Table I. Yields of Products and Product Ratios on Deamination of Amines **1** and **2**[a]

	From **1**		From **2**
Products[b]	HOAc (glacial)	HOAc–NaOAc	HOAc–NaOAc
3	43.5	35.0	29.6
4	3.4[c]	2.4[c]	0.039[c]
5	36.7	43.5	25.6
6	16.5	19.0	42.6
7	0.075[c]	0.114	2.2[c]
Ratio			
5:**6**	2.2:1	2.3:1	1:1.7
5:**4**	10.5:1	18:1	650:1
6:**7**	220:1	166:1	19:1
4:**7**	45:1	21:1	1:56

[a] Deaminations were performed at ambient temperature. [b] The monoacetates of **4–7** were obtained on deamination, and these were converted to the diols with lithium aluminum hydride. Smaller yields of three other compounds[a] resulting from hydride shift in the ions A and B. [c] These products were crystallized repeatedly with the addition of hold-back carrier[14] until the radioactivity contents were constant.

(3) The product ratios **6**:**7** (from **1**) of 166 and **5**:**4** (from **2**) of 650 provide the first measurement of a lower limit for the stereospecificity of *exo*:*endo* attack by anion (or solvent) on a classical, substituted norbornyl carbonium ion. Because of steric hindrance to *endo* attack by the 5-*endo*-phenyl or -hydroxyl groups, one might guess that these ratios are higher than the stereospecificity for *exo vs. endo* attack on the unsubstituted norbornyl cation.

Since the yields of *endo* products formed from A and B through the long routes (**1** → A → B → **7**; **2** → B → A → **4**) are so small and were measured by an indirect method[14] rather than by isolation, the question naturally arises whether these yields are real or merely reflect the limits of our experimental methods. Phrased differently, is it possible for a classical, substituted norbornyl cation to undergo 1,2-Wagner–Meerwein rearrangement to another classical ion which can then suffer *endo* attack? That the answer to this question is "yes" can be seen from the accompanying communication.[16]

(16) B. M. Benjamin and C. J. Collins, *J. Am. Chem. Soc.*, **92**, 3183 (1970).

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Wagner–Meerwein Rearrangements of Substituted Classical Norbornyl Cations[1]

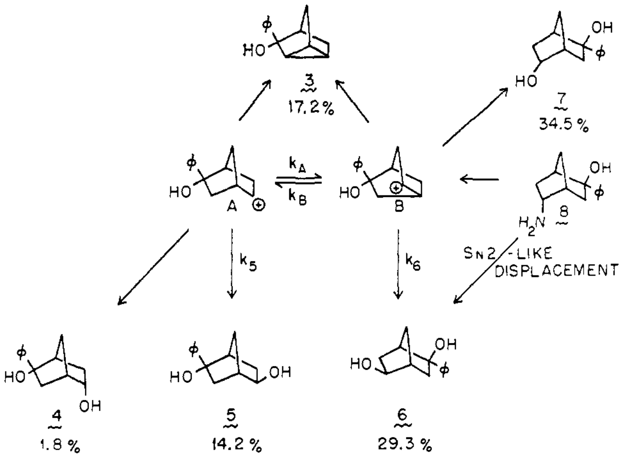
Sir:

In the preceding communication[2] we presented evidence for S$_N$2-like processes during deaminations of the substituted 2-*exo*-norbornylamines **1** and **2**.[3] We reported our measurements of the stereospecificities for *exo vs. endo* attack on the classical ions A and B and concluded that bridged nonclassical ions were unimportant during the deaminations investigated.

We report here the results of our studies of the deamination, in acetic acid–sodium acetate solution, of the *endo* amine **8**. The deamination proceeds through rearrangement of the classical ion B to the classical ion A; A then undergoes some *endo* attack to produce an isolable quantity (about 2%) of *endo*-**4**-acetate. We consider this result to be incontrovertible evidence for the survival of the classical ion A even *after* 1,2-Wagner–Meerwein rearrangement of the initially formed classical ion B; we also consider it further evidence for the unimportance of substituted, nonclassical 2-norbornyl cations during the reaction.

Previously we reported evidence that formation of the counterion by decomposition of the diazonium acetate is an important factor in the control of stereospecificity during deaminations.[4-7] We now present additional evidence and contend that it is primarily the counterion which is responsible for the "memory effects"[8] during our deaminations.

The amine **8** was subjected to deamination[9] in acetic acid–sodium acetate solution at room temperature. The mixture of products **3** and **4–7** (as the acetates) was treated with lithium aluminum hydride, and the yields of **3** and the diols **4–7** were determined spectrally (these yields are shown under the appropriate structures). In addition, the products were isolated by column chromatography. In a second deamination of **8** the yield of **4** was determined with a carbon-14 isotope dilution experiment to be 1.8%, in agreement with our estimation of the yield by isolation.



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(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

(2) C. J. Collins and B. M. Benjamin, *J. Amer. Chem. Soc.*, **92**, 3182 (1970).

(3) We preserve the same numbering system as used in the preceding paper.[2]

(4) C. J. Collins and J. B. Christie, *J. Amer. Chem. Soc.*, **82**, 1255 (1960).

(5) C. J. Collins, J. B. Christie, and V. F. Raaen, *ibid.*, **83**, 4267 (1961).

(6) C. J. Collins, V. F. Raaen, B. M. Benjamin, and I. T. Glover, *ibid.*, **89**, 3940 (1967).

(7) C. J. Collins, V. F. Raaen, and M. D. Eckart, *ibid.*, **92**, 1787 (1970).

(8) J. A. Berson, *Angew. Chem.*, **80**, 765 (1968). We disagree with Berson's argument against counterion control of "memory effects" during deamination, for he assumes that since the leaving group is N_2 such control cannot be important. In his argument Berson overlooks the very strong configuration-holding effect[4-6] of the acetate anion formed on decomposition of the diazonium acetate. See also R. Huisgen and Ch. Rüchardt, *Justus Liebigs Ann. Chem.*, **601**, 1 (1956); E. H. White, *J. Amer. Chem. Soc.*, **77**, 6011, 6014 (1955); E. H. White and C. A. Aufdermarsh, *ibid.*, **80**, 2597 (1958); **83**, 1174, 1179 (1961).

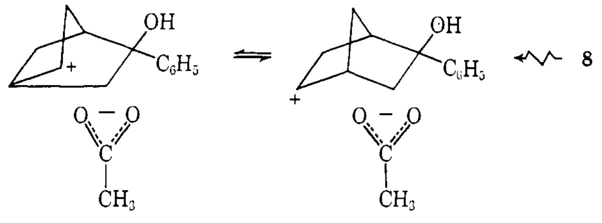
(9) The synthesis was through the following route: norbornenone + PhMgBr → 2-*exo*-phenyl-2-norbornenol (borohydration) → 2-*exo*-phenyl-2-*endo*-hydroxy-5-*exo*-norborneol (mixture) → 2-*exo*-phenyl-2-*endo*-hydroxy-5-*exo*-norbornyl tosylate (hydrolysis) → mixture of diols **5** and **6** (plus smaller yields of several other products). Diol **6** was oxidized with chromic acid to the ketone, which was converted to the oxime. The oxime was then treated with lithium aluminum hydride to yield the amine **8**. Elemental analyses and spectral data were consistent with the assigned structure.

From the data in the chart several interesting conclusions can be drawn.

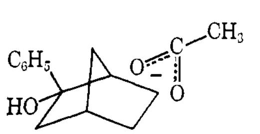
(1) The isolation of diol **4** clearly means that the classical ion A must be its precursor. Thus classical ion B (B is attacked from the *exo* direction to yield **6**, and from the *endo* direction to yield **7**) undergoes Wagner–Meerwein rearrangement to classical ion A which can be attacked from both the *exo* and *endo* directions to give **5** and **4**, respectively. There is no evidence here for a bridged nonclassical ion.

(2) The ratio of the yields of diols **5** and **6** was 1:2.1 when they were obtained from **8** and was 1:1.7 when they were obtained from the *exo* amine **2**;[2] here we have further evidence for the presence of S_N2-like processes which for **2** would produce *endo* diol **7** (2.2%), but for **8** should result in an increase in the yield of **6** as compared with **5**. In addition, S_N2-attack from the *exo* direction on **8** should be favored over *endo* S_N2 attack on **2**; from the data it can be calculated that 2.2% of the *exo* amine **2** and at least 5% of the *endo*-amine **8** undergo S_N2-like processes.

(3) The relatively high yields of **7** and **4** obtained from **8** require special comment: the *endo* diol **7** is produced in *greater* yield than the *exo* diol **6**, whereas deamination of **2** produces **6**:**7** in a ratio of 19:1. The evidence is clear for the configuration-holding ability of the counter acetate ion.[4-8] We believe that the decomposition of the diazonium acetate from **8** gives the tight ion pair B-1, which exhibits a strong tendency to collapse irreversibly to the acetate of the *endo* diol **7** (S_Ni reaction). We propose that ion pair B-1 accounts for the large yields of **7** acetate. After Wagner–Meerwein rearrangement of B-1 to the tight ion pair A-1, the configuration-holding ability of the anion is diminished, but still strong enough to produce **4**-acetate in nearly 2% yield. Compare this yield with the yield (0.04%)[2] of **4**-acetate produced on deamination of the *exo* amine **2**, where the ion pair must resemble A-II and favor collapse to *exo*-**5**-acetate. The planar representations (A-I, A-II, and B-I) of three-dimensional structures are, of course, misleading; as the structures are drawn, the anion in A-I is not *below* the cation but somewhat in front of it. From Dreiding models, at least, the collapse of A-I to **4**-acetate seems likely. We plan to prepare N-acetyl-^{14}C-N-nitroso-5-*exo*-hydroxy-5-phenyl-2-*endo*-norbornylamine (**8**) and thermally decompose it in acetic acid–sodium acetate solution. Isolation of **4**-acetate-^{14}C would provide further strong support for our explanation[10] of the present data.



A-I B-I



A-II

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(10) H. Goering and M. J. Degani, *J. Amer. Chem. Soc.*, **91**, 4506 (1969), have recently demonstrated that *syn*-7-chloro-2-*exo*-norbornyl tosylate can undergo internal return on acetolysis to form *anti*-7-chloro-2-*exo*-norbornyl tosylate. The return does not involve added labeled tosylate anion and must occur *via* a 2,6 migration of the tosylate partner in the ion pair.

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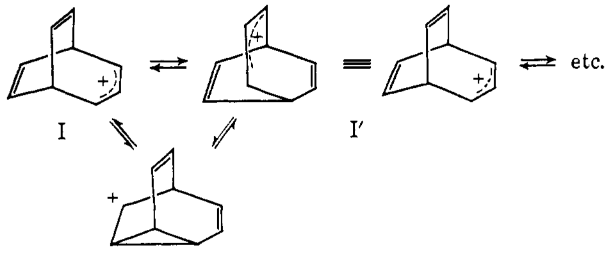
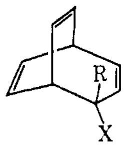
Degeneracy in the Bicyclononatrienyl–Barbaralyl Cation Rearrangement[1]

Sir:

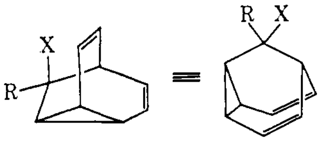
The "antibicycloaromatic"[3] bicyclo[3.2.2]nona-2,6,8-trien-4-yl cation (I) is a potentially fully degenerate $C_9H_9^+$ system.[1,2] A series of 1,2-C–C shifts ($I \rightleftarrows I' \rightleftarrows$ etc.) will eventually interconvert all of the nine CH units comprising the molecule. Other rearrangements involving I also are possible. Homoallylic participation would give the 9-barbaralyl cation (II),[2] from which I′ also could form. In fact, Goldstein and Odell have found that Lewis acids convert bicyclo[3.2.2]nona-2,6,8-trien-4-ol (III, R = H, X = OH) to barbaralol (IV, R = H, X = OH).[4] Our own results parallel this observation, which demonstrates the greater thermodynamic stability of barbaralyl (IV) over bicyclononatrienyl (III) derivatives: *e.g.*, attempted tosylation of III (R = H, X = OH) under mild conditions[5] gave only IV (R = H, X = OTs).[2] By means of deuterium labeling, we have studied the degree of degeneracy achieved during such III → IV interconversions.



I I′ II



III



IV

4-Deuteriobicyclo[3.2.2]nona-2,6,8-trien-4-yl 3,5-dinitrobenzoate (V) was prepared from bicyclo[3.2.2]-nona-2,6,8-trien-4-one[4] by $NaBD_4$ in CH_3OD reduction followed by esterification. Solvolysis of V at 75° in 60% aqueous acetone (with 10% excess lutidine) gave two products in a 1:1 ratio: 9-barbaralyl dinitroben-

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(1) Paper IV in a series on degenerate and potentially degenerate cations; for paper III see ref 2.

(2) J. C. Barborak, J. Daub, D. M. Follweiler, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 7760 (1969).

(3) M. J. Goldstein, *ibid.*, **89**, 6357 (1967).

(4) M. J. Goldstein and B. J. Odell, *ibid.*, **89**, 6356 (1967).

(5) Ethyl ether, −20°, with powdered KOH. See K. B. Wiberg and A. J. Ashe, *ibid.*, **90**, 63 (1968).