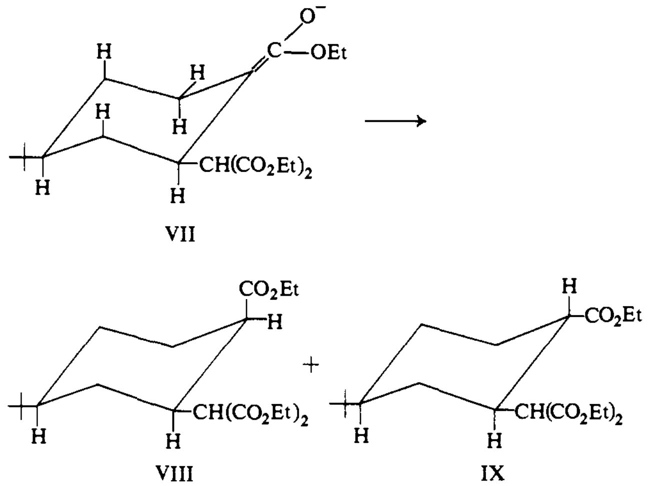


VII

VIII

IX

The above results appear to bridge the opposing views[1-4] and upholds the general hypothesis of least hindered approach[3] in such protonations.

Acknowledgment. Part of this work was supported by the Defence Research Board of Canada whom we thank.

[12] To whom inquiries should be addressed at the University of Alabama.

R. A. Abramovitch,[12] M. M. Rogic
S. S. Singer, N. Venkateswaran
Department of Chemistry, University of Alabama
University, Alabama 35486
and Department of Chemistry, University of Saskatchewan
Saskatoon, Saskatchewan, Canada
Received December 13, 1968

Kinetic Evidence for a Bishomocyclobutenium Dication[1]

Sir:

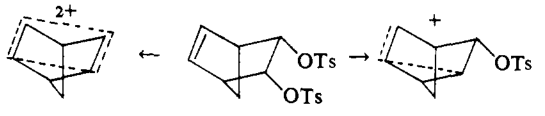
Dicarbonium ions have been recognized in structurally diverse situations.[2] A particularly elusive member of this class has been the cyclobutenium or cyclobutadiene dication (I). This ion was expected to be relatively stable, since it conforms to the Hückel rule ($n = 0$) and is isoelectronic with the known cyclopropenium ion (II).[3]


I


II

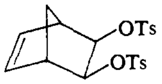
Because of the forced proximity of the charges, the stability of I is undoubtedly less than that of II, although the apparent success of several derivative syntheses[4] confirms the presence of some special stability for the cyclobutenium structure.

We wish to report kinetic evidence from the acetolysis of the conformationally rigid ditosylate of *exo-cis*-bicyclo[2.2.1]hept-5-ene-2,3-diol (III) that may implicate rapid loss of both tosylate groups to form a bishomocyclobutenium dication (IV). In the past,[5] two tosylate or brosylate groups in a molecule have been observed to undergo independent, stepwise solvolysis. Such a pathway for III would lead by way of homoallylic participation to ion V, which would absorb a molecule of solvent to form an acetoxy tosylate intermediate (in acetolysis) before losing the second tosylate group.

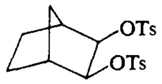


IV III V

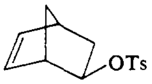
The essential kinetic argument involves comparison of the rates of the saturated and unsaturated mono- and ditosylates (III, VI–VIII). The double bond in monotosylates is known to be rate retarding, despite homoallylic assistance.[6] The second tosylate group is known to cause considerable rate retardation in a stepwise reaction, since the first-formed carbonium ion is destabilized by the remaining electron-withdrawing tosylate group.[5] If III were to lose both tosylate groups to form a cyclobutenium-stabilized dicarbonium ion (IV), the double bond would necessarily be rate enhancing (VI/III) and the second tosylate group would be much less rate retarding (VII/III).



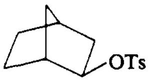
III



VI



VII



VIII

We have prepared[7] III and VI–VIII and measured their solvolysis rates by the usual titrimetric methods in buffered (KOAc) acetic acid in duplicate or triplicate at each of three or four temperatures. The rates and activation parameters at 75° are given in Table I. The rate-

---

[1] This work was supported by the Petroleum Research Fund, administered by the American Chemical Society (PRF 2970-A 4, 5), and by the National Science Foundation.

[2] H. Hart, T. Sulzberg, R. H. Schwendeman, and R. H. Young, *Tetrahedron Lett.*, 1337 (1967); I. S. Akhrem, E. I. Fedin, B. A. Kvasov, and M. E. Vol'pin, *ibid.*, 5265 (1967); H. Volz and M. J. Volz de Lecea, *ibid.*, 4675 (1966); C. U. Pittman, Jr., *ibid.*, 3619 (1967); J. S. McKechnie and I. C. Paul, *J. Am. Chem. Soc.*, **89**, 5482 (1967); B. E. Fleischfresser, W. J. Cheng, J. M. Pearson, and M. Szwarc, *ibid.*, **90**, 2172 (1968); D. M. Brouwer, *Chem. Commun.*, 515 (1967).

[3] R. Breslow, J. T. Groves, and G. Ryan, *J. Am. Chem. Soc.*, **89**, 5048 (1967); D. G. Farnum, G. Mehta, and R. G. Silberman, *ibid.*, **89**, 5048 (1967).

[4] D. G. Farnum and B. Webster, *ibid.*, **85**, 3502 (1963); H. H. Freedman and A. E. Young, *ibid.*, **86**, 734 (1964); H.-E. Sprenger and W. Ziegenbein, *Angew. Chem. Intern. Ed. Engl.*, **7**, 530 (1968); also see M. H. Benn, T. S. Sorenson, and A. M. Hogg, *Chem. Commun.*, 574 (1967), for mass spectral evidence.

[5] S. Winstein, C. Hanson, and E. Grunwald, *J. Am. Chem. Soc.*, **70**, 812 (1948); S. Winstein, E. Grunwald, R. E. Buckles, and C. Hanson, *ibid.*, **70**, 816 (1948); S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, **70**, 821 (1948); A. C. Cope, S. Moon, and P. E. Peterson, *ibid.*, **81**, 1650 (1959); A. C. Cope and G. W. Wood, *ibid.*, **79**, 3885 (1957).

[6] The subject has been discussed by M. Hanack and H.-J. Schneider, *Angew. Chem. Intern. Ed. Engl.*, 6, 672 (1967).

[7] The unsaturated diol was prepared from bicyclo[2.2.1]heptadiene according to the procedure of Y. F. Shealy and J. D. Clayton, *J. Am. Chem. Soc.*, **88**, 3885 (1966). We thank Dr. Shealy for sending us the experimental details. An nmr analysis of the *exo-cis* and *endo-cis* isomers leaves no doubt concerning the stereochemistry of the product (M. C. Thorpe, private communication). The unsaturated monoalcohol was synthesized by the method of S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Org. Chem.*, 31, 2733 (1966). Hydrogenation of these materials yielded the saturated compounds. All the tosylates were crystalline and pure by our analytical techniques.

retarding effect of the double bond in the monotosylates (VIII/VII) is seen to be about 3.5; the retarding effect of the second tosylate group in the saturated systems (VIII/VI) is about 350,000. The unsaturated ditosylate under scrutiny (III) reacts more rapidly than the saturated ditosylate (III/VI = 500) and somewhat more slowly than the unsaturated monotosylate (VII/III = 200), *i.e.*, the double bond in III is rate accelerating and the second tosylate group is much less rate retarding than in VI. The composite rate acceleration for III is thus at least 1700 (500 × 3.5 or 350,000/200). These observations are those expected for nearly concerted loss of both tosylate groups to form a cyclobutenium-stabilized dicarbonium ion. The stepwise mechanism, in which the molecule passes through a monocarbonium ion (V), an acetoxy tosylate, and another monocarbonium ion, can also furnish a rationale of the data.[8]

Table I. Kinetic Parameters for Solvolysis in Buffered Acetic Acid at 75°

Comp	Rate, sec^{-1}	ΔH^*, kcal/mol	ΔS^*, eu
III	8.6×10^{-6}	27.6	−3
VI[a]	1.7×10^{-8}	31.4	−4
VII	1.7×10^{-3}	21.2	−11
VIII	5.9×10^{-3}	22.2	−5

[a] Because this compound solvolyzes so slowly, the rate at 75° had to be extrapolated from measurements at higher temperatures with the aid of the Arrhenius equation.

If the two tosylate groups ionize almost simultaneously to form a dicarbonium ion, the first-order rate should be constant throughout time. The unsaturated ditosylate III solvolyzes with a constant rate or with a slight upward drift in rate, as has been noted previously.[5] If the reaction were stepwise, the situation would be much more complicated,[9] because the intermediate acetoxy tosylate might be expected to react at a different rate from the ditosylate. The solvolysis rate of the saturated ditosylate VI, and of other similar systems,[5] was observed to decrease significantly. These contrasting observations for III and VI are consistent with (but do not require) a dicarbonium ion mechanism in the first case and a stepwise reaction in the second.

The products of the reaction appear to be two isomeric bicyclo[2.2.1]heptenyl diacetates and two tricyclo[2.2.1.$0^{2,6}$]heptyl diacetates. The product distribution was invariant after one, two, three, four, or five half-lives. Analysis of the reaction mixture after one half-life revealed only product diacetates and starting-material ditosylate, but no acetoxy tosylates.

The kinetic behavior of III and the product studies are consistent either with a dicarbonium ion intermediate (IV) or with an acetoxy tosylate that reacts at least as rapidly as III. The rate of III relative to VI–VIII is most easily explained in terms of the dicarbonium ion pathway, although a rationale can also be constructed from the two-step mechanism.[8] We hope to obtain further evidence concerning the mechanism from deuterium labeling in the products and from secondary deuterium isotope effects. We are also examining other similar systems for this effect.[10]

---

(8) Explanation of the rate data in terms of the stepwise mechanism would have to argue that homoallylic participation in III is better able to separate the positive charge from the remaining tosylate group than can σ participation in VI.

(9) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1961, pp 166–169.

(10) An excited-state effect that we interpret as analogous to the interaction in intermediate IV has been reported by J. J. Bloomfield and R. E. Moser, *J. Am. Chem. Soc.*, **90**, 5625 (1968).

(11) Alfred P. Sloan Fellow, 1968–1970.

(12) National Science Foundation Graduate Fellow, 1966 to the present.

Joseph B. Lambert,[11] **Allen G. Holcomb**[12]
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

Received December 23, 1968

Germanium Atoms. Reactions with Germane and Silane[1]

Sir:

Recent interest in the chemistry of silicon atoms[2] prompts us to report observations on the reactions of recoiling germanium atoms. Striking similarity between germanium and silicon atoms has been found in analogous reaction systems.

Germanium atoms were produced from gaseous germane by recoil from the nuclear transformation $^{76}\text{Ge}(\text{n},2\text{n})^{75}\text{Ge}$. Reaction mixtures at 2.2 atm were irradiated with a fast-neutron flux of *ca.* 10^8 neutrons/(cm^2 sec), as described previously for silicon experiments.[3] In addition to ^{75}Ge (half-life, 82 min), very low activities of other radioactive germanium and gallium isotopes were produced, since germane of natural abundance was irradiated. None of the other activities interferes with the analysis of ^{75}Ge. The cross section for formation of ^{75}Ge increases rapidly from the threshold energy of 9.35 MeV to 1.82 barns for 14.5-MeV neutrons.[4] That free, neutral germanium atoms are indeed produced under these conditions is indicated by the calculated recoil energy, 4×10^4 eV, sufficient to rupture all bonds in the precursor molecule, and also by calculations of charge-transfer cross-section maxima according to the resonance rule.[5]

Irradiation of pure germane with fast neutrons produced germane and digermane as the sole volatile radioactive products detected by standard radio-vapor-chromatographic methods.[3] Radioactive products were compared with authentic materials on three different columns and the identity of the radio-nuclide verified by decay analysis and γ-ray spectroscopy on individually trapped, separated products. The product ratio $\text{H}_3{}^{75}\text{GeGeH}_3 : {}^{75}\text{GeH}_4 = 5.0 \pm 0.8$ is identical within experimental error with the product ratio $\text{H}_3{}^{31}\text{SiSiH}_3 : {}^{31}\text{SiH}_4 = 4.8 \pm 0.9$ ob-

---

(1) AEC Standard Technical Report No. COO-1713-8.

(2) See P. P. Gaspar, S. A. Bock, and C. A. Levy, *Chem. Commun.*, 1317 (1968), for recent references.

(3) P. P. Gaspar, S. A. Bock, and W. C. Eckelman, *J. Amer. Chem. Soc.*, **90**, 6914 (1968).

(4) E. B. Paul and R. L. Clarke, *Can. J. Phys.*, **31**, 267 (1953).

(5) (a) H. S. Massey and E. H. Burhop, "Electronic and Ionic Impact Phenomena," Clarendon Press, Oxford, 1952, p 441; (b) J. B. Hasted, "Physics of Atomic Collisions," Butterworth & Co., Ltd., London, 1964, p 420; (c) but for examples of large charge-transfer cross sections at velocities low compared to maxima predicted by the resonance rule, see G. K. Lavrovskaya, M. I. Markin, and V. L. Tal'roze, *Kinetics Catalysis* (USSR), **2**, 21 (1961).