# MINIMIZING CHANGES IN INTERNAL STRAIN IN UNIMOLECULAR
NUCLEOPHILIC DISPLACEMENT REACTIONS

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This communication describes a study of unimolecular (S_N1 or "limiting")[1] nucleophilic displacements in which effects due to changes in internal strain should be unusually small. An adjoining communication by Sargent and Harrison describes a related study.[2]
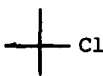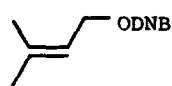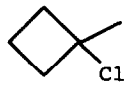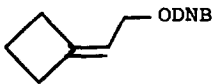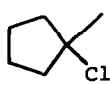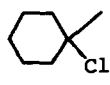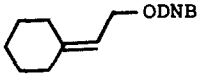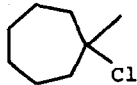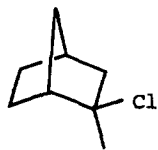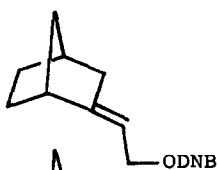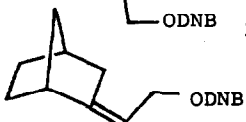
Changes in (1) bond angle, (2) torsional, and (3) non-bonded interaction strains are thought to contribute to the difference in energy between an alkyl derivative and the carbonium ion[3] formed by its ionization.[4,5,6] For example, the large range observed for solvolysis rates of tertiary chlorides 1-5 has been ascribed to variations in the magnitudes of these strain factors.[4-8] A quantitative evaluation of these strain factors, such as supplied by the treatments of Foote[10] and Schleyer,[6] is needed when rates for forming specific carbonium ion structures must be estimated. For example, a precise estimate of the effect on ionization rate of the change in strain energy on forming 13 from 2-norbornyl precursors is an essential part of the well-known efforts to decide on the basis

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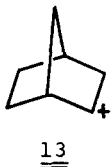
of rate data if the norbornyl cation has structure 13 or instead a structure such as 14 in which sigma electrons are delocalized.[11]

In the compounds, 7-12, used in this study, an alkene carbon corresponds to the carbon at which ionization occurs in 1-6. This c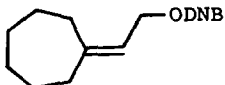arbon will bear a significant part of the charge of the allylic cation formed during solvolysis, but the geometry at this carbon should not change greatly since optimal geome-

Table I.   Solvolysis Rates of Alkyl Chlorides and of Allylic
3,5-Dinitrobenzoates

Alkyl Chloride[a]		$k \times 10^6$ sec^{-1}	Allylic 3,5-dinitrobenzoate[b]		$k \times 10^5$ sec^{-1}
<u>1</u>		8.4^c	<u>7</u>		3.1
<u>2</u>		0.62^c	<u>8</u>		1.0
<u>3</u>		367^c	<u>9</u>		13.7
<u>4</u>		2.95^c	<u>10</u>		2.7
<u>5</u>		319^c	<u>11</u>		5.3
<u>6</u>		1970^d	<u>12a</u> <u>12b</u>		26.9^e

^aIn 80% aqueous ethanol at 25°.

^bIn 80% aqueous acetone at 100°.

^cRef. 5.

^dCalculated from the rate [H. C. Brown and F. J. Chloupek, <u>J. Amer. Chem. Soc.</u>, <u>85</u>, 2322 (1963)] in ethanol assuming that the ratio of rates of <u>6</u> and <u>3</u> is the same in 80% aqueous ethanol as in ethanol.

^eRate exhibited by a mixture composed of 60% <u>12a</u> and 40% <u>12b</u>.

tries of (unstrained) alkene and carbonium ion carbons are identical. The steric environment at the carbon at which ionization occurs should be relatively constant in 7-12. Therefore, changes in internal strain, variable in ionizations of 1-6, might be nearly constant in ionizations of 7-12.

The first-order solvolysis rates of 7-12[12] are listed in Table I. Adherance to first-order behavior of a mixture of 12a and 12b and recovery after partial reaction of an ester mixture with nearly the same composition suggest that 12a and 12b have similar solvolysis rates. The products, determined by nmr spectra of reaction solutions buffered with lutidine,[13] were generally mixtures of unrearranged primary alcohols and their tertiary allylic isomers. Other products, probably dienes, were formed in significant amounts in the reactions of 9 and 11.

The range of solvolysis rates exhibited by 7-11 suggests the presence of influences other than the particular internal strain factors that have been considered to affect solvolyses of the corresponding saturated systems (1-5). The arrow in 15 indicates a non-bonded interaction, not present in solvolyses of 1-6,

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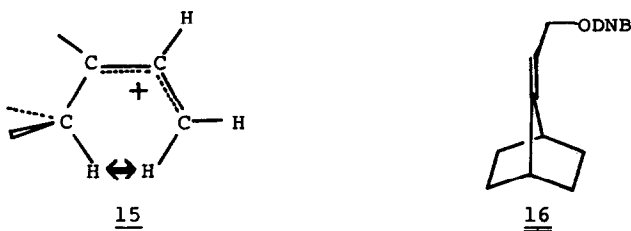
that might be partly responsible for the small differences observed between rates of 7,9,10 and 11 — this interaction should be minimal in the ion formed from 9 but might inhibit planarity of the allylic system in the ion formed from 10 and in most conformations of the ions formed from 7 and 11.[14] However, the particulary low rate exhibited by 8, a system in which this interaction should be minimal, must be attributed to some other cause. Ionization may be inhibited by some factor associated with the small internal bond angle.[15] For example, the difference in strength between the double bond of the starting material and the corresponding partial double bond of the allylic cation might be greater in a strained than in an unstrained system - such a difference might be caused by the high s character[16] of an external hybrid orbital of a carbon in a strained ring. Alternatively, ionization could be slowed in strained systems such as 8 by increased angle strain if the force constant for in-plane bending at the tertiary ring carbon is greater in the cation than in the neutral alkene. The norbornyl esters (12) exhibit a particularly high solvolysis rate in spite of an internal bond angle[6,10] lower than in any system except 8 and the possible incursion in the solvolysis of 12a of the strain factor illustrated in 15. Formation of an ion stabilized by sigma delocalization (such as depicted in 14) may be responsible for the enhanced rate.[17]

References

1. A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Company, Inc., New York, 1962; C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon," Elsevier Publishing Co., Amsterdam, 1963.

2. G. D. Sargent and M. J. Harrison, Tetrahedron Letters, 3699 (1970).

3. In the solvolyses in Table I, ionization should be rate-determining[1] and the transition states should closely resemble [G. S. Hammond, J. Amer. Chem. Soc., 77, 334 (1955)] the resultant carbonium ions.

4. H. C. Brown, R. S. Fletcher, and R. B. Johannesen, J. Amer. Chem. Soc., 73, 212 (1951). See also P. D. Bartlett, Bull. Soc. Chim. France, 100C (1951); H. C. Brown, J. Chem. Soc., 1248 (1956).

5. H. C. Brown and M. Borkowski, J. Amer. Chem. Soc., 74, 1894 (1952).

6. P. von R. Schleyer, J. Amer. Chem. Soc., 86, 1854, 1856 (1964).

7. Unusually large electronegativity of the ring carbons and delocalization involving the unshared electron pairs in the leaving group and the ring carbons also have been suggested as contributors to the reduced reactivity of small ring systems [J. D. Roberts and V. C. Chambers, J. Amer. Chem. Soc., 73, 5034 (1951)].

8. Delocalization of electron density from sigma bonds in the cyclobutyl ring has been suggested to be a factor stabilizing transition states in solvolyses of cyclobutyl derivatives.[9]

9. R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, J. Amer. Chem. Soc., 81, 4390 (1959); K. B. Wiberg and J. G. Pfeiffer, ibid., 92, 553 (1970); K. B. Wiberg and G. Szeimies, ibid., 92, 571 (1970), and references cited therein.

10. C. S. Foote, J. Amer. Chem. Soc., 86, 1853 (1964).

11. Studies related to the structure of the norbornyl cation have been reviewed critically [G. D. Sargent, Quart. Rev. (London), 20, 301 (1966)].

12. Elemental analyses and ir and nmr spectra of 7-12 and of all other new compounds are in accord with the structures assigned to them. Efforts to effect a preparative separation of mixtures of 12a and 12b or of the corresponding alcohols were not successful.

13. Lutidine slowed isomerization of the products without significantly changing the solvolysis rates.

14. The van der Waals radius of hydrogen is assumed to be 1.2 A [L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, New York, 1960, Chap. 7].

15. Compound 16, that exhibits a low solvolysis rate,[2] also has a small internal bond angle at the tertiary allylic carbon and may be susceptible to the strain factor illustrated in 15.

16. C. A. Coulson and W. E. Moffitt, Phil. Mag., 40, 1 (1949); A. D. Walsh, Trans. Far. Soc., 45, 179 (1949).

17. Sargent and Harrison have suggested that similar delocalization[9] of electrons of 2,3-sigma bonds may also affect the solvolysis rates of 8 and 9.[2]