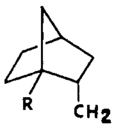
data from the unsubstituted system[4] and gives values of the *multiplicative memory effect*[9] and of the competition ratios for "far" *vs.* "near" ring expansion.

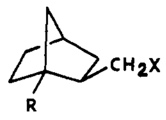
Based on the values given in Table I,[10] the effect of γ-methyl substitution on the multiplicative memory effect (MME) in the present system amounts to a factor of about 6 in the intramolecular "near"–"far" comparison and about 13 in the comparison with the parent system. The square roots of these values, 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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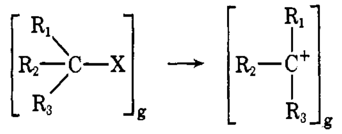
On the Relationship between the Relative Kinetic Effect of Substitution and the Absolute Magnitude of the Activation Energy in Carbonium Ion Reactions. Stereoselectivity in Carbonium Ion Ring Expansions of the 1-Methyl-7-norbornylcarbinyl System[1]

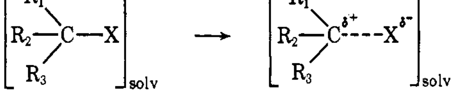
Sir:

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.

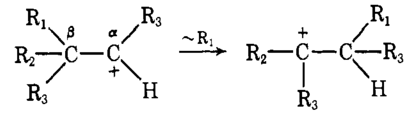
(2) (a) D. P. Stevenson as quoted by A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 42; (b) D. Bethell and V. Gold, "Carbonium Ions," Academic Press, New York, N. Y., 1967, p 66 ff.

(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).

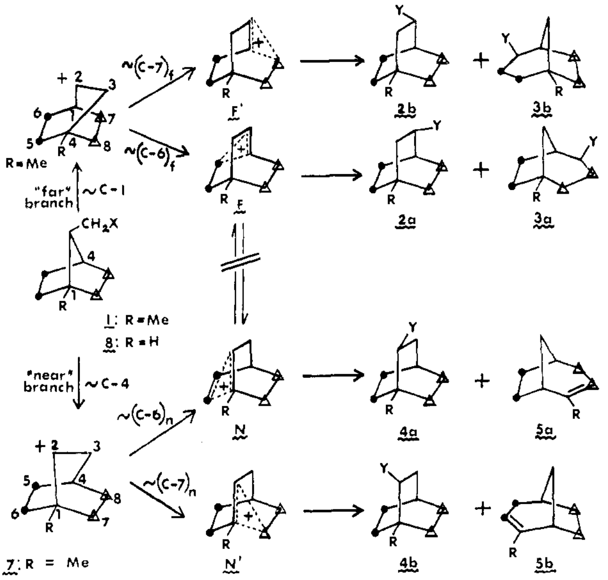
of a substituent at C-β on the rate of a carbonium ion rearrangement (eq 3) as evidenced by magnifications of



$$R_1R_2R_3\overset{\beta}{C}-\overset{\alpha}{\underset{+}{C}}R_3H \xrightarrow{\sim R_1} R_2-\overset{+}{\underset{R_3}{C}}-CR_1R_3H \qquad (3)$$

the memory effect in ring expansions of 1-methyl-7-norbornylcarbinyl derivatives (Scheme I).

Scheme I



There are three mechanistic branching points in the multiple rearrangements initiated by ring expansion of this system (Scheme I). Competition between migrations of C-1 and C-4 in the ring-expansion step leads to cations in which the charge is, respectively, remote from ("far") or adjacent to ("near") the methyl group. In each of these branches, further rearrangement must choose between anti and syn ring members C-6 and C-7, migrations of which, respectively, preserve "memory" or destroy it by crossover.

The overall distribution of ring-expanded products, % (**4a** + **4b** + **5a** + **5b**) *vs.* % (**2a** + **2b** + **3a** + **3b**) (R = Me), combined with the information (see below) that interconversion between the doubly rearranged "far" (F) and "near" (N) (R = Me) cation systems is negligible, gives directly the competition ratio for the initial ring expansion (C-4 *vs.* C-1). Specific isotopic marking (● or Δ = CHD) of one bridge of the starting material **1**, isolation of the doubly rearranged products **3** and **5** (R = Me), and appropriate degradation[6] permit determinations of the distributions **3a**/**3b** and **5a**/**5b** (R = Me) and hence of the competition for migration of anti (C-6) and syn (C-7) ring members in both the "near" and "far" branches. Solvolyses of the *p*-nitrobenzenesulfonate **1**-ONs and nitrosative deaminations of the amine hydrochloride **1**-NH_3Cl give the results reported in Table I.

Despite the enhanced stability of tertiary cation N (R = CH_3) over that of secondary cation F (R = Me), the ratio of products from the "far" and "near" branches is very close to unity in all of the reactions. If the two rearrangement steps (*e.g.*, ~C-1 and ~C-6) were concerted, one would have to attribute the near-equal distribution to the fortuitous circumstance that enhancement of the migratory aptitude of C-1 just balances the effect of cationic stability. This balance should be perturbed as the structure of the transition state changes in response to wide variations in solvent and leaving group. The distribution between "far" and "near" products shows no such variation (Table I), and therefore the rearrangements are more simply interpreted with a stepwise mechanism in which the migrations are successive rather than simultaneous.

Table I. Product Distributions in the Ring Expansion Double Rearrangement of 1-Methyl-7-norbornylcarbinyl Derivatives

		Product			
		"Far" branch[a] select.		"Near" branch[a] select.	
Reactant	Conditions[b]	%	**3a/3b**[e]	%	**5a/5b**[e]
1-ONs[c]	HOAc, 118°	52	2.3	48	8.1[e]
1-ONs[d]	HOAc, 118°		2.3		7.3
1-ONs[c]	HOAc, 78°		2.6		9.0
1-ONs[c]	HCO_2H, 100°	48	3.4	52	11.6
1-ONs[c]	H_2O–dioxane, 100°	52	2.5	48	8.1
1-ONs[c]	Me_3CCO_2H, 110°		1.9		6.2
1-NH_3Cl[c]	HOAc, $NaNO_2$, 25°	55	2.2	45	6.2
1-NH_3Cl[c]	H_2O–HOAc, $NaNO_2$, 25°	56	4.8	44	10.1

[a] "Far" branch products consisted mainly of **2** and **3** (R = Me). "Near" branch products consisted mainly of olefin **5** (R = Me) except in deamination and formolysis where substantial amounts of the corresponding tertiary alcohols and 1-methylbicyclo[3.2.1]oct-2-yl formate, respectively, appeared. Per cent yields refer to ring expanded products only. [b] Acetolyses carried out with NaOAc buffer, formolyses and hydrolyses with pyridine buffer, and trimethylacetolyses with sodium trimethylacetate buffer. [c] Δ = CHD, ● = CH_2. [d] Δ = CH_2, ● = CHD. [e] Estimated uncertainty in this ratio is about 10%.

The selectivities **3a**/**3b** (R = Me) in the "far" branch are very similar to those previously reported[7,8] for the deuterium-labeled 7-norbornylcarbinyl system lacking the methyl group. A comparison of the selectivity ratios (Table I) **5a**/**5b** *vs.* **3a**/**3b** (R = Me) shows that methyl substitution enhances the preference for (and probably the absolute rate of) the memory-preserving migration of C-6 *vs.* C-7 in the "near" branch over that in the "far" branch (Scheme I) by factors in the range of 2–4, an effect of virtually the same magnitude as those observed in two other systems.[5]

In eq 3, where R_3 = alkyl, rearrangement of an alkyl group (R_1) converts a secondary cation to a secondary one if R_2 = H and to a tertiary one if R_2 = alkyl. The present data suggest that the free-energy benefit ($\Delta\Delta F^{\ddagger}$) of methyl for hydrogen substitution at the site of a developing cationoid center (C-β) in such rearrangements is about 0.4–1.1 kcal/mol as compared to an overall $\Delta F^{\ddagger}$ for the process of less than 6 kcal/mol.[9] This value and the 1.3–2.2-kcal/mol diminution by a 6-methyl substituent of the activation energy for a

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(6) For details, see J. W. Foley, Ph.D. Thesis, University of Wisconsin, 1969.

(7) J. A. Berson and M. S. Poonian, *J. Amer. Chem. Soc.*, **88**, 170 (1966).

(8) J. A. Berson, M. S. Poonian, and W. J. Libbey, *ibid.*, **91**, 5567 (1969).

(9) (a) M. Saunders and E. L. Hagen, *ibid.*, **90**, 6882 (1968). (b) The β-substituent effect in eq 3 refers to a process in which one carbonium ion is converted into another. It should not be confused with the β-substituent effect in anchimerically assisted solvolysis, which refers to a process in which a covalent substrate is converted to a carbonium ion.

6,2-hydride shift in norbornyl cation[10] (overall $\Delta F^{\ddagger}$ = 5.9 kcal/mol[11]) can be combined with the data pertaining to eq 1 and 2 to give a monotonic curve that extrapolates to near-zero substituent effect at zero overall $\Delta F^{\ddagger}$.

[10] J. A. Berson, R. G. Bergman, J. H. Hammons, and A. W. McRowe, *J. Amer. Chem. Soc.*, **89**, 2581 (1967).

[11] G. A. Olah and A. M. White, *ibid.*, **91**, 3957 (1969).

[12] The partial support of this work by National Institute of General Medical Sciences Predoctoral Fellowship No. 5 F01 GM 33291 (1966–1969) and by an NSF Traineeship (1965–1966) is gratefully acknowledged.

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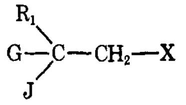
Deaminative and Solvolytic Ring Expansion. Relative Migratory Aptitudes of Ring Members and β Substituents[1]

Sir:

The intermediates in carbonium ion processes usually distribute themselves among several competing reaction pathways with far less discrimination in nitrosative deaminations than in solvolytic reactions.[2] Although agreement has not been universal on the mechanistic details of deaminations, there seems to be general acceptance of the hypothesis that loss of molecular nitrogen is an exceptionally facile process. This compresses the energy scale for the hierarchy of possible reactions that follow upon (or accompany) it and hence damps out the selectivity.[2] We were startled therefore to find (in the course of other studies) a widespread apparent reversal of this behavior. The present paper documents a number of examples of selectivity which are much *greater* in deaminatively induced ring expansions than in the solvolytic counterparts.

The competing paths we use to examine selectivity are the migration of a β substituent (R_1) and the migration of a β ring member (G, J) in carbinyl derivatives of the general formula **1**.[3] The groups G and J



$$\mathrm{G{-}C(R_1)(J){-}CH_2{-}X}$$

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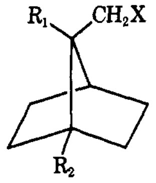
correspond to ring members of the series of bicyclic substrates **2**–**7**.



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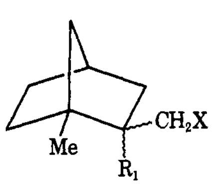

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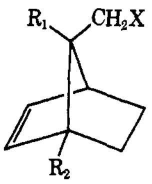

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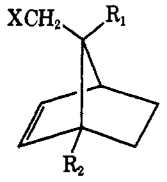

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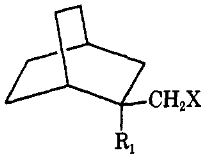

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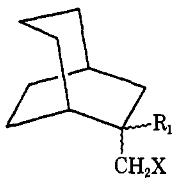

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The selectivity (ring expansion/migration of the β substituent) is based upon the total amount of product of each type in each of the reactions. Some of the details of product characterization already have been reported[4,5] and others will appear in forthcoming papers.

The data shown in Table I indicate that in the solvolytic reactions (X = OBs, ONs, or Br), the selectivity

Table I

Substrate	R_1	R_2	Medium	Selectivity (ring exp/~R_1) X = ONs[a]	X = NH_2[b]
2	H	H	HOAc	17 ± 3[a]	>200
			HCO_2H	23	
			Aq dioxane[c]	15	
			Aq HOAc		>200
2	CH_3	H	HOAc	7.5	>200
2	H	CH_3	HOAc	3	241[e]
			HCO_2H	11	
			Aq dioxane[c]	2	
			Aq HOAc		325[e]
3	*exo*-H		HOAc	7.9	
			Aq acetone[d]	3.3	
			Aq dioxane[c]	3.9	
			Aq HOAc		16
3	*endo*-H		HOAc	6.5	
			Aq acetone[d]	5.8	
			Aq dioxane[c]	5.1	
			Aq HOAc		7.5
4	H	H	HOAc	1.5	96[e]
			HOAc		>200
			Aq HOAc		>200[e]
			HOAc, $AgClO_4$	1[f]	
5	H	H	HOAc	18	29
			Aq HOAc		82
			HOAc, $AgClO_4$	2–4[f,g]	
4	CH_3	H	HOAc	2.5	>200[e]
5	CH_3	H	HOAc	40	59[e]
4	H	CH_3	HOAc	0.3	62[e]
5	H	CH_3	HOAc	3.2	17[e]
6	H		Aq dioxane[c]	0.5	7.5,[h] 7.5[i]
7	*exo*-H		HOAc	0.17	
7	*endo*-H		HOAc	0.14	

[a] In some cases, *p*-bromobenzenesulfonates were used. [b] Deamination with sodium nitrite in acetic acid or 9:1 H_2O–HOAc (v:v) unless otherwise indicated. [c] 60:40 dioxane–H_2O (v:v). [d] 75:25 acetone–H_2O (v:v). [e] X = NH_3Cl. [f] X = Br. [g] Ratio increases with temperature between 25 and 125°. [h] At 25° with a small amount of HOAc added. [i] At 100° with a small amount of HOAc added.

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[1] This work was supported in part by grants from the National Institute of Arthritis and Metabolic Diseases (AM-07505), the National Science Foundation (GP-6212X and GP-11017X), the Petroleum Research Fund (Type C grant), administered by the American Chemical Society, and the Wisconsin Alumni Research Foundation. An institutional grant to Yale University (GU-2730) is also gratefully acknowledged.

[2] For an excellent review with references to the extensive literature, see E. H. White in "The Chemistry of the Amino Group," S. Patai, Ed., Wiley, New York, N. Y., 1968, Chapter 8.

[3] In many cases, direct displacement of the leaving group X without rearrangement occurs in these systems, but since there is sometimes an appreciable bimolecular component in this type of reaction,[4] we exclude it from consideration here.

[4] (a) J. A. Berson, M. S. Poonian, and W. J. Libbey, *J. Amer. Chem. Soc.*, **91**, 5567 (1969); (b) J. A. Berson, D. S. Donald, and W. J. Libbey, *ibid.*, **91**, 5580 (1969).

[5] J. A. Berson, J. J. Gajewski, and D. S. Donald, *ibid.*, **91**, 5550 (1969).