During ionization the tosyl C–O bond is pictured to lengthen somewhat (Fig. 1) but not to "break" in attaining the transition state. Figure 1—one of many steric possibilities—depicts the situation found in axial cyclohexyl and *endo*-2-norbornyl derivatives, where strain relief accompanies ionization and steric acceleration results.

Bond angle, torsional, and nonbonded strain effects are sufficient in most cases to account quantitatively for observed solvolysis rates within 10^1 (Table I). Corrections for inductive effects ordinarily are not necessary for the compounds considered, except for those with a double bond or aryl ring β to the reaction site. The inductive term, $^1/_8$ in rate,[9] is applied in such cases. In this treatment, other effects expected to influence reaction rates (hyperconjugation, steric hindrance to solvation, etc.) do not appear to be important. Anchimeric assistance is considered in a separate communication.[10] Table I lists a representative display of compounds of diverse type ranging about 10^{10} in rate correlated satisfactorily by this treatment. The average deviation is $10^{\pm 0.25}$. Extension of these ideas to other systems and to other reactions is being pursued.

Acknowledgment.—Partial support of this work by a grant from the Petroleum Research Foundation is acknowledged with thanks.

(9) A. Streitwieser, *Chem. Rev.*, **56**, 571 (1956).
(10) P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1856 (1964).
(11) Alfred P. Sloan Research Fellow.

FRICK CHEMICAL LABORATORY PAUL VON RAGUÉ SCHLEYER[11]
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY

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The Nonclassical Carbonium Ion Problem: Reaction Rates[1]

Sir:

Three properties have become associated with "nonclassical" carbonium ions: (1) enhanced rates of formation, provided the precursor geometry is suitable (high "*exo–endo*" rate ratios of epimeric precursors); (2) high stereospecificity of kinetically controlled product formation; and (3) heightened propensity toward rearrangement. Carbonium ions with one or more of these unusual properties have often been assigned bridged structures implying increased stabilization by simultaneous and substantial charge delocalization over more than one carbon atom.[2] Recently, this concept has been questioned forcefully.[3] Rapidly equilibrating simple ions have been advanced as an alternative structural proposal.[3,4]

Of the three unusual properties associated with "nonclassical" ions, only one, enhanced reaction rate, can serve to distinguish between these structural alternatives. Both bridged and rapidly equilibrating ions would rearrange readily and both might give products with high stereospecificity.[3] Enhanced rates can be associated with simple carbonium ions only in two well-defined instances: (1) if the carbonium ion precursor suffers from steric or conformational strains, and these strains are relieved on ionization; or (2) if direct rearrangement to a more stable ion, *e.g.*, from a potential primary to a tertiary ion, occurs during the ionization process. In the latter situation both the less stable simple ion and the bridged ion intermediates are by-passed, and there is also no possibility of rapidly equilibrating ions.

For a symmetrical nonclassical ion, in the absence of steric and conformational effects, enhanced rate of formation can only be associated with a bridged structure for the intermediate. The related and equivalent simple ions and their transition states must be less stable than those of bridged structure, by definition.

Acetolysis rates of a variety of secondary aliphatic tosylates can be calculated with unexpected accuracy by assessing bond angle, torsional, and nonbonded strain contributions; inductive terms are included only for unsaturated compounds.[5a] Tosylates such as *endo*-2-norbornyl, *endo*-2-norbornenyl, and *endo*-2-benznorbornenyl are successfully treated[5a]; there is no reason to suspect that the same approach should fail for their *exo* counterparts. Table I lists data for compounds for most of which anchimeric assistance has previously been postulated in the literature. The calculated rates[5a] are generally less, and are often greatly less, than those actually observed. These differences, estimates of the magnitude of anchimeric assistance, are listed in the last column of Table I.

The author believes this evidence is compelling for the existence of bridged carbonium ions. For compounds which either are symmetrical or cannot rearrange to a more stable ion, *e.g.*, **3, 10, 15, 17,** the marked rate enhancements observed cannot reasonably and consistently[5] be explained on other than an electronic (delocalized) basis. In addition, compounds such as **6** and **12,** related by a common ionic pathway, must give a bridged ion, since *both* solvolyze with considerable anchimeric assistance. It would appear likely that most of the compounds with appreciable rate enhancement (Table Ia) give bridged ions on solvolysis.

The second group (Table Ib), with but slight anchimeric assistance ($<10^2$), is borderline. Low rate enhancements in stereochemically favorable situations indicate that bridged ions, if present, must be of energy

(1) Presented at the Gordon Conference on Hydrocarbon Chemistry, Colby Jr. College, New London, N. H., June, 1963, and at the 146th National Meeting, American Chemical Society, Denver, Colo., Jan., 1964, Abstracts, p. 7C.

(2) For reviews see (a) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; (b) J. A. Berson in P. de Mayo, Ed., "Molecular Rearrangements," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3; (c) C. W. Rees and B. Capon, *Ann. Rept. Chem. Soc.* (London), **59,** 207 (1962); M. D. Johnson, *ibid.*, **58,** 167 (1961), and preceding articles in the same series.

(3) H. C. Brown in "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, pp. 140–158, 174–178; H. C. Brown and F. J. Choupek, *J. Am. Chem. Soc.*, **85,** 2322 (1963); H. C. Brown and H. M. Bell, *ibid.*, **85,** 2324 (1963) (*cf.*, however, S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85,** 2324 (1963)); H. C. Brown, F. J. Choupek, and M. H. Rei, *ibid.*, **86,** 1246, 1247, 1248 (1964).

(4) See, *e.g.*, (a) C. J. Collins and B. M. Benjamin, *ibid.*, **85,** 2519 (1963); C. J. Collins, M. M. Staum, and B. M. Benjamin, *J. Org. Chem.*, **27,** 3525 (1962); W. A. Bonner and T. A. Putkey, *ibid.*, **27,** 2348 (1962), and earlier papers therein cited; (b) J. A. Berson and D. Willner, *J. Am. Chem. Soc.*, **84,** 675 (1962); **86,** 609 (1964); J. A. Berson and P. Reynolds-Warnhoff, *ibid.*, **84,** 683 (1962); **86,** 595 (1964); H. M. Walborsky, J. Webb, and C. G. Pitt, *J. Org. Chem.*, **28,** 3214 (1963); (c) P. S. Skell and R. J. Maxwell, *ibid.*, **84,** 3963 (1962); (d) E. J. Corey and J. Casanova, Jr., *ibid.*, **85,** 165 (1963); E. J. Corey, J. Casanova, Jr., P. A. Vatakencherry, and R. Winter, *ibid.*, **85,** 169 (1963); (e) P. von R. Schleyer, D. C. Kleinfelter, and H. G. Richey, Jr., *ibid.*, **85,** 479 (1963); (f) E. J. Corey and R. L. Dawson, *ibid.*, **85,** 1782 (1963); E. J. Corey and H. Uda, *ibid.*, **85,** 1788 (1963); (g) T. Norin, *Tetrahedron Letters*, **No. 1–2,** 37 (1964).

(5) (a) P. von R. Schleyer, *J. Am. Chem. Soc.*, **86,** 1854 (1964); *cf.* (b) C. S. Foote, *ibid.*, **86,** 1853 (1964), and Ph.D. Thesis, Harvard University, 1961.

TABLE I
ESTIMATION OF THE MAGNITUDE OF ANCHIMERIC ASSISTANCE BY THE METHOD OF REFERENCE 5a

No.	Tosylate	Ketone[a] ν_{CO}, cm.$^{-1}$	ϕ, deg.	GS − TS, kcal. nonbonded	log rel. rate Calcd.	log rel. rate Obsd.[a]	log anch. assistance
	(a) Anchimeric assistance > 10^2						
1	*anti*-8-Dicyclopentadienyl	1780	60,60	0.3	−8.8[b]	4.33	13.1
2	*anti*-7-Norbornenyl	1780	60,60	0.3	−8.8[b]	4.11	12.9
3	7-Dibenznorbornadienyl	1792	60,60	0.1	−11.3[b]	−0.79	10.5
4	*anti*-7-Benznorbornenyl	1792	60,60	0.3	−10.3[b]	−1.22	9.1
5	7-Quadricyclyl	1746[c]	60,60	0.0	−4.9	3.31[d]	8.2
6	3-Nortricyclyl	1762	60,60	0.3	−6.2[b]	1.82	8.0
7	*anti*-8-Bicyclo[3.2.1]oct-2-enyl	1758[e]	60,60	0.2	−6.1[b]	−0.13[e]	6.0
8	7-*syn*-Norbornenyl	1780	60,60	0.1	−8.9[b]	−3.28	5.6
9	Cyclobutyl	1791	0,0	0.0	−4.2	0.99	5.2
10	*exo*-2-Benznorbornenyl	1756	0,45	0.3	−2.8[b]	1.63	4.4
11	*exo*-8-Bicyclo[3.2.1]octyl	1752	60,60	0.3	−4.4	−0.21	4.2
12	*exo*-2-Norbornenyl	1745	0,45	0.3	−1.4[b]	2.42	3.8
13	Cholesteryl	1721	60,60	0.0	−1.7[b]	2.01	3.7
14	*exo*-2-Bicyclo[2.2.2]oct-5-enyl	1735	0,60	0.4	0.5[b]	4.10	3.6
15	*exo*-2-Norbornyl	1751	0,40	0.3	−0.6	2.71	3.3
16	*endo*-2-Bicyclo[2.2.2]oct-5-enyl	1735	0,60	0.1	−0.7[b]	2.49	3.2
17	2-Bicyclo[2.1.1]hexyl	1764[f]	0,60	0.2	−3.3	−0.37[g]	2.9
18	Epicholesteryl	1721	60,60	0.4	−1.4[b]	1.40	2.8
	(b) Anchimeric assistance < 10^2						
19	Cyclopropyl	1815	0,0	0.0	−7.2	−5.32	1.9
20	9-Bicyclo[3.3.1]nonyl	1726	60,60	0.6	−1.0	0.48	1.5
21	*exo*-Trimethylenenorborn-*exo*-2-yl	1751	0,40	0.3	−0.6	0.84[h]	1.4
22	*cis*-3-Bicyclo[3.1.0]hexyl	1739[i]	0,40[j]	0.0	−0.2[b]	1.14[i]	1.3
23	*axial*-2-Bicyclo[3.2.1]octyl	1717	50,60	0.6	0.4	1.62	1.2
24	2-Bicyclo[2.2.2]octyl	1731	0,60	0.4	0.9	1.85	0.9
25	*equat.*-2-Bicyclo[3.2.1]octyl	1717	50,60	0.2	0.1	0.47	0.4
26	*trans*-3-Bicyclo[3.1.0]hexyl	1739[i]	0,40[j]	0.6[i]	0.2[b]	0.17	0.0
27	*syn*-8-Bicyclo[3.2.1]oct-2-enyl	1758[e]	60,60	1.1	−5.5	−5.54[e]	0.0
28	Cyclooctyl	1703	40,40?[k]	0.0?	2.8	2.76	0.0
29	Cyclononyl	1703	40,40?[k]	0.0?	2.8	2.70	−0.1
30	Cyclodecyl	1704	40,40?[k]	0.0?	2.7	2.98	+0.3
31	Cycloundecyl	1709	40,40?[k]	0.0?	2.1	2.05	0.0

[a] Data, unless otherwise indicated, taken from Foote.[5b] [b] Corrections for inductive effects: −0.9 in log k for each double bond or phenyl ring and −0.5 in log k for each cyclopropane ring β to the reaction site.[5a] [c] P. R. Story and S. R. Fahrenholtz, *J. Am. Chem. Soc.*, **86**, 1270 (1964). [d] H. G. Richey, Jr., and N. C. Buckley, *ibid.*, **85**, 3057 (1963); P. R. Story and S. R. Fahrenholtz, *ibid.*, **86**, 527 (1964). [e] N. W. LeBel and L. A. Spurlock, *Tetrahedron*, **20**, 215 (1964). [f] Value for 5,5-dimethylbicyclo[2.1.1]hexan-2-one (J. Meinwald and P. G. Gassman, *J. Am. Chem. Soc.*, **85**, 57 (1963)). [g] At 75° (J. Meinwald, Abstracts, 18th National Organic Chemistry Symposium, American Chemical Society, Columbus, Ohio, June, 1963, p. 39). [h] See ref. 2b. [i] S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83**, 3235 (1961). [j] Our experience [M. M. Donaldson, Ph.D. Thesis, Princeton University, 1958; *Dissertation Abstr.*, **22**, 738 (1961)] with locked cyclopentane rings suggests this estimate. [k] J. Sicher in P. B. D. De la Mare and W. Klyne, Ed., "Progress in Stereochemistry," Vol. 3, Butterworths, London, 1962, Chapter 6; V. Prelog and J. G. Traynham in P. de Mayo, "Molecular Rearrangements," Vol. 1, Interscience Publishers, Inc., 1963, Chapter 9.

more nearly comparable with classical ions.[6] Compounds **25–31** have no significant anchimeric assistance and the data do not require the formulation of bridged intermediates. Further implications of this treatment will be discussed in the full report.

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(6) See Table I*i*, and ref. 4b, f, and g with regard to compounds **22**, **23**, and **24**.

(7) Alfred P. Sloan Research Fellow.

FRICK CHEMICAL LABORATORY PAUL VON RAGUÉ SCHLEYER[7]
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY

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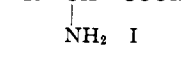
Reactions in Strong Acids. II.[1] New Concept in Amino Acid Chemistry: C-Derivatization of Amino Acids[2]

Sir:

In an extension of the results discussed in the first paper of this series,[1] a new type of amino acid chemistry has been established. The chemistry of amino acids (I), as presently known, consists of transformations of functional groups already present in these molecules[3];



their (intact) hydrocarbon moities (R) have not been subjected to chemical reactions.[4] The reason for this is obviously the high reactivity of the functional groups, relative to the inertness of the hydrocarbon chain. In principle, free-radical-type reagents would be expected to overcome this inertness, provided that

(1) Part I: J. Kollonitsch, V. Verdi, M. Boskin [Reactions in Strong Acids. I. Side-Chain Chlorination of Alkylpyridines and Alkylthiazoles in Concentrated Sulfuric Acid], submitted to *Tetrahedron Letters*.

(2) Presented in part at the XIXth International Congress of Pure and Applied Chemistry, London, July 10–17, 1963.

(3) See Greenstein and Winitz, "Chemistry of Amino Acids," Vol. 1–3, John Wiley and Sons, Inc., New York, N. Y., 1961; also Th. Wieland, *et al.*, in E. Muller, Ed., "Methoden der Organischen Chemie," (Houben-Weyl), 4th Ed., Vol. XI/2, Thieme Verlag, Stuttgart, 1958, p. 321.

(4) Irradiation of amino acid solutions by high-energy radiation (X-ray, ultraviolet light, etc.), long known only to degrade amino acids,[3] recently was used to induce complex cleavages leading to rearrangement of the C-skeletons [G. Ferrari and R. Cultrera, *Nature*, **190**, 326 (1961)].