ate College, Texas A&M University, for a research fellowship for S. D. A.

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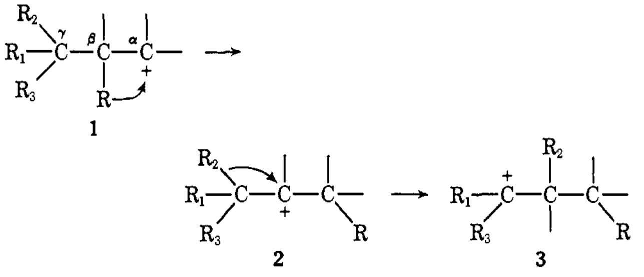
Magnification of the Memory Effect by Methyl Substitution. The Ring Expansions of the 1-Methylnorborn-2-enyl-7-*anti*- and -7-*syn*-carbinyl and the 1-Methyl-*endo*- and -*exo*-2-norbornylcarbinyl Systems[1]

Sir:

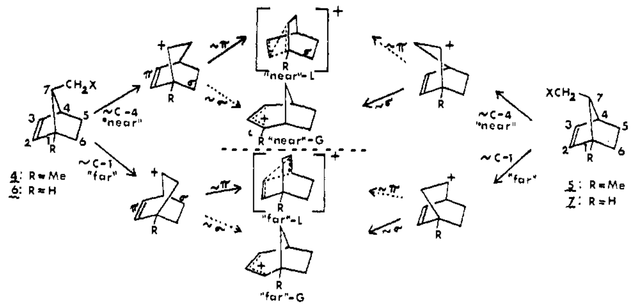
Consecutive multiple carbonium ion rearrangements (*e.g.*, **1** → **2** → **3**) frequently select between two potential migrating groups (R_1 and R_2), even though in principle there is an opportunity for complete symmetrization, quasisymmetrization, or crossover at the once-rearranged intermediate stage **2**. Competition between stereochemical symmetrization or crossover and the second rearrangement **2** → **3** determines the magnitude of this type of "memory effect."[2] One might expect that alkyl for hydrogen substitution of the nonmigrating group (R_3) γ to the original cationic charge, in providing a means for generation of a more stable doubly rearranged ion (**3**, R_3 = alkyl), would favor rearrangement more than symmetrization in **2** and thereby magnify the memory effect. In this and the accompanying paper,[3] we report experiments that demonstrate this phenomenon. The results provide the first roughly quantitative estimate of the amount by which a substituent so placed enhances the specific rate of rearrangement of a carbonium ion.



Because the starting materials are unsymmetrically substituted, the double rearrangements of 1-methylnorborn-2-enyl-7-*anti*- and -7-*syn*-carbinyl derivatives **4** and **5** (Scheme I) permit not only an external comparison with the previously studied unsubstituted parent systems[4] **6** and **7** but also an internal one, since the selectivities on the "far" side (methyl group remote from the site of charge) serve as calibration points for those on the "near" side.

Scheme I predicts the occurrence of four distinct sets of products in proportions that will be determined by the competitions ~C-4 *vs.* ~C-1 and ~π *vs.* ~σ shown. Memory-destroying crossover steps are shown with dashed arrows. The products expected or conceivable by analogy with the unsubstituted series[2,5,6] are those derived from the four cations[7] "near"-L, "near"-G, "far"-L, and "far"-G. Unambiguous independent syntheses and characterizations of these 23 potential ring-expanded products as well as those of several side products support the structural assignments.[8]

Scheme I



The validity of the analogy with the unsubstituted system is demonstrated in each case when independent generation of the product-forming cationic intermediate by acetolysis of the corresponding once-rearranged substrate, namely the appropriate 1- (or 4-) methylbicyclo[2.2.2]oct-5-en-2-yl *p*-toluenesulfonate (**8**-OTs → "near"-L, **9**-OTs → "near"-G, **10**-OTs → "far"-L, and **11**-OTs → "far"-G), gives the predicted products. Crossover between the cation systems, although detectable at 120°, is negligibly small at 35°.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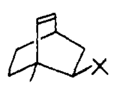
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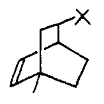
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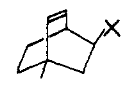
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The results of ring expansions of the syn and anti systems by way of intermediates generated in the nitrosative deamination of the amines at room temperature are reported in Table I, which also includes

Table I. Memory Effects in Deaminations

	Product ratio from amine system[a]			
	Parent		1-Methyl	
Type of product ratio	Syn (**7**-NH_2)	Anti (**6**-NH_2)	Syn (**5**-NH_2)	Anti (**4**-NH_2)
Total "near"/total "far"	1.00[g]	1.00[g]	2.0[f]	0.84[d]
Memory effect (ME)[b]				
"Near"[h]	3.3[c]	33[c]	20[g]	65[g]
"Far"[h]			6.5[d]	33[d]
Mult ME (MME)				
"Near"[h]	110[e]		1300[e]	
"Far"[h]			215[f]	

[a] Refers to ring-expanded products only. [b] ME = G/L product ratio from syn, L/G product ratio from anti. [c] Reference 4b. [d] Estimated uncertainty ±15%. [e] Estimated uncertainty ±30%. [f] Estimated uncertainty ±20%. [g] By symmetry. [h] Applies only to 1-methyl series.

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(2) For a review, see J. A. Berson, *Angew. Chem., Int. Ed. Engl.*, 7, 779 (1968).

(3) J. A. Berson and J. W. Foley, *J. Amer. Chem. Soc.*, 93, 1297 (1971).

(4) (a) J. A. Berson and J. J. Gajewski, *ibid.*, **86**, 5020 (1964); (b) J. A. Berson, J. J. Gajewski, and D. S. Donald, *ibid.*, 91, 5550 (1969).

(5) (a) H. L. Goering and M. F. Sloan, *ibid.*, **83**, 1992 (1961); (b) H. L. Goering, R. W. Greiner, and M. F. Sloan, *ibid.*, **83**, 1391 (1961); (c) H. L. Goering and D. L. Towns, *ibid.*, **85**, 2295 (1963).

(6) N. A. LeBel and J. E. Huber, *ibid.*, **85**, 3193 (1963).

(7) The significance of the twisted cation notation is discussed elsewhere.[2,4]

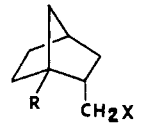
(8) J. W. McKenna, Ph.D. Thesis, University of Wisconsin, 1970.

data from the unsubstituted system[4] and gives values of the *multiplicative memory effect*[9] and of the competition ratios for "far" *vs.* "near" ring expansion.

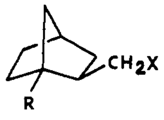
Based on the values given in Table I,[10] the effect of γ-methyl substitution on the multiplicative memory effect (MME) in the present system amounts to a factor of about 6 in the intramolecular "near"–"far" comparison and about 13 in the comparison with the parent system. The square roots of these values, which are in the range 2–4, roughly approximate the enhancements of selectivity.

The enhancements are of about the same magnitude as those observed in the 1-methyl-2-norbornylcarbinyl (see below) and 1-methyl-7-norbornylcarbinyl[3] systems. In those cases, it is possible to equate the enhancement with an increase in the ratio of the rate constant for the second rearrangement (k_r) to that for symmetrization or crossover (k_c). In the **4**–**5** case, for reasons already given,[2,9] this ratio is not directly accessible, but the uniformity of the γ-methyl effect makes it seem likely that the underlying cause is the same here. Since the "far"-side memory effect seems to differ but little from that in the unsubstituted case,[10] it seems unlikely that the observed "near"-side enhancement factor of 2–4 results from fortuitous large and almost equal increases in *both* k_r and k_c. More plausibly, it probably represents largely the enhancement of k_r.

Methyl substitution produces very large enhancements of selectivity in both deaminative and solvolytic reactions of the 1-methyl-2-norbornylcarbinyl systems **12** and **13**, the substituted derivatives showing lower limits for the multiplicative memory effects ranging between 1450 and 64,000, by far the largest ever observed. Appropriate treatment[11] of the previous data for the parent endo case[12a,13] (**14**-OBs) and comparison with the data from **12**-ONs indicate that methyl substitution here again enhances the ratio k_r/k_c by a factor of about 2–4.



12: R = Me
14: R = H



13: R = Me

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[9] In systems such as the syn–anti pairs **5**–**4** and **7**–**6**, crossover can occur by formation of a quasisymmetrical intermediate, *e.g.*, a bicyclo[2.2.2]oct-2-en-5-yl cation, from either member of the pair. Since an unknown "natural" ratio controls the partitioning of this intermediate in further rearrangement,[2] a memory effect will manifest itself only as a difference in product ratios from syn and anti substrates. The multiplicative memory effect (MME), *i.e.* $[(G/L)_{syn}][(L/G)_{anti}]$, is a useful method of presenting the data. If there is no memory effect, the MME is necessarily unity, no matter what the "natural" partition ratio. If there is a memory effect, the MME is a good index of its size. Since the MME contains terms from the ring expansions of both members of an epimeric pair, a memory effect, even if present in only one member of the pair, will surely be detected.

[10] Bridgehead methyl substitution apparently also slightly increases the MME value on the "far" side as compared to that of the unsubstituted system. The effect, amounting to a factor of about 2, seems to be outside experimental error but is definitely smaller than that on the "near" side.

[11] J. B. E. Allen, Ph.D. Thesis, University of Wisconsin, 1970.

[12] (a) J. A. Berson and P. Reynolds-Warnhoff, *J. Amer. Chem. Soc.*, **84**, 682 (1962); **86**, 595 (1964); (b) W. Kraus and P. Schmutte, *Tetrahedron*, **24**, 1537 (1968).

[13] J. A. Berson and D. Willner, *J. Amer. Chem. Soc.*, **84**, 675 (1962); **86**, 609 (1964).

[14] National Science Foundation Graduate Fellow, 1966–1969.

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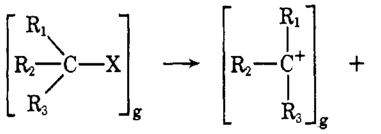
On the Relationship between the Relative Kinetic Effect of Substitution and the Absolute Magnitude of the Activation Energy in Carbonium Ion Reactions. Stereoselectivity in Carbonium Ion Ring Expansions of the 1-Methyl-7-norbornylcarbinyl System[1]

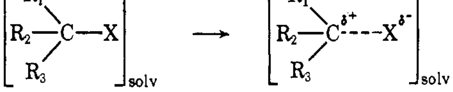
Sir:

Reactions creating carbonium ions are greatly facilitated by alkyl for hydrogen substitution at the developing cationoid center. The effect is largest for gas-phase ionizations (eq 1), where the overall free energy of activation is large ($\Delta F^{\ddagger}$ for R_2 = H $\sim$ 150 kcal/mol, $\Delta\Delta F^{\ddagger}$ between R_2 = Me and R_2 = H $\sim$ 18 kcal/mol[2]), but even in reactions of much lower overall $\Delta F^{\ddagger}$, the substituent effect remains a substantial one.



(1)

Thus, in "limiting" solvolysis (eq 2), $\Delta\Delta F^{\ddagger}$ $\sim$ 11 kcal/mol, $\Delta F^{\ddagger}$ $\sim$ 25 kcal/mol.[3] The shape of any correlation that may exist between the relative kinetic effect of substitution and the absolute magnitude of the activation energy in reactions of this type is not obvious.



(2)

In particular, does the curve extrapolate monotonically to zero substituent effect as the overall $\Delta F^{\ddagger}$ tends to smaller values? Although this seems intuitively reasonable,[4] there are no strong theoretical reasons for excluding the possibility that at very low $\Delta F^{\ddagger}$, $\Delta\Delta F^{\ddagger}$ may vanish or even change sign. In this and the accompanying paper,[5] we provide points for the lower end of the correlation by an examination of the effect

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[1] The partial support of this work by the National Science Foundation through Grants No. GP-6212X, GP-11017X, and GU-2730, by the Wisconsin Alumni Research Foundation, and by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

[2] (a) D. P. Stevenson as quoted by A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 42; (b) D. Bethell and V. Gold, "Carbonium Ions," Academic Press, New York, N. Y., 1967, p 66 ff.

[3] J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2542 (1970).

[4] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, pp 162–168.

[5] J. A. Berson, J. M. McKenna, and H. Junge, *J. Amer. Chem. Soc.*, **93**, 1296 (1971).