVA LAPIDOT
DAVID SAMUEL

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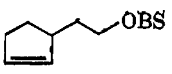
Ring Closure to the Bicyclooctyl System in the Solvolysis of 3-(Δ^2-Cyclopentenyl)propyl Brosylate[1,2]

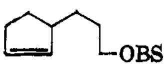
Sir:

In recent years the investigation of cyclizations of unsaturated sulfonate esters under solvolytic conditions has been fruitful both from a theoretical and from a synthetic viewpoint. Confirming evidence for the unique stability of the 2-norbornyl cation was obtained from solvolytic studies on 2-(Δ^3-cyclopentenyl)ethyl sulfonates,[3] while similar studies have contributed evidence concerning nonclassical cations of the bicyclo[3.2.1]octyl and bicyclo[2.2.2]octyl systems.[4] Even the acetolysis of 5-hexenyl *p*-nitrobenzenesulfonate yielded interesting data concerning the character of the cyclohexyl carbonium ion.[5] In this communication we wish to describe some of our results concerning the solvolysis of 3-(Δ^2-cyclopentenyl)propyl brosylate (I) and the related compounds 2-(Δ^2-cyclopentenyl)ethyl brosylate (II) and 3-cyclopentylpropyl brosylate (III).

I



II



III

The alcohols corresponding to the brosylates were prepared by standard techniques and had properties

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(2) This work was supported in part by the Petroleum Research Fund, administered by the American Chemical Society (Grant No. 1272-A4).

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identical with those listed in the literature.[6] These were converted to brosylate esters in the usual way; brosylates I and II were oils which liberated 96 to 98% of the theoretical amount of sulfonic acid on acetolysis, while III melted at 40–41° and gave the correct analysis for carbon and hydrogen content.

Kinetic data are presented in Table I. Good first-order kinetics were obtained in all cases; in particular, acetolysis of I was very reproducible and free of drift.

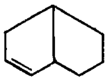
TABLE I

SOLVOLYTIC RATE CONSTANTS (SEC.$^{-1}$ × 10^5)

Solvent	Ethanol (80°)	Acetic acid (80°)[a]	97% formic acid (70°)
k_1 for I	13.8 ± 1.0	1.55 ± 0.05[b]	25.7 ± 3.5
k_1 for II	7.16 ± 0.33	0.278 ± 0.010	...
k_1 for III	13.4 ± 1.0	0.411 ± 0.012[c]	1.32 ± 0.14

[a] Containing 0.036 M sodium acetate, 0.030 M brosylate. [b] At 70°, $k_1 = (5.70 \pm 0.05) \times 10^{-6}$ sec.$^{-1}$; at 100°, $k_1 = (9.80 \pm 0.04) \times 10^{-5}$ sec.$^{-1}$. [c] At 70°, $k_1 = (1.47 \pm 0.03) \times 10^{-6}$ sec.$^{-1}$; at 100°, $k_1 = (2.63 \pm 0.04) \times 10^{-5}$ sec.$^{-1}$

The products of acetolysis, and in the case of I, formolysis, were reduced with lithium aluminum hydride and analyzed by vapor phase chromatography, using 1,2,3-tris(2-cyanoethoxy)propane as the stationary phase. Components were identified by comparison of retention times and infrared spectra with those of authentic samples. On acetolysis in the presence of excess sodium acetate, II and III yielded only the corresponding acetates. On the other hand, I yielded a complex mixture of acetolysis products. After reduction, this mixture consisted of 20% *cis*-bicyclo[3.3.0]-oct-2-ene (IV), 25% *cis,trans*-bicyclo[3.3.0]octan-2-ol (V), 1.7% *cis,cis*-bicyclo[3.3.0]octan-2-ol (VI), 0.8% *cis*-bicyclo[3.3.0]octan-1-ol (VII), 11% *exo*-bicyclo-[3.2.1]octan-8-ol (VIII), and 41.7% uncyclized alcohol. In formic acid (in the presence of excess sodium formate), the products of I were entirely cyclized, and, after reduction, consisted of 1.6% IV, 4.6% VI, 4.5% VII, 66% V, and about 23% VIII. The vapor phase chromatographic peaks due to V and VIII overlap slightly and the relative amounts of these two compounds may be somewhat in error.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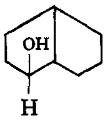
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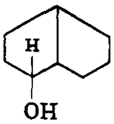
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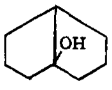
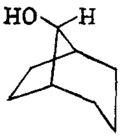
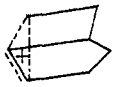

VII


VIII

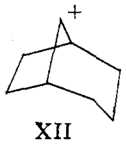
It is obvious from the kinetic and product data that the bridged ion IX[7] is not readily accessible from II in acetic acid solution. The fact that the rate of acetolysis of II is actually slower than that of III is not surprising, and is probably due both to a somewhat greater amount of steric hindrance at C-1 and a modest inductive effect of the double bond in II. It has been observed that 4-pentenyl and *trans*-4-hexenyl *p*-nitrobenzenesulfonate both solvolyze in acetic acid at about 75% of the rate of the *n*-hexyl sulfonate ester.[5]

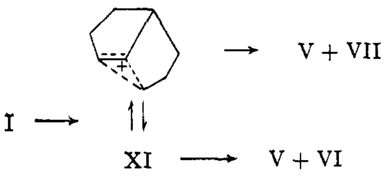

IX

In the case of I it is clear that intramolecular participation of the double bond competes with the normal process of solvolysis in acetic acid, and takes over completely in the more highly ionizing formic acid. In ethanol, a relatively nucleophilic solvent, the effect probably disappears, as evidenced by the identical rates of ethanolysis for I and III.

The amount of rate enhancement and the degree of cyclization of I are extremely similar to those observed in the case of 2-(Δ^3-cyclohexenyl)ethyl brosylate.[4b] Ignoring ground state energy differences between the two unsaturated brosylates, this suggests that the intermediate ion produced by cyclization of I might be very roughly of the same stability as the bicyclo[2.2.2]oct-2-yl nonclassical ion.[8] However, the pattern of cyclization products obtained from I cannot be rationalized on the basis of a single intermediate carbonium ion. The cyclized substitution products obtained from I are the same as those obtained by solvolysis of *cis*-4-cycloocten-1-yl,[9] *cis,trans*-bicyclo[3.3.0]oct-2-yl,[10] and *exo*-bicyclo[3.2.1]oct-8-yl[11] sulfonate esters, although the relative amounts of each product vary greatly among the different cases. Of critical importance is the fact that little or none of the epimer of VIII (*endo*-bicyclo-[3.2.1]octan-8-ol, X) is formed. If I merely cyclized to a mixture of ions XI and XII, one would expect to obtain both possible products from XII, inasmuch as one *does* obtain all those corresponding to XI. A scheme similar to one suggested by Foote and Woodward for the acetolysis of *exo*-bicyclo[3.2.1]octan-8-yl tosylate[11] would most simply explain our results and is shown below.


XI


XII



In terms of this scheme, the bridged ion would produce only V and VIII, while XI would yield V and VI. The tertiary derivative, VII, formed by hydride ion migration, and the elimination product, IV, probably also arise from XI. Whether the bridged ion, ion XI, or a mixture of the two is the initial ionization product of I has not yet been determined.

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[12] National Institutes of Health Predoctoral Fellow, 1963–1964.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK 27, NEW YORK

W. D. CLOSSON
GEORGE T. KWIATKOWSKI[12]

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