# ORGANIC REACTION MECHANISMS · 1968

*An annual survey covering the literature dated December* 1967 *through November* 1968

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Edited by

**B. CAPON** University of Glasgow

**C. W. REES** University of Leicester

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# Preface

This fourth volume of the series is a survey of the work on organic reaction mechanisms published in 1968. For convenience, the literature dated from December 1967 to November 1968, inclusive, was actually covered. The principal aim has again been to scan all the chemical literature and to summarize the progress of work on organic reaction mechanism generally and fairly uniformly, and not just on selected topics. Therefore, certain of the sections are somewhat fragmentary and all are concise. Of the 3500 papers which have been reported, those which seemed at the time to be more significant are normally described and discussed, and the remainder are listed.

Our other major aim, second only to the comprehensive coverage, has been early publication since we felt that the immediate value of such a survey as this, that of "current awareness", would diminish rapidly with time. In this way we have been fortunate to have the expert cooperation of the English office of John Wiley and Sons.

To improve the scope and speed of coverage of the increasing volume of literature on reaction mechanisms we decided, this year, to enlist several new authors. We have been very fortunate in the expert and enthusiastic colleagues who have joined us, and are particularly grateful to them all for meeting our demanding deadlines. We are also grateful to Dr. M. J. Perkins who, whilst not wanting any further editorial responsibility, kindly agreed to continue as a contributor.

The organization of the earlier volumes has been retained, though there are more sub-headings and the subject index, which is cumulative, has been enlarged. We welcome suggestions for improvement in future volumes.

We thank Mr. D. L. Forster and Miss Angela Williams for their tireless help, especially with the indexes.

April 1969

B.C.
C.W.R.

# Contents

CHAPTER 1

# Carbonium Ions[1]

B. Capon

*Chemistry Department, The University, Glasgow*

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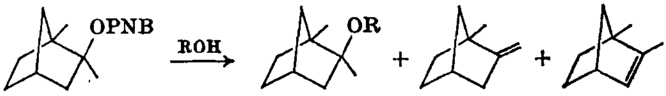
## Bicyclic Systems

*Derivatives of norbornane and related compounds.* Goering and Humski have shown that methanolysis and hydrolysis in aqueous acetone of optically active 1,2-dimethyl-*exo*-2-norbornyl *p*-nitrobenzoate (**1a**) yields optically active products. The hydrolysis yields the *exo*-alcohol with 9% and the exocyclic olefin (**1b**) with 63% retention of optical activity, and the methanolysis yields the *exo*-methyl ether and (**1b**) with 8 and 60% retention respectively.



**(1a)** **(1b)**

| | | | |
|---|---|---|---|
| R = H | **11** | **35** | **54%** |
| R = Me | **37** | **26** | **37%** |

Possibly the olefin is formed from an asymmetric ion pair and racemization competes with solvent capture, or alternatively a separate elimination reaction

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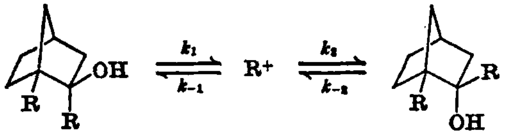
[1] (a) G. A. Olah and P. von R. Schleyer (Ed.), *Carbonium Ions*, Vol. 1, John Wiley, New York, 1968, (b) J. A. Berson, "Memory Effects and Stereochemistry in Multiple Carbonium Ion Rearrangements", *Angew. Chem. Intern. Ed. Engl.*, 7, 779 (1968), (c) W. Hückel, "Kryptionen-Reaktionen", *Ann. Chem.*, **711**, 1 (1968), (d) W. Hückel, "Die Entwicklung der Hypothese von Nichtklassischen Ion", *Sitzungberichte Heidelberger Akad. Wiss.*, **1967/68**, 291.

is superimposed on the carbonium ion process. These interpretations would mean respectively that at least 60 or 10% of the ionization is unassisted.[2]

In a complementary investigation Goering, Brown and Schwene have determined the rate and equilibrium constants for the acid-catalysed interconversion of the norbornanols and the 1,2-dimethyl-norbornanols in aqueous dioxan (equation 1).[3] The experimentally determined constants for the



(1)

***exo*-R$_s$OH, R = H**
***exo*-R$_t$OH, R = Me**

***endo*-R$_s$OH, R = H**
***endo*-R$_t$OH, R = Me**

processes defined in equations (2) and (3) are related to the constants of equation (1) as follows:

$$\text{active } exo\text{-ROH} \xrightarrow{k_\alpha} \text{inactive products} \tag{2}$$

$$exo\text{-ROH} \underset{k_{1\text{-}endo}}{\overset{k_{1\text{-}exo}}{\rightleftharpoons}} endo\text{-ROH}(K_{eq} = k_{1\text{-}exo}/k_{1\text{-}endo}) \tag{3}$$

$$k_\alpha = k_1;\ k_\alpha/k_{1\text{-}exo} = (k_{-1}/k_{-2}) + 1;\ \text{and } (k_{-1}/k_{-2})\,K_{\text{eq}} = k_1/k_2.$$

The temperature variation of $k_1$, $k_2$, $k_{-1}/k_{-2}$, and $K_{\text{eq}}$ were determined and the Arrhenius energies of activation and the standard enthalpy changes, plotted in Figure 1, determined. The differences in the energies of activation for ionization of the norbornanols is about 3.5 kcal greater than that for the ionization of the 1,2-dimethylnorbornanols. This was attributed to $\sigma$-delocalization in the transition state for ionization of *exo*-norbornanol, and since torsional effects[4] may be more important in the tertiary than in the secondary system (see ref. 3 below however) this figure sets a lower limit. When a diagram corresponding to Figure 1 is constructed using free energies of activation, the secondary and tertiary *exo-endo* transition state differences are much closer (within ca. 1 kcal). The conclusions to be drawn from references 2 and 3 therefore seem to be that $\sigma$-delocalization is not a significant factor in determining the *exo*:*endo* rate ratio for the ionization of 1,2-dimethylnorbornyl derivatives; that analysis of the equilibria and rate data for the interconversion of the alcohols in terms of Arrhenius energies of activation suggests that a sub-

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[2] H. Goering and K. Humski, *J. Am. Chem. Soc.*, **90**, 6213 (1968).

[3] H. L. Goering, C. Brown and C. B. Schewene, *J. Am. Chem. Soc.*, **90**, 6214 (1968).

[4] See *Organic Reaction Mechanisms*, **1967**, 1.

stantial part, but probably not all, of the greater rate of ionization of *exo*- over *endo*-2-norbornanol results from σ-participation, but that analysis in terms of free energies of activation suggests that the contribution of σ-participation is relatively small. The problem therefore is to decide which analysis is correct.

Brown and Rei[5] have carried out a similar analysis in terms of free energies of activation for the solvolyses in aqueous dioxan of the 1,2-dimethylnorbornyl *p*-nitrobenzoates (using the equilibrium constant for the alcohols). The difference in the free-energy levels of the transition states for ionization of the *exo*- and *endo*-isomers is 4.2 kcal, similar to that for the ionization of the norbornanols and of the norbornyl acetates in acetic acid (5.5 kcal).[6] These results therefore suggest that, if these systems are comparable, there is negligible σ-participation in the reactions of the *exo*-norbornyl derivatives. Torsional effects appear to be unimportant in causing the rate of solvolysis of 2-methyl-*endo*-2-norbornyl *p*-nitrobenzoate to be slow, because this compound reacts more slowly than 1,2-dimethyl-*endo*-2-norbornyl *p*-nitrobenzoate. If a torsional effect,[4] resulting from a decreased dihedral angle between the *exo*-2- and 1-substituents in the transition state were important, it should be larger when they are both methyl.

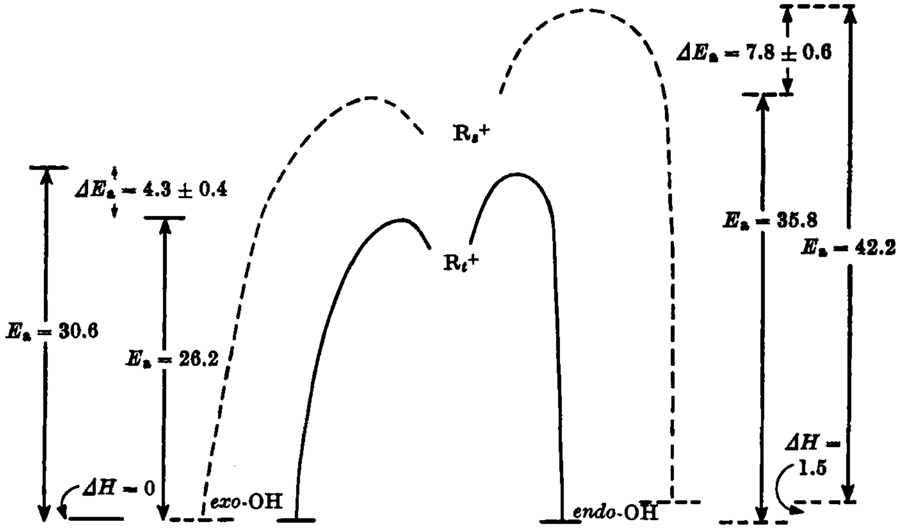

**Figure 1. Energy diagrams for acid-catalysed equilibration of norbornanol (dashed lines) and 1,2-dimethylnorbornanol (solid lines).**

Complementary to the work reported last year on the pinanyl → bornyl

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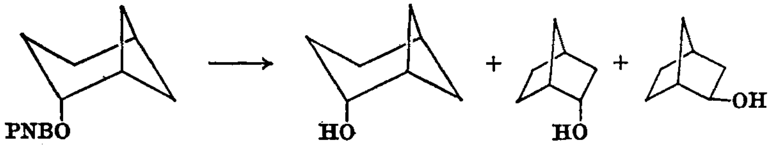
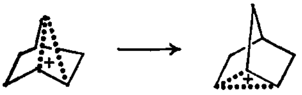
[5] H. C. Brown and M.-H. Rei, *J. Am. Chem. Soc.*, **90**, 6216 (1968).

[6] See *Organic Reaction Mechanisms*, **1965**, 14.

rearrangement,[7a] an investigation of the norpinanyl → norbornyl rearrangement has now been reported. The reaction of norpinan-2-ol with toluene-*p*-sulphonyl chloride yields *endo*-norborn-2-yl toluene-*p*-sulphonate. The solvolysis of norpinan-2-yl *p*-nitrobenzoate (**2a**) in aqueous acetone yields, after 30% conversion, a mixture consisting of 3.5% norpinan-2-ol, 34% *endo*-norbornan-2-ol and 62.5% *exo*-norbornan-2-ol. The unsolvolysed *p*-nitrobenzoate contains substantial quantities of *endo*-norborn-2-yl *p*-nitrobenzoate and some *exo*-norborn-2-yl *p*-nitrobenzoate. Decomposition of the norpinan-2-yl diazonium ion generated by the photolysis of norpinan-2-one toluene-*p*-sulphonylhydrazone also yielded a mixture of norpinanyl, and *exo*- and *endo*-norbornyl derivatives. The proportion of *exo*-norbornyl derivative was higher in the less nucleophilic solvent trifluoroethanol than in EtOH. When the reaction was carried out in a mixture of $D_2O$–DONa–dimethoxyethane the *endo*-norbornanol contained deuterium only at position 1, but in the *exo*-norbornanol the deuterium was scrambled equally between positions 1 and 2. These results suggest that the *exo*-norbornyl derivatives are formed from a non-classical norbornyl cation (**2c**), but that this is preceded by another non-classical ion (**2b**) with a strong tendency to react from the *endo* direction. The results are not compatible with just one non-classical norbornyl cation being an intermediate.[7b]



(**2a**)



(**2b**) (**2c**)

Collins and Lietzke have made an interesting analysis of Roberts, Lee, and their coworkers' isotopic labelling experiments on the solvolysis of norbornyl and cyclopent-3-enyl arenesulphonates.[7c] The $^{14}C$-labelling experiments on the formolysis of 2-*exo*-norbornyl *p*-bromobenzenesulphonate indicate that the rate constant for the 3,2-hydride shift is about 10 times slower than that for the 6,2-hydride shift. The $^{14}C$-labelling experiments with 2-(cyclopent-3′-enyl)-[2-$^{14}C$]ethyl *p*-nitrobenzenesulphonate (**3**)[8] were also discussed. The occur-

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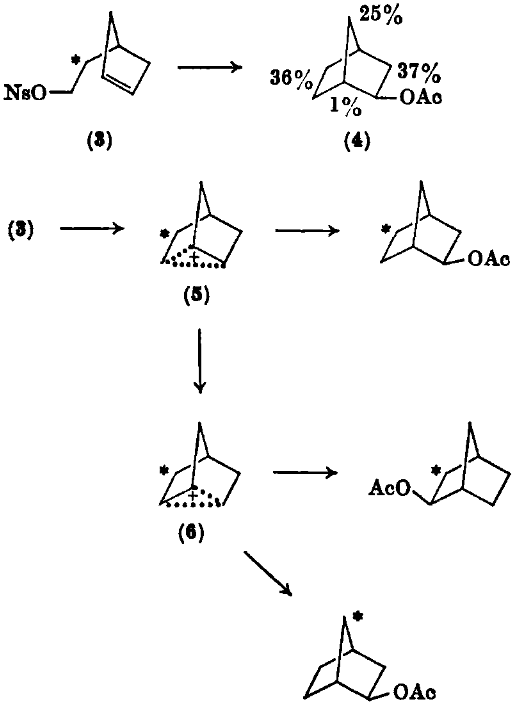
[7a] See *Organic Reaction Mechanisms*, **1967**, 2.

[7b] W. Kirmse and R. Siegfried, *J. Am. Chem. Soc.*, **90**, 6564 (1968).

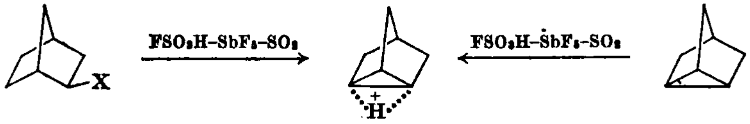
[7c] C. J. Collins and M. H. Lietzke, *J. Am. Chem. Soc.*, **89**, 6565 (1967).

[8] See *Organic Reaction Mechanisms*, **1966**, 28.

rence of more label at $C_{(3)}$ and $C_{(5)}$ than at $C_{(7)}$ of the norbornyl acetate (**4**) formed from (**3**) indicates that non-classical ions (**5**) and (**6**) cannot be the sole product-forming intermediates.



The species obtained on dissolving *exo*-norbornyl halides in strongly acidic solvents like $FSO_3H–SbF_5–SO_2$ is not a 2-norbornyl cation but a protonated nortricylene (**7**). This was indicated by the Raman spectrum which is very



(**7**)

similar to that of nortricyclyl derivatives but different from norbornyl ones. The same species could be generated by dissolving nortricyclene in $FSO_3H–SbF_5–SO_2$ at –80°. The NMR spectrum is also consistent with this structure. It consists of signals at $\delta = 5.2$ (4 protons), 3.1 (1 proton), and 2.1

(6 protons) which were ascribed respectively to the 4 equivalent protons attached to the cyclopropane ring, the bridgehead proton and the 6 methylene protons. When nortricyclene was dissolved in $FSO_3D$–$SbF_5$–$SO_2$ at −78° a similar spectrum was obtained, except that the signal at $\delta = 5.2$ corresponded to only 3.1 protons. The protonated cyclopropane was considered to be an edge-protonated species with the 4 protons equivalent on the NMR time scale through scrambling round the ring by way of a "corner protonated transition state". This equivalence could also be achieved by interconversion with a small concentration of norbornyl cation which undergoes a Wagner–Meerwein shift but not a 2,3-hydride shift. When the ion is quenched in pyridine the major identifiable product is nortricyclene.[9]

Details of Schaefer and Weinberg's measurement of the secondary deuterium isotope effect of the polarimetric rate constant for the solvolysis of *exo*-[3,3-$^2H_2$] norbornyl bromide in aqueous acetic acid have been reported. The value $k(H)/k(D) = 1.04$ per deuterium is strikingly different from that for the solvolysis of the *endo*-isomer, 1.16 per deuterium, and is similar to that obtained in $S_N2$ reactions. This supports the view that there is participation by the 1,6-bonding electrons, but the observation that 7,7-deuteration causes no isotope effect suggests that there cannot be very much delocalization in the transition state. The value of 1.16 for the *endo*-compound and the value of 1.28 for the $\alpha$-isotope effect on solvolysis of [2-$^2H$]*endo*-norbornyl bromide suggest that here there is a high degree of bond breaking in the transition state. This is in accord with the view that departure of the bromine is sterically hindered and that the transition state is not reached "until a larger-than-normal degree of bond breaking has occurred".[10] Similar results have been reported for the acetolysis of the [3,3-$^2H_2$]norbornyl toluene-*p*-sulphonates; $k(H)/k(D)$ for the *exo*-isomer was 1.014 and for the *endo*-isomer was 1.26.[11]

In contrast to these results the isotope effects for the solvolysis of [3,3-$^2H_2$]-2-phenylnorborn-2-*exo*-yl and -2-*endo*-yl *p*-nitrobenzoate in 60% aqueous acetone are $1.18 \pm 0.02$ and $1.15 \pm 0.02$ at 35° respectively. This is consistent with the view that these compounds react by similar mechanisms and that the much greater rate for the *exo*-isomer does not result from participation. These results also of course lend support to the view that the different isotope effects obtained with the *exo*- and *endo*-norbornyl compounds are the result of different mechanisms.[12]

Similar isotope effects were also found for the solvolysis in aqueous acetone of [3,3-$^2H_2$]-2-methylnorborn-2-*exo*-yl and -2-*endo*-yl *p*-nitrobenzoate

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[9] G. A. Olah, A. Commeyras and C. Y. Lui, *J. Am. Chem. Soc.*, **90**, 3882 (1968); see *Organic Reaction Mechanisms*, **1965**, 23—25; **1966**, 12.

[10] J. P. Schaefer, M. J. Dagani, and D. S. Weinberg, *J. Am. Chem. Soc.*, **89**, 6938 (1967); see *Organic Reaction Mechanisms*, **1965**, 21.

[11] J. M. Jerkunica, S. Borčić and D. E. Sunko, *Chem. Comm.*, **1967**, 1302.

[12] J. P. Schaefer, J. P. Foster, M. J. Dagani and L. M. Honig, *J. Am. Chem. Soc.*, **90**, 4497 (1968).

[$k$(H)/$k$(D) = 1.334 and 1.306 respectively]. An intermediate value (1.162) was obtained for the acetolysis of 1,7,7-trimethyl[3,3-$^2H_2$]norborn-*exo*-2-yl toluene-*p*-sulphonate (isobornyl toluene-*p*-sulphonate).[13a] The isotope effect for the solvolysis of 2-[$^2H_3$]methylnorborn-*exo*-2-yl chloride in aqueous EtOH is 1.22 at 25°, very similar to that found with 1-methylcyclohexyl and 1-methylcyclopentyl chloride.[13b]

Brown and Takeuchi have reported several striking examples of solvolyses of *t*-norbornyl derivatives which show high *exo*:*endo* rate ratios not ascribable to participation by the 1,6-electrons in the reactions of the *exo*-compounds. Thus, 2-*p*-anisyl-*exo*-norbornyl chloride is ethanolysed $5 \times 10^{11}$ times faster than *exo*-norbornyl chloride. It therefore seems likely that the introduction of a 2-*p*-anisyl-substituent must eliminate participation, especially as it has been shown that the much more effective participation found in the solvolysis of *anti*-7-norbornenyl derivatives is absent in reactions of 7-*p*-anisyl-*anti*-7-norbornenyl derivatives (see p. 30). Nevertheless 2-*p*-anisyl-*exo*-norbornyl *p*-nitrobenzoate is hydrolysed 284 times faster than its *endo*-isomer in 80% aqueous acetone at 25°. This *exo*:*endo* rate ratio, similar to that for the acetolysis of the norbornyl toluene-*p*-sulphonates, cannot arise from participation, and steric and/or torsional effects are a likely cause.[14] It is altered only slightly on going to the 2-phenyl-, 2-*p*-trifluoromethylphenyl-, and 2-*p*-nitrophenyl-norbornyl *p*-nitrobenzoates, and since steric and torsional effects presumably remain constant, there can also be no participation in the reactions of the *exo*-isomers of these compounds. The 2-*p*-nitrophenylnorbornyl compounds react at similar rates to the 2-methylnorbornyl *p*-nitrobenzoates,[15] and the *exo*:*endo* rate ratios are similar (2-*p*-nitrophenyl, 114; 2-methyl, 180). The electronic demands in the reactions of the 2-methyl compounds must be approximately the same as those in the reactions of the 2-*p*-nitrophenyl compounds, and it seems unlikely that participation is an important factor contributing to the observed *exo*:*endo* rate ratio.[16]

Even more striking results were obtained with the 2-*p*-anisyl-3,3-dimethylnorbornyl compounds (2-*p*-anisylcamphenylyl) as the *exo*-*p*-nitrobenzoate was hydrolysed 44,000 times faster than its *endo*-isomer. Here the introduction of the 3,3-dimethyl substituents has little effect on the rate for the *exo*-isomer but a 147-fold rate-decreasing effect with the *endo*-isomer.[17] This effect is significantly larger than that found on introducing 3,3-dimethyl substituents into norbornyl toluene-*p*-sulphonate, when there is about a 9-fold decrease in

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[13a] J. M. Jerkunica, S. Borčić and D. E. Sunko, *Chem. Comm.*, **1968**, 1488.

[13b] K. L. Servis, S. Borčić and D. E. Sunko, *Tetrahedron*, **24**, 1247 (1968).

[14] H. C. Brown and K. Takeuchi, *J. Am. Chem. Soc.*, **90**, 2691 (1968).

[15] See *Organic Reaction Mechanisms*, **1965**, 9.

[16] K. Takeuchi and H. C. Brown, *J. Am. Chem. Soc.*, **90**, 2693.

[17] H. C. Brown and K. Takeuchi, *J. Am. Chem. Soc.*, **90**, 5268, 5270 (1968).

the rate of acetolysis.[18] The one factor which has not been fully explored to account for the *exo*:*endo* rate differences with 2-arylnorbornyl derivatives is steric inhibition of resonance. All the results could be explained if an *exo*-2-aryl substituent were unable to conjugate as well as an *endo* one with the developing cationic centre in the transition state. In the solvolysis of 2-*p*-methoxy-

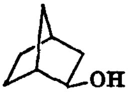
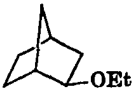
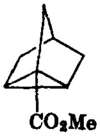
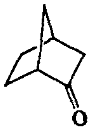
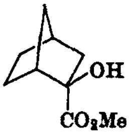
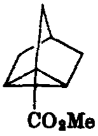
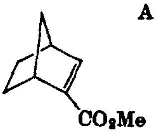
| 1-Substituent | Relative Rate at 25° | Product | | | |
|---|---|---|---|---|---|
| H | 1 |  |  | | |
| $CO_2Me$ | $4.9 \times 10^{-4}$ |  <br>38% |  <br>8.6% |  <br>4.4%<br>(8) |  <br>9.4% |
| $OCOCH_3$ | $2.4 \times 10^{-3}$ |  <br>(9) | | | |
| NHCOPh | 1.1 | (9) | | | |
| $NH_2$ | 46 | (9) | | | |
| $CO_2^-$ | 4.0 |  <br>35% |  <br>45% |  <br>11% | |
| | |  <br>7% |  <br>2% | After treatment with diazomethane | |

Figure 2.

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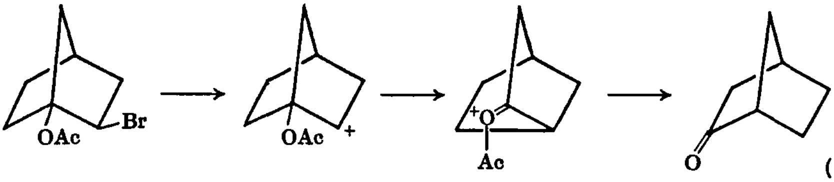
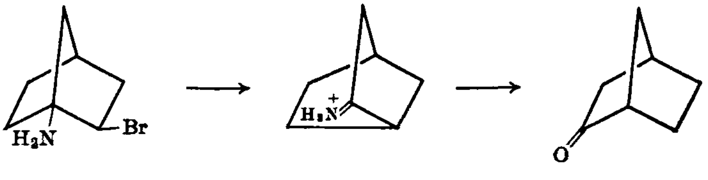
[18] See J. A. Berson, in *Molecular Rearrangements* (Ed. P. de Mayo), Interscience Publishers, 1963, part 1, p. 177.

phenylnorborn-2-*exo*-yl derivatives the 2-*p*-methoxyphenyl group decreases the free energy of activation by ca. 16 kcal mole$^{-1}$. To account for all the 4.4 × 10$^{4}$-fold slower rate of solvolysis of *endo*-compared to *exo*-2-*p*-anisyl-3,3-dimethylnorbornyl *p*-nitrobenzoate in terms of steric inhibition of resonance, it would be necessary to say that the *exo*-2-*p*-methoxyphenyl group provides 5.2 kcal mole$^{-1}$ less stabilization in the transition state than an *endo*-one. It is difficult to decide just how reasonable this is, but experiments with 2-(2′,6′-dimethylphenyl) norbornyl compounds would probably provide the answer.

An interesting investigation of the solvolysis in 80% aqueous EtOH of 1-substituted *exo*-2-norbornyl bromides has been reported by Wilt and Wagner (see Figure 2). The 1-methoxycarbonyl compound reacts very slowly and it was suggested that there was no participation by the 1,6 $\sigma$ electrons. A classical ion, which yielded substitution products solely by *exo*-attack, was postulated as an intermediate. The high proportion of nortricyclyl derivative (**8**) was attributed to conjugation between the developing cyclopropane ring and the carbonyl group in the transition state for proton loss from position 6 of this classical ion. The 1-acetoxy compound was also thought to react without participation, but here the initially formed classical ion must rearrange (equation 4a). A similar rearrangement occurs with the 1-benzamido and 1-amino compounds, but the higher rates of reaction suggest that the rearrangement may be concerted with ionization (e.g. equation 4b). It was suggested that the relatively small rate increase observed with the 1-amino group may result from steric inhibition of the overlap of the nitrogen lone-pair orbital with the developing *p* orbital at $C_{(1)}$. The 2-carboxy compound may also react with participation.[19a]



(4a)



(4b)

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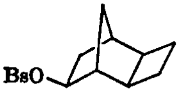
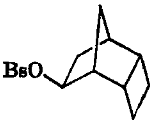
[19a] J. W. Wilt and W. J. Wagner, *J. Am. Chem. Soc.*, **90**, 6135 (1968).

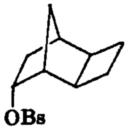
Acetolysis of (**10a**), (**10b**) and (**10c**) all yield the *exo-exo* acetate (**10d**). The *exo-endo* *p*-bromobenzene sulphonate (**10b**) is converted into the *exo-exo* isomer (**10a**) prior to acetolysis.[19b]



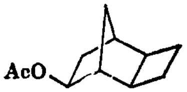
(**10a**)



(**10b**)

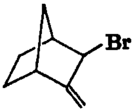


(**10c**)



(**10d**)

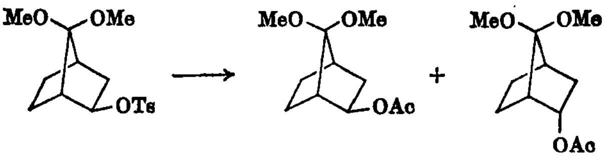
Treatment of *exo*-3-bromo-2-methylenenorbornane (**11a**) with silver acetate in 50% aqueous acetone gave a mixture of *exo*-3-hydroxy-2-methylenenorbornane, 2-hydroxymethylnorbornane, and their acetates. No *endo*-C$_{(3)}$-product was obtained. Reaction presumably proceeds via ion (**11b**) which is not bridged. Therefore exclusive *exo*-attack on a non-equilibrating unbridged 2-norbornyl cation is possible (see pp. 279, 280).[20]



(**11a**)

(**11b**)

Gassman and Marshall have extended their investigation of the acetolysis of the 2-toluene-*p*-sulphonoxy-bicyclo[2.2.1]heptan-7-ones[21] to the corresponding dimethyl acetals. The *endo*-isomer reacts with neighbouring group participation by a methoxyl group (see p. 71). The *exo*-isomer (**12**) yields 66% of a mixture of the corresponding acetates consisting of 95.5% *exo*- and 4.5% *endo*-isomers. The rate is 1/200th that for *exo*-norbornyl toluene-*p*-sulphonate (see also pp. 20–22).[22]



(**12**) 95.5% 4.5%

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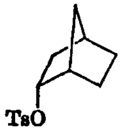
[19b] R. R. Sauers, S. B. Schlosberg and P. E. Pfeffer, *J. Org. Chem.*, **33**, 2175 (1968).

[20] C. W. Jefford and W. Wojnarowski, *Chem. Comm.*, **1968**, 129.

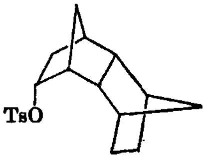
[21] See *Organic Reaction Mechanisms*, **1965**, 26, **1966**, 10.

[22] P. G. Gassman and J. L. Marshall, *Tetrahedron Letters*, **1968**, 2433.

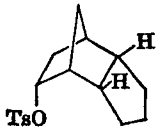
The relative rates of acetolysis of (**13**), (**14a**) and (**14b**) are 1.0:22:0.1. Whereas the slowness of the reaction of (**14b**) was attributed to steric hindrance to ionization,[23] the high rate of (**14a**) may be the result of steric acceleration. The difference in rates between (**14a**) and (**14b**) does not arise from differences in angle strain, since the carbonyl stretching frequencies of the corresponding ketones are identical (1743 $cm^{-1}$).[24]



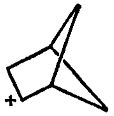
**(13)**



**(14a)**



**(14b)**



**(15)**

There have been several investigations of additions to norbornenes and related compounds which have some bearing on the structure of the 2-norbornyl cation.[25] The steric course of electrophilic additions to bicyclo[2.1.1]hexene is similar to that of additions to norbornenes. Thus oxymercuration, addition of DOAc in the presence of $D_2SO_4$, and of HCl in $CH_2Cl_2$ occur exclusively *cis*, whereas addition of 2,4-dinitrobenzenesulphonyl chloride occurs exclusively *trans*. It seems unlikely that these can have occurred via a classical ion (**15**) since, unlike the ion from norbornene, this would be symmetrical and should yield equal amounts of *cis*- and *trans*-isomers. It is possible that ion-pairing could control the steric course in the addition of DCl, but difficult to see how this could be so with the $D_2SO_4$-catalysed addition of AcOD. The results therefore suggest that the mechanism does not involve a carbonium ion and, in view of the closeness of this system to norbornene, that the mechanism here does not as well. This implies that the products of additions to norbornenes are irrelevant to the structure of the 2-norbornyl cation in solvolysis reactions.[26a]

Oxymercuration with mercuric acetate of 7,7-dimethylnorbornene and *syn*-7-bromonorbornene yields *exo*-products exclusively. It was considered that a factor other than steric effects must cause addition to norbornene to occur from the *exo*-face, otherwise the 7,7-dimethyl and *syn*-7-bromo-substituents would have caused *endo*-addition to occur.[26b]

Addition of HCl to 1-chloronorbornene occurs much more slowly than to

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[23] See *Organic Reaction Mechanisms*, **1967**, 3.

[24] I. Rothberg, *Chem. Comm.*, **1968**, 268.

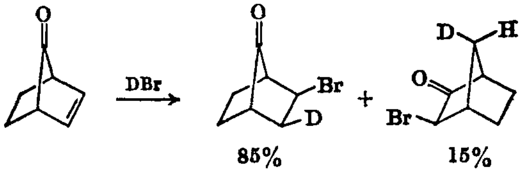
[25] For previous work see *Organic Reaction Mechanisms*, **1967**, 5.

[26a] F. T. Bond, *J. Am. Chem. Soc.*, **90**, 5326 (1968).

[26b] T. G. Tidwell and T. G. Traylor, *J. Org. Chem.*, **33**, 2614 (1968); see also W. C. Baird and M. Buza, *ibid.*, p. 4105.

norbornene and 2-chloronorbornene, and the product is more than 99.5% of 1-*exo*-3-dichloronorbornene. This was considered to indicate that bridging in the transition state was unimportant as a 1-chlorosubstituent should stabilize a bridged ion.[27]

The addition of hydrogen and deuterium halides to norbornen-7-one yield a mixture of unrearranged and rearranged halides (e.g. equation 5). No *endo*-products were obtained.[28] This behaviour contrasts with that of *exo*-2-toluene-*p*-sulphonoxynorbornan-7-one which on acetolysis yields a mixture of *exo*- and *endo*-products.[21]



(5)

Addition of acetic acid to *endo*-trimethylenenorbornene yields a higher proportion of *endo*-trimethylenenorborn-*exo*-2-yl acetate than addition to *exo*-trimethylenenorbornene does, indicating that the sole product-forming intermediate is not a non-classical ion.[29]

The rates of the chromic acid oxidation of norbornanols and related compounds have been compared to the rates of solvolysis of the corresponding toluene-*p*-sulphonates.[30]

The interconversion of sativene and cyclosativene involves a substituted norbornyl cation.[31a] The reactions of 2-methylisoborneol and 2-methylfenchols with $HNO_3$ have been studied.[31b]

A structural investigation of norbornane and 1,4-dichloronorbornane in the vapour state by electron diffraction has been reported.[32]

More details have been published of the products of acetolysis of [*exo*, *exo*-2,3-$^2H_2$]-*anti*-7-norbornyl toluene-*p*-sulphonate (**16**) (equation 6). The 3% of 2-acetoxybicyclo[3.2.0]heptane is not all (**17**) but contains about 5% of (**18**). This does not come from rearrangement of the initially formed ion pair (**19**) to (**20**) since this should collapse to (**21**) faster than it reacts with solvent, and hence unreacted (**16**) should contain (**21**), but this was not found. It was

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[27] A. J. Fry and W. B. Farnham, *Tetrahedron Letters*, **1968**, 3345.

[28] R. Caple, H. W. Tan and F. M. Hsu, *J. Org. Chem.*, **33**, 1542 (1968).

[29] S. J. Cristol and G. C. Fusco, *J. Org. Chem.*, **33**, 106 (1968); see also *Organic Reaction Mechanisms*, **1965**, 15; **1966**, 5.

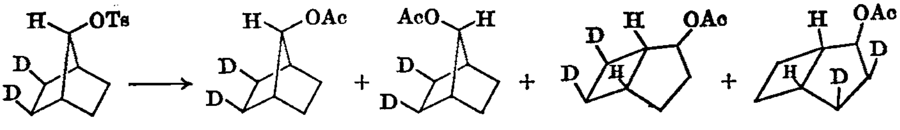
[30] R. Baker and J. Hudec, *Tetrahedron Letters*, **1968**, 4715; see also ref. 24.

[31a] L. Smedman and E. Zavarin, *Tetrahedron Letters*, **1968**, 3833.

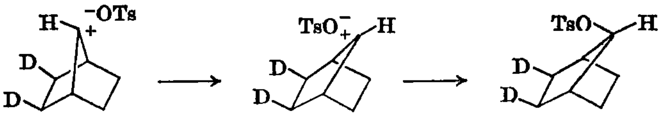
[31b] H. Toivonen, *Tetrahedron Letters*, **1968**, 3041.

[32] J. F. Chiang, C. F. Wilcox and S. H. Bauer, *J. Am. Chem. Soc.*, **90**, 3149 (1968).

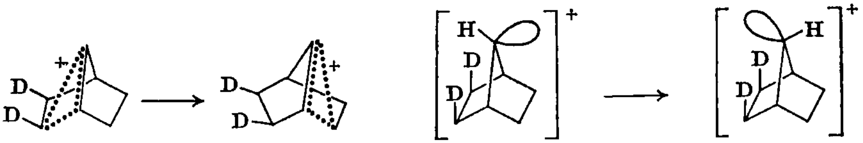
suggested instead that a non-classical (**22**) or non-planar ion (**24**) intervened and that these underwent rearrangement to (**23**) or (**25**). The 10% of 7-bicyclo[2.2.1]heptyl acetate of inverted configuration must then have resulted half from (**23**) or (**25**) and half from an $S_N2$ displacement.[33]



(**16**) (**17**) (**18**) (6)



(**19**) (**20**) (**21**)



(**22**) (**23**) (**24**) (**25**)

*Other bicyclic systems.* A detailed investigation of the solvolysis of bicyclo-[3.2.1]oct-2-yl, bicyclo[2.2.2]octyl arenesulphonates, and related compounds has been reported by Goering and Fickes. Acetolysis and hydrolysis in 80% aqueous acetone of bicyclo[3.2.1]oct-*endo*-2-yl toluene-*p*-sulphonate (**26**) are accompanied by ion-pair return. In both solvents racemization of optically active starting material is faster than solvolysis with $k_\alpha/k_t$ ca. 5 and 3 respectively. The product of acetolysis is mainly the corresponding *endo*-acetate, but there is also a small amount of *exo*-acetate and bicyclo[2.2.2]oct-2-yl acetate formed. Owing to the ion-pair return only about 20% of the *endo*-acetate is formed directly from optically active starting materials, but of this more than 99% is racemic. On addition of $LiClO_4$ only a "normal" salt effect was found, and the ratio $k_\alpha/k_t$ was reduced slightly, suggesting that ion-pair return is occurring from intimate ion pairs. These results were interpreted in terms of a non-classical ion (**27a**) which leaks to (**27d**). As discussed below this was thought to occur by way of classical ions (**27b**) and (**27c**).[34]

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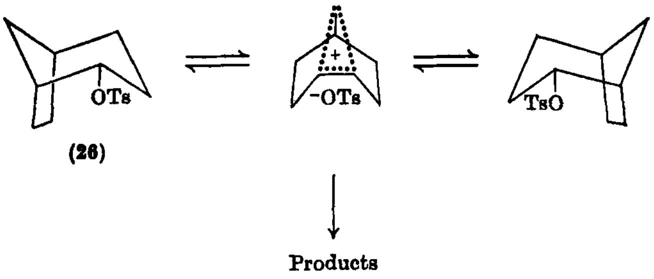
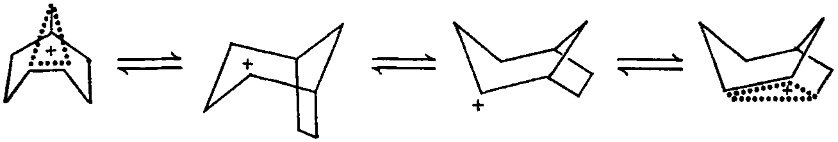
[33] P. G. Gassman, J. M. Hornback and J. L. Marshall, *J. Am. Chem. Soc.*, **90**, 6238 (1968); see *Organic Reaction Mechanisms*, **1967**, 15. See also F. B. Miles, *J. Am. Chem. Soc.*, **90**, 1265 (1968).

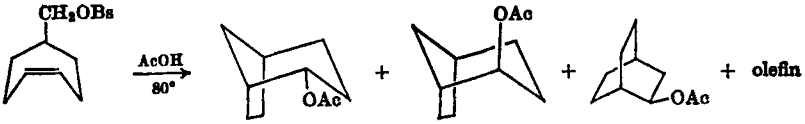
[34] H. L. Goering and G. N. Fickes, *J. Am. Chem. Soc.*, **90**, 2848 (1968).

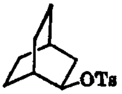
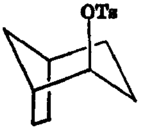
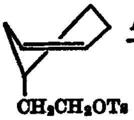




(27a) (27b) (27c) (27d)

The products of solvolysis of bicyclo[3.2.1]oct-*endo*-2-yl toluene-*p*-sulphonate (**26**) and cyclohept-4-enylmethyl *p*-bromobenzenesulphonate (**28**) are the same, but the proportions are slightly different (see equations 7 and 8). It was postulated that both substrates ionize to give an ion pair containing the

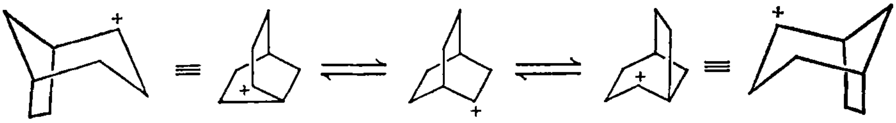


| | | | | | | |
|---|---|---|---|---|---|---|
| (28) | | 92.3% | 4.1% | 3.6% | 0% | (7) |
| (26) | $\xrightarrow[80^\circ]{AcOH}$ | 83.9% | 8.0% | 5.2% | 2.9% | (8) |
| <br>(29) | $\xrightarrow[49^\circ]{AcOH}$ | 0.4% | 46.2% | 53.4% | 13% | (9) |
| <br>(30) | $\xrightarrow[49^\circ]{AcOH}$ | 0.6% | 45.5% | 53.9% | 15% | (10) |
|  | $\xrightarrow[100^\circ]{AcOH}$ | | 46% | 54% | | (11) |

same non-classical ion, but that the position of the counter ion depends on the starting material. At present it is not clear if the small difference in the proportions of the products results from the counter ions being different or being differently situated in the ion pair. Bicyclo[2.2.2]oct-2-yl and bicyclo-[3.2.1.]oct-*exo*-2-yl toluene-*p*-sulphonate (**29** and **30**) yield the same mixture of products (see e.g. equations 9 and 10) but they are to a large extent interconverted prior to solvolysis, and so any small differences would have been obscured. The mixture was very similar to that reported previously[35] for the acetolysis of 2-(cyclohex-3′-enyl)ethyl *p*-bromobenzenesulphonate (see equation 11). The initially formed ion pair from this compound would have the counter ion differently situated to that from (**29**) and (**30**), and this result therefore suggests that the stereochemistry of the ion pair has little effect in controlling the composition of the products.

One interesting point is that the proportion of bicyclo[2.2.2]oct-2-yl acetate to bicyclo[3.2.1]oct-*exo*-2-yl acetate, obtained from the acetolysis of the corresponding toluene-*p*-sulphonates at 49°, is 1.2, whereas the proportion obtained from bicyclo[3.2.1]oct-*endo*-2-yl toluene-*p*-sulphonate is 0.6. Therefore these products cannot have been formed wholly from the same intermediates in the different reactions. As the difference cannot be attributed to the location of the counter ion it was suggested that the conversion of non-classical ion (**27a**) into (**27d**) proceeded by way of classical ions (**27b**) and (**27c**) and that the excess of bicyclo[3.2.1]oct-*exo*-2-yl acetate formed from (**26**) is formed from one of these (probably **27b**).[36]

Evidence that non-classical ion (**27d**) can also revert to a classical ion was obtained from a determination of the products of solvolysis of optically active bicyclo[2.2.2]oct-2-yl and bicyclo[3.2.1]oct-*exo*-2-yl toluene-*p*-sulphonate. If these reactions proceeded wholly via non-classical ion (**27d**) they should yield unracemized products. On the other hand if rapidly interconverted classical ions (**32**) and (**31**) were involved, racemic products should be obtained since the 1,6- and 1,8-bonds of (**32**) are equivalent and their migration should yield enantiomeric forms of (**31**) at equal rates. After correcting for the interconversion of the toluene-*p*-sulphonates prior to hydrolysis the results given in Table 1 were obtained. The formation of partially racemized products suggests that non-classical ion (**27d**) cannot be the sole intermediate and its partial


(**+31**) (**32**) (**−31**)

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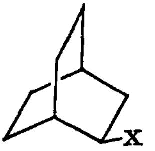
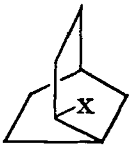
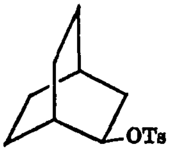
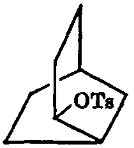
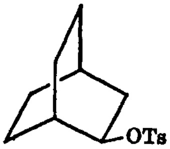
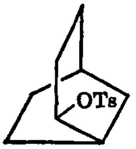
[35] S. Winstein and P. Carter, *J. Am. Chem. Soc.*, **83**, 4485 (1961).

[36] H. L. Goering and G. N. Fickes, *J. Am. Chem. Soc.*, **90**, 2856 (1968).

**Table 1. Optical purities of solvolysis products derived from optically active bicyclo[2.2.2]octan-2-yl and bicyclo[3.2.1]oct-*exo*-2-yl toluene-*p*-sulphonate.**

| | Optical purity % | |
|---|---|---|
| |  |  |
| | Acetolysis (48.86°) X = OAc | |
|  | 53 | 72 |
|  | 59 | 77 |
| | 80% Aqueous acetone (48.86°) X = OH | |
|  | 78 | 93 |
|  | 83 | 94 |

racemization via a classical ion as shown in Scheme 1 was proposed. The possibly slightly greater amount of racemization in the products from bicyclo-[2.2.2]oct-2-yl toluene-*p*-sulphonate than in those from bicyclo[3.2.1.]oct-*exo*-2-yl toluene-*p*-sulphonate, could arise from the direct formation of classical ion (**33** ≡ **32**) on ionization of the former. The possibility of twisted[37]

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[37] An X-ray crystallographic investigation of the structure of bicyclo[2,2,2]octane-1,4-dicarboxylic acid indicates that it does not have a twisted structure; O. Ermer and J. D. Dunitz, *Chem. Comm.*, **1968**, 567; a similar investigation of the structure of 1-*p*-bromobenzene sulphonyloxymethyl bicyclo[2.2.2]octane indicates a very small angle of twist; A. F. Cameron, G. Ferguson and D. G. Morris, *J. Chem. Soc.* (B), **1968**, 1249.