acetone–water to make up a final solution of 95% aqueous acetone v/v. The two solutions were put in the two arms of a Y-shaped reaction vessel and mixed at the desired temperature. For each run seven to ten samples (3–5 ml) were withdrawn at various time intervals to cover until 85% reaction. These aliquots were then added to benzene (5 ml) and the organic layer washed with water (by this procedure the thiocyanate is not solvolyzed appreciably). The aqueous solution was titrated for acid with standard aqueous sodium hydroxide.

The determination of isothiocyanate was carried out by reacting with excess piperidine. The amine reacts readily with the isothiocyanate to give quantitatively N-(4,4′-dimethylbenzhydryl)-N′-(cyclopentamethylene)thiourea, while the thio compound does not interfere. The excess amine was then titrated and the following procedure was used. Aliquots (2 ml) of the reacting solution were added to benzene (5 ml) and washed with water. The aqueous layer was extracted with 3-ml portions of benzene, the organic extracts were collected and the aqueous washing was discarded. A 0.1 *M* solution of piperidine (2 ml) in benzene was added and the solution allowed to stand for 30 min at room temperature. The benzene layer was extracted with 10 ml of 0.02 *N* HCl and water and the collected aqueous portions were titrated with 0.01 *N* NaOH. In some experiments the isothiocyanate was determined by ir. The wavelength was selected at 2050 cm^{-1} corresponding to the absorption maximum for the isothiocyanate. A Perkin-Elmer Model 21 double beam instrument was used. The results were in good agreement with those obtained by titration. The product ratio [acid]/[R-NCS] did not change appreciably within a given run and this provides evidence for the stability both of the alcohol and the isothiocyanate under the reaction conditions. A solvolysis experiment carried out on 4,4′-dimethylbenzhydryl isothiocyanate confirmed this point. When the isothiocyanate (5×10^{-2} *M*) was allowed to stand in 95% acetone with 0.2 *M* $NaClO_4$ at 25° no appreciable formation of acid was detected after 48 hr corresponding to about ten half-lives for the thiocyanate.

Table IV

$100f^a$	A_{NaSCN}	A_{R-NCS}	A_{R-SCN}	$A_{R-SCN}(1-f)/A_{R-NCS}f$
2.75	950	81.0	19.0	8.30
3.20	930	77.3	21.3	8.35

[a] Fraction of isomerization; [R-SCN] = 5×10^{-2} *M*; [NaSCN] = 2×10^{-2} *M*; $NaClO_4$ + NaSCN = 0.2 *M*; temperature = 25°.

The rate of formation of acid and isothiocyanate follows a first-order law with deviations which stay within 5% at least up to 85% reaction both in the absence and in the presence of salts ($NaClO_4$ and/or NaCN). A run carried out at $NaClO_4$ = 0.2 *M* is reported in detail as follows (reaction, % ($10^5 k_{tot}$, sec^{-1})): 12.6 (15.0), 21.7 (13.6), 41.1 (14.8), 54.5 (14.6), 68.3 (14.7), 85.0 (14.7). On the contrary in an experiment carried out in the presence of 0.0486 *M* *sym*-collidine under the identical conditions the first-order rate coefficient showed a large decrease, as shown below (thiocyanate ion was determined by bromide titration): 17.7 (14.65), 31.4 (14.11), 44.3 (11.02), 52.9 (10.67), 59.4 (9.70).

Exchange. The same procedure for the preparation of the initial solution as that described for solvolysis runs was used. The work-up and the counting procedures have been described.[2a]

Partition of Radioactivity between Thiocyanate and Isothiocyanate. The detailed method has been previously described.[2b] The specific activities of the ionic thiocyanate, A_{NaSCN}, of the organic thiocyanate, A_{R-SCN}, and of the isothiocyanate, A_{R-NCS}, which have been observed at 2% isomerization are reported in Table IV. The specific activities are expressed in arbitrary units, having set A_{NaSCN} = 1000 at time zero. In the last column the ratio of total activities on the two species R-SCN and R-NCS is given.

Memory Effects in Multiple Carbonium Ion Rearrangements. I. The Ring-Expansion Route to Cations of the Bicyclo[2.2.2]octenyl Series[1]

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Abstract: Ring expansions of 2-norbornenyl-*syn*-7-carbinyl substrates in a variety of carbonium ion reactions lead to twice-rearranged products *via* intermediates different from those generated from the *anti* isomers. The major products from the *syn* system are in the G series previously encountered by Goering in solvolyses of bicyclo[2.2.2]-oct-5-en-2-*endo*-yl derivatives, whereas those from the *anti* system give mainly products (L series) observed by LeBel from bicyclo[2.2.2]oct-5-en-2-*exo*-yl derivatives. The specificity of the second rearrangement step is not perfect, however, and some "memory" is lost by crossover from the *syn* system to the L series and from the *anti* system to the G series. The product-forming twice-rearranged cations show all the characteristics of the typical G and L intermediates, but the latter two cations when generated from bicyclo[2.2.2]oct-5-en-2-yl substrates do not cross over appreciably. An extra intermediate or reaction path permitting crossover therefore must be inserted in the mechanism for the ring expansions. This intermediate is not efficiently trapped by external nucleophiles. Environmental factors such as solvent, ionic concentration, electrophilic catalysts, and variation of the leaving counterion have remarkably little effect on the selectivities of the second rearrangement step.

In the ring-expansion route to bicyclic carbonium ions, the nature of the product-forming intermediates depends markedly upon the stereochemistry of the reactant. The prototypical cases are derived from the *endo*- and *exo*-2-norbornylcarbinyl systems (**1** and **2**), which give two distinctively different intermediates. It is both plausible and convenient to refer to these as the conformationally isomeric chair and boat cyclohexyl cations **3** and **4**.[3] Whether this is the only possible

(1) This work was supported in part by grants from the National Institute of Arthritis and Metabolic Diseases (AM-07505), the National Science Foundation, the Petroleum Research Fund, and the Wisconsin Alumni Research Fund.

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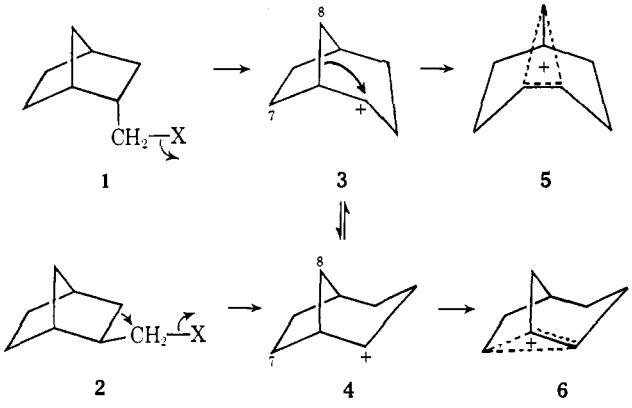
(3) (a) J. A. Berson and P. Reynolds-Warnhoff, *J. Am. Chem. Soc.*, **84**, 682 (1962); **86**, 595 (1964); (b) J. A. Berson and D. Willner, *ibid.*, **84**, 675 (1962); **86**, 609 (1964).

formulation is a matter for later consideration. For the purposes of the present discussion, the very complex pattern of behavior revealed by the previous study[3] is

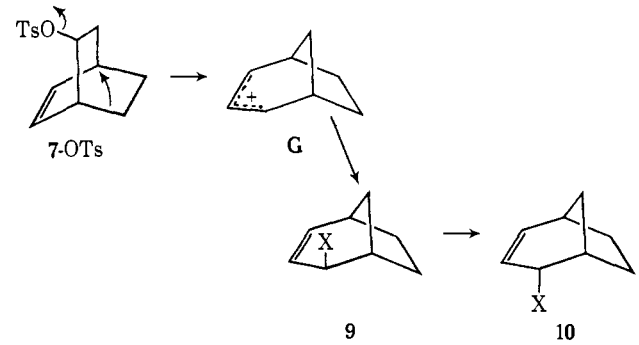


incidental to the simpler observation that the conformationally isomeric once-rearranged cations **3** and **4** interconvert at a rate that is slow relative to the rates of second rearrangement steps (**3** → **5** by migration of C-8, and **4** → **6** by migration of C-7). The specificities of these second rearrangements, which involve control of the choice of migrating group at a center remote from the initial site of heterolysis, we have called "memory effects" (with the hope that the term compensates in brevity and suggestiveness for its deficiencies in originality, precision, and elegance).

An origin for such memory effects is not difficult to propose in the case of ions **3** and **4**, where a definite barrier to conformational isomerization is readily imagined and where the stereoelectronic alignment of one of the two potential migrating bonds is more favorable in each case.[3] To know the full implications of memory effects and in particular to determine whether the existence of relatively stable conformationally isomeric pairs is a necessary condition for their occurrence, one must examine the behavior of systems in which enough rigidity is incorporated into the structure to ensure that any energy barrier separating conformations is small. The present paper, the first of several detailed reports of studies of this kind,[4,5] describes results in the 2-bicyclo[2.2.2]octenyl system.

Cations in this system are generated by more direct routes in solvolyses of 2-*endo*-bicyclo[2.2.2]-5-enyl[6] and 2-*exo*-bicyclo[2.2.2]oct-5-enyl[7] *p*-toluenesulfonates (**7**-OTs and **8**-OTs), and their properties serve as standards against which to compare the behavior of the cations produced by ring expansion.

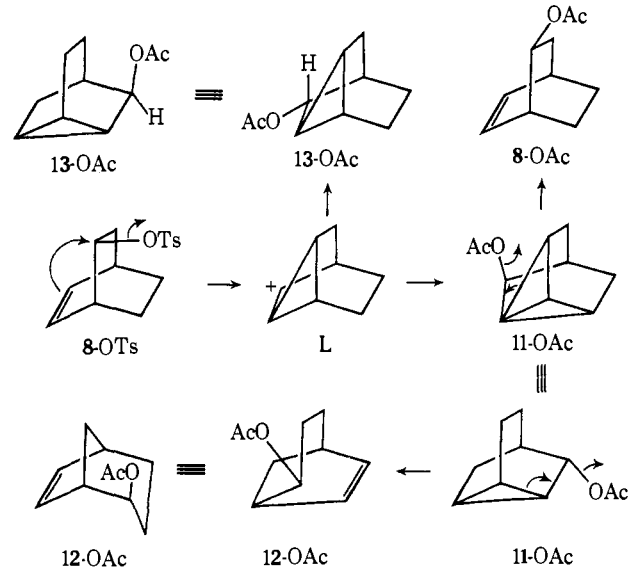
Goering and his students showed that the major kinetically controlled product of the acetolysis of the *endo*-*p*-toluenesulfonate **7**-OTs is 2-*exo*-bicyclo[3.2.1]oct-3-enyl acetate (**9**-OAc). Traces of 2-*endo*-bicyclo[3.2.1]-oct-3-enyl acetate (**10**-OAc), 2-*endo*-bicyclo[2.2.2]oct-5-enyl acetate (**7**-OAc), and 2-*exo*-bicyclo[2.22]oct-5-enyl acetate (**8**-OAc) also are formed. Under conditions of reversible carbonium ion formation, the major product acetate (**9**-OAc) is partially converted to its epimer **10**-OAc. This product pattern, the "Goering



G series

series" (G), is best understood in terms of the allylic ion **G** as the major intermediate in solvolysis of the *endo*-*p*-toluenesulfonate **7**-OTs.[6] Direct evidence for a symmetrical precursor of product **9**-OAc is provided by the observation[6] that optically active **7**-OTs leads to completely racemic **9**-OAc.

The products from the 2-*exo*-bicyclo[2.2.2]oct-5-enyl *p*-toluenesulfonate **8**-OTs, the "LeBel series" (L), are quite different. Acetolysis under kinetic control gives largely the tricyclic acetate **11**-OAc;[7] its epimer, **13**-OAc, as well as two other products, 2-*exo*-bicyclo[2.2.2]-oct-5-enyl acetate (**8**-OAc) and 2-*exo*-bicyclo[3.2.1]oct-6-enyl acetate (**12**-OAc), occur in only minor amounts. Al-



L series

though several different electronic distributions in the intermediate may be imagined, it is sufficient for our purposes to describe the first product-forming species as the tricyclic cation **L**. Under strenuous solvolysis conditions, product **11**-OAc slowly drifts toward an equilibrium mixture enriched in **8**-OAc and **12**-OAc, the latter two being formally related to **11**-OAc by the rearrangements indicated with arrows.[7]

These observations indicate that the G and L systems of cationic intermediates are mechanistically well in-

(4) For a preliminary account, see J. A. Berson and J. J. Gajewski, *J. Am. Chem. Soc.*, **86**, 5020 (1964).

(5) (a) A general but necessarily cursory survey of studies on memory effects is given by J. A. Berson, *Angew. Chem. Intern. Ed. Engl.*, **10**, 779 (1968). Closely related work is reported in the accompanying papers: (b) J. A. Berson, M. S. Poonian, and W. J. Libbey, *J. Am. Chem. Soc.*, **91**, 5567 (1969); (c) J. A. Berson, R. G. Bergman, G. M. Clarke, and D. Wege, *ibid.*, **91**, 5601 (1969); (d) J. A. Berson, D. S. Donald, and W. J. Libbey, *ibid.*, **91**, 5580 (1969); (e) J. A. Berson, D. Wege, G. M. Clarke, and R. G. Bergman, *ibid.*, **91**, 5594 (1969).

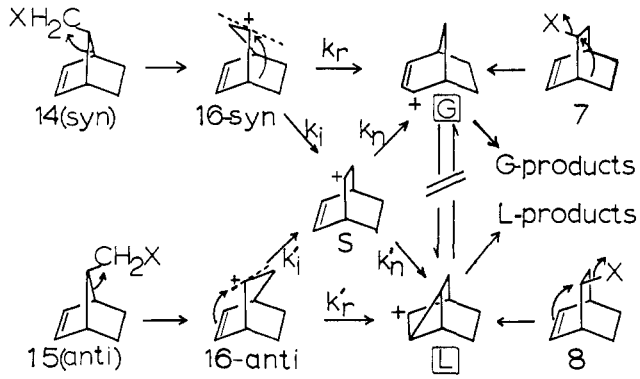
(6) (a) H. L. Goering and M. F. Sloan, *ibid.*, **83**, 1992 (1961); (b) H. L. Goering, R. W. Greiner, and M. F. Sloan, *ibid.*, **83**, 1391 (1961); (c) H. L. Goering and D. L. Towns, *ibid.*, **85**, 2295 (1963).

(7) (a) N. A. LeBel and J. E. Huber, *ibid.*, **85**, 3193 (1963); (b) *cf.* also R. R. Fraser and S. O'Farrell, *Tetrahedron Letters*, 1143 (1962).

sulated from each other. Even under equilibrating conditions where drift *within* each series permits interconversion of products, little crossover from one series to the other occurs. This clean separation between the G and L systems provides both a practical and a theoretical basis for the present study.

By an extension of the rationale used to deal with the ring expansions of the 2-norbornylcarbinyl systems,[3] one can develop a set of predictions of the behavior of the conformationally isomeric 2-bicyclo[2.2.2]octenyl cations which hypothetically might be formed by ring expansions of the *syn*- (**14**) and *anti*-2-norbornenyl-7-carbinyl (**15**) derivatives (Scheme I).

Scheme I



In the *syn* case, ring expansion might be expected to give a 2-bicyclo[2.2.2]oct-5-enyl cation **16**-*syn* in which, because of the disposition of the side-chain methylene group of the precursor, the sense of the twisting distortion is that shown. The axis of the empty p orbital at C-2 of the twisted cation **16**-*syn* lies nearly parallel to the C-1–C-7 bond, so that a second rearrangement would be expected to involve that bond in preference[8] to any other. This would produce the familiar allylic cation G, which results from *endo*-2-bicyclo[2.2.2]oct-5-enyl (**7**) solvolyses.

The *anti*-precursor (**15**) should expand to give a twisted cation **16**-*anti* in which the p orbital axis is favorably aligned for interaction with the π electrons of the C-5–C-6 double bond. The result of this would be the tricyclic cation (**L**) of the L series.

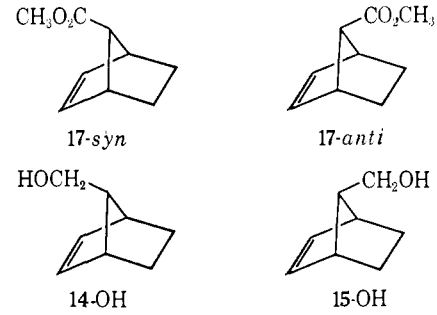
The prediction of the preference of *syn* substrate to give **G** cation and of *anti* to give **L** can be derived more generally, without reference to twisted cations or other mechanistic details, merely on the basis of analogy to the gross stereochemical results in the 2-norbornylcarbinyl systems. It is the group originally more remote from the initial reaction site that migrates preferentially in the second step.

The second rearrangement in each case can compete with conformational change, a process that erases the difference between the twisted cations, either by way of the quasi-symmetric cation **S** as a true intermediate or directly. In the latter case, **S** or a species very much like it could represent the transition state for interconversion of **16**-*syn* and **16**-*anti* cations. The scheme shown does not permit mixing of the G and L systems *after two rearrangements* by direct interconversion (**G** $\rightleftharpoons$ **L**) since this is ruled out by the behavior[6,7] already described.

The competition ratios (k_r/k_i and k_r'/k_i'), which measure rates of entrapment of the twisted species by the second bond rearrangement *vs.* conformational interconversion, determine the efficiency with which each ring expansion preserves the memory. These ratios, however, are not given directly by the product ratios from each precursor, $(G/L)_{syn}$ and $(L/G)_{anti}$, since if the quasi-symmetric ion **S** is an intermediate, it will be partitioned in accord with some unknown "natural" ratio, k_n/k_n'. The scheme is therefore noncommittal on the absolute magnitudes of the product ratios. It implies that if both $k_i \gg k_r$ and $k_i' \gg k_r'$, $(G/L)_{syn} = (G/L)_{anti}$. That is, if conformational crossover from both sides is fast relative to the second rearrangement step, there will be no memory effect. If either of these conditions does not hold, memory will be preserved and will manifest itself as a difference in product compositions. In general, $(G/L)_{syn}$ will be greater than $(G/L)_{anti}$, although because of the unknown bias imposed by the "natural" ratio k_n/k_n', either or both may be greater or less than unity.

The same framework (Scheme I) can be used for analysis of memory effects regardless of whether twisted cations **16**-*syn* and **16**-*anti* are actually *conformationally* nonidentical or differ in some other way. The elucidation of the physical basis of their nonidentity is of course the essence of the problem, but for descriptive purposes, **16**-*syn* and **16**-*anti* temporarily can be mere working hypotheses or mnemonic tags.

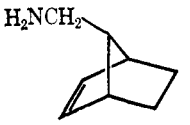
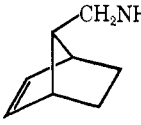
Preparation of the 2-Norbornenyl-*syn*- and -*anti*-7-carbinyl Systems. The *syn*- and *anti*-7-carbomethoxy-2-norbornenes, **17**-*syn* and **17**-*anti*, are available as a mixture from the corresponding acids, which result from carbonation of the Grignard reagent from 7-bromo-2-norbornene.[9] Separation of the esters by preparative vapor chromatography (vpc) gives each in epimeric purity of $\geq$99.5%, and lithium aluminum hydride reduction of each gives the corresponding primary alcohol **14**-OH and **15**-OH, $\geq$99.5 and $\geq$99.9% epimerically pure, respectively. The alcohols are converted to the corresponding *p*-bromobenzenesulfonates, *p*-nitrobenzenesulfonates, and amines by standard methods. Conversion to the amine hydrochlorides can be effected without involvement of the double bonds by passage of dry hydrogen chloride over a pentane solution of the amine at −78°. Ring expansions are observed in both *syn* and *anti* systems by solvolytic and deaminative generation of the cations.



(8) Although the preference is shown in the scheme as exclusive, *i.e.*, **16**-*syn* → **G** only and **16**-*anti* → **L** only, this is not a necessary feature. To the extent that some crossover by **16**-*syn* → **L** or **16**-*anti* → **G** occurs, the product distributions are conservative measures of the memory effect. For compatibility of this alternative mechanism with the experimental facts, it is only necessary that the competition ratio for rearrangement to **G** *vs.* **L** be greater from *syn*-derived "twisted" cation **16**-*syn* than from *anti*-derived "twisted" cation **16**-*anti*.

(9) (a) R. R. Sauers and R. M. Hawthorne, Jr., *J. Org. Chem.*, **29**, 1685 (1964). (b) For evidence confirming the assignments[9a] of stereochemistry see R. K. Bly and R. S. Bly, *J. Org. Chem.*, **28**, 3165 (1963).

Table I. Products (Per Cent)[a] from the Deaminations of the *syn*- and *anti*-2-Norbornenyl-7-carbinylamines, **14**-NH_2 and **15**-NH_2, in Glacial and Aqueous Acetic Acid

	Starting material and conditions							
								
	14-NH_2				**15**-NH_2			
Rx, Product (series)	HOAc RNH_2[b,k] X = OAc	HOAc $RNH_3^+Cl^-$[c] X = OAc	Aq HOAc[h,i] $RNH_3^+Cl^-$ X = OAc	Aq HOAc[h,i] $RNH_3^+Cl^-$ X = OH	HOAc RNH_2[d,k] X = OAc	HOAc $RNH_3^+Cl^-$[e] X = OAc	Aq HOAc[i,j] $RNH_3^+Cl^-$ X = OAc	Aq HOAc[i,j] $RNH_3^+Cl^-$ X = OH
7 (G)	1.3	0.6	0	0.3	0	0	0	0
10 (G)	2.6	0.3	0.2	0.9	0	0	0	0
9 (G)	69	77	6.9	74	2	3	0.2	1.3
8[n] (L)	1.3	0.7	*f*	1	5	5	*g*	7
13 (L)	0.5	0.3	0	0	2	3	0	2
11 (L)	25	22	1.5	14	89	88	9	79
12 (L)	~0	~0	0	~0	~1	~1	0	~1
Per cent excess[l] G	46	53	61	66				
G/L	2.7	3.3	4.2	4.9				
Per cent excess[m] L					96	94	96	97
L/G					48	32	45	68

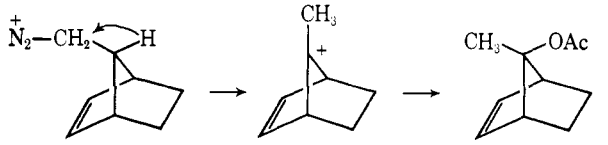
[a] Per cent of ring-expanded acetates only. Small amounts of hydrocarbons not included. Unless otherwise indicated, uncertainty ±3% of the given value. [b] Product mixture contains 20% **14**-OAc and 3% **20**-OAc. [c] Product mixture contains 16% **14**-OAc and a total of 6% of material divided among three products with retention times close to that of **20**-OAc. [d] Product mixture contains 6% **15**-OAc. [e] Product mixture contains 4% **15**-OAc and 1% **20**-OAc. [f] Products **8**-OAc + **14**-OAc = 2.2% of ring-expanded acetates. [g] Products **8**-OAc + **15**-OAc = 0.6%. [h] Product mixture contains 1.5% **14**-OAc, 6% **14**-OH, and 1% **20**-OH. [i] Product mixture contains 0.5% **14**-OH and traces of **20**-OH and **20**-OAc. [j] Ring-expanded product consists of 9% acetates and 91% alcohols. [k] The presence of the epimers of **20**-OH or **20**-OAc in small amounts cannot be excluded. [l] Per cent excess G = 100(G − L)/(G + L). [m] Per cent excess L = 100(L − G)/(L + G). [n] Value uncertain to ±10–15% of that shown.

Deaminative ring expansions of the *syn*- and *anti*-2-norbornenyl-7-carbinylamines **14**-NH_2 and **15**-NH_2 and the corresponding hydrochlorides can be effected with sodium nitrite in glacial or aqueous acetic acid at room temperature. In solvent glacial acetic acid, although small amounts of hydrocarbons and alcohols are formed, the volatile products are largely acetates. Control experiments show that the virtual absence of alcohols does not result from their conversion to acetates under the reaction conditions. The yields of monoacetate products from the *syn* series vary between 45 and 65% (corrected for recovered amine), but the *anti*-amine series gives much lower yields (10–20%). The difference is attributable to the more exposed position of the double bond in the *anti* isomer, attack upon which diverts large amounts of the starting material and the corresponding primary acetate (**15**-OAc) to nonvolatile products. Despite the low yields, the product compositions are meaningfully interpretable, since controls establish the stability of all but two of the deamination products to the reaction conditions. The only unstable ring-expanded product is **12**-OAc, *exo*-bicyclo[3.2.1]-oct-7-en-2-yl acetate, which is expected in major amount only under conditions other than kinetically controlled in the L series. The instability of this substance in the deamination environment is of minor consequence in the present work, since it enters into the quantitative evaluation of the memory effect only to a small extent.

In the aqueous acetic acid media (90% water, 10% acetic acid, v/v), the volatile products are mixtures of alcohols and acetates in approximately 10:1 ratio. Here also, the yields in the *anti* series are lower than in the *syn*. Controls demonstrate that the G/L ratio of the product alcohols does not change significantly under the reaction conditions.

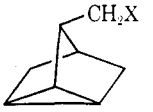
The product distributions from the deaminations (Table I) are determined by capillary vpc analyses. Identification of the major products is achieved by preparative vpc separation and spectroscopic comparison with authentic samples.

Ring expansion is a very efficient process and accounts for about 80% of the volatile products in all the deamination experiments. Small amounts of material appear as unarranged primary product and as tertiary product **20**-OAc, the latter resulting formally from vicinal hydride shift, *e.g.*, **14** → **20**-OAc.[10]



14 20-OAc

(10) Traces of nortricyclylcarbinyl products **18** are found in deamination. These are stable under the deamination conditions and consequently cannot be a source of the major products. Moreover, their conversion to unsaturated materials would require the incorporation of solvent protons, which does not occur (see below). Finally, neither deaminative nor solvolytic entry into the set of cations of the nortricyclylcarbinyl series leads to significant amounts of the products observed here.[5c] These observations exclude a hypothetical reversible formation of nortricyclylcarbinyl compounds as the mechanism of the partial crossover between the products from the *syn* and *anti* systems.

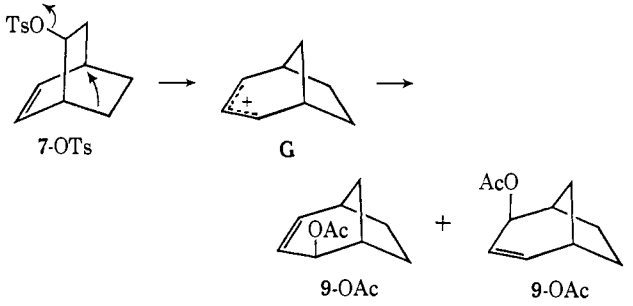


18

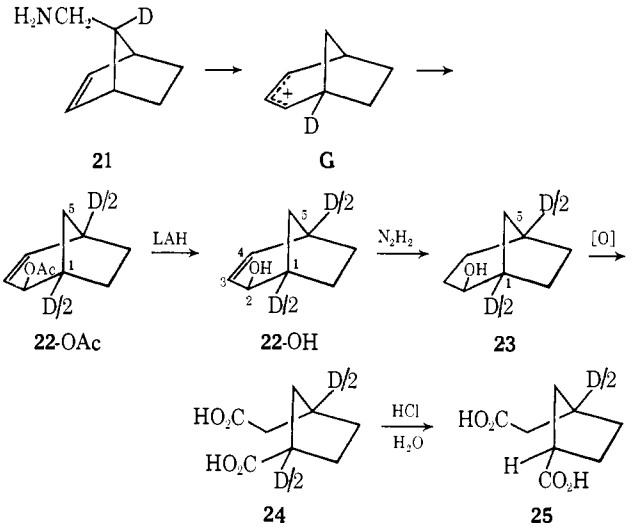
Similarly, for a number of reasons crossover cannot be attributed to a sequence involving protonation of *syn* substrate (**14**-X) to give cation

The differences between the product ratios from deamination of *syn* and *anti* substrates (Table I) demonstrate a memory effect, which operates in the predicted direction and controls the distribution as between G and L types. Although the origin and quantitative expression of this will be subjects of later discussion, it is first necessary to establish that the cations that serve as the actual product-forming intermediates for the G and L series in the ring expansions are the same as those generated by entry *via* the *endo*- and *exo*-bicyclo[2.2.2]oct-5-en-2-yl precursors (Scheme I). Support for this identification comes from comparisons of symmetry properties and chemical behavior.

The Product-Forming Intermediates in the G Series. The major product of the G series is an *exo*-bicyclo-[3.2.1]-oct-3-en-2-yl derivative, **9**-OAc or **9**-OH. The acetate **9**-OAc is formed essentially completely racemic from acetolysis of optically active *endo*-bicyclo[2.2.2]-oct-5-en-2-yl *p*-toluenesulfonate (**7**-OTs), by way of the symmetrical allylic ion **G**.[6]



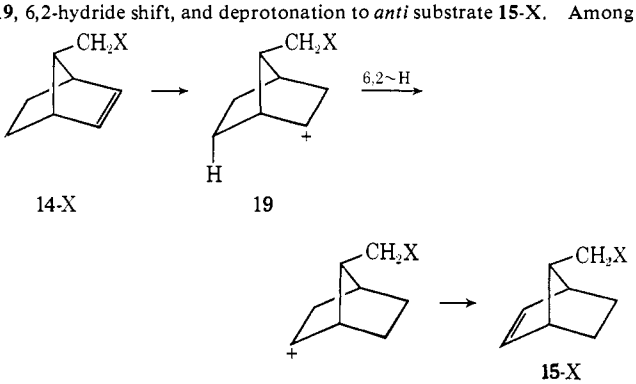
The distribution of the isotopic label in the corresponding product **22**-OAc from the deamination (in acetic acid) of 7-*anti*-deuterio-2-norbornene-7-*syn*-carbinylamine (**21**) provides some information on the nature of the **G** cations produced by ring expansion. The labeled amine **21** is prepared with 0.91 atom of D/molecule from 7-*syn*-carbomethoxy-2-norbornene-7-*anti*-*d*, which is separated from the deuterated mixture of epimers obtained from *anti*-7-carbomethoxy-2-norbornene (**17**-*anti*), sodium methoxide, and methanol-O-*d*. Deamination of **21**, isolation of the major G product, labeled allylic acetate **22**-OAc, corresponding to **9**-OAc, and reduction with lithium aluminum hydride give *exo*-2-bicyclo[3.2.1]oct-3-en-2-ol (**22**-OH). The nuclear magnetic resonance (nmr) signal at δ 2.4 of this substance is assigned to the bridgehead protons at C-1 and C-5. Its intensity in **22**-OH corresponds to 1.1 ± 0.1 H, which means that essentially all (0.9 atom of D/molecule) of the original label (0.91 atom of D/molecule) resides at C-1 and C-5. Diimide reduces **22**-OH to the saturated alcohol **23**, and an application to that substance of the degradation sequence previously used in this system[3,5b] permits the location of the deuterium label. This involves oxidation to *cis*-3-carboxycyclopentaneacetic acid (**24**) and epimerization with hot hydrochloric acid to the *trans* isomer **25**, which simultaneously removes all deuterium α to the carboxyl groups. The *trans*-acid **25** from this sequence contains 0.45 atom of D/molecule, just half the deuterium content of the starting amine **21**. The 50% of the deuterium lost in the degradation thus must reside at C-1, C-2, C-3, and/or C-4 of the allylic alcohol **22**-OH.



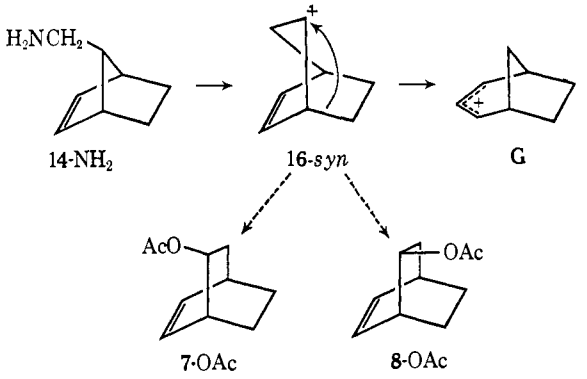
Taken together, the data from nmr and from chemical degradation are consistent only with the location of 50% of the deuterium label at each bridgehead, C-1 and C-5, of **22**-OH and hence of the acetate **22**-OAc. Furthermore, control experiments with optically active **9**-OAc (see Experimental Section) show that this result cannot be attributed to allylic rearrangement of the product acetate **9**-OAc once it is formed. The evidence thus indicates that the product-forming cation in deaminative ring expansion is the familiar symmetrical cation **G** produced by solvolysis of the *endo*-2-bicyclo[2.2.2]oct-5-en-2-yl system **7**.

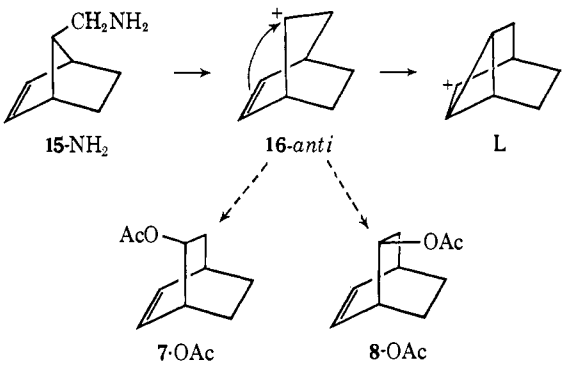
Not only is the major product, *exo*-bicyclo[3.2.1]-oct-3-en-2-yl acetate (**9**-OAc) formed from the same intermediate, but the *total distribution* of ring-expanded products in the G series is essentially the same. The percentages of *exo*-allylic acetate **9**-OAc, *endo*-allylic acetate **10**-OAc, and *endo*-bicyclo[2.2.2]oct-5-en-2-yl acetate (**7**-OAc) from solvolysis of *endo*-bicyclo[2.2.2]oct-5-en-2-yl *p*-toluenesulfonate[6] (**7**-OTs) are 99.1, 0.5, and 0.4, whereas those from the deaminative ring expansion of the *syn*-amine **14**-NH_2 are 96, 2, and 2. These figures probably differ by no more than the experimental error in the vapor chromatographic analysis, but even if the apparent discrepancy is real, the data show that at least 98–99% of the hypothetical twisted cations **16**-*syn* generated by ring expansion of **14**-NH_2 elude nucleophilic capture by the medium. Such a process would lead to formation of an "extra" amount of bicyclo-[2.2.2]oct-5-en-2-yl product and would give a product distribution richer in **7**-OAc (and/or **8**-OAc) than that obtained in direct solvolysis of **7**-OBs.

19, 6,2-hydride shift, and deprotonation to *anti* substrate **15**-X. Among



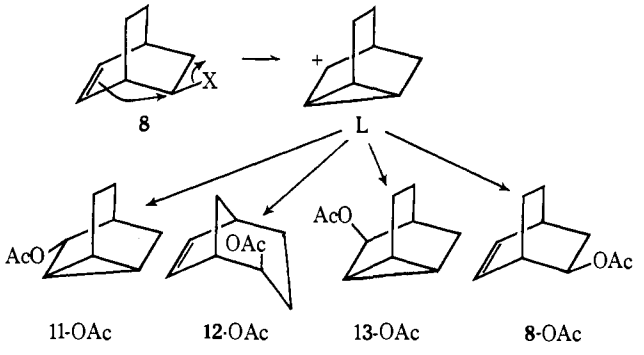
the objectionable features of this mechanism is the prediction of some **15**-OAc product from **14**-X and *vice versa*, neither of which is observed.





In ring expansion of the *anti*-amine **15**-NH_2, the amount of product of the G series is so small (Table I) that it becomes very difficult to perform an isotopic labeling experiment corresponding to that in the case of *syn*-amine **14**-NH_2. Nevertheless, the distribution of products within the G series (allylic *exo*-acetate **9**-OAc ≫ *endo*-bicyclo[2.2.2]oct-5-en-2-yl acetate (**7**-OAc) ≈ allylic *endo*-acetate **10**-OAc) is again consistent with the conclusion that essentially all of the G products arise by capture of the same intermediates as those encountered in direct solvolysis of **7**-OTs.[11]

The Product-Forming Intermediates in the L Series. Scheme I shows the tricyclic cation **L** as the precursor of the L products formed in ring expansions of both the *syn*- and *anti*-amines **14**-NH_2 and **15**-NH_2. If this is the sole source of L products, the distribution of the four acetates of this series **8**-OAc, **11**-OAc, **12**-OAc, and **13**-OAc from deaminative ring expansions in acetic acid should be independent of whether the starting amine is *syn* or *anti* and moreover should be the same as that from acetolysis of *exo*-bicyclo[2.2.2]oct-5-en-2-yl *p*-toluenesulfonate (**8**-OTs).



From either the *syn* or *anti* substrate, the distribution of L series products does not differ significantly from that obtained in acetolysis of **8**-OTs (Table II). Again, there is no indication of appreciable "extra" formation of bicyclo[2.2.2]oct-5-en-2-yl products **7**-OAc or **8**-OAc. The hypothetical twisted cation **16**-*anti* that intervenes between starting *anti*-amine **15**-NH_2 and tricyclic cation **L** seems to be as inefficiently trapped by solvent as its twist isomer **16**-*syn*. This behavior is unusual in ring expansion, since trapping of the first-formed cation by external nucleophiles frequently competes with the second rearrangement.[3-5]

(11) Although one might imagine that reversible deprotonation of carbonium ions would permit the intervention of hydrocarbon intermediates in the formation of acetate products, this possibility is excluded by direct test. Deamination of *syn*-2-norbornene-7-carbinylamine-N,N-d_2 in deuterioacetic acid gives the usual product mixture, from which the major G and L products, allylic acetate **9**-OAc and tricyclic acetate **11**-OAc, are isolated with normal isotopic abundance.

Table II. Comparison of Product Distributions in the L Series from Deaminative Ring Expansion with Those from Acetolysis of **8**-OTs

Starting material	Products, % of L series			
	8-OAc	**13**-OAc	**11**-OAc	**12**-OAc
8-OTs (*exo*-OTs)[a,c]	7 (7)	⩽3 (⩽3)	90 (93)	3 (0)
14-NH_2 (*syn*-NH_2)[b]	5	2	93	*d*
14-NH_2 (*syn*-NH_2·HCl)[b]	3	1	96	*d*
15-NH_2 (*anti*-NH_2)[b]	4	2	93	*d*
15-NH_2 (*anti*-NH_2·HCl)[b]	5	3	92	*d*

[a] In buffered HOAc, 25° (ref 7). [b] In HOAc containing $NaNO_2$, 25°. [c] Reference 7a. [d] Traces present, but product decomposes under deamination conditions. Values in parentheses adjusted by subtraction of **12**-OAc to provide comparison with deaminations.

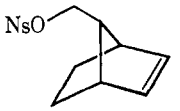
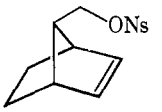
Solvolytic ring expansion of the *syn*- and *anti*-2-norbornenyl-7-carbinyl *p*-nitrobenzenesulfonates **14**-ONs and **15**-ONs occurs only to a minor extent. In contrast to the deaminations, most of the starting material in solvolysis is converted to product of unrearranged structure (**14**-OAc or **14**-OH, **15**-OAc or **15**-OH) (Table III).[12] The fraction of ring expanded product is increased somewhat in the silver perchlorate promoted solvolyses of the corresponding bromides (**14**-Br and **15**-Br), although substitution without rearrangement still predominates (Table IV). Nevertheless, even in the cases least favorable to ring expansion, enough rearranged product is formed to demonstrate the occurrence of substantial memory effects.

The strenuous conditions needed to effect reaction of the rather sluggish primary arenesulfonates cause some drift of the product compositions *within each series*, so that the distributions are not those observed in kinetically controlled solvolyses of the bicyclo[2.2.2]oct-5-en-2-yl arenesulfonates. For this reason, it is not possible to apply the criterion previously used to identify the product-forming intermediates in the deaminative ring expansions with those in the bicyclooctenyl solvolyses. Nevertheless, since the deaminations do not involve any extra product-forming intermediates, it is difficult to imagine that such species intervene in the solvolyses.

Silver ion markedly accelerates the solvolyses of the bromides, thereby permitting examination of the solvolytic ring expansion over a considerable temperature

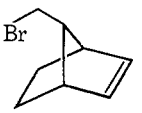
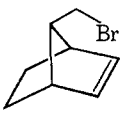
(12) (a) See also R. K. Bly and R. S. Bly, *J. Org. Chem.*, **31**, 1577 (1966); (b) H. Tanida and Y. Hata, *ibid.*, **30**, 977 (1965).

Table III. Products (Per Cent)[a] from Acetolyses[b] of *anti*- (**15**-ONs) and *syn*- (**14**-ONs) 2-Norbornenyl-7-carbinyl *p*-Nitrobenzenesulfonates

	Starting material						
	 15-ONs[c,f]				 14-ONs[h]		
	[$LiClO_4$], *M*				[$LiClO_4$], *M*		
Product (series)	0.0	0.05	0.10	0.25	0.0	0.10	0.25
7 (G)	9[d]	4[d]	7[d]	3[d,e]	2	3	3
10 (G)	4	9	4	5[e]	22	22	21[e]
9 (G)	9	15	9	13[e]	56	58	57[e]
8 (L)	74[i]	70[i]	74[i]	75[e,i]	19	18	19[e]
12 (L)	0.5	3	5	4	*g*	*g*	*g*
Per cent excess L[j]	56	46	59	57			
L/G	3.5	2.7	3.9	3.8			
Per cent excess G[k]					62	64	62
G/L					4.2	4.6	4.3

[a] Per cent of ring-expanded acetates only. Estimated uncertainty ±3% of the given value unless otherwise indicated. [b] Unless otherwise indicated, initial concentrations are R-ONs, 0.063 *M*; NaOAc, 0.068 *M*. Reactions run at 125°. [c] Total product acetates include amounts of 7-methylnorborn-2-en-7-yl acetate (**20**-OAc) varying between 6 and 19%; 7-nortricyclylcarbinyl acetate (**18**-OAc), 3–6%; five trace components of unknown structure total 0.5–3%; and unrearranged primary acetate (**15**-OAc), 52–78%. Not included are small amounts of hydrocarbon and diacetate. [d] The vpc trace for this component is broad, and to judge from the small amount of **7** in the G product from the *syn* series (where analysis is more accurate), the peak at the retention time of **7** from **15**-ONs is mostly due to an impurity. If the 9:10:7 ratio from **15**-ONs is taken to be the same as from **14**-ONs, the L/G values become 5.5, 2.9, 5.9, and 4.3. This is therefore a maximum value. [e] Value corrected for crossover of **8**-OAc. [f] When initial NaOAc concentration = 0.168 *M*, the product is 94% primary material **15**-OAc, 4% **20**-OAc, 0.5% **18**-OAc; the ring-expanded products are difficult to determine accurately because of interference by the overwhelming amount of **15**-OAc. A rough value of L/G = 6 ± 2 is obtained. [g] Not determinable because of interference by peaks of unknown trace components. [h] Total product acetates include 58–80% of primary acetate (**14**-OAc); **18**-OAc, trace; **20**-OAc, 1–2%; unknown components 2–6% (16% in 0.25 *M* $LiClO_4$, including a sixth unknown). [i] Uncertainty 6–10% of value shown. [j] Per cent excess L = 100(L − G)/(L + G). [k] Per cent excess G = 100(G − L)/(G + L).

Table IV. Products (Per Cent)[a] from Silver Perchlorate Promoted Acetolyses[d] of *anti*- (**15**-Br) and *syn*- (**14**-Br) 2-Norbornenyl-7-carbinyl Bromides

	Starting materials[e]							
								
	14-Br			**15**-Br				
Product (series)	125° 2 hr	125° 25.5 hr	75° 7.8 hr	125° 2 hr	100° 2.3 hr	75° 5 hr	50° 15 hr	25° 120 hr
7 (G)	*b*	*b*	*b*	3	1	2	3	3
10 (G)	2	4	*b*	21	19	15	11	6
9 (G)	5	5	2	58	56	50	47	56
8[c] (L)	59	91	39	15	17	29	26	20
13 (L)	9	0	9	1	2	1	3	3
11 (L)	25	0	50	3	6	4	11	13
Per cent excess L[f]	87	82	95					
L/G	14	10	42					
Per cent excess G[g]				64	51	33	23	31
G/L				4.5	3.1	2.0	1.6	1.9

[a] Per cent of ring-expanded acetates only. Estimated uncertainty ±3% of value shown unless otherwise indicated. [b] A trace (<0.1%) of this material present. [c] Values for this component are uncertain to ±10% of that shown. [d] Total product acetates include 6–10% **20**-OAc, 56–88% of unrearranged primary acetate **14**-OAc or **15**-OAc, and traces of **18**-OAc. [e] Approximate initial concentrations of reagents: substrate, 0.06 *M*; $AgClO_4$, 0.11 *M*; urea, 0.12 *M*. [f] Per cent excess L = 100(L − G)/(L + G). [g] Per cent excess G = 100(G − L)/(G + L).

range. The possibility of perturbing the memory effect through changes in the ionic strength of the reaction solutions is examined by solvolytic experiments in the presence of various concentrations of lithium perchlorate (Tables III and IV).

Quantitative Expression of Memory Effects. The product distributions of Tables I, III, and IV, when arranged according to G and L categories, permit an examination of the variation of the memory effect as a function of the initial stereochemistry (*syn* or *anti*), the leaving group (ONs, Br, or N_2^+), and the reaction conditions. The data from the two substrate systems (**14** and **15**) from Tables I, III, and IV are summarized in Tables V and VI, which also include the results of a less extensive study of hydrolysis of **14**-ONs in aqueous dioxane. The product ratios $(G/L)_{syn}$ and $(L/G)_{anti}$ are useful for conversion to free energy of activation differences, but another convenient index of selectivity is the

Table V. Memory Effects in Ring Expansions of 2-Norbornenyl-*syn*-7-carbinyl Substrates **14**-X

X	Temp, °C		—G/L[a]—	Per cent excess G
N_2^+	25	Deamin, HOAc	2.7	46
N_2^+	25	Deamin, HOAc[a]	3.3	53
N_2^+	25	Deamin, H_2O/HOAc	4.2,[b] 4.9[c]	61,[b] 66[c]
ONs^-	125	Solvol, HOAc[d]	4.2	62
ONs^-	125	Solvol, HOAc[e]	4.6	64
ONs^-	125	Solvol, HOAc[f]	4.3	62
Br^-	125	Solvol, HOAc/Ag^+	4.5	64
Br^-	100	Solvol, HOAc/Ag^+	3.1	51
Br^-	75	Solvol, HOAc/Ag^+	2.0	33
Br^-	50	Solvol, HOAc/Ag^+	1.6	23
Br^-	25	Solvol, HOAc/Ag^+	1.9	31
ONs^-	100	Solvol, H_2O/dioxane[d]	3.7	57
ONs^-	100	Solvol, H_2O/dioxane[e]	2.8	47

[a] Deamination of **14**-NH_2·HCl. [b] Acetates. [c] Alcohols. [d] No added $LiClO_4$. [e] 0.1 *M* $LiClO_4$ added. [f] 0.25 *M* $LiClO_4$ added. [g] Uncertainty in this value *ca.* ±0.4 unit.

Table VI. Memory Effects in Ring Expansions of 2-Norbornenyl-*anti*-7-carbinyl Substrates **15**-X

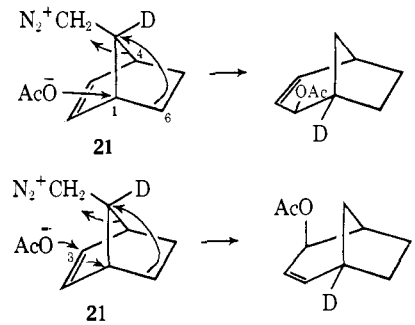
X	Temp, °C	Reaction	L/G[h]	Per cent excess L
N_2^+	25	Deamin, HOAc	48	96
N_2^+	25	Deamin, HOAc[a]	32	94
N_2^+	25	Deamin, H_2O/HOAc	45,[b] 68[c]	96, 97
ONs^-	125	Solvol, HOAc[d]	3.4	56
ONs^-	125	Solvol, HOAc[e]	2.7	46
ONs^-	125	Solvol, HOAc[f]	3.9	59
ONs^-	125	Solvol, HOAc[g]	3.8	57
Br^-	125	Solvol, HOAc/Ag^+	12[i]	85[i]
Br^-	75	Solvol, HOAc/Ag^+	42	95

[a] Deamination of **15**-NH_2·HCl. [b] Acetates. [c] Alcohols. [d] No added $LiClO_4$. [e] 0.05 *M* $LiClO_4$ added. [f] 0.1 *M* $LiClO_4$ added. [g] 0.25 *M* $LiClO_4$ added. [h] Uncertainty in this value *ca.* ±10% of figure indicated. [i] Average of 2- and 25.5-hr runs (Table IV).

"per cent excess" G or L product, a measure of the per cent efficiency with which each system (*syn* → G and *anti* → L) preserves its integrity. Note that when the L/G and G/L ratios are large, they are very sensitive to small analytical errors. In two of the deaminations of Table VI, for example, L/G changes from 32 to 48, but the per cent excess index changes only from 94 to 96%.

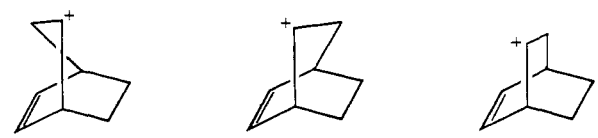
The Nature of the Memory Effects. It is immediately apparent that the direction of the memory effect in all the cases of Tables V and VI is that predicted (Scheme I) by analogy to the chair–boat cations of the 2-norbornylcarbinyl series. The product ratio $(G/L)_{syn}$ is always greater than $(G/L)_{anti}$ under a given set of conditions. The range of the effect, given by the ratio of the $(G/L)_{syn}$ value to the $(G/L)_{anti}$ one, can be quite large. It amounts to a factor of 260–320 in aqueous acetic acid deamination.

One conceivable way in which the memory effect might operate is by some kind of multicenter displacement process in which rearrangement is concerted with attack by a nucleophile. For example, in the formation of allylic acetate **9**-OAc of the G series from *syn* substrate **14**, acetate ion might attack C-1 or C-3 as C-4 and C-6 migrate. This formulation is unsatisfactory for several reasons. First, the result of the labeling experiment with **21** (the labeled counterpart of **14**) described, which produces **22**-OAc with 50% of the label at each bridgehead, requires fortuitously equal rates of attack at C-1 and C-3 of **21**. Similarly, as Table II shows, the distributions of the three products in the L series are essentially independent of the medium or substrate (*syn* or *anti*) under kinetically controlled conditions. To maintain that they were being formed by three concurrent multicenter displacements, one would have to argue that the relative rates of these independent reactions were the same in the *syn* as in the *anti* system, independent of nucleophile, and fortuitously the same as the relative rates of capture of the authentic L cation[7]



generated bys olvolysis of *exo*-bicyclo[2.2.2]oct-5-en-2-yl derivatives, **8**-OTs. The probability of these coincidences is remote. *Memory therefore must be preserved in processes passing through carbonium ions, not in bimolecular nucleophilic reactions.*

The observed memory effects establish the need to include cationic intermediates other than the quasi-symmetric one **S** and the two standard ones, **G** and **L** in the mechanism (Scheme I) of the ring expansions. We now are concerned with the physical bases for the differences between these extra intermediates **16**-*syn* and **16**-*anti*.



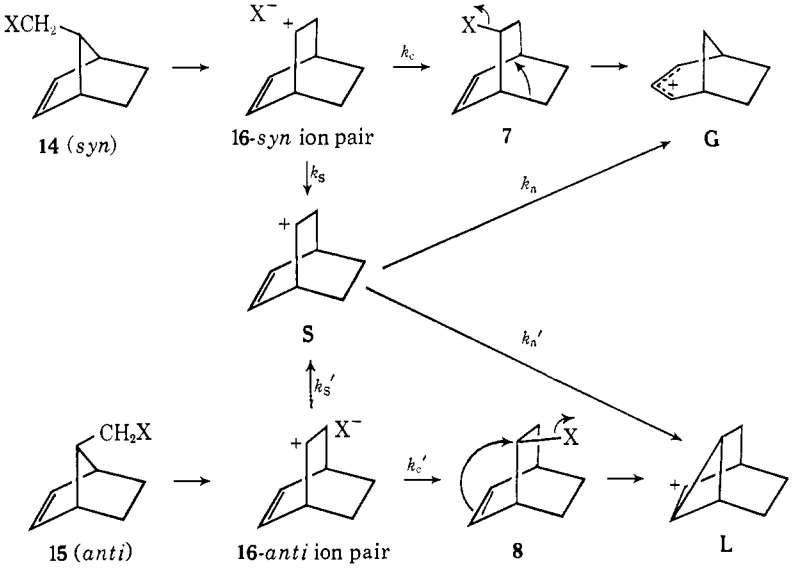
16-*syn* 16-*anti* S

In the most general terms, the differences might be imagined to have either an *intramolecular* or an *extramolecular* origin (or both) according to whether they derive from the structures of the cations themselves or from their environments in solution.

In the extramolecular category, ion-pair return[13] combined with rearrangement might conceivably provide a mechanism for the memory effect. The ring expansions then might be formulated as in Scheme II, where the roles of the "twisted" ions **16**-*syn* and **16**-*anti* of Scheme I are assumed by the ion pairs **16**-*syn* ion pair and **16**-*anti* ion pair. The differences in behavior in the *syn* and *anti* series then would result from the differences in location of the counterions in the first-formed intermediates **16**-*syn* ion pair and **16**-*anti* ion pair, each of which collapses stereospecifically to a 2-bicyclo[2.2.2]oct-5-enyl derivative, **7** or **8**. In order to account for crossover in this scheme, it is reasonable to insert a step in which solvent separates the ion pairs and produces the quasi-symmetric ion **S**. It is at this point that difficulties begin to arise with Scheme II, for the competition between collapse and separation of the ion pairs (k_c/k_s and k_c'/k_s') should be very sensitive to the nature of the solvent and of the counterion.[13] Specifically, the k_c/k_s

(13) S. Winstein and G. C. Robinson, *J. Am. Chem. Soc.*, **80**, 169 (1958), and references cited there.

Scheme II



and k_c'/k_s' ratios and hence the memory effects should decline as the ionizing power and nucleophilicity of the solvent increase. Conceivably, the product composition from one of the substrates (for example, *syn*) might be insensitive to solvent because of inefficient ion-pair return ($k_s \gg k_c$), in which case the product mixture would be controlled by the "natural ratio" k_n/k_n' for partitioning of the quasi-symmetric intermediate **S**. Scheme II then would predict that the product mixture from the *other* substrate system (*e.g.*, *anti*) would respond to solvents in one of two ways. Either it would be unresponsive for the same reason as the *syn* system ($k_s' \gg k_c'$), in which case it would give the *same* product mixture as did the *syn* system, *both* being controlled by k_n/k_n', or it would show a decline in memory effect with increasing solvent ionizing power. There is no way for Scheme II to rationalize the combination of *different* product ratios from *syn* and *anti* substrates with the absence of the predicted solvent effect. Yet it is just this combination that is observed experimentally (Tables V and VI).[14]

Although there seems to be a small effect which favors L product with decreasing temperature in the bromide solvolyses of Tables V and VI, the selectivities, especially in the *syn* series (Table V), are remarkably steady despite wide variations in solvent and counterion. Even in the *anti* series (Table VI) the apparent fluctuations in the L/G ratios in deamination probably result at least in part from the inability of the analyses to determine accurately the small amounts (2–3%) of G product.

Scheme II also is difficult to reconcile with the silver ion promoted solvolyses of the bromides, since the first intermediate then presumably would not be an ion pair but rather some kind of aggregate of the cation with AgBr. This might well return to covalent rearranged bromide (*e.g.*, 7-Br) and Ag^+, but to fit the data, such return would have to be fortuitously just about as efficient as that when X^- = ONs in the *syn* series and much more effective in the *anti*. Perhaps the most serious objection to Scheme II is its inability to account for the nitrosative deaminations, where it becomes difficult to suggest what to substitute for the counterion X^-. In the *syn* series in acetic acid, for example, the likely counterion would be acetate, but return of **16**-*syn* ion pair to covalent once-rearranged acetate **7**-OAc would quench the reaction completely, since **7**-OAc does not rearrange under the conditions. Such a scheme therefore would not even provide a path for the formation of the major product, the doubly rearranged allylic acetate derived from cation **G**.

Finally, there remains the possibility that molecular nitrogen may play the role of X^- in Scheme II. This would occur if the ion–molecule aggregate, **16**-*syn* ion pair (X = N_2), collapsed to covalent rearranged diazonium cation, **7**-N_2^+. Although such rearrangements are unknown in aliphatic systems, reports of somewhat related processes in arenediazonium ions[15] and of the capture of molecular nitrogen by benzenesulfenium ion[16] make the ion–molecule return possibility worthy of consideration. Again, however, difficulties arise in the detailed interpretation. To fit the data of Tables V and VI, covalent return of molecular nitrogen would have to be about as efficient as covalent return of bromide or *p*-nitrobenzenesulfonate (or even more so). This seems highly unlikely.

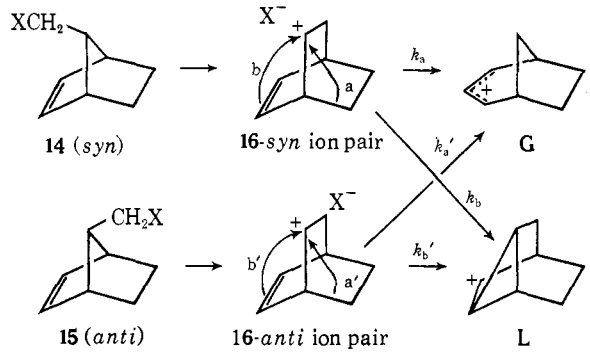
Some of the difficulties of the ion–pair interpretation of memory effects are removed if crossover between the *syn* → G and *anti* → L systems occurs not by solvolysis of the ion pairs (**16**-*syn* ion pair and **16**-*anti* ion pair) to the quasi-symmetric bicyclo[2.2.2]octenyl cation **S** (Scheme II) but rather by rearrangement directly to the **G** and **L** cations (Scheme III). In this modified ion-pair scheme, "*shielding*" *by the counterion* of one face of the cation (rather than collapse to fully covalent 2-bicyclo[2.2.2]oct-5-enyl derivative) is the means by which memory is preserved. But new difficulties arise. The efficiency of the "shielding," measured by the rate constant ratios k_a/k_b and k_a'/k_b', might reasonably be expected to be a function of the size and shape of the "shielding" group, of the nature of its interaction with the cationic center, and of the distance between the centers of charge.

(14) Direct interconversion of the epimeric ion pairs **16**-*syn* ion pair and **16**-*anti* ion pair might be substituted for crossover *via* cation **S**, but again this would have to be insensitive to environmental effects.

(15) (a) J. M. Insole and E. S. Lewis, *J. Am. Chem. Soc.*, **85**, 122 (1963); (b) E. S. Lewis and J. M. Insole, *ibid.*, **86**, 32, 34 (1964); (c) E. S. Lewis and R. E. Holliday, *ibid.*, **88**, 5043 (1966); (d) see, however, A. K. Bose and I. Kugajewsky, *ibid.*, **88**, 2325 (1966).

(16) D. C. Owsley and G. K. Helmkamp, *ibid.*, **89**, 4558 (1967).

Scheme III



The "shielding" effectiveness and hence the memory effect again should be sensitive to the nature of the leaving group and the solvent, but the data of Tables V and VI do not conform to the pattern expected from Scheme III. Furthermore, since no "excess" 2-bicyclo[2.2.2]-product is formed, one must postulate in Scheme III that the counterions in the deaminatively produced ion pairs R^+OAc or R^+OH^- which could readily capture R^+ to give stable 2-*endo*- or *exo*-bicyclo[2.2.2]octenyl products forbear to do so and are content merely to direct the carbon skeletal rearrangement.

Ion pairs may well be involved in many of the processes studied here, and our understanding of the details of their behavior is still imprecise enough to allow the possibility that they may be the cause of these observations. At present, however, the known properties of ion pairs do not provide a helpful or natural explanation of memory effects. It does not seem fruitful to speculate on what *ad hoc* subsidiary hypotheses might be invoked to shore up the ion-pair argument.

One can generalize the idea of environmental causes of the asymmetrical behavior of "twisted" cations to include not only the immediately adjacent counterion but also the ionic atmosphere and the solvation shell. In that case, a transient asymmetry might arise because Wagner–Meerwein rearrangement in the ring expansion would displace the locus of positive charge by about 1.5 Å, and unless the reorganization of the ionic atmosphere or solvent shell were fast relative to the carbon skeletal rearrangement, the freshly formed ring-expanded cation would exist in a nonequilibrium environment for the period of the relaxation time. The direction of displacement of the environment from equilibrium would depend upon the direction from which the ring expansion occurred (*syn* or *anti* starting material), so that, qualitatively at least, the ratios of rates of the two possible second, follow-up rearrangement steps (leading to **G** or **L** cations) would be unequal for the duration of the relaxation time.

The relaxation time for the ionic atmosphere under the experimental conditions in these ring expansions may be estimated[5a] to be about 10^{-9} sec. Although little is known about the absolute rates of carbonium ion rearrangements in solution, the data available in the literature[17,18] suggest that in some cases the lifetime may be short enough to be competitive with ion–atmosphere relaxation. Nevertheless, this plausible picture of the memory effect seems to be unsatisfactory.

(17) (a) M. Saunders, P. von R. Schleyer, and G. A. Olah, *J. Am. Chem. Soc.*, **86**, 5680 (1964).
(18) G. A. Olah and J. Lukas, *ibid.*, **89**, 4739 (1967).

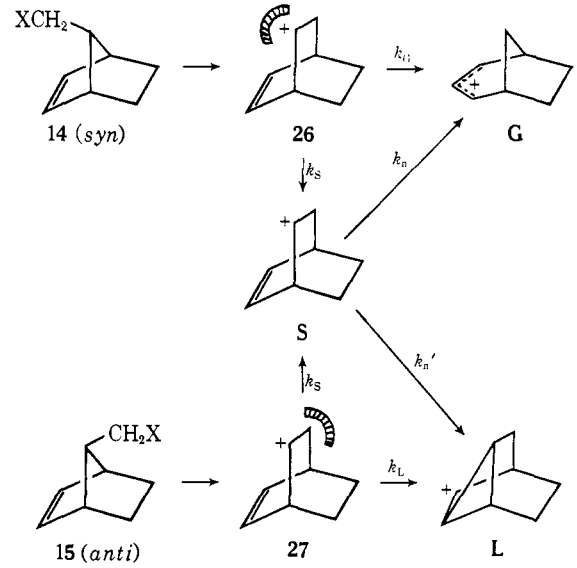
The relaxation time is alterable by adjustment of the total ionic concentration. For dilute aqueous solutions, there is a simple inverse proportionality,[19] but qualitatively, a decrease in relaxation time with increased ionic concentration is expected even under other conditions. In solvents of low dielectric constant, where extensive ion pairing occurs, the ratio b/a of actual concentrations of separated ions in two solutions of total salt concentrations B and A is given by eq 1, where

$$b/a = \frac{-K \pm \sqrt{K^2 \pm 4BK}}{-K \pm \sqrt{K^2 + 4AK}} \qquad (1)$$

K is the dissociation constant for the formation of free ions. When $K \ll 1$, as is the case in solvents like acetic acid,[19] the b/a ratio becomes approximately $(B/A)^{1/2}$. The relaxation time therefore should decrease with increase of the total salt concentration or its square root (or some intermediate relationship).

In a formal way, the asymmetric ionic-atmosphere mechanism of the memory effect can be represented as in Scheme IV. The difference between the first-formed

Scheme IV. Asymmetric Ionic Atmosphere Mechanism



ring-expanded cations **26** and **27** from **14** (*syn*) and **15** (*anti*) starting materials is symbolized by the location of the heavy curved bar, corresponding to differing distributions of the ionic atmosphere. Each of the cations **26** and **27** is capable of conversion to the same quasi-symmetric cation **S** by relaxation of the ionic atmosphere with rate constant k_s (assumed for simplicity to be the same in both cases). Competing with relaxation are intramolecular trapping steps (rate constants k_G and k_L) leading to cations **G** and **L**. The quasi-symmetric cation **S** partitions itself between two rearrangement paths with the "natural" ratio k_n/k_n'. More complexity but no major change in the picture is introduced by allowing some crossover from unsymmetrical species to the "wrong" doubly rearranged system (direct **26** → **L** or **27** → **G**).

In terms of Scheme IV, the product ratios $(G/L)_{syn}$ and $(L/G)_{anti}$ from *syn* and *anti* starting materials can be expressed as in eq 2 and 3. In general, therefore,

(19) *Cf.* H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1958, pp 54, 93.

$$(G/L)_{syn} = k_G/k_S + (k_G/k_S)(k_n/k_n') + k_n/k_n' \quad (2)$$

$$(L/G)_{anti} = k_L/k_S + (k_L/k_S)(k_n'/k_n) + k_n'/k_n \quad (3)$$

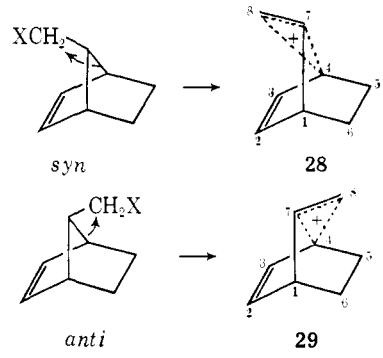
Scheme IV and eq 2 and 3 predict that the memory effect selectivities should decrease with increasing ionic concentration as a consequence of their reciprocal relationship to k_S. The data of Tables III, IV, and V give no evidence of such salt sensitivity. This finding in itself does not rule out Scheme IV, since the selectivities would not be very responsive if the "natural ratios," k_n/k_n' and k_n'/k_n, were very much larger than the salt-sensitive ratios k_G/k_S and k_L/k_S. However, in that case the product ratios would be controlled largely by the "natural" ratios. This would predict that virtually the same product mixture should be obtained from either *syn* or *anti* starting material, *i.e.*, $(G/L)_{syn}$ should be approximately the reciprocal of $(L/G)_{anti}$, which is contrary to the observations. The argument is of course closely related to that used in the previous discussion of the effect of solvent. Further evidence against the hypothesis of control of the memory effect by ionic atmosphere relaxation is given in the accompanying paper on the ring expansions of isotopically labeled 7-norbornylcarbinyl derivatives, where by symmetry the "natural ratio" is unity.[5b]

An outline exactly analogous to Scheme IV can be used as the basis for the construction of a hypothetical *asymmetric solvation* mechanism for the memory effect. The rate constant k_S then would correspond to relaxation of the solvent shell, and the other reactions would retain their earlier meaning. It is difficult to predict the magnitude of the relaxation time of the solvent shell, since there is no known correlation between such processes and phenomena (*e.g.*, dielectric relaxation, self-diffusion, etc.) which can be measured directly. Although a fuller discussion of the solvent reorganization hypothesis is deferred to a later paper,[20] it is evident from Table V that no large changes in the $(G/L)_{syn}$ value result from changes of solvent. This can be interpreted in only two ways. Either there is essentially no difference in relaxation rate between acetic acid and aqueous dioxane, or asymmetric solvation is not a major contributor to the memory effect.

Conclusions. By far the simplest interpretation of all of the data on the 2-norbornenyl-7-carbinyl ring expansions is one in which the memory effect is ascribed largely to intramolecular factors. Evidently, there are energy barriers that separate the "twisted" cations **16**-*syn* and **16**-*anti* from the quasisymmetric one **S**. These barriers might conceivably be conformational, that is, derived from the energy costs associated with angle deformations and differential nonbonded interactions between the twisted cations and the transition states for their conversion to **S**. Although molecular models give no hint of an energy minimum as twisting distortions in either direction are imposed on the eclipsed conformation **S**, this could be deceptive, and the presence of small minima cannot be ruled out. If this is the origin of the memory effect, these ring expansions constitute an exceedingly delicate probe for hitherto unsuspected conformational energy pockets.

(20) (a) J. A. Berson and J. W. Foley, paper in preparation; (b) J. W. Foley, Ph.D. Thesis, University of Wisconsin, 1969.

Some stability also might be conferred upon the twisted cations by nonclassical bonding. If the ring expansions of the *syn* and *anti* substrates occur in concert with departure of the leaving group, the first intermediates might be the nonclassical ions **28** and **29**. Al-

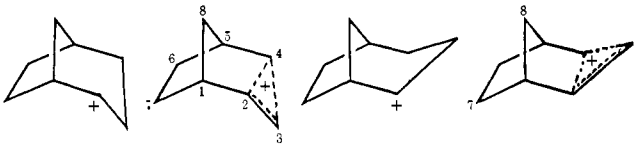


though participation of this kind in the rate-determining heterolysis does not seem to be very effective[5d,12a] and does not compete well with the major product-forming process, direct substitution on the primary carbon, it cannot be ruled out in that small portion of the solvolysis that does lead to ring expansion. It is not inconceivable that a nonclassical ion (**28** or **29**) might even be formed after the rate-determining heterolysis.

The geometry of the nonclassical ions **28** and **29** is quite unfavorable for intramolecular nucleophilic opening of the mesomeric bridge with inversion, that is, from the direction opposite the bridging atom C-4. Neither the C-1–C-6 σ electrons nor the C-2–C-3 π/C-1–C-2 σ electrons can attack C-7 from the direction that is normally[5a,21] favored in nonclassical ions. Yet it seems reasonable that the observed specificity, which preferentially involves the C-1–C-6 σ electrons in the *syn* → G system and the C-2 π/C-1–C-2 σ electrons in the *anti* → L, could result from intermediates **28** and **29**. In the *syn*-derived cation **28**, the C-2–C-3 p-orbital axes intersect the π-nodal plane (containing C-1–C-7–C-8) of the C-7–C-8 π system at a fairly small angle, and the C-1–C-2 bond axis lies almost exactly in this nodal plane. Bonding of the C-7–C-8 π system with these electrons therefore will be quite small. On the other hand, the C-1–C-6 σ electrons make an angle of about 60° with the π-nodal plane, a geometry that permits bonding interaction. Migration of the C-1–C-6 bond will be preferred, even though it lies on the same side of the π-nodal plane as C-4 and hence cannot approach from the preferred back side. That is, front-side bonding is better than no bonding at all.

In principle, the same reasoning can be applied to the 2-norbornylcarbinyl systems previously studied.[3] This merely would require that the conformationally isomeric chair and boat cations **3** and **4** be replaced with nonclassical ions **30** and **31**. The geometric relationships of the C-1–C-8 and C-1–C-7 σ bonds to the C-2–C-3 π-nodal plane correspond quite well to those in **28** and **29**, and the observed migration preferences in the second rearrangement steps (C-8 in **30** and C-7 in **31**) can be understood on the same basis. A serious difficulty

(21) (a) *Cf. inter alia*, J. A. Berson in "Molecular Rearrangements," P. de Mayo, Ed., Vol. 1, Part 3, Interscience Publishers, New York, N. Y., 1963, and references therein; (b) J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick, and D. Houston, *J. Am. Chem. Soc.*, **89**, 2590 (1967).



3 30 4 31

emerges with this interpretation, however. The previous experiments[3a] indicate that the nucleophilic solvent–lyate ion system is able to trap some of the first-formed cations (**3** or **30**) in the ring expansion of *endo*-2-norbornylcarbinyl substrate. Capture from the *endo* direction to give *endo*-2-bicyclo[3.2.1]octyl product **32** is favored over *exo* capture to give **33** by a factor of only

32 33

4. As has been pointed out,[3a] this is reasonable behavior if a classical ion (**3**) is an important product-forming intermediate, but not if the nonclassical ion **30** is the sole intermediate, since that should give *endo* product **32** with much higher specificity. No corresponding test is possible in the present cases, since the first-formed intermediates escape nucleophilic capture and proceed directly to **G** or **L** doubly rearranged cations.

Of course, it is possible that the first-formed intermediates may be classical ions in the 2-norbornylcarbinyl systems and nonclassical ions in the present ones. At least, however, nonclassical ions alone do not provide a simple interpretation for all of the memory effects.

The first-formed intermediates in the 2-norbornenyl-7-carbinyl ring expansions must be very short-lived, since even nucleophilic capture by solvent, an extremely fast reaction,[22] is unable to compete with the follow-up rearrangement step. Conceptually, this second rearrangement could have an arbitrarily low activation energy, and, in the extreme, it could be of the order of *RT*, or <1 kcal/mol at 100°. As this activation energy becomes smaller the concept of a two-step, multiple rearrangement becomes blurred until, in the limit, the reaction coordinate for rearrangement has only a single maximum. This point is discussed in more detail elsewhere,[5a] but it suffices to emphasize here that the extreme situation is one not generally encountered in studies of the memory effect. There is almost always some crossover from one system to another. Memory is not perfectly preserved. This must mean either that there is a distinct pause after the first rearrangement step, permitting the intermediate to choose between two alternate modes of rearrangement (or between symmetrization and rearrangement), or that the ring expansions take place along two or more parallel paths. In any case, if the memory-preserving pathway is a concerted double rearrangement, it is not energetically much preferred over the competing pathway(s) which lead to crossover.

Experimental Section

Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Melting points were determined on a Thomas–Hoover capillary melting point apparatus and are uncorrected. Infrared (ir) spectra were recorded on either a Perkin-Elmer Model 137 Infracord or a Beckman Model IR 8 infrared spectrophotometer in the phase indicated. Nuclear magnetic resonance (nmr) spectra were run on a Varian Associates Model A-60 or A-60A spectrometer both operating at 60 MHz. Samples were run as dilute solutions in the solvent indicated using tetramethylsilane (TMS) as an internal reference. Chemical shifts are recorded as parts per million downfield from TMS on the δ scale (unless otherwise indicated), and coupling constants are given in cycles per second (hertz). Nuclear magnetic resonance data are presented in the order (chemical shift): multiplicity, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broadened; integration; assignment.

For most analytical vpc, Barber-Colman gas chromatographs, Models 61-C and 5000, with radium ionization detectors were used. Argon was the carrier gas. The columns used with these instruments were of the open tube, capillary type and consisted of coiled lengths of stainless steel tubing, 0.01 in. i.d. coated with either Ucon LB 550X or tris(β-cyanoethoxy)propane (TCEP). New tubing was cleaned prior to coating by passing *ca.* 10 ml of chloroform or hexane through the column at 400 psi, followed by *ca.* 10 ml of the solvent in which the substrate was to be applied—usually benzene. About 2 ml of a 10% v/v solution of the substrate in benzene was passed slowly through the column at 10 psi nitrogen pressure. After the solution plug had passed through, the nitrogen flow was continued for several hours to evaporate the solvent. Spent columns were recoated successfully by first removing the old substrate by passing 5–10 ml of each of the following through the column at 400 psi: methylene chloride, acetone, water, concentrated nitric acid, water, concentrated ammonium hydroxide, water, acetone, and benzene. After coating, the columns were conditioned by placing them in an oven and slowly raising the temperature and nitrogen pressure over a period of 24 hr up to the maximum expected operating conditions and maintaining the column at these conditions for a minimum of 24 hr.[23]

All preparative and some analytical vpc was performed using Varian Aerograph A-90P, A-90P3, or A-700 Autoprep instruments equipped with thermal conductivity detectors using helium as carrier gas. A wide variety of 0.25-in. and $^3/_8$-in. diameter packed columns were used in the work reported here, and these are listed in Table VII. Table VIII gives typical retention times for most of the compounds encountered in this work. The values given in this table should be considered as relative since the absolute values of the retention times vary significantly with the condition of the columns, temperature, and pressure (flow rate).

Table VII. Vpc Columns

Column designation	Column dimensions (ft × in.)	Substrate
A (A-1)	250 (270) capillary[a]	Ucon LB-550X (50HB-2000)
B	250 capillary[a]	TCEP
C (C-1)	100 (150) capillary[a]	TCEP
D	20 × 0.375	TCEP
E	5 × 0.25	Ucon LB-550X
F	20 × 0.375	FFAP[b]
G	20 × 0.375	Ucon HB-5000
H	10 × 0.375	Carbowax 20M
I	5 × 0.25	SE 30 silicone oil
J	5 × 0.25	SF 96 silicone oil
K	15 × 0.25	Carbowax 20M
L	10 × 0.375	Ucon LB-550X
M	20 × 0.375	Ucon LB-550X
N	20 × 0.375	Ucon 50HB-2000
O (O-1)	6 (10) × 0.25	TCEP
P (P-1)[c]	6 × 0.25	Silicone gum rubber
Q	7.5 × 0.25	*d*
R	7.5 × 0.25	Carbowax 20M

[a] See text for information on preparation and dimensions. [b] Varian Aerograph's "free fatty acid phase." [c] P, 5%; P-1, 15% stationary phase. [d] γ-Nitro-γ-methylpimelonitrile.

(22) S. Winstein, *J. Am. Chem. Soc.*, 87, 381 (1965).

(23) We are indebted to Dr. R. Teranishi for advice on these procedures.

Table VIII. Typical Retention Times on TCEP (B) and UCON (A-1) Capillary Vpc Columns

Compd	Retention time on column, min B[a]	A-1[b]
20	7.5	15.3
12	14.2	30.1
14	15.9	30.5
15	16.3	30.8
18	18.5	37.0
10	18.7	35.6
9	19.4	37.0
7	19.4	34.0
8	16.3	32.0
13	21.2	41.7
11	22.8	44.5
33	19.7	
32	21.8	

[a] Column B, 250-ft TCEP capillary, at 120° and 50 psi. Widths of peaks at half-height 0.2–0.3 min. [b] Column A-1, 270-ft UCON polar 50-HB-2000 capillary, at 119° and 50 psi. Widths of peaks at half-height 0.5–0.7 min.

Quantitative vpc analysis was done by multiplying the peak height by the peak width at half-height. This method gave results consistent to within ±3% of the peak area for all but very small or poorly resolved peaks. Where larger uncertainty exists it is noted in the text. In cases where the primary unrearranged product was the major component, the distribution of ring-expanded products was determined by injection of a large enough sample to permit accurate analyses for the minor products while the major product peak went off-scale. The total amount of ring-expanded products was more accurately determinable by summation of the areas under the minor peaks and comparison with that of the major peak.

Isolation of the major products of a glacial acetic acid deamination of **14**-NH_2 (**14**-OAc, **11**-OAc, and 9-OAc) was achieved by vpc on column O and nmr spectral comparison with authentic samples. Similarly, the major product of deamination of **15**-NH_2 (**11**-OAc) was isolated and identified. Identification of the minor products was achieved by vpc retention times on two different capillary columns.

Acetic acid and **dioxane** were purified by methods described by Fieser.[24] **Pentane** was Phillips Research Grade and was distilled before use. **Pyridine**, Mallinckrodt, Reagent Grade, was distilled from solid potassium hydroxide and stored over molecular sieves. **Silver perchlorate** was dried according to Radell, *et al.*[25]

Standard Procedures. A. Lithium Aluminum Hydride Reduction of Ketones and Esters. In a typical procedure 5.52 mmol of ketone in 5 ml of diethyl ether was added dropwise over a period of 15 min to a slurry of 7.00 mmol of lithium aluminum hydride in 10 ml of diethyl ether contained in a three-necked flask equipped with reflux condenser and magnetic stirring. The system was protected from moisture with a drying tube ($CaSO_4$). After stirring for several hours to ensure complete reduction a freshly prepared, saturated solution of sodium sulfate was added carefully until the slurry turned from gray to white. A small amount of solid sodium sulfate was added to ensure a well-behaved, granular precipitate. The slurry was filtered, and the filter cake was washed well with fresh diethyl ether, boiled with 15 ml of fresh diethyl ether, and refiltered. Removal of the solvent from the combined diethyl ether solutions through a short Vigreux column gave a 91% yield of alcohol, which was purified by distillation bulb-to-bulb *in vacuo* or, when necessary by vpc.

B. Acetylation of Alcohols. Two general procedures were used. (1) To a quantity of the alcohol in at least a 15 molar excess of pyridine was added a 7 molar excess of acetic anhydride. The reaction mixture was heated at 110° in a dry atmosphere for 20 hr. Cold water was added, and after standing for at least 45 min the solution was extracted well with diethyl ether. The diethyl ether solution was washed twice with 10% hydrochloric acid (last wash acidic), twice with 1 *M* sodium bicarbonate (last wash basic), and once with saturated sodium chloride solution, and dried (Na_2SO_4). Removal of the solvent through a short Vigreux column and bulb-to-bulb distillation of the residue gave good yields of clear, water-white product. (2) To a quantity of the alcohol in ten times its molar amount of dimethylaniline was added 7 molar equiv of acetyl chloride. The reaction mixture was closed to the atmosphere and allowed to stand at room temperature for 15 hr. The solution turned blue within 15 min. The reaction mixture was diluted with saturated sodium chloride solution whereupon a slight warming occurred as the excess acetyl chloride was hydrolyzed. The solution was extracted well with pentane and the combined extracts were washed several times with small portions of 10% hydrochloric acid, once with water, and dried (Na_2SO_4). Removal of solvent through a short Vigreux column and bulb-to-bulb distillation of the residue gave excellent yields of even relatively unstable, tertiary acetates.

C. Preparation of Arenesulfonate Esters from Alcohols. The same general procedure was used for *p*-methyl-, *p*-bromo-, and *p*-nitrobenzenesulfonates. In a typical procedure 2.366 g (9.29 mmol) of *p*-bromobenzenesulfonyl chloride (freshly recrystallized from carbon tetrachloride) in 4 ml of dry pyridine was added over a period of 0.5 hr to a stirred solution at 0° of 1.002 g (8.07 mmol) of 2-norbornenyl-*anti*-7-carbinol. The solution became cloudy within 15 min. The reaction mixture was stirred at 0° for 3 hr, then stoppered and placed in a refrigerator at 5° overnight. Considerable solid was present at this time. About 1 ml of water was added and after stirring for 0.5 hr, 40 ml more water was added. The oil which formed solidified upon scratching with a glass rod. The solid was filtered off, washed well with water, sucked dry, and recrystallized from methanol giving a 90% yield of pure material.

The preparations of *syn*- and *anti*-2-norbornenyl-7-carbinyl derivatives **14**-OH, **14**-OAc, **14**-OBs, **15**-OH, **15**-OAc, and **15**-OBs gave materials which had properties in accord with those reported.[12a]

syn-**2-Norbornenyl-7-carbinyl** *p*-**nitrobenzenesulfonate** (**14**-ONs) was prepared by method C and recrystallized from methanol to give light yellow crystals, mp 100.5–101.2°.

Anal. Calcd for $C_{14}H_{15}NO_5S$: C, 54.35; H, 4.89; N, 4.52; S, 10.36. Found: C, 54.33; H, 5.08; N, 4.53; S, 10.35.

anti-**2-Norbornenyl-7-carbinyl** *p*-**nitrobenzenesulfonate** (**15**-ONs) was prepared in the same way. Recrystallization from methanol afforded light yellow crystals, mp 121.0–122.5°. Upon melting, it turned a deep red color, and it was also unstable at room temperature. After 2 days at 25° pink crystals were found in a previously purified sample; therefore, the sulfonate ester was stored at −20°.

Anal. Found for $C_{14}H_{15}NO_5S$: C, 54.38; H, 4.80; N, 4.63; S, 10.32.

2-Norbornenyl-*syn*-7-carbinyl Bromide (**14**-Br). To 0.6976 g (1.78 mmol) of 2-norbornenyl-*syn*-7-carbinyl *p*-nitrobenzenesulfonate (**14**-ONs) in 11 ml of dimethylformamide (in a dry 25-ml flask equipped with condenser and drying tube) was added 0.4230 g (3.56 mmol) of finely ground potassium bromide. The reaction mixture was heated at 60° in a dry atmosphere for 24 hr; during this time most of the potassium bromide went into solution, and a new solid appeared. The reaction mixture was diluted with 40 ml of water and the resulting cloudy solution was extracted four times with a total of 35 ml of diethyl ether. The combined extracts were washed twice with small portions of water, once with a saturated sodium chloride solution, and dried (Na_2SO_4). After removal of the solvent through a short Vigreux column, there remained 327 mg of cloudy oil which upon vpc analysis on capillary column A (110°, 50 psi) showed two peaks in a ratio of 12.9:1 at 31.5 and 37.2 min, respectively. The components were preparatively separated on column K at 120°. Under these conditions the major component eluted in 40.5 min and the minor one in 65.0 min. The ir and nmr spectra indicated that the minor component was 2-norbornenyl-*syn*-7-carbinyl formate **14**-O_2CH: ir (neat) 1724 (formate C=O), 1180 (C–O–), and 716 cm^{-1} (*cis* double bond); nmr (CCl_4) δ 7.9 (s, 1 H, aldehyde proton), 5.88 (t, 2 H, J = 1.5 Hz, vinyl protons), 4.02 (d, 2 H, J = 7.5 Hz, $>CHCH_2O-$), 2.75 (m, 2 H, C-1 and C-4 bridgehead protons), 2.10–1.50 (m, 3 H, C-7 bridge and C-5, C-6 *exo* protons), 1.38–0.83 (m, 2 H, C-5 and C-6 *endo* protons).

The major component was the title compound **14**-Br [0.2957 g (88.6%)]: ir (neat) 1335 1235, 875, 738, 715, 687, 630 cm^{-1}; nmr (CCl_4) δ 5.91 (t, 3 H, J = 1.5 Hz, vinyl protons), 3.26 (d, 2 H, J = 8 Hz, CH_2Br), 2.82 (broad, 2 H, C-1 and C-4 bridgehead protons), 2.25–1.50 (m, 3 H, C-7 bridge and C-5, C-6 *exo* protons), 1.45–0.52 (m, 2 H, C-5 and C-6 *endo* protons).

(24) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1955.

(25) J. Radell, J. W. Connolly, and A. J. Raymond, *J. Am. Chem. Soc.*, **83**, 3958 (1961).

Anal. Calcd for $C_8H_{11}Br$: C, 51.38; H, 5.93; Br, 42.74. Found: C, 51.31; H, 5.88; Br, 42.77.

2-Norbornenyl-*anti*-7-carbinyl Bromide (15-Br). To a solution of 1.623 g (4.74 mmol) of 2-norbornene-*anti*-7-carbinyl *p*-bromobenzenesulfonate (**15**-OBs) in 30 ml of dimethylformamide in a dry 50-ml flask containing a small, magnetic stirring bar and equipped with reflux condenser and drying tube, was added 1.13 g (9.48 mmol) of finely ground potassium bromide. The reaction mixture was heated at 60° with stirring for 12 hr. A small amount of the potassium bromide remained undissolved. After cooling to room temperature, 90 ml of water was added and the resulting solution was extracted four times with a total of 50 ml of diethyl ether. The combined extracts were washed twice with water, once with saturated sodium chloride solution, and dried (Na_2SO_4). The solvent was removed through a short Vigreux column leaving a cloudy liquid which showed only one peak (32.7 min) on capillary vpc column A (110°, 50 psi). The material was purified on column H at 120° and a flow rate of 133 ml/min. Under these conditions it had a retention time of 54 min. There was no indication of the presence of formate ester. The purified material weighed 0.650 g (74%): ir (neat) 1330, 1240, 735, 693, 638 cm^{-1}; nmr (CCl_4) δ 6.07 (t, 2 H, J = 2 Hz, vinyl protons), 3.03 (d, 2 H, J = 8 Hz, CH_2Br), 2.68 (broad, 2 H, C-1 and C-4 bridgehead protons), 2.2–1.38 (m, 3 H, C-7 bridge and C-5, C-6 *exo* protons), 1.38–0.65 (m, 2 H, C-5 and C-6, *endo* protons).

Anal. Calcd for $C_8H_{11}Br$: C, 51.38; H, 5.93; Br, 42.74. Found: C, 51.39; H, 5.94; Br, 42.77.

***syn*-7-Phthalimidomethyl-2-norbornene.** To a solution of 1.22 g (0.00356 mol) of **14**-OBs in 22 ml of dimethylformamide was added 0.496 g (0.0036 mol) of anhydrous potassium carbonate and 1.073 g (0.0073 mol) of phthalimide which had been recrystallized from ethanol and sublimed. The reactants were heated at reflux with vigorous stirring in a dry atmosphere for 8 hr. After this time the solution was cooled, and 70 ml of water was added to precipitate *syn*-7-phthalimidomethyl-2-norbornene. The resulting mixture was filtered under vacuum, and the solid collected was washed well with water. The solid was dissolved in 70 ml of ether, and the ethereal solution was washed with portions of a 2% sodium hydroxide solution until the washings no longer gave a precipitate (phthalimide) when acidified. The organic solution was then washed with saturated brine and dried over anhydrous sodium sulfate. Evaporation of the solvent on a rotary evaporator gave 0.781 g (86.8%) of white crystals, mp 132–134°. One recrystallization from methanol gave material: mp 133.5–134.5°; ir 1780 and 1700 cm^{-1} ($CHCl_3$).

Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.85; H, 5.78; N, 5.54.

***anti*-7-Phthalimidomethyl-2-norbornene** was prepared from **15**-OBs in the same manner. The yield of crude material was 84%, mp 86.0–87.2°. Recrystallization from methanol afforded material: mp 85.5–86.5°; ir 1780 and 1700 cm^{-1} ($CHCl_3$).

Anal. Found for $C_{16}H_{15}NO_2$: C, 75.93; H, 5.97; N, 5.57.

***syn*-2-Norbornenyl-7-carbinylamine (14-NH_2).** To 50 ml of a 25% aqueous methanol solution (by volume) was added 1.0265 g (0.00405 mol) of the *syn*-phthalimide and 13.8 g (0.35 mol) of sodium hydroxide. The solution was heated at reflux for 2 days under an atmosphere of nitrogen. After this time the reaction mixture was cooled, and an equal volume of saturated brine was added followed by enough water to dissolve the precipitated salts. The aqueous solution was extracted seven times with a total of 80 ml of *n*-pentane; the combined organic extracts were washed once with saturated brine and dried over anhydrous sodium sulfate. Careful removal of the solvent through a Vigreux column under an atmosphere of nitrogen was followed by a bulb-to-bulb distillation of the residue at 0.5 mm; the distillate, 0.415 g (83.2%) of a clear, colorless oil, *syn*-2-norbornenyl-7-carbinylamine, **14**-NH_2, was collected at −78°.

The **benzamide** was prepared by dropwise addition of benzoyl chloride to a pyridine solution of the amine. After standing for 4 hr at room temperature, the reaction mixture was poured onto cracked ice and diluted with water. The aqueous solution was extracted with ether, and the ethereal solution was washed with small portions of 2% hydrochloric acid solution until the washings were acidic; it was washed further with water, then with saturated brine and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by six recrystallizations from hexane–ethyl acetate gave *syn*-2-norbornenyl-7-carbinylbenzamide as white crystals: mp 101.8–106.5°; ir 3450 and 1650 cm^{-1} ($CHCl_3$); nmr ($CDCl_3$) 0.94 (m, 2 H, aliphatic), 1.75 (m, 3 H, aliphatic), 2.80 (bs, 2 H, bridgehead), 3.31 (m, 2 H, NCH_2), 5.87 (bs, 2 H, olefinic), 6.7 (bm, 1 H, NH), 7.45 (m, 3 H, aromatic), 7.75 (m, 2 H, aromatic).

Anal. Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.17; H, 7.28; N, 6.30.

The hydrochloride was prepared by passage (for 15 min at −78° with stirring) of dry hydrogen chloride gas over the dried pentane extracts from a basic hydrolysis of the phthalimide. Nitrogen was passed over the milky white suspension until all the pentane was driven off, and the apparatus was warmed to room temperature. The white powdery residue, *syn*-2-norbornenyl-7-carbinylamine hydrochloride, **14**-NH_2·HCl, was obtained in 70.5% yield: nmr [D_2O, chemical shifts in cps upfield (+) or downfield (−) from internal H_2O]: +217 (m, 2 H, aliphatic), +170 (bm, 3 H, aliphatic), *ca.* +100 (bm, 4 H, aliphatic), −82 (closely spaced three-line m, 2 H, olefinic).

Similarly, *anti*-norbornenyl-7-carbinylamine, **15**-NH_2, a clear, colorless liquid, was prepared in 81% yield from the *anti*-phthalimide. The **benzamide** was obtained as needles from ethyl acetate–hexane: mp 141.5–143°; ir 3450, 1650 cm^{-1} ($CHCl_3$); nmr ($CDCl_3$) 1.00 (m, 2 H, aliphatic), 1.75 (bm, 3 H, aliphatic), 2.66 (bs, 2 H, bridgehead), 3.17 (m, 2 H, NCH_2), 6.08 (bs, 2 H, olefinic), 6.30 (bm, 1 H, N*H*), 7.45 (m, 3 H, aromatic), 7.75 (m, 2 H, aromatic).

Anal. Found for $C_{15}H_{17}NO$: C, 79.37; H, 7.53; N, 6.25.

The **hydrochloride** was prepared in a manner similar to that for preparation of **14**-NH_2·HCl except that hydrogen chloride was passed over the pentane solution of **15**-NH_2 for only 2 min to avoid addition of the acid to the double bond. Removal of the solvent afforded 64.5% of *anti*-2-norbornenyl-7-carbinylamine hydrochloride, **15**-NH_2·HCl: nmr (D_2O) chemical shifts cps upfield (+) or downfield (−) from H_2O; +225 (m, 2 H, aliphatic), +180 (bm, 3 H, aliphatic), +112 (m, 4 H, aliphatic), −96 (m, 2 H, olefinic). The amine had previously been prepared by reduction of *anti*-7-cyano-2-norbornene.[12b]

Acetolysis of *syn*- and *anti*-2-Norbornenyl-7-carbinyl *p*-Nitrobenzenesulfonates (14-ONs) and 15-ONs under Varied Ionic Strength Conditions. The concentration of reagents and the acetolysis conditions were the same for all of these runs except that salts were added to vary the ionic strength of the solvolysis medium. A typical acetolysis follows.

To a 10-ml flask equipped with a reflux condenser was added 68.5 mg (0.221 mmol) of 2-norbornenyl-*syn*-7-carbinyl *p*-nitrobenzenesulfonate (**14**-ONs), 19.1 mg (0.232 mmol) of anhydrous sodium acetate, 91.0 mg (0.855 mmol) of anhydrous lithium perchlorate, and 3.42 ml of dry acetic acid. The reaction mixture was protected from moisture with a drying tube and closed to the atmosphere through a mercury bubbler. After heating for 47.6 hr at 125°, the slightly yellow solution was cooled to room temperature and 10 ml of a saturated sodium chloride solution was added. The resulting cloudy solution was extracted three times with a total of 20 ml of pentane and the combined extracts were washed twice with 1 *M* sodium bicarbonate and dried (Na_2SO_4). Careful removal of the solvent through a short Vigreux column gave 29.8 g (106% based on monoacetate product) of light yellow oil. The material was analyzed on capillary glpc columns A and B.

The results of a series of acetolyses conducted in the manner described above, but with differing amounts of added salts, are given in Table III. The results of acetolyses of the corresponding compounds **14**-OBs and **15**-OBs previously reported[4] are in fair agreement with these but were obtained with vpc columns of lower resolving power.

A side reaction resulted in addition of acetic acid to the products or substrates. This produced a difficultly volatile diacetate fraction, the presence of which in the crude reaction mixture was manifested by a high ratio of intensities of acetoxy to olefinic proton resonances in the nmr and occasionally by apparent material balances greater than 100%. Fortunately, this did not interfere with the determination of selectivities for G or L products, since control experiments showed that crossover, either directly (by interconversion of G and L products) or nominally (by preferential consumption of products of one series) was negligible under most of the solvolysis conditions. In the presence of 0.25 *M* lithium perchlorate, a correction for crossover was necessary.

Aqueous Dioxane Solvolysis of 2-Norbornenyl-*syn*-7-carbinyl *p*-Nitrobenzenesulfonate (14-ONs). In a small flask was placed 67.2 mg (0.217 mmol) of **14**-ONs, 18.7 mg (0.228 mmol) of anhydrous sodium acetate, 1.65 ml of water, and 2.47 ml of dioxane. This represents 40% v/v water in the mixture, and it was found to be the maximum allowable amount which would result in a homogeneous solution at reflux. The clear, slightly yellow solution was heated at reflux (bath at 100°) for 24.6 hr. After cooling to room tem-

perature it was poured into 10 ml of saturated sodium chloride solution. The resulting cloudy solution was extracted three times with a total of 25 ml of pentane and the combined extracts were washed once with 1 *M* sodium carbonate and dried (Na_2SO_4). Careful removal of the solvent through a short Vigreux column gave a viscous residue whose ir spectrum showed a strong hydroxyl absorption and none of the peaks associated with the sulfonate ester. For analysis the product mixture was converted directly to the acetates using standard procedure 1 in section B and was analyzed on capillary vpc column A. The yield of acetate product was 83% of theory.

This solvolysis was repeated under the same conditions except that enough anhydrous lithium perchlorate was added to make the solution 0.1 *M* in lithium perchlorate. Under these conditions the amount of primary, unrearranged material, compound **14**-OAc was so large that analysis for bicyclo[2.2.2]oct-5-en-*exo*-2-yl acetate (**8**-OAc) was impossible. The product mixture was treated under the acetolysis conditions with 0.25 *M* $LiClO_4$ under which the primary, unrearranged material **14**-OAc is partially consumed, presumably by addition of acetic acid to the double bond, but little crossover occurs. This treatment allowed an analysis to be made, but considerable error was involved in the analysis of bicyclo-[2.2.2]oct-5-en-*exo*-2-yl acetate (**8**-OAc).

Aqueous Dioxane Solvolysis of 2-Norbornenyl-*anti*-7-carbinyl *p*-Nitrobenzenesulfonate (15-ONs). Under the same conditions as previously described for the aqueous dioxane solvolysis of 2-norbornenyl-*syn*-7-carbinyl *p*-nitrobenzenesulfonate (**14**-ONs), the *anti* isomer gave a 73% yield of alcohol product which contained *ca.* 98% unrearranged material, **15**-OH. After conversion of the product to the acetates some of **15**-OAc was removed from the mixture by vpc. After two passes, analysis on column A indicated small amounts of bicyclo[2.2.2]oct-5-en-*exo*-2-yl acetate (**8**-OAc), nortricyclyl-3-carbinlyl acetate (**18**-OAc), and an unknown material shown to arise from the unrearranged, primary acetate **15**-OAc under acetolysis conditions with added lithium perchlorate. Relative to the amount of bicyclo[2.2.2]oct-5-en-*exo*-2-yl acetate (**8**-OAc) there was no detectable bicyclo[3.2.1] oct-3-en-*exo*-2-yl acetate (**9**-OAc).

Test of Stability of Bicyclo[2.2.2]oct-5-en-*exo*-2-yl Acetate (8-OAc) to the Acetolysis Conditions. A check of the purity of the bicyclo[2.2.2]oct-5-en-*exo*-2-yl acetate (**8**-OAc) by capillary vpc on column A showed only trace amounts of impurities. After subjecting **8**-OAc to the standard acetolysis conditions with added anhydrous lithium perchlorate 0.298 *M*, the acetate product was worked up as previously described. An nmr spectrum of the crude product mixture gave the correct integration for the relative amounts of olefinic, α-acetoxy, and acetoxy methyl protons indicating that relatively little of diacetate formation had occurred. Capillary vpc analysis on column A (110°, 50 psi) showed that 18% of **8**-OAc had rearranged giving 6.2% **12**-OAc, 6.3% **9**-OAc, and 5.5% of other products.

Test of Stability of 2-Norbornenyl-*anti*-7-carbinyl Acetate (15-OAc) to Acetolysis Conditions. To a dry 10-ml flask were added 21.5 mg (0.130 mmol) of 2-norbornenyl-*anti*-7-carbinyl acetate (**15**-OAc), 0.5 mg (0.006 mmol) of anhydrous sodium acetate, 29.2 mg (0.130 mmol) of sodium *p*-nitrobenzenesulfonate, 53.4 mg (0.500 mmol) of anhydrous lithium perchlorate, and 2.00 ml of dry acetic acid. A reflux condenser and drying tube were added and the system was closed to the atmosphere through a mercury trap. The solution was heated at 125° for 48 hr and worked up as previously described. The recovery was 130% based on starting acetate. The ir spectrum of the crude product indicated that the double bond had been partially destroyed as evidenced by the very low intensity of the absorption in the 700–750-cm^{-1} region. Analysis on capillary column A showed that the material in the monoacetate region of the vpc trace consisted of 66% starting acetate **15**-OAc, 12% nortricyclyl-3-carbinyl acetate, and 22% of an unidentified material which had been previously detected in amounts <1.6% in all acetolyses containing lithium perchlorate, including those in the *syn* series.

Acetolysis of 2-Norbornenyl-*anti*-7-carbinyl Bromide (15-Br). To a dry, 10-ml flask was added 48.0 mg (0.256 mmol) of 2-norbornene-*anti*-7-carbinyl bromide (**15**-Br), 22.2 mg (0.271 mmol) of anhydrous sodium acetate, 64.9 mg of *cis,trans*-decalin (internal standard), and 4.0 ml of dry acetic acid. The mixture was swirled until homogeneous and a 500-μl sample was withdrawn. The sample was diluted with 1500 μl of distilled water and extracted three times with pentane. The combined extracts were washed twice with 1 *M* sodium bicarbonate, once with water, and dried (Na_2SO_4). The solvent was removed carefully through a short Vigreux column and the residue analyzed on capillary glpc column A (110°, 50 psi). Under these conditions the decalin peaks eluted in 15.5 and 19.7 min, and the bromide (**15**-Br) in 32.9 min. The flask with a reflux condenser, drying tube, mercury bubbler, and the solution was heated at 120°. Samples were taken after 17.8 and 65.5 hr and were worked up and analyzed as described above. The analysis showed that less than 2% reaction had occurred after 17.8 hr and less than 3% after 65.5 hr. Only traces of products could be seen.

An attempt was made to catalyze the reaction with 38.8 mg (0.168 mmol) of zinc bromide, but analyses of samples taken after 12 and 87 hr of heating at 120° indicated that, although 18 and 80%, respectively, of the bromide **15**-Br had been consumed, it had been converted to difficultly volatile material, presumably by addition of acetic acid to the double bond.

Silver Perchlorate Promoted Acetolyses of 2-Norbornenyl-*syn*- and -*anti*-7-carbinyl Bromide (14-Br and 15-Br). A typical procedure follows. To a dry 10-ml flask was added under a stream of dry nitrogen 36.7 mg (0.177 mmol) of dry silver perchlorate, 31.2 mg (0.167 mmol) of 2-norbornene-*anti*-7-carbinyl bromide (**15**-Br), 19.9 mg (0.331 mmol) of urea, 2.65 ml of dry acetic acid, and 11.1 mg of decalin (internal standard). Brief swirling yielded a homogeneous solution. A 250-μl sample was withdrawn, diluted with 750 μl of water, filtered, and extracted three times with a total of *ca.* 5 ml of pentane. The combined extracts were washed several times with small portions of 10% hydrochloric acid, twice with 1 *M* sodium bicarbonate, and dried (Na_2SO_4). The pentane was removed carefully through a short Vigreux column and the residue was analyzed on capillary vpc column A (110°, 50 psi). The flask containing the remaining reaction mixture was equipped with a reflux condenser and drying tube ($CaSO_4$), and wrapped in aluminum foil to exclude light. After heating at 125° for 2 hr another 250-μl sample was withdrawn and worked up as described above. A dark deposit had formed on the walls of the flask, and heating for an additional 25.5 hr resulted in little additional reaction over the 47% observed at 2 hr. Although 87.7% of the acetate formed was unrearranged, primary material **15**-OAc, analysis for the rearrangement products was possible. The results are given in Table IV.

Acetolysis of 2-Norbornenyl-*syn*-7-carbinyl Bromide (14-Br). This acetolysis was conducted in the same manner as was the uncatalyzed acetolysis of 2-norbornene-*anti*-7-carbinyl bromide (**15**-Br). Samples analyzed after 19 and 69.5 hr indicated a loss of starting material of 4.5 and 8.1%, respectively. There was only one peak in the region of the capillary glpc trace where expected products elute, amounting to 25% of the starting material consumed. A very long retention time peak accounted for another 25% of the consumed starting material.

Test of Stability of the C-8 Acetates to the Acetolysis Conditions. Two known mixtures of acetates obtained from the acetolysis of 2-norbornene-*anti*-7-carbinyl *p*-nitrobenzenesulfonate (**15**-OAc) were resubjected to the acetolysis conditions with lithium perchlorate added to the medium in amounts which made its concentration 0.10 and 0.25 *M*. The ratio of L to G products remained constant although the over-all composition of the mixtures changed somewhat due to the conversion of the primary, unrearranged acetate **15**-OAc to less volatile products and also as a result of the small amount of crossover of bicyclo[2.2.2]oct-5-en-*exo*-2-yl acetate (**8**-OAc) to the allylic acetates of the G series, **9**-OAc and **10**-OAc, under the conditions of acetolysis at 125° in the presence of 0.25 *M* lithium perchlorate. The values given in Table III for the selectivities in these runs at high lithium perchlorate concentration are corrected on the assumption that the amount of crossover observed in the time period of the control experiment would be paralleled by a proportionate amount of crossover in the time period of the solvolysis, assuming first-order behavior for the crossover process. This is, of course, a maximum correction, since in the actual solvolysis, only part of the total amount of **8**-OAc has been exposed to the conditions for the time period of solvolysis.

Control experiments showed that crossover of L products tricyclo[3.2.1.$0^{2,7}$]oct-*endo*-5-yl acetate (**11**-OAc) and bicyclo[2.2.2]-oct-5-en-*exo*-2-yl acetate (**8**-OAc) to products of the G series amounted to <3 and <2%, respectively, under acetolysis conditions at 120° in the absence of lithium perchlorate.

Glacial Acetic Acid Deamination of *syn*-2-Norbornenyl-7-carbinylamine (14-NH_2). Freshly distilled amine (0.447 g, 0.00368 mol) was dissolved in 14 ml of dry acetic acid, and at room temperature solid sodium nitrite, 0.36 g (0.0052 mol), was added in small portions over a 3-hr period to the acetic acid solution with agitation provided by a magnetic stirring apparatus. The mixture was kept overnight and then treated with an additional 0.36 g (0.0052 mol) of sodium nitrite, which was added in small portions over a 6-hr

period. The reaction mixture was allowed to stand 90 min after addition of sodium nitrite was complete; then 50 ml of a 10% sodium hydroxide solution was added cautiously. The still acidic reaction mixture was extracted four times with a total of 75 ml of *n*-pentane; the combined organic extracts were washed with a 10% sodium bicarbonate solution until the washings were basic, then washed once with saturated brine and dried over anhydrous sodium sulfate. Evaporation of the solvent through a Vigreux column gave 0.285 g of a sweet-smelling, yellow oil: ir strong 1730, weak 1630 cm^{-1} (covalent nitrate), and very weak OH absorption. Vpc analysis of the crude material on colum A-1 is given in Table I. The acidic reaction mixture was washed with ether and then made basic by addition of a 10% sodium hydroxide solution. The basic solution was extracted with ether, and the combined ethereal extracts were washed with saturated brine and dried over anhydrous sodium sulfate. Evaporation of the solvent through a Vigreux column gave 0.120 g of light yellow oil smelling like an amine and assumed to be **14**-NH_2. Correcting for recovered starting material, the yield of acetate product in the deamination was 65%. In a separate experiment, 0.125 g of the deamination product mixture was chromatographed on silica gel using ether–pentane solutions for elution. The first materials off the column were nitrates, 0.006 g; 0.082 g of acetates were collected in the later fractions. A portion of the reaction mixture was subjected to preparative vpc on column O, and **14**-OAc, **9**-OAc, and **11**-OAc were separated and identified by their nmr spectra.

Glacial Acetic Acid Deamination of 14-NH_2·HCl. The deamination was conducted in the same manner as described above for the free amine. The yield of acetate product was 67% after correction for unreacted amine: ir 1730 and weak 1630 cm^{-1}, very weak hydroxyl absorption. The vpc analysis on column A-1 is given in Table I. No alcohols were observed in an analysis on column G.

Glacial acetic acid deamination of *anti*-2-norbornenyl-7-carbinylamine (15-NH_2) was performed in the same manner as described above for the *syn* isomer. The yield of acetate product was 16.2% after correction for recovery of 19% of unreacted amine; however, the yield is a maximum value since the tarry material formed in this deamination was slightly soluble in pentane and could have contributed to the weight of the residue obtained after evaporation of the pentane extracts. The vpc analysis on column A-1 is given in Table I: ir 1730, weak 1630 cm^{-1}, very weak hydroxyl absorption. The reaction mixture was subjected to preparative vpc on column O, and **11**-OAc was isolated and identified by its nmr spectrum.

Similarly, the glacial acetic acid deamination of **15**-NH_2·HCl gave a yield of 27% of acetates not corrected for unreacted amine. The vpc analysis on column A-1 is given in Table I. A separate analysis on column B revealed the presence of 5% **11**-OH; no other alcohols were found.

Aqueous Acetic Acid Deamination of *syn*-2-Norbornene-7-carbinylamine Hydrochloride (14-NH_2·HCl). A solution of 0.187 g (0.00117 mol) of **14**-NH_2·HCl in 2.0 ml of water and 0.27 ml of acetic acid was treated dropwise over a 3-hr period at room temperature with a solution of 0.150 g (0.00218 mol) of sodium nitrite in 0.5 ml of water; agitation was provided by a magnetic stirring apparatus. After 24 hr, solid sodium chloride was added until saturation was achieved, then the solution was extracted three times with a total of 20 ml of ether. The combined ethereal extracts were washed with a 10% sodium bicarbonate solution until the washings were basic. After an additional wash with saturated brine the organic solution was dried over anhydrous sodium sulfate. Evaporation of the solvent through a Vigreux column afforded 0.072 g of a yellow semisolid. The vpc analysis on column B is given in Table I. The aqueous reaction mixture was made basic and extracted with ether, and the combined ethereal extracts were washed with saturated brine and dried over anhydrous sodium sulfate. Evaporation of the solvent through a Vigreux column gave 0.063 g of a light yellow oil smelling like amine. Therefore, the yield of acetates and alcohols was about 85% if it is assumed this is recovered amine.

Aqueous acetic acid deamination of *anti*-2-norbornene-7-carbinylamine hydrochloride (15-NH_2·HCl) was effected by treating a solution of 0.110 g (0.00069 mol) of the substance in 2.0 ml of water and 0.2 ml of acetic acid with a solution of 0.120 g (0.00173 mol) of sodium nitrite in 0.5 ml of water added dropwise during 3 hr at 25°. After 24 hr 5 ml of saturated brine was added and the solution extracted with ether. The ethereal extracts were washed with a sodium bicarbonate solution and with saturated brine and dried over anhydrous sodium sulfate. Evaporation of the solvent gave 0.060 g of brown oil which was distilled bulb to bulb at 0.1 mm, the distillate, 0.015 g of an oil, being trapped at −78°. The glpc analysis on column B is given in Table I.

Control experiments showed that the deamination conditions produced no change in the selectivity ratios.

***anti*-7-*d*-*syn*-7-Carbomethoxy-2-norbornene.** A solution of *anti*-7-carbomethoxy-2-norbornene (**19**), 3.90 g (0.0256 mol), in 32.0 g (0.970 mol) of methanol-O-*d* containing 1.10 g (0.0204 mol) of sodium methoxide was heated at reflux for 1 week under an atmosphere of nitrogen. After this time the methanol was removed by distillation through a 7-in. spiral wire column, 28.0 g being collected. The yellow liquid remaining in the distillation flask was diluted with 5.5 ml of deuterium oxide and extracted with *n*-pentane. After drying the combined pentane extracts over anhydrous sodium sulfate, the solvent was removed through a Vigreux column leaving a clear, colorless liquid, 4.15 g. The residue was subjected to preparative vpc on column N as described above for the undeuterated esters giving 1.45 g of *anti*-7-*d*-*syn*-7-carbomethoxy-2-norbornene, and 1.52 g of *syn*-7-*anti*-7-carbomethoxy-2-norbornene, the total recovery being 76%. The latter ester was resubjected to the equilibration conditions with the recovered methanol-O-*d;* thus, an additional 0.426 g of *anti*-7-*d* ester was obtained and combined with the material from the initial exchange–equilibration experiment. The total amount of *anti*-7-*d* ester obtained was 1.816 g (44%): ir broad, weak band centered at 2130, intense 1735 cm^{-1}; nmr 1.00 (m, 2 H), 2.3 (0.1 H), 2.75 (m, 2 H), 3.13 (m, 2 H), 3.53 (s, 3 H), 5.95 (m, 2 H).

***anti*-7-*d*-*syn*-2-Norbornene-7-carbinol (14-OH-*d*)** was obtained in 95% yield by a lithium aluminum hydride reduction of the corresponding ester and purified by a bulb-to-bulb distillation at 10 mm and an air-bath temperature of 100–120°. The alcohol had 7.60 atom % excess dueterium (falling drop) or 0.912 atom D per molecule.

anti*-7-*d*-*syn*-2-Norbornene-7-carbinyl *p*-bromobenzenesulfonate 14-OBs-*d was prepared as described above for the undeuterated compound. The yield of material after recrystallization from methanol was 91%, mp 89.8–90.8°. The compound contained 6.20 and 5.99 atom % excess deuterium (duplicate falling drop) or 0.930 and 0.898 atom of D per molecule, respectively.

***anti*-7-*d*-*syn*-7-Phthalimidomethyl-2-norbornene** was prepared in the same manner as the undeuterated material. The compound was obtained in 71.6% yield after one recrystallization from methanol, mp 132.0–132.5°, and contained 6.06 atom % excess deuterium (falling drop) or 0.909 atom of D per molecule.

Deamination of *anti*-7-*d*-*syn*-2-Norbornene-7-carbinylamine. Hydrolysis of 1.6 g (6.37 mmol) of the deuterated phthalimide in a manner similar to that used in the undeuterated series gave amine which was dissolved immediately in 40 ml of acetic acid and deaminated as described above by addition of 1.415 g (0.0206 mol) of sodium nitrite. A cold solution of 21 g of sodium hydroxide in 50 ml of water was added cautiously to the solution which was cooled with an ice bath. Enough water was added to dissolve the precipitated salts, and the resulting solution was extracted four times with a total of 180 ml of *n*-pentane. After the pentane extracts had been washed with portions of a 10% sodium bicarbonate solution until the washings were basic and with saturated brine, the organic solution was dried over anhydrous sodium sulfate. Evaporation of the solvent through a Vigreux column at atmospheric pressure gave 0.320 g of a brown, sweet-smelling, oily residue: ir intense 1735 cm^{-1}, weak 1630 cm^{-1}, very weak 2250 cm^{-1}. The entire product was cleaved with lithium aluminum hydride giving 0.20 g of a light yellow semisolid. One-half of the mixture was subjected to preparative vpc on column O-1 with 8.5 mg of **9**-OH-*d*, bicyclo[3.2.1]oct-3-en-2-*exo*-ol, being obtained after two cycles. This material was contaminated with 3% of its epimer, **10**-OH-*d*, and 3–4% of an unknown compound. Electronic integration of the nmr spectrum of this material and comparison to an undeuterated sample of **9**-OH indicated that 1.1 ± 0.1 atom of H was present in the resonance signal at δ 2.40 of **9**-OH-*d*. The nmr spectrum did not permit detection of the small amount of **10**-OH.

Diimide Reduction of the *d*-Alcohol Mixture. Isolation of *exo*-Bicyclo[3.2.1]octan-2-ol-*d*. The remaining portion of the alcohols obtained from the deamination and subsequent cleavage was dissolved in 15 ml of methanol and 10.2 g (0.0523 mol) of dipotassium azodicarboxylate was added. Dipotassium azodicarboxylate had been prepared by addition of azodicarbonamide (Aldrich Chemical Co.) to an excess of a 40% potassium hydroxide solution. The salt was collected by filtration under vacuum, washed with methanol, and dried in a desiccator at 5 mm overnight. Under nitrogen and

with vigorous stirring provided by a large magnetic stirring bar, glacial acetic acid was added dropwise to the yellow slurry until all the color was gone; approximately 10 ml of acetic acid was used, and addition took place over a 90-min period. The resulting mixture was filtered and the solids were washed well with ether. A 10% sodium bicarbonate solution was added to the combined ethereal solutions with swirling until the aqueous layer was basic; the organic layer was separated, and the aqueous layer was extracted three times with ether. The ether extracts were combined with the original ethereal solution and were washed with saturated brine and dried over anhydrous sodium sulfate. Evaporation of the solvent through a Vigreux column gave 0.115 g of a light yellow solid. This mixture was subjected to preparative vpc on column O-1, and 0.030 g of *exo*-bicyclo[3.2.1]octan-2-ol-*d* (**23**) was obtained. It was homogeneous by analysis on column B.

Degradation of *exo*-Bicyclo[3.2.1]octan-2-ol-*d* to *trans*-3-Carboxycyclopentaneacetic Acid. To 0.2 ml of concentrated nitric acid cooled with an ice–acetone bath was added 0.030 g (0.0024 mol) of the above *exo*-bicyclo[3.2.1]octan-2-ol-*d* in small portions over a period of 1 hr. After standing 0.25 hr at room temperature the reaction mixture was placed on a steam bath for 40 min. The brown solution was cooled, diluted with 3 ml of saturated brine, and extracted three times with a total of 20 ml of ether. The ethereal extracts were washed with saturated brine and dried over anhydrous sodium sulfate. Evaporation of the solvent under a stream of nitrogen gave 0.047 g of a yellow powder which was recrystallized once from ethyl acetate–hexane giving 0.023 g of a light yellow powder. The powder was placed in a sealed tube with 0.8 ml of 10% hydrochloric acid solution and heated to 180° for 16.5 hr. After this time the tube was cooled and opened, and the contents were diluted with 3 ml of saturated brine. The solution was extracted with ether, and the ethereal extracts were washed with saturated brine. After drying over anhydrous sodium sulfate, the solution was stripped of solvent under a stream of nitrogen. Recrystallization of the residue from ethyl acetate–hexane gave 0.0145 g of crystalline solid, mp 128–131° with prior softening at 125° (lit.[3a] mp 129.5–131° for *trans*-3-carboxycyclopentaneacetic acid). The diacid contained 3.74 atom % excess deuterium (falling drop) or 0.448 atom of D per molecule.

Optical Stability of the Allylic Acetate 9-OAc When Subjected to the Deamination Conditions. Optically active 9-OH[6a] with $[\alpha]^{24.5}D$ +96.7° (*c* 1.3 $CHCl_3$) was acetylated with acetic anhydride in pyridine on a steam bath overnight and subjected to the glacial acetic acid deamination conditions, reisolated as usual, and cleaved with lithium aluminum hydride. Sublimation gave 99+% of pure **9**-OH, $[\alpha]^{23}D$ +90.4° (*c* 1.3, $CHCl_3$).

Diimide Reduction of Optically Active 9-OH. Optically active **9**-OH with $[\alpha]^{22.5}D$ +167.5 (*c* 2.3, $CHCl_2$) was reduced with diimide generated from dipotassium azodicarboxylate in a manner similar to that described above with the deuterated alcohols. The saturated alcohol, *exo*-bicyclo[3.2.1]octan-2-ol, was isolated by preparative vpc on column O-1 and sublimed. Its rotation, $[\alpha]^{26}D$ −13.06° (*c* 2.7, $CHCl_3$), was in exact agreement with the reported retention of optical activity when **9**-OPhth was catalytically hydrogenated and saponified.[26]

Stability of Optically Active 9-OH on Column O. Optically active **9**-OH with $[\alpha]^{24.5}D$ +96.7° (*c* 1.3, $CHCl_3$) was subjected to preparative vpc on column O under the same conditions used to separate **9**-OH-*d* from the mixture derived from deamination. After sublimation the alcohol had an $[\alpha]^{24.5}D$ +92.5° (*c* 1.6, $CHCl_3$).

***syn*-2-Norbornene-7-carbinylamine-N-d_2 (14-ND_2) and Its Deamination in Acetic Acid-O-*d*.** *syn*-2-Norbornene-7-carbinylamine hydrochloride, **14**-$NH_2 \cdot HCl$, was prepared as described above from 1.40 g (0.00552 mol) of phthalimide and dissolved in 5 ml of deuterium oxide (99.8% isotopically pure). The nmr spectrum of this solution contained a hydroxyl resonance which integrated for four hydrogens, roughly twice as much as expected from the solvent alone. The aqueous solution was made basic with sodium methoxide and extracted with *n*-pentane. The pentane solution was dried over anhydrous sodium sulfate. Evaporation of the solvent through a Vigreux column followed by distillation of the residue as described above afforded 0.647 g of a clear colorless liquid which was dissolved immediately in 20 ml of acetic acid-O-*d* containing 5% acetic anhydride as determined by nmr. Deamination was conducted as described above with 1.3 g (0.019 mol) of sodium nitrite. After the isolation procedures described above, 0.240 g of a light yellow oil was obtained. The entire product was cleaved with lithium aluminum hydride and both **9**-OH and **10**-OH were isolated by preparative vpc on column O. The spectra including electronic integration gave no indication of the presence of deuterium in these alcohols. Falling drop deuterium analyses showed that **9**-OH contained 0.22 atom % excess deuterium or 0.026 atom of D per molecule, and **10**-OH contained 0.19 atom % excess deuterium or 0.023 atom of D per molecule.

(26) H. L. Goering and G. N. Fickes, *J. Am. Chem. Soc.*, **90**, 2862 (1968).