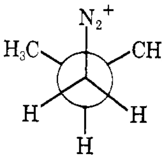
The fact that the route C:route D ratio is constant and is solvent (but not temperature)[11] independent suggests that the rearranging precursor ions, either **1i′** or **1d**$^+$, are the "same" in all media (*i.e.*, they are in the same states of solvation) and that the ratio of hydride to methyl shift reflects the ratio of their respective precursor conformers: **4** and **5** (a and b) (of **1i′** and **1d**$^+$). The sum of these species, however, *increases* with *increasing solvating* power of the medium.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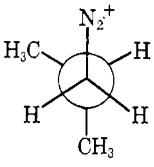
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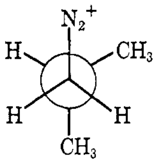
5b

From these and related experiments with other *primary* aliphatic amines[8b,15] it can be concluded that carbonium ions are not formed by unimolecular fission of the corresponding diazonium ion. In these systems carbonium ions are apparently only formed by concerted rearrangement processes.

[15] Similar results are obtained from *n*-butylamine and neopentylamine.

[16] NASA Fellow, 1963–1966.

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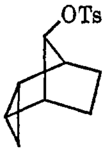
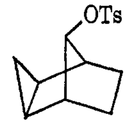
Rates of Solvolysis of 2-Cyclopropylethyl Brosylates[1]

Sir:

The ability of the cyclopropyl group to interact with a positive center separated from it by one carbon atom has been the subject of much recent discussion,[2] and some striking examples have been reported; for example, I solvolyzes[2a] 10^{14} times faster than isomeric II and 10^3 times faster than the analogous norbornenyl derivative III in which the cyclopropane ring in I is replaced by a double bond. Therefore, although little anchimeric assistance is observed in the open-chain homoallylic system IV[3] ($k_{\mathrm{IV}}/k_{n\text{-butyl}}$ = 3.7, for formolysis), the possibility exists that the solvolysis of esters of 2-cyclopropylethanol (V) might be significantly assisted.


I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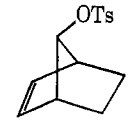
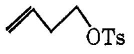
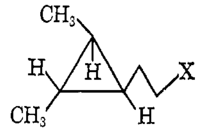
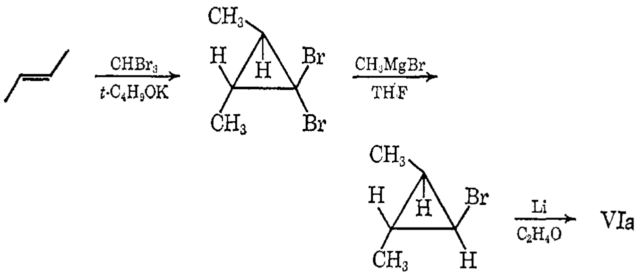

III


IV


Va, X = OH
b, X = OBs


VIa, X = OH
b, X = OBs

Sauers and Ubersax[2b] have examined the formolysis of the brosylate of V-α,α-d_2 and claim that their results can be explained "without recourse to intermediates other than classical ones. If such intermediates are involved they cannot be the sole intermediates." In view of their uncertainty (their experiments could not demonstrate the presence or absence of participation) further work is clearly needed; we have accordingly measured the rates of formolysis of the brosylate of V and its dimethyl derivative VI, and compared them with the corresponding rate for ethyl brosylate. Vb was prepared from the alcohol;[4] Va by the method of Tipson.[5,6] VIb was likewise prepared from VIa, which in turn was obtained by the following route.[7,8]



Solvolysis of Vb in anhydrous formic acid containing sodium formate[9] at 85°, followed by treatment with lithium aluminum hydride, gave the alcohols VII, VIII, IX, and Va, in agreement with previous work.[2b,10] The rates of formolysis were measured spectrophotometrically in anhydrous formic acid containing sodium formate (5% excess over ester) at 75°; the results are shown in Table I. The rates were unaffected by addition of larger excesses of sodium formate.

Table I. First-Order Rate Constants (k_1) for the Solvolysis of Brosylates in Anhydrous Formic Acid at 75°

Compound	$k_1 \times 10^5$, sec^{-1}	Relative rate
EtOBs	4.26	1.00
Vb	3.94	0.93
VIb	13.30	3.12

The fact that VIb solvolyzes about three times faster than Vb must be attributed to participation by the cyclopropyl group, for introduction of methyl substituents into the β position of simple alkyl tosylates

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[1] This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.

[2] (a) H. Tanida, T. Tsuji, and T. Irie, *J. Am. Chem. Soc.*, **89**, 1953 (1967); M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967); (b) R. R. Sauers and R. W. Ubersax, *J. Org. Chem.*, **31**, 495 (1966); (c) G. E. Cartier and S. E. Bunce, *J. Am. Chem. Soc.*, **85**, 932 (1963); (d) M. A. Eakin, J. Martin, and W. Parker, *Chem. Commun.*, 955 (1967); (e) R. R. Sauers and J. A. Beisler, *Tetrahedron Letters*, 2181 (1964); (f) J. Haywood-Farmer, R. E. Pincock, and J. I. Wells, *Tetrahedron*, **22**, 2007 (1966); (g) R. R. Sauers, J. A. Beisler, and H. Feilich, *J. Org. Chem.*, **32**, 569 (1967); (h) P. K. Freeman and D. M. Balls, *Tetrahedron Letters*, 437 (1967); (i) C. F. Wilcox, Jr., and R. G. Jesaitis, *ibid.*, 2567 (1967); (j) M. Hanack and H. M. Ensslin, *ibid.*, 4445 (1965); (k) S. Winstein, P. Bruck, P. Radlick, and R. Baker, *J. Am. Chem. Soc.*, **86**, 1867 (1964).

[3] K. L. Servis and J. D. Roberts, *ibid.*, **87**, 1331 (1965).

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

[5] R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

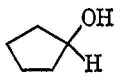
[6] All new compounds gave satisfactory analyses, etc.

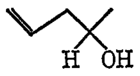
[7] P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 3409 (1956).

[8] D. Seyferth and B. Prokai, *J. Org. Chem.*, **31**, 1702 (1966).

[9] In the absence of base (sodium formate), Vb reacted rapidly in formic acid by opening of the cyclopropane ring; this was established by the rapid disappearance of the nmr signals corresponding to cyclopropane protons.

[10] Sauers and Ubersax[2b] give the following ratios for alcohols VII, VIII, IX, and Va: 36:12:17:35.


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).

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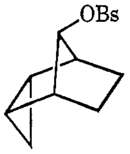
Received November 2, 1968

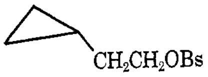
Solvolyses of 2-Cyclopropylethyl Brosylate[1]

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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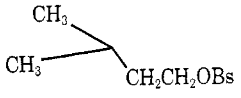
III

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).