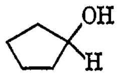
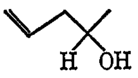


VII



VIII

IX

has little effect on the rate of formolysis,[11] and the same would surely be true for the corresponding brosylates. However, the degree of participation is evidently small; indeed, Vb solvolyzed more slowly than ethyl brosylate. A difference of this kind would be expected if the reaction involved no participation, since cyclopropyl should exert an inductive effect analogous to that of unsaturated groups.[12]

Our results are therefore consistent with the tentative suggestion of Sauers and Ubersax[2b] that participation is unimportant in the formolysis of Vb; at the same time, they imply that the cyclopropane is a potentially effective neighboring group, being able to participate if aided by methyl substitution.

On the other hand, cyclopropyl seems to be a less effective neighboring group than vinyl, judging by a comparison of the relative rates of formolysis of allylcarbinyl tosylates, with and without methyl substituents,[3,13] with those for the cyclopropyl derivatives in Table I. The fact that I solvolyzes much faster than III cannot therefore be attributed to a greater innate ability to participate on the part of cyclopropyl than of vinyl; it is presumably due either to ring strain or to the fact that the geometry of I is even more ideally suited to participation by the cyclopropyl group than is that of III for participation by the π electrons of the double bond.[14]

[11] S. Winstein and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1120 (1952).

[12] It is generally agreed that the carbon orbitals used to form exocyclic bonds in cyclopropane must be close to sp^2 in hybridization.

[13] Servis and Roberts[3] found that substitution of a *cis*- or *trans*-methyl group in the terminal position of allylcarbinyl tosylate gave rate accelerations of 165 and 770, respectively, when compared to *n*-butyl tosylate.

[14] G. D. Sargent, R. L. Taylor, and W. H. Demisch, *Tetrahedron Letters*, 2275 (1968).

Michael J. S. Dewar, J. Milton Harris
Department of Chemistry, The University of Texas
Austin, Texas 78712

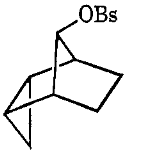
Received November 2, 1968

Solvolyses of 2-Cyclopropylethyl Brosylate[1]

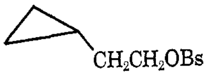
Sir:

Intense interest has been focused on the potential interaction of cyclopropane with cationic species in situations in which the cyclopropyl ring and the cation are insulated by a saturated group, *i.e.*, homocyclopropylcarbinyl or 2-cyclopropylethyl systems.[2] Theoretical considerations indicate a large stabilization energy for a 2-cyclopropylethyl cation.[2c] To the extent that a transition state for ionization approaches the geometry of this hypothetical ion, large rate enhancements might be anticipated. Enhancement of the rates of solvolysis for systems of this type have varied from none[2g,j] to 10^{14} in the case of I.[2k,l]

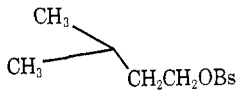
In reactions involving carbonium ions of unsubstituted 2-cyclopropylethyl compounds, product analyses and isotope labeling studies indicate extensive rearrangement of the carbon skeleton.[2b,f] It can also be deduced that the propensity for cyclopropyl migration is intermediate between that of phenyl and hydrogen.[2d] The rates of solvolysis of 2-cyclopropylethyl brosylate (II) have been determined to obtain evidence to ascertain whether the rate is enhanced by cyclopropyl participation and whether rearrangement occurs at the kinetically measured ionization stage or in a subsequent step. Isoamyl (2-isopropylethyl) brosylate (III) has been used for rate comparisons as the best available approximation to the geometrical requirements of the cyclopropylethyl system.[3]



I



II



III

2-Cyclopropylethyl brosylate was prepared from 2-cyclopropylethanol[5] and purified by recrystallization from ether–pentane; it had a melting point and an nmr spectrum which agreed with that reported.[2f] Isoamyl brosylate was prepared and purified in a similar manner. Rates were determined titrimetrically by standard procedures to an indicator end point for ethanolyses and acetolyses and by potentiometric titration for formolyses. Rate constants were determined graphically from linear first-order plots which include data from at least three half-lives using experimental infinity titers taken at ten half-lives.

Table I. Solvolytic Rate Constants

Solvent	Temp, °C	2-Cyclopropylethyl[a] $k \times 10^5$, sec^{-1}	Isoamyl[a] $k \times 10^5$, sec^{-1}
97% EtOH	75.01	4.40	4.66
CH_3CO_2H	110.30	4.29[b]	4.40[b]
CH_3CO_2H	119.43	7.89[b]	
CH_3CO_2H	129.97	20.1[b,d]	20.9[b,e]
HCO_2H	59.98	0.710[c]	0.652[c]
HCO_2H	75.02	3.13[c,f]	2.85[c,g]

[a] Brosylate concentration is 0.02–0.03 *M*. [b] 0.035 *M* sodium acetate. [c] 0.046 *M* sodium formate. [d] $\Delta H^{\ddagger} = 23.34$ kcal/mol, $\Delta S^{\ddagger} = -18.22$ eu. [e] $\Delta H^{\ddagger} = 23.55$ kcal/mol, $\Delta S^{\ddagger} = -17.52$ eu. [f] $\Delta H^{\ddagger} = 22.06$ kcal/mol, $\Delta S^{\ddagger} = -16.06$ eu. [g] $\Delta H^{\ddagger} = 21.93$ kcal/mol, $\Delta S^{\ddagger} = -16.63$ eu.

---

[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[2] (a) S. Winstein and J. Sonnenberg, *J. Amer. Chem. Soc.*, **83**, 3235 (1961); (b) G. E. Cartier and S. E. Bunce, *ibid.*, **85**, 932 (1963); (c) S. Winstein, P. Bruck, P. Radlick, and R. Baker, *ibid.*, **86**, 1867 (1964); (d) M. Hanack and H. M. Ensslin, *Tetrahedron Lett.*, 4445 (1965); (e) K. B. Wiberg and G. Wenzinger, *J. Org. Chem.*, **30**, 2278 (1965); (f) R. R. Sauers and R. W. Ubersax, *ibid.*, **31**, 495 (1966); (g) J. Haywood-Farmer, R. E. Pincock, and J. I. Wells, *Tetrahedron*, **22**, 2007 (1966); (h) R. R. Sauers, J. A. Beisler, and H. Feilich, *J. Org. Chem.*, **32**, 569 (1967); (i) P. K. Freeman and D. M. Balls, *Tetrahedron Lett.*, 437 (1967); (j) C. F. Wilcox and R. G. Jesaitis, *ibid.*, 2567 (1967); (k) H. Tanida, T. Tsuji, and T. Irie, *J. Amer. Chem. Soc.*, **89**, 1953 (1967); (l) M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967).

[3] It can be estimated from available data[2e,4] that the inductive effect of a "nonconjugated" cyclopropane is electron withdrawing by a factor of 6–15 on the rates of solvolytic reactions.

[4] H. C. Brown and J. D. Cleveland, *J. Amer. Chem. Soc.*, **88**, 2051 (1966).

[5] H. Hart and D. P. Wyman, *ibid.*, **81**, 4891 (1959).

The rates of ethanolysis, acetolysis, and formolysis of 2-cyclopropylethyl brosylate and isoamyl brosylate are virtually identical, indicating little or no rate enhancement by cyclopropane.[6] The apparent m value[7] (calculated from the rates in formic and acetic acids) for 2-cyclopropylethyl brosylate is 0.34, and for isoamyl brosylate $m = 0.33$ at 75° (ethyl tosylate has $m = 0.37$ at 75°[7]). The insensitivity of the relative rates of cyclopropylethyl and isoamyl brosylates to changes in solvent ionizing power and solvent nucleophilicity suggests that both compounds solvolyze by the same mechanism.[8] The apparent m value is typical for primary arenesulfonates,[7] and it is probable that the transition states for both of these reactions involve a large degree of nucleophilic assistance by solvent (high N character[9]).

Formolysis product analyses (0.13 M brosylate, 0.14 M sodium formate) were determined from the crude formate ester mixtures by gas chromatography. Preliminary analyses at ten half-lives of solvolysis indicate that approximately 75% of the product is 1,3-pentanediol diformate (identified by nmr spectra and comparison with an authentic sample) and that less than 15% cyclopentyl formate is formed.[2f,10] An nmr spectrum of the formolysis reaction mixture using the same concentrations as reported[2f] shows that at least 80% of the cyclopropane hydrogens are retained at 75% reaction, indicating that the products are largely determined by ring opening of 2-cyclopropylethyl formate.[11] The maximum extent of rearrangement to cyclopentyl formate, etc.,[2f,10] is therefore 25% or less. The similar kinetic behavior of II and III and the formation of cyclopropylethyl formate as the predominant kinetic product indicate that participation by cyclopropane is relatively unimportant in this system.[12]

Cyclopropane is thus a less effective neighboring group than an olefin (allylcarbinyl brosylate is seven times more reactive than n-butyl brosylate[8]).[13] However, in the norbornyl system, I, cyclopropane is 10^3 times more effective than a double bond. It is concluded that either (a) the norbornyl system is strained, and the apparent rate enhancement reflects the difference in strain of I and the corresponding olefin, or that (b) the geometrical requirements for effective cyclopropane orbital overlap with a carbonium ion center are more stringent than the requirements for double bond participation.[16,17] If the cyclopropane-ring bonds are considered to be bent orbitals with a high degree of p character, these orbitals are in effect turned in toward each other on the cyclopropane ring and are therefore less available for overlap with a nearby center than are the orbitals of a double bond. These hypotheses are currently being tested further.

---

(6) The rates could not be determined in trifluoroacetic acid buffered with sodium trifluoroacetate as the cyclopropane protons in the nmr spectrum disappear completely before 10% solvolysis occurs.

(7) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(8) K. L. Servis and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 3773 (1964).

(9) S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2700 (1951).

(10) Sauers and Ubersax[2f] isolated (in relative yields) 2-cyclopropylethanol (35%), cyclopentanol (36%), methylallylcarbinol (12%), and crotylcarbinol (17%) after $LiAlH_4$ reduction (aqueous work-up) of the crude formate esters obtained from formolysis (0.33 M brosylate, 0.71 M sodium formate) after ten half-lives.

(11) 2-Cyclopropylethanol in buffered formic acid gives predominantly 1,3-pentanediol diformate.

(12) M. J. S. Dewar and J. M. Harris, *J. Amer. Chem. Soc.*, **90**, 4468 (1968), have observed a rate enhancement in the 2-cyclopropylethyl system when methyl groups are substituted on the cyclopropane ring. We are grateful to Professor Dewar for sending us his manuscript prior to publication.

(13) Cyclopropane is also less effective than a double bond in the related neopentyl system. Acetolysis of 2-cyclopropyl-2-methylpropyl brosylate is eight times faster than the isopropyl analog[14] at 74.6°, whereas acetolysis of 2,2-dimethyl-3-butenyl brosylate is 95 times faster than its saturated analog.[15] Complete details will be published later.

(14) E. N. McElrath, R. M. Fritz, C. Brown, C. Y. Leftall, and R. B. Duke, *J. Org. Chem.*, **25**, 2195 (1960).

(15) R. S. Bly and R. T. Swindell, *ibid.*, **30**, 10 (1965).

(16) Nonbonded repulsive interaction of hydrogens on a cyclopropane ring with hydrogens attached to a carbonium ion center in the transition state for participation has recently been invoked[17] to explain the lack of rate enhancement by cyclopropane in a related system. Although the geometry may be different in the cyclopropylethyl system (the stereochemistry of cyclopropane participation is unknown), nonbonded interactions may, in part, prevent cyclopropane assistance in the transition state.

(17) G. D. Sargent, R. L. Taylor, and W. H. Demisch, *Tetrahedron Lett.*, 2275 (1968).

Yorke E. Rhodes, Toshio Takino
Department of Chemistry, New York University, University Heights
New York, New York 10453

Received March 29, 1968

Nuclear Magnetic Resonance Study of Alkali Ion Solvation

Sir:

In recent years spectroscopic techniques have been frequently applied to the studies of ionic solvation in aqueous solutions and in nonaqueous solvents. Far-infrared spectroscopy has been used for the investigation of alkali metal ion solvation in tetrahydrofuran[1,2] and in dimethyl sulfoxide.[3] While this technique is very useful for numerous nonaqueous systems, it is limited by the transparency of the solvents in the investigated spectral region, as well as by the solubilities of the inorganic salts.

A useful extension of our studies of solvation appears to be in the application of nmr spectroscopy. This technique has been widely used for the studies of solvation of, primarily transition metal ions in various solvents and has been recently reviewed in the literature.[4]

While our investigation was in progress, a communication by Schaschel and Day[5] appeared which reported similar work but in a different nonaqueous system. We wish to report here studies on the solvation of lithium, ammonium, and sodium salts by dimethyl sulfoxide.

All salts were dried under vacuum to constant weight before use. Dimethyl sulfoxide was purified first by vacuum distillation over granulated barium oxide, followed by repeated fractional crystallization. Physical properties of purified DMSO agreed well with the literature values. 1-Pentanol was kept over anhydrous

---

(1) W. F. Edgell, A. T. Watts, J. Lyford, and W. M. Risen, Jr., *J. Am. Chem. Soc.*, **88**, 1815 (1966).

(2) (a) W. F. Edgell, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 9–14, 1967, No. R149; (b) W. F. Edgell, J. Lyford, and J. Fisher, Abstracts 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 31–April 5, 1968, No. S136; (c) W. F. Edgell, personal communication.

(3) B. W. Maxey and A. I. Popov, *J. Am. Chem. Soc.*, **89**, 2230 (1967).

(4) J. F. Hinton and E. S. Amis, *Chem. Rev.*, **67**, 367 (1967).

(5) E. Schaschel and M. C. Day, *J. Am. Chem. Soc.*, **90**, 503 (1968).