Fig. 1.—Acetolysis rates of arenesulfonates and carbonyl frequencies of corresponding ketones.

**TABLE III**

| Arenesulfonate | $\nu_{C=O}$ for ketone, cm.$^{-1}$ | log $k_{rel}$ Obsd. | log $k_{rel}$ Calcd. | log (accel.) |
|---|---|---|---|---|
| Cyclopropyl | 1815[a,b] | −5.32[c] | −12.5 | 7.2 |
| Cyclobutyl | 1791[d] | 0.99[c] | −9.4 | 10.4 |
| Cyclopentyl | 1748 | 1.51[e] | −3.7 | 5.2 |
| exo-2-Norbornyl | 1751[d] | 2.71[e] | −4.1 | 6.8 |
| endo-2-Norbornyl | 1751[d] | 0.18[e] | −4.1 | 4.3 |
| 2-Bicyclo[2.2.2]octyl | 1731[d] | 1.85[f] | −1.5 | 3.4 |
| 2-Bicyclo[3.2.1]octyl (axial) | 1717[d] | 1.62[f] | 0.4 | 1.2 |
| 2-Bicyclo[3.2.1]octyl (equatorial) | 1717[d] | 0.47[f] | 0.4 | 0.1 |
| endo-2-Bicyclo[2.2.2]oct-5-enyl | 1735[g] | 2.49[f] | −2.0 | 4.5 |
| exo-2-Bicyclo[2.2.2]oct-5-enyl | 1735[g] | 4.10[h] | −2.0 | 6.1 |
| exo-2-Norbornenyl | 1745[g] | 2.42[i] | −3.3 | 5.7 |
| endo-2-Norbornenyl | 1745[g] | −1.48[i] | −3.3 | 1.8 |
| Nortricyclyl | 1762[d] | 1.82[i] | −5.6 | 7.4 |
| anti-7-Norbornenyl | 1780[j] | 4.11[j,k] | −7.9 | 12.0 |
| anti-8-Dicyclopentadienyl | 1780[l] | 4.33[m] | −7.9 | 12.2 |
| syn-7-Norbornenyl | 1780[j] | −3.28[n] | −7.9 | 4.6 |
| anti-7-Benznorbornenyl | 1792[o] | −1.22[o]. | −9.5 | 8.3 |
| exo-2-Benznorbornenyl | 1756[o] | 1.63[o] | −4.8 | 6.4 |
| endo-2-Benznorbornenyl | 1756[o] | −2.22[o] | −4.8 | 2.6 |
| 7-Dibenznorbornadienyl | 1792[p,q] | −0.79[q,t] | −9.5 | 8.7 |
| exo-8-Bicyclo[3.2.1]octyl | 1752 | −0.21[r] | −4.2 | 4.0 |
| 9-Bicyclo[3.3.1]nonyl | 1726 | 0.48[r] | −0.8 | 1.3 |
| 5,5-Dimethyl-2-bicyclo[2.1.1]hexyl | 1764[s] | 1.18[s,t] | −5.8 | 7.0 |

[a] In vapor. [b] W. B. De More, H. D. Pritchard, and N. Davidson, J. Am. Chem. Soc., 81, 5878 (1959). [c] J. D. Roberts and V. C. Chambers, ibid., 73, 5034 (1951). [d] See ref. 4b. [e] See Table I, ref. a. [f] H. L. Goering and M. F. Sloan, J. Am. Chem. Soc., 83, 1992 (1961). [g] Private communication from Dr. A. Gagnieux. [h] N. A. LeBel and J. E. Huber, J. Am. Chem. Soc., 85, 3193 (1963). [i] S. Winstein and M. Shatavsky, ibid., 78, 592 (1956); S. Winstein, H. M. Walborsky, and K. Schreiber, ibid., 72, 5795 (1950). [j] See Table I, ref. h. [k] See Table I, ref. g. [l] R. C. Cookson, J. Hudec, and R. O. Williams, Tetrahedron Letters, No. 22, 29 (1960). [m] R. B. Woodward and T. J. Katz, Tetrahedron, 5, 70 (1959). [n] S. Winstein and E. T. Stafford, J. Am. Chem. Soc., 79, 505 (1957). [o] P. D. Bartlett and W. P. Giddings, ibid., 82, 1240 (1960); W. P. Giddings, Ph.D. Thesis, Harvard, 1959. [p] Solvent not specified. [q] J. Meinwald and E. G. Miller, Tetrahedron Letters, No. 7, 253 (1961). [r] See ref. 3. [s] J. Meinwald and P. G. Gassman, J. Am. Chem. Soc., 85, 57 (1963). [t] At 75°.

rates were considered to be accelerated either by ground-state eclipsing interactions or by anchimeric acceleration. All these compounds have rates which are *faster* than the rates calculated by the correlation; the difference is the sum of rate enhancements from anchimeric acceleration and steric effects (other than those of internal angle strain).

**TABLE II**

| Arenesulfonate | $\nu_{C=O}$ for ketone (or aldehyde), cm.$^{-1}$ | log $k_{rel}$ Obsd. | log $k_{rel}$ Calcd. |
|---|---|---|---|
| Methyl | 1728[a,b] | −1.14[c] | −1.1 |
| Ethyl | 1730[b] | −1.45[c] | −1.3 |
| Benzyl | 1709[b] | 1.73[d] | 1.5 |
| trans-2-t-Butylcyclohexyl | 1700[e,f] | 2.20[f] | 2.6 |
| cis-2-t-Butylcyclohexyl | 1700[e,f] | 2.61[f] | 2.6 |

[a] Corrected from gas phase by subtracting 16 cm.$^{-1}$, which gives good agreement with solution values for acetaldehyde and propionaldehyde. [b] J. Depireux, Bull. Soc. Chim. Belges, 66, 218 (1957). [c] See Table I, ref. f. [d] S. Winstein, E. Grunwald, and H. W. Jones, J. Am. Chem. Soc., 73, 2700 (1951). [e] Solvent not specified. [f] H. Goering, R. L. Reeves, and H. H. Espy, J. Am. Chem. Soc., 78, 4926, 4931 (1956).

This novel correlation is a further demonstration of the importance of angle strain and hybridization effects in organic reactions.[2,3,4c,5] It should be possible to extend the correlation to other types of reactions involving tetrahedral ground states and trigonal transition states (or *vice versa*).[6]

**Acknowledgments.**—The least-squares program and advice on its use were kindly supplied by Dr. Paul Haake. Computation was carried out on an IBM 7090

(5) C. S. Foote, Tetrahedron Letters, No. 9, 579 (1963).
(6) Schleyer has recently extended this correlation by adding terms for torsional strain, nonbonded interactions, and inductive effects: P. von R. Schleyer, Abstracts, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan., 1964, p. 7C; P. von R. Schleyer, J. Am. Chem. Soc., 86, 1854 (1964).

at the Computing Facility of the Department of Engineering, U.C.L.A. The author is particularly indebted to Prof. R. B. Woodward for encouragement and stimulation, and to Prof. P. D. Bartlett for interest in this work, which was originally presented in part in C. S. Foote, Ph.D. Thesis, Harvard, 1961. Part of this work was supported by Petroleum Research Fund Grant No. 1428 A 1, 4.

## Estimation of Nonassisted Solvolysis Rates[1]

*Sir:*

Despite anticipated difficulties, many solvolysis rates can be calculated with high accuracy very easily, using

TABLE I

CALCULATION OF SOLVOLYSIS RATES BY EQ. 1

| No. | Compound | Ketone,[a] $\nu_{CO}$, cm.$^{-1}$ | $\phi$, deg. | GS − TS, non-bonded, kcal. | Log rel. rate Calcd. | Obsd.[a] |
|---|---|---|---|---|---|---|
| 1 | 7-Norbornyl | 1773 | 60, 60 | 0.4 | −7.0 | −7.00 |
| 2 | endo-8-Bicyclo[3.2.1]-octyl | 1750 | 60, 60 | 0.6[b] | −4.2 | −4.11 |
| 3 | endo-2-Benznorbornenyl | 1756 | 0, 40 | 0.4 | −2.4[d] | −2.22 |
| 4 | endo-2-Norbornenyl | 1745 | 0, 40 | 0.4 | −1.0[d] | −1.48 |
| 5 | 2-Adamantyl | 1727 | 60, 60 | 0.6[b] | −1.1 | −1.18 |
| 6 | Cyclohexyl | 1716 | 60, 60 | 0.0 | −0.1 | 0.00 |
| 7 | Cyclotetradecyl | 1714 | 60, 60 ? | 0.0 | +0.1 | +0.08 |
| 8 | Isopropyl | 1718 | 60, 60 | 0.0 | −0.4 | +0.15 |
| 9 | endo-2-Norbornyl | 1751 | 0, 40 | 1.3[c] | −0.2 | +0.18 |
| 10 | Cyclopentadecyl | 1715 | 60, 60 ? | 0.0 | 0.0 | +0.42 |
| 11 | cis-4-t-Butylcyclohexyl | 1716 | 60, 60 | 0.6[b] | +0.4 | +0.42 |
| 12 | Cyclododecyl | 1713 | 60, 60 ? | 0.0 | +0.3 | +0.50 |
| 13 | 2-Butyl | 1721 | 60, 60 | 0.6 | −0.3 | +0.53 |
| 14 | 3,3-Dimethyl-2-butyl | 1710 | 60, 60 | 1.2 | +1.5 | +0.62 |
| 15 | Cyclotridecyl | 1713 | 60, 60 ? | 0.0 | +0.3 | +0.66 |
| 16 | 3-Methyl-2-butyl | 1718 | 60, 60 | 1.4 | +0.6 | +0.93 |
| 17 | Cyclopentyl | 1740[e] | 0, 20 ? | 0.0 | +1.5 | +1.51 |
| 18 | Cycloheptyl | 1705 | 45, 45[f] | 0.0[f] | +2.0 | +1.78 |
| 19 | trans-2-t-Butylcyclohexyl | 1700 | 60, 60 | 0.6 | +2.2 | +2.20 |
| 20 | cis-2-t-Butylcyclohexyl | 1700 | 60, 60 | 1.2 | +2.6 | +2.61 |
| 21 | 1,4-α-5,8-β-Dimethano-perhydro-9-anthracyl | 1696 | 60, 60 | 0.6 | +2.8 | +2.67 |

[a] Data from Foote.[5]  [b] Axial cyclohexyl strain energy (E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw–Hill Book Co., Inc., New York, N. Y., 1962, p. 236).  [c] See C. F. Wilcox, Jr., M. Sexton, and M. F. Wilcox, J. Org. Chem., 28, 1079 (1963).  [d] Includes inductive factor $^1/_8$.[9]  [e] This value would appear to be better than that usually quoted (ca. 1750 cm.$^{-1}$),[3,5] see C. L. Angell, et al., Spectrochim. Acta, 926 (1959).  [f] J. B. Hendrickson, J. Am. Chem. Soc., 84, 3355 (1962).

semiempirical but quite reasonable steric and conformational considerations. None of the underlying concepts is new[2] and the principles employed are well established in organic theory.

**Bond Angle Strain.**—Bond angle strain influences the rate of processes involving a change of carbon hybridization.[2,3] The ionization of a tosylate in the system C–C(OTs)–C is inhibited by a C–C–C angle constricted to a value less than 109.5°, while a C–C–C angle greater than 109.5° facilitates ionization.[2,3] The carbonyl stretching frequency of ketones is also sensitive to the internal C–CO–C bond angle.[3,4] Foote[5] has demonstrated dramatically the linear relationship which exists between these two factors.

For quantitative evaluation of the effect of bond angle strain on secondary tosylate acetolysis rates, compounds 1, 2, 5, 11, and 21 in Table I were selected. All are in the skew conformation around the reaction site (dihedral angles 60°), and all of the tosyl groups are in the axial conformation or are in equivalent steric environments. The first term of eq. 1 was deduced from the data of Table I. $k_{rel}$ is the solvolysis rate relative to cyclohexyl tosylate in acetic acid at 25°, $\nu_{CO}$ is the carbonyl frequency (cm.$^{-1}$) of the ketone related to the secondary tosylate under consideration, and the strain is measured in kcal. Measured carbonyl fre-

quencies of ketones[3,5] vary over 130 cm.$^{-1}$; bond angle

$$\log k_{rel} = (1715 - \nu_{CO})/8 + 1.32 \sum_i (1 + \cos 3\phi_i) +$$

$$(GS - TS \text{ strain})/1.36 + \text{inductive term} \quad (1)$$

strain effects on solvolysis rates therefore should range over $10^{16}$.

**Torsional Strain.**—Torsional strain can be evaluated with equal ease.[2] From a conformational viewpoint, carbonium ions, because of their sixfold rotational barrier,[6] should be essentially equally strained whatever their rotational arrangement.[7] Torsional strain effects on solvolysis rates can therefore be assessed from ground state considerations alone: compounds with eclipsed groupings around the reaction site will solvolyze more rapidly than compounds in skewed conformations.[2]

Angle $\phi$ is defined as the average smaller torsional angle around each of the C–C bonds adjacent to the tosyl group. Values of $\phi$ can vary between 0 and 60° and may be measured from models or otherwise estimated. Torsional strain variation with $\phi$ is evaluated from the usual equation,[7] $E_{torsional} = E_r/2 (1 + \cos 3\phi)$, where $E_r$ is the barrier to single bond rotation. $E_r$ does not vary greatly with ordinary changes in substitution[7]; the value of $E_r$ adopted here, 3.6 kcal./mole, that of ethyl chloride and ethyl bromide,[7] was felt to be closest to the value expected for methyl rotation in an ethyl arenesulfonate. Activation free energies expressed in kcal. can be converted to powers of ten in rate at 25° by dividing by 1.36 ($\Delta F^* = -RT \ln k$). The second term of eq. 1 evaluates torsional strain; the maximum rate effect possible ($\phi = 0°, 0°$) is $10^{5.3}$.

**Nonbonded Interaction Strain.**—In contrast to the above terms, nonbonded strain does not appear to give rise to very pronounced rate effects, amounting to only $10^1$ or at most $10^2$ for the relatively uncrowded secondary tosylates under consideration here. In principle, both steric acceleration and steric deceleration are possible depending on whether the solvolysis transition state is less or more crowded than the ground state.[2] Steric deceleration, in fact, is but rarely encountered,[8] evidently because leaving groups are generally able to find a propitious avenue for departure. Nonbonded strain effects can be evaluated (eq. 1, third term) by estimating ground state interactions of the tosyl group from conformational analogies or from experimental values and then deciding to what extent this nonbonded strain is decreased (or increased) in going to the transition state (cf. Fig. 1).
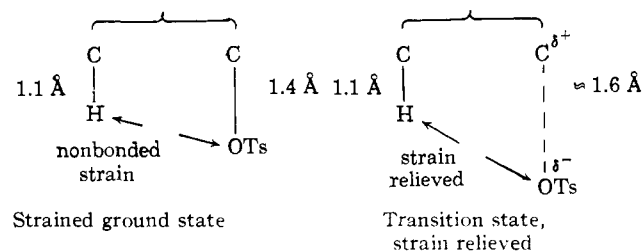


Fig. 1.—Analysis of nonbonded interactions and effect on rate.

146th National Meeting, American Chemical Society, Denver, Colo., Jan., 1964, Abstracts, p. 7C.

(2) See H. C. Brown, J. Chem. Soc., 1248 (1956), and references therein cited.

(3) P. von R. Schleyer and R. D. Nicholas, J. Am. Chem. Soc., 83, 182 (1961).

(4) J. O. Halford, J. Chem. Phys., 24, 830 (1956).

(5) C. S. Foote, J. Am. Chem. Soc., 86, 1853 (1964); Ph.D. Thesis, Harvard University, 1961.

(6) Compare CH₃BF₂ and CH₃NO₂.[7]

(7) D. J. Millen, "Progress in Stereochemistry," Vol. 3, P. B. D. De la Mare and W. Klyne, Ed., Butterworths, London, 1962, Chapter 4; D. J. Millen, Chem. Ind. (London), 1472 (1963).

(8) M. M. Donaldson, Ph.D. Thesis, Princeton University, 1958; Dissertation Absir., 22, 738 (1961).

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 $\beta$ 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.

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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]

(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).

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

(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.