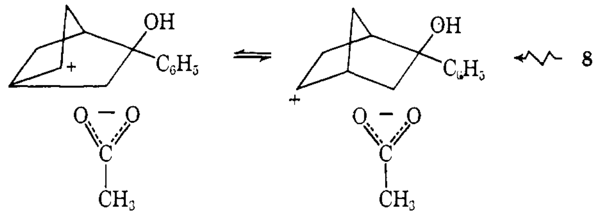
From the data in the chart several interesting conclusions can be drawn.

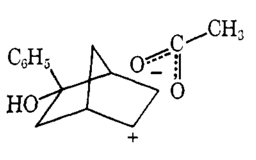
(1) The isolation of diol **4** clearly means that the classical ion A must be its precursor. Thus classical ion B (B is attacked from the *exo* direction to yield **6**, and from the *endo* direction to yield **7**) undergoes Wagner–Meerwein rearrangement to classical ion A which can be attacked from 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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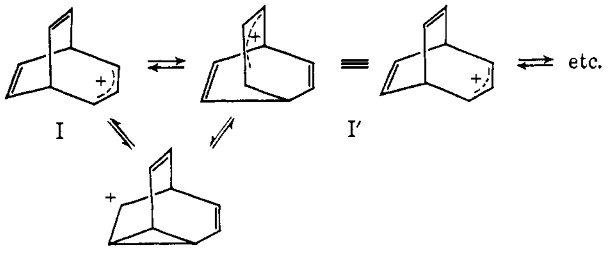
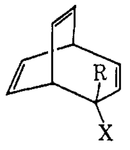
Degeneracy in the Bicyclononatrienyl–Barbaralyl Cation Rearrangement[1]

Sir:

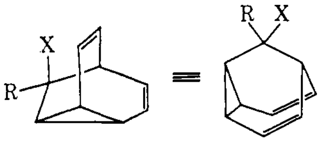
The "antibicycloaromatic"[3] bicyclo[3.2.2]nona-2,6,8-trien-4-yl cation (I) is a potentially fully degenerate $C_9H_9^+$ system.[1,2] A series of 1,2-C–C shifts ($\mathrm{I} \rightleftarrows \mathrm{I'} \rightleftarrows$ etc.) will eventually interconvert all of the nine CH units comprising the molecule. 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.



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).

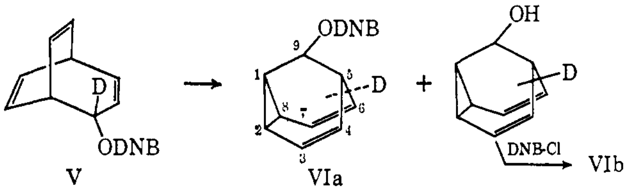
[5] Ethyl ether, −20°, with powdered KOH. See K. B. Wiberg and A. J. Ashe, *ibid.*, **90**, 63 (1968).

zoate (VIa) by return and 9-barbaralol (IV, X = OH). No bicyclo[3.2.2]nonatrien-4-ol (III, R = H, X = OH) could be detected in the product mixture under our conditions although a separate experiment showed it would survive these conditions. For convenience of purification and analysis, the latter was converted to 3,5-dinitrobenzoate (VIb). The extent of deuterium scrambling (Table I) was determined by nmr.[2] Mass spectroscopy provided additional evidence that starting materials and products had the same deuterium content (±5%). Within experimental error (±3%), VIa and VIb had identical scrambling patterns, suggesting a common rearrangement pathway. Selective rather than total degeneracy was observed. While very little deuterium was introduced into positions C_8, C_7, and C_9, totally statistical distribution over the remaining six positions was achieved.[6] The mixing mechanisms $I \rightleftarrows I' \rightleftarrows$ etc. do not take place, for these processes, through symmetrization in the intermediates, would introduce deuterium into positions 3, 7, and 9, where none is found (Table I). Likewise, simple homoallylic conversion of III (or I) to IV (or II) is ruled out, for this should introduce deuterium only to positions 2, 4, 6, and 8, but not to positions 1 and 5, where it is found experimentally in equivalent amounts (Table I).

Table I. Deuterium Scrambling in Solvolysis Products

Compd	% deuterium in various positions[a]			
	$C_{1,5}$	$C_{2,4,6,8}$	$C_{3,7}$	C_9
VIa	36	63	1	0
VIb	32	66	2	0
Statistical	22	44	22	11

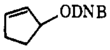
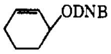
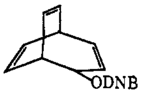
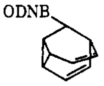
[a] The positions 1 and 5 as well as 2, 4, 6, and 8 are rendered equivalent by facile Cope interconversion; *cf.* ref 2.



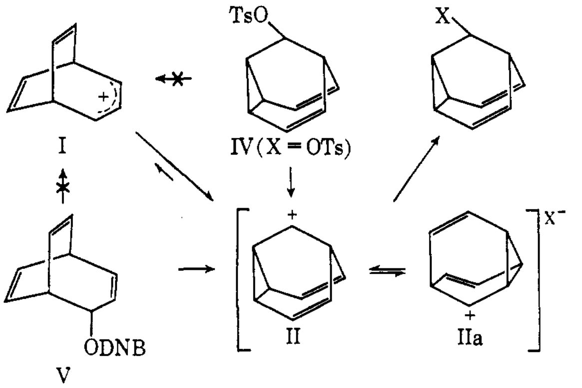
The solvolysis rate of V was comparable to that of other cyclic allylic dinitrobenzoates (Table II) and was many powers of ten greater than the rate of 9-barbaralyl 3,5-dinitrobenzoate (IV, R = H, X = ODNB). The latter compound thus was not responsible for the 9-barbaralol (IV, X = OH) observed as a reaction product from V. The data of Table II are not simple to interpret. However, the solvolysis rate of V is not unusually slow, as might be expected if ion I were formed from V and if I were destabilized through antibicycloaromaticity.[3]

Contrary to the usual situation, the three-membered ring containing barbaralyl system IV is more stable than its olefinic isomer, III.[7] This is revealed by the earlier[3] and by the present results under thermodynamic control conditions. Kinetic control would be expected for the products obtained from buffered solvolysis. Since both V and 9-barbaralyl tosylate (IV, R = H, X = OTs)[2] gave only 9-barbaralyl and not bicyclo[3.2.2]nona-2,6,8-trien-4-yl products under such conditions, we conclude that the 9-barbaralyl cation (II) is also more stable than the bicyclononatrienyl one (I). The much faster rate of reaction of V than 9-barbaralyl 3,5-dinitrobenzoate (IV, R = H, X = ODNB) is probably due to the anchimerically assisted conversion of V directly to II, avoiding the less stable I. The present and the former[2] deuterium scrambling results confirm this conclusion, that the bicyclo[3.2.2]nona-2,6,8-trien-4-yl cation (I) is not a very stable species and does not tend to form under the conditions of our experiments.

Table II. Kinetic Data for Solvolysis of Allylic 3,5-Dinitrobenzoates

Compd	k, 75°, sec^{-1} 60% aqueous acetone[a]	Relative rates	$\nu_{C=O}$, cm^{-1} [b]
	6.2×10^{-3} [c]	117	1716
	5.3×10^{-5} [c]	1	1686
	8.8×10^{-4}	17	1680[e]
	$\sim 5 \times 10^{-5}$ [d]	$\sim$0.01[d]	1716[f]

[a] Conductometric rate constants. Due to return the total ionization rates of these compounds are faster. [b] Carbonyl frequencies of the corresponding ketones; *cf.* C. S. Foote, *J. Amer. Chem. Soc.*, **86**, 1853 (1964); P. von R. Schleyer, *ibid.*, **86**, 1854, 1856 (1964). [c] W. Sliwinski, unpublished data. [d] Estimated roughly on the basis that 25° acetolyses of tosylates are generally 500 times faster than the 100° 60% acetone solvolyses of the corresponding dinitrobenzoates (J. E. Baldwin and W. D. Fogelsong, *J. Amer. Chem. Soc.*, **89**, 6372 (1967)). [e] Reference 4. [f] Reference 2.



The most concise description, consistent with the available data, is presented above. Both 9-barbaralyl (IV) and bicyclononatrienyl (V) derivatives ionize to give directly the 9-barbaralyl (II) cation or ion pair. However, this species undergoes effective threefold symmetrization (IIa)[8] rapidly, before covalent products can be formed. Such a mechanism, coupled with the

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(6) See Table I, footnote *a*.

(7) An analogy is found in the greater stability of nortricyclene over norbornene: P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 80, 1700 (1958).

(8) After submission of this paper, we became aware of related work done in S. Winstein's laboratory. J. B. Grutzner and S. Winstein (*ibid.*, **92**, 3186 (1970)) report a similar deuterium labeling solvolysis study. P. Ahlberg, D. L. Harris, and S. Winstein (*ibid.*, **92**, 2146 (1970)) and P. Ahlberg, J. B. Grutzner, D. L. Harris, and S. Winstein (*ibid.*, in press) have studied the stable 9-barbaralyl and related cations, and have presented evidence to support the degenerate rearrangement, II $\rightleftarrows$ IIa, suggested by us[2] as one of the possible scrambling mechanisms.

degenerate Cope process,[6] renders the individual CH groups in sets of barbaralyl positions (3, 7, 9) and (1, 2, 4, 5, 6, 8) equivalent. Leakage—mixing of these two sets of positions—occurs practically not at all in the experiments described here. Somewhat more leakage was found earlier during solvolysis of labeled 9-barbaralyl tosylate (IV, R = D, X = OTs):[2] 7% in 80% acetone and 26% during acetolysis. Such leakage may involve the intermediacy of the bicyclononatrienyl cation (I), formed slowly from II.

It is tempting to ascribe the apparent instability of the bicyclo[3.2.2]nona-2,6,8-trien-4-yl cation (I) to "antibicycloaromaticity."[3] However, this cation may be destabilized by the ring strain factors present in the covalent ion precursors and also by the adverse electron-withdrawing inductive effect of the two nonallylic double bonds. These factors, coupled with a favorable mechanistic pathway for conversion of V directly to II, may account for the results we have observed. We continue efforts to find unambiguous evidence for "antibicycloaromaticity" in cation I.

Acknowledgments. This work was supported by grants from the National Science Foundation, the National Institutes of Health (AI-07766), and the Petroleum Research Fund, administered by the American Chemical Society. We thank Professor J. B. Grutzner for an exchange of information.[8]

[9] National Institutes of Health Postdoctoral Fellow, 1969–1970.

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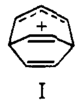
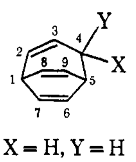
Bicycloaromaticity. The Stability and Rearrangement of the Bicyclo[3.2.2]nonatrienyl Cation[1]

Sir:

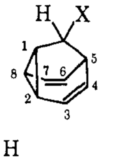
According to the theory proposed by Goldstein,[2] the bicyclo[3.2.2]nonatrienyl cation, I, should be "destabilized and antibicycloaromatic." Evidence has been presented[3] that this system undergoes a facile rearrangement to yield barbaralyl products. We now wish to report results to show that this behavior cannot be attributed to the inherent destabilization of I, but is due to the availability of a low-energy route for its conversion to the energetically favored barbaralyl system III. Data will be presented which reveals a new and interesting asymmetric deuterium scrambling reaction. Parallel studies have been undertaken by Schleyer.[4]



I



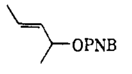
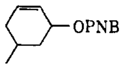
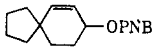
IIa, X = H, Y = H
b, X, Y = O
c, X = H, Y = OH
d, X = D, Y = OH
e, X = H, Y = OPNB
f, X = D, Y = OPNB



IIIa, X = H
b, X = OH
c, X = OPNB(*p*-nitrobenzoate)

In order to establish the degree of destabilization associated with I, we carried out the solvolysis of the *p*-nitrobenzoate, IIe[5] (mp 95–6°). Any marked rate depression of the [3.2.2] system when compared with suitable model compounds can be attributed to destabilization of the antibicycloaromatic cation. Solvolyses were carried out in 80% aqueous acetone at 100 and 125°. Only a 77 ± 1% infinity was attained at both temperatures, but work-up of the solvolysis products showed that 23% of the initial IIe had isomerized to the barbaralyl *p*-nitrobenzoate, IIIc, which is stable to the reaction conditions.[6] After correction for this competing reaction, the data gave good first-order plots and the results are shown in Table I together with model systems for comparison. After chromatographic purification the remaining solvolysis products were shown to be IIc and IIIb by comparison with authentic samples. The yield of IIc varied with the solvolysis (0–20%), but control experiments showed that IIc could be converted to IIIb under reaction conditions.[7] Thus, the rates and products of the solvolysis indicate that there is little unusual destabilization associated with the [3.2.2] cation, I. The observation of the rearranged internal return product, IIIc, shows that while I is not strongly destabilized relative to other allylic cations, it can readily rearrange to the lower energy barbaralyl cation IV.[8]

Table I. Solvolysis Data for Allyl *p*-Nitrobenzoates[a]

Compound	Temp, °C	Rate × 10^6 sec^{-1}
IIe	100	11.8 ± 1.0
IIe	125	98 ± 5
	100	12[b]
	100	3.7[b]
	100	3.8[b]

[a] In 80% aqueous acetone. [b] E. C. Friedrich, Ph.D. Thesis, University of California at Los Angeles, Los Angeles, Calif., 1961.

In the earlier work,[3] it was reported (without experimental detail) that no bicyclo[3.2.2]nonatriene, IIa, was detected in the $LiAlH_4$–$AlCl_3$ reduction of the

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[1] Supported by the National Science Foundation.

[2] M. J. Goldstein, *J. Amer. Chem. Soc.*, **89**, 6357 (1967).

[3] M. J. Goldstein and B. G. Odell, *ibid.*, **89**, 6356 (1967).

[4] J. C. Barborak and P. von R. Schleyer, *ibid.*, **92**, 3184 (1970). We thank Professor Schleyer for informing us of his results prior to publication and for agreeing to simultaneous publication.

[5] All new compounds gave satisfactory analyses and spectral properties. IIe was prepared from the corresponding alcohol IIc by conventional methods.

[6] J. C. Barborak, J. Daub, D. M. Follweiler, and P. von R. Schleyer, *ibid.*, **91**, 7760 (1969).

[7] These reactions were monitored by nmr spectroscopy on the crude solvolysis products both before and after separation by column chromatography into ester and alcohol components. Chromatography of each compound individually showed no evidence of rearrangement or decomposition on the column.

[8] We recognize that our conclusions regarding the destabilization of I rest heavily on the observation of IIc in the solvolysis product and the assumption that this material does not arise from direct solvent displacement on IIe. However, comparison with other solvolytic studies involving *p*-nitrobenzoates in these laboratories suggests that this is unlikely. The extent of deuterium scrambling observed in IIc derived from IIf should provide at least partial justification of this point. Unfortunately, in the reaction in which the deuterated products were examined, no IIc was detected by nmr.