Among the further possible conversions of the α-alkylidene ketones is reduction of the double bond, which should lead to over-all α-alkylation in good yield. Further investigations into the generation and chemistry of zinc enolates are in progress.[12]

Acknowledgment. Early experiments by Dr. Albert J. Fritsch, S.J., contributed importantly to the development of the procedure for generation of zinc enolates.

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Steric Factors in the Rates of Solvolysis of *exo*- and *endo*-2- and- 3-Bicyclo[3.3.1]nonyl Brosylates. Evidence for Steric Hindrance to Ionization in a Bicyclic System

Sir:

In the solvolysis of many bridged bicyclic compounds, the concurrent possibility of neighboring group participation hinders the assessment of the relative importance of steric effects as driving forces for reaction. We wish to report the results of an investigation of the solvolysis of *exo*- and *endo*-2- and -3-bicyclo[3.3.1]nonyl brosylates (Table I) in which steric factors are clearly responsible for the observed solvolytic activity.

Table I. Acetolysis of Brosylates[a]

Brosylate	Temp, °C	$k \times 10^5$, sec^{-1}	k_{rel}	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
Cyclohexyl	65.00	5.64			
	25.00	0.0229	1.00	27.4	1.6
endo-2	85.00	44.7			
	65.00	4.93			
	25.00	0.0240	1.05	26.6	−0.9
exo-2	45.00	31.7			
	25.00	1.81	79.1	26.9	−8.5
exo-3	25.00	21.7	948	23.2	−1.1
	17.00	7.45			
endo-3	25.00	22.5	973	24.2	−4.3
	17.00	6.87			

[a] Rates were measured titrimetrically. The solvent was glacial acetic acid containing about 2% acetic anhydride and was 0.09 *M* in sodium acetate.

Crystallographic investigations[1-4] have indicated that the preferred conformation of the bicyclo[3.3.1]nonane skeleton is the chair–chair form. However, interactions between C_3 and C_7 are sufficiently severe to cause a partial flattening of both rings and to increase the average bond angles (C_1–C_2–C_3, C_2–C_3–C_4, C_3–C_4–C_5) to a value of 114°. If the C_3 (or C_7) *endo* hydrogen is replaced by an atom such as oxygen, the magnitude of this repulsion is increased and spectral evidence indicates that the substituted ring assumes the boat conformation.[5-7] The strain attending these conformations is reflected in the reactivity of the 3-brosylates and by the fate of the cations which are formed.

The *exo*-3-brosylate solvolyzes at a rate which is 948 times greater than that of cyclohexyl brosylate; more than 90% of the product of acetolysis is bicyclo[3.3.1]nonene. The driving force for this reaction must have its source in the strain which is relieved as the reacting carbon atom undergoes rehybridization from an sp^3 to an sp^2 center, thereby minimizing the "bowsprit" interaction between C_3 and C_7. The high percentage of elimination which occurs is probably a further indication of the strained nature of the parent ring system, since reaction of the cation with solvent to form an ester would reestablish the unfavorable transannular interaction which formerly existed.[8,12]

The *endo*-3-brosylate is 973 times more reactive than cyclohexyl brosylate, and the major product of solvolysis (>90%) is again the olefin. The reactivity of this isomer is consistent with what would be expected from relief of the strain inherent in the rigid-boat conformational modification of the cyclohexane ring. It is interesting to note that, on the basis of the carbonyl frequency (1717 cm^{-1}, CCl_4), the *exo*-3- and *endo*-3-brosylates exhibit a log (rate enhancement) of 2.58 and 2.59, respectively, if bond angle strain, torsional strain, and nonbonded interaction strain terms are omitted from the Foote–Schleyer correlations.[14,15] Since the possibilities for anchimeric assistance seem remote, it is reasonable to conclude that the major fraction of these enhancements arise from the three steric factors mentioned above.

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[1] M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, **47**, 695 (1964).

[2] W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc.*, 1844 (1965).

[3] W. A. C. Brown, G. Eglinton, J. Martin, W. Parker, and G. A. Sim, *Proc. Chem. Soc.*, 57 (1964).

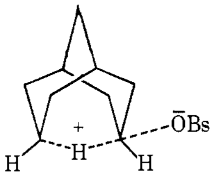
[4] I. Laszlo, *Rec. Trav. Chim.*, **84**, 251 (1965).

[5] W. D. Macrosson, J. Martin, and W. Parker, *Tetrahedron Letters*, 2589 (1965).

[6] C. Y. Chen and R. J. W. LeFévre, *J. Chem. Soc.*, 539 (1966).

[7] J. P. Schaefer, J. C. Lark, C. A. Flegal, and L. M. Honig, *J. Org. Chem.*, **32**, 1372 (1967).

[8] It is conceivable that a portion of the observed rate enhancement may result from transannular participation by hydrogen during the rate-determining step. Transannular hydride shifts between C_3 and C_7



have been observed[9] in this system as well as in reactions of medium-sized rings,[10] but attempts to detect hydrogen participation in the latter systems have been unsuccessful.[11] Since stereoelectronic factors offer an ideal opportunity for hydrogen participation in reactions of 3-substituted bicyclo[3.3.1]nonanes, we have initiated studies on appropriate deuterated compounds in an attempt to evaluate this possibility.

[9] R. A. Appleton, J. R. Dixon, J. M. Evans, and S. H. Graham, *Tetrahedron*, **23**, 805 (1967).

[10] A. C. Cope, S. W. Fenton, and C. F. Spencer, *J. Am. Chem. Soc.*, **74**, 5884 (1952), and subsequent papers in this series.

[11] V. Prelog, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **18**, 247 (1957).

[12] A rate enhancement of 948 relative to cyclohexane corresponds to a $\Delta\Delta F$ of 4.05 kcal/mole. Since the ΔF for the chair–boat equilibrium of cyclohexane is approximately 6 kcal/mole,[13] it seems reasonable to conclude that the energy difference between the chair–chair and the chair–boat conformations of the bicyclo[3.3.1]nonane skeleton is approximately 2 kcal/mole. The same figure may be obtained from a consideration of the reactivity of the 3-*endo*-brosylate (Table I).

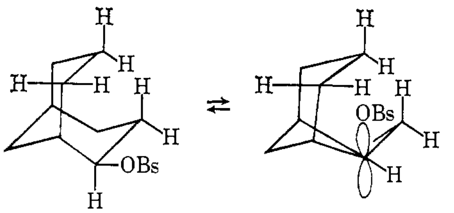
[13] A comprehensive discussion of the energetics of this system can be found in E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

[14] C. S. Foote, *J. Am. Chem. Soc.*, **86**, 1853 (1964).

[15] P. von R. Schleyer, *ibid.*, **86**, 1855, 1856 (1964).

The largest fraction of the driving force ($k_{\rm rel} = 79$) for the reaction of the *exo*-2-brosylate must arise from the relief of eclipsing strain between C_3 and C_7. As the C_2–O bond begins to stretch, C_1, C_3, and the carbinyl hydrogen on C_2 will tend toward coplanarity. This will be accompanied by a movement of C_3 away from C_7 and will reduce the magnitude of the nonbonded interaction between C_3 and C_7 in the transition state relative to the ground state. The product of solvolysis is primarily (>90%) bicyclo[3.3.1]nonene.

The behavior of the *endo*-2-brosylate is interesting since it is of the same order of reactivity as cyclohexyl brosylate. If a model of this compound is constructed,



it will be seen that, as ionization occurs and the C_3 methylene group moves away from the C_7 methylene group, the departing brosylate anion is forced into close proximity to the C_7 position.[16] As a result, any driving force which accrues from the relief of transannular interactions in the starting brosylate is negated by the establishment of an equally serious nonbonded interaction in the transition state. From a comparison of the relative rates of the *exo*-2- and *endo*-2-brosylates, it appears that steric hindrance to ionization brings about a rate decrease of 75-fold.[17]

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[16] This concept was first suggested for the solvolysis of *endo*-norbornyl derivatives by H. C. Brown. A detailed discussion of this proposal can be found in the paper by H. C. Brown, I. Rothberg, P. von R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Natl. Acad. Sci U. S.*, **56**, 1653 (1966).

[17] For a detailed study of the solvolysis of the *endo*-2-tosylate, see M. Hanack, W. Kraus, W. Rothenwohrer, W. Kaiser, and G. Wentrup, *Ann.*, 703, 44 (1967).

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Kinetics and Mechanisms of Electron-Transfer Reactions Involving Copper(I) in Perchlorate Solution[1]

Sir:

It is a well-known and often-quoted fact that copper(I) ion is unstable with respect to disproportionation (eq 1)

$$2Cu^+ = Cu^{2+} + Cu(s) \qquad (1)$$

in solutions lacking complexing anions. The equilibrium quotient for reaction 1 is 2×10^6 M^{-1} at 25–35° at ionic strength 1.13 M in the presence of perchlorate anions.[2] We have found that appropriate one-electron reductions can be used to generate quantitative yields of Cu^+ in perchlorate solution. Such metastable solutions can, moreover, be used for some time without appreciable disproportionation. Solutions are sensitive to oxygen, however, and all reactions have been studied under nitrogen which had been carefully purified of traces of oxygen. Spectrophotometric measurements, either conventional[3] or stopped-flow,[4] form the basis for all the rate studies reported here.

The reactions of copper(II) with an insufficient amount of the one-equivalent reducing agents Cr(II), V(II), and Eu(II) have been examined. The first of these (eq 2) provides a particularly useful synthetic technique, since the equilibrium lies well toward Cu^+, and since

$$Cr^{2+} + Cu^{2+} = Cr^{3+} + Cu^+ \qquad (2)$$

the other product, $Cr(H_2O)_6{}^{3+}$, is unreactive toward substances whose reactions with copper(I) we have studied. The rate equation is first order with respect to each metal ion concentration; the predominant reaction term has an inverse dependence upon $[H^+]$, but an additional term independent of $[H^+]$ was noted (eq 3). At 25.0° and $C_{ClO_4^-} = 1.00$ M, $a = 0.22$

$$d[Cu^+]/dt = (a + b/[H^+])[Cr^{2+}][Cu^{2+}] \qquad (3)$$

M^{-1} sec^{-1} and $b = 0.56$ sec^{-1}. The product was verified to be Cu^+ under the conditions of these experiments by two independent methods. The decrease in light absorption of Cu^{2+} at 7500 A ($\epsilon \sim 11$ M^{-1} cm^{-1}) corresponded quite closely to the stoichiometry given in eq 2, rather than to a 1:2 ratio of Cu^{2+}/Cr^{2+} which would be the case were supersaturated metallic copper being generated. Moreover, a number of the rate runs were carried out under conditions where the excess of Cu(II) was slight, so that pseudo-first-order kinetics was not followed. In such cases, appropriate second-order plots were nicely linear and gave the same apparent rate constant at a particular $[H^+]$ as did runs in which pseudo-first-order conditions held. On the other hand, the same experiments when calculated assuming the stoichiometry was such that $0.5Cu^0$, and not Cu^+, was formed gave nonlinear plots. Copper metal was, of course, formed in any experiment where $[Cr^{2+}]_0 > [Cu^{2+}]_0$, and also in runs where $[Cr^{2+}]$ was only slightly less than $[Cu^{2+}]$. The latter observation is consistent with a second step, $Cu^+ + Cr^{2+} = Cu^0 + Cr^{3+}$, that became important under conditions where excess Cu^{2+} was so low that adequate time remained for Cu^+ to react with Cr^{2+} to an appreciable extent. Formation of copper metal in experiments with a bare excess of Cu(II) could be prevented by slow addition of Cr(II) with continuous stirring during the addition.

Reaction of V^{2+} and Cu^{2+} in perchlorate solutions likewise produced Cu^+ although the second-order rate constant was independent of $[H^+]$. Over the range $0.04 < [H^+] < 1.0$ M, $k_V = 28$ M^{-1} sec^{-1} at 25.0°. Absence of a term varying as $[H^+]^{-1}$ and the large value of k_V compared to a are particularly noteworthy. The former is very likely an indication of an outer-sphere mechanism.[5] The high value of k_V relative to

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[1] Work performed in the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission. Contribution No. 2162.

[2] (a) W. M. Latimer, "Oxidation Potentials," 2d ed, Prentice-Hall Inc., New York, N. Y., 1952, p 185; (b) R. W. Miller, Thesis, University of Illinois, 1961; *Dissertation Abstr.*, 22, 3365 (1962), as cited by L. G. Sillén, "Stability Constants of Metal-Ion Complexes," Section I, Special Publication No. 17, The Chemical Society, London, 1964, p 17.

[3] J. H. Espenson, *J. Am. Chem. Soc.*, 86, 5101 (1964).

[4] D. W. Carlyle and J. H. Espenson, *Inorg. Chem.*, **6**, 1370 (1967).

[5] B. R. Baker, M. Orhanovic, and N. Sutin, *J. Am. Chem. Soc.*, **89**, 722 (1967), have discussed the role of $[H^+]$ in other reductions of $V(H_2O)_6{}^{2+}$.