

ORGANIC REACTION MECHANISMS · 1971

*An annual survey covering the literature
dated December 1970 through November 1971*

B. CAPON

C. W. REES

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Edited by

B. CAPON University of Glasgow

C. W. REES University of Liverpool

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Preface

This seventh volume of the series is a survey of the work on organic reaction mechanisms published in 1971. For convenience, the literature dated from December 1970 to November 1971, 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. Nearly 5000 papers have been reported, and 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 we have been fortunate to have the expert cooperation of the English office of John Wiley and Sons.

July 1972

B.C.

C.W.R.

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CHAPTER 1

Carbonium Ions¹

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Bicyclic and Polycyclic Systems

Derivatives of Norbornane and Related Compounds

¹³C and ¹H NMR and Raman spectroscopic investigations of the 1,2-dimethylnorbornyl cation have been reported.² In SbF₅-SO₂ and FSO₃H-SbF₅-SO₂, the amount of 6,2 σ delocalization is nearly identical with that in the 2-methylnorbornyl cation, but in the former the barrier to C₁C₂ Wagner-Meerwein shift is lowered so far that it cannot be frozen out on the NMR time scale even at -140°C. This low barrier results from a degenerate tertiary-tertiary rearrangement. The C-H_{6_{exo}} bond is involved to a major extent in the delocalization.

¹ S. Winstein and M. Sakai, "Non-Classical Ions and Homoaromaticity", *Kagaku No. Ryoiki*, **25**, 127 (1971); R. E. Leone and P. von R. Schleyer, "Degenerate Carbonium Ions", *Angew. Chem. Int. Ed.*, **9**, 860 (1970); W. R. Dolbier, "Mechanisms of Solvolytic Spirane Rearrangements", *Mech. Mol. Migr.* **3**, 1 (1971); R. C. Bingham and P. von R. Schleyer, *Fortschr. Chem. Forsch.*, **18**, 1 (1971); M. J. Goldstein and R. Hoffman, "Symmetry, Topology and Aromaticity", *J. Am. Chem. Soc.*, **93**, 6193 (1971).

² G. A. Olah, J. R. DeMember, C. Y. Lui, and R. D. Porter, *J. Am. Chem. Soc.*, **93**, 1442 (1971); *see Org. Reaction Mech.*, **1970**, 2.

The relative rates of 6,2- and 3,2-hydride shifts ($k_6:k_3$) are <100 and <200 in the acetolysis of Δ^3 -[1- ^{14}C]cyclopentenylethyl toluene-*p*-sulphonate and 2-*exo*-[4- ^{14}C]-norbornyl toluene-*p*-sulphonate, respectively.³ ^{14}C studies have also shown that in the solvolysis of *exo*-norbornyl *p*-bromobenzenesulphonate, isotopic scrambling occurs in the starting ester owing to internal return and also in the initial product as well as in the reaction intermediates.⁴

Deuterium tracer studies have added further evidence that classical ions generated in deaminations can survive several Wagner–Meerwein rearrangements or hydride shifts.⁵ An *endo*–*endo* hydride shift to a secondary carbonium ion has been observed in the deamination of 3-*exo*-aminobornane-2-*exo*-ol,⁶ and a 3,2-*endo*,*endo*-methyl migration in the decomposition of a triazoline.⁷ The results were interpreted in terms of open classical intermediates. β -Deuterium isotope effects have been reported to be inconsistent with anchimeric assistance in the solvolysis of *exo*-norbornyl derivatives. Differences in the force-constant change associated with the hydrogens at C-2, C-3 and C-6 in formation of the transition states for the *exo*- and *endo*-derivatives are suggested as the origin of the observed isotope effects.⁸ The observation that β -deuterium isotope effects in the solvolysis of 1,2-dimethyl-*exo*-2-norbornyl *p*-nitrobenzoate in solvents varying from 50 to 70 vol. % ethanol are directly related to the amount of elimination product is suggested as being due to rate-determining elimination in competition with substitution and internal return.⁹

Acetolysis of the epimeric *exo*-6-methoxycarbonyl-2-norbornyl *p*-bromobenzene-sulphonates proceeds through classical carbonium ions with $k_{\text{exo}}/k_{\text{endo}} = 4.4$, although some Wagner–Meerwein rearrangement occurs.¹⁰ Little positive charge was believed to reside on the migrating carbon atom in the transition state for migration. *endo*-6-Methoxycarbonyl-*exo*-2-norbornyl *p*-bromobenzenesulphonate solvolyses with anchimeric assistance and lactone formation.

In the solvolysis of α -fenchyl toluene-*p*-sulphonate (**1**) in acetic acid, a mixture of products is obtained, but the main component is 4-methylsantenyl acetate (**2**) resulting from methyl migration, Wagner–Meerwein rearrangement and hydride shift.¹¹ (**3**) is also produced by a process involving solvent assistance and hydride shift.

Rates of displacement reactions on (**4**)–(**7**) have been measured, the relative rates being found to be very similar to the reactivities observed for solvolyses. Steric interactions between the leaving group and other groups are again the determining factor.¹² Rearrangements of a series of dihydrodicyclopentadiene derivatives in orthophosphoric acid have also been studied.¹³

Low *exo*:*endo* rate ratios have been observed in the solvolysis of a number of *exo*-2,3-*o*-arylene-5-norbornyl toluene-*p*-sulphonates (**8**) and (**9**).¹⁴ A small increase in

³ C. J. Collins and C. E. Harding, *Ann. Chem.*, **745**, 124 (1971).

⁴ C. C. Lee, B.-S. Hahn, L. K. M. Lam, and D. J. Woodcock, *Can. J. Chem.*, **48**, 3831 (1970).

⁵ V. F. Raaij, B. M. Benjamin, and C. J. Collins, *Tetrahedron Letters*, **1971**, 2613; see *Org. Reaction Mech.*, **1970**, 6.

⁶ P. Wilder, Jr., and W. C. Hsieh, *J. Org. Chem.*, **36**, 2552 (1971).

⁷ S. Rengaraju and K. D. Berlin, *Tetrahedron*, **27**, 2399 (1971).

⁸ S. E. Scheppele, *Chem. Comm.*, **1971**, 592.

⁹ K. Humski, *Croat. Chem. Acta*, **42**, 501 (1971).

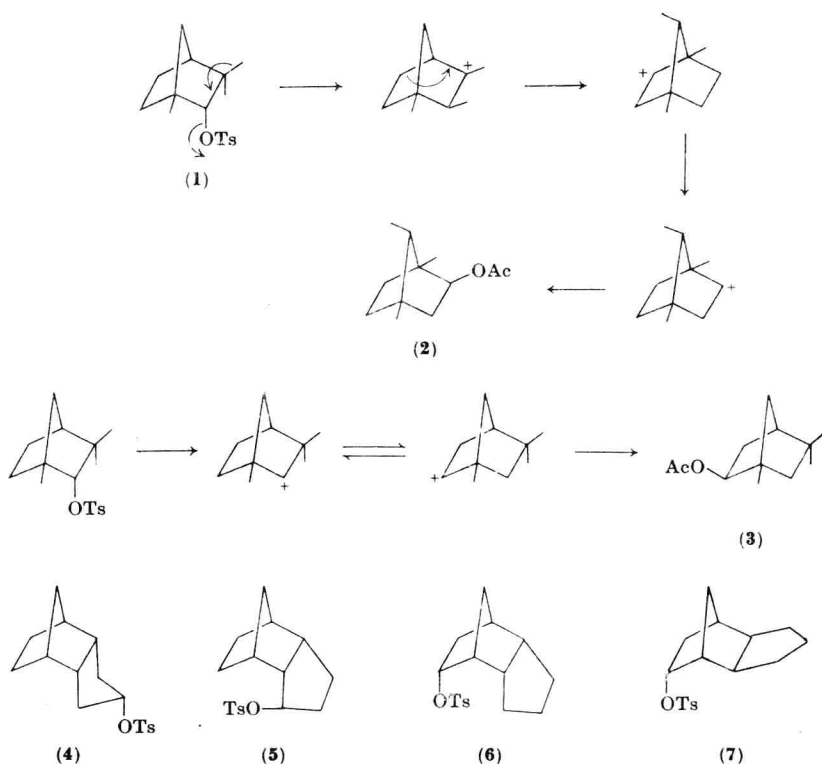
¹⁰ G. W. Oxer and D. Wege, *Tetrahedron Letters*, **1971**, 457.

¹¹ A. Coulombeau, C. Coulombeau, and A. Rassat, *Bull. Soc. Chim. France*, **1970**, 4389.

¹² I. Rothberg and R. V. Russo, *J. Chem. Soc. (B)*, **1971**, 1214.

¹³ P. Wilder, D. J. Cash, R. C. Wheland, and G. W. Wright, *J. Am. Chem. Soc.*, **93**, 791 (1971).

¹⁴ R. Baker and T. J. Mason, *J. Chem. Soc. (B)*, **1971**, 1144.



exo/endo rate ratio with change in solvent from acetic acid to formic acid was interpreted as resulting from an increasing carbon-carbon bond participation. The reactions were discussed in terms of k_A and k_S pathways but it was suggested that, in these systems, some "leakage" could occur.

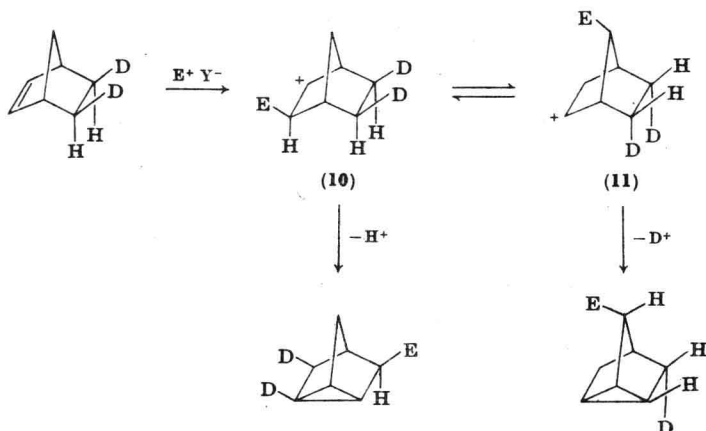
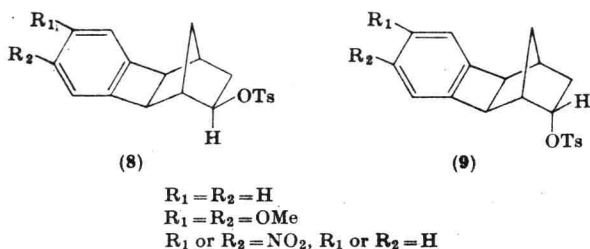
In the addition of bromine and chlorine to *exo,exo*- and *endo,endo*-5,6-dideuterionorbornene, proton loss to form a tricyclic product occurs from C-6 with *exo* and *endo* stereoselectivity, respectively.¹⁵ It was suggested that elimination could occur from (10) in bromination and from (11) in chlorination. Elimination from unsymmetrical bridged ions was also considered. Greater than 50% of *exo-cis* addition was found for hydrogen chloride and bromide to 2,3-dideuterionorbornene, and a classical norbornyl carbonium ion was suggested.¹⁶ In formic acid, methanol and hydrogen fluoride, Wagner-Meerwein rearrangement became equally important.

A detailed re-investigation has been made of the bromination of norbornene and the products have been found to consist of a mixture of five dibromides, bromonortricyclene and 2-*exo*-bromonorbornane.¹⁷ From ¹⁴C studies, 2-*exo*,3-*endo*-dibromonorbornane was

¹⁵ N. H. Verstiuk and I. Vancas, *Can. J. Chem.*, **48**, 3963 (1970).

¹⁶ J. K. Stille and R. D. Hughes, *J. Org. Chem.*, **36**, 340 (1971).

¹⁷ D. R. Marshall, P. Reynolds-Warnhoff, E. W. Warnhoff, and J. R. Robinson, *Can. J. Chem.*, **49**, 885 (1971).



shown to arise from bromonium ion (12) and also carbonium ion (13). *endo*-Attack has been observed in the reaction of bromine with *anti*-7-bromo-5-phenylbenzonorbornadiene and *syn*-7-bromo-2-phenylnorbornene.¹⁸ It was suggested that the reversal from normally observed *exo* attack is due to the reduction in the σ delocalization in the transition state for this pathway.



Palladium chloride-copper chloride catalysed addition reactions to tricyclo[4.2.1.0^{2,5}] derivatives have been studied.¹⁹ Products from two competitive reactions involving a copper(II) complex and palladium(II) complex were obtained, but neither process appeared to proceed through free carbonium ions. Reaction of camphene, norbornene, benzonorbornene and dibenzobarrelene with $Pb(OAc)_{4-n}(N_3)_n$ appears to proceed through carbonium ion intermediates.²⁰

¹⁸ R. Caple, G. M. S. Chen, and J. D. Nelson, *J. Org. Chem.*, **36**, 2870 (1971).

¹⁹ C. J. R. Adderley, J. W. Nebzydoski, M. A. Battiste, R. Baker, and D. E. Halliday, *Tetrahedron Letters*, **1971**, 3545.

²⁰ E. Zbiral and A. Stutz, *Tetrahedron*, **27**, 4953 (1971).

The 7-norbornyl cation has been generated from α -deuterio-2-bicyclo[3.2.0]heptyl *p*-bromobenzenesulphonate in acetic acid and products have been studied.²¹ Observed ¹³C chemical shifts in norbornyl derivatives have been interpreted in terms of bond lengths and inductive and steric effects.²² Special kinetic salt effects have been measured in the solvolysis of *t*-butyl bromide, *exo*-2-chloro-1- and -2-methylnorbornane, isobornyl chloride and camphene hydrochloride.²³

An intermediate diazotic acid (14) is formed in the reaction of 1,1-disubstituted hydrazines with nitrous acid, which decomposes by two alternative routes.²⁴ One involves formation of a nitrenium ion (15) which undergoes rearrangement and reaction with solvent and, in the other, nitrous oxide is lost with hydrogen transfer to the nitrogen.

Other studies include assessments of torsional effects in the [2.2.1] system;²⁵ equilibration reactions of norborneols and 1-methylnorborneols;²⁶ dependence of rates on sodium hydroxide concentration in the hydrolysis of optically active *exo*- and *endo*-norbornyl toluene-*p*-sulphonates;²⁷ sulphur-oxygen bond cleavage of secondary and tertiary toluene-*p*-sulphonates under nucleophilic solvolytic conditions;²⁸ properties of 2-aryl-norbornene oxides and the dimer formed by dehydration of the 2-*p*-anisyl derivative;²⁹ reactions of *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene *exo*-oxide;³⁰ formation of norbornylene-mercurinium ions;³¹ sulphuric acid and formic acid catalysed hydration of *endo*- and *exo*-norbornene-5-carboxylic acids;³² lactone formation from 2-*endo*-cyano-, 2-*endo*-cyanomethyl- and 2-*endo*-carboxymethyl-5-norbornenes;³³ and deamination of *endo*- and *exo*-bornylamines.³⁴

Other Bicyclic Systems

Further studies on "memory effects" have appeared. Magnification of a memory effect by substitution of an alkyl group for hydrogen of the non-migrating group R₃ in (16) γ to the original cationic charge, providing a more stable doubly rearranged ion, is reported.³⁵ In deamination reactions of (17) and (18) the effect of the γ -methyl substitution on the multiplicative memory effect was a factor of 6 for the C-1 ("near") versus C-4 ("far") ring expansion comparison and about 13 in the comparison with the parent system. However, limits ranging from 1450 to 64,000 for the multiplicative memory effects, indicating very large enhancements of selectivity by methyl substitution, were

²¹ B. Funke and S. Winstein, *Tetrahedron Letters*, **1971**, 1477.

²² J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *J. Am. Chem. Soc.*, **92**, 7107 (1970).

²³ C. A. Bunton, T. W. Del Pesco, A. M. Dunlop, and K. U. Yang, *J. Org. Chem.*, **36**, 887 (1971).

²⁴ P. G. Gassman and K. Shudo, *J. Am. Chem. Soc.*, **93**, 5899 (1971).

²⁵ S. P. Jindall, S. S. Sohoni, and T. T. Tidwell, *Tetrahedron Letters*, **1971**, 779; S. P. Jindall and T. T. Tidwell, *Tetrahedron Letters*, **1971**, 787; J. M. Mellor and C. F. Webb, *Tetrahedron Letters*, **1971**, 4025.

²⁶ A. Coulombeau and A. Rassat, *Bull. Soc. Chim. France*, **1970**, 4393.

²⁷ P. Hirsjarvi, T. Kiutamo, J. Korvenranta, E. Tenhunen, and M. Vilen, *Suom. Kemistilehti*, **43**, 519 (1970).

²⁸ P. G. Gassman, J. M. Hornback, and J. M. Piescone, *Tetrahedron Letters*, **1971**, 1425.

²⁹ T. J. Gerteisen, D. C. Kleinfelter, G. C. Brophy, and S. Sternhell, *Tetrahedron*, **27**, 3013 (1971).

³⁰ B. C. Henshaw, D. W. Rome, and B. L. Johnson, *Tetrahedron*, **27**, 2255 (1971).

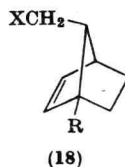
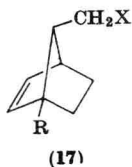
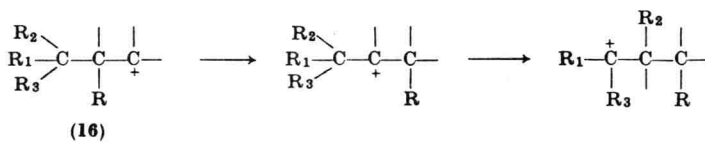
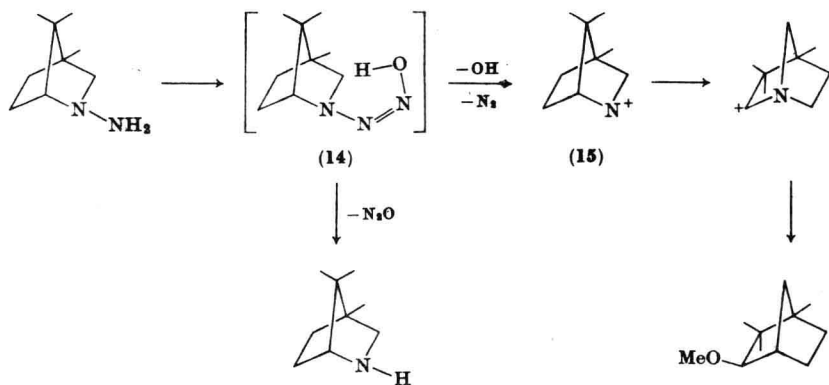
³¹ G. A. Olah and P. R. Clifford, *J. Am. Chem. Soc.*, **93**, 1261 (1971).

³² H. Geiger, *Tetrahedron*, **27**, 165 (1971).

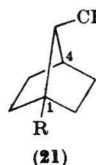
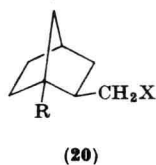
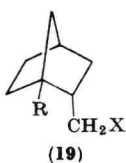
³³ T. Sasaki, S. Eguchi, and M. Sugimoto, *Bull. Chem. Soc. Japan*, **44**, 1382 (1971).

³⁴ D. V. Banthorpe, D. G. Morris, and C. A. Bunton, *J. Chem. Soc. (B)*, **1971**, 687.

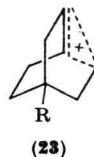
³⁵ J. A. Berson, J. M. McKenna, and H. Junge, *J. Am. Chem. Soc.*, **93**, 1296 (1971).



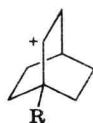
$\text{R} = \text{Me, H}$
 $\text{X} = \text{NH}_2$



"far branch"
 $\sim \text{C-1}$



"near branch"
 $\sim \text{C-4}$



found in deamination and solvolysis of the 1-methyl-2-norbornylcarbiny systems (**19** and **20**).

Evidence has been obtained that the free-energy benefit ($\Delta\Delta F^*$) of replacing hydrogen by methyl monotonically approaches zero at zero overall ΔF^* .³⁶ Thus, in reactions of 1-methyl-7-norbornylcarbiny derivatives (**21**), despite the extra stability of tertiary cation (**22**) over secondary cation (**23**), the ratio of products from "far" and "near" branches is close to unity. The data suggest that $\Delta\Delta F^*$ of methyl for hydrogen replacement at the site of a developing carbonium ion (C- β) in these rearrangements (**24**) is about 0.4–1.1 kcal mole⁻¹ compared to 6 kcal mole⁻¹ for overall ΔF^* .



Whilst the relatively unselective nature of deamination reactions compared with solvolytic processes has been accepted for some time, in some deaminations the reverse has been demonstrated.³⁷ Competing paths used to examine selectivity are migration of a β -substituent (R₁) and migration of a β ring member (G, J) in carbonyl derivatives of general formula (**25**); the series of structures (**26**)–(**31**) was examined. Deamination invariably produces an increase in preference for ring expansion over the solvolytic reactions; in some cases a selectivity ratio as large as 100 is found. The results were rationalized in terms of ground-state conformations, which in the bicyclic systems places the leaving group as far as possible from the bulky bicyclic system. In this situation migration is not favoured in the solvolytic processes, so that the migration in deamination has enhanced relative importance. Normally, in systems such as 3-phenyl-2-butyl the energies of transition states for deamination do not lie far above the barriers for internal rotation and the choice of phenyl or methyl migration depends on the distribution in the diazonium ion ground state.

"Memory effects" in formation of (**33**) and (**34**) resulting from hydride shift, and rearrangement in carbonium ion reactions of (**32**), have been shown not to result from ion-pairing effects.³⁸ The hydride shift process results in ca. 20% preservation of optical purity in *p*-bromobenzenesulphonate hydrolysis, but in deamination the hydroxyl group in the ring-expanded product replaces the migrating carbon with inversion of configuration. The results are consistent with either a slow interconversion of conformational isomers or non-classical bonding.

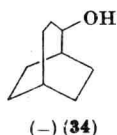
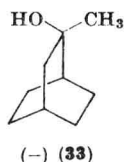
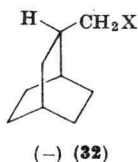
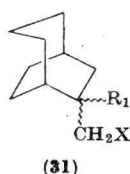
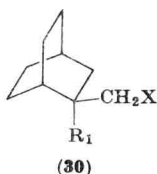
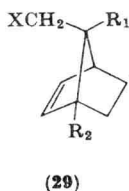
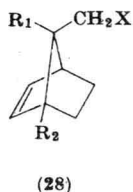
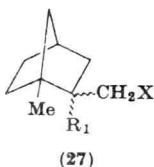
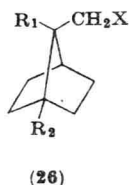
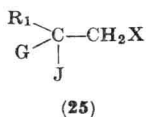
A number of studies on *trans*-fused cyclopropanes have been published. In the solvolysis of the *trans*-bicyclo[6.1.0]non-2-yl derivatives (**35** and **36**), the *trans,trans* isomer was found to be greater than 10⁴ times as reactive as the *trans,cis* isomer.³⁹ This difference arises because in (**36**) the leaving group lies over the cyclopropane ring so that only a

³⁶ J. A. Berson and J. W. Foley, *J. Am. Chem. Soc.*, **93**, 1297 (1971).

³⁷ J. A. Berson, J. W. Foley, J. M. McKenna, H. Junge, D. S. Donald, R. T. Luibrand, N. G. Kundu, W. J. Libbey, M. S. Poonian, J. J. Gajewski, and J. B. E. Allen, *J. Am. Chem. Soc.*, **93**, 1299 (1971).

³⁸ J. A. Berson, R. T. Luibrand, N. G. Kundu, and D. G. Morris, *J. Am. Chem. Soc.*, **93**, 3075 (1971).

³⁹ K. B. Wiberg and T. Nakahira, *J. Am. Chem. Soc.*, **93**, 5193 (1971); P. G. Gassman, E. A. Williams, and F. J. Williams, *J. Am. Chem. Soc.*, **93**, 5199 (1971).



poor interaction exists between the developing p -orbital and the cyclopropane ring. In reaction of (35) the developing p -orbital has its lobe directly over the bridging C—C bond. No “cross-over” in products was found for the epimeric derivatives, and the stereochemistry was the same for the two reactions. Only the *trans,trans* epimer showed scrambling in the solvolysis when the material was labelled α -D (37).

No evidence for cyclopropane participation was found in the solvolysis of 4-*trans*-bicyclo[5.1.0]octane p -bromobenzenesulphonate.⁴⁰ It was concluded that requirements for participation, which involve either the interaction of a single bent cyclopropyl bond with an orthogonal p -orbital, or the interaction of the orbitals of two different cyclopropyl carbon—carbon single bonds with two ends of the p -orbital, are not satisfied with this system. Acid-catalysed addition to *trans*-bicyclo[5.1.0]oct-3-ene occurs with product-determining protonation at the bridgehead.⁴¹ Products indicate that protonation of the cyclopropane ring is preferred over that of the double bond, which is consistent with the reactive nature of the former, as shown in solvolytic studies of analogous systems.

A bisected bishomoallylic intermediate has been suggested on the basis of similar rates and products found in the solvolysis of *endo*- and *exo*-2-bicyclo[3.1.0]hexyl 3,5-dinitrobenzoates; substitution of a 5-methyl group had a similar effect on the solvolysis of the two epimers.⁴²

⁴⁰ P. G. Gassman, J. Seter, and F. J. Williams, *J. Am. Chem. Soc.*, **93**, 1673 (1971).

⁴¹ P. G. Gassman and F. J. Williams, *J. Am. Chem. Soc.*, **93**, 2704 (1971).

⁴² E. C. Friedrich and M. A. Saleh, *Tetrahedron Letters*, **1971**, 1373.