Memory Effects in Multiple Carbonium Ion Rearrangements. III. The Effects of β-Methyl Substitution on Selectivity and Reactivity in the Ring Expansions of 7-Norbornylcarbinyl and 7-Norbornenylcarbinyl Derivatives[1,2a-d]

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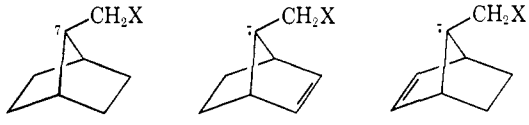
Abstract: A methyl substituent at C-7, in the β position relative to the initial site of heterolysis, causes marked changes in the products of carbonium ion reactions in the 7-norbornylcarbinyl system. Under kinetically controlled conditions of deamination in glacial acetic acid, at room temperature, almost all of the ring-expanded product from 7-methylnorbornyl-7-carbinylamine is the once-rearranged tertiary acetate, 2-methylbicyclo[2.2.2]oct-2-yl acetate, **10**-OAc. Doubly rearranged product of the 1-methylbicyclo[3.2.1]oct-*exo*-2-yl structure, **8**-OAc, is formed in acetolysis at 120° of the 7-methylnorbornyl-7-carbinyl *p*-bromobenzenesulfonate, but this is largely a product of thermodynamic control, resulting from the instability of the tertiary acetate under the solvolysis conditions. New syntheses of 7-methylnorborn-2-enyl-*anti*- and -*syn*-7-carbinyl derivatives (**12** and **13**) and of 1-methyltricyclo[3.2.-1.0^{2,7}]oct-6-yl derivatives (**26**, **27**, **32**) are described. Ring expansions of the *anti*-7-carbinyl system might be expected to parallel those in the unmethylated series by giving products derived from 1-methyltricyclo[3.2.1.0^{2,7}]oct-6-yl cation (**L′**), but this cation is unstable and suffers "crossover" to the 1-methylbicyclo[3.2.1]octenyl allylic cation of the **G′** series. In the ring expansion of the *syn* system, the **G′** cation expected as the major product of double rearrangement is more stable. The difference in product distributions shows that even though the once-rearranged cation is tertiary, a memory effect persists in the twice-rearranged products of deaminative ring expansion. An important side reaction in the *syn* system is ring closure between the double bond and the *syn*-7-carbinyl side chain to produce 1-methyltricyclo[3.3.0.0^{2,7}]octan-4-yl cation, which gives rise to five new products. Two of these are identified as the corresponding acetates by independent synthesis from 1-methyltricyclo[3.3.0.0^{2,7}]octan-4-one, for which a new synthesis is reported. Ratios of acetolysis rate coefficients at 120.4° (roughly corrected for the direct displacement component) permit the evaluation of the effect of β-methyl substitution. The ratio of rates (7-methyl/unsubstituted) is 6.3 for the *syn*-7-carbinyl system, 3.3 for the *anti*-7-carbinyl one, and 10.6 for the saturated one. The latter figure is in close (but probably fortuitous) agreement with a ratio of about 11 deduced from values in the literature for the ratio of rates of 1-methylcyclopentylcarbinyl and cyclopentylcarbinyl *p*-toluenesulfonates.

Memory effects in ring-expanding multiple rearrangements of norbornylcarbinyl (**1**),[2b] 2-norbornenyl-*syn*-7-carbinyl (**2**),[2a] 2-norbornenyl-*anti*-7-carbinyl (**3**),[2a] and other[2c,d,3] systems manifest themselves as a preference for migration in the second rearrangement step by the group more remote from the site of heterolysis. A number of questions remain on the scope of such effects and their interpretation. One of the most important and most difficult of these concerns the nature of the species formed in the first rearrangement step. It has been convenient to formulate this as a true metastable intermediate, and indeed there is compelling evidence in some[2d,3] but not all[2a,b] cases of memory effects that it can be intercepted by external nucleophiles before the second rearrangement step. This paper is the first of a series examining this transient intermediate further by experiments in which appropriate substitutions are made to control the rate of the second rearrangement step. In the present work, the strategy is to introduce a methyl group at C-7 of **1**, **2**, and **3**, thereby making the product of the first rearrangement a tertiary cation and retarding the rate of the second rearrangement. Further studies will be reported soon on systems designed to *accelerate* the second rearrangement step by methyl substitution *two* carbons removed from the site of heterolysis.



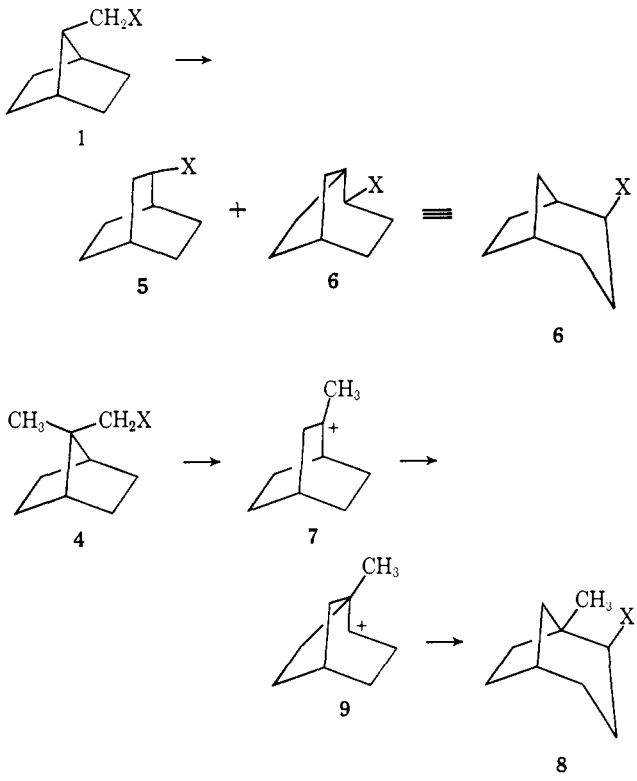
1 2 3

Ring Expansion of the 7-Methyl-7-norbornylcarbinyl System, 4. The profound modifying effect of methyl substitution becomes apparent immediately in the behavior of the 7-methyl-7-norbornylcarbinyl system, **4**. The unmethylated analog, the 7-norbornylcarbinyl system, **1**, gives ring-expanded products which are both singly (**5**) and doubly (**6**) rearranged, the memory effect being revealed by position labeling with deuterium.[2b] The cationic intermediate leading to bicyclo[2.2.2]octyl and to *exo*-bicyclo[3.2.1]octyl products **5** and **6** has positive charge at each of two secondary sites, and nucleophilic capture occurs readily at each. In the 7-methyl series, **4**, the first ring-expanded 2-methylbicyclo[2.2.2]-oct-2-yl cation, **7**, has most of the charge at one tertiary center, and capture in the doubly rearranged 1-methylbicyclo[3.2.1]oct-*exo*-2-yl form, **9**, should be much less favorable than in the unmethylated series. In practice, this bias could cause insuperable difficulties if it were

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

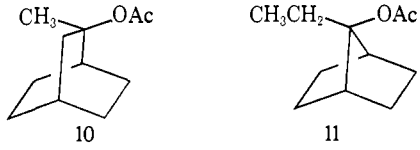
(2) For closely related studies, see papers I, II, IV, and V in this series: (a) J. A. Berson, J. J. Gajewski, and D. Donald, *J. Am. Chem. Soc.*, 91, 5550 (1969); (b) J. A. Berson, M. S. Poonian, and W. J. Libbey, *ibid.*, 91, 5567 (1969); (c) J. A. Berson, D. Wege, G. M. Clarke, and R. G. Bergman, *ibid.*, **91**, 5594 (1969); (d) J. A. Berson, R. G. Bergman, G. M. Clarke, and D. Wege, *ibid.*, 91, 5601 (1969). (e) Please address inquiries to this author at Sterling Chemistry Laboratory, Yale University, New Haven, Conn. 06520.

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



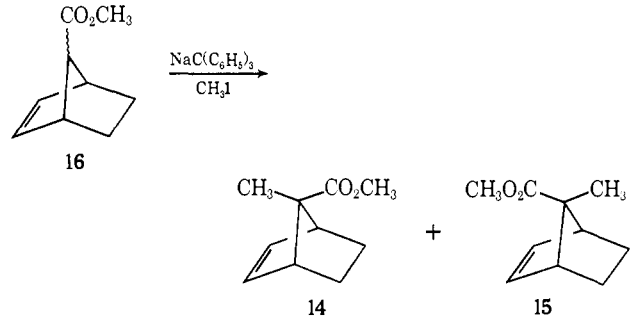
strong enough to preclude formation of doubly rearranged product **8**.

The acetolysis of 7-methylnorbornyl-7-carbinyl *p*-nitrobenzenesulfonate (**4**-OBs) at 100° does in fact give some of the twice-rearranged secondary acetate **8**-OAc. In addition to the 11.7% of this material, there are 59.1% of unrearranged primary acetate **4**-OAc, 15.5% of once-rearranged tertiary acetate **10**-OAc, and 3.6% of the product, **11**-OAc, resulting from methyl shift.



This encouraging result is deceptive, however, for it is quite likely that the desired twice-rearranged product **8**-OAc is an artifact arising from the instability (established by control experiments) of the tertiary acetate **10** under the solvolysis conditions. Further, under the milder conditions of deamination of **4**-NH_2 (room temperature, glacial acetic acid), none of the doubly rearranged product **8**-OAc is formed. Ring expansion is very efficient, but the rearrangement stops sharply after the first step, giving 90% of once-rearranged material (82% **10**-OAc, 8% **10**-OH). The remainder of the product is unrearranged primary material **4**-OAc. These results preclude the examination of the memory effect in the saturated 7-methyl compounds **4** and shift attention to the unsaturated series. The starting materials and most of the anticipated products of this study are not reported in the literature, and a number of syntheses and stereochemical assignments must be made before the ring expansion work can begin.

Synthesis of the *syn*- (and *anti*-) 7-Methylnorborn-2-enyl-*anti*- (and -*syn*-) 7-carbinyl Systems (12 and 13). A mixture of the methyl esters of *syn*-7-methylnorborn-2-enyl-*anti*-7-carboxylic acid and *anti*-7-methylnorborn-2-enyl-*syn*-7-carboxylic acid (**14** and **15**) is obtained by direct methylation (sodium triphenylmethide, methyl iodide) of a mixture of the *syn*- and *anti*-unmethylated esters **16**. The *anti*-carbomethoxy compound **14** predominates by 8:1 in the mixture, which can be separated



by preparative vapor chromatography (vpc). The stereochemical assignments to **14** and **15** rest upon an unambiguous alternate synthesis of the *syn*-carbinol, **13**-OH (Scheme I).

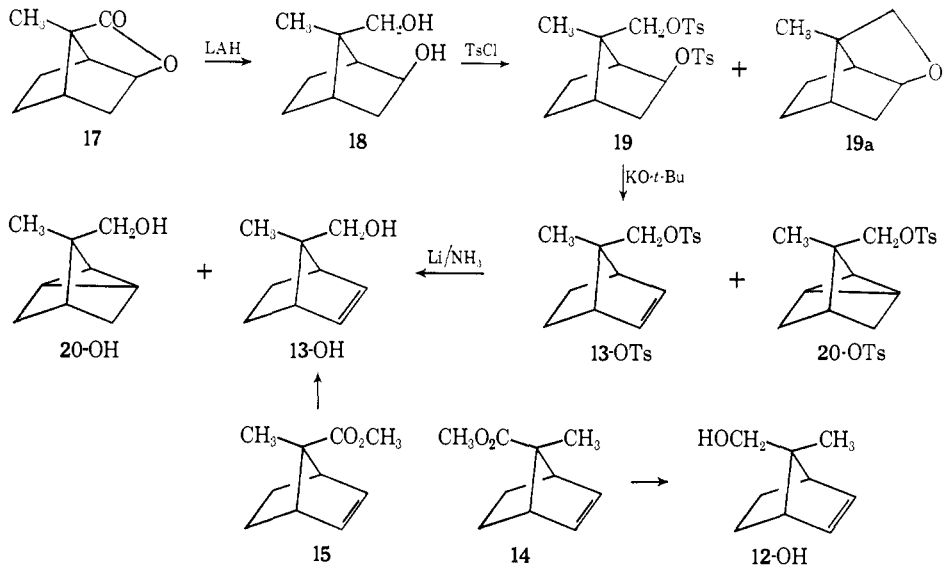
anti-7-Methyl-*exo*-2-hydroxynorbornane-*syn*-7-carboxylic acid lactone (**17**)[4] is reduced to the diol **18**, which readily forms a di-*p*-toluenesulfonate **19**, together with variable amounts of the ether **19a**. Potassium *t*-butoxide in *t*-butyl alcohol converts **19** to the unsaturated *p*-toluenesulfonate **13**-OTs, admixed with 3-methylnortricyclyl-3-carbinyl *p*-toluenesulfonate (**20**-OTs) in the approximate ratio 4:1 **13**-OTs–**20**-OTs. The mixture of *p*-toluenesulfonates is reduced by lithium in liquid ammonia[5] to a mixture of the corresponding alcohols, **13**-OH and **20**-OH, which are separated by vpc. Alcohol **13**-OH is identical with that prepared by lithium aluminum hydride reduction of the minor ester **15** from the direct methylation and is readily distinguishable from the other stereoisomer, **12**-OH, prepared from the major ester **14**. Since the direct methylation gives only modest yields of esters **14** and **15**, and moreover the *syn*-carbomethoxy compound **15** is the minor component, the alternative synthesis *via* lactone **17** affords a practical route to **13**-OH as well as a firm basis for stereochemical assignments to the entire series.

Synthesis and Characterization of the Products Expected from Ring Expansions of 12 and 13. By analogy to the reactions of the unmethylated compounds **2** and **3**,[2a] ring-expanded products from **12** and **13** are expected to fall into two categories. One of the sets of products should be related to the tricyclic cation **21** (**L'**), which would result from interaction of the double bond with the cationic site in the second rearrangement step. The other set should derive from the allylic cation **22** (**G'**). In addition, there might be either or both of the stereoisomeric products formally derivable from the once-rearranged 2-methylbicyclo[2.2.2]oct-5-en-2-yl cation **23** (see Scheme II).

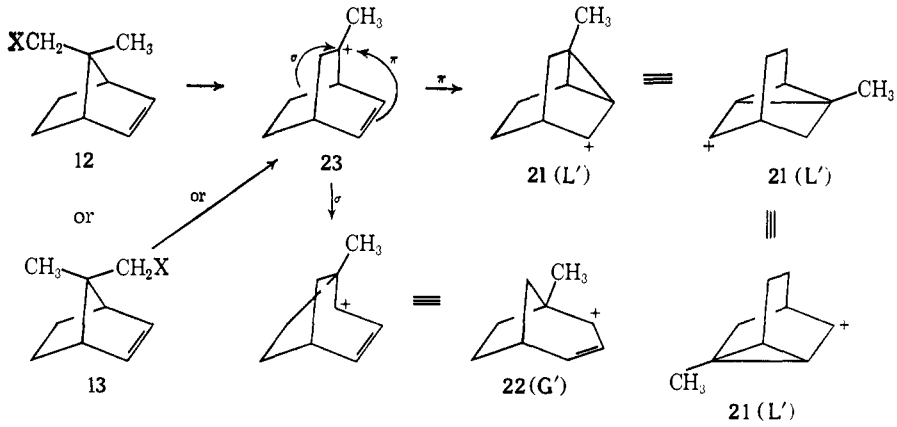
These products **24** and **25** from **23** are readily obtained as a vpc-separable mixture by the action of methyl Grignard reagent on bicyclo[2.2.2]oct-5-en-2-one.[6] Their stereochemistry is assigned[6] in part on the basis of the difference in chemical shift of the methyl protons in the parent compounds and a series of derivatives; additional grounds for the assignments come from perman-

(4) S. Beckmann and H. Geiger, *Chem. Ber.*, 94, 48 (1961).
(5) (a) W. D. Closson, P. Wriede, and S. Bank, *J. Am. Chem. Soc.*, **88**, 1581 (1966); (b) H. L. Goering and R. W. Thies, *ibid.*, 90, 2967 (1968).
(6) N. Kundu, Ph.D. Thesis, University of Wisconsin, 1966.

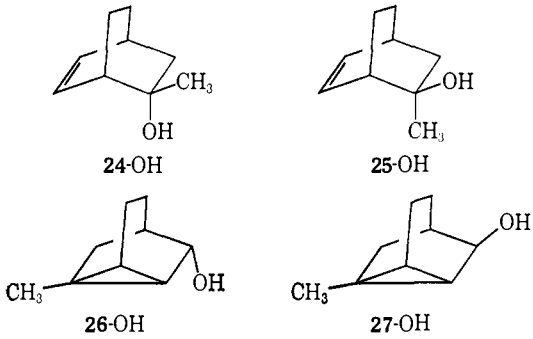
Scheme I



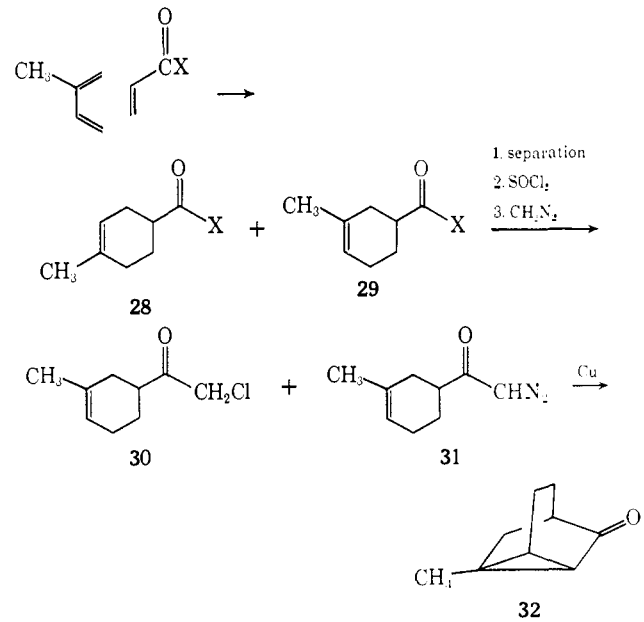
Scheme II



ganate oxidations in which the *endo*-hydroxy isomer **24**-OH gives a lactonic acid but the *exo*-hydroxy compound **25**-OH gives a dibasic hydroxy acid.[7]

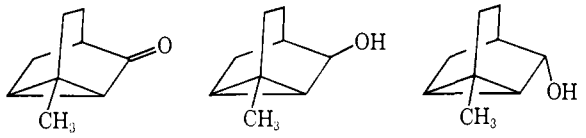


The epimeric 1-methyltricyclo[3.2.1.0^{2,7}]octan-6-ols, **26**-OH (*exo*) and **27**-OH (*endo*), which derive from cation **21** (**L**′) are obtained from the corresponding ketone, **32**, which in turn is synthesized by the sequence shown. Diels–Alder addition of isoprene to methyl acrylate gives a mixture of methyl esters of 4- and 3-methylcyclohex-3-ene-1-carboxylic acids (**28**-OCH$_3$ and **29**-OCH$_3$). Saponification to the free acids and recrystallization affords the major component, the 4-methyl isomer, **28**-OH, in pure form.[8] The desired 3-methyl isomer, **29**-OH, can be brought to about 88% purity by repeated refrigeration and filtration of a concentrated hexane solution of the mixture, which removes most of the 4-methyl isomer, **28**-OH. Conversion of the acid to the acid chloride and addition of the latter to an ethereal solution of diazomethane give the diazo ketone **31** along with the isomeric 4-methyl diazo ketone and variable amounts



(7) D. G. Morris, unpublished work.
(8) H. E. Hennis, *J. Org. Chem.*, **28**, 2570 (1963).

of chloro ketone **30**. Addition of this mixture in high dilution[9] to powdered copper suspended in boiling hexane produces 1-methyltricyclo[3.2.1.0^{2,7}]octan-6-one (**32**) admixed with unreacted chloro ketone **30** and 2-methyltricyclo[3.2.1.0^{2,7}]octan-6-one (**33**) which is present because of the approximately 12% of 4-methylcyclohex-3-ene-1-carboxylic acid (**28**-OH) in the starting material. The product is purified partially by vpc to give a 96:4 mixture of **32** and **33**, which upon reduction with lithium aluminum hydride gives a mixture of three alcohols easily separable by vpc.

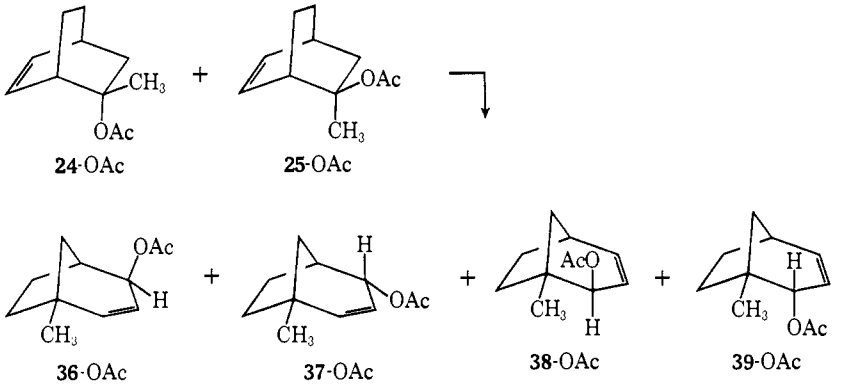


33 **34** **35**

The major component of the reduction mixture (84%) is 1-methyltricyclo[3.2.1.0^{2,7}]octan-*endo*-6-ol (**27**-OH); this stereospecificity is reminiscent of that observed in the sodium borohydride reduction of the parent ketone, tricyclo[3.2.1.0^{2,7}]octan-6-one.[10] Stereochemical equilibration (aluminum isopropoxide in isopropyl alcohol) gives a mixture of 80% *exo*-alcohol **26**-OH and 20% *endo* **27**-OH, a result that is again in accord with the observations in the parent series.[10]

The remaining two alcohols from the borohydride reduction of ketone **32** are 1-methyltricyclo-[3.2.1.0^{2,7}]octan-*exo*-6-ol (**26**-OH, 10%) and 2-methyltricyclo[3.2.1.0^{2,7}]octan-*endo*-6-ol (**34**-OH, 5%), the latter material arising from the contaminant ketone, **33**. A small amount of the 2-methyl-*exo*-6-ol (**35**-OH) undoubtedly is formed but escapes detection.

The products related to cation **22** (**G'**) are allylic alcohols, which fall into two pairs of epimers: 1-methylbicyclo[3.2.1]oct-2-en-*exo*- and -*endo*-4-ols (**36**-OH and **37**-OH), and 1-methylbicyclo[3.2.1]oct-3-en-*exo*- and -*endo*-2-ols (**38**-OH and **39**-OH). The corresponding acetates are conveniently prepared merely by heating a mixture of the two unsaturated tertiary acetates **24**-OAc and **25**-OAc at 120° in acetic acid. The two *exo* allylic acetates **36**-OAc and **38**-OAc, accompanied by the *endo* isomers **37**-OAc and **39**-OAc, are formed in nearly quantitative yield. The structures are assigned by comparison of the spectroscopic properties with those of independently synthesized[11] authentic samples.

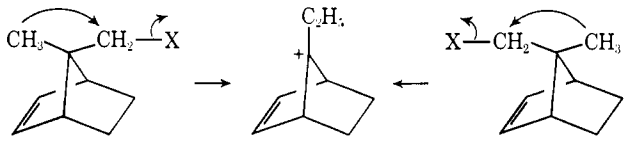


24-OAc **25**-OAc

36-OAc **37**-OAc **38**-OAc **39**-OAc

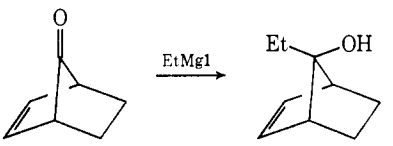
Control experiments show that this mixture of allylic acetates is formed under thermodynamically controlled conditions from ring expansion of either of the 7-methylnorborn-2-enyl-7-carbinyl systems, **12** or **13**.

A 7-ethylnorborn-2-en-7-yl cation **40** would result if vicinal methyl shift occurred before ring expansion in either **12** or **13**. Of course, the same cation need not



12 **40** **13**

necessarily be formed from both precursors, but in any case, a 7-ethylnorborn-2-en-7-ol product might be expected. One of the isomers of this structure, probably *syn*-7-ethylnorborn-2-en-7-*anti*-ol (**41**) results from the action of ethyl Grignard reagent on norborn-2-en-7-one (**42**). The stereochemistry is not critical for our purposes and is assigned here merely by analogy to the reaction of **42** and methyl Grignard reagent.[12]



42 **41**-OH

Acetolytic ring expansions are found to be unsuitable for the study of memory effects in the 7-methylnorborn-2-en-7-carbinyl system because of the instability of several of the important products to the reaction conditions (see below). There are several other aspects of the chemistry of the derived carbonium ions under acetolysis conditions that nevertheless are relevant and are described here. Nitrosative deamination conditions do permit an examination of the memory effect, and the results are given in a later section of this paper.

The sodium acetate buffered acetolyses of *syn*-7-methylnorborn-2-enyl-*anti*-7-carbinyl *p*-bromobenzenesulfonate (**12**-OBs) and the *anti*-7-methyl-*syn*-7-carbinyl isomer (**13**-OBs) at 120° for 0.5 half-life give product mixtures that are not kinetically controlled. Separate tests show that even after such relatively short exposures the two tertiary bicyclo[2.2.2]octenyl acetates (**24**-OAc and **25**-OAc), as well as 1-methyltricyclo[3.2.1.0^{2,7}]-octan-*exo*-6-yl acetate (**26**-OAc), all are converted entirely to the mixture of allylic acetates **36**-OAc, **37**-OAc,

(9) *Cf.* W. von E. Doering, E. T. Fossel, and R. L. Kaye, *Tetrahedron*, 21, 25 (1965).

(10) N. A. LeBel and J. E. Huber, *J. Am. Chem. Soc.*, 85, 3193 (1963).

(11) J. M McKenna, Ph.D. Thesis, to be submitted to the University of Wisconsin, 1969.

(12) R. K. Bly and R. S. Bly, *J. Org. Chem.*, 28, 3165 (1963).

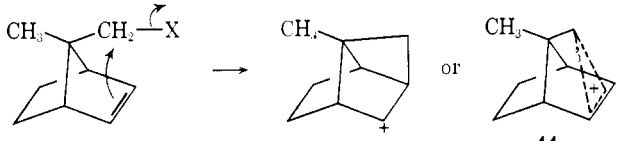
Table I. Percentage Composition of Products from the Acetolysis[a] of 12-OBs and 13-OBs

Products[b,e]	Starting material 12-OBs	13-OBs
41-OAc	26	0.8
A[c]	0	4.3
B[c]	0	6.7
C[c]	0	7.7
12-OAc	33	0
D[c]	0	15
E[c]	0	12
38-OAc[d]	9.5	7.7
37-OAc	2.6	1.5
36-OAc	29	22
13-OAc	0	22[a]

[a] The sodium acetate concentration in both runs was 0.0248 *M*. A separate run with 13-OBs in which the sodium acetate concentration was doubled produced an increase in the amount of primary product 13-OAc to 24%. The rest of the relative distribution was unchanged. [b] Products present after 0.5 half-life. These are not kinetically controlled. [c] Product from attack on the double bond by the carbinyl carbon (see text). [d] A small amount of the *endo*-allylic isomer 39-OAc undoubtedly is present but is not separated from 38-OAc under the analytical conditions. [e] 3-Methylnortricyclyl-3-carbinyl acetate is not detectable among the products.

38-OAc, and 39-OAc. The products of acetolysis from the two substrates 12-OBs and 13-OBs are given in Table I.

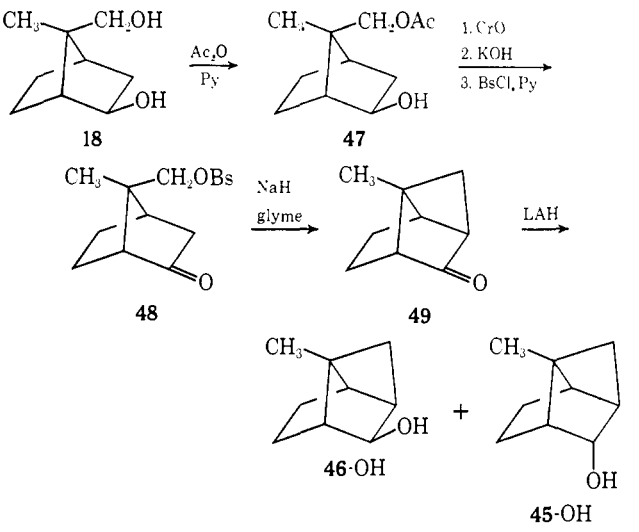
The product distribution from the *anti*-7-carbinyl substrate 12-OBs is unremarkable. It consists of some unrearranged primary acetate 12-OAc, some product of methyl shift, 41-OAc, and some of a mixture of ring-expanded allylic acetates 36-OAc, 37-OAc, 38-OAc, and 39-OAc. Acetolysis of the *syn*-7-carbinyl substrate, however, gives a sharply contrasting product mixture, which contains, in addition to a little methyl-shifted acetate 41-OAc and substantial amounts of unrearranged (13-OAc) and ring-expanded (36-OAc, 37-OAc, 38-OAc, and 39-OAc) acetates, a set of five new compounds A, B, C, D, and E, totaling almost half of the products. These materials show no olefinic proton absorption in the nmr and presumably are tricyclic. A reasonable working hypothesis would attribute their formation to interaction between the double bond and the developing positive charge on the *syn*-carbinyl side chain, giving the tricyclic cation 43 or perhaps its nonclassical variant 44.



13-OBs 43 44

Nucleophilic capture of these cations should lead to 1-methyltricyclo[3.3.0.0^{3,8}]octan-4-*endo*- (and/or -*exo*-) yl acetate, 45-OAc and/or 46-OAc. This speculation is confirmed by an independent synthesis of acetates 45 and 46, which starts with the previously described diol 18.

By careful treatment with acetic anhydride–pyridine, 18 is converted to a mixture from which the primary monoacetate 47 can be separated by column chromatography in 50% yield. Successive steps of oxidation, saponification, and *p*-bromobenzenesulfonylation give the arenesulfonoxy ketone 48, which is converted by sodium hydride to the tricyclic ketone 49 in 85% yield.

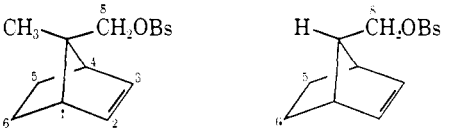


18 47 48 49

46-OH 45-OH

Lithium aluminum hydride reduction of ketone 49 gives two alcohols in a ratio of 5.6:1. The major alcohol probably has the *endo* configuration 45-OH, but a firm basis for this assignment is not now available.

Regardless of configuration, the method of synthesis and the spectroscopic data leave no doubt of the gross structure of these two alcohols. The acetate of the major alcohol from the tricyclic ketone 49 now proves to be identical in vpc retention time and ir and nmr spectra with the acetate D, the major "unknown" product from acetolysis of the *syn*-carbinyl *p*-bromobenzenesulfonate 13-OBs (Table I). The epimeric acetate from tricyclic ketone 49 has a vpc retention time identical with that of acetate B or C (Table I), which are not well resolved. Moreover, the *p*-toluenesulfonate of the major alcohol from ketone 49 (probably 45-OTs) gives upon acetolysis the same five acetates, A, B, C, D, and E, as are observed in the acetolysis of *syn*-carbinyl substrate 13-OBs (Table I). Aside from an excess of the acetate B (probably the *exo* compound, 46-OAc, epimeric with the starting 45-OTs), the relative proportions of the acetates from 45-OTs are virtually the same as those of this group from 13-OBs. Acetates A–E thus are clearly derived from tricyclic cation 43 (or 44) and its rearrangement products. These acetates amount to a total of 45% of the product mixture from *anti*-7-methyl-*syn*-7-carbinyl substrate 13-OBs (Table I). This efficient cyclization involving the *syn*-carbinyl side chain and the double bond in the 7-methyl system 13-OBs is to be contrasted with the behavior of the 7-unsubstituted analog 2-OBs, which gives no detectable cyclization products.[2a,13] It is conceivable that the 7-methyl group

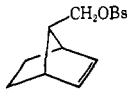
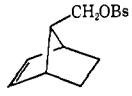
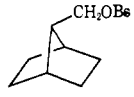
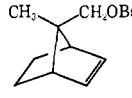
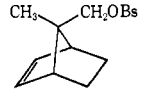
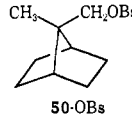


13-OBs 2-OBs

of 13-OBs causes subtle distortions of molecular geometry that might produce this difference. Compressions of the C-7, C-1, C-2 and C-7, C-4, C-3 angles, which would result from nonbonded repulsions between the 7-methyl group and the *exo* hydrogens at C-5 and C-6, would bring C-8 closer to C-2 and C-3 and thereby nar-

(13) R. K. Bly and R. S. Bly, *J. Org. Chem.*, 31, 1577 (1966).

Table II. Titrimetric Rate Coefficients for Acetolyses of *p*-Bromobenzenesulfonates at 120.4°

Substrate[d]	$k \times 10^5$, sec^{-1}
 2-OBs	1.76[a] (1.50)[c]
 3-OBs	1.37[a] (1.08)[c]
 1-OBs	2.89[a] (2.64)[c]
 13-OBs	9.40[b]
 12-OBs	4.45[b]
 50-OBs	28.0[b]

[a] Interpolated from data of ref 13. [b] This work. [c] Value corrected for bimolecular component. [d] Initial concentration about 0.02 *M*; sodium acetate initial concentration about 0.025–0.03 *M*.

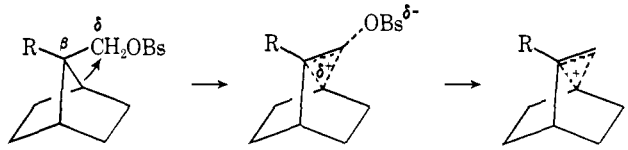
row the energy gap between the ground state and the transition state for cyclization of C-8 and C-2 or C-3. If this interaction occurred in the ionization step, it would anchimerically assist the solvolysis rate. Kinetic studies of the solvolyses of **13**-OBs and related substances provide a test of this. They also bear on the question whether the first step in the ring expansion may be anchimerically assisted and hence on whether the memory-preserving cationic intermediate so generated may be a nonclassical ion.

Acetolysis Rates. Table II shows the effect of a *syn*-double bond and of a β-methyl group on the rate of acetolysis. The first three entries of the table give values for the 7-unsubstituted compounds **2**-OBs, **3**-OBs, and **1**-OBs. They are taken from the data of Bly and Bly[13] and serve as reference points for the 7-methyl series, **13**-OBs, **12**-OBs, and **50**-OBs. The rate processes of interest here are the unimolecular components of the total displacement reaction. For some of these primary substrates, however, there is a strong presumption of a substantial bimolecular contribution, and in one case, **1**-OBs, there is definite evidence of it.[2b] Accordingly the rate coefficients should be adjusted to some fraction of the observed values. Such adjustments are small and can be made to a good approximation for part of the bimolecular component, the direct displacement by the sodium acetate buffer.[14] The corrected values are listed in parentheses in Table II.

These values, of course, still may contain a bimolecular component of unknown size because of solvent participation. This probably would not have a large effect on the search for π participation, since the contribution might be expected to remain roughly constant in comparisons between *syn* and *anti* or *syn* and saturated substrates. In evaluations of the β-methyl substituent effect, however, there would be a significantly larger bimolecular component in solvolyses of the isobutyllike 7-unsubstituted substrates than in those of the neopentyllike 7-methyl series. Therefore, the rate ratios calculated on the basis of the partially corrected values are minimum estimates of the magnitude of the β-methyl effect on the unimolecular rate.

Bly and Bly[13] have already concluded that π-bond participation is insignificant in the norborn-2-enyl-*syn*-7-carbinyl system, **2**-OBs, since the rate is not enhanced (Table II) and no products of ring closure are observed. In the 7-methyl series reported here (Table II), it would be hard to make a case for a significant rate enhancement of the solvolysis of the *syn*-carbinyl compound **13**-OBs. Although the rate is about twice as fast as that of the *anti* isomer, the increase is too small to require a special explanation. The rate for the saturated compound **50**-OBs is about three times as fast as that of the *syn* isomer, an increase comparable in sense and size with that in the 7-unsubstituted series (Table II). Thus, despite the ring closure of 45% of the product in the solvolysis of the 7-methyl-*syn*-7-carbinyl substrate, **13**-OBs, no significant rate enhancement occurs. Apparently, the interaction of the π bond of **13**-OBs with the carbinyl cationic center occurs late on the path to the rate-determining transition state, or possibly even after it.

Substitution of methyl for hydrogen at C-7 produces a modest rate enhancement in each case. The corrected ratios of acetolysis rate coefficients for the *syn*-carbinyl (**13**-OBs/**2**-OBs), for the *anti*-carbinyl (**12**-OBs/**3**-OBs), and for the saturated (**50**-OBs/**1**-OBs) pairs are 6.3, 3.3, and 10.6, respectively. Qualitatively, a rate enhancement by β-methyl substitution is consistent with a hypothetically concerted ionization ring expansion (*e.g.*, **51** → **52**), which would transfer some of the positive charge to the β position in the transition state of the rate-determining heterolysis. It is difficult, however,



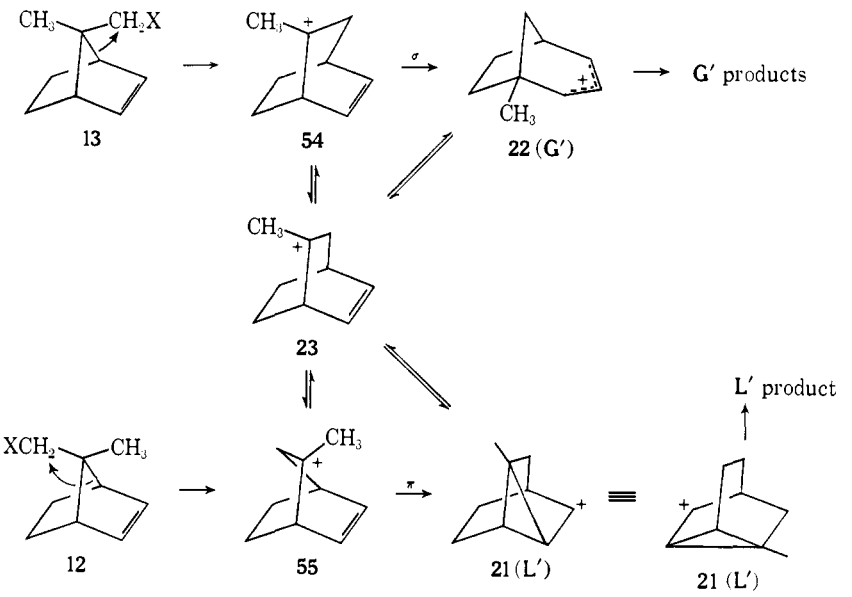
51 52 53

to decide whether the magnitude of the effect is appropriate, because the interpretation of solvolyses of simple model compounds of the neopentyl type is still controversial.[15,16] Perhaps the closest monocyclic analog of the 7-norbornylcarbinyl structure **51** is the cyclopentylcarbinyl system. Table III gives a series of acetolysis rate comparisons from the literature;[15–18] the values in parentheses are approximate ratios obtained by comparison of two rates through a common reference or a reasonable model compound.

(14) D. S. Donald, Ph.D. Thesis, University of Wisconsin, 1969, and references cited therein.

(15) (a) W. G. Dauben, J. L. Chitwood, and K. V. Scherer, Jr., *J. Am. Chem. Soc.*, **90**, 1014 (1968).
(16) W. G. Dauben and J. L. Chitwood, *ibid.*, **90**, 6876 (1968).
(17) P. D. Bartlett, W. D. Closson, and T. J. Cogdell, *ibid.*, **87**, 1308 (1965).
(18) G. Le Ny, *Compt. Rend.*, **250**, 368 (1960).

Scheme III



Relative rate comparison G of Table III shows that β-methyl substitution enhances the rate of acetolysis of a cyclopentylcarbinyl substrate by a factor of about 11. Previous workers[17-19] have suggested that relief of strain by carbon participation may provide a driving force in the solvolysis of this system. On this basis, one might expect that in 7-norbornylcarbinyl solvolyses (**51** → **52**), relief of strain might be even more pronounced; if present, however, this effect is overcome by some other factor, since the 7-norbornylcarbinyl solvolysis is slower, not faster, than the cyclopentylcarbinyl one (ratio H, Table III).

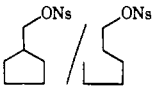
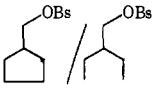
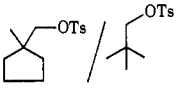
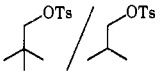
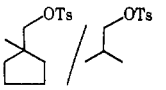
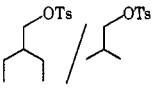
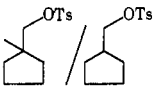
The 10.6-fold acetolysis rate enhancement by 7-methyl substitution in the 7-norbornylcarbinyl system is almost exactly the same as that in the cyclopentylcarbinyl case (Table III, G). This may well be fortuitous, but it seems reasonable to conclude that the importance, if any, of carbon participation in both the monocyclic and bicyclic systems is comparable.

The modest β-methyl effects and rather slow absolute rates observed in the present ring expansions are to be contrasted with the results of solvolyses of *exo*-norbornyl systems, which are widely (but not universally) believed to involve strong anchimeric assistance by carbon participation in a transition state leading to a nonclassical cationic intermediate. The *exo* norbornyl rates are fast,[20] and a β-methyl substituent increases the acetolysis rate by a factor of 68 at 25°.[21] By themselves, the rather feeble rate effects in the 7-norbornylcarbinyl systems could hardly form a strong basis for the postulate of a nonclassical transition state (**52**) or intermediate (**53**) in the ring expansions. Yet such ions provide one of the few consistently useful working hypotheses for the interpretation of the memory effects.[22] Thus, if the memory-preserving ions encountered[2a,b] in 7-norbornylcarbinyl or norborn-2-enyl-7-carbinyl ring expansions are nonclassical, the kinetic tests used here fail to detect them with certainty. The memory effect, which uses a symmetry property as the means of detection, is a much more sensitive probe.

(19) J. E. Nordlander, S. P. Jindal, P. von R. Schleyer, R. C. Fort, Jr., J. J. Harper, and R. D. Nicholas, *J. Am. Chem. Soc.*, **88**, 4475 (1966).
(20) J. A. Berson in "Molecular Rearrangements," Vol. 1, Part 3, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963.
(21) P. von R. Schleyer, as cited in ref 20, p 182.
(22) J. A. Berson, *Angew. Chem. Intern. Ed. Engl.*, 7, 779 (1968).

Tests for Crossover of Cation G' → L' and *Vice Versa*. Scheme III presents a basis for analysis of memory effects in the ring expansions of 7-methylnorborn-2-enyl-7-carbinyl derivatives analogous to that used[2a] for the parent 7-unsubstituted compounds. In order to preserve any of whatever stereochemical specificity is transmitted by the once-rearranged "twisted" cations **54** and **55**, it is necessary that the twice-rearranged ions **22 (G')** and **21 (L')** be trapped as products

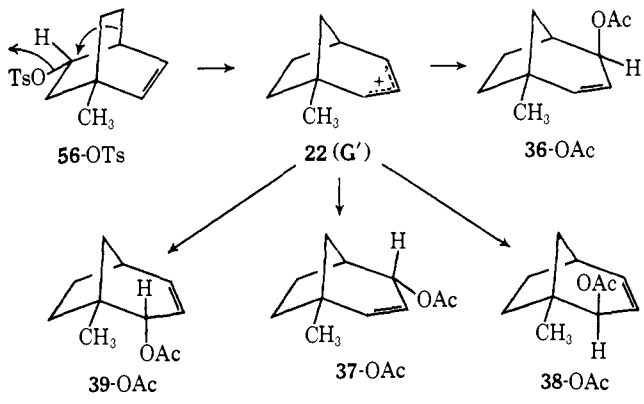
Table III. Ratios of Acetolysis Rates

Compounds	Relative rate: Code letter	Value	Temp, °C	Ref
	A	3.5	80	17
	B	2.5		18
	C	114	75	19
	D	0.33	75	14
	E	(35)	75	*a*
	F	(1)	75	*b*
	G	(11)	75	*c*
	H	13	115	13, 17, 18

[a] E ≅ CD. [b] F is assumed to be unity. [c] G ≅ E/BF.

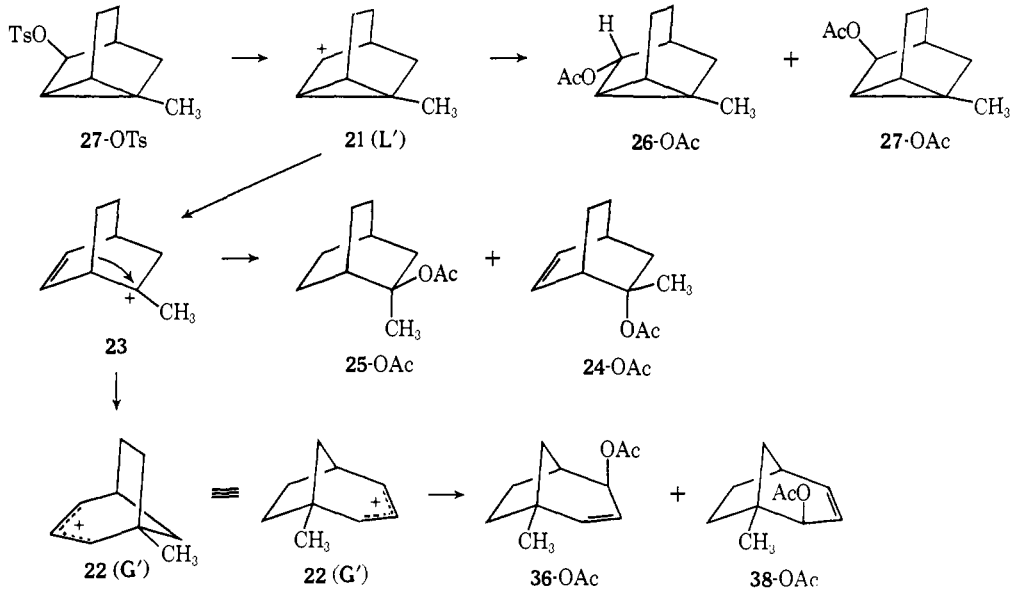
at rates that are at least competitive with the rates at which they interconvert with each other. An examination of the behavior of independently generated cations **G′** and **L′** provides some measure of how serious a problem the interconversion rate may be.

Acetolysis of 1-methylbicyclo[2.2.2]oct-5-en-*endo*-3-yl *p*-toluenesulfonate (**56**-OTs) at 40° gives a mixture of allylic acetates consisting mainly of the *exo* compounds **36**-OAc and **38**-OAc, with traces of the *endo* epimers **37**-OAc and **39**-OAc.[11] Products (*e.g.*, tricyclic compound **26**-OAc) from the **L′** cation **21**, are present in no more than minor quantities. Crossover from the **G′** to the **L′** cation series thus is slow at 40° in acetic acid, conditions similar to those used in the deaminations to be described.



To test for crossover in the reverse direction (**L′** → **G′**), we generate **L′** cations from 1-methyltricyclo-[3.2.1.0^{2,7}]oct-*endo*-6-ol (**27**-OH). The *p*-toluenesulfonate **27**-OTs is very unstable, but it is apparently formed when a cold pyridine solution of **27**-OH and *p*-toluenesulfonyl chloride is allowed to stand. It is acetolyzed by keeping in acetic acid. The acetate fraction of the resulting product mixture contains not only the expected **L′** products **26**-OAc (7.3%) and **27**-OAc (<0.5%) but also large quantities of **G′** products, the allylic acetates **36**-OAc (40%) and **38**-OAc (27%). Evidently, cation **21** (**L′**), even under these mild conditions, can cross over into the **G′** system, probably by way of some such species as tertiary bicyclic cation **23**. The presence of bicyclic acetates **25**-OAc (21%) and **24**-OAc (5–6%) in the product mixture is consistent with this scheme. These background studies indicate that whatever memory effect inheres in the double rearrangement of *syn*-carbinyl compound **13** to cation **G′** (Scheme II) will persist in the product pattern, but that in the rearrangement of *anti*-carbinyl compound **12** to cation **L′** it inevitably will be largely or wholly lost.[23]

Memory Effects in the Deaminative Ring Expansions of the 7-Methylnorborn-2-enyl-7-carbinylamines. Nitrosative deaminations of the *syn*-carbinylamine **13**-NH_2 and its *anti* isomer **12**-NH_2 in glacial acetic acid at room temperature give the mixtures of products shown in Table IV. The differences in product distributions, although small, appear to be outside of experimental error. In particular, the G′/L′ ratio from *syn*-amine **13**-NH_2 is 18 ± 2, and that from *anti*-amine **12**-NH_2 is 10 ± 2. It would seem that some memory is preserved, even in this system, where quasi-symmetrization to tertiary cation **23** (Scheme II) might be expected to compete more favorably with σ or π entrapment of "twisted" cations **54** or **55** than in the unsubstituted case. Because of the extensive crossover suffered by cation system L′, the L′/G′ ratio (or G′/L′ ratio) from *anti*- (or *syn*-) amine is not a meaningful measure of the memory effect, and experimental difficulties preclude an adjustment of the observed values to correct for crossover. Moreover, as is always the case in quasi-symmetrical rather than truly symmetrical systems,[2a] the product ratio is not directly translatable into a ratio of rates of σ entrapment *vs.* quasi-symmetrization because the "natural" partition ratio of the quasi-symmetric ion (*e.g.*, in Scheme III, the relative rates of **23** → **G′** and **23** → **L′**) is unknown. Nevertheless, it is clear that mem-



(23) It is of incidental interest to inspect the products from the tertiary bicyclic cation system **23** generated in another way. These studies are fragmentary, and results are available only for the deamination of the two amines **24**-NH_2 and **25**-NH_2. The *endo*-amino compound **24**-NH_2 gives 33% bicyclic *exo*-acetoxy compound **25**-OAc, 4% *endo* epimer **24**-OAc, 14% tricyclic L′ product **26**-OAc, and 31 and 18%, respectively, allylic G′ products **36**-OAc and **38**-OAc. The *exo*-amino compound **25**-NH_2 gives 19% **25**-OAc, 5% **24**-OAc, 15% **26**-OAc, 35% **36**-OAc, and 27% **38**-OAc.[24,25]

(24) D. S. Donald, Ph.D. Thesis, University of Wisconsin, 1969.

(25) W. J. Libbey, Ph.D. Thesis, University of Wisconsin, 1969.

Table IV. Products from the Nitrosative Deamination of the 7-Methylnorborn-2-enylcarbinylamines

	Starting material			
	12-NH_2		13-NH_2	
Product[g]	% of total[a,d,f]	% rearr[b,c]	% of total[a,d,e]	% rearr[b,c]
26 (L′)	5.4 ± 1	6.2 ± 1	3.7 ± 1	4.2 ± 1
36 (G′)	33	38	38	44
38 (G′)	23	26	29	33
24	5.5 ± 1	6.3 ± 1	4.5	5.1
25	21	24	12	14

[a] About 5% alcohols and traces of olefins formed are not included in these figures. [b] Products of ring expansion. [c] Average of two runs. [d] All values ±0.5% unless otherwise noted. [e] 1.5% 7-ethylnorborn-2-en-7-yl acetate (**41**-OAc) and 11 ± 1% **13**-OAc are formed also. [f] A trace of **41**-OAc and 13% **12**-OAc are formed also. [g] Control experiments establish the stability of all the products listed under the conditions of deamination.

ory persists in at least one of the present ring expansions and that its direction is the same as that in the systems without the methyl group[2,3] [$(G'/L')_{syn} > (G'/L')_{anti}$]. Whether its magnitude is less than that in the unsubstituted 2-norbornenyl-7-carbinyl analogs[2a] is uncertain, but qualitatively, its survival of this rather severe test considerably expands the range of structures in which this phenomenon now is expected to occur.

Experimental Section

Standard procedures and vpc analyses were carried out as described elsewhere.[2a] The letter code for identification of vpc columns is the same as the previous one.[2a] Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Lactone of *anti*-7-Methyl-*exo*-2-hydroxynorbornane-*syn*-7-carboxylic Acid (17). This compound was prepared by a slight modification of the method of Beckman and Geiger.[4] To 500 ml of 75% sulfuric acid in a 1-l. flask containing a large magnetic stirring bar was added in one portion with stirring, 50.0 g (0.331 mol) of *exo*-5-carboxy-*endo*-5-methyl-2-norbornene. The solution became homogeneous within 1 hr. Stirring was continued at room temperature for 24 hr, whereupon the clear, slightly brown reaction mixture was poured onto *ca.* 4 kg of ice. The resulting aqueous solution was extracted continuously with diethyl ether for 3 days. The slightly yellow ether extract was decolorized by boiling with activated charcoal, then filtered and dried (Na_2SO_4). Removal of the ether through a short Vigreux column gave 49.6 g of white crystals. One recrystallization from hexane gave 45.5 g of white needles, mp 121.5–124.0°. A second recrystallization from hexane gave 44.0 g (88%) of material, mp 124.0–125.0° (lit.[4] mp 125.0–126.0°).

***anti*-7-Methyl-*exo*-2-hydroxy-*syn*-7-carbinol (18).** A 250-ml, three-necked, round-bottomed flask equipped with a 125-ml dropping funnel, condenser, and drying tube, and containing a large magnetic stirring bar was flame dried under a stream of dry nitrogen. After cooling, 4.75 g (0.125 mol) of lithium aluminum hydride and 75 ml of tetrahydrofuran (freshly distilled from lithium aluminum hydride) were quickly placed in the flask and a solution of 18.59 g (0.123 mol) of lactone **17** in 50 ml of tetrahydrofuran was added from the dropping funnel to the stirred solution over a period of 1 hr. A freshly prepared saturated solution of sodium sulfate was added in small portions through the condenser until the light gray suspension turned white. The suspension was filtered and the solid salts were boiled with 50 ml of fresh tetrahydrofuran and filtered, and the filtrate was combined with the original solution. Removal of the solvent left 17.58 g (92.3% crude yield) of a white solid, mp 203.0–204.5°. One recrystallization from ether gave white crystals, mp 205.5–206.5°. The material can also be recrystallized efficiently from ethyl acetate and can be sublimed at 150° at 15 torr: ir (KBr) 3378, 2941, 1450, 1027, 1014, 1000, 966, 924, 885, 855 cm^{-1}; nmr ($CDCl_3$) δ 3.78 (2 H, AB pattern with J_{AB} = 11.5 Hz, A at 4.21, B at 3.35, CCH_2OH), multiplet superimposed on the AB pattern (1 H, $CHOH$), 2.98 (s, 2 *H*, $-OH$), complex absorption from 2.2 to 0.8 (8 H), 1.05 (s, 3 H, $-CH_3$).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.12; H, 10.14.

***anti*-7-Methyl-*syn*-7-*p*-toluenesulfonoxy-*exo*-2-*p*-toluenesulfonoxynorbornane (19).** To a flame-dried 1-l. three-necked flask equipped with condenser and dropping funnel was added 28.0 g (0.181 mol) of the above diol **18** and 150 ml of dry pyridine. The contents of the flask were protected from moisture with a drying tube and stirring was provided by a magnetic stirrer. The dropping funnel was charged with 87.0 g (0.455 mol) of *p*-toluenesulfonyl chloride (freshly recrystallized from carbon tetrachloride) and 150 ml of dry pyridine. After cooling the contents of the flask to 0°, addition was begun and was complete in 1.8 hr. Solid began to form in *ca.* 20 min. Stirring at 0° was continued for 19 hr and then for 4.5 hr at room temperature whereupon the reaction mixture was poured onto 400 g of ice. A heavy oil separated which would not crystallize. The aqueous solution was extracted three times with a total of 800 ml of diethyl ether. The combined extracts were washed with 10% hydrochloric acid until the wash was acid to congo red, *ca.* 800 ml being required, followed by 25 ml of 1 *M* sodium bicarbonate and 25 ml of saturated sodium chloride. The aqueous was made acidic with 10% hydrochloric acid and extracted once with 150 ml of diethyl ether. The ether extract was washed once with 1 *M* sodium bicarbonate, once with saturated sodium chloride, and combined with the first extracts. After drying ($CaSO_4$) the solvent was stripped off under vacuum during the latter stages, leaving 68.0 g of an amber oil which gave crude crystals upon standing in the cold for several hours. The crystals were washed twice with cold methanol and recrystallized from methanol giving 39.1 g of white powder, mp 64.5–66.5° (cloudy to 90°). Yields varied from 50 to 65% and the material was not purified further: ir (KBr) 1351, 1183, 1174 cm^{-1}; nmr (CCl_4) δ 7.50 (A_2B_2 pattern with an additional coupling in the downfield portion of J = 2.5 Hz, 8 H, J_{AB} = 9 Hz, $\Delta\nu_{AB}$ = 23.3, aromatic protons), 4.03 (AB pattern, 2 H, J_{AB} = 9 Hz, $\Delta\nu_{AB}$ = 25.5 CCH_2OTs), 4.5–4.1 (broad, 1 H, $CHOTs$) 2.45 (s, 6 H, tosyl methyls), 2.0–1.4 (m, 6 H), 1.0 (s, 3 H, methyl at C-7 position), 1.2–0.9 (m, 2 H).

A by-product produced in substantial amount in this reaction is the cyclic ether, 1-methyl-3-oxatricyclo[4.3.0.$0^{4,8}$]nonane (**19a**): ir (thin film) 2941, 1473, 1445, 1374, 1316, 1299, 1085, 1064, 1020, 1000, 933, 906, 893, 850, 823 cm^{-1}; nmr δ 3.91 (m, 1 H, $-OCH$), 3.55 (AB quartet, 2 H, J_{AB} = 7.5 Hz, $\Delta\nu_{AB}$ = 8.7 Hz, CCH_2O-), 1.75 (broad, 2 H, bridgehead protons), 1.65–0.9 (complex, 6 H), 1.04 (s, 3 H, methyl protons).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.11; H, 10.14.

2-Norbornene-*anti*-7-methyl-*syn*-7-carbinyl *p*-Toluenesulfonate (13-OTs). A suspension of 6.00 g (53.7 mmol) of potassium *t*-butoxide in 58 ml of *t*-butyl alcohol was stirred at room temperature in a one-necked flask equipped with reflux condenser and drying tube, until solution was complete. To this solution was added in one portion 5.753 g (12.4 mmol) of di-*p*-toluenesulfonate (**19**) and after stirring for several minutes at room temperature, the slightly opaque, amber solution was placed in an oil bath at 80°. Within 2 min a fine, white solid began to form. After stirring at 80° for 3 hr the reaction mixture was cooled in an ice bath and 1 ml of water was added. After *ca.* 5 min additional stirring the solution was poured into 100 ml of cold water. The two-phase liquid was extracted three times with a total of 180 ml of diethyl ether. The combined extracts were washed once with water, once with saturated sodium chloride solution, and dried ($CaSO_4$). The solvent was stripped off at aspirator vacuum yielding 3.18 g (87.6% crude yield) of slightly yellow crystals. One recrystallization from methanol gave white crystals, mp 66.6–67.0°. A second recrystallization gave material, mp 67.0–67.5°, and a third recrystallization from methanol yielded hard, white crystals, mp 67.1–67.6°. This material was later shown to be a mixture of 80% of the title compound **13**-OTs and 20% tricyclo[2.2.1.$0^{2,6}$]heptyl-3-methyl-3-carbinyl *p*-toluenesulfonate (**20**-OTs). The spectral properties of the mixture are as follows: ir (KBr) 1366, 1351, 1188, 1174, 722 cm^{-1}; nmr (CCl_4) δ 7.49 (AB q, 4 H, J_{AB} = 9 Hz, aromatic protons (the proton counts which follow are relative to these)), 5.82 (t, 1.6 H, J = 1.8 Hz, olefinic protons), 3.93 (s, 1.6 H, $>CCH_2O$ in **13**-OTs), 3.75 (m, 0.4 H, $>CCH_2O-$ in **20**-OTs), 2.46 (s, 3 H, tosyl methyl), 2.4 (m, 1.6 H), 2.0–0.8 (complex pattern, 4.4 H), 0.94 (s, 3H, $>CCH_3$).

2-Norbornenyl-*anti*-7-methyl-*syn*-7-carbinol (13-OH). In a dry, three-necked, 1-l. flask containing a large magnetic stirring bar and equipped with a Dry Ice–acetone condenser and pressure-equalizing dropping funnel was placed 4.72 g (0.68 mol) of oil-free, hexane-washed lithium wire. Approximately 240 ml of ammonia was condensed in the flask using Dry Ice–acetone cooling. Blue and bronze color formed as the ammonia came into contact with the lithium. A mixture, 5.00 g (17.0 mmol), of 80% **13**-OTs

and 20% **20-OTs**, prepared as described above, in 40 ml of dry tetrahydrofuran and 13.3 ml of absolute methanol was placed in the dropping funnel and added dropwise to the stirred solution over a period of 1.5 hr. Stirring was continued for *ca.* 10 hr with Dry Ice cooling and without cooling for 8 hr while the ammonia was allowed to escape. The ether was replenished occasionally during this time. The addition of 34 ml of methanol brought about the discharge of the residual blue and bronze colors within 0.5 hr. About 150 ml of diethyl ether and 150 ml of water were added, the layers were separated, and the aqueous layer was extracted three times with a total of 150 ml of diethyl ether. The combined extracts were washed twice with 25-ml portions of 10% sodium hydroxide, once with saturated sodium chloride solution, and dried ($CaSO_4$). Careful removal of the ether through a Vigreux column left 1.905 g of oil which solidified upon standing in the cold. Sublimation at 12–15 torr up to 80° using ice–water cooling gave 1.537 g (65%) of white, waxy material with a strong camphorlike odor. Vpc analysis on column B (110°, 50 psi) showed the presence of two compounds in a ratio of *ca.* 4:1. Compound **13-OH** was obtained pure by preparative glpc on column C at 138° and 60 psi under which conditions it had a retention time of 50 min as compared to *ca.* 65 min for the minor component, tricyclo-[2.2.1.$0^{2,6}$]heptyl-3-methyl-3-carbinol (**20-OH**). The pressure was reduced to 18 psi during collection. The collection efficiency was 79%. After sublimation to remove column bleed the title compound melted 109.5–110.6°; ir (KBr) 3300 cm^{-1}, 3030, 2915, 2849, 1015, 870, 847, 800, 714, 699; nmr (CCl_4) δ 5.88 (t, 2 H, J = 1.8 Hz, olefinic protons), 3.44 (s, 2 H, $>CCH_2O$), 2.99 (s, 1 H, $-OH$), 2.35 (broad, 2 H, C-1 and C-4 bridgehead protons), 1.80 (m, 2 H, C-5 and C-6 *exo* protons), 0.93 (s, 3 H, C-7 methyl protons), 1.1–0.7 (m, 2 H, C-5 and C-6 *endo* protons).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.67; H, 10.05.

The ***p*-bromobenzenesulfonate 13-OBs** was prepared by standard procedure (C) in 90% yield. Recrystallization from methanol gave needles: mp 80.0–81.5°; ir (KBr) 1351, 1189, 1176 cm^{-1}; nmr ($CDCl_3$) δ 7.73 (s, 4 H, aromatic protons), 5.82 (t, 2 H, J = 1.8 Hz, olefinic protons), 4.08 (s, 2 H, $>CCH_2O-$), 2.5–2.28 (broad, 2 H, C-1 and C-4 bridgehead protons), 2.1–1.2 (complex, 2 H, *exo* C-5 and C-6 protons), 1.2–0.7 (complex, 2 H, *endo* C-5 and C-6 protons), 0.94 (s, 3 H, C-7 methyl protons).

Anal. Calcd for $C_{15}H_{17}BrSO_3$: C, 50.40; H, 4.80; Br, 22.39; S, 8.97. Found: C, 50.45; H, 4.81; Br, 22.31; S, 9.07.

The 20% component of the mixture is tricyclo[2.2.1.$0^{2,6}$]heptyl-3-methyl-3-carbinol (**20-OH**) as indicated by its spectral properties, elemental analysis, and mode of synthesis. A sample was repassed as above and sublimed twice: mp 107–110°; ir (thin film) 3226 2941, 2874, 1460, 1025, 800 cm^{-1}; nmr (CCl_4) δ 3.42 (central lines of AB pattern, 2 H, J = 8 Hz, $>CCH_2OH$), complex pattern from 2.0 to 0.6 (broad peaks at 1.72, 1.58, 1.42, 1.22, and a fairly sharp peak at 1.04, 8 H), 0.93 (s, 3 H, methyl protons).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.07; H, 10.33.

2-Norbornenyl-*anti*-7-methyl-*syn*-7-carbinyl acetate (13-OAc) was obtained from the corresponding alcohol with acetic anhydride–pyridine (procedure B-1). The crude product, obtained in 93.3% yield, gave only one peak on column B (110°, 50 psi). Bulb-to-bulb distillation gave the material as a clear, water-white oil: ir (neat) 1739, 1235, 1026, 719 cm^{-1}; nmr (CCl_4) δ 5.93 (t, 2 H, J = 1.9 Hz, olefinic protons), 3.99 (s, 2 H, $-CCH_2O$), 2.40 (broad, 2 H, C-1 and C-4 bridgehead protons), 1.92 (s, 3 H, acetoxy methyl), 2.1–1.6 (m, 2 H, *exo* C-5 and C-6 protons), 1.2–0.80 (m, 2 H, *endo* C-5 and C-6 protons), 0.92 (s, 3 H, C-7 methyl).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.08; H, 8.85.

3-Methyltricyclo[2.2.1.$0^{2,6}$]heptylcarbinyl Acetate (20-OAc). This material was prepared by procedure B-1 from the corresponding alcohol. Bulb-to-bulb distillation gave a water-white liquid: ir (neat) 3067, 2967, 2882, 1739, 1464, 1387, 1377, 1235, 1032, 982, 907, 829, 800 cm^{-1}; nmr (CCl_4) δ 3.83 (AB pattern, 2 H; J_{AB} = 11 Hz, $\Delta\nu_{AB}$ = 6.93 Hz, $>CCH_2O-$), 1.97 (s, 3 H, CH_3COO), 1.78 (broad, 1 H), 1.60 (broadened singlet, 2 H), 1.24 (broadened singlet, 1 H), 1.18–0.70 (complex pattern with peaks at 1.13, 1.06, 0.90, 0.82, 0.74, 4 H), 0.94 (s, 3 H, $>CCH_3$).

7-Methyl-7-norbornylcarbinol (4-OH) was prepared by hydrogenation at atmospheric pressure of 0.2980 g (2.16 mmol) of **13-OH** in methanol using 10% palladium on charcoal. After filtration to remove catalyst and careful removal of solvent through a Vigreux column, the crude alcohol was sublimed under aspirator vacuum, up to 100°, using ice–water cooling, giving 0.2730 g (90.5%) of material: mp 152.7–153.2°; ir (KBr) 3333, 1471, 1029, 998 cm^{-1}; nmr (CCl_4) δ 3.50 (s, 2 H, $>CCH_2O$), 2.0–0.8 (complex, 10 H), 1.04 (s, 3 H, C-7 methyl).

Anal. Calcd for $C_9H_{16}O$: C, 77.10; H, 11.50. Found: C, 76.89; H, 11.23.

The ***p*-bromobenzenesulfonate (4-OBs)** was prepared in 93.5% yield by standard procedure (C). Recrystallization from methanol gave white plates: mp 72.0–73.0°; ir (KBr) 1351, 1178 cm^{-1}; nmr ($CDCl_3$) δ 7.64 (broad s, 4 H, aromatic protons), 3.99 (s, 2 H, $\equiv CCH_2O$), 2.0–0.8 (complex, 10 H), 0.99 (s, 3 H, C-7 methyl).

Anal. Calcd for $C_{15}H_{19}BrSO_3$: C, 50.14; H, 5.33; Br, 22.24; S, 8.93. Found: C, 50.12; H, 5.35; Br, 22.26; S, 8.90.

2-Norbornene-*anti*-7-methyl-*syn*-7-carbinylphthalimide. In a 25-ml one-necked flask equipped with a condenser and drying tube and closed to the atmosphere using a mercury bubbler were placed 0.3319 g (0.930 mmol) of **13-OBs**, 0.2745 g (1.86 mmol) of phthalimide (recrystallized from ethanol and sublimed), 0.1280 g (0.930 mmol) of potassium carbonate, and 5.7 ml of dimethylformamide (shaken with potassium hydroxide and distilled from calcium oxide). The initially yellow solution containing solid potassium carbonate was placed in an oil bath at 160° whereupon the solid dissolved within 20 min with the evolution of gas. In *ca.* 45 min a solid began to form and after 15 hr the orange solution was cooled to room temperature and 15 ml of cold water was added and the stirring continued for 15 min. The slightly yellow solid which formed was filtered off and washed well with water, sucked dry, and dissolved in 20 ml of diethyl ether. The ether solution was washed with 5 ml of 2% sodium hydroxide solution which gave no precipitate upon acidification. The ether solution was washed with saturated sodium chloride and dried over calcium sulfate. The ether was removed under a stream of nitrogen leaving 0.1760 g (71%) of slightly yellow powder. Recrystallization from methanol gave white crystals: mp 122.0–123.0°; ir (KBr) 1757, 1701, 1385, 1058, 911, 733, 720, 714 cm^{-1}; nmr (CCl_4) δ 7.72 (two-line pattern with weaker lines, 4 H, J = 2 Hz, aromatic protons), 6.05 (A_2X_2 pattern appearing as a triplet, 2 H, J = 1.9 Hz, olefinic protons), 3.75 (s, 2 H, $>CCH_2N<$), 2.40 (broad, 2 H, C-1 and C-4 bridgehead protons), 1.9–1.5 (m, 2 H, C-5 and C-6 *exo* protons), 1.1–0.7 (m, 2 H, C-5 and C-6 *endo* protons), 0.84 (s, 3 H, C-7 methyl).

Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41, N, 5.24. Found: C, 76.53; H, 6.39; N, 5.19.

7-Methyl-7-norbornylcarbinylphthalimide was obtained in 69% yield by the same procedure. The reaction time in this case was 22 hr. The product, recrystallized from methanol, melted at 117.0–117.5°: ir (KBr) 1776, 1721, 1389, 1346, 1058, 918, 795, 747, 724 cm^{-1}; nmr ($CDCl_3$) δ 7.70 (two lines of equal intensity with weaker lines, 4 H, J = 2 Hz, aromatic protons), 3.68 (s, 2 H, $>CCH_2N<$), three broad absorptions from 2.4 to 1.0 centered at 2.15, 1.74, 1.25), 0.89 (s, 3 H, C-7 methyl).

Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.56; H, 7.08; N, 5.13.

7-Methyl-7-norbornylcarbinylamine (4-NH_2). To a 25-ml flask equipped with reflux condenser and closed to the atmosphere with a mercury trap was added 0.1800 g (0.668 mmol) of 7-methyl-7-norbornylcarbinylphthalimide, 2.13 g (53.3 mmol) of sodium hydroxide, 5.5 ml of methanol, and 2.0 ml of water. After the system had been flushed with nitrogen, the solution was heated at reflux for 57 hr. After cooling to room temperature, 8 ml of saturated sodium chloride solution was added, followed by enough water to dissolve the precipitated salts. The aqueous solution was extracted five times with a total of 30 ml of pentane and the combined extracts were dried ($CaSO_4$) under nitrogen in a tightly closed flask. The solvent was removed carefully under nitrogen through a Vigreux column and the pale yellow oil which remained was distilled bulb to bulb at 0.3 torr up to 150° using Dry Ice cooling. A semisolid (0.0864 g, 94%) with a characteristic amine odor was obtained: ir (neat) 3226, 2933, 2857, 1587, 1417, 1042 cm^{-1}.

2-Norbornenyl-*anti*-7-methyl-*syn*-8-carbinylamine (13-NH_2) was obtained in 79% yield from 2-norbornenyl-*anti*-7-methyl-*syn*-7-carbinylphthalimide in the same manner: ir (neat) 3226, 2933, 2857, 1587, 1460, 1042, 717 cm^{-1}.

7-Ethylnorbornyl-7-yl Acetate (11). Atmospheric hydrogenation of a methanolic solution of the epimeric 2-norbornene-7-vinyl-7-ols[26,27] over 30% palladium on charcoal gave 7-ethylnorbornan-7-ol, mp 65.0–66.0° (lit.[26] mp 65.5–66.5°). Conversion to the acetate

(26) J. A. Berson and M. Jones, Jr., *J. Am. Chem. Soc.*, **86**, 5019 (1964).

(27) We are indebted to Dr. E. J. Walsh, Jr., for this sample.

using standard procedure (B-2) followed by bulb-to-bulb distillation gave water-white 7-ethylnorborn-7-yl acetate: ir (neat) 2959, 2865, 1730, 1449, 1366, 1250, 1212, 1170, 1122, 1087, 1015, 962 cm^{-1}; nmr (CCl_4) δ 2.33 (broad, 2 H, C-1 and C-5 bridgehead protons), 1.94 (s, 3 H, acetoxy methyl), complex pattern from 2.0 to 0.67 with peaks at 1.98, 1.86, 1.75, 1.55, 1.28, 1.16, 1.00, 0.88, 0.75 (13 H).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.60; H, 10.00.

2-Norbornene-*syn*-7-ethyl-*anti*-7-ol (41) was formed when a solution of 1.0194 g (9.40 mmol) of 7-ketonorbornene[27,28] in 50 ml of dry ether was added during 40 min to a Grignard reagent prepared from 28 mmol of ethyl iodide and 29.7 g-atom of magnesium. After 1 additional hr the reaction mixture was heated to reflux for 1 hr, cooled and an excess of a saturated sodium chloride solution was added carefully. The slurry was filtered and the filter cake washed well with fresh diethyl ether. The solvent was removed through a Vigreux column giving *ca.* 1.25 g of light yellow liquid whose infrared spectrum showed no carbonyl absorption and a strong hydroxyl absorption. The components of the crude product were separated on column F at 140° and 230 ml/min. Several very small, low retention-time peaks were observed along with two major peaks at 1.23 and 1.57 hr in a ratio of 3.2:1, respectively. The major component (0.8202 g, 63%) gave one sharp peak on capillary glpc column B: ir (neat) 3378, 3058, 2967, 2874, 1466, 1279, 1134, 990, 942, 876, 855, 787, 709 cm^{-1}; nmr (CCl_4) δ 5.91 (A_2X_2 pattern appearing as a triplet, J = 2 Hz, two olefinic protons), 2.35 (broad, 2 H, C-1 and C-4 bridgehead protons), 1.97 (doublet of doublets, J_1 = 8 Hz, J_2 = 2 Hz, 2 H, *exo* C-5 and C-6 protons), 1.64 (q, 2 H, J = 7.5 Hz ethylmethylene protons), 1.27 (broad, 1 H, -O*H*), 0.85 (quartet superimposed on *endo* C-5 and C-6 proton absorption, 5 H, J = 7.5 Hz).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.36; H, 10.25.

The spectra of the minor component of the reaction suggests that it is the reduction product, 2-norbornen-*anti*-7-ol.

2-Norbornene-*syn*-7-ethyl-*anti*-7-yl acetate (41-OAc) was prepared from the corresponding alcohol in 95% yield using standard procedure (B-1). Glpc analysis on capillary column B showed 6.5% unreacted alcohol. After purification on column G, analysis on capillary column B showed 0.3% of the alcohol: ir (neat), 3067, 2985, 2874, 1736, 1462, 1370, 1248, 1116, 1018, 973, 956, 714 cm^{-1}; nmr (CCl_4) δ 5.94 (A_2X_2) pattern appearing as a triplet, 2 H, J = 2 Hz, olefinic protons), 2.94 (closely spaced multiplet showing some fine structure, 2 H, C-1 and C-4 bridgehead protons), 2.16–1.5 (complex pattern with peaks at 2.12, 2.02, 2.00, 1.86, 1.81, 1.76, 1.74, 1.71, 1.67, 1.60, 1.54, two ethylmethylene and the two C-5 and C-6 *exo* protons), 1.92 (s, 3 H, acetoxy methyl), 0.77 (triplet, J = 7.2 Hz, superimposed on a doublet of doublets centered at 0.93, J_1 = 12 Hz, J_2 = 3.2 Hz; a total of five protons for the methyl part of the 7-ethyl group and the *endo* C-5 and C-6 protons).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.27; H, 8.89.

***anti*-7-Carbomethoxy-*syn*-7-methyl-2-norbornene (14).** To 93 g of a 1.2% by weight amalgam of sodium in mercury in a 250-ml round-bottomed flask fitted with a reflux condenser was added 5.39 g (1.93 mmol) of triphenylmethyl chloride in 60 ml of dry ether and the mixture was stirred magnetically at ether reflux under a nitrogen atmosphere. The mixture turned a dark red in *ca.* 1 hr, and stirring was continued for an additional 3 hr. To this mixture was added dropwise over a 30-min period 1.4 g (0.92 mmol) of a mixture of *syn*- and *anti*-7-carbomethoxy-2-norbornene (**16**) prepared by the method of Sauers,[29] in 15 ml of anhydrous ether. A nitrogen atmosphere was maintained throughout the reaction. The mixture was stirred an additional 30 min at reflux, then was cooled in an ice bath and 2.25 ml of anhydrous methyl iodide was added by pipet. The dark red color disappeared immediately. The mixture was stirred for 2.5 hr at 0°, an additional 2.25 ml of methyl iodide was added, and the reaction mixture was permitted to warm to room temperature while stirring was continued for an additional 1 hr. Water (50 ml) was added and the mixture was filtered through a Büchner funnel using Filter Cel. The aqueous and organic layers were separated, and the aqueous layer was extracted twice with 20-ml portions of pentane. The combined organic portions were washed twice with saturated brine and dried ($CaSO_4$). Removal of the solvent by distillation left a residue which was distilled bulb to bulb at 100–155° (15 mm), and 0.67 g of a liquid was recovered. This material was redistilled bulb to bulb at 100–125° (15 mm), giving 0.54 g of a colorless liquid and leaving a residue of yellow oil in the distilling bulb. Vpc analysis on a column B showed that the distillate contained six components in addition to olefins. The major peak (*ca.* 85%) subsequently was shown to be the desired ester. On the capillary TCEP column the major peak came off first. Three of the other peaks were collected by preparative vpc and identified by the nuclear magnetic resonance spectra as *anti*-7-carbomethoxy-2-norbornene, *syn*-7-carbomethoxy-2-norbornene, and a mixture of *syn*-7-carbomethoxy-*anti*-7-methyl-2-norbornene (**15**) and what appeared to be 7-carbomethoxy-7-methylnortricyclene. The separation by vpc on column D at 117° gave 0.36 g (23.5%) of the *anti*-7-carbomethoxy-*syn*-7-methyl-2-norbornene (**14**): ir (neat) 3.30 (olefinic CH), 5.79 (ester C=O), 7.59, 8.10 (ester C–O), 9.04, 11.19, 11.41, 11.78, 13.05, and 13.95 μ (*cis*-disubstituted double bond); nmr (CCl_4) δ 5.92 (triplet, 2 J = 2 Hz, olefinic protons), 3.62 (s, 3, CO_2CH_3), 2.77 (broad, 2, bridgehead 1,4 protons), 2.0–1.6 (complex, 2, *exo*-5,6 protons), 1.2–0.8 ppm (complex including a sharp singlet methyl peak at 1.1, 5, *endo*-5,6 protons and -CH_3).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.31; H, 8.51.

Norborn-2-enyl-*syn*-7-methyl-*anti*-7-carbinol (12-OH) was prepared by lithium aluminum hydride **reduction** of the ester **14**. It had mp 110.5–111.7° after bulb-to-bulb distillation: ir (KBr) 3.18 (OH), 8.90, 9.60, 9.82, 11.02, 11.45, 11.77, 13.80, and 13.98 μ; nmr (CCl_4) δ 5.93 (t, 2, J = 1.9 Hz, olefinic protons), 3.38 (s, 2, CH_2OH), 2.96 (broad singlet, 1, OH), 2.42 (broad, 2, bridgehead 1,4 protons), 1.95–1.65 (complex, 2, *exo*-5,6 protons), 1.2–0.75 (complex including a sharp methyl singlet at 1.00, 5, *endo*-5,6 protons and CH_3).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.39; H, 10.15.

The ***p*-bromobenzenesulfonate, 12-OBs**, had mp 64.5–65°.

Anal. Calcd for $C_{15}H_{17}BrSO_3$: C, 50.50; H, 4.80; Br, 22.39; S, 8.97. Found: C, 50.34; H, 4.76; Br, 22.37; S, 9.02.

The **phthalimide** had mp 129–129.5°; ir (KBr) 3.31, 5.69, 5.85, 6.87, 7.04, 7.22, 7.33, 7.46, 7.61, 9.40, 10.90, and 13.80 μ; nmr (CCl_4) δ 7.73 (complex, 4, aromatic protons), 5.93 (t, 2, J = 2 Hz, olefinic protons), 3.57 (s, 2, -CH_2N), 2.55–2.00 (complex, 4, bridgehead 1,4 and *exo*-5,6 protons), 1.3–0.8 ppm (complex pattern including a methyl singlet at 0.87, 5, *endo*-5,6 protons and CH_3).

Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.35; H, 6.45; N, 5.04.

2-Norbornenyl-*syn*-7-methyl-*anti*-7-carbinylamine. A solution of 105 mg (0.394 mmol) of 2-norbornenyl-*syn*-7-methyl-*anti*-7-carbinylphthalimide and 1.26 g (31.5 mmol) of sodium hydroxide in 3.25 ml of methanol and 1.15 ml of water was refluxed for 54 hr under a nitrogen atmosphere. Then 4.5 ml of saturated brine and enough water to dissolve the precipitate that formed was added, and this solution was extracted four times with 6-ml portions of pentane. The pentane extracts were washed once with saturated brine and dried ($CaSO_4$). The pentane was removed by distillation, then the liquid residue was distilled at 50–120° (0.8 mm) giving 41 mg (76%) of the amine. The infrared spectrum (neat) showed two absorptions due to the N–H stretching vibration at 2.92 and 3.05 μ, an absorption at 3.32 μ due to the olefinic C–H stretching vibration, and a strong band at 13.95 μ for the *cis*-disubstituted double bond. In addition the generally weak spectrum had bands at 6.2 (broad), 6.88, 7.31, 7.59, and 12.92 μ.

1-Methyltricyclo[3.2.1.0^{2,7}]octan-6-one (32). To a dry, 2-l., three-necked flask equipped with condenser, addition funnel, and mechanical stirring was added 300 ml of dry diethyl ether, 22 ml (0.28 mol) of pyridine, and 38.3 g (0.272 mol) of a mixture of 3-methylcyclohex-3-ene carboxylic acid (**29-OH**) and 4-methylcyclohex-3-enecarboxylic acid (**28-OH**) in a ratio of *ca.* 8:1, respectively.[8] Dropwise addition of a solution of 64.3 g (0.54 mol) of thionyl chloride in 300 ml of dry diethyl ether over a period of 3 hr to the stirred reaction mixture at room temperature was followed by an additional 4 hr of stirring at room temperature. The reaction mixture was protected from moisture with a drying tube. A small amount of dark material had formed during the addition and was filtered off prior to flash evaporation of the solvent at reduced pressure. The slightly dark oil obtained was distilled at reduced pressure giving 18.8 g of material distilling at 70° at 1.0 torr. This material was used without further purification: ir (neat) 2933 2890, 1779, 1445, 1385, 1287, 1277, 1174, 1142, 1089, 922, 731 cm^{-1}.

(28) P. G. Gassman and P. G. Pape, *J. Org. Chem.*, 29, 160 (1964).
(29) R. R. Sauers and R. M. Hawthorne, Jr., *ibid.*, 29, 1685 (1964).

Diazomethane was prepared by adding 55.0 g (0.366 mol) of N-nitrosomethylurea portionwise to a stirred, ice-cold, two-phase solution consisting of 160 ml of 40% potassium hydroxide in water and 525 ml of diethyl ether. After stirring for 2.5 hr at ice bath temperature, the yellow, homogeneous ether layer was decanted onto potassium hydroxide and dried in the cold for 2 hr. The dried ethereal solution of diazomethane was decanted into a 2-l. erlenmeyer flask in an ice bath and 18.8 g (0.119 mol) of the acid chloride mixture described above in 150 ml of dry ether was added dropwise with vigorous stirring over a period of 3.8 hr. The solution was allowed to warm to room temperature and was stirred overnight while open to the atmosphere. Filtration to remove a small amount of solid that had formed, and removal of solvent with a rotary evaporator, gave 17.1 g (87.5% crude yield) of amber liquid. The infrared spectrum of the crude product shows strong absorptions at 2105 and 1639 cm^{-1} as expected for a diazo ketone. There is also a moderately strong absorption at 1727 cm^{-1} which arises from α-chloro ketone side product. No attempt was made to separate the mixture at this point.

The cyclization of the diazo ketone was carried out according to the high dilution method of Doering, *et al.*[9] In a 1-l., one-necked flask was placed 600 ml of hexane, 26 g of copper powder, and a large magnetic stirring bar. The flask was equipped with a 200-ml Soxhlet extractor on top of which was placed a condenser followed by a 250-ml addition funnel. The crude diazo ketone reaction product described above was placed in the dropping funnel along with 150 ml of hexane. The system was protected from moisture with a drying tube. The hexane in the flask was heated to reflux with stirring while the diazo ketone solution was added dropwise to the condensing pool of hexane in the Soxhlet. Addition was complete after 6.75 hr. The solution was allowed to reflux for an additional 10 hr, was filtered and then concentrated in a rotary evaporator leaving 14.4 g of dark oil. Distillation at 0.15 torr through a 38-cm tantalum wire column gave two fractions: 38–40° (6.2 g) and 46–47° (3.0 g). The infrared spectra of both fractions show carbonyl absorptions at 1770 and 1721 cm^{-1}. In the lower boiling fraction the absorption at 1721 cm^{-1} was the stronger while in the higher boiling fraction the 1770-cm^{-1} absorption was more intense. The 1770-cm^{-1} band is in the range expected for the α-chloro ketone and the 1721-cm^{-1} band is at the frequency expected for the cyclized ketone. 1-Methyltricyclo[3.2.1.$0^{2,7}$]octan-6-one (**32**) was obtained pure from the lower boiling fraction by preparative vpc separation on column H (130°, 50 psi) under which conditions it began to elute in 90 min. It was incompletely separated from the much smaller amount of its higher retention time 2-methyl isomer **33**, which results from the 4-methylcyclohex-3-enecarboxylic acid (**28**-OH) in the starting material, but it could be obtained 96% pure in two passes and analytically pure by taking the cut earlier. The ketone **32** and its 2-methyl isomer **33** had retention times of 80.2 and 81.9 min, respectively, on column B (110° and 50 psi): ir (neat) 2941, 2874, 1721, 1447, 1279, 1195, 1134, 1008, 884, 864 cm^{-1}; nmr (CCl_4) δ 1.93 (broad, 6 H), 1.52 (broad, 3 H), 1.34 (s, 3 H, $-CCH_3$).

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.41; H, 8.86.

***exo*- and *endo*-1-Methyltricyclo[3.2.1.$0^{2,7}$]octan-6-ol (26-OH and 27-OH).** Lithium aluminum hydride reduction of 1-methyltricyclo-[3.2.1.$0^{2,7}$]octan-6-one (**32**), containing 4% of its 2-methyl isomer **33** (see above), using standard procedure A gave a 95% yield of a mixture showing three peaks on capillary glpc analysis, column B (108°, 50 psi) at 37.0, 37.8, and 41.1 min amounting to 10, 84.3, and 5.7%, respectively. The mixture could be separated preparatively on column H at 132° and 50 psi, conditions which gave base-line separation of all three components for 60-μl injection samples. The first peak began to elute in 65 min. The 10% component, a semisolid at room temperature, was 1-methyltricyclo[3.2.1.$0^{2,7}$]-octan-*endo*-6-ol (**27**-OH): ir (neat) 3333, 2985, 2924, 2857, 1350, 1202, 1089, 1058, 1009, 981, 876, 751 cm^{-1}; nmr (CCl_4) δ 3.78 (s, 1 H, C*H*OH), 2.42 (s, 1 H, CHO*H*), 2.1–1.3 (complex pattern with peaks at 1.80, 1.64, 1.43, 7 H), 1.22 (s, 3 H, $-CCH_3$), 1.06 (d, 1 H, J = 6.5 Hz, C-7 H), 0.73 (d with fine splitting, 1 H, J = 6.5 Hz, C-2 H).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.21; H, 10.13.

The major product of the reduction was 1-methyltricyclo-[3.2.1.$0^{2,7}$]octan-*exo*-6-ol (**26**-OH). The sodium borohydride in methanol reduction of tricyclo[3.2.$10^{2,7}$]octan-6-one is reported[10] to give 95% *exo*-tricyclo[3.2.1.$0^{2,7}$]octan-6-ol. The lithium aluminum hydride reduction reported here gave 89.4% *exo* product: ir (neat) 3425, 2985, 1342, 1198, 1064, 1030, 985, 869, 763 cm^{-1}; nmr (CCl_4) δ 4.28 (t, 1 H, J = 4 Hz, C*H*OH), 3.0 (s, 1 H, CHO*H*), 2.1–1.5 (complex pattern with peaks at 1.96, 1.92, 1.72, 1.65, 1.58, 7 H), 1.14 (s, 3 H, $-CCH_3$), 1.02 (doublet of doublets, 1 H, J = 7 Hz, J = 4 Hz, C-7 proton), 0.60 (doublet with fine splitting, J = 7 Hz, C-2 proton).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.28; H, 10.25.

The nmr of the 5.7% component corresponds exactly to the nmr of 2-methyltricyclo[3.2.1.$0^{2,7}$]octan-*endo*-6-ol (**34**-OH) and does not show the high-field absorption for the C-2 proton seen in the C-1 methyl isomer.[11]

Equilibration of 0.2448 g (1.77 mmol) of 1-methyltricyclo-[3.2.$10^{2,7}$]octan-*exo*-6-ol (**26**-OH) with 0.353 g of aluminum isopropoxide in 2.9 ml of isopropyl alcohol containing a few drops of acetone for 4.3 days at reflux gave 0.2157 g of a mixture, which vpc analysis on column E showed to be 82% **27**-OH and 18% **26**-OH. For *exo*- and *endo*-tricyclo[3.2.1.$0^{2,7}$]octan-7-ol, the equilibrium position is reported[10] to be 80% *endo*- and 20% *exo*.

1-Methyltricyclo[3.2.1.$0^{2,7}$]octan-*endo*-6-yl Acetate (27-OAc). This compound was obtained in quantitative yield from the corresponding alcohol **27**-OH using standard procedure (B-2). The crude product was purified on vpc column I at 105°, 20 psi. A trace of dimethylaniline eluted in 5.0 min and the title compound began to elute in 10.0 min: ir (neat) 3030, 1739, 1366, 1355, 1241, 1028, 997, 762 cm^{-1}; nmr (CCl_4) δ 4.98 (triplet with fine splitting, 1 H, J = 4 Hz, C*H*OAc), 1.98 (s, 3 H, $OCOCH_3$), 2.2–1.3 (complex pattern with major peaks at 2.03, 1.75, 1.62, 7 H), 1.17 (s, 3 H, $-CCH_3$), 1.3–1.0 (pattern obscured by methyl peak, 1 H, C-7 proton), 0.67 (doublet with fine splitting, 1 H, J = 7 Hz, C-2 proton).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.26; H, 8.85.

1-Methyltricyclo[3.2.1.$0^{2,7}$]octan-*exo*-6-yl Acetate (26-OAc). This compound was obtained in quantitative yield from the corresponding alcohol **26**-OH in the same manner as described above for the *exo* isomer: ir (neat) 2994, 2941, 2865, 1730, 1447, 1374, 1361, 1332, 1242, 1203, 1089, 1052, 1028, 847, 753 cm^{-1}; nmr (CCl_4) δ 4.80 (s, 1 H, C*H*OAc), 1.98 (s, 3 H, $OCOCH_3$) 1.9–1.4 (complex pattern with major peaks at 1.78, 1.72, 1.60, 1.52, 7 H), 1.25 (s, 3 H, $-CCH_3$), 1.20 (doublet with down-field half obscured by the methyl peak, 1 H, J = 8 Hz, C-7 proton), 0.83 (doublet with fine splitting, 1 H, J = 8 Hz, C-2 proton).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.20; H, 8.93.

***anti*-7-Methyl-*exo*-2-hydroxynorbornyl-*syn*-7-carbinyl Acetate (47).** In a dry 10-ml flask were placed 2.00 g (12.9 mmol) of *anti*-7-methyl-*exo*-2-hydroxynorbornyl-7-carbinol (**18**), 1.33 g (13.0 mmol) of acetic anhydride, and 3.0 ml of pyridine. The homogeneous solution was allowed to stand at room temperature for 8 hr, 1 ml of ice-cold 1 *M* $NaHCO_3$ was added, and the solution was allowed to stand for 3 hr. It was then poured on ice, made just barely acidic with cold 6 *M* hydrochloric acid, and extracted three times with a total of 25 ml of diethyl ether. The combined extracts were washed once with 1 *M* sodium bicarbonate, once with water, and dried (Na_2SO_4). Removal of the solvent through a short Vigreux column gave 2.16 g of oil showing strong hydroxyl and carbonyl absorptions in its infrared spectrum. Chromatography on alumina (30 g) gave adequate separation of the mixture. Elution with 1:1 pentane and benzene gave (0.76 g) of material which was mainly the diacetate although the hydroxyl absorption in the ir became stronger in the latter fractions. Elution with benzene and ether gave 1.0 g of monoacetate as a clear, viscous oil which gave one peak at 22 min on column J at 130° and 25 psi. Unreacted diol is eluted with methanol. Although two monoacetates are possible the nmr spectrum of the monoacetate fraction indicates that it is 95% of the primary acetate: ir (neat) 3534, 3030, 1730, 1475, 1447, 1383, 1366, 1350, 1316, 1242, 1122, 1101, 1075, 1020, 998, 971 cm^{-1}; nmr (CCl_4) δ 4.33 (AB quartet, J_{AB} = 11 Hz, $\Delta\nu_{AB}$ = 5.3 Hz, 2 H, $-CCH_2OAc$), 3.9–3.6 (complex pattern with peaks at 3.85, 3.78, 3.75, 3.68, 3.63, 1 H, C*H*OH), 2.73 (broad, 1 H, $-OH$), 1.98 (s, 3 H, $OCOCH_3$), 1.95–1.56 (broad absorption with one strong peak at 1.77, 6 H), 0.997 (s, 3 H, $-CCH_3$), 1.32–0.85 (complex pattern partially obscured by methyl singlet with peaks at 1.13, 1.11, 1.03).

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.48; H, 9.19.

***anti*-7-Methyl-2-ketonorbornyl-7-carbinyl Acetate.** In a 2-l. erlenmeyer flask was placed 500 ml of glacial acetic acid, 20 ml of water, and 0.4482 g (2.27 mmol) of *anti*-7-methyl-*exo*-2-hydroxy norbornyl-7-carbinyl acetate (**47**). The solution was cooled to ice-bath temperature and a solution of 0.235 g (2.35 mmol) of

chromium trioxide in 100 ml of water was added in one portion with vigorous swirling. The reaction flask was immediately removed from the ice bath and allowed to stand at room temperature for 3 hr. The solution had turned a greenish color by this time. A mixture of 325 ml of ice water and 25 ml of methanol was added and the resulting solution was extracted three times with a total of 300 ml of pentane. The combined extracts were washed twice with 1 *M* sodium bicarbonate (second wash basic) and dried (Na_2SO_4). Removal of the solvent through a Vigreux column gave only 39.7 mg of residue. The aqueous phase was continuously extracted with pentane for 45 hr and the pentane extract was washed with water, 1 *M* $NaHCO_3$ (basic), and dried (Na_2SO_4). The solvent was removed through a short Vigreux column leaving 0.2618 g of light yellow oil whose infrared spectrum showed a very weak hydroxyl stretch and a strong carbonyl absorption. When the aqueous phase was continuously extracted for 5 additional days only 2.3 mg of additional material was obtained. The 302.5 mg of combined, extracted material was distilled bulb to bulb at 0.05–0.03 torr up to 90° giving 230 mg of white oil which was analyzed by vpc on column J at 130° and 25 psi. Under these conditions one major and one minor (9% of total) peak were seen at 21.0 and 23.0 min, respectively. The latter peak corresponds in retention time to the starting material, **47**. When the major peak was collected it solidified to a waxy solid which induced crystallization of the distilled material: ir (thin film) 3030, 1748, 1220 (broad), 1029, 769 cm^{-1} (broad); nmr (CCl_4) δ 3.96 (AB quartet, J_{AB} = 12 Hz, $\Delta\nu_{AB}$ = 9 Hz, 2 H, $-CCH_2OAc$), 2.35–1.0 (complex pattern with major peaks at 2.27, 2.12, 1.96, 1.57, 1.42, 1.04; 8 H), 1.08 (s, 3 H, $-CCH_3$).

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.49; H, 8.30.

***anti*-7-Methyl-2-ketonorbornyl-7-carbinyl *p*-Bromobenzenesulfonate (48).** To a 10-ml flask was added 0.2013 g (1.03 mmol) of *anti*-7-methyl-2-ketonorbornyl-7-carbinyl acetate in 1 ml of methanol. A solution of 0.0876 g (1.56 mmol) of potassium hydroxide in 4 ml of methanol was added whereupon the solution turned slightly yellow. The reaction mixture was heated at reflux for 2 hr and cooled to room temperature, and 87 mg of sodium bicarbonate was added before the methanol was removed at reduced pressure. The residue was taken up in diethyl ether, filtered, and concentrated and the residue distilled bulb to bulb to 0.4 torr up to 105°. A sweet smelling, waxy solid (63 mg, 40%) sublimed which gave only one peak on glpc column J (130° and 25 psi) of retention time 9.0 min: mp 175–176°; ir (KBr) 3509, 3030, 1748, complex pattern of weak, overlapping peaks from 1460 to 1111, 1105, 1064, 1026, 957, 917, 870, 847 cm^{-1}; nmr ($CDCl_3$) δ 3.57 (s, 2 H, $-CCH_2OH$), 2.40–1.0 (complex pattern with peaks at 2.30, 2.23 (O*H*), 2.13, 1.88, 1.81, 1.61, 1.55, 1.42, 1.26, 1.07), 1.12 (s, 3 H, $-CCH_3$). Standard procedure (C) was used to prepare the *p*-bromobenzenesulfonate **48** from the alcohol in up to 91.5% crude yield of material whose melting point is unchanged from that of analytically pure material; crystallized from methanol, it had mp 98.0–99.0°; ir (KBr) 3096, 2967, 1748, 1580, 1368, 1190 cm^{-1}; nmr ($CDCl_3$) δ 7.71 (s, 4 H, aromatic), 3.92 (s, slightly broadened, 2 H, $-CCH_2OBs$), 2.45–1.30 (complex pattern with peaks at 2.15, 1.95, 1.92, 1.63, 1.55, 1.42, 8 H), 1.10 (s, 3 H, $-CCH_3$).

Anal. Calcd for $C_{15}H_{17}BrO_4S$: C, 48.30; H, 4.59; Br, 21.40; S, 8.60. Found: C, 48.16; H, 4.61; Br, 21.38; S, 8.58.

1-Methyltricyclo[3.3.0.0^{3,8}]octan-4-one (49). A 50-ml flask equipped with a condenser, drying tube, and nitrogen inlet was flamed dried and cooled while flushing with dry nitrogen. A 50% dispersion of sodium hydride in mineral oil was washed well with pentane and dried under vacuum (14 torr). To the dried flask was added 210 mg (8.76 mmol) of this sodium hydride, 20 ml of 1,2-dimethoxyethane, and 926.7 mg (2.48 mmol) of *anti*-7-methyl-2-ketonorbornyl-7-carbinyl *p*-bromobenzenesulfonate (**48**) while the system was being flushed with nitrogen. The reaction vessel was placed in an oil bath at 80° and the temperature was raised rapidly to 100°. The slurry was allowed to reflux for 5 hr, cooled to room temperature, and filtered. The solid was washed carefully with wet diethyl ether and very little reaction was observed. Most of the solvent was removed at aspirator vacuum through a short Vigreux column leaving 428.3 mg of yellow oil. This material was distilled bulb to bulb giving 287.1 mg of clear, colorless liquid with a strong camphorlike odor which tended to crystallize. There was 74.8 mg of nonvolatile residue. The volatile material sublimed rapidly at 14 torr at room temperature and distilled at *ca.* 75° (14 torr). The distilled material was further purified by preparative glpc on column J at 100° and 10 psi under which conditions it was separated from a slightly higher retention time component amounting to 3.4%. The yield of purified material was 82%. The ketone had a retention time of 22.4 min on capillary vpc column B (110° and 50 psi). It also showed one sharp peak at 26.5 min on column H at 117° and 60 psi. It had mp 79.0–80.0° in a sealed tube. It shrank and sublimed rapidly in the vicinity of its melting point: ir (thin film) 2941, 1751, 1466, 1445, 1383, 1335, 1297, 1149, 1126, 1041, 1017, 840, 818, 775, 760 cm^{-1}; nmr (CCl_4) δ 2.71 (t, 1 H, J = 2.8 Hz), 2.38 (broad, 1 H), 2.38–1.22 (complex pattern with major peaks at 2.13, 2.10, 2.06, 2.02, 1.93, 1.90, 1.88, 1.78, 1.65, 1.49, 7 H), 1.18 (s, 3 H, $-CCH_3$), 0.85 (s, 0.15 H, may be an impurity).

***exo*- and *endo*-1-Methyltricyclo[3.3.0.0^{3,8}]octan-4-ols (46-OH and 45-OH).** Lithium aluminum hydride reduction of 1-methyltricyclo[3.3.0.0^{3,8}]octan-4-one (**49**) using standard procedure A gave a mixture of two sweet-smelling alcohols in 95.6% yield. Vpc analysis on column B at 117 and 50 psi showed the presence of two components with retention times of 30.1 min (84%) and 34.9 min (16%). The mixture gave one sharp peak on column H (115°, 60 psi) at 48 min, but was well resolved and could be preparatively separated on column D (135°, 60 psi), the minor component eluting in 65 min, the major in 75 min, and a trace component at 85 min. The column pressure was reduced to 20 psi during collection. Both alcohols sublimed rapidly at atmospheric pressure and room temperature. The major alcohol had the following properties: mp 109.0–109.5° (sealed tube, shrinks prior to melting); ir (KBr) 3311, 2933, 2857, 1449, 1351, 1332, 1311, 1297, 1274, 1093, 1052, 1024, 1010 cm^{-1}; nmr (CCl_4) δ 4.06 (doublet with fine coupling, 1 H, J = 7.0 Hz, C*H*OH), 2.3–1.15 (complex pattern with peaks at 2.22, 1.88, 1.60, 1.55, 1.52, 1.49, 1.35, 1.29; 10 H), 1.09 (s, 3 H, $-CCH_3$).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.97; H, 10.21.

The minor alcohol from the lithium aluminum hydride reduction had the following properties: mp 85.0–86.0°; ir (thin film) 3333, 2941, 2857, 1449, 1370, 1096, 1058, 1011, 955 cm^{-1}; nmr (CCl_4) δ 3.74 (broadened doublet, J = 2.3 Hz, C*H*OH), 2.70–0.99 (complex pattern with peaks at 2.48, 2.35, 2.31, 2.04, 1.92, 1.49, 1.03, 0.99, 10 H), 1.08 (s, 3 H, $-CCH_3$).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.09; H, 10.23.

Standard procedure (B-2) was used to convert 38.8 mg of the mixture of alcohols described above to the corresponding acetates. Vpc analysis on capillary column B (110°, 50 psi) showed two peaks at 22.9 min (15%) and 24.0 min (85%). Both of these peaks correspond in retention time to product peaks in the acetolysis mixture obtained from 3-norbornene-*anti*-7-methyl-*syn*-7-carbinyl *p*-bromobenzenesulfonate (**13**-OBs), the major corresponding to the 14.5% component and the minor to the 6.70% component. The two acetates could be separated on vpc column D (135°, 60 psi). The major and minor acetates had retention times of 62 and 58 min, respectively, and were completely separated only for very small injection samples. The major acetate was obtained pure: ir (neat) 2950, 2865, 1733, 1466, 1379, 1362, 1314, 1247, 1085, 1047, 1029 cm^{-1}; nmr (CCl_4) δ 4.80 (doublet with fine splitting, 1 H, J = 7 Hz, C*H*OAc), 2.50–1.30 (complex pattern with peaks at 2.38, 2.25, 2.15, 1.90, 1.68, 1.59, 1.43, 9 H), 1.97 (s, 3 w, acetate), 1.10 (s, 3 H, $-CCH_3$).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.23; H, 8.98.

The *p*-toluenesulfonate of the major alcohol was obtained in quantitative yield using standard procedure C. The product was a clear oil which could not be obtained crystalline: ir (neat) 2950, 2865, 1597, 1449, 1355, 1190, 1176, 1099, 966, 901, 870, 812, 729, 665 cm^{-1}; nmr (CCl_4) δ 7.50 (A_2B_2, 4 H, J_{AB} = 8.5 Hz, ν_{AB} = 20.6 Hz, aromatic), 4.65 (doublet with small extra coupling, 1 H, J = 7 Hz, C*H*OTs), 2.42 (s, 3 H, tosyl methyl), 2.20–1.16 (complex pattern with major peaks at 2.38, 2.00, 1.90, 1.72, 1.56, 1.51, 1.43, 1.36, 1.31, 1.25, 1.19, 9 H), 1.05 (s, 3 H, $-CCH_3$).

Acetolyses of the 7-methylnorborn-2-enyl-7-carbinyl *p*-bromobenzenesulfonates (12-OBs and 13-OBs) were carried out in the usual manner.[2a] Analyses of the products were achieved with column B (100°, 50 psi). The results are given in Table I.

Acetolysis of the *p*-Toluenesulfonate of the Major Alcohol Obtained from the Lithium Aluminum Hydride Reduction of 1-Methyltricyclo[3.3.0.0^{3,8}]octan-7-one (49). In a dry 5-ml flask was placed 64.0 mg (0.218 mmol) of the *p*-toluenesulfonate of the major alcohol (probably **45**-OBs) from the lithium aluminum hydride reduction of 1-methyltricyclo[3.3.0.0^{3,8}]octan-4-one (**49**), 22.4 mg (0.273 mmol) of anhydrous sodium acetate, and 1.09 ml of dry acetic acid. It should be noted that these concentrations were unintentionally

ten times greater than those in the other acetolyses reported in this work. A condenser fitted with a mercury trap to exclude the atmosphere was added, the system was flushed with nitrogen and the flask placed in an oil bath at 50° for 18.3 hr. The slightly yellow solution was diluted with aqueous saturated sodium chloride and extracted three times with a total of 20 ml of pentane. The combined extracts were washed once with 1 *M* $NaHCO_3$, dried (Na_2SO_4), and the solvent removed carefully through a short Vigreux column. The 43.5 mg of light yellow oil which remained showed a very weak ir absorption at 1176 cm^{-1} which may be due to a trace of unreacted *p*-toluenesulfonate. Vpc analysis on capillary column B (110°, 50 psi) indicated the presence of five components in the acetate region and less than 8% of two olefins. The acetates correspond in retention times to the five acetates (A, B, C, D, E, Table I) observed in the acetolysis of **13**-OBs that are not observed in the acetolysis of **12**-OBs. The amount of each, in order of their elution, was calculated to be A, 9.9%; B, 22.5%; C, too poorly resolved; D, 39.3%; E, 28.7%. The ratio of D to E is 1.3 from **13**-OBs and 1.4 from **45**-OBs. The ratio of E to A is 2.7 from **13**-OBs and 2.9 from **45**-OBs.

Preparative Separation of the Products of the 120° Acetolysis of 13-OBs. The acetolysis of 2-norbornene-*anti*-7-methyl-*syn*-7-carbinyl *p*-bromobenzenesulfonate (**13**-OBs) gives five compounds not found in the acetolysis of the *anti* isomer (**12**-OBs) as shown in Table I. This separation was undertaken in an attempt to elucidate the structures of these compounds. The components of this mixture were partially achieved on preparative glpc column D (120°, 50 psi). Component D (Table I) was obtained pure, and its nmr and ir spectra corresponded to those of the tricyclic acetate obtained from the major alcohol (probably **45**-OH) produced in the lithium aluminum hydride reduction of ketone **49**. Components B and C were not separable under these conditions, but the nmr and ir spectra of the mixture are very much like those of D suggesting tricyclic rearrangement products similar to D. The ir and nmr spectra of component A suggested that it was also tricyclic, but the nmr spectrum obtained was rather weak due to the small material available.

Kinetics of the Acetolysis of 13-OBs, 12-OBs, and 50-OBs at 120.43 ± 0.03°. The acetic acid used in this work was prepared by allowing glacial acetic acid to reflux with an added 1% acetic anhydride for 18 hr and then distilling, taking the middle fraction and adding 1% acetic anhydride. A standard 0.02483 *M* sodium acetate in acetic acid solution was prepared and used for all the kinetic runs reported here. In typical run, 0.1882 g of **13**-OBs was placed in a volumetric flask calibrated to hold 24.885 ml, and the flask was filled with the standard 0.02483 *M* sodium acetate in acetic acid solution. This gives a solution that is 0.02107 *M* in the *p*-bromobenzenesulfonate. Approximately 2.5 ml of this solution was sealed in each of nine ampoules. The ampoules were placed in a constant-temperature bath at 120.43 ± 0.03° and the zero-time sample was removed in 20 min and placed briefly in an ice bath. The ampoule was opened when at room temperature and a pipet, calibrated to deliver 1.9914 ± 0.0008 ml, was used to withdraw the sample. Two drops of bromophenol blue indicator were added and the yellow solution was titrated to a colorless end point with the 0.01685 *M* perchloric acid solution. Samples were removed and titrated over a period of 8 hr and an infinity sample was removed and titrated after 20 hr. The data were treated in the standard manner for first-order reactions using the graphic form of the equation

$$\log \frac{V_0 - V_\infty}{V_t - V_\infty} = \frac{k}{2.303} t$$

where V_0, and V_∞, and V_t are volumes of titrant required for the samples taken at times zero, infinity and time "t," respectively, and k is the unimolecular rate constant in units of reciprocal time. The left side of this expression was plotted *vs.* time and the slope of the resulting straight line, multiplied by 2.303, gave the value of k. For compounds **13**-OBs and **12**-OBs good first-order plots were obtained to and beyond 3 half-lives. The value of k for compound **50**-OBs was calculated directly from the above equation from data obtained early in the acetolysis using the theoretical infinity titer because the samples became too colored to titrate after 2.5 hr. The infinity sample for **13**-OBs was slightly yellow and deviated from theory by 4% but the infinity sample for **12**-OBs was uncolored and within 1.6% of theoretical. The results are given in Table II.

Preparation and Acetolysis of 1-Methyltricyclo[3.2.1$0^{2,7}$]octan-*exo*-6-yl *p*-Toluenesulfonate (27-OTs). To a solution of 42.7 mg (0.308 mmol) of 1-methyltricyclo[3.2.1.$0^{2,7}$]octan-*exo*-6-ol alcohol (**27**-OH) in 0.7 ml of dry pyridine at 0° was added with stirring 99 mg (0.52 mmol) of *p*-toluenesulfonyl chloride in an additional 0.7 ml of dry pyridine. The reaction mixture was placed in a refrigerator at *ca.* 5° for 26 hr. One attempt to isolate this *p*-toluenesulfonate using the standard work-up, with extra precautions being taken to keep the solutions cold during work-up, gave a negligible amount of product, so in this run half of the still-cold reaction mixture was added without further manipulation to 4 ml of solid glacial acetic acid at *ca.* 5°. The reaction vessel was quickly warmed to 25° in a water bath and the clear, colorless solution was stirred at 25° for 15.5 hr. Addition of 10 ml of water was followed by five extractions with 6-ml portions of pentane. The combined extracts were washed twice with 1 *M* sodium carbonate solution (both washes basic), once with saturated sodium chloride solution, and dried (Na_2SO_4). Most of the solvent was removed carefully through a short Vigreux column and the residue, which contained a small amount of pyridine, was analyzed on capillary vpc columns A and B.

Glacial Acetic Acid Deamination of 2-Norbornenyl-*anti*-7-methyl-*syn*-7-carbinylamine (13-NH_2) and 2-Norbornenyl-*syn*-7-methyl-*anti*-7-carbinylamine (12-NH_2). A dry, 25-ml three-necked flask was flushed with nitrogen while 40.6 mg (0.296 mmol) of freshly distilled 2-norbornenyl-*anti*-7-methyl-*syn*-7-carbinylamine (**13**-NH_2) was washed in with 1.5 ml of dry acetic acid. The flask was equipped with a drying tube and nitrogen inlet. While stirring with a small magnetic stirrer, 53.2 mg (0.770 mmol) of sodium nitrite was added in small portions over a period of 4 hr. The solution became cloudy in *ca.* 2 hr and was stirred an additional 19 hr. The addition of 8 ml of saturated sodium chloride solution was followed by three extractions with a total of 20 ml of pentane. The combined pentane extracts were washed once with 1 *M* sodium bicarbonate (the wash was basic), once with saturated sodium chloride solution, and dried (Na_2SO_4). The solvent was removed carefully through a short Vigreux column giving 58 mg of yellow oil which was analyzed on capillary vpc columns A and B. The results are given in Table V.

In the same manner 33.8 mg of **12**-NH_2 was deaminated giving 62 mg (some solvent left) of slightly yellow oil which was analyzed on capillary vpc columns A and B. The results are given in Table V.

Control experiments were carried out in which each of the acetate products in the first column of Table V was resubjected to the above deamination conditions. In the controls, only the amine was omitted from the reaction mixture. In each case, the original acetate was recovered unchanged in high yield.