CARBONIUM IONS

VOLUME III
MAJOR TYPES (CONTINUED)

REACTIVE INTERMEDIATES IN ORGANIC CHEMISTRY

Edited by GEORGE A. OLAH
Case Western Reserve University

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CARBONIUM IONS

Edited by

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VOLUME III

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Introduction to the Series

Reactive intermediates have always occupied a place of importance in the spectrum of organic chemistry. They were, however, long considered only as transient species of short life-time. With the increase in chemical sophistication many reactive intermediates have been directly observed, characterized, and even isolated. While the importance of reactive intermediates has never been disputed, they are usually considered from other points of view, primarily relative to possible reaction mechanism pathways based on kinetic, stereochemical, and synthetic chemical evidence. It was felt that it would be of value to initiate a series that would be primarily concerned with the reactive intermediates themselves and their impact and importance in organic chemistry. In each volume, critical, but not necessarily exhaustive coverage is anticipated. The reactive intermediates will be discussed from the points of view of: formation, isolation, physical characterization, and reactions.

The aim, therefore, is to create a forum wherein all the resources at the disposal of experts in the field could be brought together to enable the reader to become acquainted with the reactive intermediates in organic chemistry and their importance.

As the need arises, it is anticipated that supplementary volumes will be published to present new data in this rapidly developing field.

In Memoriam
Saul Winstein 1912–1969

Editors' Preface to Volume I

Three years ago we undertook the task of trying to organize a survey of the field of carbonium ion chemistry in the form of an advanced monograph. Although we both have been active in research on carbonium ions, we were not fully aware, at the time the project was begun, of the vast dimensions to which the field had grown, particularly in the past two decades. To cover the entire area a very substantial effort was needed and the cooperation of a large number of colleagues and friends was necessary. We have been very gratified by the favorable response of research workers in the field to our invitations to contribute chapters in their own specialities. As the project proceeded, it became quite obvious that it would be impossible to cover all the material, as originally projected, in fewer than four volumes, if these were to be kept to manageable size.

Thought has been given to the best arrangement of chapters in these volumes. Some authors were able to produce their manuscripts more rapidly than others, and it might have been possible to assemble the volumes from unrelated chapters, in order of receipt. We have felt it better to have each individual volume maintain a coherence and identity by bringing together chapters related in subject matter to one another. Thus, a historical introduction, general aspects, and methods of investigation of carbonium ions are included in this first volume. Major types of such ions will be featured in the second volume, and the third will deal with the classical–nonclassical ion problem. The last volume will contain chapters devoted to diverse types of carbonium ions, and it will have comprehensive subject and author indexes. In addition, each volume will have short indexes.

We have not tried to alter in any way the individual author's contributions, but, hopefully, we have provided some coordination of topics to minimize overlap and to make a multiauthored book, as much as possible, an organized entity. Consequently, the different chapters reflect their authors' standpoints and philosophy. We felt particularly that exposure of the reader to views from opposing sides of topics in which there is controversy not only would be stimulating, but would further an understanding of the topic. Often, one's opinions and attitudes are influenced by a particularly persuasive argument. It is to the good to have the alternative interpretations available conveniently together, to facilitate comparison. The editors have attempted to survey the fascinating field of carbonium ions impartially by affording the many active workers an opportunity to

summarize their viewpoint and evidence. To what extent we have been successful will be decided by the readers.

We should like to express our sincere appreciation not only to the authors whose contributions made this book possible, but also to the numerous colleagues who commented on individual chapters, provided us with additional information (frequently not yet published), and called attention to many aspects of carbonium ions, whose importance we had not fully realized.

As the preparation of a monograph of this size takes a long time, we must apologize to our readers and especially to our co-authors that the unavoidable manuscript collecting and publishing delays have made it impossible to cover the literature to the last minute. In this first volume reference to the literature through 1966 is general, and in frequent instances citations to books published as late as summer, 1967, were added in the galley proof stage.

As the first volume of our monograph is going into production, the second and third volumes are practically complete and in the printer's hands. It is hoped that the whole project will be finished by the end of next year. The cooperation and excellent work of the publisher's staff made the preparation of these volumes a much more pleasant task than we could possibly have anticipated originally.

GEORGE A. OLAH
PAUL v. R. SCHLEYER

January 1968

Editors' Note to Volumes III and IV

Since publication of Volume II in 1970 three major contributors to modern carbonium ion chemistry, Professors Sir Christopher Ingold, Costin D. Nenitzescu, and Saul Winstein, died. We will all miss them. Their work will, however, continue to guide future generations. As a memento to Saul Winstein, Volume III includes the text of his 1967 Centenary Lecture to the Chemical Society of London. This lasting review on nonclassical ions, to which Professor Winstein contributed so much, is reprinted with the kind permission of the Chemical Society.

Since we no longer consider the classical–nonclassical ion problem to be of a special nature, the original outline of the series has been changed somewhat. Volumes III and IV continue with discussion of major types of ions, but do not concentrate entirely on topics related to nonclassical ions. The order of presentation of chapters has been changed somewhat, and new topics of current interest have been added. This increased length will necessitate Volume V, which will contain the overall indexes.

Whereas delays continue to plague projects of this size, with the cooperation of our authors most chapters were brought up to date in revisions. We thank them for their understanding and willingness to cope with this problem.

GEORGE A. OLAH
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October 1971

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CHAPTER 22

Nonclassical Ions and Homoaromaticity*

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University of California, Los Angeles, California

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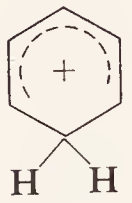
I. CLASSICAL CARBONIUM IONS

While we will be dealing in the main with nonclassical ions, it may be helpful to begin with several examples of so-called classical carbonium ions. One example is the benzenonium ion (**1**), containing a 4π-electron 5-carbon system (4π5C). A typical transient carbonium ion is represented by (**2**), these being stabilized by α-methyl substitution and generally more so by α-phenyl substitution. In the case of the phenyl substituent, the effect of conjugative electron release by phenyl more than compensates for inductive electron removal. With two and three α-phenyl substituents, one comes to the well-known benzhydryl and triphenylmethyl cations (**3**) and (**4**), respectively. While these cations are sufficiently stable to be isolated as crystalline salts, they are still extremely reactive towards water as a nucleophile. Rough estimates of the first-order rate constants for collapse

* Centenary Lecture of S. Winstein, presented before the Chemical Society (London) and reprinted with the permission of the Society from *Quart. Rev.* (*London*), **23**, 1411 (1969), in memory of Saul Winstein.

of these ions in aqueous solvents are 10^9 sec^{-1} for the benzhydryl cation and 10^5 sec^{-1} for the trityl cation (1).



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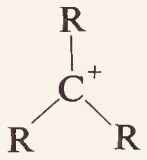

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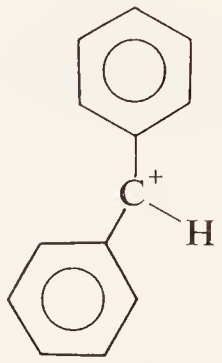

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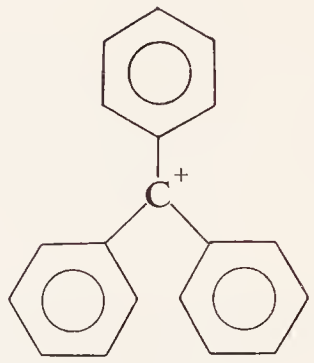
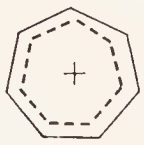


(4)

An extremely stable classical aromatic cation is the tropylium ion (2), (**5**), representing a $6\pi 7C$ system. From the work of Doering (2) and Eigen (3) one can estimate a value of 1 sec^{-1} for the first-order rate constant for collapse of tropylium ion in water as solvent. Thus, as regards reactivity towards water, cations (**3**), (**4**), and (**5**) cover a range of 9 powers of 10. Cyclopropenyl cations (4), e.g., (**7**), are also extremely stable classical aromatic cations, these being available from acid treatment of the corresponding cyclopropenol (**6**).



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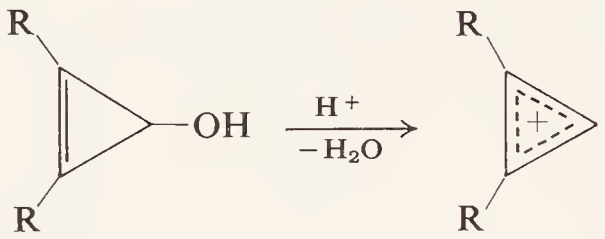
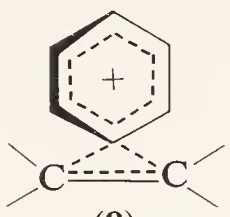


(6) (7)

II. NONCLASSICAL IONS AND NONCLASSICAL ELECTRON DELOCALIZATION

The classical cations mentioned above involve electron delocalization largely by way of familiar conjugation employing *p* π-orbital overlap. The illustrative nonclassical cations (**8**)–(**13**) involve nonclassical electron delocalization employing, at least in part, overlap of orbitals on carbon atoms between which there does not occur an additional σ-bond. Such orbital overlap is usually not π, but intermediate between σ and π.

Cation (**8**) is the phenonium (5a) ion type, resulting from β-phenyl group participation in solvolysis. Nowadays, several representative phenonium ions have been directly viewed by nmr in exceedingly non-nucleophilic



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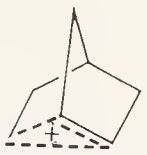

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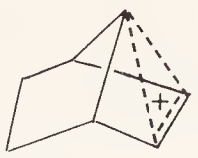

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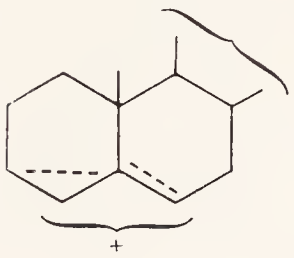

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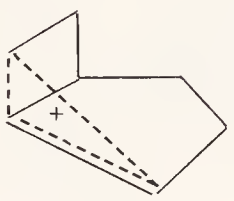

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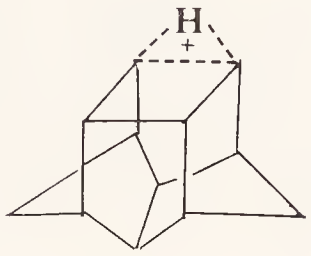


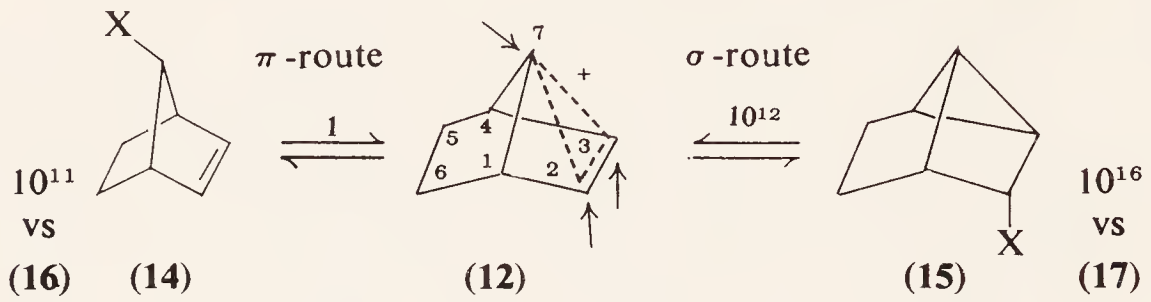
(13)

media (5b). Cations (**10**)–(**12**) contain the now familiar 2-electron 3-centre bonding arrangement (2π3C), the dotted lines representing partial bonds of bond order between 0 and 1. One of these, the norbornyl cation (**10**), was discussed in Sheffield at a Symposium on Stereochemistry by H. C. Brown. His paper has been published in *Chem. in Britain* (6), but there will not be time to comment on it in detail in my paper at this symposium. While the article in *Chem. in Britain* will undoubtedly prove to be of historical interest, I would recommend reading the actual older and more recent literature (7) for conclusive evidence that the secondary norborn-2-yl cation prefers a nonclassical structure. I plan to illustrate 2-electron 3-centre bonding more fully with the example of the norbornen-7-yl cation (8) (**12**), which has been studied, not only solvolytically, but also directly by nmr. Following this, I will hark back to the cholesteryl–*i*-cholesteryl ion (**9**), a homoallyl (9) ion, since it was this type of species which prompted the invention of the term "homoconjugation" (9) and later on led us to the concept of homoaromaticity (10). Then, a brief account of the now known homoaromatic species will be given, and, finally, we will go on to a description of current research on rearrangements of norbornadien-7-yl cations under conditions of long life.

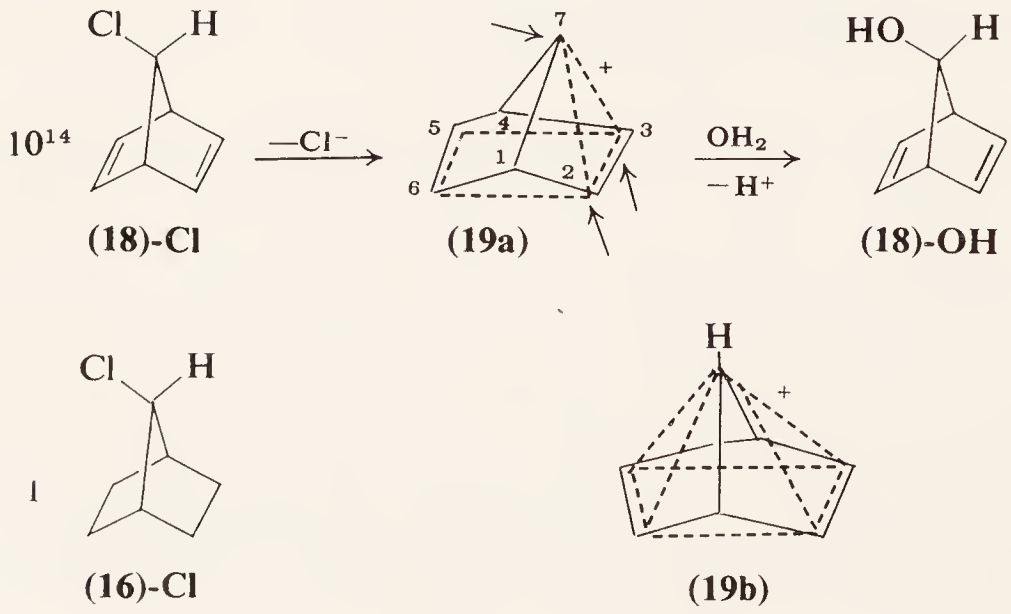
III. NORBORNEN-7-YL AND NORBORNADIEN-7-YL CATIONS

The *anti*-norbornen-7-yl cation is best represented as in (**12**). In solvolytic work it arises by anchimerically assisted ionization of an *anti*-norbornen-7-yl derivative (8a,b) (**14**) or its tricyclic isomer (8c–e) (**15**) by the so-called π- and σ-routes, respectively. These ionizations are tremendously anchimerically accelerated, the acetolysis rate of *anti*-norbornen-7-yl toluene-*p*-sulphonate exceeding that of the saturated norborn-7-yl analogue (**16**) by a factor of 10^{11}. The hydrolysis rate of the tricyclic *p*-nitrobenzoate (**15**) in

90% aqueous acetone exceeds that of its bicyclic isomer (**14**) by a factor of 10^{12}, giving a rough value of 10^{16} for the factor by which the reactivity of (**15**) exceeds that of the *endo*-norbornyl analog (**17**) without the cyclopropane ring (8e).

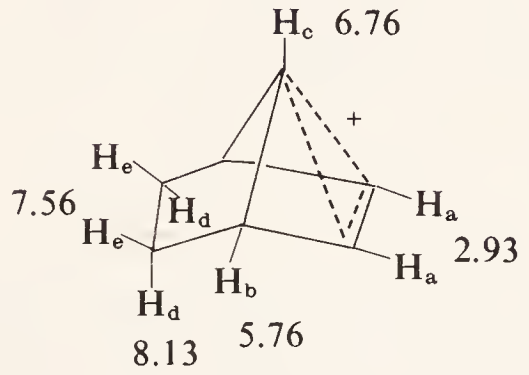


Related to the norbornen-7-yl cation (**12**) is the norbornadien-7-yl species (**19**), first studied solvolytically by Winstein and Ordronneau (11a). The reported 10^{14} factor by which the rate of solvolysis of norbornadien-7-yl chloride (**18**)-**Cl** exceeded that of the saturated norborn-7-yl analogue (**16**)-**Cl** set a world record for anchimeric acceleration (11a). Of the possible nonclassical structures for the cation visualized by these authors, the unsymmetrical one represented by (**19a**) can be chosen on the basis of the nmr spectrum first observed by Story and Saunders (12). A symmetrical structure represented by (**19b**) was also considered (11a), and this is clearly much less stable than (**19a**) (see below).



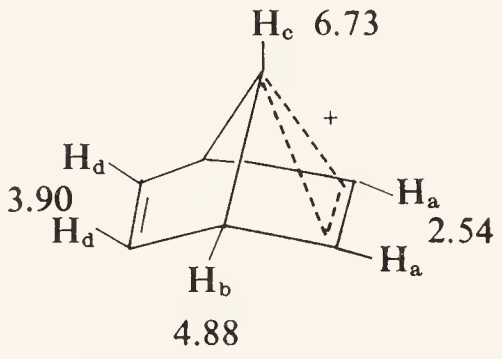
Ions (**12**) and (**19a**) react with nucleophiles at C-7 and C-2(C-3) with the C-7:C-2 product ratio in kinetic control varying markedly with the nature of the nucleophile (8,11). However, these reactions with nucleophiles such as H_2O, MeOH, $Ph{\cdot}CH_2{\cdot}OH$, MeO^-, $Ph{\cdot}CH_2O^-$, BH_4^-, and AlH_4^- are extremely highly stereospecific at both C-7 and C-2 (8,11).

Cation (**12**) may be generated by extraction of *anti*-norbornen-7-ol (**14**)-**OH** or the tricyclic ether (**15**)-**OMe** from CH_2Cl_2–CCl_4 into SO_2–SbF_5–FSO_3H at $-50°$ (8c). Similarly, cation (**19a**) is generated by extraction of norbornadien-7-ol (**18**)-**OH** into FSO_3H (11b,c). The nmr spectra of these ions (chemical shifts on the τ scale and coupling constants) are summarized in (**20**) and (**21**).



(**20**)

J_{ac}	J_{bc}	J_{cdg}
2.5	2.6	0.8 Hz



(**21**)

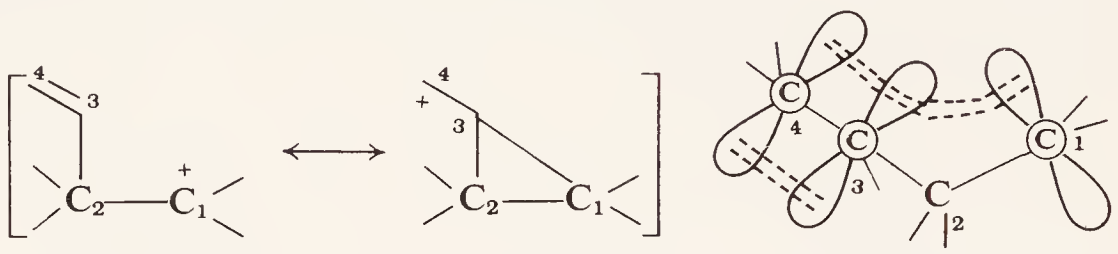
J_{ac}	J_{bc}	J_{cd}
2.7	2.8	1.0 Hz

As regards chemical shifts and coupling constants, the norbornen-7-yl cation (**12**) and the norbornadien-7-yl cation (**19a**) are quite analogous. As regards the protons on the three-centre bonded carbon atoms, the H_c proton signal occurs at high field relative to that of the H_a protons in both ions. The features of the observed nmr spectra are in good accord with a nonclassical structure allowing for the variation in charge distribution which results from hybridization changes at individual carbon atoms of a bridged ion. Actually, the bridging carbon atom in a bridged ion, e.g., C-7 in (**12**), can be expected (10c) to have considerable tendency to rehybridize from sp^2 towards sp^3. Such rehybridization increases the C-7 Coulomb integral as well as C-7–C-2 and C-7–C-3 orbital overlap. This leads to net stabilization of the bridged ion, and these very features of rehybridization at C-7 tend to diminish the charge on this atom (10c).

IV. HOMOCONJUGATION AND HOMOAROMATICITY

It was the cholesteryl–*i*-cholesteryl cation (**9**) which prompted the invention of the terms "homoallyl" and "homoconjugation" (9). The term homoallyl is made clearer with formulas (**22a–c**) which portray a carbonium

ion with a β-olefinic group and show explicitly the overlapping atomic p-orbitals on the two olefinic carbon atoms C-3 and C-4 and the cationic carbon atom C-1. The idea behind the homoallyl designation is that a methylene group (C-2) is a poor insulator of conjugation if the proper rotational positions about the C-1–C-2 and C-2–C-3 bonds are assumed. With proper rotational positions, there is very appreciable 1,3-orbital overlap of a type intermediate between σ and π. Semiempirical molecular orbital calculations suggest substantial stabilization from electron delocalization (9d,10c).



(22a) **(22b)** **(22c)**

From the above point of view, one may say that a homoallyl cation is homoconjugatively stabilized. In conjugation there is electron delocalization over adjacent carbon atoms. Homoconjugation involves electron delocalization across intervening carbon atoms, a single intervening carbon atom in the case of cation (**22**).

While it is only a short jump from "homoallyl" to "homoaromatic" it took us several years to make this extrapolation (10a). Just as for aromaticity, one criterion for homoaromaticity is increased stability or delocalization energy (DE) of a substrate due to cyclic electron delocalization, and another criterion is the ability of a substance to sustain an induced ring-current. The general idea of homoaromaticity and the nomenclature we have been employing are illustrated in Table I and Figure 1. As shown in Table I, the HMO delocalization energy of the aromatic cyclopropenyl cation is considerably greater than that of an acyclic allyl cation. For a modified version of the cyclopropenyl cation involving interruption of the σ-backbone on one side so that the 1,3-resonance interval, namely β_1, is appreciable but less than β_0, the HMO delocalization energy is also greater that that of the allyl counterpart. Such a species may be termed homoaromatic. Interruption of the σ-backbone may involve removing the σ-bond entirely or interposition of one or more methylene groups. Analogous to the allyl-cyclopropenyl–homocyclopropenyl sequence is the heptatrienyl–tropylium–homotropylium sequence. In the case of the allyl anion, ring closure to the cyclopropenyl anion involves a decrease in the HMO delocalization energy. Thus, the cyclopropenyl anion may be termed antiaromatic in the terminology of Breslow (13a) and Dewar (13b).

Analogously, the monohomocyclopropenyl anion may be called anti-homoaromatic; the monohomotropylium anion may be so designated, as well.

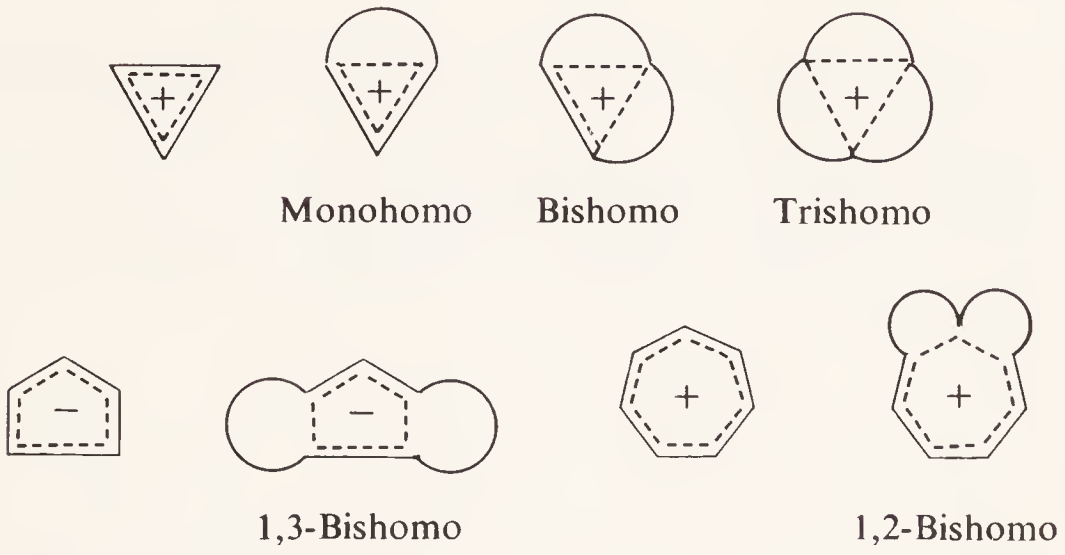
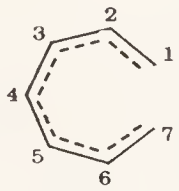
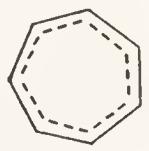
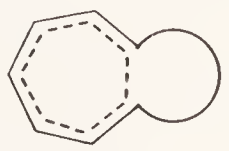


Fig. 1. Illustrative mono-, bis-, and tris-homoaromatic species.

As indicated in Figure 1, the σ-skeleton of an aromatic species may be interrupted on one, two, or three sides, and thus one can conceive of bishomocyclopropenyl and trishomocyclopropenyl species as well as monohomo-. Also visualized in Figure 1 are a 1,3-bishomocyclopenta-dienide ion and a 1,2-bishomotropylium cation. It is important to note that designations such as mono-, bis-, and tris-homoaromatic are based on

TABLE I

HMO Delocalization Energies (β Units) of Some Species

Number of Electrons						
					$\beta_1 = 0.5\ \beta_0$	
2	R^+	0.828	2.000	Aromatic	1.372	Homoaromatic
4	R^-	0.828	0.000	Antiaromatic	0.372	Antihomoaromatic
					$\beta_1 = 0.5\ \beta_0$	
6	R^+	2.055	2.988		2.423	Homoaromatic
8	R^-	2.055	2.098		1.938	Antihomoaromatic

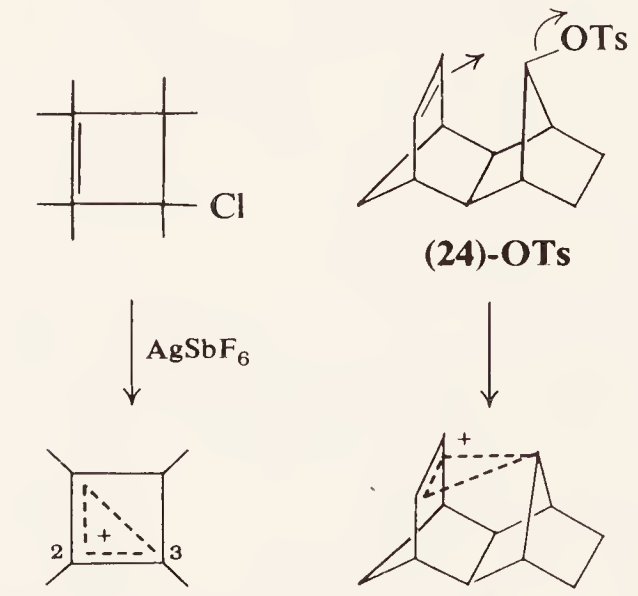
the number of sides where the σ-backbone is removed or lengthened and not on the number of methylene groups inserted on any particular side.

I will now present a partial survey or progress report on homoaromatic ions. First we shall review two-electron species, then six-electron systems and finally we shall consider nine- and ten-electron ions.

V. MONO- AND BIS-HOMOCYCLOPROPENYL CATIONS

Considering homocyclopropenyl cations, we come first to ion (**23**) studied by Katz (14). This pentamethylcyclobutenyl cation is an allylic species with an unusually important 1,3-interaction because the restraint of the four-membered ring makes for an unusually small 1,3-distance. The most important evidence for a serious 1,3-resonance integral in cation (**23**) is the uv spectrum. This shows an absorption band with λ_{max} 245 nm, intermediate between the values characteristic of allylic cations on the one hand and cyclopropenyl on the other. From the linear relation between the frequency of the long-wavelength uv absorption of a series of carbonium ions and the calculated HMO excitation energy an estimate of 0.33 β_0 is obtained for β_{13}. Thus, cation (**23**) may be appropriately called a monohomocyclopropenyl species.

Turning to possible examples of bishomocyclopropenyl species, we come to cation (**12**), discussed above, and (**25**), which we also investigated some years ago (15). The latter cation is produced by ionization of (**24**)-**OTs**, this ester ionizing some 10^{11} times as rapidly as the saturated norborn-7-yl analog as a result of tremendous anchimeric acceleration. According to our present terminology, both species (**12**) and (**25**) are bishomocyclopropenyl in type.



(**24**)-**OTs**

λ_{max} 245 nm

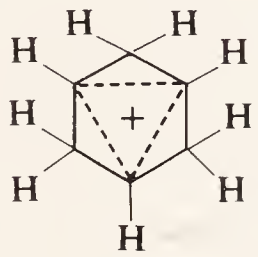
$\beta_{13} = 0.33\ \beta_0$

(**23**)

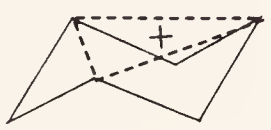
(**25**)

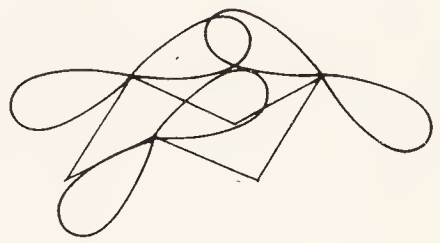
VI. THE TRISHOMOCYCLOPROPENYL CATION

The first recognized example of a trishomocyclopropenyl ion was the simple unsubstituted bicyclo[3,1,0]hex-3-yl cation (**26**) (10b,16). Atomic orbital overlap for the delocalized two-electron system is represented in (**27**). The evidence which led to the trishomocyclopropenyl formulation for the cationic intermediate from *cis*-bicyclo[3,1,0]hex-3-yl toluene-*p*-sulphonate (**28**)-**OTs** was the solvolytic behavior of this substrate compared to that of the *trans*-epimer, (**30**)-**OTs**. For labelled substrates, 3-deuteriated alcohols and esters were originally employed, but more recently we have preferred to work with 6,6-dideuteriated specimens (16c).



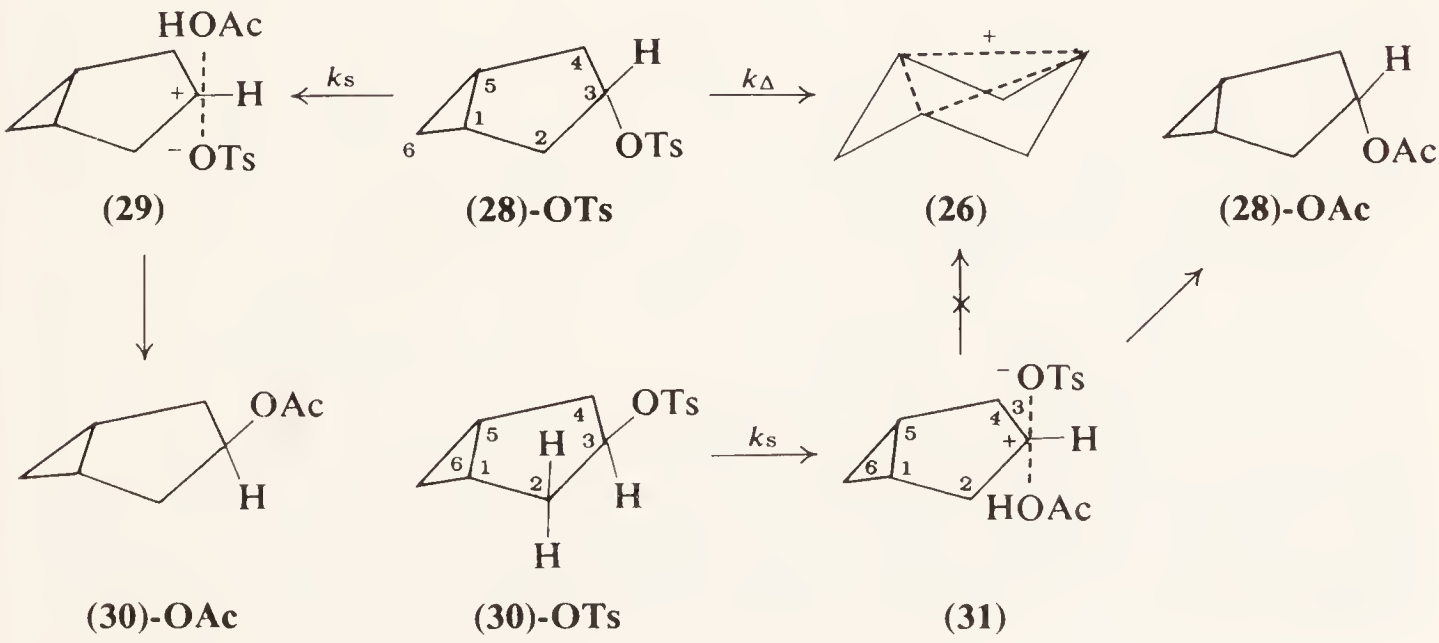
(**26**)





(**27**)

In acetolysis, the *cis*-toluene-*p*-sulphonate (**28**)-**OTs** displays a higher rate than does the *trans*-epimer. Also, it displays ion-pair return and a special salt effect. As product, it gives quantitatively the *cis*-acetate (**28**)-**OAc** with essentially complete retention of configuration (99%). The fraction of elimination product is negligible (0.3%), and no rearranged bicyclo[3,1,0]hex-2-yl or monocyclic products are observed. From dideuteriated (**28**)-**OTs** a product *cis*-acetate is observed with 1.35 ± 0.03 cyclopropane methylene protons, within experimental error of the value 1.33 predicted on the basis of the trishomocyclopropenyl intermediate.



(**29**) (**28**)-**OTs** (**26**) (**28**)-**OAc**

(**30**)-**OAc** (**30**)-**OTs** (**31**)

In acetolysis of the *trans*-toluene-*p*-sulphonate (**30**)-**OTs**, no special salt effect is observed and a number of products are formed. Here, ionization without anchimeric assistance (k_s) leads to a classical cation (**31**). The latter may obviously collapse to inverted *cis*-acetate (**28**)-**OAc**. It may also set off a series of rearrangements *via* a $2 \rightarrow 3$ hydride shift leading to a bicyclo[3,1,0]hex-2-yl cation. The latter is related to a cyclohex-3-enyl cation by ring opening, which in turn can lead to an allylic cation by hydride shift. On this basis, one can understand the complex array of acetolysis products from *trans*-tosylate, three bicyclic acetates, two monocyclic acetates, a bicyclic olefin, and two monocyclic dienes.

As regards mechanism of solvolysis of *cis*-tosylate (**28**)-**OTs**, the essentially exclusive formation of *cis*-acetate with retention of configuration and complete equilibration of the label, the absence of elimination, the lack of rearrangement to bicyclo[3,1,0]hex-2-yl and monocyclic structures, and the special salt effect and ion-pair return phenomena provide a complete contrast with the behavior of the *trans*-tosylate. All of the results are explicable on the basis of the trishomocyclopropenyl intermediate formed by anchimerically assisted ionization (k_Δ). Rate constant k_Δ evidently exceeds the rate constant for anchimerically unassisted solvolysis, k_s, by a factor of ca. 50 in acetolysis and by a somewhat smaller factor in aqueous acetone.

The most striking aspect of the solvolysis of *trans*-tosylate is the complete absence of equilibration of the deuterium label in the *cis*-acetate part of the product from (**30**)-**6D$_2$-OTs** (<0.03 cyclopropane methylene proton). Evidently, leakage from the classical cation (**31**) to the nonclassical ion (**26**) competes unusually poorly with its other reactions.

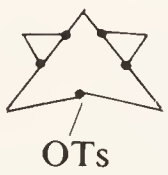
VII. OTHER TRISHOMOCYCLOPROPENYL SPECIES

Since the first trishomocyclopropenyl cation was suggested, a number of other examples have been recognized. Evidence that alkyl-substituted examples (**34**) and (**35**) occur in acetolysis of neothujyl and neoisothujyl toluene-*p*-sulphonates has been published by Norin (17). The very high relative reactivities of the "cis" epimers and the unique nature of the products as regards stereochemistry and structure are in striking accord with the trishomocyclopropenyl formulation of the carbonium ions.

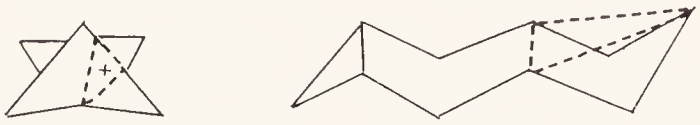
1-Methyl- and 1,5-dimethyl-bicyclo[3,1,0]hex-3-yl systems have been investigated by Yang-i Lin (18) at U.C.L.A. The high solvolytic reactivity of the *cis*-epimers relative to the *trans*, as well as the stereochemistry and deuterium scrambling in the product formation, are uniquely consistent with trishomocyclopropenyl type cations (**32**) and (**33**) in solvolysis of the *cis*-monomethyl- and dimethyl-bicyclo[3,1,0]hex-3-yl toluene-*p*-sulphonates.

As summarized in Table II, kinetic product control from the methyl substituted cations (**32**) and (**33**) favors *tertiary* rather than *secondary* product. However each type of product is formed stereospecifically in the *cis*-configuration. With 6,6-dideuteriated monomethyl substituted *cis*-toluene-*p*-sulphonate, the *tertiary* solvolysis product contains two cyclopropane methylene protons, while the secondary product contains one, in exact accord with expectations from the trishomocyclopropenyl cation (**32**) (Table III). On the other hand, the secondary product from the dideuteriated *trans*-toluene-*p*-sulphonate shows <0.02 cyclopropane methylene protons. Again, as with the unsubstituted *trans*-bicyclo[3,1,0]hex-3-yl toluene-*p*-sulphonate, there is no leakage to the nonclassical ion during solvolysis of the *trans*-toluene-*p*-sulphonate.

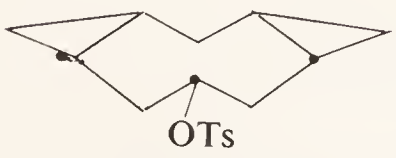
There is a somewhat more complicated example of a bicyclo[3,1,0]hex-3-yl nonclassical ion which is very instructive. This ion is generated by anchimerically assisted ionization of a substrate molecule **(36)-OTs** containing two cyclopropane rings and the tosylate group in the all-*cis* configuration (19). Either one or both of the cyclopropane rings could conceivably become involved with the developing carbonium ion centre in ionization. Thus, one might conceive of either a three-centre trishomocyclopropenyl type of ion (**37**) or other ions such as the five-center pentahomocyclopentadienyl cation (**38**). HMO calculations give a clear prediction in favor of the three center cation and this is borne out by the experimental results starting with the deuterium-labelled toluene-*p*-sulphonate. The results show clearly that only one of the cyclopropane groups in **(36)-OTs** participates in ionization with formation of a specific three-center trishomocyclopropenyl cation and this maintains its integrity until destroyed by nucleophilic attack (19).



(36)-OTs



(37)



(36)-OTs

(38)

A very striking example of a trishomocyclopropenyl cation is the intermediate (**41**) in the very recently reported hydrolysis of (**39**)-*p*-nitrobenzoate, with an *endo*-fused cyclopropane group in an *anti*-norborn-7-yl

TABLE II

Relative Rates and Products in Solvolysis of Some Bicyclo[3,1,0]hex-3-yl Systems

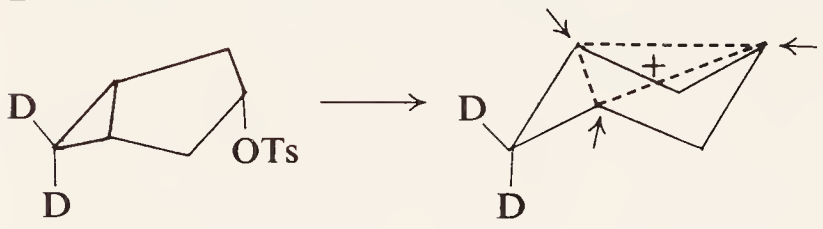
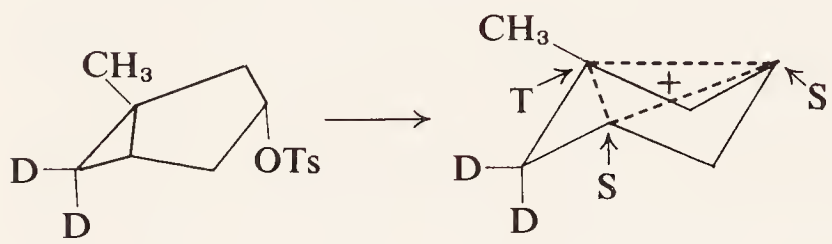
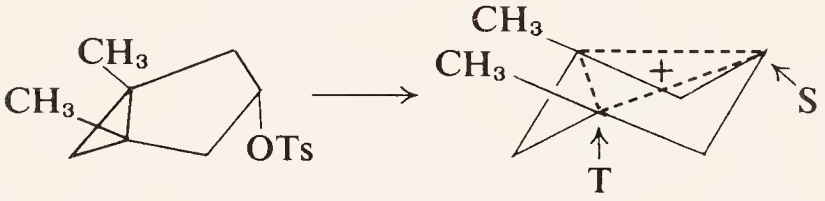
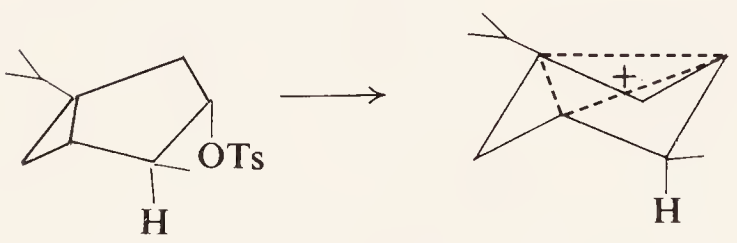
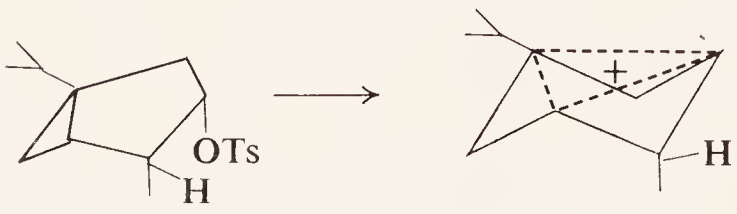
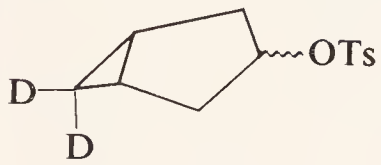
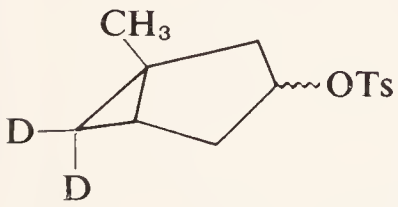
	Relative rate of *cis* ROTs	*Cis*/*trans* rate ratio
 **(28)-6D$_2$-OTs** → **(26)** 99% *cis*, 1% *trans*	1.0	40
 **(32)** 10% S; 99.7% *cis*, 90% T; 99.9% *cis*	5.1	97
 **(33)** 3% S, 97% T; 99.9% *cis*	7.0	119
 **(34)**	6.4	324
 **(35)**	9.5	922

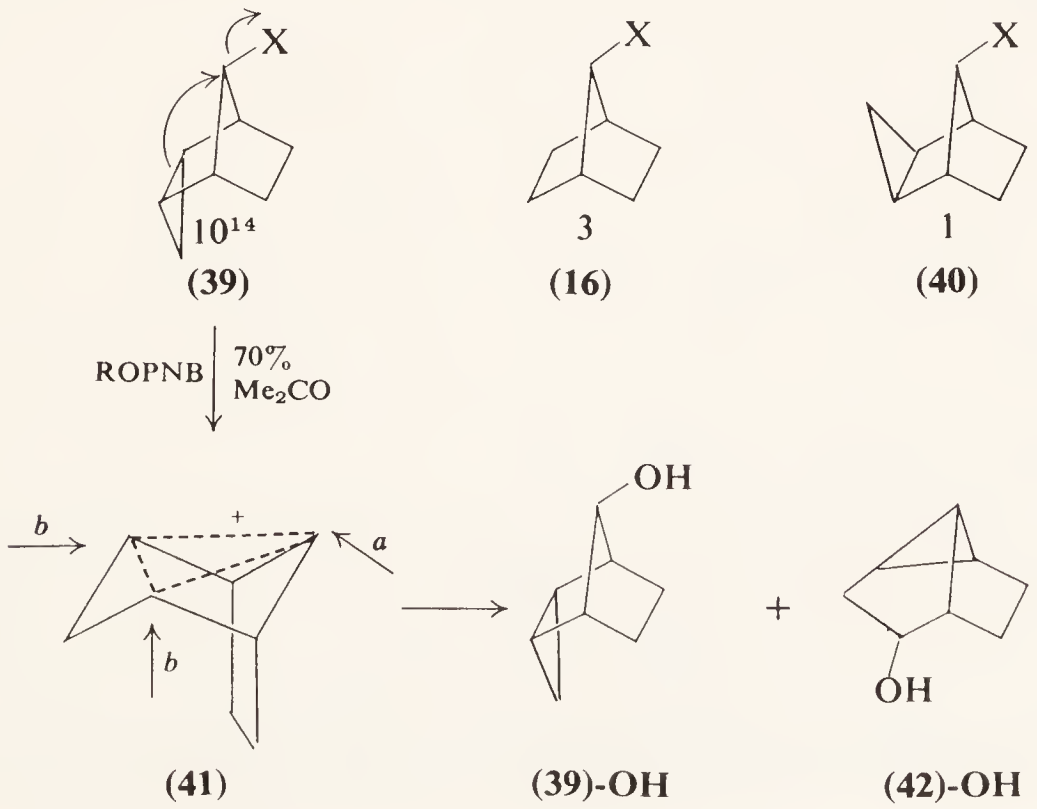
TABLE III

Deuterium Scrambling in Bicyclo[3,1,0]hex-3-yl Systems

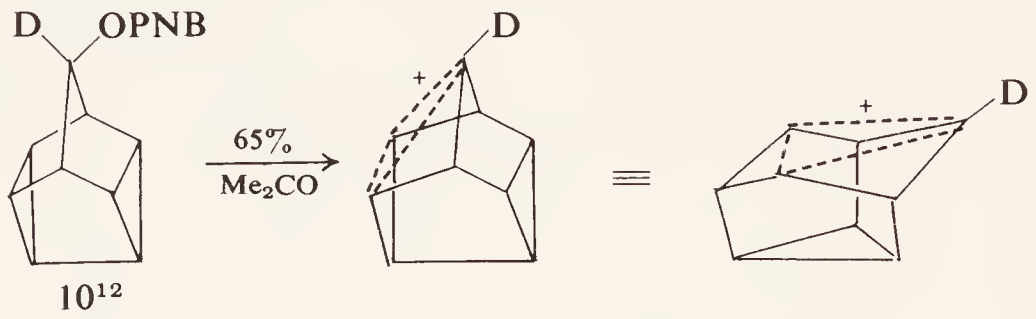
System	Cyclopropane methylene protons in *cis*-solvolysis product	
	cis-ROTs	*trans*-ROTs
	1.35	< 0.03
	T 2.03 S 1.00	S < 0.02

system (20). The isomeric ester (**40**) displays an unaccelerated rate, "face-participation" by the cyclopropane group being poor. On the other hand, "edge-participation" by the cyclopropane group in (**39**) is excellent, (**39**) being 10^{14} times as reactive as the isomeric analog (**40**). Thus, solvolysis of (**39**) equals the world record for anchimeric acceleration. Consistent with the nonclassical trishomocyclopropenyl structure (**41**) for the intermediate cation is the high stereospecificity in the formation of the alcoholic products (**39**)-**OH** and (**42**)-**OH**.

Very recently, hydrolysis of the related system (**43**) with two cyclopropane groups has been described by Coates and Kirkpartick (21). This



system is also extremely reactive, and deuterium labelling shows the intermediate to be the three-fold-degenerate ion (**44**). "Bridge-flipping" does not occur in this species during solvolysis.



10^{12}

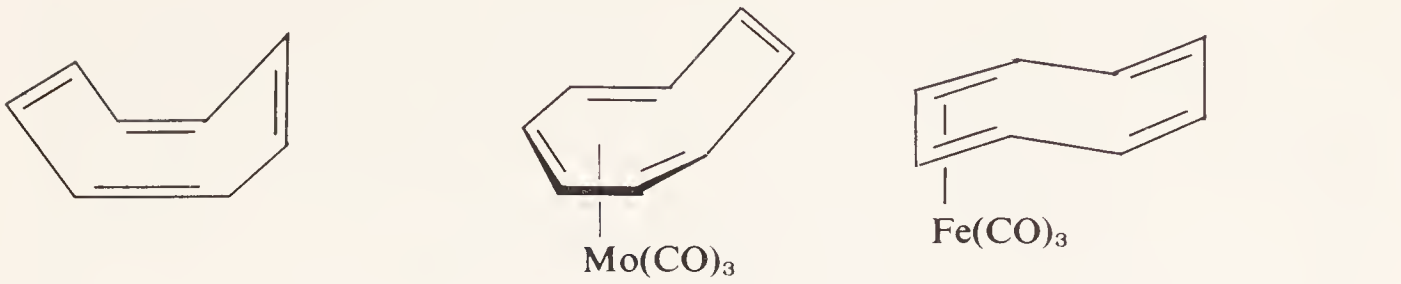
(**43**) (**44**)

VIII. HOMOTROPYLIUM CATIONS

Turning to six-electron homoaromatic systems, let us consider first the $C_8H_9^+$ ion as a possible monohomotropylium ion. This ion may be generated by protonation of cyclo-octatetraene (C_8H_8) in concentrated sulphuric acid (22a,23a). Alternatively, it may be isolated as a solid salt (22a), $C_8H_9^+SbCl_6^-$, by treatment of the hydrocarbon with HCl and $SbCl_5$. In this connection, it will be instructive to consider also the protonation of the cyclo-octatetraene transition-metal carbonyl complexes (23a,24), $C_8H_8 \cdot Mo(CO)_3$ and $C_8H_8 \cdot Fe(CO)_3$. The different electronic requirements of transition-metal atoms in their complexes exert a corresponding control on the resulting structure and thus constitute a powerful tool in the study of homoaromaticity (23a).

The observed nmr spectra of the three cations from protonation of C_8H_8 and its two complexes in H_2SO_4 are summarized in formulae (**45**)–(**47**). For $C_8H_9^+$, the spectrum displays a 5:2:1:1 proton pattern, and especially striking is the large chemical shift (5.8 ppm) between "inside" and "outside" H_b and H_a methylene protons. The nmr spectrum of $C_8H_9Mo(CO)_3^+$ with a 5:2:1:1 proton pattern and a large chemical shift between H_b and H_a (3.5 ppm), bears a striking resemblance to that of the parent $C_8H_9^+$ ion. In contrast, the nmr spectrum of $C_8H_9FeCO_3^+$ displays a 1:4:2:2 proton pattern and the methylene H_b and H_a protons display nearly the same chemical shift.

The striking similarity between the nmr spectra of the free ion and its $Mo(CO)_3$ complex and the contrast with that of the $Fe(CO)_3$ complex give one considerable insight into the electronic structure of each of the species. It seems evident that the $Fe(CO)_3$ complex may be represented to a fair approximation by the classical structure (**47**) which was preferred by Wilkinson (24b) and which is in accord with the $4\pi 5C$ preference of the Fe



(45)

$\tau_{2,3,4,5,6}$ 1.5

(46)

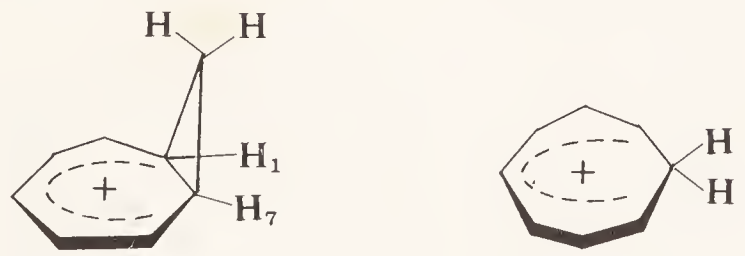
$\tau_{2,3,4,5,6}$ 3.5–4.0

(47)

τ_4 2.26

$\tau_{2,3,5,6}$ 4.62

atom. For the $Mo(CO)_3$ complex, the 6π electronic preference of Mo limits the choice of structure to cyclo-octatrienyl (**49**) or homotropylium (**46**). Only the latter is able to account for the large observed chemical shift between the "inside" and "outside" H_b and H_a protons. This assignment is strengthened by the analogy between the $Mo(CO)_3$ complex and the free ion. As regards the free $C_8H_9^+$ ion, the planar cyclo-octatrienyl structure



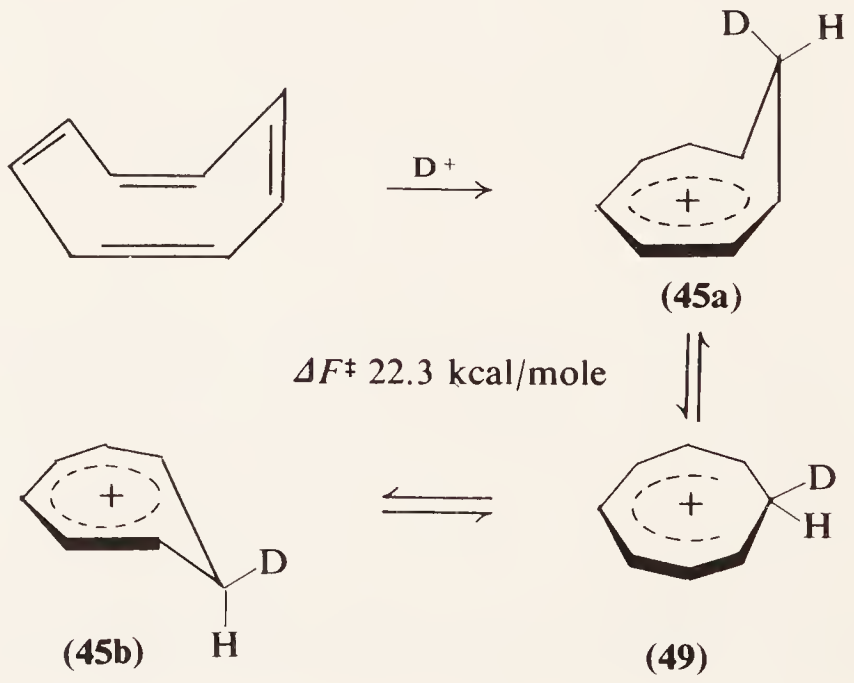
(48) **(49)**

(**49**) may be excluded because this would have magnetically equivalent H_a and H_b methylene protons. For a classical structure (**48**) with a relatively fully formed cyclopropane ring we would expect the nmr signal for $H_{1,7}$ to be at τ ca. 7 or above, a *gem* $J_{a,b}$ of 4.5–5 c/sec, and a *cis* $J_{a,1}$ (ca. 8 c/sec) larger than the *trans* $J_{b,1}$ (ca. 4–5 c/sec), by analogy with known cyclopropyl substituted carbonium ions and other cyclopropane derivatives. Such a structure is excluded by the extensive deshielding of the $H_{1,7}$

protons (τ 3.6) and the pattern of the available coupling constants, *trans* ($J_{b,1}$ 10 c/sec) being larger than *cis* ($J_{a,1}$ 7.5 c/sec). On the other hand, we should note that the nmr spectrum of the $Fe(CO)_3$ complex is just what would be expected for a structure of this type with the cyclopropane electrons excluded from the delocalized electronic system.

The available data are compelling in favor of nonclassical homotropylium structures for the free $C_8H_9^+$ ion and its $Mo(CO)_3$ complex. These involve 1,7-orbital overlap of a type intermediate between σ and π and the species may be called homoaromatic. Ring currents associated with these structures account in the main for the large chemical shift between the "inside" and "outside" methylene protons (23b).

The large chemical shift between inside and outside methylene protons in the monohomotropylium ion makes it possible to measure the rate of ring inversion in this species. This in turn leads to a value for the free-energy difference between the classical cyclo-octatrienyl cation (**49**) and the preferred homoaromatic one (23b). The rate measurement depends on the fact that there is considerable stereospecificity in the protonation of C_8H_8 in D_2SO_4 at lower temperatures ($-15°$), ca. 80% of the incoming deuterium being "inside" (23b). As observation of the solution of C_8H_8 in D_2SO_4 is continued, the intensities of the inside and outside proton signals approach the value corresponding to half a proton in each position, thus permitting the evaluation of a first-order rate constant for the (**45a**) $\rightarrow$ (**45b**) isomerization. This is 9.8×10^{-4} sec^{-1} at ca. 37° and 6.1×10^{-4} sec^{-1} at ca. 32°, corresponding to a $\Delta F^{\ddagger}$ of 22.3 kcal/mole. If the equilibration is visualized as proceeding by ring inversion through a planar form, that of the classical cyclo-octatrienyl cation (**49**), then the free energy of (**49**) is shown to be 22.3 kcal/mole higher than that of the homoaromatic monohomotropylium ion (23b).



Further insight into the electronic structure of the homotropylium ion is provided by its uv spectrum (23b). The two λ_{max} values, 232.5 nm (log ε 4.52) and 313 nm (log ε 3.48) are at somewhat higher wavelengths than those for tropylium ion (25), 217 nm (log ε 4.61) and 273.5 nm (log ε 3.63). However, it is very illuminating that the λ_{max} for uv absorption of the homotropylium ion resembles more closely the value for tropylium ion, with an HMO excitation energy (E_T) of 1.692 β, than the value to be expected for a classical planar cyclo-octatrienyl species (**49**) with negligible 1,7-interaction. The HMO excitation energy for such an ion is 0.765 β, and Deno (26) has reported λ_{max} at 470 nm for an actual heptatrienyl cation which could be taken as a model for (**49**).

An estimate can be made of the value of the 1,7-resonance integral (β_{17}) in the homotropylium ion from the position of the long-wavelength uv absorption maximum at 313 nm. It has been demonstrated that, for a large number of carbonium ions, a reasonably good correlation exists between the HMO excitation energy and the frequency of long-wavelength absorption. In order that homotropylium fit such a correlation, its HMO excitation energy must be approximately 1.45 β_0 which corresponds to $\beta_{17} = 0.73\ \beta_0$. With this β_{17}, the HMO treatment leads to a bond order of 0.56 for the 1,7-bond and values of 0.69, 0.69, and 0.65 for the π-electron 1,2-, 2,3-, and 3,4-bond orders, respectively. These values are to be compared with a π-bond order of 0.64 for the bonds in tropylium ion.

A tropylium-like electronic description of the monohomotropylium ion with a relatively even electron distribution around the C-1–C-7 carbon atom framework, together with a ring current model using a tropylium-like 1.6 Å ring radius and a six-electron induced ring current, accounts very well for the general features of the nmr spectrum of (**45**). Thus, the chemical shift of protons H_{2-6} in (**45**) is very similar to the value for H_{1-7} in tropylium ion. Such a model also accounts very well for the chemical shift between "inside" and "outside" C-8 protons (23b).

More direct evidence regarding the aromatic ring current in monohomotropylium ion comes from the volume diamagnetic susceptibility of this species measured by Dauben (27). As shown in Table IV, the χ_M value for benzene shows an exaltation, Λ, of 13.7 compared to the nonaromatic calculated value, while tropylium ion shows a Λ of 16.0 (27b). It is striking that the Λ for monohomotropylium ion is larger than that of tropylium ion. If the usual exaltation ($\Lambda = 5.2$) associated with a cyclopropane ring is subtracted from that of monohomotropylium ion ($\Lambda = 20$), the resultant Λ, namely 15, is only slightly less than the tropylium exaltation.

Homotropylium ions with "inside" and "outside" 8-chloro-substituents have been reported recently by Huisgen (28) and his co-workers. These ions have a chemical shift (Δ) between inside and outside H_b and H_a

protons identical to that for the unsubstituted homotropylium ion. Further, the rate of equilibration of the epimer 8-chloro-ions (28) is essentially the same as for the unsubstituted analog (**45**).

It is interesting to enquire how far one may proceed with substituents in the monohomotropylium ion without converting the structure into a classical one. Judging by the chemical shift (Δ) between inside and outside H_b and H_a protons and other features of the nmr spectra, 1-methyl-, 1-phenyl-, and 2-hydroxymonohomotropylium ions are still decidely homoaromatic (22b,c). Still more instructive is the 1-hydroxymonohomotropylium ion from protonation of cyclo-octatrienone (29). Even this species is decidedly homoaromatic. As in the case of the unsubstituted homotropylium ion, diamagnetic susceptibilities confirm the homoaromatic character of the 1-methyl-, 1-phenyl-, and 1-hydroxy-homotropylium species (Table IV) (27c).

TABLE IV

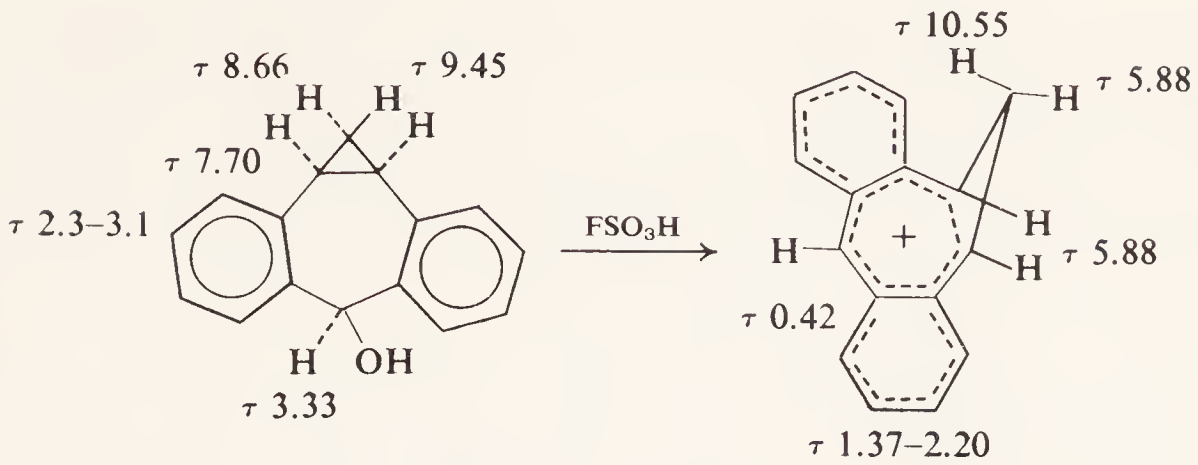
Some "Inside-Outside" Proton Δ Values and Volume Diamagnetic Susceptibilities

			Homotropylium ions					
	C_6H_6	$C_7H_7^+$	Unsub.	8-Cl	1-Me	1-Ph	2-OH	1-OH
Δ (ppm)	—	—	5.8	5.7	5.0	*ca.* 5	3.1	3.1
χ_M (obs.)	54.8	56 ± 1	72 ± 2	—	83 ± 2	120 ± 2	—	75 ± 5
χ_M (calc.)	41.1	40.0	52.0	—	63.3	100.5	—	57.4
Λ	13.7	16	20	—	20	19.5	—	18

It seemed to us that a homocounterpart of the 2,3,6,7-dibenzotropylium ion would be instructive from the viewpoint of homoaromaticity since the two benzene rings dampen considerably the gain in ΔE_π due to cyclic electron delocalization attending formation of a tropylium species. Such a dibenzohomotropylium ion (**51**) has in fact been prepared (30) from the covalent alcohol precursor (**50**). The nmr spectrum of the ion, especially the high Δ value at the methylene group, shows this species to be homoaromatic. Very recently, a monobenzohomotropylium ion has also been reported (31).

IX. A BISHOMOCYCLOPENTADIENIDE ANION

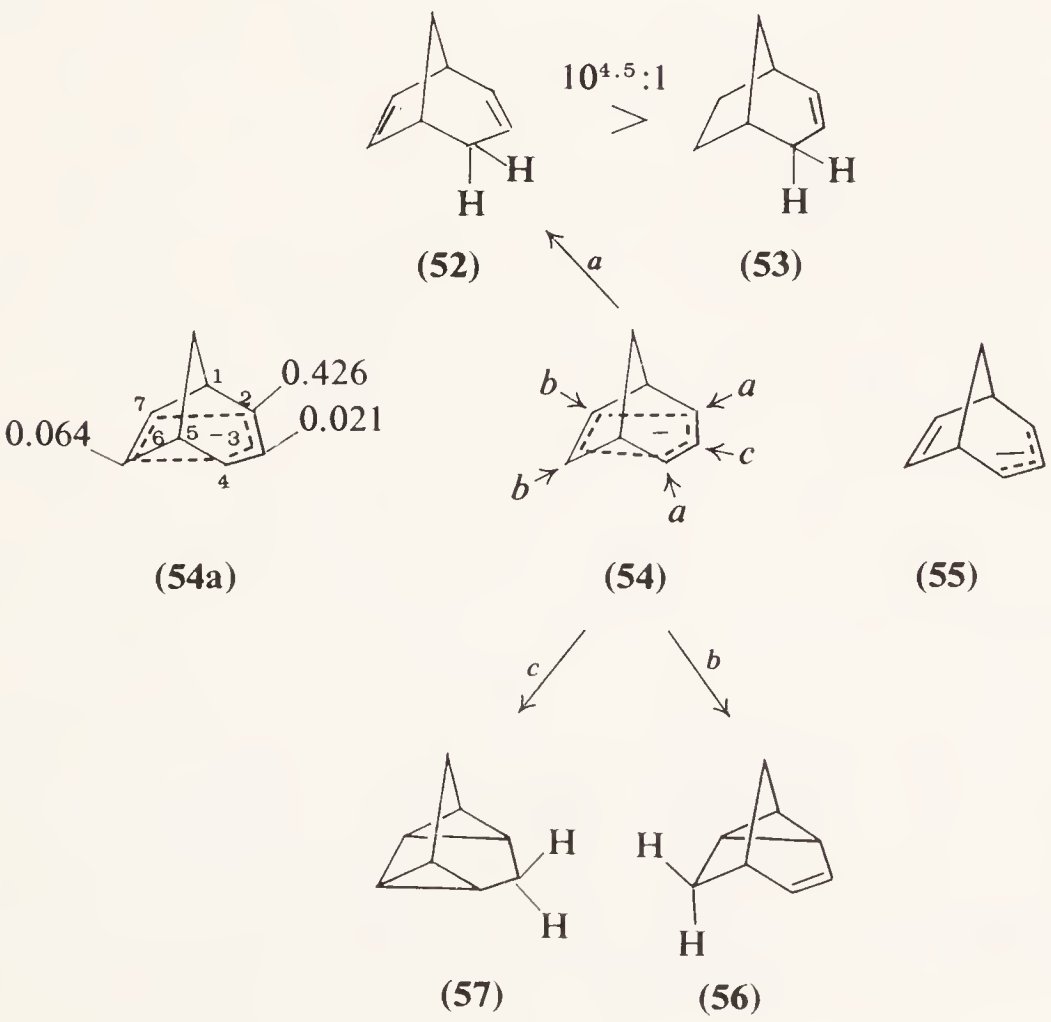
Continuing the six-electron homoaromatic theme, but switching to homocyclopentadienide ions, we shall now consider a 1,3-bishomocyclopentadienide species, namely (**54**). The possibility that this ion is an intermediate in some base-catalyzed deuterium exchanges was suggested



(50) **(51)**

by the work of Brown and Occolowitz (32a) on the relative rates of deuterium exchange of the bicyclic diene (**52**) and monoene (**53**). In dimethyl sulphoxide (DMSO) containing $KOBu^t$, diene (**52**) is more reactive in exchange than monoene (**53**) by a factor of $10^{4.5}$. This increased reactivity of the diene relative to the monoene was ascribed to the presence of the additional olefinic group in (**52**). Exchange involved only the allylic protons in the bicyclic diene and monoene, and no formation of isomeric hydrocarbons from the diene was observed.

HMO Calculations do in fact predict a bonding interaction between allylic anion and olefinic systems in carbanion (**55**). This interaction is quite appreciable even for (β_{27}/β_0) equal to 0.3, and it is specifically



(52) **(53)** **(54a)** **(54)** **(55)** **(57)** **(56)**

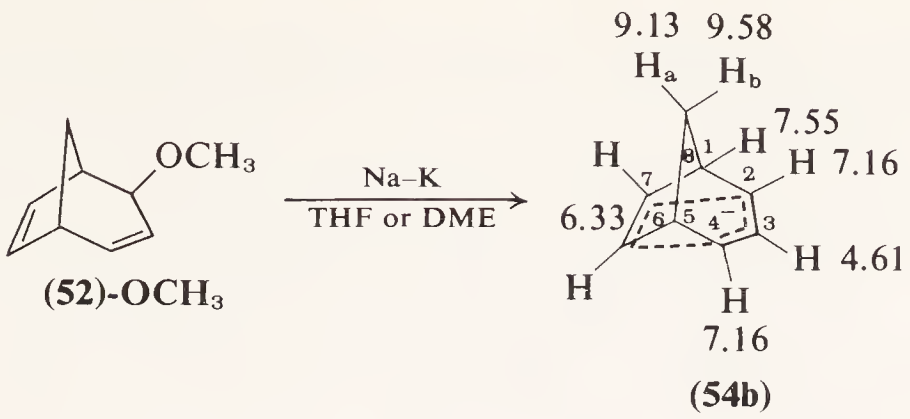
allowed for by the 1,3-bishomocyclopentadienide description (10d). The charge distribution in such an ion depends, of course, on the molecular geometry and the relative importance of the different atomic orbital overlaps. Illustrated in (**54a**) are the HMO calculated charge densities for (β_{27}/β_0) equal to 0.3. Charge is greatest at C-2 and C-4, considerably smaller at C-6 and C-7, and least at C-3.

One may visualize proton donation at the different carbanionic centers of a bishomocyclopentadienide ion (**54**), reaction at C-2 or C-4 (*a*) leading to bicyclic diene (**52**), C-6 or C-7 (*b*) giving tricyclic olefin (56), and C-3 (*c*) leading to tetracyclic hydrocarbon (**57**). One may in fact anticipate the possibility of base-catalyzed equilibration of the bicyclic, tricyclic, and tetracyclic hydrocarbons. Such equilibration of the three hydrocarbons is in fact observed (33a) using Streitwieser's catalyst–solvent system, $CsNHC_6H_{11}$ in $C_6H_{11}NH_2$, which gives much greater equilibration (and exchange) rates than does the $KOBu^t$–DMSO system. These equilibration studies in $C_6H_{11}NH_2$ have shown the relative reactivities of the three hydrocarbons to be in the sequence, bicyclic > tricyclic ≫ tetracyclic. On the other hand, thermodynamic stabilities of the three hydrocarbons are in the sequence, tricyclic > bicyclic > tetracyclic (33a).

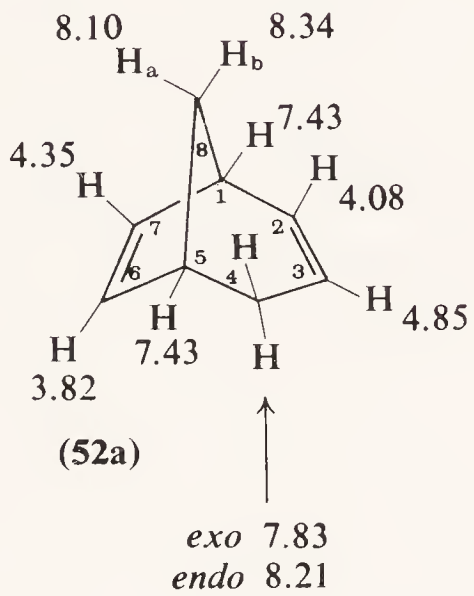
The bicyclo-octadienyl anion (**54**) is sufficiently stable to permit preparation of the potassium salt and observation of its nmr spectrum in tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) (32b,33b). On shaking in THF or DME with Na–K alloy at ca. 0°, the allylic ether (**52**)-OCH_3 reacts quite rapidly to generate the bicyclo-octadienide salt. The resulting orange carbanion solutions are only very faintly contaminated, e.g., with diene (**52**), and are stable for many hours. One of the signals in the nmr spectrum of (**54**) is observed by a solvent signal in ordinary THF or DME, but this difficulty is largely avoided in perdeuteriotetrahydrofuran. The chemical shifts on the τ-scale for the various protons in the anion (**54**) are shown in (**54b**) and these are compared with the corresponding values in the parent diene in (**52a**).

In the nmr spectrum of the anion (**54**) the signal for vinylic protons $H_{2,4}$ appears as a triplet at τ 7.16, shifted upfield by 3.1 ppm relative to H_2 in diene (**52**). The signal for $H_{6,7}$ appears as a singlet at τ 6.33, upfield by an average of 2.3 ppm relative to H_6 and H_7 in the diene. On the other hand, the signal for H_3 appears as a triplet at τ 4.62, actually slightly downfield (ca. 0.2 ppm) from H_3 in (**52**). For the bridgehead protons $H_{1,5}$ in the anion, the signal appears as a skewed triplet at τ 7.55, nearly the same position as in (**52**) (τ 7.43). The signals for the H_8 protons appear as a multiplet at τ 9.12 for H_{8a} and a doublet at τ 9.58 for H_{8b}, an average of 1.1 ppm upfield relative to the values for H_{8a} and H_{8b} in the diene.

All the features of the nmr spectrum of the anion are very much in accord



(52)-OCH_3 **(54b)**



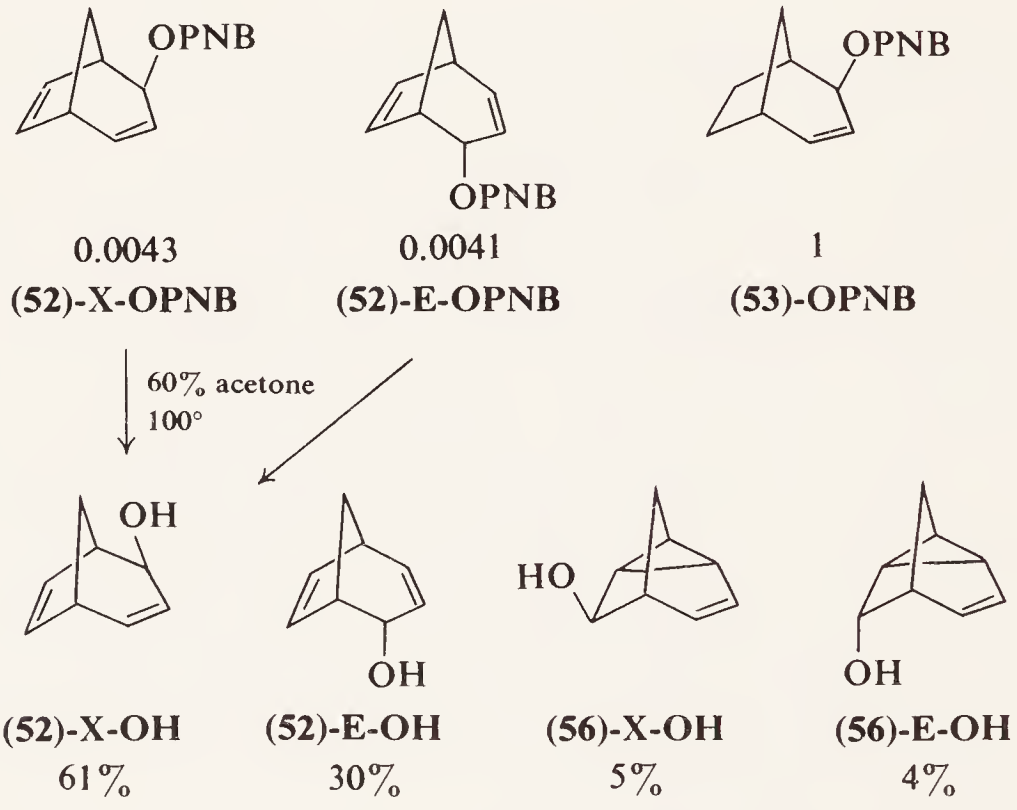
(52a)

with a delocalized bishomocyclopentadienide structure (**54**) with an appreciable aromatic ring current. Very striking is the relatively large upfield shift of the $H_{6,7}$ signal on going from diene to anion, in contrast with the negligible effect on the bridgehead 1,5 protons. The upfield shift of the $H_{6,7}$ signal by an amount ca. 2/3 as large as for $H_{2,4}$ indicates the substantial delocalization of negative charge to C-6 and C-7. The chemical shifts of the $H_{2,4}$, $H_{6,7}$, and H_3 protons relative to the values in (**52**) namely 3.1, 2.3, and -0.2 ppm, respectively, are in just the C-2,4 > C-6,7 > C-3 order for the predicted charge distribution in the anion. The slight negative shift for H_3 relative to H_3 in the diene can be ascribed to the fact that the appreciable deshielding due to the aromatic ring current more than offsets the shielding effect of the negative charge at C-3, the very atom expected to bear the least negative charge. The substantial shielding of the H_8 protons in (**54**) relative to (**52**) by 1.1 ppm may also be ascribed at least partly to a ring-current effect.

Quenching of the carbanion solutions in CH_3OH or CH_3OD produces essentially quantitatively the diene (**52**) containing $<0.5\%$ of tricyclic (**56**) or tetracyclic (**57**). The data show that kinetic control in the protonation of (**54**) favours C-2 and C-4 very strongly. As regards possible stereospecificity of the protonation, the nmr spectrum of the diene

recovered from the CH_3OD quench shows the presence of both *exo*- and *endo*-4-D in comparable amounts. Thus, no appreciable stereospecificity is evident in the protonation (33b).

Whereas the 6,7-olefinic group in the bicyclo-octadienyl anion (**54**) stabilizes it by making it a six-electron bishomoaromatic species, the situation in the corresponding cation should be different. Here, the 6,7-olefinic group makes the cation a four-electron antihomoaromatic bishomocyclopentadienyl species. Therefore, it is of some interest to see the effect of the second olefinic group in solvolysis of the bicyclo-octenyl and bicyclo-octadienyl *p*-nitrobenzoates. As might be expected, the second olefinic group in the *exo*- and *endo*-bicyclo-octadienyl *p*-nitrobenzoates (**52**)-**X-OPNB** and (**52**)-**E-OPNB** is markedly rate retarding (34), alkyl–oxygen ionization in these esters being 0.0043 and 0.0041 times as rapid as it is in the monoenyl analog (**53**)-**OPNB**. The retardation is probably even larger than can be ascribed to the rate-retarding inductive effect of the second olefinic group, in line with the antihomoaromatic designation for the first intermediate cation formed in solvolysis of the dienyl *p*-nitrobenzoates. The products of such solvolysis are very largely the *exo*- and *endo*-bicyclic allylic alcohols, together with small proportions of tricyclic alcohols (34). The exact mechanistic account of the mode of formation of these tricyclic alcohols is not yet clear.



X. MONOHOMOCYCLO-OCTATETRAENE ANION RADICAL: A NINE-ELECTRON HOMOAROMATIC

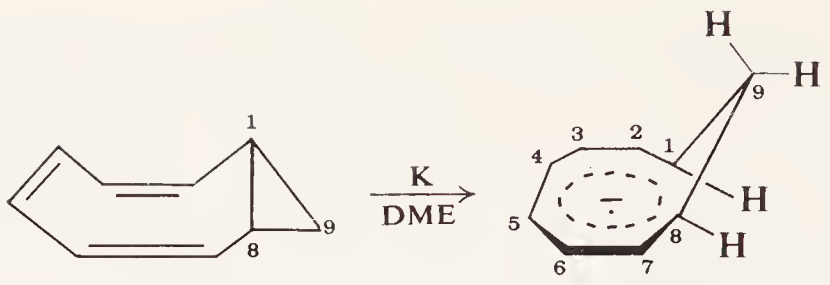
Instead of entering an antibonding olefin molecular orbital, an additional electron supplied to tub cyclo-octatetraene prefers to go into a non-

bonding molecular orbital of a planar cyclo-octatetraene (35). The HMO delocalization energy of cyclo-octatetraene anion radical is so large that aromatization is induced by donation of an electron to cyclo-octatetraene. Similarly, donation of two electrons to cyclo-octatetraene produces the aromatic 10 π-electron-containing cyclo-octatetraene dianon (36). Treatment of cyclo-octatetraene monomethylene adduct (**58**) (monohomocyclo-octatetraene) with a small amount of potassium in glyme at low temperature gives an anion radical whose esr spectrum can be observed (37,38). Compared to cyclo-octatetraene anion radical with a nine-line esr spectrum due to spin coupling of the odd electron with eight equivalent protons ($a_H = 3.209$ gauss), the monohomocyclo-octatetraene anion radical displays a relatively complex esr spectrum appropriate for a species with the symmetry of (**59**). The interpretation of the spectrum is further substantiated with the aid of the dideuterio-analog of (**59**), prepared from (**58**) containing two deuterium atoms on C-9.

As regards the structure of the anion radical species from monohomocyclo-octatetraene, it is clear that the classical structure (**60**) with a fully formed cyclopropane ring must be rejected. Such a structure would not accommodate the large a_H value observed for one of the C-9 protons. The C-9 protons are γ to the nearest radical center in (**60**), and any observed a_H values for γ-protons are always very small. The planar classical structure (**61**), with negligible 1,8 interaction, must also be rejected since the two C-9 protons are equivalent in this structure and would have equal a_H values. On the other hand, the nonclassical monohomocyclo-octatetraene anion radical structure (**59**) accommodates all features of the esr spectrum. Setting a_D equal to $2\,a_H/13$, spectra of both the protonated and deuteriated anion radical species can be well simulated as regards line positions and intensities with the set of a_H values shown for (**59**). The specific assignment of a_H values for the protons on C-1–C-8 is based on calculated spin densities at C-1–C-8 of the nonclassical anion radical (**59**). With either Hückel or the more sophisticated McLachlan (39) spin densities one predicts the sequence of a_H values as $a_{1,8} > a_{3,6} > a_{4,5} > a_{2,7}$. Calculations to simulate these observed a_H values with the aid of the McConnell relation (40), $a_H = Q\rho$, support the nonclassical structure with appreciable 1,8 overlap and resonance integrals (37).

In the monohomocyclo-octatetraene anion radical (**59**) the cyclopropane electrons are abviously included in the delocalized electronic system. An interesting and instructive contrast is provided by the anion radical prepared from the *trans*-fused monomethylene adduct of cyclo-octatetraene (37b), namely (**62**).

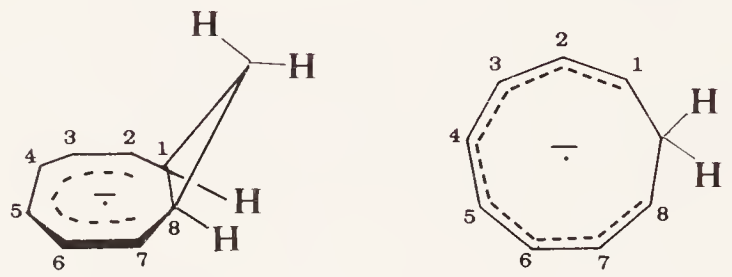
Brief treatment of (**62**) in DME with a potassium mirror at $-90°$ produces an anion radical whose esr spectrum can be recorded at $-90°$.



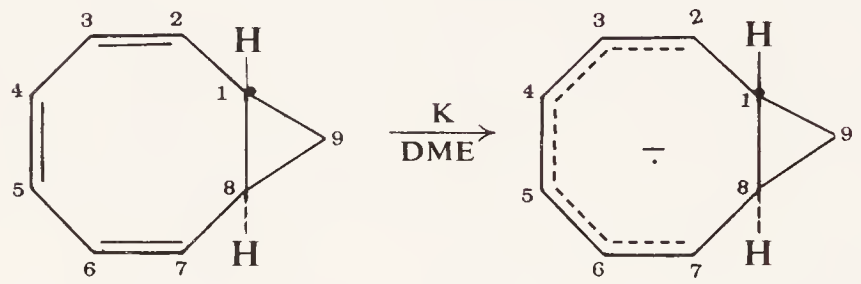
(58) (59)

H	1	2	3	4	9	9
a_H	5.72	0.87	5.12	1.99	4.54	12.18

$Q = 27.40$



(60) (61)



(62) (63)

H	1	2	3	4	9	9
a_H	5.61	8.11	< |0.10|	4.22	0.46	0.46
or	4.22		or 5.61			

$Q = 24.66$ or 27.44

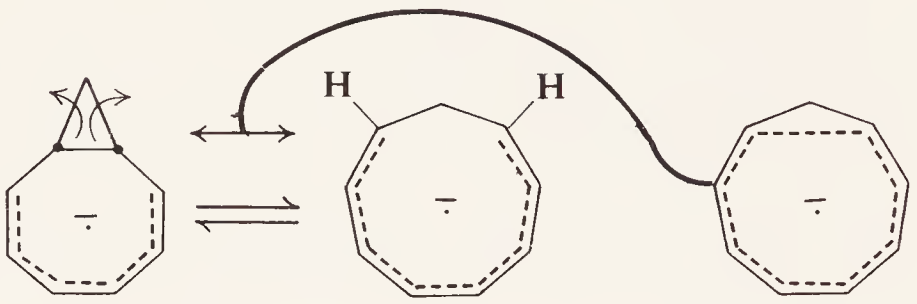
This is very different from that of (**59**). It consists of more than 60 well resolved lines spread over 37.7 gauss, and it can be simulated excellently with hyperfine splitting constants (a_H) of 8.11, 5.61, 4.22, and 0.46 gauss, each for two protons. Evidently, the a_H value for the two remaining protons must be essentially zero ($< |0.10|$ gauss). The assignment of the a_H value of 0.46 gauss to the C-9 protons is clear from the spectrum of the anion radical prepared from the 9,9-dideuterio-(**62**). In this spectrum the 0.46 gauss splitting is no longer observed. The anion radical from (**62**) showed no tendency to rearrange to (**59**) on long observation (6 hr) at $-90°$. Raising the temperature to $-60°$ caused the spectrum of the anion radical from (**62**) to disappear, with no evidence at any point of an isomerization to (**59**) (37b).

All the features of the spectrum of the anion radical from (**62**) are in line with a classical structure (**63**), the *trans*-fused analog of (**60**), containing an essentially fully closed cyclopropane ring and a hexatriene anion radical system. Such a structure is supported by the small and equal a_H values for the two C-9 protons (0.46 gauss) and the fact that the pattern of remaining a_H values is appropriate for a hexatriene anion radical system. The assignment of the a_H values to the different protons is based on calculated spin densities at C-2 to C-7 of a hexatriene π-system. With either Hückel or more sophisticated McLachlan (39) calculated spin densities one predicts the same sequence of a_H values for C-2 to C-7 and simulates the values quite well with the McConnell relation (40). A remaining ambiguity in the a_H assignments is whether the 5.61 and 4.22 values belong to C-1,8 and C-4,5, respectively, or vice versa.

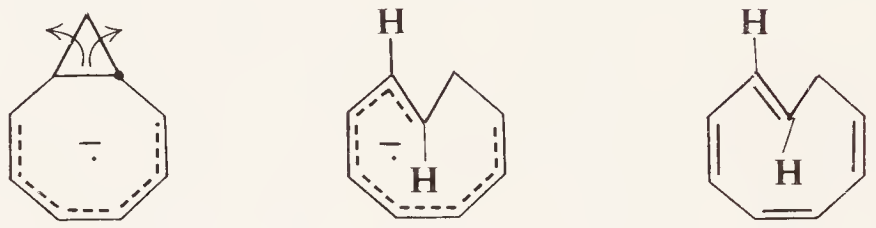
Not only can the pattern of a_H values for C-2 to C-7 in (**63**) be simulated by calculations for a hexatriene π-system, but it is experimentally quite similar to that for a known hexatriene anion radical, generated from cycloheptatriene by Levy and Myers (41). A strong argument in favor of structure (**63**) may be based on the observed Q value. Thus, the sum of a_H values, 24.66 or 27.44, for C-2 to C-7 is a reasonable value for Q. On the other hand, the sum of a_H values, 35.88, for C-1 to C-8 is well out of the range of known Q values. This strongly supports structure (**63**) with the C-1–C-8 cyclopropane electrons excluded from the delocalized π-electron system. The observed a_H value of 5.61 or 4.22 gauss for C-1,8 is also appropriate for protons β to the hexatriene anion radical system in (**63**).

The inclusion of the C-1–C-8 cyclopropane electrons in the delocalized electronic system in anion radical (**59**) and their exclusion in (**63**) is very significant. The difference between the two cases may be understood with the aid of an orbital symmetry argument of the type employed by Woodward and Hoffmann (42) for electrocyclic reactions. Examining the highest occupied molecular orbital in an octatetraene anion radical, the conversion of a cyclononatetraene anion radical (**61**) into a bicyclic hexatriene anion radical (**60**) and the reverse reaction are predicted to be disrotatory. The opening of the anion radical from *cis*-(**58**) leads to the anion radical of the all-*cis*-cyclononatetraene and geometry is favourable for a compromised delocalized electronic system intermediate in character between the bicyclic hexatriene and monocyclic cyclononatraene anion radical extremes. *Trans*-(**62**) has the C-2–C-7 hexatriene system in a nearly planar arrangement. Thus, the situation is more favorable for conjugation in the triene portion of the hydrocarbon or in a triene anion radical system than it is in the tub-like *cis*-(**58**). The disrotatory opening of anion radical (**63**) is towards a very uncomfortable *trans-cis-cis-cis*-cyclononatetraene anion radical (**64**). Models of the *trans-cis-cis-cis*-tetraene (**65**) show the relative

orientation of olefinic groups to be unfavourable for conjugation in the hydrocarbon and in the corresponding anion radical. It is also very unfavorable for a C-1–C-8 interaction in the latter. It is thus clearly more advantageous for (**63**) to remain a relatively favorable hexatriene type anion radical than to open partially or fully.



(**60**) (**61**) (**59**)

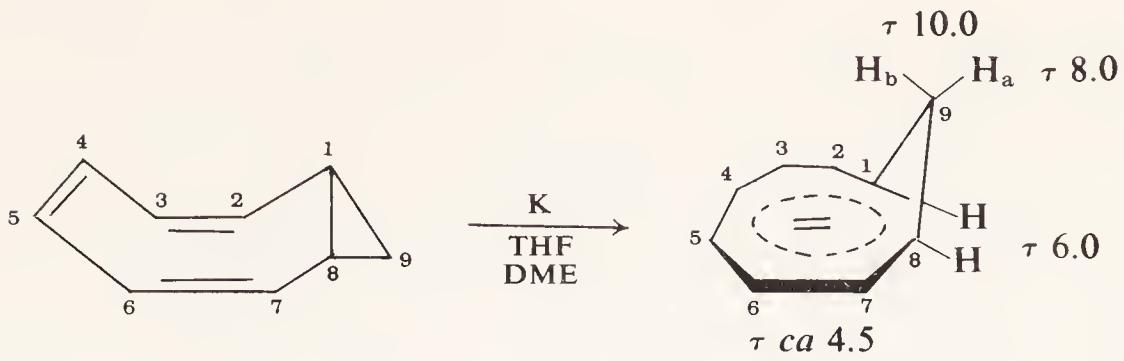


(**63**) (**64**) (**65**)

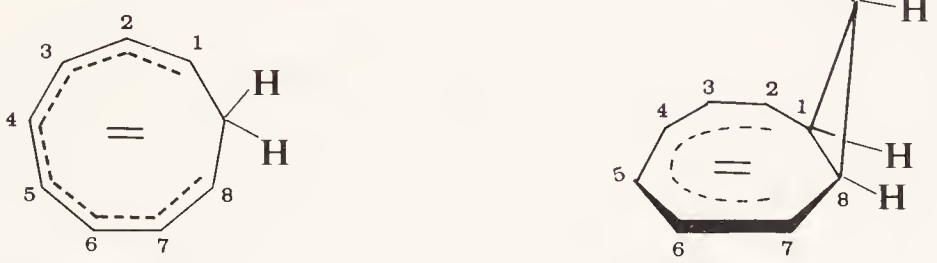
The occurrence of nonclassical electron delocalization in any particular system depends on stereoelectronic and quantum mechanical factors. This is illustrated by the pair of anion radicals just discussed, namely, classical (**63**) and nonclassical (**59**). Another illustration was provided above by the $C_8H_9^+$ species from protonation of cyclo-octatetraene. Thus, the free $C_8H_9^+$ and its 6 π-metal carbonyl complex, $C_8H_9^+Mo(CO)_3$, are nonclassical homotropylium species, while the 4π-iron complex, $C_8H_9^+Fe(CO)_3$, is a classical one.

XI. MONOHOMOCYCLO-OCTATETRAENE DIANION: A TEN-ELECTRON HOMOAROMATIC

Allowing a dilute solution of monohomocyclo-octatetraene (**58**) in THF or DME to stand at $-80°$ over a mirror of an excess of potassium gives rise to a solution of a potassium salt (43a). Only dilute solutions of this material may be obtained since precipitation of the salt occurs if the concentration is too high. If care is taken to obtain relatively complete reduction of the anion radical, satisfactory nmr spectra may be obtained for the salt species at $-60°$. The nmr spectrum of the salt solution, compared with that of the original hydrocarbon, is appropriate for the dianion species (**66**).



(58) **(66)**



(68) **(67)**

In both THF and DME as solvents, the nmr spectrum of the parent hydrocarbon (**58**) contains a six-vinyl-proton multiplet centered at τ 4.1, a three-proton complex multiplet centered at τ 8.8 for the two tertiary cyclopropane C-1,8 protons plus one of the cyclopropane C-9 methylene protons, and a one-proton multiplet at τ 10.0 for the other C-9 proton. For the dianion species in perdeuteriotetrahydrofuran, the nmr spectrum contains a complex multiplet for six protons centered at τ ca. 4.5 and multiplets for two protons at τ 6.0 and one proton at τ 10.0. The τ 6.0 signal overlaps one of the solvent signals (τ 6.40), so that the relative area of this signal is obtained by a difficult dissection and is therefore only approximate. In perdeuterio-1,2-dimethoxyethane the six-proton multiplet is centered at τ ca. 4.8, and the two-proton signal at τ 6.1 is better separated from the nearby solvent peak at τ 6.58. Also visible is a one-proton signal centered at τ 8.0 which was hidden in THF by the THF solvent peak at τ 8.25. Finally, the remaining one-proton signal occurs at τ 10.0. The nmr spectrum of the dianion from the 9,9-dideuteriated (**58**) is similar, except that no signal appears in the τ 6.8–10.5 range.

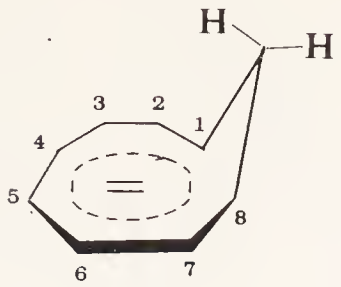
As regards assignments for the different signals in the dianion, the signal at τ 4.5 is assigned to the six C-2–C-7 protons, somewhat upfield from the vinyl proton signal in the parent hydrocarbon. The signal at τ 6.0 is assigned to the two C-1,8 protons, considerably downfield from the position of the tertiary cyclopropane protons in (**58**). The signal at τ 8.0 is assigned to the "outside" C-9 proton, this being deshielded as compared to the same proton in (**58**), while the signal at τ 10.0 is assigned to the "inside" C-9 proton.

As in the case of the anion radical (**59**), the available evidence strongly supports a homoaromatic structure (**66**) for the product from donation of two electrons to the monohomocyclo-octatetraene. A classical planar structure (**68**) with negligible 1,8-interaction is ruled out by the non-equivalence of the two C-9 protons, as well as the relatively low chemical shift of the C-2–C-7 protons. A classical structure (**67**) with a fully formed cyclopropane ring may also be rejected, since the 1,8 protons and also the 2–7 protons are too deshielded. Further, it is not easy to account for the chemical shift between the "inside" and "outside" C-9 protons on the basis of (**67**). On the other hand, all the features of the nmr spectrum are well accounted for by a homoaromatic structure (**66**) with considerable 1,8 interaction and an appreciable ring current. On this basis, the intermediate value of the chemical shift of the C-1,8 protons is easily understandable. Further, the ring current in (**66**) helps explain the chemical shift between the "inside" and "outside" C-9 protons, and also the low τ value for the C-2–C-7 "vinyl" protons. From the known relationship between the charge which a carbon atom bears and the chemical shift of a proton attached to it, one might expect the change from parent hydrocarbon to a dianion, with a double negative charge distributed over eight carbon atoms, to cause a shielding of the C-2–C-7 protons by ca. 2.5 ppm from this cause alone. The observed net effect is only ca. 0.4–0.7 ppm (THF or DME); since charge density and ring current are very probably the two most important influences on the C-2–C-7 proton chemical shifts, deshielding due to the aromatic ring current must be quite substantial.

Reactions of the aromatic 10 π-electron cyclo-octatetraene dianion as a nucleophile (36a,44) are both interesting and useful. Similar interest attaches to the chemistry of the homoaromatic counterpart of cyclo-octatetraene dianion, namely monohomocyclo-octatetraene dianion (**66**). However, only a little information is available regarding the chemistry of (**66**), specifically its behavior on protonation with methanol (43b). This gives only one main product, namely, bicyclo[6,1,0]octa-2,4-diene (**70**), obtained in over 85% yield by preparative v.p.c.

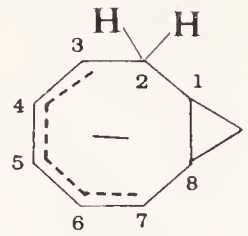
When the dianion from 9,9-dideuterio-(**58**) is quenched with MeOH the final product is pure 9,9-dideuterio-(**70**). When CH_3OD is employed in the quench of dianion (**66**) the bicyclo-octadiene product contains two deuterium atoms as judged by the mass spectrum, and the nmr spectrum shows that these are located at least very largely as in 2,3-dideuterio-(**70**). As regards possible stereo specificity of the protonations at C-2 and C-3, we do not as yet have any precise information.

Mechanistic considerations suggest that the first protonation of (**66**) occurs at C-2 and gives rise to the bicyclic anion (**69**) which then reacts at C-3 in the second protonation (43b).



(66)

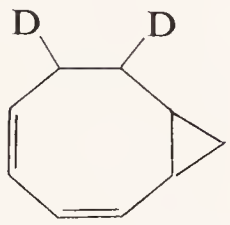
CH_3OH



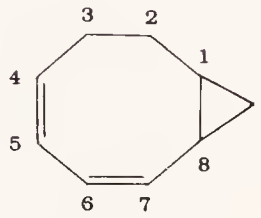
(69)

CH_3OD

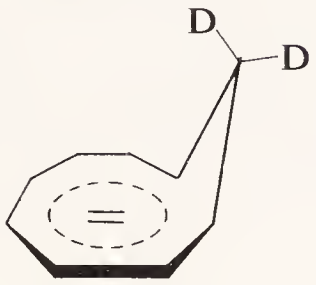
CH_3OH



2,3-D_2-(70)

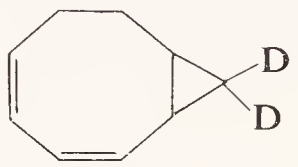


(70)



9,9-D_2-(66)

CH_3OH

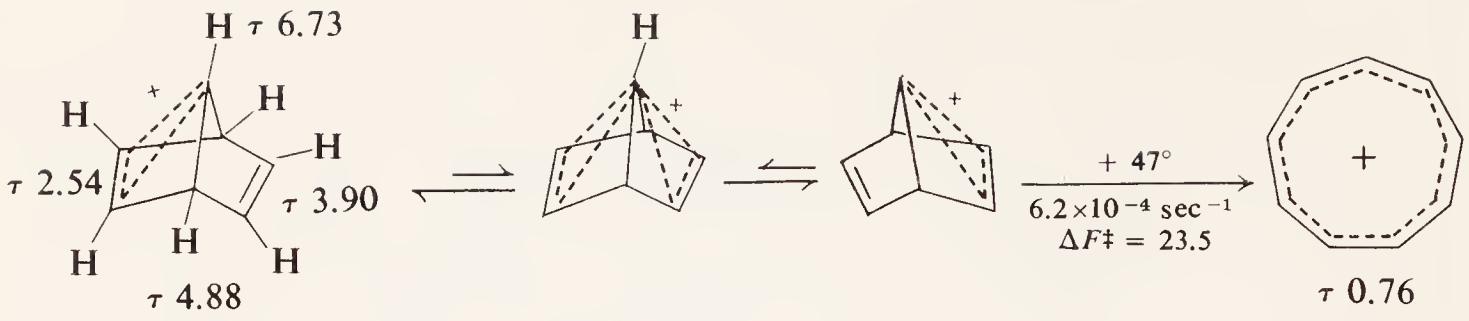


9,9-D_2-(70)

XII. FIVE-CARBON DEGENERATE REARRANGEMENT AND BRIDGE FLIPPING OF THE NORBORNADIEN-7-YL CATION

As indicated earlier, it is now possible, in extremely non-nucleophilic media, to observe directly by nmr many of the nonclassical carbonium-ion intermediates previously proposed to explain unusual rates, products, and stereochemistry in solvolytic work. It is thus possible to study directly the behavior of these species under conditions of long life. Such studies are uncovering fascinating new carbonium-ion rearrangements which will be illustrated with current work on norbornadien-7-yl cations (11).

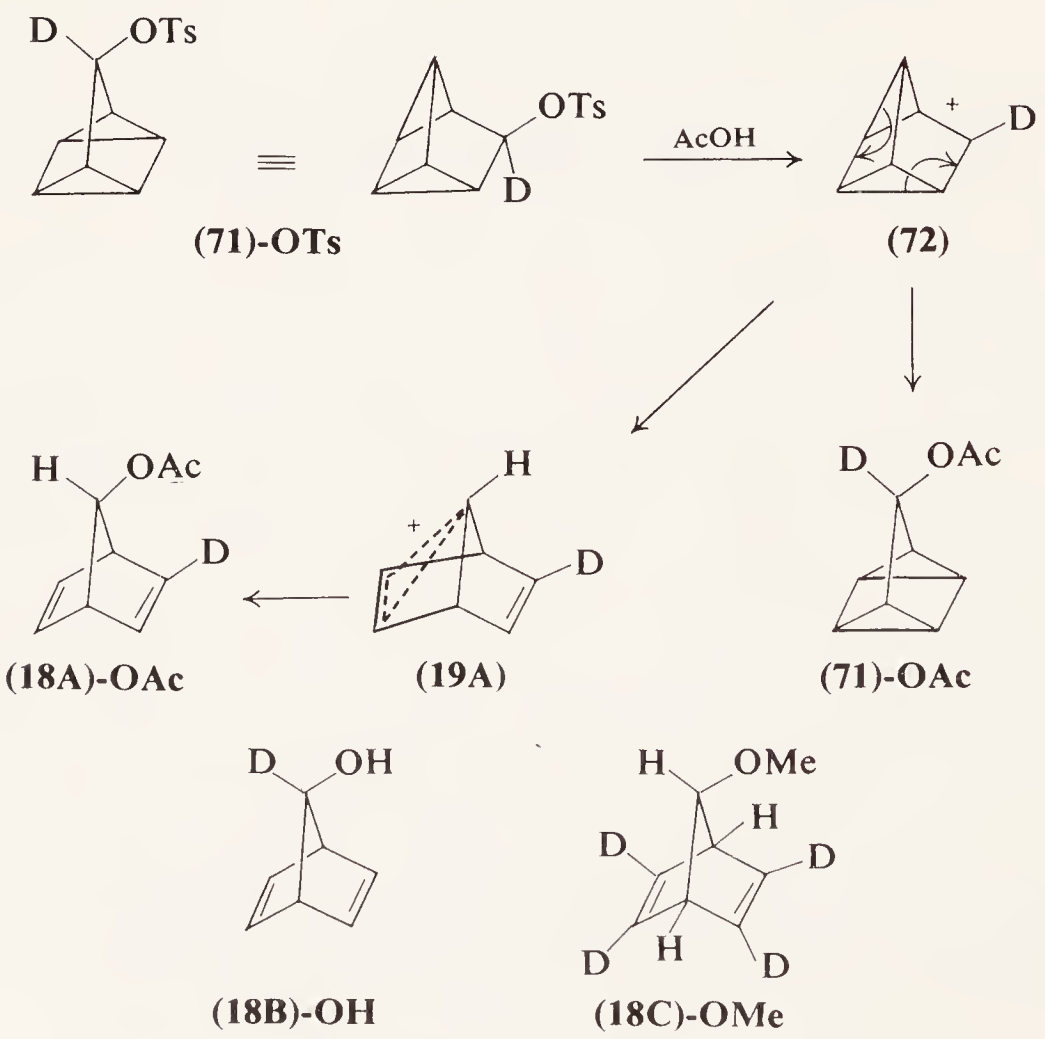
Extraction of norbornadien-7-ol from pentane or CH_2Cl_2 into FSO_3H at $-78°$ gives an FSO_3H solution of cation (11b) (**19**). Warming the solution to $+45°$ caused no noticeable broadening of the proton signals for the "bound" and "unbound" vinyl groups, thus showing that there is a substantial barrier to bridge flipping, i.e., (**19a**) $\rightleftharpoons$ (**19c**), via symmetrical (**19b**) as a transition state (or intermediate) (11c). On the other hand, extended Hückel calculations predict a relatively low value for this barrier (8 kcal; 0.35 eV) (45).



(19a) **(19b)** **(19c)** **(5)**

Cation (**19**) decomposes at 45° as evidenced by the development of some broad, undetailed nmr signals, as well as a sharp signal at τ 0.76 for tropylium ion formed in ca. 25% yield. Despite very rapid decomposition, the nmr spectrum of (**19**) could be recorded at 77°. At this temperature the τ 2.54 signal for the "bound" vinyl protons was still sharp with the coupling patterns somewhat collapsed. However, the τ 3.90, 4.88, and 6.73 signals for "unbound" vinyl, bridgehead, and bridge protons were broadened, indicating the onset of an interesting degenerate rearrangement (11b).

To study this rearrangement on a conventional rather than nmr time-scale, labelled norbornadien-7-yl precursors were employed. These were: (**18A**)-**OAc** with a *syn* vinyl deuterium obtained from acetolysis of 7-deuterioquadricyclyl OTs, (**71**)-**OTs**, via the Richey–Story rearrangement (46); (**18B**)-**OH** with a 7-deuterium obtained from 7-deuterioquadricyclanol; and (**18C**)-**OMe** with 77% of 4 vinyl deuterium atoms obtained by



(71)-OTs **(72)**

(18A)-OAc **(19A)** **(71)-OAc**

(18B)-OH **(18C)-OMe**

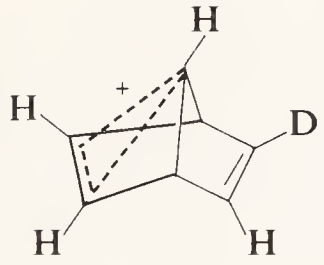
base-catalyzed exchange of norbornadien-7-yl methyl ether with $LiNDC_6H_{11}$ in $C_6H_{11}ND_2$.

In FSO_3H at $-73°$, **(18A)-OAc** displayed the four-signal spectrum of **(19)** with the intensity of the unbound vinyl signal only half as great as that for the bound vinyl; see **(19A)** in Table V (11b). When the cation solution was warmed to $-47°$, a scrambling of the deuterium label was observed with a rate constant of 3×10^{-4} sec^{-1} (Table V). However, the vinyl proton peak intensities did not approach the 1:1 ratio expected for a bridge-flip phenomenon. Rather, the peak intensities approached a 2:1·6:1·6:0:8 ratio for the bound vinyl, unbound vinyl, bridgehead, and bridge protons, respectively, as in **(19E)**. In other words, deuterium was scrambled to all positions *except* the bound vinyl! The same phenomenon was demonstrated with cations **(19B)** and **(19C)** from **(18B)-OH** and **(18C)-OMe**, respectively (Table V). At $-60°$ intially, both of these cations exhibited the same relative peak intensities as their precursors, but on warming to ca. $-50°$, these intensities approached the ratios expected for a five-carbon scrambling reaction; see **(19F)** and **(19G)** in Table V (11b).

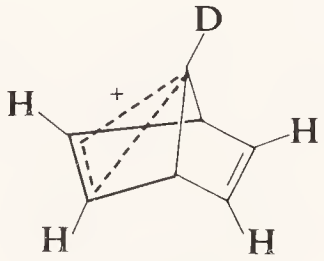
TABLE V

Rates and Free Energies of Activation of Degenerate Isomerizations of the Norbornadien-7-yl Cation

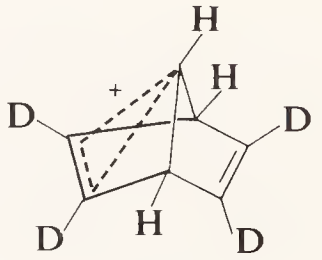
Cation



(19A)

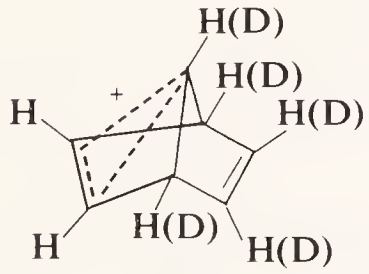


(19B)

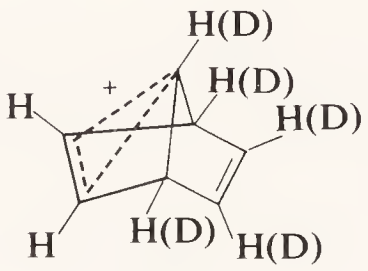


(19C)

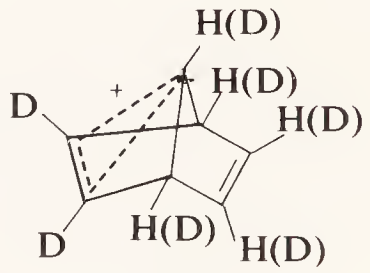
Product



(19E)



(19F)



(19G)

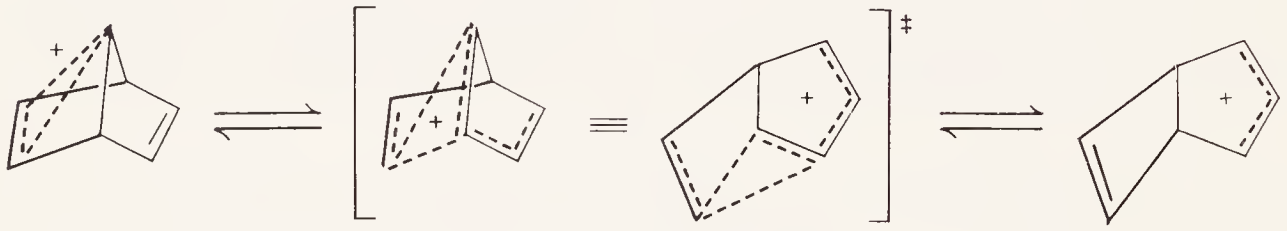
Temperature, °C	−47	−55	−50
10^4 k sec^{-1}	3[a]	1.7[b]	2[a]
$\Delta F^{\ddagger}$, kcal/mole	16.7	16.4	16.7

[a] Evaluated graphically using $\ln [(H_\infty - H_0)/(H_\infty - H_t)] = kt$, with H_∞ equal to the equilibrium amount of protium in the unbound vinyl group.

[b] Same as note a, at C-7.

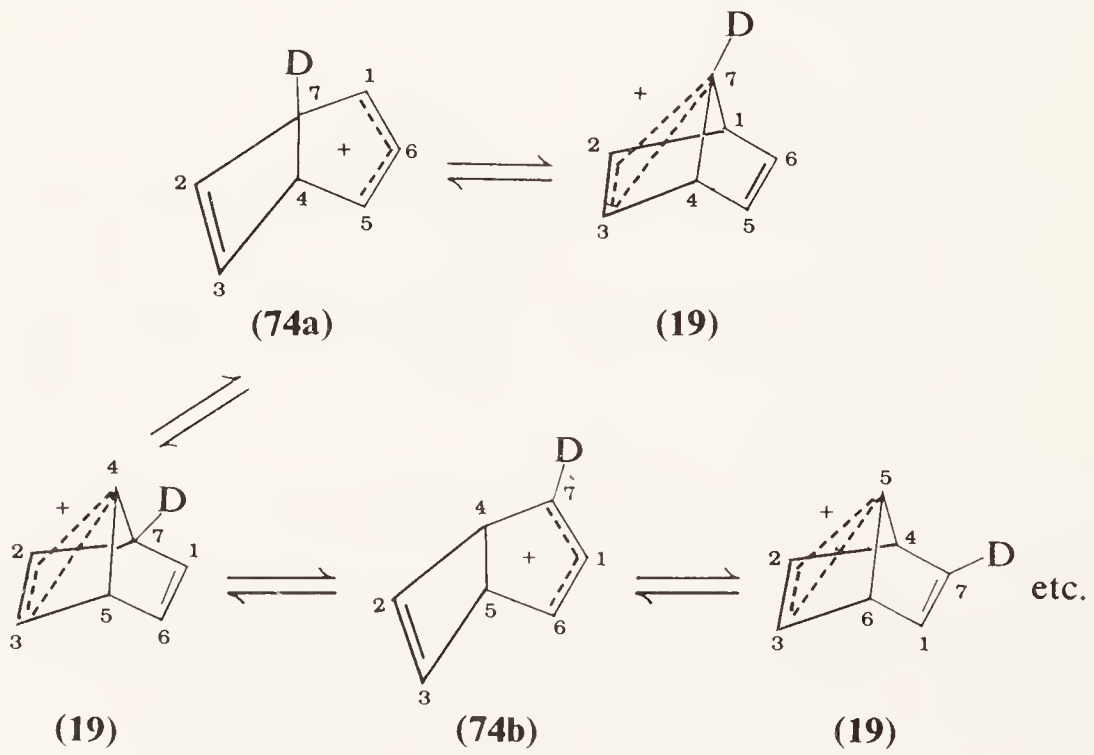
Examination of the nmr signal intensities during scrambling of (**19A**), (**19B**), and (**19C**) revealed that deuterium is incorporated sequentially at the different positions. Thus, in the case of (**19A**) and (**19C**), deuterium is first incorporated into the bridgehead, then into the bridge position. With (**19B**), deuterium appears first at the bridgehead, then in the unbound vinyl group. Thus, the isomerization may be said to occur by a stepwise circumambulatory motion of five carbons of the framework of (**19**) with respect to the two which comprise the bound vinyl function.

The simplest specific mechanism which we can conceive for the five-carbon degenerate rearrangement involves the ring contraction of (**19**) to a bicyclo[3,2,0]heptadienyl cation (**74**) by means of a 1,2-shift of a bound vinyl carbon atom from C-1 or C-4 to C-7 via a transition state such as (**73**), followed immediately by a ring expansion which leaves the same vinyl function bound to C-7.



(19) **(73)** **(74)**

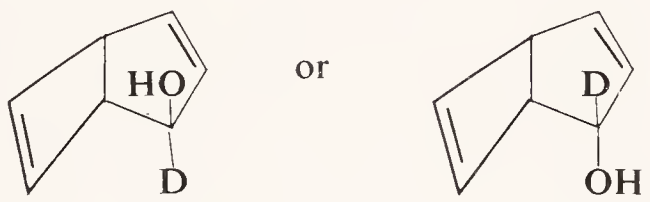
This is pictured by (**19**) ⇌ (**74a**) ⇌ (**19**) ⇌ (**74b**) ⇌ (**19**), etc., which shows the bound vinyl group working its way around the five-membered ring defined by the five other carbon atoms in (**19**). This mechanism is supported by the behavior of the *cis*- and *trans*-bicyclo[3,2,0]heptadienols, *cis*-(**75**)-**OH** and *trans*-(**75**)-**OH** in FSO_3H (11b).



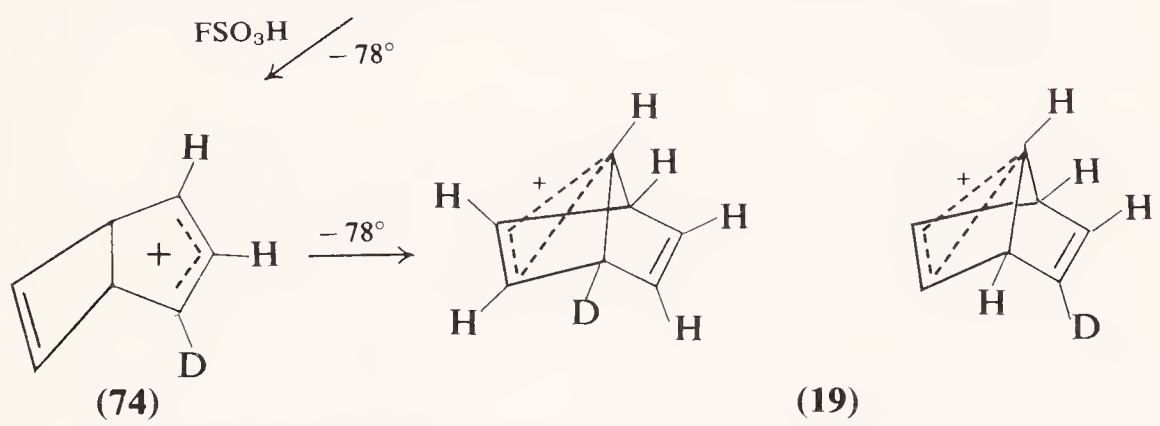
(74a) **(19)**

(19) **(74b)** **(19)**

When either *cis*-(**75**)-**OH** or *trans*-(**75**)-**OH** was extracted into FSO_3H t $-78°$, and the carbonium-ion solution was observed at $-78°$ within 120 sec, the nmr spectrum of (**19**) was obtained with no trace of a signal for a [3,2,0]-cation (**74**). Most importantly, the α-deuterio-*cis*- and -*trans*-[3,2,0]-alcohols both gave (**19**) with 2·0:1·5:1·5:1·0 ratios of signal intensities for bound vinyl, unbound vinyl, bridgehead, and bridge protons, respectively. In other words, 50% of the deuterium label appears at a bridgehead, and 50% in the unbound vinyl group. This result is in exact accord with a mechanism wherein the first formed [3,2,0]-cation ring-expands to the [2,2,1]-ion with either carbon of the cyclobutene vinyl function undergoing a 1,2-shift as the migrating vinyl group becomes the bound vinyl of (**19**). The evidence is thus strongly in favor of the ring contraction–ring expansion mechanism (11b) for the degenerate five-carbon scrambling of (**19**).



trans-(**75**)-**OH** *cis*-(**75**)-**OH**

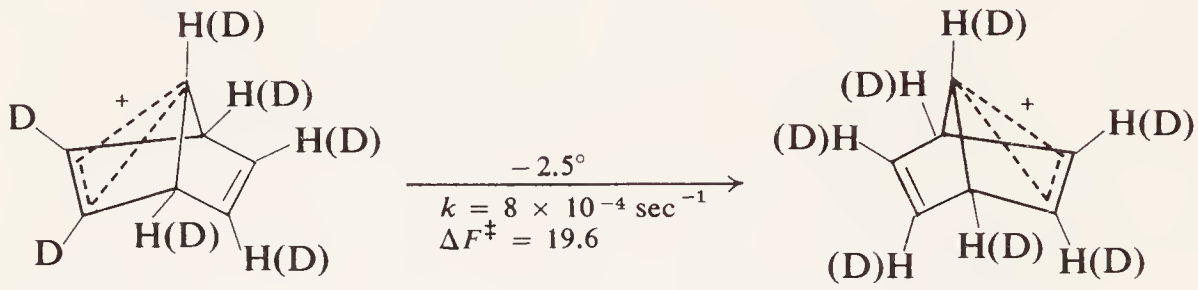


(**74**) (**19**)

As regards the equilibrium between the [3,2,0]-ion and the [2,2,1]-ion (**19**), the latter is strongly favored. A minimum figure for the rate constant for (**74**) → (**19**) is 10^{-2} sec^{-1} at $-78°$, and the rate constant for (**19**) → (**74**) at this temperature may be estimated as 1.5×10^{-6} sec^{-1} from the available data. Thus, a minimum figure for the equilibrium constant for (**74**) ⇌ (**19**) is 7000 at $-78°$.

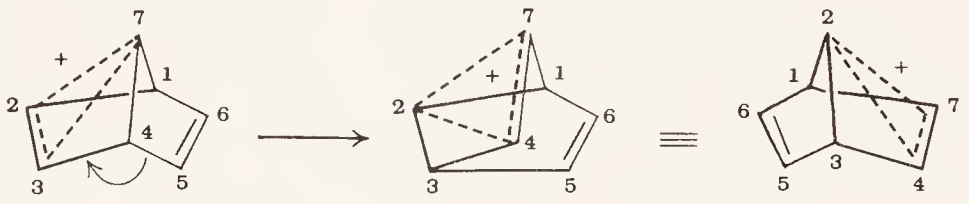
Returning to the phenomenon of "bridge-flipping," it was possible to study (11c) the equilibration of bound and unbound vinyl groups in (**19**) by observing the labelled cation (**19G**) derived from the precursor (**18C**)-**OMe** as a result of degenerate five-carbon scrambling. Cation (**19G**) has a deuterium atom at each bound vinyl position but only 2/5 of a deuterium atom at each unbound vinyl position. At ca. 0° protium incorporation

into the bound vinyl positions is indeed observed, the bound and unbound vinyl signals approaching equal intensities as in (**19H**). At $-2.5°$, $k = 8 \times 10^{-4}$ sec^{-1} and thus $\Delta F^{\ddagger}$ is 19.6 kcal/mole, some 3 kcal greater than $\Delta F^{\ddagger}$ for five-carbon scrambling.



(**19G**) (**19H**)

The value of 19.6 kcal/mole is actually a lower limit to the free-energy difference between the symmetrical and unsymmetrical structures of the norbornadien-7-yl cation. This is because bridge flipping is not the only possible mechanism for exchange of vinyl groups. For example, another plausible mechanism involves 1,2-shifts of an unbound vinyl carbon atom from C-1 to C-2, or C-4 to C-3. Such shifts move the bound vinyl group around so as to scramble C-1, C-2, C-3, C-4, and C-7. Coupled with the more rapid degenerate five-carbon rearrangement, all seven carbon atoms become scrambled (11b,c).

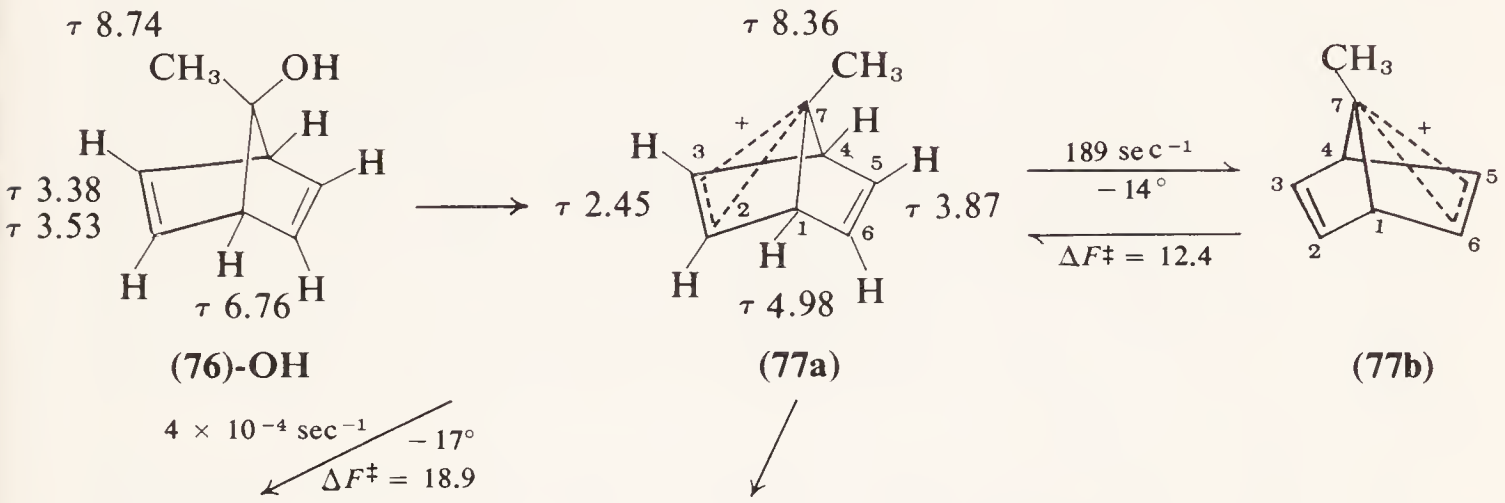


XIII. THE 7- AND 2-METHYL-NORBORNADIEN-7-YL CATIONS (11c)

One would expect a 7-methyl substituent to lower the barrier to bridge flipping, so we proceeded to examine the 7-methyl cation (**77**). As the precursor for this ion we employed alcohol (**76**)-**OH**. Extraction of (**76**)-**OH** from CD_2Cl_2 into FSO_3H at $-78°$ yielded an FSO_3H solution of (**77**) whose nmr spectrum below $-45°$ corresponds to an unsymmetrical structure. This spectrum consists of a two-proton bound vinyl quartet at τ 2.45, a broad two-proton unbound vinyl singlet at τ 3.87, a two-proton bridgehead multiplet at τ 4.98, and a methyl singlet at τ 8.36.

As the temperature is raised, the vinyl signals of (**77**) begin to broaden and eventually coalesce at $-14°$, while the bridgehead signal sharpens to a quintuplet and the methyl peak remains sharp. The fact that the bridgehead

signal actually sharpens indicates that only the magnetic environments of the vinyl protons are being averaged, so this must occur by bridge-flipping, namely (**77a**) ⇌ (**77b**). At the coalescence temperature, the first-order rate constant for bridge-flip is 189 sec^{-1} and $\Delta F^{\ddagger}$ is 12.4 kcal/mole.



Above ca. −5°, (**77**) rearranges quite rapidly to a more stable species, the 2-methyl ion (**78**). This is formed at −17° in ca. 60% yield with a rate constant of $4 \times 10^{-4}\,sec^{-1}$ ($\Delta F^{\ddagger} = 18.9$ kcal/mole). As regards conceivable mechanisms of the (**77**) → (**78**) rearrangement, the simplest is by way of a C-1 → C-2 shift of the unbound vinyl carbon C-6 in (**77**), producing (**78**) directly. Upon further heating of (**78**), decomposition occurs with no detectable formation of methyl tropylium ion.

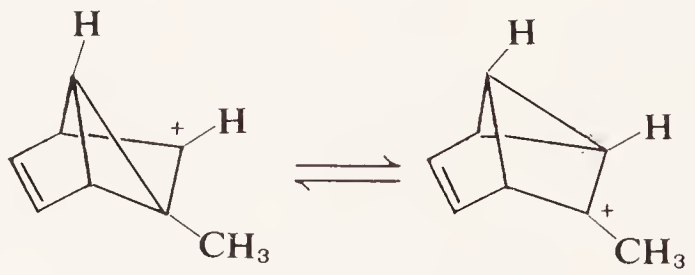
The 2-methyl ion (**78**) was identified by its nmr spectrum and the results of quenching it in MeOH. In the nmr spectrum of (**78**), signals appear at τ 3.19, 3.88, 5.11, 6.58, and 7.44 for bound vinyl, unbound vinyl, bridgehead, bridge, and methyl protons, respectively. From quenching the FSO_3H solution of (**78**) in MeOH there was isolated the corresponding *anti*-methyl ether with a correct analysis and an appropriate nmr spectrum summarized in (**79**) (solvent CS_2).

The chemical shifts of the C-7, C-2, and C-3 protons in (**19**), and in the *anti*-norbornen-7-yl ion as well, were previously explained on the basis that C-7, where considerable rehybridization from trigonal towards sp^3 is expected (10c), bears very little of the positive charge, while C-2 and C-3 carry most of it. This interpretation is strongly supported by the nmr

spectra of (**77**) and (**78**). Thus, in the nmr spectrum of the 7-methyl cation (**77**), the chemical shifts at C-2 and C-3 (and C-5 and C-6, also) are nearly the same as for (**19**) and the 7-CH_3 chemical shift is nearly as high as in covalent (**76**)-**OH**. Thus, a 7-CH_3 group, on a carbon atom bearing very little positive charge, interacts very little with the cationic electronic system and perturbs the charge distribution negligibly. As expected, however, the 2-CH_3 group in (**78**) does interact very appreciably with the cationic electronic system. Thus, in the nmr spectrum of (**78**), the chemical shift of the 2-CH_3 group is shifted downfield by 0.92 ppm and that of the 3-proton is shifted upfield by 0.74 ppm relative to the values in (**77**). One would expect (**78**) to be the most stable of the monomethyl norbornadienyl cations and this is in line with the observed substantial equilibrium constant for (**77**) $\rightleftharpoons$ (**78**).

The large barrier to bridge flipping in (**19**) ($\Delta F^{\ddagger} \geqslant 19.6$ kcal/mole) discloses the enormous gain in stability when C-7 in symmetrical (**19b**) is at least partially rehybridized and the geometry is distorted to that of unsymmetrical (**19**) where the interaction of C-7 is entirely with one of the two available olefinic groups. While a 7-methyl group has little effect on unsymmetrical (**19**), it would be expected to have a strongly stabilizing effect on symmetrical (**19b**), where olefinic electron involvement is much less, and much more positive charge resides at C-7. On this basis one can understand the substantial reduction in the bridge-flipping barrier in (**77**) relative to (**19**) by an amount equal to or greater than 7.2 kcal/mole.

The nmr spectrum of (**78**) is of interest in connection with Brown's and Deno's formulation (47a,b) of (**19**), and the norbornen-7-yl cation as well, as a pair of rapidly equilibrating tricyclic ions. On such a basis, the equilibrating tricyclic 2-methyl cation, (**80a**) $\rightleftharpoons$ (**80b**), would surely be nearly exclusively tertiary (**80b**) and the nmr spectrum would be that of (**80b**). Spectra of a number of cyclopropylcarbinyl cations are now recorded (48) and these show signals for the cyclopropane α- and β-protons



(**80a**) (**80b**)

at similar and very high field (τ ca. 7). Contrary to this, the chemical shift of the C-3 proton in the 2-methyl cation (**78**) (τ 3.19) is at lower field than the C-7 proton by 3.4 ppm, and also at lower field than the cyclopropane α-proton in known cyclopropylcarbinyl cations by at least 3 ppm. Thus,

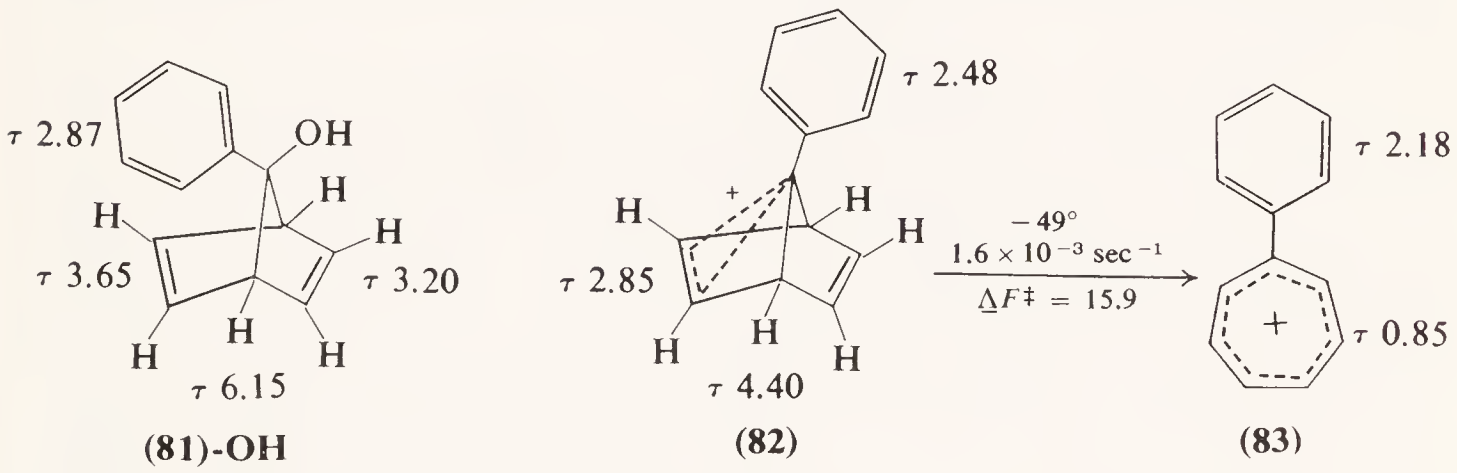
we can add a strong nmr argument to those based on chemistry and stereochemistry (8) against the equilibrating tricyclic ion formation.

XIV. THE 7-PHENYL-NORBORNADIEN-7-YL CATION (11d)

Since one would expect an even greater diminution of the bridge-flipping barrier due to a 7-phenyl substituent, we proceeded to investigate the 7-phenyl cation (**82**). The precursor to this ion was the 7-phenyl-norbornadien-7-ol (**81**)-**OH** (nmr spectrum in CCl_4). The nmr spectrum of the 7-phenyl cation (**82**) in FSO_3H at $-70°$ exhibits a sharp four-proton triplet at τ 2.85 for four equivalent vinyl protons, a two proton quintuplet at τ 4.40 for the bridgehead protons, and a five-proton broad singlet centred at τ 2.48 for the aromatic protons. Of considerable interest is the relative width of the aromatic proton signal, being only ca. 9 cps at half height. When the acid solution is diluted with SO_2, spectra may be recorded as low as $-100°$ without viscosity broadening. Even at this temperature (**82**) still exhibits a vinyl triplet broadened less than 3 c/sec.

When the temperature of the FSO_3H solution is raised, cation (**82**) undergoes a clean rearrangement to phenyltropylium ion (**83**). The first-order rate constant for appearance of phenyltropylium ion at $-49°$ is 1.6×10^{-3} sec^{-1}, corresponding to a $\Delta F^{\ddagger}$ of 15.9 kcal/mole. Ion (**83**) was identified by its nmr spectrum which exhibits a six-proton multiplet at τ 0.85 and a five-proton multiplet centered at τ 2.18. The nmr spectrum was identical to that of authentic phenyltropylium fluoroborate.

The equivalence of the four vinyl protons in the 7-phenyl cation, taken alone without considering other features of the nmr spectra, indicates that this cation is either symmetrical, or it is unsymmetrical and yet bridge-



(81)-OH **(82)** **(83)**

flipping rapidly even at $-100°$. In the latter case, assuming that the chemical shifts of the two sets of vinyls would differ by at least 40 c/sec, the rate of bridge-flip must be greater than 840 sec^{-1}, which leads to a maximum $\Delta F^{\ddagger}$ of 7.6 kcal/mole.

The chemical shifts of the vinyl protons in (**82**) provide essentially no assistance in deciding between the symmetrical and rapidly equilibrating

unsymmetrical formulations. This is because the observed chemical shift of τ 2.85 in (**82**) is not so very different from the average chemical shift of bound and unbound vinyl protons in (**19**) (τ 3.22) and (**77**) (τ 3.16), nor are they unreasonable values for a symmetrical ion.

In the case of the 7-phenyl cation (**82**), an important clue is the chemical shift and signal pattern for the aromatic protons. The spread in chemical shift for the various *o*-, *m*-, and *p*-protons is very small, the whole half-band width being 9 c/sec. On the other hand, a substantial spread in chemical shift values of the benzene ring protons is observed in carbonium ions where an α-phenyl group is tolerating considerable positive charge (49). Examples of such cations are cumyl and benzhydryl, where the difference between *meta* and *ortho* chemical shift values is 0.83 and 0.48 ppm, respectively. Not only is the signal pattern for the aromatic protons in (**82**) quite narrow, but their chemical shift is at quite high field compared to typical α-phenyl carbonium ions. In fact, the phenyl proton signal even in the extreme case of the phenyl tropylium ion (**83**) comes at definitely lower field and has much more of a spread pattern than in cation (**82**). It is thus evident that the phenyl group in (**82**) tolerates very little positive charge. Since it would undoubtedly bear a great deal of charge in the symmetrical ion, we have a strong argument that (**82**) is unsymmetrical and similar to (**19**) and (**77**). On this basis, (**19**), (**77**), and (**82**) are all three unsymmetrical norbornadienyl cations with flipping barriers of $\geqslant 19.6$, 12.4, and < 7.6 kcal/mole, respectively, in just the sequence expected for 7-H, 7-CH_3, and 7-C_6H_5 substituents (11c,d).

The new work on norbornadienyl cations described above serves to illustrate the fact that the study of carbonium ions under conditions of long life presents us with a whole host of exciting new observations and new problems in organic reaction mechanisms.

It is interesting to enquire which of the rearrangements of the norbornadien-7-yl and bicyclo[3,2,0]heptadienyl ions mentioned above are able to compete in solvolysis in typical solvolysing solvents where carbonium-ion lifetime is very short. The answer is that ring contraction, bridge-flipping, and other rearrangements of the norbornadien-7-yl cations, and ring expansion of the bicyclo[3,2,0]heptadienyl cation do not compete visibly in typical solvolytic work. Solvent capture of the cation in question is much more rapid than are these various rearrangements. On the other hand, the Richey–Story rearrangement (46) of the quadricyclyl ion (**72**) to norbornadienyl ion (**19**) does compete with product formation quite well in AcOH (46) and even better in HCOOH (11b).

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CHAPTER 23

Homoallylic and Homoaromatic Cations

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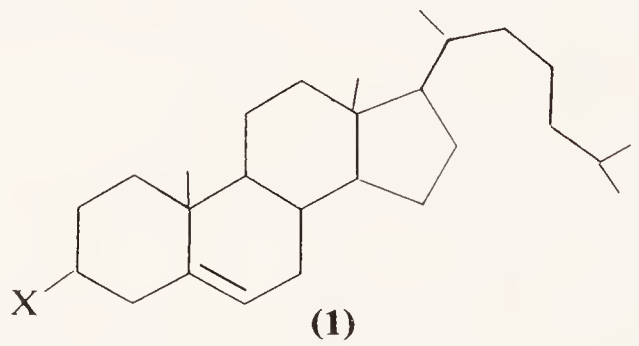
I. INTRODUCTION

Since Shoppee's first treatment (1) of the solvolysis of derivatives of Δ^5-cholestene (**1**) and other Δ^5-steroids, the observation of similar homoallylic interactions has been extended to several systems that cover a wide spectrum in relative orientations of the cationic center and the double bond. In the succeeding 23 years considerable evidence has been accumulated that demonstrates, quite convincingly, the existence of homoallylic interactions. However, a detailed analysis of such interactions is still not possible; indeed, there has yet been no unequivocal demon-



(1)

(1a) X = —Cl; **(1b)** X = —OAc; **(1c)** X = —OCH_2CH_3; **(1d)** X = —OTs
OTs = *p*-toluenesulfonate

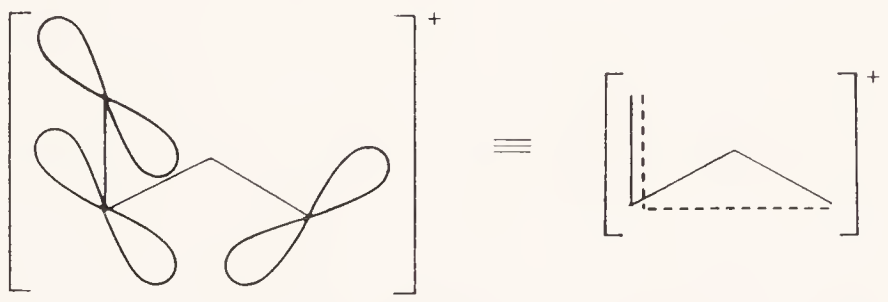
stration of the existence of homoallylic carbonium ion intermediates. Although such ions almost certainly exist as intermediates in many systems, very little is known about their structures, and what little structural

information is available has been inferred chiefly from product and kinetic analyses of solvolysis reactions.

In the last decade direct structural information has been obtained for a few, especially stable ions, principally through the observation of nuclear magnetic resonance (nmr) spectra of their complex salts. It has not been possible to distinguish unequivocally, however, in any of these cases between a true charged-delocalized, nonclassical structure and a series of rapidly equilibrating classical ions.

The questions now being asked about the structure of homoallylic ions cannot be answered completely with present-day knowledge or instrumentation. In certain favorable cases, the most widely accepted view holds that the π system of the double bond interacts to stabilize the incipient cationic center, thus lowering the energy of the transition state and leading, in some cases, to a charge-delocalized (usually through the available p orbitals) nonclassical carbonium ion. This position is usually based on the observation of solvolytic rate enhancements, the retention of configuration in solvolysis products, and, in some cases, the isolation of relatively stable carbonium ion salts.

The homoallylic concept is best illustrated by formula **2** in which both σ-type and π-type overlaps of p or near-p orbitals are utilized as simply as possible. Thus "homoallylic" delocalization exists across one or more intervening carbon atoms, and the ion is said to be "homoconjugatively" stabilized. Excellent discussions of certain homoallylic and other closely



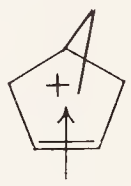
(2)

related ions are provided by Berson (2), Bartlett (3), and Hanack (4).

H. C. Brown (5,6) has maintained, however, that although the double bond of a homoallylic system plays a role in lowering the energy of the transition state in ionization, the available data are best explained through the appropriate rapidly equilibrating classical cationic intermediates **3a** and **3b**. Both Brown (6) and Deno (7) have referred, in general terms, to the electron releasing power of cyclopropyl groups to explain the stability of certain cationic intermediates. Brown (5,6) has advanced the argument that the stability associated with homoallylic cations is a conjugation phenomenon and not a structural problem.

(3a) (3b)

M. J. S. Dewar (8), on the other hand, has argued quite convincingly that most, if not all, homoallylic cations should best be represented as π complexes involving the double bond and the cationic center (e.g., **4**). Nonetheless, at least one thing is clear. Homoallylic interactions do exist and are important to the theory and practice of chemistry, even though the nature of the homoallylic intermediates has not been firmly established.



(4)

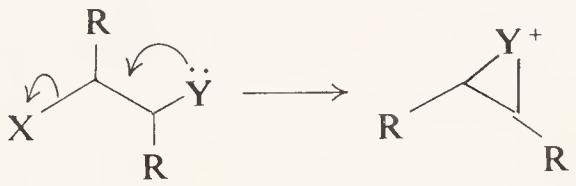
It is obvious from the following discussions of specific ions that we favor the charge-delocalized, nonclassical view in many cases, although there does seem to be little of a substantial nature to choose between this approach and the π-complex formulation of Dewar. In fact, Dewar's approach accounts very well for the apparent three-centered character of most homoallylic cations. We also note that all known homoallylic cations are $4n + 2$ electron systems. This point is developed later in the chapter. Homoallylic carbonium ions are widely referred to as "nonclassical" ions. This terminology seems inappropriate in view of the ordinary type of bonding commonly proposed for this class of ions. For the most part we substitute the term "charge-delocalized" to describe homoallylic cations.

II. BASIS FOR THE HOMOALLYLIC CONCEPT— THE "NEIGHBORING GROUP EFFECT"

The intramolecular interaction of carbonium ion centers with functional groups possessing available electrons was a concept first proposed to explain the retention of configuration observed on solvolysis of appropriately substituted halides. One of the earliest examples of this type of interaction was provided by Cowdrey et al. (9) in their investigation of the solvolysis of optically active α-bromopropionic acid, which underwent methanolysis and hydrolysis with retention of configuration. These investigators considered retention to result from stabilization of the cation in a tetrahedral conformation by the carboxylate anion. However, Winstein (10) later demonstrated that the most probable explanation involved the actual

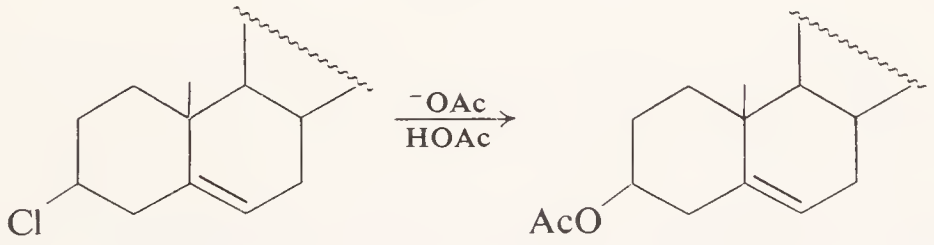
intermediacy of an α-lactone. The same explanation was also offered for other α-substituted acids by Bean et al. (11).

The "neighboring group effect" concept was extended to other systems by Lucas et al., who investigated the effect of neighboring bromine (Y) on substitution reactions (**5**) and proposed an intermediate bromonium ion (**6**) to explain the observed retention of configuration (12). They learned also that the neighboring acetoxy group exerts considerable influence on substitution reactions, leading to retention of configuration through the intermediacy of an acetoxonium ion (13).



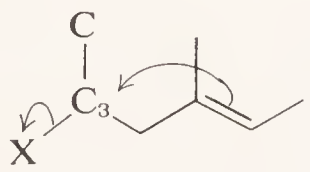
(5) (6)

Evidence for the interaction of a carbon–carbon double bond with a cationic center was first recognized by Shoppee, who found that acetolysis of cholesteryl chloride (**1a**) yielded cholesteryl acetate (**1b**), which was uncontaminated by the α-isomer **12** (1). These findings were further substantiated by detailed solvolysis studies (14) on several other Δ^5-



(1a) (1b)

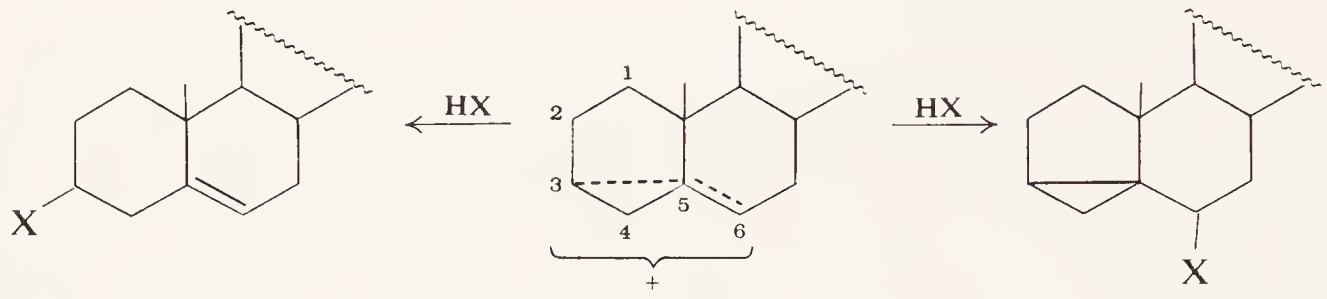
cholestene derivatives. This behavior was in sharp contrast to that observed for the corresponding saturated cholestanyl derivatives, which solvolyzed under similar conditions with substantially complete inversion of configuration. Drawing on the analogy of the α-halo acids (**9**) and the bromonium and acetoxonium ions proposed by Winstein in other systems, Shoppee postulated that retention of configuration in the solvolysis of Δ^5-cholestene (**1**) and other Δ^5-steroid derivatives was achieved similarly (i.e., by participation of the appropriately situated double bond, as illustrated in **7**).



(7)

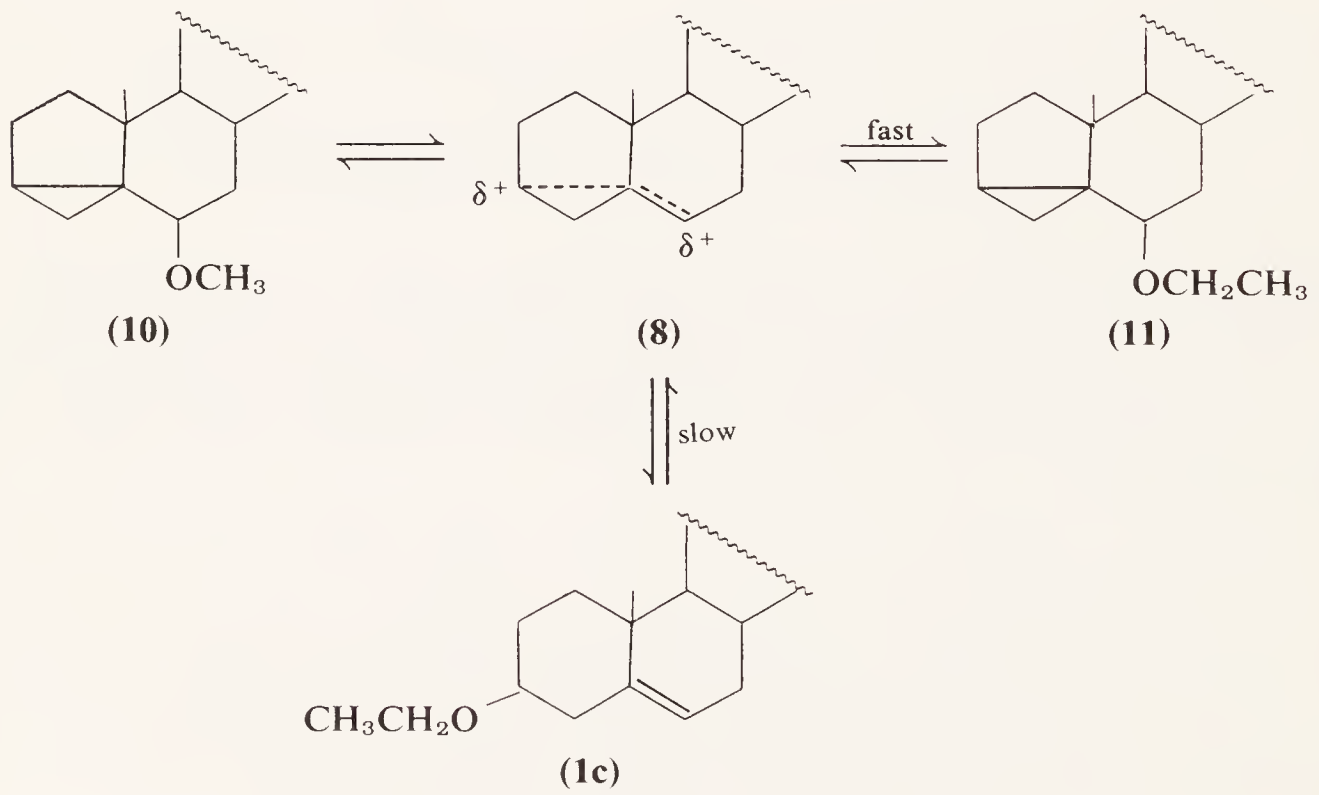
III. THE CHOLESTERYL CATION

Shoppee (1) had expressed no preference for either the tetrahedral conformation concept advanced by Ingold (9) or the bromonium ion concept (12). In a subsequent report (15), however, Winstein proposed, as one possibility, the delocalized cationic intermediate **8** (16) on the basis of kinetic and product studies. It was pointed out (15) that this scheme required that solvent (HX) react faster at C-6 than at C-3, since 3-β-cholesteryl derivatives (**1**) are more stable than 3,5-cyclocholestan-6β-yl derivatives (**9**). Thus the *i*-compounds (**9**) were the kinetically controlled products. In fact, Winstein subsequently demonstrated that *i*-derivatives (**9**) were more reactive than the corresponding cholesteryl derivatives (**1**) by a factor of $10^{7.4}$ and, furthermore, that most of this difference was due to the ground state free energy difference, ΔF° (17,18).



(1) **(8)** **(9)**

The nonclassical concept (**8**) (15) was further strengthened by Winstein's finding, shortly thereafter, that the acid-catalyzed conversion of **10** to **11** was much faster than its conversion to **1c** (19). The probable sequence is as illustrated here. Apparently, the same intermediate ion is formed from

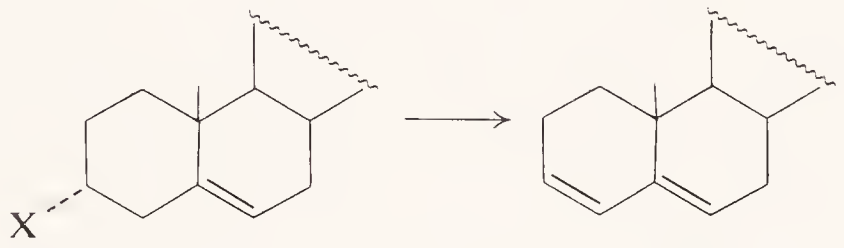


(10) **(8)** **(11)**

(1c)

cholesteryl, 3,5-cyclocholestan-6β-yl, and possibly 3,5-cyclocholestan-6α-yl derivatives, judging from product studies (17,20).

It has been further demonstrated that solvolytic acceleration by the double bond in the cholesteryl system is strongly dependent on the relative orientation of the double bond and the leaving group. The 3β-cholesteryl derivatives (**1**) show a rate enhancement (15) by a factor of about 100 over the corresponding saturated compounds and solvolyze with retention of configuration; 3α-cholesteryl derivatives (**12**), on the other hand, are less reactive than 3β-derivatives and yield, as the principal product on acetolysis, cholesta-3,5-diene (**13**) (14). Acetolysis of 3α-cholesteryl derivatives is also considerably less sensitive to changes in ionic strength (14).



(12) **(13)**

A. Summation of Characteristic Features

From the preceding discussion, the important characteristic features of the cholesteryl homoallylic ion are now beginning to emerge and may be summarized as follows.

Retention of configuration. 3β-Cholesteryl (**1**) and 3,5-cyclocholestan-6β-yl derivatives (**9**) solvolyze with complete retention of configuration.

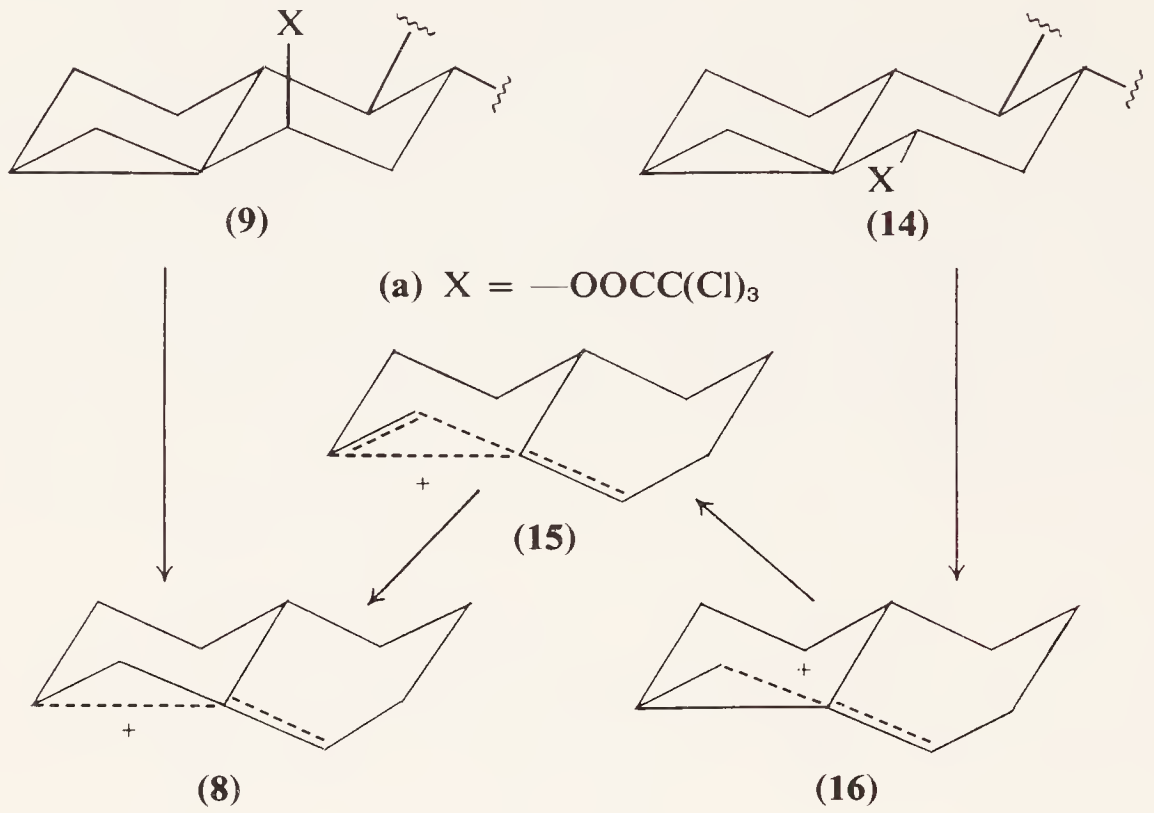
Solvolytic rate enhancement. The 5,6-double bond of 3β-cholesteryl derivatives (**1**) provides a rate enhancement factor of 100 over the corresponding saturated compounds.

Stereospecificity of interaction. Proper orientation of the leaving group for backside attack by the double bond is critical, as evidenced by the comparison of 3α- and 3β-derivatives.

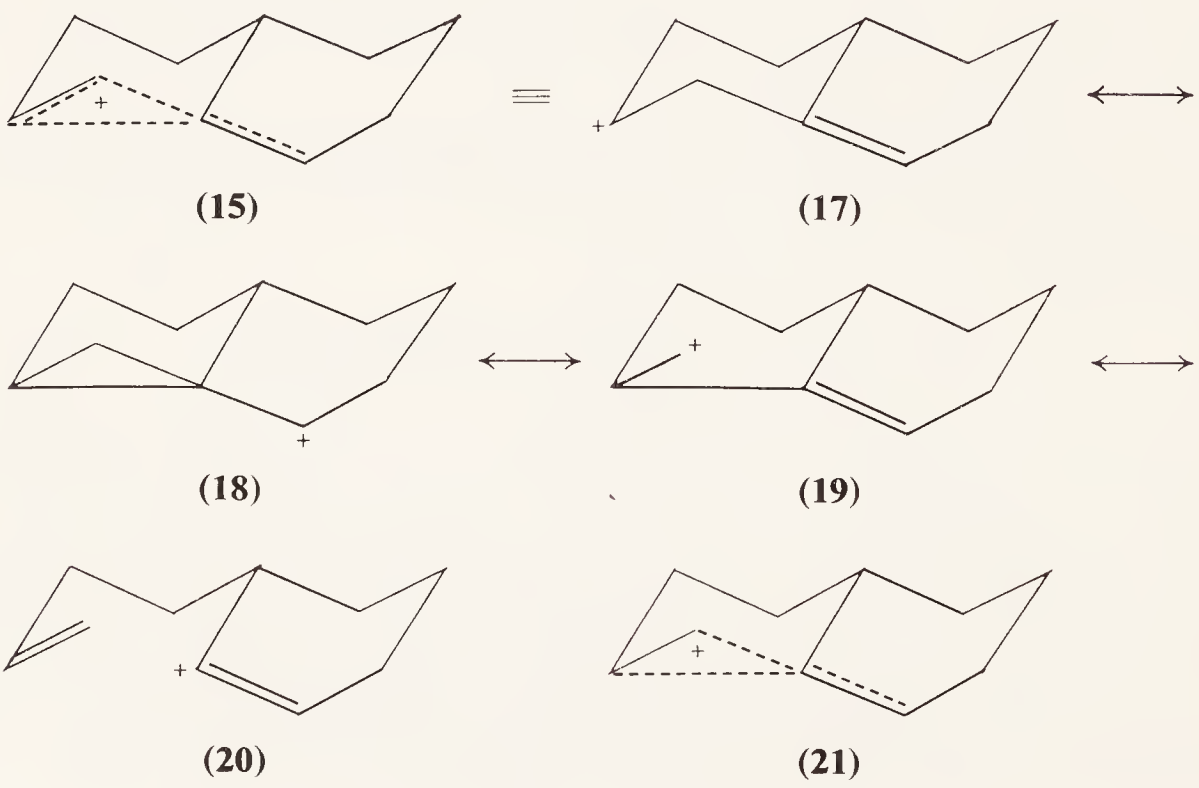
B. Structure of the Intermediate Cation

The question concerning the structure of the intermediate homoallylic cation(s) in the solvolysis of cholesteryl (**1**), 3,5-cyclocholestan-6β-yl (**9**), and 3,5-cyclocholestan-6α-yl (**14**) is still not neatly settled. Since cholesteryl *p*-toluenesulfonate (**1d**) and 3,5-cyclocholestan-6-yl trichloroacetates (**9a**, **14a**) all give essentially the same solvolysis products, in the same amounts, Winstein has suggested (20) that a common cationic intermediate is required for **1** and **9** and most likely for **14**. It was further suggested that

the symmetrical homoallylic ion (**15**), the unsymmetrical ion (**8**), and possibly its counterpart, **16**, may all be involved to various extents in the solvolysis of **1**, **9**, and **14** derivatives.

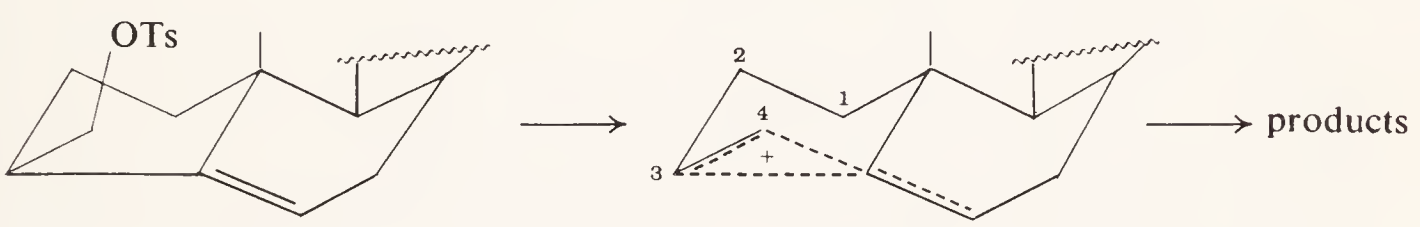


The symmetrical cation (**15**) is the resonance hybrid of **17**–**20** and involves both σ and π delocalization. We would prefer to formulate the symmetrical cation as **21**, which is a resonance hybrid of **17**–**19** and does not involve the unlikely vinyl cation resonance contributor **20**. The unsymmetrical ion (**8**) is the resonance hybrid of **17** and **18**, whereas the ion **16** is the hybrid of **18** and **19**.

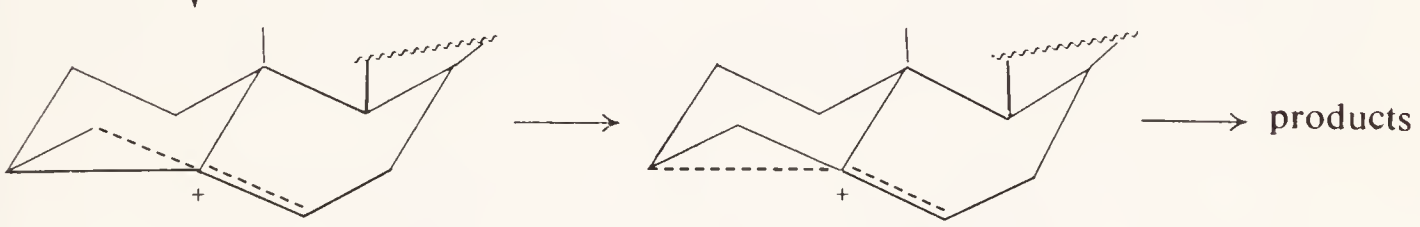


The proposed existence (17) of both symmetrical and unsymmetrical intermediates is based on the observation that both the 3,5-cyclocholestan-6-yl derivatives (**9**, **14**) solvolyze at a similar rate. If the ionization of 6β- and 6α-derivatives proceeded stereospecifically to the unsymmetrical intermediates, **8** and **16**, respectively, then, based on steric and electronic grounds, we would probably expect the 6β-derivative to solvolyze faster (17). Winstein has argued that the similarity in solvolysis rates for **9** and **14** can best be accounted for by assuming that both yield the symmetrical derivative, **15**, first. It was concluded, however, that the solvolysis data for cholesteryl derivatives (**1**) are compatible with either the unsymmetrical intermediate (**8**) or the symmetrical cation **15** (17). Clearer understanding of this system must await additional studies of the extent of internal return, of solvent effects, and of steric effects. The evidence now at hand seems compatible with the single intermediate (**8**).

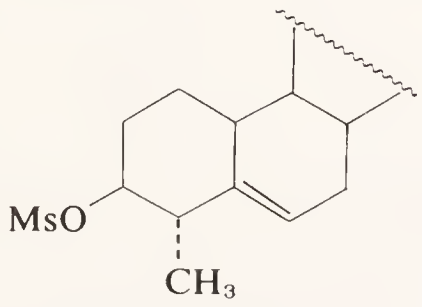
Whitham (21) recently reported evidence which, he believes, suggests that compounds **1**, **9**, and **14** ionize to the common symmetrical intermediate (**15**). It was found that, on solvolysis, 3β-hydroxymethyl-*A* norcholest-5-ene *p*-toluenesulfonate (**22**) yields the same products, and in the same amounts, as cholesteryl *p*-toluenesulfonate (**1d**). Whitham further suggested (22) that the twentyfold increase in rate observed for the solvolysis of 4α-methylcholesteryl methanesulfonate (**23**) relative to the



(22) **(15)**



(16) **(8)**



(23)

MsO = methanesulfonate

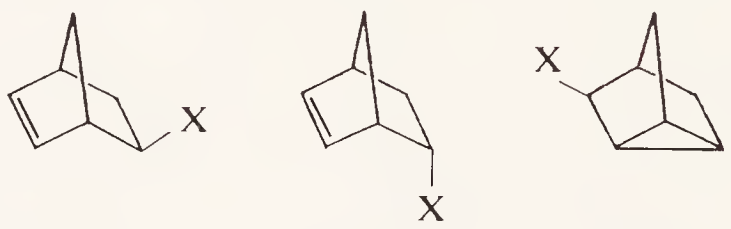
unsubstituted cholesteryl analog indicates that the symmetrical cation (**15**) is the intermediate in both systems.

It is our interpretation that, although the symmetrical intermediate (**15**) (which should most likely be formulated as in **21**) may be more important in 4α-methyl- and 4,4,-dimethylcholesteryl derivatives (23) in which a resonance structure with a cationic center at C-4 is stabilized by methyl substitution, little important contribution to the symmetrical ion (**15**) or to the unsymmetrical ion (**16**) is derived from unsubstituted derivatives. Such structures would incorporate a primary carbonium ion at C-4. This is apparently also the conclusion drawn by de Sousa and Moriarty (24) in their kinetic study of the solvolysis of 4α- and 4β-methylcholesteryl *p*-toluenesulfonates. The solvolysis of **22** probably proceeds by the formation, initially, of the higher energy ion **16** with subsequent rearrangement to **8** before reaction with solvent. The same rationale would also account for the data on solvolysis of the 6α- and 6β-derivatives, **9** and **14**.

In conclusion, it appears that the evidence at this time best supports the unsymmetrical homoallylic cation (**8**) as the sole intermediate in solvolysis of cholesteryl (**1**) and 3,5-cyclocholestan-6-yl derivatives **9** and **14**.

IV. THE DEHYDRONORBORNYL CATION

The investigation of the homoallylic interaction of a carbon–carbon double bond and a positive center was quickly extended to other systems. Winstein and co-workers recognized that the orientation of the double bond in the dehydronorbornyl molecule was suitable for an interaction of the cholesteryl type (25). It was found that *exo*-dehydronorbornyl *p*-bromobenzenesulfonate (**24a**) underwent acetolysis 7000 times faster than the corresponding *endo* isomer (**25a**)* to give, as the principal product, the tricyclic acetate (**26b**). Unlike the cholesteryl system, the ring-closed product in this system is thermodynamically more stable than the olefin

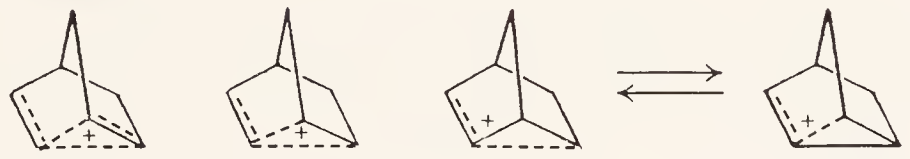


(24) **(25)** **(26)**

(a) X = —OBs; **(b)** X = —OAc; **(c)** X = —Cl; **(d)** X = —NH_2

* This system had been investigated somewhat earlier by J. D. Roberts et al. (26), who concluded that the double bond had little effect. They later showed that this report was based on results obtained from impure *endo*-2-norbornyl chloride.

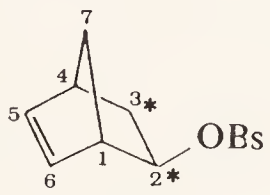
(17,27). Tricyclic derivatives (**26**) are also more reactive than the corresponding *endo*-dehydronorbornyl compounds; comparison of the brosylates reveals that the factor is 2000 (25). Although the large rate enhancement provided by the double bond in the *exo* derivative (**24a**) and the retention of configuration of the dehydronorbornyl product in solvolysis argue strongly for the existence of a homoallylic interaction, the structure of the probable intermediate homoallylic ion is in some doubt. It has been argued (17) that, since the nortricyclyl derivative (**26a**) undergoes reaction to give less norbornenyl product (**24b**) than does the *exo*-norbornenyl derivative (**24a**), the two different starting materials do not lead to the same intermediate ion. Winstein, therefore, has proposed that tricyclyl derivatives **26** yield the symmetrical ion **27** (17), whereas *exo*-2-norbornenyl compounds (**24**) first yield the unsymmetrical ion **29a**, which may then isomerize to the symmetrical ion **27** (17). As in the case of the symmetrical cholesteryl cation, we would prefer the simpler structure (**28**) for the symmetrical dehydronorbornyl cation.



(27) **(28)** **(29a)** **(29b)**

A. Labeling Experiments

Winstein's argument (17,28) was partly based on Roberts' study of ^{14}C-labeled 2-norbornenyl derivatives (**30**) (29). It was found that acetolysis of



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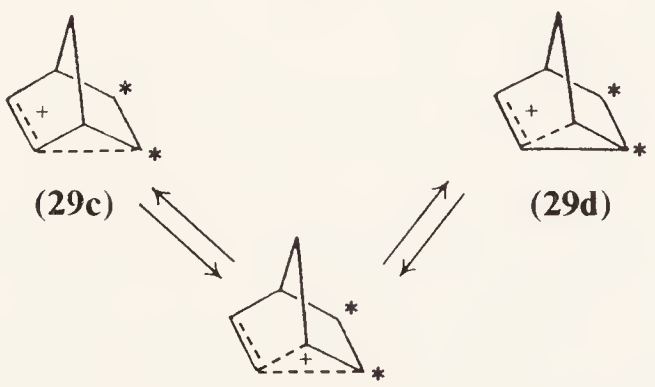


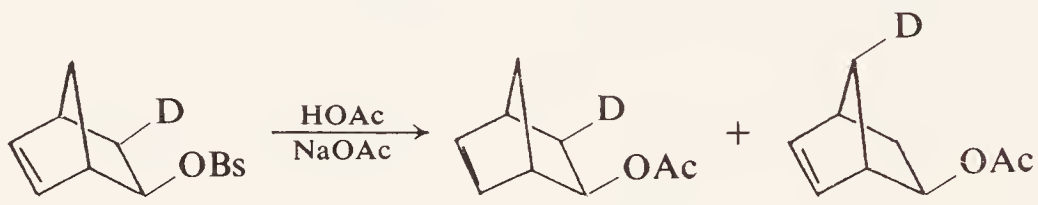
(29c) **(29d)**

(28a)

OBs = *p*-bromobenzenesulfonate

2,3-^{14}C-*exo*-2-norbornenyl *p*-bromobenzenesulfonate (**30**) yielded *exo*-2-norbornenyl acetate (**24b**) in which 38% of the ^{14}C had been lost from the 2 and 3 positions. This value was taken as the rearrangement percentage. Two possible interpretations of these data were considered (29). One possibility held that the unsymmetrical ion (**29c**) was formed initially but partially rearranged to the symmetrical intermediate **28a** subsequently. The alternative considered by Roberts was a partial equilibration of the unsymmetrical, enantiomeric ions **29c** and **29d**, presumably via the symmetrical transition state (**28a**).

Cristol (30) has recently reported that the acetolysis of *exo*-3-deuteriodehydro-2-norbornyl-*p*-bromobenzenesulfonate (**31**) yielded 7% of an equimolar mixture of the acetates **32** and **33**. The remainder of the product consisted of tricyclic material. The data were interpreted in terms of equilibrating ions of type **29a**, **b** or initial formation of a symmetrical intermediate of type **28**.



(31) **(32)** **(33)**

B. Evidence Compatible with the Unsymmetrical Cation

Operating on the very qualitative observation that all homoallylic cations so far studied may be formulated as simply as possible, utilizing both σ-type and π-type overlap of *p* or near-*p* orbitals and 2π-electron–3-carbon bonding, it is our opinion that the symmetrical homoallylic cation (**27** or **28**) is unlikely; nor is it needed to explain the data. The interconversion, **29c** $\rightleftarrows$ **29d**, should be rather facile, since 1,4-interactions are considered to be negligible (17,31), and therefore maintenance of configuration at C-5 should not be particularly important. The principal interaction of the *p* orbital at C-5 with the adjacent center at C-6 is of the π type; consequently, C-5 should behave more like an allylic center.

In acetic acid the equilibration of ions (**29c**, **d**) is incomplete, hence only 38% rearrangement is observed (29). However, Roberts finds 48% rearrangement in formic acid, a solvent in which the cations would be expected to have a greater lifetime, thus indicating that the equilibration of **29c** and **29d** is essentially complete.

The observation that tricyclic brosylate (**26a**) gives more tricyclic product than does the dehydronorbornyl derivative **24a** hardly is surprising and does not necessarily call for the intermediacy of more than one cation for two reasons. First of all, these cationic intermediates are highly

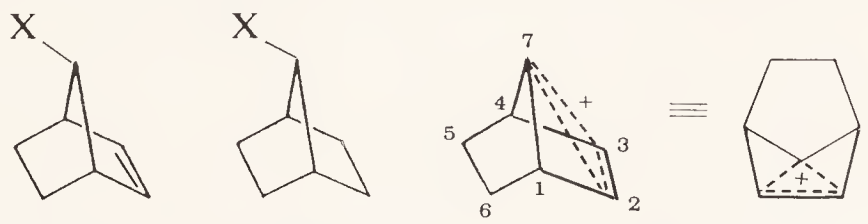
solvated, not free carbonium ions, and it seems likely that the relatively short-lived cation would give product distributions influenced by the position of the leaving group (recall that **29c** and **29d** are not completely equilibrated in acetic acid). Second, some direct displacement by solvent at C-5, whether on the brosylate itself (**26a**) or on a corresponding ion-pair intermediate, seems a distinct possibility. It is stressed again that there is no obvious reason for maintaining configuration about C-5. Retention of configuration about C-2 is required by the experimental observation, however, and we would expect it from a theoretical consideration (31) of bonding in the system, which predicts a strong 1,3 interaction between C-6 and C-2. Based on the data available, it is concluded that only the unsymmetrical, enantiomeric cations **29a** and **29b** are important in the solvolysis of dehydronorbornyl (**24**) and tricyclyl derivatives (**26**).

V. THE 7-NORBORNENYL CATION

In 1955 Winstein et al. (32) reported their observation that *anti*-7-norbornenyl-*p*-toluenesulfonate (**34a**) undergoes acetolysis at a remarkably high rate and, in fact, that this ester is more reactive than the corresponding saturated ester, 7-norbornyl-*p*-toluenesulfonate (**35a**), by a factor of approximately 10^{11}. Of equal importance was their observation that the reaction of **34a** with solvent is completely stereospecific.

A. Structure of the Nonclassical Cation

These phenomena were attributed to anchimeric assistance to ionization at C-7, provided by the π electrons of the 2,3 double bond, thereby generating the 7-norbornenyl carbonium ion, which is represented by structure **36**. Again, the dotted line notation represents bond formation



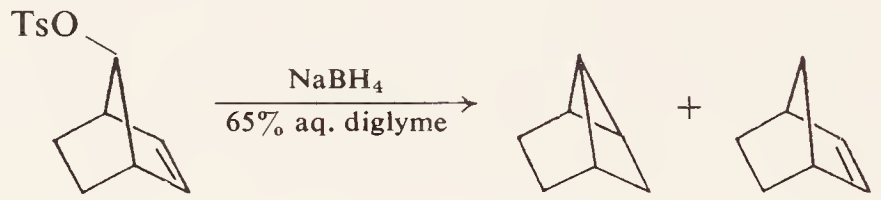
(34) **(35)** **(36)**

(34a) X = —OTs; **(34b)** X = —Cl; **(34c)** X = —OCH_3; **(34d)** X = —OH; **(34e)** X = —NH_2; **(34f)** X = —OBs

by overlap of the three available *p* orbitals. An intermediate ion of this type would, of course, preclude formation of *syn* product. Although strong interaction of the positive center with the double bond is required, we would not anticipate formation of tricyclic products by reaction of solvent at C-2 or C-3 under reversible conditions because of their higher energy (33,34).

B. Isolation of Tricyclic Products

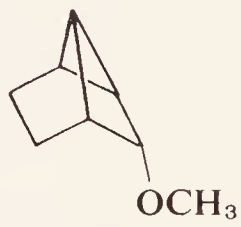
In several subsequent reports by Winstein (33,35,36), Brown (5), and Tanida (37), tricyclic products are described as being obtained from *anti*-7-norbornenyl derivatives (34) under nonequilibrium conditions. Brown and Bell (5), who solvolyzed *anti*-7-norbornenyl *p*-toluenesulfonate (**34a**) in 65% aqueous diglyme containing excess sodium borohydride, obtained a 15% yield of tricyclo[4,1,0,$1^{3,7}$] heptane (**37**) along with a 70% yield of norbornene (**38**). In a similar experiment, Winstein (35) observed



(34a) **(37)** **(38)**

approximately the same distribution. He concluded that borohydride was trapping the intermediate carbonium ion, since the rate of solvolysis of *anti*-7-norbornenyl chloride (**34b**) in 65% aqueous diglyme was the same as its rate of reduction in an aqueous sodium borohydride and sodium hydroxide solution. Sodium borohydride reduction of **34a** in dry diglyme gave the tricyclic hydrocarbon **37** in 95% yield. However, Winstein points out that it is not clear whether the reduction in anhydrous media involves a concerted reaction or prior ionization. Brown has also observed a high yield of tricyclic hydrocarbon in anhydrous media (5).

In more recent work (33,36) Winstein has carefully studied the reaction of **34a** with methoxide ion to give the ether **34c** and 2-methoxytricyclo-[4,1,0,$0^{3,7}$]heptane (**39**). Variation of the methoxide ion concentration from $3.5 \times 10^{-8} M$ to $3.98 M$ gave yields of ether (**39**) varying from 0.3 to



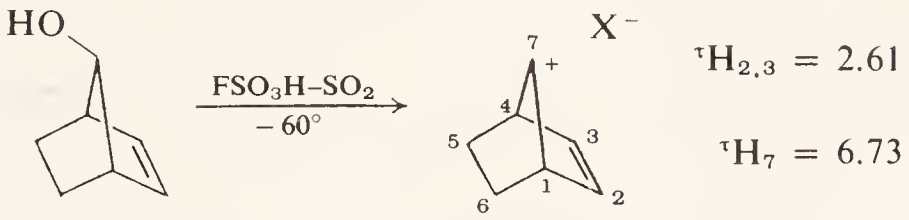
(39)

51.5%. The maximum methoxide ion concentration in the neutral, buffered methanolysis of **34a** was $3.5 \times 10^{-8} M$. Control experiments showed that the ether (**39**) is fully stable under these conditions; thus kinetic control in neutral methanolysis of **34a** yielded 99.7% **34c** and 0.3% **39**. Methoxide attack on the 7-norbornenyl carbonium ion is highly stereoselective, giving greater than 97% of the *endo* ether (**39**).

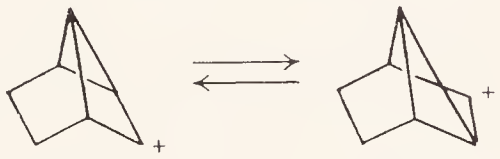
There have also been reports by Tanida (37,38) in which the *endo*-tricyclic nitrile, 2-cyanotricyclo[4,1,0,$0^{3,7}$]heptane, was isolated in low yield by treating **34b** with sodium cyanide.

C. Nmr Spectrum of the 7-Norbornenyl Cation

Considerable additional information concerning the structure of the 7-norbornenyl cation has recently been reported by Winstein (36) and by Richey (39), who performed nmr spectroscopy studies of the cation generated in strong acid. The nmr spectrum of the cation (**40**), prepared by Richey from the alcohol (**34d**), revealed identical chemical shifts for the protons at C-2 and C-3 and for those at C-1 and C-4. The nmr data are equally consistent for the delocalized ion **36** or a set of rapidly equilibrating classical ions (**41**).

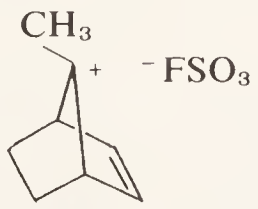


(34d) **(40)**



(41a) **(41b)**

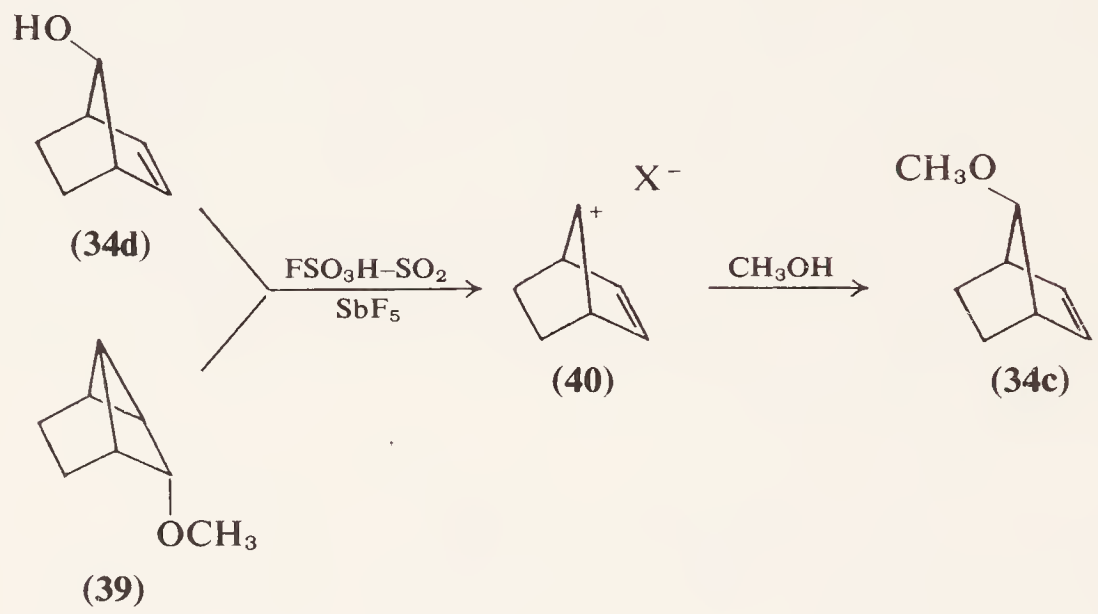
Richey has pointed out that even if the ions (**41**) are more stable than **36**, which in this case would be the higher energy transition state lying between **41a** and **41b**, the ion **36** could not be of significantly higher energy than **41** because, even at $-60°$, equilibration must be rapid. It should be noted that the multiplet representing the C-7 proton occurs at $\tau = 6.73$, whereas the multiplets for the C-2 and C-3 protons occur at 2.61, thus indicating considerably less positive charge at C-7. This is not an unreasonable chemical shift for the 7-hydrogen in structure **36**, [as we argued (40) for the 7-norbornadienyl cation] because this hydrogen, which will not lie in the plane of the cyclopropenyl-type ring, will thus be more shielded than would a similar hydrogen attached to a cyclopropenyl cation. Richey has also examined the spectrum of the cation **42** and found that introduction of a methyl group at C-7 has little effect on the chemical



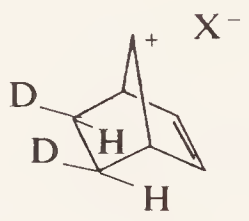
(42)

shifts of the protons elsewhere in the molecule, further indicating that little positive charge exists at C-7.

Winstein (36) was able to generate **40** from either the alcohol (**34d**) or the tricyclic ether (**39**). *anti*-7-Methoxynorbornene (**34c**) was formed in over 50% yield by quenching the solution of **40** in methanol. From the



nmr spectrum of the 5,6-*exo*-dideuterio cation **43**, Winstein was able to determine the following coupling constants: $J_{7-2,3} = 2.5$ Hz, $J_{7-endo-5,6} =$ 0.8 Hz. The $J_{7-2,3}$ value indicates considerable bond formation between C-7 and the carbon atoms of the double bond. The nmr data reported for the 7-norbornenyl cation (36,39) are analogous to those reported by us



(43)

for the 7-norbornadienyl ion (40–42); for a detailed discussion of this matter, see Section VII.

D. Comparison of the 7-Norbornenyl and Dehydronorbornyl Systems

It is apparent that *anti*-7-norbornenyl derivatives represent another homoallylic system similar to the *exo*-2-norbornenyl system (**24**), but one that differs significantly in the spatial relationship of the functionalized carbon and the double bond. A developing positive center at C-7, in contrast to the cationic center in the 2-norbornenyl molecule, would be symmetrically disposed toward the double bond, permitting interaction of the empty *p* orbital at C-7 with the π system of the 2,3 double bond. Such

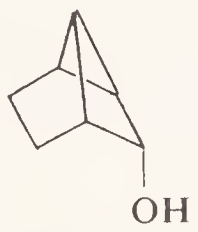
an ion would be closely related to the cyclopropenyl cation, lacking only two carbon–carbon σ bonds. In fact, Roberts et al. (43) treated this system with a simple molecular orbital technique similar to that employed by Simonetta and Winstein (31) and indicated a preference for the "bis-homocyclopropenyl" designation for the cation (**36**) to emphasize this relationship.

The effect of the more potent homoallylic orientation of the *anti*-7-norbornenyl system was illustrated by Roberts and co-workers (43), who calculated that the delocalization energy of the 2-norbornenyl cation with an unperturbed carbon skelton was 2.8 kcal, as compared with 7.7 kcal for the unperturbed 7-norbornenyl cation. The maximum net stabilization energy for **36** was estimated to be 10.5 kcal (cf. 16.6 kcal for the allylic cation). This value corresponded to a C-2–C-7 bond distance of 2.00 Å. The calculated net stabilization energy for **36** is, therefore, approximately 4 kcal higher than for the dehydronorbornyl cation **29a** (31).

Greater π participation in the *anti*-7-norbornenyl system has been cited by Tanida (44) as a possible reason for observing only products with complete retention of configuration in the nitrous acid deamination of *anti*-7-norbornenyl-amine (**34e**), whereas the deamination of *exo*-2-norbornylamine (**24d**) gave a 2% yield of *endo* products (45).

E. Examination of the Classical Ion Approach

The evidence now available relating to the 7-norbornenyl cation—i.e., the large rate enhancement afforded by the double bond, retention of configuration, nmr data, and trapping experiments with nucleophiles—appears best explained by the delocalized carbonium ion intermediate **36**. However, Brown has questioned these arguments (5,6) and prefers to describe the solvolysis intermediates from *anti*-7-norbornenyl derivatives as a rapidly equilibrating pair of classical ions (**41**). Brown has suggested, even though solvolysis of **34a** under weakly alkaline conditions gives only **34d**, that the tricyclic alcohol **44** may, in fact, be the unstable kinetic

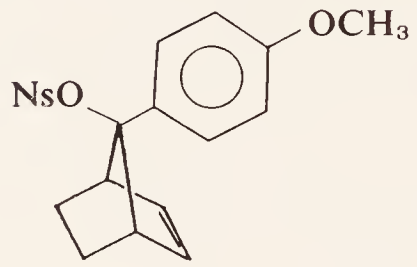


(44)

product of the solvolysis. This has been disproved by Tufariello (34), in a study revealing that the alcohol **44** was stable under alkaline hydrolysis conditions. Brown's main defense of the classical structure interpretation

must now be based on the high yield of tricyclic hydrocarbon (**37**) produced in the hydride-trapping experiments. However, the high yield of tricyclic product was obtained in anhydrous media which, as discussed previously, may involve a concerted hydride attack rather than significant prior ionization. Winstein (33,36) has pointed out that the formation of *endo* tricyclic products such as **39** is well explained by the nonclassical ion (**36**), in which attack can only be *endo*, whereas predominantly *exo* products would be expected from **41**.

A recent report by Gassman (46) showed that the rate acceleration of 10^{11}, caused by double-bond participation in **34a** solvolysis, vanished in the 7-*p*-anisyl derivative (**45**). Both the classical and nonclassical intermediates would be expected to exhibit this effect, however.

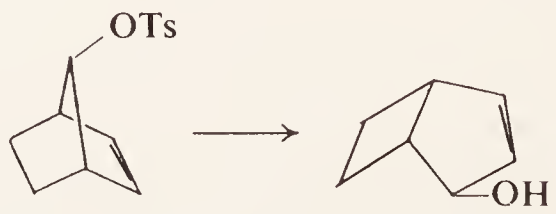


(45)

The 7-norbornenyl and several related systems are discussed in this chapter in terms of charge-delocalized, "nonclassical" intermediates because, in our opinion, the evidence now favors this interpretation. In addition, several of the delocalized structures are theoretically quite credible (31,34). In any event, as indicated in the Introduction, it hardly seems justifiable to use the term "nonclassical" for the *anti*-7-norbornenyl and 7-norbornadienyl cations, since the *p*-orbital interaction so very closely parallels that in the cyclopropenyl system.

F. The *syn*-7-Norbornenyl System

Subsequent to the report on the solvolysis of the *anti* tosylate (**34a**), Winstein and Stafford (47) reported the solvolysis of the corresponding *syn* isomer (**46**) and found that the sole product was the rearranged alcohol **47**, whose configuration was unknown but was probably as shown here. This work dramatically illustrated the importance of the orientation of the



(46) **(47)**

leaving group for stabilization of the incipient positive charge by the double bond. Although the *syn* isomer (**46**) was more reactive than the corresponding 7-norbornyl derivative (by 10^4), it was less reactive than the *anti* isomer (**34a**) by the substantial factor of 10^7, and the course of the reaction was entirely different. It was concluded (47) that the *syn* isomer was probably accelerated somewhat in solvolysis by formation of the intermediate allylic cation (direct precursor of **47**).

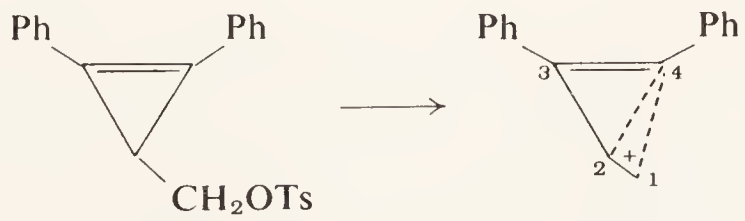
A comparison of rates of acetolysis of some norbornyl *p*-toluenesulfonate esters at 25°C (32) reveals the following:

Compound	*Relative rate*
Cyclohexyl tosylate	1
7-Norbornyl tosylate (**35**)	10^{-7}
exo-2-Norbornenyl tosylate (**24**)	10^3
endo-2-Norbornenyl tosylate (**25**)	10^{-1}
anti-7-Norbornenyl tosylate (**34a**)	10^4
syn-7-Norbornenyl tosylate (**46**)	10^{-3}
endo-2-Norbornyl tosylate (**83**)	1

Unfortunately, rate comparisons of this type are complicated and made somewhat suspect by the phenomenon of internal return. That is, ionization may take place to an ion pair, followed by collapse of the ion pair to the original compound. Consequently, the titrametric rate may be only a minimum value. An excellent discussion of this topic is provided by Berson (2).

G. The Cyclopropenyl Carbinyl Cation

The cyclopropenyl carbinyl system (**48**), which is constituted similarly to the *anti*-7-norbornenyl structure, has been investigated by Breslow (48). It was concluded that **48** solvolyzed without appreciable participation of the double bond but gave instead a bicyclobutonium-type intermediate (**49**), after the fashion of a cyclopropyl carbinyl system. It was also judged, from the relatively small effect of an anisyl substituent, that the *p* orbital of the developing positive charge at C-2 is still orthogonal to the double bond at the time of the transition state. The rearrangements of several other



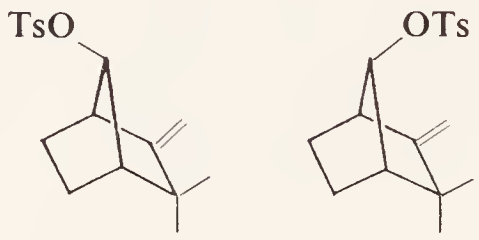
(48) **(49)**

monocyclic homoallylic compounds have been reviewed by Cope (49) and Hanack (4).

VI. THE 7-CAMPHENYL AND 2-CAMPHENYL SYSTEMS

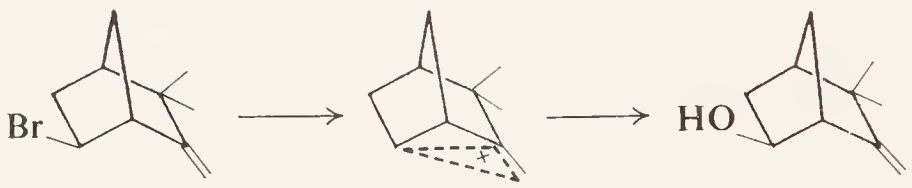
Interestingly, *anti*-7-camphenyl tosylate (**50**), which is closely related to the *anti*-7-norbornenyl system and might be expected to exhibit some evidence of homoallylic participation in solvolysis reactions, was quite unreactive; in fact, it was only about six times more reactive than 7-norbornyl tosylate (**35**) in acetolysis (50).

The *syn* isomer **51** was found to be approximately twice as reactive as **50**. In contrast to **51**, however, the *anti* tosylate does solvolyze without rearrangement. On this basis, there seems to exist some possibility of a homoallylic interaction.



(50) **(51)**

In an investigation of another system, closely related to the *exo*-2-norbornenyl structure, Dev and co-workers (51) have reported their qualitative observation of the rapid hydrolysis of **52** in aqueous dioxane (lithium carbonate) with retention of configuration. They attributed this phenomenon to the formation of the delocalized intermediate cation **53**.

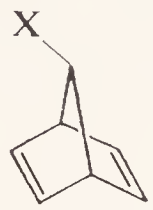


(52) **(53)**

VII. THE 7-NORBORNADIENYL CATION

The 7-norbornadienyl cation is of considerable importance to the development of carbonium ion theory, principally because of its inherent stability, which has greatly facilitated its study. When Winstein and Ordronneau (52) solvolyzed 7-norbornadienyl chloride, **54a**, they learned that it is about 800 times more reactive than *anti*-7-norbornenyl chloride (**34b**) and that the sole solvolysis product is 7-norbornadienol (**54b**). By

analogy to the *anti*-7-norbornadienyl system, a homoallylic cation, resulting from interaction of the double bonds and the incipient positive center at C-7 was proposed (52). Unlike the case of the *anti*-7-norbornenyl cation (**36**), several possibilities for charge delocalization were conceivable,



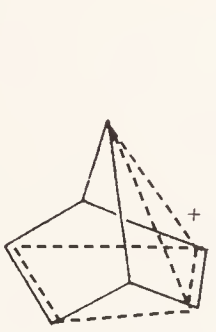
(54)

(54a) X = —Cl; **(54b)** X = —OH; **(54c)** X = —D;
(54d) X = —OCH_3; **(54e)** X = —OAc

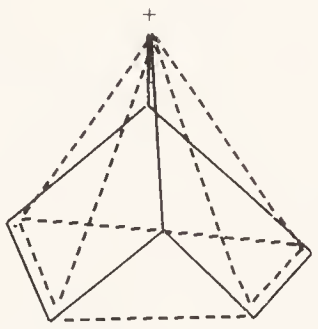
and Winstein and Ordronneau suggested three possible formulations (**55**) for the 7-norbornadienyl carbonium ion.

A. Nmr Spectra of Norbornadienyl Cations

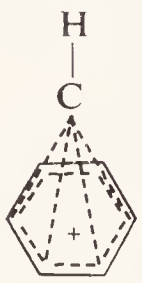
The previously cited stability of the 7-norbornadienyl cation makes it possible to obtain structural information on the whole system by the application of nmr spectroscopy. It was believed likely that the three structures (**55**) proposed by Winstein (52) for the 7-norbornadienyl cation would be distinguished by nmr. Heretofore, information on the structure of homoallylic cations had been inferred principally from a combination of kinetic and product analysis data.



(55a)



(55b)

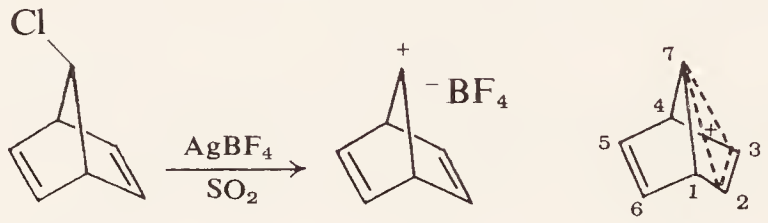


(55c)

For the nmr study, 7-norbornadienyl fluoroborate (**56**) was prepared by treatment of 7-norbornadienyl chloride (**54a**) with silver fluoroborate in liquid sulfur dioxide at low temperature (41). Examination of the nmr spectrum of **56** in sulfur dioxide and in nitromethane (40) revealed that the salt possesses an unsymmetrical structure; the spectrum indicated four different types of protons in the ratio of 2:2:2:1 (as shown in **56**). This prompted us to conclude that, of the three structures, the unsymmetrical ion **55a** was the most likely representation of the 7-norbornadienyl cation

(40). It was noted, however, that structure **57** was also compatible with all the available data.

Treatment of the sulfur dioxide solution of **56** with acetic acid yielded 7-norbornadienyl acetate (**54e**) exclusively. The absence of rearrangement in the fluoroborate salt was further indicated by reaction of **56** with 2-methoxy-2-methyl-1,3-dioxolane (**58**). The only isolable products were 7-methoxynorbornadiene (**54d**) and the dioxolenium fluoroborate salt **59** (40,53).



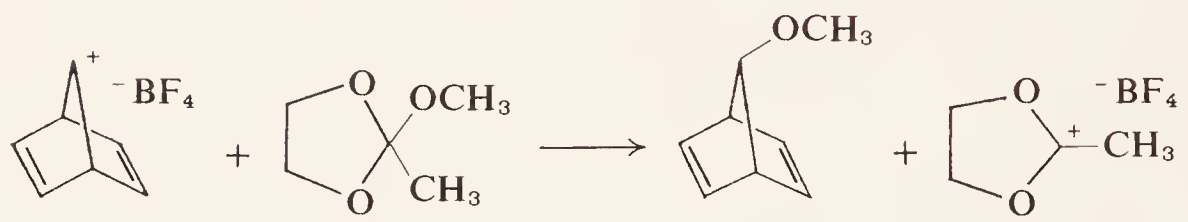
(54a) **(56)** **(57)**

$H_{2,3}: \tau = 2.42$

$H_{5,6}: \tau = 3.74$

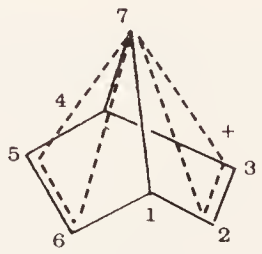
$H_{1,4}: \tau = 4.77$

$H_7: \tau = 6.52$



(56) **(58)** **(54d)** **(59)**

Subsequently, a detailed analysis of the nmr spectrum of **56** permitted the assignment and evaluation of coupling constants in the cation. It was found that $J_{7-2,3} = 2.7$ Hz, which indicated considerable bond formation between C-7 and the carbons of the double bond (42). A coupling ($J =$ 1.0 Hz) was also detected between H-7 and the upfield olefinic hydrogens H-5 and H-6. It was suggested, therefore, that a correct representation of the 7-norbornadienyl cation should possibly include some C-7–C-5,6 bonding as shown in the unsymmetrical structure **60**. It is not possible at this time



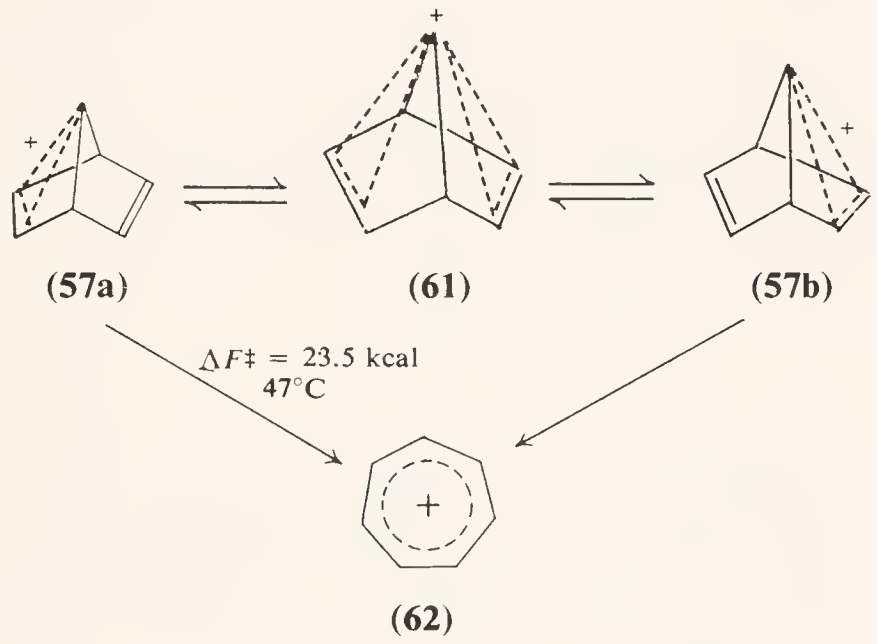
(60)

to choose between structures **57** and **60**, but in the interest of formulating all homoallylic and homoaromatic structures as simply as possible, we

continue to employ the two-electron, three-center bonding (2π–3C) represented by structure **57**, with the understanding that **60** is not ruled out. Although it is possible that the fluoroborate salt (**56**) is unsymmetrical because of the requirements of ion-pair formation, as suggested by Capon (54), we believe that this is not the case, since the spectrum observed by Richey (39) in FSO_3H–SO_2 for the 7-norbornadienyl cation is the same as that reported by us for the fluoroborate.

Further evidence that the 7-norbornadienyl cation is unsymmetrical has been obtained by employing extended Hückel calculations (55). These calculations predict a delocalization energy of 8 kcal for the unsymmetrical ion (**57**) with respect to the totally symmetrical ion (**61**).

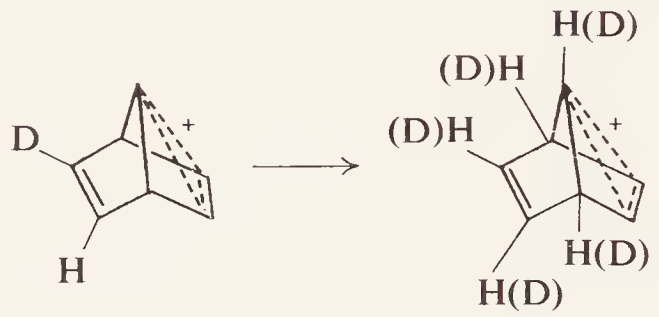
Since the nmr signals for the olefinic protons of **57** were unchanged up to 50°, we concluded (40) that a substantial barrier to **57a**–**57b** interconversion existed. This barrier can be understood by assuming that considerable energy would be necessary to move the bridge away from the double bond before any benefit from interaction with the other double bond would be felt.



In recent nmr studies employing several norbornadienyl cations, Winstein (56–58) has presented further evidence suggesting "that there is a substantial barrier to 'bridge flipping' (**57a**–**57b**) via symmetrical **61** as a transition state" (57) ($\Delta F^{\dagger} \geqslant 19.6$ kcal/mole at $-2.5°$). The cations employed in this study were generally prepared by extracting the appropriate precursor from methylene chloride or pentane into FSO_3H at $-78°$.

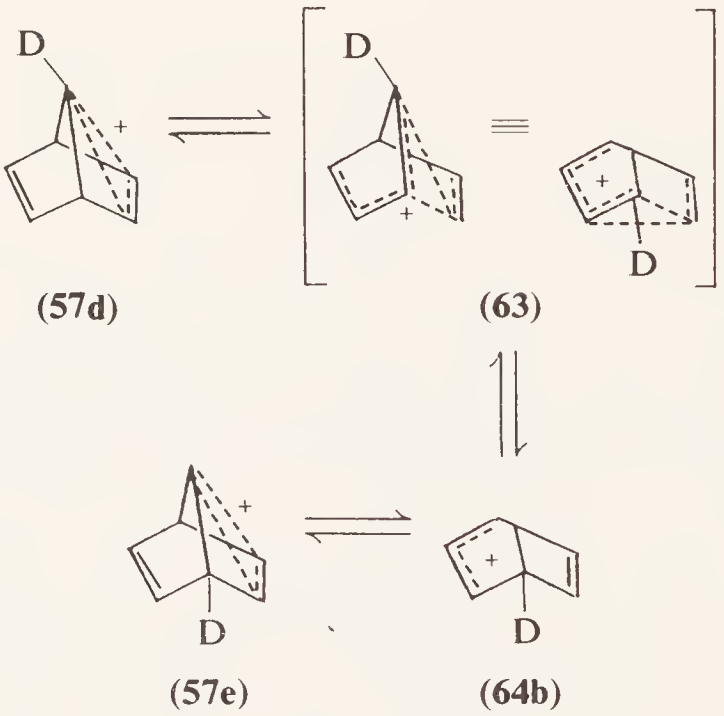
In the search for "bridge flipping" in the norbornadienyl cation, Winstein (56) observed an interesting degenerate five-carbon scrambling. The nmr spectrum of a FSO_3H solution of **57** at 77°, despite quick decomposition to **62**, exhibited a sharp signal at $\tau = 2.54$ for the "bound" vinyl protons; but the three signals for the other protons were broadened,

indicating a five-carbon rearrangement. The rearrangement could be studied in greater detail by employing labeled cations. Consequently, if a solution of deuteriocation (**57c**) was allowed to warm to approximately $-50°$, the deuterium became scrambled to all positions except the "bound" vinyl positions, as shown in **57f**. By examining the nmr spectrum of a series of labeled cations, it could be determined that the deuterium was



(57c) **(57f)**

incorporated stepwise in the five "unbound" positions; i.e., "the isomerization may be said to occur by a stepwise circumambulatory motion of five carbons of the framework of **57** with respect to the two which comprise the bound vinyl function" (56). The simplest mechanism that could be envisioned (56) for the rearrangement is illustrated by contraction of **57d** via transition state **63** to **64b**. The cation **64b** then ring expands to the bicyclic ion **57e**. The process is repeated, and the bound vinyl group works its way around the five-carbon ring defined by the other carbon atoms.

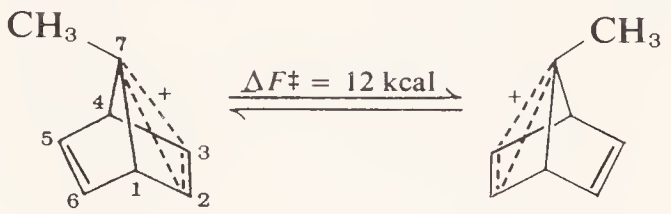


(57d) **(63)**

(57e) **(64b)**

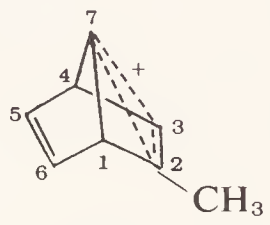
In order to observe the effects of methyl substitution on the size of the barrier to "bridge flipping" and on the nmr spectrum as well, the 7-methyl-norbornadienyl cation **65** was prepared (57). It was reported that

the two nmr signals for the vinyl protons of **65** coalesced at $-14°$, whereas the signal for the methyl group remained sharp and the bridgehead hydrogen multiplet sharpened. The latter effect is believed to indicate that only the magnetic environment of the vinyl protons is averaged and that this averaging can occur only by "bridge flipping" (**65a–65b**) (57). The $\Delta F^{\ddagger}$ for the **65a–65b** interconversion was 12.4 kcal at the coalescence temperature.



(65a) **(65b)**

$H_{2,3}: \tau = 2.45$
$H_{5,6}: \tau = 3.87$
$H_{1,4}: \tau = 4.98$
$H_7\text{-}CH_3: \tau = 8.36$



(66)

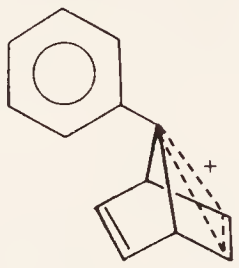
$H_3: \tau = 3.19$
$H_{5,6}: \tau = 3.88$
$H_{1,4}: \tau = 5.11$
$H_7: \tau = 6.58$
$H_2\text{-}CH_3: \tau = 7.44$

Reduction of the barrier to "bridge flipping" by approximately 7 kcal upon introduction of a methyl group at C-7 in **57** can be explained in terms of stabilizing the positive charge at C-7, thereby lowering the energy of the symmetrical transition state (**61**). Warming the fluorosulfonic acid solution of **65** resulted in its rearrangement to the more stable 2-methylnorbornadienyl cation **66** (57). Implications of the nmr spectrum of **66** are discussed in Section VII-B.

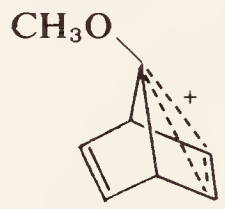
Nmr spectra of fluorosulfonic acid solutions of both the 7-phenylnorbornadienyl cation (**67**) and the 7-methoxynorbornadienyl cation (**68**) have been recorded at low temperatures (58). Not surprisingly, the barrier to "bridge flipping" is significantly reduced by these substituents.

Deno (59) has objected to a delocalized representation of the norbornadienyl cation on the grounds that the multiplet representing the C-7 proton in its nmr spectrum is too far upfield, being at $\tau = 6.5$. This objection is without substance, however. As discussed earlier in this section, a magnetic anisotropic effect probably exists to account for the

chemical shift (40). In addition, Winstein (36) has noted that the upfield position of the C-7 proton is reasonable because C-7 has a considerable propensity to rehybridize from sp^2 to sp^3 [this is equivalent to our earlier argument (40)]. Consequently, we would expect C-7 to bear less of the



(67)



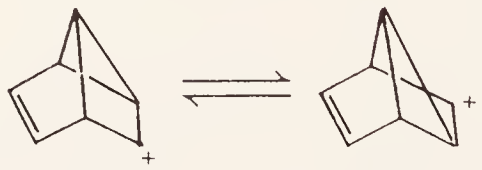
(68)

positive charge, while C-2 and C-3 carry most of it. The argument that C-7 carries less of the positive charge is supported by the behavior of the methyl group in **65**, which alters only slightly the chemical shifts exhibited by the hydrogens at all other positions of **65** relative to **57**. The 2-methyl of ion **66**, on the other hand, interacts with the cationic electronic system to change the nmr of that ion considerably, relative to **65**.

B. The Classical Structure

We conclude that, although the nmr evidence alone obviously would not differentiate between **57** and the pair of rapidly equilibrating classical ions **69a** and **69b** preferred by Brown (5,6), the total evidence—including the large rate enhancement observed in the solvolysis of **54a**, the stability of the salt **56** (to about $-10°$), the "bridge flipping" experiments, and related rearrangements—favors the delocalized, nonclassical representation (**57**).

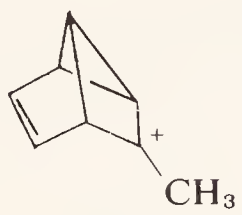
It has been suggested (5,6) that electron delocalization in the 7-norbornadienyl cation is not a matter of structure, but that we are dealing, instead, with two rapidly equilibrating cyclopropyl carbinyl cations (**69a**, **b**) resulting from a transition state in which ionization is assisted by



(69a) **(69b)**

the double bond(s). These classical ions are said to be stabilized through "electron release" by the cyclopropyl groups. Apparently, the same view is held by Deno (59). Winstein has observed (60) that Deno has uniformly omitted specific indication of electron delocalization in his representations of cyclopropyl cations, but he discusses elsewhere the now well-known

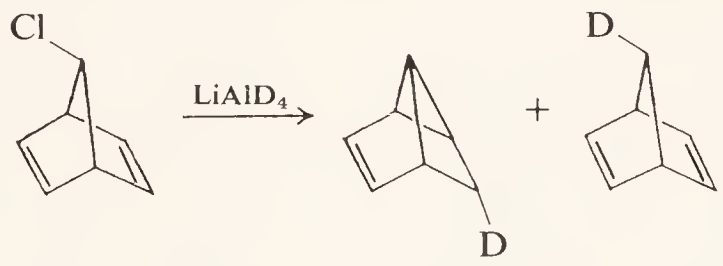
electron-releasing effect of the cyclopropyl group in cations. On the other hand, alkadienyl cations are depicted by Deno (7) in their full-blown delocalized state. Winstein points out the apparent inconsistency of this practice, considering the relative effects of vinyl and cyclopropyl groups in the stabilization of cations. Winstein (57) has further concluded that the nmr spectrum of the 2-methylnorbornadienyl cation **66** is evidence against the classical, equilibrating ions **69a** and **69b** as an accurate representation for the norbornadienyl cation. If the 2-methylnorbornadienyl cation were actually a pair of equilibrating ions, we would expect it to exist almost exclusively in the form of the tertiary ion **70** (57). Since the nmr of **66** is not compatible with the spectra of cyclopropyl carbinyl cations described by Olah (61), structure **70** can probably be ruled out as a valid representation of the ion.



(70)

C. Nucleophilic Trapping of the Cation

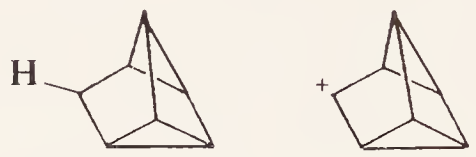
Interaction of a double bond and an incipient positive center at C-7 in the 7-norbornadienyl system has been well demonstrated chemically. It was found, e.g., that treatment of the chloride (**54a**) with lithium aluminum deuteride in ether gave the tricyclic olefin (**71**) as the major product, along with some deuterionorbornadiene (**54c**) (62). More recently, under conditions more clearly requiring a carbonium ion intermediate, Brown used sodium borohydride to obtain the undeuterated products in the same



(54a) **(71)** **(54c)**

ratio (5). Whether we view this reaction as trapping, irreversibly, the classical ions (**69**) or the delocalized cation (**57**), the results indicate that a large percentage of the charge is located at the olefinic carbons (C-2, C-3). Brown (6b) has concluded that the reduction data rule out the *endo*-bonded structures (**55**) originally proposed by Winstein (52). Since no

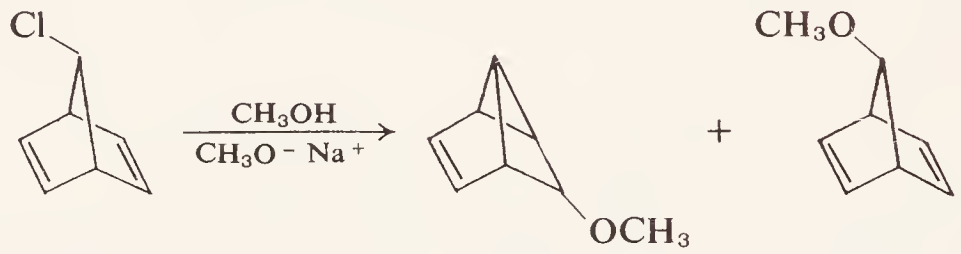
quadricyclane (**72a**) was detected in either investigation, it is unlikely that the quadricyclyl cation **73** plays an important role in descriptions of the 7-norbornadienyl cation **57**. This and other such interpretations must be



(72a) **(73)**

made with caution, however, because a clear relationship between carbonium ion character or composition and the products of hydride trapping of that carbonium ion has not yet been drawn.

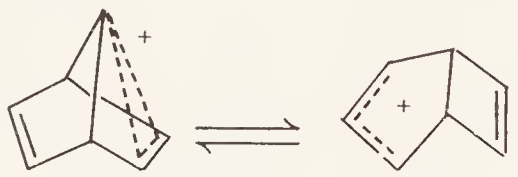
More recently, Tanida (38) has reported the formation of substantial amounts of the tricyclic derivative **74** along with some **54d** upon methanolysis of **54a** in the presence of sodium methoxide. No implications were drawn from this work as to the structure of the intermediate cation involved.



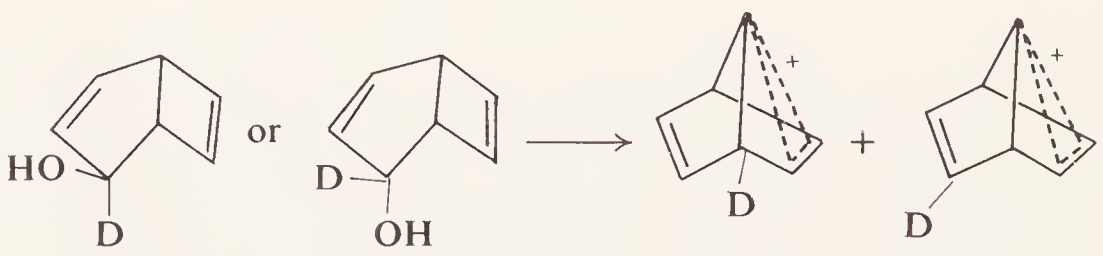
(54a) **(74)** **(54d)**

D. Interrelation of the Bicyclo[3.2.0]heptadienyl and 7-Norbornadienyl Cations

As discussed in Section VII-A, Winstein (56) postulated that the bicyclo[3.2.0]heptadienyl cation (**64a**) was an intermediate in the 5-carbon



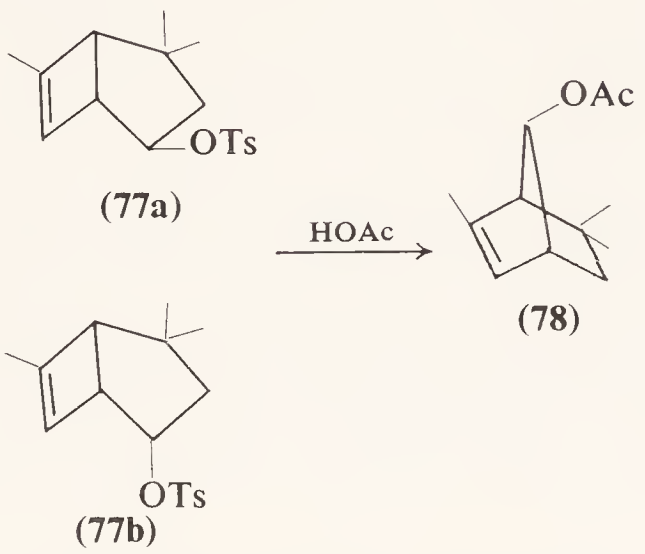
(57) **(64a)**



(75) **(76)** **(57e)** **(57c)**

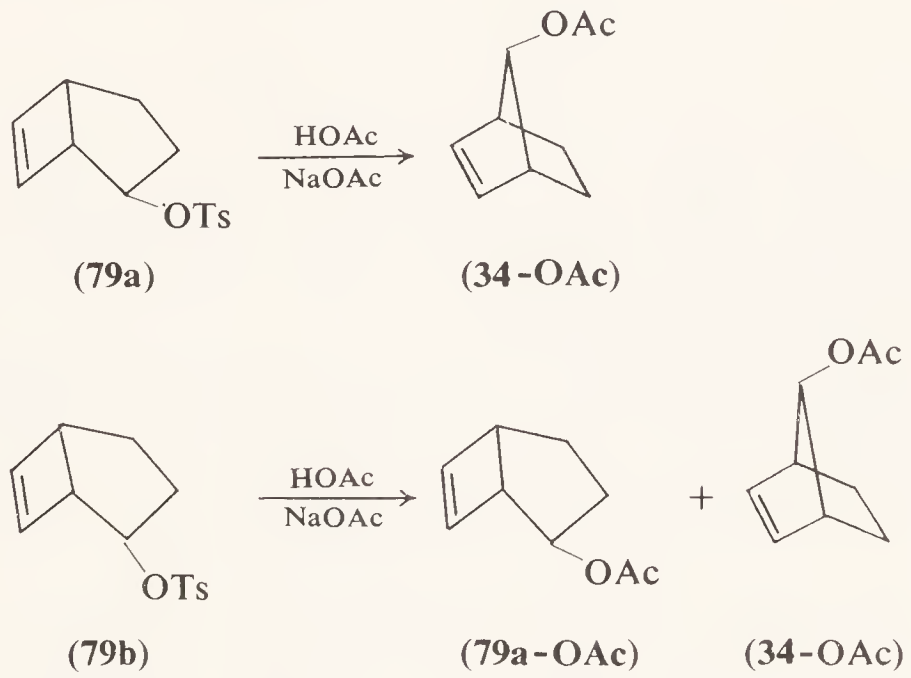
degenerate rearrangement of the norbornadienyl cation **57**. Evidence for this mechanism was provided by the rearrangement in fluorosulfonic acid of the alcohols **75** and **76** to a 50:50 mixture of the salts **57c** and **57e**. It was also noted that the rearrangement is extremely facile, being complete in 120 sec at $-78°$. The equilibrium constant for **64a** $\rightleftarrows$ **57** was estimated to be 7000 at this temperature. Clearly, the norbornadienyl cation is strongly favored in the equilibrium.

Whitham (63) has observed a similar rearrangement in solvolysis of the epimeric bicyclo[3.2.0]hept-6-en-2-yl tosylates **77a** and **77b**, which both give the *anti*-7-acetate **78**.



(77a) **(78)** **(77b)**

We have examined the unsubstituted compounds analogous to **77** and find that the *exo* tosylate **79a** solvolyzes 1600 times faster than the *endo* epimer **79b** in acetic acid at 50°. Furthermore, **79a** gives only *anti*-7-norbornenyl acetate (**34-OAc**); the *endo* epimer yields both **34-OAc** and the *exo* acetate **79a-OAc** (64b).

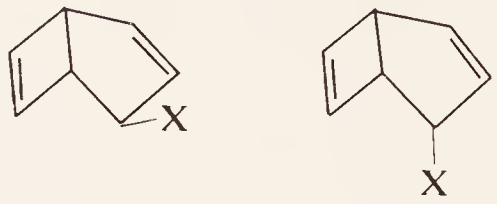


(79a) **(34-OAc)**

(79b) **(79a-OAc)** **(34-OAc)**

We have shown (64) that the ring expansion observed for **75** and **76** does not occur upon solvolysis of the *exo*- and *endo*-*p*-nitrobenzoates **80b** and

81b in aqueous acetone. The rates observed for the solvolyses of **80b** and **81b** were approximately the same, and mixtures of **80a** and **81a** were the only products isolated. From this information we concluded that the allylic double bond must stabilize the carbonium ion center to the extent



(80) **(81)**

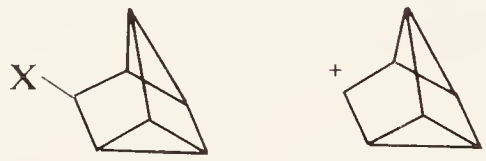
(80a) X = —OH; **(80b)** X = —OpNB

OpNB = *p*-nitrobenzoate

that participation by the homoallylic double bond is not important, even though the homoallylic double bond is more favorably oriented for interaction with a developing positive center in the early stages of ionization. Nor were any rearranged products observed on solvolysis in acetic acid. It is apparent that interconversion of **64a** and the norbornadienyl ion (**57**) becomes important only in solvents that provide long-lived carbonium ions.

E. The Quadricyclyl Cation

Several investigatiors have shown that quadricyclyl derivatives (**72**) do not generate the same cation as that derived from 7-norbornadienyl

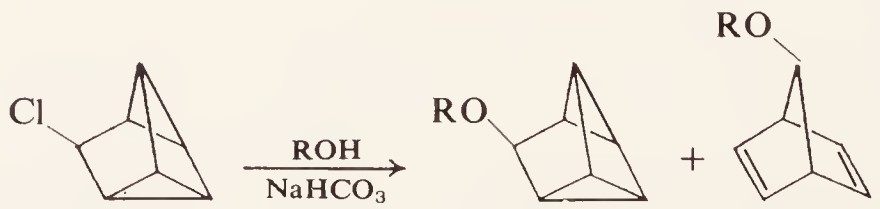


(72) **(73)**

(72a) X = —H; **(72b)** X = —D; **(72c)** X = —Cl; **(72d)** X = —OH;
(72e) X = —OTs; **(72f)** X = —OBs; **(72g)** X = —ONs

ONs = *β*-naphthalene sulfonate

derivatives (65,66). Solvolysis of 7-quadricyclyl chloride (**72c**) in aqueous ethanol containing excess sodium bicarbonate, e.g., gave a product consisting of 75% quadricyclyl derivatives and 18% 7-norbornadienyl

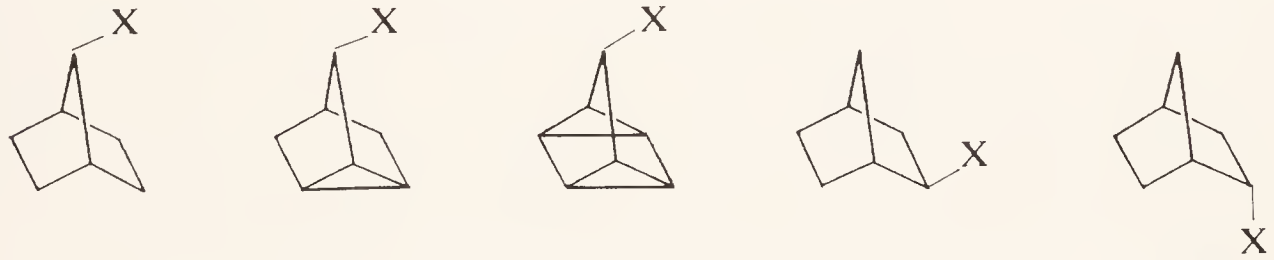


(72c) 75% 18%

derivatives (66). In acetic acid, containing excess potassium acetate, the proportion of 7-norbornadienyl product was higher (65,67) and varied with time (68).

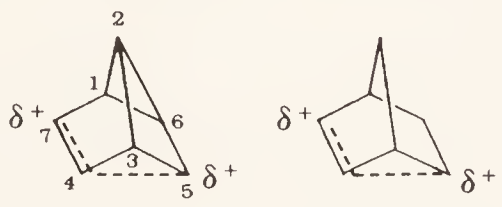
Quadricyclyl derivatives were also remarkably reactive (65,66), being approximately 10^9 more reactive than the corresponding 7-norbornyl derivative and less reactive than the *anti*-7-norbornenyl derivative (**34**) by a factor of only 100 or less (66). However, as Richey pointed out (65), tricyclic derivatives (**26**) are less reactive than the corresponding quadricyclyl derivatives by a factor of only 30 to 40, indicating that the effect of the second cyclopropyl ring in quadricyclyl derivatives is fairly negligible. Even though introduction of a cyclopropyl ring into **82** or **83** will also generate **26**, the 7-norbornyl molecule (**35**) constitutes a better model, since it already contains most of the structural factors present in **26** which serve to destabilize the cation. Comparison of **82** and **26** reveals that, in this instance, the cyclopropyl ring has a slight retarding effect.

Approximate relative rates for acetolysis of the *p*-bromobenzenesulfonates at 25° (65,69)



(35)	(26)	(72)	(82)	(83)
1	6×10^8	10^{10}	7×10^9	1.5×10^7

In order to account for the reactivity of quadricyclyl derivatives in solvolysis reactions, we proposed that the intermediate quadricyclyl carbonium ion was stabilized by charge delocalization as shown in **84** (66). This structure was based on Winstein's formulation of charge delocalization in the dehydronorbornyl cation (**29a**) and accounts for the observation that quadricyclyl derivatives are only slightly more reactive than the

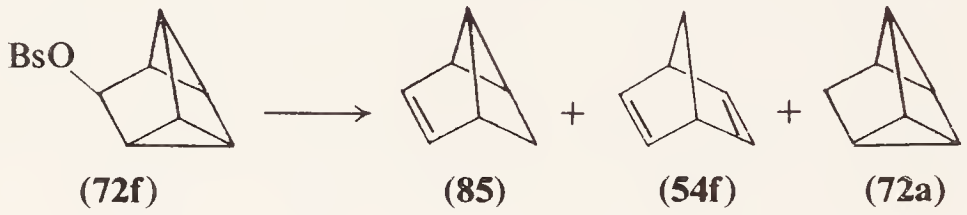


(84) **(29a)**

corresponding tricyclic compounds. It is noteworthy that models of the spatial relation of the cationic center to the cyclopropyl rings in the

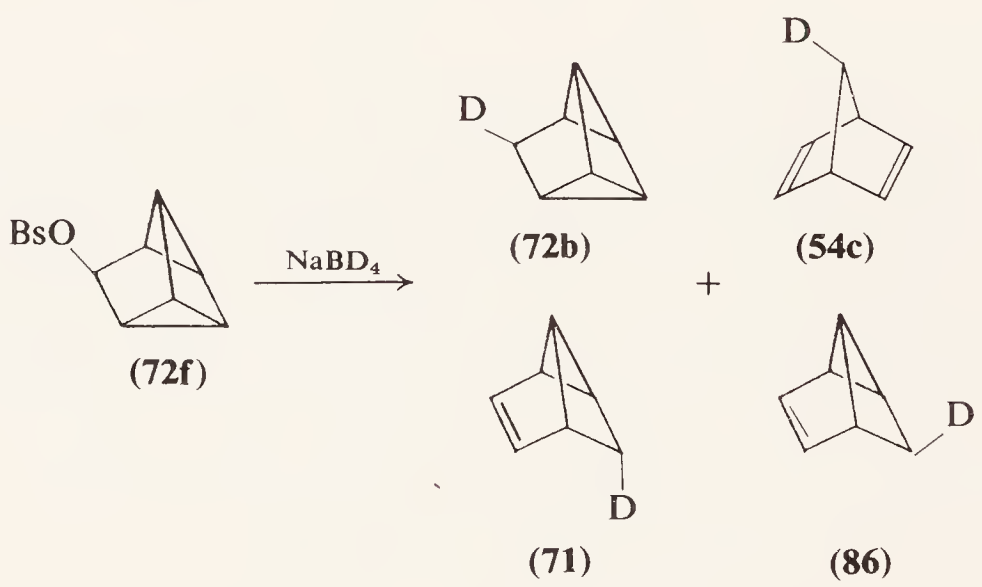
quadricyclyl carbonium ion (**73**) make it look very nearly the same as it is in the preferred conformation of the dimethyl cyclopropyl carbonium ion as determined by Olah (70).

In an attempt to determine the mode of charge delocalization in the quadricyclyl cation by trapping it irreversibly with hydride (5), we solvolyzed quadricyclyl chloride (**72c**) in aqueous ethanol in the presence of sodium borohydride, but the hydrocarbon product consisted solely of quadricyclane (**72a**) (66). The same result was obtained on treating the brosylate (**72f**) with sodium borohydride in anhydrous diglyme. More recently, however, in an experiment using 80% aqueous diglyme as the solvent, the brosylate (**72f**) yielded a hydrocarbon product that consisted of 10% tricyclene (**85**) and about 1% norbornadiene (**54f**) in addition to quadricyclane (**72a**) (67). Since the tricyclene **85** could have arisen from



(**72f**) (**85**) (**54f**) (**72a**)

reduction of the 7-norbornadienyl cation (**57**), particularly since some norbornadiene was formed, the reaction was repeated using sodium borodeuteride. Nmr analysis of the products revealed that approximately 10% of the tricyclene consisted of *exo*-deuteriotricyclene (**86**) and the remainder of *endo*-deuteriotricyclene (**71**) (67). Reduction of 7-norbornadienyl chloride (**54a**) under similar conditions produced only **71** and **54c**, in agreement with previous results (62).



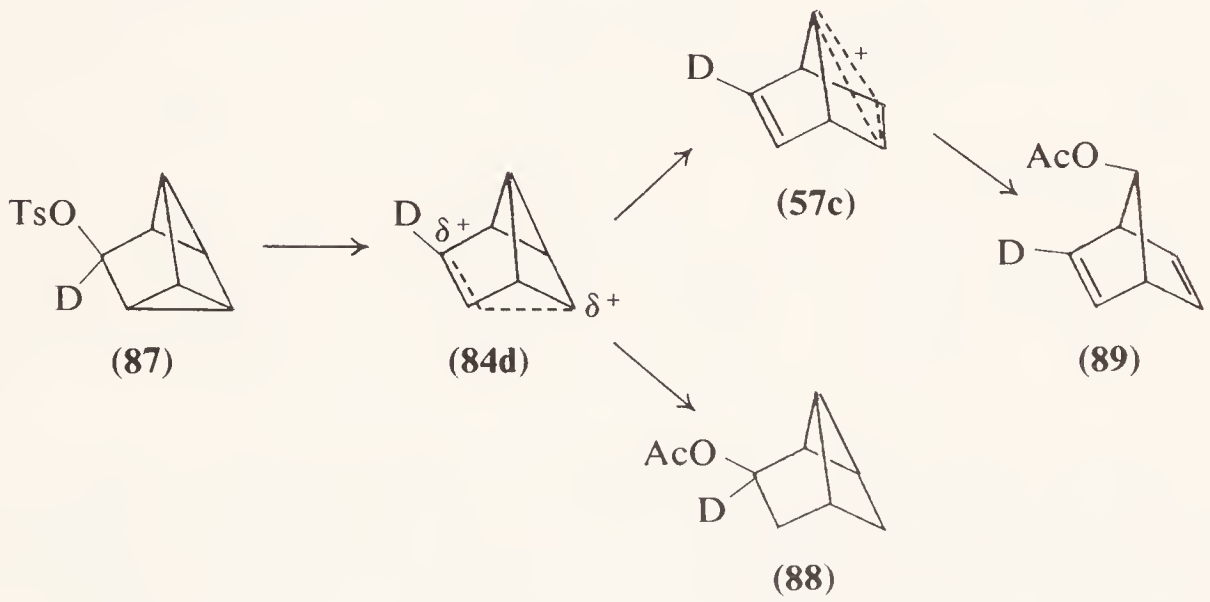
(**72f**) (**72b**) (**54c**) (**71**) (**86**)

It was proposed that **86** arose from reduction of the quadricyclyl cation (**84**) at C-5 and that **71** and the deuterionorbornadiene **54c** were generated by reduction of the 7-norbornadienyl cation (**57**), produced by rearrange-

ment of **84**. The ratio of **71** to **54c** was within experimental error of that usually found upon reduction of the 7-norbornadienyl cation (**57**) (5,62). Although these data support the structure **84**, the conclusions are based on the assumption that all the hydrocarbon product arises from a cationic intermediate. Since the yield of **86** was very low, caution must be exercised. The formation of **86** can probably be considered significant in spite of this limitation, however, for the most likely alternative to a cationic intermediate is direct displacement by deuteride on the brosylate (**72f**), and this reaction would be expected to be relatively more important in anhydrous diglyme. In fact, neither **71** nor **86** was obtained in this solvent (66).

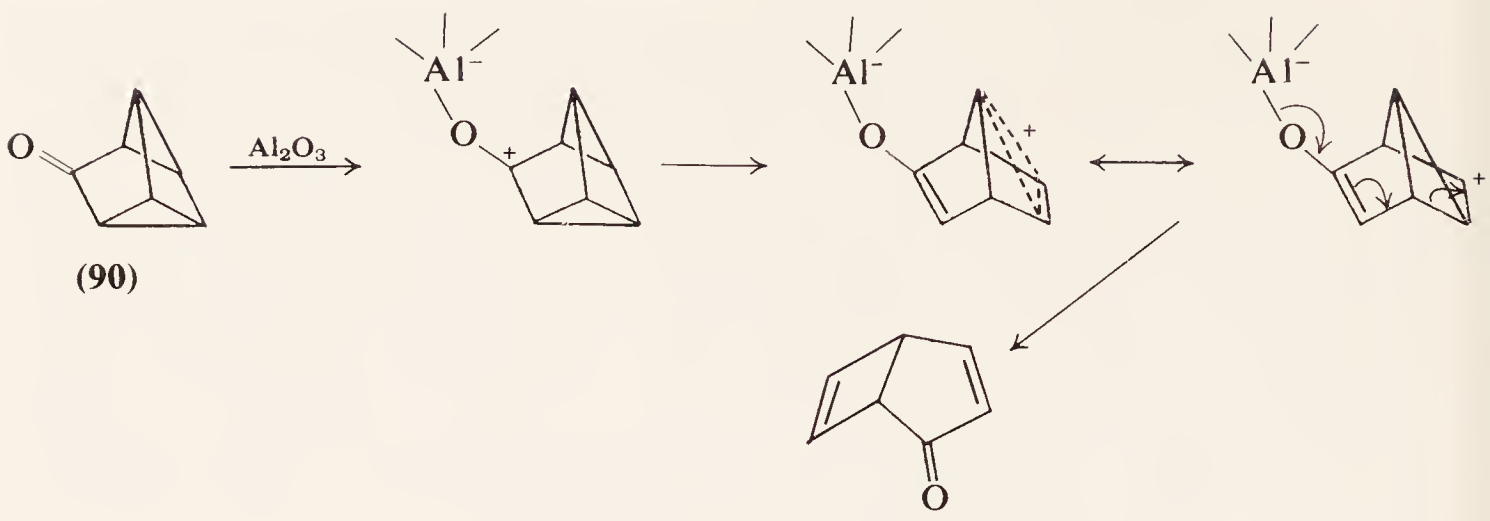
F. Interrelation of the Quadricyclyl and 7-Norbornadienyl Cations

Isomerization of the quadricyclyl cation (**84**) to the 7-norbornadienyl cation (**57c**), obviously a rather facile process, follows the general rearrangement path suggested by Richey (65) and by ourselves (66). Acetolysis of the deuterium-labeled tosylate **87** generated a product consisting of an approximately 50:50 mixture of **88** and **89** (67). Our version of this sequence is shown in the equation:



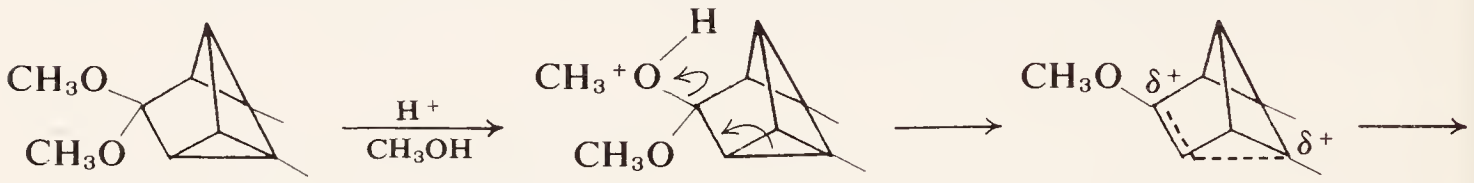
As indicated, the hydrogens of the quadricyclyl cation (**84d**) are not scrambled by rearrangement, thereby excluding a structure in which the positive center is delocalized over two or more equivalent carbons. Furthermore, this experiment revealed that the isomerization of the quadricyclyl cation to the 7-norbornadienyl cation is highly stereospecific and, in addition, that the 7-norbornadienyl cation (**57**) retains its configuration, once it is formed. This rearrangement scheme is also consonant with that depicted for the quadricyclanone **90** to bicycloheptadienone (**91**) conversion (71).

More evidence for the proposed isomerization scheme has been provided

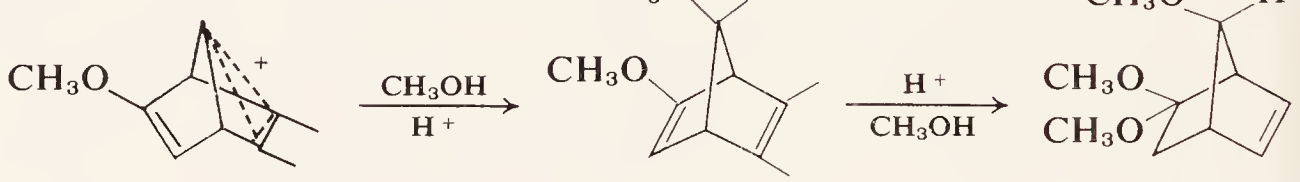


(90) (91)

by the work of Gassman (72,73), in which rearrangement of the quadricyclyl derivative **92** to the norbornadienyl derivative **94** was found to occur in weakly acidic methanol. The **92** → **94** rearrangement mechanism preferred by Gassman (73) is illustrated. An alternative mechanism proposed by Gassman (73) involves the highly delocalized intermediate ion (**95**);

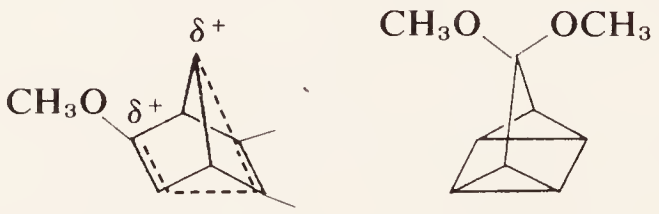


(92) (93)



(94)

on the basis of our preceding discussion, however, this mechanism is considered unlikely. Gassman goes on to point out that a mechanistic rationale for the rearrangement including classical ions does not satisfactorily explain the stereospecific incorporation of the methoxy function. In a related study (74), the demethylated derivative **96** was observed to undergo rearrangement at a rate approximately 10^5 times slower than **92**.



(95) (96)

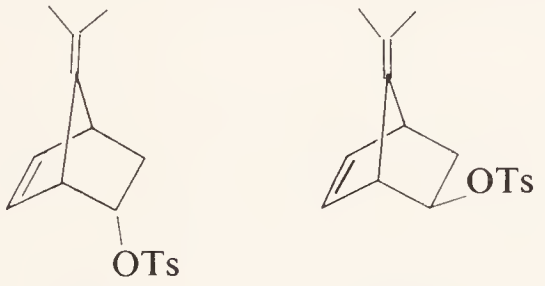
It may be concluded, then, that the 7-quadricyclyl (**84**) and 7-norbornadienyl (**57**) cations are separate and distinct species and behave

similarly to other homoallylic cations studied earlier, especially with respect to retention of configuration, spatial relationship of the interacting centers, stereospecificity of the homoallylic interaction, and apparent charge delocalization patterns. With respect to the last-mentioned feature, there is an increasingly long list of homoallylic cations which, like **57** and **84**, appear to be stabilized by interaction of the positive center, principally, with only one of the available unsaturated centers.

VIII. OTHER DIENYLIC CATIONS

A. The 7-Isopropylidene Norbornenyl System

An example of a diene system in which the positive center appears to interact with only one of the double bonds is provided by DePuy, who found that *endo*-7-isopropylidene-5-norbornenyl-2 *p*-toluenesulfonate (**97**) underwent acetolysis with a rate enhancement of 10^4 over the corresponding tosylate (**25**) lacking the isopropylidene group and, moreover, that acetolysis occurred with complete retention of configuration (75). On the other hand, the *exo* tosylate **98**, which also solvolyzed with rate enhancement, gave only the rearranged acetate **99**. The corresponding dihydro tosylates **100** and **101** behaved analogously.



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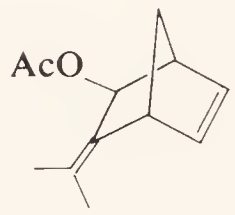

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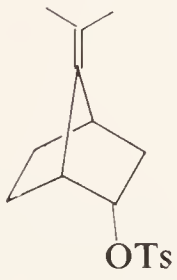

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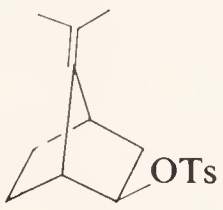

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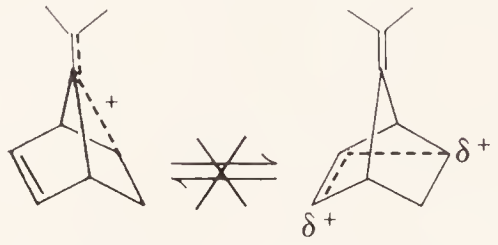


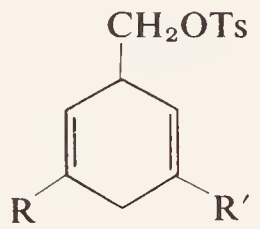
(97a) **(98a)**

These results were interpreted (75) to indicate that, although a positive charge was formed at C-2 in both cases, no common intermediate cation was formed; indeed, the two cations **97a** and **98a** were distinct and separate under the reaction conditions.

B. The 1,4-Dihydrobenzyl Cation

In similar fashion, Chapman and Fitton were able to demonstrate that primary assistance to ionization in acetolysis of 1,4-dihydrobenzyl

tosylates (**102**) is due principally to only one of the double bonds (76). This conclusion was reached by observing that the effect of substituents, R and R′, was not multiplicative. For example, even though 3-methyl-1,4-dihydro-



(102)

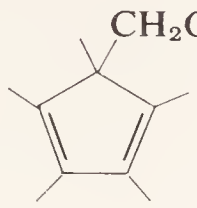
benzyl tosylate (**102**, R = CH_3, R′ = H) is 22 times more reactive than 1,4-dihydrobenzyl tosylate (**102**, R = R′ = H) itself, the dimethyl derivative (**102**, R = R′ = CH_3) is only 46 times more reactive. If both double bonds had participated equally, of course, the rate enhancement factor for the dimethyl derivative would have been approximately the square of that for the methyl derivative. It was noted in this report (76) that the geometry of the homoallylic system of the 1,4-dihydrobenzyl tosylates is quite similar to that of cholesteryl tosylate.

C. Pentamethylcyclopentadienyl Carbinyl Cation

Somewhat similar mechanistic considerations apply in the pentamethylcyclopentadienyl carbinyl system (**103**) investigated by de Vries (77) and by Winstein (78), who found that acetolysis of the tosylate (**103**) was anchimerically accelerated over neopentyl tosylate (taken as an appropriate model] by a factor of about 10^{10}. Although the solvolysis data strongly indicated the intermediacy of an electron delocalized homoallylic carbonium ion, several modes of charge delocalization were conceivable. Both the unsymmetrical structure (**104**) and the symmetrical structure (**105**) were considered (78).

In the light of data collected since 1960, a reasonable prediction for the structure of this ion should be **106**, in which the second double bond has a relatively small effect on the stability. It would also seem likely that **106** would be in equilibrium with, or at least interconvertible with, **107**. The kinetically controlled product of the acetolysis of **103** was reported to be the hydrocarbon (**108**); the equilibrium product was the acetate (**109**).

Winstein (79) has subsequently reported the nmr spectrum of a cation generated by extraction of **108** from chloroform solution into fluorosulfonic acid. This cation, which Winstein now believes is the true intermediate in the solvolysis of **103**, is represented as **110**. Cation **105** is now rejected (79) as a possible intermediate in the solvolysis reaction on the grounds that it is a four-electron bishomocyclopentadienyl cation and is



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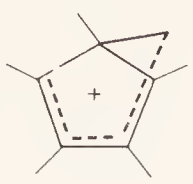

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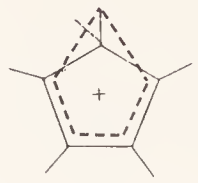

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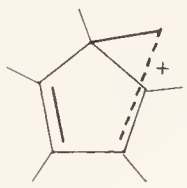

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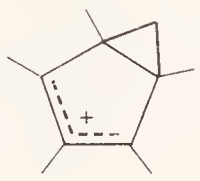

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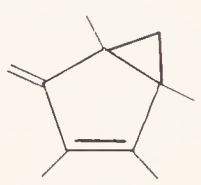

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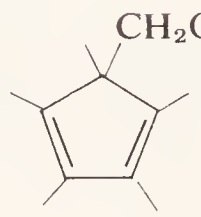
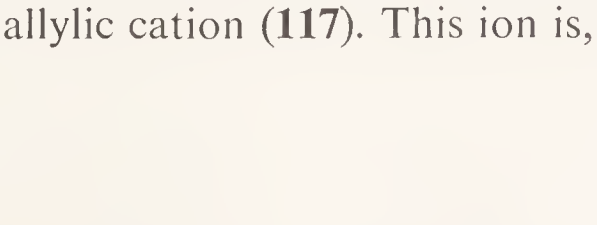


(109)

antihomoaromatic (see Section XIII). We observe, however, that Winstein's nmr data are equally consistent with **106** $\rightleftarrows$ **107**, which constitutes a 2π–3C system.



(108) **(110)**

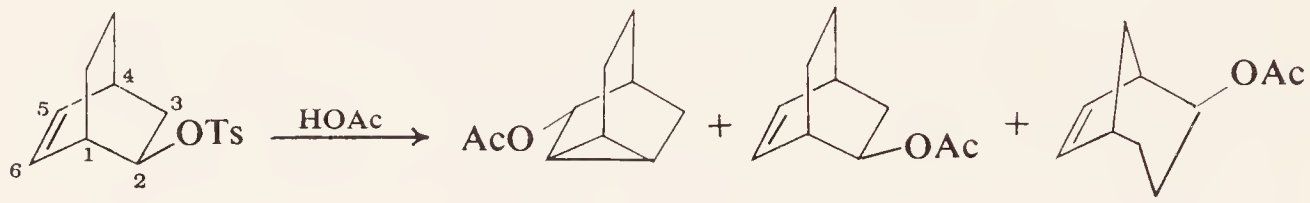
IX. THE BICYCLOOCTENYL CATIONS

A. The Bicyclo[2.2.2]octenyl System

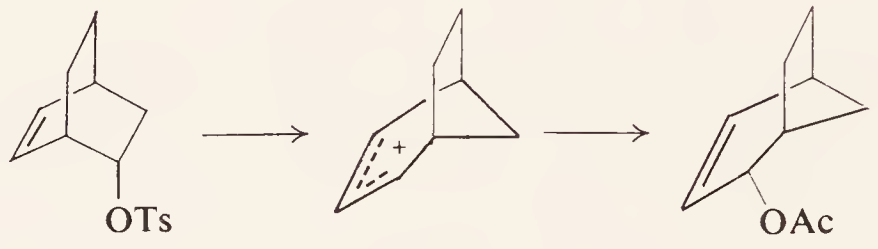
The 2-substituted bicyclo[2.2.2]-5-octenyl structure provides yet another homoallylic system of considerable interest. LeBel and Huber (80) have reported the solvolysis of *exo*-bicyclo[2.2.2]oct-5-en-2-yl *p*-toluenesulfonate (**111**) and have concluded that the double bond provides a rate enhancement of at least 4×10^5—a factor which yields an *exo*/*endo* rate ratio notably greater than that observed for the dehydronorbornyl system. As indicated (80), however, an *exo*/*endo* rate comparison is difficult, not only because of probable internal return but because the *endo* compound (**112**) that was used to provide the model, unassisted rate also shows rate enhancement, as demonstrated by Goering and Towns (81). The *endo* tosylate (**112**) appeared to ionize directly to the allylic cation (**113**) (81).

In their very thorough study (80), LeBel and Huber found that acetolysis of **111** gave 90% tricyclic acetate (**114**), 7% **115**, and 3% rearranged acetate (**116**); they suggested that the observed rate enhancement and solvolysis products were consistent with the direct formation of the unsymmetrical homoallylic cation (**117**). This ion is, of course, analogous

to that proposed for the dehydronorbornyl system by Winstein (17). LeBel also considered the possibility of the formation of rapidly equilibrating classical cations, as discussed earlier in this chapter for the 7-norbornenyl cation (Section V).

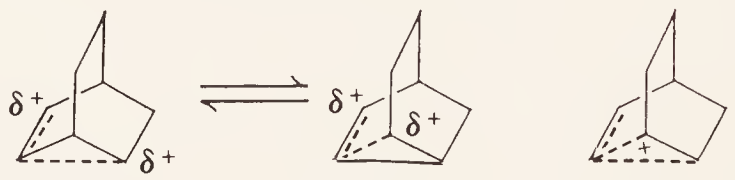


(111) **(114)** **(115)** **(116)**



(112) **(113)**

Unlike the dehydronorbornyl system, the stereochemistry of the reaction of **117** with solvent at C-5 is observable. The sole tricyclic product (**114**) results from *endo* attack at C-5, which LeBel explains by observing that the *endo* side of the molecule is less hindered. *Endo* attack by solvent at C-2, however, was considered to be precluded by partial bond formation between C-2 and C-6. The small percentage of rearranged acetate (**116**) was presumed to arise from formation of the symmetrical ion (**118**). Isomerization of **117a** to **117b** could also account for the rearranged product (**116**) and would be analogous to the scheme discussed in Section IV for ^{14}C scrambling in the dehydronorbornyl cation.



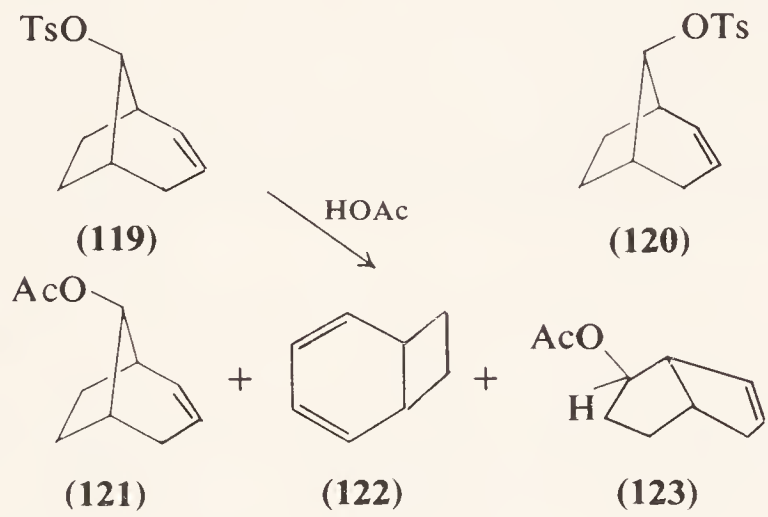
(117a) **(117b)** **(118)**

B. The Bicyclo[3.2.1]octenyl System

The bicyclo[3.2.1]octenyl system has also been investigated by LeBel's group (82), and some interesting comparisons to the *anti*-7-norbornenyl system are drawn. The 8-substituted bicyclo[3.2.1]octenyl molecule (**119**) contains a double bond whose orientation with respect to the leaving group is somewhat different from the *anti*-7-norbornenyl double bond and

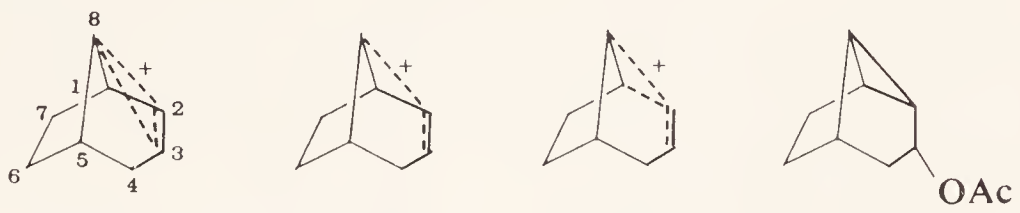
is, therefore, quite helpful to our understanding of homoallylic cationic structure.

The *anti* tosylate **119** underwent acetolysis about 2.6×10^5 faster than the corresponding *syn* tosylate **120** (82), thereby providing a strong argument in favor of homoallylic participation by the double bond in solvolysis of **119**. The products of acetolysis, in addition to the unrearranged acetate **121**, consisted of the bicyclic diene **122** and the rearranged acetate **123**. Consideration of the large *anti*/*syn* rate ratio, coupled with the product analysis data,* led LeBel and Spurlock (82) to consider three



(119) **(120)** **(121)** **(122)** **(123)**

possible homoallylic intermediate cations; the bishomocyclopropenyl ion (**124**), by analogy to the *anti*-7-norbornenyl cation; the unsymmetrical homoallylic cation (**125**) of the type and geometry considered for the cholesteryl, dehydronorbornyl, and others; and the symmetrical homoallylic cation (**126**), also considered for the cholesteryl and dehydronor-



(124) **(125)** **(126)** **(127)**

bornyl cations. Cation **124** was rejected on the grounds that the C-3–C-8 distance is probably too great for significant 1,4 interaction. It is true that the 1,4 interaction would undoubtedly be smaller than the 1,3 interaction, but the difference between structures **124** and **125** would seem to be only one of degree. LeBel regarded structure **125** as most probable, but he considered the symmetrical structure **126** as a distinct possibility. Structure **126** was also considered to be a reasonable model for the transition state

* Unrearranged acetate (**121**) derived from **119** showed 100% retention of configuration, whereas the *syn* tosylate (**120**) yielded considerable unrearranged acetate of inverted configuration.

in formation of the ionic precursor of **123**. Unlike the cholesteryl or dehydronorbornyl systems, however, none of the ring-closed acetate **127** was obtained.

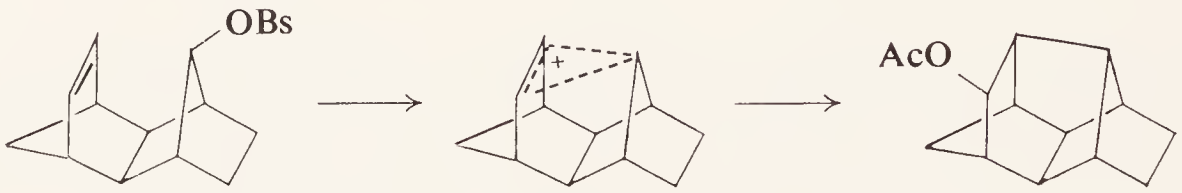
Rate comparisons of some related *p*-toluenesulfonates (82)

Cyclohexyl	1
anti-7-Norbornenyl (**34a**)	7.7×10^3
Δ^3-Cyclohexenyl	0.74
anti-Bicyclo[3.2.1]oct-2-en-8-*yl* (**119**)	0.75
syn Tosylate (**120**)	2.9×10^{-6}

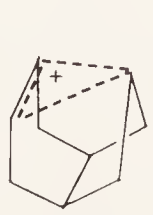
It is noteworthy, as pointed out by LeBel, that **119** and Δ^3-cyclohexenyl tosylate, which are structurally related, are of nearly identical reactivity.

X. "BIRDCAGE" CATIONS

Another interesting homoallylic system is provided by the "birdcage" hydrocarbon precursors investigated by Winstein and co-workers. The *p*-bromobenzenesulfonate **128**, e.g., undergoes acetolysis to the saturated acetate **129** at a rate only four times less than the acetolysis rate of *anti*-7-norbornenyl brosylate (**34f**). Winstein and Hansen (83) attributed the very large rate enhancement and the formation of **129**, the sole product, to the intermediacy of the homoallylic, nonclassical cation **130**. This system provides a unique orientation of the double bond and the incipient cation as illustrated in **130a**. Conceptually, this cation (**130**) is quite similar to that proposed for the bicyclic system (**131**) investigated previously by Leal and Pettit (84). Pettit's ion was isolated as a yellow solid perchlorate salt, but its structure was assumed from its mode of preparation and from ultraviolet spectral data.



(128) **(130)** **(129)**



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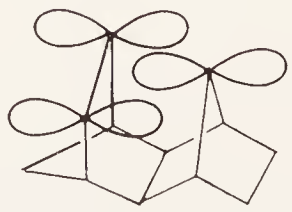
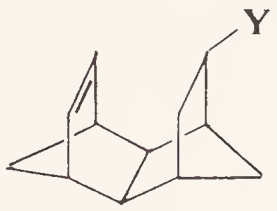


(130a)

The closely related octahydrodimethanonaphthyl system **132** (85) constitutes another interesting homoallylic system; here the *p* orbitals of the cation are again parallel, but the system differs from **130** in that the presumed intermediate cation (**133**) is unsymmetrical with respect to the



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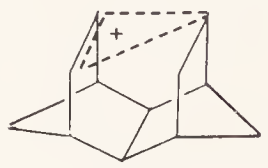
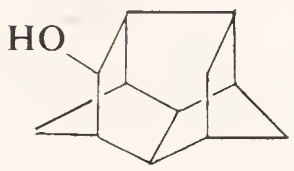


(133)

double bond. Derivatives of this structure are even more reactive than their corresponding *anti*-7-norbornenyl derivatives (**34**) by a factor of approximately 10 (85). The products of the hydrolysis of the trifluoroacetate **132**, in addition to **134**, include the "birdcage" hydrocarbon **135** and the rearranged alcohol **136**.



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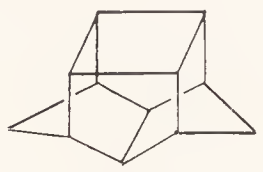

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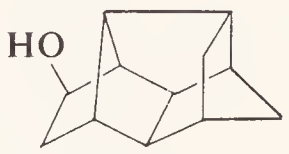
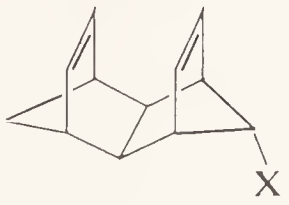


(136)

The *endo*, *endo*-dimethanonapthadienyl system (**137**) provides an example of possible π-electron participation from both remote and homoallylic double bonds (86). The only product isolated from the hydrolysis of the *p*-nitrobenzoate **137a** was the *anti* alcohol **137b**. It was postulated (86) that the highly delocalized intermediate (**138**) accounted for both the high rate of solvolysis (10^3 times greater than the corresponding *anti*-7-norbornenyl derivative) and the retention of configuration by the product (**137b**).



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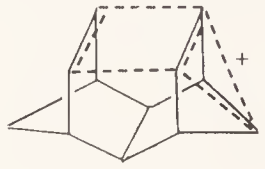


(138)

(a) X = —OpNB; **(b)** X = —OH

XI. OTHER HOMOALLYLIC SYSTEMS

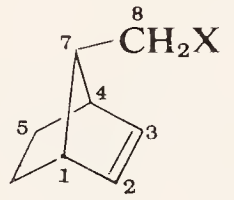
Many other homoallylic systems have been investigated. Since it would not be practical to discuss all such examples in this chapter, we have included in this section those systems which do not fall into any major

category by weight of numbers or by intensity of investigation but which do add to carbonium ion theory.

A. The (7-Norbornenyl)methyl System

The acetolyses of (*syn*- and *anti*-7-norbornenyl)methyl *p*-bromobenzenesulfonates (**139a**, **140a**) and of the corresponding saturated (7-norbornyl)-methyl *p*-bromobenzenesulfonate (**141a**) were originally reported by Bly and co-workers (87). The system was of interest as a test for the importance of overlap geometry on the amount of π participation in solvolysis, particularly since, *a priori*, the system appeared to be perfect in all respects for double-bond participation.

In the original work (87) it was learned that the major isolated products from acetolysis of the unsaturated brosylates (**139a** and **140a**) were the corresponding unrearranged acetates, **139b** and **140b**, respectively. Both



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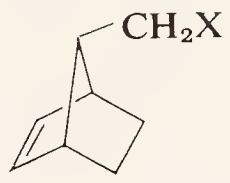
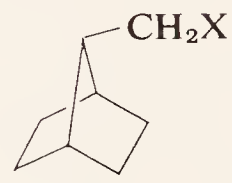
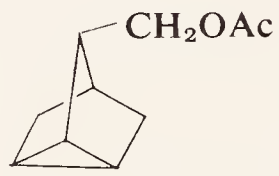


(140)

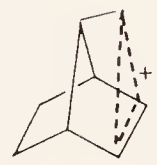


(141)

(a) X = —OBs; **(b)** X = —OAc; **(c)** X = —OTs; **(d)** X = —NH_2



(142)

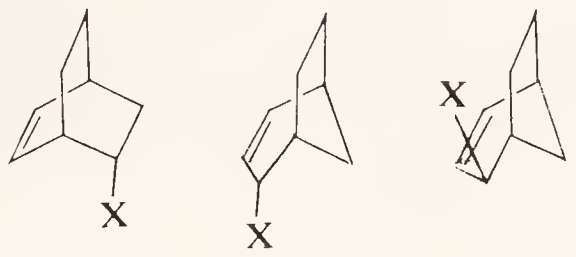


(143)

brosylates (**139a**, **140a**) gave a small amount of the tricyclic acetate **142** as the only other reported product (87). Bly (87) estimated a small anchimeric assistance factor of 5 to 6 for the *syn* brosylate (**139a**) and proposed the delocalized homoallylic structure **143** for the intermediate in acetolysis. Sauers and Hawthorne observed (88) that the *syn* tosylate (**139c**) solvolyzed somewhat faster than the *anti* isomer **140c**.

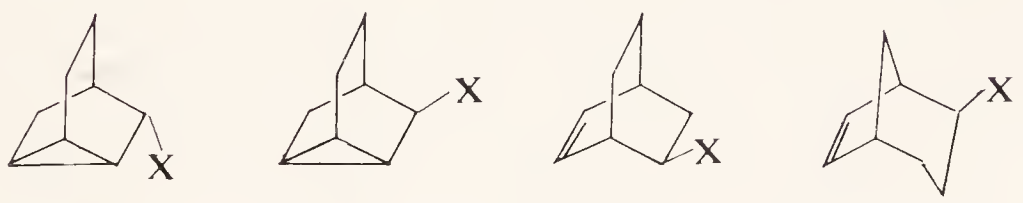
Berson and Gajewski (89) also found that the acetolysis of **139a** and **140a** resulted principally in unrearranged acetates. However, close examination of the reaction mixture revealed some minor, but very interesting, rearranged products in acetolysis of both isomers. It was observed that the *syn* isomer (**139a**) on acetolysis gave a mixture of two sets of products. One set was nearly identical in substance and in ratio to the products (**144**, **145**, **112**) that Goering (81) had obtained from *endo*-bicyclo[2.2.2]octenyl tosylate (**112a**). The other set of products was similar

in all respects to those LeBel (80) obtained from the acetolysis of *exo*-bicyclo[2.2.2]octenyl tosylate (**111a**). In addition, a small amount of the *exo* derivative **146b** was obtained. Deamination of the *syn* amine (**139d**) gave similar results yielding "Goering" alcohols (G-alcohols) and "LeBel" alcohols (L-alcohols) in a ratio of approximately 2.5:1.



(112) **(144)** **(145)**

Goering products

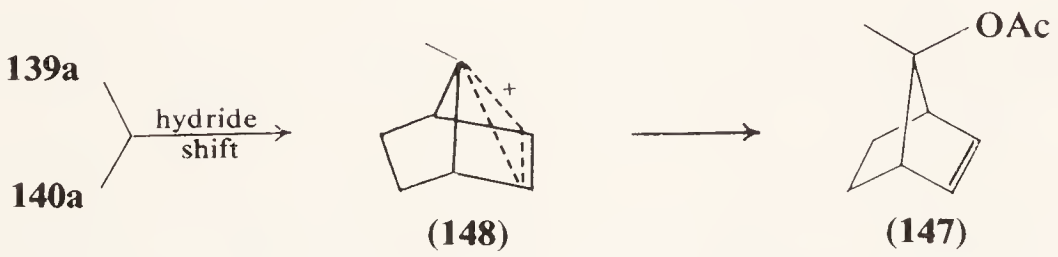


(114) **(146)** **(111)** **(116)**

(a) X = —OTs; **(b)** X = —OAc; **(c)** X = —OBs

LeBel products

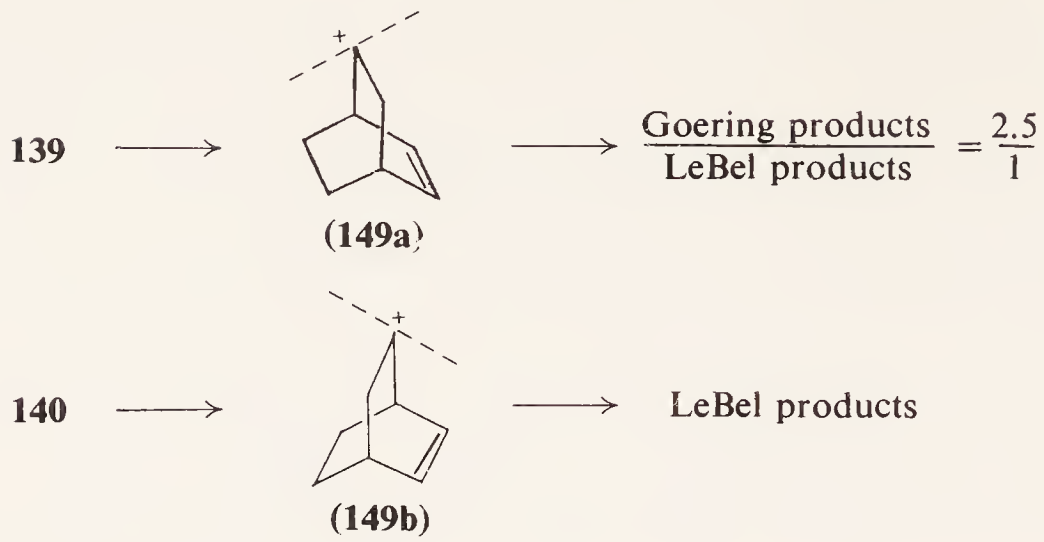
The *anti* isomers (**140a**, **140d**), on the other hand, gave almost exclusively L-products (**114**, **146**, **111**), acetates from **140a** and alcohols from **140d**. Also observed among the minor products was the acetate **147**, which could arise from the homoallylic cation **148**, derivable from **139a** or **140a** by hydride shift from C-7 to C-8 (89).



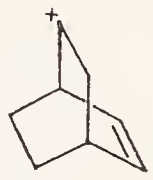
(148) **(147)**

Based on the G and L product data, it was concluded that the *syn* derivatives (**139**), in undergoing ring expansion, generate intermediates distinctly different from those of the *anti* derivatives (**140**). The intriguing possibility was considered that **139** and **140** generate the deformationally isomeric ions **149a** and **149b** (89).

Following this argument to its conclusion requires that both intermediates, **149a** and **149b**, rearrange or form a homoallylic nonclassical



cation within a vibrational period. As pointed out by Berson (89), interaction of the empty *p* orbital and the double bond in **149b** traps the cation into the L-system, whereas delocalized interaction of the C-4–C-5 bond with the empty *p* orbital of **149a** traps the cation into the G-system. It



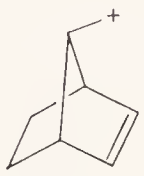
(149)

would appear from the differences in stereospecificity that π trapping in the **149b** system is more efficient than σ trapping of the intermediate **149a**. Berson states "the most likely path for crossover (G to L products) is the single twitch by which **149a** or **149b** can relax to **149**" (89).

In a very thorough recent study, Bly (90) examined the acetolysis of brosylates **139a**, **140a**, and **141a**. In contrast to the report by Berson (89), in which no actual amounts of the various products were given, Bly records the yields of all products isolated from **139a** and **140a** solvolyses. As previously reported (87,89), the major products from the acetolysis of **139a** and **140a** were the corresponding unrearranged acetates (**139b**, **140b**). The products from the acetolysis of brosylate, **139a**, of mechanistic interest, consisted of 10% G products (**144b**, **145b**), 0.5% L-product (**111b**), and 0.6% acetate **147**. From acetolysis of the *anti* isomer (**140a**) there was obtained after one-half of one half-life less than 3% L-products (**114b**, **146b**, **111b**), no G-products, and 6% acetate **147**. Bly did not detect some of the minor products reported by Berson.

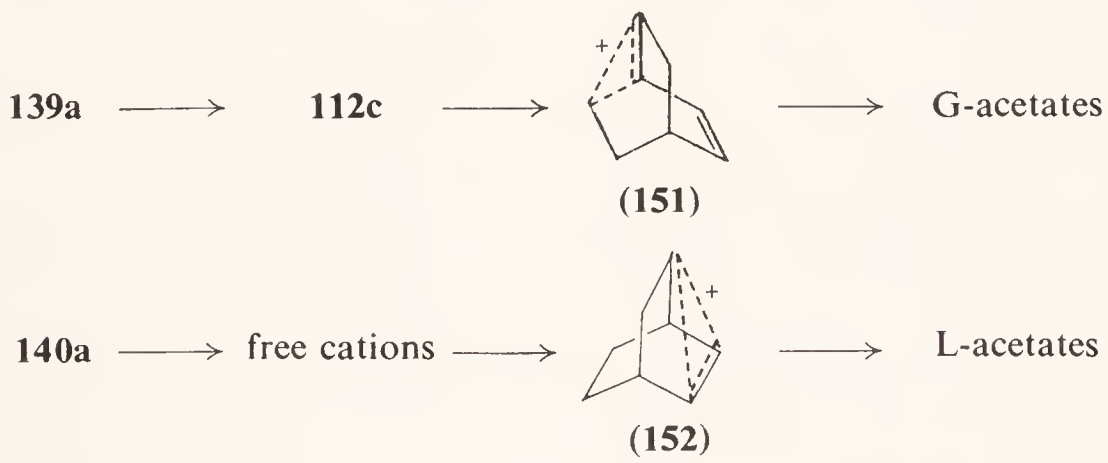
By use of a detailed σ^* treatment, Bly concludes that **139a** derives little or no anchimeric assistance from π-electron delocalization as represented by intermediate **143**. It was also argued (90) that the intermediate cation (**143**) was probably not involved in the rate-determining step,

since no products were obtained that would result from attack of solvent at C-2 or C-3 of **143**, nor did any tricyclic products result from rearrangement of the same cation. Based on the somewhat analogous 7-norbornenyl cation (**36**), however, we would not even expect to isolate a product resulting from solvent attack at C-2 or C-3. The argument for excluding cation **143** must, therefore, rest on the fact that no rate enhancement was observed. Bly attributes the lack of assistance to the absence of π-π overlap (due to the great C-8–C-2,3 distance) and to the absence of σ-σ overlap (due to the unfavorable geometry—**150**).



(150)

In order to account for all the rearranged G and L products, the acetate **147** (which arises in different amounts from **139a** and **140a**), and the different effect of added salt on the rates of solvolysis of the same two derivatives, Bly proposed that brosylates **139a** and **140a** undergo acetolysis by different mechanisms. It was proposed (90) that **139a** is converted to the cation **151**, which, in turn, yields G-acetates. On the other hand, it was postulated that the L-intermediate **152** arises through a series of "free"



carbonium ion intermediates. The crossover of G to L intermediates is believed to occur before the ion **151** has fully developed. The ions **151** and **152** can be compared with the ions **113** and **117**, respectively, which, according to Goering (81) and by LeBel (80), lead to the same products.

The work of Bly (90), then, has caused us to question whether the rearranged products in the solvolyses of **139a** and **140a** can be explained on the basis of the deformationally isomeric ions **149a** and **149b** proposed by Berson (89). Although it is obvious that much work remains before an unequivocal answer can be made to the questions raised by these reports

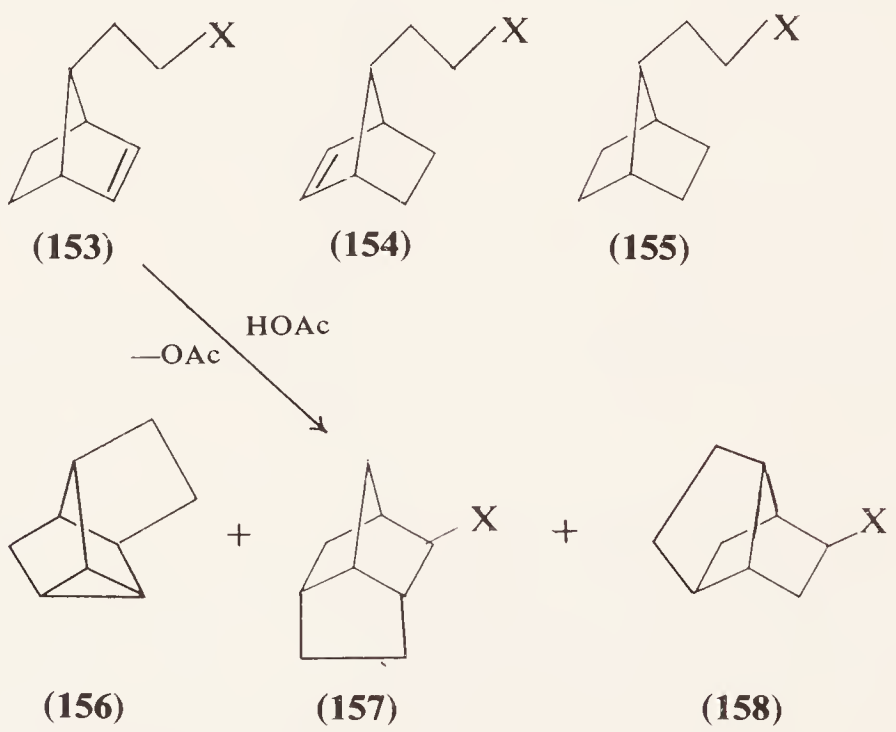
(87–90), such investigations would seem to hold considerable promise for obtaining the detailed information required for advancing carbonium ion theory.

B. The 2-(7-Norbornenyl)ethyl System

The acetolysis of 2-(*syn*- and *anti*-7-norbornenyl)ethyl and 2-(7-norbornyl)ethyl *p*-bromobenzenesulfonates (**153a**, **154a**, **155a**) have recently been investigated by Bly (91,92) and Youssefyeh (93).

Since the brosylate **153a** is geometrically more ideal for π-electron participation in ionization because the carbon bearing the leaving group can approach the double bond more closely than is possible in the case of the previously discussed brosylate (**139a**), it was postulated that the former, in contrast to **139a**, would undergo acetolysis with great rate enhancement (92). That this was, in fact, the case was confirmed, when **153a** was found to undergo acetolysis at a rate approximately 1.9×10^5 greater than the *anti* brosylate (**154a**), 1.4×10^5 times greater than the saturated analog **155a**, and only twofold less than *anti*-7-norbornenyl *p*-bromobenzenesulfonate (**34f**).

Bly (92) learned that the ultimate product from the acetolysis of **153a** consists of 22% deltacyclane (**156**), 42% *exo*-2-brendyl acetate (**157b**), and 36% *exo*-4-brexyl acetate (**158b**). Stopping the solvolysis reaction after a short time resulted in the isolation of a considerable amount of *exo*-2-brendyl brosylate (**157a**), but no *exo*-4-brexyl brosylate (**158a**). The



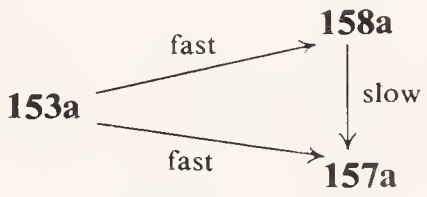
(153) **(154)** **(155)**

(156) **(157)** **(158)**

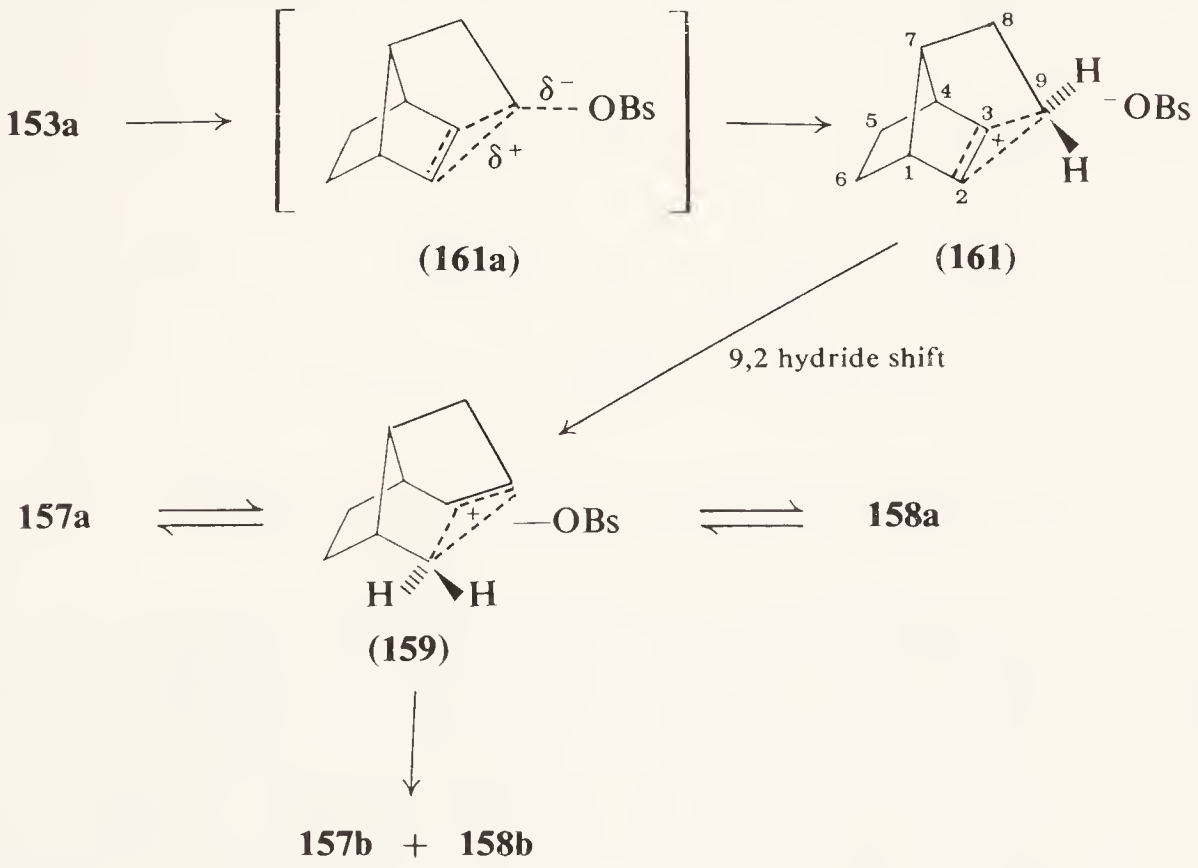
(a) X = —OBs; **(b)** X = —OAc

solvolysis of either **153a**, **157a**, or **158a** gave the same final products, in which the acetate ratio, **157b**:**158b**, was invariant. A detailed kinetic study showed that about 40% of the brosylate **153a** returns to the saturated

brosylate **157a**, which then solvolyzes more slowly. The amount of **153a** returned is independent of added *p*-bromobenzenesulfonate, indicating that **157a** is formed by ion-pair return instead of external ion return (92). Bly noted (92) that **158a** is probably formed during the acetolysis of **153a** but, as Nickon (94) has shown, it is so reactive that only an undetectable steady state concentration would be formed under the conditions used. Bly was able to confirm the presence of **158a** by examining the solvolysis of **153a** by nmr in carbon tetrachloride. For this medium the following reaction scheme was devised (92):

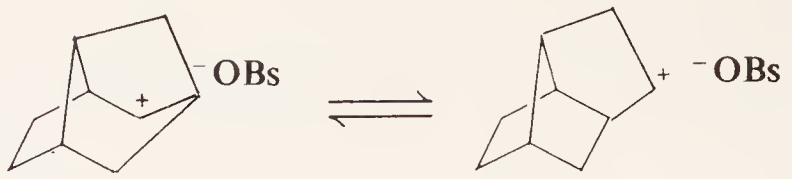


Bly considered three mechanistic interpretations to account for the data. The scheme outlined below appears to accommodate the experimental data best, especially when compared with the solvolysis data for the analogous

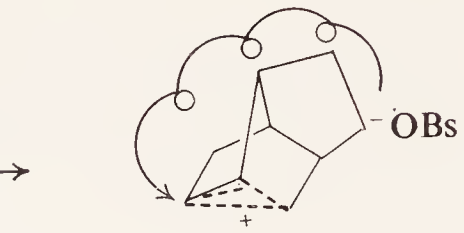


2-(Δ^3-cyclopentenyl)ethyl system, which is discussed in the next section. As usual, it was not possible to decide between the nonclassical ion pair (**159**) or the rapidly equilibrating, classical ion pair (**160a**, **160b**).

Bly noted (92) that the data on ion-pair return probably eliminate the originally proposed mechanism (91) in which the intermediate **161** was envisioned to rearrange via a 6,2 hydride shift to the intermediate **162**. If



(160a) **(160b)**



(162)

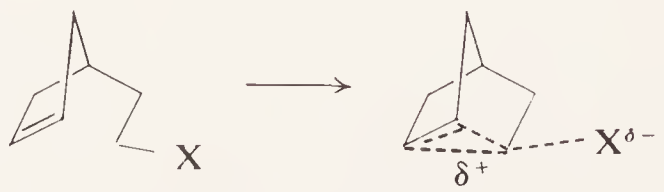
this occurred, there would be a large net charge separation in **162** (95) and "the anion of the new ion pair(s) would then have to diffuse rapidly, without dissociating, to the opposite side of the cation before returning" (92) to the brosylates **157a** and **158a**. Carbonium ion theory will profit from further careful, detailed studies of this type.

The closely related brosylate (**163**) apparently derives little rate enhancement from interaction of the ionizing center with the double bond. Allred and Maricich report a k_{unsat}/k_{sat} of about 15 (96).

(163)

C. The 2-(Δ^3-Cyclopentenyl)ethyl Structure

The *syn* brosylate **153a** is, of course, perfectly analogous to the 2-(Δ^3-cyclopentenyl)ethyl derivatives (**164**) recently investigated in several laboratories. Bly has estimated that the reactivity of **153a** exceeds that of **164** by about 1500 times. The higher reactivity of the former brosylate was attributed to the greater nucleophilicity of the more highly strained norbornene double bond, rather than to a greater stability of transition state **161a** as compared with transition state **165** (92). It goes without



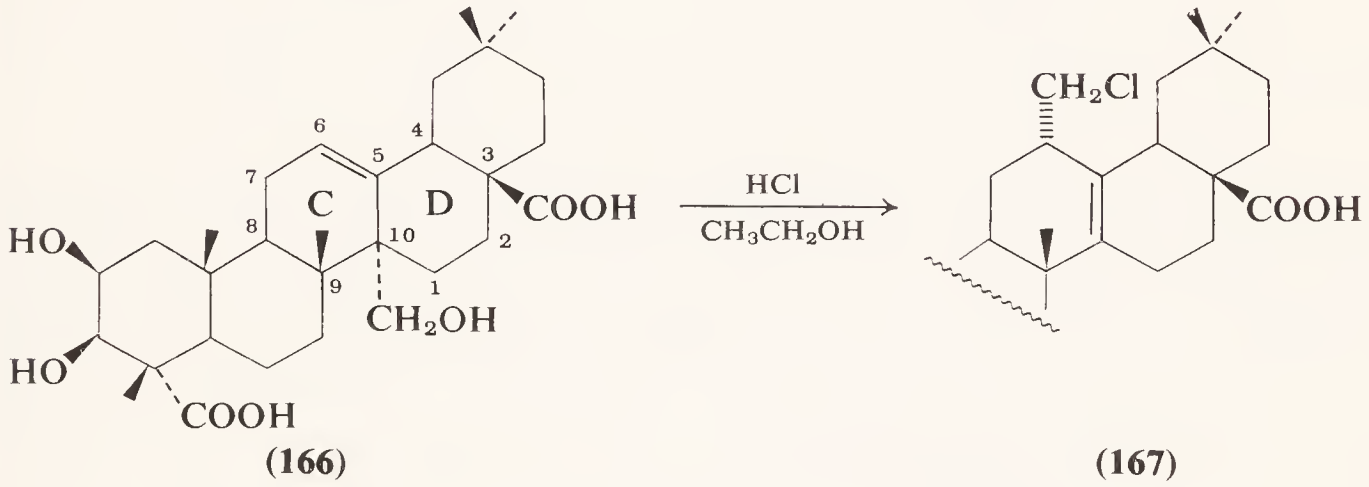
(164) **(165)**

saying, of course, that double-bond nucleophilicity has no importance except for whatever information the term may yield to estimate the relative energies of molecular ground and transition states. Several derivatives of **164** undergo solvolysis with rate enhancement and with ring closure to the norbornyl system. This topic is treated in another chapter, but for leading references see the series of papers by Bartlett and co-workers, and the papers by Closson and Kwiatkowski, Collins and Lietzke, Spurlock et al., and Lee and Lam (97).

D. Selected Systems Involving *i*-Steroid-Type Rearrangements

Homoallylic cations have been proposed as intermediates in several systems involving rearrangements similar to the *i*-steroid rearrangement discussed in Section III. A review of this and related rearrangements has been published by Wendler (98).

Pelletier (99) has suggested that homoallylic cations participate in the conversion of presenegenin (**166**) to senegenin (**167**) using ethanolic hydrochloric acid. It was proposed that the transformation of **166** to **167** could best be formulated as conversion of the homoallylic ion **168**, depicted

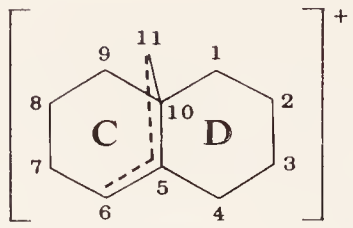


(166) **(167)**

as a resonance hybrid of the canonical forms (**168a**, **b**), to the new homoallylic ion (**169a**, **b**). Pelletier further suggested that **168a**, **b** and **169a**, **b** were interconnected via the cyclobutonium ion **170**. Through a series of transformations of various related compounds, it was shown that attack by nucleophile at C-6 of cation **168** or at C-10 of cation **169** led to *i*-steroid-type products, formed under kinetic control. Senegenin (**167**), formed by attack of nucleophile at C-11 of cation **169**, was determined to be the product of thermodynamic control.

The same type of mechanistic rationale had been proposed by de Mayo (100) for the rearrangement of **171**.

Tadanier (101,102) has examined the solvolysis of the related Δ^5-19-methanesulfonoxy steroid **172** under a variety of reaction conditions, and



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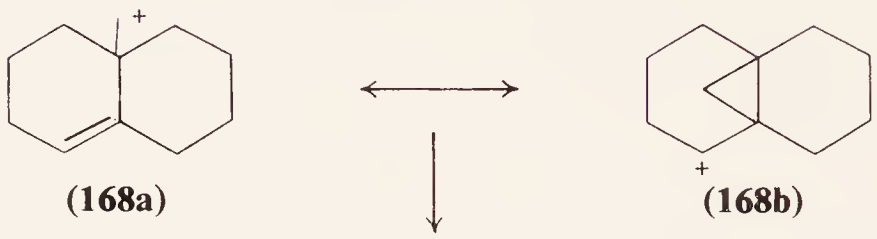
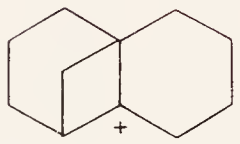
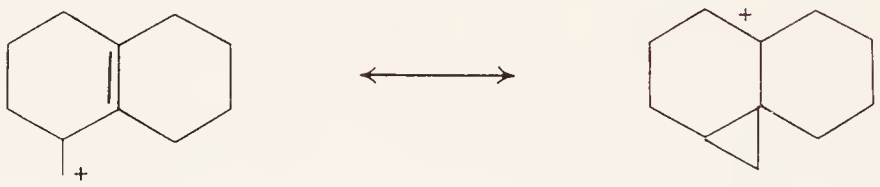


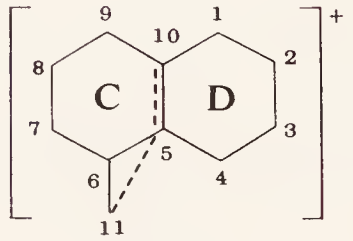
(168a) **(168b)**



(170)



(169a) **(169b)**



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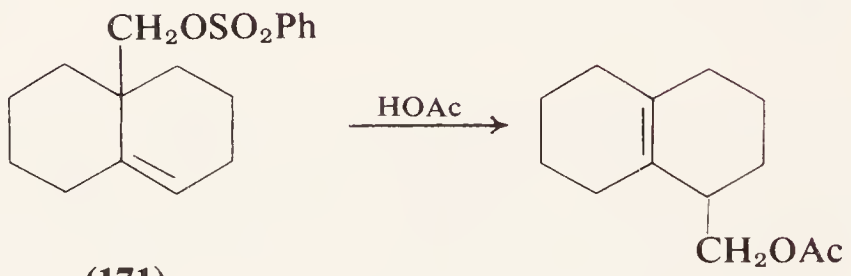
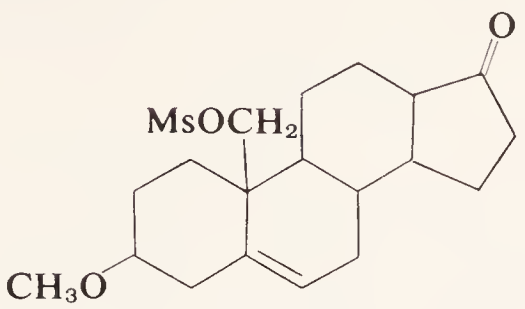


(171)

his results were consistent with those obtained by Pelletier (99) and de Mayo (100). The product of the thermodynamically controlled acetolysis was **173** and, based on the structures of the products **173, 174, 175**, and other minor products obtained from the solvolysis of **172** under several sets of conditions and transformations of those products, Tadanier proposed that the isomeric homoallylic cations **176** and **177**, can best explain the observed results. Tadanier further concluded that a large energy barrier exists between **176** and **177** and "that rearrangement of cation **176** to **177**, which



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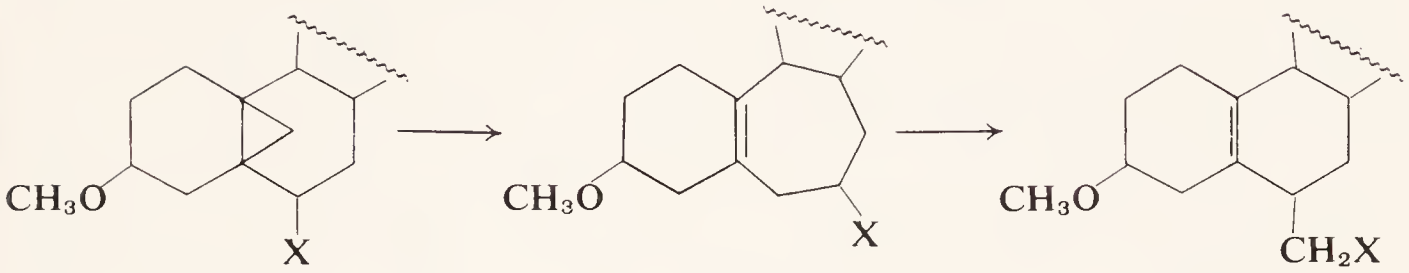
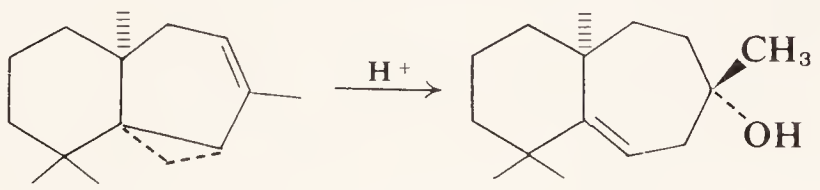


(174) (175) (173)

occurs in the conversions of **172** and **174** to **175** and **173**, is essentially irreversible" (102).

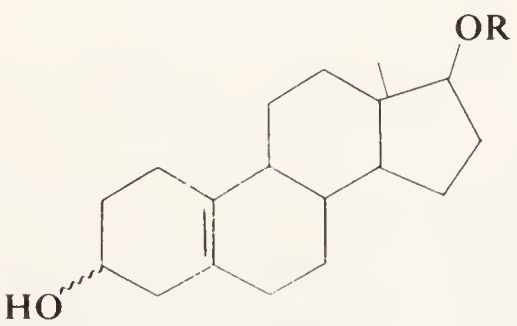
(176) (177)

Analogy for parts of the mechanistic proposals discussed in this section can be found in the work of Dauben and Friedrich (103), in which the mechanism of the acid-catalyzed hydration of thujopsene (**178**) to widdrol (**179**) was investigated. *i*-Steroid-type rearrangements have also been



(178) (179)

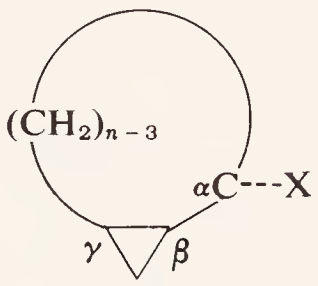
reported by Levine (104) for the steroids represented by **180**.



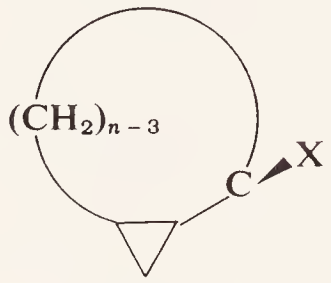
(180)

E. Homoallylic Cations as Intermediates in Certain Homoallylic Ring Expansions

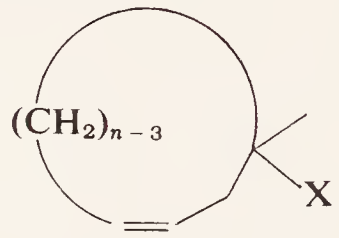
Cope (105) has shown that in the early stages of the acetolysis of either the *anti* alcohol **181a** or its *syn* isomer **182a**, where $n = 7$, mixtures of the *anti* and *syn* acetates **181b** and **182b** occurred, along with some **183b**. Extended reaction times permitted the exclusive formation of the *cis* ring-expanded product 3-cycloocten-1-yl acetate **183b**. Goering reported no ring-expanded product in the solvolysis of **181c** and **182c**, where $n = 6$; the absence of retention of configuration at C_α was noted (106).



(181)



(182)



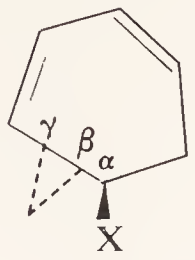
(183)

(a) X = —OH; **(b)** X = —OAc; **(c)** X = —OpNB

Unique homoallylic ring expansions, both for unsaturated and saturated medium-ring-size alcohols of type **181** and **182** have recently been reported by Winstein (107,108). The products of those expansions studied by Winstein differ from the previously discussed ring-expansion products of Cope (105) in that a high degree of retention of configuration was achieved. Data reported for **184** serve to illustrate Winstein's findings for all the unsaturated systems studied.

Solvolysis of the *p*-nitrobenzoate **184a** in 80% aqueous acetone gave a 65% yield of **184b**, with less than 2% epimerization; trienol (**185**) was also obtained, in 15% yield. Treatment of **184a** with dilute perchloric acid yielded only the trienol **185**. Not only is configuration at C_α maintained in the nonexpanded solvolysis product **184b**, but olefin formation (ring-expanded product) of **185** is also stereospecific. In this case, the *trans*-trienol (**185**) is formed from *anti-p*-nitrobenzoate (**184a**). Solvolysis of *syn* compounds (**182**), conversely, gave *cis*-ring-expanded alcohols (**183a**); retention of configuration at C_α in the unexpanded product **182a** was observed.

Winstein rationalized that the stereospecificity of these reactions was due to the intermediacy of the nonclassical homoallylic ion **186**. He and his colleagues believed that all the reactions of the *anti* derivatives studied proceeded as shown in the transformation of **187** to **188** through the intermediacy of the ion **186** (107). In order for the C_β–C_γ bond to participate in the ionization of the *anti* derivatives, a *trans* relationship of H_1 and H_2



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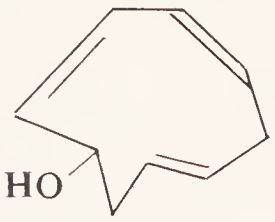
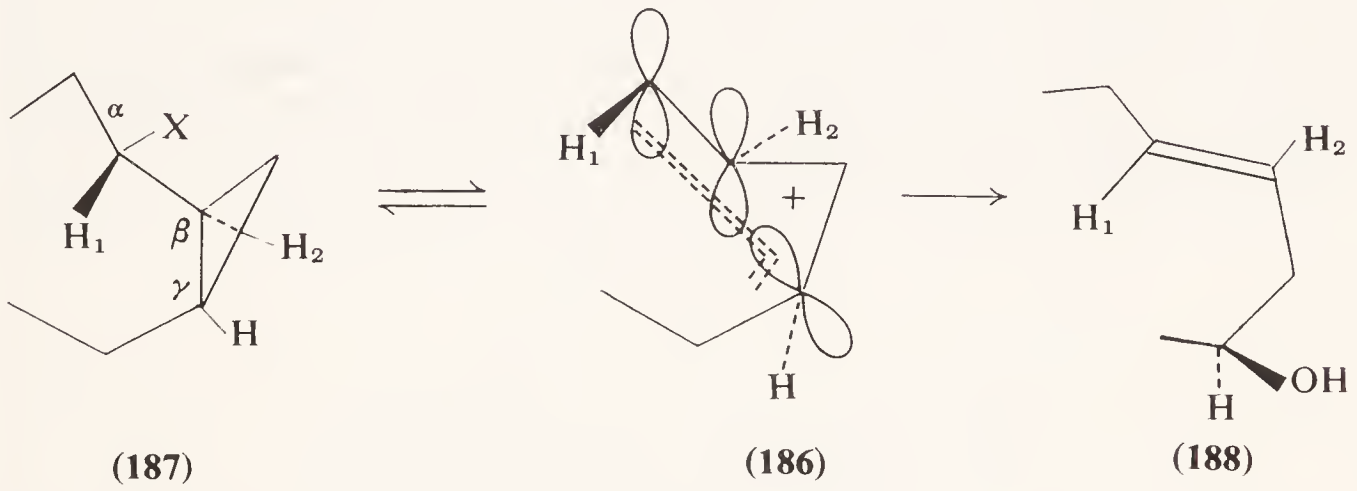


(185)

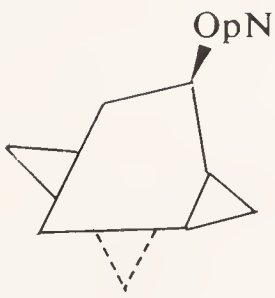
(a) X = —OpNB; **(b)** X = —OH

would be necessary, as shown in **186**. A *cis* relationship of H_1 and H_2 would be necessary for the *syn* derivatives to give the expected products. These stereoelectronic factors led Winstein to predict that inversion of configuration at C_γ should also occur (107).

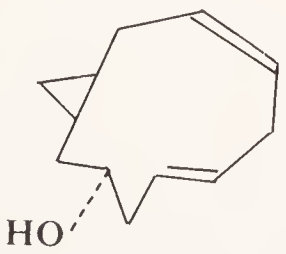


(187) **(186)** **(188)**

That inversion of configuration at C_γ did, in fact, occur was demonstrated by the reactions of **189** and a number of similar systems (108). Solvolysis of the *p*-nitrobenzoate (**189**) in 80% aqueous acetone yielded a 25:75 mixture of bis-expanded **190** and mono-expanded **191**, respectively. On the other hand, treatment of **189** with dilute perchloric acid led only to



(189)



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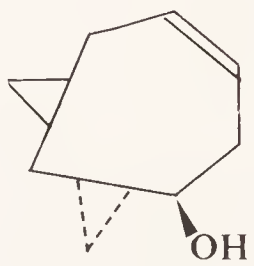
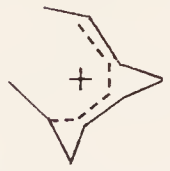


(191)

the bis-expanded alcohol **190** (108). A bishomopentadienyl cation (**192**) was postulated as a possible intermediate in the formation of at least some of the bis-expanded product (**190**).



(192)

Thus the larger ring systems undergo expansion with a stereospecificity not found in the smaller rings. Winstein states that "until more ring systems are investigated it is not clear which ones can be expected to yield the stereospecific results described" (107).

F. The Allylcarbinyl Cation

The simplest possible homoallylic system (**193**) has received the attention of Servis and Roberts (109), who estimate a rate enhancement factor of 3.7 in the formolysis of allylcarbinyl tosylate (**193**), by comparison with *n*-butyl tosylate. It was also found that **193** gives the same products as cyclobutyl tosylate. Delocalized bicyclobutonium ion intermediates were proposed to account for their observations. This system is discussed in greater detail in another chapter.

(193)

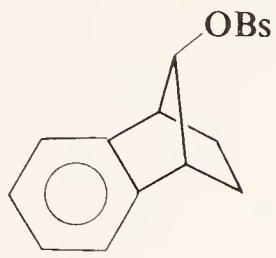
XII. HOMOBENZYLIC CATIONS

Recent work has revealed that homobenzylic systems furnish interesting parallels to certain of the homoallylic systems just discussed. The initial research of Bartlett and Giddings (110) on the solvolysis of 2- and 9-substituted benzonorbornenes has been extended by Wiley (111), Tanida (112–116), Winstein (117), and Brown (118) to systems bearing substituents on the benzene ring. Tanida has recently reviewed some of his work on homobenzylic and homoallylic cations (119). It has been found that the benzene ring, like the double bond, also provides a strong driving force to ionization.

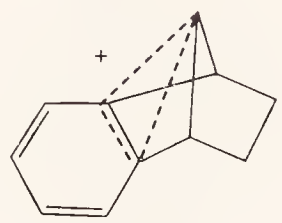
A. *anti*-9-Benzonorbornenyl Sulfonates

In the initial work on this system, Bartlett and Giddings (110) demonstrated that *anti*-9-benzonorbornenyl brosylate (**194**) undergoes acetolysis to give exclusively the corresponding unrearranged acetate. The fused benzene ring provides acceleration to ionization at C-9 but, in this instance, it is considerably inferior to the double bond, supplying about 7 rather than 14 kcal decrease in free energy of activation, as estimated for the *anti*-7-norbornenyl transition state (110). Translated into rate factors,

the brosylate **194** was more reactive than the 7-norbornyl brosylate **35f** by about 6×10^5 or, in other words, more than 10^5 less reactive than *anti*-7-norbornenyl brosylate **34f**. The intermediate cation for acetolysis of **194** was depicted as the structure **195** (110). It was reasoned that the benzene ring is less effective, relative to the double bond, in assisting ionization at



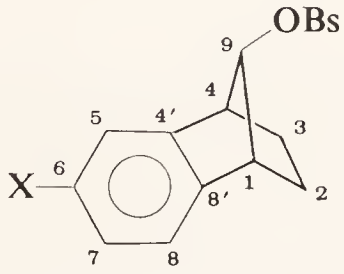
(194)



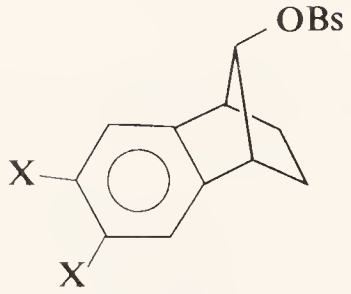
(195)

C-9 because the realignment of atomic orbitals required by structure **195** occurs at the expense of some of the aromatic stabilization energy.

Tanida et al. (112–114) have examined in great detail the effect of both 6 and 6,7 substituents on the rate of solvolysis of the *anti*-9-benzonorbornenyl brosylates (**196**, **197**). The range of reactivity of **196** as the substituent X was varied from methoxy to nitro was found to be 386,000 (112).



(196)

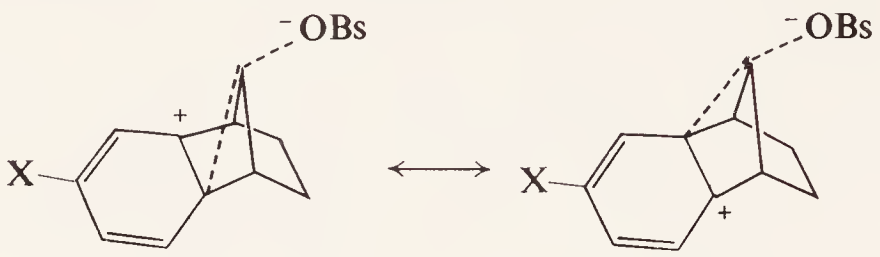


(197)

As might be expected (120), the 6-methoxy substituent had a relatively small effect on the rate of acetolysis, increasing it by a factor of 54 over the brosylate (**194**). The 6-nitro substituent, on the other hand, decreased the acetolysis rate by the large factor of 10^5, but, significantly, not below that for 7-norbornyl brosylate **35f**, itself. The rate data for **196** correlated well with $[\sigma + \sigma^+]$. This was interpreted (112) as a possible indication that both σ and π complexes are important in the transition state which could be modeled as internal aromatic substitution. The rate data also correlated well with the Hammett relation, $\log (k_x/k_h) = \rho(\sigma_m{}^+ + \sigma_p{}^+)/2$ (113). This was taken to indicate that the solvolysis involved simultaneous participation by the *meta* and *para* substituents of the aromatic ring. Consequently, the transition state leading to ionization was depicted as **198a** $\leftrightarrow$ **198b** (113). As pointed out by Bartlett (121), the transition state (**198a**, **b**), written in valence bond notation, must include both the structures

shown, as well as the bond structures common to all "σ-complex" transition states, with charge at positions 5, 6, 7, and 8.

In order to decide between the two possible Hammett relationships and the resulting implications for the transition state, both the 6,7-dimethoxy



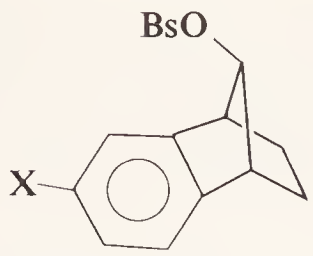
(198a) **(198b)**

and 6,7-dimethyl derivatives of **197** were prepared (113). It was found that one methoxy (or methyl) substituent at C-6 (**196**) accounted for an increase in rate by the factor of 54 (or 5.7) over the brosylate (**194**). However, two methoxy (or methyl) substituents (**197**) increased the rate by a factor of 3000 (or 36), which was approximately the square of the value for one substituent. It was thus concluded that $\sigma_m^+ + \sigma_p^+$ is most likely the correct correlation and, therefore, the transition states involved in the solvolyses of **194**, **196**, and **197** are probably symmetrical with respect to C-4′–C-8′ (113).

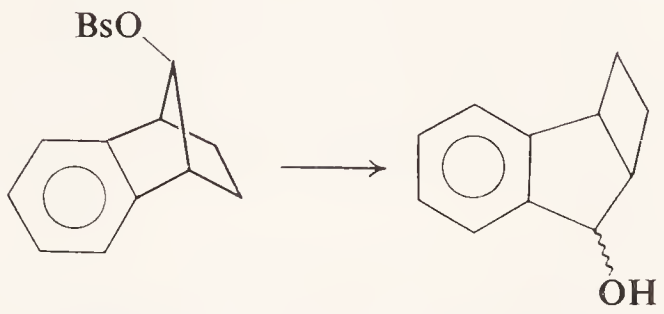
1. Comparison of the anti *and* syn*-9-benzonorbornenyl and 9-methyl benzonorbornen-9-*(anti *and* syn*)-yl Arenesulfonates*

Subsequent to the report describing the solvolyses of the *anti* brosylates (**196**), Tanida (114) published the results of his investigation of the solvolysis of the corresponding *syn* isomers (**199**). The range in rate values for the series **199** as the substituent X was varied from methoxy to nitro was only a factor of 43, compared to 386,000 for the **196** series. Tanida points out that this observation "substantiates the fact that significant participation (homobenzylic conjugation) such as in the acetolysis of **196** is absent in that of **199**" (114). The only solvolysis products isolated from the brosylate (**200**) were the rearranged alcohols **201**, the predominant epimer being *anti*. It is interesting to note that despite complete rearrangement—most likely by formation of a stabilized benzylic carbonium ion with participation of the 1,2 carbon–carbon bond (114)—the brosylate **200** undergoes acetolysis with little rate enhancement (a factor of approximately 30 relative to 7-norbornyl brosylate). The lack of rate acceleration in this case is in sharp contrast to the previously discussed *syn*-7-norbornenyl tosylate (**46**).

Tanida also examined the solvolysis of both the *anti* and *syn* tosylates **202** and **203**. The *anti*:*syn* rate ratio was determined to be 493, compared

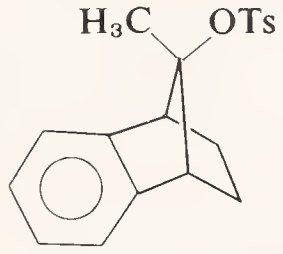


(199)

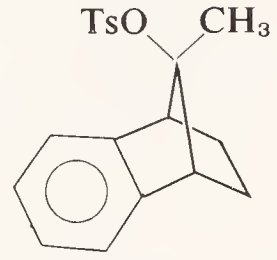


(200) **(201)**

with an *anti*:*syn* ratio of 2400 for the demethylated analogs **194** and **200**. It was also determined that the methyl substituent increased the rate of solvolysis by factors of 86,700 and 18,000 in the cases of the *syn*-arenesulfonates and the *anti*-arenesulfonates, respectively.



(202)



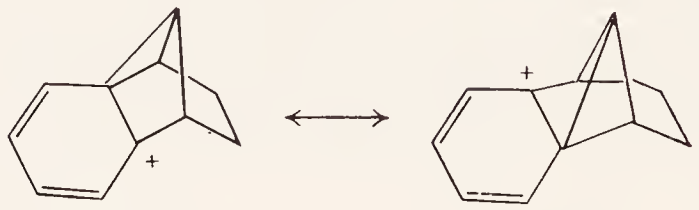
(203)

As Tanida indicates (114), tertiary carbonium ions should be stable enough to require little or no participation, and, therefore, both the amount of stabilization provided by π participation and the magnitude of the *anti*:*syn* (or *exo*:*endo*) rate ratio should decrease as the cationic center is made more stable by the introduction of electron-releasing substituents. It was believed that the *anti*-9-benzonorbornenyl structure would provide a good test for this hypothesis, since very large π participation is generally accepted for this system (122). That there may be some homobenzylic participation in the *anti* series despite methyl substitution is indicated by comparing **194**, **200**, **202**, and **203**, where we find a small decrease, by a factor of 4.9 (2400/493) in the *anti*:*syn* rate ratio with methyl substitution (at C-9) and a small change in the CH_3:H rate ratio factor from 18,000 (*anti* series) to 87,700 in the *syn* series. However, Tanida (114) feels that the differences are probably too small to consider this a valid test.

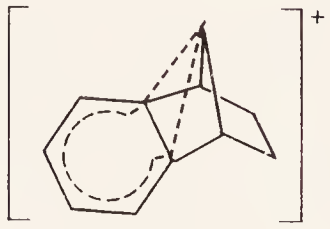
2. *Structure of the* anti-*9-Benzonorbornenyl Cation*

Tanida (112–114) has presented strong evidence that the transition state for the solvolysis of *anti*-9-benzonorbornenyl derivatives is symmetrical with respect to the benzene ring. We know that even though a symmetrical transition state is indicated, the intermediate cation formed subsequent to the transition state need not be of the same symmetry. Winstein, however, has suggested that evidence for a symmetrical transition state in the *anti*-9-benzonorbornenyl system would be considered evidence for a symmetrical intermediate, and he has cited the work of Tanida as one of the most powerful pieces of supporting evidence for the 7-norbornenyl cation non-classical structure (**36**).

The cation can most likely be formulated in valence-bond notation with structures **204a** and **204b**, as well as the other required bond structures displaying positive charge at positions 5, 6, 7, and 8, or more simply, as the delocalized structure **205**. As Bartlett has suggested (121), charge in-



(204a) **(204b)**



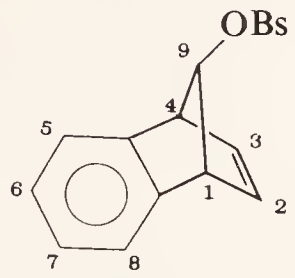
(205)

corporation into a phenonium ion ring seems to prevent any really classical ion intermediate in this system.

B. Other *anti*-9-Homobenzylic Systems

A comparison of the acetolysis rates of brosylate **194** and the *anti*-9-benzonorbornadienyl brosylate **206** revealed that the double bond enhances the acetolysis rate by a factor of only 100 (110). The second double bond (*syn*) in the 7-norbornadienyl system (**54**), by contrast, gave a rate increase of 800-fold over the *anti*-7-norbornenyl system. Although there is a possibility of some sort of front-side stabilization of the cationic center at C-9 by the double bond, Bartlett felt that the most likely explanation of the role of the *syn* double bond was to increase the C-1–C-9–C-4 bond angle from its value just under 100° (110). This effect, which would tend

to stabilize the transition state, should also serve to raise the energy of the ground state. This argument has been questioned by Gassman (46), who suggested that if such a bond angle effect does exist, it must be relatively small.



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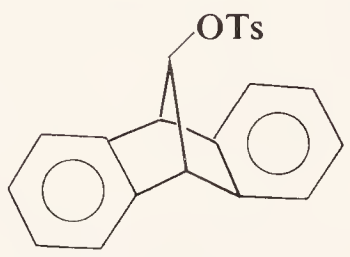


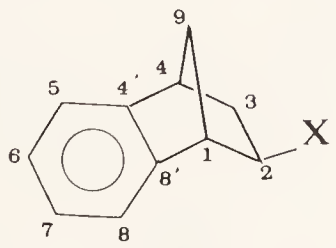
(207)

Meinwald and Miller concluded from the acetolysis of dibenzonorbornadienyl tosylate (**207**) that the *syn* benzene ring has little effect on the stability of the intermediate cation and that there probably is no symmetrical ion incorporating the benzene rings equally (123). Dibenzonorbornadienyl tosylate (**207**) was, in fact, about twice as reactive as *anti*-9-benzonorbornenyl brosylate (**194**) at the same temperature.

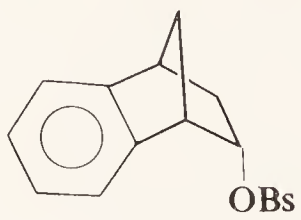
Cristol et al. (124) have investigated the dibenzobicyclo[3.2.1]octadiene system and have presented a comparison with several other homoallylic systems whose reaction paths are also highly dependent on the relative orientation of the leaving group and the unsaturated π center.

C. The 2-Benzonorbornenyl System

It was originally reported that *exo*-3-benzonorbornenyl brosylate (**208a**) underwent acetolysis at a rate 7500 times greater than the corresponding *endo* brosylate (**209**) to yield, exclusively, the unrearranged acetate **208a** (110). The *exo*:*endo* rate ratio was calculated at 25° from an erroneously



(208)

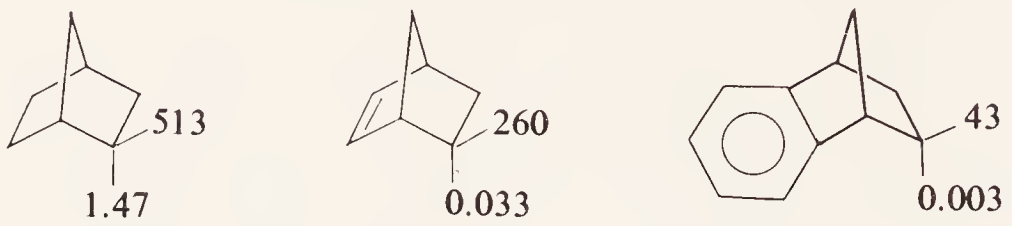


(209)

(a) X = —OBs; **(b)** X = —OAc; **(c)** X = —Cl

extrapolated rate for the *endo* isomer. The ratio has now been corrected to a value of approximately 15,000 through independent calculations by Winstein (117), Brown (118), and Tanida (116). If the corrected rate for the acetolysis of **209** is used, the relative reactivities [for acetolysis at 25°

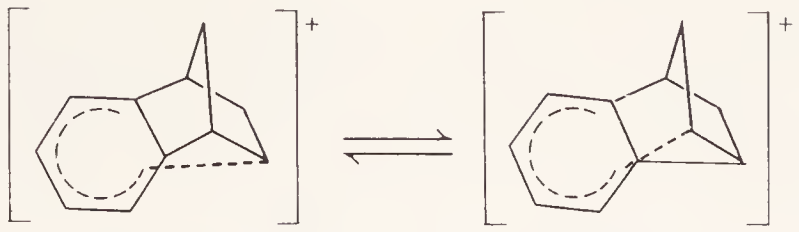
relative to cyclohexyl *p*-bromobenzenesulfonate] for 2-norbornyl, 2-norbornenyl, and 2-benzonorbornenyl *p*-bromobenzenesulfonates can now be restated as shown (112,116):



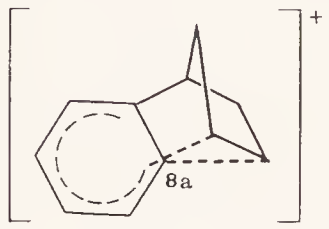
Bartlett (110) attributed part of the absolute rate decrease observed for both the *exo* and *endo* brosylates **208a** and **209** to greater sp^2-sp^3 polarization at C-1–C-8′ and at C-4–C-4′, thereby making development of a positive charge at C-2 less favorable than in the case of the 2-norbornenyl brosylates **24a** and **25a**. It was also proposed that part of the rate decrease was due to benzene ring resistance to deformation by the strain imposed by the bicycloheptenyl structure; thus the shared carbons must use more truly sp^2 orbitals than the corresponding olefinic carbons in the 2-norbornenyl molecule.

Accepting the supposition that the foregoing arguments apply equally well to the *exo* and *endo* isomers, and bearing in mind that the *endo* rate is an extrapolated value, then the *exo*:*endo* ratio for the benzonorbornenyl brosylates **208a** and **209** is approximately twice that reported for *exo*- and *endo*-2-norbornenyl brosylates **24a** and **25a** (25). Consequently, the benzene ring appears to be twice as effective as the double bond in assisting ionization at the C-2 position. But, as previously discussed, the benzene ring is considerably inferior to the double bond in assisting ionization at C-9 (C-7).

On the basis of the high *exo*:*endo* rate ratio and retention of configuration on solvolysis, the delocalized, unsymmetrical, homoallylic structure **210a** was proposed to represent the intermediate cation in the solvolysis of **208a** (110). This intermediate portrays the benzene ring intruding upon the ionization just as if electrophilic aromatic substitution were taking place at C-8*a* of the norbornene structure (125). Later, however, Giddings and Dirlam (126) reported that acetolysis of optically active **208a** gave racemic product, and they reasoned that the cationic intermediate **211** was more compatible with their result. It was proposed that **211** could "be formed either directly in the rate-determining step with anchimeric assistance from both σ and π electrons or subsequently from cation **210a**" (126). Bartlett (125) has observed that "pending a fuller investigation," the symmetrical cation (**211**) could be looked upon as the transition state for equilibration of the ions **210a** $\rightleftarrows$ **210b**; rapid equilibration would explain the racemic product equally well. Cristol (127) noted



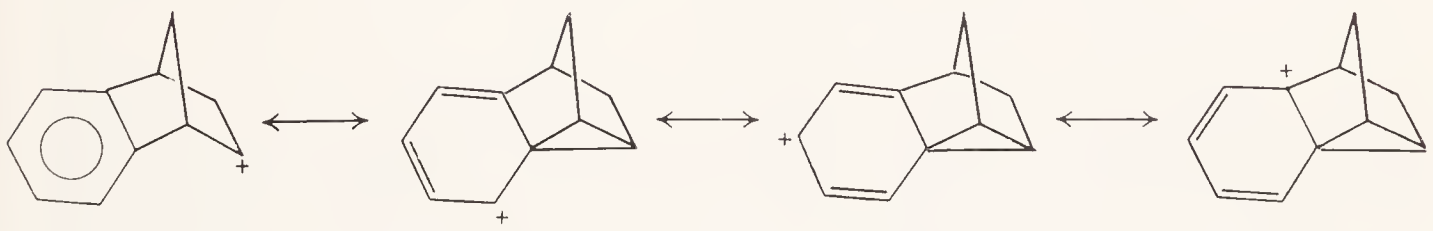
(210a) **(210b)**



(211)

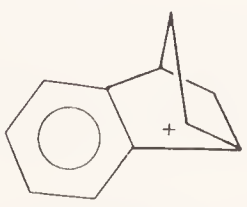
that the work of Giddings and Dirlam (126) did not demonstrate that loss of optical activity in solvolysis of **208a** by internal return could be neglected.

In order to avoid confusion of terms and symbolism, it should be noted that the cation **210a** involves only homobenzylic participation, utilizing both σ-type and π-type overlap of p or near-p orbitals but involving only the π electrons of the benzene ring. The resonance structures contributing to the dotted-line structure **210a** are **212a–212d**.



(212a) **(212b)** **(212c)** **(212d)**

The structure **211**, on the other hand, denotes ionization that is accelerated both by the benzene π electrons (homobenzylic participation) and the σ electrons of the C-1–C-8*a* bond (carbon participation). Nonetheless, the ion **211** is frequently referred to as involving simply carbon participation. The contributing resonance structures represented by **211** are **212a–212d** and **213**.

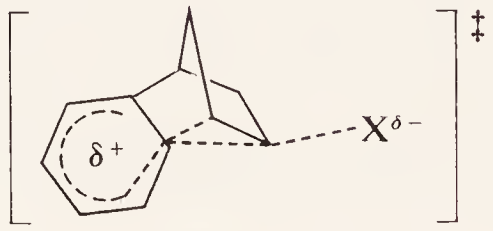


(213)

Recently Brown (128) chose the 2-benzonorbornenyl system to test his hypothesis that carbon participation is unimportant in the solvolysis

of norbornyl derivatives. Anchimeric assistance in the norbornyl molecule can involve only σ electrons. Thus the 2-benzonorbornenyl system, which is really quite different *a priori* from the norbornyl system in the type of anchimeric assistance provided to ionization, was chosen as a test for carbon participation in the norbornyl system.

Brown and Tritle (128) argued that the high *exo*:*endo* rate ratio in the 2-benzonorbornenyl system was not due to an abnormally high *exo* rate, but, rather to a very slow *endo* rate. They proposed that, as in the norbornyl system, the *endo* rate was slow because of steric inhibition to ionization. The evidence in favor of this position was based on the premise that if carbon participation was important, the degree of participation in the transition state (**214**) should become less as stabilizing groups are introduced into the C-2 position (128). Consequently, Brown introduced methyl and phenyl substituents at C-2 and found that the *exo*:*endo* rate



(214)

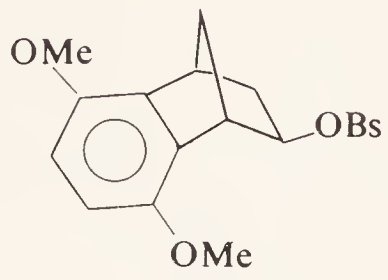
ratio changed from 15,000 for hydrogen to 6500 for methyl to 4300 for phenyl. It was observed that "Certainly there is no change in the *exo*:*endo* rate ratio of the magnitude one might have predicted for the major decrease in carbon participation which should have accompanied the introduction of a highly stable tertiary benzylic carbonium center at position 2" (128). Brown further remarked "The results are clearly more consistent with the steric explanation than that based on carbon participation."

Brown also argued (128) that both the amount of carbon participation and the magnitude of the *exo*:*endo* rate ratio would drop as deactivating substituents were introduced into the aromatic ring, provided carbon participation was responsible for the high *exo*:*endo* rate ratio in the 2-benzonorbornenyl system. Therefore, he proposed "to establish the effect of substituents in the aromatic ring before making a final decision" (128).

1. The Effect of Aromatic Substituents

The effect of aromatic substituents on the solvolysis rate of a 2-benzonorbornenyl derivative (**215**) was first studied by Wiley (111), who learned that two methoxy groups provided a rate enhancement of 27-fold

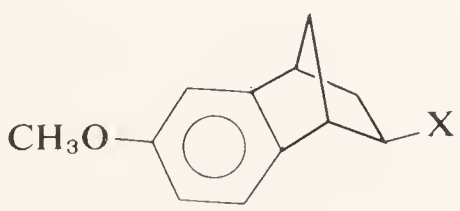
over the unsubstituted analog **208a**; thus some homoallylic participation by the benzene ring in the transition state was indicated.



(215)

Considerable recent work has been reported by Winstein (117), Brown (118), and Tanida (129,130) concerning methoxy substituent effects on the acetolysis rates of 2-benzonorbornenyl derivatives. Brown (118) has also observed the effect of nitro substituents.

Winstein (117) reported that the homo-*p*-methoxy brosylate **216a** undergoes solvolysis 150 times faster than the unsubstituted 2-benzonorbornenyl brosylate **208a**, and Brown (118) observed a rate acceleration of 210 for the chloride **216b** over the unsubstituted chloride **208c**. Brown emphasized that this is "the largest rate acceleration yet observed for a neighboring '*p*-anisyl' group" (118). For the homo-meta-methoxy brosylate **217**, there was observed (117) a slight rate retardation relative to **208a**. Rate enhancement by *p*-methoxy and rate retardation by *m*-methoxy is expected for anchimerically assisted acetolysis involving phenyl participation (117). The rate enhancement factors of 150 and 210 correspond to a ρ value ($\rho\sigma^+$ treatment) similar to values reported for intramolecular and intermolecular Friedel-Crafts reactions. This is not surprising in view of the proposed similarity to electrophilic aromatic substitution.



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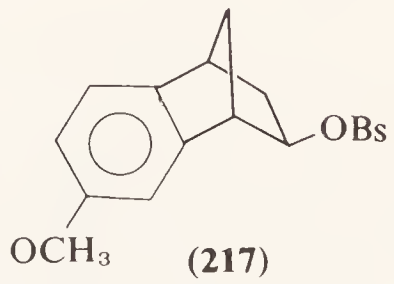


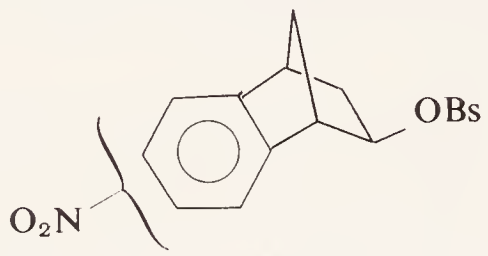
(217)

(216a) X = —OBs; **(216b)** X = —Cl

The observed large rate enhancement factors correlate well with the very large estimated *exo*:*endo* rate ratios of 8.3×10^5 (117) for the homo-para-methoxy-2-benzonorbornenyl brosylates and 3.2×10^6 (118) for the homo-para-methoxy-2-benzonorbornenyl chlorides. Both the absolute rate increases due to the methoxy substituent and the *exo*:*endo*

rate ratio are considerably larger than the corresponding numbers observed for the methoxy-9-benzonorbornenyl brosylates **196** and **199**. These findings are in accord with Bartlett's results (110), in which the benzene ring was found to be more effective in assisting ionization at C-2 than at C-9.

In a study of the effect of nitro substituents, Brown (118) has used a mixture of the mono-homo-para- and mono-homo-meta-nitro brosylates (**218**) along with the corresponding *endo* isomers (**219**). It was felt that the mixture of isomers did not require separation for analysis because of the similarity in σ^+ values for *m*-nitro and *p*-nitro substituents. The *exo*:*endo* rate ratio for **218**:**219** was a minimum of 94 as opposed to an *anti*:*syn* rate ratio of 4.4 for the nitro derivatives of **196** and **199** (114). Some un-



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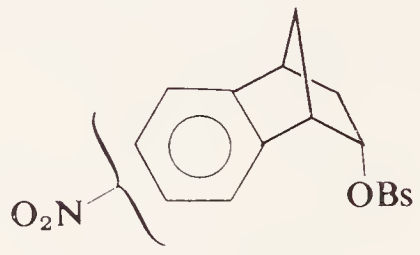


(219)

certainty is introduced into the comparison of the ratios cited because the rates were measured at very different temperatures. Brown contended that "if the nitro substituent in **218** effectively cancels out π participation from the aromatic ring, then the 15,000 *exo*:*endo* rate ratio [rate ratio for **208a**:**209**] involves a factor of 160 for π participation and a factor of 94 for steric and torsional contributions (118). His suggestion (118) that there may be residual π participation even with the highly deactivating nitro group seems a likely possibility, especially because of the great rate enhancement caused by the "*p*-anisyl" group.

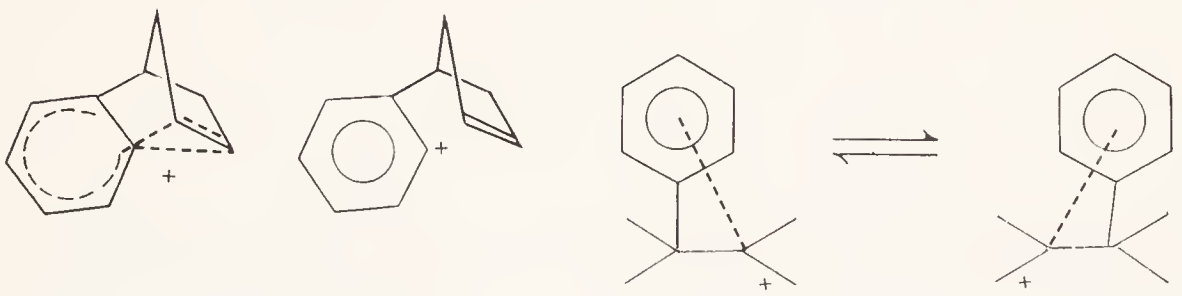
2. Structure of the 2-Benzonorbornenyl Cation

The substituent studies clearly established that homobenzylic participation in the transition state is the dominant factor contributing to the high *exo*:*endo* rate ratios in solvolysis of the secondary 2-benzonorbornenyl systems. Brown now refers (118) only to π participation in the solvolysis of **208**; no longer is **208** mentioned as a model for carbon participation in the norbornyl system. Even though there is only a small difference in the *exo*:*endo* rate ratios for the tertiary 2-methyl and 2-phenyl derivatives, it is evident that Brown's indirect method of testing for anchimeric assistance in the secondary derivatives has failed. Nonetheless, the high *exo*:*endo* rate ratios obtained from the tertiary derivatives may be due mainly to steric and torsional contributions. As Winstein concluded

"It is still not clear where ionization changes from anchimerically assisted to essentially unassisted as 2-R groups are added" (117).

Thus the nature and structure of the 2-benzonorbornenyl cationic intermediate are still in some doubt. Any proposed cation must be consonant with the large homobenzylic participation and retention of configuration but loss of optical activity from the starting material. We hold that the cation **211**, proposed by Giddings (126), or the ion **220**, constructed by Winstein (117), are at best, higher energy transition states formed either by simultaneous anchimeric assistance from both σ and π electrons (where σ participation seems very unlikely) or subsequently from **210a**. The critical difference between **211** and **220** is that **220** involves the additional, high-energy phenyl cation resonance contributor **221**.

On this basis, and by analogy to the 2-norbornenyl cation, we prefer to consider the symmetrical cation **211** an approximation to the higher energy transition state for the **210a** $\rightleftarrows$ **210b** interconversion. The data of Giddings are, after all, equally compatible with the simpler structure **210**, provided the equilibration of **210a** and **210b** is sufficiently rapid. Brown proposed that a similar equilibrating pair of intermediates, **222a** and **222b** best explains the solvolysis data for certain β-phenylethyl derivatives. In fact, many of the conflicting arguments presented by Brown (131) and Cram (132) concerning the existence of the phenonium ion are directly related to the question of the nature of the 2-benzonorbornenyl cation. This matter is discussed at greater length in Chapter 27.



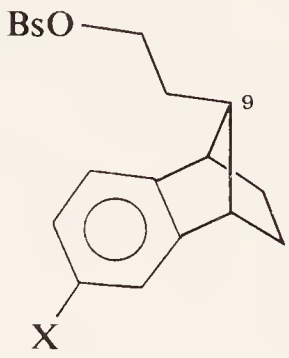
(220) **(221)** **(222a)** **(222b)**

D. The 2-(*syn*-9-Benzonorbornenyl)ethyl System

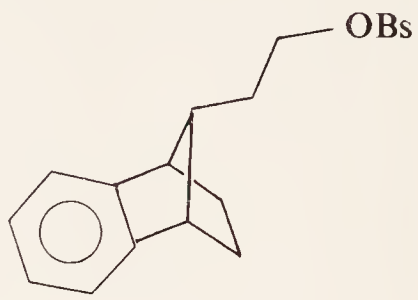
The substituent effect studies of Tanida (112–115) on benzonorbornenyl brosylates, discussed previously, have been accepted as evidence for π participation in these systems. In a continuation of his probe for homobenzylic participation, Tanida has recently reported the results of a rate and product study of acetolysis of a series of 6-substituted 2-(*syn*-9-benzonorbornenyl)ethyl brosylates (**223**), along with that of one *anti* epimer (**224**) (133).

Solvolysis of the *anti* brosylate **224** yielded only unrearranged acetate, whereas solvolysis of the *syn* brosylate derivatives **223** yielded various

proportions of unrearranged acetates and rearranged benzhydrindanyl hydrocarbons and acetates represented by the general structures **225** and **226**. In addition to a large percentage of unidentified material, solvolysis of the brosylate **223b** gave almost exclusively rearranged products **225a** and **226a**. It was assumed and semiquantitatively verified by kinetic and



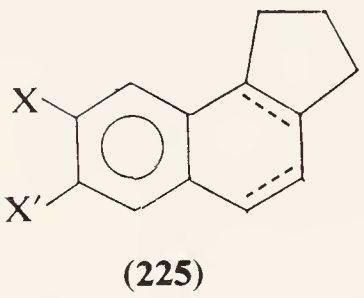
(223)



(224)

(a) X = —H; **(b)** X = —OCH_3; **(c)** X = —F;
(d) X = —Cl; **(e)** X = —NO_2

product analysis that unassisted solvolysis gives only unrearranged product; anchimerically assisted solvolysis leads only to rearranged products.



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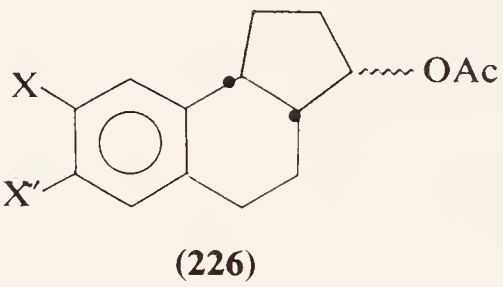


(226)

(a) X = —OCH_3; X′ = H
(b) X = —H; X′ = —OCH_3

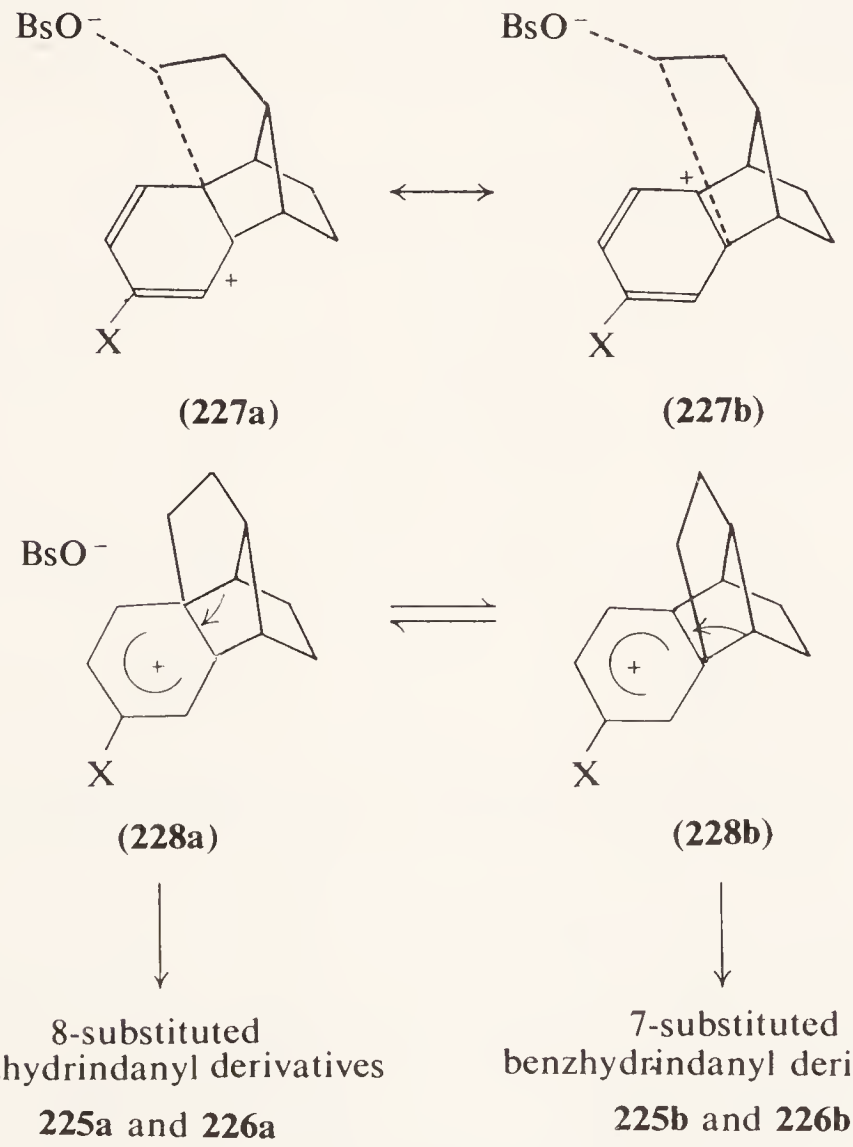
The brosylate **223a** was found to solvolyze 20 times faster than the *anti* isomer **224**. This is to be compared to a *syn*:*anti* ratio of 1.9×10^5 reported by Bly (92) for the 2-(7-norbornenyl)ethyl brosylates **153a** and **154a**. The *syn*:*anti* rate ratio of 20 for the epimers **223a** and **224** is, however, in line with the k_u/k_s ratio reported by Bartlett (97) for 2-(Δ^3-cyclopentenyl)ethyl tosylate (**164**) and its saturated analog. In the same report it was demonstrated that this ratio can vary by large factors, depending on solvent and leaving group. Meaningful correlation of data of this type from several laboratories will be difficult until more detailed studies like those performed by Bartlett have been carried out.

The substituent effects found for derivatives of **223** are much less dramatic than those obtained for *anti*-9-benzonorbornenyl derivatives (**196**). For instance, **223** yielded a $k_{OCH_3}:k_{NO_2}$ ratio of only 146. However, the kinetic data correlate well with $[\sigma_p^+ + \sigma_m^+]$ and generate a large, negative ρ value, which, as discussed previously, indicates increasing

participation as activating substituents are introduced into the benzene ring. Tanida also noted that the accelerating effect of the methoxy substituent is much too large to be explained in terms of the inductive effect of the benzene ring, and the acetolysis, therefore, must be aided by π-electron delocalization in the transition state.

Tanida believes the data support a symmetrical transition state of the type represented by **227a** and **227b** (133). As pointed out previously, a completely symmetrical, delocalized, homoallylic transition state would explain the data and would also correlate well with the symmetrical transition states proposed by Bly (92) and Bartlett (97) for similar systems.

Tanida accounted for the rearranged products by the mechanism represented in **228**. This mechanistic scheme is probably oversimplified, however, since solvolysis of **223b** reportedly gives no 7-substituted derivatives (**225b**, **226b**) and, furthermore, much of the product was unidentified.



XIII. HOMOAROMATIC CATIONS

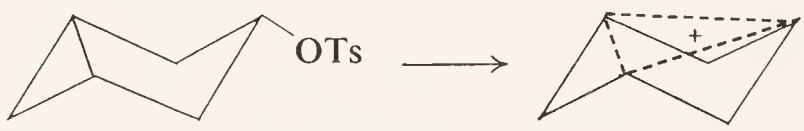
As indicated earlier in this chapter, Roberts (43) has referred to the *anti*-7-norbornenyl cation (**36**) as a bishomocyclopropenyl cation, thus

indicating its relation to the cyclopropenyl cation, i.e., one carbon is separated from the other two by more than one σ bond. Winstein has labeled all such systems homoaromatic and refers to cation **36** as a bishomoaromatic species (134). As pointed out by Winstein in his definitive review on homoaromaticity (134), the allyl cation **229**, the cyclopropenyl cation **230**, and its monohomo derivative **231** provide an operational illustration of homoaromaticity. The monohomo derivative **231** is termed

(229) **(230)** **(231)**

homoaromatic because its Hückel MO delocalization energy, although less than that for the aromatic cation **230**, is greater than that for **229**, since its 1,3 resonance integral β_1 is large but, owing to the insertion of the methylene group, is less than β_0. The "mono-", "di-", etc., terms of homoaromatic terminology refer only to the number of sides of the cation on which the σ backbone is lengthened or removed.

In 1959, Winstein et al. (135) reported the discovery of a probable trishomocyclopropenyl cation (**232**) derived from the 3-bicyclo[3.1.0]-hexyl system (**233**). This ion (**232**), as depicted by Winstein, is a symmetrical homolog of the cyclopropenyl cation and is wave mechanically analogous to it (136,137). It differs, however, in that the orbital overlap is



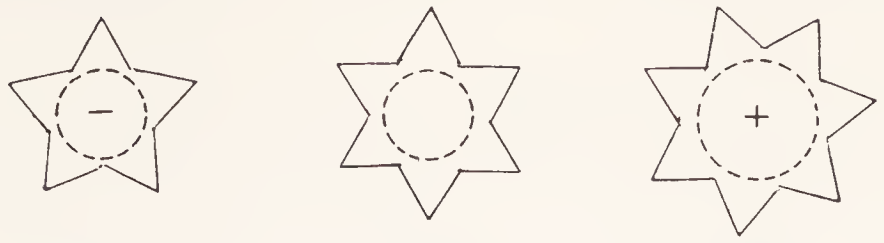
(233) **(232)**

more σ than π, and the 1,3 overlap and exchange integrals are smaller in magnitude than the corresponding 1,2 integrals of the cyclopropenyl cation (136,137).

Since the early work by Winstein involving the trishomocyclopropenyl cation (**232**), many other systems have been investigated and termed homoaromatic. Yet none of the other original systems postulated by Winstein to be homoaromatic—i.e., pentahomocyclopentadienide anion (**234**), hexahomobenzene (**235**), or heptahomotropylium cation (**236**)—has yielded to experimental realization (136,138).

A. The 3-Bicyclo[3.1.0]hexyl Cation

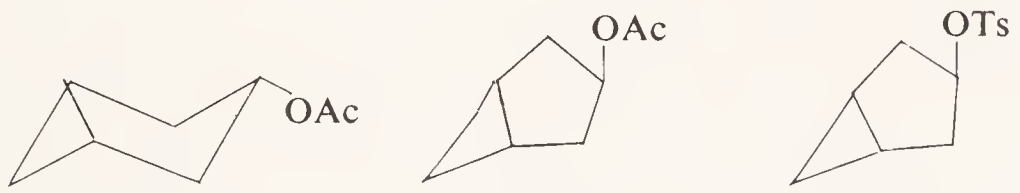
In a recent paper (139), Winstein has thoroughly reexamined and expanded much of his earlier work (140,141) on the 3-bicyclo[3.1.0]hexyl



(234) (235) (236)

system. Although the evidence presented is not unequivocal, it strongly supports the homoaromatic concept expressed by the trishomocyclopropenyl cation (**232**) as the intermediate in the solvolysis of *cis*-3-bicyclo[3.1.0]hexyl toluenesulfonate (**233**). It was found, e.g., that acetolysis of the *cis* tosylate (**233**), which is properly constituted for backside participation by the cyclopropyl group during ionization, yielded at least 98% *cis* acetate (**237**) with the remainder of the reaction product consisting of the *trans* acetate (**238**) and olefin (139).

In contrast to his earlier work (140) in which he found that acetolysis of the *trans* tosylate **239** gave only the *cis* acetate **237** and olefin, Winstein has

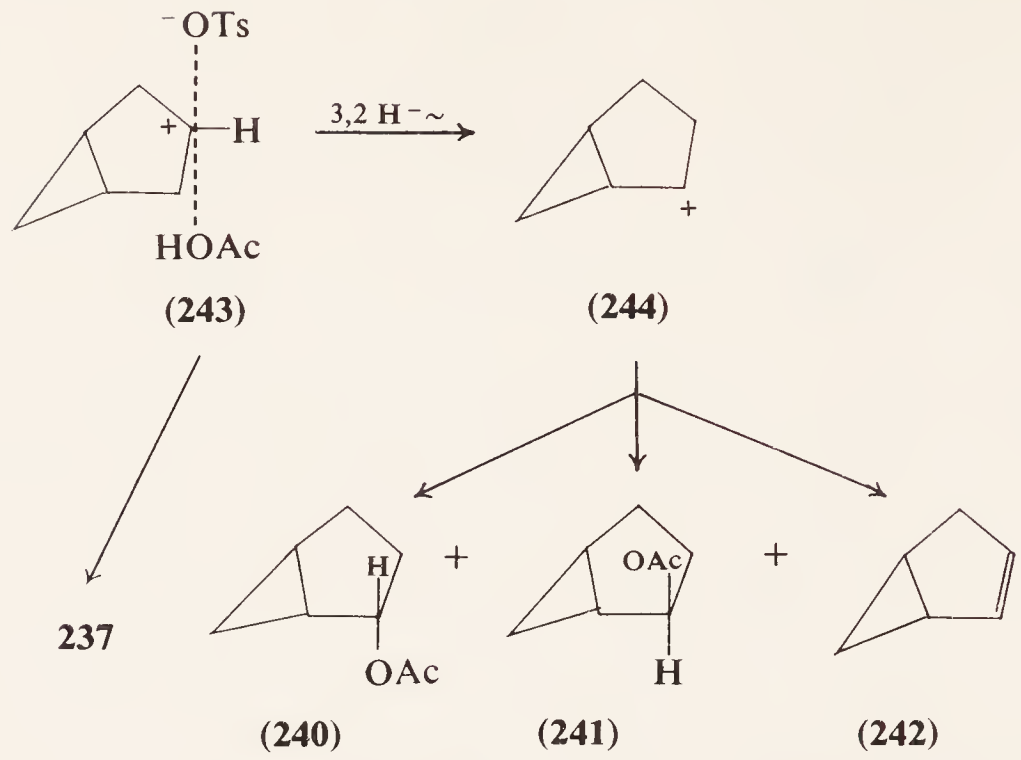


(237) (238) (239)

now reported that acetolysis of **239** yielded a complex mixture of three bicyclic acetates, **237**, **240**, and **241**, and two monocyclic acetates, the five accounting for 70% of the product. The remaining 30% of the product consisted of one bicyclic olefin (**242**) and two monocyclic olefins (139). The major product was the *cis* acetate (**237**), which constituted approximately 40% of the total reaction mixture. Winstein pictures all the products from acetolysis of the *trans* tosylate **239** to arise by unassisted solvolysis (k_s) through the classical-type transition state (**243**). The acetates **240** and **241** and the olefin **242** are presumed to result from the intermediate cation **244**, formed by a 3,2 hydride shift; the major product (**237**) can be visualized simply as the result of backside attack by solvent (139). All other "*trans*" products can arise from various rearranged carbonium ions.

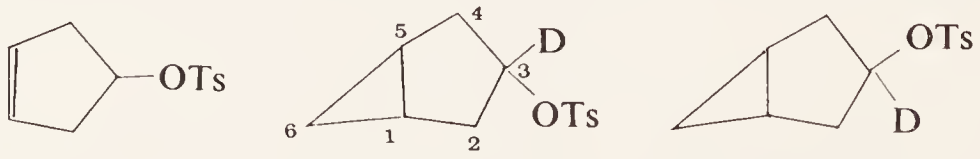
Comparison of the relative apparent reactivities of the epimeric tosylates **233** and **239** does not offer strong evidence for the homoaromatic cation **232**. The *cis*:*trans* rate ratio varies from a value of 47 in formolysis to 36 in acetolysis (139).

More compelling evidence for the trishomocyclopropenyl cation is furnished from the rate data by the observation that the *cis* tosylate (**233**)



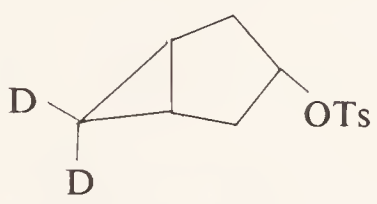
is subject to a substantial special salt effect on addition of lithium perchlorate; on the other hand, the *trans* tosylate **239** shows little effect (140). Winstein has argued convincingly (142) that the "special" effect of lithium perchlorate is due essentially to elimination of ion-pair return from solvent-separated ion pairs and, moreover, that this phenomenon is only important in the case of relatively stable cations, usually thought to possess unique structures (140,142); the unique structures are presumably charge-delocalized, nonclassical ones. Thus the acetolysis data for **233** are treated in the same way as those for the 3-anisyl-2-butyl system, which showed a comparable salt effect (142). The unique nature of the intermediate cation from the *cis* tosylate **233** is further emphasized by Winstein's failure to observe a special salt effect in acetolysis of the closely related Δ^3-cyclopentenyl tosylate (**245**) or for cyclohexyl or cyclopentyl tosylate (140). Confirmatory evidence is reported by Bartlett and Rice (143), who found no indication of homoallylic participation by the double bond on solvolysis of Δ^3-cyclopentenyl bromide in aqueous acetone. In this system (**245**), apparently the strain energy of bending is greater than the stabilization energy so gained.

Some of the strongest supporting evidence for the trishomoaromatic cation **232** has been provided by deuterium-labeling experiments. In early work, Winstein reported that the *cis* tosylate (**246**) was converted quantitatively to *cis* acetates containing deuterium equally distributed over C-1, C-3, and C-5, in keeping with a symmetrical, nonclassical intermediate.

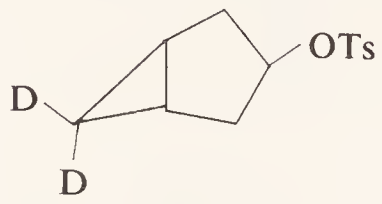


(245) (246) (247)

The *trans* tosylate (**247**), by comparison, suffered very little deuterium scrambling (141). However, **247** was contaminated with **246** and, as mentioned previously, many products from the solvolysis of the *trans* tosylate **239** went undetected in the earlier work. In later reports on deuterium-labeling experiments (139), Winstein has chosen to work with the 6,6-dideuteriotosylates **248** and **249**, probably because of simpler and more reliable nmr analysis; isotope effects on solvolysis are also eliminated. Nmr analysis of the acetate from **248** indicated the presence of 4/3 cyclopropane methylene protons, as expected for a cation in which C-2, C-4, and C-6 become equivalent. Reisolation of the unreacted *cis*-deuteriotosylate **248** followed by determination of the extent of deuterium scrambling with



(248)

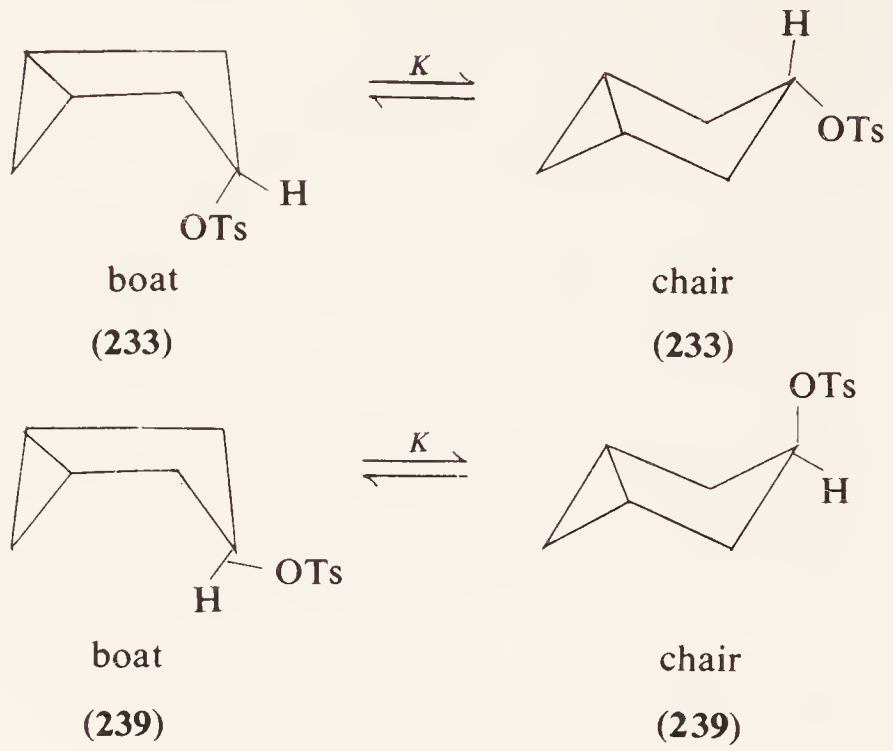


(249)

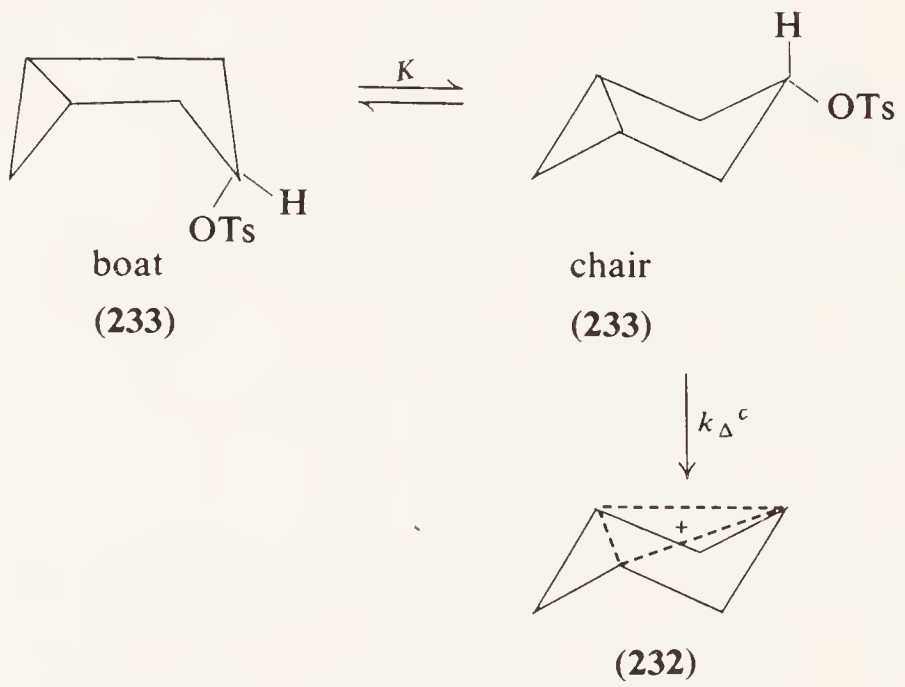
time permitted the calculation of k_{eq} for internal return and provided verification of the earlier interpretation of the special salt effect.

In sharp contrast to the label scrambling observed in acetolysis of the *cis* tosylate **248**, the *trans* isomer **249** showed no migration of deuterium in the *cis* acetate product **237**-d_2. Assuming the intermediacy of the classical ion **243** for solvolysis of *trans* tosylate **239**, these results indicate that no leakage occurs from the classical ion **243** to the nonclassical ion **232**. In any event, there is ample analogy for this phenomenon (134,139). The explanation for nonleakage rests on the assumption that the 3-bicyclo-[3.1.0]hexyl derivatives exist predominantly in the boat conformation. The evidence for a boat conformation is based on comparison of the observed nmr coupling constants with the constants calculated for a chair, a boat, and a planar five-membered ring by use of the Karplus equation. Also, it is known that various thujyl derivatives prefer the boat conformation (139). Winstein states "the *trans* tosylate **239** with a preferred boat conformation, has no reason to ionize to a cation with a chair conformation. Instead, the classical cation **243** probably contains a relatively flat five-membered ring, and an unusual amount of reorganization would be required for conversion to the chairlike nonclassical ion **232**" (139). The important and unknown factor here is undoubtedly the role of solvent.

Even though the existence of the trishomocyclopropenyl cation (**232**) has not been proved, the rate acceleration, the stereochemistry and nature of the solvolysis products, the special salt effect, and the deuterium scrambling are all compatible with the nonclassical intermediate **232**, derived from anchimerically assisted ionization k_{Δ}.



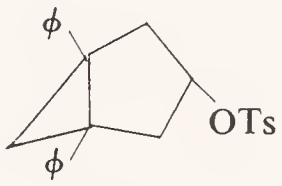
The ratio of k_Δ to unassisted solvolysis k_s is about 50, based on previously discussed product information for acetolysis of the *cis* tosylate **233**. Winstein noted (139) that this value is somewhat low compared to k_Δ/k_s ratios for other nonclassical systems. The low ratio is attributed to the preferred boat conformation for the 3-bicyclo[3.1.0]hexyl systems. Winstein proposes that the boat-to-chair equilibrium constant K is very small, but once chair-**233** is formed it ionizes to cation **232** with a normally fast $k_\Delta{}^c$. However, since K is considerably less than unity and the apparent k_Δ is expressed by $(K/1 + K)k_\Delta{}^c$, the apparent k_Δ is much less than the actual $k_\Delta{}^c$ (139). Obviously, it would be very valuable to know the value of K.



In papers that appeared before the latest report by Winstein (139) on the 3-bicyclo[3.1.0]hexyl cation, Corey (144,145) took exception to the

trishomoaromatic concept represented by the structure **232**. It was found (144) that, in the nitrous acid deamination of the *cis*- and *trans*-3-bicyclo-[3.1.0]hexyl amines, each amine led to a mixture of *cis*- and *trans*-3- and *cis*- and *trans*-2-bicyclo[3.1.0]hexanols (precursors of **237**, **238**, and **240**, **241**, respectively). The complex reaction mixture was taken to indicate that both amines were deaminating classically and that the trishomoaromatic concept of Winstein was thereby weakened (144). However, as Winstein has noted (139), the very nature of the deamination reaction would lead us to expect both amines to deaminate classically. A great similarity between the products obtained by Corey from deamination and those obtained from solvolysis of the *trans* tosylate **239** was pointed out (139).

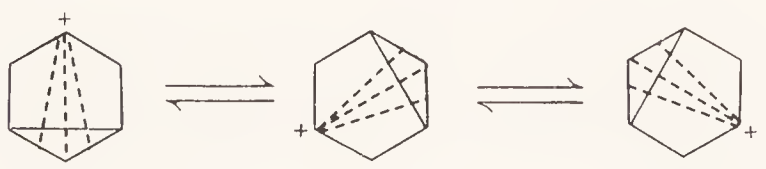
In order to further test their hypothesis that the trishomocyclopropenyl cation **232** was not an important intermediate, Corey and Uda (145) studied the solvolysis of *cis*-diphenyl-*p*-toluenesulfonate (**250**). It was believed (145) that the phenyl groups, which occupy 1,5 positions, should stabilize a



(250)

trishomocyclopropenyl cation relative to either the starting material or the classical ion. The tosylate **250**, however, was two or three times less reactive than the unsubstituted tosylate **233** and yielded only rearranged products. It was concluded from the rate data that the phenyl groups provided little or no anchimeric acceleration. It is possible, however, that the inductive effect of the phenyls is greater than estimated by Corey and Uda (145) and that this effect could be as high as a factor of 100 (110).

Corey was led to propose that solvolysis occurs through the intermediacy of a set of rapidly equilibrating classical ions (**251a**, **251b**, and **251c**) in which the positive center is weakly interacting with the cyclopropyl ring.



(251a) **(251b)** **(251c)**

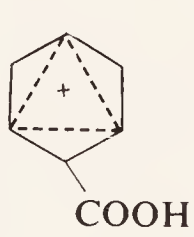
Winstein has taken very sharp exception (134,139) to the Corey proposal. It was pointed out that the phenyl group, owing to its opposing inductive and conjugative effects, is a very poor probe for positive charge development at a particular center. Winstein argued that the phenyl substituents

affect the boat-to-chair equilibrium constant K and both the anchimerically assisted ionization constants $k_\Delta{}^c$ and k_Δ (139). Dewar has also taken issue with Corey's argument that phenyl groups should stabilize the cationic structure **232** (146). Winstein further notes that extended Hückel calculations (147) predict greater stability for the trishomocyclopropenyl cation **232** than either a classical ion or the phenyl substituted ions **251a**, **251b**, and **251c** (139).

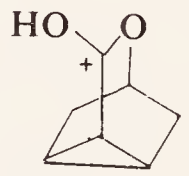
B. Nmr Spectra of the 3-Bicyclo[3.1.0]hexyl Cation

Further information on the structure of the cation has been sought from nmr spectra. In his original report (148), Olah concluded that the nmr spectrum of the fluoroborate salt of the cation supported the trishomocyclopropenyl formulation **232**. Subsequently, however, it was argued (149) that although the nmr spectrum indicated only two types of hydrogens in a 2:1 peak area ratio and thus rather definitely eliminated a classical structure, several nonclassical structures were possible, including a simple cyclohexyl allylic ion. Nevertheless, the possibility exists that the spectrum could result from a time average of equilibrating classical ions.

Following to Olah's report, Sauers published findings (150) on the nmr spectrum of a cation in 80% sulfuric acid, which was interpreted as being most consistent with the structure **252**. Sauers was able to effect an 80% recovery of the corresponding lactone from sulfuric acid solution. Deno (151) has taken issue with Sauers's proposal (**252**) and states that the cyclopropyl carbonium ion structure **253** is more compatible with the nmr data.

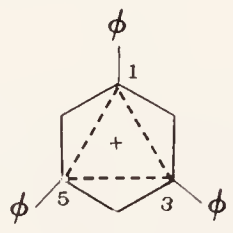


(252)

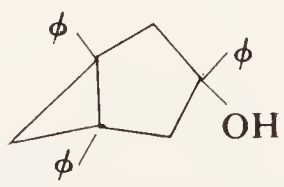


(253)

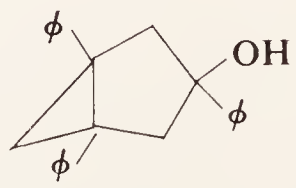
Broser (152) has recently reported the nmr spectrum of a cation generated in a CH_3NO_2–$SOCl_2$–$SbCl_5$ solution, which was believed to be most consistent with the trishomocyclopropenyl structure **254**. The cation



(254)



(255)

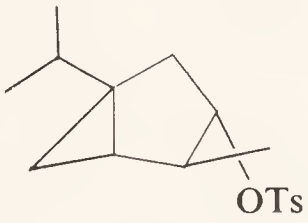


(256)

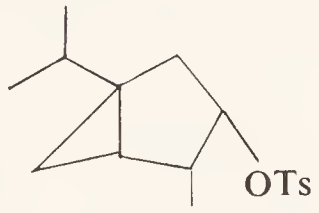
formulated as **254** could be generated from either the *cis* alcohol **255** or the *trans* alcohol **256**. This interpretation is regarded as questionable, however, since the spectrum was obtained at a rather high temperature and the starting alcohol was apparently not regenerated from the cation.

C. Other Possible Trishomocyclopropenyl Species

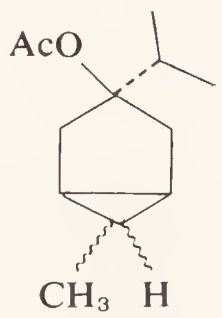
Several examples of solvolyses of alkyl-substituted 3-bicyclo[3.1.0]hexyl systems have recently been reported. Norin (153) has found that the *cis* isomers, (−)-neothujyl (**257**) and (+)-neoisothujyl (**257a**) *p*-toluenesulfonates, undergo acetolysis at a rate at least 700 times faster than the corresponding *trans* isomers, (−)-thujyl (**258**) and (+)-isothujyl (**258a**) *p*-toluenesulfonates, and, in addition, yield acetates of retained configuration. Much of the large *cis*:*trans* rate ratio is due to an abnormally slow rate for the *trans* isomers **258** and **258a** as compared with the unsubstituted *trans* isomer **239**. The data of Norin (153) show a very poor correlation between k_Δ/k_s and the *cis*:*trans* rate ratios, whereas Winstein found a good correlation for the unsubstituted compounds **233** and **239**. Surprisingly, Norin also found that the main acetolysis product from the *cis* isomers **257** and **257a** was not the tertiary acetate (**259**).



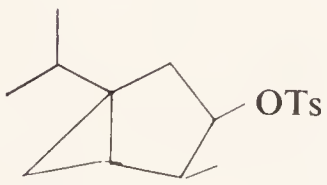
(**257**)



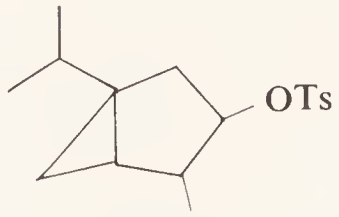
(**257a**)



(**259**)

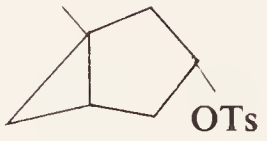


(**258**)

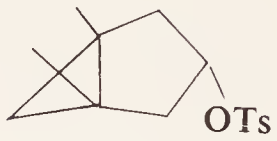


(**258a**)

Winstein (134) has extended his investigations to the solvolysis of 1-methyl- and 1,5-dimethyl-3-bicyclo[3.1.0]hexyl tosylates (**260**, **261**). The



(260)

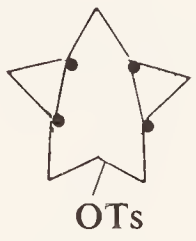


(261)

acetolysis products obtained were almost exclusively *cis* and, in contrast to Norin's work, the products were almost exclusively tertiary acetates as well. It was found that the monomethyl tosylate **260** solvolyzed five times as fast as its unsubstituted analog **233**, whereas the dimethyl tosylate **261** reacted seven times faster (134). These data contrast with those reported by Tanida (114) and by Bartlett (97) for other systems in which a symmetrical, nonclassical intermediate was invoked and in which introduction of a second substituent increased the rate factor by its square. Resolution of this difference must await further, detailed, substituent studies.

A derivative of another interesting system, originally visualized by Winstein (141) as a possible source of the pentahomocyclopentadienide anion **234**, has been investigated (154). In acetolysis, the *cis* tosylate **262** was found to be more reactive that the *trans* isomer **263** by a factor of 52; after appropriate workup, **262** gave as the principal product the corresponding *cis* alcohol **262–OH**, along with several other products, one of which was believed to be the hydrindanol **264**.

(262)



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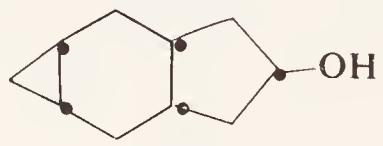
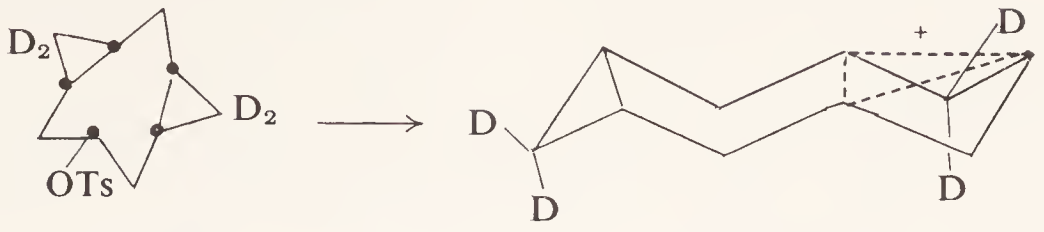
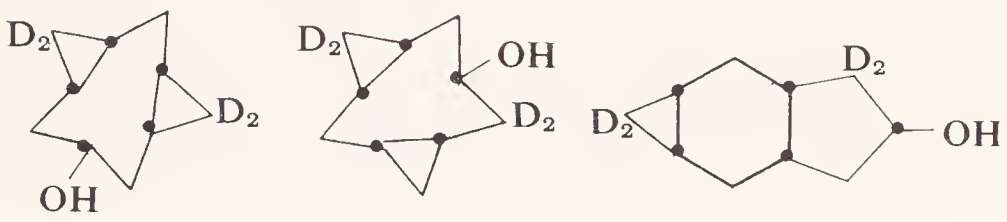


(264)

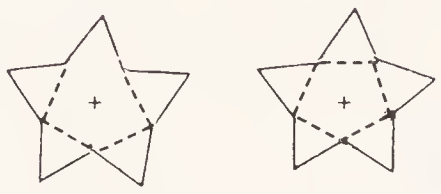
The technique of deuterium labeling was again instructive in ascertaining the mode of charge delocalization. Acetolysis of the tetradeuterio tosylate **265** yielded the alcohols **266** and **267**, with deuterium scrambling as indicated in the figures, and the deuteriohydrindanol **268**. The kinetic and product analysis results were considered to be most consistent with the intermediacy of the nonclassical trishomocyclopropenyl-type cation **269**. The three-centered ion **269** was also the cation favored by a Hückel LCAO–MO calculation which indicated a delocalization energy of 2.000 β_1. It is interesting that the five-centered cation **270** gave a smaller calculated delocalization energy (1.464 β_1); the other possible five-centered cation **271** was, of course, of higher energy still (1.236 β_1). The implication again, as found throughout the study of homoallylic and homoaromatic cations, is that these systems are $4n + 2\pi$ electron systems.



(265) (269)

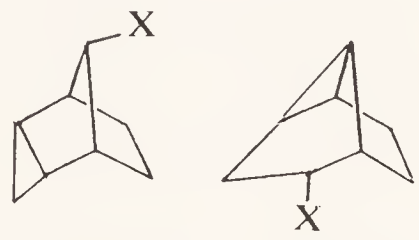


(266) (267) (268)



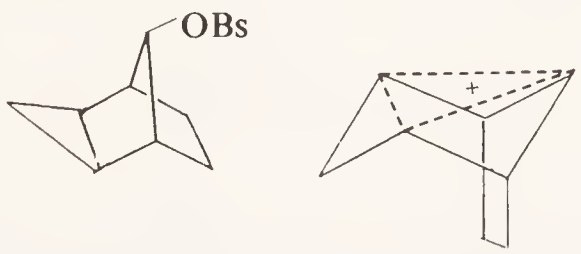
(270) (271)

Recently both Tanida (155) and Battiste (156) have reported the solvolysis of yet another system for which the intermediacy of a nonclassical trishomocyclopropenyl-type cation was proposed (156). It was found that *endo-anti*-tricyclo[3.2.1.$0^{2,4}$]octan-8-*yl* *p*-nitrobenzoate **272a** underwent solvolysis at a rate 10^{14} times greater than that for 7-norbornyl *p*-toluenesulfonate (**35a**). By contrast, the *exo-anti-p*-bromobenzenesulfonate **273** has been reported to undergo solvolysis at a rate three times slower than that of **35a** (157). The *p*-nitrobenzoate **272a** also solvolyzes with partial rearrangement and ion-pair return to yield a mixture of **272b** and



(272) (274)

(a) X = OpNB; (b) X = —OH



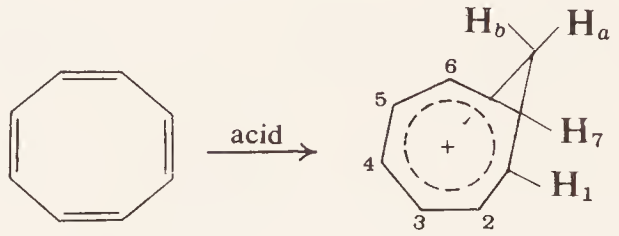
(273) (275)

274a, **b**. The latter two products comprised more than 70% of the reaction material (155).

It was suggested that the high solvolytic reactivity of **272a** relative to the 7-norbornyl system **35a** is best rationalized by the intermediacy of the nonclassical trishomocyclopropenyl-type cation **275**.

D. Homotropylium Cations

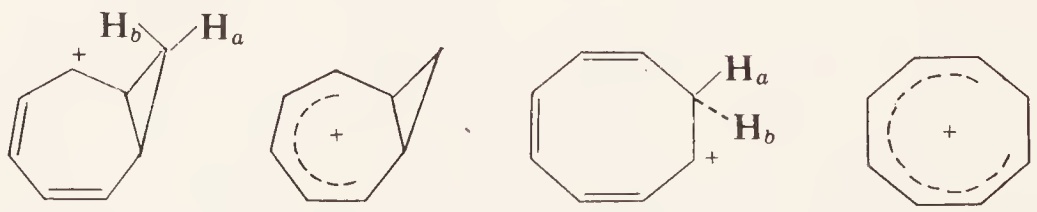
A very strong case for the existence of many examples of homotropylium cations has been presented by Winstein (134). The homotropylium cation is formulated as having the 6-electron monohomoaromatic structure (**276**).



(277) **(276)**

Pettit (158) first reported the preparation of a salt of this ion, the stable hexachloroantimonate **276**, which resulted from treatment of cyclooctatetraene (**277**) with antimony pentachloride and hydrochloric acid. In his original paper (158), Pettit depicted the cation produced from **277** as either the classical, cyclopropyl cation **278** or the homotropylium cation **276**; it is clear that the nonclassical structure was favored. The possibility of a planar cyclooctatrienyl structure (**279**) was quickly eliminated by the large chemical shift (5.8 ppm) between hydrogens H_a and H_b in the nmr spectrum. These hydrogens would be expected to be magnetically equivalent in structure **279**. Both **278** and **279**, formulated by Pettit as shown, are more economically written as in **278a** and **279a**.

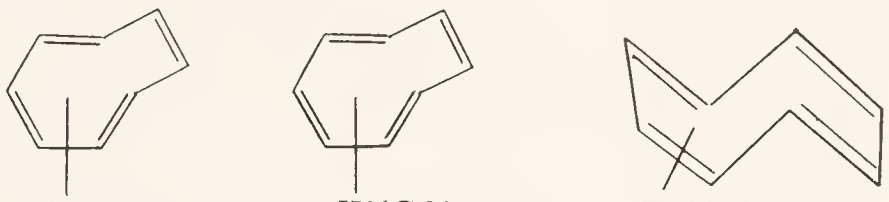
Solutions of cyclooctatetraene in concentrated sulfuric acid and in deuteriosulfuric acid have now been extensively studied by Pettit (159,160) and by Winstein (161,162). Winstein (134,161) has also investigated the protonation of cyclooctatetraenemolybdenum tricarbonyl (**280**) and



(278) **(278a)** **(279)** **(279a)**

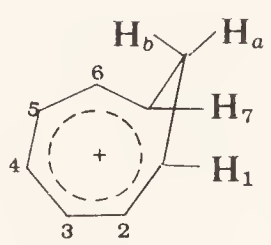
cyclooctatetraenetungsten tricarbonyl (**281**) and has drawn a comparison with the cyclooctatetraeneiron tricarbonyl (**282**) protonation study of

Wilkinson (163). Again, the data do not permit an unequivocal conclusion, but support is lent to the monohomoaromatic 6-electron system represented by the structure **276**.



(280) **(281)** **(282)**

Some of the strongest evidence supporting the homotropylium cation structure is provided by the nmr studies of Pettit (158,160) and Winstein (134,161,162). Pettit, working with the nmr spectrum of **276** prepared by dissolving **277** in concentrated sulfuric acid, found a 5:2:1:1 proton pattern as in **276**—nmr. The large difference in chemical shift between H_a and H_b (5.8 ppm) was attributed to a substantial ring current, in which H_b is shielded and H_a, lying almost in the plane of the ring, is deshielded (158).



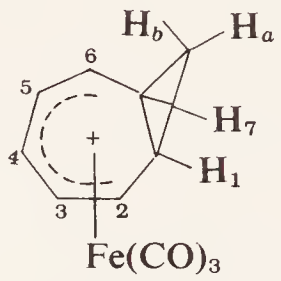
(276-nmr)

(5) $H_{2,3,4,5,6}$; $\tau = 1.4$
(2) $H_{1,7}$; $\tau = 3.4$
(1) H_a; $\tau = 4.8$
(1) H_b; $\tau = 10.6$

We now know that cyclooctatetraeneiron tricarbonyl (**282**) has a 1,3-diene bonded structure in solution (164). Thus it is interesting to consider a discovery by Wilkinson. He found (163) that **282**, upon treatment with either concentrated sulfuric acid or aqueous hydrogen tetrafluoroborate, gave the classical ion **283**, in accord with the 4π–5C preference of the iron atom (161). This behavior, of course, is in contrast to that of the homotropylium system (**276**). The nmr spectrum of **283** displayed a 1:4:2:2 proton pattern and, in contrast to that of the monohomotropylium ion **276**, has a very small chemical shift between H_a and H_b.

The classical bicyclic structure **283**, which can be pictured as forming

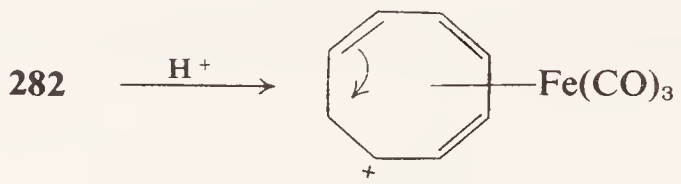
via the homoallylic intermediates **283a** and **283b** (163), was further confirmed by sodium borohydride reduction to the bicyclic complex **284**.



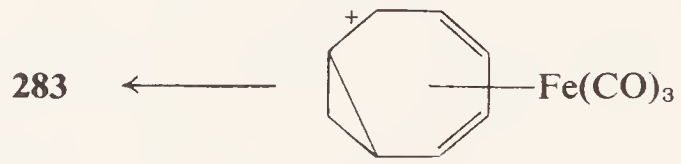
(283)

(1) H_4; $\tau = 2.26$
(4) $H_{2,3,5,6}$; $\tau = 4.62$
(2) $H_{1,7}$; $\tau = 7.48$
(1) H_b; $\tau = 8.47$
(1) H_a; $\tau = 8.65$

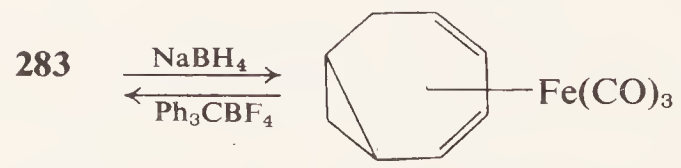
The cation **283** could be regenerated from **284** by hydride abstraction with triphenylmethyltetrafluoroborate; the starting material (**282**) could be



(283a)



(283b)

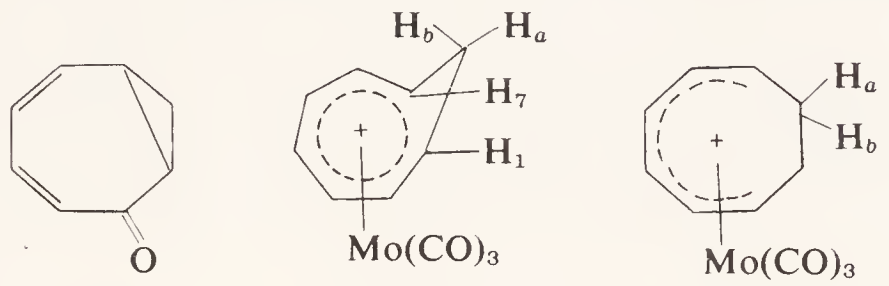


(284)

regenerated from **283** with base. Pettit (165) has further substantiated the classical structure (**283**) by converting the tetrafluoroborate salt of **283** to homotropone (**285**) through a series of reactions.

Winstein has strengthened the case for the monohomotropylium cation through an nmr study (161) of cation **286**, generated by protonation of cyclooctatetraenemolybdenum tricarbonyl (**280**). The complex (**280**) has 6π–6C olefin-to-metal bonding and would be expected to yield a 6π–7C arrangement on protonation, thus essentially limiting the possible cationic

structures to either **286** or **287** (161). The resulting nmr spectrum is very similar to that reported for the simple homotropylium cation **276** (158,161). The spectrum displays the same 5:2:1:1 proton pattern, as well as a large chemical shift between protons H_a and H_b, thereby eliminating structure **287** in which these two protons would be equivalent. Possibly the structure assigned to complex **286** could be strengthened by reduction and regeneration experiments of the type reported by Wilkinson for **283** (163).



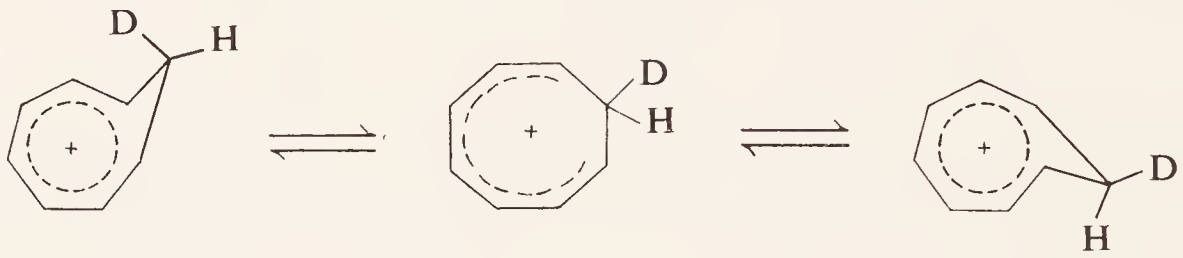
(285) **(286)** **(287)**

For further evidence of the difference between the nonclassical structure (**276**) and the classical structure (**283**), Winstein (161) has determined the coupling constants $J(H_a–H_1)$ (*cis*), $J(H_b–H_1)$ (*trans*), and $J(H_a–H_b)$ for **276** and found that they are not in accord with those predicted and obtained by Wilkinson for the fully formed cyclopropane ring in the classical structure **283** (163).

Deno (151) has, in effect, taken exception to the nonclassical homotropylium structure (**276**) and proposed that all the properties of the cation are best represented by the structure **278a**, for which "no unusual hybridization other than cyclopropyl conjugation is required to rationalize the stability" (151). It is never made clear what Deno means by "cyclopropyl conjugation." Apparently he envisions some electron-releasing power of the cyclopropyl ring for which no resonance structures can be written. Both Winstein (161) and Pettit (160) have shown the fallacy of Deno's statement. Pettit points out the large differences in chemical shifts of the four "cyclopropyl" protons in **276** compared with the small chemical shift differences in "normal" cyclopropylcarbonium ions. He also emphasizes the previously discussed difference in coupling constants for "cyclopropyl" protons in **276** and **283** to mitigate against structure **278a**. The absence of any bicyclo[5.1.0]octane derivatives on reaction of **276** with lithium aluminum hydride or sodium acetate was noted (160). Treatment of **276** with sodium acetate followed by catalytic hydrogenation gave cyclooctyl acetate and cyclooctane, along with several unidentified products (158).

The monohomotropylium character of **276** has been more clearly defined by Winstein, using ring inversion experiments and correlations of the ultraviolet spectrum of the ion with that of the closely related tropylium cation **62** (162).

It was originally reported that protonation of cyclooctatetraene (**277**) was nonstereospecific, since its treatment with deuteriosulfuric acid led to nmr signals of equal intensity for protons H_a and H_b (**276**) (158). Winstein has now demonstrated that if **277** is dissolved in deuteriosulfuric acid at $-10°$, the nmr spectrum indicates that about 80% of the deuterium becomes attached from the inside of the ring. Continued observation of the nmr spectrum reveals that the signals for protons H_a and H_b approach the value of one-half proton each, as observed by Petitt. The nmr data yielded a value for $\Delta F^{\ddagger}$ of 22 kcal/mole for the isomerization, **288a** $\rightleftarrows$ **288b**. Winstein pictured the isomerization to proceed via ring inversion through the planar species **289**; thus **289** is calculated to have a free energy 22 kcal/mole greater than the homoaromatic cation **288** (162). It was also



(288a) **(289)** **(288b)**

learned that the ultraviolet spectrum of **276** more closely resembles the spectrum of tropylium ion **62** than the anticipated spectrum of the planar cyclooctatrienyl ion **279a**. Employing Streitwieser's observation (166) that a good correlation exists between the frequency of long-wavelength absorption and the Hückel MO excitation energy, the monohomotropylium ion **276** was found to have an appreciable $\beta_{1,7}$. The bond orders for the cation **276** were also very similar to those for tropylium ion (162). From these observations, Winstein concludes that the homotropylium ion (**276**) has, as expected, the essentially even electron distribution around the C-1 through C-7 framework, in accord with the appreciable ring current indicated by its nmr spectrum.

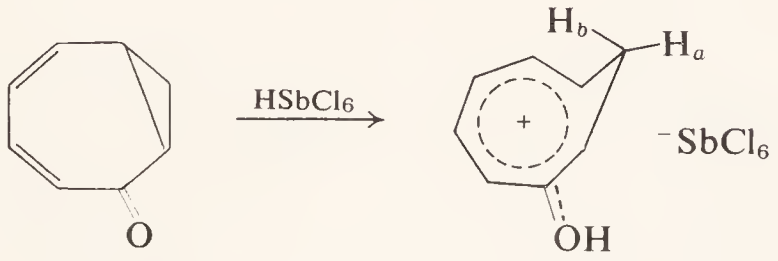
Further evidence for the ring current is provided by Winstein's application (162) of the Johnson-Bovey equation (167) to calculate chemical shifts due to induced ring currents. Based upon a 1.6-Å ring radius and a 6-electron system, a value of 5 to 6 ppm for the chemical shift between protons H_a and H_b was obtained; the observed value is 5.8 ppm.

Indication of an aromatic ring current for **276** is also provided by its diamagnetic susceptibility exaltation. Dauben has defined the exaltation Λ of a compound as the difference between the molar susceptibility χ_m exhibited by a compound and that predicted (χ'_m) for the identical but not cyclically delocalized structural counterpart: $\Lambda = \chi_m - \chi'_m$ (168a). Winstein has reported (134) unpublished work of Dauben and Laity in

which the value of Λ for the monohomotropylium cation **276** was determined to be 18, compared with a value of 19.5 for tropylium ion. For benzene, $\Lambda = 13.7$ (168a). Dauben, however, has indicated (168b) that the χ_m values used in the calculations of Λ for **276** and **62** as reported by Winstein (134) have not yet been determined accurately. This appears to be a minor difficulty, and the method holds much promise for determining the aromatic character of molecules.

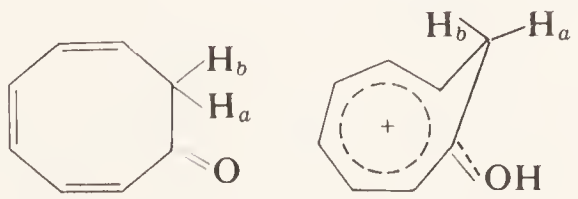
Several substituted monohomotropylium-type cations have now been prepared. The experiments, in general, were carried out to determine the effect of substituents on the aromaticity of the system. Other important information relating to the reactions of cyclooctatetraene and substituted cyclooctatetraenes with electrophiles has also been obtained from such studies.

Pettit (165) has reported that the protonation of homotropone (**285**) gave a crystalline hexachloroantimonate salt with an implied structure, **290**. Pettit appeared to favor structure **290** on grounds of the high basicity of **285** and large chemical shift between inside and outside protons (H_a and H_b) of 3.1 ppm. A stronger case for the structure **290** could have been made if the starting ketone had been regenerated and if a more detailed nmr analysis had been given. There seems little doubt, nevertheless, that **290** has appreciable homoaromatic character, even with the hydroxyl substituent.



(285) **(290)**

Winstein believed (169) that the high-energy cyclopropane ring present in **285** tended to favor the nonclassical structure (**290**); therefore, he proposed that cyclooctatrienone (**291**) would be a better system in which to study the effect of a hydroxyl group on homotropylium character. Winstein reasoned that the nmr of **291** in strong acid, at an unspecified low temperature, is compatible with the homotropylium oxide structure **292**. It was



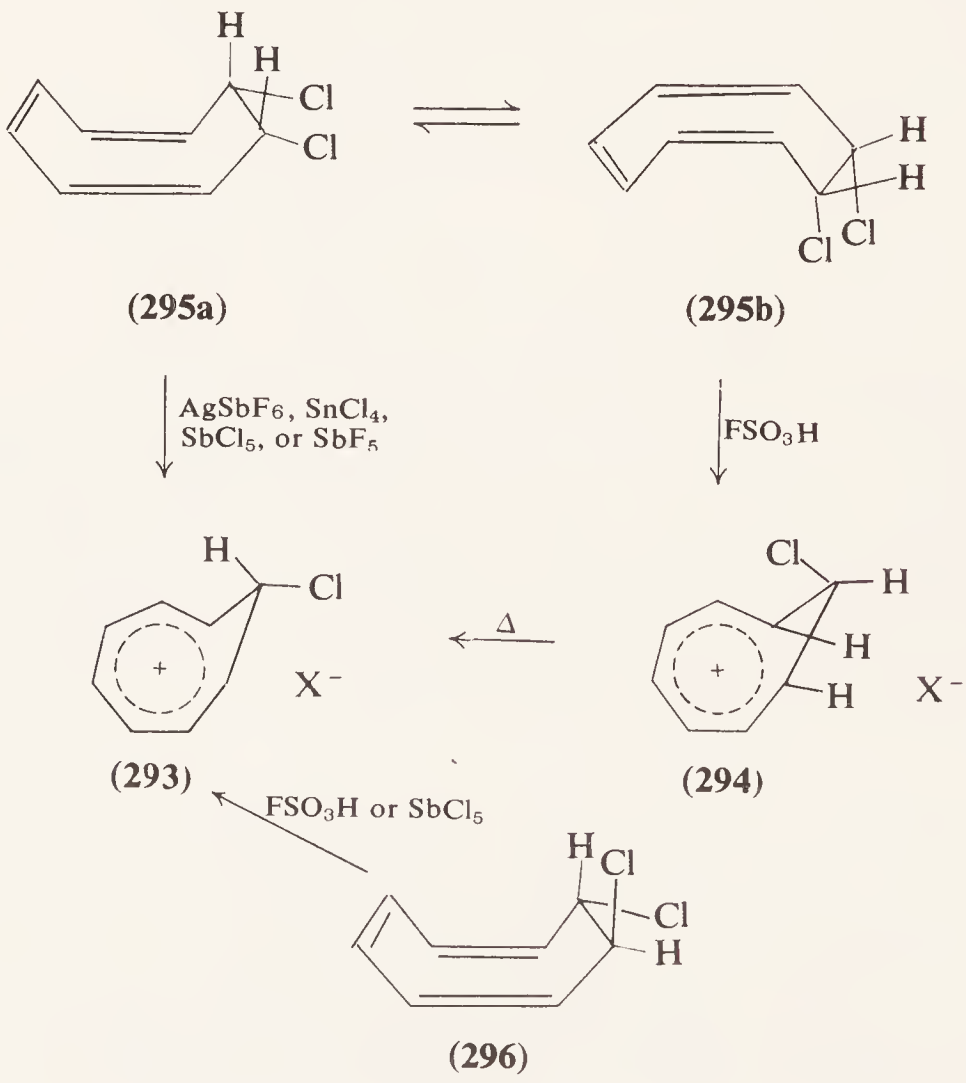
(291) **(292)**

found that the differences in chemical shift between the inside and outside protons ($\Delta H_a H_b$) for the ketone **291** in sulfur dioxide and for the conjugate acid **292** were 0.81 and 3.1 ppm, respectively. Winstein concludes that this 2.3-ppm difference is large enough to justify assigning the homotropylium structure to **292** and, therefore, that the powerful electron-releasing hydroxyl substituent does not convert the cation to a classical species (169).

The structural assignment for **292** is strengthened by the observation that starting ketone **291** can be regenerated from it. Comparison of the ultraviolet and nmr spectra of **292** with those of the conjugate acid of tropone also lent support.

The recent report of the generation of stable *exo*- and *endo*-8-chlorohomotropylium salts **293** and **294** (170) further substantiates some of the earlier work of Winstein and of Pettit. Fluorosulfonic acid, it appears, selectively attacks the *endo* conformer (**295b**) of *cis*-7,8-dichlorocycloocta-1,3,5-triene to yield the *endo*-8-chlorohomotropylium salt (**294**). The *exo* salt **293** can be generated by a variety of reagents from the dichlorotriene conformer **295a** or by removal of the *endo* chlorine from *trans*-7,8-dichlorocyclooctatriene (**296**) using either stannic pentachloride or fluorosulfonic acid. The selectivity and the kinetical control of the ionizations are not explained (170).

If allowance is made for the effect of chlorine, the nmr spectra of **293**



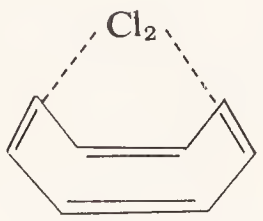
(295a) **(295b)**

(293) **(294)**

(296)

and **294** are in accord with the previously described spectrum of homotropylium cation (**276**). The triplet assigned to the *endo*-8-hydrogen is shifted upfield to $\tau = 8.2$ by the aromatic ring current, whereas the *exo*-hydrogen is deshielded and is found $\tau = 2.5$. Total isomerization of the *endo* isomer **294** to the *exo* isomer **293** takes place if the solution of **294** is warmed to 30°. Nmr kinetic measurements for the first-order isomerization yield a value for $\Delta H^{\ddagger}$ of 24 kcal/mole. Huisgen (170) postulated that the isomerization takes place by ring inversion as previously discussed for the equilibration of *endo*-8-*d*-homotropylium cation (**288a**) (162).

The same communications (170) presented strong evidence that the *endo*-chlorohomotropylium cation **294** is an intermediate in the formation of the *cis*-dichloride **295**. It was found that *exo*-8-chlorohomotropylium ion (**293**) and the *endo*-isomer (**294**), when treated with tetraethylammonium chloride, yielded the *trans*-dichloride **296** and the *cis*-dichloride **295**, respectively. Therefore, it may be concluded that both homotropylium cations undergo *endo* attack by chloride anion. The initial chloronation is pictured as occurring through the *endo*-transition state (**297**) for maximum π overlap with the attaching electrophile. The second step, chloride anion attack on **294**, is believed to occur *endo*, since "π overlap between the orbitals at positions 1 and 7 of the homotropylium ion is substantially larger on the underside than on the side of the C-8 bridge" (170), as shown in **297a**; *cis* dichloride **295** results.



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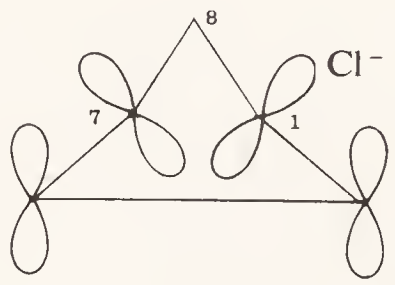
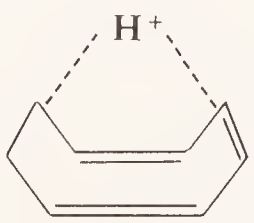


(297a)

Huisgen's observations in the case of chloronation of cyclooctatetraene seem to correlate with the findings of Winstein (162) and Pettit (159), in which deuteration of cyclooctatetraene and methylcyclooctatetraene occurred *endo*, from the direction of greater π overlap, as depicted in **298** and **299**. On the other hand, deuteration of the molybdenum complex



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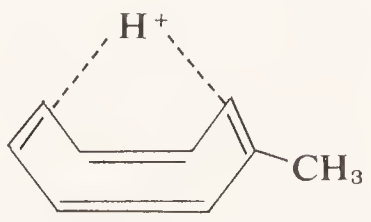
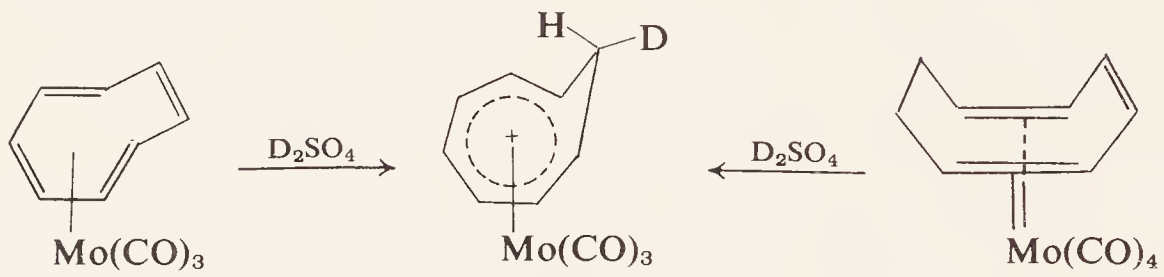


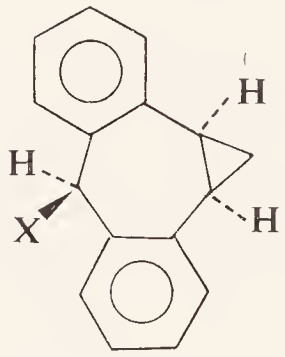
(299)

(**280**) initially gave the *exo*-deuterio compound **300**. Winstein has also observed exclusive *exo*-deuteration of cyclooctatetraenemolybdenum tetracarbonyl (**301**), which exists, most likely, in the tub conformation, to give with simultaneous loss of carbon monoxide, the monohomotropylium cation (**300**) (171).



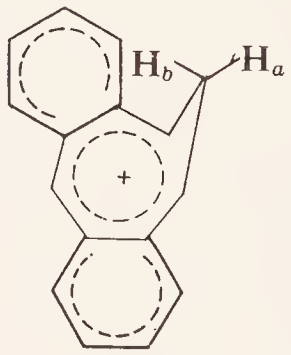
(280) **(300)** **(301)**

In an effort to observe the effect of benzene rings on the monohomotropylium cation, Winstein studied the *cis*-dibenzohomotropyl derivative **302a** (172). Treatment of compound **302a** with strong acid yielded the substituted homotropylium cation **303**, for which the nmr data were in accord with a strong ring current in the *B* ring, as assessed by the usual large chemical shift for inside and outside protons ($\Delta H_a H_b$ = 4.7 ppm).



(302)

(302a) X = —OH;
(302b) X = —OCH_3

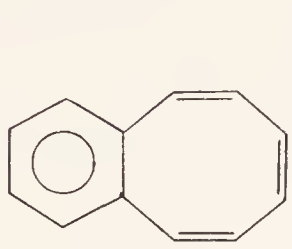


(303)

The structure proposed for **303** was further substantiated by quenching a sulfuric acid solution of **303** in methanol to yield the starting ether derivative **302b**.

The case for a strong homoaromatic interaction in the benzohomotropylium cation (**304**), prepared from benzocyclooctatetraene (**305**), is somewhat weaker (173). The $\Delta H_a H_b$ value was found to be 3.9 ppm; however, part of this difference was ascribed to the "nonsymmetrical disposition of H_a and H_b with respect to the benzene nucleus" (173). Part of the chemical shift between H_a and H_b was probably due to homo-

tropylium character, however, since the classical 4π–5C complex (**306**) exhibited a $\Delta H_a H_b$ of only 1.6 ppm. The case for **304** is also weakened by the absence of quenching or regeneration experiments.



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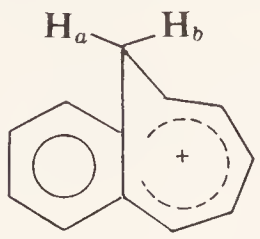

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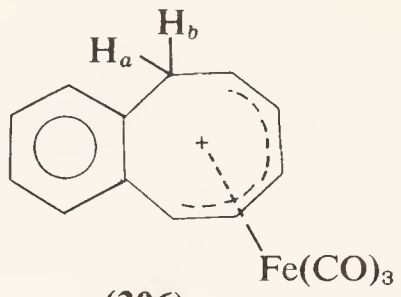

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CHAPTER 24

The 2-Norbornyl Cation

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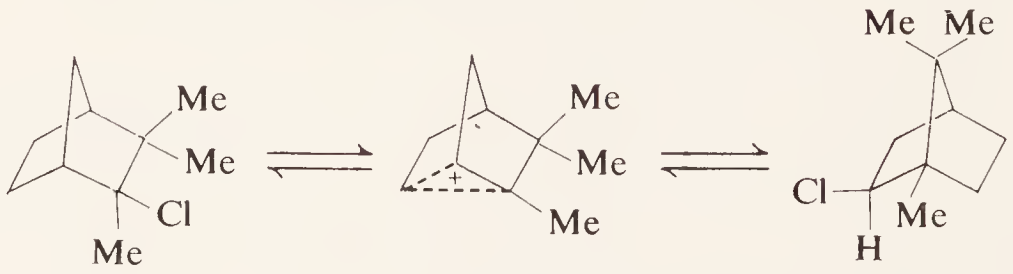
I. INTRODUCTION

The 2-norbornyl cation may well be the most thoroughly investigated yet least thoroughly understood reactive intermediate known to organic chemists. Seldom, if ever, has a single species been the subject of so many ingenious experiments conceived by so many eminent investigators utilizing such a variety of sophisticated methods. Despite the intensity of this effort, the structure of the 2-norbornyl cation remains an enigma.

In 1939 Wilson et al. (1) advanced the hypothesis that a mesomeric, bridged ion (**2**)* is involved in the rearrangement of camphene hydro-



(**1**) (**2**) (**3**)

* The actual formalism (**2**) was first advanced by H. B. Watson (2), who attributed the initial suggestion of a mesomeric intermediate to Sir C. K. Ingold.

chloride (**1**) to isobornyl chloride (**3**) (3,4). This suggestion, which in recent years has been the source of intense controversy, brought forth little comment and no effort at experimental verification for a decade. Not until publication of the elegant and exhaustively thorough studies of Winstein and Trifan (5,6) on the solvolysis of the epimeric 2-norbornyl brosylates did this proposal receive a firm experimental foundation. The substance of this investigation and its further elaboration by the Winstein school (7,8) have received extensive review (9–17) and need only be summarized here.

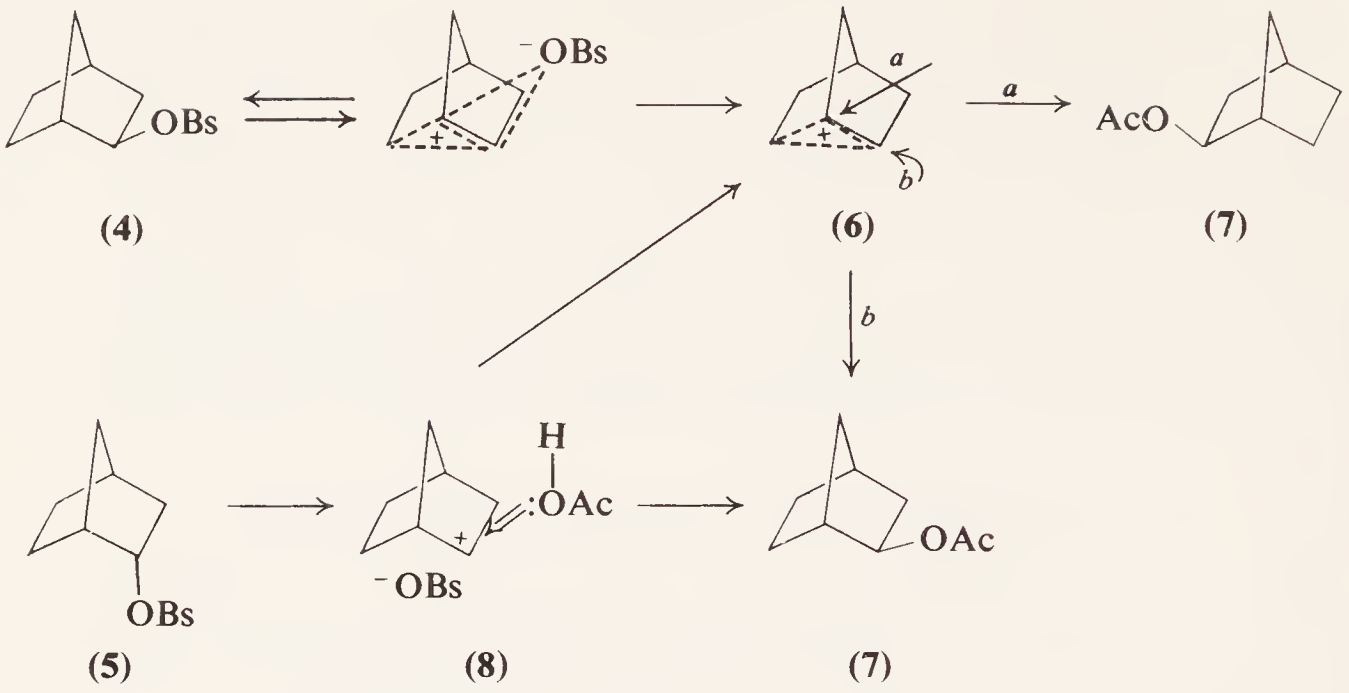
A. Solvolysis of 2-Norbornyl Arenesulphonates

Winstein and Trifan (5–7) found that the rate of solvolysis of *exo*-2-norbornyl brosylate (*p*-bromobenzenesulfonate) (**4**) relative to that of the *endo*-epimer was 350 in acetic acid at 25°C. The product of solvolysis of *exo*-2-norbornyl brosylate in acetic acid, ethanol, or aqueous acetone was found in all cases to possess only the *exo* configuration. When optically active brosylate was employed, the product was completely racemic, and the rate of racemization exceeded the rate of solvolysis, as determined by the rate of formation of *p*-bromobenzenesulfonic acid. The ratio of polarimetric to titrimetric rate constants, which decreased with increasing Y value (18) for a series of solvents, ranged from 3.46 in acetic acid to 1.40 in 75% aqueous acetone (19).

The solvolysis of *endo*-2-norbornyl brosylate (**5**) also yielded products with solely the *exo* configuration. In contrast to the behavior of the *exo*-epimer, optically active *endo*-2-norbornyl brosylate yielded product in which 7 to 8% of the optical activity was retained. In this case, no significant difference between the rate of racemization and rate of formation of *p*-bromobenzensulfonic acid was observed.

Reinvestigation (8) of the products of acetolysis of the epimeric 2-norbornyl brosylates using vapor-phase chromatography confirmed the exclusive *exo* stereochemistry of the substitution products, but revealed that significant elimination accompanies solvolysis. At 25° *exo*-norbornyl brosylate on acetolysis yields 95.6% acetate and 4.4% hydrocarbon; at 75° the *endo* brosylate gives rise to a product mixture composed of 87.3% acetate and 12.7% hydrocarbon. The acetate product in both cases is more than 99.7% *exo*-2-norbornyl acetate. The hydrocarbon product is a mixture of nortricyclene and norbornene in the approximate ratio of 39:1 (20).

Winstein and Trifan argued that the enhanced rate of solvolysis of the *exo*-epimer relative to that of *endo*-2-norbornyl brosylate could only be explained in terms of an intramolecular displacement reaction involving nucleophilic attack by the electrons of the C-6–C-1 σ bond on C-2 during heterolysis of the C-2–O bond in the *exo*-epimer. Since stereoelectronic considerations require "backside" attack in direct nucleophilic displace-



ment reactions*, participation of the C-6–C-1 bond during heterolysis of *endo*-2-norbornyl brosylate is geometrically prohibited. In principle, comparable participation by the C-1–C-7 σ bond is stereoelectronically feasible during solvolysis of the *endo* brosylate, but such participation would involve further straining the already highly strained five-membered ring formed by carbon atoms 1, 2, 3, 4, and 7 of the norbornyl nucleus. This increase in strain might well be expected to more than offset the decrease in free energy associated with σ-electron delocalization (5–7, 16,17).

Winstein and Trifan further contended that the symmetrical bridged ion (**6**) is most likely both the direct product of ionization of the *exo* brosylate and the immediate precursor of the product *exo*-acetate (**7**). This conclusion followed from their analysis of the discrepancy between polarimetric and titrimetric rate constants as a function of solvent nucleophilicity. These data are best interpreted in terms of initial ionization to an intimate ion pair (21,22),† whose cationic fragment must already possess either a symmetrical structure or a totally equilibrated pair of enantiomeric structures. This ion pair is capable of collapsing to give *racemic* brosylate; or, less frequently, it may react with solvent to form product. The relative frequency of product formation should, of course, increase with increasing nucleophilicity of the solvent, and this relationship was, in fact, observed.

Winstein and Trifan conceded that at least three alternatives to the formation of a symmetrical bridged ion (**6**) could lead to racemization within the ion pair itself. A Wagner-Meerwein migration of C-6 from C-1

* For a discussion of this point and leading references, see Ref. 17, pages 5–7.

† For a discussion of the role of ion pairs in solvolytic reactions, together with leading references, see Refs. 21 and 22.

to C-2, a hydride shift from C-3 to C-2, or a 1,3 hydride shift from C-6 to C-2 all convert a classical 2-norbornyl cation into its enantiomer. If any of these processes were rapid relative to ion-pair collapse, the observed optical behavior could be explained in terms of classical carbonium ions alone. None of these processes can account for the observed ionization rate differential between the *exo*- and *endo*-brosylates, however.

Winstein and Trifan also argued that a bridged structure was necessary to explain the absolute stereospecificity observed for both product formation and ion-pair return during solvolysis of *exo*-2-norbornyl brosylate. A classical 2-norbornyl cation would be expected to give at least some *endo*-2-norbornyl acetate; in fact, *all other factors being equal*, a definite preference for *endo* attack might be expected to result both from backside solvent participation in the ionization process and from leaving-group shielding to *exo* solvent attack on the classical carbonium ion.* The bridged ion (**6**), on the other hand, can react only by backside nucleophilic attack on one of the atomic orbitals involved in the multicenter bond. Attack in this manner at either C-1 or C-2 perforce yields only *exo*-2-norbornyl acetate.

Solvolysis of *endo*-2-norbornyl brosylate (**5**) was postulated to proceed via unassisted ionization to a classical 2-norbornyl cation coordinated with solvent on the side opposite to the departing group (**8**). It was then envisaged that this ion either reacted directly with the coordinated solvent molecule to give optically active *exo*-acetate or, to a much larger extent, rearranged to the symmetrical bridged ion (**6**). Rearrangement to the bridged ion (**6**) was regarded as necessary to explain the abnormally high degree of racemization and absolute stereospecificity attending the formation of products in solvolysis of the *endo*-brosylate. On the basis of the observed kinetics of this reaction, together with the kinetics of racemization and solvolysis of the *exo*-epimer, Winstein and Trifan were able to exclude a number of possible alternative explanations for this behavior.

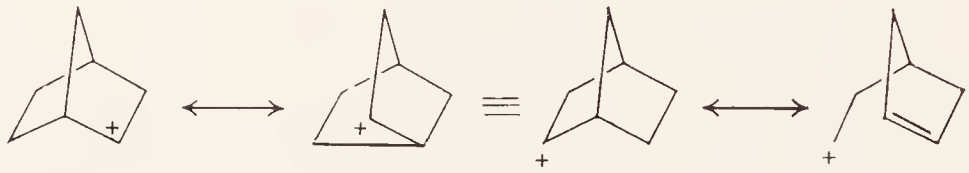
B. Formulation of the Nonclassical 2-Norbornyl Cation

The dashed lines drawn in structural formulas **2** and **6** were intended by the original proponents of these structures to represent "partial" covalent bonding between the atoms connected by the lines. The somewhat ambiguous designation of "partial bonding" has been further confused by

* In this context, it is pertinent to note that even α-phenylneopentyl tosylate on acetolysis yields the corresponding acetate with 10% net inversion of configuration. Not only must this system offer severe hindrance to backside solvent approach during ionization, it unequivocably proceeds through a reactive intermediate which, being benzylic in nature, presumably has a planar configuration at the site of ionization. For an extensive discussion of this general phenomenon, see Ref. 17, pp. 59 et seq.

the tendency of different authors, and even the same author at different times, to represent the same structural concept by means of formulas with a varying number of dashed lines. Thus Winstein and Trifan first (5) formulated the 2-norbornyl nonclassical cation with two dashed lines (**9**) in a manner directly analogous to structure **2**; but subsequently (6,7) they adopted a formulation containing three dashed lines (**6**).

(9) **(6)**

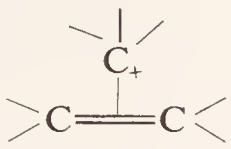


(6a) **(6b)** **(6c)**

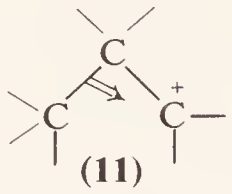
Several other formulations for ions of this type have been offered (23–25), but none has been put to extensive use.

Winstein's introduction of the third dashed line in **6** was neither arbitrary nor capricious. It was designed to suggest explicitly the contribution of a third canonical form (**6c**) to this mesomeric cation. The previous formulation of this ion (**9**), like the formulation **2** (2) for the analogous mesomeric ion postulated by Wilson et al. (1), represented contributions from only canonical forms **6a** and **6b**.

Although no direct chemical evidence for contributions of form **6c** to the mesomeric hybrid was available at the time formulation **6** was first presented, this formulation did reflect, without discriminating between them, the suggestions of both Dewar (23) and Walsh (27) regarding the bonding in such an ion. Dewar believed that this bonding consisted of a dative bond between a pair of π electrons and a bridging atom that "maintained its valency and stereochemistry." This concept was formulated as **10**. Dewar further asserted that only π electrons were capable of such dative bonding, since σ electrons were inhibited sterically from such participation. Walsh (27) disagreed and maintained that the bonding in ions such as **6** is best described in terms of dative bonding from a pair of σ electrons to the third atom, a concept which might be formulated as **11**. Walsh (27) also appears to have been first to suggest a direct analogy between the bonding in nonclassical carbonium ions and that in the boron hydrides (28), with which these ions are isoelectronic. Ingold (29) also conceived of the bridged ion as involving a strong interaction between carbon–carbon bond σ electrons and the cationic center. He introduced the term "synartetic ion" for such species, which he described as possessing "a split single bond *fastening together* the locations of a split ionic charge."



(10)



(11)

It is important to note that, although the Dewar and the Walsh-Ingold descriptions of bonding in a nonclassical ion differ on the state of hybridization of the three atoms bearing the electron deficiency, they are in complete accord in suggesting that *each of the three atoms sharing the electron deficiency is directly bound to the other two by means of a single electron-pair bond.* This description requires direct overlap not only between a single atomic orbital of C-6 and suitably oriented atomic orbitals at both C-1 and C-2 in **6**, but also direct overlap between these latter two orbitals as well. The dashed line between C-1 and C-2 in **6** thus represents a finite contribution of this direct overlap between atomic orbitals on C-1 and C-2 to the molecular orbital formed by the linear combination of atomic orbitals on C-1, C-2, and C-6. In this manner the dashed line takes on a definite significance analogous to the familiar solid line in organic structural formulas. *Throughout this chapter, a dashed line is employed to represent the overlap of two atomic orbitals, where each atomic orbital contributes to a multicenter molecular orbital containing two electrons*; a solid line represents the overlap of two atomic orbitals where each contributes to a two-centered molecular orbital containing two electrons.

From the foregoing discussion, we can conclude that the defining characteristic of the nonclassical (30), bridged, synartetic (29), or mesomeric (1) 2-norbornyl cation, as formulated by Winstein and Trifan (6,7) (**6**), is the delocalization of *sigma*-bonding electrons (9,11). (In conformity with our prior suggestion (9), we refer to **6** as a bridged cation.) A possible orbital structure for **6**, as suggested by Streitwieser (31), is presented in Figure 1.

The application of extended Hückel theory (32) to the 2-norbornyl cation problem suggests a structure very similar to that of Figure 1, except that minimum energy is obtained when C-6 is sp^2 hybridized (33). This

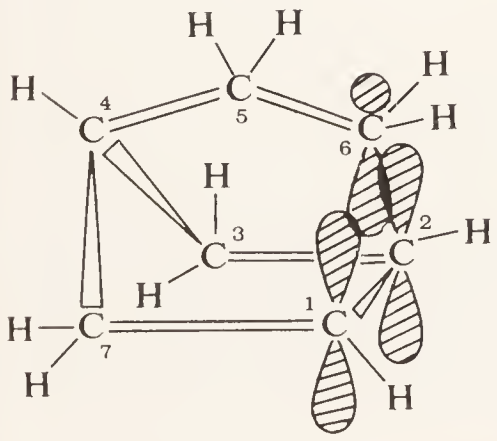


Fig. 1. Possible orbital structure of the nonclassical bridged 2-norbornyl cation [after Streitwieser (31)].

calculation attributes a stabilization of 51 kcal/mole to the bridged structure relative to a wholly classical structure for the 2-norbornyl cation. Since this energy differential appears unreasonably large even to its author, and since the calculation perforce ignores the influence of solvation, the significance of this result must remain in question.

C. Objections to the Bridged-Ion Postulate

Over the last few years, increasing opposition has been raised to the bridged formulation (**6**) of the 2-norbornyl cation. The nature of, and the basis for, this opposition have been summarized in three reviews by Brown (34–36), who is by far the most outspoken and most articulate advocate of this position. Brown's position may be summarized briefly as follows: (*1*) the observed *exo*/*endo* rate ratio for the solvolysis of the 2-norbornyl brosylates, rather than resulting from an enhanced rate for the *exo*-epimer as suggested by Winstein and Trifan (5–7), may be due to a retarded rate for the *endo*-epimer; (*2*) the peculiar U-shaped structure of the norbornyl nucleus might well abnormally hinder *endo* approach to a classical 2-norbornyl cation and thus result in the exclusive formation of *exo* derivatives as products; (*3*) the skeletal rearrangements attendant upon generation of the 2-norbornyl cation (discussed later) could result from the rapid equilibration of two enantiomeric classical cations as well as from the intervention of a symmetrical bridged ion; (*4*) efforts to confirm the charge delocalization implicit in the bridged structure (**6**) have in several cases proven unsuccessful; (*5*) efforts to confirm the special stability attributed to **6** relative to the classical 2-norbornyl cation have not succeeded. The questions raised when Brown's neoclassical thesis is juxtaposed with the earlier nonclassical concept of the 2-norbornyl cation have generated considerable experimental effort in recent years. There are four principal questions to which this work has been addressed:

1. Is the 2-norbornyl cation a single symmetrical species or is it a rapidly equilibrating mixture of enantiomers?
2. Does the *exo* orientation of products derived from the 2-norbornyl cation result from stereoelectronic or from steric prohibition to *endo* attack?
3. Is the rate of solvolysis accelerated for *exo*-2-norbornyl derivatives or is it retarded for *endo*-2-norbornyl derivatives?
4. Is the 2-norbornyl cation a charge-delocalized species or a charge-localized species?

In surveying the chemistry of the 2-norbornyl cation and its analogs, it is well to keep these questions clearly in mind. Were any of these questions to be answered unambiguously, the storm of controversy now surrounding

the structure of the 2-norbornyl cation would considerably abate, if not dissipate altogether.

II. HYDRIDE SHIFTS

A. 6,2 (6,1) Hydride Shifts

The structural rearrangement required by the intervention of the symmetrical bridged ion (**6**) was subjected to experimental scrutiny by Roberts, Lee, and Saunders (30,37). *Exo*-2-norbornyl brosylate labeled with ^{14}C at the 2- and 3-positions was subjected to acetolysis, and the product, *exo*-2-norbornyl acetate, was systematically degraded. If racemization of optically active brosylate results either from intervation of the bridged ion (**6**) or from rapid equilibration of a classical 2-norbornyl cation with its enantiomer by means of a Wagner-Meerwein migration of C-6 from C-1 to C-2, 25% of the total initial ^{14}C should be found at each of the 1-, 2-, 3-, and 7-positions in the acetate produced. The experimental result is presented in Table I.

TABLE I

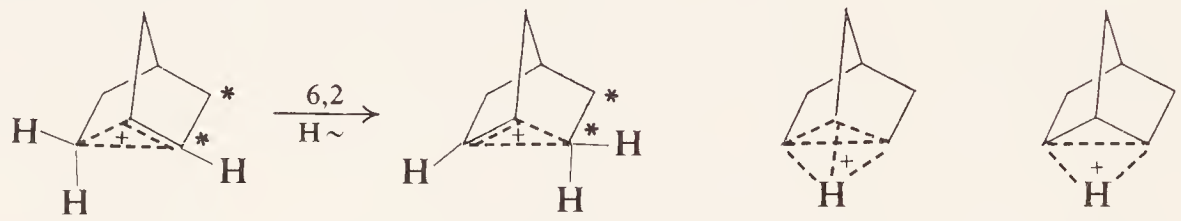
Calculated and Experimental Isotopic Distributions for the 2-Norbornyl Acetate Formed on Acetolysis of *exo*-2-Norbornyl [2,3-$^{14}C_2$]-Brosylate

	^{14}C Activity, %			
Calculated for	C-2 + C-3	C-1 + C-4	C-7	C-5 + C-6
Bridged ion (**6**)	50	25	25	0
6,2 Hydride shift	50	0	0	50
3,2 Hydride shift	100	0	0	0
Nortricyclonium ion (**12**)	33	17	17	33
55% (**6**) and 45% (**12**)	42.5	21.25	21.25	15
Found (30, 37)	40	23	22	15

This result clearly establishes that the complete racemization attending solvolysis of the *exo*-brosylate cannot result primarily either from a 6,2 hydride shift or from a 3,2 hydride shift; however, the presence of ^{14}C at positions 5 and 6 in the product acetate establishes beyond question that 6,2 hydride migrations do occur to a significant extent during this reaction. To account for the observed ^{14}C distribution, Roberts et al. suggested the intervention of an even more highly symmetrical ion than the bridged ion (**6**), namely, the nortricyclonium ion **12**, in which carbon atoms 1, 2, and 6 are totally equivalent. Nucleophilic attack by solvent at any of these positions

leads to racemic *exo*-2-norbornyl acetate. The ^{14}C distribution could be fitted within the limits of experimental error by assuming that the initial formation of **6** was followed by partial rearrangement to **12** to the extent of 45% in acetic acid. Since rearrangement to **12** would be expected to compete more favorably with reaction of **6** with solvent in less nucleophilic solvents, this hypothesis is consistent with the experimental observation (30,37) that ^{14}C scrambling is more extensive in formic acid but significantly restricted in aqueous acetone.

Roberts et al. regarded **12** as an intermediate; but Winstein and Trifan (6) had argued, and Roberts (37) agreed, that ^{14}C scrambling could also be interpreted as arising from the interconversion of one bridged ion (**6**) into another (**6a**) by means of 6,2 and 6,1 hydride shifts. [Positions 1 and 2 on the norbornyl nucleus are totally equivalent in the bridged ion (**6**).] The two bridged ions **6** and **6a** are identical except for the position of radioactive carbon.

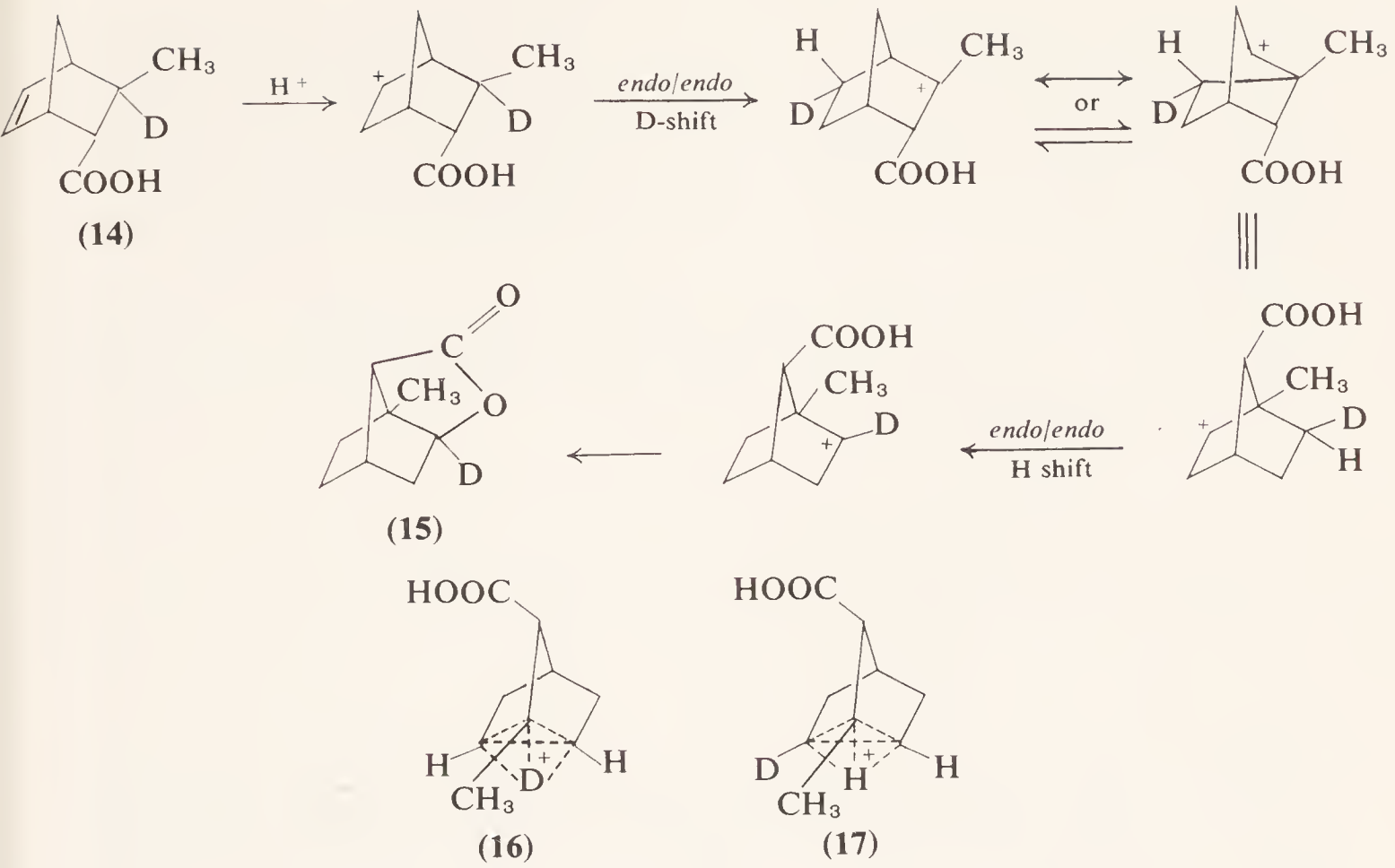


(6) (6a) (12) (13)

Winstein and Trifan (6,38) suggested that an "edge-protonated" cyclopropane intermediate or transition state (**13**) might well be involved in this transformation, rather than the "face-protonated" cyclopropane species, the nortricyclonium ion **12**, suggested by Roberts (30,37).

Although there is no experimental evidence which permits a distinction between these two hypotheses for the parent 2-norbornyl cation, the intervention of a nortricyclonium-type intermediate or transition state is inconsistent with the observed behavior of two substituted 2-norbornyl cations. Treatment of acid (**14**) with 50% sulfuric acid results in formation of lactone (**15**), which was shown to be contaminated by less than 3% of the analogous C-2 protio species (39). This result is consistent with the following sequence of reactions, where the cations are shown as classical for clarity, but which would be equally valid for bridged species. The formation of **15** would be inconsistent with the formulation of the transition states for the initial D shift (**16**) and the subsequent H shift (**17**) as nortricyclonium ions, since it is inconceivable that **17** could lead exclusively to 2-deuterio lactone (**15**), while **16**, which differs only in the location of deuterium, could be totally prohibited from yielding 2-protio lactone.

Similarly, Collins and Benjamin (40,41) have shown that the hydride-shifted products derived from the solvolysis of tosylates **18** and **19** must


CH3
D
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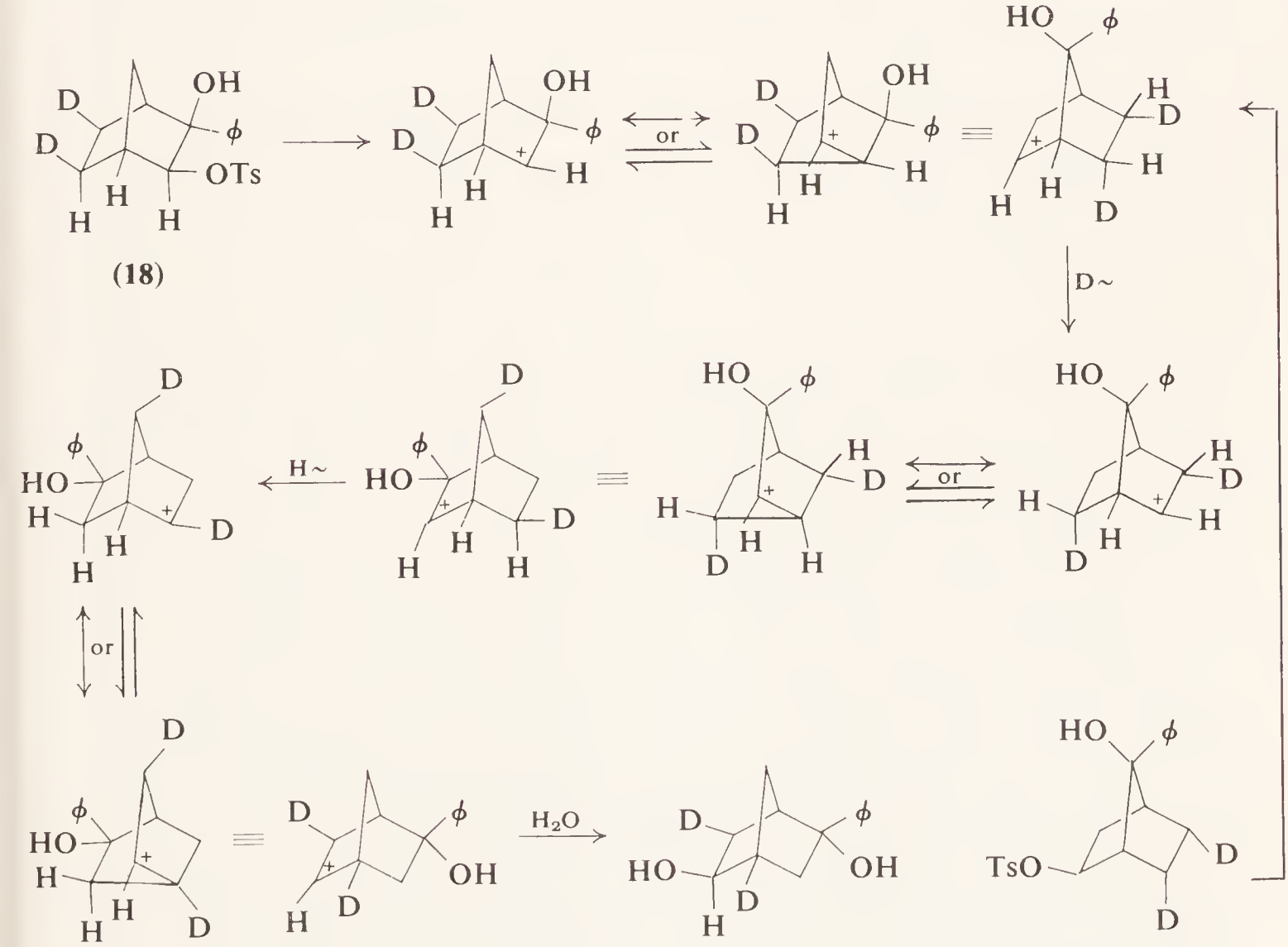
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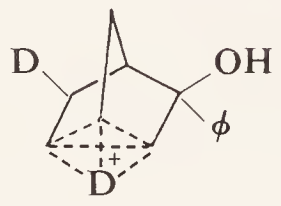
arise from discrete consecutive steps (6,1, 6,2, and 1,2 hydride shifts), a result incompatible with "face-protonated" nortricyclonium ions as intermediates or transition states. For example, solvolysis of tosylate **18** in aqueous acetone at 100° yields, among several products, alcohol **20**. The preceding sequence is proposed as the most economical rationale for this observation.

The structures **21** and **22** constitute the only rational "face-protonated" ("face-deuterated") species that could be postulated to intervene during solvolysis of tosylate **18**.



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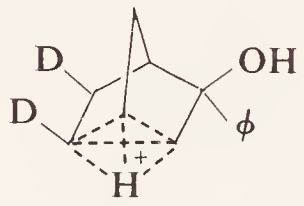


(22)

Since it is inconceivable that **21** could yield products containing bridgehead deuterium, and since it is equally implausible that **22** could yield products bearing deuterium on nonadjacent carbon atoms, the observed formation of alcohol (**20**) precludes consideration of these two species as the sole precursors for hydrogen (deuterium) shifted products.

B. 3,2 Hydride Shifts: Their Rate Relative to 6,2 (6,1) Shifts

Dills (42) has demonstrated that the data of Roberts et al. (30,37) for the ^{14}C isotopic distribution in the product of formolysis of a mixture of *exo*- and *endo*-2-norbornyl (2,3-$^{14}C_2$) brosylates cannot be accounted for solely on the basis of the skeletal rearrangements implied by **12**, considered either as an intermediate or as a transition state; and he has calculated the extent to which 3,2 hydride shifts must occur to explain the data quantitatively. Roberts et al. (30,37) had logically demonstrated that 3,2 hydride shifts do not occur during acetolysis of the *exo*-brosylate.

An elegant investigation involving the direct observation of the 2-norbornyl cation by the technique of nuclear magnetic resonance (43–45) has recently shed further light on the 3,2 and 6,2 (6,1) hydride shifts attending the formation of that ion. The nmr spectrum of the ion, generated as the SbF_6^- salt by dissolution of 2-norbornyl fluoride or chloride in SbF_5 or a mixture of SbF_5 and liquid SO_2, is markedly and significantly temperature dependent. At $-120°$ the 60 MHz nmr spectrum of 2-norbornyl fluoride dissolved in a mixture of SbF_5, SO_2, and SO_2F_2 consists of three peaks: -321 (relative area, 4); -189 (relative area, 1); and -132 (relative area, 6) Hz from external tetramethylsilane. Above $-60°$ these peaks begin to broaden, and at $-23°$ they coalesce to a single peak. The

high-temperature spectrum is interpreted to indicate time-average equivalence of all protons in the 2-norbornyl cation. Such equivalence is possible only if three events are occurring rapidly and simultaneously: (*1*) the formation of a bridged ion (**6**) or the rapidly reversible Wagner-Meerwein migration of C-6 from C-1 to C-2, (*2*) hydride migration from C-6 to C-2 (or C-1), and (*3*) hydride migration from C-3 to C-2. The low-temperature spectrum is postulated to arise as a result of a diminished rate for the third of these events. The result of this "freezing out" of the C-3, C-2 hydride migrations is the generation of three magnetically distinct sets of protons: the four protons bonded to C-1, C-2, and C-6; the single proton bonded to C-4; and the six protons bonded to C-3, C-5, and C-7.

From the temperature dependence of the spectrum, one can determine a rate constant for the 3,2 hydride migrations as a function of temperature. This rate constant has the value of 10^4 sec^{-1} at 12.9° and 72 sec^{-1} at −46°. The activation enthalpy for this shift is found to be 10.8 ± 0.6 kcal/mole. By making the arbitrary assumption that the rate of Wagner-Meerwein migration (or bridged-ion formation) equals the rate of 6,2 (or 6,1) hydride shift, Saunders et al. (44) were able to calculate that the rate constant for these processes must exceed 3×10^5 sec^{-1} even at −120°. If the preexponential factor were 10^{13} for these processes, this rate would correspond to an activation energy of less than 5.5 kcal/mole. Furthermore, comparison of the minimum rate for the 6,2 hydride shift with that for the 3,2 hydride shift extrapolated to −120° demonstrates that the former exceeds the latter by at least a factor of $10^{8.8}$. Unfortunately, these experiments are unable even to suggest whether the 2-norbornyl cation under these conditions exists as a bridged ion or as a rapidly equilibrating pair of enantiomeric classical ions.

NOTE ADDED IN PROOF: For the results and discussion of more recent spectroscopic investigations of the 2-norbornyl cation and some substituted 2-norbornyl cations, see Refs. 203–212.

Lee and Lam (46) have recently provided additional data bearing on the structural rearrangements that accompany generation of the 2-norbornyl cation. By systematic degradation of the product of solvolysis of *exo*- and *endo*-2-^{3}H-2-norbornyl brosylate, they were able to determine what percentage of that product arose from cations that had attained each of three varying degrees of symmetry: (*1*) C-1 and C-2 equivalent; (*2*) C-1, C-2, and C-6 equivalent; and (*3*) all carbon atoms equivalent. These data, for both acetolysis and formolysis, are presented in Table II.

Equivalence of C-1 and C-2, of course, results simply from the formation of the bridged ion (**6**) or from the rapid equilibration of the two Wagner-Meerwein related enantiomers of the classical 2-norbornyl cation. Equivalence of C-1, C-2, and C-6 requires the additional intervention of

TABLE II

Extent of Rearrangement Accompanying Generation of the 2-Norbornyl Cation Calculated for Tritium Distribution in the Solvolysis Product of *exo*- and *endo*-2-Norbornyl-2-^{3}H-Brosylate (46)

Consequence of Rearrangement	Contribution, %			
	Acetolysis			
	exo		*endo*	Formolysis
	25°	45°	reflux	*exo*, 25°
C-1, C-2 equivalent	45	55	43	43
C-1, C-2, C-6 equivalent	45	38	47	22
Complete equivalence	10	7	5	35

6,2 (6,1) hydride shifts; for total equivalence, the additional intervention of both 6,2 and 3,2 hydride shifts is needed. The results of Lee and Lam (46) are in accord with the earlier results of Roberts and co-workers (30,37), which they complement, in demonstrating both that 6,2 hydride shifts are highly competitive with solvent capture of the 2-norbornyl cation and that the intrusion of 3,2 hydride shifts is much more pronounced in the less nucleophilic solvent, formic acid. In contrast to the earlier work (30,37), however, these data suggest that even in acetic acid, 3,2 hydride shifts occur to a significant extent prior to attack by solvent on the 2-norbornyl cation. Of particular interest is the experimentally significant *decrease* in the percentage of product derived from 6,2 hydride shifts as the temperature is raised from 25 to 45°. This indicates that the activation energy for solvent capture of the 2-norbornyl cation exceeds that for the 6,2 hydride shift. From these data, Berson (47) calculates that solvent capture has the higher activation energy by 4.65 kcal/mole. This, of course, also represents the minimum absolute value for the activation energy for capture of the 2-norbornyl cation in acetic acid.

Both Collins and Lietzke (48) and Berson and co-workers (47) have subjected the ^{14}C data of Roberts and co-workers (30,37) and the tritium label data of Lee and Lam to detailed and sophisticated analysis. From these data they have been able to calculate the rate constants for the 3,2 and 6,2 hydrogen migrations relative to that for solvent capture of the 2-norbornyl cation. From the results of extensive work in his own laboratory on the chemistry of various methyl 2-norbornyl cations (47,49–52), Berson has been able also to estimate the relative rate constants for tertiary to secondary 3,2 and 6,2 hydride shifts. These data are presented in Table III.

TABLE III

Rates of 3,2 and 6,2 Hydrogen Migration Relative to Rate for Solvent Capture of the 2-Norbornyl Cation

	Reactant[a]	Solvent	Temperature °C	k_s/k_3[b]		k_s/k_6[b]	
				Ref. 48	Ref. 47	Ref. 48	Ref. 47
1.	*A*	HOAc, NaOAc	25	>20	—	1 ± 0.25	1.76
2.	*A*	HOAc NaOAc	45	>120	—	1.55 ± 0.35	2.88
3.	*B*	HOAc, NaOAc	45	>20		1.9 ± 0.6	2.7
4.	*B*	Aq. acetone	45	—	—	—	8.34
5.	*C*	HOAc, NaOAc	100	—	>122 8.7 (*t*, *s*)		
6.	*D*	HOAc, NaOAc	100	—	—	—	0.81 (*t*, *s*)
7.	*D*	Aq EtOH	100	—	—	—	2.18 (*t*, *s*)
8.	*A*	HCOOH, HCOONa	25	>30	—	1.25 ± 0.25	—
9.	*B*	HCOOH, HCOONa	Reflux	1.5 ± 1.0	—	0.17 ± 0.1	—

[a] *A* = *exo*-2-norbornyl-2-^{3}H-brosylate (46), *B* = *exo*-2-norbornyl[2,3-^{14}C] brosylate (30,37), *C* = *endo*-3-methyl-*exo*-2-norbornyl brosylate (47), *D* = *endo*-6-methyl-*exo*-2-norbornyl brosylate (52).

[b] k_s = Pseudo-first-order rate constant for capture of cation by solvent; k_3 = rate constant for 3,2 hydride shift; k_6 = rate constant for 6,2 (6,1) hydride shift. Unless otherwise indicated, k_3 and k_6 refer to migration from secondary carbon to secondary carbon; (*t*, *s*) indicates migration from tertiary to secondary carbon.

The agreement among comparable values of k_s/k_3 and k_s/k_6 in Table III is quite good, considering that the data were taken on four different compounds in three different laboratories and that the two methods of treating the data differed substantially. These data are in qualitative agreement with those determined by the nmr technique (44) for k_6/k_3; i.e., the 6,2 hydride shift occurs more rapidly in all cases than the 3,2 hydride shift. There is considerable uncertainty, however, regarding the quantitative accuracy of the values for k_3/k_s.

The best fit to the original isotope position data (30,37) that yielded the rate ratios listed in entry 3 of Table III also predicts 1% ^{14}C at C-3 of the product 2-norbornyl acetate. The data of Lee and Lam (46) at 25° (entry 1) also indicate the presence of 1% of the tritium label at C-3 of the acetolysis product. If we credit these findings, then k_6/k_3 is calculated to be equal to 10 to 20. Some uncertainty surrounds this result, however, since Collins

and Lietzke have demonstrated logically that the 5 to 6% tritium found at C-3 in the formolysis product of *exo*-2-norbornyl-2-^{3}H-brosylate must arise to a large extent from processes not involved in the initial solvolysis reaction. If such nonkinetically controlled products also arise in the acetolysis reactions, the calculated k_6/k_3 ratios would be too low. Entries 2 and 5 in Table III suggest that the *minimum* value for k_6/k_3 is in the range 30 to 80. Entries 8 and 9 suggest that k_6/k_3 is somewhat lower in formic acid (10–24) than in acetic acid. If the true value for k_6/k_3 in formic and acetic acids does lie between 10 and 100, as the data of Table III suggest, it would appear that the relative rate of these processes is not independent of solvent. This conclusion results from the observation (47) that extrapolation of the low-temperature nmr data (44) to 25–100° yields values of k_6/k_3 on the order of 4×10^3 to 3×10^4. If this difference in k_6/k_3 between non-hydroxylic media and hydroxylic media proves to be real, the past practice (53) of employing the rates observed by nmr techniques as approximations to rates under solvolytic conditions will have to be discontinued.

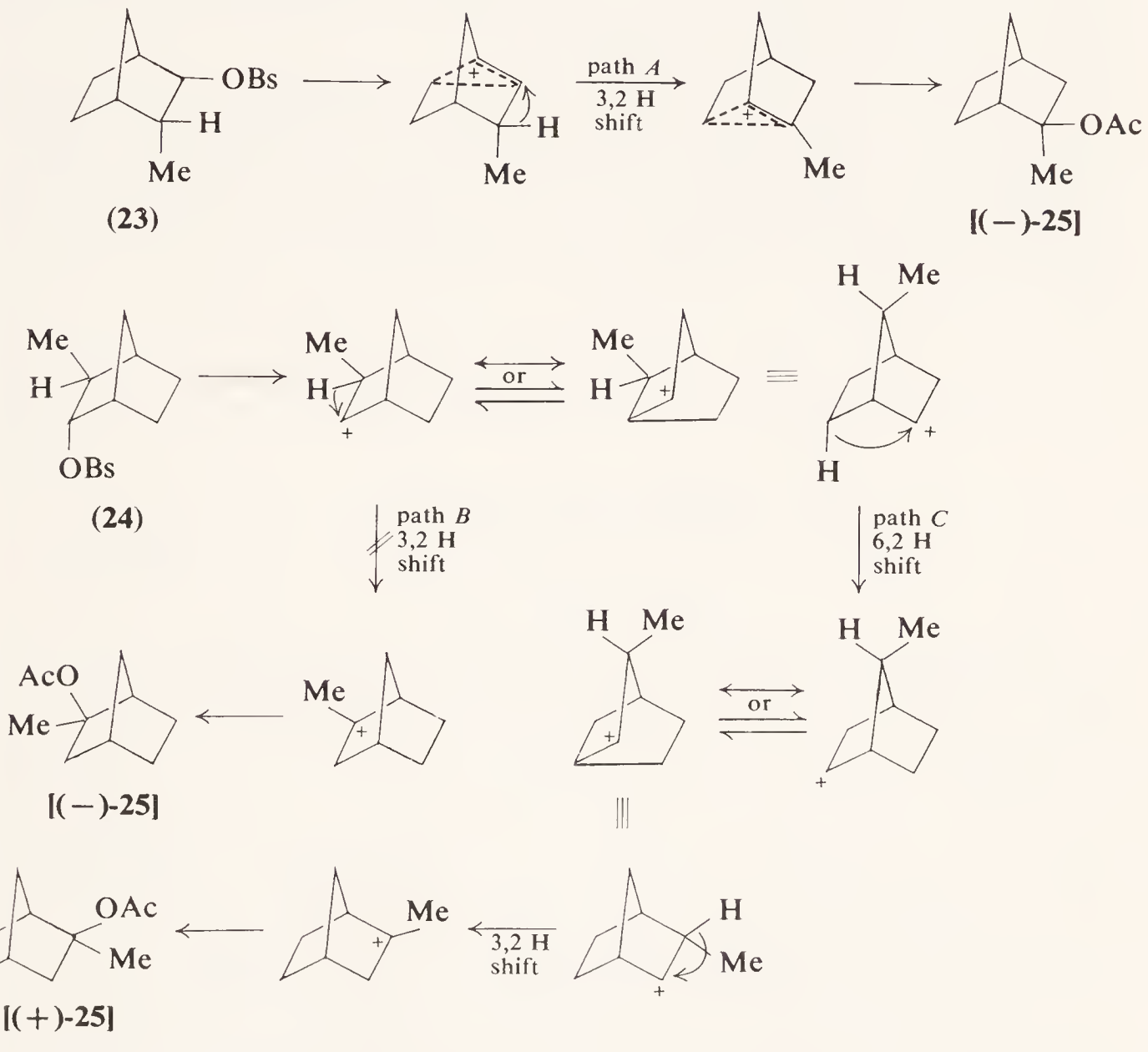
Entries 5 and 6 (cf. entry 3) lead to the interesting conclusion that the rates for hydride migration from tertiary carbon relative to those from secondary carbon lie between 5 and 15 for both 6,2 and 3,2 hydride shifts. (The upper value of the range for 6,2 shifts results from the estimation (47) that k_s/k_6 at 100° should be reduced by a factor of 3 for comparison with data taken at 45°.) Thus it is clearly implied that in the transition states for these migrations the donor carbon atom bears only a small fraction of the total positive charge associated with the cation. For the 6,2 shift, Berson et al. (47) have rationalized that this inference is consistent with an edge-protonated cyclopropane structure for the transition state. Theoretical calculations (54) suggest that most of the charge associated with such a structure is borne by the bridging proton. No rationale for the low sensitivity of 3,2 hydride shifts to alkyl substitution has been offered, although Berson and co-workers (52) have proposed possible molecular orbital models for the reaction.

C. Stereochemistry of 6,2 (6,1) and 3,2 Hydride Shifts

Another intriguing aspect of the chemistry of 6,2 and 3,2 hydride shifts in the 2-norbornyl cation is their remarkable and contrasting stereochemistry. In demonstrating the discrete and sequential nature of the 6,2 (6,1) hydride shifts in the reactions of acid **14** and tosylate **18**, both Berson and Grubb (37) and Collins and Benjamin (40) showed conclusively that these migrations exclusively follow an *endo*, *endo* pathway. By contrast, a number of investigations* have demonstrated that 3,2 shifts involve a strong, if not total preference for the *exo*, *exo* pathway.

* For a summary more complete than that presented here, see Refs. 16 and 55.

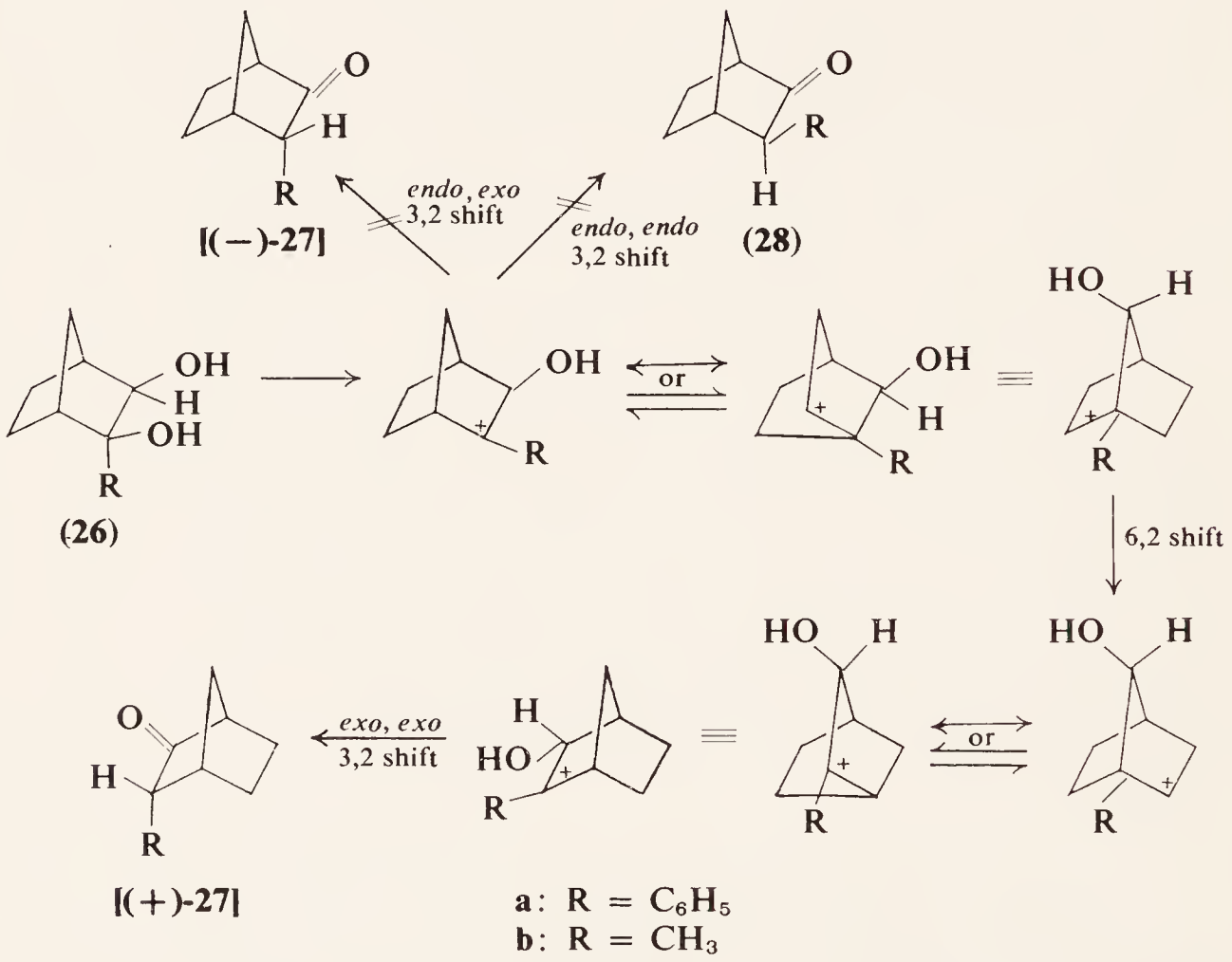
This preference has been established for 3,2 hydride migration in a secondary norbornyl cation most clearly and elegantly by Berson and his co-workers (49), who investigated the acetolysis of both 3-*endo*-methyl-2-*exo*-norbornyl brosylate (**23**) and 3-*exo*-methyl-2-*endo*-norbornyl brosylate (**24**). Both brosylates lead to a complex mixture of acetates, but a small percentage of 2-methyl-*exo*-2-norbornyl acetate (**25**) is formed from each. In each case, acetate **25** formally results from a 3,2 hydride shift in the



initially formed 3-methyl-2-norbornyl cation, followed by attack of acetate ion on the tertiary cation thus derived (paths *A* and *B*). By a series of careful stereochemical correlations, Berson and his co-workers were able to show that both the optically active brosylates **23** and **24** actually employed in the investigation would lead to the formation of levorotatory acetate **25** if the simple mechanistic pathway just outlined were followed. The sign and magnitude of rotation of acetate **25** formed on acetolysis of optically active 3-*endo*-methyl-2-*exo*-norbornyl brosylate (**23**) show that the compound is formed with 105 ± 5% retention of optical purity and that it belongs to the stereochemical series that results from direct *exo*-vicinal hydride shift in the 3-*endo*-methyl-2-norbornyl cation (path *A*). In

sharp contradistinction, acetolysis of 3-*exo*-methyl-2-*endo*-norbornyl brosylate (**24**) yielded dextrarotatory acetate **25**. The sterochemical inversion attendant upon formation of acetate **25** from brosylate **24** is most readily interpreted as resulting from the series of reactions outlined as path *C*. The magnitude of the rotation of the (+)-acetate **25** isolated from this reaction sets a minimum of 90% in selectivity of path *C* over path *B*. A more sophisticated analysis of his results led Berson to infer that the *exo*-vicinal hydride shift (path *A*) is at least 100 times more efficient than the *endo*-vincinal hydride shift (path *B*).

An equally detailed investigation of the mechanism of the pinacol rearrangement of 2-*endo*-phenyl-2,3-*cis*-*exo*-norbornanediol (**26a**) to 3-*endo*-phenyl-2-norbornanone (**27a**) (56) carried out by Collins and co-workers (57) provides evidence for strong preference for *exo*, *exo* 3,2 hydride migration in a tertiary norbornyl cation.



a: R = C_6H_5
b: R = CH_3

By employing optically active diol **26a**, Collins et al. established that the product of the reaction was not that which would result from a direct *endo*, *exo* 3,2 shift, (−)-ketone **27a**, but rather its enantiomer, (+)-ketone **27a**. By employing both ^{14}C and tritium labels, they also demonstrated that product formation did not involve phenyl migration but did occur with migration of the original 3-*endo*-hydrogen. Thus the reaction must involve an initial 6,2 shift followed by a subsequent *exo*, *exo* 3,2 shift as outlined. Since the product of a direct *endo*, *endo* 3,2 shift (**28a**) is thermodynamically more stable than ketone **27a**, and since there is no

reason to suspect that any of the intermediate cations formed along the route to the observed product should introduce an extraneous kinetic bias toward formation of ketone **27a**, the observed relative yield of ketone **27a** to ketone **28a** should provide at least a good first approximation to the preference for *exo*, *exo* over *endo*, *endo* migration for this system. This ratio is now estimated to be $\geqslant 200$.

More recently, Berson and co-workers (49) have found that *endo*-3-methyl-*cis*, *exo*-2,3-norbornanediol (**26b**) rearranges in aqueous sulfuric acid exclusively to *endo*-3-methyl-2-norbornanone (**27b**). As little as 0.03% of the epimeric ketone **28b** could have been detected in the product, but was not. Assuming that this reaction follows the pathway established for the phenyl analog **26a**, although this was not explicitly demonstrated, it is possible to calculate that the *exo*, *exo* pathway is preferred to the *endo*, *endo* by a factor of at least 3300.

A strong preference for *exo*, *exo* 3,2 methyl migration has been established for the 2,3,3-trimethylnorbornyl (58), 2,3,3-trimethyl-1-hydroxynorbornyl (59), and 2,3-dimethyl-3-β-carboxyethylnorbornyl (60) cations.

D. Interpretation of the Stereospecificity of 3,2 Hydride Shifts

1. The Bridged-Ion Postulate

The most widely advanced explanation for the high stereospecificity of 3,2 shifts involves the bridged-ion postulate (9,16,49,55–60). The bridged formulation of the 2-norbornyl cation requires that nucleophilic attack at C-2 (C-1) occur from the backside of the orbital involved in the multicentered bond (i.e., from the *exo* direction) by analogy to the stereochemical course of simple S_N2 displacement reactions (17). This restriction must perforce extend to the attack of intramolecular, as well as extramolecular, nucleophiles. Berson (49) has pointed out that more rigorous quantum mechanical arguments lead to the same expectation with respect to the stereochemistry of 3,2 migrations within a bridged ion. The strong preference for *exo*, *exo* 3,2 migration which is observed experimentally has thus been cited as evidence for the bridged-ion formulation, since, in a classical 2-norbornyl cation, the *exo* and *endo* substituents at C-3 would seem to be indistinguishable in their stereochemical relationship to C-2.

Brown (36) has suggested that the exclusive *exo* capture of the 2-norbornyl cation by external nucleophiles might be a consequence of the rapid equilibration of the two enantiomeric cations which are interconverted by Wagner-Meerwein migration of C-6 from C-1 to C-2, or vice versa.* The rapid oscillation of the C-5, C-6 two-carbon bridge inherent in this process

* For a more detailed exposition of this suggestion, but in a different context, see Ref. 61.

would, in Brown's conception, prevent an accumulation of solvent (nucleophile) in the *endo* direction and thereby favor substitution from the *exo* direction. This postulated process has been aptly dubbed "the windshield wiper effect." Since it is difficult to envisage how the windshield wiper effect could influence the stereochemical course of attack by *internal* nucleophiles, the observed strong preference for *exo*, *exo* 3,2 migration indicates that there must be some additional factor controlling the stereochemistry of attack on the 2-norbornyl cation. These observations have led Berson to express a preference for the bridged-ion formulation (49,62).

Sargent (62) has questioned the viability of the windshield wiper effect as a mechanism for explaining the stereospecificity of attack by external nucleophiles on the 2-norbornyl cation in light of its inability to account for comparable effects in the case of the closely related 2-bicyclo[2.2.2]octyl and 2-bicyclo[3.2.1]octyl cations (64).*

Brown (35) and Schleyer (65) have questioned the stereoelectronic explanation for the specificity of 3,2 migrations based on a bridged structure for the 2-norbornyl cation. They argue that as the substituent at C-2 is made more capable of stabilizing a classical cation, the bridged structure for the cation should become less important (see p. 1128) and the transition state for 3,2 migration less subject to the stereoelectronic constraints imposed by such an ion. Yet the preference for *exo*, *exo* 3,2 migration appears to be equally as strong in the tertiary 2-methyl (49,58–60), 2-phenyl (57), and even 2-*p*-anisyl-2-norbornyl cations (66), as in the secondary 2-norbornyl cation.

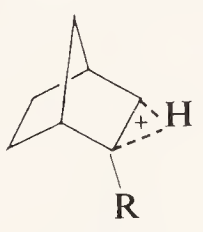
This invariance in the degree of stereoselectivity as a function of classical cationic stability of the migration terminus has caused both Brown (35) and Schleyer (65) to propose alternate explanations for this phenomenon. Berson (49) has cautioned against drawing conclusions from the invariance of data which all show total preference for one path over another; he points out that wide variations in actual sensitivity may underlie an apparent insensitivity generated merely by the limitations of available experimental technique. Berson thus appears to attribute to the tertiary 2-norbornyl cations a predominantly bridged structure, even though the stability of this structure may be less relative to the classical cation than for the secondary cation.

2. *Steric Hindrance to* endo, endo *Migration*

Brown has suggested an alternative steric explanation for the stereoselectivity of 3,2 migrations. He argues that the transition state for an

* For a summary of citations to additional comment on the windshield wiper effect, see Ref. 49, note 33.

endo, *endo* 3,2 shift would place the migrating group "very close to the 5,6-ethylene bridge" (35). This statement appears to imply that the *exo*, *exo* pathway might well be favored because the transition state is less sterically crowded than that for the *endo*, *endo* shift. Berson (49) and Schleyer (65) have taken issue with this suggestion. They point out that during *exo*, *exo* migration the migrating group would be forced to brush past the *syn*-7-hydrogen, whereas in the transition state for the *endo*, *endo* shift, the migrating group must be more or less symmetrically disposed between the *endo*-5 and *endo*-6 hydrogens. Thus the transition state for *exo* migration might well be as crowded, if not more crowded than that for *endo* migration. For the case in which the migrating group is hydrogen, the nonbonded distances appear to be too short to give rise to any serious steric inhibition to either *exo* or *endo* migration (65). Finally, for hydrogen migration from or to a tertiary center, the transition state for *exo* migration (**29a**) places the substituent group (R) in the sterically less favorable pseudo-*endo*-position, as contrasted with its sterically more favorable pseudo-*exo*-orientation in the transition state for *endo* migration (**29b**). This last effect should, if anything, introduce a steric bias in favor of the *endo*, *endo* migration pathway (65).



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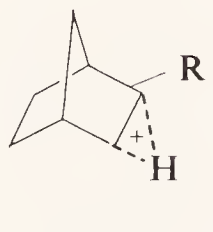
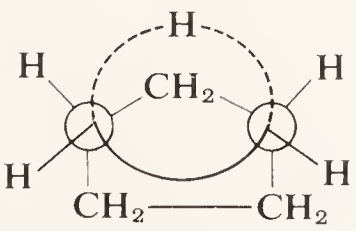


(29b)

3. Torsional Effects

Schleyer (65) has proposed yet another rationale for the marked preference for *exo*, *exo* as opposed to *endo*, *endo* 3,2 migrations in the 2-norbornyl cation and its analogs. He notes that molecular models permitting incorporation of "bent bonds" into the three-membered ring present in the transition state for 3,2 migration reveal a marked difference in *torsional* interactions for the *exo* as opposed to the *endo* transition state. The transition state for *exo* migration (**30**) possesses a nearly ideally skewed arrangement of substituents about the C-1–C-2 and C-3–C-4 bonds. By sharp contrast, in the transition state for *endo* migration (**31**), the arrangements about these two bonds are virtually wholly eclipsed.



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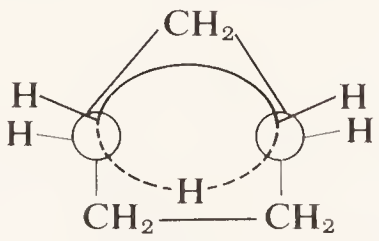
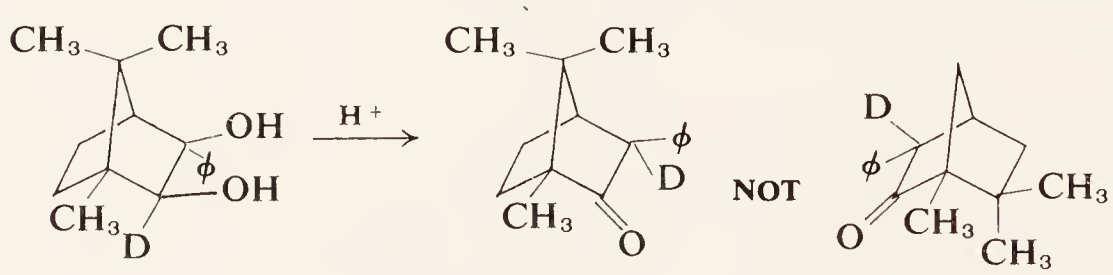


(31)

If we assume that the torsional interactions inherent in the partial bonds to hydrogen in these transition states are characterized by a torsional potential function comparable with normal carbon–hydrogen bonds, we can estimate the difference in energy between transition states **30** and **31** to be as much as 6 kcal/mole. The excess torsional strain inherent in transition state **31** relative to transition state **30** should be largely insensitive to the nature of substituents at C-2 and C-3, the cationic stability of the ion, and the nature of the migrating group. For these reasons, Schleyer concludes that torsional effects offer the best explanation for the observed marked preference for *exo*, *exo* 3,2 migrations.

4. An endo, endo 3,2 *Hydride Shift*

The first apparent exception to the generalization that 3,2 hydrogen migrations take exclusively an *exo*, *exo* stereochemical pathway has been reported by Bushell and Wilder (67). They find that the pinacol rearrangement of *endo*-3-phenyl-2,3-*exo*, *cis*-bornanediol (**31a**) leads to formation of *exo*-3-phenylcamphor (**31b**) in 80% yield. Deuterium incorporated at the *endo*-2-position in the starting material is found to an extent greater than 90% at the *endo*-3-position in the product. From these results, Bushell and Wilder conclude that the rearrangement involves a simple *endo*, *endo* 2,3 hydride shift. These results differ significantly from those obtained by Collins and co-workers (57) for the acid-catalyzed pinacol rearrangement of *endo*-2-phenyl-2,3-*exo*, *cis*-norbornanediol (**26a**) (p. 1116), which differs from diol **31a** only in lacking the three methyl groups. If the present rearrangement followed the same mechanistic pathway as is inferred for diol **26a**, the expected product would be ketone **31c**. Bushell and Wilder offer no rationale for the dichotomy in mechanism for the reaction of the seemingly similar diols **26a** and **31a**. Do the results obtained with the bornanediol **31a** reflect a thermodynamic bias against accumulation of **31c**, which possesses two unfavorably oriented bulky *endo* substituents, rather than a kinetic preference for *endo*, *endo* hydrogen migration? The apparent ability of an *endo*, *endo* hydride shift to compete with other processes in this system lends added support to the inference drawn from kinetic studies (p. 1132) that classical 2-phenyl-2-norbornyl cations are either lower, or more nearly equal in energy relative to the bridged structure than is the case for secondary 2-norbornyl cations.



(31a) **(31b)** **(31c)**

E. Summary

Since the invariance in preference of *exo*, *exo* 3,2 migrations as a function of classical cation stability casts some doubt on the stereoelectronic explanation for this phenomenon, and since torsional effects appear to provide a possible alternative rationale, we conclude that the stereoselectivity in the attack of internal nucleophile on the 2-norbornyl cation fails to provide conclusive evidence for a bridged structure for the ion.

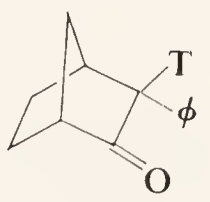
III. THE STEREOCHEMISTRY OF PRODUCTS DERIVED FROM THE 2-NORBORNYL CATION

If stereospecificity of attack by internal nucleophiles on the 2-norbornyl cation fails to provide unambiguous evidence for the structure of the ion, we are prompted to inquire whether the observed stereospecificity of attack by external nucleophiles can provide such evidence.

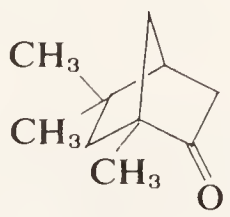
A. Steric Hindrance to *endo* Approach

There is a considerable bulk of experimental evidence which, by analogy, strongly supports Brown's contention that addition to the sp^2-hybridized carbon atom of a classical 2-norbornyl cation should occur preferentially from the *exo* direction (36). For example, each of the following reactions of bicyclo[2.2.1]heptene proceeds virtually exclusively via attack on the double bond from the *exo* direction: benzyne addition (68), diene addition (69), 1,3-dipolar addition (70), dihalogenocarbene addition (71), methylene addition (72), sulfenium addition (73), oxymercuration (74,75), halogenation (76), epoxidation (77,78), hydroxylation (77,79), and hydroboration (36). Similarly, the sodium enolate of bicyclo[2,2,1]heptan-2-one (2-norbornanone) reacts with methyl iodide in ether solution to give 97% *exo*-3-methyl-bicyclo[2.2.1]heptan-2-one and less than 3% of its *endo*-epimer (80).

With 3-*endo*-phenyl-2-norbornanone-3-^{3}H (**32**), loss of tritium through base-catalyzed exchange with solvent occurs more rapidly than epimerization to the more stable 3-*exo*-phenyl epimer (81). Both 2-norbornanone (82,83) and isofenchone (82) (**33**) exchange their 3-*exo*-hydrogens for deuterium [and vice versa (84)] more rapidly than their 3-*endo*-hydrogens. Chromic acid oxidation is less selective, but still



(32)

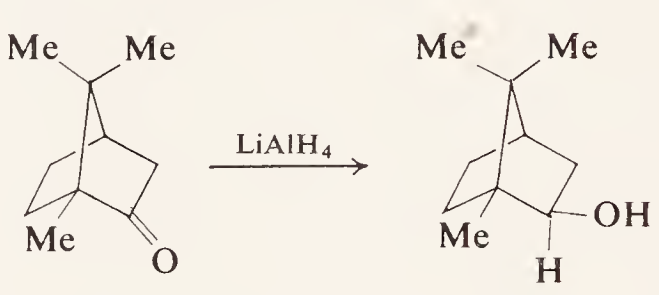


(33)

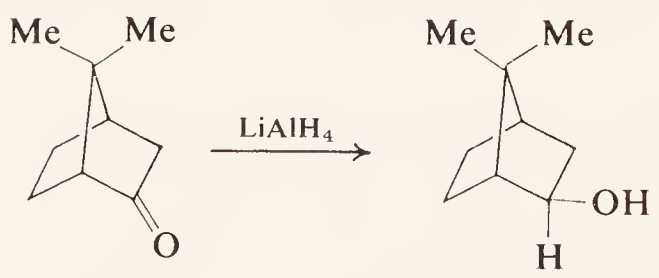
involves more rapid cleaveage of the *exo*-carbon–hydrogen bond in *endo*-2-norbornanol than the *endo*-carbon–hydrogen bond in *exo*-2-norbornanol [relative rate = 2.5 (85), 6.5 (86)]. Similarly, additions to the trigonal carbon atom of 2-norbornanone proceed selectively from the *exo* direction.* Reduction of this ketone with lithium aluminum hydride (87,88) and sodium borohydride (87,89), e.g., gives an excess of *endo*- over *exo*-2-norbornanol in the ratio of 10:1 (87) and 5:1 (87) [6.2:1 (89)], respectively.

B. The Influence of a *syn*-7-Methyl Substituent

Since steric preference for *exo* attack on the trigonal carbon atom of a classical 2-norbornyl cation predicts the same product stereochemistry as the necessity for backside attack on a bridged norbornyl cation (**6**), the exclusive formation of *exo*-substituted products in the solvolysis of 2-norbornyl brosylate gives no clue to the nature of the product-forming intermediate. Berson (90) has called attention to certain systems in which this ambiguity apparently is removed. He points out that the presence of a *syn*-7-alkyl group seems to increase the steric hindrance toward *exo* attack on a trigonal carbon atom at the 2-position of the norbornyl skeleton to such an extent that *endo* attack is actually preferred. On reduction with lithium aluminum hydride, camphor (**34**) gives isoborneol (**35**) in high yield (91), and apocamphor (**36**) gives apoisoborneol (**37**) in 91% yield (88).



(34) (35)

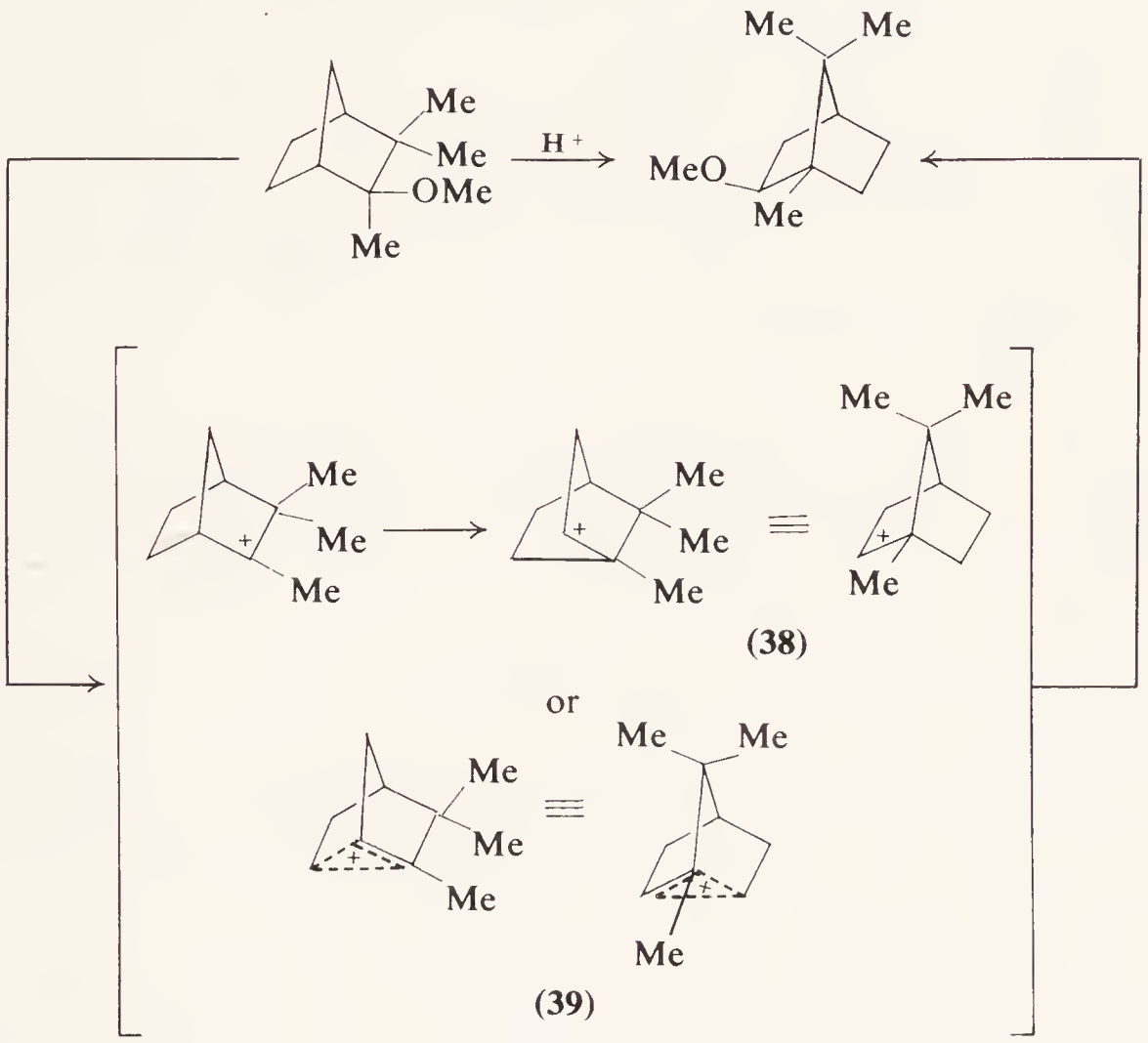


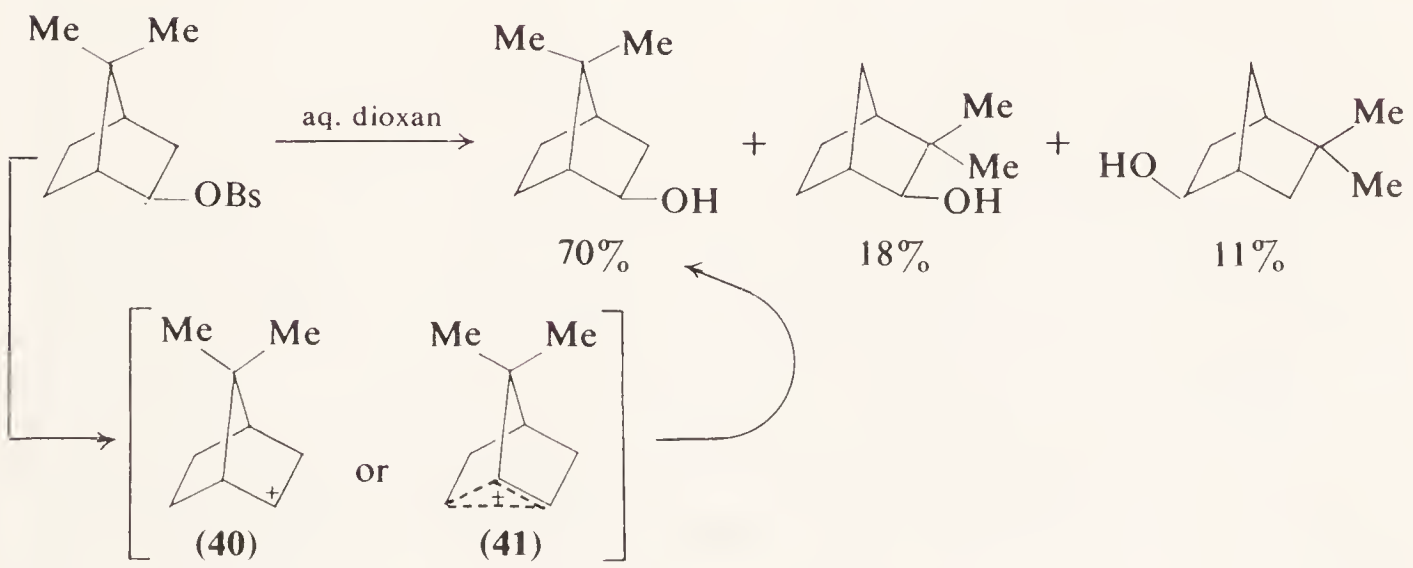
(36) (37)

Since *endo* approach is sterically favored in the hydride reactions, by analogy, this approach should also be favored in the attack of nucleophiles on the corresponding classical C-2 cations. Nevertheless, the car-

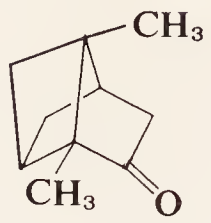
* These reactions, which include Grignard addition, metal hydride reductions, and sodium-alcohol reduction, have been summarized for a number of substituted bicyclo[2.2.1]heptan-2-ones in Refs. 16 and 55.

bonium ion reactions of these systems give *exo* products exclusively (92–96). These results have been interpreted (16,87) as incompatible with steric control of nucleophilic attack on the classical ions **38** and **40**, but in full accord with the postulated intervention of the bridged ions **39** and **41** as product-determining intermediates.

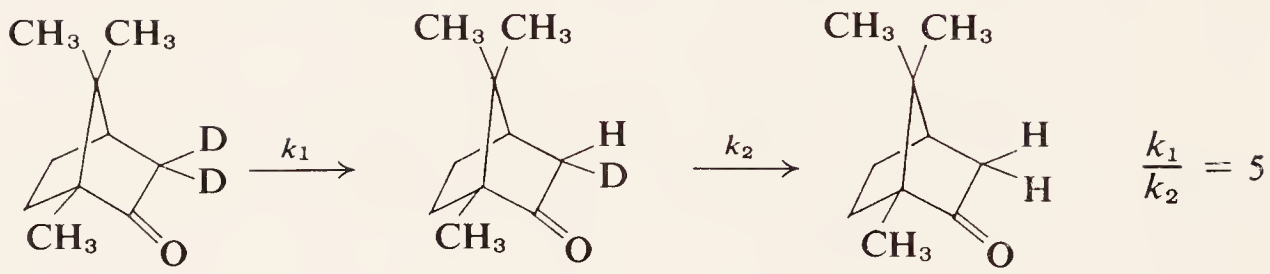




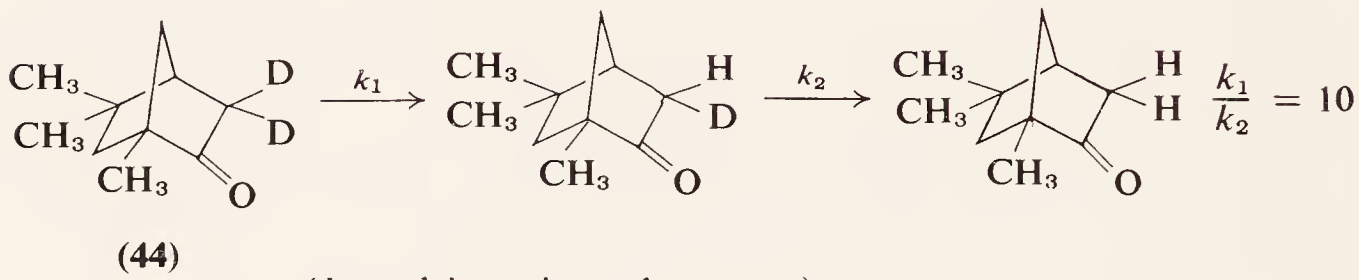
The results of subsequent investigations have introduced some ambiguity into this interpretation. Both camphor (82) (**34**) and carvone-camphor (84) (**42**) bear methyl groups *syn* to the two-carbon bridge



(42)



(43)



(44)

(k_1 and k_2 estimated; see text)

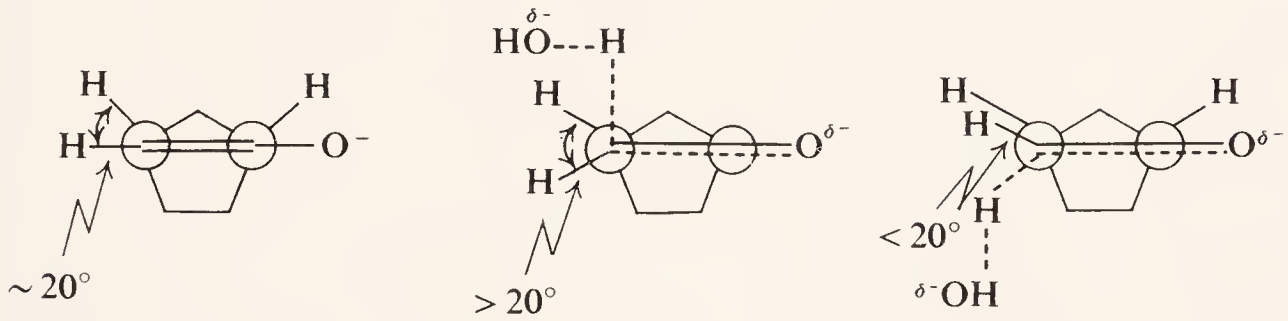
embodying the carbonyl function, and both compounds exchange their *exo*-3-hydrogens for deuterium [and vice versa (84)] more rapidly than their *endo*-3-hydrogens. The stereoselectivity of exchange in these cases is comparable with that for their analogs lacking the *syn*-7-methyl group; e.g., under conditions that result in 80% of the α,α-dideuteriocamphor (**43**) suffering some exchange, the product consists of camphor-d_1 and camphor-d_0 in the ratio of 4.3:1; under the same conditions, however, 93% of α,α-dideuterioisofenchone (**44**) reacts to yield isofenchone-d_1 and isofenchone-d_0 in the ratio of 5.2:1. The similarity in these ratios clearly indicates that the presence (in **43**) or absence (in **44**) of a *syn*-7-methyl group has little influence on either the rate of *exo*-3-deuterium abstraction or the relative ease of protonation of the resulting enolate anion from the *exo* direction. The ratios also demonstrate that the presence (in **44**) or absence (in **43**) of an *endo*-5-methyl group has little influence on the rate of *endo*-3-deuterium abstraction, and, by the principle of microscopic reversibility, deuteration (protonation) of the enolate anion from the *endo* direction. It thus appears that the enolization and exchange reactions of substituted 2-norbornanones are remarkably insensitive to classical steric effects.

In fact, by assuming that monodeuterated ketone is generated from **43** and **44** only by *exo*-3-hydrogen exchange (84), and by treating *exo* and

endo exchange as consecutive pseudo-first-order reactions (97), we estimate an *exo*/*endo* exchange rate ratio of 5 for α,α-dideuteriocamphor (**43**) and 10 for α,α-dideuterioisofenchone (**44**). This result suggests that the presence or absence of a *syn*-7-methyl group or an *endo*-5-methyl group influences the relative rate of *exo*/*endo*-3-hydrogen exchange by, at most, a factor of 2. The same result also demonstrates that enolization of 2-norbornanones, although it does involve some preference for *exo*-3-hydrogen abstraction, is not nearly as stereospecific as the capture of 2-norbornyl cations. For this reason, we must question whether the results of these investigations are of any assistance in predicting the direction of attack on a classical *syn*-7-substituted 2-norbornyl cation.

NOTE ADDED IN PROOF: For more recent quantitative studies of the relative rates for *exo* and *endo*-deprotonation of 2-norbornanone and substituted 2-norbornanones, see Refs. 253–255.

Rate ratios of 5 to 10 for *exo*/*endo*-3-hydrogen exchange are susceptible to interpretation on the basis of torsional effects (65) alone. Schleyer (65) has pointed out that protonation of the 2-norbornyl enolate anion (**45**) from the *exo* direction results in a transition state (**46**) in which the unfavorable nearly eclipsed (dihedral angle 20°) H–C-3–C-4–H torsional interaction is somewhat relieved. By contrast, protonation from the *endo* direction involves a transition state (**47**) in which this interaction is made more severe, i.e., more nearly eclipsed.



(45) **(46)** **(47)**

A rough calculation permits a quantitative approximation of the magnitude of this torsional effect. Assuming various geometries for the transition state, we can quickly conclude that the torsional differences between that for *exo* protonation (**46**) and that for *endo* protonation (**47**) will be maximized if C-3 has rehybridized to such an extent that the H–C-3–C-4–H dihedral angle for **46** is 40° and that for **47** is 0°. Since all other torsional interactions are comparable for these two transition states, the difference in activation free energy to be ascribed to torsional effects is simply the difference in energy between a 40 and a 0° torsional arrangement *for a single pair of bonds*. This can be roughly approximated

by one-third the difference in energy between an eclipsed ethane conformation and one that is 40° skewed; the energy difference is given (98) by

$$\frac{1}{3}\cdot\frac{2.90}{2}\,[\cos(0°) - \cos(120°)] = 0.714 \text{ kcal/mole}$$

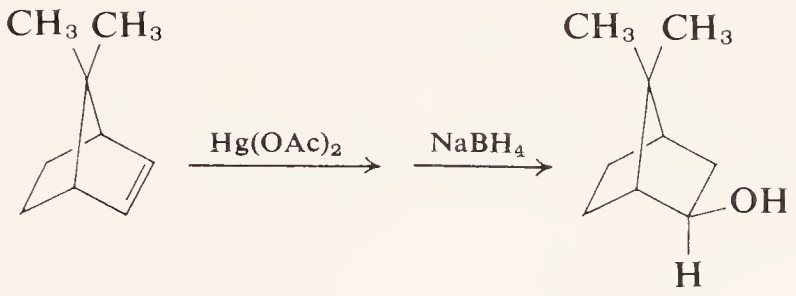
Conversion of an activation free energy difference of 0.714 kcal/mole to relative rates at 25° yields a value of 3.3. If Schleyer's concept of torsional effects is correct, and if it produces an *exo*/*endo* protonation rate ratio of the magnitude here calculated, there seems to be little evidence that protonation of the 2-norbornyl enolate anion is subject to the classic steric bias which is suggested (34–36) to preclude *endo* attack upon the 2-norbornyl cation.

1. The Failure of syn*-7-Methyl Substituents to Inhibit* exo *Attack*

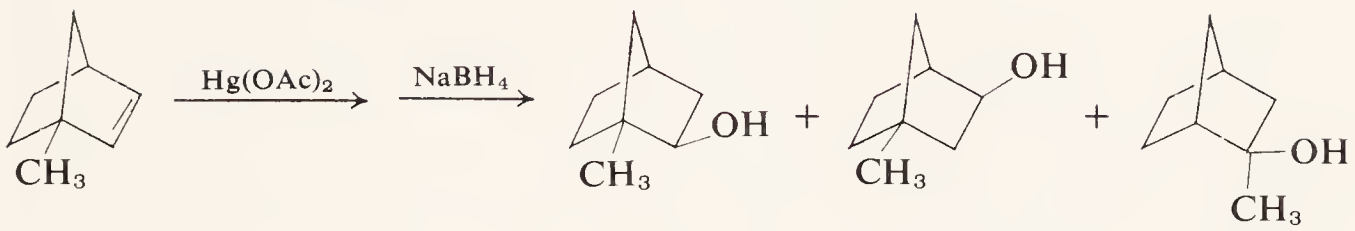
A more compelling objection to the postulate that *syn*-7-substituents should render attack on a classical 2-norbornyl cation less favorable from the *exo* than from the *endo* direction is raised by the steric course of oxymercuration of 7,7-dimethylnorbornene (**48**) (75). Despite the presence of a *syn*-7-methyl substituent, this olefin yields solely apoisoborneol (**49**) on oxymercuration-demercuration. Brown (75) argues that, although oxymercuration shows many of the characteristics of reactions thought to involve carbonium ion intermediates (e.g., a strong Markovnikov directing effect of substituents attached to the double bond), at least two observations militate against invoking the intervention of bridged ions as a rationale for this stereochemical result.

First, oxymercuration-demercuration of 1-methyl-2-norbornene (**50**) results in an equal yield of 1-methyl-*exo*-2-norbornanol (**51**) and 1-methyl-*exo*-3-norbornanol (**52**) and only a small amount of rearranged product, 2-methyl-*exo*-2-norbornanol (**53**) (75). In another context, Brown (96) and Schleyer (100) have suggested that, were formation of the two bridged ions **54** and **55** a competitive process, bridged ion **54** should predominate as a result of the stabilizing influence of the 1-methyl group directly attached to the electron-deficient center. Preferential formation of this bridged ion should lead to a kinetic bias against formation of 1-methyl-*exo*-3-norbornanol and to substantial, if not exclusive, formation of tertiary alcohol **53**.

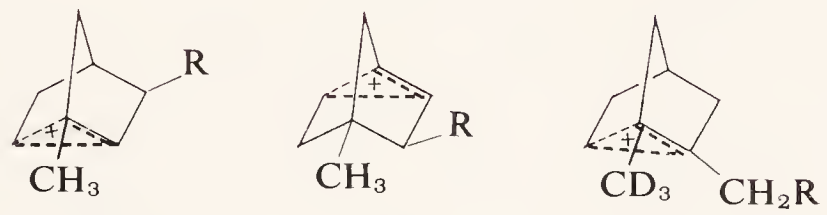
Second, oxymercuration-demercuration of 1-methyl-d_3-2-methylenenorbornane (**56**) yields 1-methyl-d_3-2-methyl-*exo*-2-norbornanol (**57**) without detectable scrambling of the methyl-d_3 group (96). Intervention of a symmetrical bridged ion (**56a**) in this reaction would be expected to result in total methyl-d_3 scrambling.



(48) **(49)**

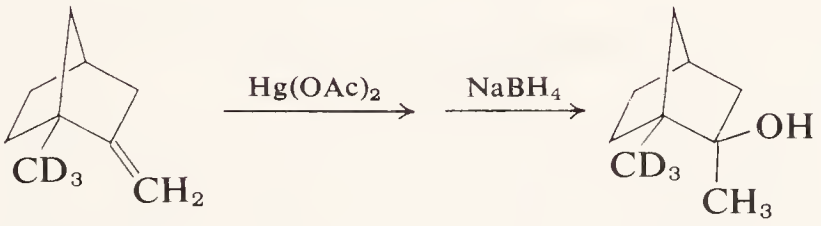


(50) **(51)** 48% **(52)** 48% **(53)** 4%



(54) **(55)** **(56a)**

R = HgOAc



(56) **(57)**

The latter observation would seem unambiguous in excluding the intervention of a bridged ion in the generation of a tertiary 2-norbornanol by oxymercuration. The former result, however, is less definitive in excluding the intervention of bridged ions in oxymercuration reactions leading to secondary 2-norbornanols, since little independent evidence exists to indicate the extent to which one would expect charge delocalization to C-1 in *the transition state for oxymercuration* of a 2-norbornene (e.g., **54** or **55**). Nonetheless, there is no clearcut evidence for the intervention of bridged ions in this reaction. In the absence of such evidence, we must conclude that factors other than bridging may lead to exclusive *exo* substitution in additions to norbornenes even in the presence of a *syn*-7 substituent. By inference, we must also conclude that the same factors might also lead to exclusive *exo* attack upon the sp^2-hydridized carbon atom of a *syn*-7-substituted 2-norbornyl classical cation.

C. Torsional Effects

Schleyer (65,99) has suggested that torsional considerations may play a role in determining the preference for *exo* attack in both the additions to norbornenes and the capture of 2-norbornyl cations. Torsional effects appear to be capable of explaining no more, and perhaps somewhat less, than a tenfold preference for *exo* as opposed to *endo* attack on the 2-norbornyl cation (see calculation, p. 1125). For an addition to norbornene, involving simultaneous rehybridization at both C-2 and C-3, torsional effects might account for a 10 to 100-fold preference for *exo* addition. Thus although torsional effects may be significant in determining the stereochemistry of many additions to norbornene, they must contribute little to the process that effects the dramatic steric control in attack of nucleophiles on the 2-norbornyl cation. A strong suggestion that torsional effects are not paramount in determing the *exo* orientation in oxymercuration of norbornenes is found in the observation that 2-methylene norbornene, on oxymercuration-demercuraction, yields 2-methyl-*exo*-2-norbornanol containing 0.5% of epimeric alcohol (96). As Schleyer (65) points out, there should be no marked torsional preference for *exo* attack on this exocyclic double bond, yet the striking stereoselectivity of attack on norbornene itself remains in evidence in this case as well.

D. Stereospecific Product Formation in the Absence of Kinetic Evidence for Bridging

It is important to note that whatever explanation is finally adopted to explain the stereoselectivity of attack on the 2-norbornyl cation, that explanation must account for the manifestation of such stereoselectivity even for the capture of ions for which there is little or no *kinetic* evidence for bridging. Kinetic evidence bearing on the structure of the 2-norbornyl cation is discussed in detail in a subsequent section, but it is pertinent here to consider at least two ions for which such criteria provide no compelling argument for a bridged structure, even though the ions are captured with high stereoselectivity from the *exo* direction.

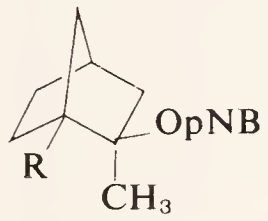
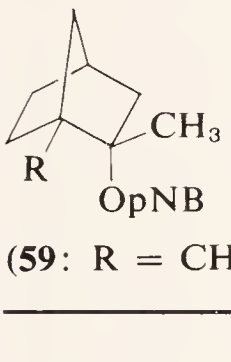
1. 2-Methyl-2-Norbornyl Cations

Were there significant charge delocalization to C-1 during generation of the 2-methyl-2-norbornyl cation, a presumed concomitant to bridging, we would expect the substitution of a methyl group at that position to stabilize the incipient cationic charge, resulting in an enhanced rate of formation of this ion. Relative to their respective 2-methyl analogs, therefore, the rate of solvolysis of 1,2-dimethyl-*exo*-2-norbornyl *p*-nitrobenzoate (**58**) should be greater than that of 1,2-dimethyl-*endo*-2-norbornyl *p*-nitrobenzoate (**59**),

which cannot directly give rise to a bridged ion. As indicated by the data in Table IV, this expectation is not realized. Substitution of a 1-methyl group for hydrogen enhances the rate of solvolysis of the *exo*-ester **58** by a factor of 4.3 and that of the *endo*-ester **59** by the virtually identical factor of 4.8 at 50° (101).

TABLE IV

Rates of Solvolysis for 2-Methyl-2-Norbornyl p-Nitrobenzoates (101)

Compound		$k_1 \times 10^6$, sec^{-1} 50°	$k_1 \times 10^6$, sec^{-1} 75°	Relative rates, 50°, R = CH_3/R = H
 (**58**: R = CH_3)	R = H	2.2	41.2	
	R = CH_3	9.4	121	4.3
 (**59**: R = CH_3)	R = H	0.012	0.20	
	R = CH_3	0.057	1.1	4.8
	OpNB = *p*-nitrobenzoate			

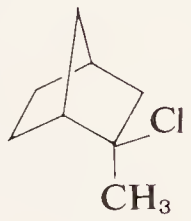
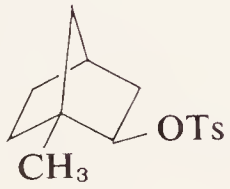
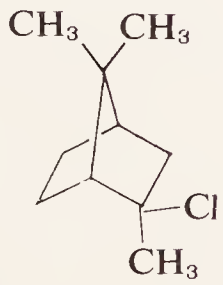
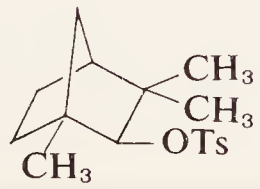
These results clearly demonstrate the absence of significant charge delocalization to C-1 in the transition state for solvolysis of the 2-methyl-*exo*-2-norbornyl *p*-nitrobenzoates. Nevertheless, irreversible capture of the 2-methyl-2-norbornyl cation by $NaBH_4$ in 65% aqueous diglyme occurs from the *exo* direction with marked stereospecificity (70:1; see Table V). Under the same conditions, the 2,7,7-trimethyl-2-norbornyl cation appears to suffer exclusive *exo* attack (Table V).

*2. 2-*p*-Anisyl-2-Norbornyl Cations*

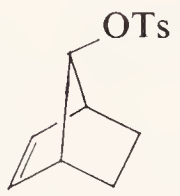
The *exo*/*endo* ratio of 284 for solvolysis of the epimeric 2-*p*-anisyl-2-norbornyl *p*-nitrobenzoates (103) differs little from the values for acetolysis of the unsubstituted epimeric 2-norbornyl tosylates—(280) (104)—and brosylates—(350) (5,6). There is substantial reason to doubt that the *exo*/*endo* rate ratio for the 2-*p*-anisyl system can result to any significant extent from C-6–C-1 σ-bonding electron participation, however. One of the most dramatic examples of carbon–carbon bonding electron participation is found in the observation (105) that acetolysis of *anti*-7-norbornenyl

TABLE V

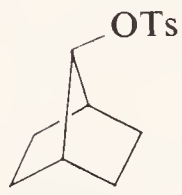
Solvolysis Products of Several 2-Methyl-2-Norbornyl Cation Precursors Formed in the Presence of 1.8M $NaBH_4$ in 65% Aqueous Diglyme (102)

Precursor	R	Yield, % R R OH CH_3	R R H CH_3	R R CH_3 H	R R CH_2	R R CH_3
	H	57	35	0.5	3	3
	H	56	42	0.6	0.8	0.8
	CH_3	5	56	0	3.1	4
	CH_3	7	65	0	19	2

tosylate (**60**) is accelerated over that of its saturated analog (**61**) by a factor of 10^{11}. Gassman and co-workers (106) have recently shown that 7-*p*-anisyl-*anti*-7-*p*-nitrobenzoate (**62**) undergoes solvolysis in 90% aqueous acetone at a rate only about 2.5 times greater than that of its saturated analog (**63**).

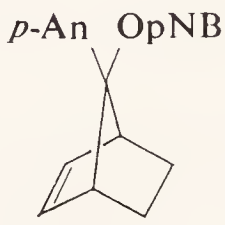


(**60**)

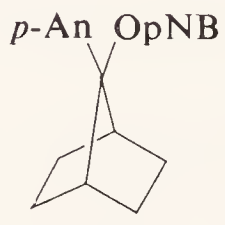


(**61**)

Relative rates of solvolysis: 10^{11} 1



(**62**)



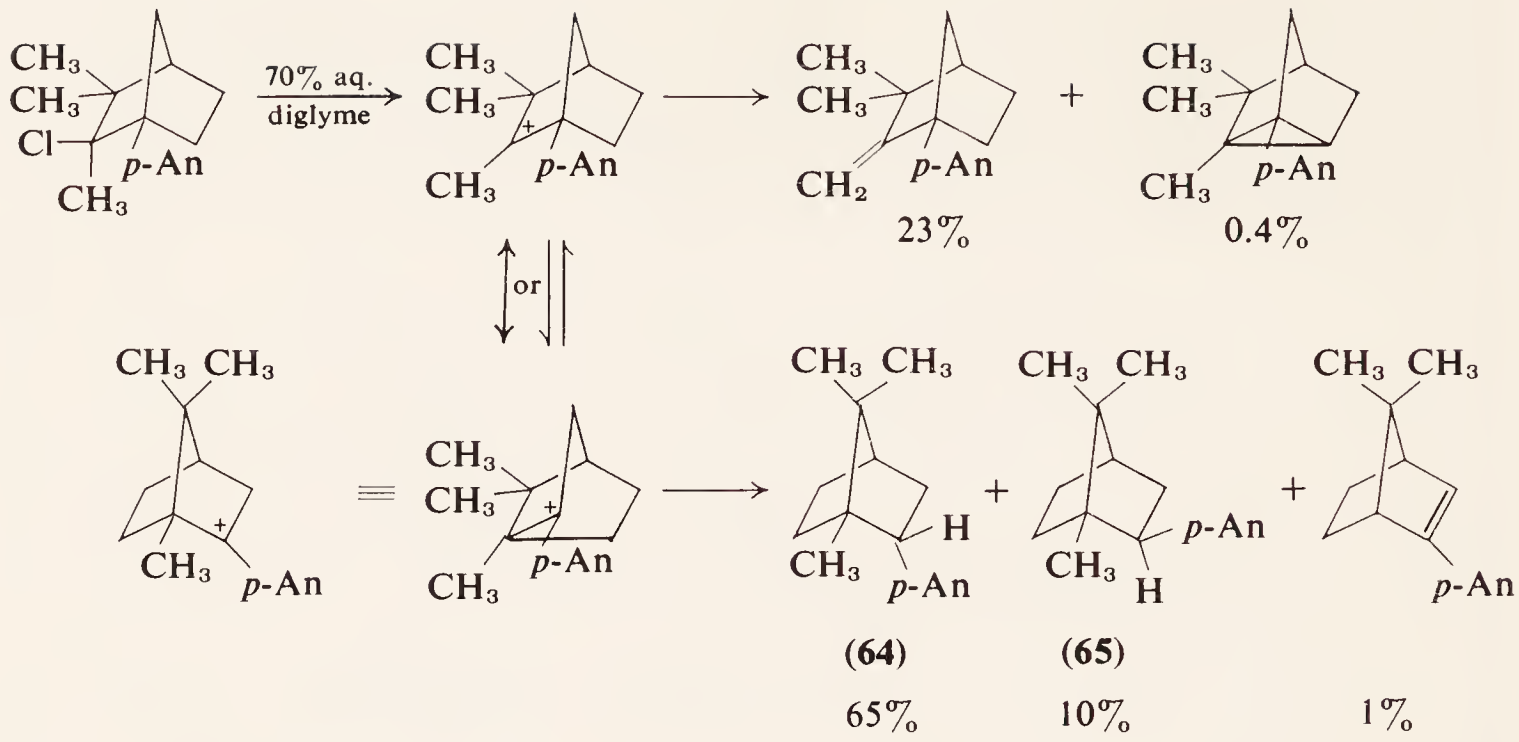
(**63**)

Relative rates of solvolysis: 2.5 1

It is difficult to see why the effect of the *p*-anisyl group in eliminating participation by the π electrons in the 7-norbornenyl system would not be duplicated by elimination of σ-electron participation during generation of the 2-*p*-anisyl-norbornyl cation. Again, however, the 2-*p*-anisyl-2-norbornyl cation, when captured by $NaBH_4$ in diglyme, yields 2-*p*-anisylnorbornane in which the configuration of the 2-hydrogen is $\geqslant 98\%$ *exo* (103). This thus constitutes a second system in which marked stereoselectivity is demonstrated for capture of a 2-norbornyl cation for which kinetic evidence presents no compulsion to postulate a bridged structure. Unlike the behavior of the 2-methyl-2-norbornyl cation, however, introduction of a *syn*-7-methyl group causes a marked *reduction* in the stereoselectivity for capture of the 2-*p*-anisyl-2-norbornyl cation by $NaBH_4$.

E. *endo*-Attack on a 2-Norbornyl Cation

The 1,7,7-trimethyl-2-*p*-anisyl-norbornyl cation yields a mixture of both *p*-bornylanisole (**64**) and *p*-isobornylanisole (**65**) in which the former, the product of *exo* attack, predominates by only a factor of 6.5 (102). This result clearly establishes that a 2-norbornyl cation is susceptible to attack from the *endo* direction. It is difficult to interpret this observation utilizing only classical steric effects or torsional effects. The presence of a 1-methyl substituent appears to generate very little, if any, nonbonded interaction with an *exo*-2-substituent. (Note the absence of significant acceleration



resulting from relief of steric strain in solvolysis of the 1,2-dimethyl-2-norbornyl *p*-nitrobenzoates, p. 1129.) Why then should the presence of the 7,7-dimethyl substituents result in significant onset of *endo* capture of the 2-*p*-anisyl-2-norbornyl cation when these substituents fail to induce such behavior in other 2-norbornyl cations (see previous discussion)? In seeking to resolve this enigma, we will probably be obliged to invoke the well-documented enormous ability of *p*-anisyl to stabilize a classical cationic center. One such suggestion, which is consistent with the observations, but for which there is, as yet, no compelling experimental justification, follows.

F. The Possibility of Bridging Within Tertiary 2-Norbornyl Cations

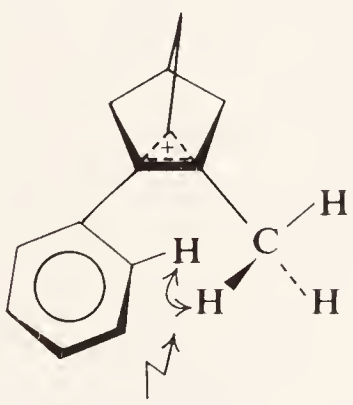
1. A Suggested Rationale

The 2-norbornyl cation is capable of existing both as a bridged ion and as one of a pair of classical ions which are interconverted, presumably via the bridged ion, by Wagner-Meerwein migration of C-6 from C-1 to C-2 and vice versa. Each of these three ions is in equilibrium with the other two. The principal driving force for bridged-ion formation is relief of strain within the norbornyl skeleton, not charge delocalization. The hybridization of the carbons involved in the three-centered bridged ion and the nature of the bonding within the ion is such that electron-releasing substituents are able to stabilize the bridged ion to an extent comparable with but not identical to their ability to stabilize a classical cation.

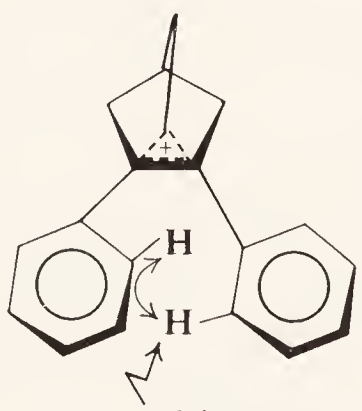
This model suggests that charge delocalization will not be extensive for unsymmetrically substituted 2-norbornyl cations. Thus we can use it to explain the observation that bridged ions yield kinetically controlled products derived from attack at that carbon best able to accommodate the positive charge as a classical cation (108–111). Since the model postu-

lates only a slight differential in the relative ability of substituents to stabilize positive charge for the bridged structure as opposed to a classical structure, it explains the preservation of those characteristics associated with bridging (e.g., *exo*/*endo* rate differentials and stereoselective capture), even for 2-norbornyl cations for which a classical structure should be highly stabilized. The driving force for bridging is postulated to be relief of strain, however; therefore, the equilibrium between classical and bridged ions should be acutely sensitive to any substitution that would increase steric strain in passing from a classical to a bridged structure. Such a strain increment might arise in various ways (see p. 1154), but it seems inevitable in the case of a 1,2-disubstituted 2-norbornyl cation in which at least one of the substituents is aryl.

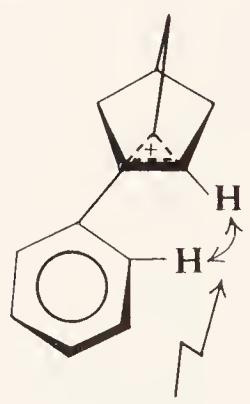
In order to demonstrate this point, we must postulate a structure for the bridged cation consonant with the requirements of the proposed model. Since the model requires that substituents exert a comparable stabilizing effect on both the bridged and classical cations, the hybridization of the carbon atoms to which those substituents are attached must be the same for both ions. A structure in which this requirement is met, i.e., one in which both C-1 and C-2 are sp^2 hybridized in the bridged ion, is that of Streitwieser (Fig. 1). This model requires that the carbon atoms at positions 1, 2, 3, and 7 assume near coplanarity. For an aryl substituent at C-1 or C-2 to exercise its full conjugative, electron-releasing, stabilizing influence, it too must achieve near coplanarity with these four carbon atoms. The presence of a substituent at C-1 in such a bridged 2-arylnorbornyl cation (**66**, **67**) will introduce significant nonbonded interactions not found in the unsubstituted 2-arylnorbornyl cation **68**.



(66)



(67)



(68)

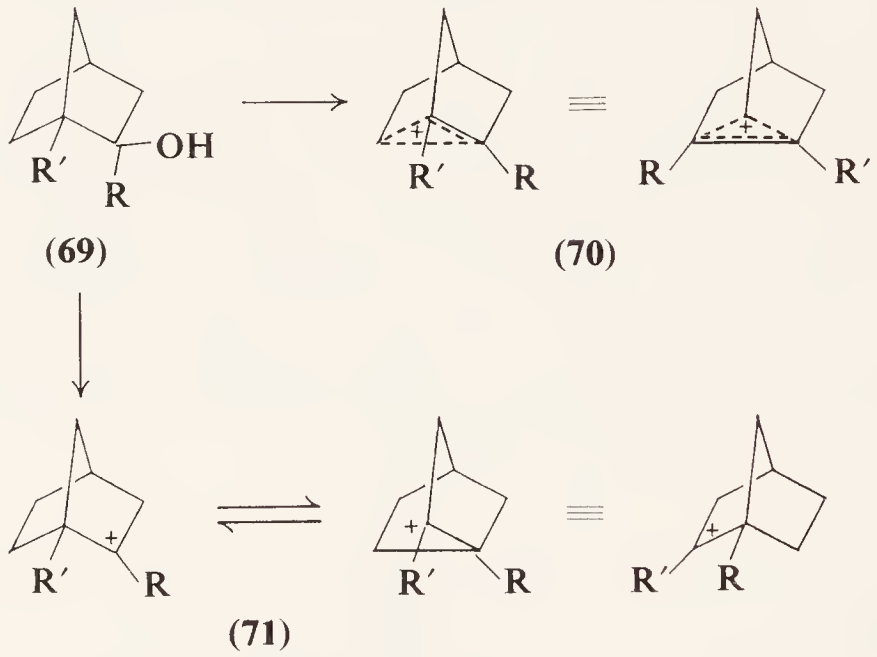
Any distortion of this ion which leads to relief of the unfavorable nonbonded interactions without disturbing the π overlap between the aryl group and the cationic center produces a geometry more resembling that of the classical 2-arylnorbornyl cation. For such ions, then, the equilibrium between bridged and classical cations might well favor the classical ion.

The combination of the presence of both the 1-methyl group, which would serve to favor the classical over the bridged ion species, and the *syn*-7-methyl group, which would hinder *exo* attack on the classical ion, could explain the striking susceptibility of the 1,7,7-trimethyl-2-*p*-anisylnorbornyl cation to *endo* attack, as contrasted with the absence of *endo* attack on the unsubstituted 2-*p*-anisylnorbornyl cation.

2. 1,2-Diaryl 2-Norbornyl Cations

An additional example of 1-substitution leading to preference for the classical structure for a 2-arylnorbornyl cation may be found in the behavior of the 1,2-di-*p*-anisylnorbornyl cation.

Schleyer et al. (112) determined the ultraviolet spectral behavior, the thermodynamic stability, the nmr spectra, and the chemical behavior of a series of mono- and diaryl substituted 2-norbornyl cations. Their results can be exemplified by the following data, obtained for the carbonium ions generated, on the one hand, from 2-*p*-anisylnorbornene, and on the other hand, from 1,2-di-*p*-anisyl-*endo*-2-norbornanol (**69b**).



a: R = *p*-CH_3O—C_6H_4—, R′ = H
b: R = R′ = *p*-CH_3O—C_6H_4—

These investigators found that the carbonium ions generated from both alcohols **69a** and **69b** by dissolution in concentrated sulfuric acid gave ultraviolet spectra with maximum absorption at the same wavelength, 381 mμ. The carbonium ion from alcohol **69a** was found to be half-formed in 41% sulfuric acid and was therefore judged to be thermodynamically more stable than the carbonium ion from alcohol **69b**, which was half-formed in 51% sulfuric acid. The carbonium ion generated from the disubstituted alcohol **69b** underwent bromination and sulfonation with half-times of less than 1 min, under conditions in which the carbonium ion generated from 2-*p*-anisylnorbornene was not brominated at all and

required more than 3000 hr for 50% sulfonation. At room temperature, the nmr spectrum of the carbonium ion generated from the disubstituted alcohol **69b** showed doublet absorption in the aromatic region characteristic of four equivalent protons *meta* to the methoxyl group and four equivalent protons *ortho* to the methoxyl group of the anisyl ring. At $-70°$, however, the two peaks lost detail and collapsed into a single broad peak; the authors interpreted this phenomenon as an indication of impending nonequivalence of the two aryl rings.

The authors point out that all these results are irreconcilable with a structure for the carbonium ion generated from alcohol **69b** which involves simultaneous conjugation of both aryl rings with the electron-deficient center. The extended conjugation present in such a system compared with that found in the monoaryl-substituted carbonium ion surely should (*1*) provide a substantially different chromophoric system, resulting in ultraviolet absorption at longer wavelengths; (*2*) yield enhanced thermodynamic stability; (*3*) render the two aryl groups equivalent, regardless of temperature, and cause them to give rise to identical proton signals in the nmr; and (*4*) result in both aromatic nuclei offering resistance to electrophilic substitution comparable with that demonstrated by the monoaryl-substituted carbonium ion, by virtue of possessing reduced electron density in the π system of each of the benzene rings. On all counts, the experimental findings preclude such extended conjugation in the carbonium ion arising from the disubstituted alcohol **69b**. On these grounds, Schleyer et al. conclude that "diarylnorbornyl carbonium ions possess rapidly equilibrating simple ion structures" (112). If this inference is correct, the absence of bridging could be rationalized as resulting from the unfavorable nonbonded interactions (**67**), which would be generated in the bridged ion when one or both of the aryl groups is so oriented as to permit π overlap with the electron-deficient center. (For a possible alternative interpretation of the same data, see Ref. 113.)

Inspection of models demonstrates that the methyl–methyl nonbonded interactions present in the bridged 1,2-dimethyl-2-norbornyl cation are less severe than those inherent in 1-substituted 2-arylnorbornyl cations.*

* This comparison can be made more nearly quantitative by utilizing substituted ethylenes as models to assess the magnitude of the nonbonded interactions between substituents at C-1 and C-2 in the norbornyl cation. The heats of hydrogenation of *cis*- and *trans*-2-butene differ by only 1 kcal/mole (114), whereas those of *cis*- and *trans*-stilbene differ by 5.7 kcal/mole (115). Since to a first approximation these differences represent the nonbonded steric repulsion between two methyl as opposed to two phenyl substituents attached *cis* to two adjacent sp^2-hybridized carbon atoms, the difference between them indicates the excess nonbonded strain energy present in the 1,2-diphenyl-2-norbornyl bridged cation as compared with the 1,2-dimethyl-2-norbornyl bridged cation.

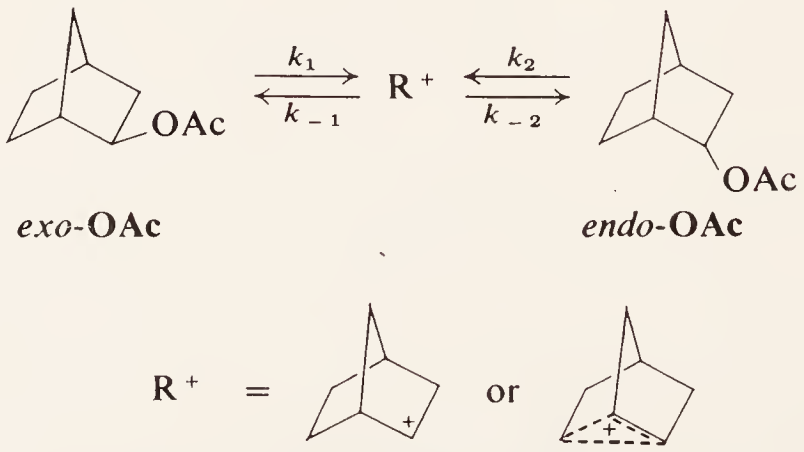
We might well anticipate, therefore, that 1,2-dimethyl-2-norbornyl cations would exhibit properties explicable in terms of a bridged structure to a much greater extent than would 1-substituted-2-arylnorbornyl cations.

G. The Interrelation of Kinetic and Stereochemical Criteria for Bridged-Ion Formation

In his more recent critiques of the 2-norbornyl cation, Brown (34,35) has argued that high *exo*/*endo* solvolysis rate ratios and high stereoselectivity for *exo* capture are not independent criteria for probing the structure of this ion. He points out that it is not the "amount of bridging that may or may not be present in the free ion" which controls the stereoselectivity of substitution, but that "it is the amount of bridging in the *exo* transition state, or whatever factor is responsible for the difference in stability of the two transition states, that will control the distribution of the norbornyl cation between *exo* and *endo* products." If the leaving group present in the transition state for ionization is identical to the nucleophile present in the transition state for cation capture, then the principle of microscopic reversibility ensures that the same factor that determines the *exo*/*endo* ionization rate ratio must also determine the *exo*/*endo* product distribution. Two such systems have been investigated and have yielded strongly contrasting results.

1. Equilibration of the Epimeric 2-Norbornyl Acetates

Goering and Schewene (116) have examined the $HClO_4$-catalyzed racemization and epimerization of optically active 2-norbornyl acetate. By determining the rate constant for irreversible equilibration of both *exo*- and *endo*-acetate, the equilibrium constant for epimerization, and the rate of racemization of *exo*-acetate, these authors were able to obtain values for the *exo*/*endo* ratio for both ionization to (k_1/k_2), and acetic acid capture of (k_{-1}/k_{-2}) the 2-norbornyl cation. These ratios are presented in Table VI and the apparent activation energies derived from them appear



in Figure 2. It is clear, as expected, that the partition ratios for ion capture k_{-1}/k_{-2} do indeed parallel the ionization rate ratios k_1/k_2. The magnitudes

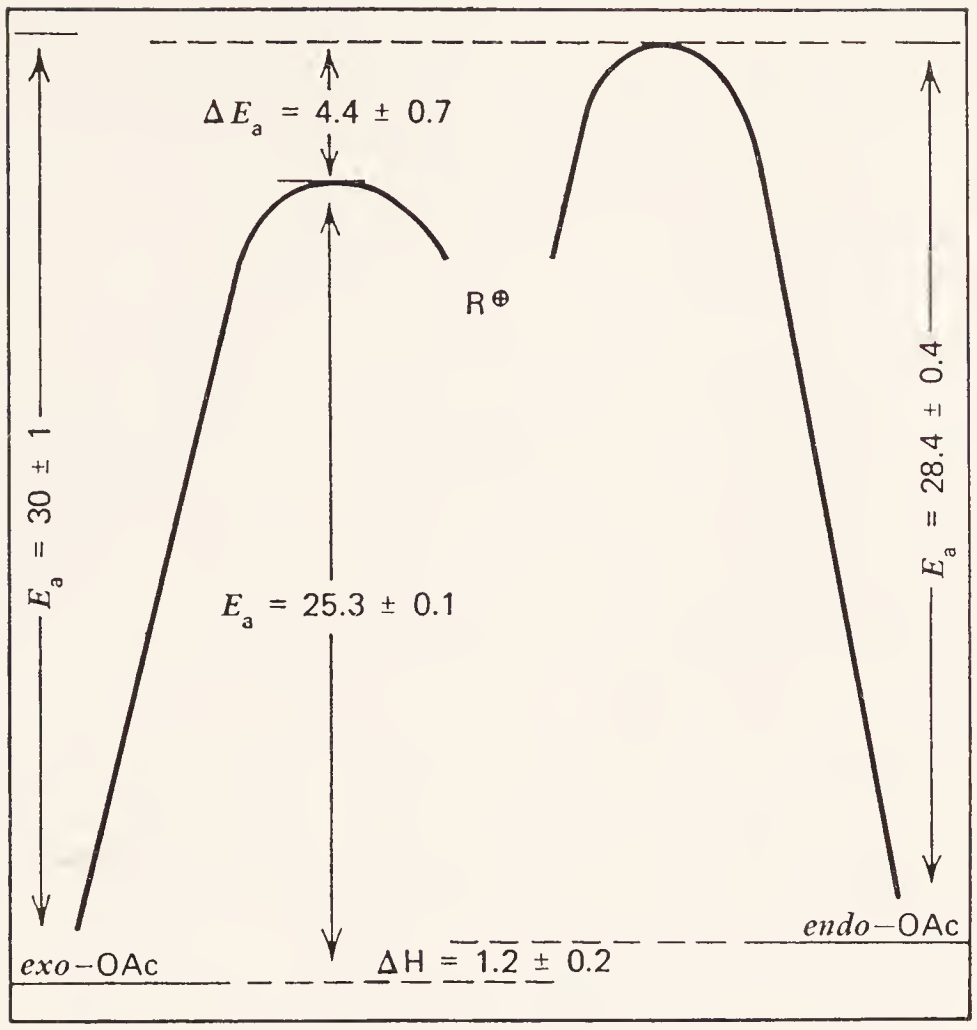


Fig. 2. Apparent activation energies (E_a) for acid-catalyzed reactions of *exo*-2-norbornyl acetate (*exo*-OAc) and *endo*-2-norbornyl acetates (*endo*-OAc) and ΔH for equilibration.

of both k_1/k_2 and k_{-1}/k_{-2} are comparable with those determined by or estimated from solvolysis of the epimeric 2-norbornyl brosylates (5–7). Goering and Schewene cite the lower energy of the transition state for *exo* capture (ionization) as important evidence for the bridged structure for the intermediate carbonium ion. They suggest that *endo* capture, which they were able to detect to the extent of 0.05 ± 0.02% from acetolysis of *exo*-2-norbornyl tosylate in the presence of acetate ion at 100°, probably involves initial isomerization of the bridged ion to the classical 2-norbornyl cation. If this is the case, ΔE_a (4.4 ± 0.7 kcal/mole) represents a lower limit for the difference in energy between the bridged and classical 2-norbornyl cations.

Since he feels that there is no kinetic evidence for bridging in the transition states of norbornyl systems not undergoing rearrangement to more stable intermediates, Brown (35) concludes that the results of Goering and Schewene are "more compatible with the alternative proposal that the transition state for the *exo*-acetate is normal, with the higher energy for the *endo* transition state arising from steric strain."

TABLE VI

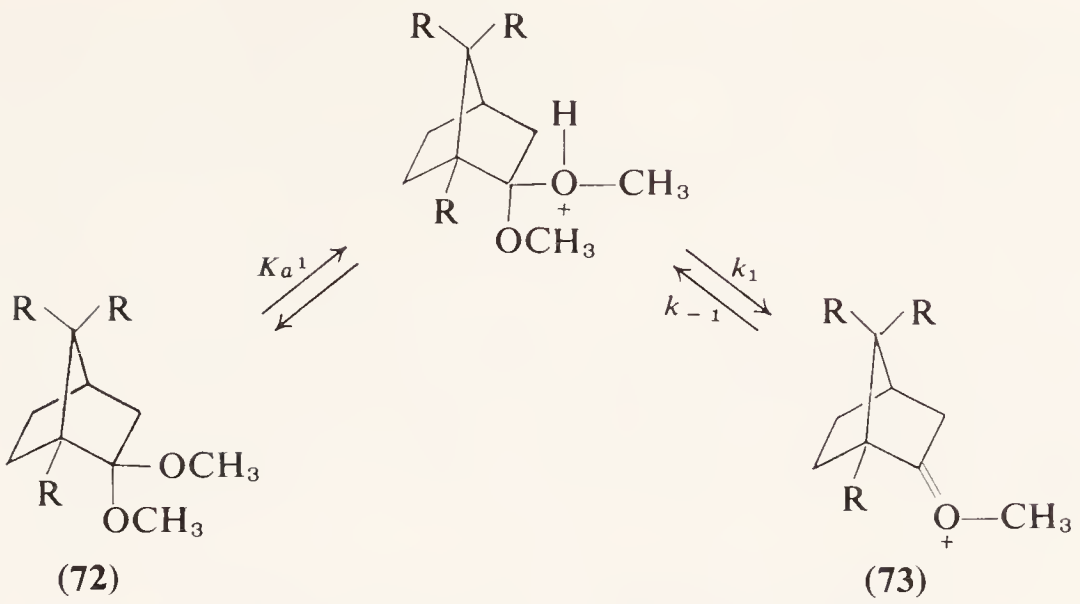
***exo/endo* Ionization and Capture Ratios for Acid-Catalyzed Equilibration of 2-Norbornyl Acetates in Acetic Acid**

Temperature °C	Ratio	
	k_{-1}/k_{-2}	k_1/k_2
24.92	9140 ± 880	1480 ± 190
36.61	6800 ± 470	1180 ± 100
48.90	5070 ± 290	953 ± 87
78.46	2810 ± 100	629 ± 49
99.41	1980 ± 190	479 ± 53

The work of Goering and Schewene seems to lack internal evidence that would allow one to choose between these alternative interpretations. Comparison with the results of the following related investigation, however, prompts the author to favor the interpretation of Goering and Schewene.

2. Camphor and Norcamphor Dimethyl Ketals: Precursors for Classical 2-Norbornyl Cations

Traylor and Perrin (117) have examined the kinetics of acid-catalyzed methoxyl exchange for camphor (**72b**) and norcamphor dimethyl ketals (**72a**) in methanol-d_4. As in the acetate epimerization study (116), the kinetic analysis of this reaction is simplified by the necessity for the transition state for ionization of the protonated *exo* (*endo*) methoxyl group to be identical to that for *exo* (*endo*) methanol capture by the intermediate 2-methoxy-2-norbornyl cation (**73**). Since ionization is the rate-limiting step for exchange and the basicities of the *exo* and *endo* ketal oxygens can be assumed to be nearly equal ($K_a^1 \approx K_a^2$), the *exo/endo* ionization rate ratios (k_1/k_2) can be determined from the rate of disappearance of the *exo* and *endo*–OCH_3 nmr signals resulting from exchange for –OCD_3. In this manner, Traylor and Perrin found values of k_1/k_2 equal to 16 and 0.1 for 2-norcamphor dimethyl ketal (**72a**) and camphor dimethyl ketal (**72b**), respectively. These ionization *exo/endo* rate ratios compare with 1600 (polarimetric) for the 2-norbornyl brosylates (5–7), 1480 at 25° for the 2-norbornyl acetates (116), and about 10^5 for the isobornyl/bornyl chlorides (29). Since it is most difficult to conceive of any marked difference in steric interactions in the transition state for ionization of protonated methoxyl on the one hand, and, e.g., protonated acetate on the other, Traylor and Perrin conclude that their results are best interpreted on the basis of the intermediacy of a classical 2-methoxynorbornyl cation. Such an interpretation requires some special effect, e.g., bridging, to account for



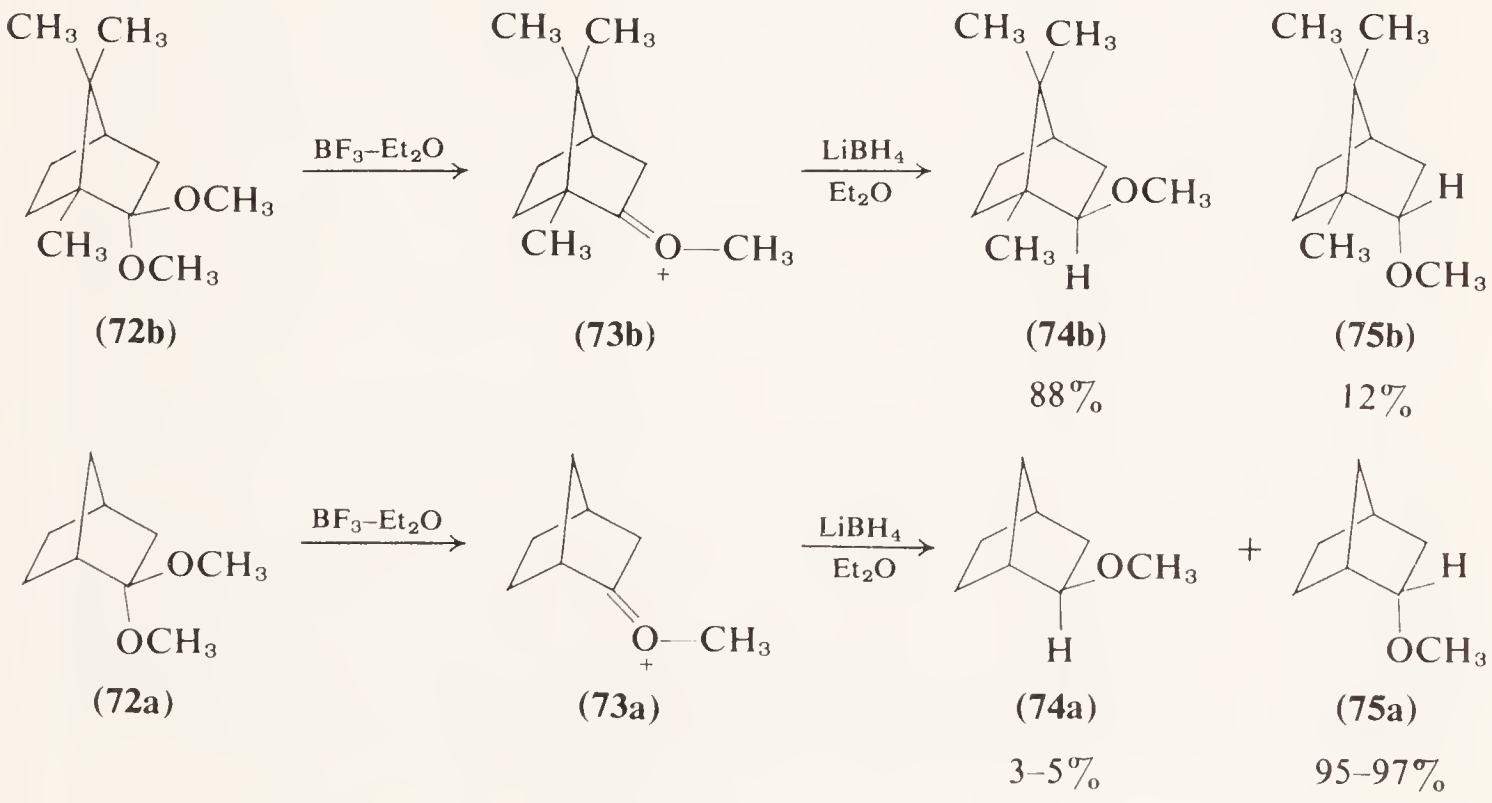
(72) (73)

(72a) R = H
(72b) R = CH_3

high *exo*/*endo* reactivity ratio observed by Goering and Schewene (116) for the 2-norbornyl acetates.

Treatment of diethyl ether solutions of the dimethylketals (**72**) with boron trifluoride etherate followed by addition of lithium borohydride yielded a mixture of *exo*- (**74**) and *endo*-2-methyl ethers (**75**).

If we assume the intermediacy of the same ion as is formed in the exchange reaction, we find a close correspondence between the *exo*/*endo*



(72b) **(73b)** **(74b)** 88% **(75b)** 12%

(72a) **(73a)** **(74a)** 3–5% **(75a)** 95–97%

hydride capture ratios—0.13 for **73b** and ca. 24 for **73a**—and the *exo*/*endo* ionization ratios. The value of 0.13 for the *exo*/*endo* ratio for hydride capture of cation **73b** appears all the more dramatic upon recalling that the hydride capture ratio for the 2,7,7-trimethylnorbornyl cation (Table V) exceeds 130.

Traylor and Perrin suggest that their results define the behavior to be expected of classical 2-norbornyl cations, thus providing a basis for estimating steric effects and anchimeric assistance in other bicyclo[2.2.1]-heptyl systems. Since they conclude that there is no carbon bridging in the transition state for departure of methanol, which is the rate-limiting step in the exchange reaction, Traylor and Perrin attribute the *exo*/*endo* ionization rate ratio of 16 for **72a** to steric hindrance to *endo* departure of methanol. This value probably overestimates the magnitude of steric deceleration for ionization of *endo*-2-norbornyl brosylate, tosylate, acetate, etc., since the *exo*/*endo* reactivity ratio for **72a** most likely reflects some enhancement in the rate of *exo* ionization derived from relief in the transition state of the ground state strain between the *endo*-6-hydrogen and the *endo*-6-oxygen. The magnitude of this adverse ground state interaction may be estimated from the ΔH for equilibration of the epimeric 2-norbornyl acetates (1.2 kcal/mole; see Fig. 2) (116) or the ΔG for equilibration of the epimeric 2-norbornanols (1.0 kcal/mole) (118).

If all this ground state strain is relieved as the *endo*-2-methoxy swings away from the *endo*-6-hydrogen during rehybridization of C-2 in the approach to the transition state for *exo* ionization for **72a**, a sixfold rate enhancement would be expected. Thus only a factor of 16/6, or ca. 3, remains to be allocated to the effect of steric deceleration of *endo* ionization. If accepted, this analysis allows a quantitative estimation, i.e., <1 kcal/mole, of the extent to which steric interactions in the transition state for *endo* ionization (capture) exceed those in the *endo* ground state.

This model predicts that nonbonded steric effects alone would generate an *exo*/*endo* reactivity ratio of 3 for the 2-norbornyl arenesulfonates or acetates* and an *exo*/*endo* product partition ratio of ca. 16 for capture of a classical 2-norbornyl cation by acetic acid or water. Torsional effects might increase these ratios to values of 10 to 30 and 48 to 160, respectively (see p. 1125).† The results of Traylor and Perrin, when interpreted as involving

* The assumption that methoxy, acetoxy, and tosyloxy substituents should all have comparable steric requirements is supported by the near identity of their steric *A* factors in cyclohexane systems (119).

† Absence of a clear definition of the structure of the transition state leading to cation **73** makes it impossible to judge how much torsional considerations influence the *exo*/*endo* reactivity factor observed by Traylor and Perrin. If this transition state resembles a protonated ketone, little torsional effect would be expected (65); if it resembles a methoxy carbonium ion, the usual effect might be anticipated.

the intermediacy of a classical 2-methoxy-2-norbornyl cation, thus confirm Brown's earlier suggestion (34–36) that *exo*-2-norbornyl arenesulfonates might solvolyze more rapidly than their *endo*-epimers, and that the 2-norbornyl cation might collapse preferentially to yield *exo* products, even in the absence of σ bridging. However, even when the effects observed by Traylor and Perrin are inflated by the torsional effect postulate, their magnitude falls short by a factor of at least 50 of explaining quantitatively both the high *exo*/*endo* reactivity ratios and the stereoselectivity in *exo*-product formation observed by both Winstein (5–7) and Goering and Schewene (116).

H. The Deamination of 2-Norbornylamine: Possible Formation of a Classical 2-Norbornyl Cation

Direct evidence bearing on the stereochemical fate of the unsubstituted classical 2-norbornyl cation may be contained in the results of two investigations of the deamination of optically active *exo*- and *endo*-2 norbornylamines in acetic acid. The results published by Corey and his co-workers (120), together with those obtained in the more thorough investigation of these reactions by Berson and Remanick (121), are summarized in Table VII.

The results obtained by the two groups agree quite well within the limits of experimental error, with the exception of the value for retention of optical purity in the products from deamination of *endo*-2-norbornylamine. In this case the value obtained by Berson is most likely the more accurate, since it was obtained by actual measurement of racemization. Corey, on the other hand, employed an indirect deuterium-scrambling technique, which, as Berson (121) has pointed out, is more susceptible to the intrusion of experimental artifacts.

On the basis of his findings that the deaminations of *exo*- and *endo*-2-norbornylamine yield virtually identical product mixtures, both in terms of the retention of optical purity and in terms of the *exo*/*endo* substitution ratio, Corey (120) postulated that both reactions proceed through a common intermediate. Since optically active product cannot be derived from the symmetrical nonclassical 2-norbornyl cation (**6**), Corey further suggested that this common intermediate must closely approximate in structure a classical 2-norbornyl cation.

Berson's more sophisticated experimental approach enabled him to distinguish some essential differences among the products derived from the epimeric 2-norbornylamines (121): (*1*) the *endo*-amine yields approximately twice as much *endo*-acetate as does the *exo*-amine; (*2*) the retention in optical purity of the *exo*-acetate is "substantially greater" in the product from the *endo*-amine than in that from the *exo*-amine; (*3*) finally, and most

TABLE VII

Products from the Deamination of Optically Active *exo*- and *endo*-2-Norbornylamines in Acetic Acid

Product	From *exo*-epimer[a]		From *endo*-epimer[a]	
	Yield, %	Optical purity, %	Yield, %	Optical purity, %
Total acetate[b]	87 (85.5)[e]	—	80	—
Total alcohol[b]	10 (9)[e]	—	16	—
Total nitrate[b]	2 ± 0.5	—	4	—
Total *exo*[b]	97 ± 1[f] (96 ± 1)	—	95 ± 1[g] (95 ± 1)	—
Total *endo*[b]	1.85 ± 0.45[f] (4 ± 1)	—	4.8 ± 0.5[g] (5 ± 1)	—
endo-Acetate[c]	2 ± 0.5	—	4.7 ± 0.5	85 ± 12
exo-Acetate[c]	98	11 ± 2	95.3	18 ± 0.6
endo-Alcohol[d]	ca. 1	—	5.3 ± 0.5	—
exo-Alcohol[d]	ca. 99	—	94.7	—
Total products		13 (15)		21 (16)

[a] Unless otherwise indicated, the uncertainty in the values quoted should be taken as 0.5 to 1%. The values in parentheses are those of Corey and his co-workers (120); the others are those of Berson and Remanick (121).

[b] Percentage of total recovered product.

[c] Percentage of acetate product fraction.

[d] Percentage of alcohol product fraction.

[e] *exo*-Epimer only.

[f] Calculated by assuming 98% of total nitrate to be the *exo*-epimer.

[g] Calculated by assuming 95% of total nitrate to be the *exo*-epimer.

significantly, little, if any, racemization is observed in the *endo*-acetate derived from the *endo*-amine. This final distinction clearly eliminates the possibility that all the products of the deamination of both *exo*- and *endo*-2-norbornylamine come from a single common intermediate. Were this the case, the extent of racemization for both *endo* and *exo* products would necessarily be identical. Clearly, then, the racemization encountered in the course of these reactions cannot derive solely from the Wagner-Meerwein interconversion of two enantiomeric 2-norbornyl classical ions (120). A further analysis of Berson's results, however, did permit him to establish that the extent of rearrangement in the *racemic portion* of the product was identical for the deamination of *exo*- and *endo*-2-norbornylamine. For this reason, Berson suggested that the intermediate giving rise to racemic product is common to both reactions (121).

The following mechanism appears to be consistent with the experimental results for these reactions. Deamination of *endo*-2-norbornylamine results

in the generation of a classical 2-norbornyl cation, which either reacts with nucleophile (acetate ion, nitrate ion, acetic acid, or water) or rearranges over a finite energy barrier to the bridged 2-norbornyl cation. The *exo* approach to the classical 2-norbornyl cation is favored over the *endo* approach by a factor of approximately 4 to 6:1. [In the absence of ion-pair effects, this ratio would be identical to the ratio (percentage optical purity *exo*-acetate: percentage *endo*-acetate product), which in this case is 4.1 ± 0.4.] Deamination of *exo*-2-norbornylamine proceeds via two competing mechanisms: (*1*) with participation of the 6,1 bonding pair to yield the bridged 2-norbornyl cation directly and (*2*) unassisted generation of the classical 2-norbornyl cation. The classical 2-norbornyl cation generated from the *exo*-amine is identical to that generated from *endo*-2-norbornylamine, except for the position of the gegenion of any intervening ion pairs. Consequently, it should both rearrange to the bridged ion and react directly with nucleophiles to give optically active products. In this case the ratio (percentage optical purity of *exo*-acetate: percentage total *endo*-acetate product) has the value 6 ± 2.5. On the basis of this mechanism, the intermediate leading to racemic products suggested by Berson and Remanick (121) as common to the deamination reaction for both the *exo*- and *endo*-2-norbornylamines would be identical to the bridged ion that is postulated (6) to give rise to racemic products in acetolyses of the two epimeric 2-norbornyl brosylates.

The foregoing mechanism has the advantage of being able to account for the following experimental observations.

1. The optical purity of the *endo*-acetate is significantly greater than that of the *exo*-acetate in the mixture produced from the deamination of the *endo*-amine. Optically active products can only come from the classical 2-norbornyl cation. Similarly, *endo*-acetate can only be derived from attack on the classical cation, whereas *exo*-acetate can come from both the classical cation and the symmetrical bridged ion. The departure from complete retention of optical purity in the *endo*-acetate can be explained in terms of some equilibration of the initially formed, vibrationally excited (122) classical cation with its enantiomer, possibly via the bridged ion (120).

2. The inferred intervention of a common precursor for the racemic portions of the mixture from the deamination of both the *exo*-amine and the *endo*-amine.

3. The difference in optical purity of the *exo*-acetate products and the difference in the *exo*/*endo* product ratios encountered between deamination of *endo*-amine on the one hand and *exo*-amine on the other. Since only the classical 2-norbornyl cation can give rise either to optically active products

or to *endo* product, the proportion of these will be diminished in the deamination of the *exo*-amine by the extent to which the bridged ion is formed directly.

The mechanism is also consistent with an expected decrease in the extent of the participation of the 6,1 bonding pair in the formation of the 2-norbornyl cation by deamination, as contrasted to its formation by solvolysis. Diminished participation is expected because the highly exothermic, direct loss of nitrogen from the aliphatic diazonium ion requires only a small activation energy—ca. 5 kcal/mole (120,123)—in comparison with that required for solvolysis of sulfonate—ca. 20–25 kcal/mole (6,120). Streitwieser (123) has suggested that a decrease in activation energy for ionization to a carbonium ion results in a compression of the difference in activation energies between competing routes to ionization. Due to this compression, there are more nearly equal rates of reaction along these competing reaction paths; in this case, 6,1 bonding pair participation and unassisted ionization. Martin and Bentrude (124) have elaborated on this theme, pointing out that if the activation enthalpy terms for the competing reaction paths are monotonously low, then the reaction with the lower activation entropy should prevail. Corey (120) has noted that the activation entropy for assisted deamination should exceed that for unassisted ionization, since participation requires the simultaneous excitation of the C-6–C-1 bending mode and the carbon–nitrogen stretching mode of vibration, whereas simple ionization requires the excitation of only the carbon–nitrogen stretching mode.

Corey (120) has called attention to the probability of significant involvement of cation-acetate ion pairs in these reactions on the basis of the results of related deaminations in acetic acid (125). Ion pairs of this type would be expected to yield a high value for percentage *endo*-acetate product in the deamination of the *endo*-amine and a high value for percentage optical purity of *exo*-acetate in deamination of the *exo*-amine, when compared with the value that would be determined solely by the difference in steric hindrance to nucleophiles approaching a classical 2-norbornyl cation from either the *endo* or *exo* direction. This expectation is borne out by the relative magnitudes of the ratio (percentage optical purity of *exo*-acetate): (percentage *endo*-acetate product) for the deamination of the *endo*- and *exo*-amines, ca. 4 and 6, respectively. These ratios can thus be used to set minimum and maximum limits on the *exo*/*endo* product ratio for nucleophilic attack by acetate or acetic acid on a classical 2-norbornyl cation. The remarkable agreement of this ratio with the equilibrium constant (ca. 4) for interconversion of *exo*- and *endo*-2-norbornanols (118) may be more than coincidental.

The validity of this method of obtaining an experimental value for the

exo/*endo* product ratio resulting from nucleophilic attack on a classical 2-norbornyl cation would be vitiated if we accepted Berson and Ben-Efraim's suggestion (126) that the optically active *exo*-acetate obtained in the deamination of *endo*-2-norbornylamine results from a direct nucleophilic displacement by solvent. Corey (120) rejected this idea on the basis of the low activation energy for deamination, which should result in the reaction path of minimum activation entropy; the transition state for a bimolecular displacement reaction certainly would have a more negative entropy than that for direct ionization. Berson and Remanick (121) countered this objection by citing Streitwieser's proposal (123) that the decreased activation energy for deamination should enhance the extent to which direct displacement could compete with simple ionization as compared, e.g., with acetolysis of *endo*-2-norbornyl brosylate (which yields *exo*-acetate, which is only 7–8% optically pure). Without passing on the relative merits of these two theoretical arguments,* the author is forced to conclude that direct displacement by solvent can only be of minor significance in the deamination of the epimeric 2-norbornylamines. This conclusion is based on the proved absence of such a displacement reaction in the closely related decomposition reaction of *N*-nitrosoamides (122, 128,129†).

In summary, the foregoing interpretation of the amine deamination studies by Corey and his co-workers (120) and by Berson and Remanick (121) sets the extreme upper limit of the *exo*/*endo* product ratio derived from nucleophilic attack by acetate ion or acetic acid on a classical 2-norbornyl cation at 8.5:1. This value is of the same order of magnitude as that observed by Traylor and Perrin (117) for capture of the 2-methoxy-2-norbornyl cation, which they presume to be classical. Both values are less by at least 2 orders of magnitude than those observed by Winstein et al. (5–7) and Goering and Schewene (116) for capture of the 2-norbornyl cation under conditions for which they postulate the intermediacy of a bridged ion. It remains difficult to interpret these discrepancies on the basis of steric factors alone.

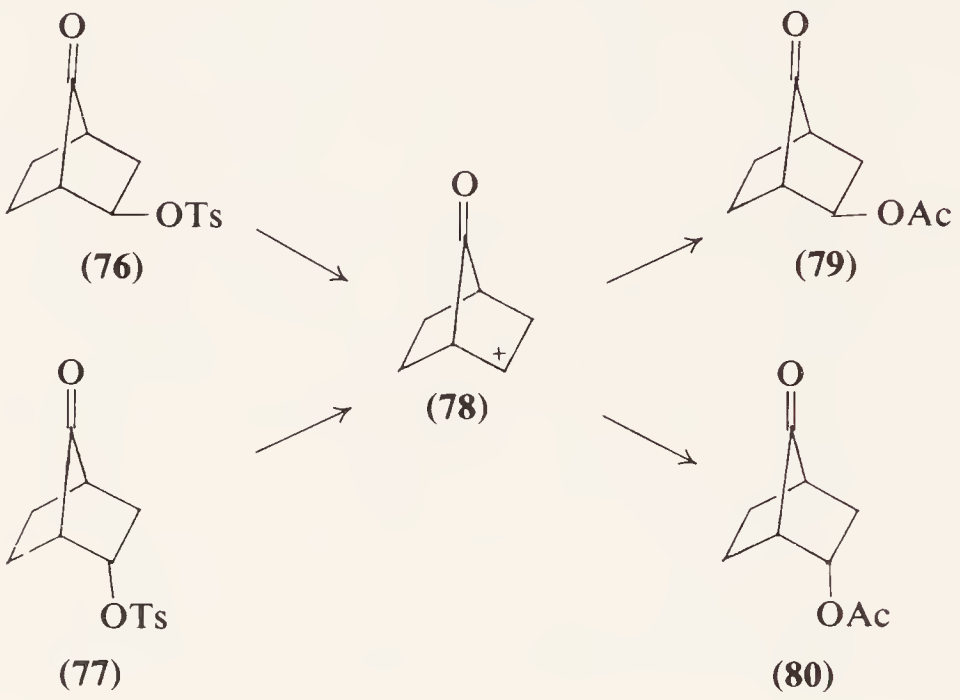
I. The Solvolysis of the 7-oxo-2-Norbornyl Tosylates and Related Derivatives

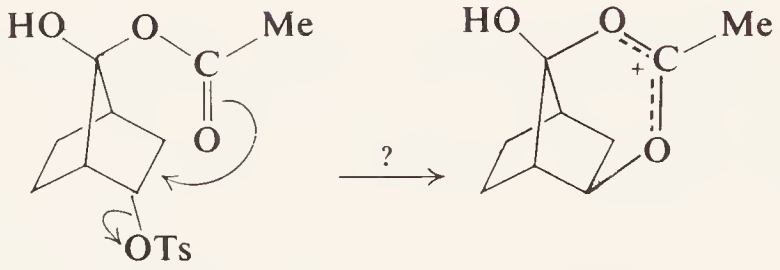
The formation of *endo*-oriented substitution products has also been observed in the solvolyses of 7-oxo-*exo*- (**76**) and 7-oxo-*endo*-2-norbornyl tosylates (**77**). At 25°, the rate of acetolysis of the *endo*-tosylate (**77**)

* In his review of the deamination reaction, Ridd (127) has considered these arguments on a theoretical basis and, in accord with the position taken here, concludes that displacement by solvent is most unlikely.

† White (129) suggests that the mechanisms of deamination of amines and of the decomposition of *N*-nitrosoamides are not only analogous but actually overlap.

exceeds that for the *exo*-tosylate by a factor of 6. Surprisingly, the 7-oxo-group appears to exert little, if any, rate-retarding inductive effect upon the solvolysis of the *endo*-tosylate (**77**), since its rate of acetolysis at 25° is virtually indistinguishable from that of *endo*-2-norbornyl tosylate (6). Gassman and Marshall suggest that these results are best interpreted by assuming that both the *endo*- (**77**) and *exo*-oxotosylates (**76**) undergo





(**81**) (**82**)

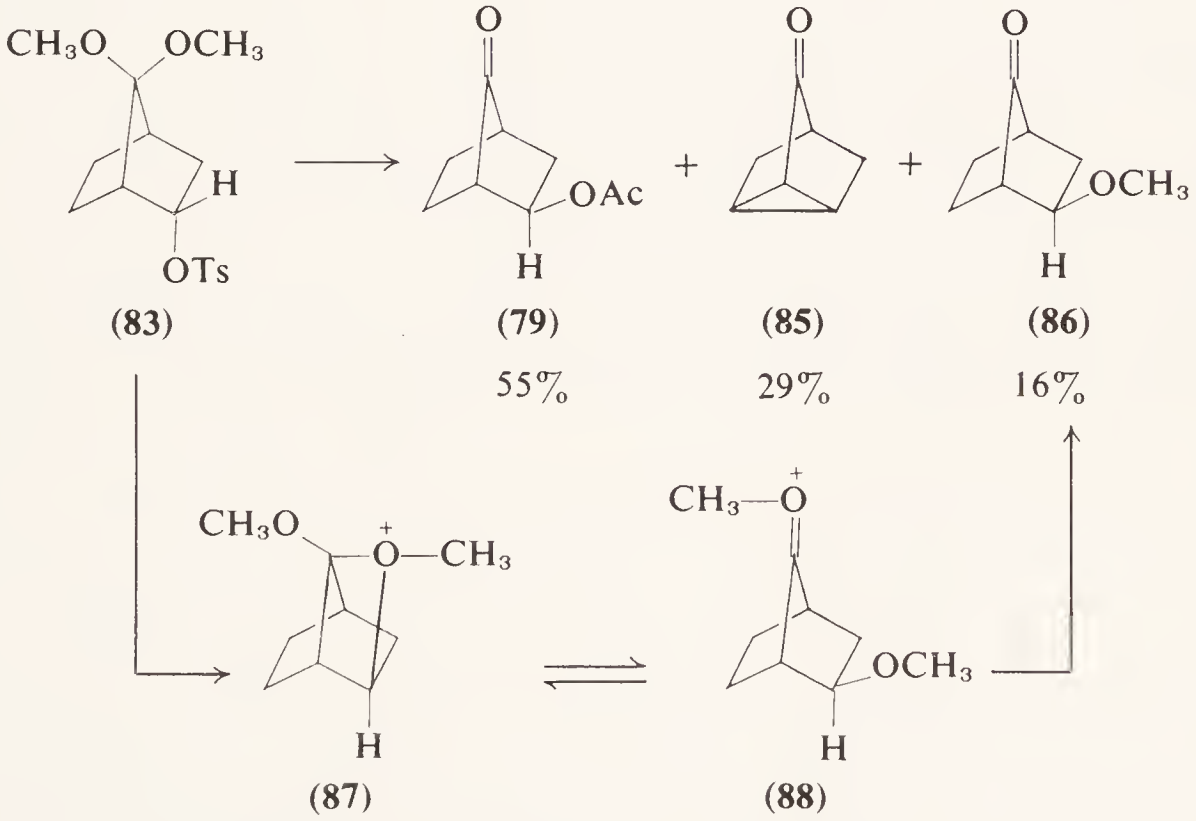
unassisted ionization to a classical 7-oxo-2-norbornyl cation (**78**). Presumably, participation of the C-6–C-1 bonding electrons does not accompany ionization of the *exo*-tosylate (**76**), because the inductive effect of the adjacent 7-oxo-group renders untenable the development of positive charge density at C-1, which must accompany this process.

Gassman and Marshall found that acetolysis of the *exo*-oxotosylate (**76**) yielded a mixture of products consisting of 34% *endo*- (**80**) and 66% *exo*-2-acetoxy-7-oxonorbornane (**79**). The *endo*-oxotosylate (**77**) also yielded a mixture of the same two acetates, but it contained only 2% of the *endo*-2-acetoxy-7-oxonorbornane (**80**). These results are consistent with the formation in each case of the classical 7-oxo-2-norbornyl cation. Normal leaving-group shielding of the cation and backside solvent participation in its formation would lead one to expect a preponderance of acetate of configuration inverted relative to starting tosylate to be generated in each case. The predominance of *exo*-acetate found in both product

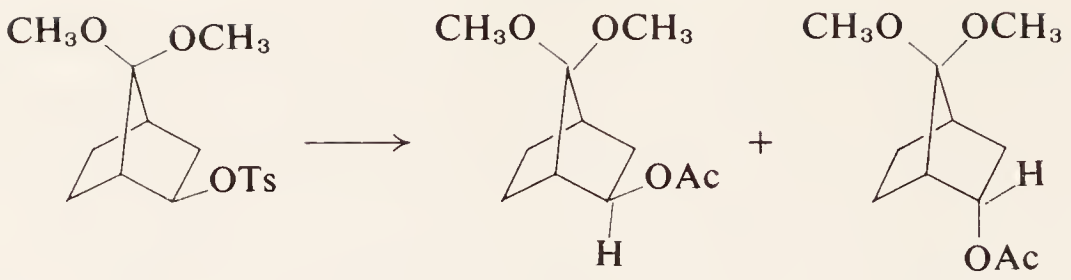
mixtures confirms the widely held belief that the 2-norbornyl cation should be less accessible from the *endo* side, but the isolation of 34% *endo*-acetate (**80**) from solvolysis of the *exo*-oxotosylate (**76**) makes it graphically clear that steric considerations alone cannot account for the exclusive formation of products of *exo* stereochemistry from a 2-norbornyl cation.

Gassman and Marshall considered and rejected the possibility that acetolysis of the *endo*-oxotosylate (**77**) proceeds via an intermediate acetoxonium ion (**82**) formed by initial addition of acetic acid to the 7-oxo-group followed by intramolecular participation of the carbonyl oxygen of the acetoxy-group (**81**). They considered such a mechanism most unlikely because participation of this type is precluded during ethanolysis, for which the *exo*/*endo* solvolytic rate ratio at 100° for the epimeric 7-oxo-2-norbornyl tosylates is only 2.1 (cf. 0.4 for acetolysis at 100°).

More recent results reported by Gassman and Marshall (131) revive the possibility that the *exo*- (**76**) and *endo*-oxotosylates (**77**) solvolyze by different mechanisms and becloud the interpretation placed on the previous work. These investigators find that acetolysis of *endo*-7,7-dimethoxy-2-norbornyl tosylate (**83**) yields only products containing a 7-keto function, whereas its *exo*-epimer (**84**) yields only products containing 7,7-dimethoxy substituents.



Since the *endo*-tosylate (**83**) yields only ketonic products and its epimer (**84**) produces only ketal-type products, Gassman and Marshall (131) conclude that the two tosylates must solvolyze by different mechanisms. The formation of 7-oxo-*exo*-2-norbornyl methyl ether (**86**) from acetolysis of *endo*-tosylate **83** leads these investigators to postulate that this reaction



(84) **(89)** 95.5% **(90)** 4.5%

(Percentages indicate relative yields. Absolute yields of total products were 70 and 66% from **83** and from **84**, respectively.)

involves methoxyl participation to generate **87** as the initial cationic intermediate. Cation **87** could presumably interconvert readily with cation **88**, which, by transfer of a methyl group to acetic acid, could serve as a logical precursor for ketoether **86**. Although cation **87** hardly seems an attractive precursor to the major products of the reaction—ketoacetate **79** and nortricyclanone (**85**)—the intervention of this ion was thought to be necessary to explain the ketonic nature of the products. This conclusion was prompted by the observation that ketalacetates **89** and **90** were stable to the reaction conditions and that nortricyclanone dimethylketal did not yield significant amounts of either **79** or **85** when decomposed in buffered acetic acid.

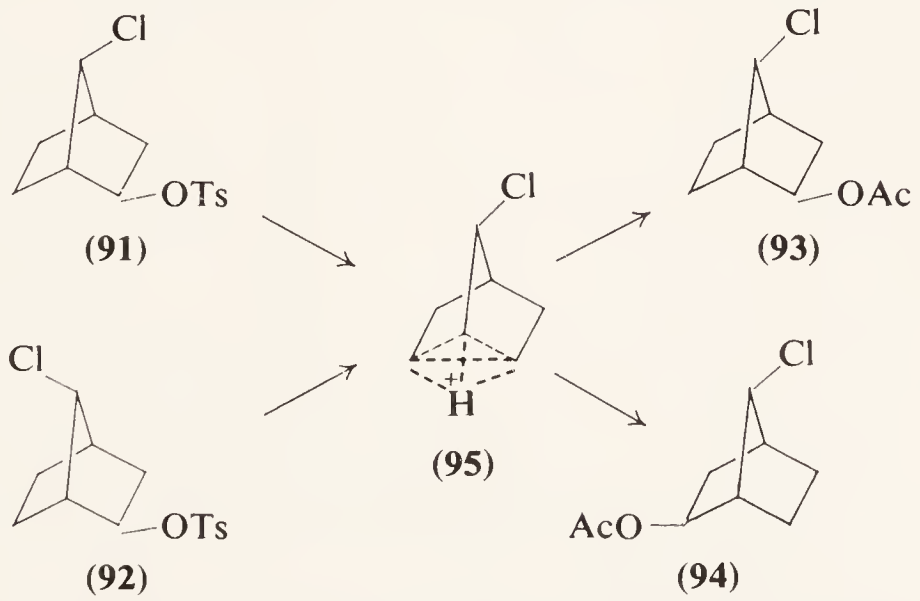
From the nature of the products formed by acetolysis of *exo*-tosylate **84**, Gassman and Marshall concluded that cation **87** does not intervene in this reaction. They suggest that the mixture of *exo*- (**89**) and *endo*-acetates (**90**) arises from attack on a classical 7,7-dimethoxy-2-norbornyl cation, perhaps in the form of a solvent-separated ion pair. No explanation was advanced for the apparent failure of this ion to interconvert with cation **87**, although such a process would seem to be most facile, given the central role assigned to methoxyl participation in the solvolysis of *endo*-tosylate **83**.

The observation that methoxyl may participate during ionization of *endo*-tosylate **83** reopens the possibility that acetolysis of *endo*-oxotosylate **77** involves intramolecular acetoxyl participation (**81** → **82**). Thus the near equality of the acetolysis rate constants for the *exo*- (**76**) and *endo*-oxotosylates (**77**) cannot be employed as *prima facie* evidence for the generation of a classical 7-oxo-2-norbornyl cation (**78**). The intervention of an acetoxonium ion (**82**) could provide a plausible explanation for the markedly higher *exo*/*endo* product partition ratio observed for solvolysis of the *endo*- (**77**) as opposed to the *exo*-oxotosylate (**76**). The formation of such an intermediate cannot at the same time account for the significant yield of *endo*-acetate (**80**) formed in the acetolysis of 7-oxo-*exo*-2-norbornyl tosylate (**76**). The most likely precursor for the products of this reaction remains a classical 2-norbornyl cation, and the high yield of *endo*-acetate

(**80**) remains to challenge those who would argue that *endo* attack on such an ion is precluded solely by steric inhibition.

NOTE ADDED IN PROOF: Gassman and MacMillan (217) have cautioned that *all* 7-oxygenated 2-norbornyl tosylates may solvolyze by mechanisms different from that of the unsubstituted system and therefore are inappropriate substrates with which to test the postulate that significant charge delocalization may accompany the formation of the parent 2-norbornyl cation.

One disturbing feature remains concerning the postulate (130) that the adverse inductive effect of the 7-keto group renders untenable participation by the C-6–C-1 σ-bonding electrons during solvolysis of 7-oxo-*exo*-2-norbornyl tosylate. Were this the case, other comparable electron-withdrawing substituents would be expected to produce similar kinetic and stereochemical consequences. This expectation is borne out in the acetolysis of 7,7-dimethoxy-*exo*-2-norbornyl tosylate (**84**): this reaction is retarded by a factor of 245 (25°) relative to acetolysis of *exo*-2-norbornyl tosylate; it also produces *endo*-acetate (**90**) in significant yield (4.5%) (131). The expectation that significant yields of *endo* product should be formed from acetolysis of *syn*- (**91**) and *anti*-7-chloro-*exo*-2-norbornyl tosylate (**92**) is not confirmed by the published data (132), however, even though both these tosylates solvolyze at a rate virtually identical to that for 7,7-dimethoxy-*exo*-2-norbornyl tosylate (**84**). Roberts and his co-workers (132) reported that both chlorotosylates yield the same (ca. 1:1) mixture of *syn*- (**93**) and *anti*-7-chloro-*exo*-2-norbornyl acetates (**94**), but that no *endo*-acetate was detected in the product mixture. The nearly identical yield of acetate of retained structure and acetate derived from a 6,2 hydride shift was interpreted as strong evidence for the intervention of a hydrogen-bridged ion (**95**). The absence of 3-chloro-*exo*-2-norbornyl acetate from



the product mixture was taken to reflect low cationic charge at C-1 in the bridged ion, due to the adverse inductive effect of the 7-chloro substituent.

According to the interpretation of Gassman and Marshall (130,131), this adverse inductive effect should result, at least to some extent, in the formation of classical 2-norbornyl cations in this system, and these ions should be subject to attack from the *endo* direction. A conflict between the Gassman and Marshall prediction and the results of Roberts and co-workers (132) may be more apparent than real, however. The analysis of the product mixture from the acetolysis of the 7-chlorotosylates, conducted without the benefit of vapor-phase chromatography, rests on infrared comparison of the chlorohydrins formed by $LiAlH_4$ reduction of the product mixture with authentic mixtures of *syn*- and *anti*-7-chloro-*exo*-2-norbornanols (132). It seems likely that as much as 10% of *endo* product might have remained undetected by this technique. This analysis obviously bears repeating, utilizing more sensitive analytical procedures.

NOTE ADDED IN PROOF: The products (219) and the kinetics (220) of acetolysis of the 7-chloro-2-norbornyl tosylates have been reinvestigated.

IV. KINETIC CRITERIA FOR BRIDGED-ION FORMATION

The rate of acetolysis of *exo*-2-norbornyl brosylate (**4**) exceeds that of its *endo*-epimer by a factor of 350 (25°) when measured titrimetrically and by a factor of ca. 1600 when followed polarimetrically (see p. 1101) (5–8). Since the rate constant for the *endo*-brosylate differs from that of cyclohexyl brosylate (7) by less than a factor of 2, Winstein and Trifan (5,6) concluded that the acetolysis of *exo*-2-norbornyl brosylate must be accelerated. If we attribute this acceleration to participation by the C-6–C-1 bonding pair of electrons, then the initially formed ion must differ in structure from a classical 2-norbornyl cation. This follows from the fact that simple Wagner-Meerwein rearrangement involving migration of C-6 from C-1 to C-2 results merely in the formation of the enantiomer of the classical 2-norbornyl cation which would be generated by simple ionization of *exo*-2-norbornyl brosylate. Since an enhanced rate must reflect a lower transition state free energy, which in turn must reflect a first intermediate of lower free energy, it is inconceivable that ionization with participation could generate an accelerated rate of solvolysis for *exo*-2-norbornyl brosylate, *unless that participation were to result in the formation of a first intermediate more stable than the classical 2-norbornyl cation.* Unambiguous demonstration that solvolysis of *exo*-2-norbornyl brosylate is attended by anchimeric assistance must then constitute positive evidence for the formation of a bridged ion similar, if not identical, to that originally proposed by Winstein and Trifan (5–8).

Brown (34–36) has proposed an alternative explanation for the observed *exo*/*endo* rate ratio in the solvolysis of the 2-norbornyl brosylates. He

suggests that the rate of solvolysis of *exo*-2-norbornyl brosylate may be normal, rather than being enhanced, and that the rate of solvolysis of *endo*-2-norbornyl brosylate, rather than being normal, may, in fact, be diminished (36). For these reasons, he contends that the ratio of the solvolytic rate constants of the epimeric 2-norbornyl brosylates may not provide evidence for a driving force (i.e., for σ delocalization) in the solvolysis of the *exo*-epimer. To support his suggestion that the *endo*-brosylate may solvolyze unusually slowly, Brown argues that the peculiar geometry of the norbornyl ring skeleton requires that the departing brosylate anion pass unusually close to the *endo*-hydrogen atom on C-6 if it is to follow a path perpendicular to the plane of the incipient carbonium ion at C-2. He thus suggests that the transition state for ionization of the *endo*-sulfonate is sterically destabilized with respect to the ester itself, and this results in a deceleration for ionization of the *endo*-sulfonate relative to the *exo*-epimer.

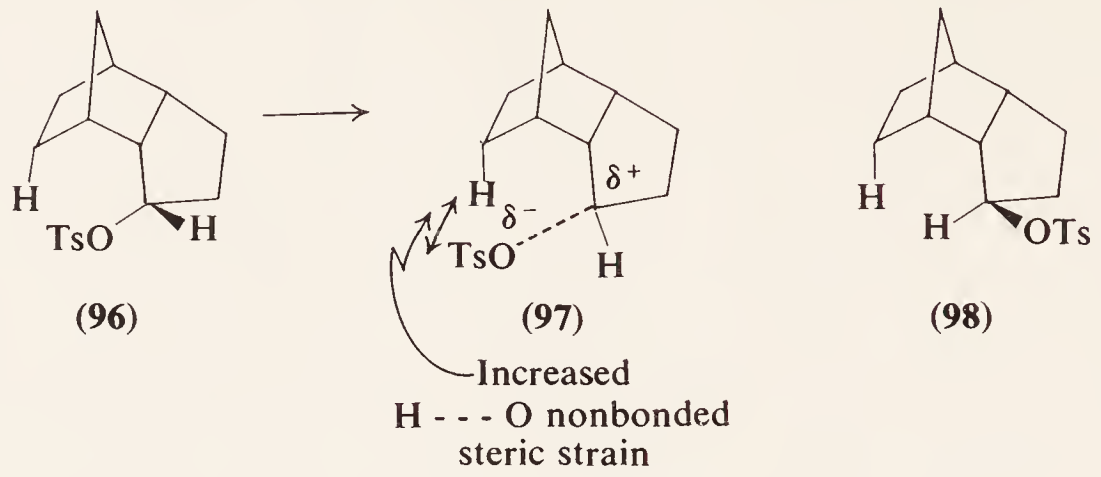
To decide between these differing interpretations of the *exo*/*endo* rate ratio for the 2-norbornyl brosylates, we must come to grips with three fundamental questions:

1. Is steric deceleration of solvolysis an unambiguously demonstrable phenomenon?
2. Can steric deceleration of solvolysis be clearly demonstrated for substituted 2-norbornyl derivatives, and, if so, to what extent can this demonstration be extrapolated to the unsubstituted system?
3. What consequences should devolve from σ participation in solvolysis of substituted *exo*-2-norbornyl derivatives, and to what extent can the presence or absence of these consequences be proven experimentally?

A. Steric Deceleration of Solvolysis

A handful of examples of steric deceleration of solvolysis have now been reported. Perhaps the clearest of these is found in the observation that the rate of acetolysis of *endo*-5,6-trimethylene-*exo*-8-norbornyl tosylate (**98**) exceeds that of its epimer (**96**) by a factor of 5.7 (133). Since the influence of torsional and bond angle strain (see p. 1160) on the rate of ionization should be identical for these two epimers, and since ground state nonbonded strain for the *endo*-tosylate exceeds that of its epimer by ca. 1.9 kcal/mole (134), the usual assumption (135) that nonbonded strain is fully relieved in the transition state for carbonium ion formation would lead to the prediction that the rate of the *endo*-tosylate should *exceed* that of the *exo* by approximately a factor of 25. The absence of any apparent mechanism (e.g., σ participation) by which the rate of the *exo*-tosylate could be enhanced, prompts the conclusion that solvolysis of the *endo*-tosylate is

retarded by an increase in nonbonded strain of approximately 1 kcal/mole (RT ln 5.7) between ground state (**96**) and transition state (**97**).

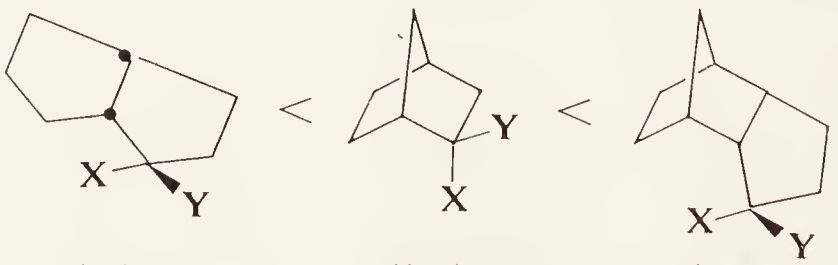


(96) (97) (98)

Inspection of models reveals that, if the tosylate-leaving group is constrained to depart by a route that even approaches perpendicularity with the plane of the developing carbonium ion during solvolysis of *endo*-tosylate **96**, it must, indeed, pass very close to the *endo*-2-hydrogen. In this respect, it seems that the system, qualitatively at least, offers more extreme steric hindrance to ionization than does solvolysis of *endo*-2-norbornyl brosylate (136–138). For this reason we might take the value of 1 kcal/mole as *an upper limit* for the magnitude of the increase in nonbonded interaction experienced by the leaving group in passing from ground state to transition state during solvolysis of *endo*-2-norbornyl brosylate.

Brown and his co-workers (137) have examined the rates of solvolysis of the tertiary *p*-nitrobenzoates **101a** and **101b** corresponding to the secondary tosylates **98** and **96**. In this case they find that the *exo*/*endo* rate ratio is 4300. Comparison with the results in the secondary system (*exo*/*endo* rate ratio, 5.7) reveals that a major contribution to this ratio must come from relief in the transition state of the adverse *endo*-8-methyl, *endo*-2-hydrogen nonbonded interaction present in the ground state of *exo*-*p*-nitrobenzoate **101a**; i.e., solvolysis of the *exo*-*p*-nitrobenzoate must be sterically accelerated.

This coupling of steric effects, steric deceleration of *endo* ionization and steric acceleration of *exo* ionization, tends to becloud the significance of the observation that *exo*/*endo* ionization ratios increase as the U-shaped character of the bicyclic skeleton is enhanced in the series



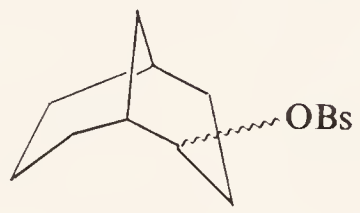
(99) (100) (101)

(a) X = CH_3, Y = *p*–nitrobenzoate

(b) X = *p*–nitrobenzoate, Y = CH_3

Even if we accept the assumption (136,137), verified only for the 2-methyl-2-norbornanols (139), that *endo*-methyl and *endo*-oxygen engender nearly identical unfavorable ground state nonbonded interactions, we can only conclude that, for this series of compounds, these interactions are not relieved as extensively in the transition state for ionization of the *endo*-*p*-nitrobenzoates as in that of the *exo*-*p*-nitrobenzoates.

Steric deceleration of ionization for the *endo*-epimer has also been invoked to explain the *exo*/*endo* rate ratio (ca. 75) for solvolysis of the epimeric 2-bicyclo[3.3.1]nonyl brosylates (**102**) (140). This is a much more



(102)

flexible system than the norbornyl skeleton, and it features significant nonbonded interactions not involving substituents attached to the carbon atom bearing the leaving group which may be relieved by ionization. Therefore, the relevance of the foregoing observation to the question of steric deceleration of ionization for *endo*-2-norbornyl derivatives is diminished.

B. Steric Deceleration in Solvolysis of *endo*-2-Norbornyl Arenesulfonates

With respect to the question of possible steric deceleration of ionization, the solvolyses of the epimeric 6,6-dimethyl-2-norbornyl *p*-toluenesulfonates (tosylates) (**103**, **104**) (104) furnish contrasting and intriguing results. Inspection of the *exo*/*endo* rate ratio (Table VIII) alone would lead to the conclusion that even a bulky methyl group in the *endo*-6-position fails to hinder ionization of an *endo*-2-sulfonate. If we consider the rate of acetolysis of each of the epimeric esters relative to the corresponding unsubstituted 2-norbornyl tosylate, however, we see that *both* the substituted esters (**103** and **104**) are retarded relative to their unsubstituted analogs.

The rate deceleration exhibited by the *endo*-tosylate (**103**) (ca. 16) is readily explained by the arguments put forth by Brown to postulate an abnormally slow rate for *endo*-2-norbornyl tosylate, i.e., increased steric strain in the transition state. Whether this result can be cited to support a similar effect in the solvolysis of *endo*-2-norbornyl tosylate itself is open to contention. The act of replacing the *endo*-6-hydrogen atom of the norbornyl nucleus by a methyl group not only increases the bulk of the *endo*-6 substituent, but it also alters the effective position or "center of gravity" of that substituent in a way that places it more directly in the path of the departing sulfonate anion. This change in position occurs because the bond length between C-6 and the *endo* substituent is increased from 1.09 to

1.54 Å when hydrogen is replaced by methyl. Thus we can argue that the sulfonate anion departs along a line that avoids increased interaction with the comparatively small hydrogen atom located close to C-6 but results in significant interaction with the more bulky group centered at a greater distance from C-6 (141). This concept is presented schematically in Figure 3.

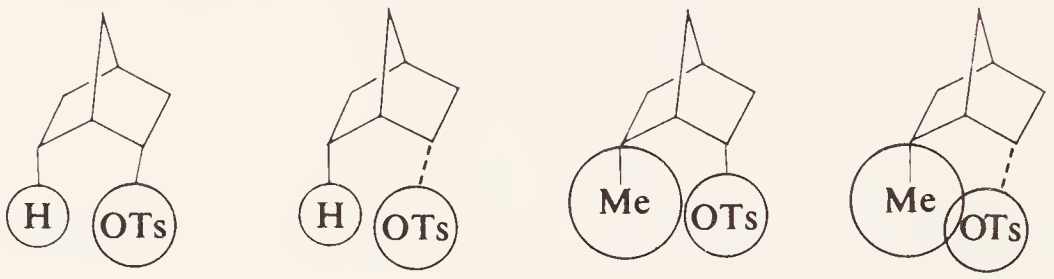


Fig. 3

C. Steric Inhibition to Bridged-Ion Formation

Another example of the steric inhibition phenomenon, steric deceleration of solvolysis, may be found in the lethargic solvolysis of *endo*-5,6-trimethylene-*endo*-2-norbornyl tosylate (**105**), which undergoes acetolysis 11 times more slowly than *endo*-2-norbornyl tosylate itself (Table VIII) (142). Steric inhibition to solvation of the resulting carbonium ion has been offered as an alternative explanation for the retarded solvolysis rates of **103** and **105** (141).

Although the retarded solvolytic rates for tosylates **103** and **105** can be explained in terms of classical intramolecular steric effects, no such rationalization presents itself in the case of the epimeric *exo*-tosylates **104** and **106**, which solvolyze at rates retarded by the factors of 20 and 21, respectively, relative to *exo*-2-norbornyl tosylate. It is tempting to argue that this rate diminution reflects steric hindrance to solvent approach to the *endo* side of C-2 and resultant inferior solvation of the transition state. Such an interpretation is rendered suspect, however, by the observation that tosylates **108** and **110** also undergo acetolysis at rates retarded by the factors of 73 and 107, respectively, relative to *exo*-2-norbornyl tosylate (Table VIII). The ease of solvent approach to C-2 from the *endo* side in these substituted norbornyl tosylates can hardly differ significantly from that in *exo*-2-norbornyl tosylate itself. It seems implausible, therefore, to try to use steric arguments to account for the effect of substitution at C-6 on the facility with which a classical carbonium ion may be generated at C-2. On the other hand, the diminished solvolytic rates of tosylates **104**,

106, **108**, and **110** can be readily explained by postulating that the transition state for their ionization fails to approach the character of the nonclassical, bridged norbornyl cation. As Donaldson (141) has pointed out, inspection of models reveals that conversion of 6,6-dimethyl-*exo*-2-norbornyl tosylate into a transition state leading to a nonclassical ion results in a marked increase in nonbonded interactions between the methyl groups on C-6 and the hydrogen atoms on C-1 and C-2. To the extent that these nonbonded interactions exceed in severity those present in the ground state of **104**, the favorable contribution to the free energy of the reaction associated with charge delocalization or decreased angle strain in the bridged ion will be offset. Similarly, Donaldson (141) argues that as the geometry of the nonclassical ion is approached in the transition state for solvolysis of tosylate **106**, the five-membered ring formed by the *endo*-trimethylene bridge must become distorted. The free-energy increase associated with this distortion thus partially counteracts the free-energy decrease associated with bridged-ion formation, so that the overall rate acceleration associated with C-6 participation is less than that exhibited by *exo*-norbornyl tosylate. Similar arguments can be applied to explain the retarded rates of solvolysis for sulfonates **108** and **110**.

In summary, although it appears that bulky *endo* substituents at C-6 bring about some steric deceleration in the ionization of *endo*-2-norbornyl sulfonates, the effect of the same substituents on solvolysis of the *exo*-sulfonates seems to imply just as strongly that the C-6–C-1 bonding electrons participate in the transition state for *exo*-2-norbornyl tosylate itself.

The possibility that bridged-ion formation can be impeded by placing structural constraints on the ability of C-6 to bond simultaneously to C-1 and C-2 has been further tested by Corey and Glass (144). In order to minimize the possibility that the structural feature of the molecule that provides the constraining force might also introduce extraneous features such as ambiguous inductive effects or possible steric hindrance to solvation, these investigators synthesized the *endo*- and *exo*-tosylates **111** and **112**, respectively. To understand that the 4,5-*exo*-trimethylene bridge should provide the desired constraint, we need only recall that a bridged 2-norbornyl cation must resemble the transition state for the simple Wagner-Meerwein migration of C-6 from C-1 to C-2. As such, the bridged ion must be intermediate in structure between the two Wagner-Meerwein related classical cations. If one of these cations possesses a structural feature resulting in increased steric strain relative to the other, then the energy of the intermediate bridged ion must be higher than it would be were this feature absent. This is precisely the case for the two ions **113** and **114**.

TABLE VIII

Relative Rates of Acetolysis of Sulfonate Esters at 25°

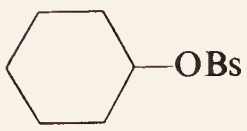
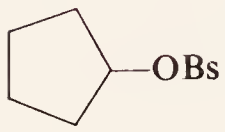
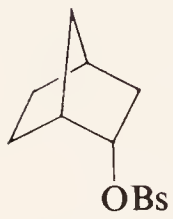
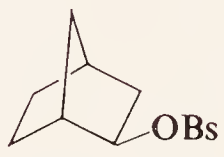
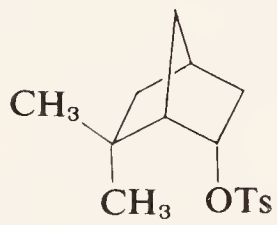
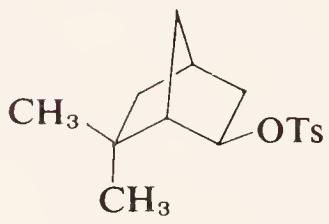
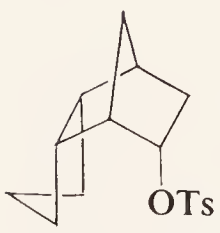
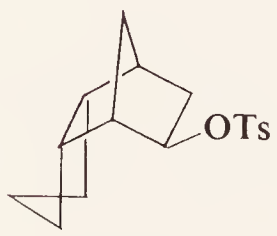
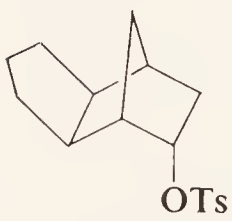
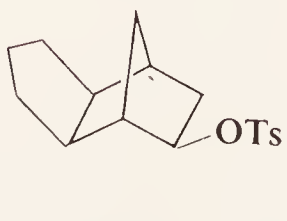
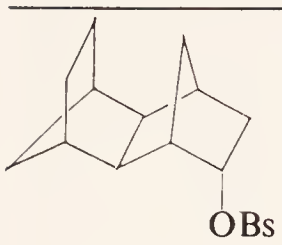
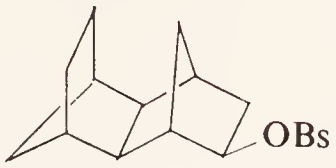
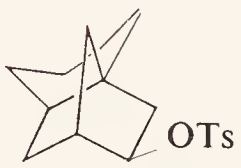
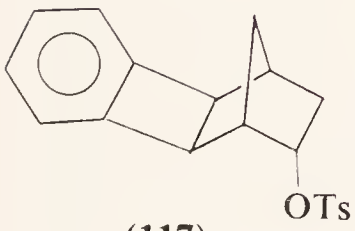
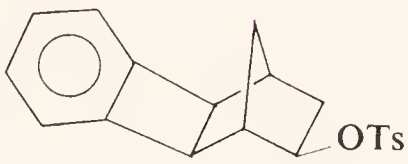
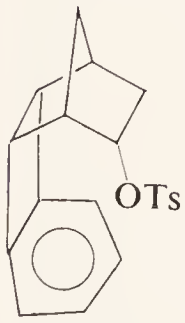
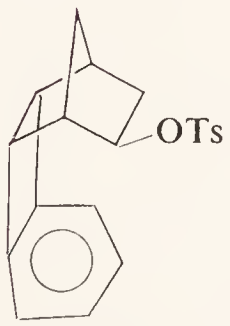
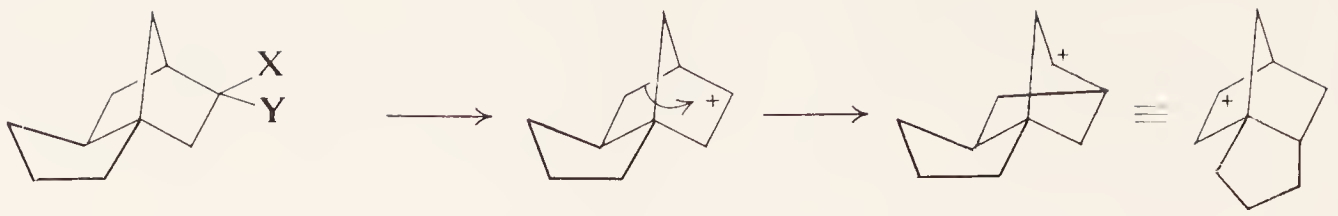
Compound	Relative rate	Compound	Relative rate	*exo*/*endo* rate ratio	Reference
	1.0				7
	32				7
 **(5)**	1.47	 **(4)**	517	350	5,6
 **(103)**	0.090[a]	 **(104)**	25.4[a]	222	104
 **(105)**	0.062[a]	 **(106)**	9.52[a]	153	142
 **(107)**	0.25[a]	 **(108)**	2.76[a]	11.2	142

TABLE VIII (*Continued*)

Compound	Relative rate	Compound	Relative rate	*exo*/*endo* rate ratio	Reference
 **(109)**	0.22[a]	 **(110)**	4.89	22	143
 **(111)**	0.67[a]	 **(112)**	5.7	8.5	144
 **(117)**	0.107[b]	 **(116)**	0.186[b]	1.74	145
 **(119)**	0.00281[b]	 **(118)**	0.714[b]	254	145

[a] Rate relative to cyclohexyl tosylate at 25°C.

[b] Rate relative to cyclohexyl tosylate at 75° [S. Winstein, E. Grunwald, R. E. Buckles, and C. Hanson, *J. Am. Chem. Soc.*, **70**, 816 (1948)].



(111) X = H, Y = OTs

(112) X = OTs, Y = H

(115a) X = OAc, Y = H

(115b) X = H, Y = OAc

(113)

(114)

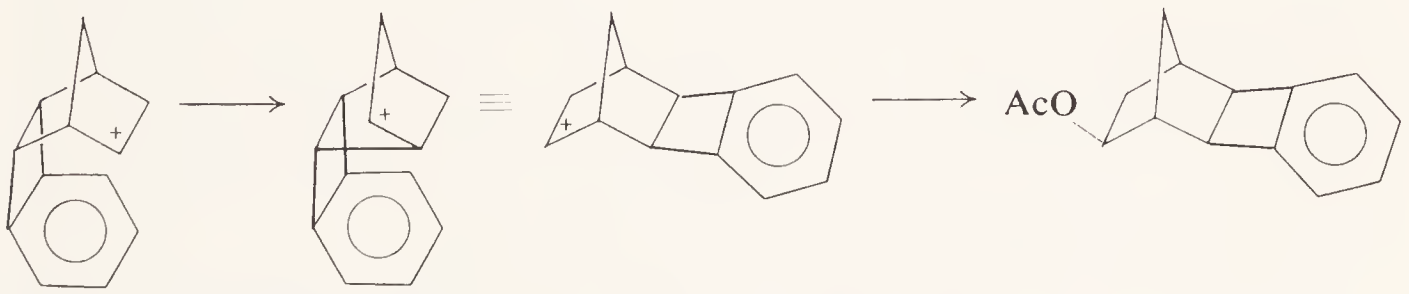
In cation **114**, the 4,5-trimethylene bridge is *endo* fused. Corey and Glass estimate that this *endo* fusion results in angle strain in the five-membered ring formed by the trimethylene bridge which exceeds that for the *exo* fused ring by 6–8 kcal/mole. If the 1600-fold *exo*/*endo* rate differential for solvolysis of the unsubstituted 2-norbornyl arenesulfonates is due largely to bridged-ion formation, the *exo*/*endo* rate ratio for tosylates **112** and **111** should be less, since the increasing angle strain in the trimethylene bridge generated by approach to the geometry of the bridged ion should serve to offset, at least partially, the stabilization associated with bridged-ion formation. If the parent *exo*/*endo* rate differential is due largely to steric inhibition to ionization, however, the remote location of the trimethylene bridge should ensure that a comparable *exo*/*endo* rate ratio would be observed for acetolysis of tosylates **112** and **111**. The observed relative rates for *exo*-tosylate **112**, *endo*-tosylate **111**, and *endo*-2-norbornyl tosylate are 3.4:0.4:1.0, respectively. The presence of the 4,5-trimethylene bridge results in a decrease in the *exo*/*endo* rate ratio from 1600 to 8.5 without any substantial effect on the rate of solvolysis for the *endo*-tosylate. Although this result is consistent with the bridged-ion hypothesis, it finds no rationale in terms of steric inhibition to ionization.

One feature of the solvolysis of tosylates **111** and **112** requires further clarification before the kinetic results can be accepted as unambiguous evidence for the bridged-ion concept. The product mixture from the acetolysis of each tosylate was found to contain ca. 92% *exo*-acetate **115a**, but less than 4%, if any, *endo*-acetate **115b**. As Brown (34,35,133) has noted, the factors that determine the *exo*/*endo* ionization rate ratio should also, at least to a first approximation, control the *exo*/*endo* product partition ratio (see p. 1136). Further work is needed to clarify the mechanistic basis for the high stereospecificity of product formation that persists in this system despite the low *exo*/*endo* reactivity ratio. (For two additional examples of this phenomenon, see pages 1159 and 1175.)

One final example serves to illustrate the profound steric effect which substituents at the 5,6-position can exert on the solvolysis of both *exo*- and

endo-2-norbornyl arenesulfonates. Baker and Hudec (145) have examined the acetolyses of the four isomeric 3,4-benzotricyclo[4.2.1.$0^{2,5}$]non-3-en-7-yl tosylates: *exo*, *exo* (**116**), *endo*, *endo* (**117**), *endo*, *exo* (**118**) and *endo*, *endo* (**119**). Comparison of the acetolysis rate constant for the *exo*, *endo*-tosylate (**117**) (Table VIII) with that for *endo*-2-norbornyl tosylate demonstrates that the only effect of the *exo*-fused substituent on the rate of departure of the leaving group is the expected approximately tenfold rate-retarding inductive effect (17). The *exo*/*endo* rate ratio for tosylates **116** and **117** (1.7) reveals the dramatic effect exerted by the *exo*-fused substituent in retarding the ionization rate for the *exo*-oriented leaving group. The only apparent explanation for this phenomenon is, once again, steric destabilization of bridged-ion formation. The rate of solvolysis of the *endo*, *endo*-tosylate **119** is less by a factor of 38 than that of the *exo*, *endo*-tosylate **117**. This diminution presumably represents steric inhibition to departure of the *endo*-oriented leaving group by the bulky *endo*-fused benzene ring. Comparison of the acetolysis rate constants for the *exo*, *exo*-tosylate **116** and the *endo*, *exo*-tosylate **118** reveals that the latter is accelerated by a factor of ca. 4. A similar factor relates the acetolysis rates for tosylates **106** and **108** and doubtless originates in relief of the ground state nonbonded repulsion between the *endo*-2-hydrogen and the *endo*-6-substituent as C-2 rehybridizes from sp^3 toward sp^2 during ionization.

Despite the low *exo*/*endo* reactivity ratio for tosylates **116** and **117**, Baker and Hudec (145) find that the only product from acetolysis of both tosylates is the *exo*, *exo*-acetate **120**. Similarly, tosylates **118** and **119** also yield only *exo*, *exo*-acetate **120**, presumably as the result of Wagner-Meerwein conversion of the initially formed ion **121** to the *exo*-fused ion **122**. (Rapid isomerization of tosylate **118** to tosylate **116** also occurred under solvolytic conditions.)



(121) **(122)** **(120)**

As with the work of Corey and Glass (144), the disparity between the low *exo*/*endo* reactivity and the high *exo*/*endo* product partition ratio represents grounds for further inquiry into the mechanism of these solvolyses.

D. Semiempirical Calculations of the Rate Constant for Unassisted and Unimpeded Ionization of 2-Norbornyl Arenesulfonates

Despite the firm experimental evidence for steric inhibition to ionization in other systems (particularly tosylates **96**, **103**, **105**, and **119**), there exists no direct experimental evidence for the operation of this phenomenon in the solvolysis of *endo*-2-norbornyl brosylate itself. The most straightforward method by which to probe for its possible intrusion, of course, would be to compare the rate of solvolysis of *endo*-2-norbornyl brosylate with that of a suitable model compound that is clearly incapable of suffering steric inhibition to ionization. The difficulty in applying this technique is in obtaining a model compound identical to *endo*-2-norbornyl brosylate with respect to angle strain, torsional strain, and nonbonded repulsions.*

In the absence of such an ideal model compound, efforts have been made to correct the observed rate for some model compounds for the anticipated effect of the structural differences between the model and *endo*-2-norbornyl brosylate. This approach is greatly facilitated by the dramatic demonstration by Foote (146) that the influence of internal bond angle strain on the rate of ionization of a secondary arenesulfonate may be estimated directly from the carbonyl stretching frequency of the corresponding ketone. Noting the virtual identity in the carbonyl stretching frequencies for cyclopentanone (1748 cm^{-1}) and 2-norbornanone (1751 cm^{-1}), Brown (34,35) has suggested that cyclopentyl derivatives are better models for 2-norbornyl derivatives than are cyclohexyl derivatives (carbonyl stretching frequency for cyclohexanone, 1716 cm^{-1}). Sargent (147) has pointed out that this argument disregards the differing effects of ground state torsional interactions in these systems. By correcting for the increased relief of torsional strain that accompanies the ionization of cyclopentyl derivatives relative to that for 2-norbornyl derivatives, Sargent (147) estimates that, in the absence of other special effects (e.g., anchimeric assistance or steric inhibition to ionization), 2-norbornyl derivatives should be *less reactive* than cyclopentyl derivatives by a factor of 33. Experimentally we find that at 25° *endo*-2-norbornyl brosylate is 21 times *less* reactive and *exo*-2-norbornyl brosylate is 16.1 (titrimetrically) times *more reactive* than cyclopentyl brosylate toward acetolysis (Table VIII).

Schleyer (135) has developed an elegant generalized method for predicting the rates of acetolysis of secondary tosylates relative to the rate for cyclohexyl tosylate. Since this method takes into account the effects of internal angle strain, torsional strain, and nonbonded interactions,

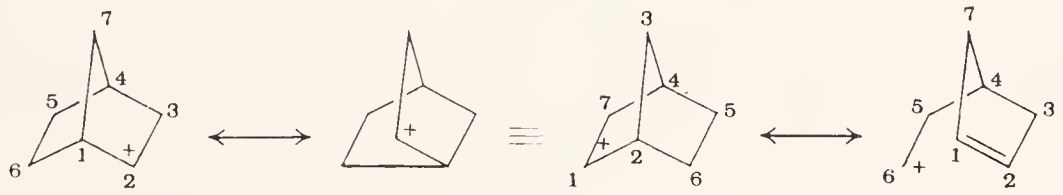
* For more complete discussion of the influence of these three factors on the rates of solvolytic reactions and of methods by which their magnitude may be estimated, see Ref. 9 and the references therein cited.

as well as inductive effects, any significant deviation from the predicted relative rate may be fairly attributed to anchimeric assistance (positive deviation) or steric inhibition to ionization (negative deviation). When compared with predicted values, the observed acetolysis rate constant for *endo*-2-norbornyl brosylate shows an insignificant positive deviation, whereas that for *exo*-2-norbornyl brosylate shows a 2000-fold positive deviation.

The only conclusion that can be drawn from the calculations of Sargent (147) and Schleyer (135) is that the rate of acetolysis of *endo*-2-norbornyl brosylate is not slowed by steric inhibition to solvolysis, but rather is in remarkable agreement with prediction. Conversely, both calculations lead to the conclusion that the acetolysis of *exo*-2-norbornyl brosylate is accelerated. Schleyer (135) considers this acceleration compelling evidence for the formation of a bridged ion.

E. Charge Delocalization as a Concomitant to Bridged-Ion Formation

Extensive effort has been expended in attempting to verify the delocalization of positive charge implied by the bridged structure for the 2-norbornyl cation. This structure (**6**) represents a hybrid of three contributing structures:



(6a) **(6b)** **(6c)**

To the extent that structures **6b** and **6c** contribute to the hybrid, electron deficiency is established at C-1 and C-6, respectively. In order to probe for this electron deficiency, the effect of substituents at C-1, C-6, and C-7 on the rate of solvolysis of 2-norbornyl derivatives has been examined. Since a transition state resembling the bridged ion in character can be achieved for ionization of an *exo*-2-leaving group, but not for ionization of *endo*-2-derivatives, electron-releasing substituents at these positions should enhance the *exo*/*endo* reactivity ratio. Similarly, electron-withdrawing substituents should decrease the *exo*/*endo* rate ratio.

1. Substitution at C-1

1-Methyl (**123**) and 1-ethyl-*exo*-2-norbornyl tosylate (**125**) undergo acetolysis at rates enhanced by factors of 51 and 78 (Table IX), respectively, relative to that of *exo*-2-norbornyl tosylate (148). Since the acetolysis of both 1-alkyl-*endo*-2-norbornyl tosylates (**124** and **126**) is accelerated by

TABLE IX

The Effect of Substituents on the Rates of Solvolysis of *exo*- and *endo*-2-Norbornyl Tosylate

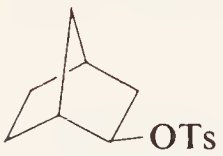
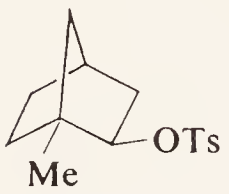
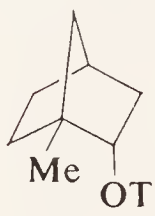
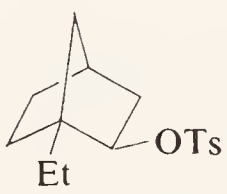
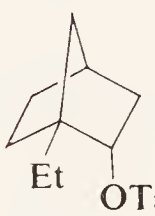
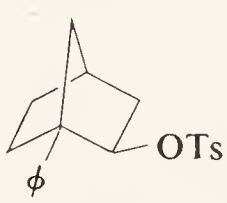
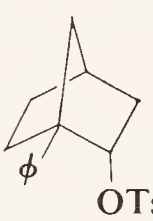
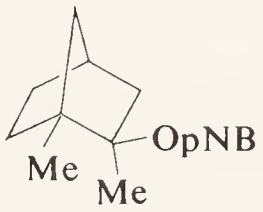
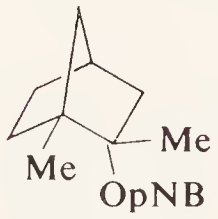
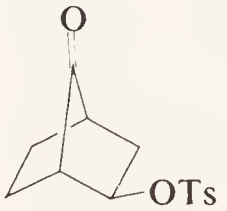
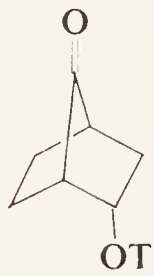
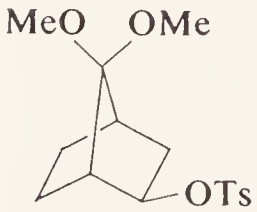
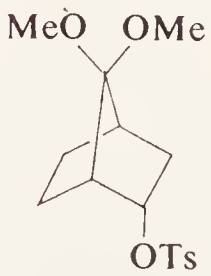
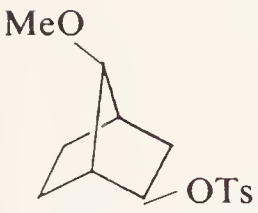
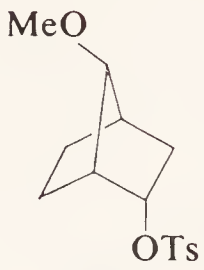
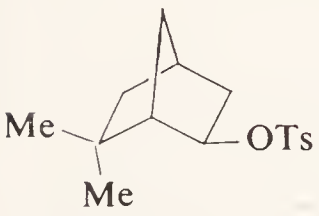
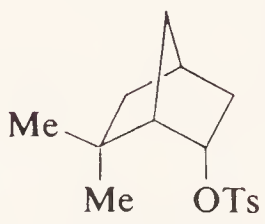
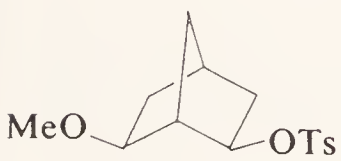
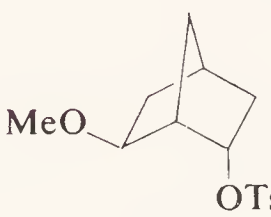
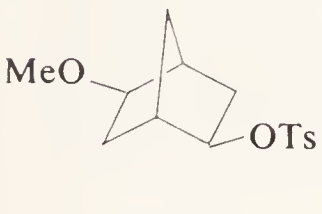
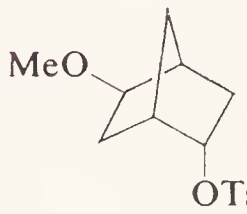
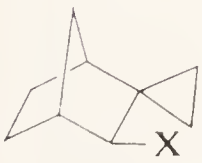
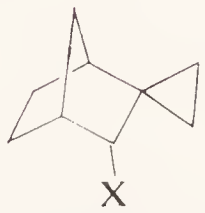
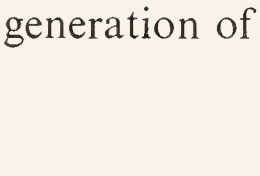
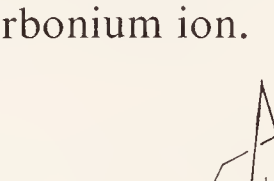
Compound	Relative rate	Compound	Relative rate	*exo*/*endo* rate ratio	Reference
	1.00		1.00	280	104
 **(123)**	51.2	 **(124)**	1.13	12,700	148
 **(125)**	77.8	 **(126)**	1.13	19,300	148
 **(127)**	3.91	 **(128)**	0.684	1,600	148
 **(129)**	4.3[a]	 **(130)**	4.8[b]	165	101
 **(76)**	0.000617	 **(77)**	1.05	0.165	130
 **(84)**	0.00427	 **(83)**	ca. 0.14[c]	ca. 8[c]	131

TABLE IX (*Continued*)

Compound	Relative rate	Compound	Relative rate	*exo*/*endo* rate ratio	Reference
 **(131)**	0.081	 **(132)**	0.38	60	151
 **(104)**	0.0395	 **(103)**	0.054	206	104
 **(133)**	0.14	 **(134)**	0.40	98	151
	0.014		0.044	89	151
 **(143)** **(143a)** X = OdNB **(143b)** X = OH	(a) 817[d]	 **(144)** **(144a)** X = OdNB **(144b)** X = OH	(a) —	3.2[e]	168

(*continued*)

TABLE IX (*Continued*)

Compound	Relative rate	Compound	Relative rate	*exo*/*endo* rate ratio	Reference
 **(145)**	(a) 4.12 (b) ca. 10[f]	 **(146)**	(a) 316 (b) —	3.9 3.1[e]	169 169

(145a) X = OTs
(145b) X = OdNB
(145c) X = Br
(145d) X = OH

(146a) X = OTs
(146b) X = OdNB
(146c) X = OH

OTs = *p*-toluenesulfonate OpNB = *p*-nitrobenzoate
OdNB = 3,5-dinitrobenzoate

[a] Rate relative to that of 2-methyl-*exo*-2-norbornyl *p*-nitrobenzoate in 60% aqueous dioxane at 50°.

[b] Rate relative to that of 2-methyl-*endo*-2-norbornyl *p*-nitrobenzoate in 60% aqueous dioxane at 50°.

[c] Estimated; see text.

[d] Rate relative to *exo*-2-norbornyl 3,5-dinitrobenzoate in 70% aqueous acetone at 100°.

[e] For solvolysis in 70% aqueous acetone at 125°.

[f] Estimated by comparison with rate of solvolysis of **143a** in 70% aqueous acetone at 125°.

less than 20% relative to *endo*-2-norbornyl tosylate (148), this constitutes clear evidence for σ participation during ionization of the *exo*-tosylates. However, this observation fails to prove that there is bridged-ion formation, since, for these unsymmetrically substituted 2-norbornyl derivatives, simple Wagner-Meerwein migration of C-6 from C-1 to C-2 results in the generation of a tertiary carbonium ion.

Since the transition state for such migration would be expected to reflect, at least partially, the enhanced stability of the incipient tertiary cation, an accelerated rate would be anticipated from this process as well as from formation of the alkyl-substituted bridged ion.

Interestingly, 1-phenyl-*exo*-2-norbornyl tosylate (**127**) undergoes acetolysis at a rate enhanced over that of *exo*-2-norbornyl tosylate itself by only a factor of 3.9 (Table IX). For a series of 1-aryl-*exo*-2-norbornyl tosylates, the rate constants for acetolysis are well correlated by the Hammett σ-ρ treatment when σ values are employed. The results are less well correlated when σ^+ values are used (148). These two observations—the modest rate-enhancing effect of phenyl and the better correlation with σ values—have been interpreted as indicating that only a small amount of the positive charge developing in the transition state for ionization is transmitted to C-1 (16,35).

Since this conclusion would seem to be at odds with the significant effect of 1-alkyl substitution, Sargent (149) has suggested that the aryl-substitution data may indicate that the interaction of the 1-aryl substituents with the incipient cationic center is inductive. He notes that the usual stabilization by aryl substituents is mesomeric and that, for such stabilization to be felt in the transition state for ionization of the *exo*-2-norbornyl tosylates, rehybridization at C-1 sufficient to generate an orbital suitable for overlap with the aryl π system would have to occur. The apparent discrepancy between the effect of aryl and alkyl substituents (whose stabilizing influence is largely, if not purely, inductive) could be resolved by postulating that hybridization at C-1 in the transition state is not suitable for effective mesomeric interaction with the exocyclic aryl substituents. Winstein appears to express similar sentiments when he states, without further elaboration, that "there are good reasons to expect carbon bridging to lag behind C–X ionization at the transition state" (150).

The ambiguity attending interpretation of the observed rate-enhancing effect of the 1-methyl substituent in solvolysis of 1-methyl-*exo*-2-norbornyl tosylate is removed when we consider the rate of solvolysis of 1,2-dimethyl-*exo*-2-norbornyl *p*-nitrobenzoate (**129**) relative to that of 2-methyl-*exo*-2-norbornyl *p*-nitrobenzoate (101). Since on ionization the dimethyl ester **129** would yield the same carbonium ion with or without Wagner-Meerwein migration of C-6 from C-1 to C-2, any significant rate-enhancing influence of the 1-methyl group could be fairly attributed to stabilization of an incipient bridged ion. The observation that a 1-methyl substituent leads to slight and virtually identical rate enhancements (Table IX) for solvolysis of both 1,2-dimethyl-*exo*-2- (**129**) and 1,2-dimethyl-*endo*-2-norbornyl *p*-nitrobenzoate (**130**), relative to their counterparts lacking the 1-methyl substituent, constitutes positive evidence for the absence of significant

charge delocalization to C-1 during ionization of 2-methyl-*exo*-2-norbornyl derivatives. For reasons to be discussed subsequently (p. 1175), this result cannot be extrapolated to yield structural information regarding the transition state for generation of secondary 2-norbornyl cations.

No reports of the influence of electron-withdrawing substituents at C-1 on the rate of solvolysis of 2-norbornyl derivatives have yet appeared in the literature. Such investigations should prove most instructive, since the ambiguity in mechanism produced by the introduction of electron-releasing substituents—namely, the possible intervention of simple Wagner-Meerwein rearrangement concerted with ionization—would be absent.

2. Substitution at C-7

The influence of electron-withdrawing substituents at C-7 has been investigated. Reasoning that the presence of a carbonyl group at C-7 should destabilize contributing structure **6b** and thus raise the energy of the bridged ion relative to that of a classical 2-norbornyl cation, Gassman and Marshall (130) investigated the solvolysis of the two epimeric 7-*oxo*-2-norbornyl tosylates (**76** and **77**). Their observation that the presence of the 7-oxo-substituent reduces the *exo*/*endo* reactivity ratio from 280 (25°)for the unsubstituted tosylates to 0.17 for tosylates **76** and **77** seems to provide dramatic evidence for bridged-ion formation in the unsubstituted system. The subsequent observation (131) that ionization of 7,7-dimethoxy-*endo*-2-norbornyl tosylate is assisted by intramolecular methoxyl participation raises the possibility that acetolysis of 7-oxo-*endo*-2-norbornyl tosylate (**77**) may proceed by a mechanism different from that of its *exo*-epimer (see p. 1147). If this were the case, the diminished *exo*/*endo* rate ratio for acetolysis of tosylates **76** and **77** would not, in itself, constitute evidence that the 7-keto function exerts a selective rate-retarding influence on the acetolysis of *exo*-tosylate **76**.

Acetolysis of *anti*-7-methoxyl-*endo*-2-norbornyl tosylate (**132**), which cannot involve intramolecular methoxyl participation, is retarded only slightly (relative rate, 0.38) with respect to acetolysis of *endo*-2-norbornyl tosylate (Table IX). The *anti*-7-methoxyl substituent exerts a somewhat more profound rate-retarding influence (0.081) on solvolysis of the *exo*-tosylate **131** (151). This differential rate-retarding effect is consistent with the postulated delocalization of charge to C-1 during solvolysis of the *exo*-tosylate.

Comparison of the acetolysis rates for 7-methoxy (**131**) and 7,7-dimethoxy-*exo*-2-norbornyl tosylate (**84**) reveals that the rate-retarding effect produced by the second methoxyl is virtually identical to that of the first. (The rate of the 7,7-dimethoxy-tosylate **84** relative to *exo*-2-norbornyl tsoylate calculated by assuming an additive rate-retarding methoxyl effect

is 6.6×10^{-3}. The observed relative rate is 4.19×10^{-3}.) This observation justifies the assumption that, *in the absence of methoxyl* participation, the rate-retarding effect of the second methoxyl on the acetolysis of 7,7-dimethoxy-*endo*-2-norbornyl tosylate (**83**) should also be comparable to that of the first. So assuming, we calculate an *unassisted* acetolysis rate constant of 0.14 for 7,7-dimethoxy-*endo*-2-norbornyl tosylate (**83**) relative to *endo*-2-norbornyl tosylate. On this basis we estimate an *exo*/*endo* reactivity rate ratio of ca. 8 for the epimeric 7,7-dimethoxy-2-norbornyl tosylates.

Since the rate-retarding effects of the differently oriented *syn*- and *anti*-7-methoxyl substituents are *observed* to be virtually identical for solvolysis of *exo*-tosylates **84** and **131**, it would not seem possible to attribute their selective influence on the rate of departure of the *exo*-oriented leaving group to special steric, dipole, or solvation effects. Consequently, the author considers the dramatic decrease in the *exo*/*endo* reactivity ratio brought about by substitution of inductively electron-withdrawing methoxy groups at C-7 to be firm evidence for significant charge delocalization to C-1 in the transition state for ionization of unsubstituted *exo*-2-norbornyl arenesulfonates.

3. Substitution at C-6

Rather than being enhanced (104), the rate of acetolysis of 6,6-dimethyl-*exo*-2-norbornyl tosylate (**104**, Table VIII) is less by a factor of 25 than that for *exo*-2-norbornyl tosylate itself. This observation has been called (35) incompatible with the postulated delocalization of positive charge to C-6 in the 2-norbornyl bridged ion. Since the solvolytic behavior of this tosylate is best interpreted in terms of steric inhibition to bridged-ion formation (p. 1155), this conclusion appears unwarranted. If the *gem*-dimethyl substituent prevents bridged-ion formation or significantly increases the free energy of the bridged ion by generating adverse non-bonded interactions, it can hardly serve as a valid probe for electronic effects that may operate within an ion not similarly destabilized.

More convincing evidence for the absence of significant charge delocalization to C-6 in the transition state for 2-norbornyl cation formation may be found in the sevenfold *rate-retarding* effect (Table IX) of an *exo*-6-methoxyl substituent (151). Since α-methoxyl substitution stabilizes carbonium ions to a greater extent than α-methyl substitution, Stang and Schleyer (151) suggest that this result provides no indication of positive charge delocalization to C-6 in the solvolysis transition state of *exo*-6-methoxyl-*exo*-2-norbornyl tosylate (**133**). As for phenyl groups, however, the stabilizing effect exerted by α-methoxyl groups at a cationic center must be mesomeric. Even if bridged-ion formation does result from solvolysis of the *exo*-6-methoxy tosylate **133**, but rehybridization of C-6 sufficient to

provide an orbital suitable for π overlap with the oxygen lone pair is not achieved in the transition state, we would expect the methoxyl group to exert only a destabilizing inductive influence. In this context, it is interesting to note that an *exo*-6-methoxyl substituent depresses the solvolysis rate for *endo*-2-norbornyl tosylate (which cannot react via a charge-delocalized transition state) less than for the *exo*-tosylate. The temptation to place special emphasis on this result is tempered by the observation that an *exo*-5-methoxyl substituent has an even more profound rate-retarding influence on the solvolysis of both *exo*- and *endo*-2-norbornyl tosylate than does the *exo*-6-methoxyl group (Table IX). This effect does not appear to be anticipated by either classical or nonclassical theory.

On theoretical grounds, Winstein has suggested that charge delocalization to C-6 in the bridged 2-norbornyl cation should be relatively minor (150,152). Piccolini and Winstein (152) calculate that the hybridization at C-6 will tend toward sp^3 in the bridged ion (**6**). They argue that such hybridization results in a larger Coulomb integral and consequent increase in C-6–C-1 and C-6–C-2 orbital overlap, and tends to diminish charge at C-6, as well.

4. Deuterium Substitution

Deuterium substitution has been employed to probe for bridged-ion formation during solvolysis of *exo*-2-norbornyl derivatives. The k_H/k_D kinetic isotope effect has been determined for solvolysis of each of the four isomeric 2-norbornyl-6-*d* brosylates (**135–138**) by two independent groups of investigators (153,154) utilizing different techniques. The agreement in their results (Table X) is remarkable, considering the problems generated by the rapid deuterium epimerization at C-6 (and possible deuterium scrambling to C-1 and C-2) caused by internal return. One group (153) minimized this problem by making very accurate measurements of instantaneous acetolysis rates in the initial stages of the reaction when deuterium epimerization should be insignificant. Murr and co-workers (154) followed the solvolyses through several half-lives, but were able to demonstrate by means of calculations assuming maximum possible scrambling that their experimental results were not contaminated by extraneous isotope effects derived from such scrambling.

Since γ-isotope effects in general are unity or slightly inverse (155–157), both groups of investigators conclude that the k_H/k_D value of 1.10 observed for the *exo*-brosylates **135** and **136** is inconsistent with solvolysis via a classical transition state. The suggestion is offered (153) that this abnormally high isotope effect may originate in vibrational changes in the C-6–H(D) bonds brought about by participation of the C-6–C-1 bonding electrons. The identity of k_H/k_D for *exo*- and *endo*-deuterium substitution

at C-6 is in accord with the equivalence of these protons in the bridged ion, which the transition state for solvolysis is presumed to resemble (153).

If the solvolysis of *endo*-2-norbornyl brosylate is to some extent retarded through destabilization of the transition state by an increase in, rather than relief of, the unfavorable *endo*-2-oxygen, *endo*-6-hydrogen nonbonded repulsion, we would expect the smaller effective steric requirement of deuterium to lead to an enhanced rate for solvolysis of *endo*-2-norbornyl-*endo*-6-*d* brosylate (**138**). Just this prediction was offered by Brown in 1961 (36), but the data of Table X demonstrate that the experimental results do not substantiate this prediction. We can only conclude that, if steric hindrance to ionization is operative in the solvolysis of *endo*-2-norbornyl brosylate, its magnitude is insufficient to be reflected in the k_H/k_D ratio for *endo*-6-deuterium substitution.

Substitution of deuterium at C-2 and C-3 also results in k_H/k_D ratios for solvolysis of *exo*-2-norbornyl derivatives (Table X) which are more consistent with σ participation than with ionization via a classical transition state (158,159). Schaefer et al. (158) have reported k_H/k_D values for solvolysis of the epimeric 2-norbornyl-3,3-d_2 bromides **139a** and **140a**. The k_H/k_D ratio for the *exo*-bromide (**139a**) is 1.04 per deuterium atom polarimetrically determined; this is one of the lowest secondary isotope effects recorded for limiting S_N1 solvolysis. An even smaller k_H/k_D ratio, 1.014, is reported for acetolysis of *exo*-2-norbornyl-3,3-d_2 brosylate (1.84 atoms of deuterium per molecule) (159).

Deuterium isotope effects are generally thought to originate in a hyperconjugative interaction between neighboring alkyl groups and the adjacent incipient cationic center (160). There appears to be a good correlation between the magnitude of these effects and the degree to which positive charge is developed at the cationic center in the transition state for ionization (161). The low k_H/k_D ratio for *exo*-2-norbornyl derivatives is thus taken to reflect charge delocalization away from C-2 in the transition state for ionization, presumably as the result of σ participation (158).

In sharp contrast with the results obtained with the *exo*-bromide, the k_H/k_D ratio for solvolysis of *endo*-2-norbornyl-3,3-d_2 bromide (**140a**)—1.16 per deuterium atom—is the largest ever observed for any secondary bromide (158). Again, similar results are reported for the corresponding brosylate (k_H/k_D = ca. 1.13 per deuterium atom) (159).

These results are interpreted to reflect highly developed positive charge at C-2 and an abnormally high degree of bond breaking in the transition state for solvolysis of *endo*-2-norbornyl derivatives (158). Schaefer and co-workers (158) suggest that steric hindrance to departure of the leaving group might require a larger-than-normal degree of bond breaking in the transition state for solvolysis. To support this interpretation, they point

TABLE X

Kinetic Isotope Effects for Solvolysis of 2-Norbornyl Derivatives

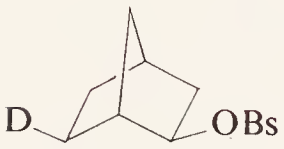
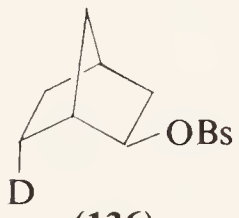
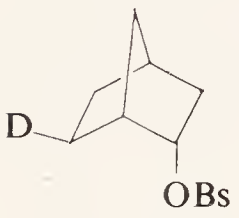
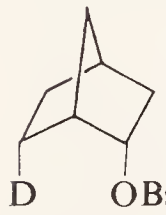
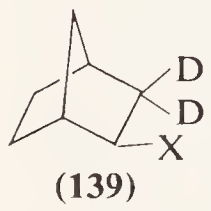
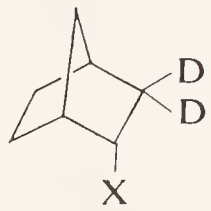
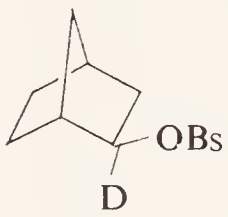
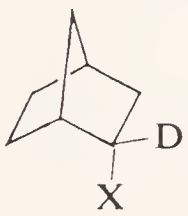
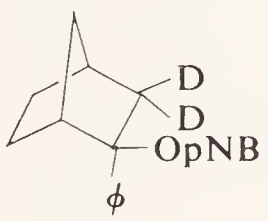
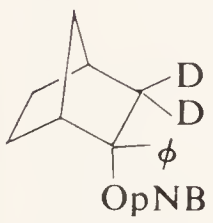
Compound	k_H/k_D per deuterium atom	Solvent	Temperature, °C	Reference
 **(135)**	1.097 ± 0.011	HOAc–1% Ac_2O	44.4	153
	1.09 ± 0.03	HOAc–KOAc	24.9	154
	1.09 ± 0.01	80% Ethanol	24.9	154
 **(136)**	1.082 ± 0.009	HOAc–0.7% Ac_2O	44.3	153
	1.11 ± 0.01	HOAc–KOAc	24.9	154
	1.11 ± 0.01	80% Ethanol	24.9	154
 **(137)**	1.021 ± 0.012	HOAc–1% Ac_2O	65.0	153
	0.98 ± 0.01	HOAc–KOAc	70.1	154
	1.00 ± 0.02	80% Ethanol	49.1	154
 **(138)**	0.998 ± 0.009	HOAc–1% Ac_2O	65.0	153
	0.99 ± 0.02	HOAc–KOAc	70.1	154
	0.97 ± 0.01	80% Ethanol	49.1	154
 **(139)**	(a) 1.04[a]	HOAc–H_2O–NaOAc	51.25	158
	(a) 1.02[b]			
	(b) 1.01[c]	HOAc–1% Ac_2O	44.3	159
(139a) X = Br **(139a)** X = Br **(139b)** X = OBs				
 **(140)**	(a) 1.16	50% Ethanol	60.21	158
	(b) ca. 1.13[c]	HOAc–1% Ac_2O	65.0	159
(140a) X = Br **(140b)** X = OBs				

TABLE X (*Continued*)

Compound	k_H/k_D per deuterium atom	Solvent	Temperature, °C	Reference
	1.10	HOAc	30.02	162
	(a) 1.20	HOAc	50.07	162
	(b) 1.28[d]	50% Ethanol	60.21	158
(a) X = OBs (b) X = Br				
 **(141)**	1.09 ± 0.02	60% Dioxane	39.50	163
 **(142)**	1.08 ± 0.02	60% Dioxane	62.50	163

OBs = *p*-bromobenzenesulfonate OpNB = *p*-nitrobenzoate

[a] Determined polarimetrically.
[b] Determined titrimetrically.
[c] Calculated on the basis of 1.84 atoms of deuterium per molecule.
[d] Calculated from the rate of solvolysis of *exo*-2-norbornyl-2,3,3-d_3 bromide by assuming that α- and β-deuterium isotope effects are additive.

out that the α-isotope effect for solvolysis of *endo*-2-norbornyl bromide ($k_H/k_D = 1.28$) exceeds that for the corresponding tosylate ($k_H/k_D = 1.20$) (163). Since for all other recorded cases the α-deuterium isotope effect for tosylate solvolysis exceeds that for bromide solvolysis, they suggest that in this instance the greater bulk of bromide compared with oxygen requires greater bond breaking in the solvolysis transition state. There may be merit in this interpretation, but the basis for the presumed connection between the magnitude of nonbonded interactions present in the transition state and the extent to which bond breaking should occur is not obvious. If the interpretation is correct, the increased hindrance to ionization of the bromide ought to be reflected in an increased *exo*/*endo* reactivity ratio for solvolysis of the epimeric 2-norbornyl bromides. Unfortunately, data reported for these bromides prevent such comparison, since they were obtained in different solvents at different temperatures.

Schaefer and co-workers argue that their interpretation of the basis for the differing β-deuterium kinetic isotope effects for solvolysis of the epimeric 2-norbornyl bromides is supported by their more recent data on the solvolysis of 2-phenyl-*exo*- (**141**) and 2-phenyl-*endo*-2-norbornyl-3,3-d_2 *p*-nitrobenzoate (**142**) (163). Unlike the parent system ratios, the k_H/k_D ratios of these tertiary 2-norbornyl derivatives are indistinguishable from one another within the limits of experimental error (Table X). Noting that the k_H/k_D ratios for the two 2-phenyl-2-norbornyl *p*-nitrobenzoates are close to those obtained for the α-phenethyl system (164), Schaefer et al. conclude that the transition state for solvolysis of the 2-phenyl-2-norbornyl *p*-nitrobenzoates must be classical. Since solvolysis via a presumed classical transition state results in k_H/k_D ratios that are identical for the *exo*- (**141**) and *endo*-derivatives (**142**), Schaefer et al. (163) argue that the wide disparity in these ratios for the *exo*- (**139a**) and *endo*-2-norbornyl bromides (**140a**) indicates a fundamental difference in the transition states for solvolysis of these two derivatives. They further contend that, since the difference is in the direction anticipated for participation during solvolysis of the *exo*-bromide (**139a**), these results provide compelling evidence for the bridged-ion postulate.

The differing α-deuterium kinetic isotope effects for solvolysis of *exo*- ($k_H/k_D = 1.10$) and *endo*-2-norbornyl brosylate ($k_H/k_D = 1.20$) have also been advanced as support for the bridged-ion hypothesis (162). Citing Streitwieser's (165) conclusion that neighboring group participation in the transition state for ionization should decrease the magnitude of the α-deuterium isotope effect, Lee and Wong (162) decided that the lower k_H/k_D ratio for solvolysis of the *exo*-brosylate constitutes evidence for participation by the C-6 and C-1 bonding electrons. The force of this interpretation is blunted by the possibility that deuterium scrambling via

internal return may have diminished the k_H/k_D ratio observed for solvolysis of *exo*-2-norbornyl-2-*d*-brosylate by Lee and Wong (162).

F. The Influence of Substituents that Stabilize Positive Charge at C-2

There appears to be general acceptance (11) of the thesis advanced by Winstein and co-workers (166) several years ago that the importance of neighboring group participation should diminish as an incipient cationic center is stabilized by substitution. When this doctrine is applied to the 2-norbornyl cation problem, we conclude that classical stabilization of positive charge at C-2 should lead to a diminished *exo*/*endo* reactivity ratio, if the source of the high ratio observed for the unsubstituted 2-norbornyl derivatives lies in an enhanced rate for the *exo*-epimer due to C-6, C-1 bonding-electron participation. If, on the other hand, some steric (34–36) or torsional (65) factor gives rise to the high *exo*/*endo* rate ratio, this ratio should be relatively insensitive to changes in substituents whose only effect is to stabilize incipient cationic charge.

This analysis and the line of investigation prompted by it have led Brown and co-workers to examine the solvolytic behavior of a number of epimeric tertiary 2-norbornyl *p*-nitrobenzoates and chlorides.* The data obtained from these investigations are instructive, but they are necessarily complicated because replacing the *endo*-2-hydrogen by an alkyl or aryl group introduces a driving force for solvolysis of the *exo*-epimers which is not present in the unsubstituted secondary derivatives—i.e., relief of the unfavorable ground state *endo*-6-hydrogen, *endo*-2-substituent nonbonded interaction. No such additional driving force is present for solvolysis of the tertiary *endo*-epimers relative to their secondary counterparts. If the observed *exo*/*endo* reactivity ratios for the tertiary systems are to be compared with those characteristic of the secondary derivatives, they must be corrected downward to neutralize the influence of this extraneous steric effect. Only if this correction is made will the comparison be a true measure of the effect of substituents in stabilizing positive charge at the incipient cationic center. Any estimate of the appropriate magnitude for this correction is necessarily uncertain. Before examining the results of Brown's investigations, then, it is instructive to consider two systems in which cationic stabilization at C-2 is effected *without* the introduction of extraneous steric complication.

G. Charge Stabilization by Structural Modification at C-3

The high solvolytic reactivity of both allylic and cyclopropyl carbinyl systems is well established (14,17). In the case of allylic derivatives, this

* For a selective summary of the results and Brown's interpretation of them, see Refs. 34 and 35.

reactivity is associated with the ability of the adjacent vinyl group to stabilize the incipient carbonium ion by simple π-electron delocalization. The stabilizing influence of neighboring cyclopropyl is less well understood, but it now appears that it may originate in pseudo-π-overlap between the developing *p* orbital at the incipient cationic center and two bent carbon–carbon bonds of the adjacent cyclopropane ring (167).

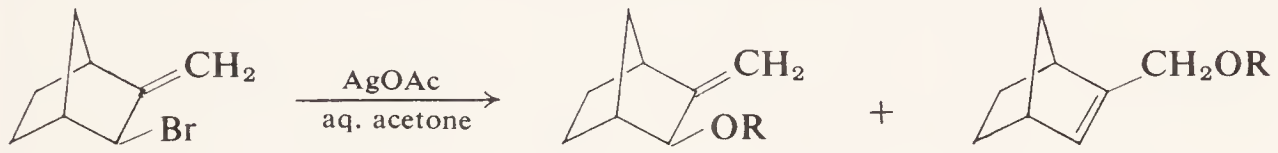
Wilcox and Jesaitis (168,169) have sought to employ vinyl and cyclopropyl as stabilizing substituents in order to determine whether the high *exo*/*endo* reactivity ratio for solvolysis of simple 2-norbornyl derivatives derives from σ participation by the C-6, C-1 bonding pair (5–7) or from steric inhibition to departure of the *endo*-oriented leaving group. By incorporating the stabilizing substituent at C-3, they were able to maintain much the same steric environment at the ionization site (C-2) as is present in the unsubstituted secondary system. This permits direct comparison of the *exo*/*endo* rate ratios obtained for the stabilized esters (**143**, **144** and **145**, **146**) with 280, the rate ratio characteristic of the epimeric 2-norbornyl tosylates (Table IX). As outlined previously, we expect diminished *exo*/*endo* ratios for **143**, **144** and **145**, **146** if σ participation accompanies solvolysis of simple *exo*-2-norbornyl derivatives. We expect the high *exo*/*endo* rate ratios to be maintained if they are of steric origin. The observed rate ratios (Table IX), 3.2 for **143**/**144**, 3.9 for **145a**/**146a**, and 3.1 for **145b**/**146b**, clearly support the bridged-ion hypothesis.

Since 1260 (38), the *exo*/*endo* rate ratio found for acetolysis of the epimeric camphenilyl [3,3-dimethyl-2-norbornyl] brosylates, is comparable to that for the unsubstituted brosylates, it is unlikely that the low ratios observed by Wilcox and Jesaitis (168,169) are artifacts derived from replacing the C-3 hydrogens by more bulky substituents. The possibility that the diminished *exo*/*endo* ratios for esters **143** and **144** might derive from some unrecognized ground state steric effect is removed by the observation (168) that equilibration of the corresponding alcohols (**143c**, **144c**) leads to an *exo*/*endo* composition (ca. 2:1) comparable to that for the 2-norbornanols themselves (ca. 4:1) (118).

As expected, the presence of the cyclopropyl substituent leads to a marked increase in the rate of solvolysis of *p*-nitrobenzoates **143** and **144** relative to their unsubstituted 2-norbornyl analogs (Table IX). A similar, expected acceleration for ester **145** due to the presence of the *exo*-methylene substituent is not realized. It is suggested that the stabilizing influence of the adjacent vinyl group may be offset by the destabilizing effect of a decreased C-1–C-2–C-3 bond angle. Although conjugation with a double bond generally decreases the carbonyl stretching frequency of a ketone by ca. 40 cm^{-1}, the difference in carbonyl stretching frequency between norcamphor and 3-methylenenorcamphor is only 13 cm^{-1}. If the difference

of 27 cm^{-1} is attributed to increased angle strain in the latter ketone, the Foote correlation (146) predicts a thousandfold rate retardation for acetolysis of tosylate **145b** relative to *exo*-2-norbornyl tosylate.

Despite their decreased *exo*/*endo* reactivity ratio, solvolysis of both *p*-nitrobenzoates, **143** and **144**, produces *exo*-alcohol **143b** in high (89–93%) yield. Similarly, when the cation that presumably results from ionization of esters **145** and **146** is generated by treatment of the corresponding bromide (**145c**) with silver acetate in 50% aqueous acetone, it yields only a mixture of *exo*-alcohol **145d** and 2-hydroxymethylnorborn-2-ene (**147a**) and their corresponding acetates, **145e** and **147b** (170). No trace of *endo*-



(145c) **(147)**

(145d) R = H **(147a)** R = H

(145e) R = CH_3CO **(147b)** R = CH_3CO

alcohol **146d** could be detected. The parallel between these product distributions and those derived from solvolysis of tosylates **111** and **112** (144) and tosylates **116** and **117** (145), which also display low *exo*/*endo* reactivity ratios, is noteworthy. Wilcox and Jesaitis (168) suggest that the continued preference for *exo* attack by solvent, even in the absence of a corresponding preference for leaving-group departure, may be related to a difference in the charge states for nucleophile and leaving group in their respective transition states and to the consequent difference in the resemblance of these transition states with the alcohol or ester ground states. The basis for the apparently general noncorrelation of *exo*/*endo* reactivity ratios with the corresponding product distribution ratios deserves much greater scrutiny than it has received to date.

H. Substitution at C-2

In order to probe for charge delocalization from the 2-position during solvolysis of *exo*-2-norbornyl derivatives, Brown and co-workers have explored the kinetic behavior of a number of tertiary 2-norbornyl chlorides and *p*-nitrobenzoates (101,103,171–177). Brown (34,35,36,103,177) reasons that the presence of 2-substituents that are increasingly capable of stabilizing cationic charge should lead to a progressive diminution in σ participation by the C-6–C-1 bonding electron pair, if, indeed, such participation is operative in the solvolysis of simple secondary 2-norbornyl derivatives. Such a diminution should reflect itself in two ways: (*1*) a smaller rate-enhancing substituent effect than is observed for systems incapable of stabilization by σ participation and (*2*) diminished *exo*/*endo* rate ratios.

A diminished rate-enhancing substituent effect should result, since the stabilization of the transition state for solvolysis of the secondary derivatives (derived from charge delocalization as a result of σ participation) will be decreased by the extent to which such participation is diminished for solvolysis of the tertiary derivatives. More simply, the rate of a reaction proceeding via a charged-delocalized transition state will be less responsive to substitution at a given site than will the rate for a reaction in which charge is localized at that site. Brown (35,175) illustrates this point by noting that replacement of α-hydrogen by methyl (178) increases the limiting rate of solvolysis of isopropyl chloride by a factor of 55,000. Similarly, the rate-enhancing effect brought about by replacing methyl (178) by phenyl (179) for solvolysis of *t*-butyl chloride is 4580. For reactions proceeding through charge-delocalized transition states, these factors are much less: *t*-cumyl chloride (179) solvolyzes only 1800 times more rapidly than α-phenethyl chloride (180) and 1,1-diphenylethyl chloride (175) solvolyzes only 50 times more rapidly than *t*-cumyl chloride (179). This point is illustrated schematically in Figure 4.

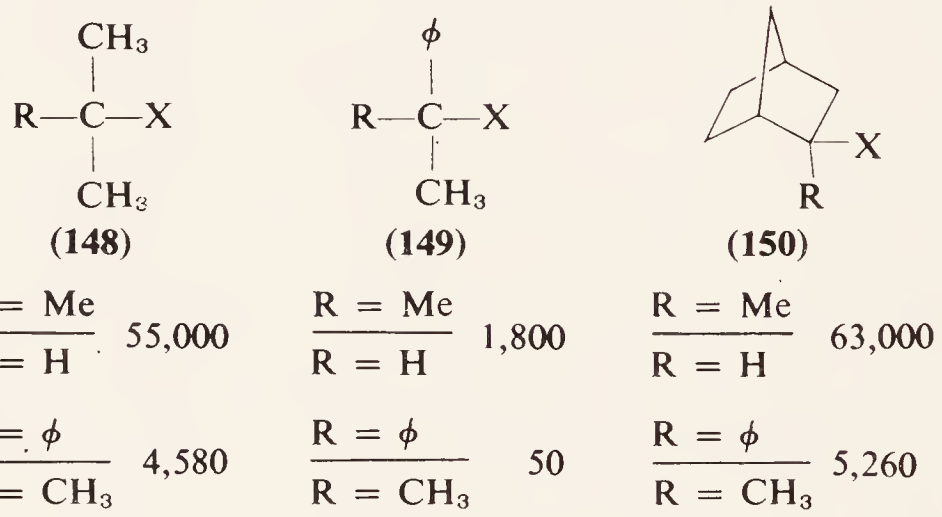


Fig. 4. The effect of substituents on the rates of reactions proceeding through charge-localized and charge-delocalized transition states and a comparison of their effect in the 2-norbornyl system.

Noting that the rate-enhancing effects of replacing hydrogen by methyl and methyl by phenyl for solvolysis of 2-norbornyl derivatives (Fig. 4) are virtually identical to those for reactions proceeding through charge-localized transition states (**148**) and much smaller than those for reactions proceeding through charge delocalized transition states (**149**), Brown (35,175) concludes that "there is no detectable stabilization of the transition state by participation and its accompanying delocalization of charge" (35) for solvolysis of the *exo*-2-norbornyl derivatives.

As noted previously, direct comparison of the rate ratios obtained for the tertiary *exo*-norbornyl system (**150**) with the two model systems **148** and **149** (Fig. 4) is invalid, since the tertiary (R = Me):secondary (R = H) rate ratio for **150** will reflect, at least in part, relief of the unfavorable ground state *endo*-2-methyl-*endo*-6-hydrogen nonbonded repulsion. If the magnitude of this repulsion were only 2 kcal/mole, and if the nonbonded strain were totally relieved in the solvolysis transition state, the corrected R = Me:R = H rate ratio would be comparable to that observed for the delocalized transition state model system **149**.

Prior to the availability of an experimental estimate for the magnitude of this interaction, Sargent (9) calculated that it might be as great as 3 kcal/mole. Subsequently, Rei and Brown (139) carried out the acid-catalyzed equilibration of the epimeric 2-methyl-2-norbornanols in aqueous dioxane. At equilibrium, they found the ratio of 2-methyl-*exo*-2-norbornanol to 2-methyl-*endo*-2-norbornanol to be 1.3. Since the *exo*/*endo* distribution for 2-norbornanol itself is ca. 8 at 25°,* this result suggests that the magnitude of the *endo*-6-hydrogen-*endo*-2-methyl repulsion energy in 2-methyl-*exo*-2-norbornanol is only ca. 1.1 kcal/mole.

Alternatively, if we ascribe all the free energy difference between *endo*- and *exo*-2-methylnorbornane to the methyl, 6-*endo*-hydrogen repulsion present in the *endo*-epimer, data on the direct equilibration of these two hydrocarbons, catalyzed by sulfuric acid (181), permits us to estimate a value of 1.0 kcal for the magnitude of this interaction.

Full relief of the 1.1-kcal, methyl, hydrogen nonbonded repulsion at the transition state will enhance the rate of solvolysis of a 2-methyl-*exo*-2-norbornyl derivative by a factor of 6 (25°) relative to a system that reacts without comparable strain release. To correct for this extraneous steric effect, we must thus divide the observed tertiary:secondary (R = Me: R = H) rate ratio for system **150** by 6 in order to compare it properly with model systems **148** and **149**. When this correction is made, we obtain a value (10,500) which is exactly intermediate between that for the charge-localized model (**148**) and that for the charge-delocalized model (**149**). In the author's opinion, this result indicates that the transition state for solvolysis of *secondary exo*-2-norbornyl derivatives does involve some charge delocalization, but it is less extensive than in the transition state for formation of benzyl-type cations (system **149**).

1. The Influence of Substitution at C-2 on the exo/endo *Rate Ratio*

Brown (34,35,101,103,173,177) has also called attention to the apparent insensitivity of the *exo*/*endo* rate ratios for solvolysis of 2-norbornyl

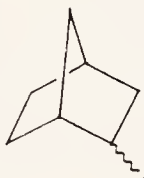
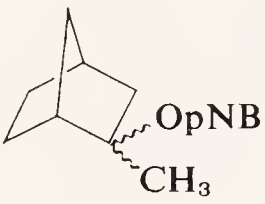
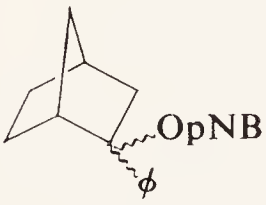
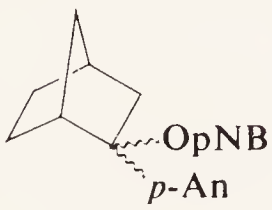
* Extrapolated by Rei and Brown (139) from data presented in Ref. 118.

derivatives to the cation-stabilizing ability of a 2-substituent. Since the *endo* derivatives solvolyze without σ participation, and since σ participation should diminish for the *exo* derivatives as the incipient cation is stabilized by substitution, we would expect *exo*/*endo* rate ratios to diminish with substitution. The observed *exo*/*endo* rate ratios for a series of representative 2-norbornyl derivatives are summarized in Table XI.

To a first approximation, the transition state geometry for ionization of the secondary *endo*-esters must closely resemble that for ionization of the tertiary *endo*-esters. No new ground state steric interactions are introduced by the presence of an *exo*-oriented alkyl or aryl group. Introduction of an

TABLE XI

***exo*/*endo* Rate Ratios for Solvolysis of 2-Norbornyl Derivatives as a Function of the Electron-Releasing Ability of a 2-Substituent**

Compound[a]	*exo*/*endo* rate ratio (observed)	*exo*/*endo* rate ratio (corrected[b])	Reference
 OBs	1600[c]	1600[c]	6
 OpNB, CH_3	183	27.5	101
 OpNB, ϕ	143	23.8	177
 OpNB, *p*-An	284	47.4	103

[a] OBs = *p*-bromobenzenesulfonate; OpNB = *p*-nitrobenzoate; *p*-An = *p*-anisyl.

[b] Corrected for extraneous steric effects; see text.

[c] Ratio of polarimetric rate constants. This ratio is chosen because it represents the rate ratio for ionization; since the solvolyses of the tertiary derivatives show no signs of complication due to internal return, the rate ratios for solvolysis are a true reflection of the rate ratios for ionization.

endo-oriented 2-alkyl or aryl substituent does raise the ground state energy for the tertiary *exo*-esters. Relief of this interaction in the transition state provides a driving force for solvolysis of the tertiary *exo* derivatives not present in their secondary counterpart. Thus a valid comparison of the secondary and tertiary *exo*/*endo* rate ratios can be made only if we first correct the tertiary rate ratios to remove the component derived from this extraneous steric effect, which does not contribute to the secondary *exo*/*endo* rate ratio. For the 2-methyl-2-norbornyl derivatives, this correction can be made by dividing the observed *exo*/*endo* ratio by 6 (see previous section). For the 2-aryl derivatives, no experimental measure of the magnitude of this correction factor is available, but Sargent (9) estimates that the nonbonded repulsion energy engendered by an *endo*-2-phenyl group should be similar to that of an *endo*-2-methyl substituent. Brown (173) has implied that the steric effect of phenyl should be more pronounced than that for methyl. If this is the case, the correction factor should be greater than 6 for the 2-aryl-2-norbornyl *exo*/*endo* rate ratios. Table XI summarizes the corrected *exo*/*endo* rate ratios for the tertiary 2-norbornyl derivatives obtained by dividing the observed values by a factor of 6.

When the corrected tertiary *exo*/*endo* rate ratios presented in Table XI are compared with that for the parent secondary system, two striking features of the data emerge. First, it is clear that the tertiary *exo*/*endo* ratios *are* markedly lower than the secondary ratio; second, the tertiary rate ratios are all markedly similar to one another.

The simplest conclusion to be drawn from these data is that the tertiary solvolyses all proceed without σ participation but that solvolysis of *exo*-2-norbornyl brosylate must proceed via a charge-delocalized transition state.

The absence of charge delocalization in the transition state for solvolysis of the 2-alkyl-*exo*-2-norbornyl *p*-nitrobenzoates is confirmed by noting that the *exo*/*endo* rate ratios for the epimeric 1,2-dimethyl *p*-nitrobenzoates are slightly *less* than the ratio for the esters lacking the 1-methyl substituent (101) (p. 1162).

Takeuchi and Brown (177) have found that a series of 2-aryl-2-norbornyl *p*-nitrobenzoates undergo solvolysis in 80% aqueous acetone at rates that are well correlated by the Hammett σ–ρ relationship.

Rho values of -3.96 and -3.77 are obtained for the *exo*- and *endo*-epimers, respectively, when rates are plotted against σ^+ constants. The absence of significant σ participation in the transition state for solvolysis of the *exo*-epimers seems to be indicated by the fact that correlation is best achieved with σ^+ constants, and by the similarity in the ρ values for the two series of epimers.

It must be noted that even after correction for the influence of extraneous steric effects, the *exo*/*endo* reactivity ratios found for solvolysis of the tertiary 2-norbornyl *p*-nitrobenzoates are still quite pronounced. This result is in sharp contrast to the results obtained with secondary 2-norbornyl derivatives whose structures incorporate steric (pp. 1154–1159) or charge-stabilizing features (pp. 1173–1175) that preclude σ participation during ionization. The *exo*/*endo* reactivity ratio observed for these derivatives in no case exceeds a value of 4. Even the *exo*/*endo* reactivity ratio for loss of methanol from protonated 2-norbornyl dimethyl ketal (**72a**) (117), when corrected for the rate-enhancing relief of the *endo*-2-oxygen, *endo*-6-hydrogen nonbonded repulsion that accompanies departure of *exo*-oriented methanol, is less than 3 (see p. 1140).

Both Schleyer (65) and Brown (177) have suggested that the maintenance of high *exo*/*endo* reactivity ratios for solvolysis of tertiary 2-norbornyl derivatives, even in the demonstrated absence of σ participation, may be due to a blend of steric (34–36,147) and torsional (65)* effects. It is not clear, however, why these effects should be more pronounced for the formation of 2-alkyl and 2-aryl-norbornyl cations than for the nonassisted generation of secondary norbornyl cations or the 2-methoxy-2-norbornyl cation.

I. Summary

In summary, we find that structural features tending to stabilize electron deficiency at C-2 lead to reduced *exo*/*endo* rate ratios for solvolysis of 2-norbornyl derivatives. This result provides support for the postulate that solvolysis of *exo*-2-norbornyl brosylate is promoted by σ participation leading to the formation of a bridged ion (5–7). Even when this participation is suppressed, *exo*-2-norbornyl derivatives react more rapidly than their *endo*-epimers. This result is surprising, since the ground state energy of *endo*-2-norbornanol exceeds that of *exo*-2-norbornanol by ca. 1 kcal/mole (118). If the same relationship holds for the corresponding brosylates, the usual assumption that the transition state for ionization resembles the resultant classical cation leads to the prediction that the *endo*-brosylate should ionize some six times more rapidly because of relief of steric strain. This realization suggests either that steric inhibition to ionization (34–36, 138) retards the solvolysis of the *endo*-brosylate, or that torsional interactions lead to transition states of differing energies for ionization of the epimeric brosylates (65), or that both effects are operative. If in the transition state for *endo*-oriented leaving-group departure, nonbonded inter-

* See page 1128. Note that the torsional factors favoring collapse of the 2-norbornyl cation by attack from the *exo* direction will, by the principle of microscopic reversibility, equally favor generation of the cation by departure of an *exo*-oriented as opposed to an *endo*-oriented leaving group.

actions were neither relieved nor increased relative to the ground state, an *exo*/*endo* rate ratio of unity would be expected, barring the intrusion of torsional effects. A realistic estimate (p. 1140) places the maximum expected *increase* in nonbonded interactions in the transition state relative to the ground state at 1 kcal/mole. Similarly, torsional effects seem incapable of providing a differential between *exo*- and *endo*-ionization transition state energies greater than 1 kcal/mole (p. 1126). If one of these effects were operative, a maximum *exo*/*endo* rate ratio of 6 would be anticipated. If both were operative, an *exo*/*endo* ratio as large as 35–40 might result. It is worth noting that for all cases in which no σ participation is expected, the *exo*/*endo* rate ratios, when corrected to neutralize the influence of extraneous steric effects, all lie within or extremely close to this range (Table XI). Thus it is safe to conclude that the *exo*/*endo* rate ratio for solvolysis of the 2-norbornyl brosylates (1600) contains *at least* a factor of 40 (i.e., half the rate differential), and perhaps a factor of 400 or more, which must be attributed to σ participation. However, we cannot ignore the possibility that steric and torsional effects also contribute to the rate differential.

J. Activation Volume as a Probe for Charge Delocalization

le Noble and co-workers (182) have suggested that the volume of activation of a solvolysis reaction may be employed as a probe for charge delocalization in the transition state. This suggestion depends on the observation that ionization reactions are attended by a significant net decrease in volume resulting from the electrostrictive forces of the ions on surrounding solvent molecules. These volume changes are influenced by the degree of dispersion of the charge: for n charges of q, the decrease in volume is twice as great as that occasioned by $2n$ charges of $1/2q$ (183). le Noble and Yates contend that if *exo*-2-norbornyl brosylate solvolyzes at a rate enhanced by participation of the C-6–C-1 bonding electrons in the transition state (5–7), the incipient cationic charge will be dispersed over at least two centers (C-1 and C-2) so that the volume of activation will be less negative than it would be, were the incipient cationic charge localized at a single center. The experimentally determined values for the volume of activation at atmospheric pressure in 94% aqueous acetone at 40° for cyclopentyl brosylate, *endo*-2-norbornyl brosylate, and *exo*-2-norbornyl brosylate are -17.7, -17.8, and -14.3 cm^3/mole, respectively.

le Noble and Yates argue that these results not only indicate σ participation in solvolysis of *exo*-2-norbornyl brosylate, but strongly suggest that there is no significant steric hindrance toward ionization of *endo*-2-norbornyl brosylate (34,35,138). They argue that steric inhibition of ionization would produce a transition state more closely resembling the reactant, so that the development of ionic character would be diminished. Such a reduction in the development of charge separation in the transition

state should result in diminished restriction of solvent molecules and a consequent less negative volume of activation. Within the limits of experimental error (± 0.5 cm^3/mole), the activation volume for solvolysis of *endo*-2-norbornyl brosylate is identical to that of cyclopentyl brosylate, for which no steric inhibition of ionization is conceivable; therefore, le Noble and Yates conclude that no such inhibition occurs for the case of *endo*-2-norbornyl brosylate.

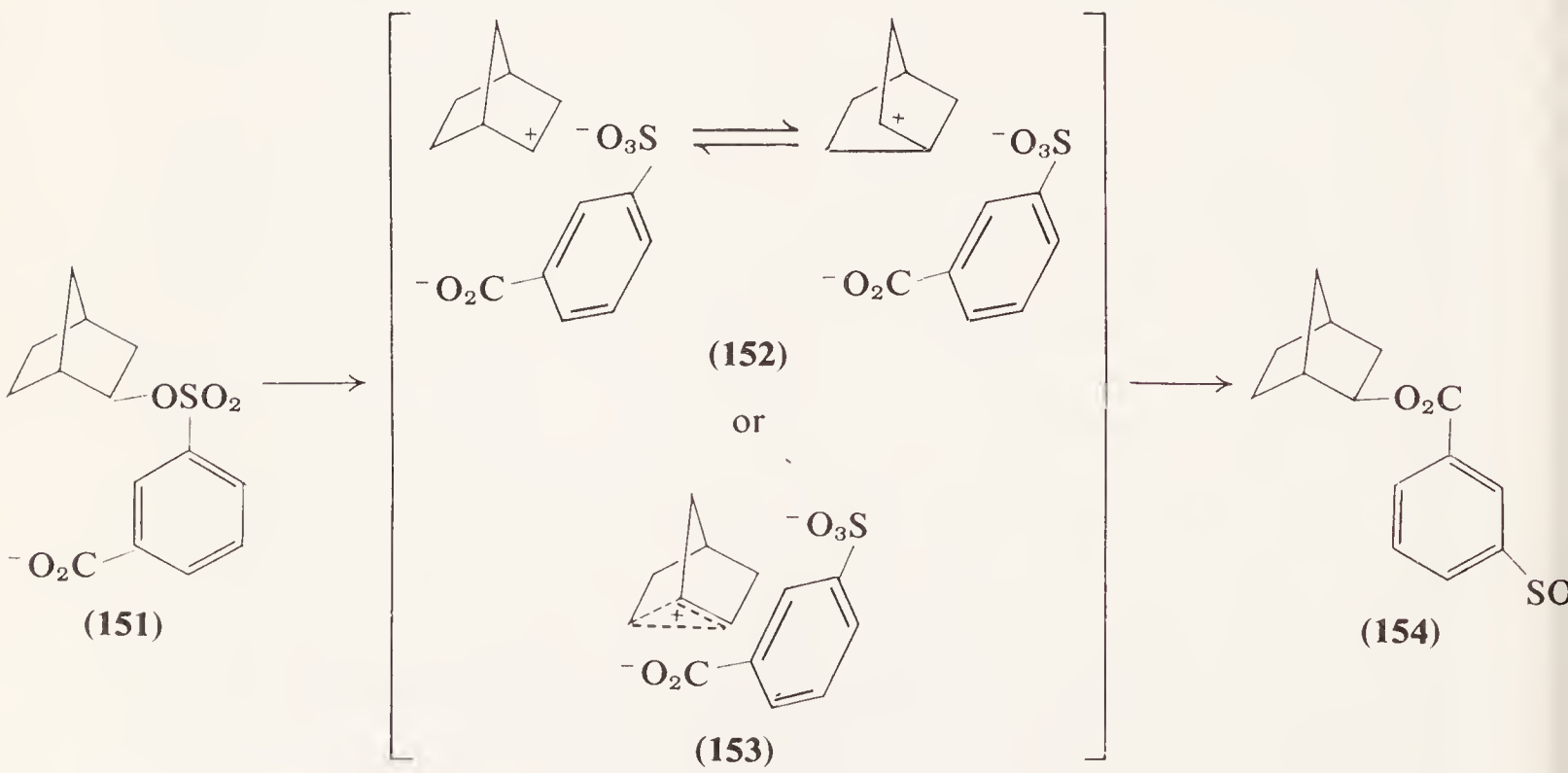
The application of this technique is open to several reservations. Perhaps the most serious of these is the tacit assumption that, in the absence of some unusual feature (σ participation or steric inhibition of ionization), the degree of ionic charge developed in the transition state is relatively equal for molecules of rather differing structure. Second, as le Noble and Yates admit, it does not allow for the possibility that steric hindrance to solvation may be reflected more strongly in the volume of activation than in the free energy of activation. In addition, it fails to take into account the possibility that certain molecules might possess some structural feature that disproportionately affects the partial molar volume of either the ground state or the transition state.

V. PROBING FOR SYMMETRY IN THE 2-NORBORNYL CATION

A. Attempts to Trap an Asymmetrical 2-Norbornyl Cation

1. *The Solvolysis of* exo-*2-Norbornyl* m-*Carboxybenzenesulfonate*

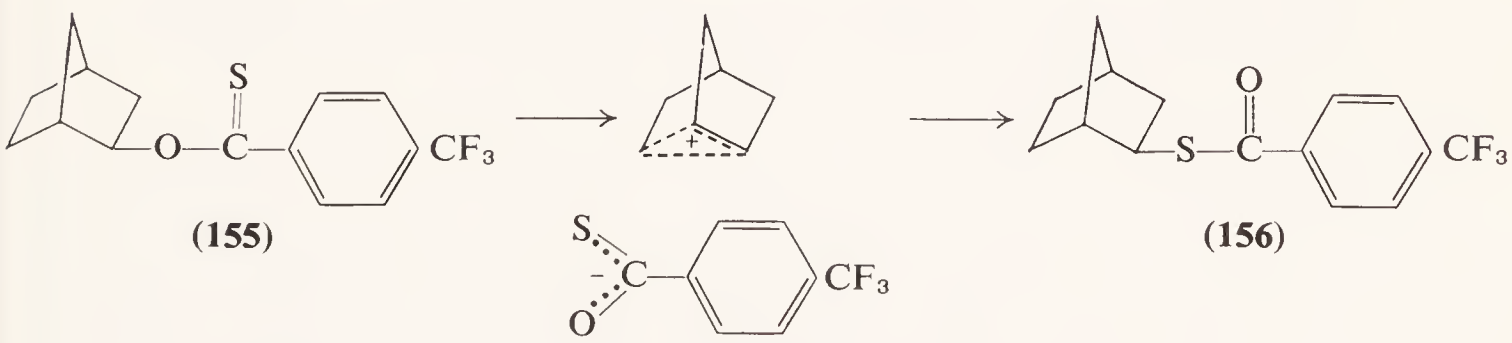
Corey and his co-workers (184) have carried out the solvolysis of optically active *exo*-2-norbornyl *m*-carboxybenzenesulfonate (**151**) in both *t*-butyl alcohol and aqueous tetrahydrofuran. During the solvolysis, one



equivalent of base was slowly added to ensure ionization of the carboxylic group on the unchanged sulfonate at all times. The *exo*-2-norbornanol obtained by hydrolysis of the reaction product, the carboxylic ester **154**, was found to be optically inactive within the limits of experimental error. Corey maintains that, if the intermediate carbonium ion formed from the sulfonate **151** existed as a classical 2-norbornyl cation in rapid equilibrium with its enantiomer (**152**), it should surely collapse to give product with some net retention of optical activity. He takes this position because only a minute molecular movement is required for the carbonium ion to recombine with the carboxylate anion of the leaving group.* On the basis of his experimental results, Corey thus concludes that, if the solvolysis of *exo*-2-norbornyl arenesulfonates does not yield the bridged ion (**153**) but rather a pair of interconverting unsymmetrical ions (i.e., **152**), "the interconversion rate is so rapid that for chemical purposes the ion may be taken as symmetrical" (184).

2. *The Solvolysis of* exo-*2-Norbornyl* p-*trifluoromethylthionbenzoate*

Smith and Petrovich (186) have arrived at the identical conclusion from the results of their investigation of the solvolysis of optically active *exo*-2-norbornyl *p*-trifluoromethylthionbenzoate (**155**) in acetic acid and aqueous ethanol. In acetic acid at 140°, the rate of racemization is equal to the rate of disappearance of the thion ester (**155**); this is interpreted as indicating that ion-pair return by oxygen to C-1 is not important in this system. The products of the reaction, in addition to 73% *exo*-2-norbornyl acetate, include 16% *exo*-2-norbornyl *p*-trifluoromethylthiobenzoate (**156**). Since the thioester (**156**) isolated from the reaction mixture is, within the limits of experimental error, totally racemic, Smith and Petrovich conclude that the 2-norbornyl cation must be symmetrical toward ion-pair return by sulfur.

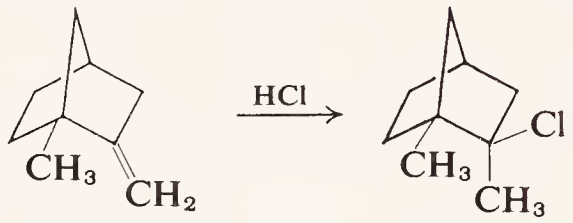


* The validity of this argument rests on its inherent assumption that the rate of ion-pair collapse to form product should exceed the rate of Wagner-Meerwein migration of C-6 from C-1 to C-2. Skell and Maxwell (184) have cautioned that this condition does not universally prevail.

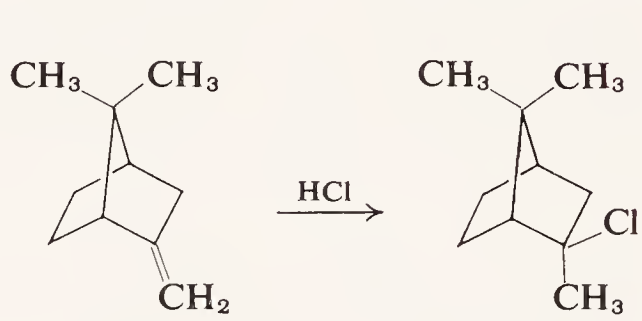
3. Absence of a Symmetrical Intermediate in the Hydrochlorination of 1-Methyl-d_3-2-Methylenenorbornane

Brown and Liu (187) have shown that rapid hydrochlorination (188) of both 1-methyl-2-methylenenorbornane (**157**) and α-fenchene (**159**) produces the corresponding tertiary *exo*-chlorides, **158** and **160**, respectively, in high yield. Brown suggests that past experience (189), the exclusive formation of tertiary chlorides, and the *exo* orientation of chloride in the product (**160**) derived from α-fenchene,* all indicate that these reactions involve the generation of intermediate carbonium ions.

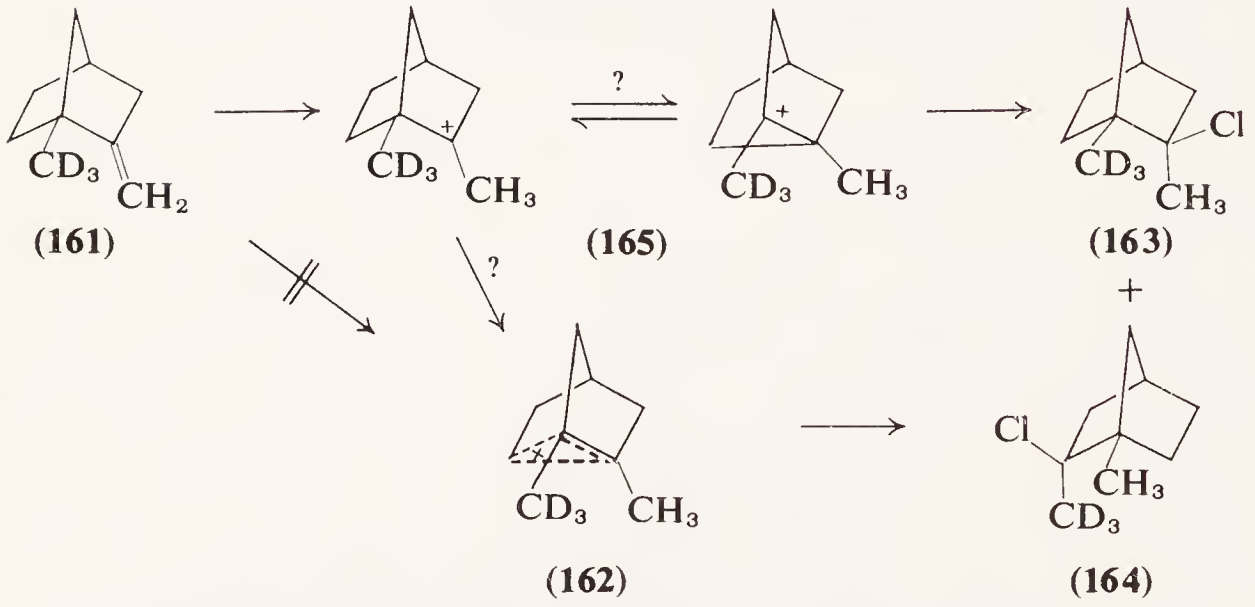
If the addition to 1-methyl-d_3-2-methylenenorbornane (**161**) involved the intermediacy of the bridged cation **162**, we would expect the product to consist of equal mixtures of 1-methyl-d_3-2-methyl- (**163**) and 1-methyl-2-methyl-d_3-*exo*-2-norbornyl chloride (**164**). When hydrochlorination was



(157) **(158)**



(159) **(160)**

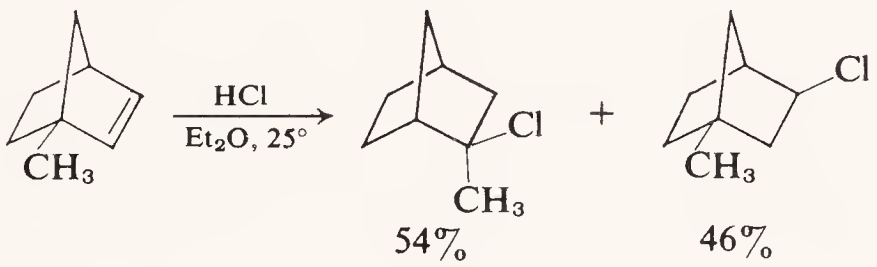


(161) **(165)** **(163)** **(162)** **(164)**

* For reactions not involving carbonium ion intermediates, the presence of a *syn*-7-methyl substituent generally results in *endo* attack on an sp^2-hybridized carbon atom at the 2-position of the norbornyl skeleton (see p. 1122).

carried out rapidly at 0° in the absence of excess acid, the ratio of chlorides **163** and **164** obtained corresponded to only 35–56% scrambling of the trideuteriomethyl label, depending on reaction conditions. Brown (187) feels that these results exclude the bridged ion **162** as the sole product forming intermediate in this reaction but that they are consistent with the intermediacy of a pair of rapidly equilibrating classical ions (**165**), which react with chloride somewhat more rapidly than they interconvert. The data could also be reconciled by postulating initial formation of a classical 1,2-dimethyl-2-norbornyl cation, which reacts with chloride and rearranges to the bridged ion (**162**) at comparable rates.

Although the hydrochlorination reaction certainly exhibits the properties commonly associated with reactions that proceed via carbonium ion intermediates, it may not involve cations identical to those formed by solvolytic processes. Certainly the character of the transition states for cation generation differ for the two reactions. For example, although a 1-methyl substituent markedly enhances the rate of solvolysis of *exo*-2-norbornyl tosylate (p. 1161), it exerts no apparent directing influence on the addition of HCl to 1-methylnorbornene (99):

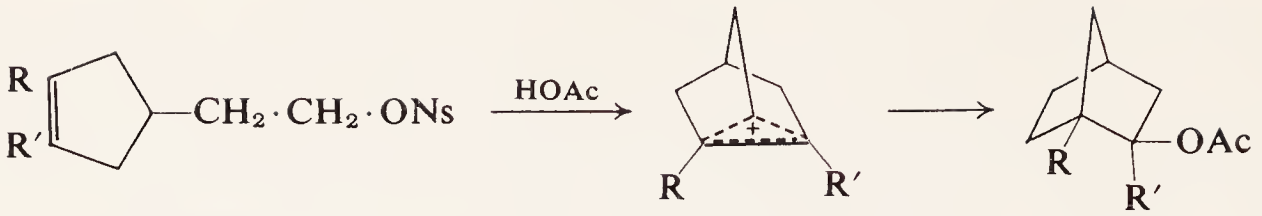


54% 46%

Until the intermediates and the transition states that lie along the reaction coordinate for the hydrochlorination reaction are more thoroughly understood, it is probably unwise to draw generalized inferences from the results of such reactions.

B. Presence of a Symmetrical Intermediate in the Solvolysis of 2-(Δ^3-Cyclopentenyl)ethyl *p*-Nitrobenzenesulfonates

Indirect evidence bearing on the structure of the 2-norbornyl cation comes from the investigations of the solvolytic ring closure of derivatives of 2-(Δ^3-cyclopentenyl)ethanol. Both the tosylate (190–192) and *p*-nitrobenzenesulfonate (193) (nosylate) (**166a**) of this alcohol undergo acetolysis to yield exclusively *exo*-2-norbornyl acetate (**168a**). The rate of acetolysis of nosylate **166a** exceeds that of its saturated analog, 2-(cyclopentyl)ethyl nosylate, by a factor of ca. 95 (193). This has been interpreted (192–193) as conclusive evidence for direct participation of the double bond in displacing the arenesulfonate anion.



(166) **(167)** **(168)**

ONs = *p*-$O_2N \cdot C_6H_4 \cdot SO_2$-

(166a) R = R′ = H
(166b) R = H, R′ = CH_3
(166c) R = R′ = CH_3

(169) **(170)**

By investigating the effect of methyl substitution on the double bond on the rate of this solvolytic ring closure, Bartlett and Sargent (194) have been able to infer the structure of the transition state for this reaction. They found that 2-(3-methyl-Δ^3-cyclopentenyl)ethyl nosylate (**166b**) and 2-(3,4-dimethyl-Δ^3-cyclopentenyl)ethyl nosylate (**166c**) undergo solvolysis at rates greater than that of 2-(Δ^3-cyclopentenyl)ethyl nosylate (**166a**) by factors of 7 and 38.5, respectively. Thus the introduction of a second methyl group on the double bond has a rate-enhancing effect (a factor of 5.5) nearly identical to that of the initial introduction of a single methyl group into the unsubstituted system. From this result, Bartlett and Sargent conclude that at the transition state for the reaction, the carbon atoms at both ends of the double bond must sense the development of the incipient positive charge to nearly the same extent. This requires a transition state in which the incipient positive charge is delocalized over three carbon atoms (**169**), and it rules out the intervention of a less symmetrical transition state (**170**). The resemblance of transition states **169** and **170** to the bridged and classical formulations for the 2-norbornyl cation is obvious. Bartlett and Sargent further contend that a reaction starting from a symmetrical ground state (**166**) and passing through a symmetrical transition state (**169**) must eventually produce a symmetrical initial intermediate (**167**).

In implying that a bridged 1,2-dimethyl-2-norbornyl cation (**167c**) intervenes in the solvolysis of nosylate **166c**, the results of Bartlett and Sargent differ from those obtained by Brown and Liu (187) for hydrochlorination of 1-methyl-2-methylenenorbornane (**157**). This represents another example of solvolysis and hydrochlorination reactions leading to differing

conclusions regarding the charge distribution within a presumed cationic intermediate. Further study is required to reveal the basis for these discrepancies.

The observation that a symmetrical (bridged) 1,2-dimethyl-2-norbornyl cation results from solvolysis of nosylate **166c** is not in irreconcilable conflict with the inference that such an ion does not appear to be the immediate product of ionization of 1,2-dimethyl-*exo*-2-norbornyl *p*-nitrobenzoate (p. 1165). Sargent (9) has commented at length on the probability that bridging, if it occurs at all, should lag behind ionization during solvolysis of tertiary *exo*-2-norbornyl derivatives. Similar behavior would not be expected for a primary nosylate (e.g., **166c**).

C. Possible Evidence for an Unsymmetrical 2-Norbornyl Cation

The conclusion that ionization of 2-(Δ^3-cyclopentenyl)ethyl arenesulfonates results in the initial formation of a symmetrical 2-norbornyl cation (194) does not preclude the possibility that subsequent rearrangement might lead to other intermediates of differing structure. Collins and Lietzke (48) have suggested that the distribution of ^{14}C in the 2-norbornyl acetate formed by acetolysis of 2-(Δ^3-cyclopentenyl)-2-^{14}C-ethyl nosylate (195) (**171**) may reveal the intervention of a classical 2-norbornyl cation. The ^{14}C distribution data (average of two independent runs) obtained by Lee and Lam (195) are summarized in Figure 5. The degradative scheme employed did not distinguish the distribution of ^{14}C between the positions within the following pairs: C-2 and C-3, C-1 and C-4, and C-5 and C-6. Attack by solvent on the initially formed intermediate (**172**) results in ^{14}C located only at C-5.

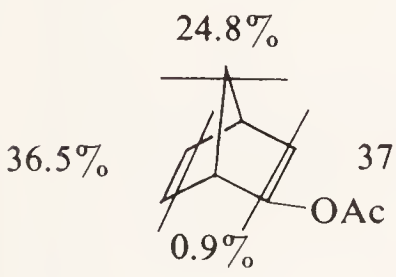
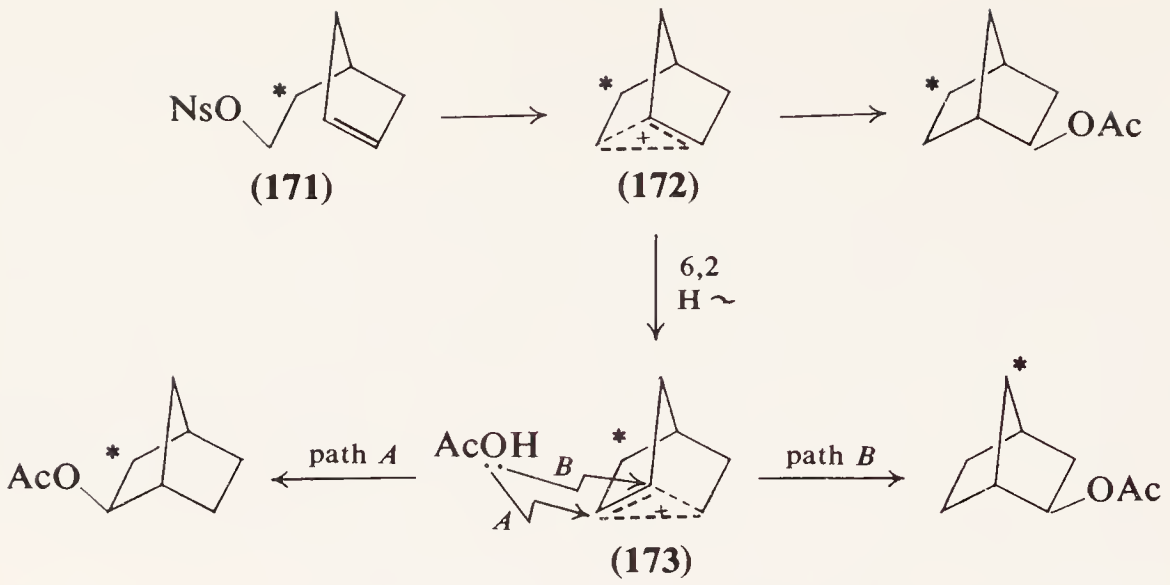


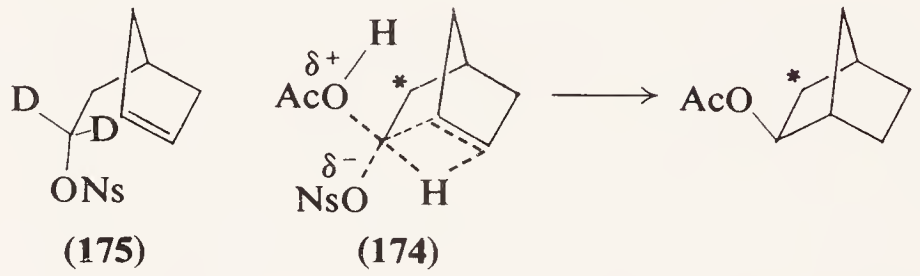
Fig 5. Distribution of ^{14}C in the acetolysis product of 2-(Δ^3-cyclopentenyl)-2-^{14}C-ethyl *p*-nitrobenzenesulfonate.

A 6,2 (or 6,1) hydride shift converts bridged ion **172** into its ^{14}C isomer **173**. Attack by solvent on **173** should lead to an equal distribution of ^{14}C between C-3 and C-7.

The data presented in Figure 5 clearly demonstrate that this expectation is not realized. To an extent well beyond the range of experimental error, the amount of ^{14}C at C-2, C-3 exceeds that at C-7. Lee and Lam (195)

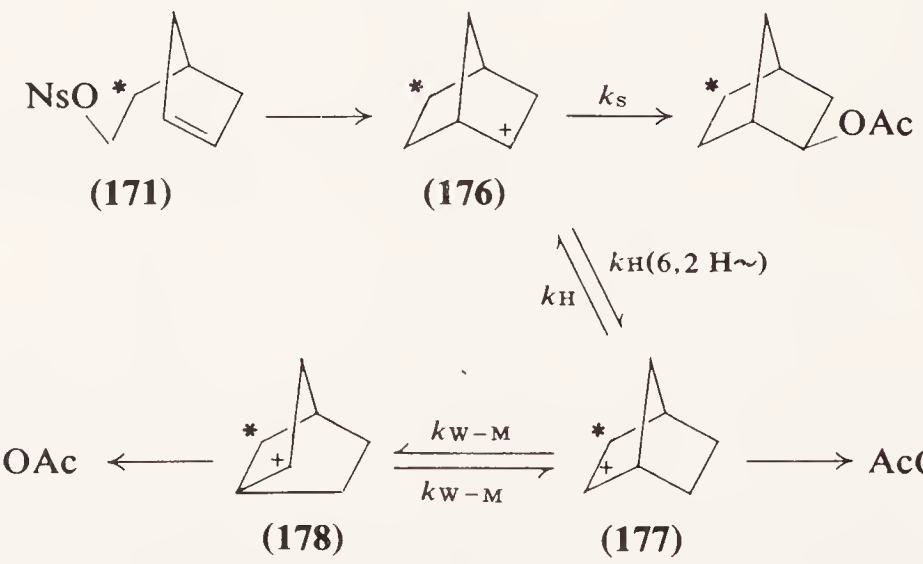


suggested that the excess ^{14}C at C-2, C-3 could be accounted for by postulating that an S_N2-like displacement involving concerted hydride migration (**174**) might compete with the formation of bridged ion **172** via normal π-assisted ionization.



Such a process seems unlikely, however, in light of the observed isotope effect ($k_H/k_D = 1.13$) (162,196) for acetolysis of dideuterio nosylate **175**, which appears too small to support the postulated concerted hydrogen migration during the rate-determining step.

Collins and Lietzke (48) note that the observed ^{14}C distribution data can be easily accommodated by a mechanism for solvolysis of nosylate **171** which involves only classical cations. The scheme would be equally

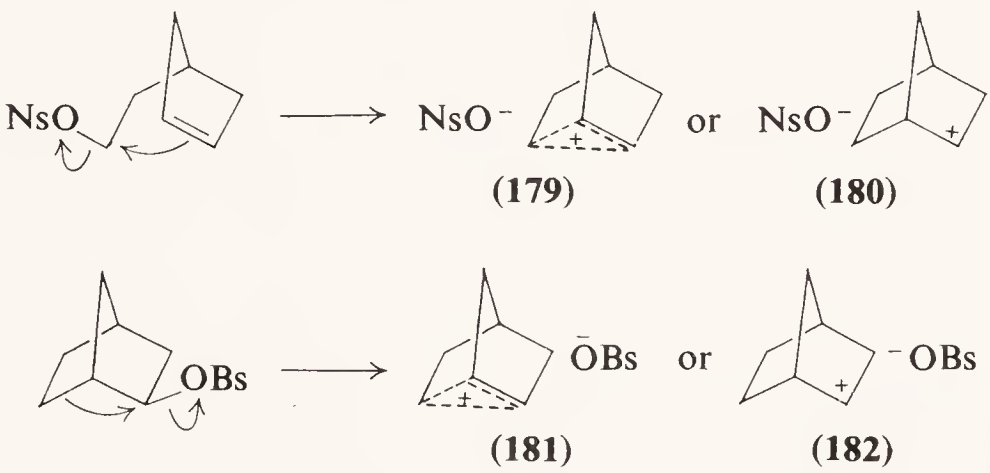


adequate, however, if the initial intermediate (**176**) were the bridged ion **172**. Collins and Lietzke were able to demonstrate that with $k_S/k_H = 0.022$

and $k_S/k_{W-M} = 0.33$, the ^{14}C product distribution data predicted by this scheme are within experimental error identical to those obtained by Lee and Lam (195).

These rate ratios, calculated to explain the behavior of the postulated intermediates **176–178** cannot be employed to explain the fate of the 2-norbornyl cations generated by solvolysis of either *exo*- or *endo*-2-norbornyl brosylate. They imply far too low a rate for Wagner-Meerwein interconversion (k_{W-M}) of the two enantiomeric classical 2-norbornyl cations and far too high a rate for 6,2 hydride migration (k_H) relative to the rate of solvent attack upon the cation (k_S) to explain the high degree of racemization (5–7) (p. 1101) and the comparatively limited amount of hydride migration accompanying these reactions.

Bartlett and co-workers (190–192,194) have noted that the environment of the 2-norbornyl cation formed by π-assisted solvolysis of 2-(Δ^3-cyclopentenyl)ethyl nosylate (**179**) differs fundamentally from that of the cation generated by σ-assisted solvolysis of *exo*-2-norbornyl brosylate (**181**). For the latter, the leaving group shields the face of the cation toward which solvent must approach in order to initiate product formation. For the former, the leaving group is well displaced from this face of the cation.



(179) **(180)**

(181) **(182)**

Collins and Lietzke suggest that the position of the leaving group may decrease k_S for attack on **182** relative to attack on an unshielded cation (e.g., **180**). They suggest further that by helping to localize positive charge, the leaving group may decrease k_H for **182** relative to the rate that would be observed in its absence. In essence, they postulate that the symmetry properties thus far ascribed to the bridged 2-norbornyl cation may be largely due to ion-pair effects, which allow the interconversion of two classical norbornyl cations to become rapid relative to other processes. However, such effects do not seem to explain the peculiar kinetic behavior of the 2-norbornyl derivatives, for which a rationale exists in bridged-ion formation. Indeed, Collins and Lietzke (48) emphasize that they take no particular stand in favor of the scheme outlined previously. Nonetheless, their suggestion will undoubtedly prompt further investigation into the

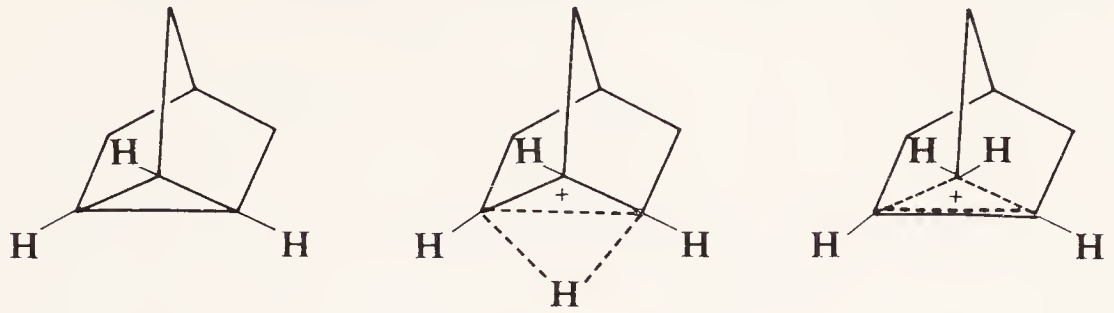
potential role of ion-pair effects in the chemistry of the 2-norbornyl cation. We cannot help but note, in conclusion, that realization of the role that ion-pair effects can play in solvolysis reactions was among the first real dividends to come from investigation of the chemistry of this intriguing intermediate (6,197).

D. Direct Observation of the 2-Norbornyl Cation by Raman Spectroscopy

The nmr spectrum of the 2-norbornyl cation (43–45), even when obtained at low temperatures, fails to establish whether this species exists in the form of a bridged ion (**6**) or as a classical, unsymmetrical cation in rapid equilibrium with its enantiomer. One reason for the inadequacy of nmr to make this distinction is that the Wagner-Meerwein interconversion of the two enantiomeric classical cations might well be rapid relative to the time required for interaction of the cation with radio frequency radiation. Thus the spectrum obtained might well reflect a time-averaged environment for the protons giving rise to absorption; the existence of such an environment would in turn imply elements of symmetry for the cation which, at any instant in time, it does not actually possess. This ambiguity would not complicate interpretation of the infrared or Raman spectra of the cation, since the time required for interaction of radiation of the frequency appropriate for obtaining such spectra with the cation is on the order of that required for only a single molecular vibration. It is inconceivable that, on this time scale, time averaging could impart to two rapidly interconverting classical 2-norbornyl cations the symmetry properties expected of a bridged ion.

Olah and co-workers (198) have recently obtained the Raman spectrum of the 2-norbornyl cation generated by dissolution of *exo*-2-norbornyl chloride in an FSO_3H–SbF_5–SO_2 solvent mixture at $-80°$. The spectrum of the cation exhibits a marked similarity to those of nortricylene and 3-bromonortricyclene, but it differs significantly from those obtained for norbornane and the 2-norbornyl halides. The similarity of the spectrum of the cation to that of nortricylene (**183**), coupled with the presence of a band in the spectrum at 3110 cm^{-1}, which is characteristic of the presence of a cyclopropane ring, lead Olah et al. to suggest that the 2-norbornyl cation is in fact protonated nortricylene (**184**). It is not obvious, however, how the Raman spectral properties of the cation exclude the bridged structure (**6**) originally proposed by Winstein and Trifan (5–7). Both possess the same skeletal structural geometry at the cationic site, namely, that of an isosceles triangle, and both bear a marked resemblance to nortricyclene. Although the Raman spectral results of Olah et al. may leave unresolved some fine points regarding the structure of the 2-norbornyl cation, they do seem unambiguous in excluding the classical cation as a

possibility. We may still question, however, whether the inferences drawn from this investigation remain valid for a 2-norbornyl cation generated in a less acidic, more strongly solvating, more nucleophilic medium.



(183) (184) (6)

ADDENDUM

Since the completion of the manuscript much research pertinent to the structure of the 2-norbornyl cation has been reported. In order to alert the reader to the continuing activity in this area, I present here by citation only a representative sample of this more recent work, the results of which in several cases require modification of interpretations presented in this chapter.

Two related and extremely important investigations reported by Goering and Humski deserve special attention. By isolating products of retained configuration from the solvolysis (90% aqueous acetone) of optically active 1,2-dimethyl-*exo*-2-norbornyl *p*-nitrobenzoate, they have demonstrated that, to the extent of *at least* 10%, this reaction proceeds via unassisted ionization to yield an asymmetric (classical) carbonium ion (199). Goering and Humski (200) realized that if ionization of 1,2-dimethyl-*exo*-2-norbornyl *p*-nitrobenzoate is unassisted, then the high γ-deuterium isotope effect ($k_H/k_D = 1.10$) ascribed to participation during solvolysis of 6-d-*exo*-2-norbornyl brosylate (page 1168) should be markedly diminished for solvolysis of 6-deuterated 1,2-dimethyl-*exo*-2-norbornyl *p*-nitrobenzoate. Since they observe $k_H/k_D = 1.02$ for solvolysis of 6,6-d_2-1,2-dimethyl-*exo*-2-norbornyl *p*-nitrobenzoate, these investigators conclude that the large γ-deuterium isotope effect for solvolysis of the unsubstituted *exo*-norbornyl system is, indeed, a manifestation of assisted ionization to a bridged ion. Goering (201) and Brown (202) and their co-workers have independently carried out the experiments requisite to construction of a "Goering-Schewene diagram" (page 1137) for the 1,2-dimethyl-2-norbornyl system, but they appear to reach differing conclusions regarding its significance.

A number of stable substituted 2-norbornyl cations, as well as the parent ion itself, have now been observed spectroscopically in strongly acidic, nonnucleophilic media. Utilizing the combined results of proton

and ^{13}C nmr and Raman spectroscopy, Olah and co-workers conclude that under these conditions the parent 2-norbornyl cation is symmetrical and σ-delocalized (203–208), that the 2-methyl-2-norbornyl cation is non-equilibrating and partially σ-delocalized (208–210), and that the 1,2-dimethyl-2-norbornyl cation is asymmetrical, rapidly equilibrating and partially σ-delocalized (210). These investigators also conclude that, like the 1,2-dimethoxy-2-norbornyl cation previously investigated by Nickon and Lin (211), the 2-hydroxy and the 2-methoxy-2-norbornyl cations (210) lack any significant σ-delocalization. They also concur (209) with Farnum and Mehta (212), whose earlier spectroscopic observations of the 2-phenyl-2-norbornyl cation led them to the conclusion that that cation also lacks significant σ-delocalization.

There is continued interest in the possibility that σ-delocalization in the transition state for solvolysis of *exo*-2-norbornyl derivatives may be revealed by observing the effect of substituents at positions remote from the ionization site (213–222). Gassman and MacMillan (217) have cautioned that 7-oxygenated systems are inappropriate for this purpose, since the oxygen functions appear to alter the mechanism of solvolysis, in some cases in ways not yet fully understood, from that which is operative in the unsubstituted norbornyl system (*cf.* page 1145). The kinetics (220) and products (219) of the acetolysis of the 7-chloro-2-norbornyl tosylates have been reinvestigated (*cf.* page 1149).

Several investigations bearing on the origin of the high rate and product *exo*/*endo* ratios for solvolysis of tertiary 2-norbornyl derivatives have been reported (224–233).

Electrophilic (234–243) and free radical (244–246) additions to norbornene and substituted norbornenes have been examined in an attempt to probe more deeply the stereochemical factors that may influence the preferential direction of attack on an sp^2 hybridized carbon at the 2-position of the norbornyl skeleton. Bartlett and co-workers (247) have described an extensive investigation of the stereochemistry of atom transfer to the 2-norbornyl and the 2-methyl-2-norbornyl free radicals generated by perester decomposition.

The rates and consequences of the hydride shifts which attend the formation of the 2-norbornyl cation have been the subject of several additional investigations (248–252).

Other topics discussed in this chapter that have received further attention include the base catalyzed α-hydrogen exchange of 2-norbornanones (253–255), deamination of 2-norbornyl amines (256–257), and solvolysis of 2-norbornyl derivatives for which the 6,1 $\rightarrow$ 6,2 Wagner-Meerwein shift is sterically constrained (258,259). Several other recent publications (260–267) also describe research pertinent to the subject of this chapter.

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CHAPTER 25

Cyclopropylcarbonium Ions

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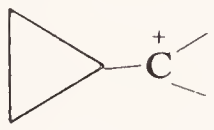
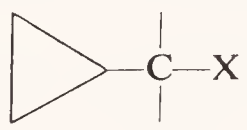
The unique properties of cyclopropylcarbonium ions (**1**) warrant a chapter devoted solely to them. Cyclopropyl is remarkably more effective than other alkyl groups in stabilizing carbonium ions. The unusual



(1)

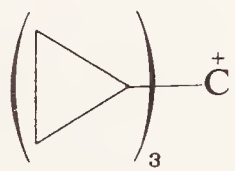
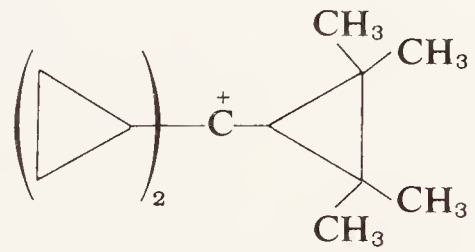
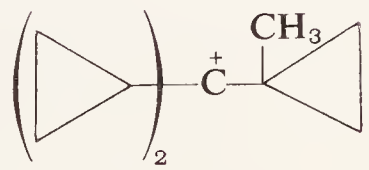


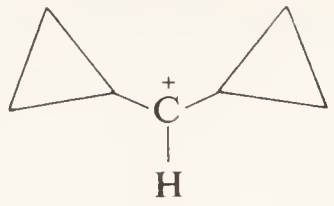
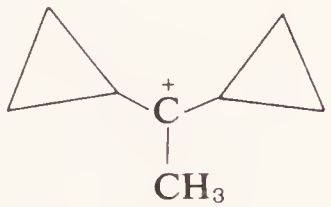
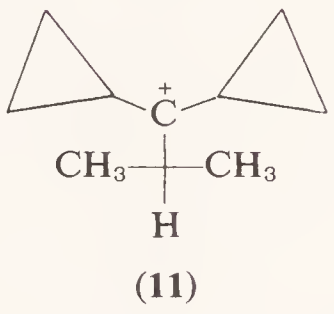
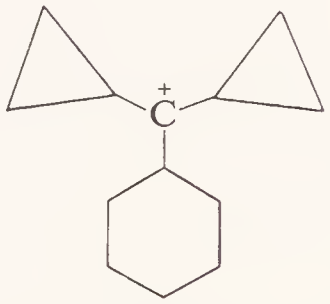
(2)

stabilities of cyclopropylcarbonium ions were inferred initially from the rapid rates of solvolysis reactions of cyclopropylmethyl derivatives (**2**), which have been reviewed (1–4). Recent studies of cyclopropylcarbonium ions as long-lived species in solution have confirmed their stabilities and furnished much additional information about their properties; these investigations have been reviewed briefly (3).

TABLE I

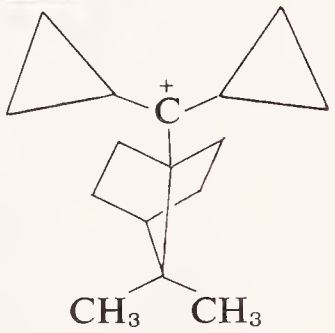
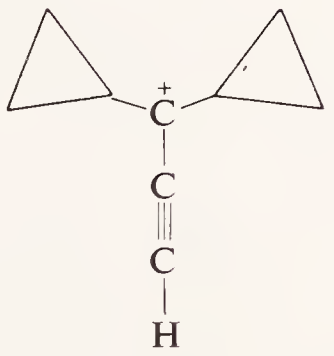
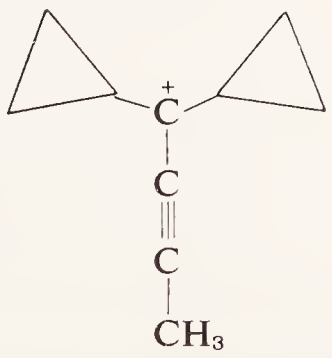
Nmr Spectra of Cyclopropylcarbonium Ions[a]

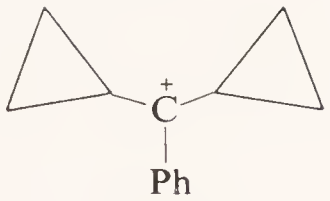
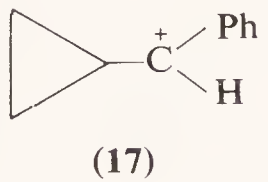
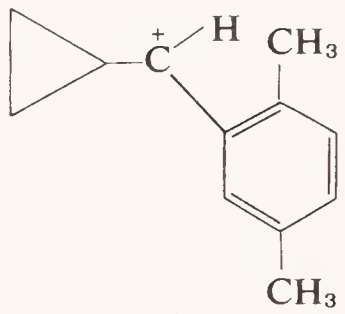
Ion	α-H's[b,c]	β-H's[b,c]	Other H's[c] and assignment	Solvent[d]	Temperature,[e] °C	Reference system[f]	References
 (6)	2.26 (*s*)			H_2SO_4	25	TMAC	7
	2.26 (*s*)			CF_3CO_2H	−25	TMAC	7
	2.26 (*s*)			25% SO_3–75% H_2SO_4	25	TMAC	7
	2.26[g]			CH_2Cl_2[h]	−25	TMAC	7,10
	1.85[i] (*s*)			SO_2[j]	−65	int. TMS	11
	2.14 (*s*)			FSO_3H–SbF_5–SO_2	−60	ext. TMS	11
 (7)	2.3–2.4	2.48 (*m*)	1.25 (*s*) CH_3	CH_2Cl_2[h]	−25	TMAC	7,10
 (8)	2.25 (*s*)		1.57 (*s*) CH_3	FSO_3H	−50	TMAC	12

 **(9)**	2.92–3.45	2.35–2.74	8.14 (t, J = 13 Hz) C^+H	FSO_3H–SbF_5–SO_2	−60	ext. TMS	11,13
	2.9–3.5	2.3–2.8	8.24 (t, J = 13 Hz) C^+H	FSO_3H	−50	TMAC	7,8,14
 **(10)**	3.00 (m)	2.60[i] (m)	2.28 (s) CH_3	FSO_3H	−30	int. $CHCl_3$	8,14
 **(11)**	2.60[i] (m)		1.28 (d, J = 7 Hz) $C(CH_3)_2$ (CH is buried under cyclopropyl H's)	FSO_3H	−50	int. $CHCl_3$	8,14
 **(12)**	2.56 (m)		1.68 (m) cyclohexyl H's	FSO_3H	−30	TMAC	8

(*continued*)

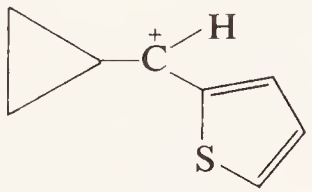
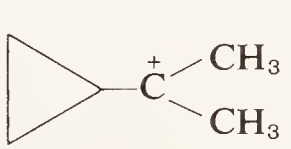
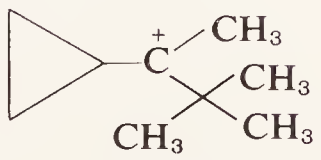
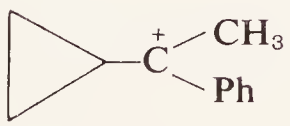
TABLE I (*Continued*)

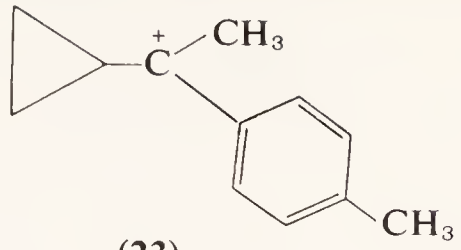
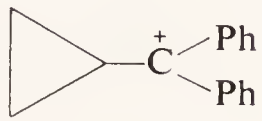
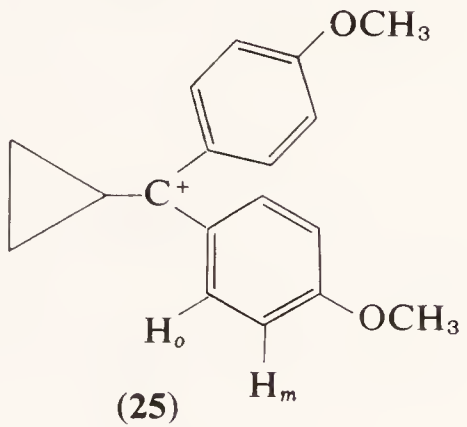
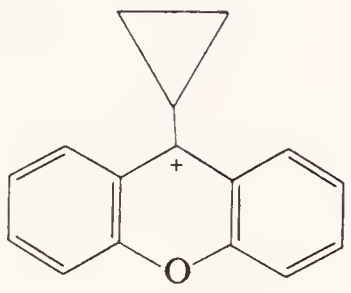
Ion	α-H's[b,c]	β-H's[b,c]	Other H's[c] and assignment	Solvent[d]	Temperature,[e] °C	Reference system[f]	References
 **(13)**	2.84 (*m*)	2.47 (*m*)	1.1 (*s*) CH_3 1.82–2.25 bicyclic ring H's	FSO_3H	−30	TMAC	8
 **(14)**	3.60–4.00	2.78–3.00	5.58 (*s*) ≡CH	FSO_3H–SO_2	−60	TMAC	9
 **(15)**	3.40–3.88	2.47–2.83	2.43 (*s*) CH_3	FSO_3H–SO_2	−60	TMAC	9

 **(16)**	3.00–3.30	2.45–2.85	7.55–8.10 aryl H's	FSO_3H–SbF_5–SO_2	−60	ext. TMS	11,13
 **(17)**	2.86–3.28	2.33–2.62	7.15–8.42 aryl H's (C^+H is buried under aryl H's)	FSO_3H–SbF_5–SO_2	−60	ext. TMS	11,13
 **(18)**	2.96–3.32	2.40–2.86	2.04 (*s*), 2.33 (*s*) CH_3's; 7.3–8.20 aryl H's (C^+H is buried under aryl H's)	FSO_3H–SbF_5–SO_2	−60	ext. TMS	11,13

(*continued*)

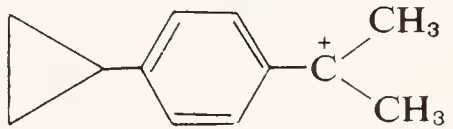
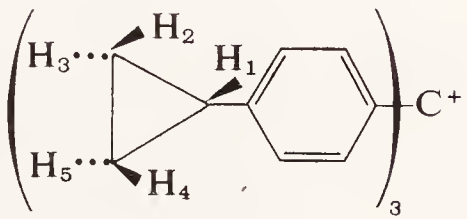
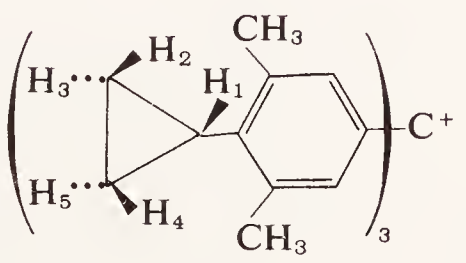
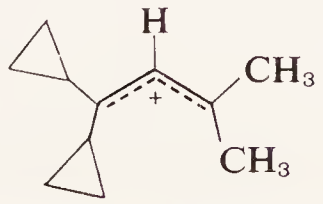
TABLE I (*Continued*)

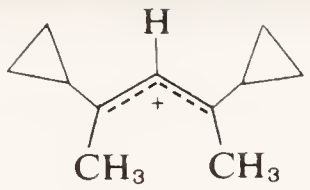
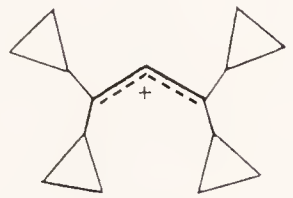
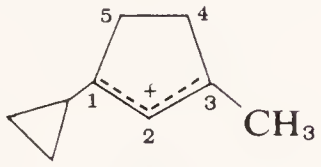
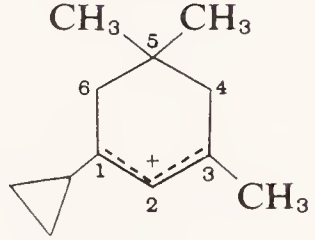
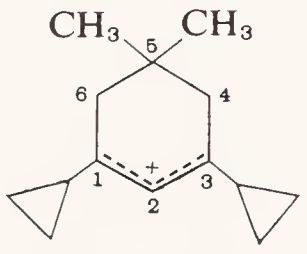
Ion	α-H's[b,c]	β-H's[b,c]	Other H's[c] and assignment	Solvent[d]	Temperature,[e] °C	Reference system[f]	References
 **(19)**	2.80–3.37	2.20–2.70	7.85–8.95 thiophene H's (C^+H is buried under thiophene H's)	FSO_3H–SbF_5–SO_2	−60	ext. TMS	11
 **(20)**	3.44–3.95		2.60 (*s*) CH_3 3.14 (*s*) CH_3	FSO_3H–SbF_5–SO_2	−60	ext. TMS	11,13
 **(21)**	3.17–3.56	2.30–2.90	1.10 (*s*) $C(CH_3)_3$ 2.40 (*s*) C^+CH_3	FSO_3H–SbF_5–SO_2	−60	ext. TMS	11,13
 **(22)**	3.56–3.90	2.82–2.98	2.52 (*s*) CH_3 7.34–8.27 aryl H's	FSO_3H–SbF_5–SO_2	−60	ext. TMS	11,13

 **(23)**	3.37–3.88	2.52–2.75	2.25 (*s*) aryl CH_3 2.47 (*s*) C^+CH_3 7.23–8.25 [$(AB)_2$ system] aryl H's	FSO_3H–SbF_5–SO_2	−60	ext. TMS	11,13
 **(24)**	3.40–3.95	2.35–2.74	7.30–7.85 aryl H's	FSO_3H–SbF_5–SO_2	−60	ext. TMS	11,13
 **(25)**	3.24–3.78	1.76–1.98 2.13–2.40	4.26 (*s*) OCH_3 6.98, 7.56 [$(AB)_2$ system, J_{AB} = 8.5 Hz] H_m, H_o	FSO_3H	−60	TMAC	12
 **(26)**	2.71–3.31	1.27–1.55 1.77–2.13	7.85–9.18 aryl H's	FSO_3H	—	TMAC	12

(*continued*)

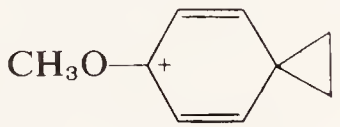
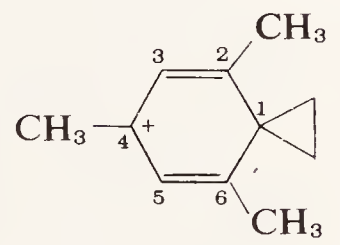
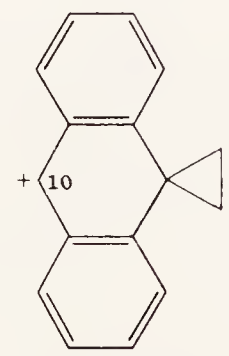
TABLE I (*Continued*)

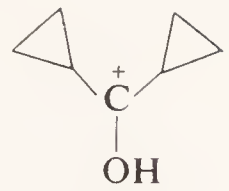
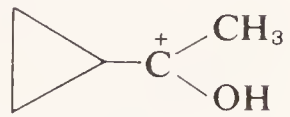
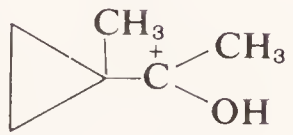
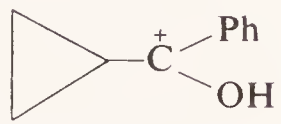
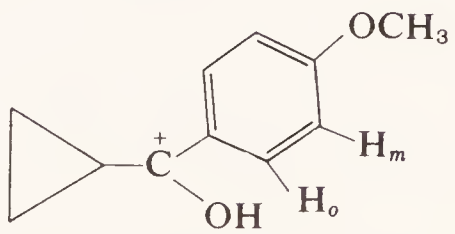
Ion	α-H's[b,c]	β-H's[b,c]	Other H's[c] and assignment	Solvent[d]	Temperature,[e] °C	Reference system[f]	References
 (27)	2.20–2.63	1.18–1.82	3.15 (*s*) CH_3 7.50, 8.58 [$(AB)_2$ system, J_{AB} = 8.5 Hz] aryl H's	FSO_3H–SO_2	−60	TMAC	12
 (28)	2.246 (*m*)	1.161 (*m*) H_3 and H_5 1.461 (*m*) H_2 and H_4 J_{12} = 8.25 Hz J_{24} = 9.05 Hz J_{13} = 4.80 Hz J_{25} = 6.89 Hz J_{23} = −4.88 Hz J_{35} = 9.78 Hz	7.02 [center of $(AB)_2$ quartet] aryl H's	CF_3CO_2H–$(CF_3CO)_2O$	—	int. TMS	15
 (29)	2.07 (*m*) J_{12} = 9.1 Hz J_{13} = 6.5 Hz J_{23} = −4.9 Hz	0.84 (*m*) H_3 and H_5 1.38 (*m*) H_2 and H_4 J_{24} = 9.1 Hz J_{25} = 6.9 Hz J_{35} = 9.8 Hz	−2.65 (*s*) CH_3 −7.33 (*s*) aryl H's	CF_3CO_2H–$(CF_3CO)_2O$	—	int. TMS	15
 (30)	buried under other absorptions	2.10–2.40	2.40 (*s*), 2.50 (*s*) CH_3's 6.39 (*s*) CH	H_2SO_4	—	TMAC	12

 **(31)**[k]	2.47–2.67	1.87–2.17	2.20 (*s*) 7.50 (*s*)	CH_3's CH	H_2SO_4	−5	TMAC	12
 **(32)**	2.20–2.68	1.60–2.04	5.95 (*s*)	CH	CF_3CO_2H	−12	int. TMS	12
 **(33)**	2.2–2.6		2.73 (*s*) 3.29 (*s*) 7.23 (*s*)	CH_3 H's on C-4 and C-5 H on C-2	H_2SO_4	25	TMAC	7,10
 **(34)**	~2.3–2.7		0.98 (*s*) ~2.3–2.7 2.44 (*s*) 7.32 (*s*)	$C(CH_3)_2$ H's on C-4 and C-6 CH_3 on C-3 H on C-2	CF_3CO_2H	−25	TMAC	7,10
 **(35)**	2.4 (*m*)	2.0[i] (*m*)	1.06 (*s*) 2.50 (*s*) 7.20 (*s*)	$C(CH_3)_2$ H's on C-4 and C-6 H on C-2	H_2SO_4	25	TMAC	7,10

(continued)

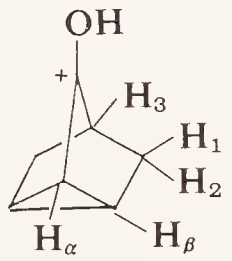
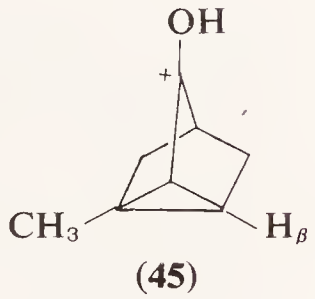
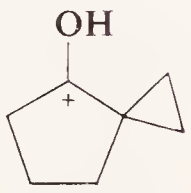
TABLE I (*Continued*)

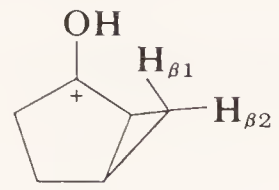
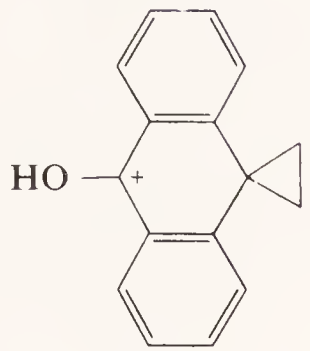
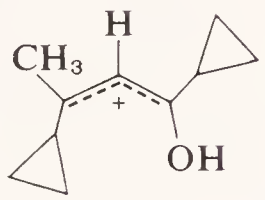
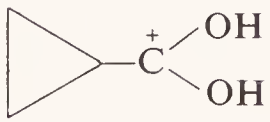
Ion	α-H's[b,c]	β-H's[b,c]	Other H's[c] and assignment	Solvent[d]	Temperature,[e] °C	Reference system[f]	References
 **(36)**	(none)	3.47 (*s*)	4.25 (*s*) OCH_3 7.47 (*d*) } [$(AB)_2$ system] 8.12 (*d*) } H's of 6-membered ring	SbF_5–SO_2	−70	ext. TMS	16
 **(37)**	(none)	3.77 (*s*)	2.39 (*s*) CH_3's on C-2 and C-6 2.60 (*s*) CH_3 on C-4 7.66 (*s*) H's of 6-membered ring	SbF_5–SO_2	−60	ext. TMS	17
 **(38)**	(none)	3.44 (*s*)	7.73 (*t*) four aryl H's 8.20 (*t*) four aryl H's 9.64 (*s*) H on C-10	SbF_5–SO_2	−55	ext. TMS	18

 **(39)**	2.07 (*m*)	2.05 (*m*)			H_2SO_4	—	TMAC	19
 **(40)**	2.61 (*m*)	2.25 (*m*)	2.77 (*s*)	CH_3	H_2SO_4	—	TMAC	19
 **(41)**	(none)	1.97 (*m*) 2.20 (*m*)	1.43 (*s*) 2.55 (*s*)	CH_3 C^+CH_3	H_2SO_4	—	TMAC	12
 **(42)**	2.95–3.40	2.38 (*m*)	7.60–8.30	aryl H's	H_2SO_4	40	ext. TMS	13
 **(43)**	3.08 (*m*)	2.12 (*m*)	4.05 (*s*) 7.22 } 8.30 }	OCH_3 [$(AB)_2$ system, J_{AB} = 8.5 Hz] H_m, H_o	H_2SO_4	—	TMAC	19

(*continued*)

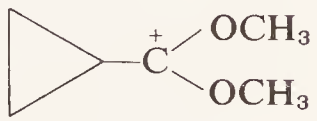
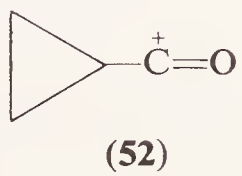
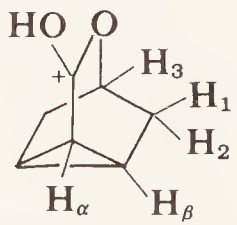
TABLE I (*Continued*)

Ion	α-H's[b,c]	β-H's[b,c]	Other H's[c] and assignment	Solvent[d]	Temperature,[e] °C	Reference system[f]	References
 **(44)**	2.24 (*t*)	3.40 (*d*) (J_{AB} = 4.5 Hz)	2.22, 2.83 [$(AB)_2$ system, J_{AB} = 11 Hz] H_1 and H_2 2.77 (*s*) H_3	H_2SO_4	—	TMAC	19
 **(45)**		3.37 (*d*) (J_{AB} = 4.5 Hz)	(other complex absorptions not assigned)	H_2SO_4	—	TMAC	19
 **(46)**	(none)	2.32 (*q*, center of A_2B_2 system) (other complex absorptions not assigned)		H_2SO_4	—	TMAC	19

 **(47)**		2.11 (*m*)	$H_{\beta1}$ or $H_{\beta2}$ (probably $H_{\beta2}$) (other complex absorptions not assigned)	H_2SO_4	—	TMAC	19
 **(48)**	(none)	3.18 (*s*)	7.7–9.2 (*m*) aryl H's	H_2SO_4	—	ext. TMS	18
 **(49)**[k]	2.15–2.55	1.10–1.40 1.50–1.85	2.07 (*s*) CH_3 6.15 (*s*) CH	CF_3CO_2H–H_2SO_4	—	TMAC	12
 **(50)**	{2.02 (*m*) 1.8 (*m*)	1.79 (*m*) 1.78 (*m*)		H_2SO_4 H_2SO_4	— 35	TMAC TMAC	19 20

(*continued*)

TABLE I (*Continued*)

Ion	α-H's[b,c]	β-H's[b,c]	Other H's[c] and assignment	Solvent[d]	Temperature, °C	Reference system[f]	References
 **(51)**	1.90–2.34	1.78 (*s*) 1.87 (*s*)	4.46 (*s*) OCH_3	H_2SO_4	—	TMAC	12
 **(52)**	2.8 (*m*)	2.76 (*m*) 3.1 (*m*)		60% SO_3–40% H_2SO_4	35	TMAC	20
				SO_2[l]	−60	ext. TMS	21
 **(53)**	2.60 (*t*) (A$_2$B system, J_{AB} = 7 Hz)	2.91 (*d*)	1.89, 2.20 [(AB)$_2$ system, J = 15 Hz] H_1, H_2 5.45 (broad) H_3	H_2SO_4	—	CH_3SO_3H	22,23

[a] In ppm relative to tetramethylsilane (TMS); positive numbers represent absorptions downfield from the standard.

[b] An unsubstituted cyclopropyl group contains five hydrogens of three kinds (α-, *cis*-β, and *trans*-β) and will exhibit an AA′BB′C or AA′BB′X spectrum. Such spectra are expected to contain a multitude of bands, since the coupling constants between all hydrogens in cyclopropyl groups are large. Spectra of few cyclopropylcarbonium ions have been analyzed completely. Instead, the absorptions due to α- and to β-hydrogens are reported variously in terms of the approximate centers of the multiplets, the approximate ranges of the multiplets (weak bands on the fringes of the multiplets are not noted, of course), or the positions of prominent peaks within the multiplets.

[c] The following abbreviations are used: *s* = singlet, *m* = multiplet, *d* = doublet, *q* = quartet, *t* = triplet.

[d] H_2SO_4 indicates concentrated sulfuric acid.

[e] Probably 25–35°C when not specified.

[f] The reference system used for the calibration of each spectrum is indicated: TMAC represents tetramethylammonium chloride used as an internal reference and assumed to absorb at 3.10; int. (internal) $CHCl_3$ and ext. (external) benzene were assumed to absorb at 7.27 and int. CH_3SO_3H at 6.76; the absorption of ext. TMS presumably was assigned a value of zero. Any inconsistencies in the chemical shifts assigned to different reference systems probably are too small to affect the discussion in this chapter.

[g] This absorption shows some evidence of fine structure.

[h] The anion probably has the average composition $AlCl_3(OH)^-$.

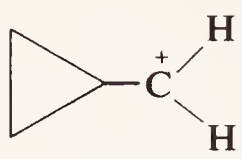
[i] Estimated by this author from the spectrum in the reference.

[j] The anion is reported to be BF_4^-, although $BF_3(OH)^-$ or other hydroxylated species also may be present (cf. Ref. 7).

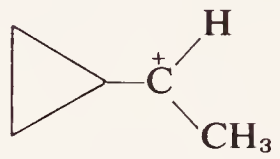
[k] The stereochemistry of the ion is not known.

[l] The anion is SbF_6^-.

This chapter is particularly concerned with the studies of stable solutions of cyclopropylcarbonium ions. Such studies at present extend neither to the least stable ions, such as **3** and **4**, nor to many interesting but more complex ions. Chapter 26 deals with the wealth of information about such ions which is available from detailed studies of solvolysis reactions.



(3)

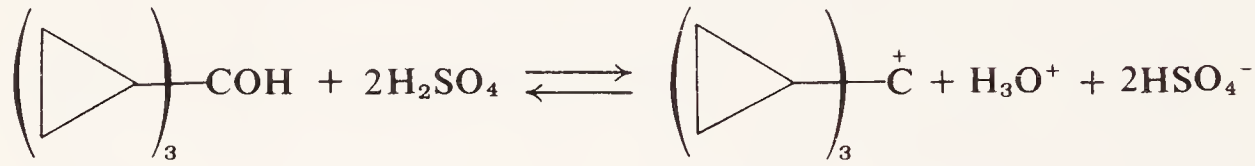


(4)

Cyclopropylcarbonium ions are represented in this chapter by solid-line structures, e.g., **1**, **3**, and **4**. The problem of their more exact representation is deferred to Section VIII.

I. PROOF OF EXISTENCE

Existence of the tricyclopropylcarbonium ion (**6**) as a stable species in solution is firmly established. This ion can be prepared (5,6) by dissolving



(5) **(6)**

tricyclopropylmethanol (**5**) in concentrated sulfuric acid. The resulting solution exhibits an *i*-factor of 4 as required by the balanced equation for ionization of an alcohol to a carbonium ion (5). The presence of a new species in the solution is evident from the intense ultraviolet absorption (λ_{max} 270 mμ, ε 22,000) (5). Recovery of the parent alcohol by careful addition of the sulfuric acid solution to aqueous base indicates that the new species can hardly be polymeric or have a structure greatly different from that of the alcohol (5). The nmr spectrum of the solution consists of a single absorption at 2.26 (5–7).* The position of this absorption, downfield from the complex multiplets observed for the cyclopropyl hydrogens of tricyclopropylmethanol, is consistent with the influence of a positive charge.

Existence of other cyclopropylcarbonium ions as stable species is predicated principally on the mode of preparation (Section II) and on the nmr spectra (Section III) of their solutions. Convincing evidence for the presence of most of the proposed cyclopropylcarbonium ions is furnished

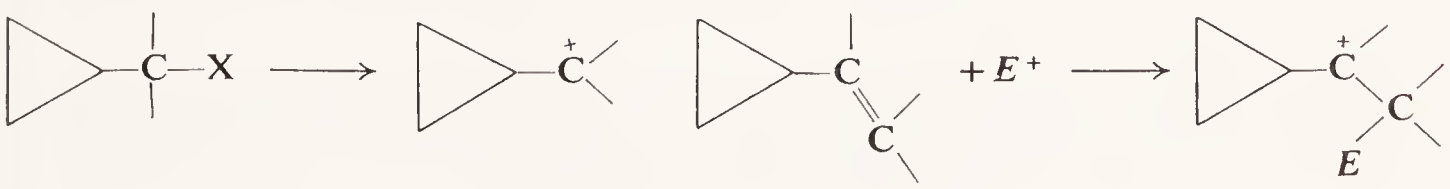
* Throughout this chapter, chemical shifts are expressed in parts per million (ppm) relative to tetramethylsilane; positive numbers represent absorptions downfield from the standard.

by the indication of the number of hydrogens of different kinds provided uniquely by nmr spectroscopy. That nmr spectra have been reported for almost all the cyclopropylcarbonium ions that have been studied as stable species attests to the leading role played by nmr spectroscopy in these investigations. Thus the compilation in Table I of most reported nmr spectra of such ions serves as a nearly complete list of cyclopropylcarbonium ions that have been directly observed. Ultraviolet spectra (Section IV) reported for solutions of several of the ions are in accord with the presence of carbonium ions but provide no specific structural information. Only a few of the ions have been converted to neutral compounds of known structure.

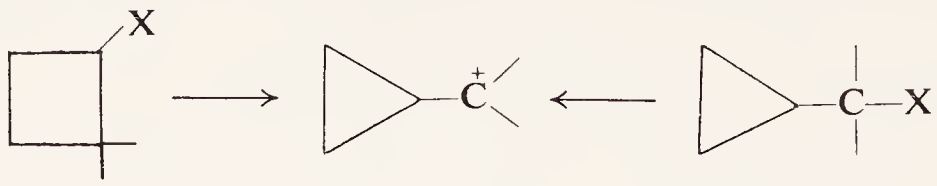
Cyclopropylcarbonium ions are assumed to be intermediates in many reactions in which their lifetimes are short and their concentrations never high enough to permit their detection by spectral means. Demonstration of the intermediacy of ions in such reactions rests on elucidation of the reaction mechanisms. The problems involved in inferring information about possible carbonium ion intermediates from data such as are obtained by kinetic and product studies are common to consideration of other classes of carbonium ions and are not discussed in this chapter. However, this problem has been reviewed for nucleophilic displacement reactions (1,24).

II. PREPARATION

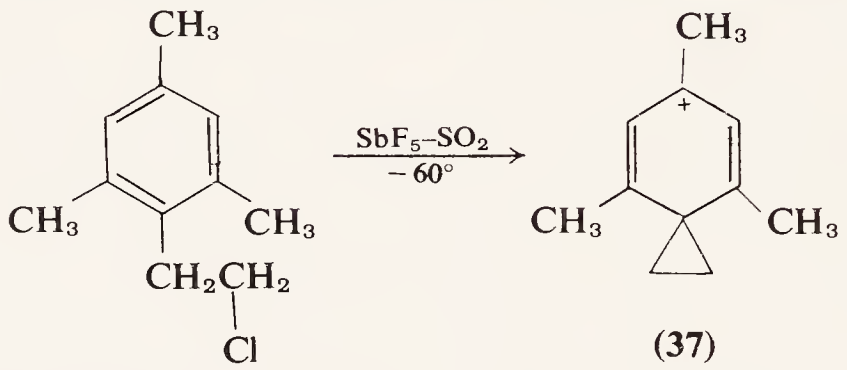
The variety of cyclopropylcarbonium ions that have been observed as stable species is illustrated by the structures in Table I. The tricyclopropylcarbonium ion (**6**), the first cyclopropylcarbonium ion to be directly observed, was prepared by adding tricyclopropylmethanol (**5**) to concentrated sulfuric acid (5,6). Most of the stable solutions of cyclopropylcarbonium ions that have since been studied were also prepared by addition to strong acid solutions of compounds with the same skeletal structures as the derived ions. In this manner ions **8–32** and **38** were prepared from alcohols, alkenyl cations **33–35** from dienes, hydroxycarbonium ions **39–49** from the corresponding ketones, dihydroxycarbonium ion **50** and acyl cation **52** from cyclopropanecarboxylic acid, dimethoxycarbonium ion **51** from trimethoxycyclopropylmethane, and cation **53** from the corresponding lactone. Cyclopropylcarbonium ions as transient intermediates also are generated frequently from reactions of cyclopropylmethyl derivatives and



from electrophilic additions to cyclopropylalkenes. Reactions of cyclobutyl derivatives (not illustrated in this chapter) in some instances lead to the same transient ions furnished by cyclopropylmethyl derivatives.

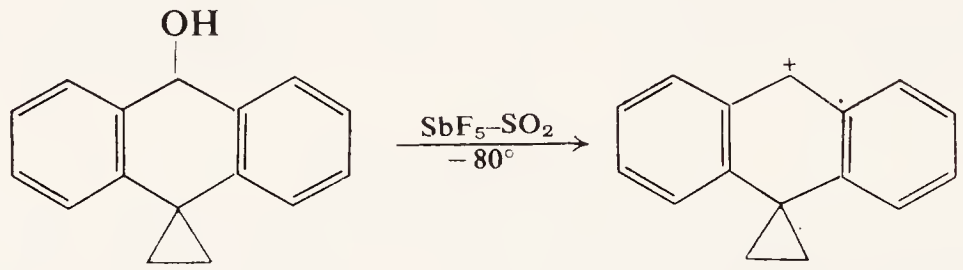


β-Arylethyl chlorides were used to prepare solutions of **36** (16) and **37** (17),



(37)

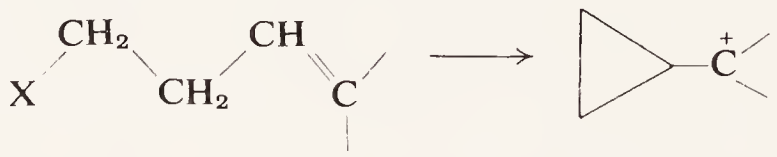
and an alcohol already containing a cyclopropane ring to prepare a solution of **38** (18). The spectra of these solutions seem consistent with



(38)

the phenonium ion structures **36–38**, which are considered here to be cyclopropylcarbonium ions.* Cram proposed in 1949 that "phenonium ions" were intermediates in acetolyses of the *p*-toluenesulfonate esters of the isomeric 3-phenyl-2-butanols (27). Considerable evidence has since been found for the existence of such ions as intermediates in some, but not all, nucleophilic displacement reactions of β-arylethyl derivatives. The preparation of stable solutions of such ions by Winstein and Olah and their collaborators provides striking confirmation of Cram's hypothesis. Phenonium ions are reviewed in Chapter 27 of this volume.

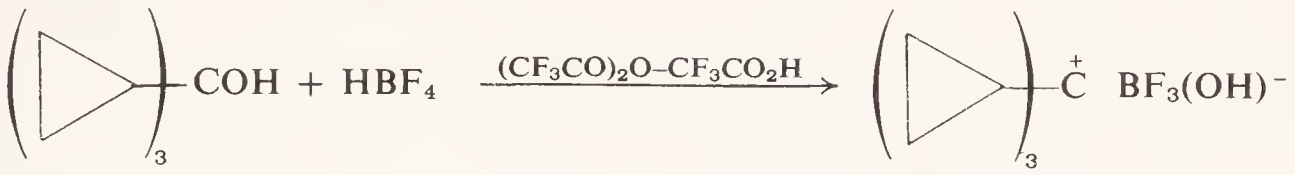
Reactions of β-arylethyl derivatives to form cyclopropylcarbonium ions



* Nmr spectra of other solutions thought originally to contain phenonium ions (25) are now known to be of other species (26).

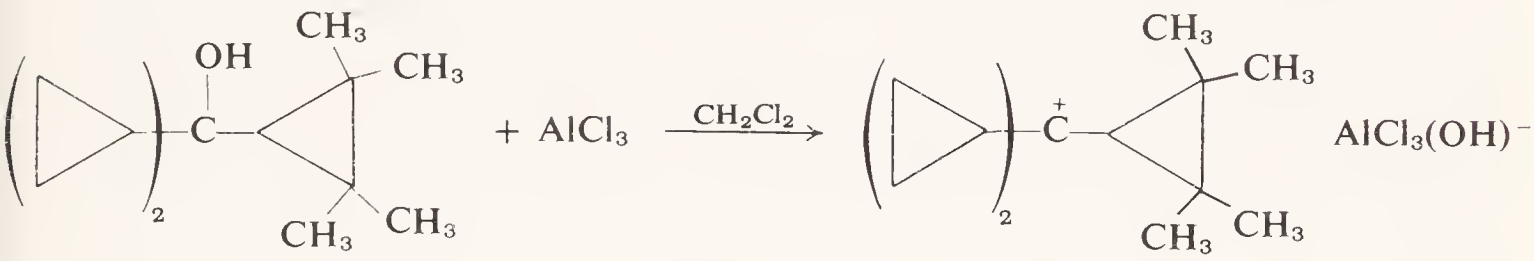
have counterparts in reactions of β-vinylethyl derivatives. Such "homoallylic" systems often lead partly or completely to transient cyclopropylcarbonium ions.* None of the ions in Table I were prepared in this fashion, but homoallylic formation of some closely related ions is discussed in Section VIII. Homoallylic systems are described by Story and Clark in Chapter 23.

Few of the cyclopropylcarbonium ions studied in solution have been isolated as salts. A solid salt, with an anion of average composition



(6)

$BF_3(OH)^-$, was prepared from tricyclopropylmethanol (7). Treatment of alcohols with aluminum chloride in dichloromethane also was used to



(7)

prepare solutions of ions **6** and **7** but the salts were not isolated (7,10). A salt of cation **52** was produced by reaction of the acyl fluoride with antimony pentafluoride (21).

(52)

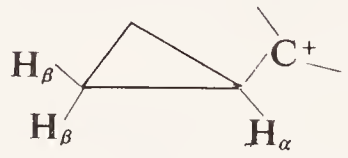
III. NMR SPECTRA

Nmr spectroscopy has been indispensable for establishing the structures of cyclopropylcarbonium ions. It has been hardly less important in suggesting the distributions of charge in the ions, the effectiveness of cyclopropyl relative to other groups in delocalizing the charge, and the geometries (discussed in Section VII) of the ions. The numbers of hydrogens of

* The word "homoallylic," coined to describe such systems (28), suggests possible interaction between the double bond and the reactive center, although they are formally separated by an intervening saturated carbon.

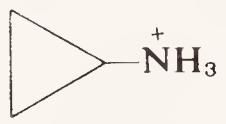
different types and the chemical shifts of each of these types of hydrogens, with few exceptions, seem consistent with the structures given in Table I.

The absorptions of the cyclopropyl hydrogens of the ions appear strikingly downfield from the absorption at 0.22 of cyclopropane.* It is expected that a hydrogen absorption will be shifted downfield by the presence of a positive charge and that the magnitude of the shift will be proportional approximately to the amount of charge on the carbon to which the hydrogen is attached (3). The large downfield shift of the β-hydrogens (see **54**) of the cyclopropyl groups must be due to conjugation



(54)

which places considerable positive charge on the β carbons. The shift of the β-hydrogen absorptions cannot be caused only by an inductive effect of the positive charge, since the β-hydrogens then would be affected much less than the α-hydrogens. The cyclopropylammonium ion, in which presumably only an inductive effect operates, exhibits an nmr spectrum† (19)



with the α-hydrogen multiplet 1.90 ppm below the β-hydrogen multiplet (α-hydrogens at 2.83 and the β-hydrogens at 0.93). In contrast, the chemical shifts of the α- and β-hydrogens of the tricyclopropylcarbonium ion (**6**) are equal, and in the spectra of many other ions, the β-hydrogen absorptions are only slightly upfield from the α-hydrogen absorptions.‡

The absorption of the β-hydrogens of the cyclopropyl group is found to shift downfield with decreasing ability of the other substituents of the carbonium ion to absorb the positive charge. This downfield shift reflects greater positive charge on the β-carbons as the result of increasing conjugation by the cyclopropyl group. For example, the cyclopropyldimethylcarbonium ion (**20**) exhibits its β-hydrogen absorption unusually far downfield; in contrast, cations in which the charge is delocalized more extensively, e.g., 9-cyclopropyl-9-xanthyl (**26**), 1,1,3,3-tetracyclopropylallyl (**32**),

* In carbon tetrachloride relative to internal tetramethylsilane (29).

† In concentrated sulfuric acid relative to internal tetramethylammonium chloride as 3.10.

‡ A report (30) that the dicyclopropylcarbonium ion (**9**) also exhibits a single nmr absorption in concentrated sulfuric acid solution may be in error (cf. Table I).

and 1,3-dicyclopropyl-5-5-dimethylcyclohexenyl (**35**), exhibit much smaller downfield shifts of the β-hydrogen absorptions. Steric and long-range shielding (31) effects of substituents should be nearly the same in the cyclopropylphenylmethylcarbonium ion (**22**) and its *p*-methyl homolog (**23**), yet the carbonium ion stabilizing effect of the *p*-methyl group results in a considerable upfield shift of the β-hydrogens. The cyclopropylphenylhydroxycarbonium ion (**42**) and its *p*-methoxy counterpart (**43**) provide a similar comparison.

The effectiveness of cyclopropyl relative to other substituents in absorbing positive charge can be inferred by comparing nmr spectra of cyclopropylcarbonium ions with those of related carbonium ions having other substituents. The data of Table II demonstrate that absorptions of hydrogens of cyclopropyl-substituted carbonium ions are upfield from the absorptions of the corresponding methyl-substituted ions. Steric and long-range shielding effects of substituents must be relatively small on the absorptions indicated in these examples.* This systematic difference in chemical shifts is attributed, at least in part, to greater absorption of positive charge by a cyclopropyl than by a methyl substituent. The greater charge density in a cyclopropyl group results in decreased charge density in the remainder of the ion. Similar comparisons of nmr spectra of related cyclopropyl-, phenyl-, and hydroxy-substituted carbonium ions suggest that cyclopropyl must also be more effective than phenyl but less effective than hydroxyl in absorbing charge.

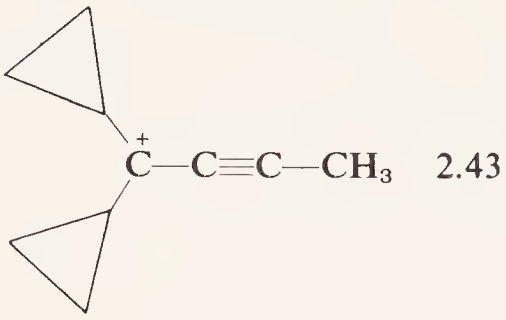
Effects of substituents on charge distribution in ions are more commonly deduced (Section V) by comparing either rates of formation of ions from neutral compounds or equilibria between ions and neutral compounds. Such experiments provide *differences* in stability between the ions and the precursors. These differences will not parallel absorption of charge by the substituents if substituents conjugate significantly in the precursors or alter the steric repulsions that accompany any changes in geometry in forming carbonium ions from neutral precursors. On the other hand, nmr shifts exhibited by an ion are characteristic of the ion only and independent of the precursor. In many instances, however, the seemingly ideal assessment of charge distribution by means of nmr shifts must be complicated by long-range shielding effects of substituents.

The insensitivity to medium of the spectrum of the tricyclopropylcarbonium ion suggests that specific bonding of this ion to solvent must be minimal, consistent with assuming that charge is significantly delocalized

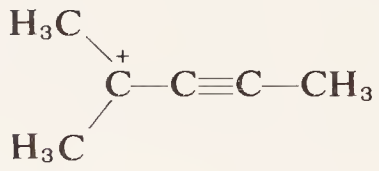
* It is assumed that the shielding effect of a cyclopropyl group in the ions is not of considerably greater magnitude than observed (32) in neutral compounds.

TABLE II

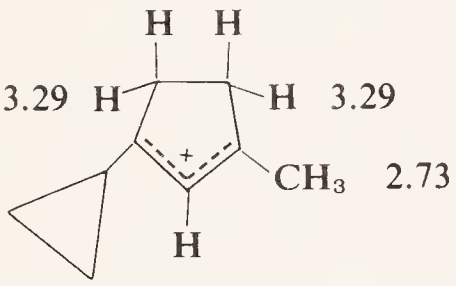
Nmr Absorptions of Related Cyclopropyl- and Methyl-Substituted Carbonium Ions[a,b]



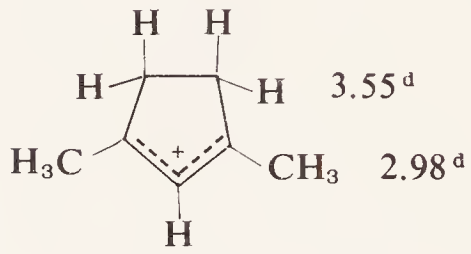
2.43



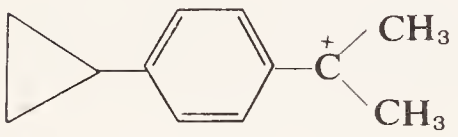
3.13[c]



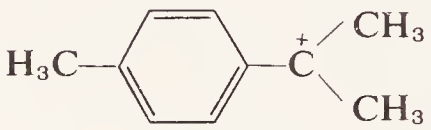
7.23



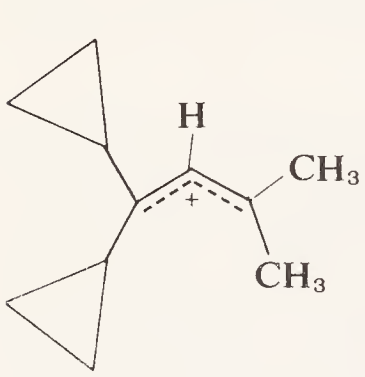
7.64[d]



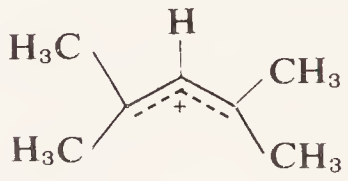
3.15



3.33[e]



2.40 and 2.50



2.95 and 2.97[d]

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[a] Data are taken from Table I unless otherwise indicated.

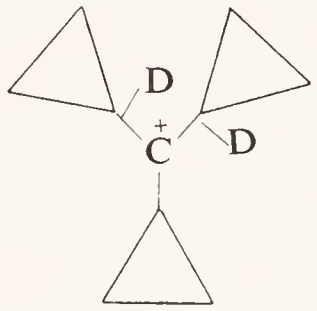
[b] Chemical shifts expressed in parts per million relative to tetramethylsilane; positive numbers represent absorptions downfield from the standard.

[c] In fluorosulfonic acid–antimony pentafluoride–thionyl chloride fluoride at −60° relative to external tetramethylsilane [C. U. Pittman, Jr., and G. A. Olah, *J. Am. Chem. Soc.*, **87**, 5632 (1965)].

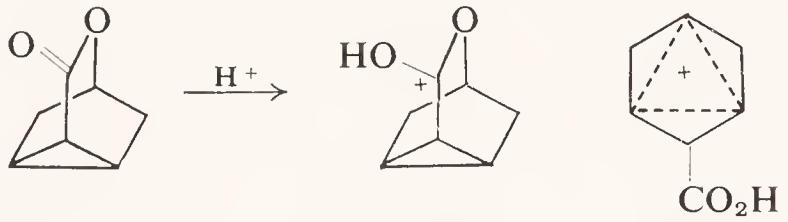
[d] In concentrated sulfuric acid relative to tetramethylammonium chloride as 3.10 [N. C. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **85**, 2991 (1963)].

[e] In fluorosulfonic acid–sulfur dioxide at −60° relative to tetramethylammonium chloride as −3.10 (12).

throughout the ion.* That a single nmr absorption, rather than a complex multiplet, is exhibited by this ion is attributed to a coincidence of the chemical shifts of the α-, *cis*-β, and *trans*-β hydrogens. In fact, some fine structure is detectable in a spectrum of this ion in dichloromethane (10). There is no evidence for any equilibration process: the appearance of the spectrum is not significantly temperature dependent, the single absorption represents all 15 hydrogens of the ion, and the deuteriums in the α,α-dideuterotricyclopropylcarbonium ion in concentrated sulfuric acid solution exchange neither with the solvent hydrogens nor with the β-hydrogens (7).



Structure **53** is proposed for the ion originally thought to be **55** (22). As has been noted (3,23), the nmr spectrum seems more compatible with the cyclopropylcarbonium ion structure **53** (cf. particularly the spectrum of **44**), and there is more precedent for this structure.



(53) **(55)**

IV. ULTRAVIOLET SPECTRA

The intense ultraviolet absorption (λ_{max} 270 mμ, ε 22,000) exhibited by the tricyclopropylcarbonium ion (**6**) in sulfuric acid solution has no counterpart in the spectra of other alkylcarbonium ions.† The cyclopropyldimethylcarbonium ion (**20**) and the dicyclopropylcarbonium ion (**9**) also are reported to exhibit intense absorptions in the same region (33). No

* In contrast, absorptions of some hydroxycyclopropylcarbonium ions (19) in sulfuric acid solutions have been observed to shift downfield with increasing acid concentration, even at acidities at which protonation of the parent ketones is virtually complete. Hydrogen bonding to solvent by the hydroxyl group of such an ion presumably is responsible. The hydrogen bonding decreases as acid strength increases (and a_{H_2O} decreases). Decreased hydrogen bonding leads to a decrease in the ability of the hydroxyl group to conjugate with the positive charge and a resultant increase in the amount of charge in the remainder of the ion.

† The spectra of *t*-alkyl cations have no significant absorptions above 210 mμ (33).

theoretical descriptions of the electronic transitions responsible for the absorptions of these saturated cyclopropylcarbonium ions have been published. However, the large extinction coefficients indicate that sizable transition moments are associated with the absorptions.

Ultraviolet spectra of other cyclopropylcarbonium ions are contained in Table III, and spectra of some related ions are included for purposes of

TABLE III

Ultraviolet Spectra of Carbonium Ions and Equilibria Between Carbonium Ions and Their Neutral Precursors

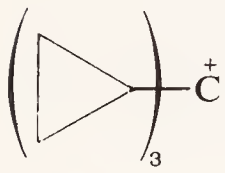
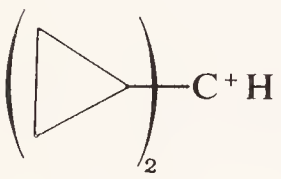
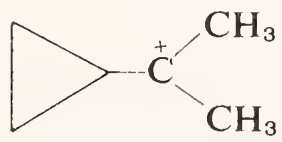
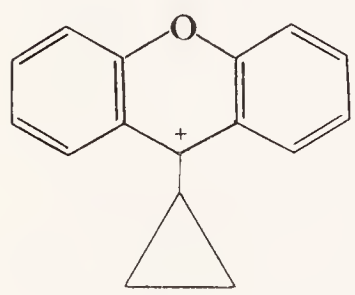
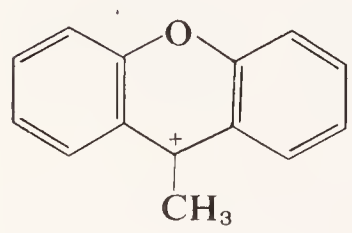
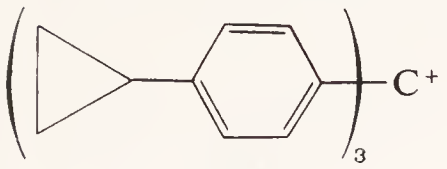
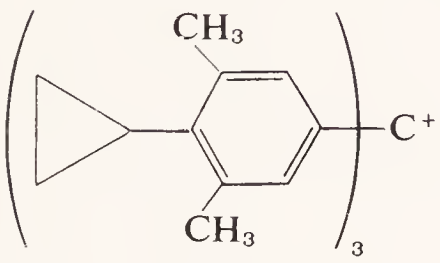
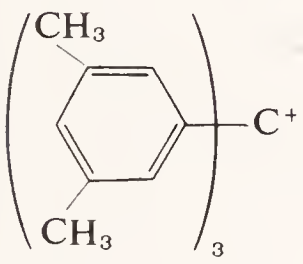
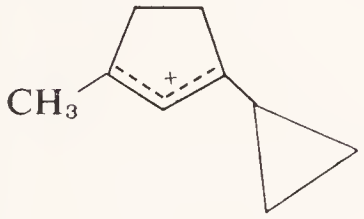
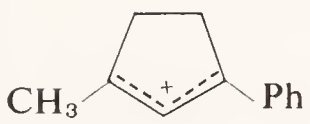
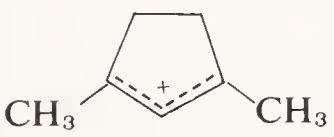
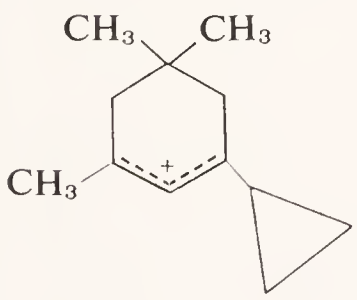
Ion	Percentage H_2SO_4 at which ion is half-formed	pK (Acidity scale used to define pK)	Ultraviolet absorption, $\lambda_{max}(\varepsilon)$	References
	22	-2.34 (H_R)	270 (22,000)[a] 270 (22,600)[b]	7 33
Ph_3C^+	50	-6.63 (H_R)		34
	—	—	273 (12,200)[b]	33
	—	—	289 (10,800)[b]	33
	—	—	377 (42,000)[a]	10
	—	—	366 (33,000)[a]	35

TABLE III (*Continued*)

Ion	Percentage H_2SO_4 at which ion is half-formed	pK (Acidity scale used to define pK)	Ultraviolet absorption, $\lambda_{max}(\varepsilon)$	References
 **(28)**	41[c]	−4.9 (H_R)	—	15
 **(29)**	50[c]	−6.5 (H_R)	—	15
	50[c]	−6.5 (H_R)	—	15
	12	−0.46 (H_0)	309 (28,000)[a]	7,36
	50	−3.4 (H_0)	—	7,36
	35	−2.1 (H_0)	275 (11,000)[a]	7,36
	—	—	333 (56,000)[a]	7,36

(*continued*)

TABLE III (*Continued*)

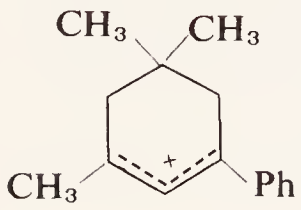
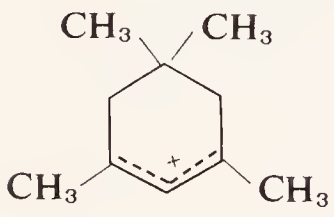
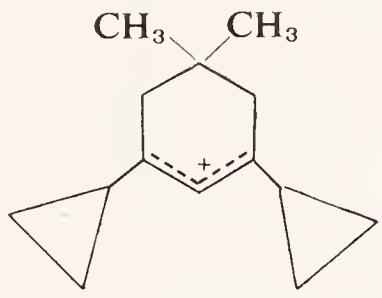
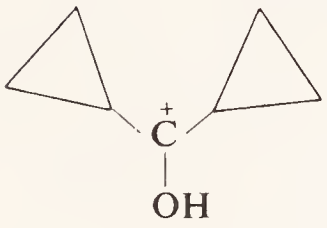
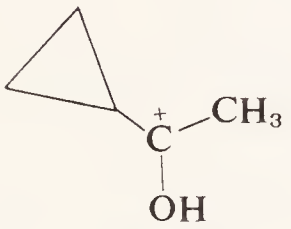
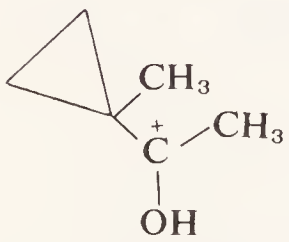
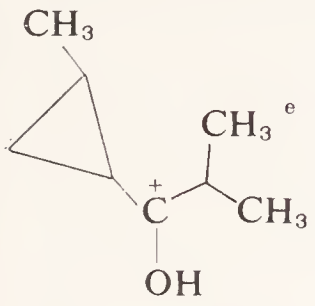
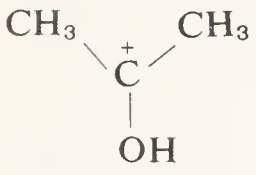
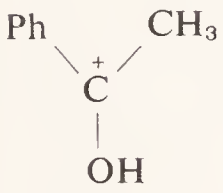
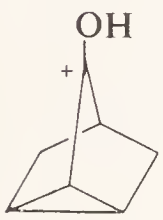
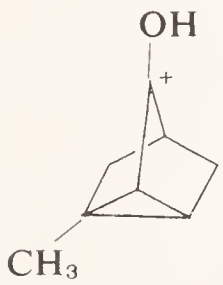
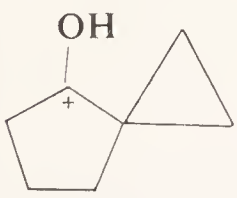
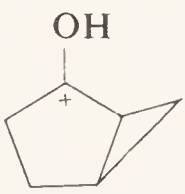
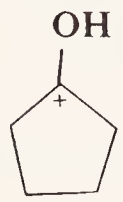
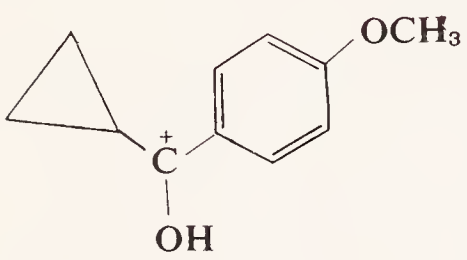
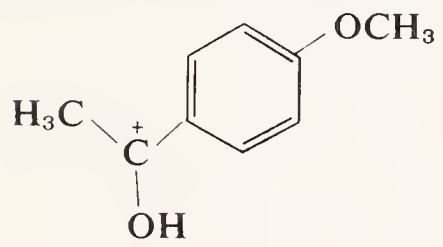
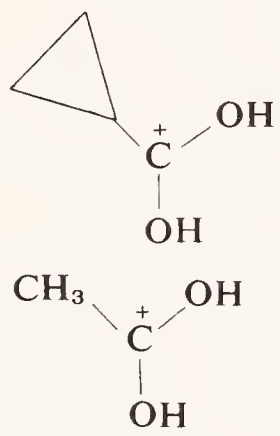
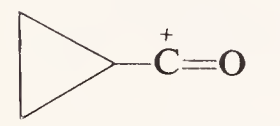
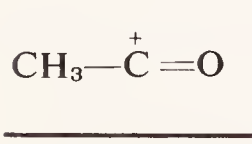
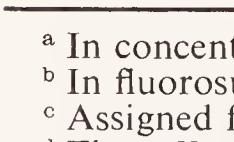
Ion	Percentage H_2SO_4 at which ion is half-formed	pK (Acidity scale used to define pK)	Ultraviolet absorption, $\lambda_{max}(\varepsilon)$	References
	52	-3.6 (H_0)	—	7,36
	50	-3.4 (H_0)	314 (9,100)[a]	7,36
	1.2	0.6 (H_0)	364 (33,000)[a]	7,36
	62.6	-4.8 (H_0)[d]	235 (16,700)[a]	19
 **(40)**	70.4	-5.7 (H_0)[d]	222 (10,400)[a]	19,12
 **(41)**	67.3	-5.3 (H_0)[d]	234 (9,300)[a]	12

TABLE III (*Continued*)

Ion	Percentage H_2SO_4 at which ion is half-formed	pK (Acidity scale used to define pK)	Ultraviolet absorption, $\lambda_{max}(\varepsilon)$	References
	71–72	−5.8 (H_0)[d,f]	~233[a,g]	10
	82[h]	−7.2 (H_0)	<190[a]	38
	74.0[h]	−6.15 (H_0)	—	39
 **(44)**	79.7	−6.9 (H_0)[d]	249 (2,900)[a]	19
 **(45)**	[80.6][i]	[−7.0 (H_0)][d,i]	[257 (4,400)][a,i]	19
 **(46)**	71.0	−5.8 (H_0)[d]	243 (7,300)[a]	19
 **(47)**	75.6	−6.4 (H_0)[d]	232 (5,500)[a]	19

(*continued*)

TABLE III (*Continued*)

Ion	Percentage H_2SO_4 at which ion is half-formed	pK (Acidity scale used to define pK	Ultraviolet absorption, $\lambda_{max}(\varepsilon)$	References
	84[h]	−7.5 (H_0)	—	38
	—	—	350 (34,200)[a]	19
	—	—	348 (33,200)[a]	19
	82[j] 73[h]	−7.2 (H_0)[f] −5.99 (H_0)	— —	20 40
	77[j] 77[h]	−6.5 (H_0)[f] −6.52 (H_0)	— —	20 40
	23% SO_3– 77% H_2SO_4[j]	—	—	20
	15% SO_3– 77% H_2SO_4[j]	—	—	20

[a] In concentrated sulfuric acid at room temperature.
[b] In fluorosulfonic acid–antimony pentafluoride at −60°.
[c] Assigned from the reported pK using the H_R values in Ref. 34.
[d] The pK refers to H_0 at half-formation, although the data are not sufficiently precise to tell if this function is followed satisfactorily. Protonation equilibria of simple ketones such as acetone and cyclohexanone do follow this function (38).
[e] The stereochemistry is not specified.
[f] Assigned from the percentage H_2SO_4 for half-formation using the tabulation of H_0 values of Paul and Long (37).
[g] Estimated by this author from the spectrum in the reference.
[h] Determined from the reported pK using the tabulation of H_0 values of Paul and Long (37).
[i] This value is not reliable because the ion decomposed rapidly.
[j] This value was determined using nmr spectra.

comparison. Absorptions of cyclopropylcarbonium ions are always at longer wavelengths and of greater intensity than absorptions of the corresponding methylcarbonium ions.

The conjugation of cyclopropyl groups with positive carbon, apparent from the ultraviolet spectra of cyclopropylcarbonium ions, has a counterpart in some neutral compounds. Attachment of a cyclopropyl in place of an alkyl group to aromatic rings or to carbon–carbon, carbon–oxygen, or carbon–nitrogen double bonds leads usually to a shift of the $\pi \rightarrow \pi^*$ absorption to longer wavelengths and often to an increase in intensity of this absorption.*

V. STABILITIES

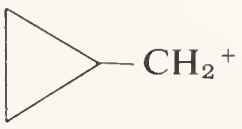
The conclusion that cyclopropyl groups are more effective than methyl or even phenyl groups in stabilizing carbonium ions can be drawn from studies of ions both in the gas phase and in solution. We refer here to thermodynamic stabilities of the ions relative to precursors, not to lifetimes of the ions under given conditions.

The abilities of substituents to stabilize CH_3^+ in the gas phase are suggested by appearance potentials (42) given in Table IV for the reaction

$$Y{-}CH_3 + e^- \longrightarrow Y{-}CH_2^+ + 2e^- + H\cdot$$

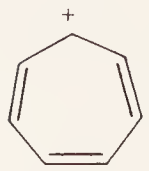
TABLE IV

Appearance Potentials of Monosubstituted Methyl Cations (42)

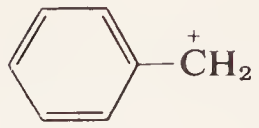
Ion	Appearance potential relative to CH_3^+, eV	Stabilization relative to CH_3^+, kcal/mole
CH_3^+	(0)	(0)
$CH_3{-}CH_2^+$	−1.58	36
$Ph{-}CH_2^+$	−2.38	55
	−2.52	58
$HO{-}CH_2^+$	−2.59	60

Cyclopropyl is better than phenyl but poorer than hydroxyl at stabilizing CH_3^+ if it is assumed that no excess energy is involved in the formation of the products and that the $C_4H_7^+$ ion formed from methylcyclopropane is the cyclopropylcarbonium ion. The stabilizing ability of cyclopropyl relative to phenyl is perhaps even greater than indicated. The ion formed

* This subject has been reviewed briefly (41).



(56)



(57)

from $PhCH_3$ probably is the cycloheptatrienyl cation (**56**), not the benzyl cation (**57**) (43). To the extent that the loss of H· is synchronized with rearrangement to the more stable cycloheptatrienyl cation, the observed appearance potential is more negative than would be required for formation of the hypothetical benzyl cation. Although chemists ordinarily are concerned with carbonium ions in solution, the order of appearance potentials of ions in the gas phase seems to correlate qualitatively with their stabilities in solution. Application of mass spectroscopy to the study of carbonium ions is described in Chapters 2 and 3 in Volume I.

Available data involving equilibria in solution between cyclopropylcarbonium ions and neutral precursors are summarized in Table III. Data for several related ions with phenyl or alkyl instead of cyclopropyl substituents are included for purposes of comparison.

The change in concentration of the tricyclopropylcarbonium ion with changing concentration of sulfuric acid (7) fits the equation

$$\log \frac{C_{R^+}}{C_{ROH}} = pK_{R^+} - H_R$$

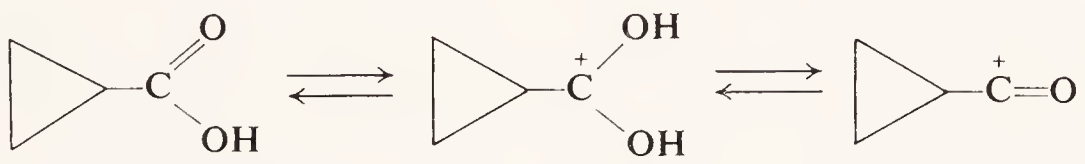
for which the values of H_R were obtained from measurements of equilibria between triarylcarbonium ions and triarylmethanols (44). Since the data conform to the equation, specific bonding of this ion to solvent must be as small as that of a triarylcarbonium ion (44), presumably because of comparable delocalization of charge. Extensive delocalization also is indicated by half-formation of the tricyclopropylcarbonium ion at much lower acidity ($pK = -2.34$) than half-formation of the triphenylcarbonium ion ($pK = -6.63$). Steric inhibition to coplanarity of the phenyl groups, as discussed by Freedman in Chapter 28, somewhat reduces their ability to delocalize the charge of the triphenylcarbonium ion. However, a similar factor may also be involved in the tricyclopropylcarbonium ion (see Section VII).

The superiority of cyclopropyl over phenyl in stabilizing carbonium ions is evident also from the data for cycloalkenyl cations. The changes in concentration of these cations with changing sulfuric acid concentration fit the equation

$$\log \frac{C_{BH^+}}{C_B} = pK - H_0$$

Adherence of the equilibria to this equation, as discussed by Deno in Chapter 18 in Volume II, suggests that these carbonium ions are in equilibrium with dienes. Conjugation in the precursors of the ions was not significant in affecting the comparisons either of the formation of the tricyclopropyl- with the triphenylcarbonium ion in solution or of the formations of various substituted methyl cations in the gas phase. However, the effects of substituents in stabilizing alkenyl cations are reduced to the extent that these substituents also stabilize the precursor dienes,* although the large effects on the ions of cyclopropyl groups are unmistakable.

The data for hydroxycyclopropylcarbonium ions also indicate that cyclopropyl is more effective than phenyl in stabilizing carbonium ions and, in addition, that two cyclopropyl groups are far more effective than one cyclopropyl plus one methyl group. The relatively high acidities needed to form hydroxycyclopropylcarbonium ions from the parent ketones and the relatively small effects of replacing methyl by cyclopropyl substituents should not be taken to indicate that cyclopropyl does not conjugate effectively in these ions. The ability of cyclopropyl groups to stabilize ions is reflected only partially in the equilibrium measurements because of significant conjugation in the neutral ketones. A cyclopropyl substituent has even less effect on the equilibria between a carboxylic acid and a dihydroxycarbonium ion (**58** $\rightleftarrows$ **50**) and between a dihydroxycarbonium ion and an acyl cation (**50** $\rightleftarrows$ **52**).

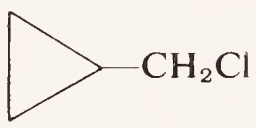


(58) **(50)** **(52)**

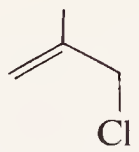
The unusual stability of cyclopropylcarbonium ions had been inferred from rapid rates of solvolysis reactions of cyclopropylmethyl derivatives more than a decade before the data presented earlier in this section were available. In the first such study, Roberts and Mazur (47) found that the

* Conjugation of a cyclopropyl group with carbon–carbon double bonds and with aryl groups probably involves somewhat less energy than the equivalent, relatively weak, conjugation of a phenyl group. Resonance energies of -2.1 kcal/mole (minus indicates destabilization) for cyclopropylethylene and of $+0.6$ kcal/mole for phenylcyclopropane have been estimated by comparing heats of hydrogenation (calculated from heats of combustion) with those of the corresponding isopropyl compounds (45). A resonance energy of $+1.8 \pm 0.8$ kcal/mole has been estimated (46) for phenylcyclopropane by comparing its heat of combustion with that estimated from group contributions.

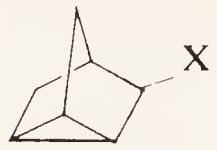
solvolysis rate in ethanol–water of cyclopropylmethyl chloride (**59**) actually exceeds that of β-methylallyl chloride (**60**) by a factor of 40.*



(59)



(60)

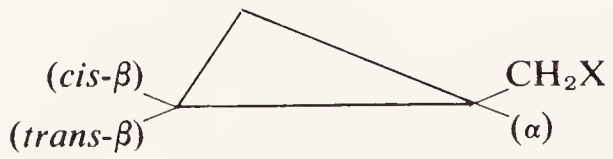


(61)

Some solvolysis studies have since provided such important information on ion stabilities that they must be mentioned here despite the emphasis in this chapter on data obtained from direct observations of ions. However, estimates of carbonium ion stabilities from rate data are subject to more problems of interpretation than are estimates from equilibrium data. Correlation of increasing carbonium ion stabilities with increasing solvolysis rates is meaningful only to the extent that stabilities of transition states parallel thermodynamic stabilities of the ions. Even in reactions in which a cyclopropylcarbonium ion clearly is formed in the rate-determining step, the transition state of this step may not always resemble closely the ion that is ultimately formed. In addition, intermediate ions in solvolysis reactions may be more closely associated with solvents or other nucleophiles than are ions in the environments, deficient in good nucleophiles, in which they are studied as stable species.

Hart and his co-workers have provided a striking demonstration of the effect of cyclopropyl groups in work summarized in Table V (6,30,49). Each replacement of an isopropyl by a cyclopropyl group results in a rate enhancement of 10^2–10^3. Even three cyclopropyl groups must be able to contribute significantly to the stabilization of an incipient ion.

The effects of substituents at the α- and β-carbons of cyclopropyl rings on solvolysis rates of cyclopropylmethyl derivatives (**62**) are shown by the



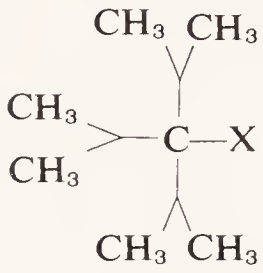
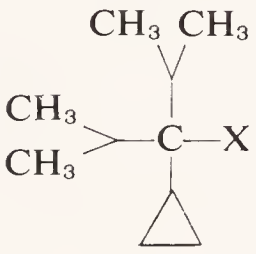
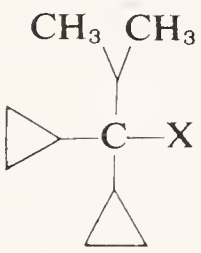
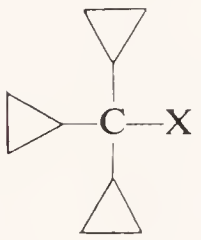
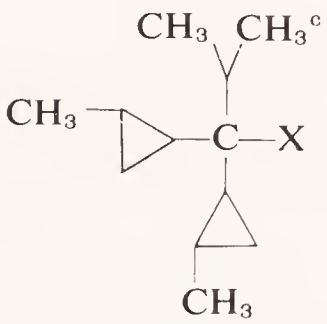
(62)

data in Table VI (50), drawn mostly from the comprehensive study of Schleyer and Van Dine (51). Significant and nearly multiplicative rate accelerations are caused by β-methyl groups, and a much larger acceleration is caused by a β-alkoxy substituent. The effect of substituents provides

* In another early study (121), the ethanolysis of cyclopropylmethyl benzenesulfonate was investigated. Solvolysis rates of nortricyclyl derivatives (**61**) had been reported previously (48); however, it is more difficult to infer from these rates the extent of stabilization of a carbonium ion by a cyclopropyl group.

TABLE V

Relative First-Order Rate Constants for Solvolyses in Aqueous Dioxan

Compound	Relative rates for X = *p*-nitrobenzoate[a]	Relative rates for X = benzoate[b]
	(1.00)	—
	246	—
	23,500	(23,500)
	—	25,300,000
	124,000	—

[a] In 80% aqueous dioxane at 60° (49).
[b] In 95% aqueous dioxane at 25° (6,30).
[c] The stereochemistry of the ring methyl groups is not specified.

TABLE VI

Relative First-Order Rate Constants for Solvolyses of Cyclopropylmethyl Derivatives (62) Substituted in the Cyclopropyl Ring

Cyclopropyl substituents	Relative rate
None	1
α-Methyl[a]	5.0
cis-β-Methyl[a]	8.2
trans-β-Methyl[a]	11.0
cis-β-*cis*-β′-Dimethyl[a]	82
cis-β-*trans*-β′-Dimethyl[a]	80
trans-β-*trans*-β′-Dimethyl[a]	124
β,β-Dimethyl[a]	92
trans-β,β,β′-Trimethyl[a]	490
β,β,β′,β′-Tetramethyl[a]	1570
trans-β-Ethoxy[a]	940
α-Phenyl[b]	1.3
cis-β-Phenyl[c]	0.62
trans-β-Phenyl[c]	2.19
trans-β-*trans*-β′-Diphenyl[d]	0.37

[a] 3,5-Dinitrobenzoates in 60% aqueous acetone at 100° (51).

[b] Benzenesulfonates in acetic acid at 20° (52).

[c] β-Naphthalenesulfonates in 90% aqueous dioxane at 25° (58).

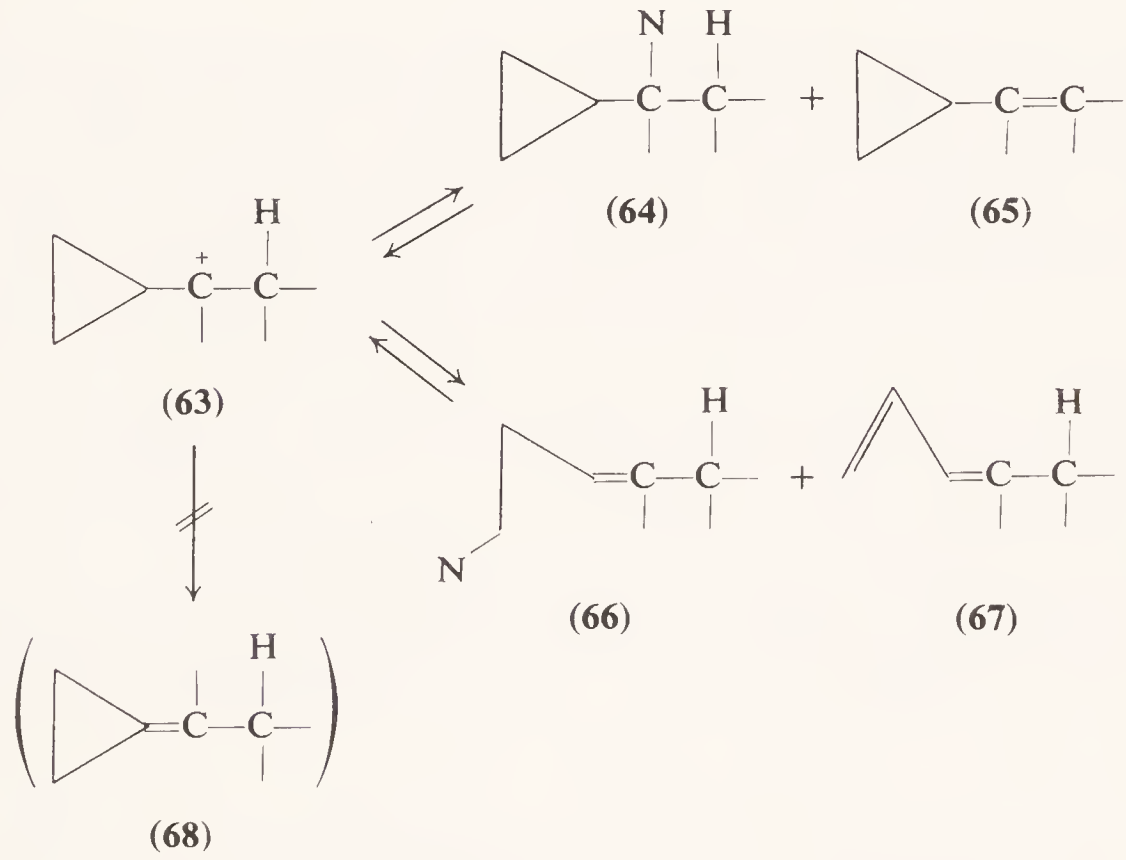
[d] *p*-Toluenesulfonates in ethanol at 30° [R. Breslow, J. Lockhart, and A. Small, *J. Am. Chem. Soc.*, **84**, 2793 (1962), and Ref. 53].

another indication of the presence in the cyclopropyl rings of considerable positive charge in the transition states of such solvolyses and probably, therefore, in the resultant ions as well. The equal effects of methyls at the β- and β′-carbons suggest that these carbons are equivalent in the cyclopropylcarbonium ion. The small effects of phenyl substituents can be attributed in part to conjugation of cyclopropyl and aryl groups in the neutral starting materials. Incomplete formation of ions in the transition state also may be involved. In an incompletely formed ion, the electron-withdrawing inductive effect of phenyl might counterbalance its electron-releasing conjugative effect. Alternatively, the structure of the ions (Section VIII) or the nature of the orbitals at the β-carbons (59) may be such that phenyl is unable to conjugate with its usual efficiency. Equilibrium data involving substituted cyclopropylcarbonium ions would be desirable.

VI. REACTIONS

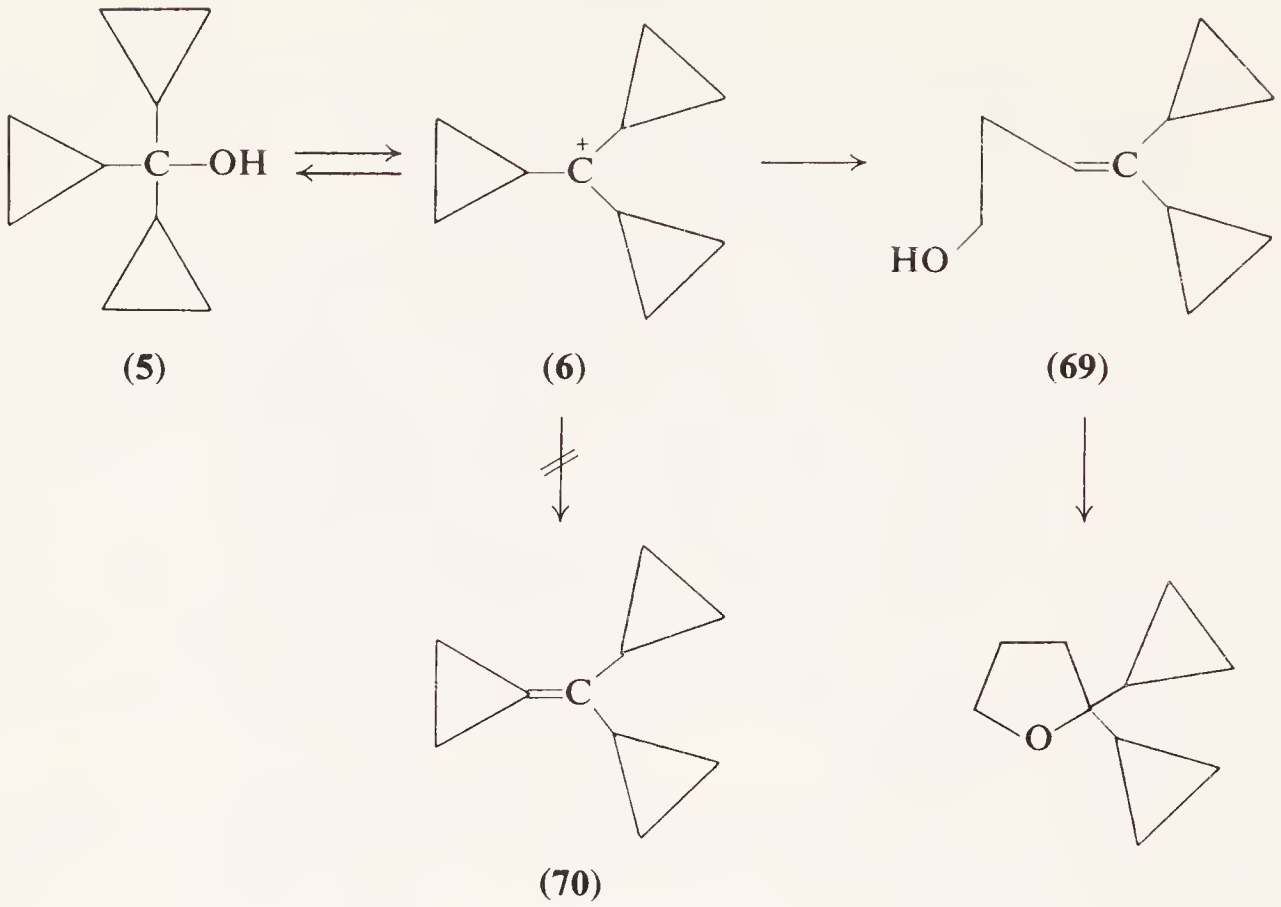
Cyclopropylcarbonium ions do not react readily with electrophiles, although such reactions are characteristic of neutral cyclopropane rings. This insensitivity to electrophilic attack must be due to deactivation of the cyclopropyl rings by the positive charge. Some of the carbonium ions listed in Table I are stable for hours in such strong electrophilic media as fluorosulfonic acid, striking evidence for the extent of this deactivation. Stability toward electrophilic attack should be least in ions in which cyclopropyl groups are least exposed to the effects of a positive charge, i.e., in those ions in which the charge is most absorbed into other groups. The more rapid disappearance of the tricyclopropylcarbonium ion (**6**) in 20% sulfur trioxide–80% sulfuric acid than in concentrated sulfuric acid (7) may be attributable to incursion of electrophilic attack on this ion in which charge is so extensively delocalized.

The reactions of cyclopropylcarbonium ions (**63**) with nucleophiles usually lead to one or more of products **64–67**. Formation of highly



strained methylenecyclopropanes (**68**) is not observed. Unrearranged products (**64** and **65**) usually are formed more rapidly than are rearranged products (**66** and **67**). However, the rearranged products are more stable and ultimately predominate if product formation is reversible.

The reactions of the tricyclopropylcarbonium ion (**6**) illustrate these generalizations. Only tricyclopropylmethanol (**5**) is isolated after addition of a sulfuric acid solution of this ion to an excess of aqueous base (7,10). Adherence of data for the equilibrium between **5** and **6** to the H_R acidity function and the observation that the α-hydrogens of the ion do not

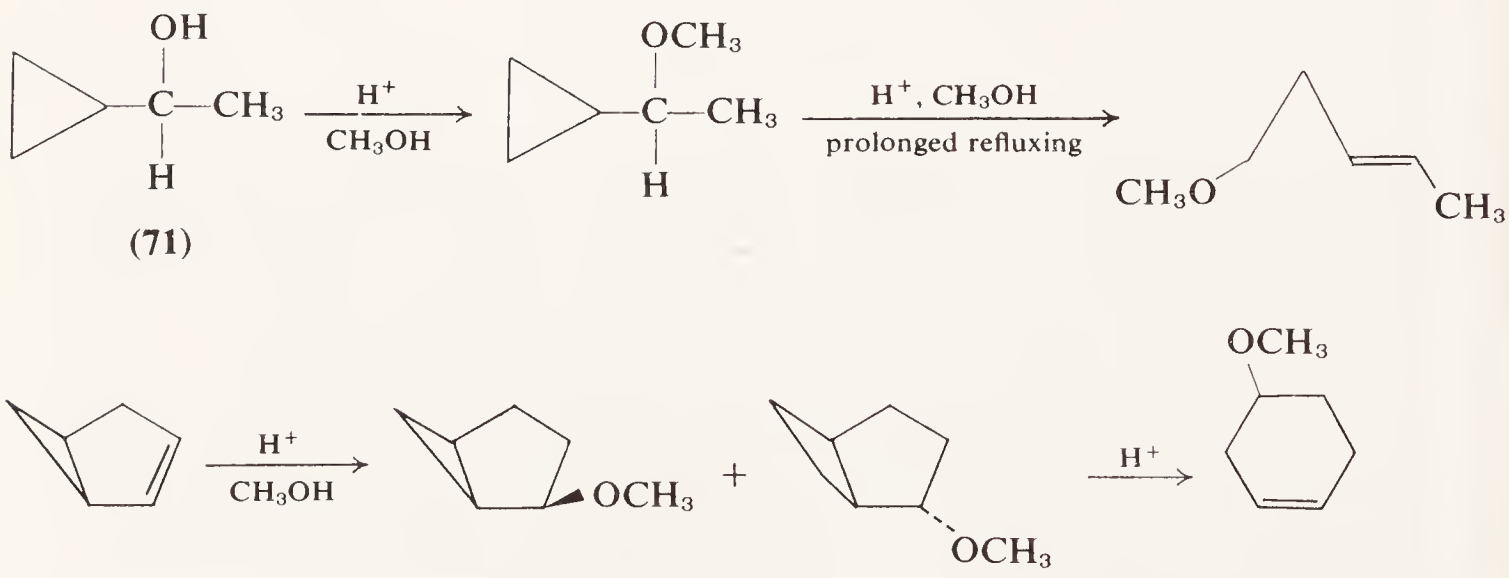


(5) (6) (69)

(70)

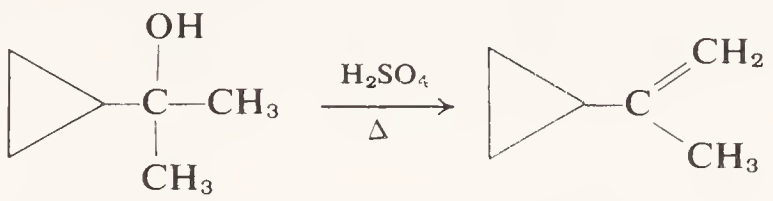
exchange with solvent hydrogens in concentrated sulfuric acid are other indications that the ion is not in equilibrium with an olefin (**70**) (7). Addition of a sulfuric acid solution of the ion to water furnishes 1,1-dicyclopropyltetrahydrofuran, presumably via initial formation of **69** (7,10). The formation of tricyclopropylmethanol is the most rapid reaction of the ion, of course, but since the solution still is acidic, the alcohol is in equilibrium with the ion and the more stable product is eventually obtained. For successful recovery of the unrearranged alcohol, it is essential to use a rapid dispersal technique in adding the solution of ion to base so that the change of the medium from acidic to basic occurs quickly.

Most reactions thought to proceed through short-lived cyclopropylcarbonium ion intermediates also lead to unrearranged compounds if

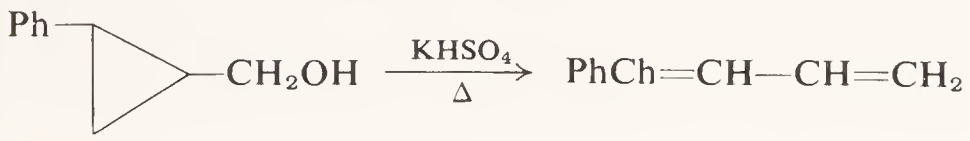


(71)

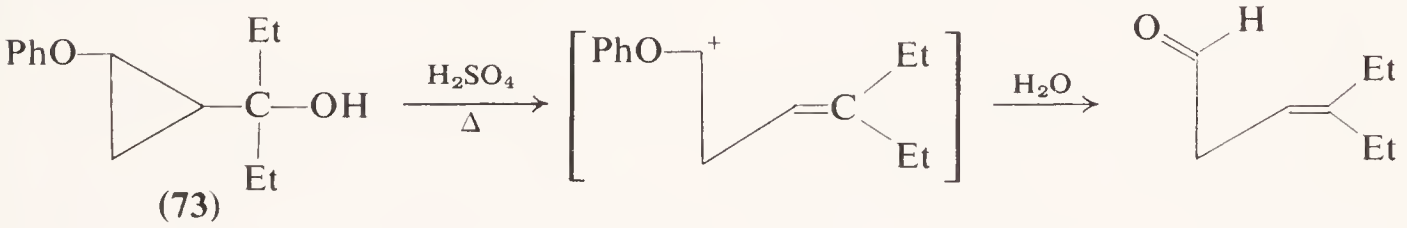
product formation is irreversible.* The preparations of unrearranged ethers from an alcohol (61) or an olefin (62) are typical, although prolonged reactions furnish more stable products, in which the cyclopropyl rings have been cleaved. Dehydration of 2-cyclopropyl-2-propanol in good yield to an unrearranged olefin is yet another example (63).



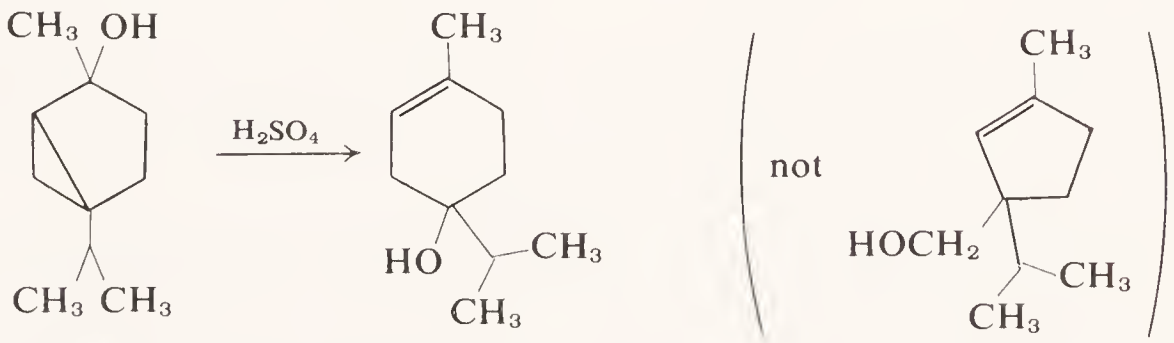
The rate of the ring-opening reaction of the tricyclopropylcarbonium ion (**6**) in sulfuric acid solutions is first order in activity of water and first order in concentration of ion (7). That bimolecular attack on the six β-carbons is slower than attack on the trigonal carbon, which forms a less stable product, is in accord with Hammond's postulate (64); the transition state for attack on the trigonal carbon should be of lowest energy, since this is the site in the ion at which charge is best localized in the transition state. Preferential attack on the trigonal carbon would be expected in most cyclopropylcarbonium ions except perhaps in simple ions, e.g., **3**, in which this carbon is primary (see Section VIII). To the extent that bimolecular ring opening is important, the lifetime of an ion will be increased by decreasing the concentration of nucleophiles. Hence the lifetime of the tricyclopropylcarbonium ion (**6**) increases with increasing concentration of sulfuric acid due to decreasing activity of water.



(**72**)



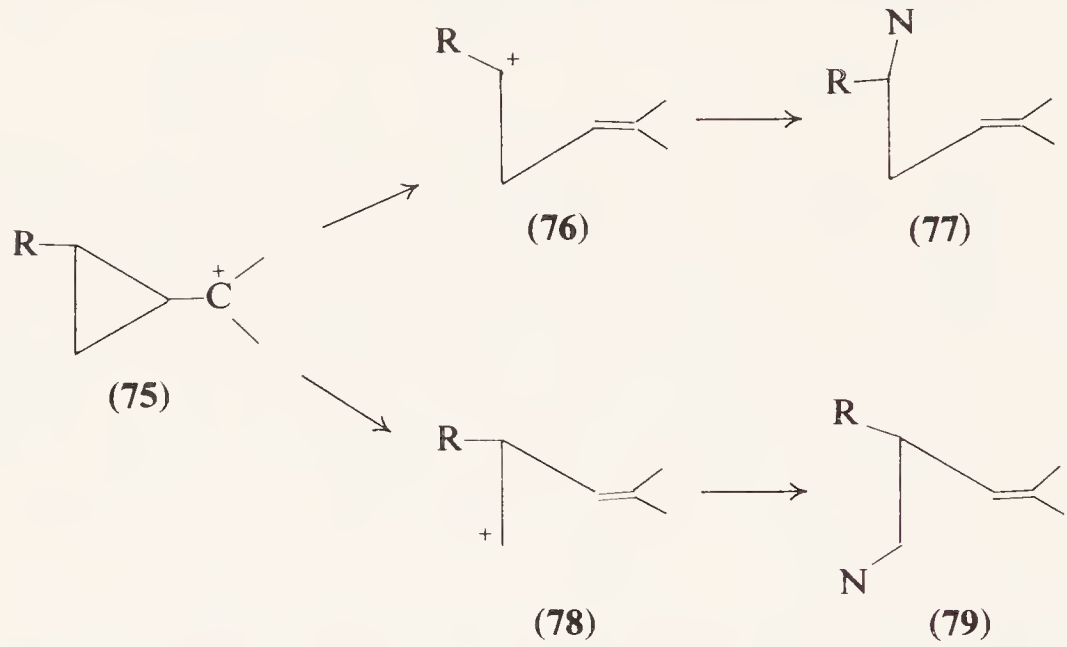
(**73**)



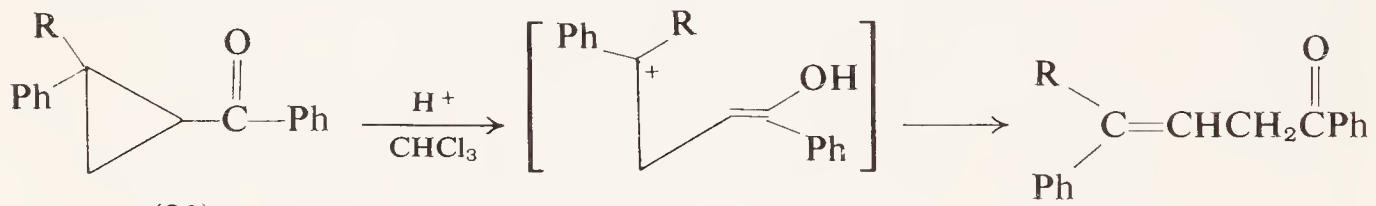
(**74**)

* Examples are found in Refs. 2 and 60.

The bimolecular mechanism found for the ring-opening reaction of the tricyclopropylcarbonium ion (**6**) with water probably does not extend to all ring openings of cyclopropylcarbonium ions. The formation of products such as those reported for reactions of **72** (65), **73** (66), and **74** (67) can be explained more readily in terms of a unimolecular isomerization of a cyclopropylcarbonium ion (**75**) to form **76**—the more stable of the isomeric acyclic ions **76** and **78**.* Such a process should produce **77**, whereas



bimolecular attack on **75** should lead instead to **79**.† In related ring openings of β-arylcyclopropyl ketones (**80**), a unimolecular mechanism is



(**80**)

suggested by the substituent effects on the rates summarized in Table VII‡ (69).

In contrast, the acyclic 1-substituted-3-butenes obtained by deamination of cyclopropylmethylamine (70) and by treatment of cyclopropylmethanol with Lucas reagent (47) may form by bimolecular attack on cyclopropylcarbonium ion intermediates. Prior isomerization to an acylic cation (**81**)

* Further examples and references are given in Ref. 65. It is conceivable that some isolated products are not formed in the initial ring cleavage; e.g., the cyclohexenol obtained from **74** might have formed by isomerization (involving equilibration with the carbonium ion) of its cyclopentenol isomer.

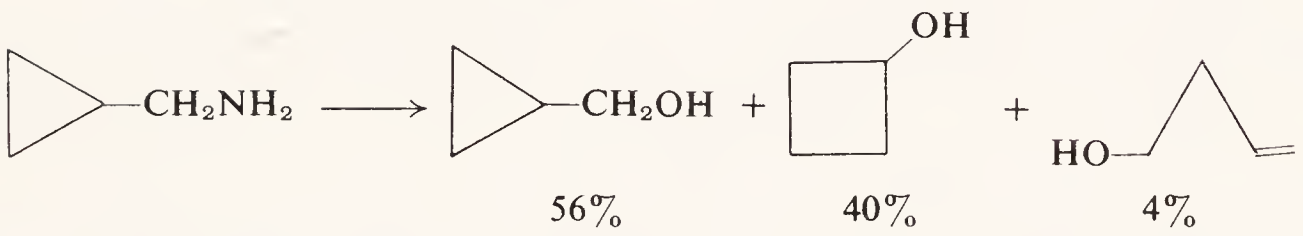
† Probably not all β-substituted cyclopropyl compounds furnish products that can be ascribed to formation of the most stable ion. Some possible exceptions exist (68), although they occur in complex systems.

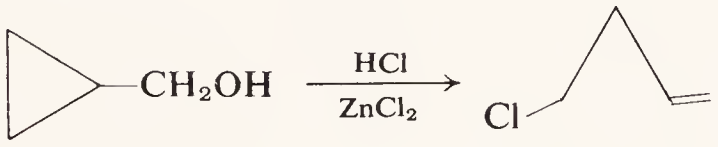
‡ It is assumed that a significant portion of the large effect of substituents can be ascribed to the ring-opening step rather than to the protonation step.

TABLE VII
Relative Pseudo-First-Order Rate Constants for Acid-Catalyzed Ring Opening of Cyclopropyl Ketones (80) in Chloroform (69)

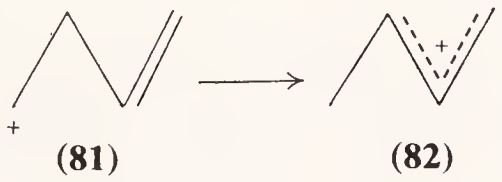
R	Relative rate[a]
H	1
Phenyl	71
p-Methoxyphenyl	63,000

[a] These are rates of disappearance of optical activity when optically active starting materials are used. The rates of formation of rearranged products may be slightly less.

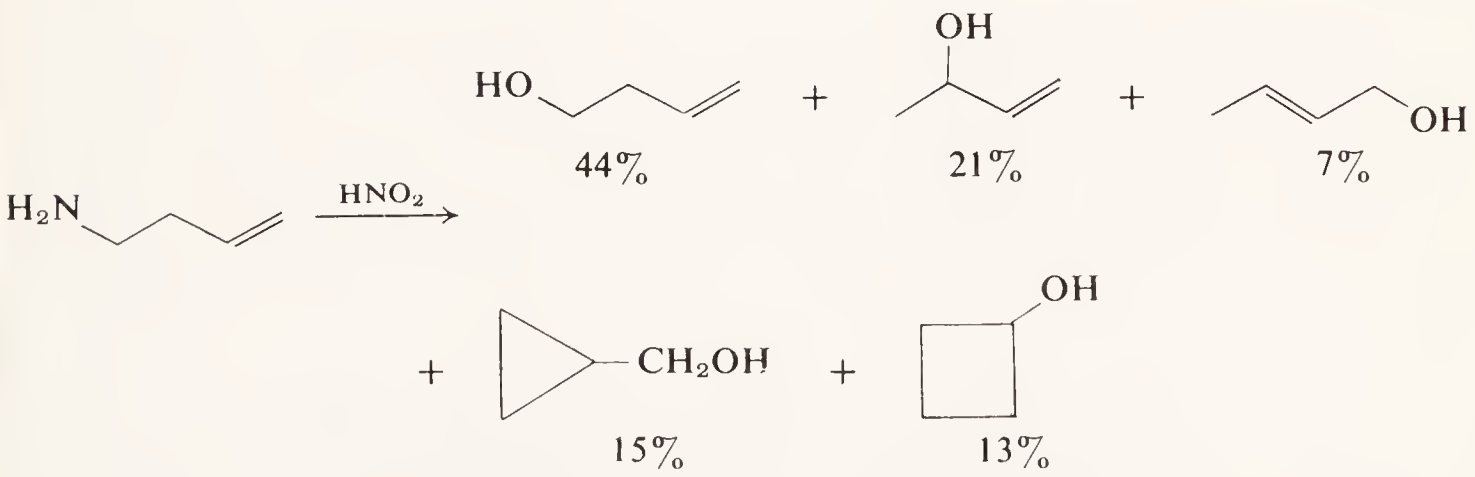




may not be responsible for the acyclic products because deamination of 1-amino-3-butene, which must furnish **81**, gives additional products that probably result from a hydride shift in **81** to form alkenyl cation **82** (70).*



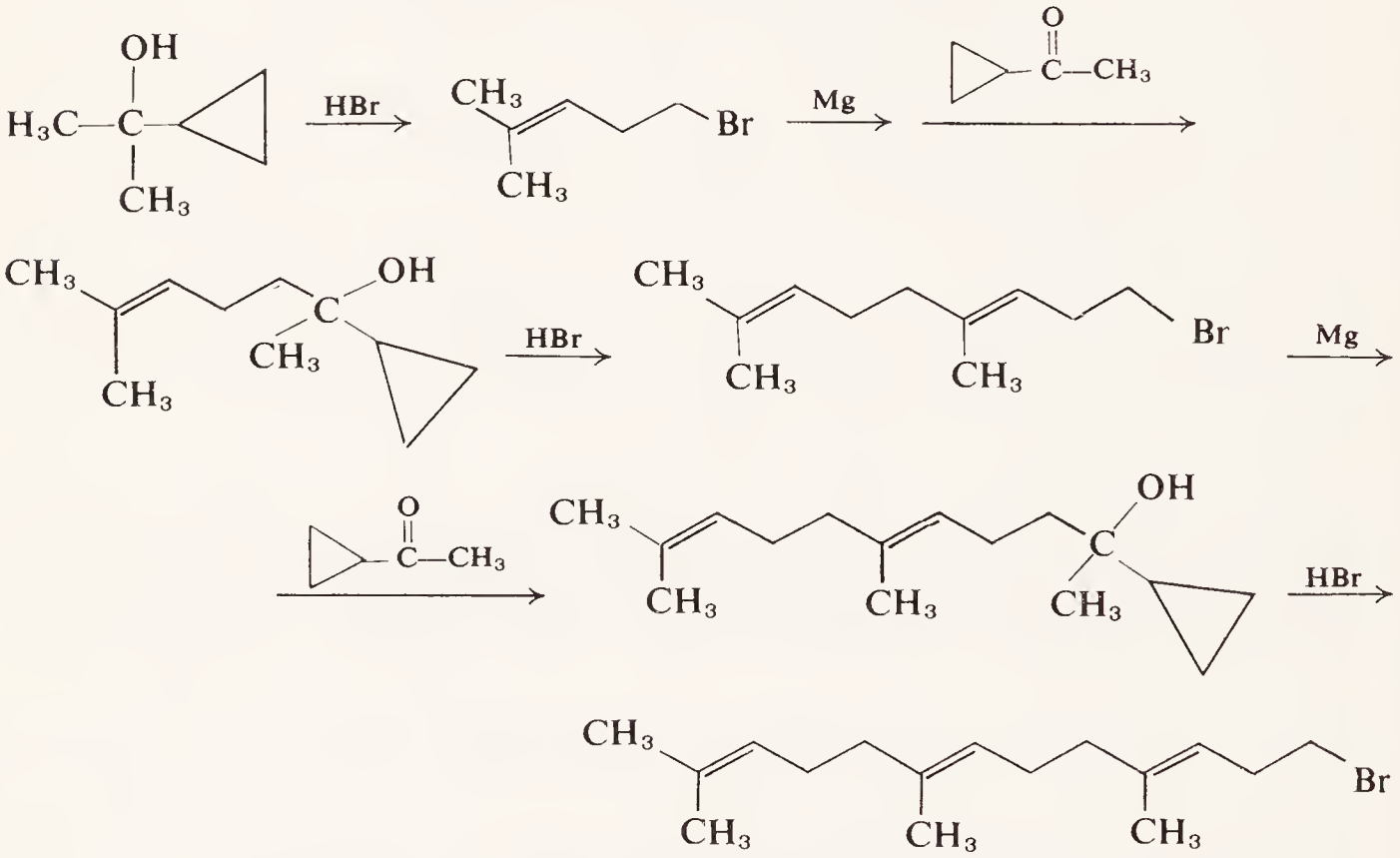
(81) **(82)**



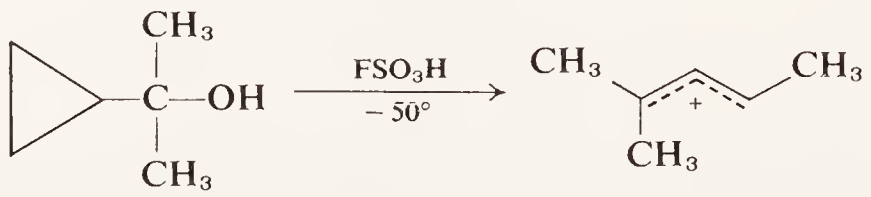
* However, the formation of different product mixtures from the same cation generated in different ways might be due to differences in "encumbrance" of the cation, as discussed by Keating and Skell in Chapter 15 of Volume II.

Further kinetic studies of the molecularity of ring opening are needed. β-Substituents that stabilize carbonium ions should favor unimolecular over bimolecular ring opening and increase formation of ring-opened products at the expense of unrearranged products. The degree of charge delocalization in the ion also may influence ring opening. With increased delocalization, the rate of unimolecular ring opening should decrease, since the rearranged ion (**76**) will become relatively less stable in comparison to the cyclic ion (**75**). Bimolecular ring opening also may be influenced by delocalization, since the leaving group should become poorer as charge is drained from the trigonal carbon.

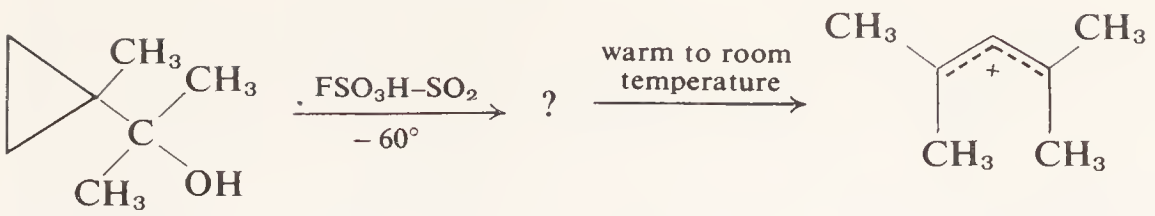
Potential synthetic applications of the ring-opening rearrangement of cyclopropylcarbonium ions are apparent from the foregoing examples. The synthesis of isoprenoid-like chains is a striking example of its use (71).



Some attempts to prepare solutions of cyclopropylcarbonium ions have led instead to isomeric carbonium ions as illustrated for reactions of **83** (14), **84** (12), and **85** (12). Cyclopropylcarbonium ions must be transient intermediates in these reactions because, under identical conditions, stable solutions of cyclopropylcarbonium ions are formed from closely related



(83)



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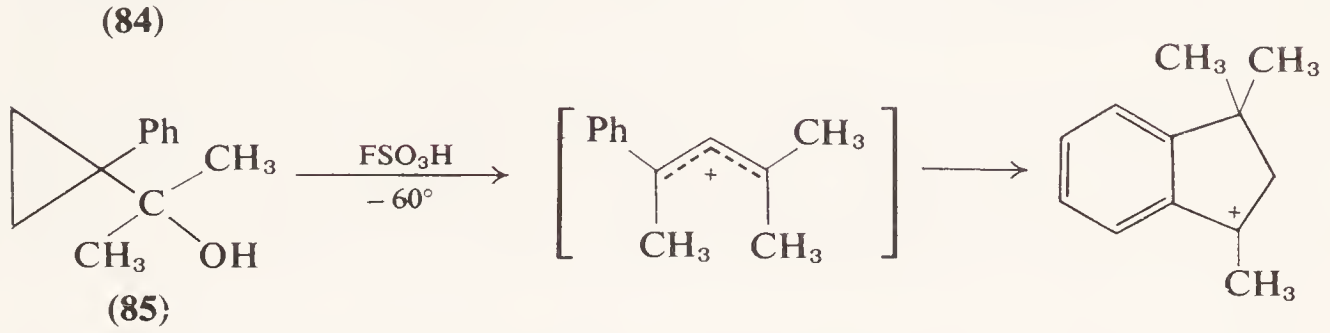
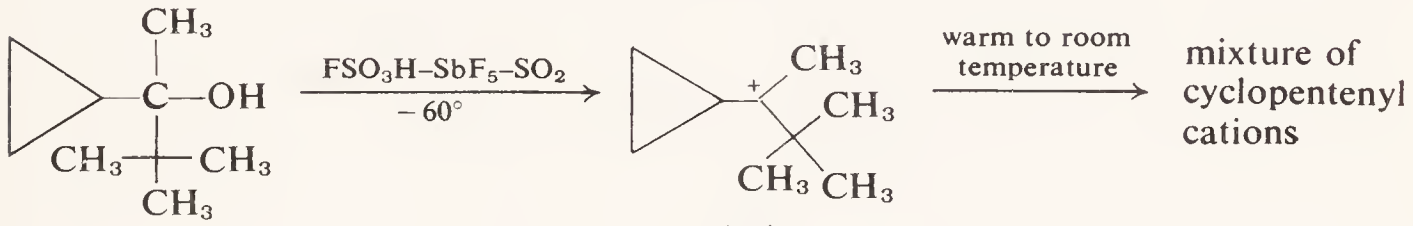


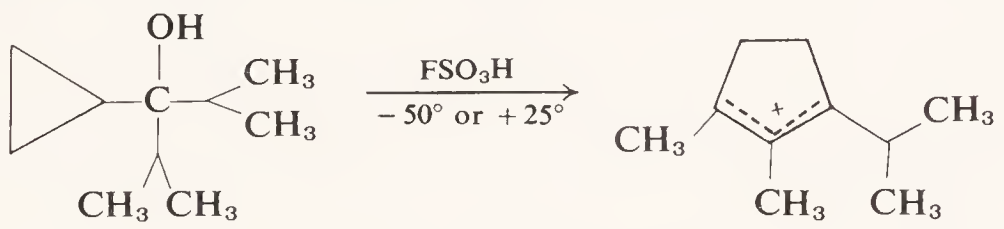
(85)

precursors. The cyclopropylmethyl-*t*-butylcarbonium ion (**21**) can be observed at low temperature but isomerizes on warming to room temperature (11,13). Formation of cyclopentenyl cations from **21** and from



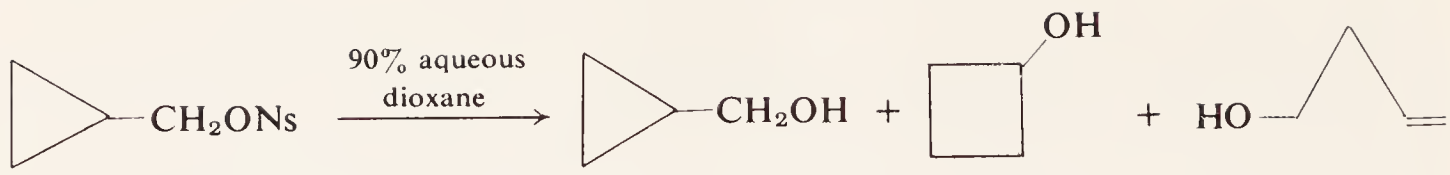
(**21**)

cyclopropyldiisopropylmethanol (14) involves oxidation as well as rearrangement of cyclopropylcarbonium ions. The sequences of steps in these complex transformations have not been elucidated.



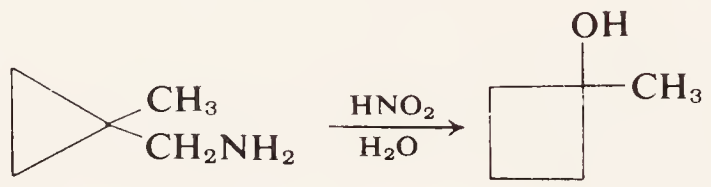
Successful preparation in fluorosulfonic acid of many ions that cannot be observed in concentrated sulfuric acid undoubtedly is attributable not only to the greater acidity of the medium but also to its low freezing point, which permits preparation of solutions at dry ice temperatures where rearrangements and other reactions are slower. Products of isomerizations to alkenyl cations are not observed in solvolysis reactions that involve cyclopropylcarbonium ions as transient intermediates. The lifetime of an ion before reaction with a nucleophile is brief in a typical solvolysis reaction. On the other hand, lifetimes of cyclopropylcarbonium ions are long in strongly acidic media, and time is available for rearrangements that are too slow to be observed under ordinary reaction conditions.

Cyclobutyl derivatives are significant products of reactions of unsubstituted cyclopropylmethyl derivatives as seen in the hydrolysis of the β-naphthalenesulfonate of cyclopropylmethanol (58) or the deamination of

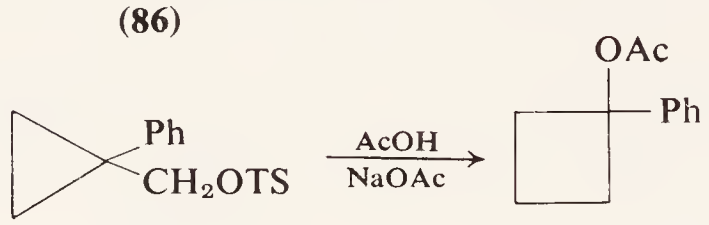


ONs = β-naphthalenesulfonate 58% 42% trace

cyclopropylmethylamine (see p. 1239) (47,70). In fact, exclusive formation of cyclobutyl products is found in similar reactions of cyclopropylmethyl systems with methyl (54,56) or phenyl (52,55) substituents at C-2 (**88**).* In contrast, cyclobutyl compounds are not ordinarily observed as products



(86)

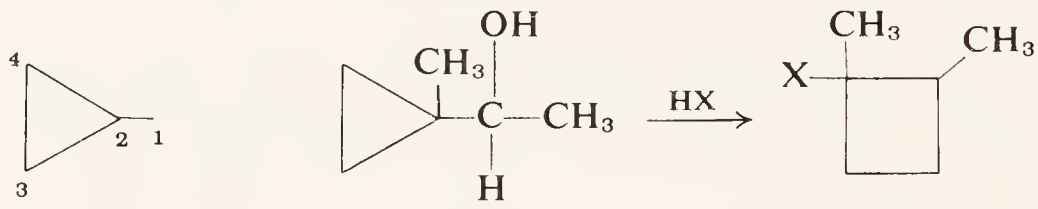


(87)

OTs = *p*-toluenesulfonate

of reactions of cyclopropylmethyl derivatives with carbonium ion stabiliz-

ing substituents on C-1 (see **88**), although probably they would be more



(88) **(89)**

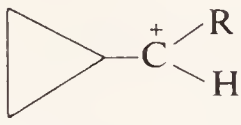
stable than the unrearranged cyclopropylmethyl compounds that often are isolated.† Those rearranged products that form, presumably under conditions where initially unrearranged products are in equilibrium with the carbonium ion, are reported to have 3-penten-1-yl structures. For example, acid-catalyzed exchange of the hydroxyl group of methylcyclopropylmethanol (**71**), a reaction that proceeds through the carbonium ion, is at least 10^3 times more rapid than formation of rearranged products (75); reaction of **71** with other acidic reagents leads to unrearranged or to

* Even if the trigonal carbon of the carbonium ion is primary, cyclobutyl products are not formed in systems where such products would be unusually strained (72).

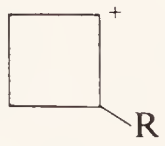
† An equilibrium mixture of cyclobutyl chloride and cyclopropylmethyl chloride at 25° contains these isomers in a ratio of 36:1; similarly, cyclopropylmethanol can be isomerized in good yield to cyclobutanol (74).

3-penten-1-yl products (see the reaction with acidic methanol on p. 1236) (76).* However, some *cis*- and *trans*-1,2-dimethylcyclobutyl derivatives are formed in reactions of **89** with acids (77).

Formation of cyclobutyl products in only a few systems can be rationalized in terms of the stabilities of carbonium ion structures **90** and **91**. These



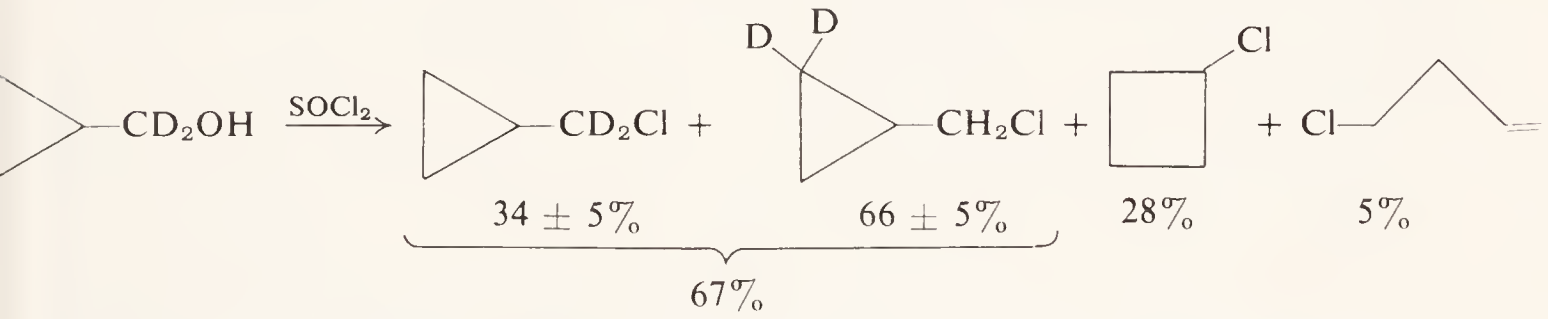
(90)



(91)

structures may be regarded either as discrete ions in equilibrium or as contributing structures† of a resonance hybrid (see Section VIII). Variation of R will greatly affect the stability of **90** but should have little effect on **91**. If **90** and **91** are regarded as discrete ions in equilibrium, then it must be concluded that when R = H their rates of reaction with nucleophiles are such as to lead to formation of nearly equal amounts of cyclopropylmethyl and cyclobutyl products; if these structures are regarded instead as resonance forms, then the contribution of **91** to the hybrid (or more appropriately, to the hybrid in the transition state for nucleophilic attack) must be important to explain the significant amount of cyclobutyl product. Introduction of a stabilizing group (R) is sufficient to render **90** either the predominant ion in the equilibrium mixture or the predominant contributor to the resonance hybrid. Formation of cyclobutyl products from **86**, **87**, and **89** is consistent with this explanation, since the methyl or phenyl groups in these systems stabilize **91** but not **90**.

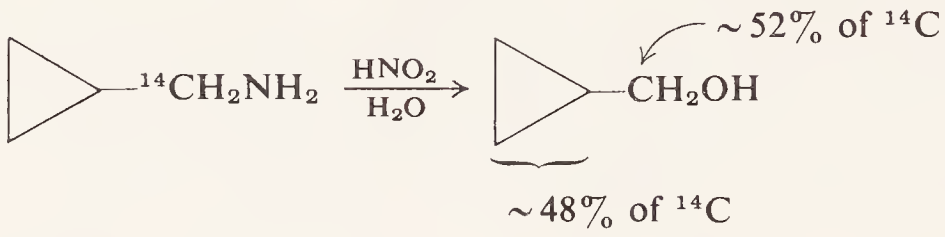
Interconversion of "methylene" carbons (C-1, C-3, and C-4 in **88**), discovered by Roberts and his co-workers, is another rearrangement of



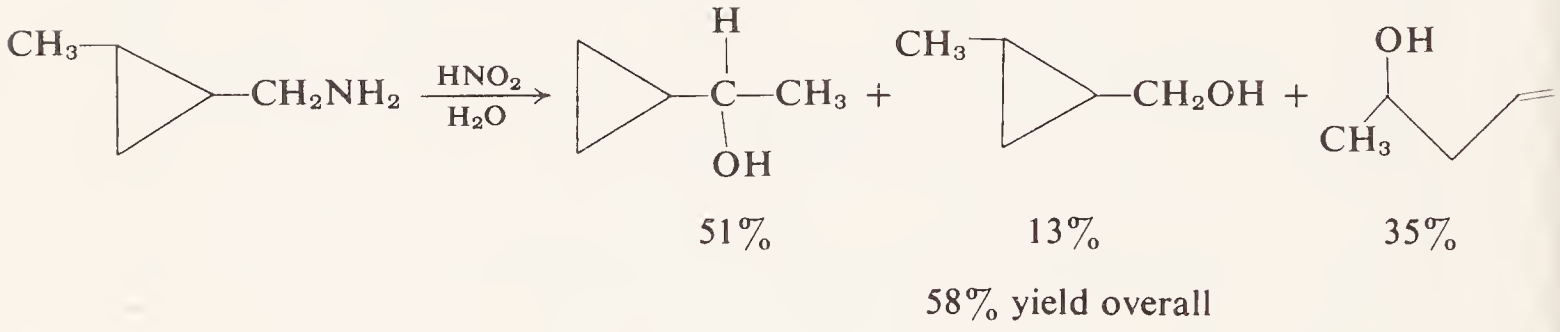
* Examples are reactions with acidic methanol [Pearson and Langer (61)], with aqueous formic acid [Favorskaya et al. (76)], with aqueous hydrogen bromide [Julia et al. (76)], and with Lucas reagent [Hanack and Eggensperger (76)]. A recent report (M. Julia, private communication) that **71** in aqueous perchloric acid furnishes some *trans*-2-methylcyclobutanol suggests that cyclobutanols may have been overlooked as products in some other reactions.

† If **90** and **91** are discrete ions, then equilibrium concentrations are established rapidly, since nearly equivalent product mixtures are obtained from cyclopropylmethyl and cyclobutyl starting materials (e.g., Refs. 47, 58, 70, 74).

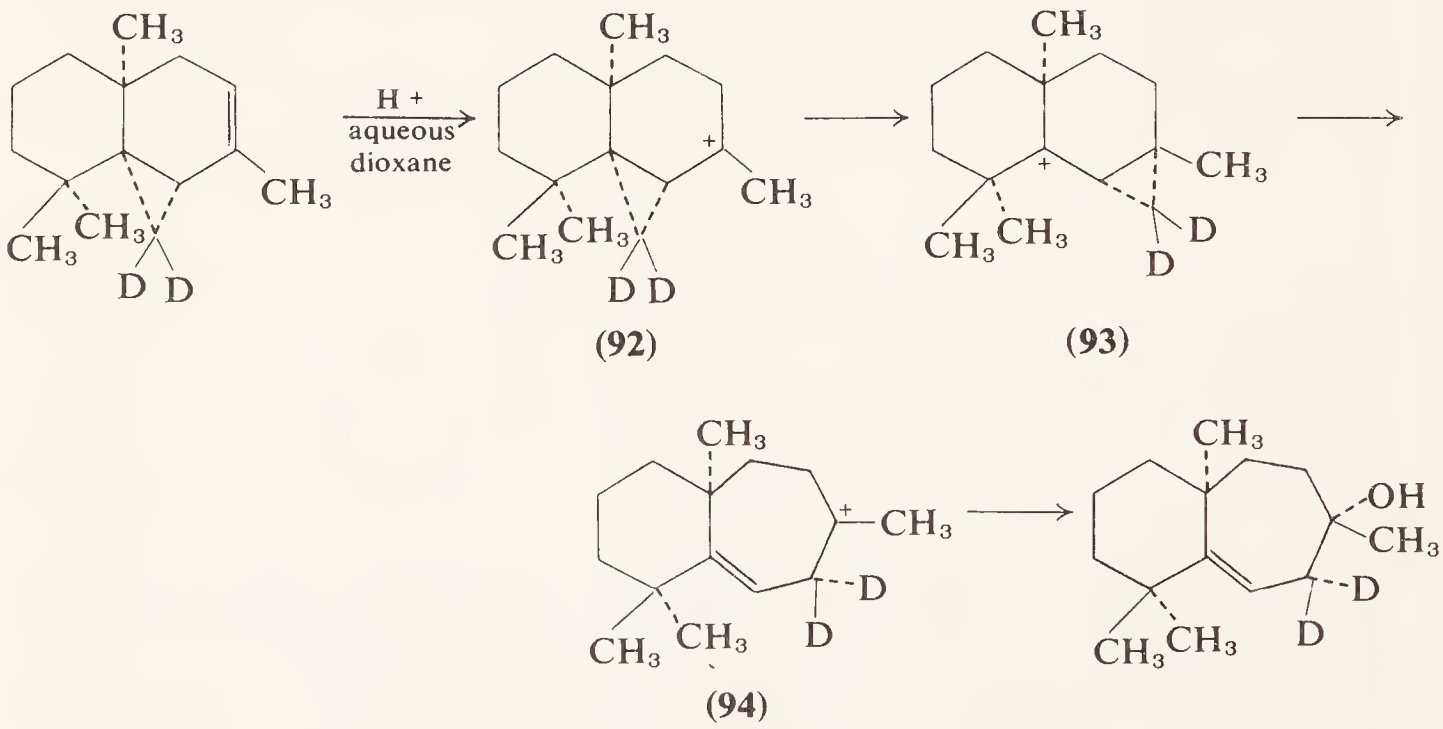
cyclopropylcarbonium ions. For example, the methylene carbons are equilibrated completely in a conversion of labeled cyclopropylmethanol to the corresponding chloride (74). Isotopic scrambling is significant, but not complete, in the deamination of cyclopropylmethylamine, indicating that the rates of interconversion of methylene carbons and of reaction of



the ion with water must be comparable (78,79). Such a rearrangement is responsible for the formation of methylcyclopropylmethanol in the deamination of (2-methylcyclopropyl)methylamine (80). It can be rational-



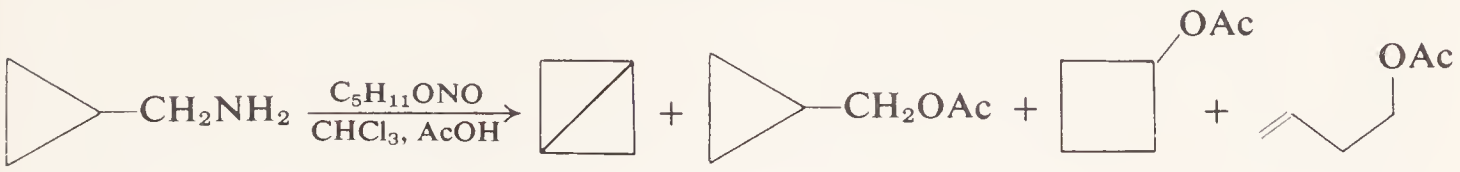
ized that the product of the acid-catalyzed rearrangement (81) of the tricyclic sesquiterpene thujopsene arises by formation of a cyclopropylcarbonium ion (**92**) that undergoes a similar rearrangement (to **93**).*



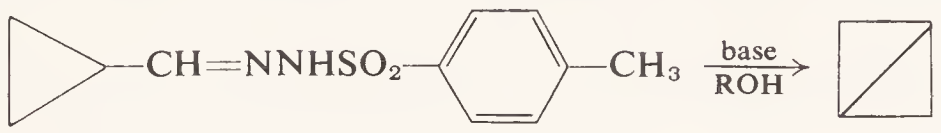
Formation of bicyclo[1.1.0]butanes may be another reaction of cyclopropylcarbonium ions. Diazotization of cyclopropylmethylamine in chloro-

* Alternatively (see Section VIII), **92**–**94** can be regarded as contributing structures of a resonance hybrid.

form with amyl nitrite and a minimal amount of acetic acid furnishes



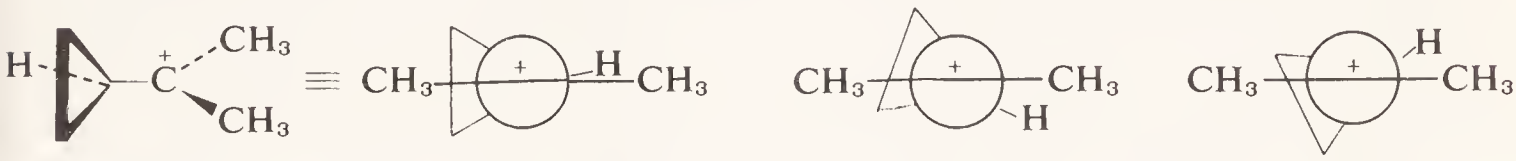
bicyclo[1.1.0]butane as the major product; the expected cyclopropylmethyl, cyclobutyl, and 3-buten-1-yl acetates also are formed, however (82). Bicyclobutane, not observed in more protic media (see, e.g., the deamination on p. 1239), may be derived from intramolecular reactions of cations which are energetic and only weakly solvated in this poorly nucleophilic environment (82).* The *p*-toluenesulfonylhydrazone of cyclopropanecarboxaldehyde reacts with bases in alcoholic solvents, but less significantly



in aprotic solvents, to furnish bicyclo[1.1.0]butane as a major product (84,85). Cyclopropyldiazomethane probably is formed in these reactions and protonated by the alcoholic solvents, but the position of protonation and the mode of decomposition to bicyclobutane are not certain (85,86).

VII. GEOMETRY

The observation by Pittman and Olah that the methyl groups of the cyclopropyldimethylcarbonium ion exhibit independent nmr absorptions requires that this ion have a structure in which the methyls are different (11,13). It is simplest to assume that the ion has the "bisected" (3) geometry (**95**). However, other possibilities such as a tilted form (**96**) or a rapid

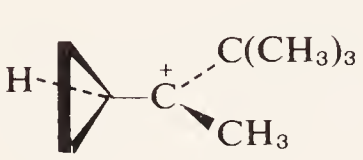


(95) **(96)** **(97)**

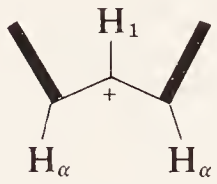
equilibration between such forms (**96** ⇄ **97**) also are consistent with the spectrum. The methyl absorptions show no broadening at −35°, indicating

* Deoxideation of the potassium salt of cyclopropylmethanol by bromoform also yields some bicyclo[1.1.0]butane, perhaps also through intramolecular reactions of cations (82). The observation of bicyclo[1.1.0]butane in these reactions raises the possibility that it might be formed in other reactions that furnish cyclopropylcarbonium ions in solvents of limited nucleophilicity. Bicyclobutane could easily be missed, since it reacts rapidly with acids to furnish cyclobutyl and cyclopropylmethyl products (83).

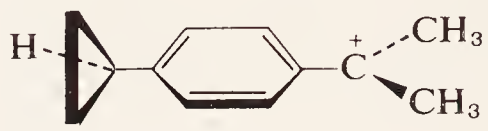
that interconversion of the methyl groups must have an energy barrier of at least 8–10 kcal/mole. That the cyclopropylmethyl-*t*-butylcarbonium ion shows no more than one methyl and one *t*-butyl absorption is attributed to the presence of only the sterically more favorable conformational isomer **98** (11). The large value of the coupling constant (J = 13 Hz) between



(98)



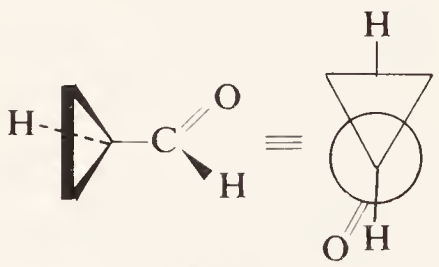
(99)



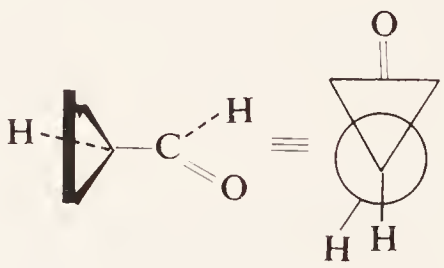
(27)

H_1 and H_α in the dicyclopropylcarbonium ion has been cited as favoring an *anti* relation of these hydrogens as found only in bisected conformational isomer **99** (11,13,14). The other ions listed in Table I probably have the bisected geometry when it is sterically feasible. However, their nmr spectra do not provide evidence for this geometry. For example, the absorptions exhibited at − 60° by the hydrogens of the two sides of the aromatic ring of the *p*-cyclopropylphenyldimethylcarbonium ion (**27**) are identical, as are those of the hydrogens of the two methyl groups of the cyclopropyldimethoxycarbonium ion **51** (12). However, the smaller amounts of charge absorbed by the cyclopropyl rings of these ions may result in much lower energy barriers to rotation around the cyclopropyl–C^+ bonds, and thus an averaging of the nmr absorptions of hydrogens on both sides of the ions.

Neutral compounds in which a cyclopropyl group is conjugated with an sp^2 carbon also show a preference for the bisected geometry, strong supporting evidence for this geometry in cyclopropylcarbonium ions. An electron diffraction study of gaseous cyclopropanecarboxaldehyde is interpreted to indicate that bisected conformational isomers **100** and **101** are



(100)

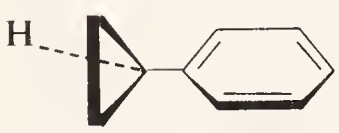


(101)

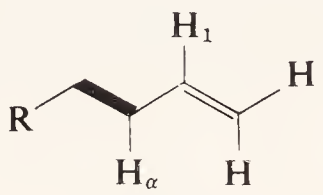
present in nearly equal amounts and are separated by a barrier in excess of 2.5 kcal/mole (87).* The stable conformations of ethane derivatives are

* Temperature and solvent dependence of the coupling constant between the aldehydic and α-protons of cyclopropanecarboxaldehyde in solution have been interpreted as indicating that conformational isomer **100** predominates, although a small amount of a gauche conformational isomer in which the carbonyl group is eclipsed

usually those with staggered bonds, and the same generalization applies to molecules such as propylene and isopropylcarboxaldehyde (91) if the double bonds are regarded as two bent single bonds. The "*s-trans*" rotational isomer (**100**) is normal, but the "*s-cis*" isomer (**101**) with eclipsed single bonds at opposite ends of a carbon–carbon single bond is unusual, and its presence must be a result of conjugation between the cyclopropyl and carbonyl groups. Electron diffraction studies suggest that cyclopropyl methyl ketone and cyclopropanecarbonyl bromide also exist predominantly in bisected conformations (92). The temperature dependence of chemical shifts of *ortho* hydrogens in arylcyclopropanes has been interpreted as an indication that the most stable conformational isomer has the bisected geometry (**102**), even though nonbonded interactions must be more serious

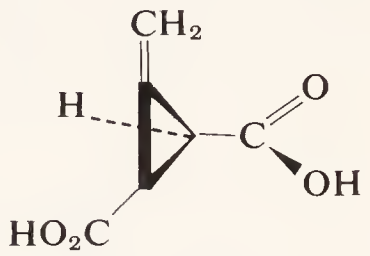


(**102**)



(**103**)

R = —H, —NCO, or —CO_2H



(**104**)

in **102** than in other conformational isomers (93). Similarly, studies of the temperature dependence of chemical shifts and coupling constants of vinylcyclopropane (94) and of two substituted vinylcyclopropanes (95) (**103**) suggest that the bisected conformations with H_1 and H_α *anti* (**103**) are of lowest energy, although gauche conformations (rather than the bisected conformations with H_1 and H_α *syn*) are of next highest energy.* X-ray crystallographic studies of cyclopropanecarboxhydrazide (97) and of Feist's acid (98) (**104**) show that these molecules have approximately bisected geometries; it must be recognized, however, that factors other than conjugation may greatly influence geometries in solids.

Further indications of the preferred geometry of cyclopropylcarbonium ions can be sought by trying to estimate the extent of conjugation in ions that have restricted geometries. For example, **44** and **46** must have bisected

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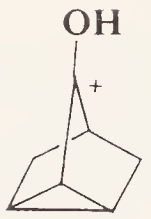
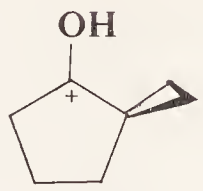
by a carbon–carbon bond of the cyclopropyl ring also is present (88). Yet the data can also be explained in terms of the presence only of **100** and **101**. The chemical shifts of the methyl groups of a series of cyclopropyl methyl ketones also can be rationalized by assuming the presence only of bisected conformational isomers (89).

The conclusion (90) that the nmr spectrum of cyclopropyl methyl ketone indicates the presence of isomers that do not interconvert rapidly at the temperature of observation (presumably room temperature) must be incorrect.

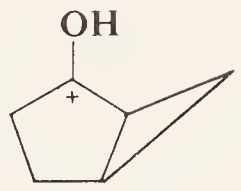
* The conclusion that only bisected conformations are significantly populated was drawn from a study of nmr and infrared spectra of *trans*-1,2-dicyclopropylethylene and vinylcyclopropane (96).



(44)



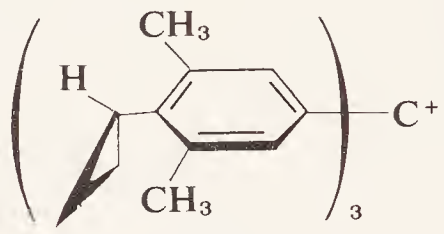
(46)



(47)

geometries but **47** must have a tilted geometry. The observation that the ultraviolet absorptions (Table III) of **44** and **46** are at much longer wavelengths than that of **47** could be taken as an indication that the bisected geometry leads to more efficient conjugation.* However, the compounds differ greatly in substitution of the cyclopropyl rings, a factor known to affect the spectra,† as well as in other respects, so any conclusion is tenuous. In a better chosen comparison, the cyclopropyl ring of **28** can assume a bisected conformation as shown in **105** or any other conformation, but that of **29** is constrained by bulky flanking methyl groups to

(105)



(106)

conformations closer to that shown in **106**. The pK_R's in Table III indicate that **28** is more stable than the unsubstituted triphenylmethyl cation. However, this stabilization by cyclopropyl groups is absent in **29**, although the methyls have little effect in the absence of a cyclopropyl group (15). These data suggest that a bisected conformation is necessary for maximum conjugation by the cyclopropyl ring. The β-hydrogen absorptions in the nmr spectrum of **28** are deshielded 0.53 ppm relative to the similar absorptions of the triarylmethanol precursor, but those of **29** are deshielded only 0.38 ppm relative to the precursor, another suggestion of decreased conjugation in **29** (15). A study of hydrolysis rates of related compounds is summarized in Table VIII (100). The *p*-cyclopropyl group shows a rate-accelerating effect considerably greater than that of a *p*-isopropyl group. However, even though one flanking methyl group only slightly reduces the accelerating effect of the cyclopropyl group, two flanking methyl groups reduce its effect below that of an isopropyl group (when a correction is made for the small accelerating effect of the methyl groups). One methyl group might not greatly affect one of the two bisected conformations, but two methyl groups will prohibit both bisected conformations.

* The spectra of the unprotonated ketone precursors of **46** and **47** show a similar difference and have been interpreted to indicate the extent of conjugation, as have spectra of other fused ring ketones (99).

† Cf. the ultraviolet spectra of **40** and **41** and of **44** and **45** (Table III).

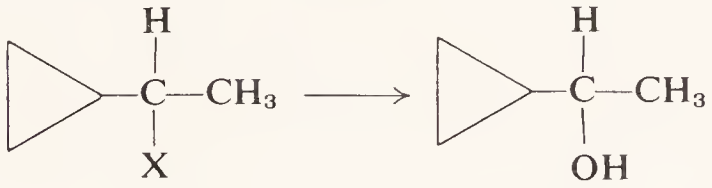
TABLE VIII

Relative First-Order Rate Constants for Hydrolyses of Substituted 2-Phenyl-2-Chloropropanes in 90% Aqueous Dioxane at 25° (100)

Substituents	Relative rate
(Hydrogen)	1
4-Isopropyl	17.8
4-Cyclopropyl	157[a]
3-Methyl[b]	2.00
3-Methyl-4-cyclopropyl	172[a]
3,5-Dimethyl	3.9
3,5-Dimethyl-4-cyclopropyl	37.1[a]

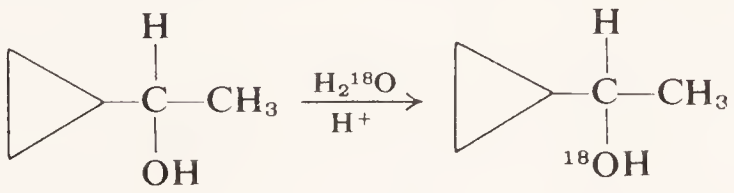
[a] Extrapolated from data at lower temperatures.
[b] Ref. 101.

Stereochemical studies of some solvolysis reactions also are consistent with a bisected structure. Deamination of optically active methylcyclopropylmethylamine (102), hydrolysis of optically active *N*-methyl-4-

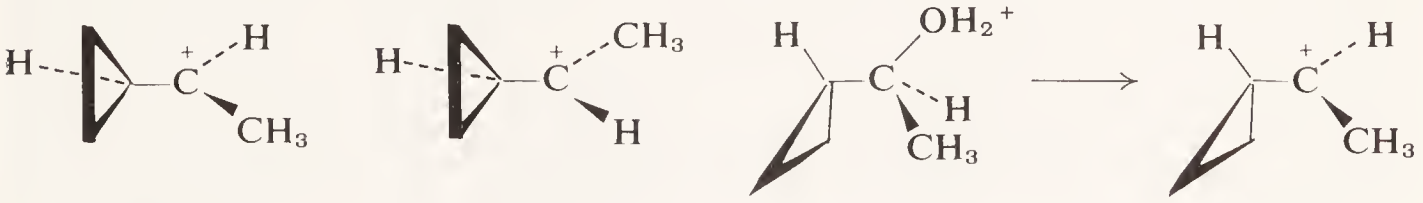


(71)

(cyclopropylmethylcarbinyloxy)pyridinium salts (102), and hydrolysis of the *p*-nitrobenzoate of optically active methylcyclopropylmethanol (103), lead to racemic methylcyclopropylmethanol (**71**). Similarly, the rate of exchange of the hydroxyl group is nearly equal to the rate of racemization of methylcyclopropylmethanol (75). These results suggest that the cyclo-



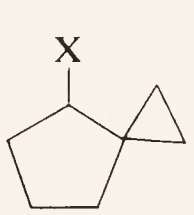
propylmethylcarbonium ion is optically inactive. Therefore, the optically inactive bisected structures (**107** and **108**) are favored, because single



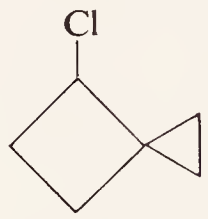
(107) **(108)** **(109)**

enantiomers of the dissymmetric ions of other geometries, e.g., **109**, might be generated from the optically active starting materials. However, it is possible that an optically active ion forms but racemizes before reacting with water.

Solvolysis rates of a variety of systems of fixed geometry [e.g., **61** (48), **110** (104), and **111** (106)] have been studied; however, the rates are complicated by factors other than the geometric relationship between the cyclopropyl ring and the trigonal carbon.

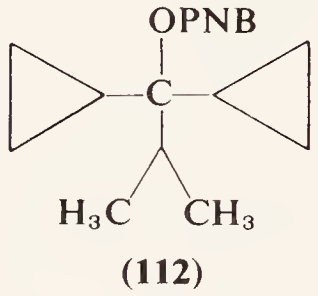


(110)



(111)

It is impossible for the cyclopropyl groups of **112** to attain the bisected geometry when methyl groups are present, and this may be why the effects on the solvolysis rate of **112** of the methyls at the β positions of the cyclo-



(112)

OPNB = *p*-nitrobenzoate

propyl rings (see Table V) are small compared to the effects of similar substitution on cyclopropylmethyl systems (Table VI). In addition, the great stability of the ion from **112** may reduce substituent effects. Even in the tricyclopropylcarbonium ion, it may not be sterically possible for the three rings to be in exactly the bisected geometry.

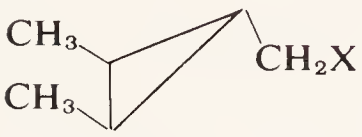
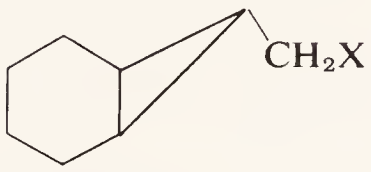
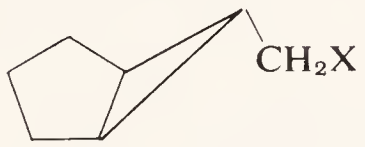
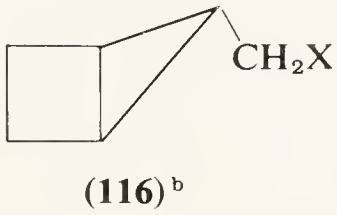
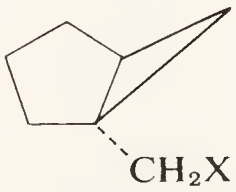
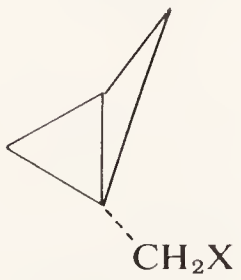
In discussing the geometry of cyclopropylcarbonium ions, only the conformational isomerism possible around the cyclopropyl–C^+ bond has been considered. It is equally important to know other aspects of the geometries of such ions. For example, are the bond lengths and angles of the cyclopropyl rings similar to those in neutral cyclopropyl compounds, or are the rings greatly distorted?

Solvolysis rates of the cyclopropylmethyl derivatives summarized in Table IX* have been interpreted in terms of changes in bond lengths on forming the ions. Schleyer and Van Dine suggest that C-3–C-4 (see **88**) is shorter and C-2–C-3 is longer in cyclopropylcarbonium ions than in neutral precursors (51). The decrease in rate in the series **114–116** (cf. also

* Some similar data not included in Table IX are found in Refs. 51 and 73.

TABLE IX

Relative First-Order Rate Constants for Solvolyses of Substituted Cyclopropylmethyl Derivatives

Compound	Relative rate
	1
 **(113)**[a]	124
 **(114)**[a]	220
 **(115)**[a]	40
 **(116)**[b]	1.3
 **(117)**[c]	700
 **(118)**[d]	> 1000

[a] 3,5-Dinitrobenzoates in 60% aqueous acetone at 100° (51).

[b] *p*-Toluenesulfonates in acetic acid at 17° (107).

[c] *p*-Nitrobenzoates in 60% aqueous acetone at 100° (105).

[d] *p*-Nitrobenzoates in 90% aqueous acetone at 118.6° (108).

with monocyclic analog **113**) may be due to increasing difficulty in shortening C-3–C-4 because of the small strained rings bridging these carbons. The rapid solvolysis rates of **117** and **118** [cf. the relative rate factor of about 55 calculated from the data of Table VI for an α plus a *trans*-β methyl substituent (51)] may be attributable to relief of strain in the second ring due to lengthening of C-2–C-3.

The geometries of cyclopropylcarbonium ions could be determined with greatest certainty by X-ray crystallographic studies of stable salts (Section II). Results of such studies are not yet available, but bond lengths and bond angles of cyclopropanecarboxaldehyde (87), cyclopropyl methyl ketone (92), and cyclopropanecarbonyl bromide (92), determined by electron diffraction studies, are normal for cyclopropane rings. Although conjugation of cyclopropyl with a trigonal carbon must be considerably less in carbonyl compounds than in carbonium ions, these observations suggest that the conjugation in cyclopropylcarbonium ions is not necessarily accompanied by tremendous distortion or rearrangement of the cyclopropyl rings.

VIII. BONDING

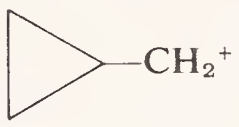
The great stabilities of cyclopropylcarbonium ions are undoubtedly attributable to significant absorption of the positive charge by the cyclopropyl rings. The characteristic downfield shifts of the β-cyclopropyl hydrogens observed in the nmr spectra of these ions are a reflection of this delocalization of charge. An inductive effect cannot be responsible for the absorption of charge since, compared to other alkyl groups, cyclopropyl is weakly electron withdrawing by induction.*

The stability of cyclopropylcarbonium ions may be due in some measure to loss of part of the ring strain of the ion precursors as well as to charge delocalization (this problem is discussed in Refs. 113 and 114). A cyclo-

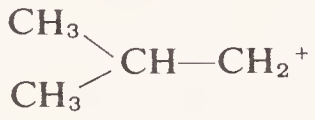
* The effect of inductive electron withdrawal by cyclopropyl groups is noted in the pK_A's of cyclopropanecarboxylic acids [(112), see also Ref. 109], the pK_B's of cyclopropylamines (112), and the dipole moments of cyclopropyl compounds (45,110,112). Taft σ^* values of +0.11 [T. L. Brown, *J. Am. Chem. Soc.*, **80**, 6489 (1958)], −0.27 [A. Allerhand and P. v. R. Schleyer, *ibid.*, **85**, 866 (1963)], and −0.475 [L. A. Jones and C. K. Hancock, *J. Org. Chem.*, **25**, 226 (1960)] have been estimated for the cyclopropyl group. The positive value was based on the intensities of infrared absorptions of aliphatic alcohols containing cyclopropyl groups. However, the negative values—estimated from correlations of spectral data using compounds in which cyclopropyl groups are conjugated with unsaturated functions—may result from opposing inductive and conjugative effects. Similarly, the Hammett σ of −0.21 for a *p*-cyclopropyl substituent (111), essentially the same as σ's of other *p*-alkyl substituents, may be the result of cancellation of inductive and conjugative effects.

propylcarbonium ion will be formed more rapidly and favored in an equilibrium to the extent that the considerable strain of the cyclopropyl ring of the precursor is decreased in the transition state leading to the ion and in the ion itself. However, relief of strain can hardly be the sole factor in stabilizing cyclopropylcarbonium ions. The observation that two, or even three, cyclopropyl groups contribute approximately equally to the stabilization of ions is difficult to rationalize in terms of stabilization that involves only relief of strain. In addition, stabilization by cyclopropyl is apparent in the *p*-cyclopropylphenyldimethylcarbonium ion (**27**), both from nmr evidence (Section III) and from rate data (115) (see Tables VIII and XII), although considerable relief of ring strain seems less likely than in some of the simpler ions.

Even though cyclopropylcarbonium ions have been represented by solid line structures such as **3** in this chapter, charge distribution in these ions is



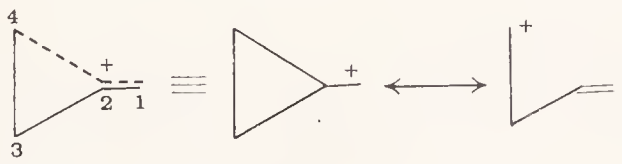
(3)



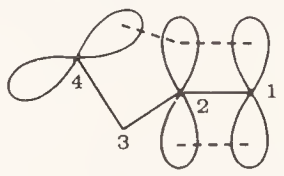
(119)

clearly dissimilar to that in the isopropylcarbonium ion (**119**), which is usually represented in a similar manner. Several descriptions of the charge delocalization in cyclopropylcarbonium ions have been considered.

The "unsymmetrical homoallylic" ion (**120**) is the resonance hybrid of **121** and **122** (47,113). Maximum stabilization energies (delocalization

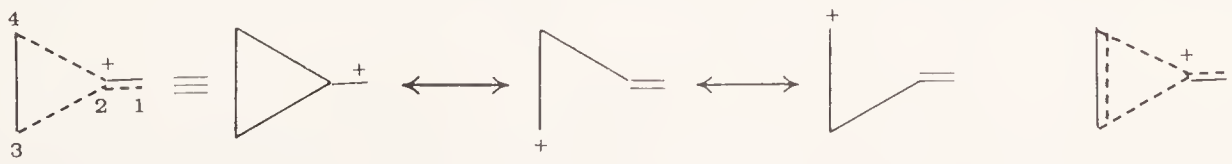


(120) **(121)** **(122)**



(123)

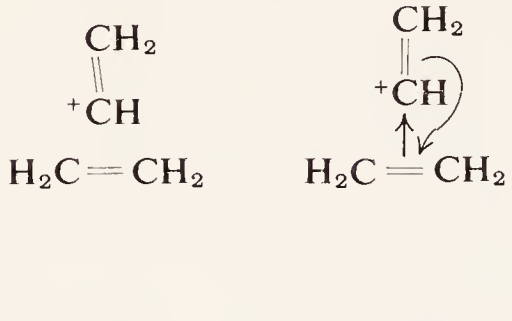
energies minus strain energies) of ca. 6 (116) and 4 (117) kcal/mole have been predicted for this ion on the basis of molecular orbital calculations that consider the overlap of the *p*-orbitals shown in **123** as a function of the C-2–C-3–C-4 bond angle (118). The "symmetrical homoallylic" ion (**124**) is the resonance hybrid of **125**–**127** (17,113,116). This ion differs from



(124) **(125)** **(126)** **(127)** **(128)**

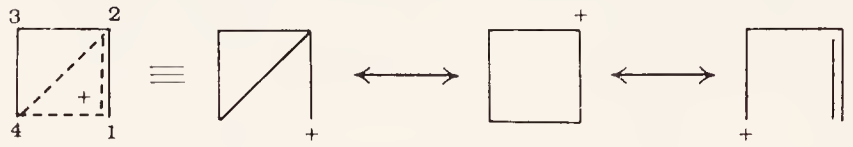
the ion previously considered in that both C-3 and C-4 are involved in delocalization. Representation (18,114) **128** of the symmetric homoallylic

ion implies an added resonance contribution from **129**. In an equivalent representation, the cyclopropylcarbonium ion has been regarded as a π



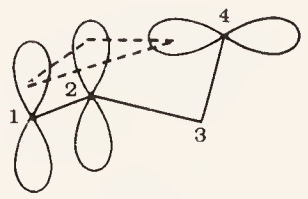
(129) **(130)** **(131)** **(132)**

complex (**130**), stabilized not only in the manner represented by the short, straight arrow, but also by the back coordination indicated by the long, curved arrow (119). It has been proposed (119) that the geometry of the π complex is either symmetrical as in **131** (resembling **128**) or distorted as in **132**. The "bicyclobutonium" ion (**133**) is the resonance



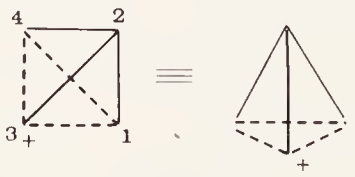
(133) **(134)** **(135)** **(136)**

hybrid of **134–136** (79). This ion differs from the homoallylic ions in having significant bonding between C-1 and C-4 and hence significant positive charge at C-2. A maximum stabilization energy of about 11 kcal/mole is predicted for this ion on the basis of a molecular orbital calculation in which the overlap appearing in **137** is considered as a function of several bond



(137)

angles (117). Ion **133** is assumed to be in rapid equilibrium with closely related isomers* in which C-1, C-3, and C-4 have interchanged positions. The "tricyclobutonium ion" (78,79,121) (**138**), in which C-1, C-3, and C-4



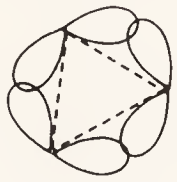
(138)

(if unsubstituted) are equivalent, is not a possible description, since these carbons are not always equilibrated completely in reactions thought to

* There are 12 isomers (6 pairs of enantiomers) (120).

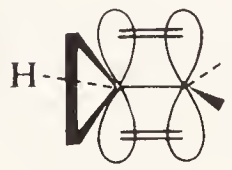
proceed through cyclopropylcarbonium ions (79). Calculations also indicate that this structure is unfavorable: the ground state would be orbitally degenerate if the methylene hydrogens were disposed as in cyclopropane (three above and three below the plane of the methylene carbons) (117,122), and the energy would be unfavorably high if the six methylene hydrogens lay in one plane (117).

The description of bonding in cyclopropylcarbonium ions can be approached instead by considering the orbitals in a cyclopropane ring and their interaction with an adjacent *p*-orbital, assuming that the geometry of the cyclopropyl ring is not greatly altered by its attachment to a positive carbon. The great differences between the chemical and physical properties of cyclopropane and those of other alkanes, cyclic or acylic, have led to descriptions of bonding in cyclopropane quite different from those accepted for other alkanes. These descriptions agree in predicting considerable *p* character in orbitals in the plane of the cyclopropane ring. Coulson and Moffitt (123) found that the calculated energy of cyclopropane is reduced if the two orbitals at each carbon used to form the ring bonds do not have sp^3 hybridization. Minimum energy is achieved if these orbitals are at an angle of 104° and have $sp^{4.12}$ hybridization as shown in **139** (124).* Conjugation in cyclopropylcarbonium ions can be



(139)

attributed to overlap as shown in **140** (cf. **128**) between the *p* orbital of the positive carbon and the orbitals with high *p* character of the adjacent ring



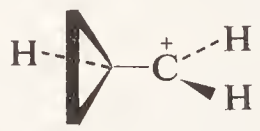
(140)

* Walsh (125) considered instead that the ring carbons have essentially sp^2 hybridization. The carbons are bonded by overlap in the plane of the ring of the three *p* orbitals on adjacent carbons and also by overlap of three sp^2 orbitals, one contributed by each carbon, directed toward the center of the ring. Four electrons occupy the molecular orbitals formed by overlap of the *p* orbitals and two electrons occupy the molecular orbitals formed by overlap of the central sp^2 orbitals. More recent molecular orbital calculations (126) predict, in agreement with the Walsh and Coulson-Moffitt models, high *p* character for the electrons of the carbon–carbon bonds of cyclopropane.

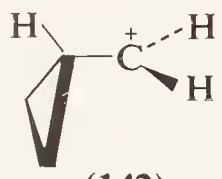
carbon (3,7,11,13). Conjugation in neutral compounds between cyclopropyl rings and groups with sp^2 carbons would be pictured similarly. In fact, conjugation was first depicted in this manner in the report of a study of conjugation between three-membered rings and carbonyl groups (127). However, the conjugation is intensified in carbonium ions because of the electron deficiency of the carbon adjacent to the cyclopropyl ring. This overlap predicts the bisected geometry for cyclopropyl groups attached to sp^2 carbons in accord with experimental evidence. Using his extended Hückel method, Hoffmann has calculated that the bisected structure of the cyclopropylcarbonium ion is about 9 kcal/mole more stable than a structure obtained by rotating 90° around the cyclopropyl–C^+ bond (122). Similarly, the "*s-trans*" (**100**) and "*s-cis*" (**101**) rotational isomers of cyclopropanecarboxaldehyde are calculated to be about 6 and 4 kcal/mole more stable, respectively, than the form obtained by rotating by 90° around the cyclopropyl–CHO bond of either (128).*

All the representations of cyclopropylcarbonium ions discussed previously have the merit, not shared by the solid-line structures used in this chapter, of keeping clearly in the foreground the considerable charge delocalization in these ions. However, these representations differ in their predictions of properties, and these predictions should be compared with the conclusions about structure reached from experiments described earlier in this chapter.

Schleyer and Van Dine used methyl substituents to demonstrate that both β-carbons contribute equally to delocalization in the transition state for cyclopropylcarbonium ion formation (51); this suggests that equally substituted β-carbons, if not prevented by structural restraints, are placed equivalently in a cyclopropylcarbonium ion. Structures both of the bisected geometry (**141**) and of geometry **142** fit this requirement. However,



(**141**)



(**142**)

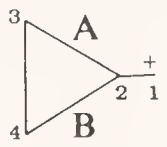
the evidence discussed in Section VII favors the bisected geometry. Of the descriptions of bonding in cyclopropylcarbonium ions, **128**, **130**, and **140** are in accord with the bisected geometry (as is **138**, but this representation has been ruled out on other grounds), and it seems that these models could be easily extended to the description of di- and tricyclopropylcarbonium ions. Some direct bonding from C-1 to C-3 and C-4, not indicated explicitly by these representations, could also be involved.

* Molecular orbital calculations have also been reported for cyclopropylethylene (45) and phenylcyclopropane (129).

Although **140** or **128** may be preferred, other structures cannot be much higher in energy. The rapid equilibration of C-1, C-3, and C-4 (**88**) in some ions requires that transition states or intermediates in which C-1 becomes equivalent with C-3 or C-4 be easily attainable. The similar mixtures of cyclopropylmethyl and cyclobutyl products obtained from cyclopropylmethyl and cyclobutyl systems can be rationalized in terms of rapidly equilibrating cyclopropylmethyl (**90**) and cyclobutyl (**91**) ions instead of a common ion. If this explanation is correct, however, then an ion such as the bicyclobutonium ion (**133**), which could represent a transition state for the rapid equilibration of **90** and **91**, cannot be much higher in energy. The bicyclobutonium ion structure (**133**) explains more economically than do **128** or **140** the formation of sizable amounts of cyclobutyl products from some systems. However, C-3 and C-4 are not equivalent in the bicyclobutonium ion. Moreover, this structure implies considerable charge at C-2; yet, in spite of the proximity of C-2 to the trigonal carbon (C-1), nmr spectra do not indicate an unusual amount of charge at that position, and effects of substituents at C-2 on solvolysis rates are smaller than of substituents at C-3 and C-4.

It is possible that no one structure can describe satisfactorily all cyclopropylcarbonium ions. Primary ions (e.g., **3**) in which such great demand for conjugation is placed on the cyclopropyl ring perhaps differ considerably in structure from the more stable cyclopropylcarbonium ions. Despite many efforts to elucidate details of the structures of cyclopropylcarbonium ions from solvolysis rates,* direct spectral and X-ray crystallographic studies of the simplest ions may ultimately provide the most convincing evidence of structure.

Although bisected structures in which bonds A and B (**143**) are equivalent may lead to the greatest conjugation, structural factors in some ions

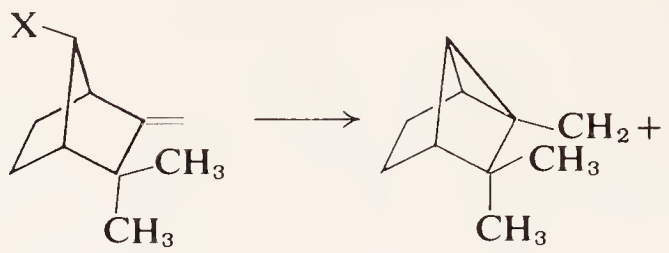


(143)

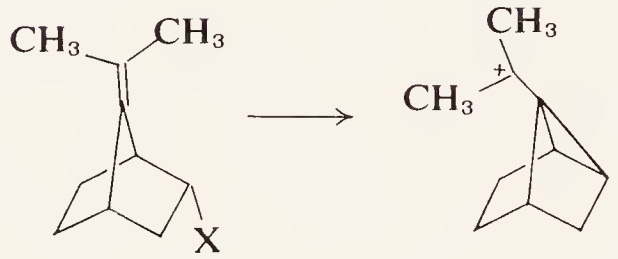
(even apart from any difference in substituents at C-3 and C-4) may prevent bonds A and B from being essentially equivalent. For example, structural restraints may force bonds A and B to be quite different in the

* In addition to the interpretations of such studies discussed in Sections V and VII, solvolysis rates have been interpreted in terms of the ease of forming bicyclobutonium ions [recent references are (73) and (107)]. The structures of the ions have also been considered in relation to such diverse phenomena in solvolysis reactions as secondary deuterium isotope effects (57,130) and heat capacities of activation (131).

ions formed as intermediates in reactions of bicyclic, homoallylic systems **144** (132) and **145** (133), notwithstanding the possibility that these ions may

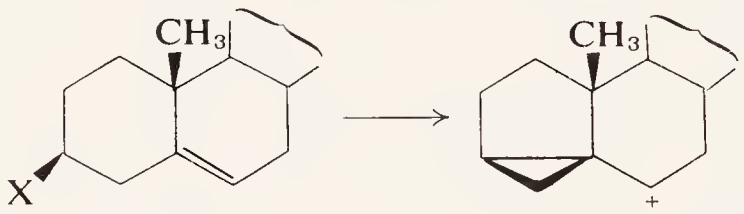


(144)



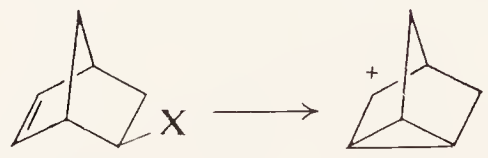
(145)

have considerable cyclopropylcarbonium ion character. However, bonds A and B could be relatively similar in the intermediate formed from the much studied cholesteryl system (**146**). (Reactions of this system have been reviewed; see Ref. 134.) Transition states of reaction steps in which

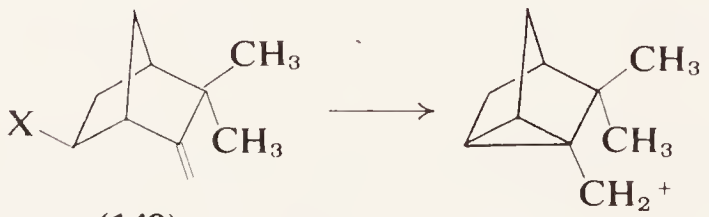


(146)

cyclopropylcarbonium ions are generated, of course, may be less symmetrical than the ions. For example, bonds A and B can be identical in the ions formed from **147*** and **148** (136), but must differ significantly in the transition states for formation of these ions.



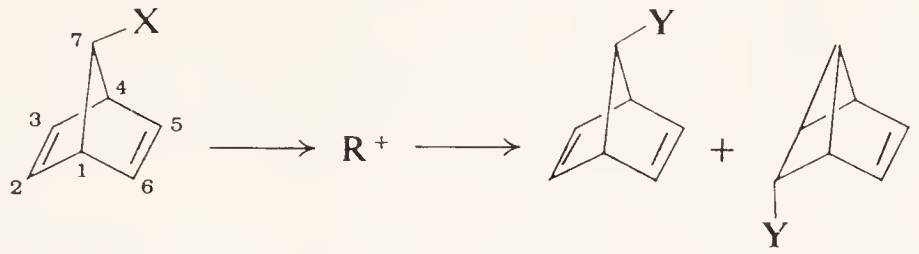
(147)



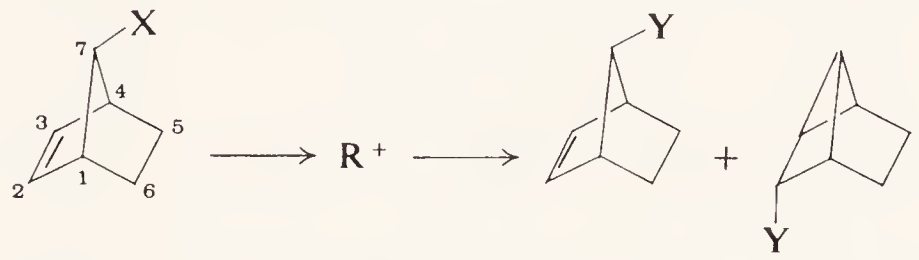
(148)

* Reactions of this system have been reviewed (135).

Cations such as those formed from 7-norbornadienyl (**149**) and *anti*-7-norbornenyl (**152**) systems certainly are related to the other cations

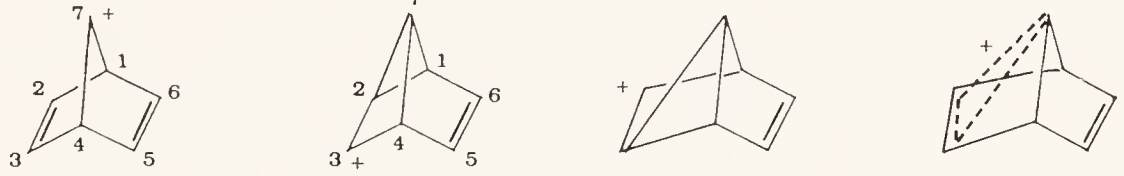


(149) **(150)** **(151)**

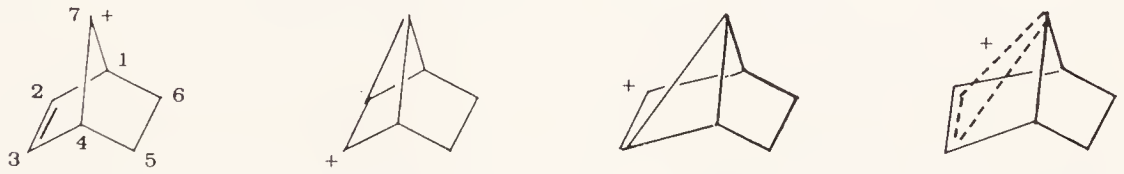


(152) **(153)** **(154)**

discussed in this chapter, but their structures may be dictated by the ring systems. The rapid formation of **150** (137,138) and of **153** (139–142) suggests that these ions are stabilized by some interaction involving the double bonds that is not indicated by structures **155** and **159**. It has been



(155) **(156)** **(157)** **(158)**

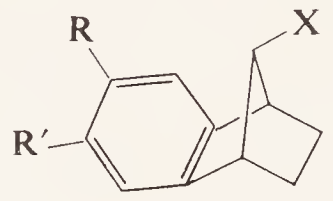


(159) **(160)** **(161)** **(162)**

proposed that these ions have the stabilization afforded by cyclopropylcarbonium ion structures **156** and **160** (3,143). However, "symmetrical" structures **158** and **162** in which the bridge carbon (C-7) is located symmetrically with respect to the formal double bond have also been proposed for these ions (140,141). These structures resemble bicyclobutonium ions (**133**) in which C-1 and C-2 are identical, and it is possible that they are particularly favored because of the ring structures of the ions. Such structures have been called bishomocyclopropenyl (140) to indicate the resemblance of the conjugated system to that of the cyclopropenyl cation, although the framework connecting the conjugating carbons suffers two interruptions.

Reactions involving **150** (137,138,143–145) and **153** (139,141–143,146, 147) form products from attack at C-7 and at C-2, consistent with either the cyclopropyl (**156** and **160**) or symmetrical (**158** and **162**) structures but not with **155** and **159**. However, the high stereoselectivity of attack at C-2 (to form **151** and **154** instead of their epimers) observed with both ions is more in accord with the symmetrical structures.

The effects of aryl substituents on the acetolysis rate of the *p*-bromobenzenesulfonate of the related benznorbornenyl system **162a** are also in



(162a)

X = *p*-bromobenzenesulfonate

accord with a symmetrical structure for the intermediate ion (148). The data in Table X indicate that a second methoxyl or methyl group exerts almost exactly the same rate-accelerating effect as the first.

TABLE X

Relative First-Order Rate Constants for Acetolyses of Benznorbornenyl *p*-Bromobenzenesulfonates (162a) at 77.6° (148)

R, R′	Relative rate
H, H	1
CH_3, H	5.7
CH_3, CH_3	36
OCH_3, H	54
OCH_3, OCH_3	3000[a]

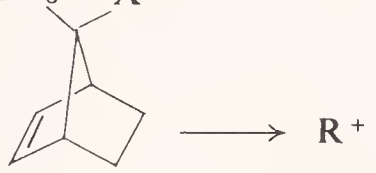
[a] Calculated from data at lower temperatures.

Nmr spectral observations of these ions also indicate that structures **155** and **159** cannot be correct. The spectrum of **150*** shows multiplets with relative areas 1:2:2:2 (at 3.48, 5.23, 6.26, and 7.58) (150). A structure in which C-2 and C-3 are not identical with C-5 and C-6 is necessary to

* The fluoroborate salt in sulfur dioxide relative to internal tetramethylsilane. Dissolving 7-norbornadienol in fluorosulfonic acid furnishes a similar spectrum (149).

explain the observation of four multiplets. A structure with nonequivalent double bonds also has been predicted on the basis of extended Hückel calculations (151). In addition, **155** is not consistent with the observation that absorption of the hydrogen at C-7 is upfield from all other absorptions of the ion. However, the number of absorptions is that expected for **158** and the upfield absorption of the hydrogen at C-7 can be rationalized on the basis of such a structure (147). Structure **156** is consistent with the position of absorption of the C-7 hydrogen, but to be consistent with the observation of equivalent absorptions of hydrogens at C-2 and C-3 (and also at C-5 and C-6 and at C-1 and C-4), **156** must be in rapid equilibrium with its isomer **157**.

Similar structures, **162** or **160** $\rightleftarrows$ **161**, for **153** and additional evidence for the significant involvement of only one double bond of **150** in dispersing the positive charge are suggested by similarities of the nmr spectra of **153** and **150**. The spectrum of **153** also shows equivalent absorptions for hydrogens at C-2 and C-3 (147,149). The chemical shifts (147,149) of hydrogens at C-2 and C-7 and coupling constants that involve these hydrogens are remarkably similar in the spectra of **150** and **153**. Since absorptions of similar hydrogens in **163** and **153** have nearly identical



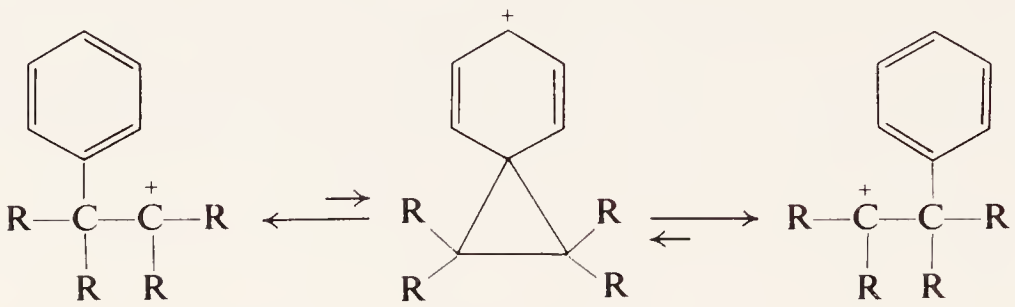
(163)

chemical shifts, it is reasonable that relatively little positive charge may reside at C-7—another indication that **155** and **159** are poor representations of these ions (149).

Even if cyclopropylcarbonium ion structures should prove to be the best representations of these ions, the energies of symmetrical structures cannot be much higher. Symmetrical structures represent midpoints for the equilibration of isomeric cyclopropylcarbonium ion structures and these equilibrations would have to be rapid to be consistent with the nmr results.

The relative strengths of bonds in cyclopropylcarbonium ions will be affected by substituents as well as by structural restraints. A carbonium ion stabilizing substituent at C-3 of **143** should decrease the strength of bond A, but introduction of such a substituent at C-1 should increase the strengths of bonds A and B. For example, the new cyclopropyl carbon–carbon bond in the ion formed from **144** may be particularly weak because the formal charge is placed on a primary carbon. With sufficient stabilization by substituents at C-3, an acyclic structure can be more stable than its cyclopropyl counterpart.

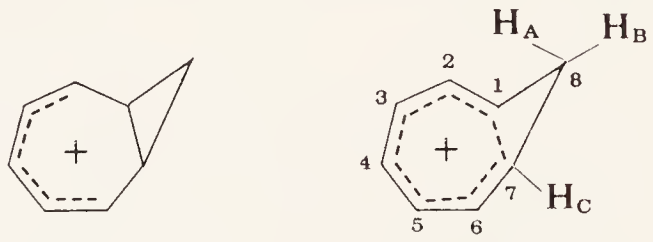
Such effects of substituents on relative stabilities of phenonium ion and isomeric acyclic structures have been noted. The nmr spectra of **36–38** (Table I) are in accord with the assigned phenonium ion structures. However, **165** (R = CH_3) apparently is less stable than its acyclic counterpart **164**, since the nmr absorptions of the phenyl group are thought to be



(164) **(165)** **(166)**

in accord with **164** (26). In contrast to the observed phenonium ions (**36–38**), **165** is not stabilized by substituents on the six-membered ring, but **164** is stabilized by methyl substituents. Even in this system, however, the phenonium ion structure (**165**) must be nearly as stable as **164**. The single nmr absorption for the methyl groups at $-60°$ requires their rapid equilibration, most probably by interconversion of **164** and **166**; **165**, as the midpoint of the path between **164** and **166**, could not be of much higher energy. The corresponding phenyl substituted ion also may exist as a rapidly equilibrating mixture of isomers, **164** $\rightleftarrows$ **166** (R = phenyl) (26).

The effects of substitution also are seen to an extreme degree in the cation generated by protonation of cyclooctatetraene (152–154). This cation could be regarded as a typical cyclopropylcarbonium ion **167**,

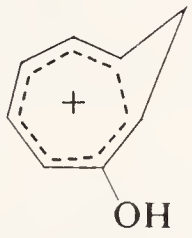


(167) **(168)**

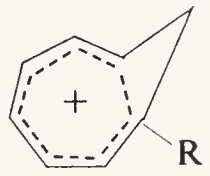
although for reasons of symmetry bonds A and B (**143**) would have to be equivalent. However, there is evidence for major contributions by C-1 and C-7, but not by C-8, to a conjugated system; and the unsymmetrical homoallylic structure **168**, which indicates a cyclic conjugated system, seems a better representation of this ion. Structure **168** has been designated homotropylium (155,156) to indicate that the conjugated system, although it resembles the system of the tropylium ion, is contained in a framework that requires electron delocalization to bridge a saturated carbon.

The ultraviolet absorptions (154) (232.5 mμ, ε 33,000 and 313 mμ, ε 3000 in sulfuric acid), at somewhat longer wavelengths than those (157) of the tropylium ion (217 mμ, ε 41,000 and 273.5 mμ, ε 4350), are at much shorter wavelengths than anticipated for the absorption of a pentadienyl cation conjugated with a cyclopropyl ring.

The nmr spectrum of the ion in concentrated sulfuric acid relative to external tetramethylsilane exhibits peaks at −0.67, 5.10, 6.42, and 8.47 having relative areas of 1:1:2:5 (158). The number of peaks is consistent with structure **167** or **168** (but not with a planar cyclooctatrienyl cation structure). However, the absorption of one of the single hydrogens is considerably upfield and the absorption of the other considerably downfield from the β-hydrogen absorptions of cyclopropylcarbonium ions. These absorptions can be rationalized, however, by assigning the upfield absorption to H_A of **168** and attributing the unusual chemical shift to shielding due to a substantial ring current; H_B is almost coplanar with the seven-membered ring, and its absorption could be shifted downfield by the deshielding effect of the ring current (152,154,159). Coupling constants J_{AB}, J_{AC}, and J_{BC} are different from those usually observed for hydrogens of cyclopropyl rings (158). Ions **169** (155) and **170** (153), which contain



(169)

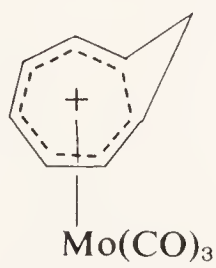


(170)

R = CH_3 or phenyl

stabilizing substituents, also exhibit upfield shifts of H_A and downfield shifts of H_B that are large, although somewhat smaller than those exhibited by the unsubstituted ion.

Some confirmation of the conclusions about the structures of these ions is provided by the contrasting properties of the molybdenum **(171)** and



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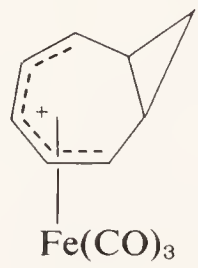


(172)

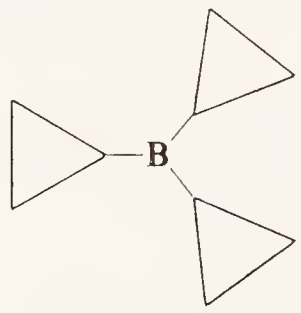
iron **(172)** tricarbonyl complexes. Molybdenum has a preference for bonding with 6 π electrons but iron with only 4 π electrons. The nmr spectrum of the molybdenum complex is similar to the spectra of **168–170** and shows

large H_A and H_B shifts (158,160). In contrast, the nmr spectrum of the iron complex is that expected for the presence of an essentially intact cyclopropyl ring (158,159); the chemical shifts (161,162) of the H_A and H_B absorptions are nearly identical, and the coupling constants (162) are typical of those exhibited by hydrogens of cyclopropyl rings.

IX. RELATED STUDIES

The conjugation found in cyclopropylcarbonium ions certainly is not unique and should be sought in compounds and intermediates in which cyclopropyl groups or positive carbons or even both are lacking. Conjugation between cyclopropyl groups and positive carbons must be related to the weaker conjugation observed between cyclopropyl groups and functions, e.g., carbonyl, vinyl, and aryl, which, in common with carbonium ion carbons, possess sp^2 carbons. The existence of such conjugation was postulated in the nineteenth century by Perkin (163), by Kishner in 1913 (164), by Robinson in 1916 (165), and by Kohler and Conant the following year (166) to explain unusual physical and chemical properties of cyclopropyl compounds. The effects of conjugation have since been noted on such widely varied properties of cyclopropyl compounds as nmr spectra (19), Raman frequencies and intensities (41), ultraviolet spectra (41), optical rotatory dispersion spectra (167), molar refractivities (41), and heats of combustion (41).

Tricyclopropylborane, isoelectronic with the tricyclopropylcarbonium ion, exhibits an nmr spectrum that provides evidence for cyclopropyl–



boron conjugation. The β-hydrogen multiplet is centered at 0.69 and the α-hydrogen multiplet at -0.25 in carbon tetrachloride relative to internal tetramethylsilane (168). The downfield position of the β-hydrogen absorption is not typical of boranes,* but is consistent with conjugation between cyclopropyl and the electron-deficient boron, which renders the β-carbons relatively positive and the boron relatively negative.

Three-membered rings such as oxiranes, aziridines, and thiiranes might also conjugate with sp^2 carbons. Data concerning carbonium ions with

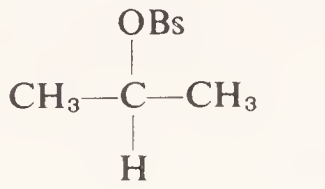
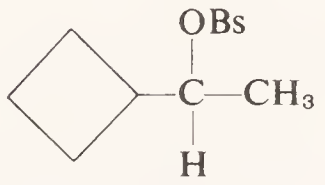
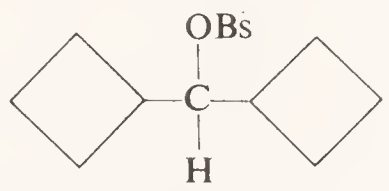
* The α- and β-hydrogen absorptions of triethylborane have chemical shifts nearly the same as those of ethyl groups in saturated aliphatic hydrocarbons (169).

such substituents are not available. However, ultraviolet spectra of some neutral compounds containing these substituents adjacent to carbonyl or aryl groups are reported to show evidence of conjugation. Ultraviolet spectra of compounds containing oxirane groups are reviewed in Ref. 170. References to the ultraviolet spectra of ketones containing aziridine groups are given in Ref. 171, and ultraviolet spectra of aryl-substituted thiiranes and oxiranes are discussed in Ref. 172.

Other groups, such as cyclobutyl, with small C–C–C bond angles, might be expected to stabilize carbonium ions more than do substituents with tetrahedral bond angles. In fact, replacement of methyl by cyclobutyl groups leads to increased solvolysis rates in the series of *p*-bromobenzenesulfonates listed in Table XI (173). Similarly, solvolysis rates of cyclo-

TABLE XI

Relative First-Order Rate Constants for Acetolyses of *p*-Bromobenzenesulfonates

Compound	Relative rate	Reference
	1	174
	510	173
	2200	173

butylmethyl bromide (175), cyclobutylmethyl *p*-toluenesulfonate (114,176), cyclobutylmethyl *p*-bromobenzenesulfonate (177), and 2-cyclobutyl-2-propyl *p*-nitrobenzoate (114) are large compared with those of acyclic model compounds (114).* These rate accelerations probably are due more to relief in the transition states of some of the ring strain of the cyclobutyl groups than to unusual delocalization of charge by essentially intact

* Rate data available for compounds in which cyclobutyl rings are part of more complex ring systems are more difficult to interpret (176,178).

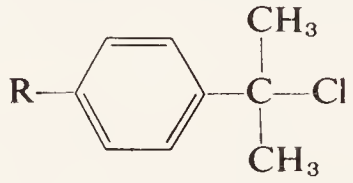
cyclobutyl rings. This conclusion is consistent with the observation that a second cyclobutyl group exhibits a much smaller effect than the first on a solvolysis rate and is reinforced by the data (115) of Table XII that indicate

TABLE XII

Relative First-Order Rate Constants for Hydrolyses of 2-(*p*-Alkylphenyl)-2-Chloropropanes (173) in 90% Aqueous Acetone (115)

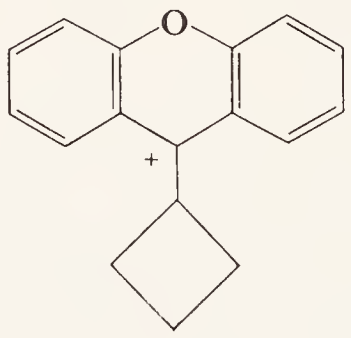
R	Relative rate
Hydrogen	1
Methyl	26.4
Cyclopropyl	125
Cyclobutyl	20.7
Cyclopentyl	23.7
Cyclohexyl	19.6
Isopropyl	18.8

that a *p*-cyclobutyl group does not cause an unusual rate acceleration in

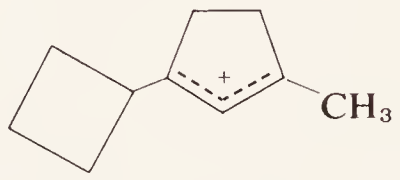


(173)

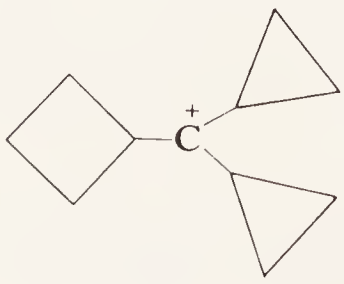
the hydrolysis of **173**, a system in which ring enlargement in the transition state should be particularly unfavorable.



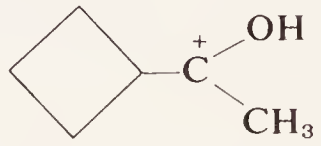
(174)



(175)

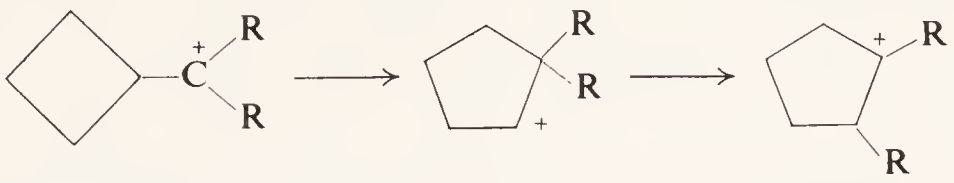


(176)



(177)

Nmr spectra of cyclobutylcarbonium ions **174–177** have been observed (12). Attempts to prepare stable solutions of cyclobutylcarbonium ions (**178**) sometimes lead instead to cyclopentyl cations (**180**) (12). However,



(178) **(179)** **(180)**

this rearrangement is prevented in **174–177** by the presence of groups R that are effective at stabilizing **178** but have little effect on the stability of **179**, an intermediate in the rearrangement. The absorptions of the hydrogens of **175–177** are almost identical with those exhibited by the corresponding methyl ions, but considerably downfield from absorptions of equivalent hydrogens in the corresponding cyclopropyl ions. On the basis of the discussion in Section III, these observations suggest that an intact cyclobutyl group resembles methyl rather than cyclopropyl in its ability to stabilize carbonium ions. This conclusion is supported by the observation that the pK of **177** (approximately -6.9) is much closer to that of the corresponding methyl than to that of the corresponding cyclopropyl ion (see Table III) (12).

X. ACKNOWLEDGMENTS

The following persons kindly provided unpublished data: H. C. Brown, N. C. Deno, R. Hoffmann, M. Julia, J. C. Martin, G. A. Olah, R. R. Sauers, P. v. R. Schleyer, H. Shechter, K. B. Wiberg, and the late S. Winstein. I am grateful to the following persons for helpful comments on the preliminary manuscript for this chapter: D. E. Applequist, P. D. Bartlett, H. C. Brown, N. H. Cromwell, R. Hoffmann, M. Julia, P. v. R. Schleyer, P. R. Story, and S. Winstein. I particularly want to thank N. C. Deno for frequent discussions, my other colleagues in the Chemistry Department at Penn State for their constant encouragement and stimulation, and Jane Richey for valuable assistance in the preparation of this manuscript.

XI. ADDENDUM

The manuscript for this chapter was completed in the spring of 1966, although some newer results were inserted in a revision made near the end of that year and some minor corrections have since been made. The additional information now available, as well as the passage of time, render some of the discussion dated, and the organization in places seems

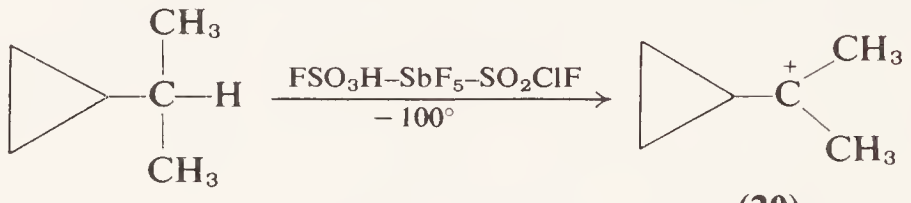
artificial. Nevertheless, for ease in relating the newer to the older studies, the original organization is retained in this Addendum. Considerable information from solvolysis studies is included, but emphasis remains on studies of stable solutions of cyclopropylcarbonium ions, which now include the methylcyclopropylcarbonium ion (**4**) and the unsubstituted cyclopropylcarbonium ion (**3**). Chapter 26 in this volume, by Wiberg, Andes, and Ashe, as well as other reviews (179,180), are concerned particularly with solvolysis reactions in which cyclopropylcarbonium ions are intermediates.

A. Proof of Existence

Proving the existence of cyclopropylcarbonium ions now seems superfluous. Nevertheless, the mode of preparation and the nmr spectra continue to be the only evidence for the existence of most cyclopropylcarbonium ions as stable species in solution. Only a few additional solutions—including, however, those of the unsubstituted cyclopropylcarbonium ion (**3**) (181,182)—have been allowed to react with nucleophiles to demonstrate that the resulting neutral compounds have structures reasonably derived from cyclopropylcarbonium ions.

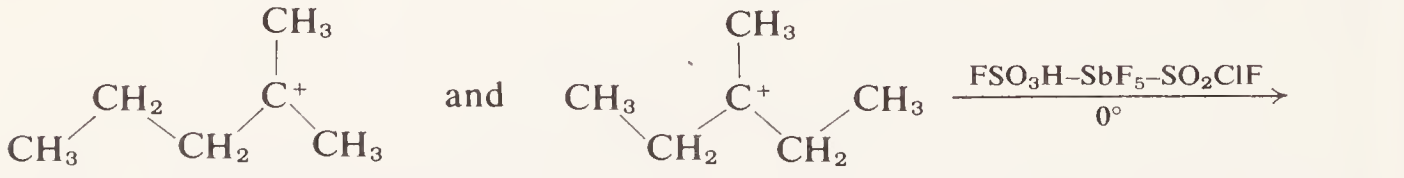
B. Preparation

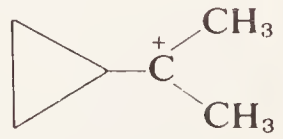
Formation of cyclopropylcarbonium ions by loss of a nucleophile from a cyclopropylmethyl derivative now includes the loss of hydride; the dimethylcyclopropylcarbonium ion (**20**), accompanied by a mixture of tertiary hexyl cations, is formed from isopropylcyclopropane, and in the same medium, the unsubstituted cyclopropylcarbonium ion (**3**) is formed



(20)

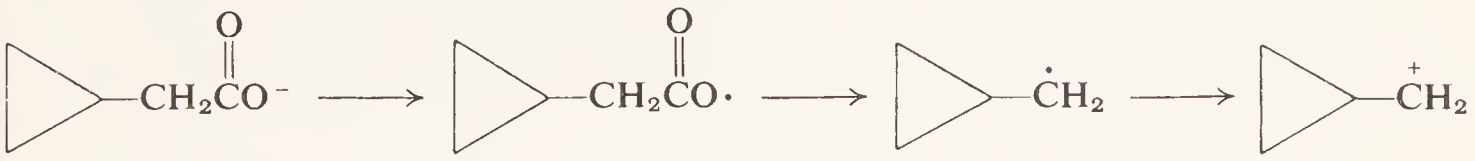
from cyclobutane (181). Formation of **20** in this medium from two tertiary hexyl cations also is reported (181). Generation of the cyclopropylcarbonium ion as a transient intermediate by anodic oxidation of the





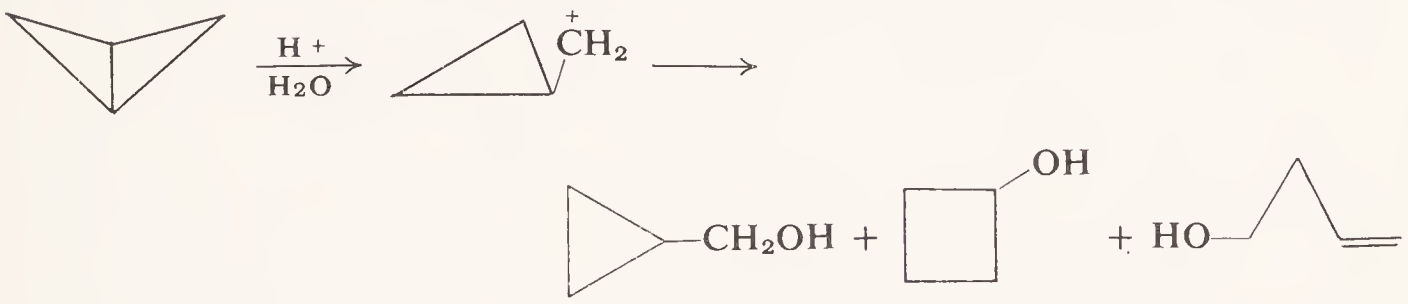
(20)

anion of cyclopropylacetic acid presumably involves removal of an electron from the cyclopropylmethyl radical (183).

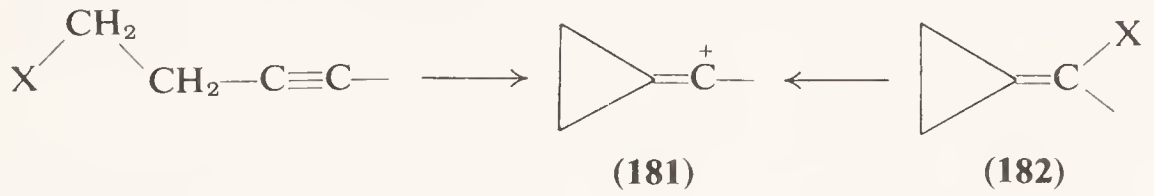


To explain the formation of products of rearranged structure in the gas-phase pyrolysis of a substituted cyclopropylmethyl acetate, it has been proposed that the reaction proceeds in part by ionization in the gas phase to a cyclopropylcarbonium ion (184). However, Lewis and Newman have established that rearranged products formed in the pyrolysis of cyclopropylmethyl trifluoroacetate under similar conditions arise largely and perhaps completely from a heterogeneous process (185).

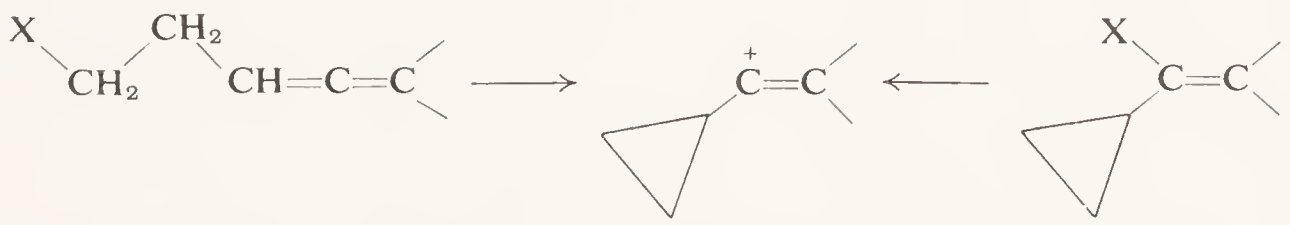
To the formation of cyclopropylcarbonium ions by electrophilic additions to cyclopropylalkenes can be added their formation by similar additions to the strained σ bonds of bicyclobutanes (186). For example, acid-catalyzed hydration of bicyclobutane furnishes the products expected from intermediacy of the cyclopropylcarbonium ion (187).



Reactions of "homoallylic" systems that furnish cyclopropylcarbonium ions as transient intermediates now have counterparts in reactions of "homopropargylic" and "homoallenic" systems that furnish cyclopropylidenemethyl (**181**) and α-cyclopropylvinyl (**183**) cations, respectively; this



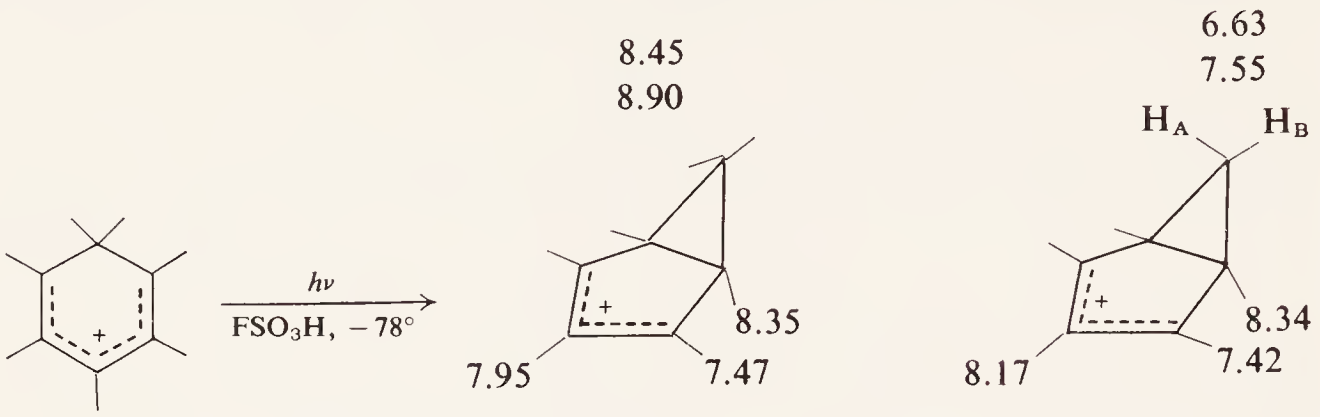
(181) **(182)**



(183) **(184)**

subject has been reviewed briefly by Hanack (188). Vinyl cations having the general structures **181** (189) and **182** (190) also are generated by solvolysis reactions of the corresponding vinyl halides (**182** and **184**).

Cyclopropylcarbonium ions have been generated photochemically. Stable solutions of bicyclo[3.1.0]hexenyl cations are prepared in high yields by photolyses of cyclohexadienyl cations (191–194), e.g., **186** from **185** (191). Presumably the bicyclic cations form by a disrotatory closure



(185) **(186)** **(187)**

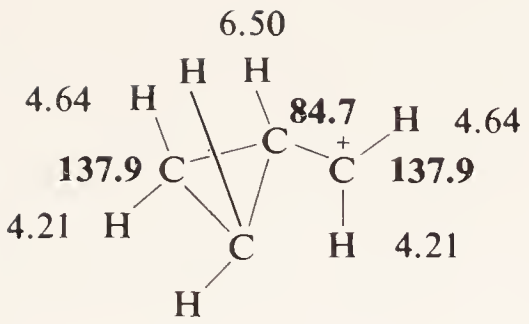
(193) that is "allowed" in the first excited state (195). Thermal rearrangements of **186** (191) and **187** (192) and of similar hexamethyl (191) and tetramethyl cations (193) to the corresponding cyclohexadienyl cations, although exothermic, have values of $\Delta F^{\ddagger}$ of 17–20 kcal/mole. Substantial energy barriers are expected, since the conrotatory course for electrocyclic ring opening allowed in the ground state is sterically precluded; therefore, the conversion, if concerted, must proceed via "forbidden" disrotatory opening. Zwitterions containing a bicyclo[3.1.0]hexenyl cation system have been proposed as transient intermediates in photochemical rearrangements of 2,5-cyclohexadienones (196), and zwitterions containing a cyclopropylcarbonium ion grouping as transient intermediates in photochemical rearrangements of esters of 3-cyclopropylpropenoic acids (197).

C. Nmr Spectra

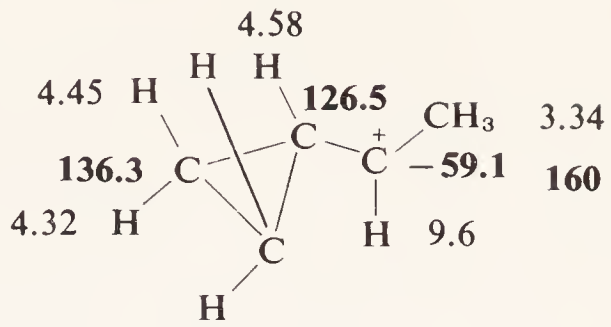
The extension of observations of proton nmr spectra to the methylcyclopropylcarbonium ion (182,198) and to the unsubstituted cyclopropylcarbonium ion (**3**) (182), and the observations of ^{13}C spectra (182) of cyclopropylcarbonium ions represent major advances.

Proton and ^{13}C (boldface) chemical shifts measured by Olah and his co-workers for **3** and **4** and under the same conditions for the previously observed dimethylcyclopropylcarbonium ion (**20**) are indicated on the structures (182).* The major features of the ^{13}C spectra of **20** and **4** can be predicted on the basis of their proton spectra: (*1*) the methyl carbons of **20** exhibit distinct absorptions, (*2*) the absorptions of the methyl carbons of **20** are considerably upfield from that (-135.4) of the methyl carbons of

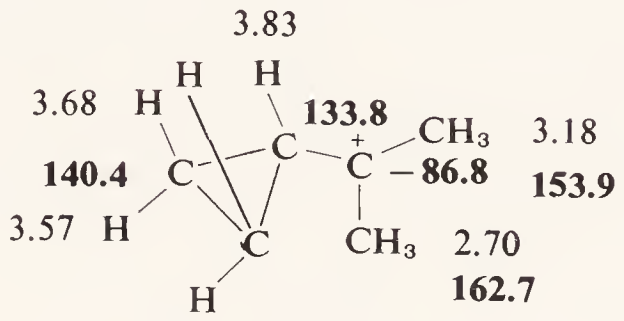
* The spectra were taken at $-70°$ of solutions generated by dissolving the corresponding alcohols in SbF_5–SO_2ClF. Proton chemical shifts are expressed as ppm downfield from external TMS, and ^{13}C chemical shifts as ppm upfield from CS_2.



(3)



(4)



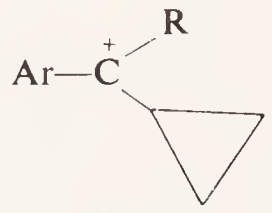
(20)

the *t*-butyl cation, (*3*) the absorption of the β-cyclopropyl carbons of **20** is considerably downfield from the value (196.3) exhibited by the carbons of cyclopropane, and (*4*) the spectra of **4** and **20** differ in ways generally consistent with the difference in their stabilities. Similarly, the proton nmr spectrum of **4** differs from that of **20** in ways expected because of the difference in their stabilities. It is probable that only one bisected conformation of **4**—presumably that shown—is present in significant amounts, since only single sets of ^{13}C and of proton absorptions are noted. The small magnitude ($J = 1.2$ Hz) of the coupling constant between the methyl hydrogens of **20** is suggested as a further indication that considerable positive charge has been absorbed by the cyclopropyl ring (199). A coupling constant of $J = 0.9$ Hz between the α-cyclopropyl hydrogen and the upfield methyl hydrogens of **20** is consistent with a bisected structure and with the previous assignment of the upfield methyl absorption to that methyl group lying over the cyclopropyl ring (199).

The ^{13}C and proton nmr spectra of **3** differ significantly from those of **4** and **20**. The ^{13}C and proton spectra indicate that the three methylene carbons are identical, at least on the nmr time scale, but that the two hydrogens of each methylene group are different. The absorptions of the two groups of methylene hydrogens are coupled with the lone hydrogen ($J = 6.5$ Hz for the absorption at 4.21 and $J = 8.0$ Hz for the absorption at 4.64), but surprisingly, they are not coupled with each other. The equivalence in the nmr spectra of the methylene groups is not surprising, since it is known from solvolysis studies (Section VI) that these nonequivalent groups nevertheless equilibrate rapidly. Such equilibration should lead to absorptions that are weighted averages of those charac-

teristic of the interconverting structures.* However, both the ^{13}C and the proton chemical shifts differ markedly from the values that would be extrapolated from values of **20** and **4**. For example, the predicted ^{13}C shift for the methylene carbons would be about 100, but 137.9 is observed; similarly, the predicted proton chemical shift of the methylene hydrogens would be ~7, but 4.21 and 4.64 are observed. The structural problem of the cyclopropylcarbonium ion is discussed in Section XI-H.

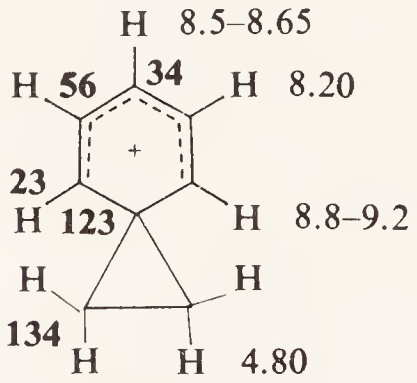
Other nmr observations include the proton spectra of a series of ions of structure **188** (200).† A full account of the study of the proton nmr spectra



(188)

R = H, CH_3, or OH

of "phenonium" ions **36** and **37** has appeared (201), and proton (201–205) and ^{13}C (205) spectra of other phenonium ions, including the parent ion **189** (205), have been reported. Proton and ^{13}C (boldface) chemical shifts of **189** are indicated on the structure (205).‡ Absorptions of the hydroxyl hydrogens of several hydroxycyclopropylcarbonium ions (**190**) have been



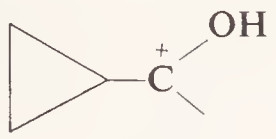
(189)

observed (200,206). At low temperatures in FSO_3H–SbF_5–SO_2, exchange of the hydroxyl hydrogen with hydrogens of the medium is sufficiently slow that their nmr absorptions are not averaged. The chemical shifts of the hydroxyl hydrogens of these cyclopropylcarbonium ions generally are

* Such equilibration in **4** and **20** would have little effect on the spectra, since the structures that place the most charge on the carbons bearing the methyl substituents would dominate in the equilibrium mixtures.

† The spectrum of **23** recorded at $-80°$ was essentially the same as that reported previously (Table I) except for nonequivalence of the hydrogens *ortho* to the formally positive carbon; the spectrum of **17** differed significantly from that reported previously.

‡ Proton chemical shifts are expressed as ppm downfield from external TMS, and ^{13}C chemical shifts as ppm upfield from CS_2.



(190)

upfield from those of similar alkylcarbonium ions, consistent with the assumption that considerable charge is absorbed by the cyclopropyl rings. Nmr spectra of several bicyclo[3.1.0]hexenyl cations have been reported (191–194,207). The proton chemical shifts* of **186** (191) and **187** (192) are indicated on the structures.

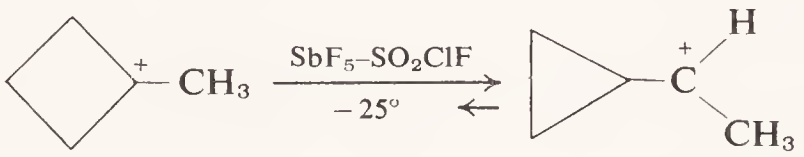
NOTE ADDED IN PROOF. In contrast to the only slight resolution of fine structure noted in a spectrum of the tricyclopropylcarbonium ion (**6**) taken at 60 MHz (Section III), Olah (private communication) has obtained a spectrum at 300 MHz that exhibits discrete absorptions for the α- and β-hydrogens.

D. Ultraviolet Spectra

Ultraviolet spectra (33) of some aryl-substituted cyclopropylcarbonium ions not included in Table III are reviewed by Olah, Pittman, and Symons in Chapter 5 of Volume I. The ultraviolet spectra of two phenonium ions have been reported (204).

E. Stabilities

Evidence for the stabilities of cyclopropylcarbonium ions has continued to accumulate from kinetic studies of reactions in which such ions are intermediates, but from only a few studies of equilibria involving cyclopropylcarbonium ions. At $-25°$, **191** or **3** isomerizes to an equilibrium



(191) **(3)**

mixture containing only about 2% of **191**; therefore, the secondary cyclopropylcarbonium ion is more stable ($\Delta F \sim 2$ kcal/mole) than the tertiary cyclobutyl cation (198). A concentration of sulfuric acid required for half-formation of the methylhydroxycyclopropylcarbonium ion (**40**) in close agreement with that in Table III is obtained from a plot of chemical shift of the methyl proton nmr absorption against the strength of the sulfuric acid (208).† A pK for the hydroxydicyclopropylcarbonium ion (**39**) in

* The chemical shifts are in ppm downfield from internal dichloromethane taken as 5.30.

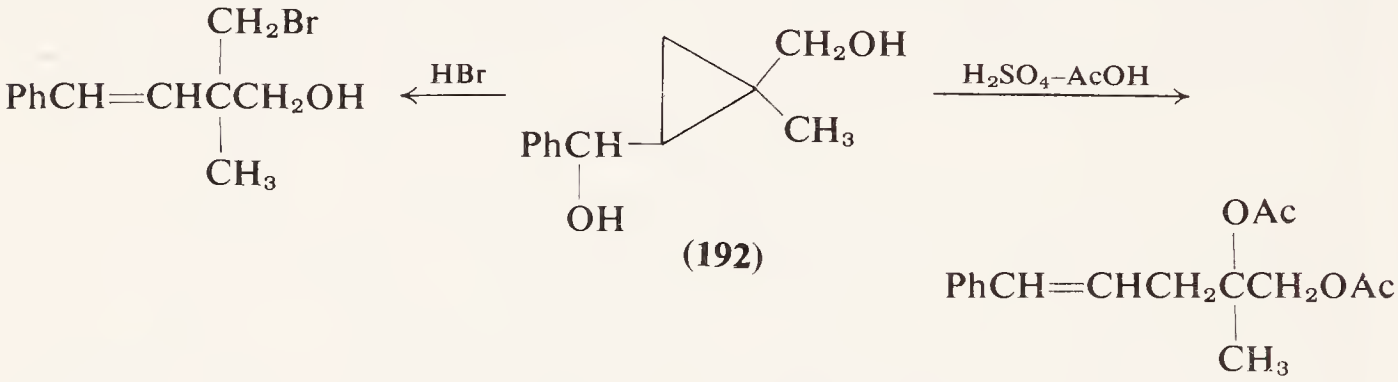
† The problem encountered with some other hydroxycyclopropylcarbonium ions, described in the footnote on page 1223, apparently was not serious.

good agreement with that in Table III was obtained from a correlation between pK and the heat of transfer of carbonyl bases from carbon tetrachloride to fluorosulfonic acid (209).

F. Reactions

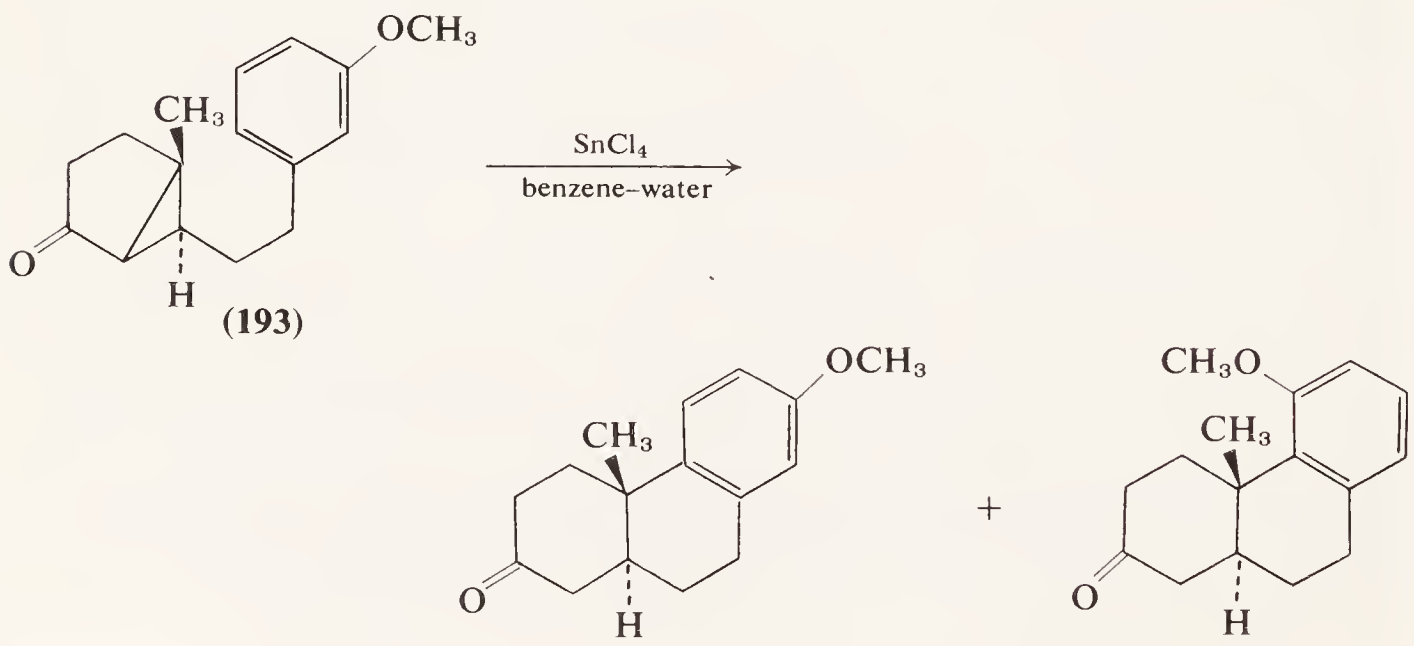
The characteristic reactions of cyclopropylcarbonium ions outlined in Section VI are sufficient to explain the gross structures of the products obtained in recently reported reactions involving cyclopropylcarbonium ions. However, newer studies have revealed some finer aspects, particularly stereochemistries, of three rearrangements observed for cyclopropylcarbonium ions: ring opening leading to 3-buten-1-yl products, ring expansion leading to cyclobutyl products, and interconversion of methylene groups leading to isomeric cyclopropylmethyl products.

Whether ring opening of cyclopropylcarbonium ions to 3-buten-1-yl systems is unimolecular or concerted with attack by a nucleophile is discussed in Section VI, with the conclusion that examples of both processes probably exist. The direction of ring cleavage of some compounds (68,180,210), e.g., **192** (210), is found to depend on the reagent and

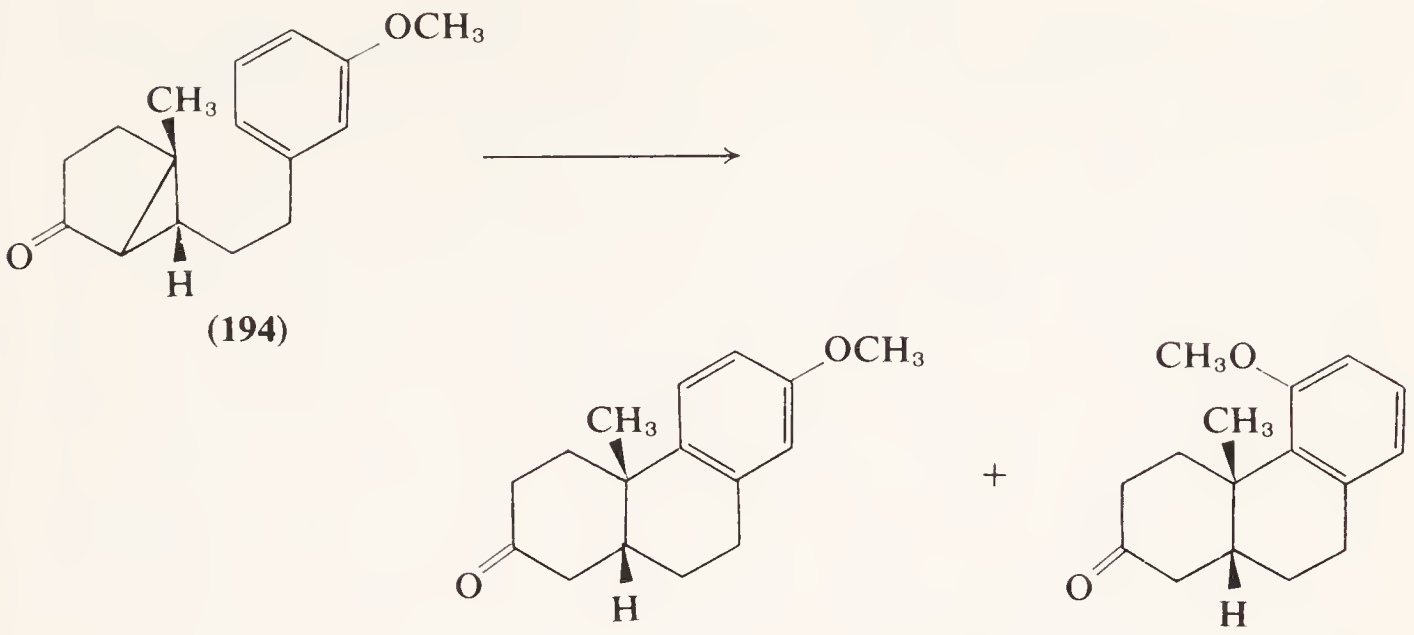


(192)

conditions. This variation could be due to the different nucleophilicities of the reagents involved—attack of a cyclopropylcarbonium ion (at the less hindered carbon) by the strongly nucleophilic bromide but not by the less nucleophilic acetic acid being faster than unimolecular ring opening (to the more stable acyclic ion).



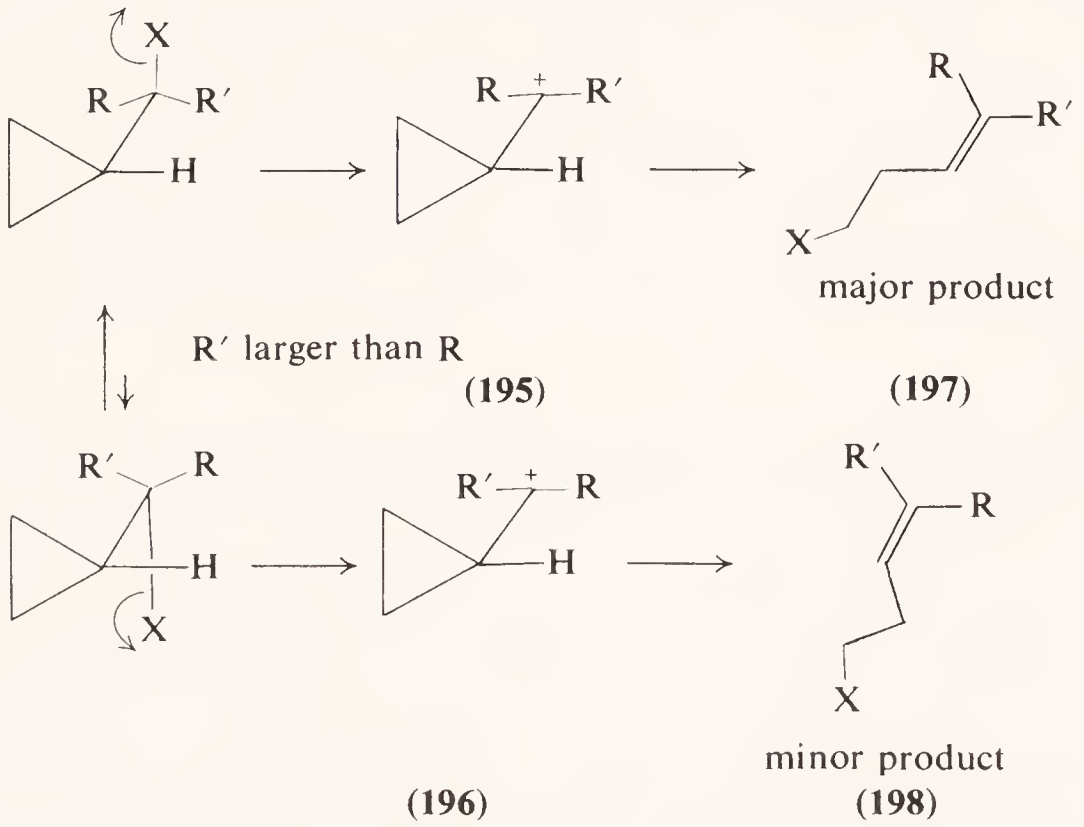
(193)



(194)

Examples have been reported of isomerizations to 3-buten-1-yl systems in which a double bond or aryl ring within the molecule acts as the nucleophile, leading to synthesis of a new ring (211,212). The stereospecificity of the ring closures of **193** and **194** suggests that involvement of the aryl ring is concerted with cleavage of the cyclopropyl ring (211).

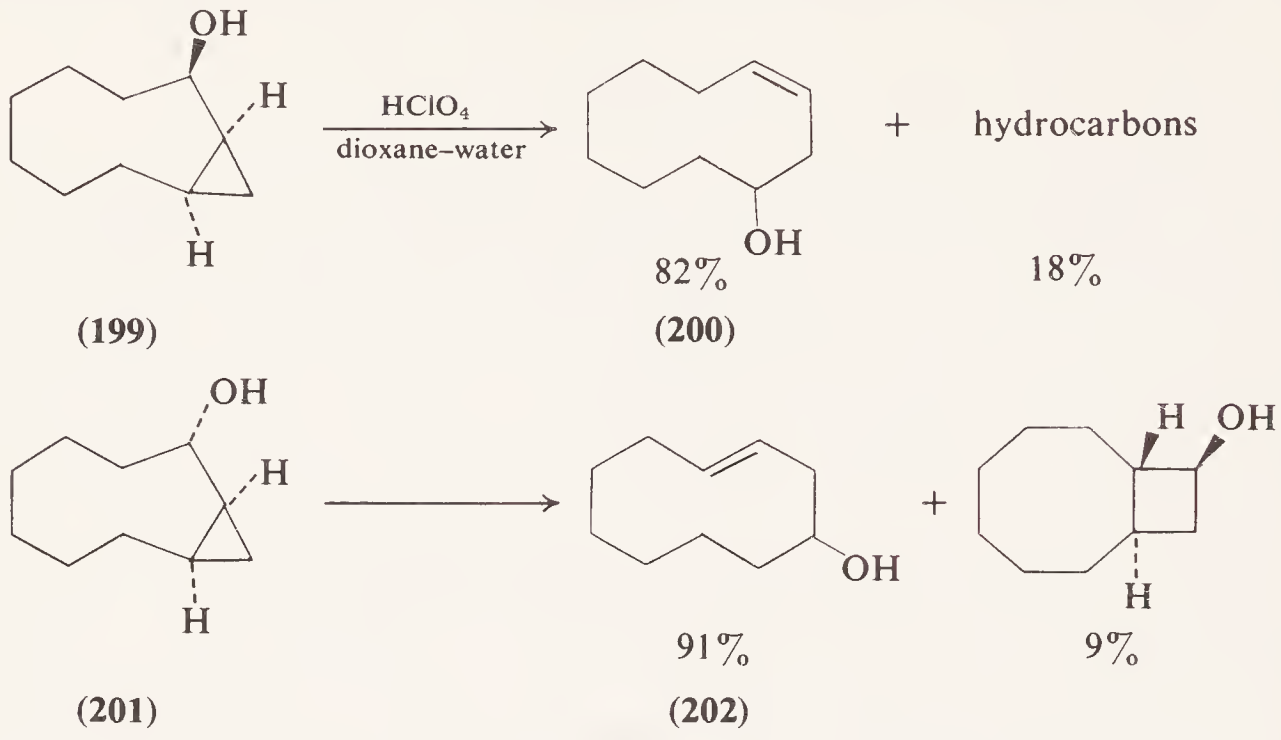
The stereochemistry of double-bond formation in ring opening has been studied in several systems and has been partially reviewed (213). Cleavages of simple cyclopropylmethyl systems furnish product mixtures in which the dominant isomers (**197**) have the bulkier groups *trans* (214). These results



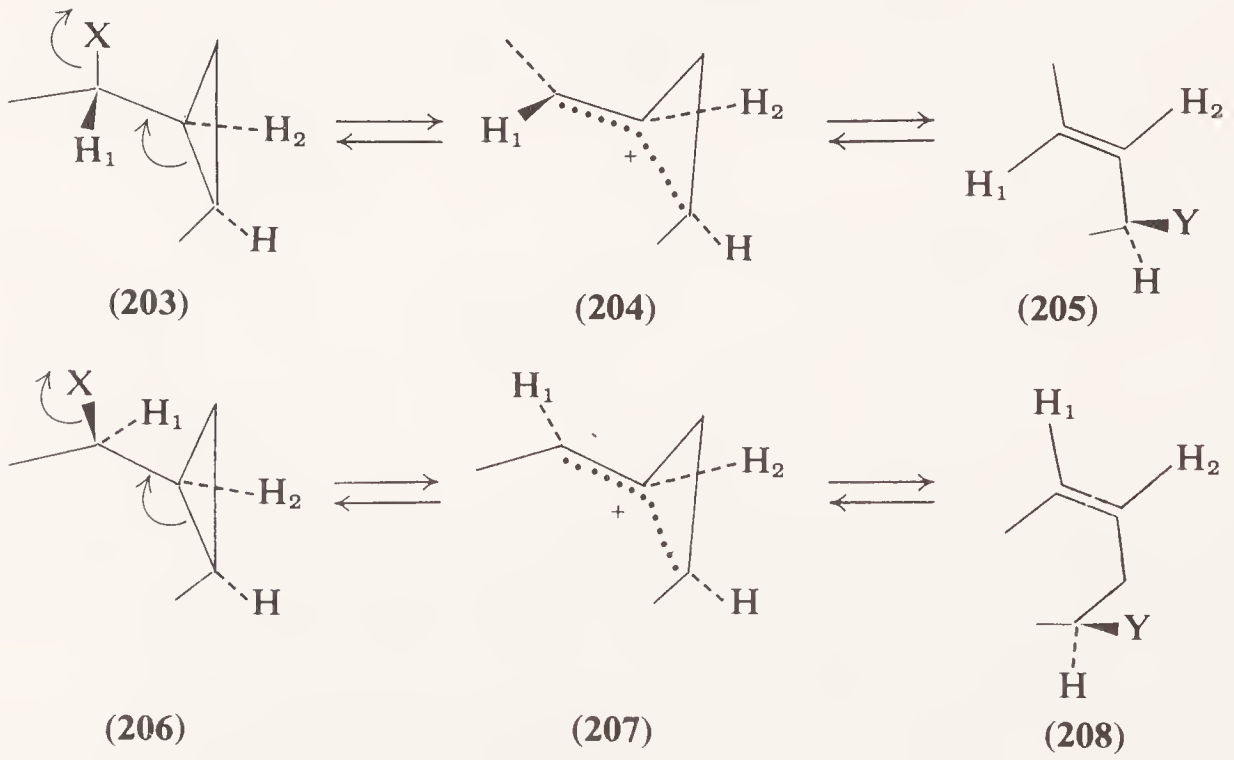
can be rationalized in terms of more rapid formation of bisected cation **195** than of **196**, because less strain is involved in a transition state for its formation. The isomeric cations should not interconvert, and their opening should be stereospecific.

In cationic reactions of *syn*- and *anti*-bicyclo[7.1.0]-2-decyl (215–217) and bicyclo[8.1.0]-2-undecyl (215,216) derivatives, alkenes are formed with

high stereospecificity. For example, alkene products **200** and **202** are formed from **199** and **201** with stereospecificities exceeding 99.7% (217).

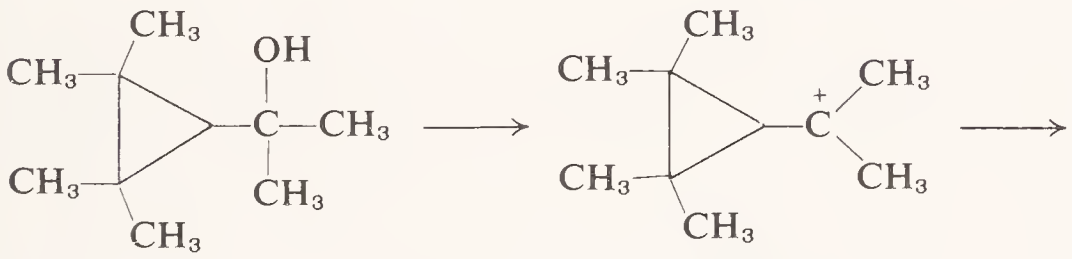


It is apparent that the *syn* and *anti* derivatives give rise to discrete ions that do not interconvert before product formation and do open stereospecifically. The cations could differ as do **195** and **196**. Cations isomeric in this way would not be possible in smaller ring systems. In fact, solvolysis reactions of *syn*- and *anti*-bicyclo[*n*.1.0]-2-alkyl derivatives in which *n* is 8 (215,216), 7 (215–217), and 6 (218,219), lead to significantly different product mixtures; but this difference diminishes when *n* is 5 (220) and vanishes when *n* is 4 (103,221) or 3 (222). Winstein and his co-workers proposed that the isomeric cations have unsymmetrical homoallylic structures **204** and **207** in which the charge is delocalized predominantly to the more substituted β-cyclopropyl carbon, the discrete cation obtained

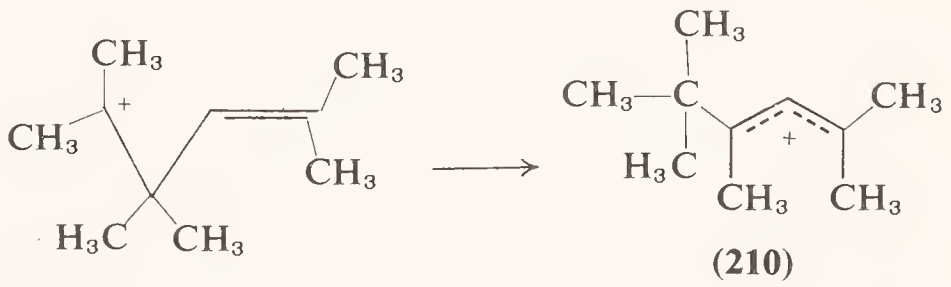


from each epimer resulting from cation formation occurring from a conformation that permits using the more substituted arm of the cyclopropane ring as the leaving group departs (215,217). Structures **204** and **207** also explain the observations that solvolysis products of unrearranged structure (**203** and **206**) are formed with retention of configuration in the larger (but not in the smaller) ring systems and that, in a suitably substituted system (216), the nucleophile is observed to add with inversion in forming **205** and **208**. However, the effect of an alkyl substituent on stability of the cation, if solely responsible for the formation of isomeric cations, must be much greater than observed in the data in Table VI.* Perhaps conformational factors on stabilities of transition states for ionization (and its reverse) are responsible at least in part for the stereospecificities observed.

Some observations have been made concerning the isomerizations of cyclopropylmethyl to allyl cations. Attempts to form the hexamethylcyclopropylcarbonium ion (**209**), even at $-125°$, lead to observation only of the 1-*t*-butyl-1,3,3-trimethylallyl cation (**210**), perhaps formed via the



(209)

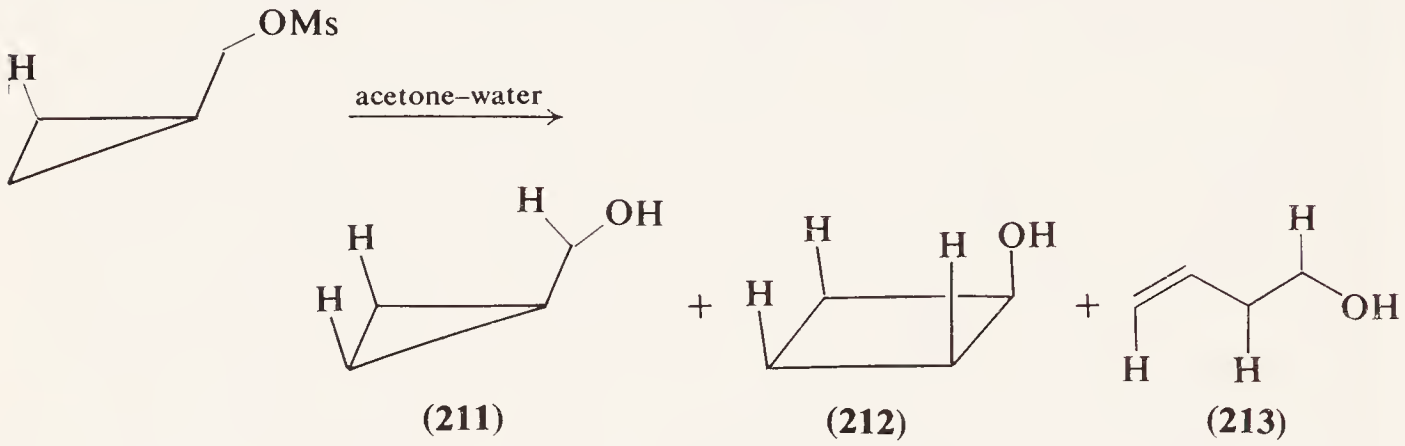


(210)

acyclic intermediate shown (224). The dimethylcyclopropylcarbonium ion (**20**) is much more stable to rearrangement than is **209**, but at higher temperatures rearranges to the 1,1,3-trimethylallyl cation at rates dependent on the medium, $\Delta F^{\ddagger} = 14.3$ kcal/mole in FSO_3H–SO_2ClF but ~18 kcal/mole in SbF_5–SO_2ClF (224). No deuterium was incorporated into **210** or into the 1,1,3-trimethylallyl cation generated in FSO_3D–SO_2ClF, eliminating mechanisms for their formation that involve protonation of the cyclopropane ring.

* It has been suggested that cyclopropylmethyl dinitrobenzoate (Table VI) may solvolyze with substantial acyl-oxygen cleavage (217). However, the observation that four β-methyl groups have nearly as great an effect on the solvolysis of this system as on a tertiary cyclopropylmethyl *p*-nitrobenzoate (223) seems contrary to this proposal.

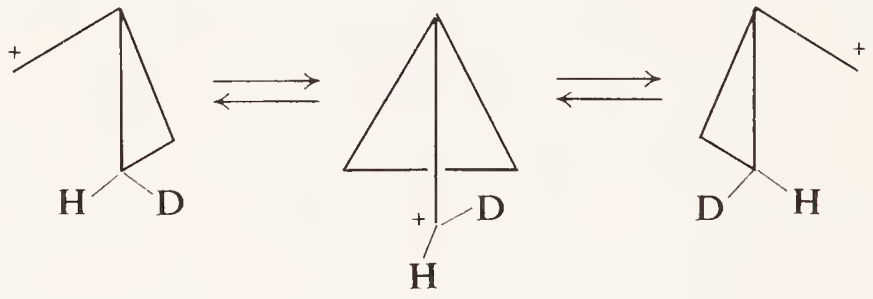
In cationic reactions of cyclopropylmethyl systems, the cyclopropylmethyl products resulting from interconversion of methylene groups and the cyclobutyl products are formed with high stereoselectivity. In a particularly elegant experiment, a derivative of the parent system, deuterated except for one position, was hydrolyzed to give products **211–213** in which, within experimental error (large for the vinyl H in **213**), the hydrogen was only at the indicated positions (225).



(211) **(212)** **(213)**

OMs = methanesulfonate

The interconversion of methylene groups, represented with bisected structures **214–216**, must proceed with inversion of the migrating carbon at each rearrangement. This stereochemistry is consistent with the con-

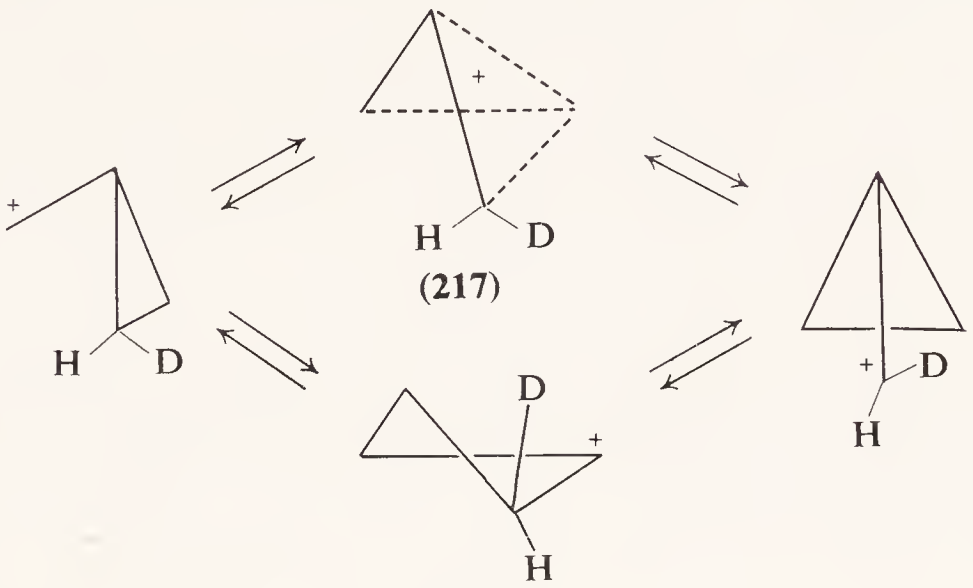


(214) **(215)** **(216)**

clusion from nmr observations that the *cis*- and *trans*-methylene hydrogens retain their identity on the nmr time scale even though the methylene carbons are equivalent. Inversion at the migrating carbon has been shown in other systems, e.g., by appropriate deuterium labeling in the cyclopropylmethyl to cyclopropylmethyl (**92** → **93**) rearrangement in the conversion of thujopsene to widdrol (226). Variable temperature studies of nmr spectra of bicyclo[3.1.0]hexenyl cations provide evidence for a similar rearrangement (191,193,207,227). For example, at higher temperatures, the absorptions due to the three types of methyl groups on the cyclopentenyl ring of **186** coalesce to a single absorption, presumably because they have become equivalent on the nmr time scale as a result of rapid rearrangement of the methylene carbon (191). However, the absorptions of the *syn*- and *anti*-methyl groups on the methylene carbon remain discrete, indicating that inversion at this carbon accompanies each migra-

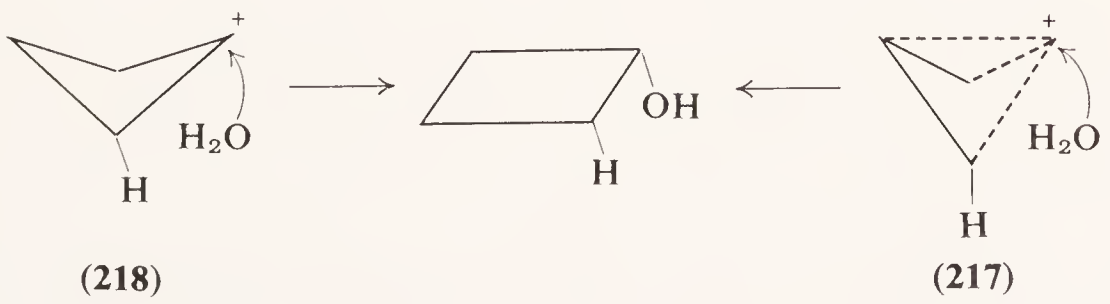
tion,* as predicted for suprafacial 1,4-sigmatropic rearrangements (229). It has been estimated that the rate of rearrangement of **186** with inversion at the migrating carbon exceeds that with retention by $>50{,}000$ (191).

The rearrangement of methylene groups might pass through a transition state or intermediate resembling **217**. Alternatively, the rearrangement might proceed via a cyclobutyl cation if the cation is "puckered" (**218**)



rather than planar to preserve the stereochemical distinction between methylene substituents (187).

The stereoselectivity observed in the formation of **212** from **210** also is noted in other cationic interconversions of cyclopropylmethyl and cyclobutyl derivatives (217–219,230). The question of the number and structures of cationic intermediates linking cyclopropylmethyl and cyclobutyl reactants and products is not yet resolved. However, planar cyclobutyl cations cannot be intermediates because they would lead to loss of stereochemistry. The stereochemical observations would be rationalized if cyclobutyl products were formed from puckered (187) cyclobutyl cations, e.g., **218**, or from **217**. The 3-buten-1-ol (**213**), also formed stereoselectively, could arise from ring opening of the cyclobutyl cation as well as from that of the cyclopropylmethyl cation (187,225).



* Rearrangement with inversion at the migrating carbon also is indicated by studies of products of reactions in which bicyclo[3.1.0]hexenyl cations are intermediates (228).

A thorough study has shown that, on treatment with aqueous perchloric acid, methylcyclopropylmethanol (**71**) yields a significant amount of *trans*-2-methylcyclobutanol, which is converted much more slowly to the expected acyclic alkenols (231). In Section VI M. Julia's finding was noted that **71** in aqueous perchloric acid furnishes some *trans*-2-methylcyclobutanol; this suggests that transient cyclobutyl products may have formed but were not noticed in other reactions.

On the basis of further work with other systems (reviewed in Ref. 232), it now seems more certain that the bicyclobutane formed in the reaction of base with the *p*-toluenesulfonylhydrazone of cyclopropanecarboxaldehyde arises from the cyclopropylcarbonium ion.

G. Geometry

Additional evidence supports the conclusion (Section VII) that the bisected geometry maximizes the conjugation between a cyclopropyl group and a positive carbon.

By double resonance studies, activation parameters of $E_a = 13.7 \pm 0.4$ kcal/mole and $\log A = 12.2 \pm 0.4$ have been determined for the interconversion of the methyl groups of the cyclopropyldimethylcarbonium ion (**20**) (199). Since interconversion might occur by a process other than rotation around the cyclopropyl–C^+ bond, these parameters represent a lower limit to the energy difference between the most stable (presumably bisected) geometry for this ion and the geometry [presumably "perpendicular" (233) (**142**)] of the highest energy attained by rotation.

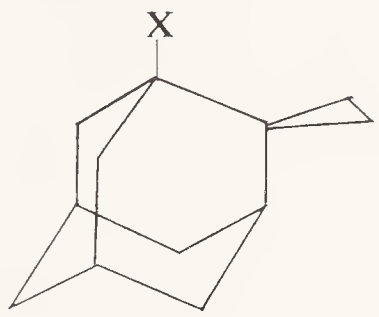
Additional evidence that bisected structures are preferred in compounds in which a cyclopropyl ring is attached to a neutral trigonal carbon supports the assignment of bisected structures to cyclopropylcarbonium ions. Microwave spectra of cyclopropanecarboxaldehyde (234) and the acid fluoride of cyclopropanecarboxylic acid (235) are consistent with bisected structures and with barriers to rotation of 4.4 and 5.2 kcal/mole, respectively. An electron diffraction study of gaseous vinylcyclopropane suggests an equilibrium mixture at 20° of 75 ± 6% of the *s-trans* (bisected) form and 25 ± 6% of a gauche form (236).* Nmr studies of cyclopropyl ketones (238) and of esters of 3-cyclopropylpropenoic acids (239) have been interpreted in terms of the dominance of bisected conformations. An X-ray crystallographic study of cyclopropanecarboxamide shows that it has a bisected conformation (240) in the crystal.

Results concerning the structures of cyclopropyl-substituted free radicals are significant to the extent that these species resemble the more electron-

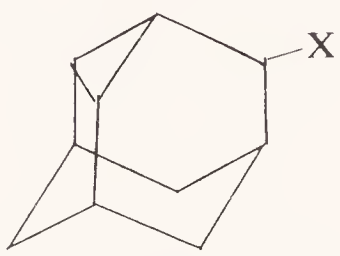
* This conclusion seems more certain than the conflicting inferences from nmr studies of vinylcyclopropanes, reviewed in Ref. 213; see recent publications (237).

deficient carbonium ions. From its recently observed electron spin-resonance (esr) spectrum, it was concluded that the cyclopropylmethyl radical has a bisected conformation and that a portion of the spin (~ 5–10%) is donated to an antibonding ring orbital antisymmetric with respect to the plane of symmetry (241). From esr and endor investigations of neutral and charged π radicals with cyclopropyl substituents, it was also concluded that the cyclopropyl group preferentially adopts a bisected conformation (242). This preference is accentuated by positive but attenuated by negative charge at the trigonal carbon to which the cyclopropyl group is attached. A strong preference for the bisected conformation was noted also in cyclopropyl-substituted semidiones (243).

Further information about the preferred geometry of cyclopropylcarbonium ions is provided by solvolysis studies of systems of restricted geometry; a few of these are mentioned here. In contrast to the rate accelerations of $\sim 10^4$–10^5 typical of cyclopropyl groups, the cyclopropyl group in adamantyl system **219** decreases solvolyses rates to only 10^{-2}–



(219)

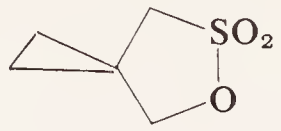


(220)

10^{-3} those of model compounds (233,244). Therefore, the constraint of the cyclopropyl ring to a perpendicular geometry in this system leads to a deceleration of $\sim 10^7$, corresponding to an energy difference of ~ 10 kcal/mole between the transition states leading to bisected and perpendicular ions, and indicating an energy difference at least as great between the ions. A linear correlation of $\log k$ with σ_I for a series of compounds including **219** suggests that the inductive effect of the cyclopropyl group is the major factor in determining its effect on the solvolysis rate of **219**, all conjugative interaction having been suppressed (244). In fact, comparison with the data of Table VIII suggests that, in spite of the flanking methyl substituents, the cyclopropyl group of 2-(3,5-dimethyl-4-cyclopropyl)-2-chloropropane still exerts about one-half its maximum conjugative stabilization during hydrolysis (244).* By contrast, the cyclopropyl group constrained to a bisected geometry in adamantyl system **220** exerts a normal, rate-accelerating effect on a solvolysis reaction (245).

* Presumably some conjugative intersection remains also in ion **106**.

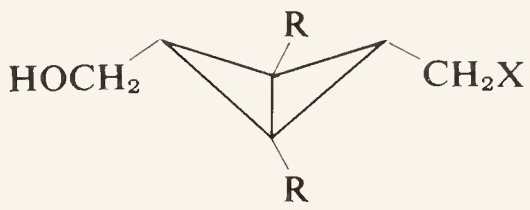
The considerable solvolytic reactivity of a vinyl halide of structure **182** is not surprising, since the resulting linear vinyl cation (**181**) is constrained to a bisected geometry and the orientation of the leaving group permits maximum conjugative interaction during ionization. By contrast, hydrolysis of sultone **221** occurs without significant acceleration by the cyclo-



(221)

propyl group (246); even though there are no constraints on the geometry of the cyclopropylcarbonium ion after its formation, the orientation of the leaving group does not permit concerted formation of a bisected structure.

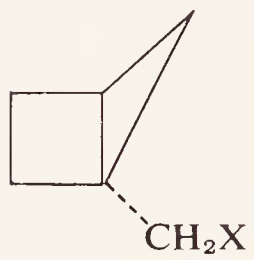
Systems **222** (247) and **223** (249) can be added to Table IX, in which the solvolysis rates had been interpreted in terms of changes of bond lengths during ionization.*



(222)

relative rate (247,248) ~ 0.6

R = $CH_3CH_2CH_2$



(223)

relative rate 400,000

It has been observed that charge-transfer frequencies of complexes of substituted benzenes, including cyclopropyl and several substituted cyclopropyl groups as substituents, correlate with the effects of the substituent groups on the rates of solvolysis reactions (250). Since the absorption process is vertical, it was concluded that a cyclopropyl group must be able to effectively delocalize a developing positive charge without alteration of its geometry or motion toward the positive center.

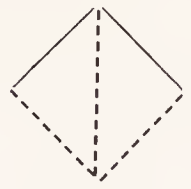
H. Bonding

Additional evidence indicates that cyclopropyl is significantly electron withdrawing when compared with other alkyl groups (251), so that absorption of charge by cyclopropyl groups must be solely by conjugation.

A few of the conclusions about possible structures for the cyclopropylcarbonium ion and for species involved in its reactions that have been reached from molecular orbital calculations, using methods that consider σ electrons, are now summarized.

* A fuller account of the work with **116** and further data on systems of structure **115** have appeared (248).

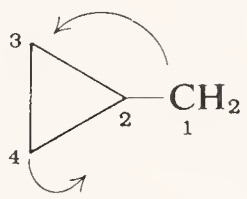
From extended Hückel calculations, Baldwin and Foglesong found that the bisected conformation (**141**) of the cyclopropylcarbonium ion is 9 kcal/mole more stable than the perpendicular conformation (**142**) (252). Energies of the "asymmetrical bicyclobutonium ion" (**217**) in several



(**217**)

geometries were calculated, and it was suggested that ions of this structure intervene in the cyclopropylmethyl–cyclopropylmethyl and cyclopropylmethyl–cyclobutyl interconversions.

From CNDO calculations, Wiberg and Pfeiffer found that the bisected conformation (**141**) is 20 kcal/mole more stable than the perpendicular conformation (**142**) (253,254). However, a 30° rotation from the bisected conformation increased the energy only by about 4 kcal/mole (253). Again from CNDO calculations, Wiberg and Szeimies found that a path (**224**) for the cyclopropylmethyl–cyclopropylmethyl interconversion in which C-1 approaches C-3 from the backside as the C-3–C-4 bond



(**224**)

is broken is of higher energy than a path (also consistent with the stereochemical results) proceeding by a puckered cyclobutyl cation (187). Isomerization of the cyclopropylmethyl to the puckered cyclobutyl cation by bending C-1 toward C-3 has only a small activation energy. It also was concluded that disrotatory opening and closing is preferred for the cyclobutyl to 3-buten-1-yl interconversion. Trindle and Sinanoğlu reached the same conclusions about the cyclobutyl to cyclopropylmethyl and the cyclobutyl to 3-buten-1-yl interconversions by application to several $C_4H_7^+$ species of a reformulation of the Woodward-Hoffmann approach in the language of localized (CNDO) orbitals (255).

From an *ab initio* calculation, Radom et al. (256) found that the bisected conformation (**141**) of the cyclopropylcarbonium ion is 17.5 kcal/mole more stable than the perpendicular conformation (**142**). Other reports include application of an ASMO-SCF method to **141** and **142** (257); application of CNDO methods to several $C_4H_7^+$ species (258), to the

mono-, di-, and tricyclopropylcarbonium ions (259), to the cyclopropylidenemethyl cation (**181**) (260), and to the 3-buten-1-yl cation (261); and application of extended Hückel and CNDO methods to the 2-phenylethyl to phenonium ion transformation (262).

The conclusions reached in Section VIII that cyclopropylcarbonium ions generally have bisected geometries and that the bonding can be represented by essentially equivalent representations **128** or **140** still seem reasonable. It was noted that the least stable ions, e.g., the parent ion (**3**), were the most likely to have significantly different structures. In fact, the rapidity of rearrangements in many cyclopropylcarbonium ion systems indicates that other structures that must be intermediates or transition states in the rearrangements cannot be of much higher energy. The recently observed nmr spectra of the methylcyclopropylcarbonium ion (**4**) are in accord with a structure essentially the same as those of more stable cyclopropylcarbonium ions. Indeed, the observation of the spectrum of the 1-methylcyclobutyl cation (**191**) shows unequivocally that this related cyclobutyl cation is a discrete species. However, chemical shifts of the nmr absorptions of the unsubstituted cyclopropylcarbonium ion (**3**) differ substantially from those predicted by reasonable extrapolations from the spectra of more stable ions. We are not certain whether these large differences result only from dramatically increased absorption of charge by the cyclopropyl ring in a structure otherwise similar to those of the more stable ions, or instead, result from a significantly different structure for the parent ion.

Although symmetrical bisected structures (**128** or **140**) may generally be most stable, it was recognized in Section VIII that geometric factors or substituent effects in some systems may favor other structures. Additional evidence is in accord with the conclusion that 7-norbornadienyl and 7-norbornenyl cations have bicyclobutonium-like structures—**158** and **162**, respectively—presumably because of favorable geometrical factors (263, 264). It was earlier concluded on the basis of nmr observations that a rapidly equilibrating mixture of **164** and **166** (R = CH_3) was more stable than the corresponding phenonium ion (**165**); the opposite conclusion now is reached on the basis of newer and somewhat different spectra (202).* However, the discussion of effects of substituents on the relative stabilities of **164–166** remains valid; nmr spectra and quenching results indicate that with the introduction of a *p*-trifluoromethyl substituent, which should destabilize **165** but have little effect on **164** and **166**, the equilibrating ions become more stable than the corresponding phenonium ion (202). Additional

* The discussion of the stabilities of **164–166** when R = phenyl no longer is meaningful—the precursor used to prepare the solution employed for nmr observations had the wrong structure (202).

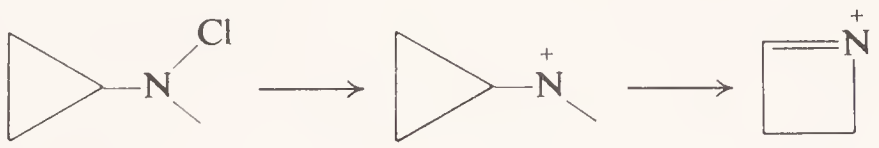
evidence is in accord with the conclusion that the carbonium ion resulting from protonation of cyclooctatetraene has unsymmetrical homoallylic structure **168**, presumably because of the relation of the conjugated system of **168** to that of the aromatic tropylium ion (263). Further proof for this structural assignment comes from the observation in the nmr spectrum of **187** of chemical shifts of H_A and H_B more characteristic of cyclopropylcarbonium ions than are the corresponding absorptions of **168**. This difference is to be expected, since strong delocalization as in **168** of the ring cyclopropyl bond of **187** would lead to a structure resembling the "antiaromatic" cyclopentadienyl cation.

I. Related Studies

It seems evident that the conjugating ability of the cyclopropyl group depends on the degree of electron deficiency of the carbon to which it is attached. A growing body of evidence from kinetic (265) and esr (241–243) studies indicates the presence of conjugation in cyclopropyl-substituted free radicals similar to, yet considerably smaller than, conjugation known in cyclopropylcarbonium ions. Additional thermodynamic evidence supports the previous conclusion that the conjugation of cyclopropyl groups with functions such as vinyl and aryl is quite weak (266), probably weaker than the conjugation of cyclopropyl groups with carbonyl functions (234,235).

Further studies of tricyclopropylborane and of other cyclopropylboranes, neutral species isoelectronic with cyclopropylcarbonium ions, have not provided any further evidence indicating the presence of strong cyclopropyl-boron conjugation (267).

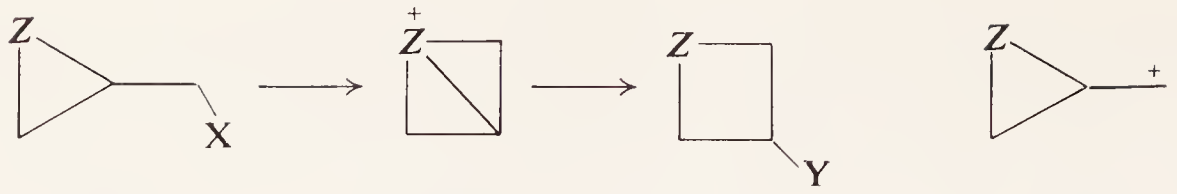
The products obtained from solvolysis of a halide of general structure **225** suggest the intermediacy of **227** (268). Ion **227** might have formed from rearrangement of a discrete cyclopropylnitrenium ion (**226**), isoelectronic



(225) **(226)** **(227)**

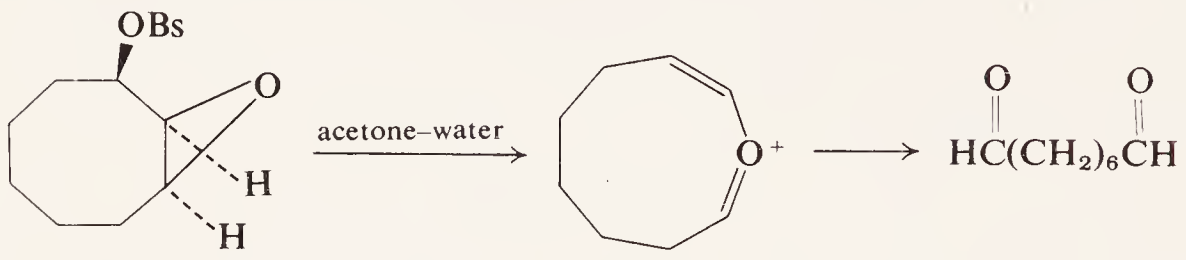
with a cyclopropylcarbonium ion, although alternatively, **226** might only contribute to a transition state for a rearrangement to **227** that is concerted with ionization of **225**.

Studies of solvolysis reactions of heteroatom systems of general structure **228** where $Z = 0$ (269,270), N (271), or S (269,272) indicate that direct participation by nonbonded electrons of the heteroatom to form 1-heterobicyclobutonium ions (**229**) dominates over ionization to heteroatom-containing counterparts (**230**) of the cyclopropylcarbonium ion. Hydrolysis



(228) (229) (230)

of 9-oxabicyclo[6.1.0]non-2-yl *p*-bromobenzenesulfonate (**231**), a system in which direct participation by oxygen would be difficult sterically,* yields



(231)

OBs = *p*-bromobenzenesulfonate

mainly suberaldehyde: this conversion is formally analogous to the cyclopropylmethyl to 3-buten-1-yl transformation; the epimer of **231** yields mainly products of unrearranged skeleton (274). The solvolysis rates of **231** and its epimer are estimated to be only 10^{-6}–10^{-7} those of the corresponding bicyclo[6.1.0]non-2-yl systems, suggesting that, in the absence of direct participation by the oxygen, the oxirane ring is far less effective than a cyclopropyl ring in stabilizing a developing carbonium ion.

A full account of the study summarized in Table XII has been published (275).

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* For a qualitative report of a reaction of another such system, see Ref. 273.

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CHAPTER 26

Cyclopropylcarbinyl and Cyclobutyl Cations

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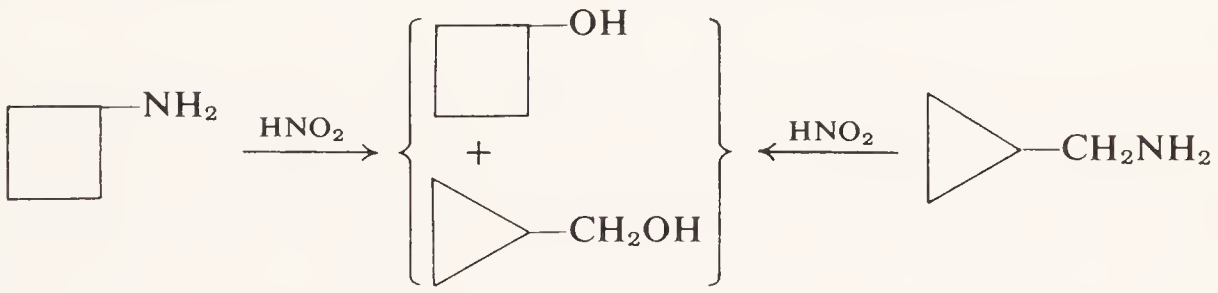
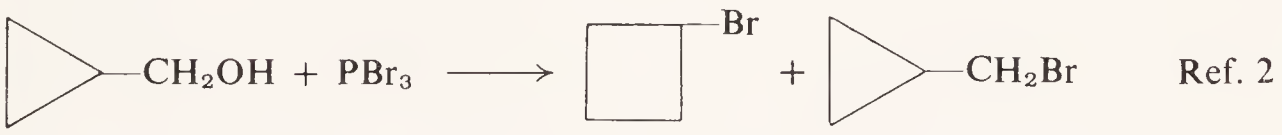
I. INTRODUCTION

In 1907 Demjanov reported the remarkable observation that both cyclobutylamine and cyclopropylcarbinylamine react with nitrous acid to give mixtures of cyclobutanol and cyclopropylcarbinol (1):



Subsequently, a number of similar observations were made. These include:



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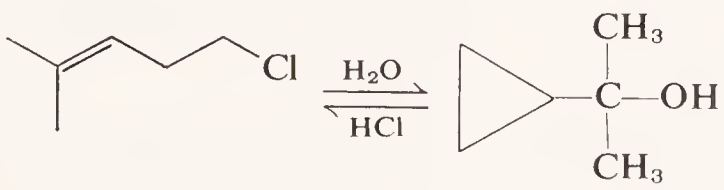

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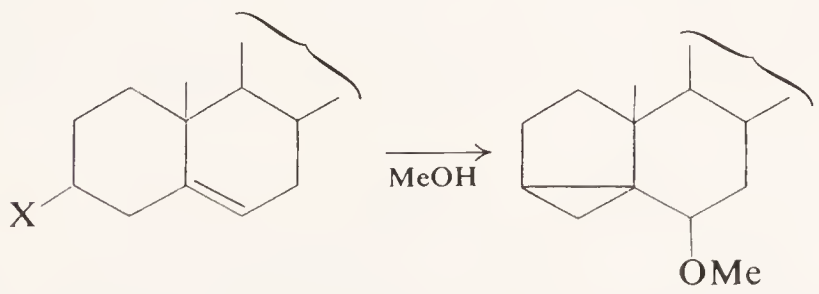

Ref. 4

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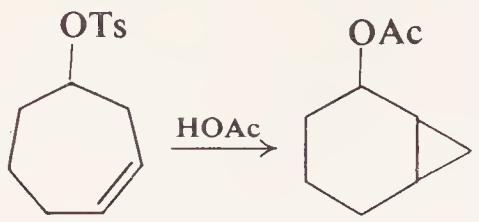
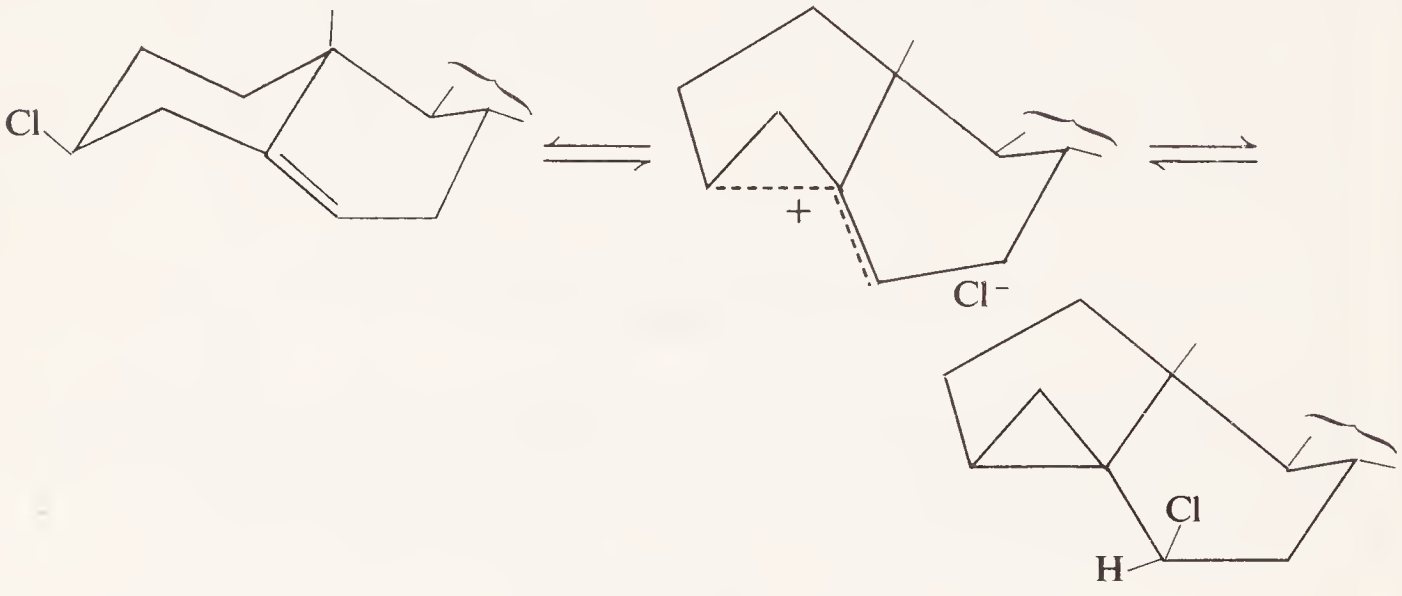


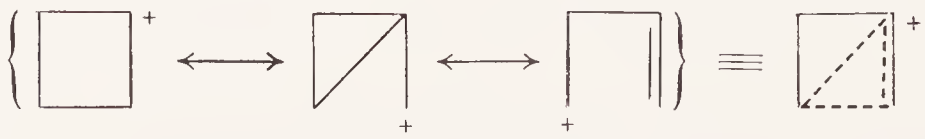
Ref. 5

Up until 1948, no satisfactory explanation had been presented for these interconversions. Starting in 1948, however, a parallel development of two explanations began. Winstein and Adams (6), as well as Dodson and Riegel (7) suggested that the cholesteryl-*i*-cholesteryl rearrangement involved an unsymmetrical homoallylic cation



This concept was developed in a number of papers (8–16) and was reviewed in some detail (17). Because of the relatively small difference in reactivity between the two epimeric-*i*-cholesteryl chlorides, Winstein and Kosower were led to propose that the intermediate cation was a symmetrical homoallylic ion in which the plane containing the cationic center was essentially perpendicular to the plane of the cyclopropane ring (17). They also pointed out the importance of considering the difference in ground state energy between the cyclopropylcarbinyl and allylcarbinyl derivatives and suggested that this would explain the difference in reactivity between the cholesteryl-*i*-cholesteryl system and the dehydronorbornyl-nortricyclyl case.

Roberts and his co-workers suggested that the reaction of cyclobutyl, allycarbinyl, and cyclopropylcarbinyl derivatives proceeded via a common intermediate, which they called a bicyclobutonium ion (18–22). This ion was considered to be a resonance hybrid of the following canonical structures:



The ion so constructed may be attacked at any one of the positively charged sites, giving cyclobutyl, cyclopropylcarbinyl, and allylcarbinyl

derivatives. Evidence for such a formulation includes ^{14}C tracer studies indicating that extensive scrambling of the label occurred after the formation of the ion(s) and kinetic data revealing that both cyclopropylcarbinyl and cyclobutyl derivatives reacted at rates considerably greater than would be expected based on reasonable models.

A third proposal has been made by Brown (23), who suggests that the cyclopropylcarbinyl cation is in equilibrium with the classical cyclobutyl cation and that both react with solvent to give products. The presumably more stable cyclopropylcarbinyl cation is favored at equilibrium, but because of its lower energy, it is less reactive to solvent than the cyclobutyl cation. In this interpretation, the ratio of products is not simply related to the ratio of the cations in equilibrium.

Recently presented nmr evidence clearly shows that the tertiary cyclopropylcarbinyl ions have an unrearranged structure. These data are reviewed in detail in Chapter 25. There remains then the question of the nature of the intermediate cations in the ionization of primary and secondary cyclopropylcarbinyl derivatives, of cyclobutyl derivatives, and of allylcarbinyl derivatives. The evidence relating to these cases is considered here.

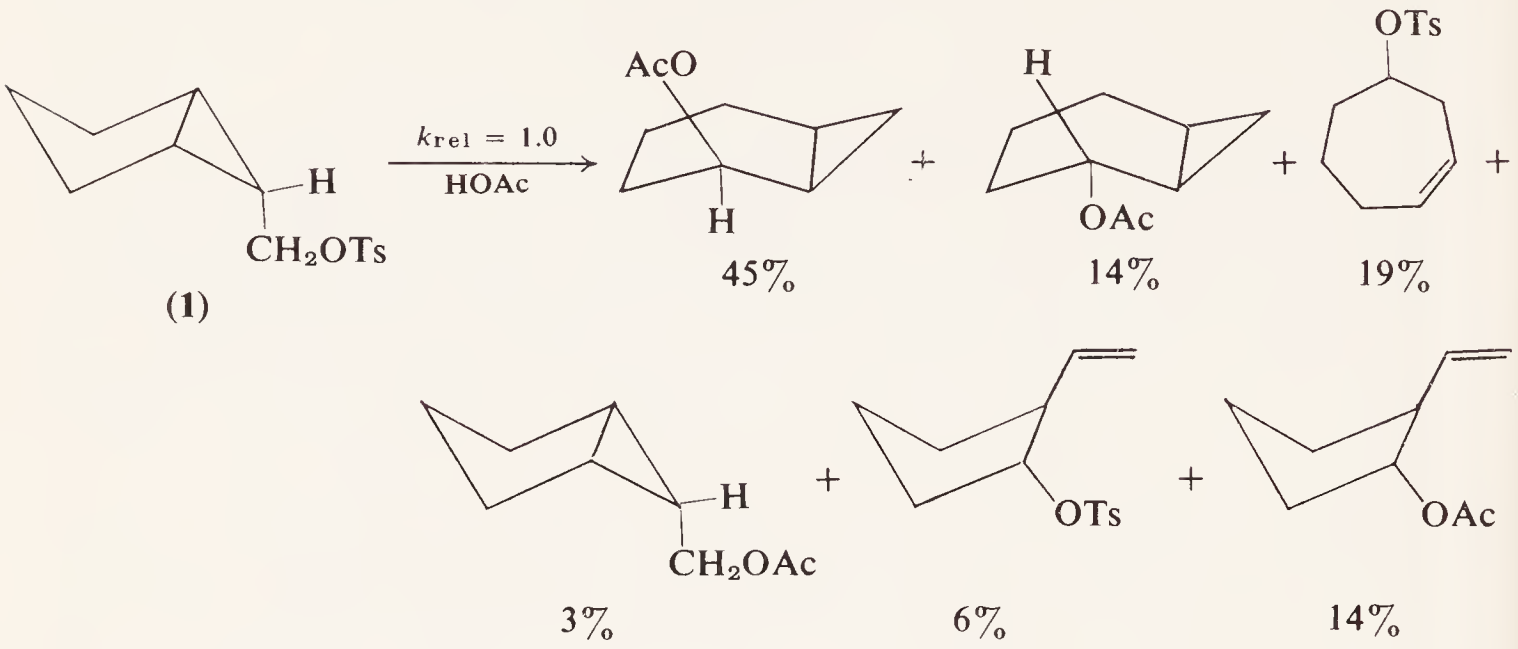
In order to facilitate our discussion, it is desirable first to define a cyclopropylcarbinyl cation, a bicyclobutonium ion, and a homoallylic ion, as the terms are used here. The cyclopropylcarbinyl ion involves the interaction of the cyclopropyl carbon–carbon bonds with the empty *p* orbital of the cationic center, the cyclopropane ring retaining essentially its original geometry. The bicyclobutonium ion has a geometry resembling cyclobutane, with considerable interaction of the C-3 atom with the cationic center. The homoallylic ion has overlap between the empty *p* orbital and the nearest *p* orbital of the double bond. From these definitions, the symmetrical homoallylic ion must be either a bicyclobutonium ion or a cyclopropylcarbinyl cation, depending on its geometry.

The foregoing definitions appear to provide a reasonable basis for discussion, since they are relatively close to a consensus of current usage and since they lead to sufficiently different geometries. It must, of course, be recognized that intermediate geometries are not unlikely and that one or more of the abovementioned ions may have energies considerably higher than the others and thus be of little importance.

II. CYCLOPROPYLCARBINYL DERIVATIVES

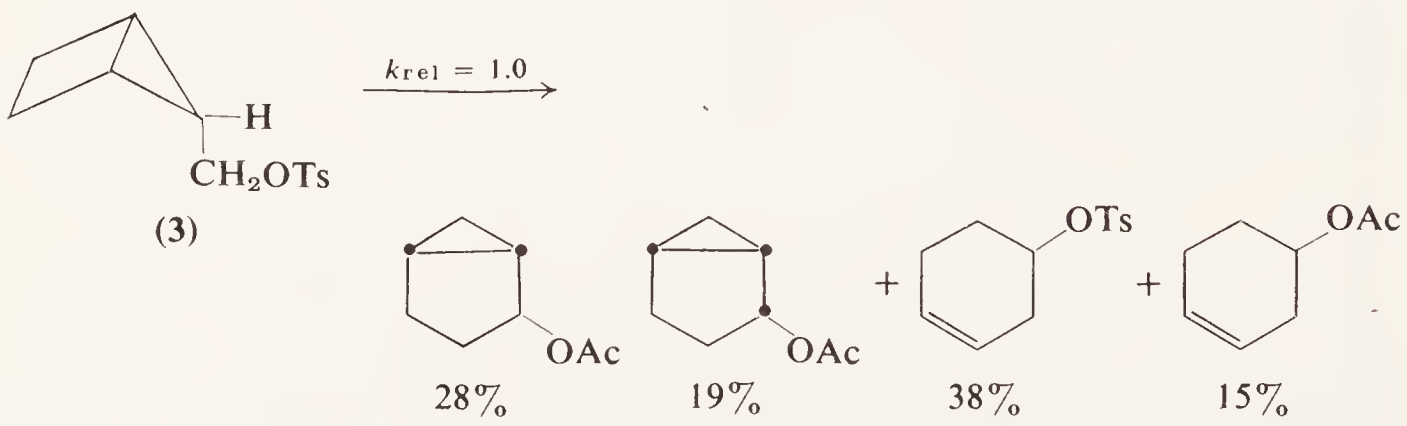
The range of structural modifications possible with cyclopropylcarbinol itself is rather limited. Therefore a study of bicyclic compounds possessing the cyclopropylcarbinyl unit is of considerable significance. It is convenient to begin a discussion of the reactions of this group of compounds

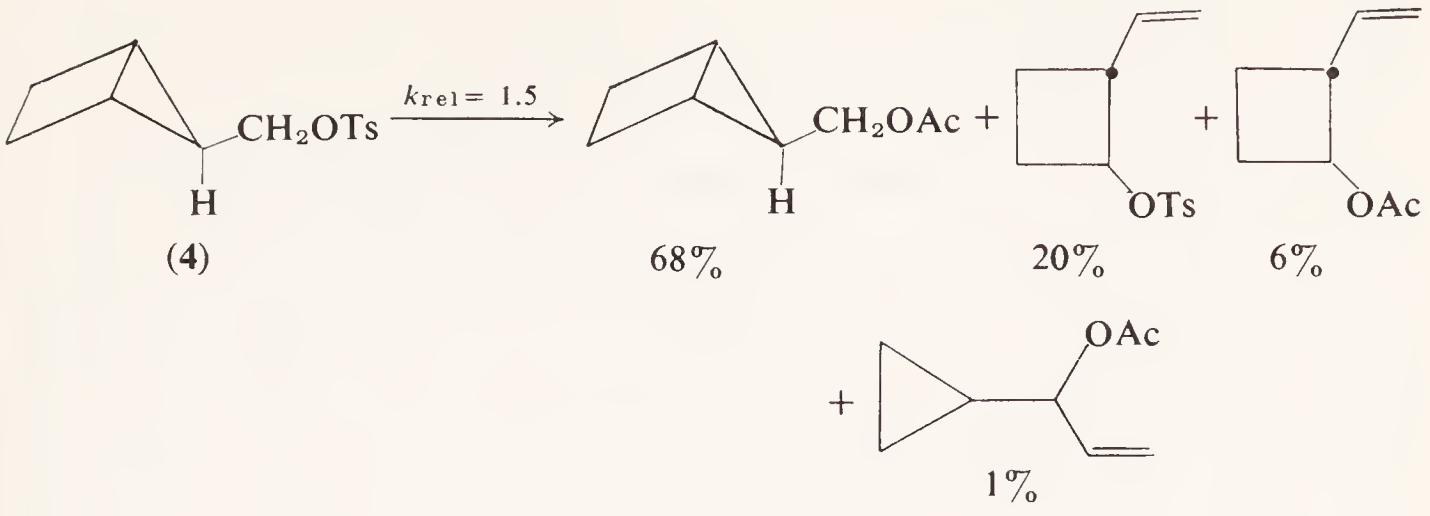
by examining the reactions of bicyclo[3.1.0]hexane-6-methyl tosylate (24,25). The products and relative rates of acetolysis are



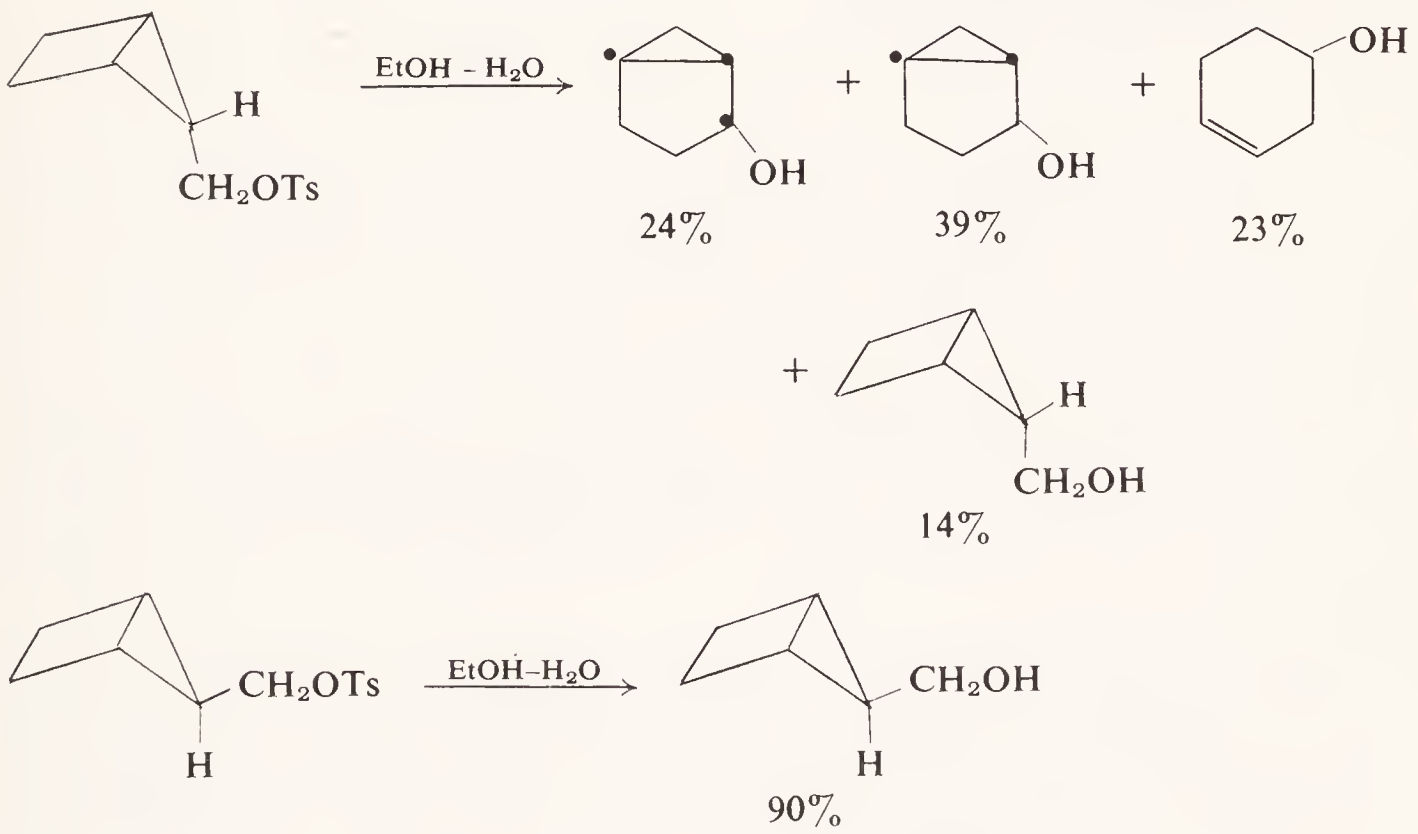
The two striking features of the foregoing observations are that the rates of reaction are essentially the same even though the products are different and that, except for the vinylcyclopentyl products, there is no crossover in products from the two isomers.

Very similar results were obtained with the bicyclo[2.1.0]pentane-5-methyl tosylates (25,26). Here again, the rates of reaction of the two





isomers are essentially the same, although the products are different. Furthermore, in this case there is no crossover in products. The rate of reaction of **3** was 1/38 that of **1**. Solvolysis in aqueous ethanol produced the following information about the nature of the reaction.



The ether products were formed in similar proportions. The *exo*-tosylate now gave only unrearranged products, and the unrearranged alcohol became a significant product from the *endo*-tosylate.

Since the rates of solvolysis of each *exo-endo* pair are essentially the same despite a significant difference in products, the structure of the activated complexes must be close to that of the reactants. Coupled with the observation of unrearranged products in the aqueous ethanol solvolyses, this similarity indicates that the ion should be a cyclopropylcarbinyl cation. The questions that remain are: (*1*) what is the structure of the cyclopropylcarbinyl cation formed in solvolyses? and (*2*) why are

different products formed in the solvolyses of the pairs of isomeric tosylates? These questions are considered in turn.

A. Structure of the Cyclopropylcarbinyl Cation Formed in Solvolyses

Nmr studies of stable tertiary cyclopropylcarbinyl cations have provided good evidence for a bisected structure in which the empty *p* orbital achieves maximum interaction with the ring carbon–carbon bonds (27,28a) (Fig. 1). The activation energy for rotation of the carbinyl carbon was found to be relatively high (28b). A similar interaction has been found in other cases in which a cyclopropane ring interacts with an electron deficient *p* orbital (29–34)

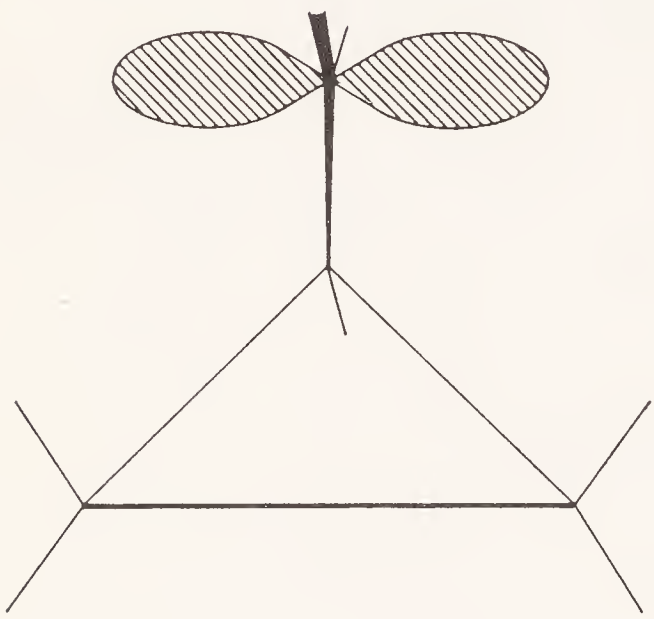
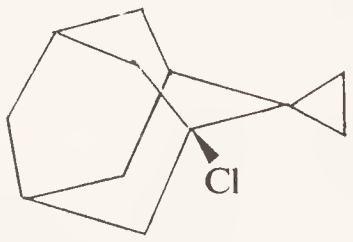
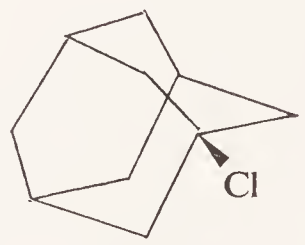


Fig. 1. Preferred geometry of the cyclopropylcarbinyl cation.

Considerable evidence is now available to support the assumption that a similar species is formed in the solvolytic reactions; e.g., the solvolysis of **A** was found to occur 10^{-3} times as rapidly as that of adamantyl tosylate (**B**) (35,36). In **A**, the empty *p* orbital is forced to assume the unfavorable



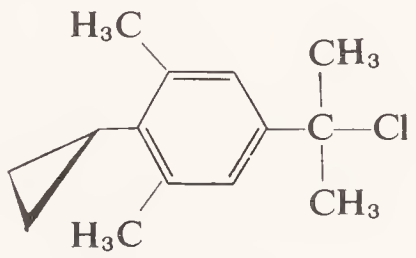
(A)



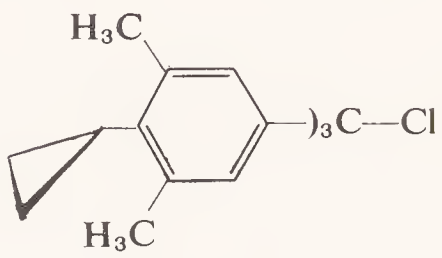
(B)

"perpendicular" conformation. As a result, no stabilization is found, but rather, rate retardation results from the inductive effect of the cyclopropane ring.

Another method of forcing a cyclopropyl ring into an unfavorable geometry involves the introduction of flanking *o*-methyl groups in compounds such as **C** and **D**. The rate of solvolysis of **C** is less than that of the derivative without the methyl groups (37), and the pK_{R^+} for the formation of the cation derived from **D** was found to be less favorable than that from the corresponding alcohol without the methyl groups (38). Nmr data indicate charge transfer from the cyclopropane ring to the aromatic ring; this means that the stabilization occuring in the absence of the methyl groups is due to an interaction between the cyclopropyl ring and the adjacent *p* orbital of the benzene ring via the "bisected" geometry. It



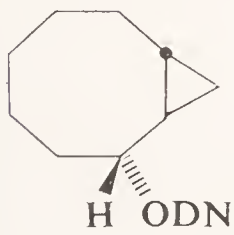
(C)



(D)

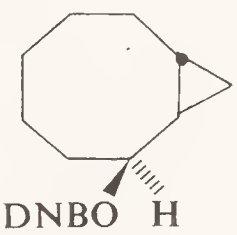
appears that a number of other reactions are best accommodated by assuming that the "bisected" geometry is favored (39).

A further indication of the geometrical requirements for a stabilizing interaction between the cyclopropane ring and the developing *p* orbital in the activated complex is found in the solvolysis of the *trans*-fused bicyclo-[6.1.0]nonan-2-ol derivatives (40,41). A comparison of the rates of solvolysis with those for the corresponding *cis*-fused derivatives (42) is provided in **E**–**H**. The ratio of rates for **E** and **F** is 18,000 whereas that for



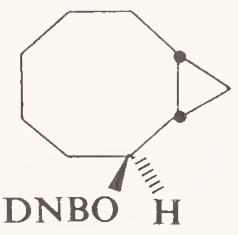
$k_{rel} = 18{,}200$
(*trans-trans*)

(E)



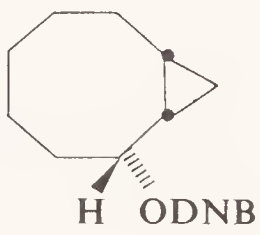
$k_{rel} = 1$
(*trans-cis*)

(F)



$k_{rel} = 65$
(*cis-trans*)

(G)



$k_{rel} = 1410$
(*cis-cis*)

(H)

the *cis* isomers **G** and **H** is only 0.05. The remarkably low rate of solvolysis of **F** must be attributable to its unusual geometry in which the leaving group lies over the cyclopropane ring, making it difficult to achieve a stabilizing interaction between the developing *p* orbital and the cyclopropane ring in the activated complex (Figure 2).

The effect of ring size on the reactivity of bridged cyclopropylcarbinyl derivatives reveals interesting trends. Data for both 1,2- and 2,3-bridged

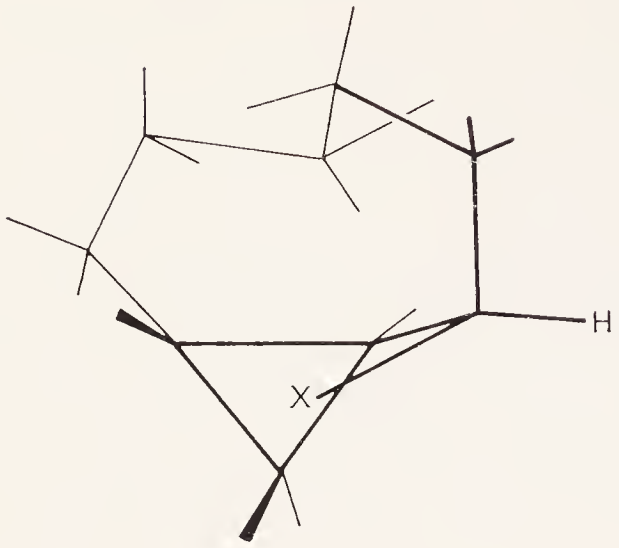
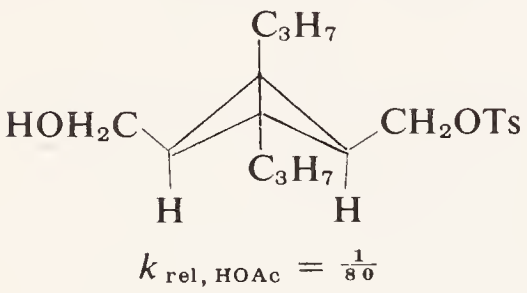


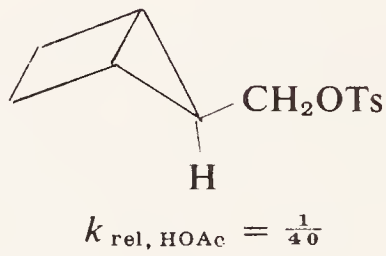
Fig. 2. Geometry of *trans*-bicyclo(6.1.0)-nonan-*cis*-2-ol.

compounds are shown. With the 2,3-bridged compounds, the normal trend is toward slightly lower rates when the bridging ring is decreased in size. On the other hand, an opposite and much larger trend is found with the 1,2-bridged derivatives. If the bridging bond were involved in the



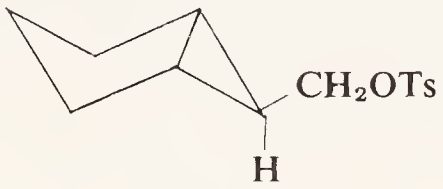
$k_{rel, HOAc} = \frac{1}{80}$

Ref. 43



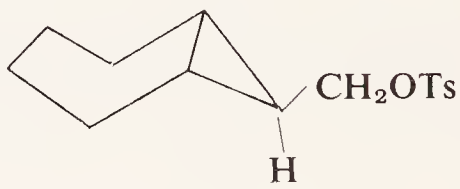
$k_{rel, HOAc} = \frac{1}{40}$

Ref. 26



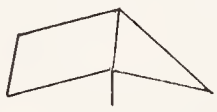
$k_{rel, HOAc} = 1$

Ref. 24



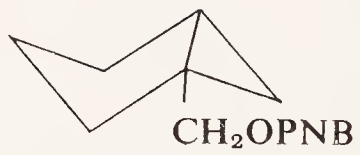
$k_{rel, HOAc} = 5$

Ref. 44



$k_{rel, 60\%\ aq.\ acetone} = 550$

Ref. 45



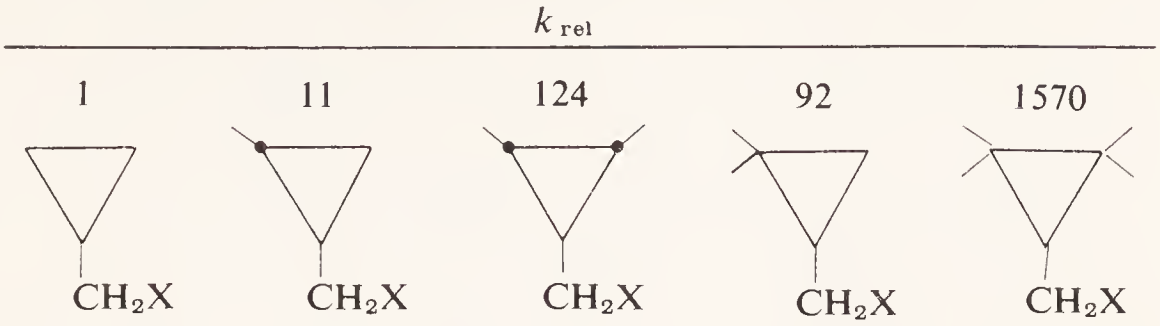
$k_{rel, 60\%\ aq.\ acetone} = 1$

Ref. 46

stabilization of the ion, we would expect an increase in ring strain to lead to an increase in rate, since a certain amount of the strain would be relieved on going to the activated complex. The results are then in agreement with the previous formulation, for only the 1,2 and 1,3 bonds are involved in the stabilization of the cation, and the 2,3 bond is not. The effect of the size of the 2,3-bridging ring is considered later.

Another important set of observations which are in agreement with "bisected" geometry for the cyclopropylcarbinyl cation are those of

Schleyer and Van Dine (47) dealing with the solvolytic reactivity of methyl-substituted cyclopropylcarbinyl derivatives.



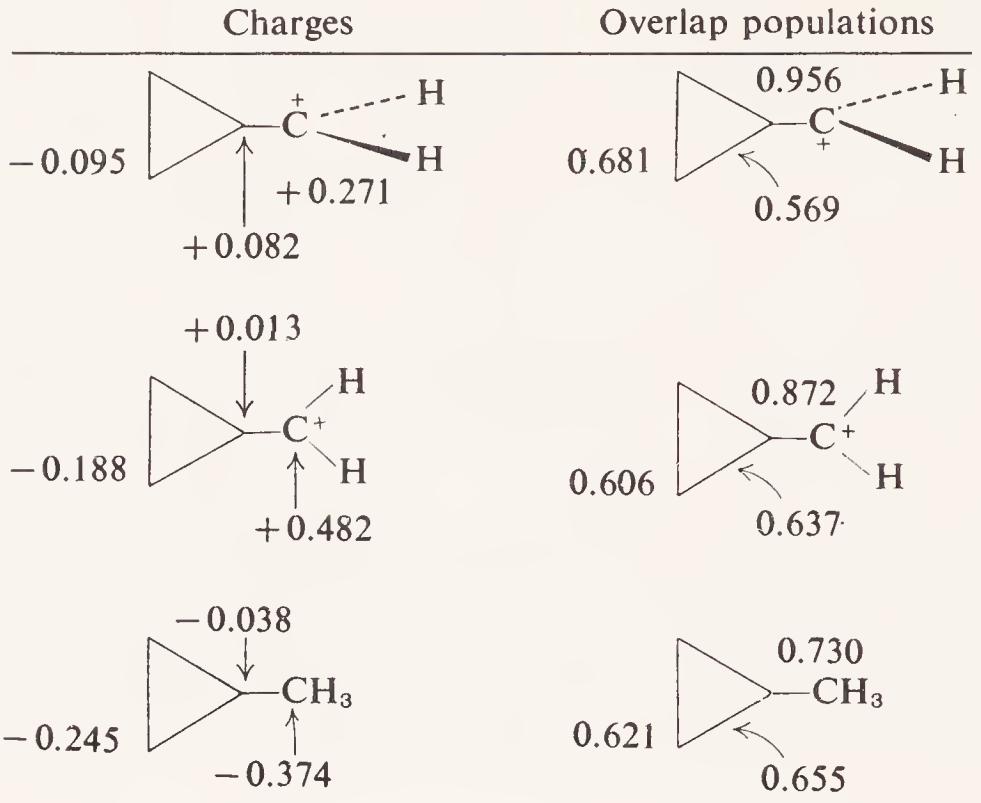
Here, the change in free energy with increasing methyl substitution is almost a linear function of the number of methyl groups. Thus 2,3-dimethyl and 2,2-dimethyl derivatives react at essentially the same rate. These data appear to require a symmetrical cyclopropylcarbinyl cation.

Further evidence favoring a symmetrical ion comes from studies of optically active cyclopropylcarbinyl derivatives. Roberts and Vogel (48), Richey and Richey (49), and Goering and Rubenstein (50) found essentially complete racemization in the solvolytic reactions of cyclopropylmethylcarbinyl derivatives and concluded that the very small amount of inversion found could arise from an S_N2 displacement reaction. An unsymmetrical ion might be expected to give partially optically active product. Corresponding results were obtained with the norcaranols (50). Successive replacement of isopropyl groups in triisopropylcarbinol by cyclopropyl results in essentially constant decrease in free energy of activation (51); and this observation, too, seems best accommodated by a symmetrical cyclopropylcarbinyl cation. If the ion were unsymmetrical, we might expect steric effects to decrease the effectiveness of the third cyclopropyl group.

The evidence just cited for symmetrical cyclopropylcarbinyl cations in solvolytic reactions, coupled with the data on the structure of the stable tertiary cyclopropylcarbinyl cations, provides a definitive argument for this structural unit. It would then seem appropriate to consider quantum chemical calculations that have been made concerning this species. The earlier calculations (52–54) were made using the π-electron approximation. Although they are of historical interest, it is doubtful if these calculations add much to the problem, since the fundamental assumption of the π-electron method is the noninteraction of π and σ electrons. This separation into two groups does not apply to the cases discussed here because of the nonplanar geometry.

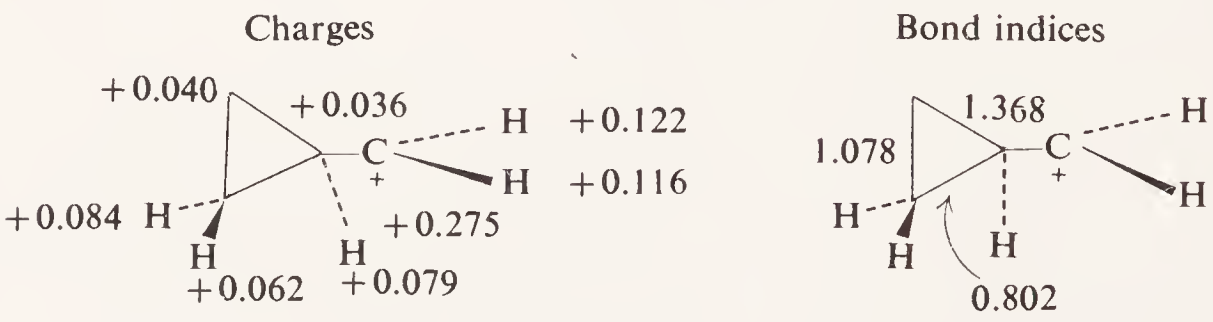
The extended Hückel theory developed by Hoffmann (55) is of considerable value here because it permits simultaneous treatment of σ and π electrons. The application of this method to the cyclopropylcarbinyl cation has been reported (56) and it was found that the ion with the empty p orbital parallel to the C2-C3 ring bond should be 9 kcal/mole more

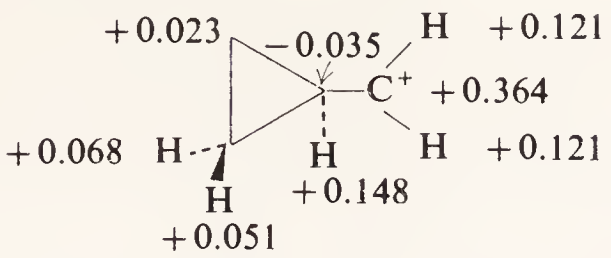
stable than the conformation in which the empty orbital has been rotated by 90°. The charges and overlap populations were

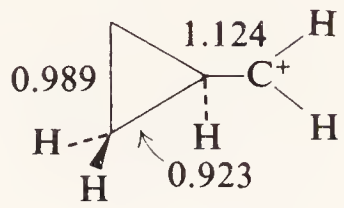


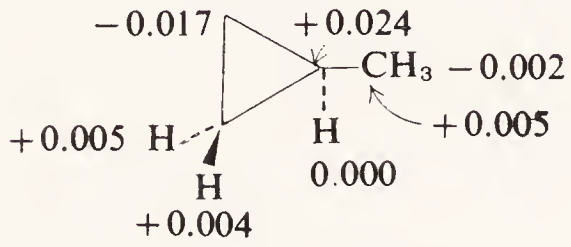
Charge delocalization is clearly predicted for the first ion, leading to a stronger exocyclic bond, an increase in the 2,3-overlap population, and a decrease in the 1,2-overlap population over the second ion. The predictions are in good agreement with the experimental findings.

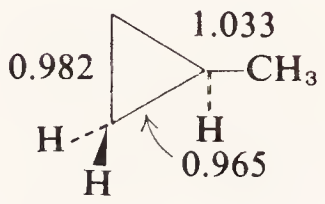
One major difficulty with the extended Hückel method using Hoffmann's parameters is that, because charge separation in hydrocarbons is exaggerated, it is difficult to interpret the results. The one-electron methods generally lead to excessive charge separation. A self-consistent field modification of the extended Hückel method has been developed by Pople et al. (57). This method, designated as CNDO is still approximate, but it does include interaction among electrons and leads to self-consistent field molecular orbitals. In contrast to the extended Hückel method, CNDO leads to a very reasonable charge distribution in hydrocarbons and thus it is of interest to apply it to the cyclopropylcarbinyl case. The results summarized are due to Wiberg (58).











The first ion is predicted to be about 20 kcal/mole more stable than the second. It can be seen that the first leads to considerable charge delocalization, an increase in the 1,4 bond index and an increase in the 2,3 bond index. Thus the results are qualitatively the same as those obtained using the extended Hückel method. In a quantitative sense, however, the numbers are quite different.

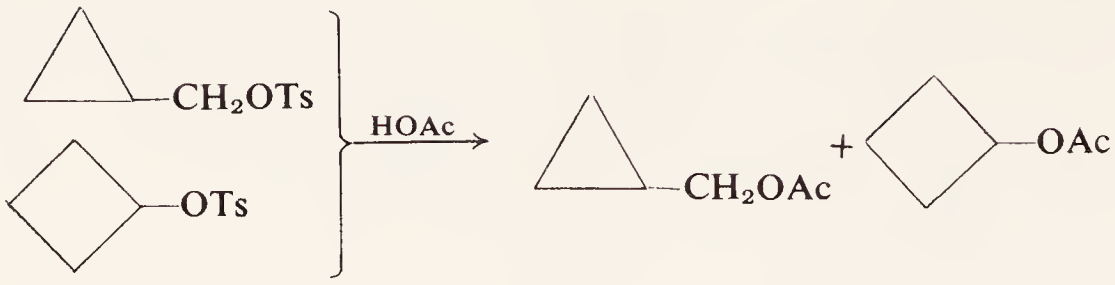
The large decrease in the 1,2 bond index should be accompanied by an increase in bond length. When the strain associated with a small ring fused across this bond is partially relieved in going to the ion, the observed rate increase occurs. The small increase in the 2,3 bond index should result in a decrease in bond length. Thus the strain associated with a small ring fused across the 2,3 bond will be increased on going to the ion, and a rate decrease should be found in comparison to larger rings. We see then that the results of the calculations are in very good agreement with the effect of ring size on the rates of solvolysis of bridged cyclopropylcarbinyl derivatives.

Other calculations have also been carried out (59,60). The ASMO-SCF procedure (61) gives a barrier to carbinyl rotation of 19 kcal/mole and the NDDO (62) method gives 22 kcal/mole. An *ab initio* calculation gave the barrier as 17.5 kcal/mole (63).

B. Nature of the Products and Stereochemistry of Transformations

In the previous section, the main emphasis is on the structure and conformation of the intermediate formed in the solvolysis of cyclopropylcarbinyl derivatives. We now consider the products of the reactions and pay special attention to the stereochemistry of the products and to the question of the difference (if any) between symmetrical and unsymmetrical ions.

The products of solvolysis of some simple cyclopropylcarbinyl and cyclobutyl derivatives are summarized here.



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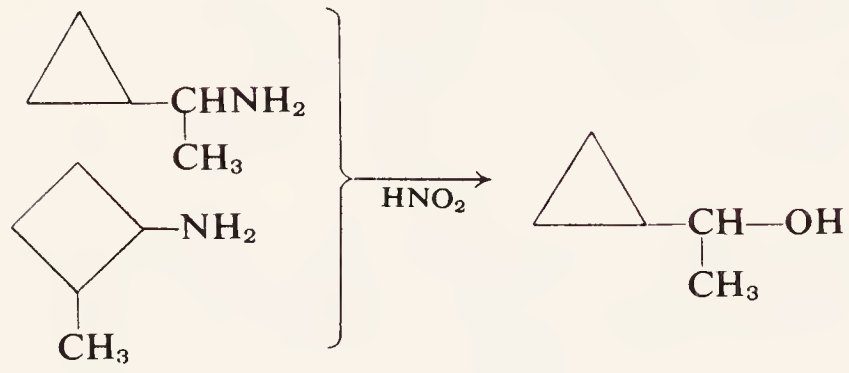
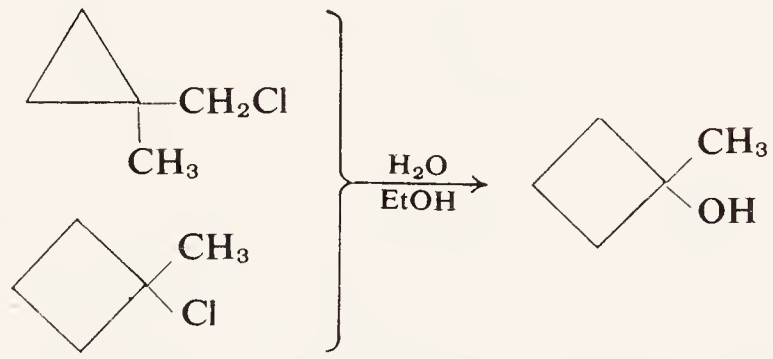


Ref. 64



Ref. 65

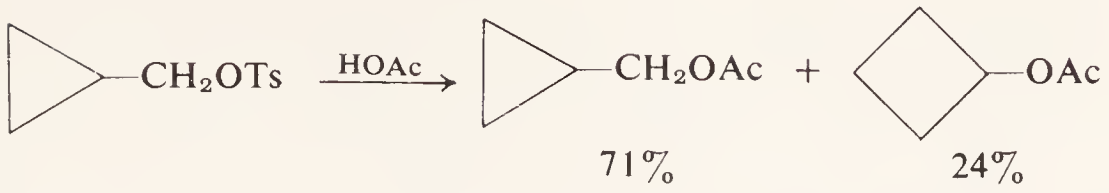
For each of the three pairs of compounds, the products are essentially the same, starting with either the cyclopropylcarbinyl or the cyclobutyl derivative. It is, however, possible to effect changes in the product distribution as indicated.* In some cases, the more nucleophilic solvent leads to a larger proportion of unrearranged product.

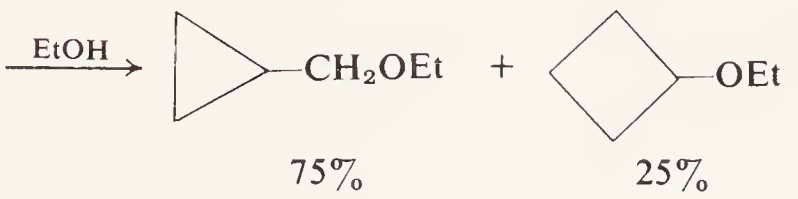
These reactions have been considered in terms of a common bicyclobutonium ion intermediate. However, the more recent evidence suggests that the species initially formed from the cyclopropylcarbinyl derivative is the cyclopropylcarbinyl cation. We may then ask if this could be a common ion from which all the products are derived. The effect of solvent nucleophilicity on product composition suggests that this is not the case, and that the cyclobutyl products are formed via a different ion. The nature of this species is considered in the next section.

In this connection, the mode of carbon scrambling in the cyclopropylcarbinyl cation must also be considered. Roberts and co-workers (19) have found extensive but not complete scrambling during deamination (67).†

* The solvolysis of cyclopropylcarbinyl tosylate in ethanol was reported to give only cyclopropylcarbinyl ethyl ether. However, this appears to be incorrect (J. Longanbach, Ph.D. dissertation, Yale University, 1969).

† Scrambling has also been studied using deuterium substitution with quite similar results (67). Majerski et al. found that the degree of scrambling was less when the stronger nucleophilic BH_4^- was used instead of water in trapping the intermediate.





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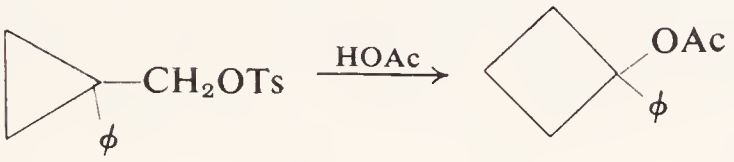
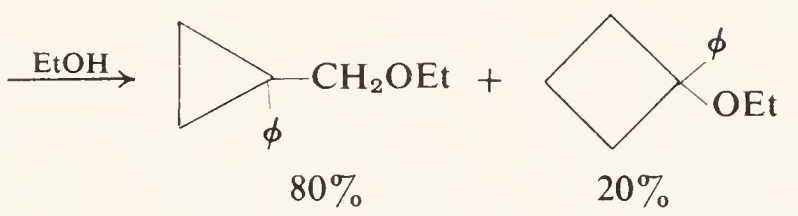
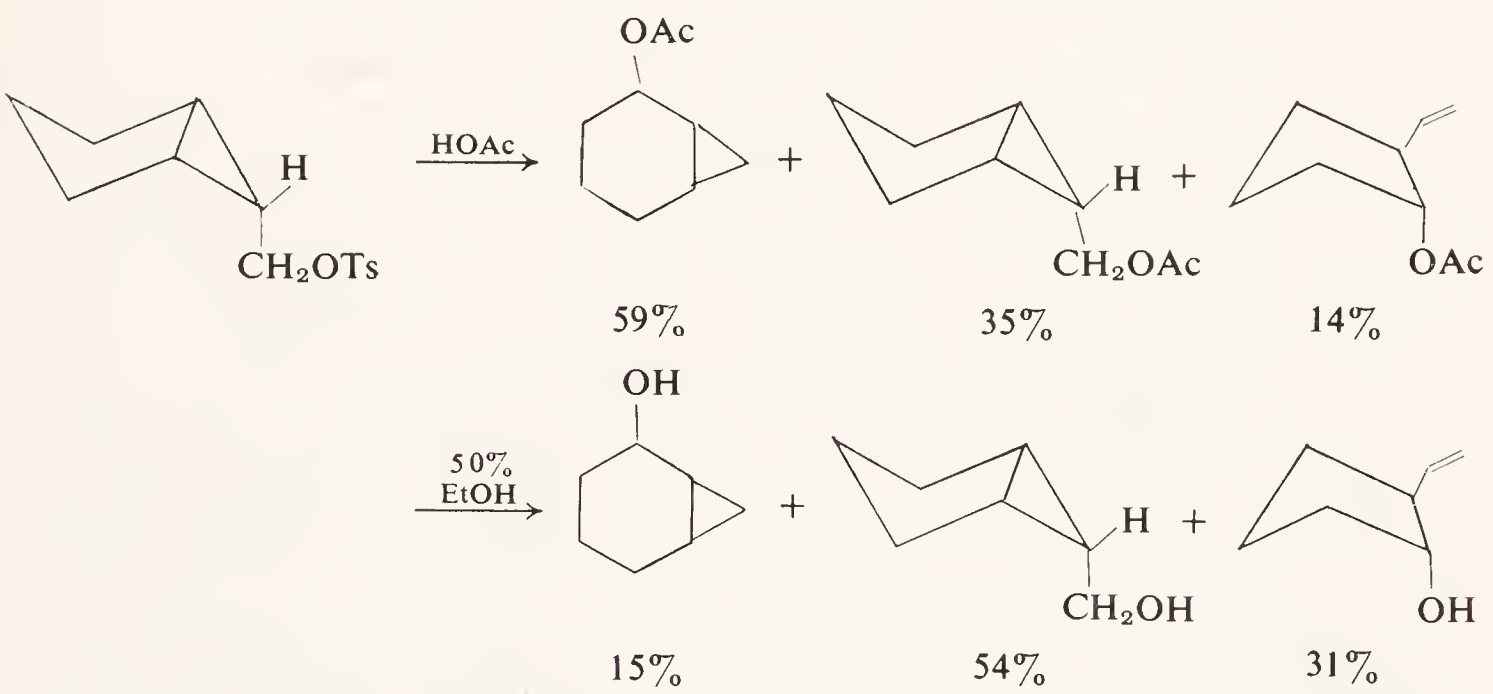
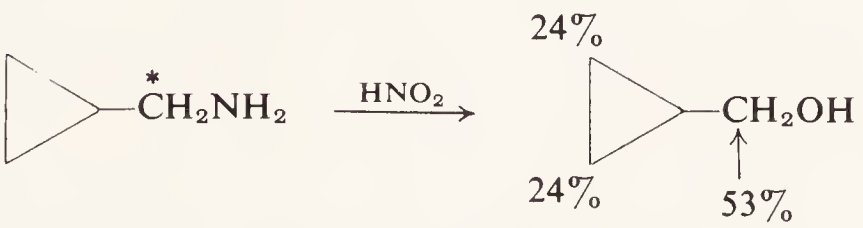




Ref. 66



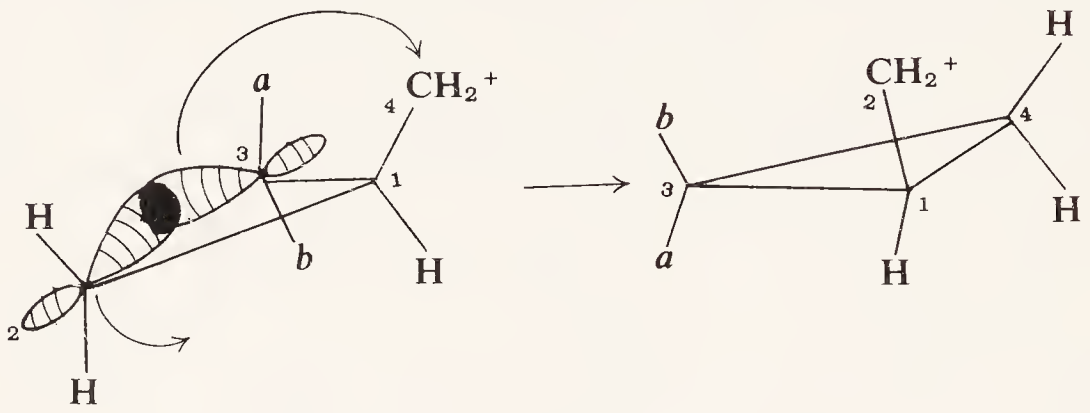
Ref. 26



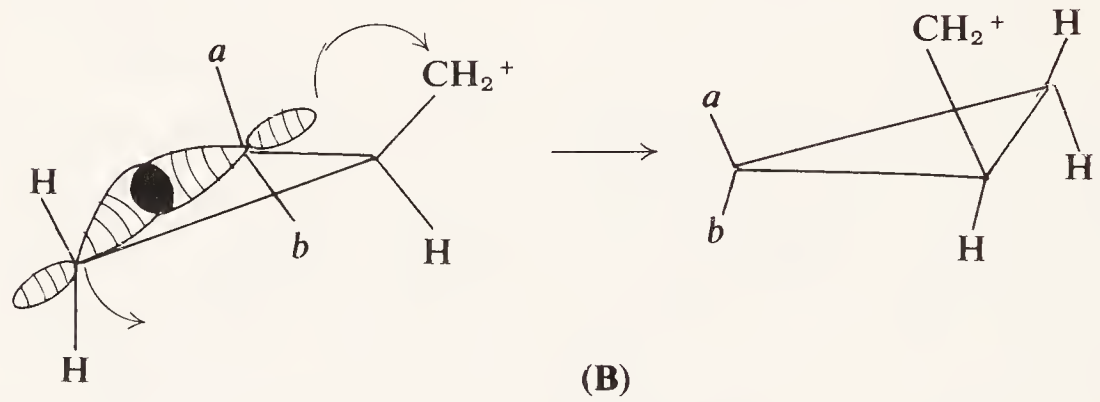
The scrambling may occur via cyclopropylcarbinyl-cyclobutyl interconversion,

however, it may also occur via a direct interconversion between cyclopropylcarbinyl ions.

Such a transformation could occur in either of two ways. First (**A**) a direct interaction of the 2,3 bond with the cationic center would lead to inversion at one of the methylene groups. Second (**B**) the backside of one of the orbitals forming the 2,3 bond could interact with the cationic center, leading to no change at the methylene group. The stereochemistry of the



(A)



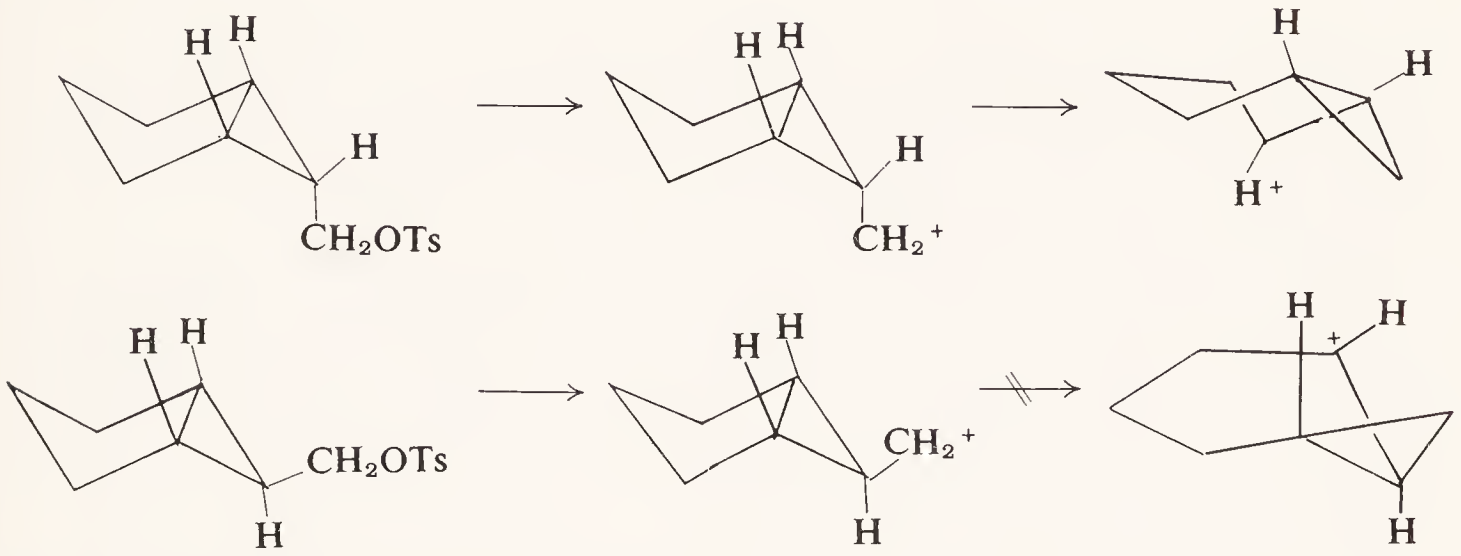
(B)

rearrangement has been determined (68,69) and it was found that the latter course was correct. The possible mechanisms are then **B** and one in which a *puckered* cyclobutyl cation is an intermediate (or activated complex). Molecular orbital calculations suggest that the path via the puckered cyclobutyl cation is the more probable (68).

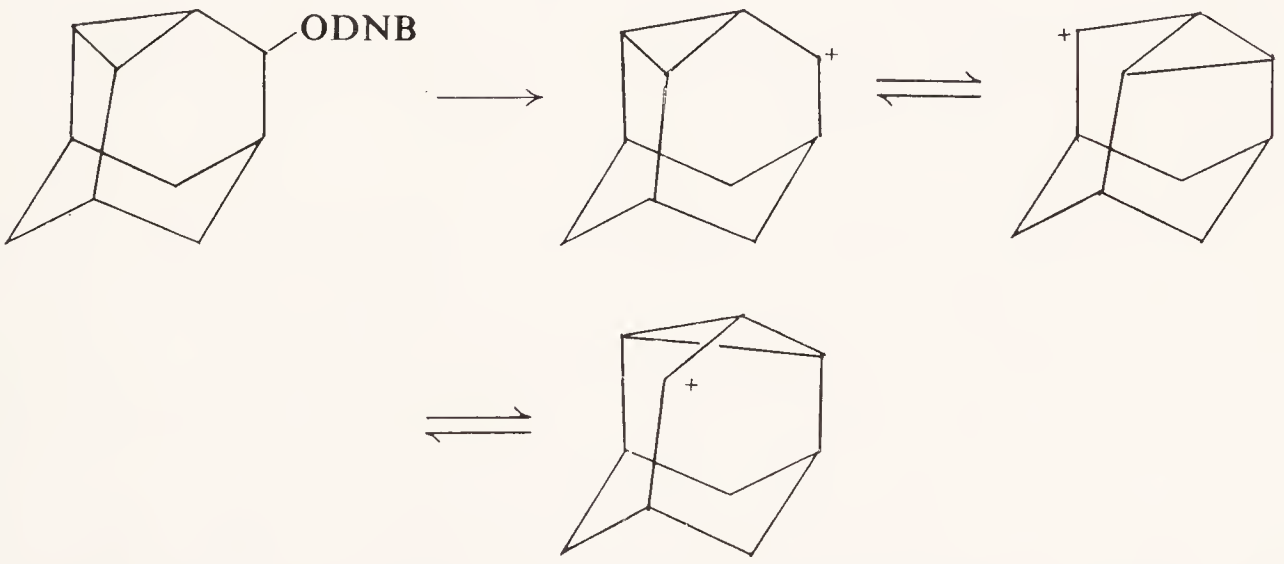
The proton nmr spectrum of the ion derived from cyclopropylcarbinol (or cyclobutanol) in SbF_5–SO_2ClF at $-80°$ has three bands of areas 1:3:3 whereas the ^{13}C spectrum has only two bands of areas 1:3 (70). The single proton in the former case corresponded to the single carbon in the latter. The structure of the ion is not clear. The spectrum is easily explained if we assume that the ion is the cyclopropylcarbinyl cation, which rapidly undergoes the degenerate cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement. The stereochemistry described previously requires that there be two nonmixing sets of three protons (the carbinyl hydrogen, which lies over the ring with the *cis*-ring hydrogens, and the carbinyl hydrogen, which

is away from the ring with the *trans*-ring hydrogens). This fits the observed spectrum well. However, equilibrating *puckered* cyclobutyl cations also could explain the spectrum (see the next section).

The stereochemistry just described is that required to explain the observations concerning the products derived from the bicyclo[3.1.0]-hexane-6-methyl tosylates (25). The *endo*-isomers rearranged to a secondary cyclopropylcarbinyl cation, whereas the *exo*-isomers did not. With the *endo*-isomers, the rearrangement will lead to the *cis*-fused norcaranyl or northujyl ions. However, a similar rearrangement of the *exo*-isomers could lead only to the *trans*-fused ions, and thus rearrangement will not occur:

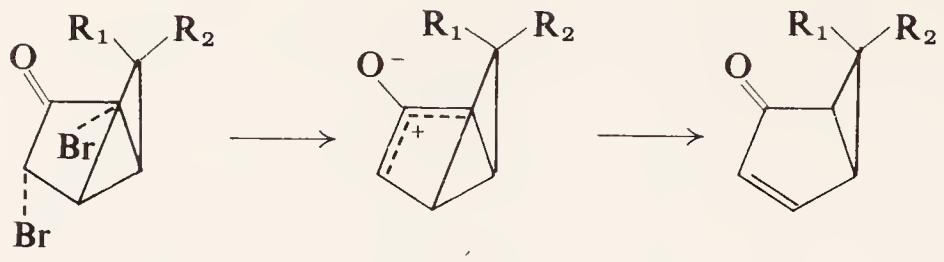


The stereochemical course described is also necessary for the label-scrambling process involving 8,9-dehydro-2-adamantyl derivatives (71); it is also needed to explain the stereochemistry of the rearrangement of the

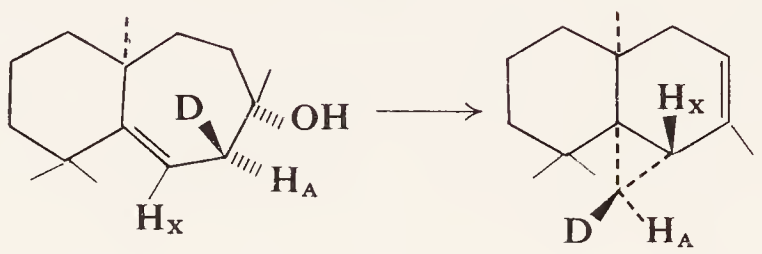


Favorskii-like intermediate (**G**) derived from the bicyclo[3.1.0]hexan-3-ones (72,73). Furthermore, the same course is required by the stereochemistry of the conversion of widdrol-7*d* (**H**) to thujopsene (**I**) (74).

Other cases in which a rearrangement of one cyclopropylcarbinyl cation to another appears to be an attractive possibility include the conversion



(G)



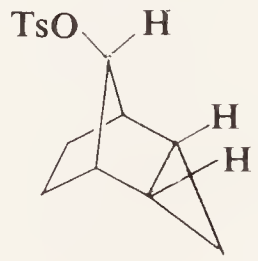
(H) (I)

of 9-hydroxymethyloctalin to 1-hydroxymethyl octalin (75), the rearrangements of 19-hydroxy-Δ^5 steroids (76), and the conversion of presenegenin to senegenin (77). It has been suggested that this rearrangement is involved in some biogenetic transformations (78).

The rearrangement products derived from cyclopropylcarbinyl cations (cyclobutyl and allylcarbinyl derivatives) are also formed stereospecifically. Because this matter is closely tied to the nature of the ions formed from these types of compounds, a discussion of the stereochemistry of these processes is postponed to later sections.

We may now consider the reactions of other cyclopropylcarbinyl derivatives. Important data are summarized in Tables I–III. The low reactivity of nortricyclyl tosylate relative to other cyclopropylcarbinyl tosylates at first appears surprising, since the nortricyclyl cation should have the proper geometry for a symmetrical cyclopropylcarbinyl cation. The low rate of reaction is probably a reflection of the additional strain introduced into the molecule on converting a tetrahedral carbon to trigonal.

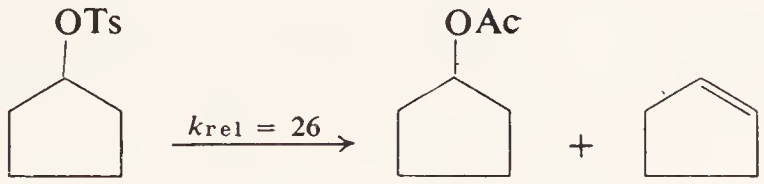
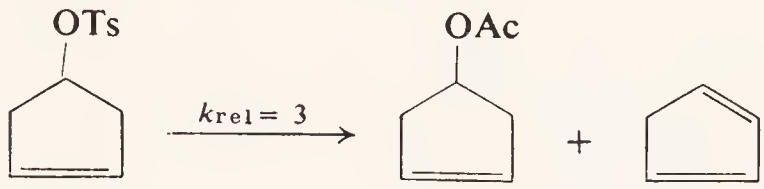
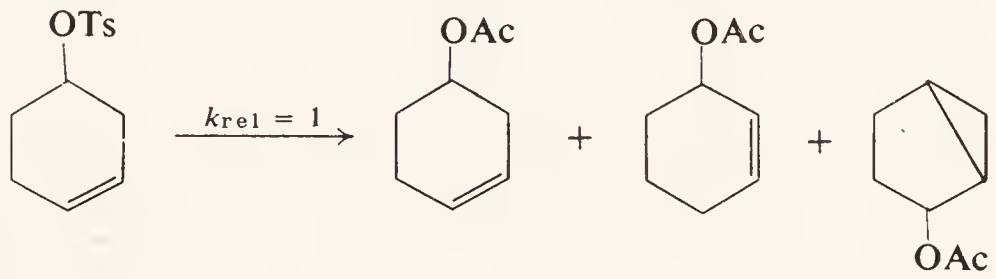
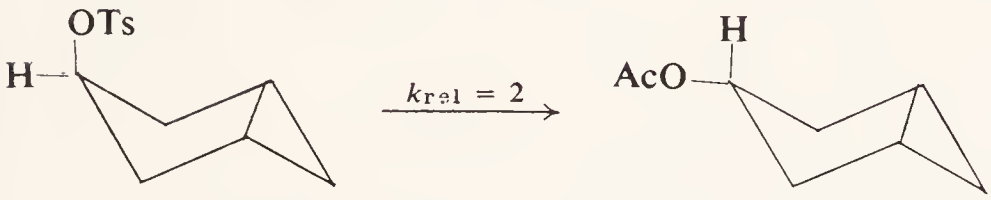
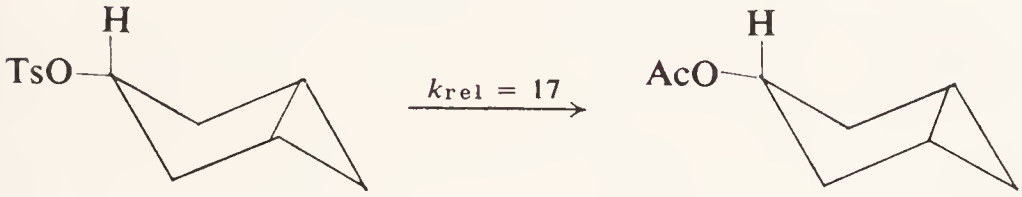
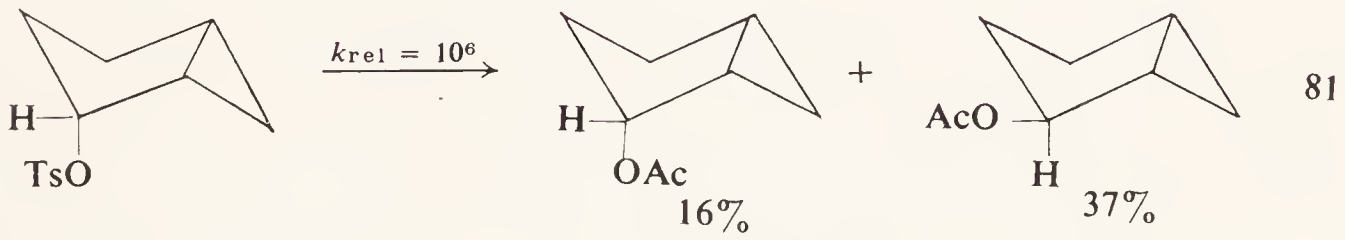
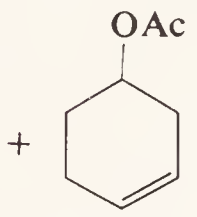
In considering the other compounds, we may first note the large difference in reactivity between the bicyclo[3.1.0]hexyl-2 and -3 tosylates. There is an interaction between the cyclopropane ring and the reaction center in the 3-tosylates as indicated by label scrambling in a deuterium-labeled derivative (80), but this seldom leads to a significant rate acceleration (91). However, when the cyclopropane ring is attached to a strained center, and the developing orbital is constrained to being close to the cyclopropane ring, as with **J**, a large rate increase may be found (92).



(J)

TABLE I

Relative Rates of Acetolysis of Cyclic Tosylates

Compounds	Ref.
	—
	—
	79
	80
	
	81
	

(*continued*)

TABLE I (*Continued*)

Relative Rates of Acetolysis of Cyclic Tosylates

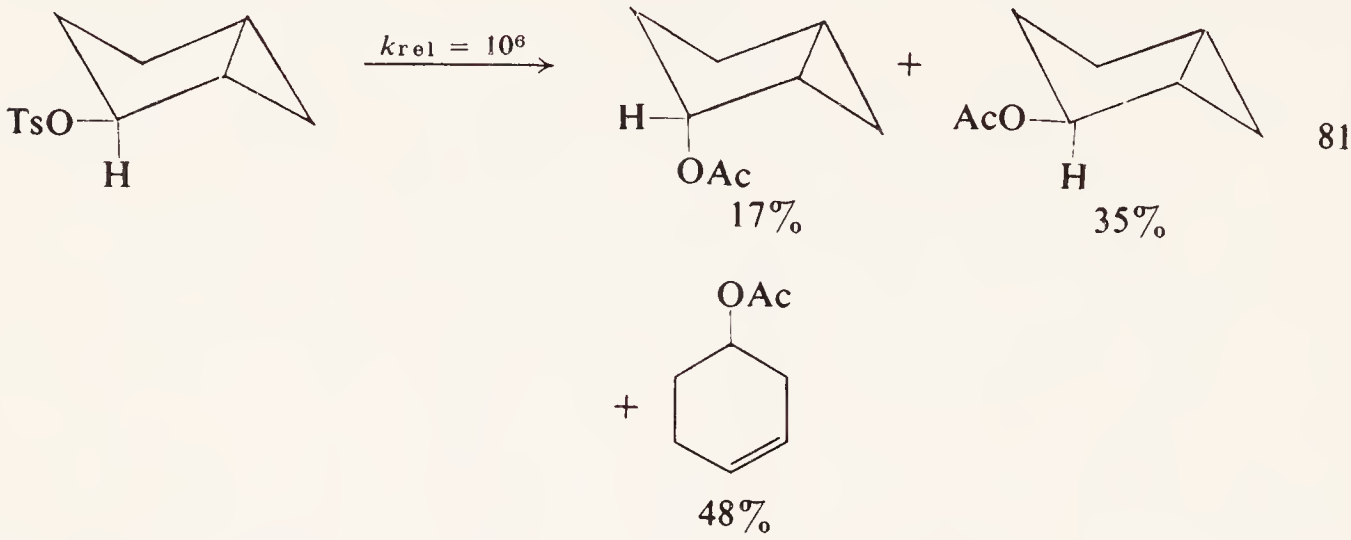
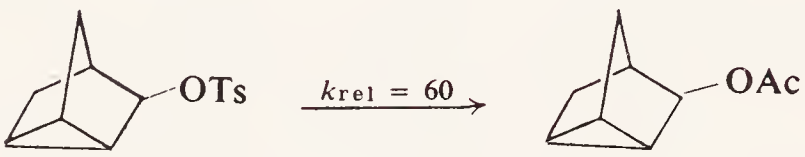
Compounds	Ref.
	81
	81,82

TABLE II

Relative Rates of Solvolysis of Cyclic *p*-Nitrobenzoates[a]

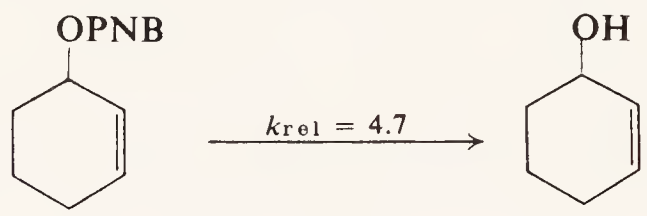
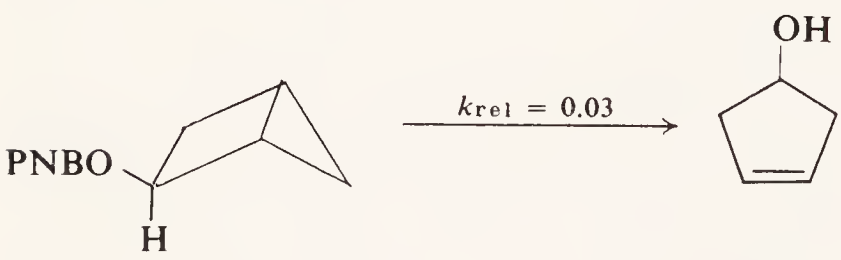
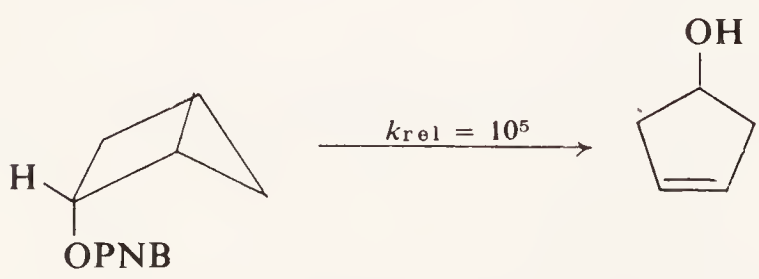
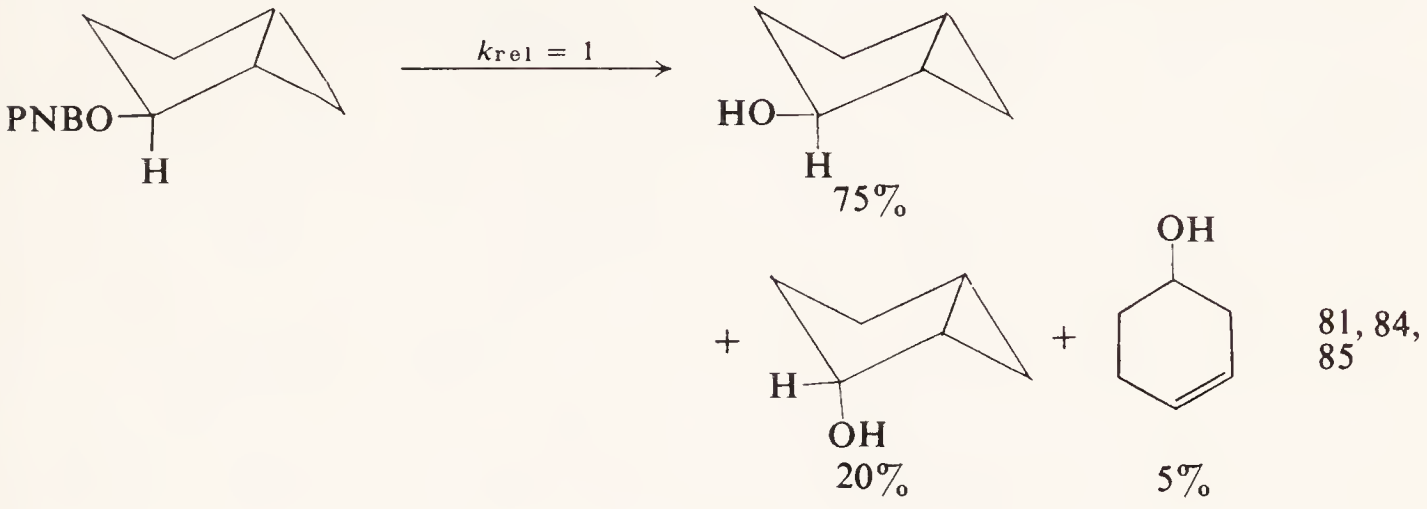
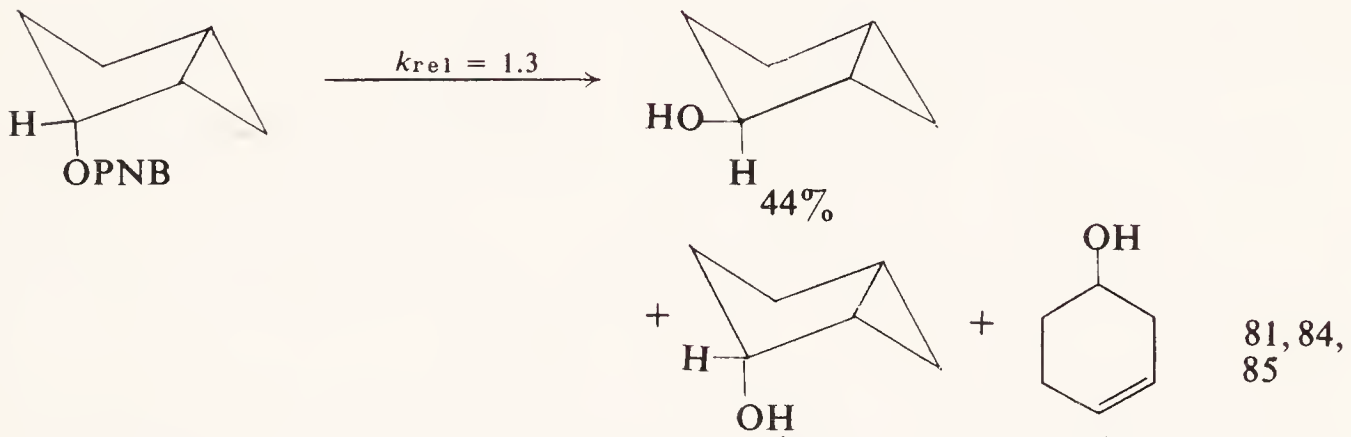
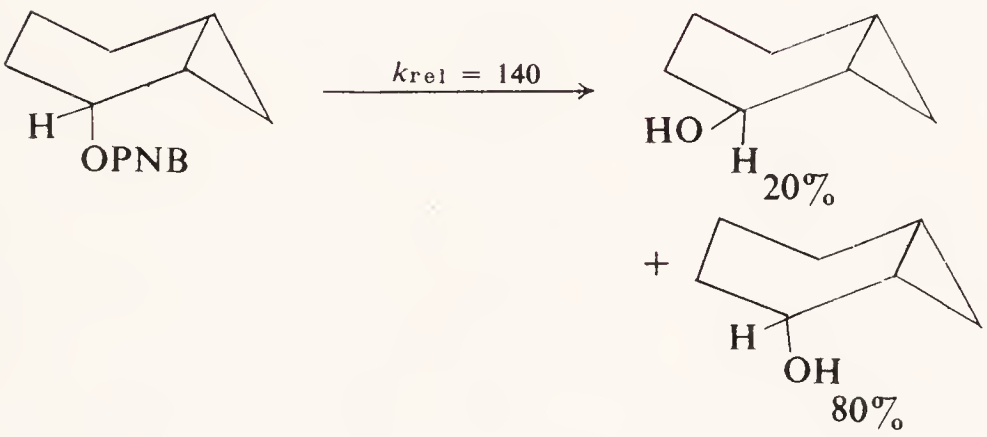
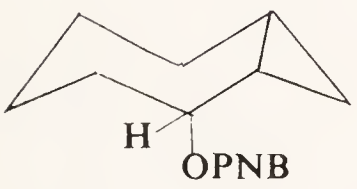
Compounds	Ref.
	81
	83
	83

TABLE II (*Continued*)

Relative Rates of Solvolysis of Cyclic *p*-Nitrobenzoates[a]

Compounds	Ref.
	81, 84, 85
	81, 84, 85
	81,86
	81

(*continued*)

TABLE II (*Continued*)

Relative Rates of Solvolysis of Cyclic *p*-Nitrobenzoates[a]

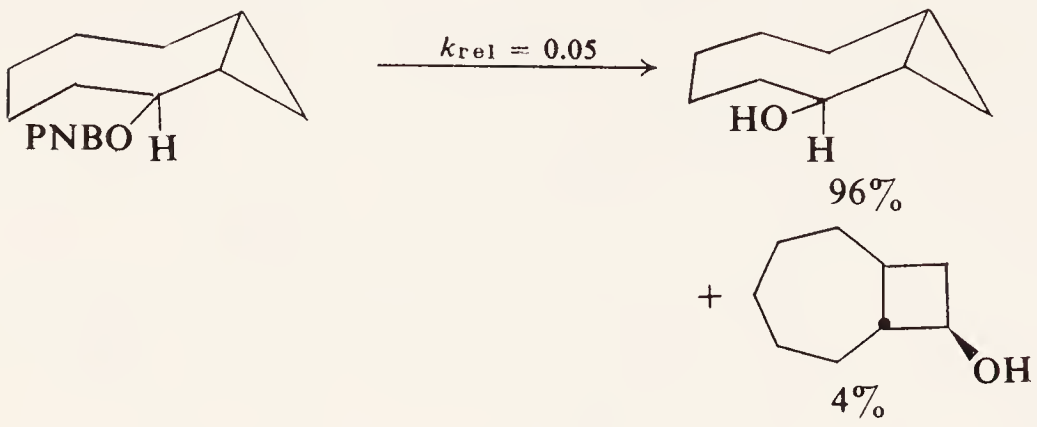
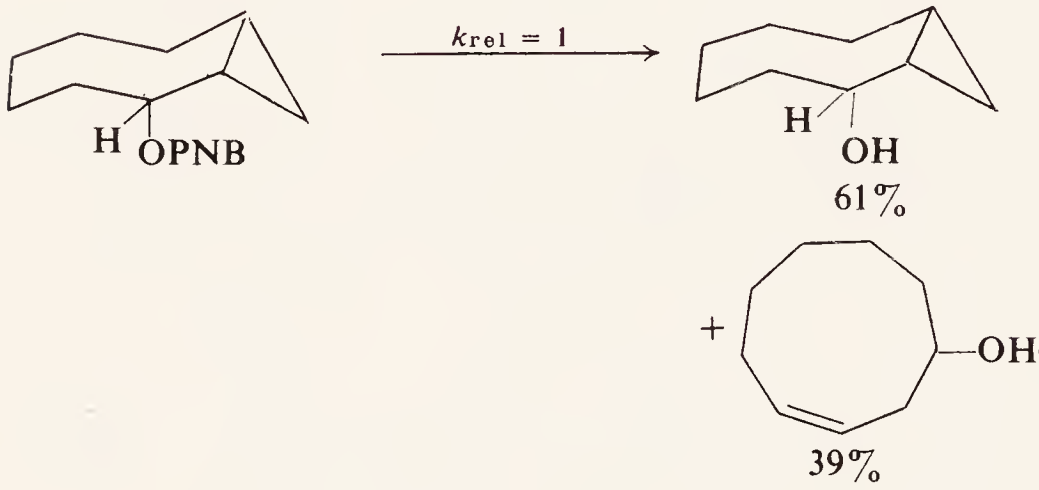
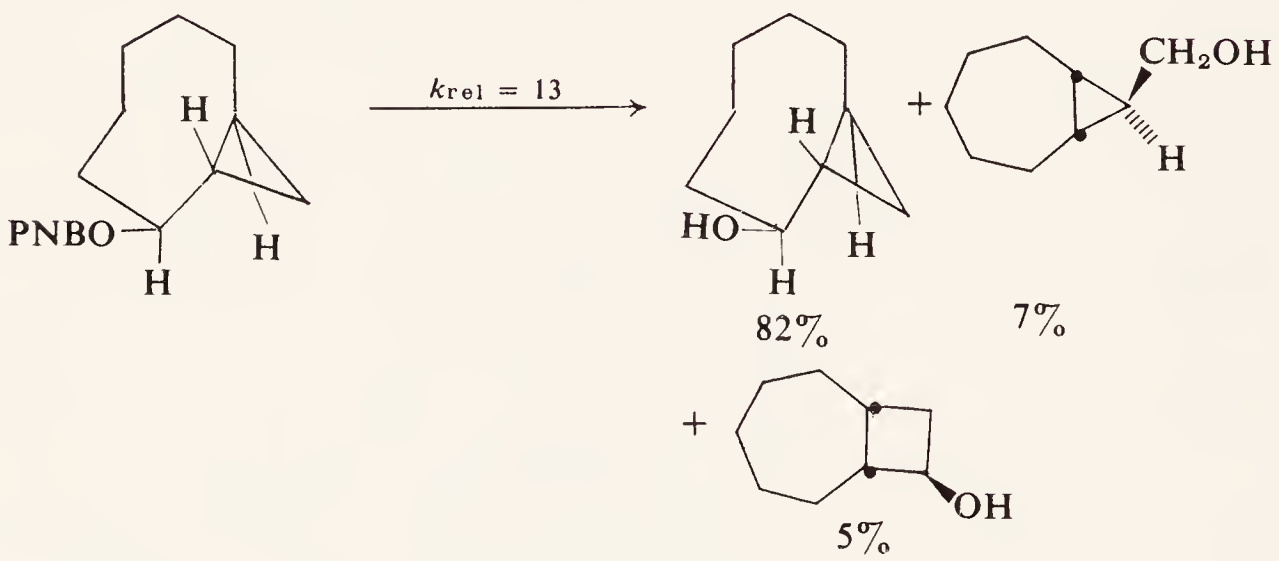
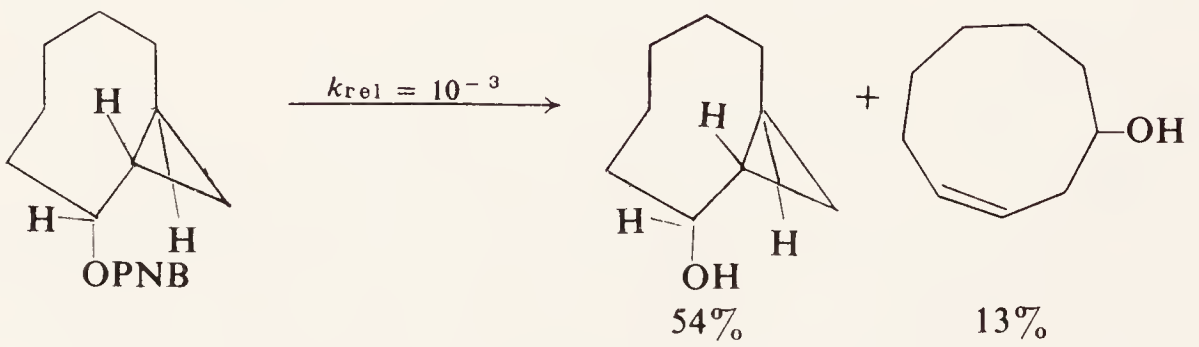
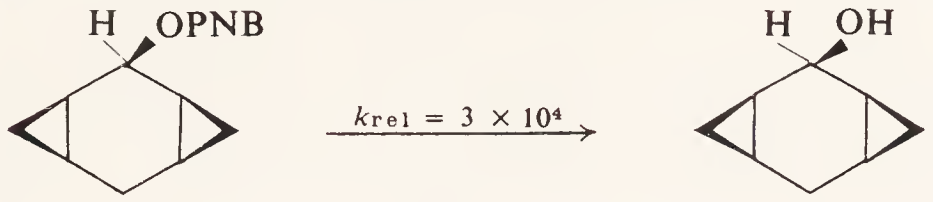
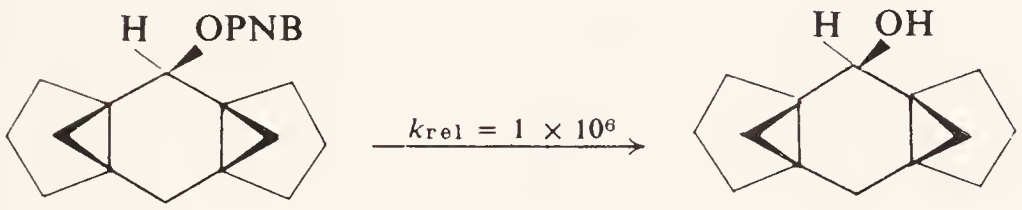
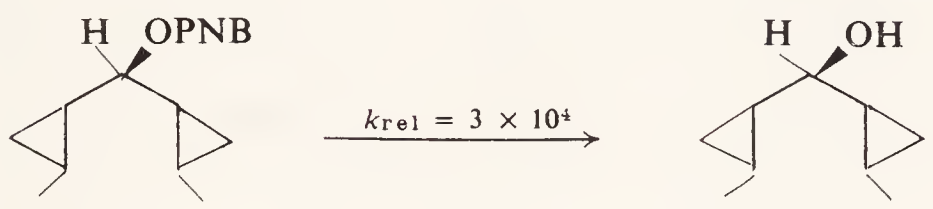
Compounds	Ref.
	42
	42
	40,41
	40,41

TABLE II (*Continued*)

Relative Rates of Solvolysis of Cyclic *p*-Nitrobenzoates[a]

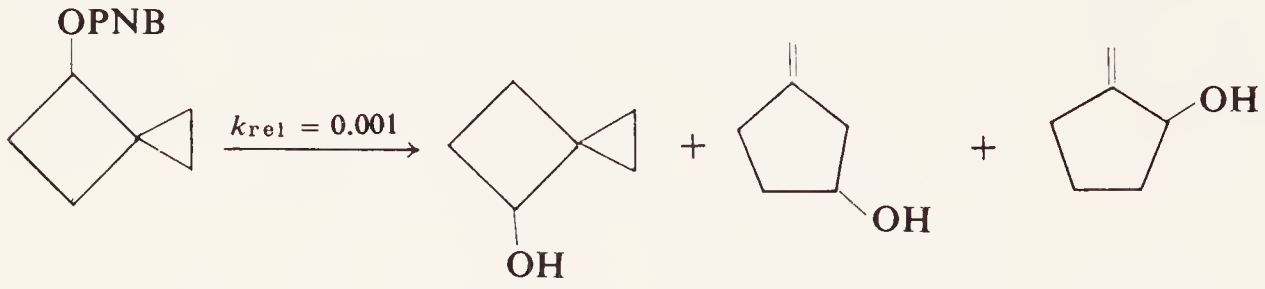
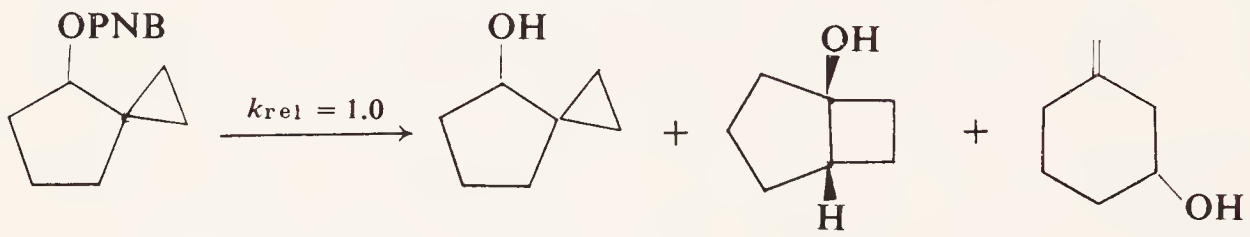
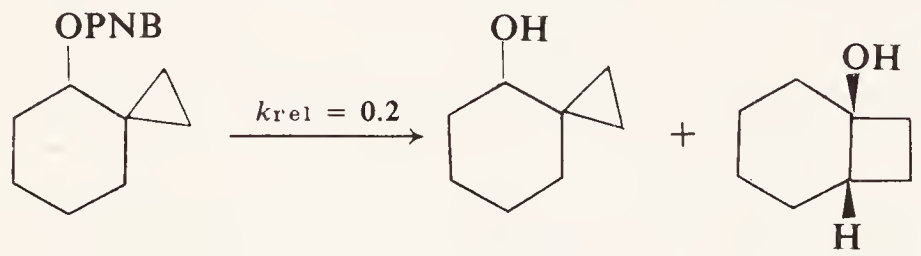
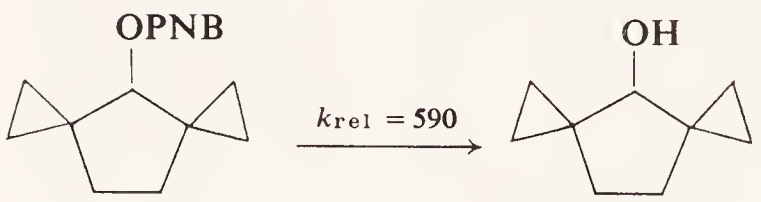
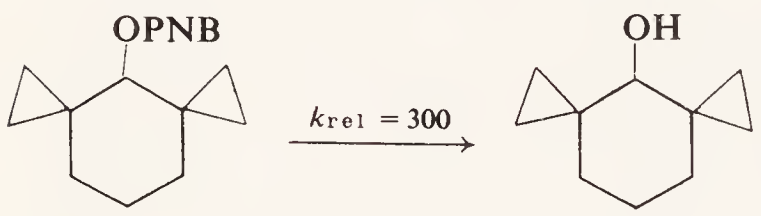
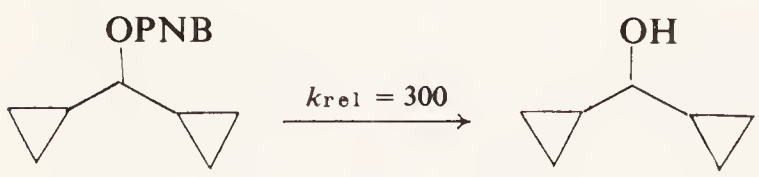
Compounds	Ref.
	86
	86
	86

One of the interesting aspects of the remaining cases is the remarkable range of reactivity. The bicyclo[2.1.0]pentane derivatives have an unusually large *exo*/*endo* rate ratio, which we consider further when the stereochemistry of the reaction of cyclobutyl derivatives is discussed. The more reactive isomer derives its high reactivity (83) from a concerted ring opening, which relieves a large part of the ring system's 53 kcal/mole (93) strain energy. The other *cis*-fused compounds with a single cyclopropane ring have similar reactivities. The differences in rate are probably due to the fused ring, which prevents the ion from fully reaching the "bisected" geometry. The *trans*-fused bicyclo[6.1.0]nonyl derivatives have a relatively large *cis*/*trans* rate ratio, which, as indicated previously, arises from the unusual geometry of the *trans*-*cis* isomer in which the leaving group lies over the cyclopropane ring (40,41). Finally, when two cyclopropane rings are attached to the reacting center, a further large increase in reactivity is observed (86).

The *cis*- and *trans*-bicyclo[3.1.0]hexyl-2 derivatives react at essentially the same rate, and the two isomers lead to identical product mixtures in acetic acid. The small difference in rate is due to a difference in ground state energy of the reactants (84). In aqueous acetone, the product compositions for the two bicyclo[3.1.0]hexyl-2 *p*-nitrobenzoates were not the same, the *trans*-isomer giving significantly more *trans* product than does

TABLE III

Relative Rates of Solvolysis of Spiro-*p*-Nitrobenzoates

Compounds	Ref.
	87,88
	87–89
	87,90
	90
	90
	90

the *cis*-isomer (81). The product ratio appears to be quite sensitive to leaving group and solvent, for with other leaving groups and aqueous ethanol, the ratio was the same for both isomeric reactants (84,85).

The bicyclo[5.1.0]octyl-2 and bicyclo[6.1.0]nonyl-2 cases provide clear cases of isomeric reactants giving different products. The bicyclo[6.1.0]-nonyl-2 case is particularly instructive because there is essentially no

crossover in products with any of the four isomers, and the products are formed stereospecifically. Thus the *cis-trans* isomer gives the *trans*-fused bicyclo[5.2.0]nonan-8-ol, whereas the *trans-trans* isomer gives the *cis*-fused bicyclo[5.2.0]nonan-8-ol. In each case, the predominant product is the alcohol corresponding to the reactant.

The results make it clear that there are a minimum of four different cations in this system. A similar conclusion is reached with the *cis*-fused bicyclo[5.1.0]octanols by a study of racemization of optically active or deuterium-labeled reactants (94). Here, the *cis-cis* reactant gave both racemized and deuterium-scrambled products, whereas the *cis-trans* reactant gave neither racemized nor scrambled products.

The only way of accommodating these results is to propose that, for a pair of epimeric reactants, one or both of the ions formed is an unsymmetrical cyclopropylcarbinyl cation and the barrier separating the ions corresponds to a barrier to conformational change in the cycloheptane or cyclooctane ring. Figure 3 presents the results of CNDO calculations on the barrier to rotation of the carbinyl group in the cyclopropylcarbinyl cation (95). It appears that a 30° rotation from the symmetrical form ($\alpha = 0°$) leads only to a small decrease in stabilization. The changes in bond indices are shown in Figure 4.

The results suggest that the unsymmetrical conformer in which only one cyclopropane carbon–carbon bond is involved is only slightly destabilized with respect to the symmetrical species. It appears that the unsymmetrical ions may be fairly common whenever there may be a geometrical constraint. The nature of the species involved in such cases receives further consideration in the next section.

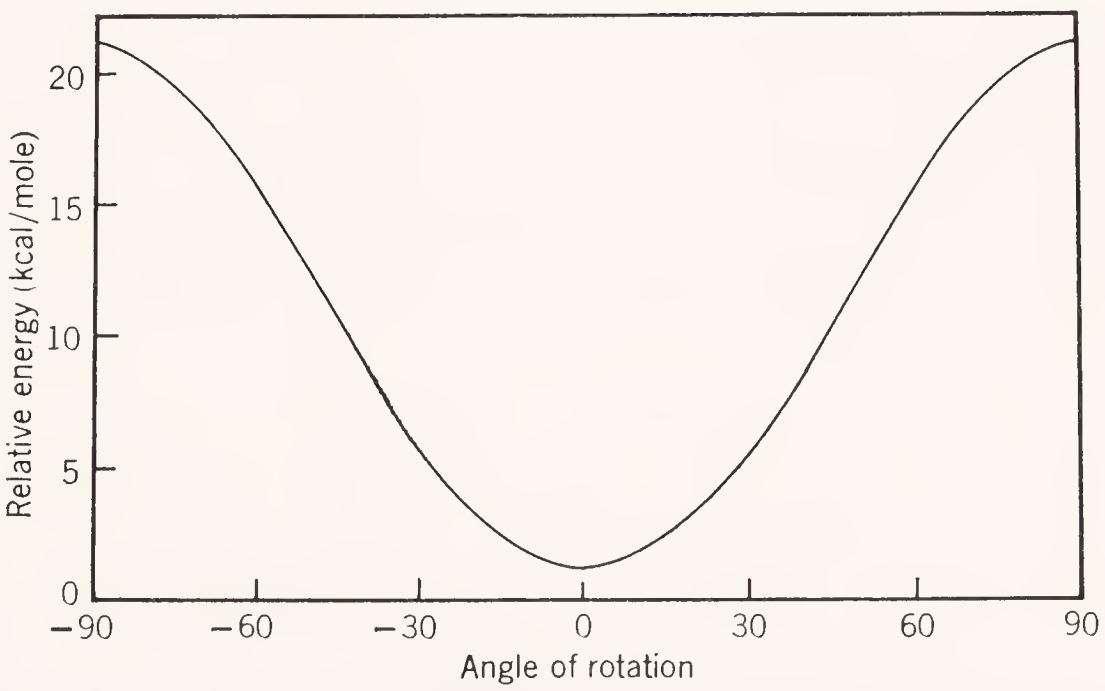


Fig. 3. Change in energy of the cyclopropylcarbinyl cation as the cationic center is rotated.

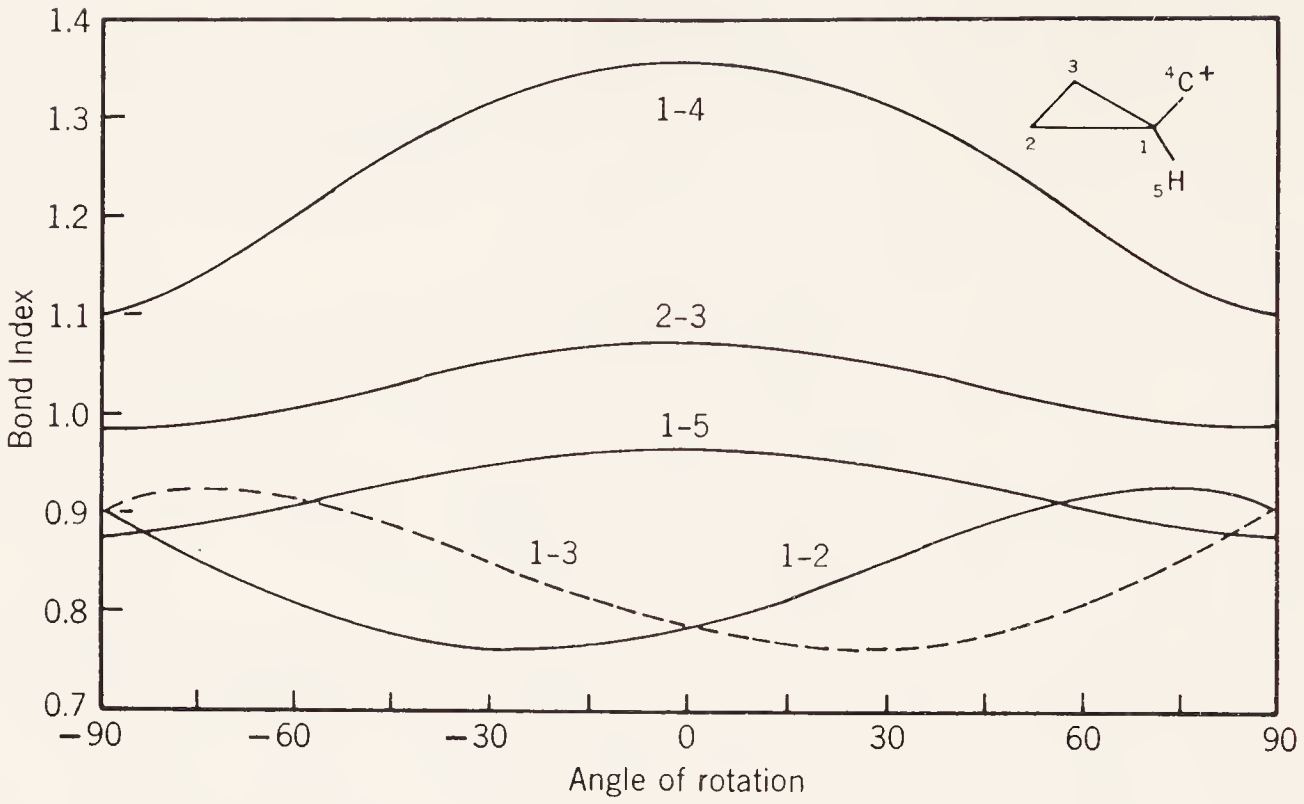
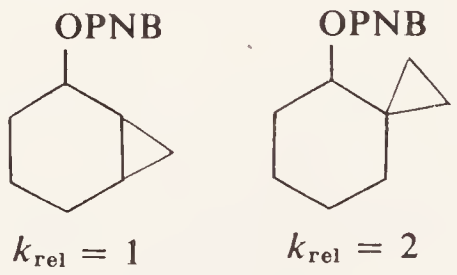


Fig. 4. Change in bond indices with rotation of the cationic center in the cyclopropylcarbinyl cation.

The bond index (58) changes are of some interest. In the symmetrical structure ($\alpha = 0°$), the 1,4 bond index is a maximum and decreases steadily as the methylene group is rotated. However, owing to the hyperconjugative interaction between the empty *p* orbital and the C-1–H-5 bond, the value at 90° rotation is still greater than unity. Correspondingly, the 1,5 bond index decreases by 0.1 on going from 0 to 90°. The 2,3 bond index is largest at 0°, corresponding to the relatively low values of the 1,2 and 1,3 indices. As the methylene group is rotated, the 1,2 and 1,3 indices change so that the bond more directly involved with the empty orbital has the lower bond index.

At first it might seem that it should be possible to obtain information on the geometrical requirements for interaction between the cyclopropane ring and the empty *p* orbital by comparing the bicyclic cases (Table II) with the spiro compounds (Table III). There is, however, very little difference in reactivity.



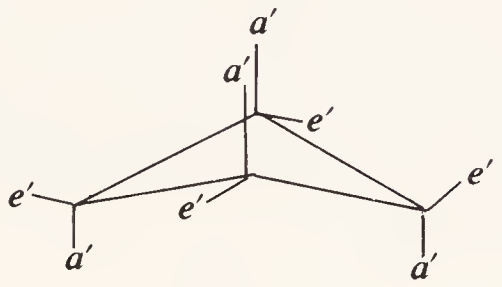
The two types of ring fusion both lead to an increase in strain. It is

probable that strain effects are at least as important as the difference in conjugative effects in determining the reactivity of compounds of this type.

III. CYCLOBUTYL DERIVATIVES

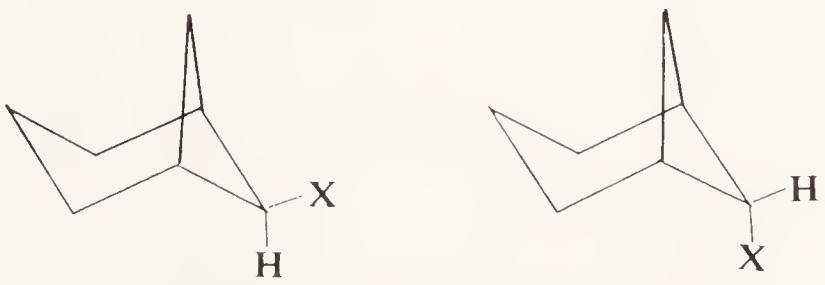
The cyclobutane ring is known to be puckered (96). The distortion from planarity leads to a decrease in C–C–C bond angle which is energetically unfavorable. However, up to a certain point this unfavorable bond angle is more than counterbalanced by the decrease in torsional strain (97). The minimum energy for the molecule is then found when the ring has been bent out of planarity by about 35° (98).

As a result of this distortion, the hydrogens (or other substituents) occupy positions corresponding to the axial and equatorial positions on a cyclohexane ring.

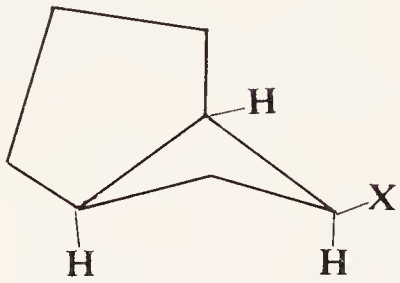


With monosubstituted cyclobutanes, we would expect the substituent to occupy the equatorial position; indeed, considerable evidence for this view has been obtained (96,99). In discussing the reactions of cyclobutane derivatives, it would be valuable to know the difference in reactivity between axial and equatorial substituents. These data may be obtained from an examination of bridged cyclobutanes.

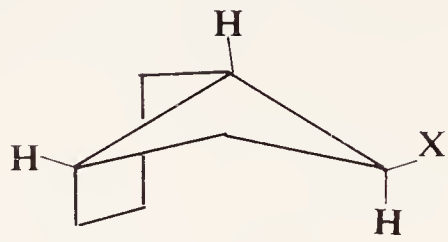
Cyclobutanes having a 1,3 bridge are relatively rigid and possess fixed axial and equatorial positions. The case of 1,2-bridged derivatives is more complex. In a *cis*-fused derivative, one of the bridging atoms is attached to an equatorial position and the other to an axial position. Thus a substituent on a methylene group may occupy an equatorial position regardless of whether it is *cis* or *trans* to the bridging ring.



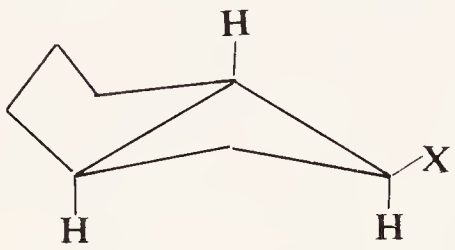
1,3-bridged fixed conformations

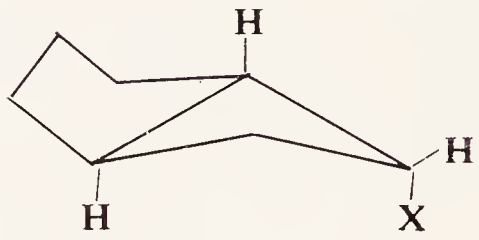


cis-1,2 bridged
cis substituent



cis-1,2 bridged
trans substituent

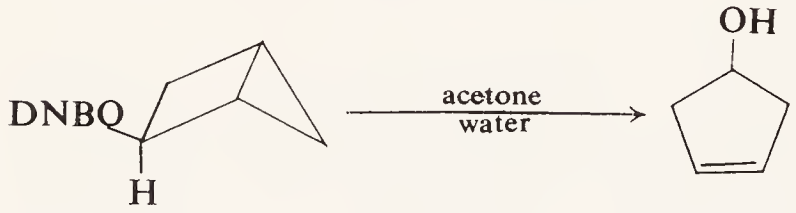




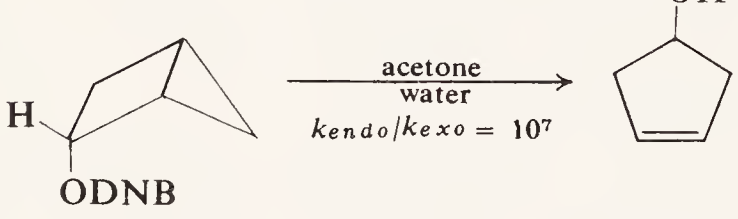
trans-1,2 bridged
fixed conformations

This may be contrasted with the *trans*-1,2 fused derivatives for which one epimer takes the axial position and the other the equatorial position.

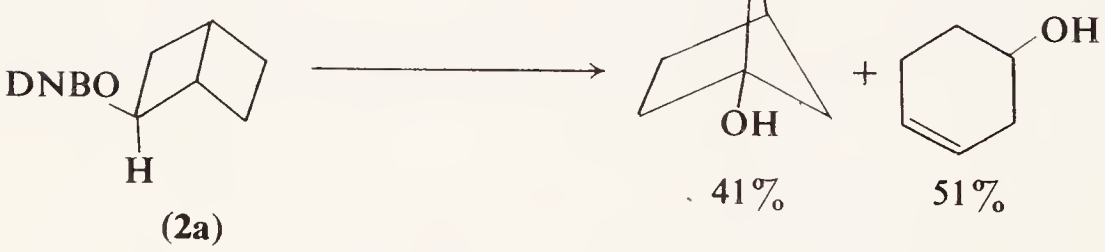
It is convenient to begin the consideration of the solvolysis of cyclobutyl derivatives by examining the reactions of the *cis*-fused bicyclo[*m*.2.0]alkyl derivatives **1–4**. It can be seen that an allylcarbinol is an important product in many cases.



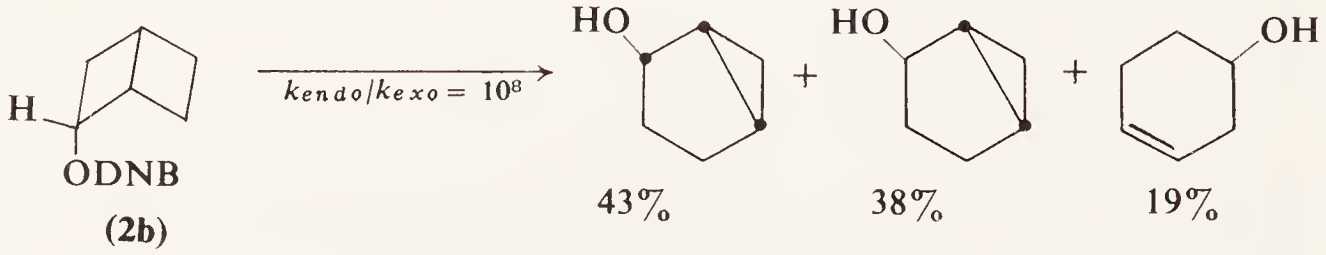
(1a) Ref. 83



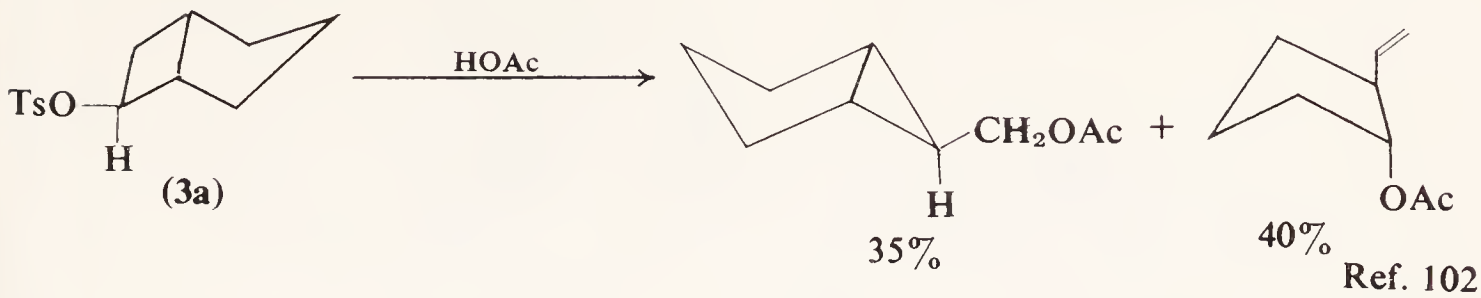
(1b) Ref. 83



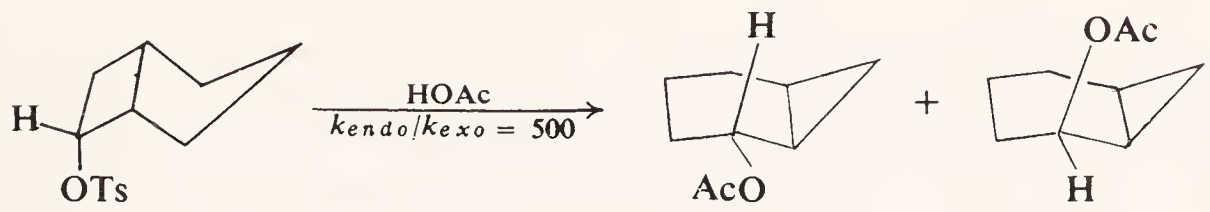
(2a) Ref. 100



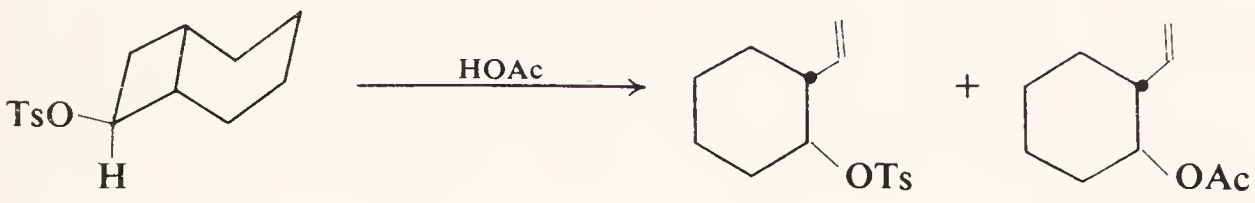
(2b) Ref. 101



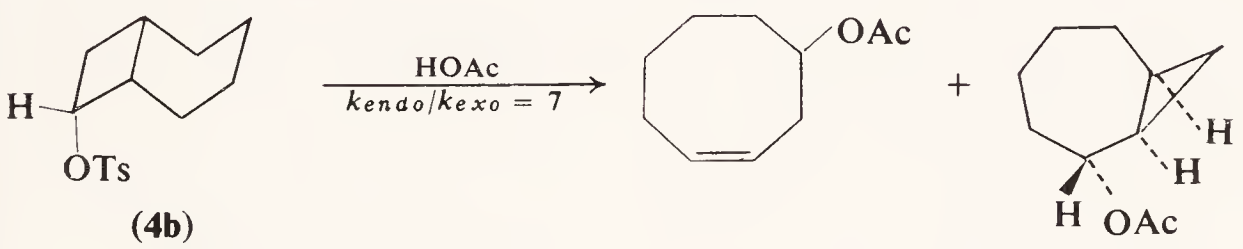
(3a) 35% 40% Ref. 102



(3b) 20% 80% Ref. 102



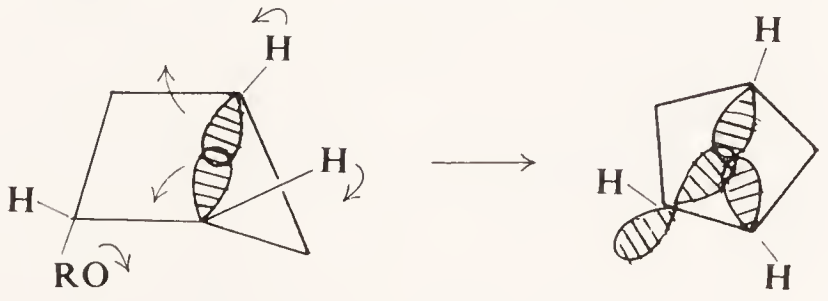
(4a) 53% 47% Refs. 95,103

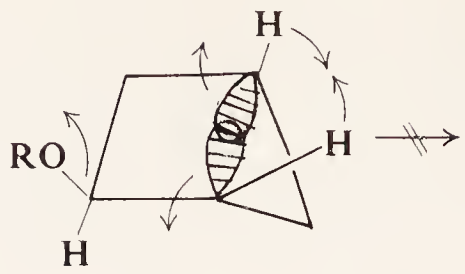


(4b) 64% 32% Refs. 95,103

Molecular orbital calculations suggest that the allowed mode of ring opening to an allylcarbinyl ion is a disrotatory process (104). The reaction would be expected to occur in a fashion giving maximum overlap between the orbitals of the bond being broken and the backside of the developing empty *p* orbital. This would be similar to the ring opening that occurs in the solvolysis of cyclopropyl derivatives (105).

Let us first examine the bicyclo[2.1.0]pentan-2-ols (83). In the case of the *endo*-isomer, the required bond movement results in the bridgehead hydrogens moving away from each other and a weakening of the central bond. This produces a relief of strain and leads to a large rate acceleration. In the case of the *exo*-isomer, a similar orbital participation process would require that the bridgehead hydrogens move toward each other. This would be an energetically unfavorable process, and the compound reacts only at the rate expected from a cyclopropylcarbinyl derivative.

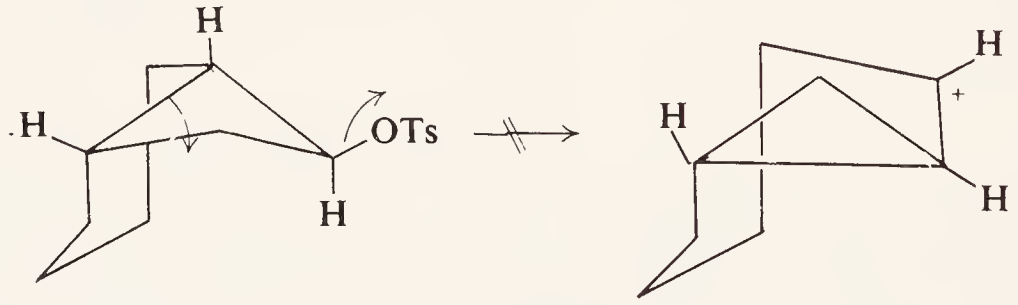




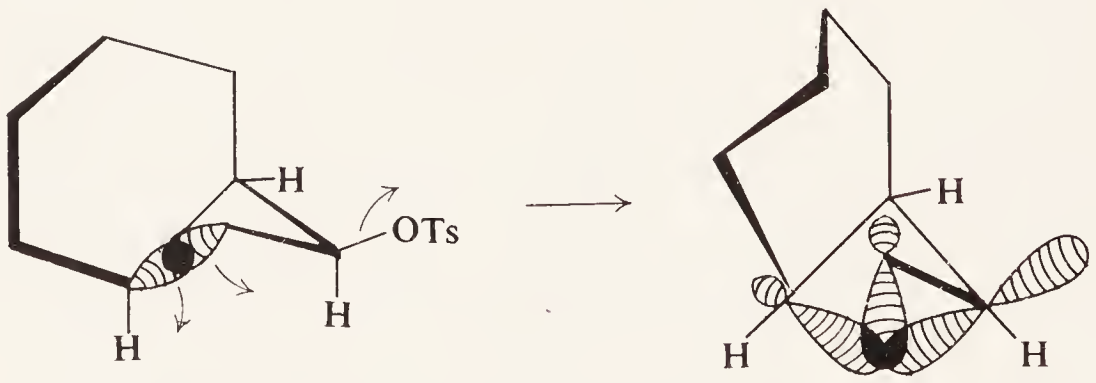
The bicyclo[2.2.0]hexanols give about the same *endo/exo* rate ratio because they have a similar geometry and the strain relief on going to the allylcarbinyl product is about the same as for the bicyclo[2.1.0]pentanols.

The smaller *endo/exo* rate ratio found with the bicyclo[3.2.0]heptyl derivatives is expected, since the strain in the system is considerably less. With the bicyclo[4.2.0]octyl derivatives, the normal conformation would probably have a puckered cyclobutane ring in which the bridgehead carbon–hydrogen bonds no longer lie in one plane. The steric restrictions on the bond movements are thereby relieved, leading to only a small *endo/exo* rate ratio.

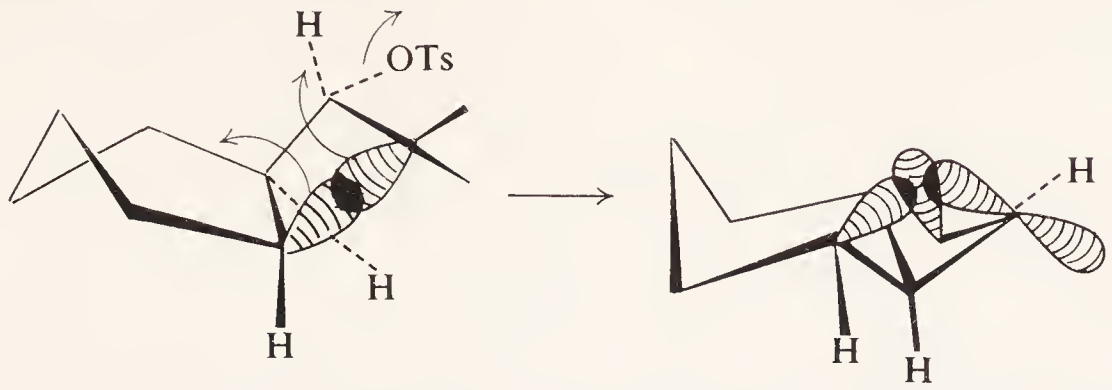
The change in products between pairs of epimers deserves comment. The reaction of **4a** does not give a bicyclo[5.1.0]octyl-2 cation because it would of necessity be *trans* fused.



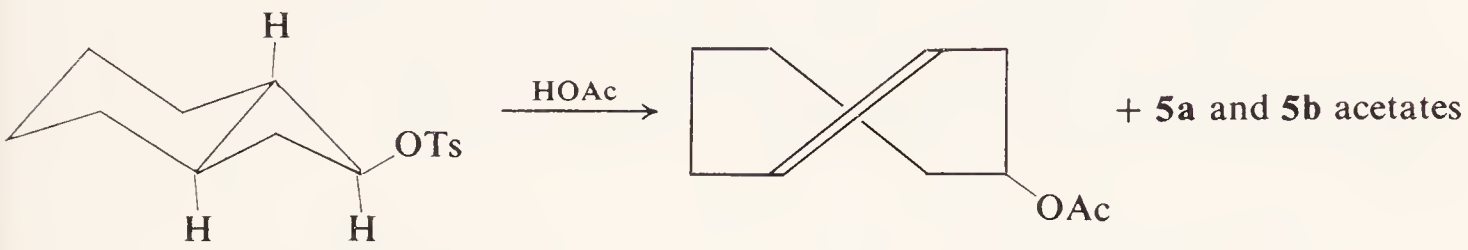
The reaction of **4b** could lead to vinylcyclohexyl acetate as well as the observed products. However, examination of the process leading to the vinylcyclohexyl cation reveals that it would be accompanied by the conversion of the cyclohexane ring to the boat form.



This is not energetically favorable, and the alternate reaction occurs. The formation of vinylcyclohexyl acetate from **4a**, on the other hand, will convert the somewhat flattened cyclohexane ring in the reactant to its normal chair form.

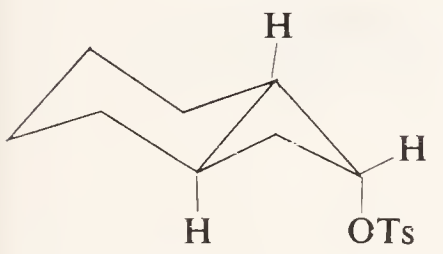


The *trans*-fused bicyclo[4.2.0]octyl-6 derivatives react in a fashion quite different from that of the *cis*-fused counterparts.



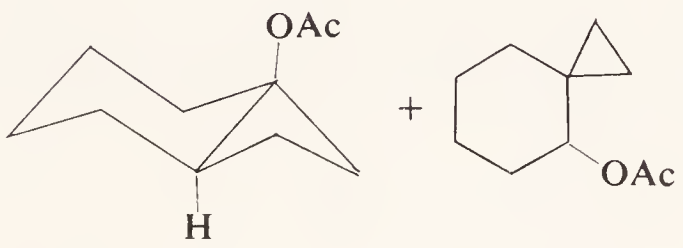
+ **5a** and **5b** acetates

(5a)



HOAc →

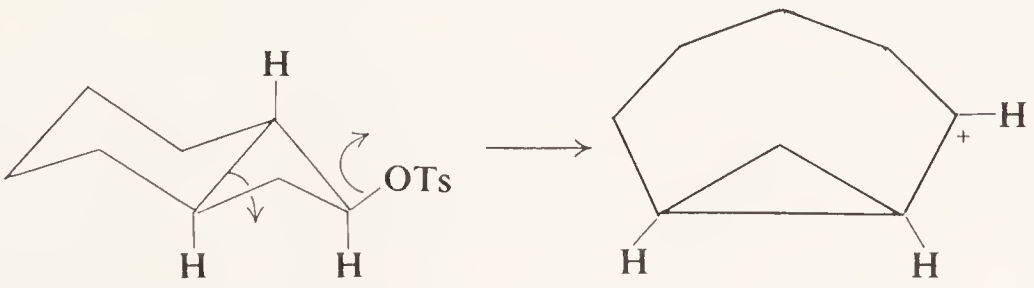
(5b)

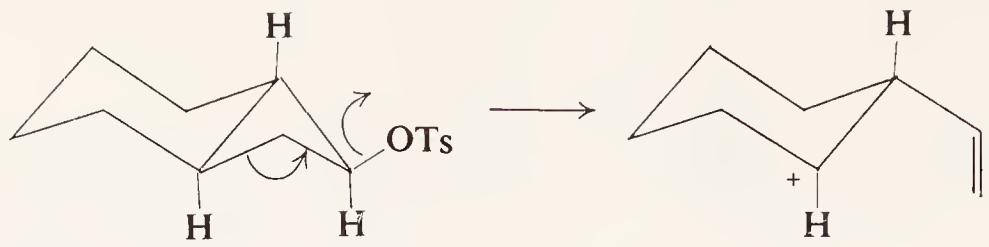


+ **5a** and **5b** acetates

Both epimers have a low reactivity (less than 1/100 that of **4a** and **4b**) and give major amounts of unrearranged products. The reaction of **5b** is not surprising because no carbon–carbon bond is properly located for participation in the ionization step. However, the bridgehead hydrogen is *trans* to the leaving group, and we know that the first two products result from the bridgehead ion thus produced. Similarly, if the axial hydrogen at the adjacent methylene group were to participate in the loss of the tosyl group, the resultant ion could be attacked by solvent to give both **5a** and **5b** acetates.

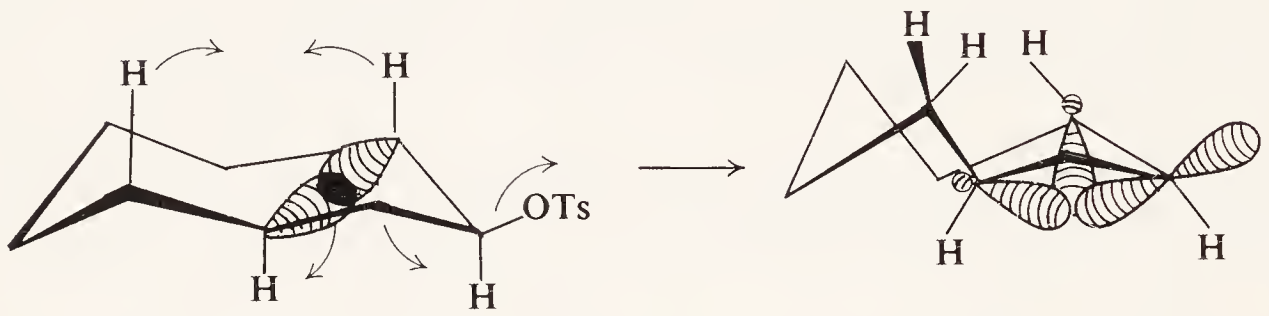
A simple consideration of the reaction of **5a** suggests that it should give





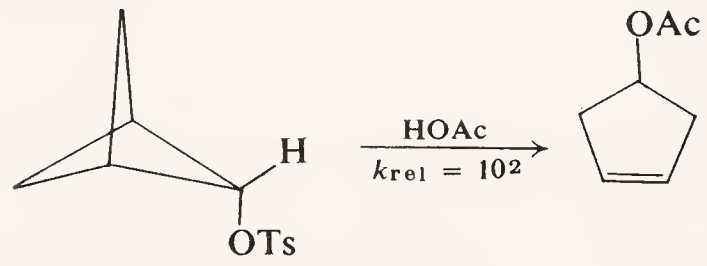
However, these products are not formed, and we have instead a *trans*-cyclooctene derivative. The latter is about 9 kcal/mole less stable than a *cis*-cyclooctene (106). Thus the process appears to lead to the thermodynamically less stable of the possible products.

The reaction of **5a** can be understood in terms of the orbital participation scheme outlined previously. Ionization with participation would lead to significant hydrogen–hydrogen and carbon–hydrogen nonbonded repulsion.



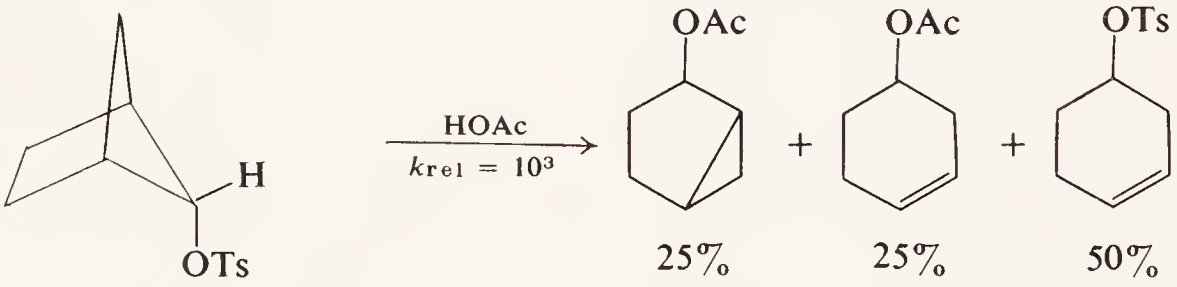
Thus the reaction does not follow this course, is quite slow, and yields the relatively unstable *trans*-cyclooctenol as the product.

Let us now turn to the 1,3-bridged cyclobutyl derivatives and some of the available data.



Ref. 107

(6)

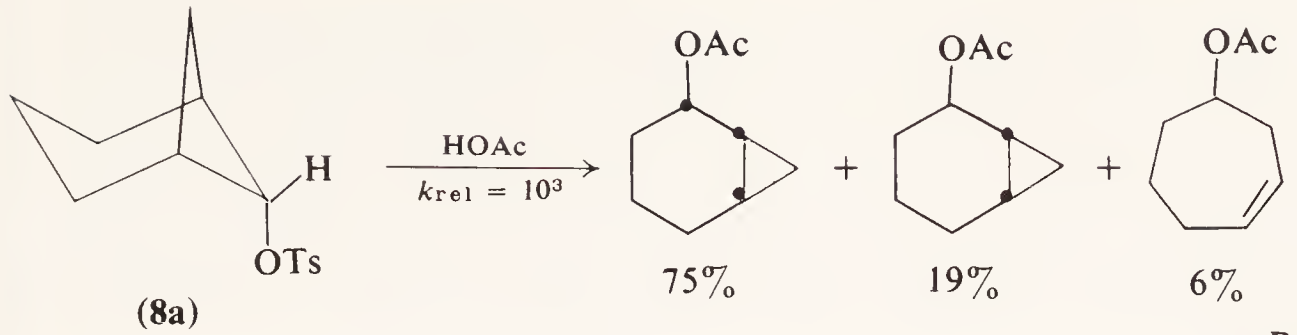


Ref. 108

(7a)

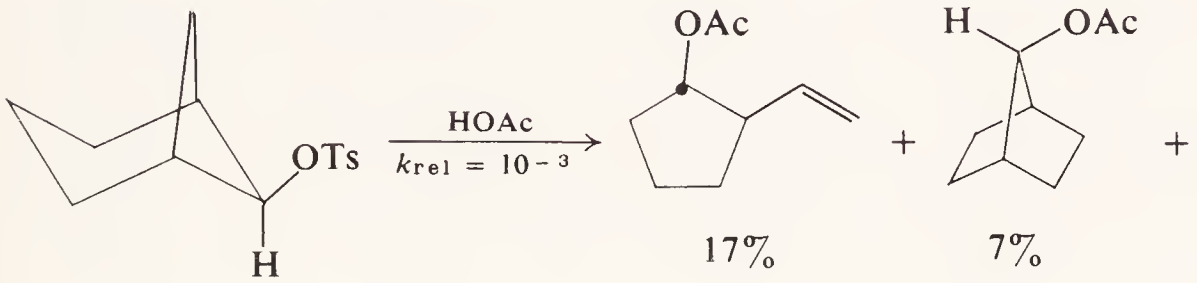
Ref. 108

(7b)

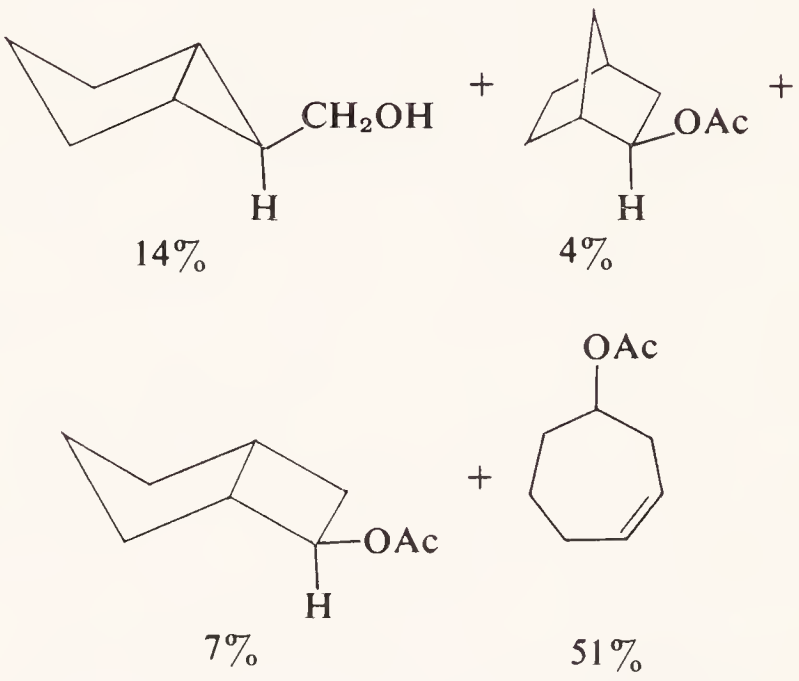


(8a)

Ref. 109

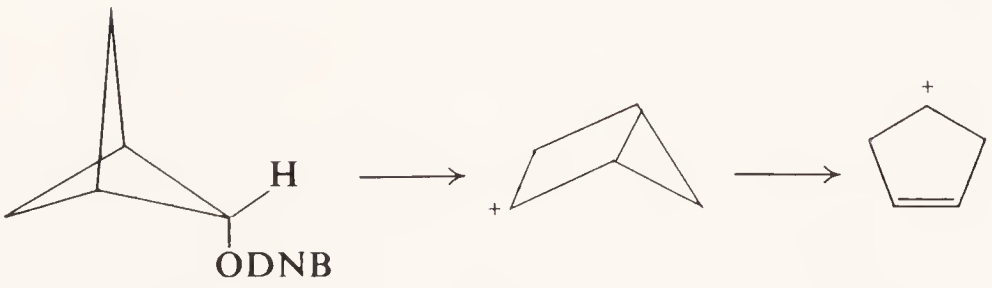


(8b)



Ref. 109

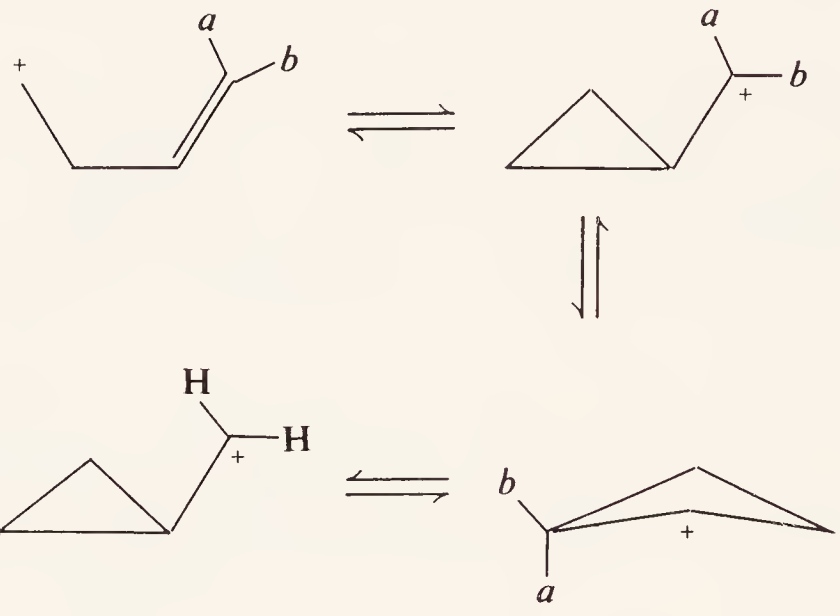
The *endo*-isomers are all about 10^3 more reactive than cyclobutyl itself, and they lead to products that correspond to an initial rearrangement to a secondary cyclopropylcarbinyl cation



In view of the high reactivity compared to cyclobutyl, it seems probable that rearrangement accompanies the ionization step. The disrotatory ring opening discussed previously will lead to strain relief on going to the activated complex (104).

The *exo*-isomers cannot rearrange by a concerted disrotatory path because of their geometry. Furthermore, the leaving group is axial, and no cyclobutane carbon–carbon bond is located so that it may participate in the ionization step. As a result, the *exo*-isomers have particularly low reactivity. The difference in reactivity between **7b** and **8b** probably results from the difference in bond angle at the reactive site [84.5° in **7b** (110) and 88° in **8b**].

The foregoing data indicate the nature of the important rearrangement processes leading to allylcarbinyl or cyclopropylcarbinyl products. It is important to note that all these processes are stereospecific, as were the rearrangements of the cyclopropylcarbinyl reactants. It is now clear that all these rearrangement processes may be described as



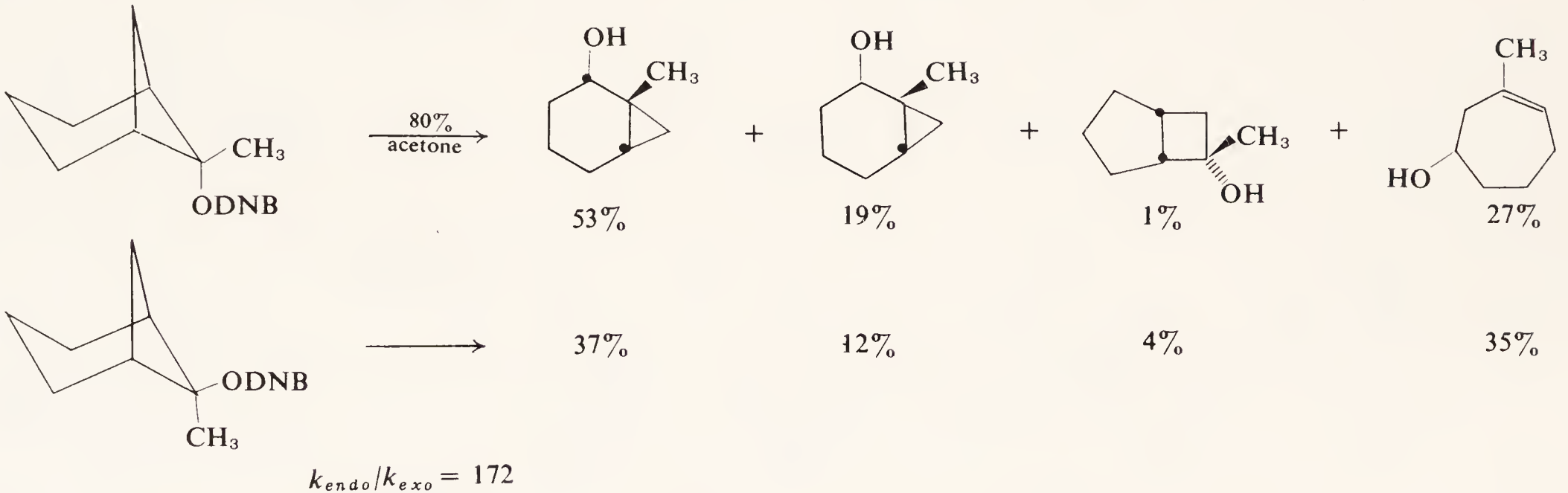
A major characteristic of the bicyclic compounds previously discussed is their tendency to rearrange. This may indicate either that the cyclobutyl cation that might be formed is not particularly stable or that there is considerable driving force from strain relief. It should be possible to suppress rearrangement by increasing the stability of the cyclobutyl cation via substitution of an electron releasing group at the α-carbon. The results of such an investigation (111) appear in Table IV.

In the bicyclo[3.1.1]heptyl case, the relatively unreactive *exo*-derivatives give the normal rate increases with α-substitution. The *endo*-isomers, however, produce a relatively small rate increase, and this is especially true in comparing the unsubstituted with the methyl-substituted derivatives. Since even with phenyl substitution, all the products are rearranged, the high rates of reaction of the *endo* derivatives must be due to a driving force from rearrangement. With a *p*-anisyl substituent, some unrearranged product is finally formed.

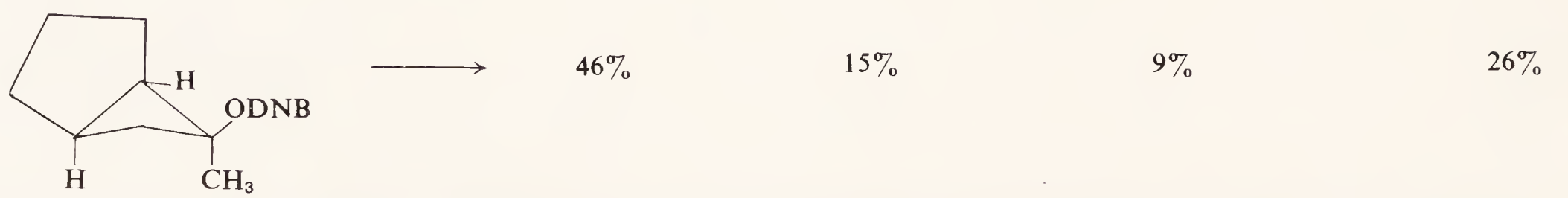
The bicyclo[3.2.0]heptyl case is similar. For the unsubstituted compounds, the k_{endo}/k_{exo} rate ratio is 500 (cf. 10^6 for the bicyclo[3.1.1]heptyl

TABLE IV

Effect of α-Substitution on the Solvolysis of Bicyclic Cyclobutyl Derivatives (111)



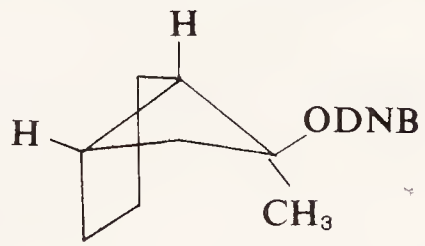
$k_{endo}/k_{exo} = 172$
$k^{CH_3}_{endo}/k^{H}_{endo} = 19$
$k^{CH_3}_{exo}/k^{H}_{exo} = 12{,}000$



(*continued*)

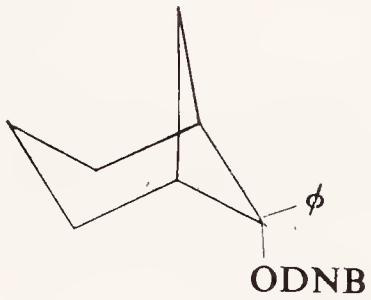
TABLE IV (*Continued*)

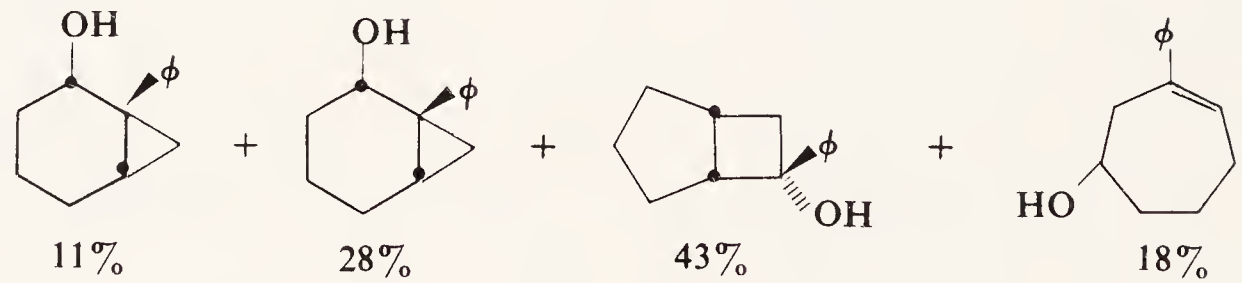
Effect of α-Substitution on the Solvolysis of Bicyclic Cyclobutyl Derivatives (111)



47% 15% 6% 23%

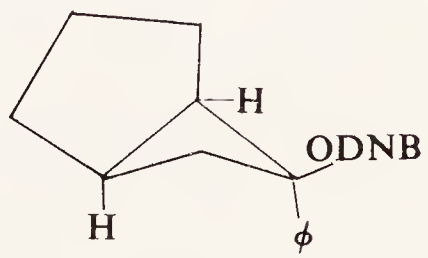
$k_{endo}/k_{exo} = 12$





11% 28% 43% 18%

$k^{\phi}_{endo}/k^{CH_3}_{endo} = 3.2$

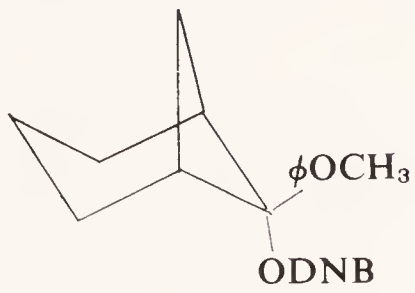


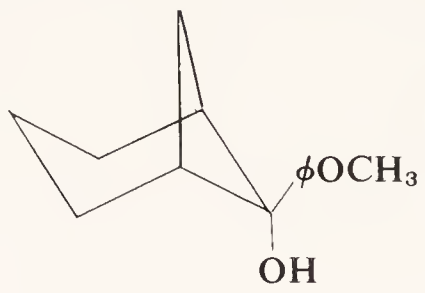
18% 31% 43% 8%

$k^{\phi}_{endo}/k^{CH_3}_{endo} = 82$

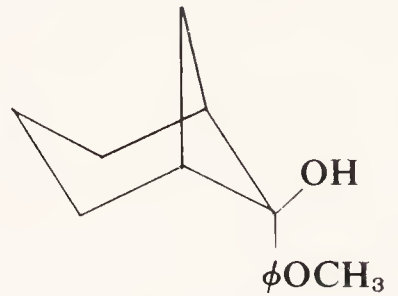
TABLE IV (*Continued*)

Effect of α-Substitution on the Solvolysis of Bicyclic Cyclobutyl Derivatives (111)

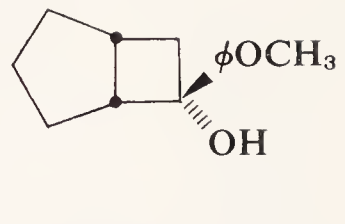




50%

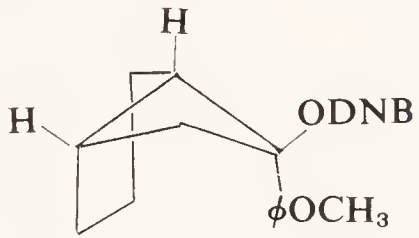


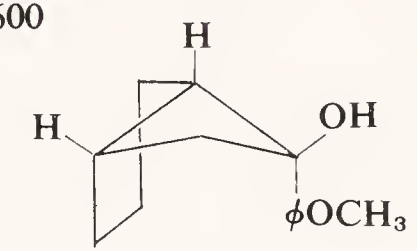
22%



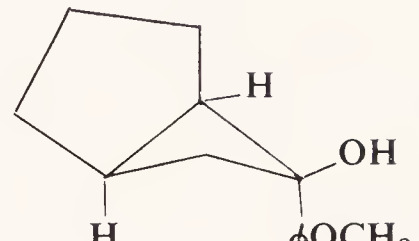
17%

$k_{endo}^{\phi OCH_3}/k_{endo}^{\phi} = 600$



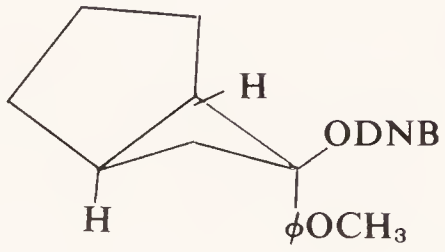


84%



16%

$k_{endo}^{\phi OCH_3}/k_{endo}^{\phi} = 3000$



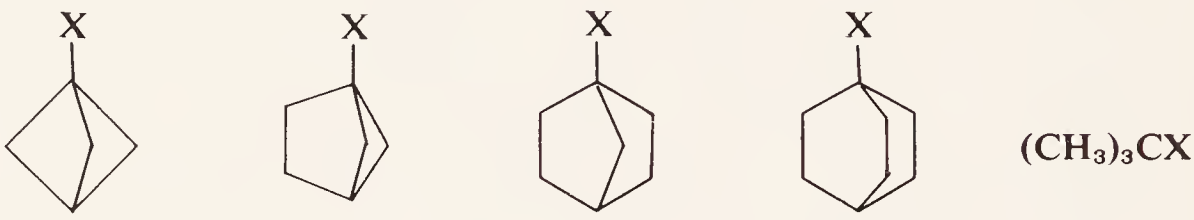
84%

16%

$k_{endo}^{\phi OCH_3}/k_{exo}^{\phi OCH_3} = 0.05$

series). This drops to 12 with methyl substitution and to 0.2 with anisyl substitution. The proportion of unrearranged products increases from 6 to 9% with methyl substitution, to 43% with phenyl substitution, and to 100% with *p*-anisyl substitution. These data do not suggest any large stabilization for a cyclobutyl cation.

Another way of obtaining tertiary cations in this series of bicyclic compounds is to place the leaving group at the bridgehead. This does lead to enhanced rates when one of the rings is cyclobutyl (122,113).



Whereas the normal trend toward lower rates with increasing angle strain at the bridgehead is found through the 1-norbornyl derivative, the still smaller rings lead to increased rates. The products from the latter are entirely rearranged, suggesting again that the rate acceleration is due to strain relief in the activated complex.

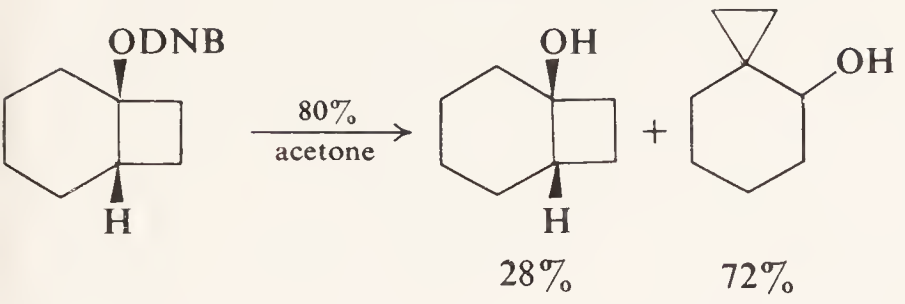
With the bicyclo[3.2.0]heptyl and bicyclo[4.2.0]octyl systems, the rings may be fused either *cis* or *trans*. Investigations of the corresponding bridgehead derivatives have yielded the data in Table V (114). Neglecting the internal return and olefinic products, each *cis-trans* pair gave essentially the same ratio of products. The same ratios also were obtained from the spiro-cyclopropylcarbinyl derivatives, suggesting one or more common intermediates. The increased rate of reaction of the *trans*-fused compounds again may be attributed to strain relief on ionization to the *cis*-derived ion.

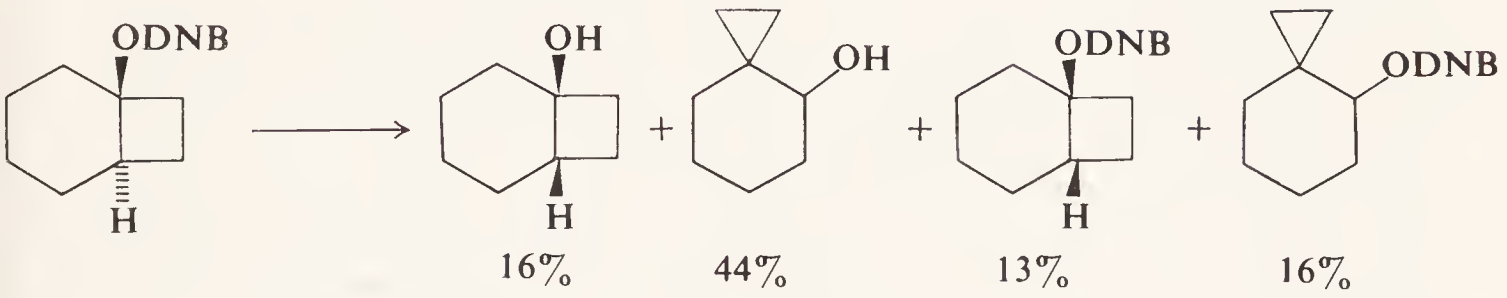
Before continuing further, it is appropriate to consider theoretical treatments of the cyclobutyl cation. The structure of the cation has been considered using both the extended Hückel (115,116) and CNDO (58) methods. Davis and Ohno concluded from their calculations that the most stable conformation of the cation had a planar ring, whereas Baldwin and Foglesong decided that the more stable conformation had a puckered ring. In agreement with the earlier CNDO calculations (58), the latter authors concluded that a 1,3 interaction should be important in stabilizing the cyclobutyl cation. One difficulty with obtaining minimum energy geometries in the foregoing calculations is that the parameters used do not lead to the observed carbon–carbon bond lengths.

Further CNDO calculations have been carried out (104), using parameters that were optimized for hydrocarbons (117). Here, the minimum energy conformation was calculated to be puckered by about 80°. The charge distribution and bond indices are shown below. The large 1–3

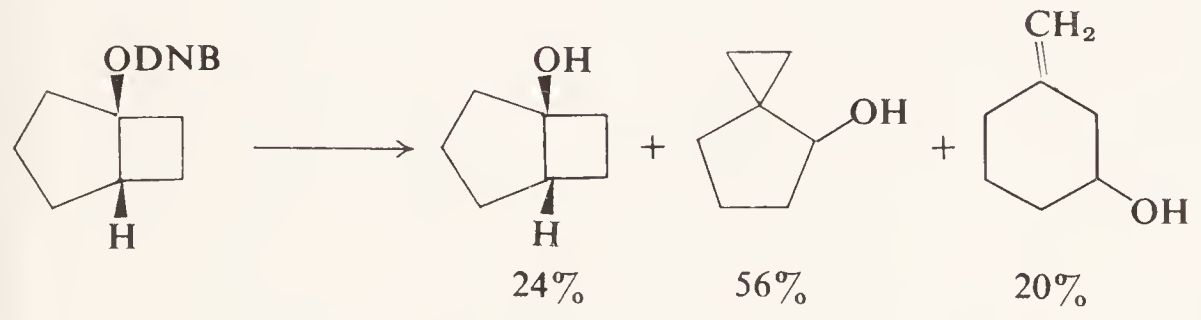
TABLE V

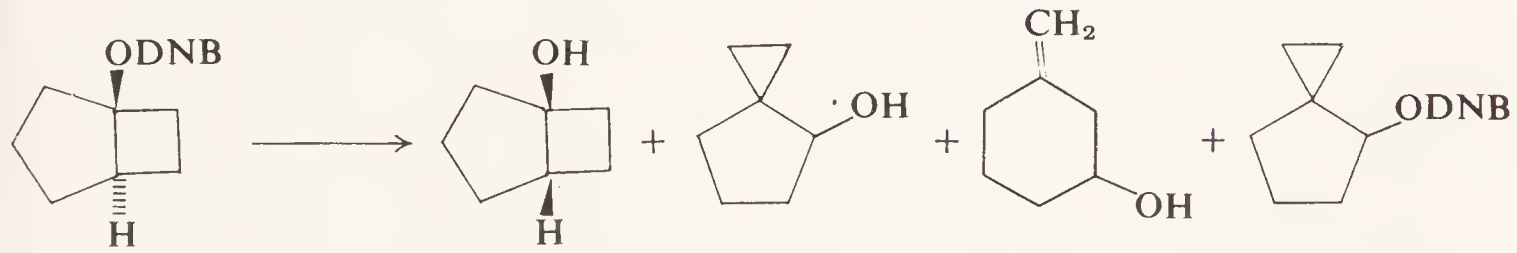
Solvolysis of Bridgehead-Substituted Bicyclo[3.2.0]heptanes and Bicyclo[4.2.0]octanes





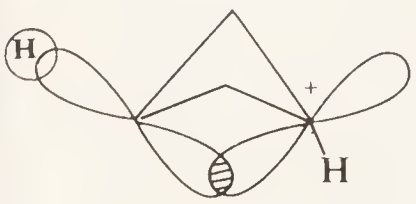
$k_{trans}/k_{cis} = 17$

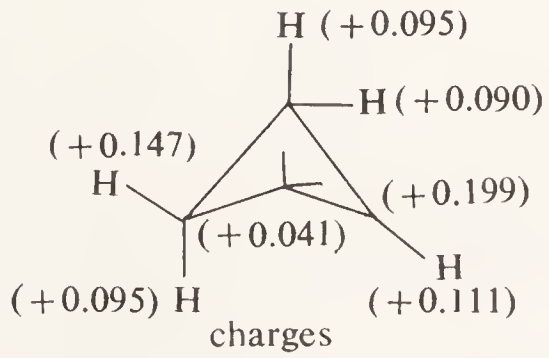




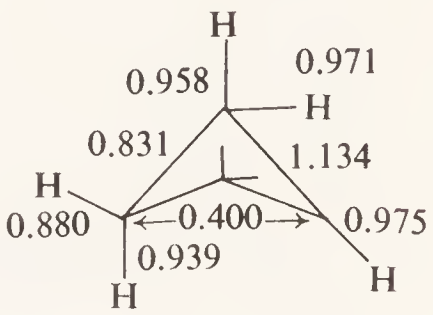
$k_{trans}/k_{cis} = 4 \times 10^5$

bond index results from the strong interaction between the empty *p* orbital and the *p* component of the orbital holding the *exo*-3-hydrogen. The species thus formed might appropriately be called a symmetrical bicyclobutonium ion (58).





charges



bond indices

A calculation dealing with the pathways by which the puckered cyclobutyl cation may be opened to a homoallyl ion suggests that only a disrotatory mode is electronically allowed (104). This is in good agreement with the experimental results given previously.

One general difficulty with the current semiempirical molecular orbital methods is their tendency to overstress the stabilization that results from multiple bonding at a carbon (118). Thus the stabilization of nonclassical ions is overemphasized by these procedures. It is not possible at the present time to know how much stabilization (if any) actually results from the calculated 1-3 interaction in the cyclobutyl cation. All that can be said with certainty is that, if the cyclobutyl cation is an intermediate in the conversion of one cyclopropylcarbinyl cation to another, it must be puckered in order to account for the stereochemistry of the process.

The foregoing discussion was confined to bicyclic derivatives because of their ability to define and control conformations. Much valuable information is available concerning simpler substituted cyclobutyl tosylates. Some of these data are summarized in Table VI.

The only product formed from the 3-phenyl derivatives is the corresponding allylcarbinyl derivative; this and the cyclopropylcarbinyl derivatives are the major products from the 3-alkylcyclobutyl tosylates. In all these cases, however, both isomers are less reactive than cyclobutyl

TABLE VI

Rates of Solvolysis of Substituted Cyclobutyl Tosylates

Compound	k_{rel}[a]	k_{trans}/k_{cis}	Ref.
cis-3-Phenyl	1/375	74	119
trans-3-Phenyl	1/5	—	119
cis-3-*p*-Tolyl	1/250	77	119
trans-3-*p*-Tolyl	1/3	—	119
cis-3-*p*-Chlorophenyl	1/770	69	119
trans-3-*p*-Chlorophenyl	1/11	—	119
3,3-Diphenyl-	1/1000	—	120
cis-3-*t*-Butyl	1/125	18	121,122
trans-3-*t*-Butyl	1/7	—	121,122
cis-3-Isopropyl	1/16	6	123
trans-3-Isopropyl	1/3	—	123
cis-3-Ethoxy	1/2300	12	119
trans-3-Ethoxy	1/190	—	119
cis-3-Chloro	1/50,000	3	119
trans-3-Chloro	1/15,000	—	119

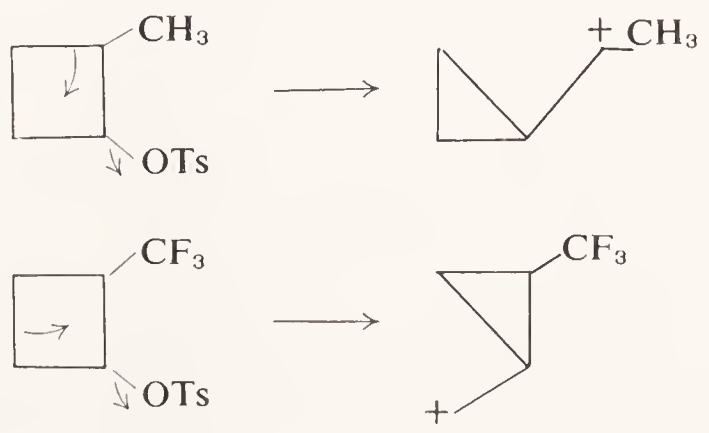
[a] Relative to cyclobutyl tosylate (= 1.0).

tosylate, and the *cis*-isomer is generally much less reactive than the *trans*-isomer. These data are not accommodated by the formation of either a cyclobutyl cation or an allylcarbinyl cation. The *trans*/*cis* ratio cannot be explained by the former ion, and the low reactivities of the phenyl-substituted compounds argue against the latter.

All the data appear to fit if we suggest that a cyclopropylcarbinyl ion is formed in the usual stereospecific fashion directly in the ionization step. The solvolysis of 2-arylcyclopropylcarbinyl tosylates (124) leads to the same allylcarbinyl product as the 3-arylcyclobutyl tosylates, and both groups of compounds lead to the same value of ρ (-1.6). In the cyclobutyl series, the *trans*-3-substituted compound should be less stable than the *cis*-isomer, which has two pseudo-equatorial groups. The *trans*-3-arylcyclobutyl tosylates would lead to the *trans*-2-arylcyclopropylcarbinyl ions, which should be more stable than the *cis* ions [*cis*-disubstituted cyclopropanes are generally less stable than the *trans*-isomers (125)]. Thus the *trans* compounds, which are destabilized in the reactant and not destabilized in the initial product ion, should be more reactive than the *cis* compounds, which are destabilized in the product ion.

When the substituent is attached to the 2-position of the cyclobutyl derivative, marked rate acceleration is normally found. The acetolysis of 2,2-dimethylcyclobutyl brosylate occurs 10^3 times more rapidly than the 3,3-dimethyl compound (126). Wiberg and Nelson (127) found that *cis*-2-methylcyclobutyl tosylate was 22 times as reactive as cyclobutyl tosylate, and 3.3 times as reactive as the *trans*-isomer. The only product was methylcyclopropylcarbinyl acetate. The solvolysis of 2-trifluoromethylcyclobutyl tosylate gave a markedly different result, with 70% of the product being 2-trifluoromethylcyclopropylcarbinol (128). Unfortunately, kinetic data are not available.

It now appears that potential cation-stabilizing groups in the 2-position lead to rearrangement in the ionization step so that the group is placed adjacent to the positive charge. Conversely, electron-withdrawing groups force the rearrangement to proceed so that the group is placed away from the cationic center.

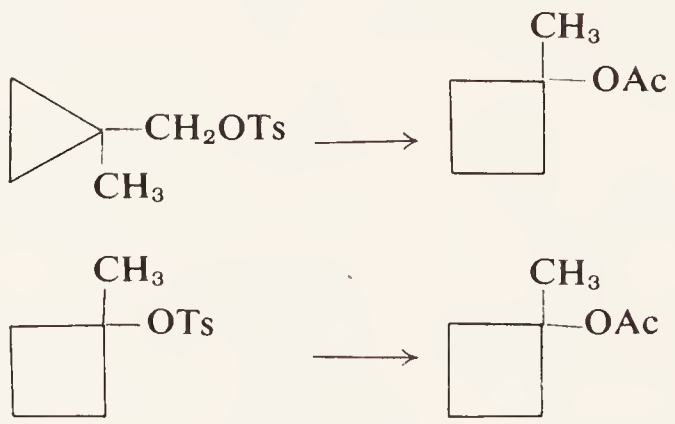


It seems reasonable to conclude that all secondary cyclobutyl derivatives having a reactivity comparable with or greater than that of cyclobutyl tosylate rearrange to a cyclopropylcarbinyl cation in the ionization step. There appears to be no evidence requiring the formation of a secondary cyclobutyl cation in these cases. These conclusions apply not only to the solvolyses just discussed, but also to the large body of data dealing with the deamination of cyclobutylamines. The products and the stereochemistry of the reaction correspond well to those found in the solvolyses (129–132).

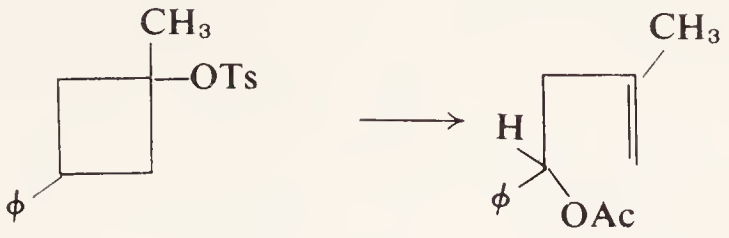
The one case in which a secondary cyclobutyl cation appears to be an intermediate is the solvolysis of 3-ethoxycyclobutyl tosylates (119). Here both the *cis*- and *trans*-isomers gave as the only products a mixture of *cis*- and *trans*-3-ethoxycyclobutanol, and the same ratio was obtained from each reactant.*

Since both isomers react at a very much slower rate than cyclobutyl tosylate, there is no reason to think that the ion is other than an unstabilized classical cyclobutyl cation. With a stronger electron-withdrawing group in the 3-position (chlorine), only S_N2-type solvolytic reactions were observed (119).

The tertiary cases appear to furnish a more promising area for possibly finding a nonclassical cyclobutyl cation, since in some cases unrearranged cyclobutyl compounds are formed as products. Thus 1-methylcyclopropylcarbinyl tosylate undergoes solvolysis to give 1-methylcyclobutanol as the only product (134). With a suitable electron-releasing group, the tertiary cyclobutyl derivative becomes the major product, suggesting that the tertiary cyclobutyl cation has become more stable than the primary cyclopropylcarbinyl cation. This, however, is probably due mainly to the intrinsic difference in energy between primary and tertiary ions. When a more stable product may be formed, the reaction takes a different course. 1-Methyl-3-phenylcyclobutyl tosylate forms as the major product the allylcarbinyl derivative (119)



* Similar results have been obtained in the deamination of the corresponding amines (133).



Again, the data do not present a case for a nonclassical cyclobutyl cation.

The nmr spectrum of the ion derived from 1-methylcyclobutanol in antimony pentafluoride at low temperature has been examined (135). The spectrum consisted of a quartet with a relative area of 2 and a heptet with a relative area of 1. This is consistent with a methylcyclobutyl cation in rapid equilibrium with the corresponding cyclopropylcarbinyl cation, and it clearly shows that the ion is not a static methylcyclobutyl cation. A similar conclusion has been reached in a study of the formation of 1-methylcyclobutanol from (β-methylallyl)carbinylamine with nitrous acid (136).

A variety of other studies of cyclobutyl derivatives have been carried out. As examples, the secondary kinetic isotope effects associated with the solvolyses of both the cyclobutyl and cyclopropylcarbinyl derivatives have been carefully examined (137). The solvolysis of highly alkyl-substituted cyclobutyl tosylates have been investigated with regard to both reactivity and product composition (138–141). These compounds have the extra complication of interactions involving the additional alkyl groups, but generally they behave in a manner analogous to the less substituted compounds.

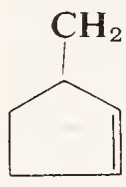
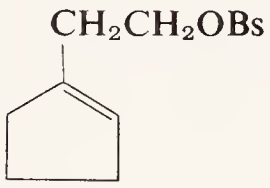
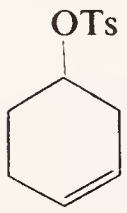
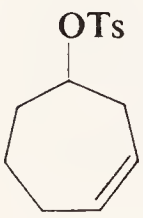
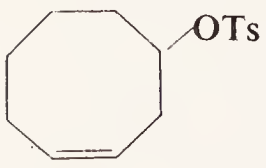
IV. ALLYLCARBINYL DERIVATIVES

In the previous sections, we presented evidence for the cyclopropylcarbinyl and cyclobutyl cations as discrete species which are in equilibrium with each other. In many cases, allylcarbinyl derivatives react at accelerated rates to give cyclopropylcarbinyl derivatives. Here we consider the nature of the cationic species formed and the activated complex leading to the ion. The subject of homoallylic ions is not covered in detail, since they are discussed in Chapter 23. The emphasis is on the relation of these ions to the cyclopropylcarbinyl and cyclobutyl cations.

A major question with the allylcarbinyl derivatives is whether the double bond participates in the formation of the activated complex. Such participation should be manifested by an increased rate of reaction, and a common test is to compare the rate of acetolysis of the given compound with that of the saturated analog. Some typical data are recorded in Table VII. Whereas no rate increase is found with allylcarbinyl itself and Δ^3-cyclohexenyl tosylate, large rate increases occur with other compounds.

TABLE VII

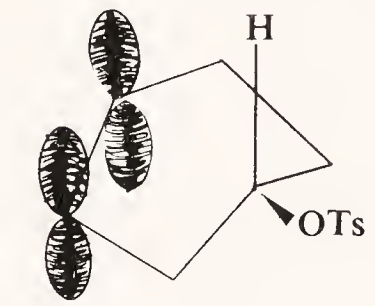
Rate Acceleration with Allylcarbinyl Derivatives

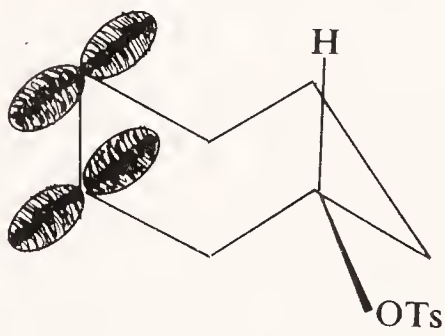
Compound	k/k_{sat}, HOAc	k/k_{sat}, EtOH	Ref.
$CH_2{=}CH{-}CH_2{-}CH_2{-}OBs$	0.5	0.5	143
$H_2C{=}CH{-}C(CH_3)_2{-}CH_2OBs$	60	—	144
$H_3C{-}C(CH_3){=}CH{-}CH_2CH_2{-}OTs$	1200	—	145
$H_3C{-}C(CH_3){=}CH{-}C(CH_3)_2{-}CH_2OBs$	10^7	—	146
	10	4.4	147
	40	1.1	148
	0.1	—	149
	10	—	150
	2	—	151

In at least some cases, the rate ratio is solvent dependent, decreasing in more nucleophilic solvents. This suggests that the double bond must compete with the solvent for stabilization of the cationic center. In order to see maximum participation, the reactions probably should be carried out in a solvent of low acidity and low nucleophilicity, e.g., trifluoroethanol (142).

The rate acceleration observed with open-chain compounds is important but difficult to interpret, because several conformations are available to them. Since similar effects are found in both open-chain and cyclic compounds, it seems reasonable to attempt to apply conclusions drawn from the behavior of the latter to the former.

Possibly the most important observation concerns the large increase in reactivity on going from 3-cyclohexenyl tosylate to 3-cycloheptenyl tosylate and 3-cyclooctenyl tosylate. The cyclohexenyl derivative is forced to have the empty *p* orbital roughly parallel to the *p* orbitals of the double bond. The addition of another methylene group to the ring leads to a favorable conformation in which the empty *p* orbital is directed toward the *p* orbitals of the double bond.



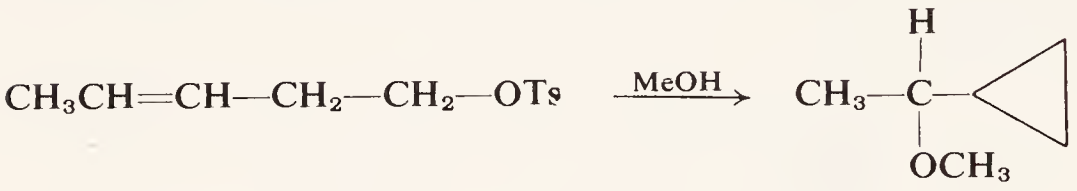


The final result of this interaction with the cycloheptenyl derivative is the norcaranyl ion. The activated complex may have a structure similar to an unsymmetrical homoallylic ion, or it may have a structure similar to the norcaranyl ion (which, as indicated previously, is probably a symmetrical cyclopropylcarbinyl cation). One way of obtaining an answer is to determine whether the activated complexes for the solvolysis of norcaranyl derivatives and 3-cycloheptenyl derivatives have similar heats of formation. These data could be derived from the heats of formation of the reactants,

the heat of solution of the reactants, and the activation enthalpies for the two acetolysis reactions. Unfortunately, the necessary thermochemical data are not yet available, although they are being obtained in this laboratory.

A rough estimate of the difference in energy between the two activated complexes may be made, however. The activation energies are 22 kcal/mole for the cycloheptenyl tosylate and ca. 16 kcal/mole for the norcaranyl tosylates, giving a difference of 6 kcal/mole. This is very close to the difference in energy between propylene and cyclopropane (8 kcal/mole), indicating that the energies of the two activated complexes cannot differ by more than a few kilocalories per mole and may indeed be almost the same.

Most of the reactions of allylcarbinyl derivatives may be explained on the basis of the formation of a cyclopropylcarbinyl cation. This may be seen from the cholesteryl-*i*-cholesteryl conversion and from a variety of other reactions (152), including the following:



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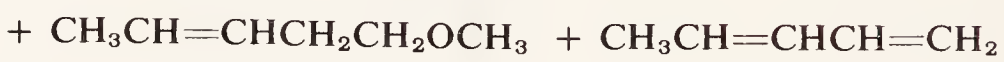

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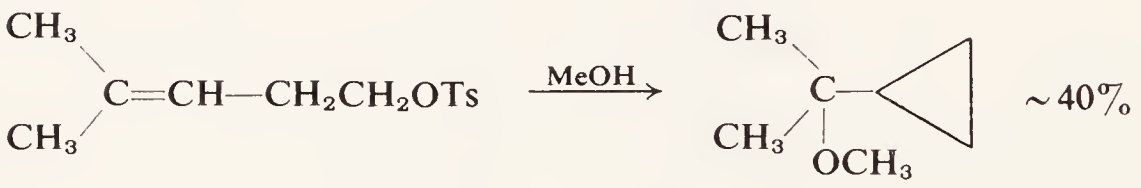

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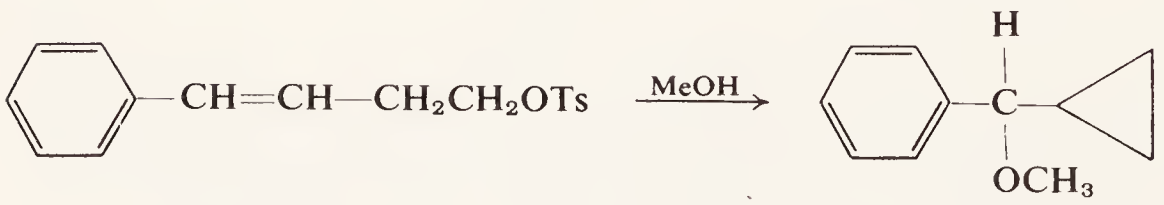

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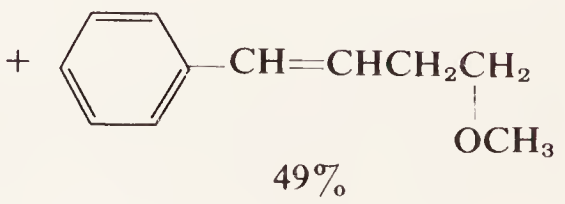

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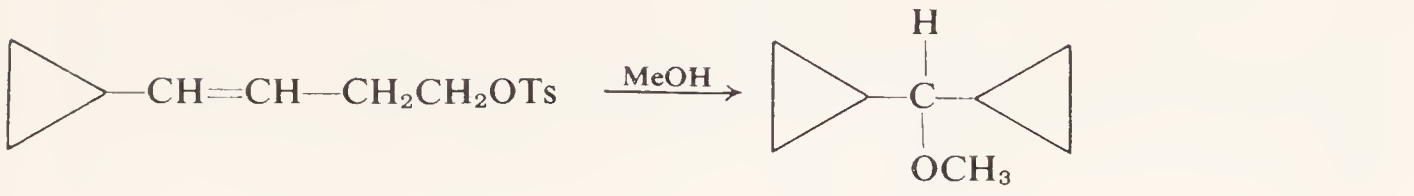

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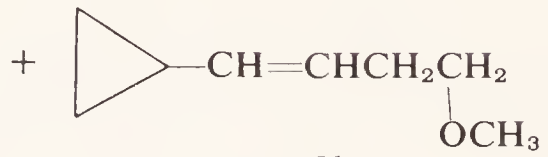

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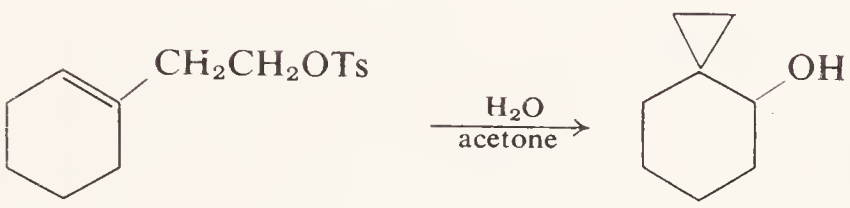

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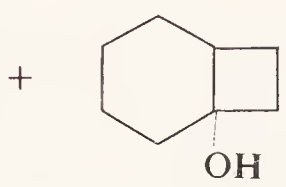

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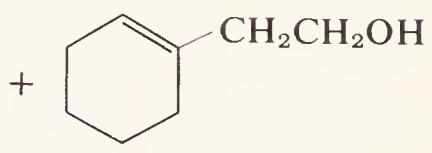
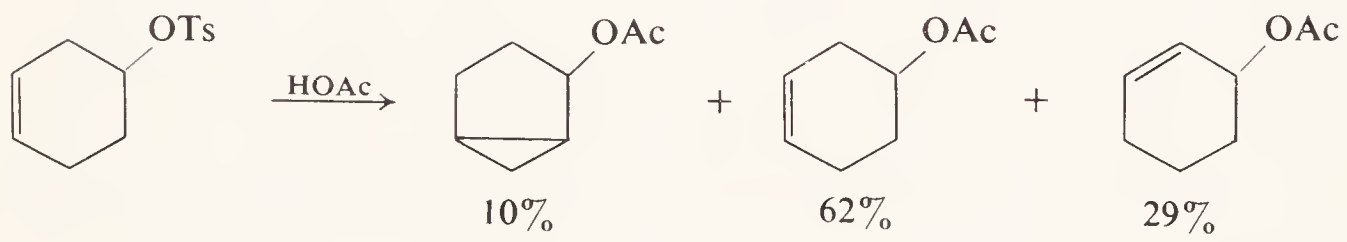
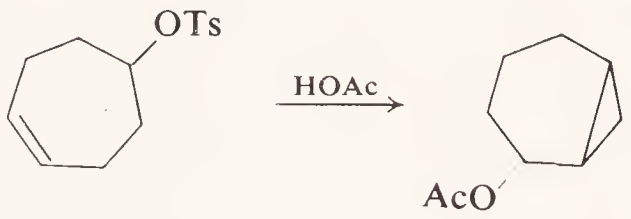


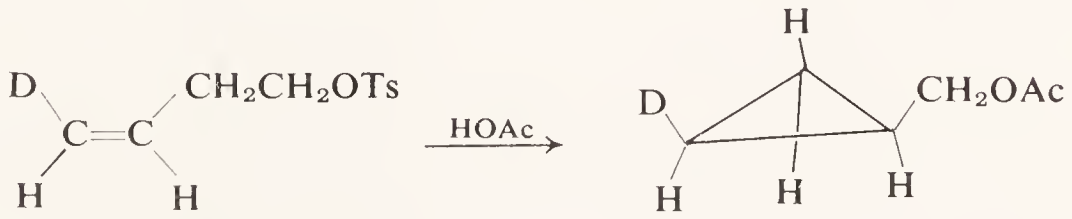
2%



10% 62% 29%

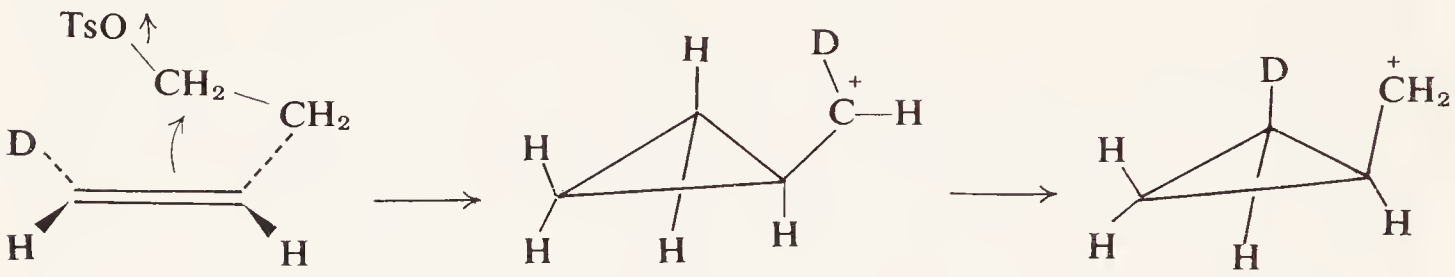


The stereochemistry of the conversion of allylcarbinyl species to cyclopropylcarbinyl and cyclobutyl derivatives and of the reverse transformations have been examined in a number of ways. In the unsubstituted case, deuterium substitution has been used (153).



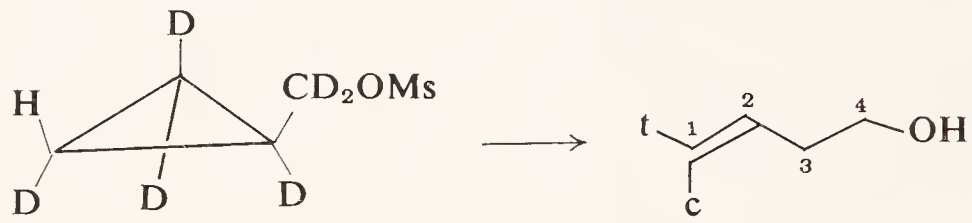
The amount of deuterium in each of the three methylene groups was essentially the same, indicating complete equilibration of the carbons.

This is in good agreement with earlier data (19). However, the deuterium is predominantly *cis* to the carbinyl group. This situation may arise as follows:



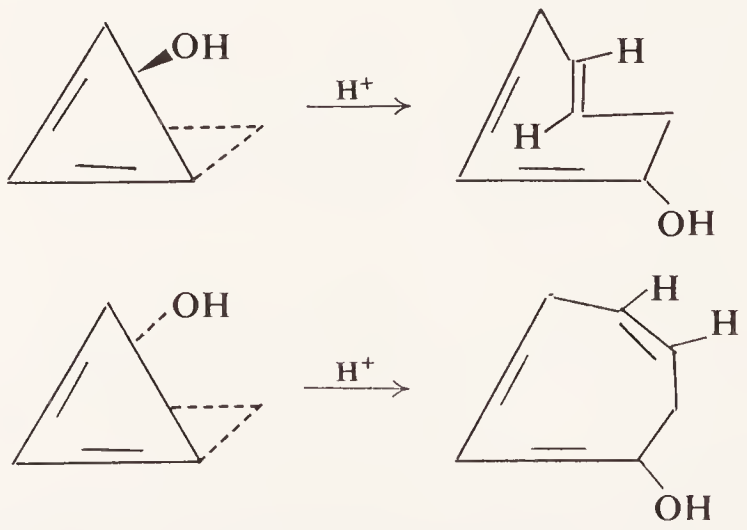
The double-bond participation step might be expected initially to give the ion in which the deuterium lies on the side of the cyclopropane ring. A cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement would then transfer the deuterium to the ring; but in accord with the stereochemical course discussed previously, the deuterium will appear *cis* to the carbinyl group.

The reaction also has been examined in the reverse direction, giving the same results (154). At C-1, the proton appeared essentially only at the



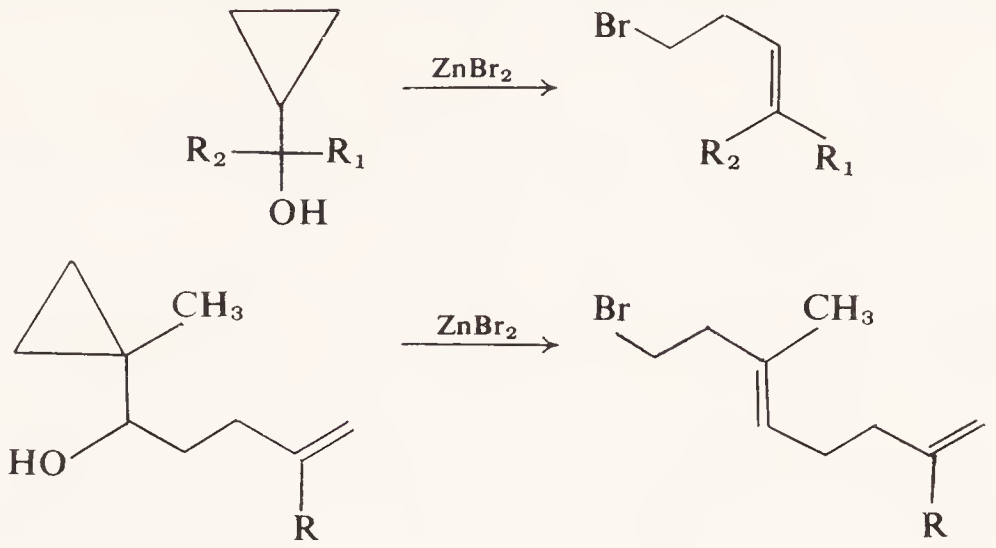
cis position. The proton was of course also distributed among the other positions.

In more complex systems, the stereochemistry of these transformations was investigated by Winstein et al. (155). They found that the conversion of cyclopropylcarbinyl derivatives to their allylcarbinyl counterparts proceeded with retention of configuration at C_α and inversion at C_γ. An example of the consequences of this stereochemistry is



Further detailed studies of this class of transformations has been carried

out by Julia et al. (156). The transformation of cyclopropylcarbinyl derivatives to olefins has been utilized as a synthetic method for the preparation of *trans*-trisubstituted olefins with high stereospecificity (157).



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CHAPTER 27

Phenonium Ions

The Solvolysis of β-Arylalkyl Systems

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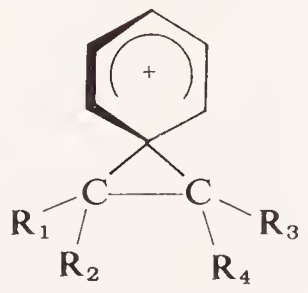
Two full decades have elapsed since the publication of the first evidence for the intermediacy of discrete, σ-bridged phenonium ions (**1**) in the solvolysis of β-arylalkyl systems (1a). Since then, probably few other topics in physical organic chemistry have been as widely or thoroughly studied. In spite of this, not many other theories in organic chemistry have



(1)

been surrounded by such extended, often heated controversy as has been associated with the idea of participation by neighboring aryl groups in solvolysis reactions. Controversy usually fosters further research, and the result is that our current view of β-aryl participation has greatly benefited from many advances in general solvolysis theory. The vast phenonium ion literature has been summarized on several occasions in the recent past (2,3), and several excellent summaries of phenonium ion chemistry have appeared recently in publications dealing with solvolysis reactions in general (5–9).

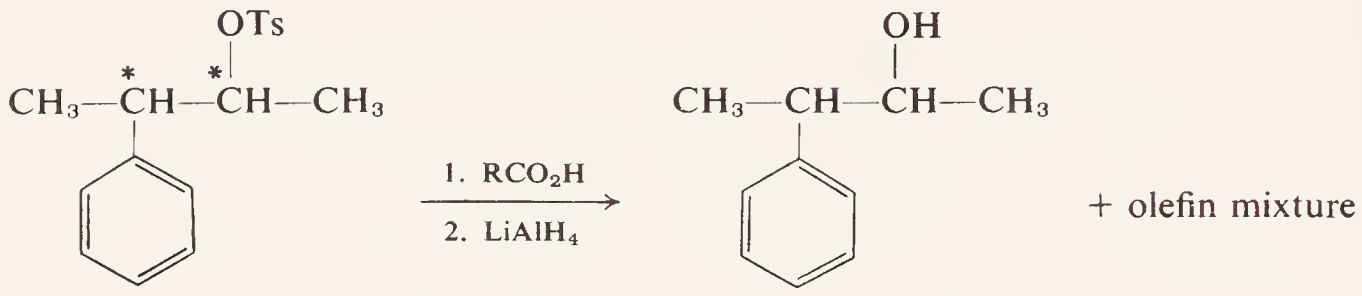
However, more than a half-decade has elapsed since the appearance of the last "summary papers" which reviewed the case for (2) and against (3) interpretations of the behavior of β-arylalkyl systems in terms of anchimeric assistance and phenonium ion intermediates. During this time, new, definitive results have appeared from several laboratories, and a highly refined perspective on the problem has become available, especially from work that has appeared only during the past few years. Viewed within its new framework, much of the old controversy appears to vanish (4). The time, therefore, appears most appropriate for a comprehensive summary of the past 22 years of research into the intermediacy of phenonium ions, from the first report (1a) to the beginnings of the resolution of the controversy (4). Accordingly, the first portion of this chapter is structured to provide as detailed a review as possible of the development of current thought regarding the behavior of β-arylalkyl systems, with emphasis on the particular features that most probably were responsible for much of the controversy in interpretation. The latter portion of the chapter is devoted largely to a quantitative refinement of the concepts outlined in previous sections, with particular emphasis on a quantitative correlation between rate enhancements and product control exercised by neighboring aryl groups.

I. DEVELOPMENT OF THE PHENONIUM ION INTERPRETATION; STEREOCHEMICAL STUDIES IN THE 3-PHENYL-2-BUTYL SYSTEM

In 1949 the first contribution (1a) was published in a comprehensive series of papers dealing with the stereochemical outcome of a selected group of solvolysis reactions. Following Winstein's demonstration of the ability of a neighboring bromine atom to control the stereochemistry in the solvolysis of the diastereomeric 3-bromo-2-butanols (10), Cram (1a) adapted this approach to the study of a neighboring phenyl group and examined the solvolysis of the optically active diastereomeric 3-phenyl-2-butyl tosylates, **2a-OTs** and **2b-OTs**. Cram was led to this problem by the observation that 3-(2-methyl-3,5-dihydroxyphenyl)-2-butanol, a deg-

radation product of citrinin, racemized when heated with acid, even though *two* asymmetric centers were present (1f).

The 3-phenyl-2-butyl tosylate (**2a-, 2b-OTs**) system contains two asymmetric centers and thus exists as four stereomers, whose configurations have been established (1e). Acetolyses and formolyses were conducted on optically pure tosylates, the ester products were converted to alcohols, and the alcohols and olefins were analyzed. The results are tabulated in Chart 1*a*.

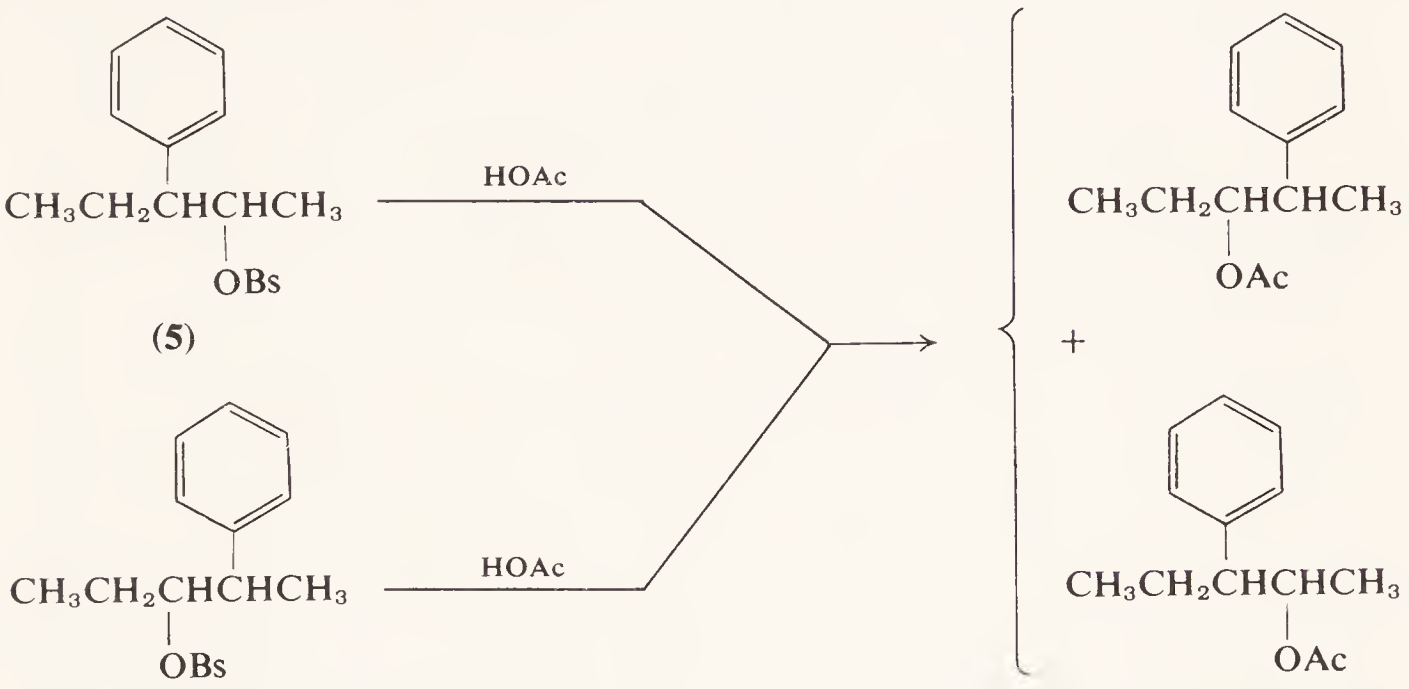


1. L-*threo* (**2a-OTs**); CH_3COOH; 75°	53% 94% racemic *threo* 0.6% L-*threo* 1.2% L-*erythro* 4.8% racemic *erythro*	35%
2. L-*threo* (**2a-OTs**); HCOOH; 25°	70% >99% racemic *threo* <0.1% L-*threo* <0.01% L-*erythro*	—
3. D-*erythro* (**2b-OTs**); CH_3COOH; 75°	68% 98% D-*erythro* 2% D-*threo*	23%
4. D-*erythro* (**2b-OTs**); HCOOH; 25°	71% >99% D-*erythro* <0.5% D-*threo*	—

Chart 1*a*. Products of Solvolysis of *threo*- and *erythro*-3-Phenyl-2-butyl Tosylates (1a).

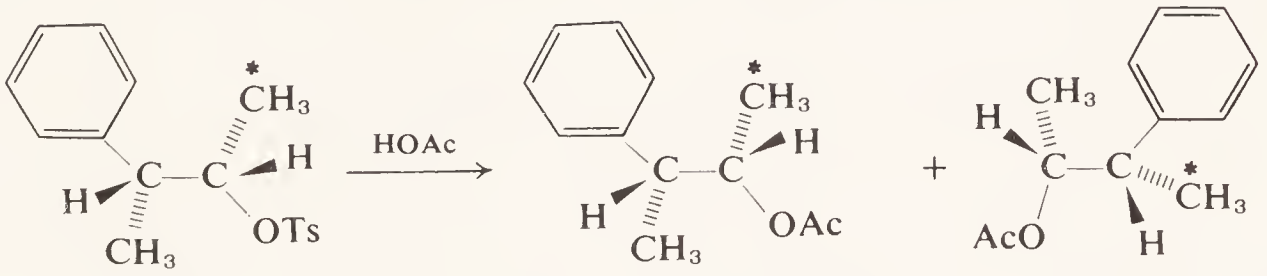
The most striking result in the solvolysis of **2a-OTs** and **2b-OTs** is that the *threo* diastereomer (**2a**) gives almost wholly racemic ester product, but the *erythro* diastereomer (**2b**) gives ester product with virtually complete retention of optical activity. Yet both diastereomers give ester products with more than 95% gross *retention of diastereomeric configuration* (i.e., *threo*-OTs gives *threo*-OAc).

That actual migration of the phenyl ring had occurred in about one-half of the product was demonstrated by Cram using the isomeric phenylpentyl brosylates (1c). Acetolysis of either 3-phenyl-2-pentyl brosylate (**5**) or 2-phenyl-3-pentyl brosylate (**6**) gave the same mixture of isomeric phenylpentyl acetates. The stereochemical structures of the pair of products in each case were those predicted by analogy with the behavior of the 3-phenyl-2-butyl system (**2a**, **2b**). Phenyl migration in both **2a-OTs** and

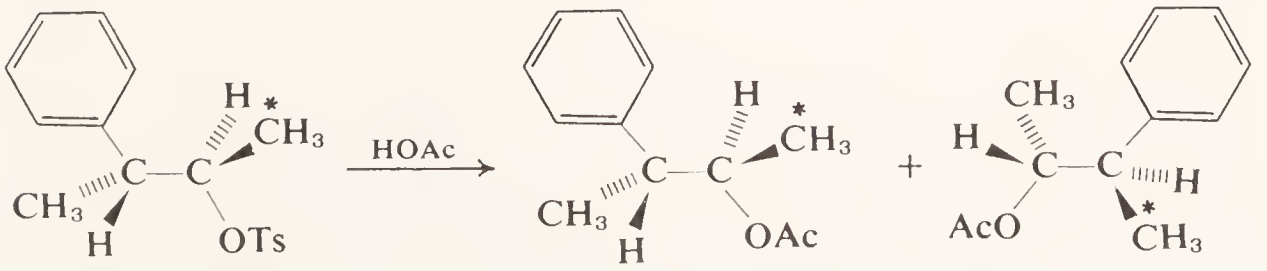


Same isomeric mixture from **5** or **6**

2b-OTs was also demonstrated by acetolysis of optically pure diastereomers which had been labeled (11) at C-1 with ^{14}C. The resulting racemic *threo*-acetate was hydrolyzed to alcohol, which was reresolved. Upon resolution, the L-*threo* enantiomer was found to have all the radioactive label at C-1 and the D-*threo* enantiomer at C-4. Thus rearrangement occurred to the



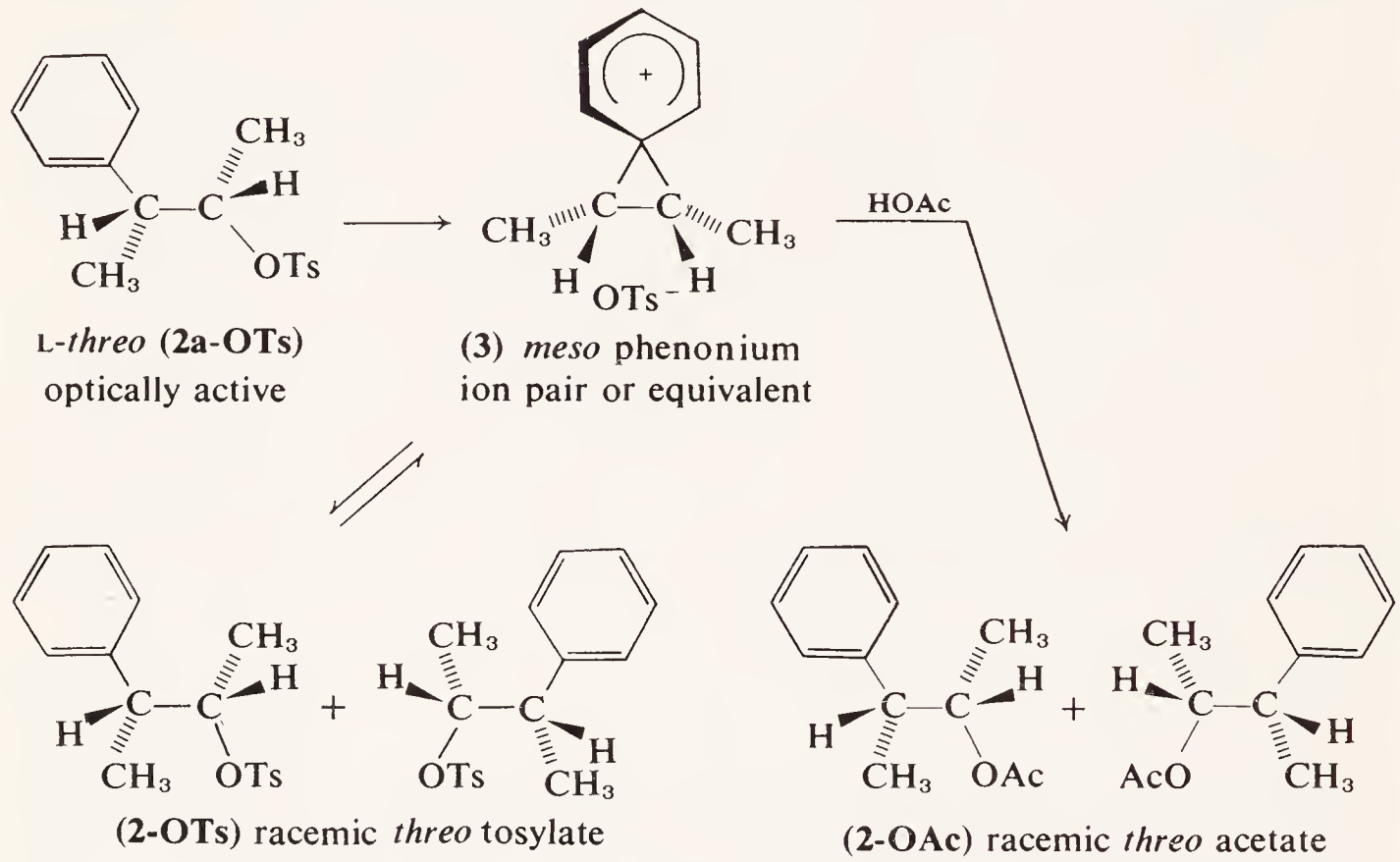
L-*threo* (**2a-OTs**-1-^{14}C) L-*threo* (**2a-OAc**-1-^{14}C) D-*threo* (**2a-OAc-4-**^{14}C)

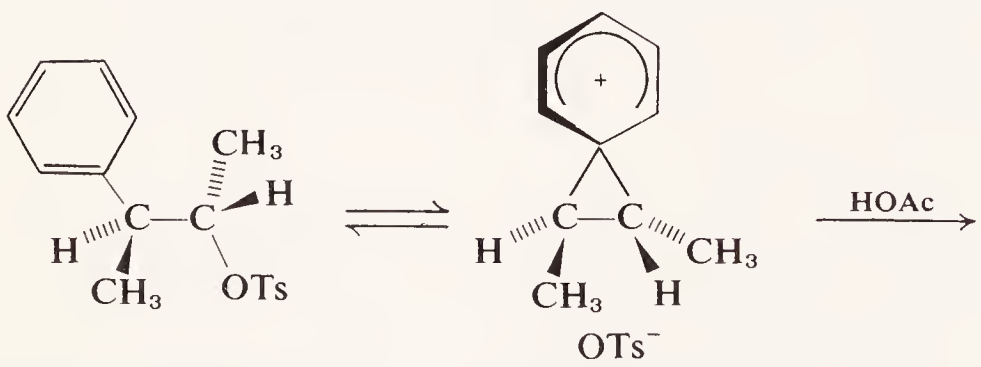


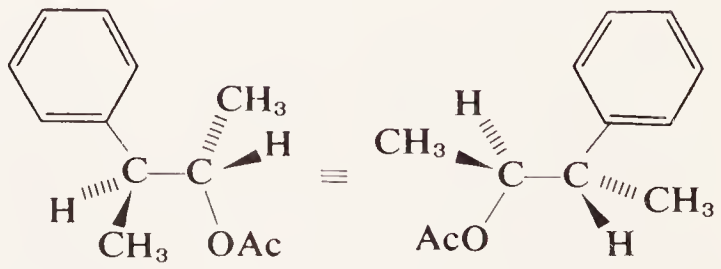
L-*erythro* (**2b-OTs**-1-^{14}C) L-*erythro* (**2b-OAc**-1-^{14}C) L-*erythro* (**2b-OAc-4-**^{14}C)

extent of about 50%. It was also demonstrated that rearrangement occurs similarly in the *erythro* series.

Before the picture was made more complex with further data and more detailed product analyses, these initial results were explained most economically with the postulation of the well-known spirocyclic "phenonium" ion (**3**, **4**) formed in a concerted fashion with the departure of the sulfonate anion. [Actually, the first aryl-bridged ion was proposed as early as 1927 (1g) to explain 1,2-phenyl migration in pinacolic rearrange-







(**2b-OAc**) optically active *erythro* acetate

ments.] The optically inactive *meso* phenonium ion (**3**) generated from the active *threo* substrate must give racemic *threo* product by solvent attack either at C_β or C_α from the side opposite the phenonium bridge. Similarly, the optically active phenonium ion (**4**; point group C_2) generated from active *erythro* substrate must give optically active *erythro* acetate by the same mode of solvent attack.

Largely through further extensive investigation by Cram (1), additional information was obtained on the 3-phenyl-2-butyl system, suggesting that phenonium ion formation in the acetolysis and formolysis of **2a-OTs** and **2b-OTs** was not the sole process involved. The new data also provided a more intimate picture of the overall reaction pathway.

For example, concurrent with the parallel studies by Winstein on the phenomenon of internal return (12,13) Cram's reinvestigation (1b) of the stereochemical processes occurring in the solvolysis of the *threo* diastereomer (**2a**) revealed that racemization of the starting tosylate occurs faster than carboxylate ester product formation, and this to a greater extent in acetic acid than in formic acid. It was found that, after one acetolysis half-life, recovered unreacted L-*threo* tosylate (**2a-OTs**) had undergone 94% racemization. In contrast, but by the same mechanism, D-*erythro* tosylate (**2b-OTs**) was recovered optically pure. When formic acid was used as solvent, the unreacted L-*threo*-tosylate (**2a-OTs**) was 18% racemized during one solvolytic half-life. When D-*threo*-brosylate (**2a-OBs**) was acetolyzed for 1.5 solvolytic half-lives in the presence of 1*M* potassium tosylate, the recovered *racemic threo* sulfonate ester was about 75% brosylate and 25% tosylate. Likewise, L-*erythro* brosylate (**2b-OBs**) after 1.5 solvolytic half-lives gave optically active *erythro* sulfonate ester that was about 65% brosylate and 35% tosylate. These results can be summarized as follows. Of the racemic *threo* acetate produced in acetolysis, 20% comes directly from optically active starting material and 80% comes from racemized starting material; or, racemization (tosylate + acetate) is about 5 times solvolysis in rate. In formolysis, 75% of the racemic *threo* formate produced comes directly from optically active starting material and 25% from racemized starting material, or racemization (tosylate + formate) is about 1.3 times solvolysis in rate. These racemization rates are in quantitative agreement with those determined from kinetic studies by Winstein (12). The rate of loss of optical activity (k_α) of **2a-OTs** was found to be 4.4 times faster than the titrimetric rate of acetolysis ($k_{t\,HOAc}$), and 1.2 times faster than the titrimetric rate of formolysis ($k_{t\,HOF}$) (12). Furthermore, the sulfonate ester racemization reactions must occur through intermediates that allow tosylate and brosylate anion exchange to occur without *threo–erythro* interconversion.

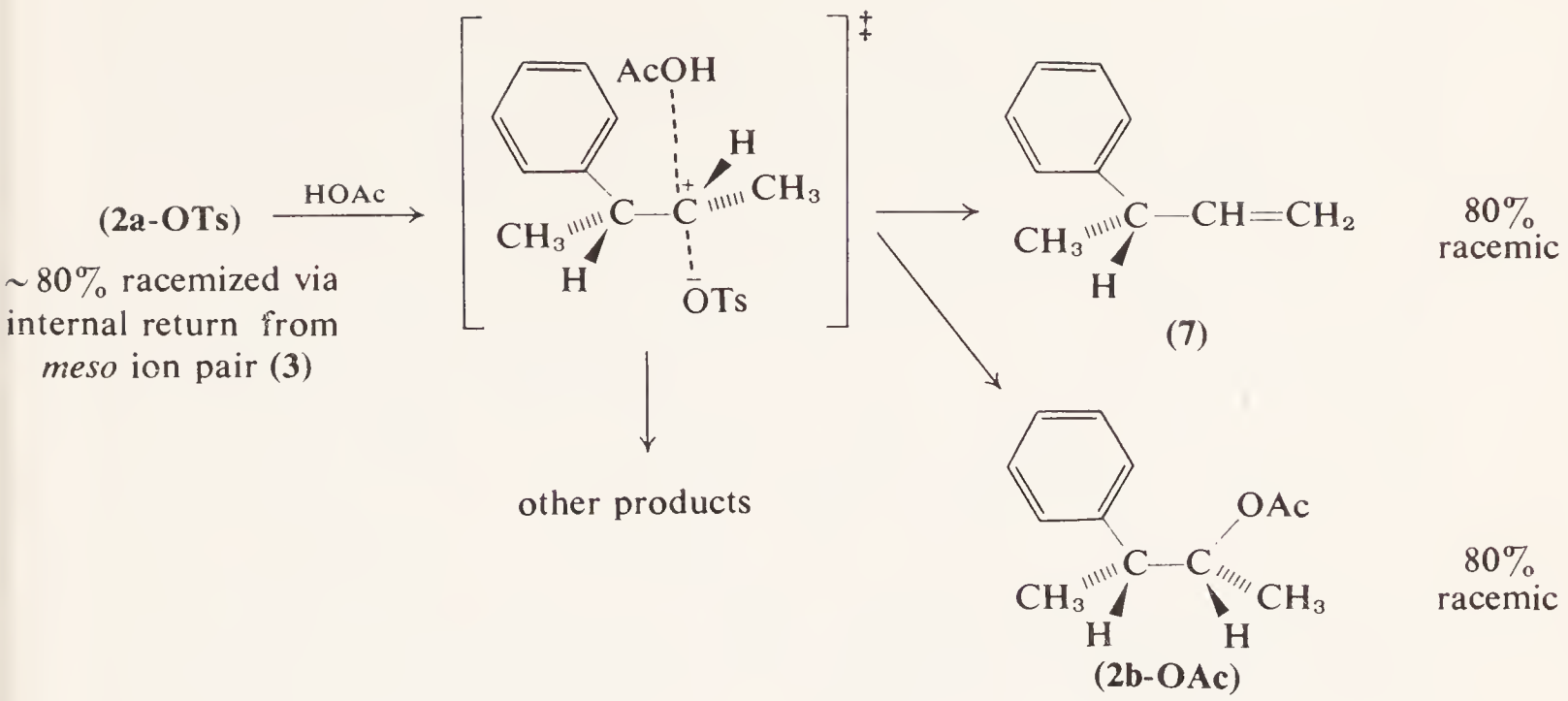
These results can be accommodated by the phenonium ion interpretation with the modification that the actual intermediates are phenonium

sulfonate *ion pairs* (1b), which return to starting materials as well as dissociate to go on to product; all processes, of course, occur with the same stereochemical consequences of attack, regardless of the attacking species (i.e., either OBs^-, OTs^-, or HOAc). (See also Section IV-B-1.) In the poorer ion-pair-dissociating solvent (12,13) acetic acid, collapse of the ion pair to the covalent state is faster than reaction with solvent, or k_α/k_t is relatively high. The reverse is true in formic acid, and k_α/k_t approaches unity.

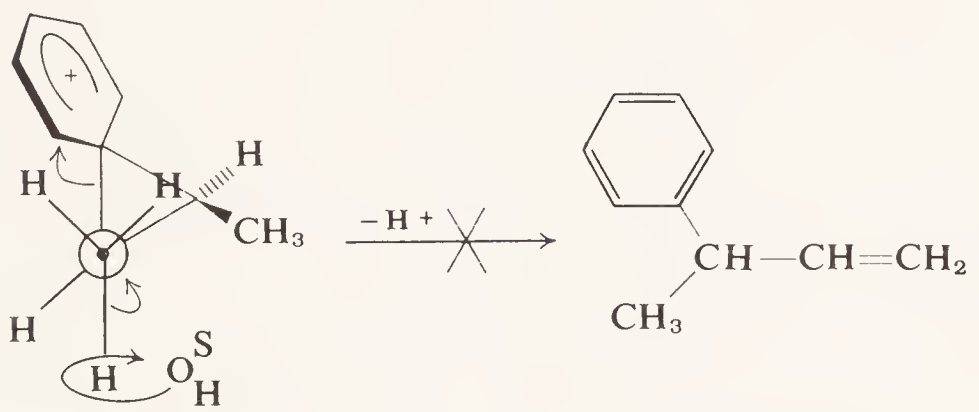
The overall stereospecificity of the ionization processes can be expressed quantitatively in terms of the k_α/k_t ratios (11,12) and the product distributions. The acetolysis and racemization of L-*threo* tosylate (**2a-OTs**) occurred at a rate $4.4 \times (94/6) = 69$ times as fast to give racemic *threo* tosylate and acetate as to give active or racemic *erythro* acetate. Likewise, the formolysis and racemization of L-*threo* tosylate occurred at a rate $1.2 \times (99/0.01) = 10{,}000$ times as fast to give *threo* as to give *erythro* material. In other words, *threo* tosylate ionizes in acetic acid with *retention* of configuration 69 times as fast as with *inversion* ($k_r/k_i = 69$). In formic acid *threo* starting material upon ionization gives *threo* 10,000 times as fast as *erythro* product ($k_r/k_i = 10^4$). In acetolysis, D-*erythro* tosylate ionized and gave back a mixture of tosylate and acetate in which *erythro* dominated over *threo* by a factor of $4.2 \times 98/2 = 206$ ($k_r/k_i = 206$). [In these calculations the small computation errors contained in the original work (1b) have been corrected.] At the time these results were obtained, no analogy from simple open carbonium ion theory could explain retention/inversion (k_r/k_i) ratios of 10^2–10^4, and, indeed, none can today, as we show later in this and subsequent sections. The evidence is compelling in favor of major phenyl control over the stereochemical outcome of these reactions.

Much attention has also been given to that portion of the solvolysis of **2a-OTs** and **2b-OTs** which involves processes other than the postulated phenonium sulfonate ion-pair formation, return, and solvent capture.

For example, acetolysis of the optically active *threo* derivative (**2a-OTs**) actually produces only a 50% yield of racemic *threo* acetate, the product expected from the *meso* intermediate **4**. A 35% yield of an olefin mixture is also produced in the acetolysis of **2a-OTs**. A detailed analysis (1d) of this mixture led Cram to conclude that conjugated olefins, which comprised about three-fourths of the olefin mixture, arose from the tertiary benzylic cation formed via 1,2 hydride shift. Tertiary acetate, from the tertiary benzylic cation, was apparently unstable at the higher acetolysis temperatures; but some of this material was isolated after acetolysis at lower temperatures. A 9% yield (ca. one-fourth of the olefins) of 3-phenyl-1-butene (**7**) was obtained, and Cram concluded from its optical purity (80% racemized) and other data that it arose via an aryl-unbridged secondary ion pair from partially racemized tosylate (**2-OTs**) that had



previously undergone ionization to the *meso* bridged ion pair (**3**) and internal return. If **7** had arisen directly by elimination from the *meso* phenonium ion pair (**3**), it would have been 100% racemized; this was not the case.



(3) *meso* (7) 100% racemized; not found

It is even less likely (1d) that conjugated olefin could have been produced from the bridged ion pair (**3**), because of the rigid, unfavorable dihedral angle—120° instead of 180° or 0°—between the 2- and 3-hydrogens and the departing phenyl ring (see also Section IV-B-1). Although there is no reason to suppose that *all* eliminations must be forbidden from bridged arenonium ions such as **3** and **4** (and such eliminations may indeed occur in special instances, see Section VII-A-2), the conclusions of Cram's earlier product studies (1d) appear to be supported by more recent data on related systems (14,15). Two cases (see Section IV-B-1, 2) were examined in which the data suggest that essentially the entire reaction proceeded with anchimeric assistance; here the products contained little or no olefin, and even the small amount of olefin formed was not conjugated with the aryl group (14,15). Therefore, regardless of whether hydride shift was involved,

the chances are that phenonium ion pair **3** was not a direct intermediate in the formation of olefin from **2a**. Unfortunately, a similar study of the olefinic products from the formolysis of **2a** and **2b** was not carried out, since the olefins were unstable to the conditions of their formation.

It is also clear that an additional 6.6% of the acetate product from the acetolysis of **2a-OTs** could not have arisen by direct solvent attack on the bridged ion pair (**3**). Most of this is a mixture of racemic and optically active *erythro* acetate. Here, *inversion* of configuration has occurred about the carbonium center, brought about by backside solvent attack either on an aryl-unbridged ion pair or on covalent starting material. (See Sections V–VIII for detailed discussions of this dichotomy.) Predominant inversion is almost always found for simple solvolysis of secondary systems in the absence of anchimeric assistance (16–19). As expected, the *erythro* acetate was 80% racemized, indicating that it, too, although not formed *directly* from a bridged ion pair (e.g., **3**), originated ultimately from starting material that had become partially racemized through aryl-assisted ionization and internal return.

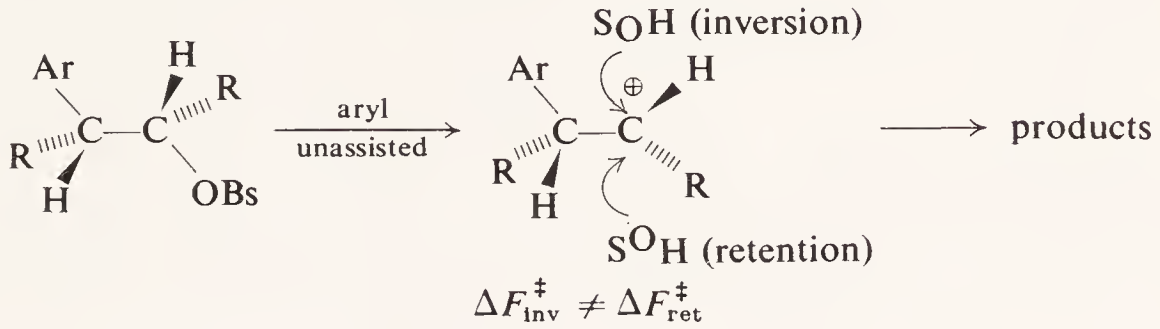
Since the phenonium ion interpretation (1,2) treats aryl participation as occurring simultaneously and in competition with nucleophilic solvent participation (1a–e,2,12,19,20) (see Section V for a full discussion), the incursion of simple acetolysis of optically active or racemized **2-OTs** is compatible with the assumption that the nucleophilic capability of the phenyl ring in **2a** or **2b** is only about an order of magnitude greater than that of the acetic acid solvent (2,20).

There remains a small but quite significant bit of product data that must be included in a complete phenonium ion interpretation. Of the acetate product formed, 0.6% is *optically active threo*, in which there is *retention* of configuration about the reacting carbon. More correctly, since the starting tosylate (**2a-OTs**) was 80% racemized via the bridged ion pair (**3**), about 2.4% of racemic *threo* acetate also must have arisen by the same solvolytic process that gave the 0.6% active *threo* acetate, yielding about 3% total *threo* acetate which could not have arisen by solvent attack on the bridged ion (**3**). This poses no great difficulty, since almost all simple secondary solvolyses can and do result in some degree of retained configuration by any of several means (16–19). A small amount ($\approx$3%) of *threo* acetate arises, then, along with the *erythro* acetate, by way of the competing simple aryl-unassisted solvolysis (2,12,20).

Cram's more complete rationalization of the excess active *threo* acetate is that the small amount of this product arises as a result of *asymmetric induction** by the neighboring carbon atom during the course of the

* Asymmetric induction is often encountered when organometallic reagents are added to carbonyl compounds with α-chiral centers. The ratio of diastereomers produced usually ranges from 2 to 4 (20a).

anchimerically unassisted solvolysis (20). In principle, even in the limiting case of a completely open cation, the diastereomeric transition states for solvent attack to give either inversion (active *erythro*) or retention (active *threo*) must have different activation energies ($\Delta F^{\ddagger}_{inv} \neq \Delta F^{\ddagger}_{ret}$):

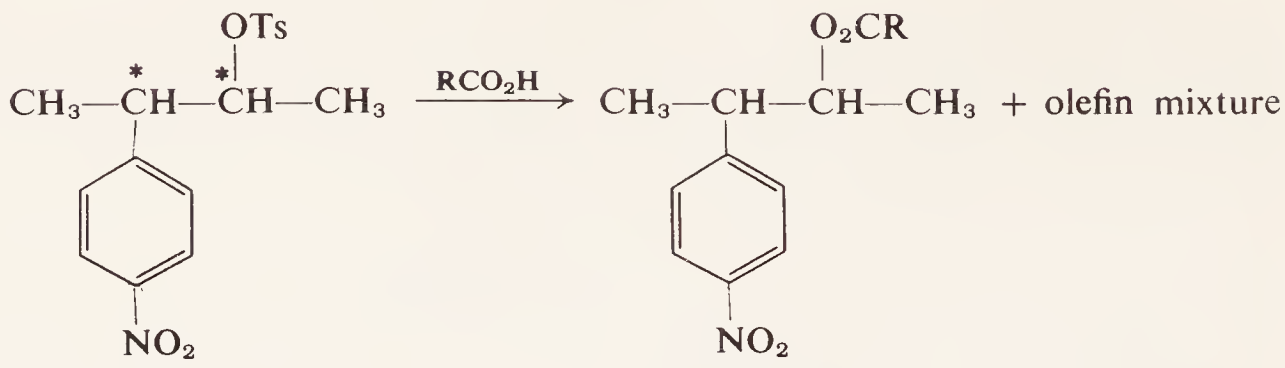


Winstein's picture of symmetrically and unsymmetrically solvated ion pairs (12) in the simple solvolysis of **2a-OTs** explains the results in a similar way.

In order to determine the behavior of the 3-phenyl-2-butyl system in the absence of aryl bridging, Cram studied the solvolysis of the *p*-nitro derivative of 3-phenyl-2-butyl tosylate (21). Very little migration, equilibration, or bridging is expected from the highly deactivated, nitrated aryl neighboring group in this system, but the remote *p*-nitro group in no way modifies the steric situation in the vicinity of the two asymmetric carbon atoms.

The results are summarized in Chart 1*b*. As expected on the basis of the stereochemical course of substitution of many simple secondary systems investigated previously (16–19), the 3-(*p*-nitrophenyl)-2-butyl tosylate system underwent solvolysis with a high degree of *inversion* of configuration. In acetolysis of the *threo* isomer, the retention/inversion rate constant ratio $k_r/k_i = 0.075$, and for the *erythro* isomer, $k_r/k_i = 0.11$. In contrast, for the parent system, $k_r/k_i = 69$ for tosylate racemization and acetolysis of the *threo* isomer (**2a-OTs**), and $k_r/k_i = 206$ for the tosylate scrambling (11) and acetolysis of the *erythro* diastereomer (**2b-OTs**).

Thus introduction of a nitro group many bond-lengths away from the reaction site leads, in acetolysis, to modification of the retention/inversion rate constant ratios by factors of 900–1800. In formolysis, the retention/inversion rate constant ratios change by factors of about 23,000. *These large factors strongly indicate that an increase in the nucleophilic character of the aryl group is responsible for directing the course of substitution in favor of retention.* This trend is further exemplified if a methoxyl group is introduced in the *para* position of the 3-phenyl-2-butyl tosylate system (14). (The 3-*p*-anisyl-2-butyl system is discussed more fully in Section IV-B-1.) In acetolysis, $k_r/k_i = 10^3$ for the *p*-methoxy-*threo* system. Thus during passage from the *p*-nitro to the *p*-methoxy substituent, this ratio changes by a factor of at least 13,000. These ratios reflect the relative abilities of



1. L-*threo*; *p*-NO_2-**2a-OTs** CH_3COOH; 100°	13% 7% *threo* (60 ± 30% racemized) 93% *erythro*	68%
2. L-*threo*; *p*-NO_2-**2a-OTs** HCOOH; 50°	11% 30% *threo* (84 ± 7% racemized) 70% *erythro*	72%
3. L-*erythro*; *p*-NO_2-**2b-OTs** CH_3COOH; 100°	9% 10% *erythro* 90% *threo*	57%
4. L-*erythro*; *p*-NO_2-**2b-OTs** HCOOH; 50°	9% 37% *erythro* 63% *threo*	59%

Chart 1*b*. Products of Solvolysis of *threo* and *erythro* 3-*p*-Nitrophenyl-2-butyl Tosylate.

solvent and aryl group to act as competing nucleophiles (2,12) at the rear of the carbon carrying the tosyl group. The *p*-nitrophenyl group loses out to solvent, the phenyl dominates over solvent by more than two powers of ten, and the *p*-methoxyphenyl dominates over solvent by four powers of ten. Thus, on stereochemical grounds alone, we can rule out static aryl-unbridged ions, *but not equilibrating aryl-unbridged or partially bridged ions* (see next section), as the source of the high retention observed in solvolysis of the 3-phenyl-2-butyl system. Phenonium ion pairs can furnish an explanation of how configurational integrity is maintained at two asymmetric centers throughout the solvolyses in both the *threo* and *erythro* series, why rearrangement occurs to the extent of 50% in each series, why non-rearranged product arises with high retention, why rearranged material is generated with inversion at each secondary carbon, and, finally, why these unique stereochemical relationships are destroyed by the simple act of putting a nitro group in place of hydrogen in the *para* position of the phenyl group.

Cram's utilization of the nucleophilically deactivated *p*-nitrophenyl group to suppress β-aryl participation (21) was the first reported application of such a technique, and it is now among the more useful tools for the study of β-arylalkyl systems. The general method of aryl deactivation has seen wider application more recently in the quantitative evaluation of aryl-unassisted solvolysis rates in a number of systems, as outlined in succeeding sections (III-B; VII-A-1).

The phenonium ion interpretation of the 3-phenyl-2-butyl system is summarized in its present form as follows. The principal mode of reaction is ionization to bridged phenonium ion pairs, leading to carboxylate and sulfonate esters with retention of diastereomeric configuration. Next in importance is the hydride shift mechanism, which produces about three-fourths of the olefins. The least predominant pathway is reaction of the unbridged secondary ion pair, which produces one-fourth of the olefins (as well as esters with both inverted and retained configuration) in ratios that are influenced by the adjacent asymmetric carbon atom.

II. THE CHALLENGE TO THE PHENONIUM ION INTERPRETATION; RAPIDLY EQUILIBRATING IONS

Brown has objected in the past (3) (see Note added in Proof)*, to the phenonium ion interpretation, submitting that all three of the solvolytic pathways described previously for the 3-phenyl-2-butyl system can be consolidated into a single set of rapidly equilibrating, unbridged ions or ion pairs, which are partitioned into the observed products. Largely because of what he considered a lack of significant rate enhancements in this system upon solvolysis (see Section III-B-1), Brown postulated that there was no appreciable interaction between the neighboring phenyl ring and the developing carbonium center during the ionization step. In systems where small rate enhancements are found, Brown has postulated varying degrees of relatively weak π briding to the aryl ring in the "open" ions. (A full discussion appears in Sections V and VI.) The resulting open or weakly π-bridged ion pair, however, is in rapid equilibrium with the phenyl-rearranged species, the rate of migration being great enough to prevent rotation about the C_α–C_β bond axis and to produce backside shielding of the intermediate cation from solvent attack in much the same manner as in the phenyl-bridged species **3** or **4** (Chart **2**). The high degree of retention

* NOTE ADDED IN PROOF. Recent key results, many of them from Brown's laboratories, have made it increasingly apparent that rapidly equilibrating, aryl-unbridged cations were not the solution to the 3-phenyl-2-butyl problem. Consequently, Brown's present position differs significantly from that summarized here (3). His latest and most refined viewpoint (4b) is discussed in Sections VII and VIII.

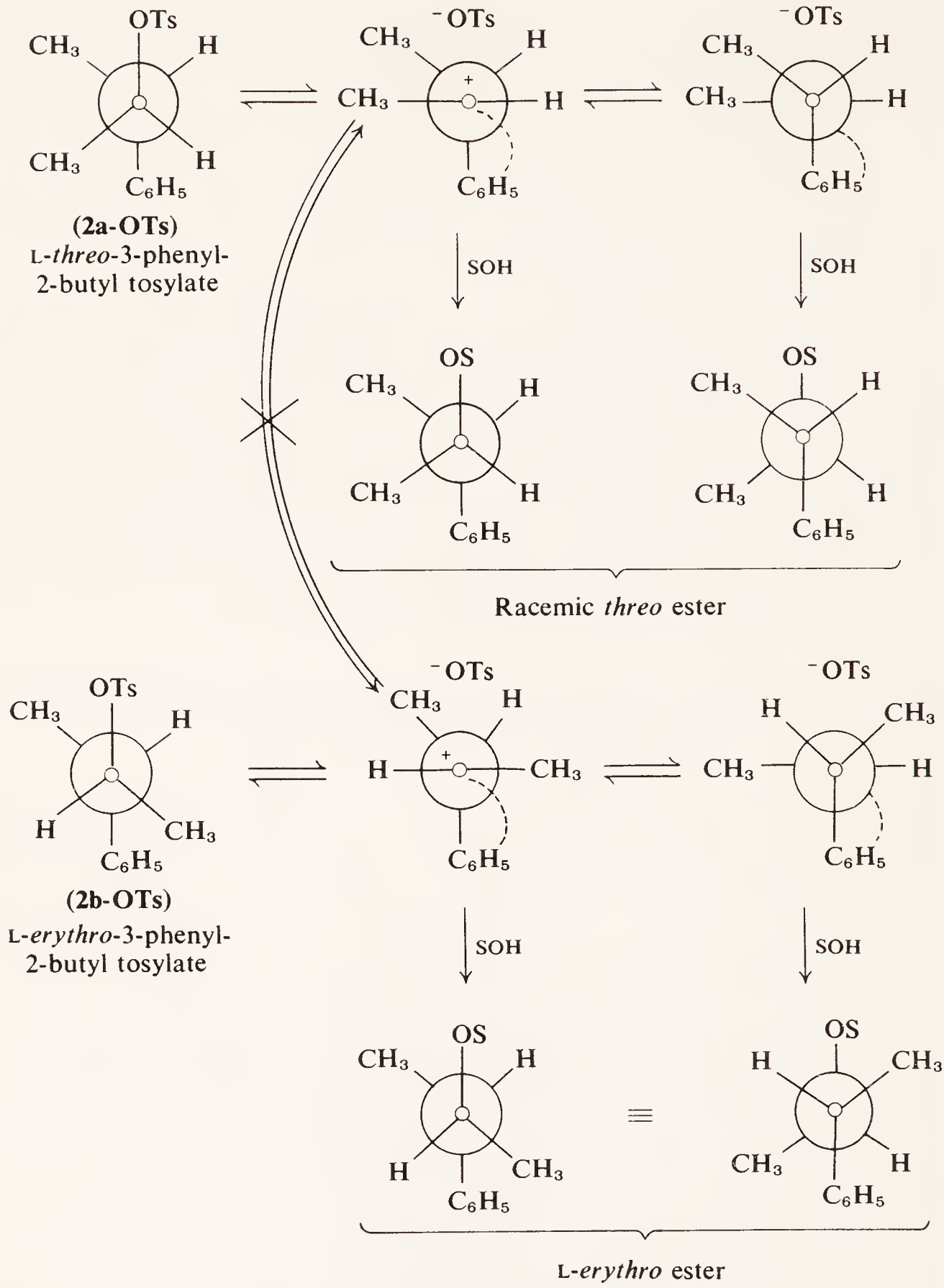


Chart 2. Retention of Diastereomeric Configuration by a Dynamic Pair of Rapidly Equilibrating Cations.

of diastereomeric configuration in the ester product has been rationalized (3,23) with this scheme. Although the equilibration between the unbridged cations would be rapid enough to prevent rotation and shield the backside of the ion, complete equilibration may not be achieved by the time the solvolysis reaction is over, precluding complete racemization of the ester product with retained diastereomeric configuration. This would explain,

for example, the ca. 3% optically active *threo* acetate produced from **2a-OTs**. Other reactions, such as elimination, can also occur from the same set of equilibrating intermediates. In contrast, the phenonium ion interpretation (2,20) requires several simultaneous reaction paths to explain the multiplicity of products (see Section V for a full discussion).

It is of historical interest to note here that Winstein, not Brown, actually was the first to publish a consideration of a dynamic pair of equilibrating cations as an alternative to a bridged ion (22).* His reasons for abandoning this formulation were never stated explicitly in print.

Cram has argued that, on the time scale of attack on the intermediate by a solvent molecule, the situation of the bridged phenyl ring cannot be simulated by a pair of ions in rapid equilibrium in which the phenyl ring is migrating (2,21). In a rapidly equilibrating pair of open cations, the bridged species is merely a transition state (see Brown's energy diagrams in Ref. 3), so that, according to Cram, the aryl ring really spends most of its time at the migration origin or terminus. As a result, the solvent about to attack the intermediate actually "sees" an open, unshielded cation, much the same as in the nonmigrating *p*-nitrophenyl derivative (21).

It is difficult to conceive of definitive experiments that might yield *direct* evidence for the intermediacy of a dynamic pair of cationic intermediates. Indeed, for secondary systems, e.g., **2a** and **2b**, no such results have yet been reported. (In primary and tertiary systems, static open, equilibrating open, and σ-bridged cations have been observed directly by nmr in strong acid media. These are discussed in detail in Section IV-C-3.) However, Collins and his co-workers produced the first direct solvolytic evidence of a rapidly equilibrating set of secondary benzylic cations. Some degree of stereochemical control was observed.†

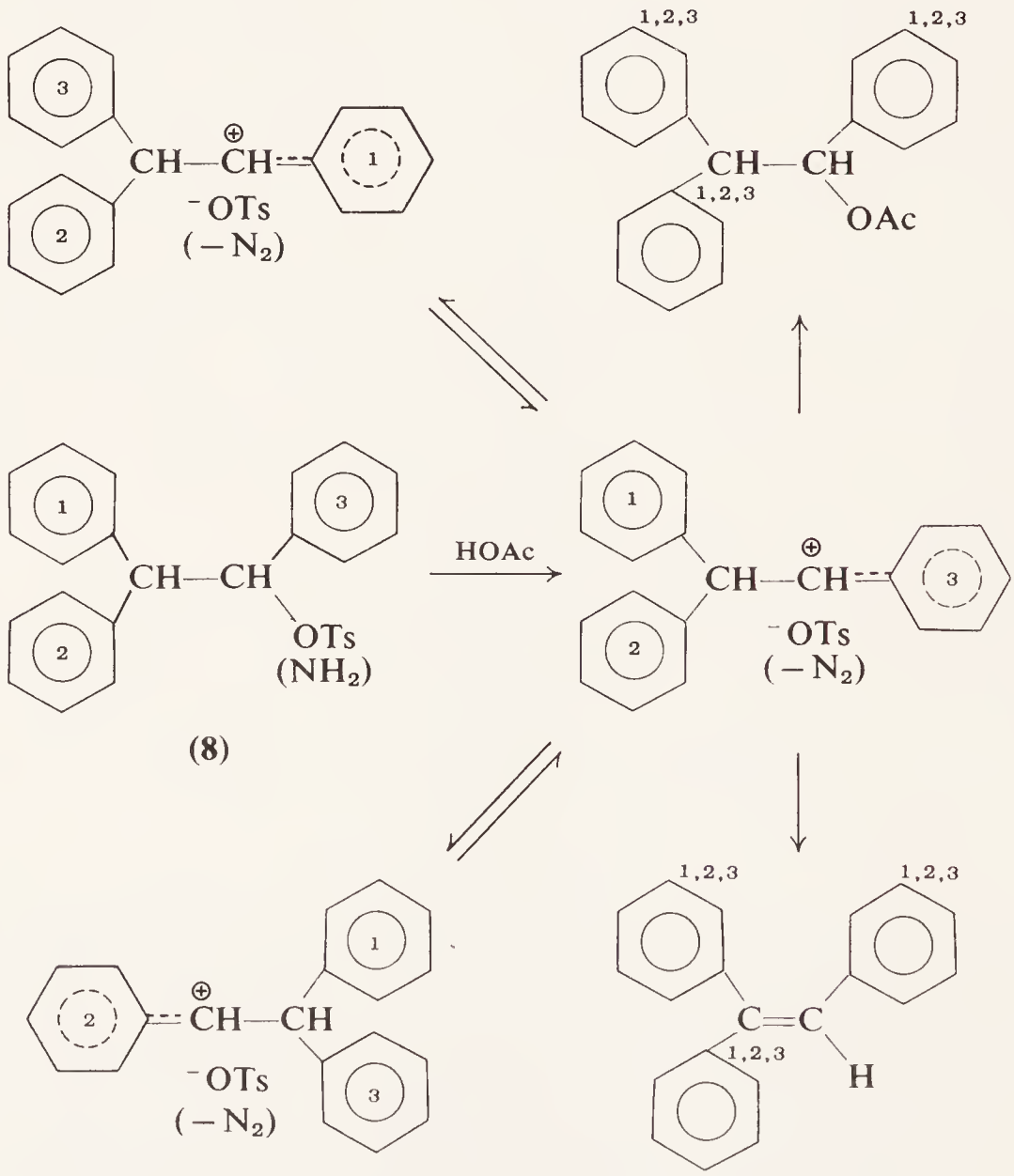
Acetolysis of 1,2,2-triphenylethyl tosylate (**8**), which was doubly labeled with ^{14}C in the aryl and alkyl groups, gave rise to acetate in which all three phenyl groups had undergone equilibration, as evidenced by aryl–^{14}C scrambling. From their rate of equilibration, a C_α–C_β equilibration rate could be calculated using open ion models which agreed with the observed C_α–C_β equilibration rate (25a).

* In order to dispel any doubt that he did not originate the idea of rapidly equilibrating ions, Brown (23,24) has often called attention to Winstein's early proposals (22), especially in connection with β-aryl participation. However, these references neglect to mention that Winstein hardly used this interpretation in the bulk of his neighboring group publications, and not at all since 1952 for β-arylalkyl systems.

† Collins and his co-workers have applied extensive treatments which appear to lend some quantitative support to Brown's alternative formulations for the solvolytic processes occurring with the 3-phenyl-2-butyl and related systems. An excellent recent summary of Collins' position on this subject is found in Ref. 28b.

The further discovery that there is no internal return (25b) in this system strongly suggests the intermediacy of a set of rapidly equilibrating, unbridged ions (ion pairs) which can yet control product stereochemistry, since the acetate product arises with a slight excess of retention (k_r/k_i = 1.2–1.4). Deamination of 1,2,2-triphenylethylamine (26,27) yielded analogous results, with a slightly greater degree of retention of configuration (k_r/k_i = 2–3). Deamination reactions are considered in detail in Section IV-A-2.

Although these results clearly suggest that bridged ions may not be the only species capable of producing retention of configuration, due caution must be applied when these results are extrapolated to the 3-phenyl-2-butyl system. In the first place, although the 1,2,2-triphenylethyl system (**8**), indeed gives an excess of retention of configuration in ester products, as opposed to the predominant inversion expected with static, aryl-unbridged ions (16–19), the observed k_r/k_i values for **8** (k_r/k_i = 1.2–3) fall far short of the 10^2–10^4 observed for **2a** and **2b**.* Second, the triphenyl



* See, however, Ref. 28a and, especially, Ref. 28b, pp. 315ff.

system (**8**) is benzylic at the initially formed carbonium center; therefore it is considerably more stable, and less requiring of β-phenyl assistance, than the phenylbutyl system.

Most recently, Collins has performed a series of calculations from which he has derived a set of rate constants (28) for the various processes that might be involved in a set of rapidly equilibrating 3-phenyl-2-butyl cations, including rotation about the central C_α–C_β bond axis, aryl migration, and ion-pair capture.

III. USE OF STEREOCHEMICAL AND KINETIC TECHNIQUES IN THE STUDY OF β-ARYLALKYL SYSTEMS

The preceding sections of this chapter have logically stressed stereochemical rather than kinetic studies in the discussion of phenonium ion interpretations, since stereochemical studies formed primarily the extensive basis on which Cram formulated his interpretations (1a–1e,2). Cram has always emphasized the power of the stereochemical probe of mechanism (1a–1e,2), and it is useful at this point, before surveying the general phenonium ion literature, to review the scope, significance, and limitations of both the kinetic and stereochemical approaches to the study of the solvolysis of β-arylalkyl systems.

A. Stereochemical Control as a Criterion of Mechanism in the Solvolysis of β-Arylalkyl Systems

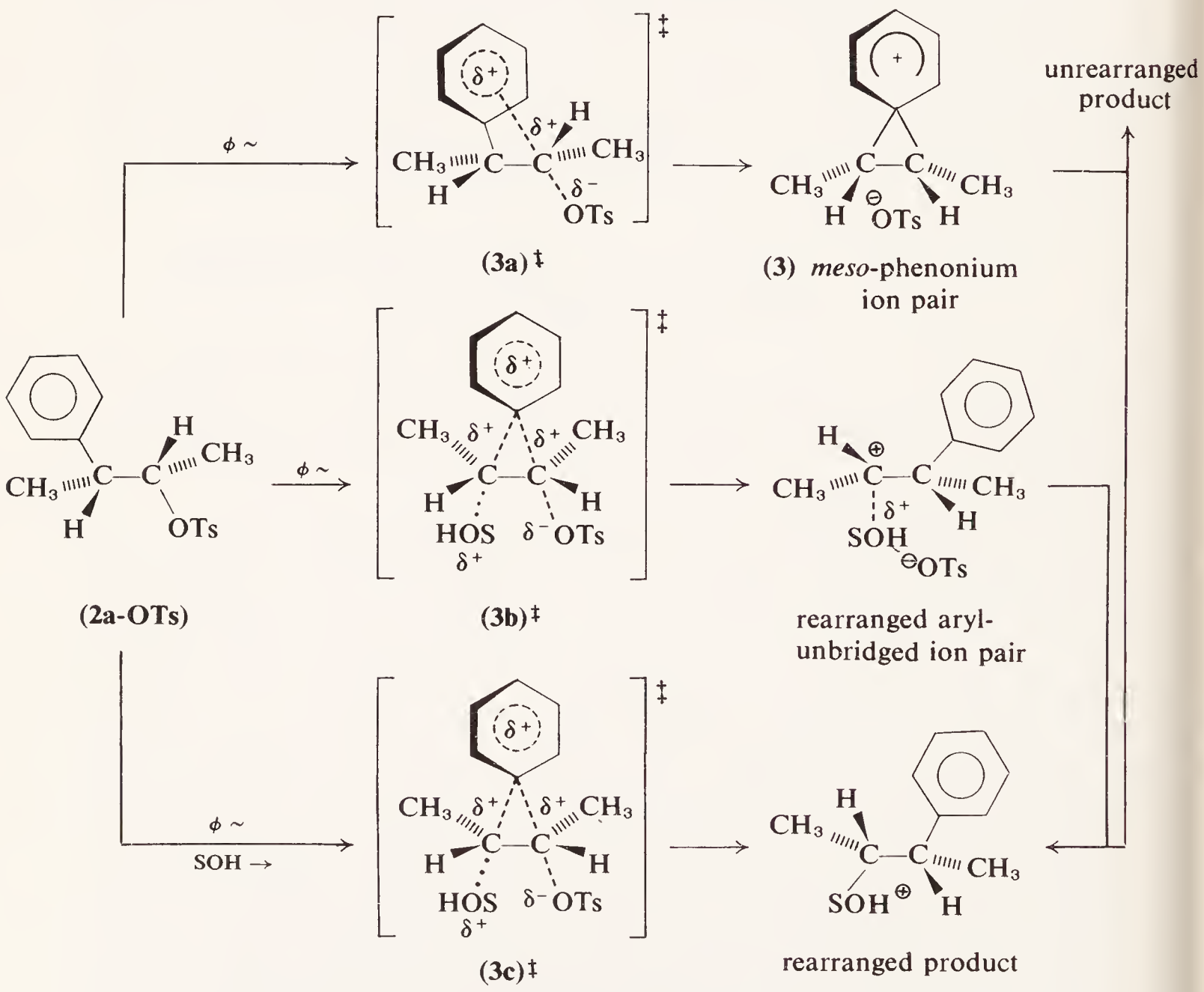
Both the kinetic and stereochemical methods for the detection of neighboring-group participation in ionization and of the intermediacy of bridged ions require carefully chosen model compounds in which such participation is absent.

Kinetic measurements are an energy parameter and *alone* do not differentiate between bridged ions and bridged transition states. *Rate comparisons reflect only differences in activation free energies, and therefore no information about structure after the rate-determining transition state is available*. For example, β,β,β-triphenylethyl tosylate (**23**, p. 1395) solvolyzes several powers of 10 faster than do model compounds, but there is a good possiblity that the rearranged unbridged ion is the first intermediate (31g). Even in systems theoretically capable of producing a symmetrically bridged ion, rate-enhancement data *alone* provide information only about the first phase of the solvolysis reaction coordinate. For example, if it were known only that the rate of ionization of *threo*-3-phenyl-2-butyl tosylate in acetic acid was 210 times that of its *p*-nitro derivative (p. 1372), we could safely say that the parent phenyl group participated in ionization. However, this kinetic information without the accompanying stereochemical

information (Charts 1*a*,*b*) concerning products would not differentiate cleanly between bridged ions or rearranged aryl-unbridged ions, or even covalent product as the first energy minimum after the rate-determining transition state(s).* Of course, once analogies have been established between stereochemical and kinetic results, then the kinetic tool becomes sharper.

In contrast, configurational changes provide a structural parameter which, with proper locations of asymmetric centers, gives a means of monitoring the structural changes past the rate-determining transition state all the way to product. The stereochemical probe is also very sensitive, and a small amount of a stereoselective component can be detected

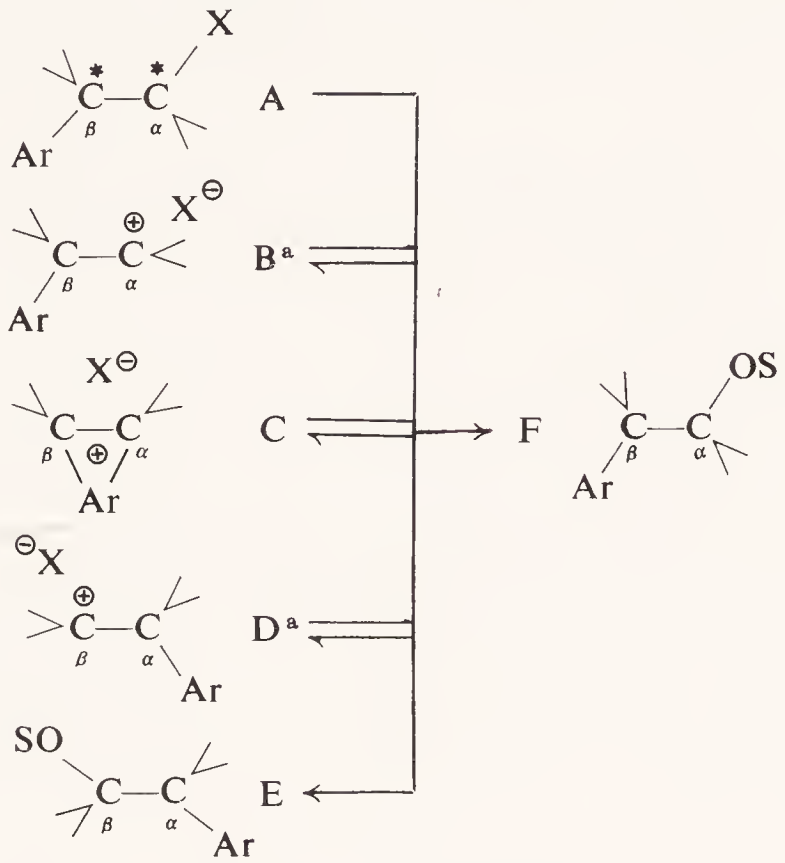
* For example, β-aryl participation in the rate-determining ionization stage of the solvolysis of *threo*-3-phenyl-2-butyl tosylate (**2a-OTs**) could be conceived of as proceeding via any of several transition states (**3a**‡, **3b**‡, **3c**‡) these, in turn, collapsing in different ways:



An accelerated ionization rate, of course, cannot distinguish among the various versions of **3**‡; stereochemical studies (rearrangement, configuration, etc.) can.

in the presence of mainly nonstereospecific processes. A large amount of stereochemical data concerning the solvolysis of β-aryl systems can be formulated in terms of Cram's original scheme (29) which is summarized in Chart 3.

General Sequence of Possible Intermediates



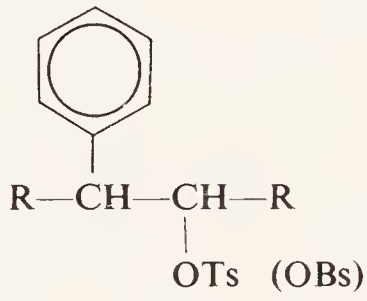
Specific Intermediate Sequence	Stereochemistry at	
	C_β	C_α
A → E	Inversion	Inversion
A → C → E	Inversion	Inversion
A → C → F	Retention	Retention
A → B → E	Inversion	Retention + inversion
A → B → F	Retention	Predominant inversion (16–19)[b] to racemization[c]
A → D → E	Retention + inversion	Inversion
A → B → C → E	Inversion	Retention + inversion
A → B → C → F	Retention	Retention + inversion
A → C → D → E	Retention + inversion	Inversion
A → B → D → E	Retention + inversion	Retention + inversion
A → B → C → D → E	Retention + inversion	Retention + inversion

[a] Degree of (nucleophilic) solvent involvement depends on particular system (16–19)
[b] Primary and most secondary systems.
[c] Most tertiary and secondary benzylic systems.

Chart 3. General Stereochemical Scheme for the Solvolysis of β-Arylalkyl Systems.

Aryl-unbridged ions, formed with solvent participation (19) where the leaving group is tosylate, halide, or other groups without an initial positive charge, give high inversion when the site of substitution is primary or secondary and much lower net inversion when the site is tertiary or benzyl. The actual values vary with the ionizing power of the solvent and with its nucleophilicity (19). With diazonium nitrogen (or protonated oxygen) as the leaving group (see Section IV-A-2), a tendency toward inversion is also visible but much less pronounced, although relatively few systems have been studied.

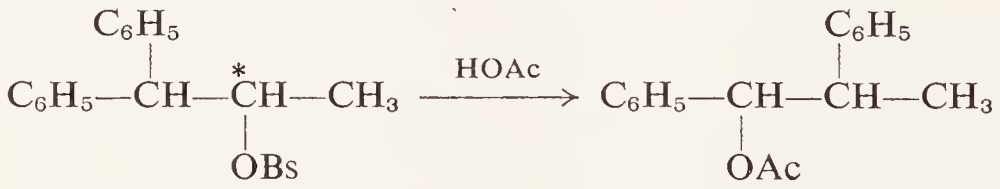
In Chart 3, the arrows imply the appropriate transition states and the letters are starting materials, ions, or products. A mechanistic designation can be made by appropriate use of letters and arrows. For example, A → E designates starting material going to rearranged product with all bond-making and breaking processes occurring in the same transition state. No such mechanism has been demonstrated to date. The solvolyses of 3-phenyl-2-butyl tosylate (**2-OTs**) (1a-1b), of 3-phenyl-2-pentyl tosylate (**5-OTs**) (1c), of 2-phenyl-3-pentyl tosylate (**6-OTs**) (1c), of 4-phenyl-3-hexyl tosylate (**9**; R = C_2H_5) (20), and of 2,5-dimethyl-4-phenyl-3-hexyl brosylate (**9**; R = *i*-C_3H_7) (30a), as well as of 2-phenyl-1-propyl brosylate (**13**, see p. 1385) all gave stereochemical results consistent with the A → C → E and A → C → F schemes dominating the reaction (phenonium ion mechanism).



(9)

R = CH_3CH_2— ; $(CH_3)_2CH$—

An illustration of the A → C → D → E (or the less probable A → D → E) sequence is found in the results of acetolysis of optically pure 1,1-diphenyl-2-propyl brosylate (**10-OBs**) to give both diastereomers of optically pure 1,2-diphenyl-1-propyl acetate (**10a-OAc**) (30c).



(10-OBs) **(10a-OAc)**

Similarly, the neophyl system, discussed in detail on page 1387, typifies

solvolysis with complete rearrangement via an A → D → E mechanism involving an aryl-bridged transition state. (The notion of A → C → D → E seems less likely, and C is undetectable here as an energy well as the system cascades downhill in energy to a relatively stable tertiary cation; but such a scheme cannot be absolutely ruled out. See page 1389.)

In typical unsymmetrical, nonrearranging β-arylalkyl systems, the stereochemical probe of a mechanism usually consists of determination of the retention/inversion ratios at the carbon atom undergoing substitution. Aryl participation leads to retention of configuration, and simple solvolysis, involving backside solvent attack (16–19) (pp. 1356–1358, 1456ff), leads to predominant inversion of configuration. Thus a distinction between mechanisms A → C → F (retention) and A → B → F (inversion) is possible.

A classical example of the competitive interplay between mechanisms A → C → F and A → B → F is the regular increase in the degree of retention of configuration in the solvolysis of 1-phenyl-2-propyl tosylate (**14-OTs**, Section IV-B-2) as solvents of progressively weaker nucleophilicity are employed. Clearly, A → C → F is becoming more predominant and A → B → F less favored as the solvent becomes less able to solvate and/or attack the backside of the developing aryl-unbridged intermediate cation. In the acetolysis and formolysis of the skeletally similar 1-paracyclophanyl-2-propyl system (**81-OTs**, Section IV-D), near-complete retention of configuration implicated A → C → F as the predominant or sole process, depending on solvent.

Similar conclusions were drawn from studies of the 1,2-diphenyl-1-propyl brosylates (**10a-OBs**) (30a,30e) and 1,2-diphenyl-2-methyl-1-butyl tosylate (29b) systems. In both systems, A → B → F and A → C → F sequences competed, the outcome depending on medium.

Solvolysis of typical symmetrical tertiary systems (see, e.g., Sections IV-C-1 and IV-C-3) gives stereochemical results consistent with A → B $\rightleftarrows$ D → E(F). (In some cases small amounts of stereochemical control suggest a possible minor contribution from A → B $\leftrightarrows$ C $\leftrightarrows$ D → E(F).) Similarly, the A → B $\leftrightarrows$ D → E(F) sequence best accounts for the observed stereochemistry and label-scrambling data for the acetolysis of 1,2,2-triphenylethyl tosylate (**8-OTs**, pp. 1361ff) (25–27). Scheme A → B $\leftrightarrows$ C $\leftrightarrows$ D → E(F) cannot be absolutely ruled out, but its intervention seems highly unlikely. The small net retention observed in solvolyses of this system may be taken to suggest that a minor part of the reaction occurs by schemes in which B and/or D are absent. But how much direct phenonium ion formation and capture could have occurred as a *minor* reaction (A → C → E) without disturbing the overall statistical analysis on which the claims for *exclusive* open ions rest (25–27) is not certain.

To sum up, the foregoing stereochemical examples support the long-held beliefs (31) (Section IV-C) that tertiary (and many benzylic secondary) systems solvolyze with little if any aryl participation and that aryl-unbridged ions B and/or D intervene in such reaction sequences. But when B and D would be simple primary or unhindered secondary carbonium ions, their intervention in the Wagner-Meerwein sequence appears to depend on the particular system and its environment. Among the more important considerations in such cases is the precise nucleophilic role of the solvent (16–19) in any aryl-unassisted process that may occur. This subject is discussed fully in Sections V–VIII.

With regard particularly to the 3-phenyl-2-butyl case (**2**), Cram's extensive evidence, summarized in Section I, indicates that the stereochemical behavior of this system is not at all like that of simple secondary models (16–19). Cram has consistently maintained (2,21) that this stereochemical evidence *alone*, qualitatively supported by the kinetic data, suffices to prove the predominant intermediacy of bridged phenonium ions [**3**,**4**; A → C → E(F) in Chart 3] in the ester-forming reaction of the 3-phenyl-2-butyl system. The other two authors of this chapter must certainly agree that the 3-phenyl-2-butyl stereochemical results have no analogy in the theory of *simple* aryl-unbridged carbonium ions, and as such they are not inconsistent with an interpretation based on the intermediacy of discrete, bridged phenonium ions (1a–1f,2,20,21,29,30). However, these two authors also believe that until very recently (Sections V–VIII), some disturbing problems were unsatisfactorily resolved. For example, the high retention/inversion ratios of $\sim 10^2$–10^4 for the acetolysis and formolysis of the 3-phenyl-2-butyl system, which Cram contrasted with the predominant *inversion* characteristic of the solvolysis of simple secondary systems (16–19), were determined from the combination of substitution product ratios with internal return data, but without taking the significant yields of olefin into account. (28b) Until very recently, there also was insufficient *quantitative* agreement between the *stereochemistry* and the *independently* determined *rate* data for the solvolysis of the 3-phenyl-2-butyl system (**2**) to warrant summary dismissal of Brown's alternative interpretations (3,23,28b). The problem of *apparent* rate-product discrepancies, described in detail in the remaining portions of this section, is encountered often in a comprehensive review of many systems (Section IV) and will be treated quantitatively in Sections V–VIII.

B. Rate Enhancement as a Criterion of Mechanism in the Solvolysis of β-Arylalkyl Systems

The classic, pioneering studies of Winstein and his co-workers dealing with the phenomenon of participation by neighboring groups (31) estab-

lished that an *accelerated solvolysis rate* due to transition state energy lowering must be observed if such participation is operative. Although the stereochemical profile (Section III-A) provides information about structural changes occurring throughout the *entire reaction coordinate* and therefore can elucidate the nature of the intermediate(s) involved (1a–1e,2,20,21,29,30), the kinetic data tell us about neighboring-group involvement in the *rate-determining transition state*. Solvolysis rate enhancements are said (31) to provide a measure of the *driving force* for neighboring-group participation.

The usual expression for the solvolysis rate enhancement is the ratio k_t/k_s, which is the factor by which the observed rate k_t is faster than it would be in the absence of anchimeric assistance, k_s. The total rate constant is usually expressed as the sum of the assisted (k_Δ) and "normal" (k_s) rates: $k_t = k_\Delta + k_s$. Winstein has often also expressed the driving force quantitatively as $L = RT \ln (k_t/k_c)$, where k_c is the originally used term for a limiting (**lim**) S_N1 process without any assistance (31). (See Section VI for a full discussion.) The driving force, in turn, is furnished by the degree of stabilization of the ionization transition state through charge delocalization into the neighboring system.

Long before H. C. Brown began his intensive efforts to reopen the neighboring group question (3a,b), the following important statement appeared in the original 1949 paper (1a) published by Cram, the first phenonium ion investigator:

> On the other hand, kinetic determinations of the comparative rates of the liberation of *p*-toluenesulfonic acid from the *p*-toluenesulfonate of [the diastereomeric 3-phenyl-2-butanols] and 2-butanol in glacial acetic acid showed that these reactions all take place with very little difference in rate. Since [2-butyl] does not, and [the diastereomers of 3-phenyl-2-butyl] do rearrange, the breaking of the carbon–oxygen bond in the latter molecules cannot be much aided energetically by the formation of a new carbon–carbon bond in a cycle, or there would be divergence in the activation energies, and hence the rates of the reaction, in the two types of molecules.

So, from the very beginning, what was to become the principal stumbling block to convincing kinetic arguments, was clearly recognized. Of course, since this first statement of the "rate-product quandary," the importance of internal return and inductive effects as effective solvolysis rate depressors has been recognized, and these factors have played no small role in the developing controversy. Nevertheless, lack of appreciable *uncorrected* rate enhancement is a characteristic of many symmetrical systems for which phenonium ions have been proposed as intermediates. The following detailed discussions of many systems of various types makes this quite evident.

1. Kinetic Effects in the Solvolysis of the 3-Phenyl-2-Butyl System

Not only does 3-phenyl-2-butyl tosylate solvolyze "with very little difference in rate" from the parent 2-butyl system, but the reaction is actually *slower* for the phenyl derivative. The titrimetric rate constant for the acetolysis of *threo*-3-phenyl-2-butyl tosylate was found to be 0.6 that for the parent 2-butyl system (31g). Clearly, at first glance, there was no apparent driving force indicating concerted participation by the phenyl ring in ionization.

In the light of Winstein's parallel studies concerning internal return in other neighboring group systems (13), reexamination of the *threo*-3-phenyl-2-butyl system revealed that return was indeed occurring; and the initial ionization step, if it was taken as being equal to the rate of racemization k_α, was found to occur at a rate that was 4.4 times faster than the rate of solvolysis k_t in acetic acid and 1.2 times faster in formic acid (12). (There have been some doubts expressed (32,33) concerning the question of the identity of k_α and the true rate of ionization.) Reduction of internal return in the latter solvent is due to its increased ability to promote dissociation of ion pairs (12,13). Applying a correction in acetic acid, 3-phenyl-2-butyl was said to *ionize* faster than 2-butyl by a factor of 0.6 × 4.4, or about 3. This was still a very small factor compared with the large effects, often several powers of 10 in magnitude, which were being observed at the time in other systems (31).

It was also recognized that, because of the sp^2–sp^3 bond dipole between the phenyl ring and the aliphatic side chain, the aromatic ring should actually depress the aryl-unassisted rate inductively, and so the crude factor of 3 in anchimeric acceleration should be corrected for the inductive depression. The history of the long and varied search for the "true" inductive effect of a β-phenyl ring merits in itself sufficient attention for a separate section; but a concise summary, with leading references, appears elsewhere (35). The use of "inductive effects" has often been misleading when the incorrect assumption was made that these are constant parameters for a given group. The inductive effect of any given neighboring group is different for each system and in each solvent, and it is not freely interchangeable among different systems. [Schleyer has determined a variety of inductive effects by reliable kinetic means (36–39) for several key systems.] Briefly, values for this elusive retardation parameter for a β-phenyl ring have ranged from a factor of 10 to 1.4 (34–37). Taking the most commonly used (35) factor of 8–10 as the rate-depressing inductive effect of a nonparticipating β-phenyl ring, Cram calculated a corrected value for the anchimeric acceleration in the *ionization* of 3-phenyl-2-butyl tosylate (**2a-OTs**) as a factor of 24–30 (2). More recently, Cram has proposed (21b)

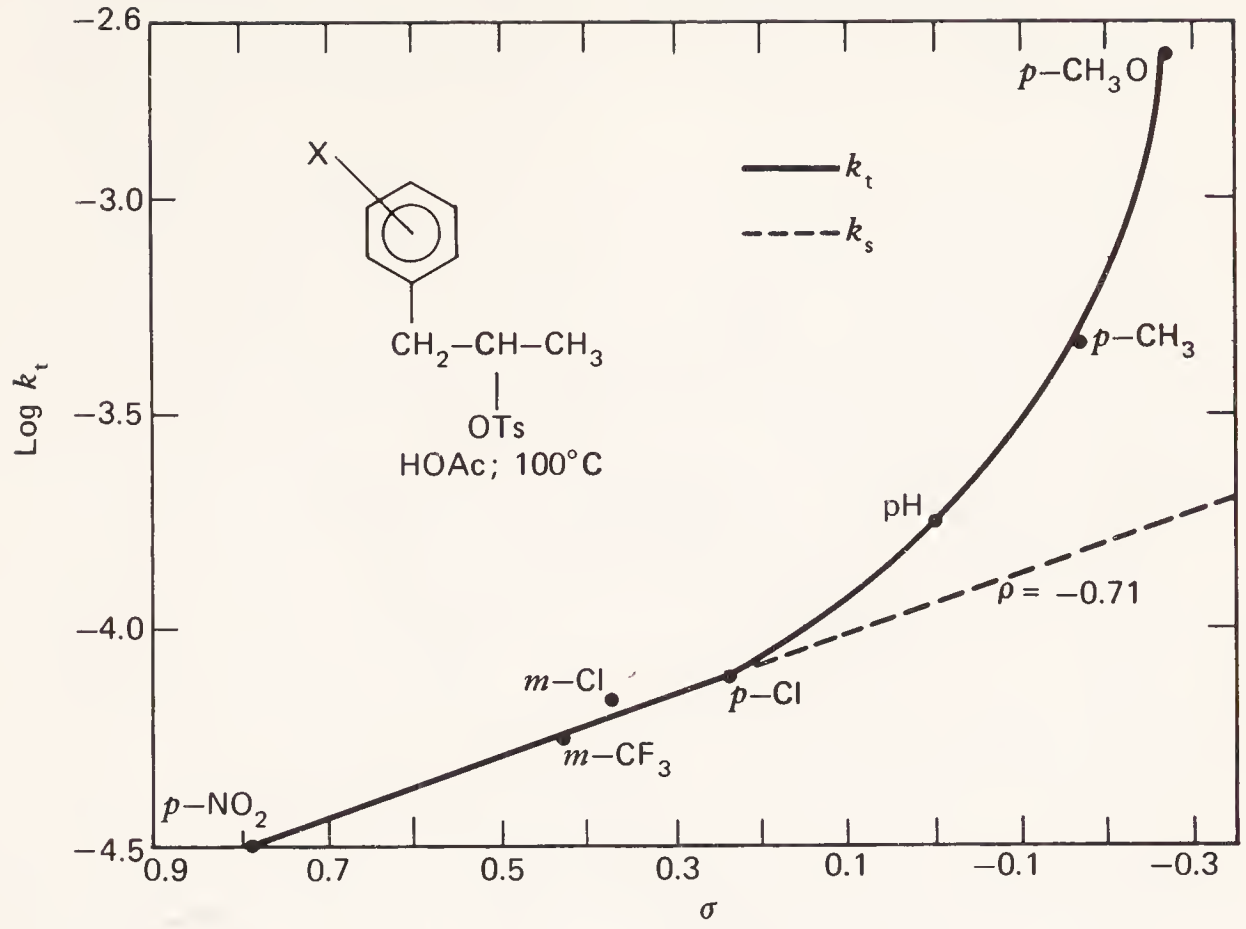


Fig. 1*a*. Hammett treatment of acetolysis (100°) of 1-aryl-2-propyl tosylates (39a).

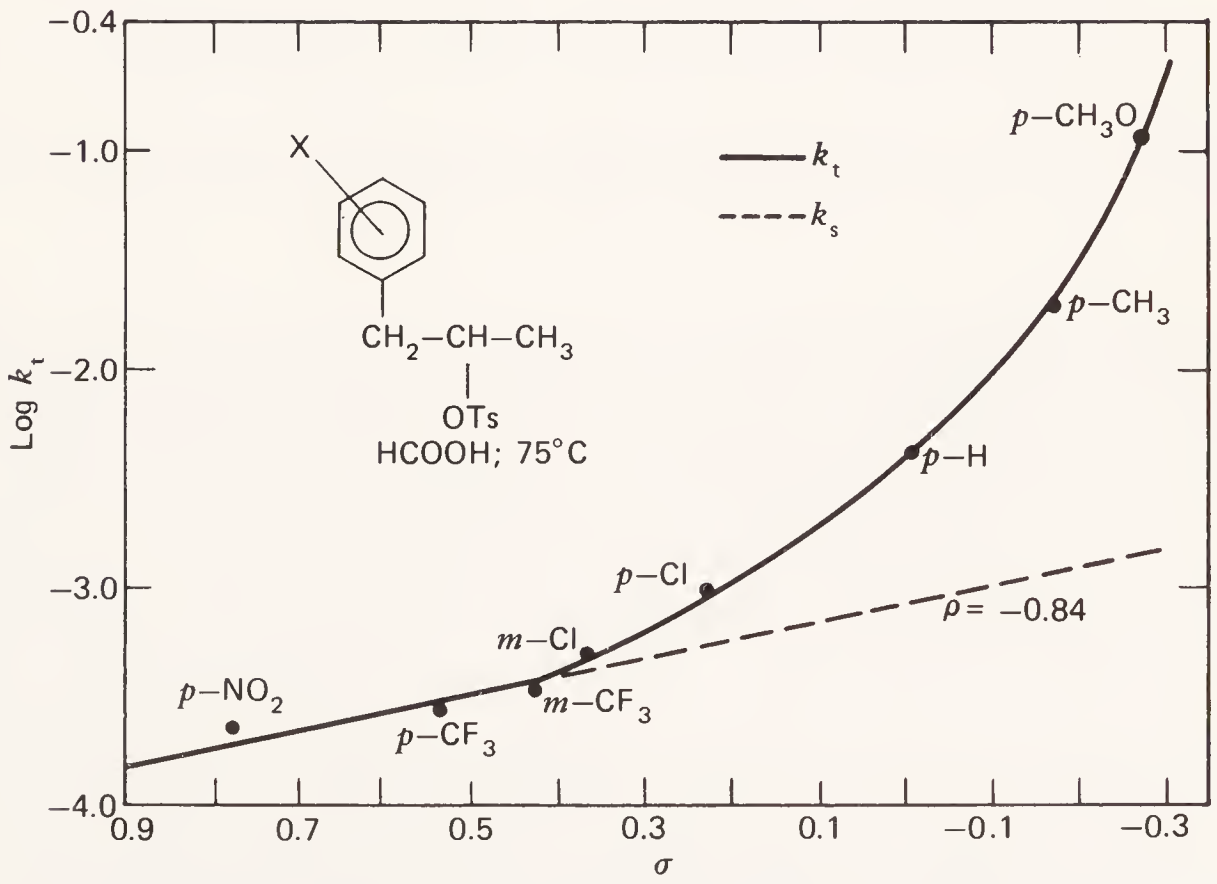


Fig. 1*b*. Hammet treatment for formolysis (75°) of 1-aryl-2-propyl tosylates (39a).

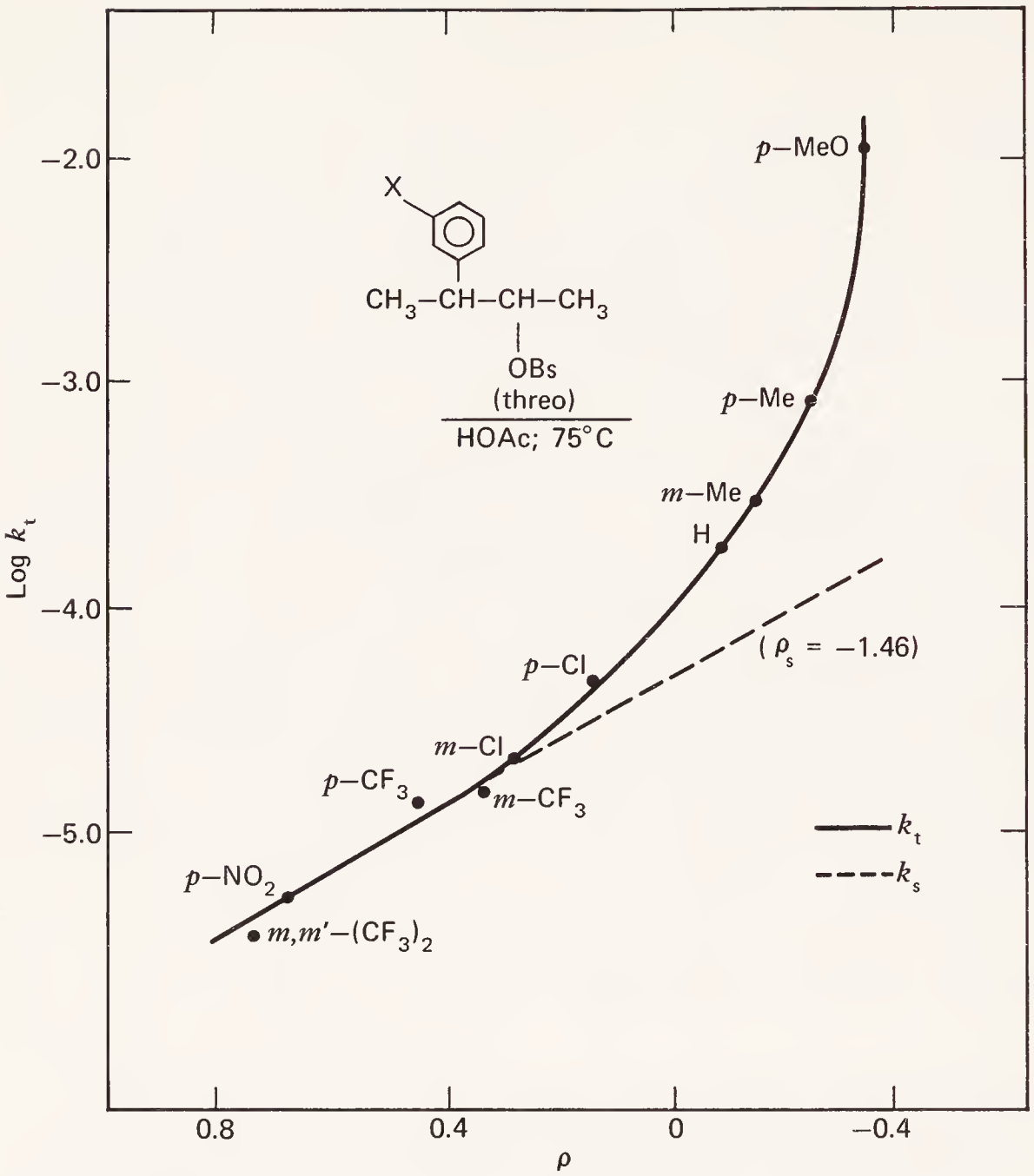


Fig. 1*c*. Hammett treatment of acetolysis (75°) of *threo*-3-aryl-2-butyl brosylates (4,38).

a rate enhancement as high as a factor of 43 for phenyl-assisted ionization, based on an inductive effect estimated from rate and product comparisons between 3-phenyl-2-butyl tosylate (**2a-OTs**) and its *p*-NO_2 derivative.*

Recently several studies have been carried out to attempt to refine and correlate more precisely the large body of kinetic data for the 3-phenyl-2-butyl (**2**) and related systems. Both Brown (4,38) and Schleyer (4a,36,39) have utilized more accurate, precise methods for determining k_s (31), the

* A qualitative idea of the increase in competitive phenyl participation in the ionization of *threo*-3-phenyl-2-butyl brosylate (**2a**) as solvent nucleophilicity is decreased is obtained from the following phenyl (**2a**)/*p*-nitrophenyl (*p*-NO_2-**2a**) ionization rate ratios: $k_\alpha^{2a}/k_\alpha^{p\text{-}NO_2\text{-}2a} = 2 \times 10^2$ (HOAc); $\sim 6 \times 10^2$ (HCOOH); $\sim 4 \times 10^4$ (CF_3COOH).

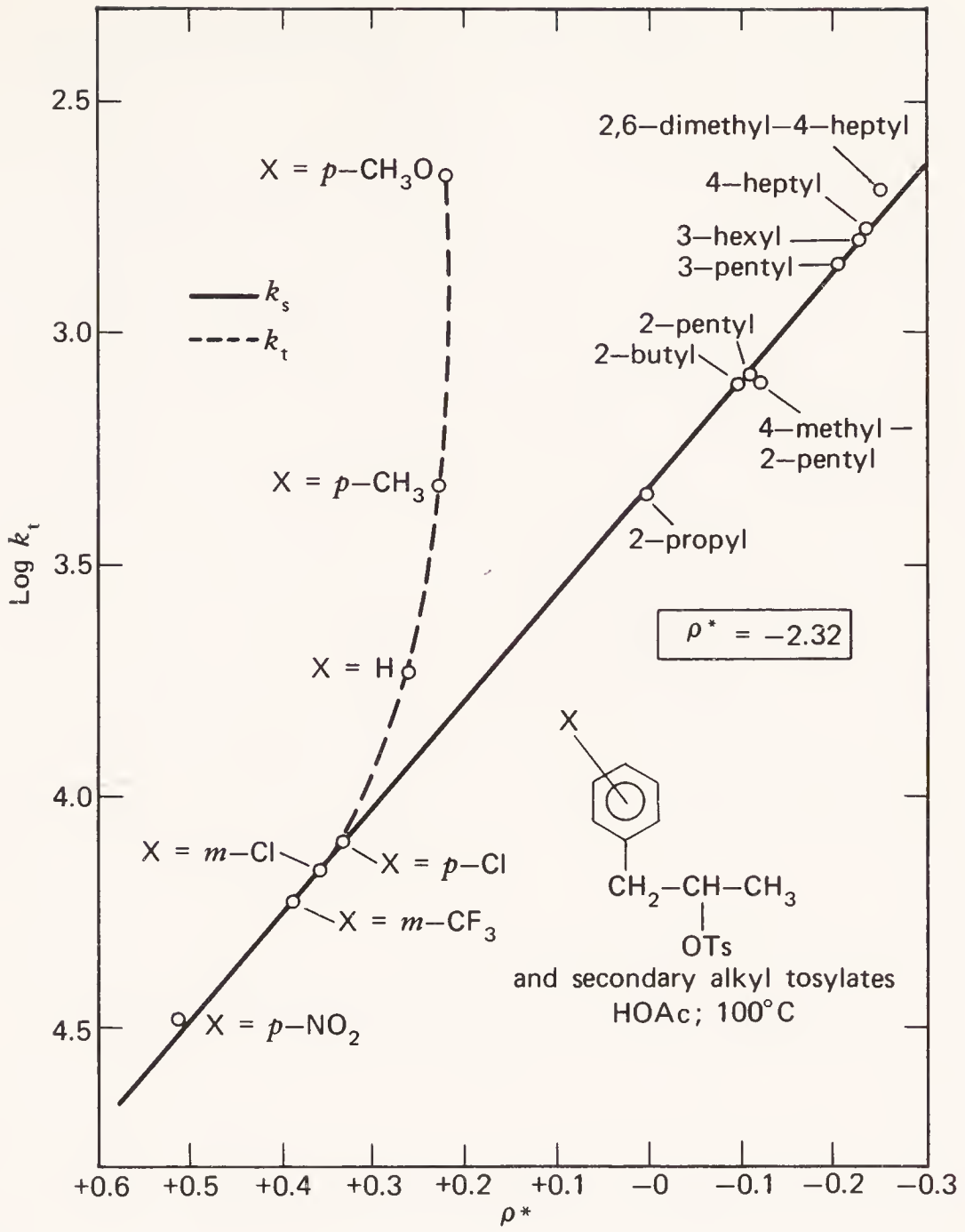


Fig. 2*a*. Taft treatment of acetolysis (100°) of secondary systems (39a); for non-participating systems: $k_t = k_s$.

anchimerically unassisted rate constant, for several primary and secondary β-arylalkyl systems, without reference to some unsubstituted "model" compound. These methods consist of determining the solvolysis rates of a series of deactivated members of the particular β-arylalkyl system under consideration (e.g., the trifluorotolyl, nitrophenyl, and halophenyl derivatives), which undergo little or no participation, applying either Hammett (e.g., Fig. 1) or Taft (40)* (e.g., Fig. 2) correlations (Table II; Section IV-A-3-b) and extrapolating these lines (ρ_s) through the appropriate σ or σ^* constants for the compounds suspected of anchimeric acceleration. For deviating points, the ratio of the observed titrimetric rate constant to the extrapolated unassisted rate constant k_t/k_s, gives a measure of the titrimetric (i.e., solvolysis, not ionization) rate enhancement. Alternatively,

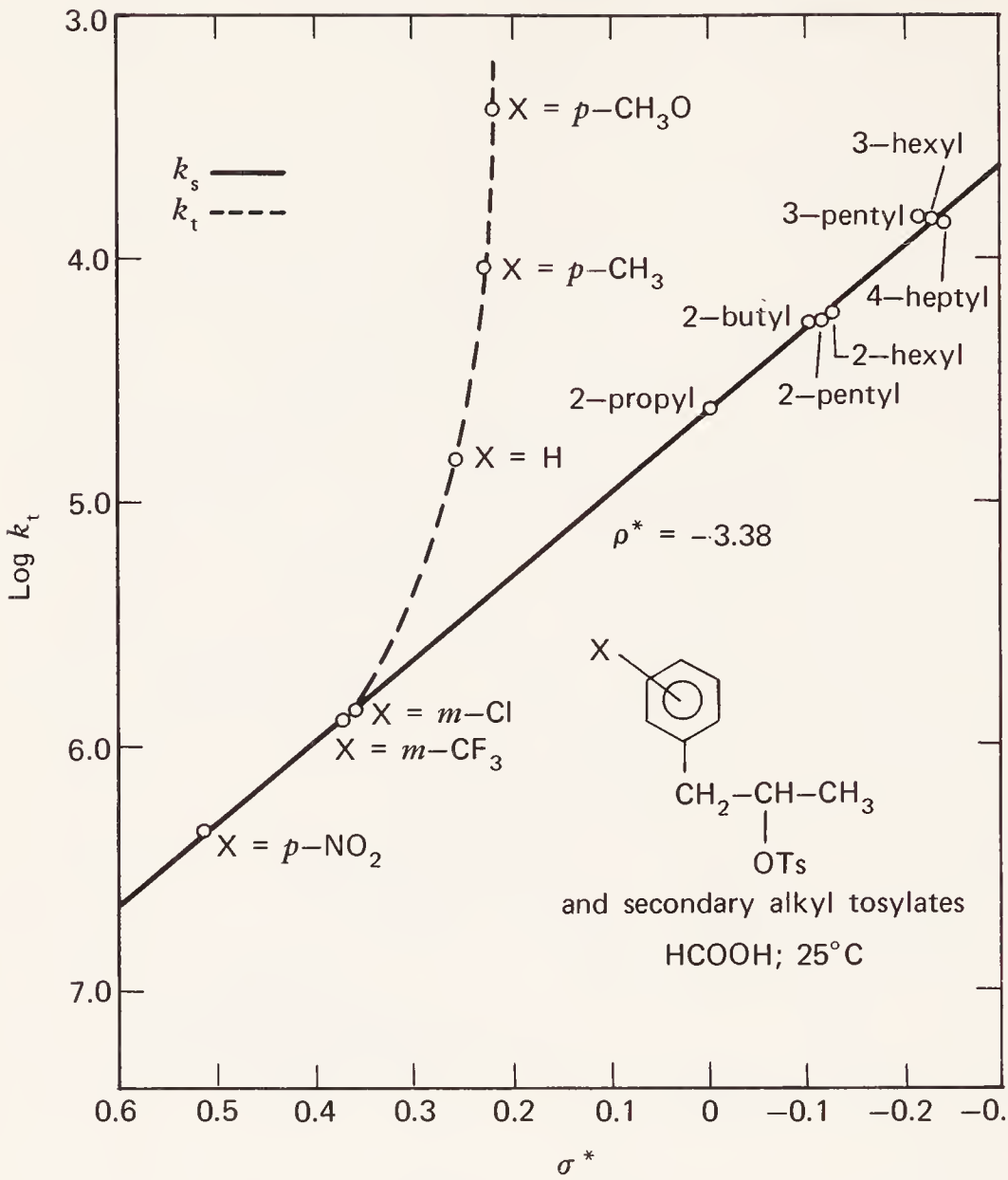


Fig. 2*b*. Taft (40) treatment of formolysis (25°) of secondary systems (39a); for nonparticipating systems: $k_t = k_s$.

racemization or scrambling rates could be used throughout an entire series, giving the *ionization* rate enhancements (k_α/k_s) directly. Figures 1 and 2 provide representative examples both of the Hammett and Taft* (40) treatments, respectively.

Using a Hammett approach (4,38c), Brown found a titrimetric rate enhancement (k_t/k_s) for 3-phenyl-2-butyl brosylate of a factor of 2.5–4.0 in acetic acid, in agreement with Streitwieser's Taft-determined value, and a factor of 24 in formic acid. Correcting these factors for internal return (k_α/k_t) gives the *ionization* rate enhancements (k_α/k_s) as 11–18 and 29, respectively. These latter values (4,38) are to date probably the most reliable magnitudes of ionization rate enhancements available for the

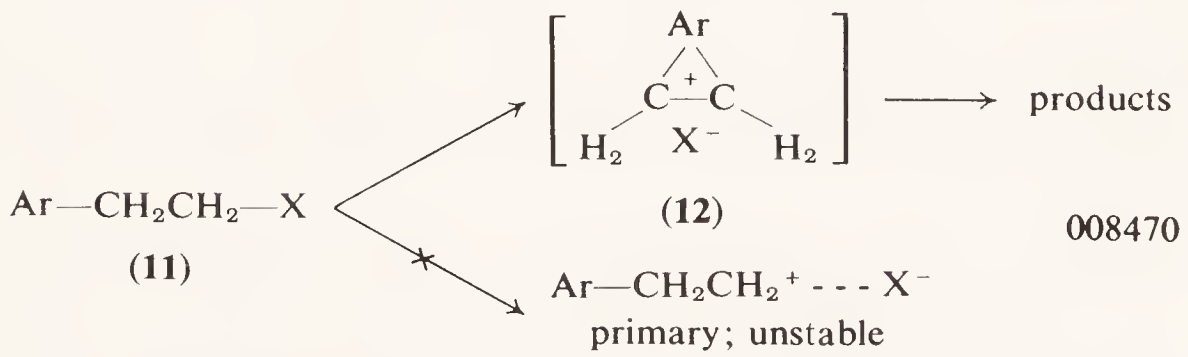
* The first use of this type of Taft correlation in a solvolytic reaction is due to Streitwieser (40).

acetolysis and formolysis of the 3-phenyl-2-butyl (**2**) system. If the aryl-unassisted (k_s) pathway involves an *open** (i.e., nonnucleophically solvated) carbonium ion, then it appears that the corresponding ionization transition state stabilization energies, only ca. 1.5–2.0 kcal/mole, are not reflective of the type of strong aryl–carbon bond implicit in a symmetrically σ-bridged phenonium ion (**1**, **3**, **4**) (1a,3,38) and are insufficient in the absence of further information to dictate such extensive stereochemical product control. Thus Cram's "rate-product quandary" has not been fully resolved on the basis of bridged versus open* ions; it still poses an apparent dilemma. Brown's argument (3,23,38) for rapidly equilibrating open* ions, formed with little or no aryl participation in the ionization transition state, was offered as an "escape from this dilemma" (3b). However, it remains to be shown that much of the "dilemma" arising from the foregoing kinetic results is due to the failure to assess accurately the degree of rate acceleration (i.e., *solvent* assistance) in the so-called unassisted (k_s) pathway. This subject is best treated after many more systems have been reviewed. Accordingly, the problem of the rate/product discrepancy is resumed in Section V.

IV. SURVEY OF GENERAL β-ARYLALKYL SOLVOLYSIS STUDIES

A. Kinetics and Rearrangements in Primary Systems

It might be expected that the β-phenylethyl system (**11**; Ar = C_6H_5) would be one of the best places to look for β-aryl participation—since an initially formed primary unbridged cation would be too unstable, the probability of stabilization via anchimeric assistance is increased. In addition, participation through direct rearrangement to a more stable



* Precise definitions are in order. Cram has consistently used the term "open" ion to describe an ion that is aryl-unbridged *but nucleophilically solvated* (2,21). However, this may lead to confusion, since an "open" ion or ion pair more generally has been used to refer to an ion that is totally nonnucleophilically solvated, either by neighboring group or by solvent (see Sections V–VIII). In order to be consistent with the recent general solvolysis literature, we shall use the term "open" ion *only* to desribe such an ion: nucleophilically unbound either to the aryl group, to the solvent, or to the leaving group.

cation, a reaction type to be discussed later, is ruled out by the symmetry of the β-phenylethyl structure, making it a model system in which to search for bridged phenonium ion intermediates (**12**) as well.

Accordingly, the β-phenylethyl (or, more commonly, β-phenethyl) system has received from many workers a lengthy, detailed scrutiny second in thoroughness only to that accorded the ancestral 3-phenyl-2-butyl cases.

This section deals first with the parent β-phenylethyl system, followed by discussions of several β-methyl- and β-aryl-substituted primary systems, and a series of polynuclear β-arylethyl substrates.

1. Kinetics and Rearrangements in the β-Arylethyl Series

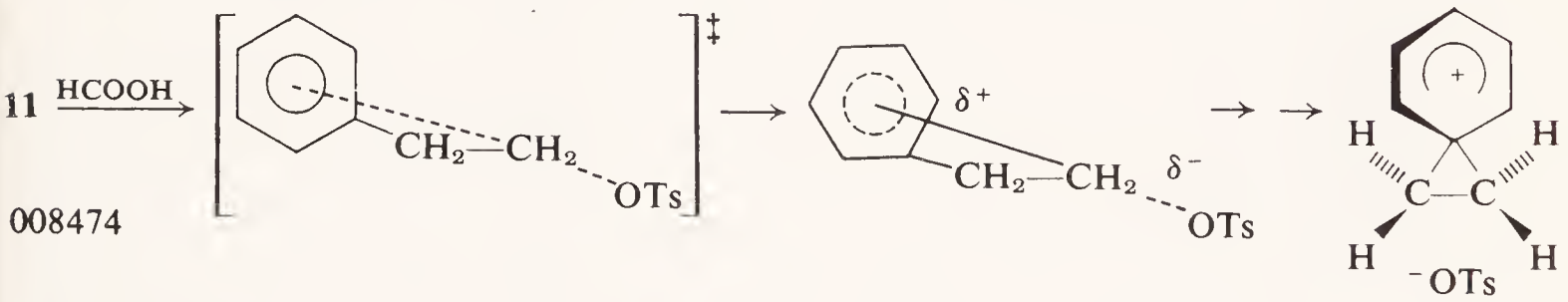
The first studies of possible anchimeric assistance in the acetolysis of the parent β-phenylethyl system were carried out by Winstein (41a) during the course of his earlier general investigations of neighboring-group participation (31). Even after the usual rough correction for the inductive effect of the β-aryl group, his conclusion concerning the parent phenyl system was as follows (41): "There are no clear indications from the kinetics that phenyl participation is very important in acetic acid, although the data would be consistent with some successful competition of phenyl with solvent participation."

Uncorrected rate data (41) showed that β-phenylethyl tosylate underwent ethanolysis and acetolysis at rates that were 0.24 and 0.37 times as fast, respectively, as the corresponding solvolysis rates of ethyl tosylate. Only in formic acid was the uncorrected rate of the β-phenyl derivative faster, by a factor of 2, than the model ethyl system. These and allied data led Winstein to conclude that both ethanolysis and acetolysis proceed predominantly via the anchimerically unassisted (k_s) pathway. In contrast, the enhanced ionizing power of formic acid results in domination of nucleophilic phenyl participation, and the phenyl-assisted pathway (k_Δ) predominates.

The degree of C_α–C_β equilibration that actually occurred under these conditions is evident from the scrambling results (see Table I). Only 0.6% ^{14}C scrambling accompanies ethanolysis (42), leaving little doubt of the near-complete predominance of the k_s route. Early results of buffered acetolysis, 11% scrambling (42), point to still minor aryl participation. The presence of the acetate buffer, however, has the effect of increasing the proportion of the k_s pathway. Compound **11**, being primary, is particularly sensitive to S_N2 reaction with added nucleophiles. Significant internal return (42b) is also a complication attendant to the acetolysis of **11**. More recent results in unbuffered acetic acid obtained by Coke and co-workers

(43) (Table I) give a more complete picture of the detailed processes involved. The degree of ^{14}C scrambling in the acetate product was shown to increase with increasing reaction time, as the starting tosylate became scrambled through internal return. An estimated degree of rearrangement amounting to 24–30% scrambling was determined by extrapolation to time = 0 (see Table I). In formic acid, where internal return is very small (42b), substantial aryl involvement is indicated by ^{14}C label equilibration to the extent of 90% (42).

Saunder's deuterium-scrambling results (Table I) in buffered media (44) are in reasonably good agreement with the ^{14}C scrambling results in buffered media (42). Saunders also determined secondary α- and β-deuterium isotope effects for the acetolysis and formolysis of **11**. In acetic acid, small (3–4%) α- and β-deuterium isotope effects were taken as evidence for the lack of significant β-phenyl participation in the ionization transition state. A relatively large (17%) α-deuterium effect and the absence of any β-deuterium effect in formic acid was interpretated as evidence against a normal, aryl-unassisted mechanism; formolysis instead proceeded with substantial aryl participation (44). Saunders argued against a symmetrically bridged first transition state and intermediate in the aryl-assisted formolysis pathway on the basis of the unexpected inequality of the α- and β-deuterium effects. A near-symmetrically aryl-bridged first transition state was reasonably expected to exhibit similar α- and β-D isotope effects. Therefore, the observed effects were rationalized in terms of an unsymmetrically bridged transition state followed immediately by an unsymmetrically bridged first intermediate [Hammond's postulate (48)], the latter, in turn, leading to the symmetrically bridged intermediate phenonium ion **12**.



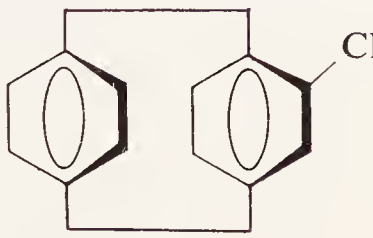
(12)

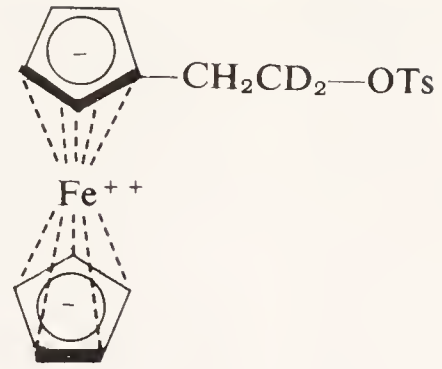
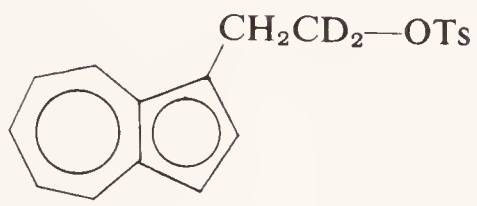
Gregoriou (49) has recently cited a series of similar isotope effects in the solvolysis of the 3-phenyl-2-butyl system (**2a**) as evidence in support of the same sequence of unsymmetrical and symmetrical transition states and intermediates in that system* as was proposed for the β-phenylethyl

* Gregoriou has proposed a general unified theory of solvolysis mechanism which, among other things, has suggested that extreme interpretations of β-arylalkyl solvolysis in terms of either fully σ-bridged or equilibrating totally unbridged species as

TABLE I

Rearrangements in the Solvolysis of β-Arylethyl Substrates; Ar—CH_2CH_2—X

Substrate	Solvent	Reference	2 × Percentage Rearrangement[a]	Remarks
C_6H_5—$CH_2{}^{14}CH_2$—OTs	EtOH	42	0.6	
	HOAc	42	11.0	Acetate-buffered
	HOAc	43	24–30	Unbuffered; extrapolated to time = 0[b]
	HCOOH	42	90	Formate-buffered
	CF_3COOH	56	100	CF_3COO^--buffered
C_6H_5—CH_2CD_2—OTs C_6H_5—CD_2CH_2—OTs	HOAc	44	20	Acetate-buffered; avg. of α- and β-D results
	HCOOH	44	80	Formate-buffered; avg. of β- and α-D results
p-CH_3O—C_6H_4—$CH_2{}^{14}CH_2$—OTs	EtOH	41c	48	Not corrected for internal return
	HOAc	41c	104	Not corrected for internal return
	HOAc	43b	98–100	Not corrected for internal return
	HOAc	43b	88	Unbuffered; extrapolated to time = 0[b]
	HCOOH	41c	102	Internal return unimportant
2,5-di-CH_3—C_6H_3—CH_2CD_2—OTs	80% aq. acetone	50a	52	
	HOAc	50a	92	Not corrected for internal return
 CH_2CD_2—OTs	HOAc	50a	0	See Section IV-D and Table VIII
	HCOOH	50a	0	See Section IV-D and Table VIII

	80% aq. acetone	50b	0	See Section IV-D
α-$C_{10}H_7$—$CH_2{}^{14}CH_2$—OTs	HOAc	47a	92	Not corrected for internal return[c]
	HCOOH	47a	100–101	Internal return unimportant
β-$C_{10}H_7$—$CH_2{}^{14}CH_2$—OTs	HOAc	47b	68	Not corrected for internal return
	HCOOH	47b	86	Internal return unimportant
α-$C_{10}H_7$—CH_2CD_2—OTs	HOAc	46	92	Not corrected for internal return
9-$C_{14}H_9$—CH_2CD_2—OTs	aq. dioxane	69a	100	Primary alcohol was only 15% of product. 85% was the bridged spiroalcohol (**27**-OH)
	HOAc[d]		100	Acetate-buffered; no internal return detected.[d]

[a] 2 × percentage rearrangement = "percentage scrambling," or the total percentage of molecules involving phenyl migration.

[b] Extrapolation to time = 0 (see Ref. 43), gives a measure of aryl rearrangement in the product acetate, formate, etc., in the absence of substrate scrambling through internal return.

[c] At 50% reaction, the starting tosylate was 76% scrambled.

[d] R. N. McDonald and J. R. Curtis, *J. Am. Chem. Soc.*, **93**, 2530 (1971).

system (**11**) (44). Acetolysis of **2a-OTs** led to small, nearly equal (ca. 7%) 1-D and 4-D (α-CD_3 and β-CD_3) isotope effects (49a), as well as small, nearly equal (ca. 10%) 2-D and 3-D (α- and β-D) isotope effects (49b). In contrast, formolysis and trifluoroacetolysis of **2a-OTs** led to small 4-D (β-CD_3) isotope effects (ca. 1%) but relatively large 1-D (α-CD_3) isotope effects (16–17%) (49a), and to small 3-D (β-D) isotope effects (1-4%) but normal 2-D (α-D) isotope effects (ca. 13–14%) (49b).

In fact, Cram had long ago proposed that symmetrically bridged phenonium ions (**3**, **4**) in the acetolysis of the 3-phenyl-2-butyl system (**2**) could be preceded by first-formed unsymmetrically bridged transition states and intermediates (30b). If symmetrical first intermediates immediately preceded by near-symmetrically bridged transition states had been involved, we would have expected the *erythro* diastereomer (**2b**), which yields phenonium ion **4** with *trans* methyl groups, to solvolyze substantially faster than the *threo* diastereomer (**2a**), which leads to bridged ion **3** with *eclipsed* methyls. Cram actually found (30b) a negligibly *small* difference between the acetolysis ionization rates for systems 2a and 2b.

Very recently, phenyl-1-^{14}C isotope effects have been determined for the acetolysis of **11-ONs** (45). The absence of any ^{14}C isotope effect for the parent phenyl derivative was taken as evidence for the lack of significant phenyl participation in the ionization transition state.

Almost every β-arylalkyl system that has been investigated has been probed for maximum possible aryl participation by activated neighboring groups, most commonly the *p*-methoxyphenyl (*p*-anisyl) group. For β-*p*-anisylethyl nosylate (**11-ONs**; Ar = *p*-$CH_3O\phi$), aryl-1-^{14}C isotope effect studies have been reported recently (45). In contrast to the parent system (**11**; Ar = ϕ), significant *p*-anisyl participation was evidenced by an aryl-1-^{14}C isotope effect of 1.03 (45).

The β-*p*-anisylethyl system (**11**; Ar = *p*-$CH_3O\phi$) has been studied extensively for many years. The earliest kinetic studies by Winstein (41a–41c) clearly showed the competitive predominance of the aryl-assisted (k_Δ) mechanism in both the acetolysis and formolysis of this substrate. Somewhat surprisingly, even with such an activating substituent, the enhanced nucleophilicity of ethanol, coupled with the extreme sensitivity of primary systems to nucleophilic solvent participation (51), was

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sole intermediates are both unsatisfactory. Some of the specific features of Gregoriou's unified theory (49) forecast the more recent refinements which have contributed to ultimate resolution of the phenonium ion controversy (4,38,39). Unfortunately, the bulk of Gregoriou's published work was not widely available, and only certain aspects of it have very recently become readily accessible. Leading references to the rest of Gregoriou's work are found in Ref. 49.

sufficient to shift the solvolysis over primarily to the aryl-unassisted (k_s) mechanism in that solvent. Scrambling results (Table I) are consistent with these conclusions.

An analysis of activation entropies, $\Delta S^{\ddagger}$, was also made by Winstein for the solvolysis of the parent (**11**; Ar = ϕ) and *p*-anisyl (**11**; Ar = *p*-$CH_3O\phi$) β-arylethyl derivatives (41), and this parameter has often been suggested as a diagnostic tool for the detection of neighboring-group participation (41b,50a). In the case of primary systems such as **11**, the activation entropy is particularly sensitive to neighboring-group participation, since, in the latter's absence, considerably negative entropies will be expected because of the largely bimolecular nature of the anchimerically unassisted (k_s) solvolysis (51). Winstein indeed found highly negative activation entropies for anchimerically unassisted or weakly assisted primary systems, e.g., ethyl and β-phenylethyl (EtOH; HOAc) (41b), of the order of -15 to -20 eu. In contrast, $\Delta S^{\ddagger}$ for anchimerically assisted systems was found to be about 10 eu *more positive* (41b). This entropy difference has been confirmed by recent, more refined studies on primary β-arylethyl systems (39b). [It has been shown that the difference in anchimerically assisted and unassisted activation entropies for secondary systems (4,38,39) is not as large as for the primary systems (39b,41b,50a)].

Brown has probed the degree of β-aryl participation in **11** by comparing substituent effects with the π-delocalized benzyl system (52). In the latter substrate, a *p*-CH_3O/H factor of ca. 10^5 is observed (52), far larger than the corresponding *p*-CH_3O/H factors found for the β-arylethyl system—30 for acetolysis (41) and 76 for formolysis (52). It was argued (52) that the benzyl system should provide an electronic model for charge delocalization into the aryl ring in a β-arylalkyl system, should the ionization transition state in the latter case approach a fully σ-bridged structure. The observed difference of ca. 10^3 in *p*-CH_3O/H rate ratios between the benzyl and β-phenylethyl (**11**) systems led Brown to suggest that the enhanced rate of solvolysis of β-*p*-anisylethyl tosylate reflected a type of participation such that the ionization transition state resembled a π complex. On this basis, it was argued that the first intermediate was then best represented by a pair of rapidly equilibrating, partially π-bridged cations or ion pairs, rather than by a fully bridged anisonium ion (52) [Hammond postulate (48)]. (See, however, Section IV-A-6.)

2. *Reactive Leaving Groups and "Supersolvents" in Primary Systems*

The likelihood of β-aryl participation is increased, in general, by destabilization of the incipient carbonium center. A neutral leaving group, incapable of forming stable ion pairs once free from the substrate, can give rise to a considerably destabilized, so-called hot carbonium ion. Loss of

free nitrogen from diazonium ions (deamination) is a common means of generating such "hot" cations, but such reactions are not easily studied kinetically. The solvolysis of alkylmercuric perchlorates generates similarly unstable cations (through the loss of free elemental mercury), but this type of reaction in general does show clean kinetic behavior which is easily studied (53,54).

Jensen and Ouellette (53) found that acetolysis of β-phenylethylmercuric perchlorate (**11**; Ar = ϕ; X = $HgClO_4$) proceeded 8.3 times faster than that of ethylmercuric perchlorate. Here a sizable uncorrected rate enhancement by a β-phenyl ring indicated fairly certainly that the bulk of the solvolysis was proceeding with aryl participation, since proper inductive correction could only increase the rate enhancement. The rate-enhancing effect of the β-phenyl group was even more striking in formic acid, where an uncorrected factor of 30 was observed. In later work, Ouellette (54) estimated the phenyl inductive effect as about a factor of 3 in both solvents, and he proposed corrected anchimeric acceleration factors of 25 in acetic acid and 90 in formic acid. These rate-enhancement factors were said to correspond to a 95%-assisted ($k_\Delta/k_t = 0.95$) acetolysis and a 99%-assisted formolysis. (The significance of such rate relationships is discussed in Section VI.)

Participation by β-aryl groups also can be enhanced by substantial reduction in solvent nucleophilicity, such that competing solvent participation in ionization is markedly reduced. This is especially true in primary systems, which solvolyze largely by S_N2 mechanisms. Recently trifluoroacetic acid has become increasingly prominent as a solvent of extremely low nucleophilicity, as well as high ionizing power (55).

Nordlander found that β-phenylethyl tosylate (**11-OTs**; Ar = ϕ) solvolyzed more than 3000 times faster in trifluoroacetic acid than ethyl tosylate (34). Clearly, β-aryl participation is completely dominant under these conditions (34). As we would expect on the basis of this kinetic result, the product trifluoroacetate, formed exclusively, showed complete scrambling of an α-^{14}C label (Table I), indicating virtually complete aryl control both of the rates and the products (34).

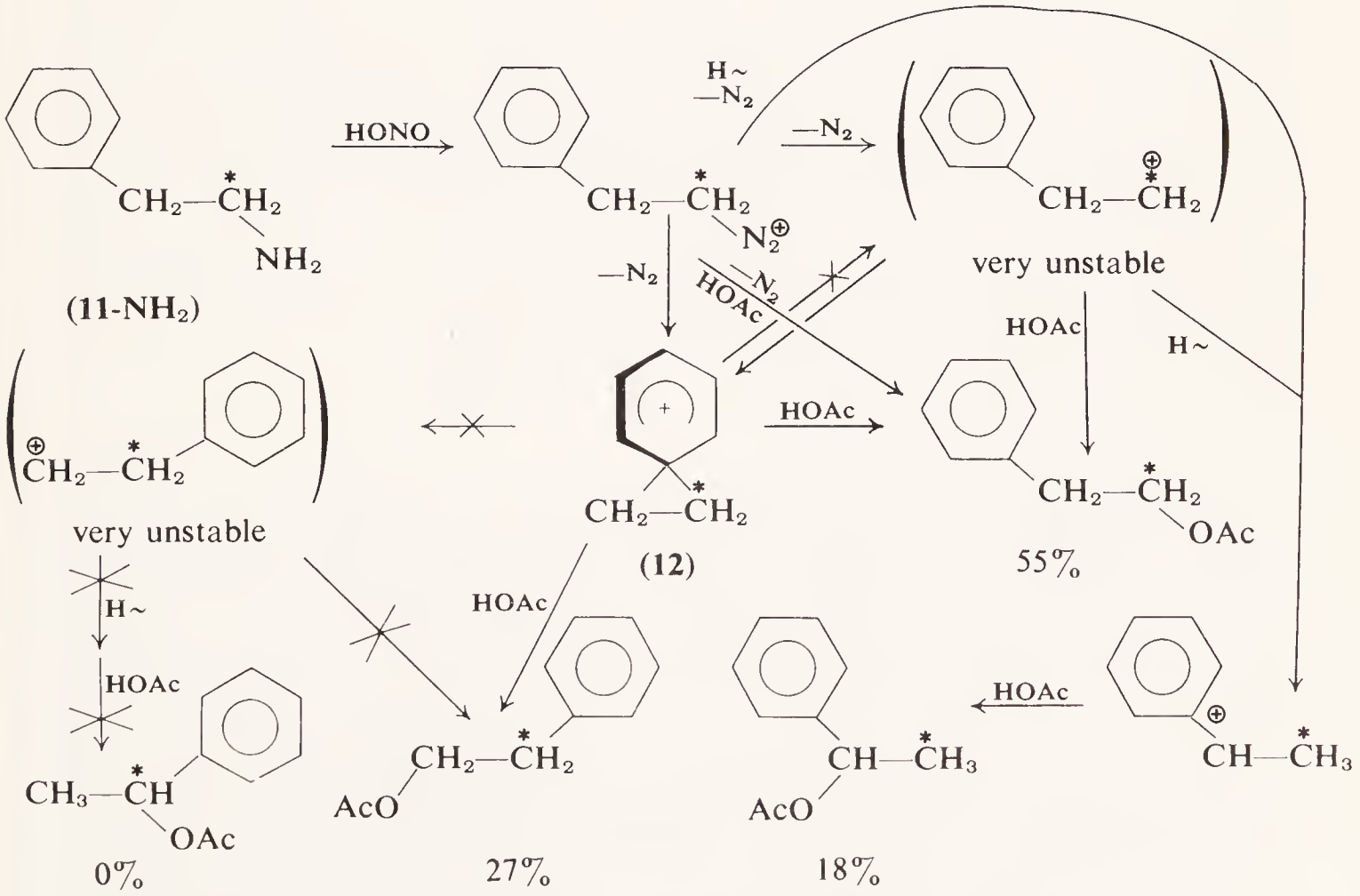
Other examples of a greatly increased contribution from nucleophilic aryl participation in the weakly nucleophilic solvent trifluoroacetic acid are provided elsewhere in this chapter (3-phenyl-2-butyl, p. 1372; 1-phenyl-2-propyl, p. 1404). In all cases, the marked but gradual increase in phenyl involvement as solvent is varied through the standard sequence, $ROH \rightarrow HOAc \rightarrow HCOOH \rightarrow CF_3COOH$, can be explained most logically by the decrease in solvent nucleophilicity throughout the solvent sequence.

The deaminative loss of neutral nitrogen from an alkyldiazonium ion

leads to a cationic species which, like that generated from demercuration (53,54) does not benefit from ion pairing with the *proximate** leaving group. Most probably, backside solvent assistance (16–19) is also reduced in deaminations, as in trifluoroacetolyses (55). (See, however, Refs. 56,57.)

Although the exothermic deaminations are seldom clean enough to study kinetically, the high-energy carbonium ion intermediate gives rise to product patterns that are markedly different from those found in the normal solvolyses of sulfonates, halides, etc. The deamination of β-phenylethylamine (**11-NH$_2$**; Ar = C_6H_5) is an example.

Deaminative acetolysis of ^{14}C-labeled β-phenethyl amine (**11-NH$_2$**; Ar = C_6H_5) gave β-phenethyl acetate with 27% phenyl rearrangement (54% C_α–C_β scrambling) (58,59)—about double the rearrangement found in unbuffered acetolysis of the tosylate (43) and about five times that found in buffered acetolysis (42) (Table I). Furthermore, acetolysis of the tosylate produced no hydride-shifted α-phenethyl acetate, but deaminative acetolysis gave an 18% yield of hydride-shift product. What is more striking is that the 18% yield of 1-phenylethyl acetate (product of hydride shift) had undergone essentially no shift of isotopic label (59). Thus it is demonstrated unequivocally that the phenyl shift was not followed by



* In deaminations, it is unlikely to expect ion pairing of the type R–X → $R^+ \cdots X^-$. However, see C. J. Collins, J. B. Christie, and V. F. Raaen, *J. Am. Chem. Soc.*, **83**, 4267 (1961) for evidence of ion pairing of the type R—N=N—X → $R^+//X^- + N_2$.

hydride shift. If open, phenyl-rearranged carbonium ion had intervened, and if this open ion had behaved as the unrearranged open ion (which is undoubtedly a precursor of at least some of the hydride migrated material), then the isotopic label of the 1-phenylethyl acetate would have been scrambled. These data strongly support a mechanism in which a phenonium ion is formed from either alkyl diazonium ion or possibly from a "hot"* primary carbonium ion, and this phenonium ion goes directly to rearranged and unrearranged acetate. In other words, any unrearranged, highly unstable primary β-phenethyl cation formed by loss of nitrogen is immediately converted either to stabler cations, e.g., phenonium ion (**12**) and rearranged benzylic α-phenethyl cation, or to β-phenethyl acetate. Primary cation is never again formed in the reaction coordinate, e.g., by "leakage" from the phenonium ion (**12**). Alternatively, the unrearranged primary cation may even be bypassed altogether; nitrogen conceivably could be directly displaced* in the diazonium ion either by β-phenyl, β-hydrogen, or solvent, or all of these (56,57,59).

Cram's much earlier study of the deaminative acetolysis of 3-phenyl-2-butylamine (**2-NH$_2$**) gave similar results and led to the same conclusions regarding the probable lack of nucleophilic assistance in carbonium ion formation with N_2^+ as leaving group.* Deamination of optically pure *threo* and *erythro*-3-phenyl-2-butylamine (**2a-NH$_2$** and **2b-NH$_2$**) in acetic acid gave a product pattern quite different from that observed for tosylate acetolysis (60). The *threo* amine gave acetate with 32% methyl migration, 24% hydrogen migration, 12% phenyl migration; the remaining 32% acetate (which was not rearranged) had 15% retained and 17% inverted configuration. The *erythro* amine gave acetate with 6% involving methyl migration, 20% hydrogen migration, and 74% of combined product of phenyl rearrangement and nonrearrangement. Of this latter fraction, 68% was of retained and 6% of inverted configuration.

* NOTE ADDED IN PROOF. The problem of whether or not diazonium nitrogen is displaced directly by solvent, neighboring group, and so on (56,57), or decomposes first to a cationic species, is still a matter of some uncertainty (59). Collins has provided an excellent recent summary of the deamination literature up to 1971 [C. J. Collins, *Accts. Chem. Res.*, **4**, 315 (1971)], and the bulk of the evidence, at least for secondary systems, seems to point toward the intermediacy of a carbonium ion, whose features and behavior differ substantially from solvolytically generated intermediates. (Some of the reasons for this will become apparent from the discussions in Sections V-VIII.)

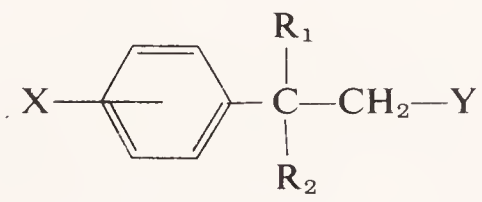
For deaminations of primary systems, however, available evidence appears to favor external and internal direct displacement as predominant pathways (56,57,59). Support for the nonintermediacy of "hot" or any carbonium ions during the deaminative solvolysis of primary amines is obtained from the observation that primary carbonium ions cannot be generated even in superionizing media (see Section IV-C-3).

These results were interpreted (60) with a mechanism invoking ground state control of products (57,60). Loss of nitrogen from the alkyldiazonium salt occurred without assistance from either solvent or neighboring group, and the "hot" open carbonium ion formed in this manner reacted faster with solvent or neighboring group than the rate of rotation about the C_α–C_β bond axis. The product pattern was predictable on the basis of the principles of open-chain conformational analysis (60). Thus the relative amounts of methyl, hydrogen, and phenyl migration corresponded to the expected relative ground state populations of the conformations in which methyl, hydrogen, and phenyl, respectively, were *anti* to the departing diazonium ion (60).

3. Kinetics and Rearrangements in β-Substituted Primary β-Arylalkyl Systems

The symmetry properties of the parent β-arylethyl system (**11**) rule out participation by the neighboring β-aryl ring in the form of a direct rearrangement to a more stable classical cation. Where substantial charge destabilization by the aryl group has been demonstrated, the transition state and first intermediate are best represented as some form of bridged species (σ or π complexes are not for the moment considered as alternatives to each other).

A large number of other primary systems has been extensively examined in which the symmetry of the parent system has been altered through further β-substitution (**11a**; R_1 and/or R_2 = CH_3, Ar, etc.). In several of these β-substituted β-arylalkyl substrates where participation by the β-aryl



(11a)

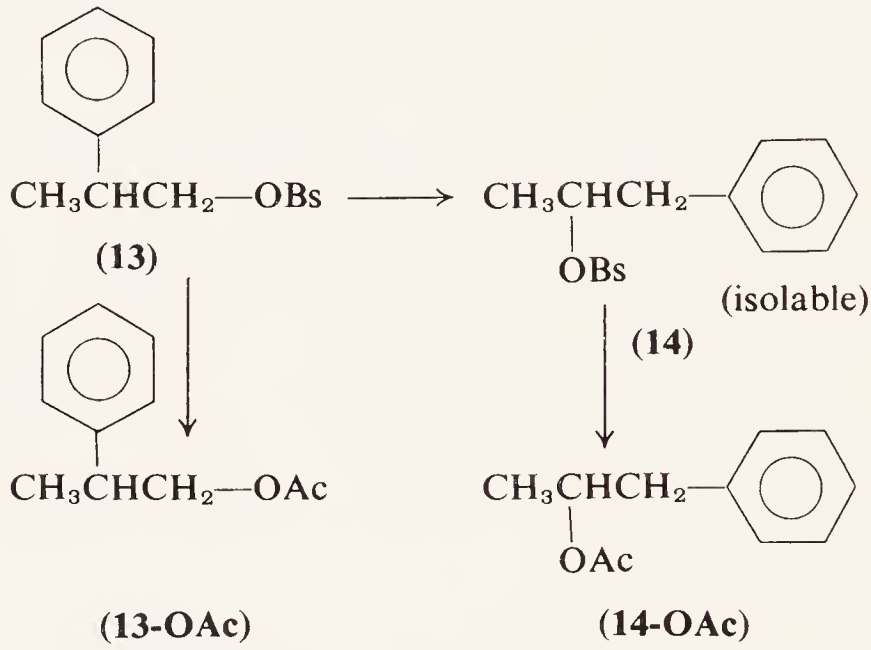
group has been demonstrated, the first intermediate following the aryl-bridged transition state need not be a phenonium ion, especially if aryl migration generates a much more stable rearranged carbonium ion. Conceivably, the aryl-bridged transition state could collapse directly to the stable rearranged cation.*

a. The 2-Aryl-1-propyl System. In the acetolysis with rearrangement of the simplest β-substituted β-arylalkyl system, 2-phenyl-1-propyl

* The bridged phenonium ion intermediate could possibly be a local energy minimum in the exothermic path to the stable, rearranged cation from the phenonium transition state.

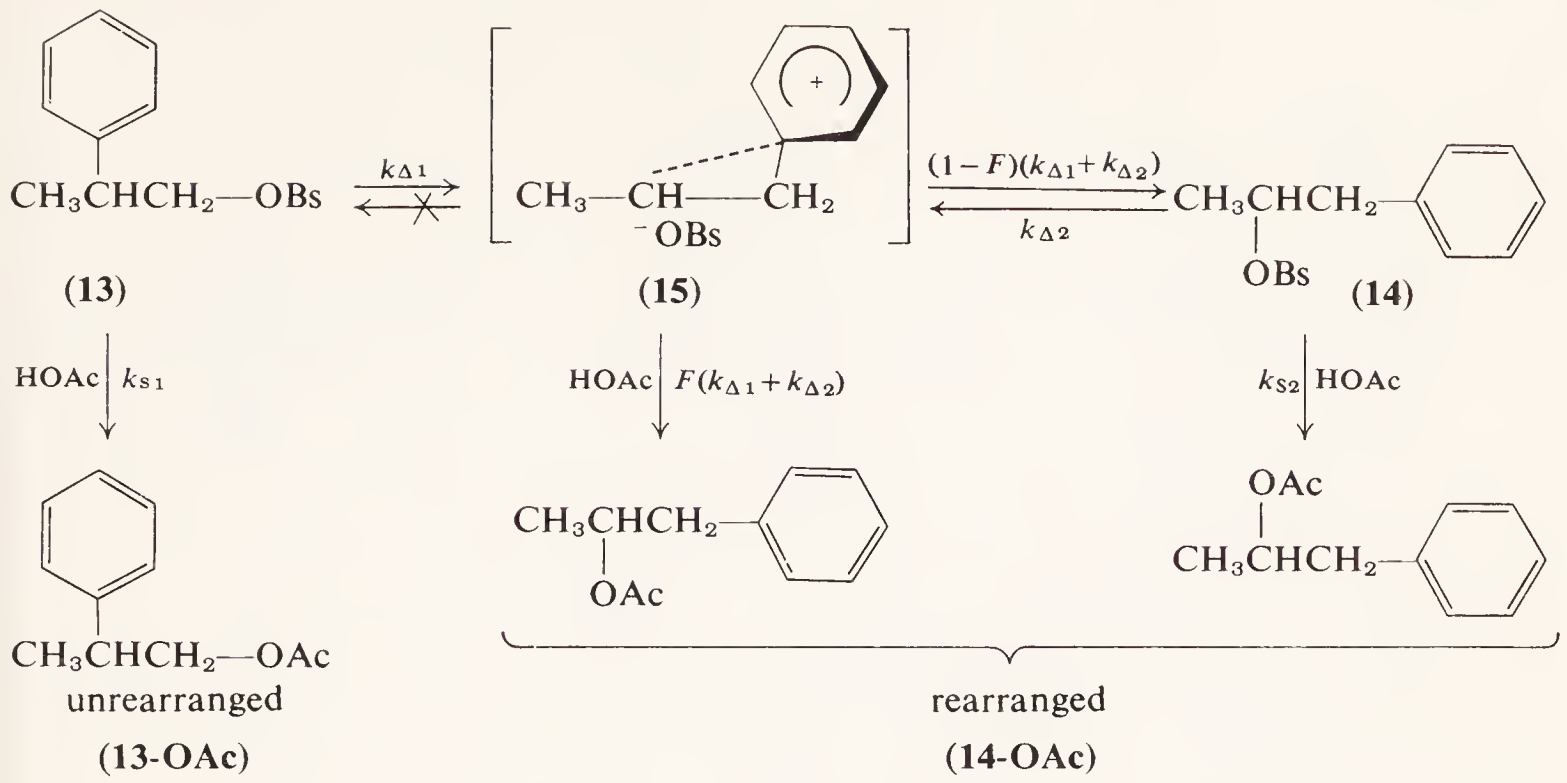
brosylate (**13**), a good case can be made for the intermediacy of a phenonium ion. [The 2-phenyl-1-propyl system (**13**) was first studied by Winstein (61a) with regard to substituent effects on participation.]

A distinguishing feature of this system is that, on acetolysis, the rearranged product of internal return, **14**, accumulates and can be isolated as the solvolysis proceeds. This occurs because the rate of rearrangement of **13** into **14** is faster than the rate of solvolysis of either isomer. Although the rearrangement route is from a primary system to the more stable secondary one, an aryl-bridged intermediate in this case may, nevertheless,



intervene during the rearrangement. This is suggested from a brief consideration of the solvolysis of **14**, the rearranged isomer. Acetolysis of **14-OTs** has been shown (36,39) to proceed with moderate phenyl participation ($k_t/k_s \sim 1.6$, by three methods of analysis; see Section IV-B-2 for full details of the solvolytic behavior of **14**). Owing to the symmetry of **14**, phenyl participation can *only* involve a phenonium ion intermediate (cf. Section IV-B-2). Therefore, it certainly appears reasonable that an aryl migration route leading *into* isomer **14** should also involve the same, or a similar, aryl-bridged intermediate (**15**), by microscopic reversibility. In fact, the acetolysis of **13-OTs** was recently used by Winstein (61c) as a measure of the importance of ion-pair return in the acetolysis of **14-OTs**, obviously on the assumption that both systems shared the same phenonium ion intermediate for aryl-assisted solvolysis.

If we employ Winstein's terminology (31,41,61), designating the aryl-assisted ionization rate constant as k_Δ and the aryl-unassisted rate constant as k_s, the acetolysis of **13** may be represented in more detail as shown on the following page. The reaction represented by $k_{\Delta 1}$ must be an essentially irreversible step, since the acetolysis of **14-OTs** gives an insignificant amount of primary ester (**13-OAc**) (39,80) (See Section IV-B-2).



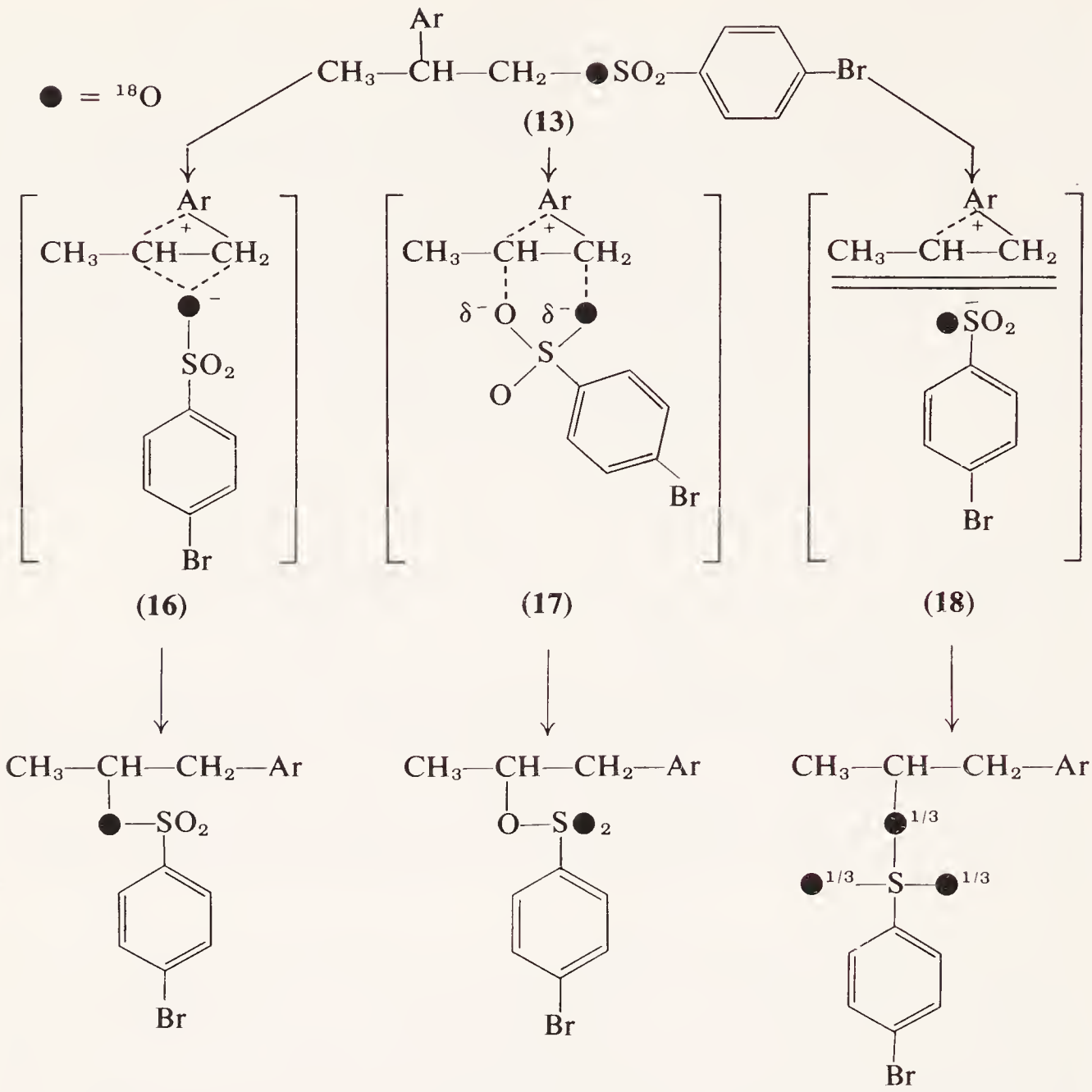
The usual scheme for treating anchimeric assistance with internal return is to designate as F the fraction of bridged ions that goes on to (substitution) product, and as $(1 - F)$ that fraction which returns to (in this case rearranged) starting material. (This subject is treated fully in Section VII.) These terms are incorporated into the representation of the acetolysis of **13**.

A novel technique was applied by Denney (62) to the acetolysis of **13** in an attempt to gain more detailed information as to the nature of the bridged ion pair **15** Solvolysis of **13** labeled with ^{18}O in the sulfonate ester oxygen was carried out, in order to distinguish between possible ion pairs **16**, **17**, and **18**.

Intervention of any of these three intermediates should produce characteristically different ^{18}O distribution in the rearranged brosylate. Actually, when Ar = phenyl, the observed ^{18}O distribution (ca. 0.66 of the ^{18}O remained as sulfonate ester oxygen) indicated that ion pair **16** was the predominant, though not exclusive, intermediate. It appears reasonable, however, that the intermediate is an "intimate" ion pair (13), so intermediate **17** rather than **18** is the most likely cause of the reduction in the amount of retained ester ^{18}O.

When Ar = *p*-anisyl, acetolysis of labeled **13** resulted in complete ^{18}O label scrambling in the recovered rearranged brosylate; this is best explained in terms of a much less "tight" ion pair (12,13) approaching **18**. A very similar set of experiments with the *threo*-3-phenyl-2-butyl system (**2**) is described in Section IV-B-1.

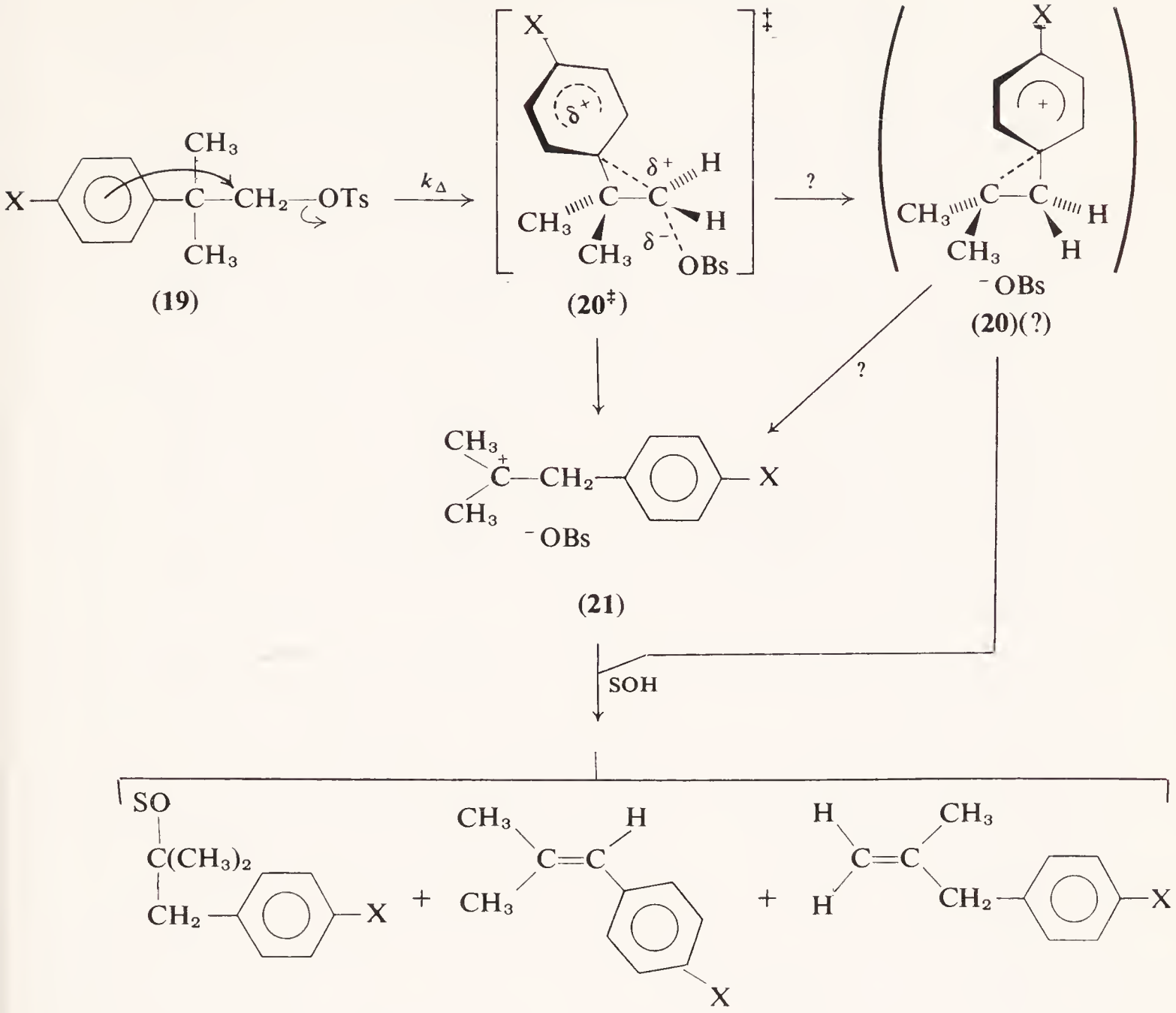
b. The 2-Aryl-2-methyl-1-propyl (Neophyl) System. Winstein first studied the parent neophyl system and concluded that ionization occurred almost exclusively via the anchimerically assisted (k_Δ) route (31g,63).



Acetolysis of neophyl tosylate (**19**; X = H) resulted completely in rearranged products, consisting largely of olefins and ester arising from phenyl migration (>99%) (64). In addition, a small amount (~0.3%) of methyl-rearranged olefin was detected. None of the unrearranged product, neophyl acetate, was observed (64). (Of course, olefin formation directly from unrearranged **19** is impossible.) The finding of methyl migration (64) is in conflict with the earlier report (63a) of no methyl migration and 0.3% unrearranged ester. However, unlike Saunders's experiments (64), the earlier work (63a) did not benefit from the as-yet-undeveloped gas chromatograph.

Additional product discrepancies exist in that the original report (63a) listed ~30% rearranged ester in the products, whereas the later work (64) reported only ~5% of this product, the large majority of rearranged product being olefinic. This condition may be partially accounted for by temperature differences—75° (63a) versus reflux (64).

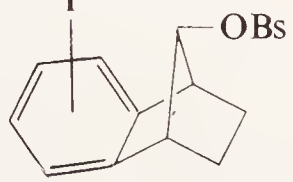
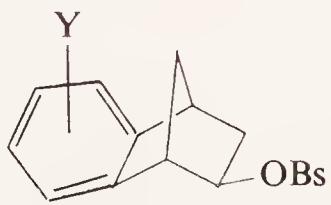
Formolysis of the neophyl system also led to essentially the same results, no unrearranged product being detected (64).

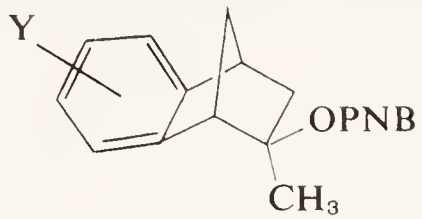


Originally, the bridged phenonium ion **20** was proposed as an intermediate in the phenyl-assisted acetolysis of **19** (63). Although the bridged ion (**20**) cannot be directly ruled out as an energy minimum, it appears reasonable that the aryl-bridged transition state (**20**‡) could lead directly to the rearranged tertiary cation (**21**) as the first intermediate (52). The driving force for this participation could be the large increase in stability of the tertiary cationic intermediate relative to the primary species (which would intervene in the anchimerically unassisted solvolysis of **19**), as well as the possible relief of steric crowding at the initially quaternary β-carbon atom. In the 2-phenyl-1-propyl system **13** just discussed, it was inferred that the rearrangement intermediate was the same bridged ion shown to be involved in the solvolysis of the rearranged secondary system **14**. By this reasoning, phenonium ion **20** appears unlikely in the acetolysis of **19**, since there is strong evidence that the solvolysis of the rearranged tertiary system, as with nearly all tertiary systems, goes essentially with neither

TABLE II

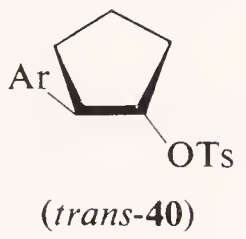
Hammett Correlations of Solvolyses of β-Arylalkyl Systems

Substrate	Rate constant	Ref.	Solvent	Correlation of participating systems versus the Hammett-Brown σ^+ constants: ρ^+	Yukawa plot[a,f]: ρ	Yukawa plot[a,f]: r
1. Neophyl brosylates; **19**; Ar—$C(CH_3)_2CH_2$—OBs	k_t	63a	HOAc	−3.0	−3.7	0.51
2. *anti*-9-benzonorbornenyl brosylates	k_t	98	HOAc	−5.1[d]	−4.5	1.04
 (*anti*-**53-OBs**)						
3. *exo*-2-benzonorbornenyl brosylates	k_t	99a,b	HOAc (77.6°)	−3.3	—	—
	k_t	99a,b	HOAc (100°)	—	−3.3	1.04
 (*exo*-**54-OBs**)						
4. *endo*-2-methyl-*exo*-2-benzonorbornenyl *p*-nitrobenzoates	k_t	100c	50% aq. acetone	−1.9	−1.1	1.5



(*exo*-**62-OPNB**)
R = CH_3

5. *threo*-3-aryl-2-butyl brosylates; **2a**; Ar—$CH(CH_3)CH(CH_3)$—OBs	Fk_Δ[b]	4	HOAc	−2.7	−3.9	0.46
6. *trans*-2-arylcyclopentyl tosylates	Fk_Δ[b,c]		HOAc	—	−4.8	0.33

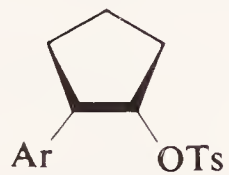
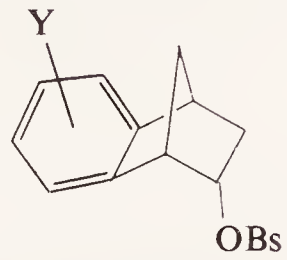
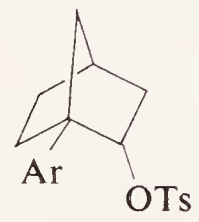


(*trans*-**40**)

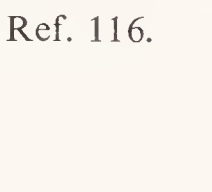
7. 1-aryl-2-propyl tosylates; **14**; Ar—CH_2CHCH_3 (OTs)	Fk_Δ[b]	39a	HOAc	−2.0	−2.8	0.50
	Fk_Δ[b]	39a	HCOOH	−2.0	−3.5	0.37
8. β-arylethyl tosylates; **11**; Ar—CH_2CH_2—OTs	Fk_Δ[b]	39b	HOAc	−2.4	−3.4	0.57

(*continued*)

TABLE II (*Continued*)

Correlation of Nonparticipating Systems versus the Regular Hammett σ Constants						
Substrate	Rate constant	Ref.	Solvent	ρ	Yukawa plot[a,f]	
					ρ	r
9. *cis*-2-arylcyclopentyl tosylates	k_t	38a,78	HOAc	−1.6	−1.7	−0.1
 (*cis*-**40**)						
10. *endo*-2-benzonorbornenyl brosylates	k_t	99c	HOAc	−1.3	−1.5	0.0
 (*endo*-**54-OBs**)						
11. 1-aryl-*endo*-2-norbornyl tosylates	k_t	37	HOAc	−1.1	−1.1	0.4
 (**61**)						

12. 1-aryl-2-methyl-2-propyl chloride; **70-Cl**; $Ar—CH_2—C(CH_3)_2—Cl$	k_t		aq. EtOH	-1.1[g] -0.93[h]	—	—
13. *threo*-3-aryl-2-butyl brosylates; **2a**; $Ar—CH(CH_3)CH(CH_3)—OBs$	k_s[b,e]	4	HOAc	-1.5	-1.4	0
14. *trans*-2-arylcyclopentyl tosylates;	k_s[b]	89	HOAc	-1.05	—	—



(*trans*-**40**)

15. 1-aryl-2-propyl tosylates **14**; $Ar—CH_2CHCH_3$ (OTs)	k_s[b,e]	39a	HOAc HCOOH	-0.71 -0.84	-0.70 -0.82	0 0
16. β-arylethyl tosylates; **11**; $Ar—CH_2CH_2—OTs$	k_s[b,e]	39b	HOAc	-0.10	—	—

[a] Log k/k_0 plotted versus $\sigma + r(\sigma^+ - \sigma)$. Cf. Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Japan*, **32**, 971 (1959).

[b] k_t separated into Fk_Δ and k_s with either a Hammett or a Taft (40) treatment. See Figs. 1 and 2, and discussion in Section VII-A-1.

[c] H. C. Brown and C. J. Kim, unpublished results, based on data in Ref. 38b.

[d] Plotted versus $(\sigma_m^+ + \sigma_p^+)/2$.

[e] For deactivated substrates only.

[f] We gratefully acknowledge the generous assistance of Dr. Wallace F. Sliwinski, Princeton University, in writing a computer program to perform the least-squares Yukawa-Tsuno[a] treatments reported in the table.

[g] Ref. 115.

[h] Ref. 116.

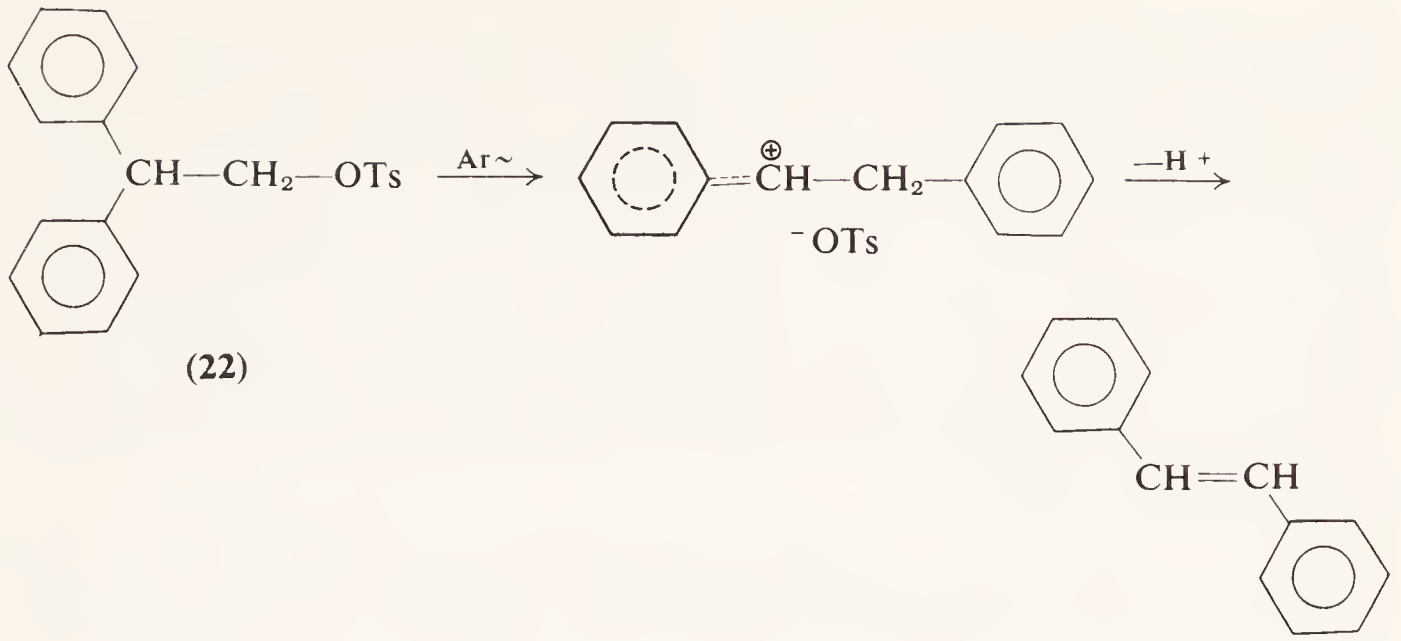
aryl participation nor arylonium ion intermediates (see **70**, Y = H, Section-IV-C-2) for the parent phenyl substrate. Of course, there is no *direct* evidence which rules **20** out entirely.

Regardless of the nature of the intermediate ion pair, aryl participation in the solvolysis of **19** results in substantial charge delocalization into the aryl ring in the bridged transition state leading to the rearranged cation; and this is expected to manifest itself, e.g., in a relatively large negative Hammett ρ, correlating against the σ^+ constants (36–39). Indeed, the propensity of **19** toward aryl participation is so great that, over a range of both activating and deactivating aryl substituents (**19**; X = *p*-CH_3O to *p*-NO_2), a reasonably good correlation against σ^+ was obtained (63a), with a ρ^+ of -3 (Table II). The Hammett behavior of this and other participating systems is contrasted in Table II with that of systems where solvolysis occurs without aryl participation. These latter systems, as expected, correlate better against σ, with less negative slopes ($\rho \lesssim -1$). These data strongly suggest that, in the neophyl system (**19**), considerable positive charge is indeed delocalized into the β-aryl ring in the rate-determining aryl-bridged transition state (**20**‡); but there is no need to interpose a phenonium ion intermediate between this transition state and the rearranged ion.

It has been demonstrated very recently that the acetolysis of even the highly deactivated *p*-nitroneophyl brosylate (**19**; X = *p*-NO_2) proceeds with predominant participation by the *p*-nitrophenyl group (65); ca. 72% of the acetolysis products arise from *p*-nitrophenyl migration and the balance from methyl migration (ca. ~25%) and solvolysis without rearrangement (ca. ~2.5%). This is further indication of the tendency of the parent neophyl system exclusively to favor anchimerically assisted (k_Δ) solvolysis.

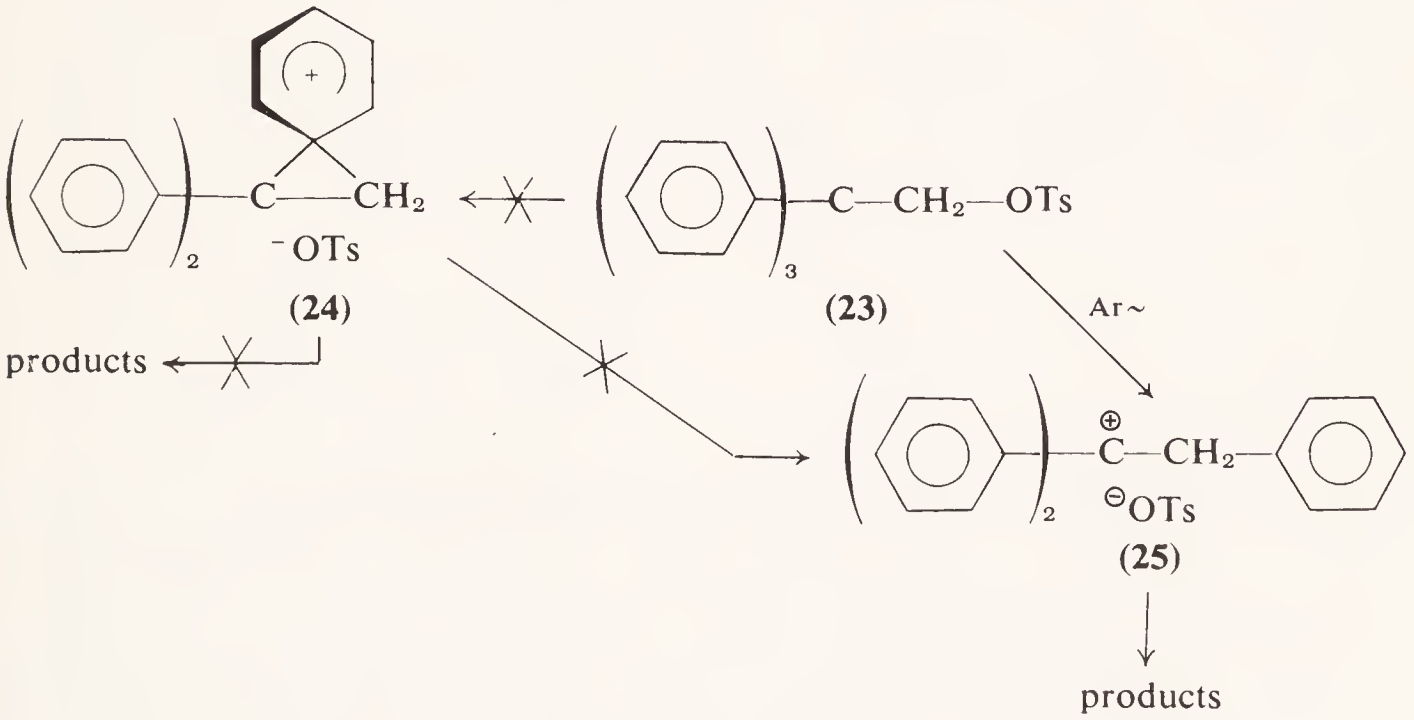
4. Solvolysis and Rearrangement of β_n-Polyarylethyl Systems

a. Two β-phenyl Groups; β,β-Diphenylethyl Tosylate. Early studies (31g) of the β,β-diphenylethyl system, **22**, indicated clearly that most of the acetolysis reaction involved aryl participation. The only reported product was *trans* stilbene, formed via aryl migration (31g). Rate comparisons with ethyl tosylate as a model for nonassisted behavior were considered infeasible, since such primary solvolyses are essentially bimolecular. Neopentyl tosylate was used as the standard of reference. [More recent, work suggests that neopentyl tosylate may not have been a good model (31g) for unassisted behavior. Evidence that has accumulated suggests that the neopentyl system solvolyzes exclusively with methyl participation (66).] It was found that **22** acetolyzed 53 times faster than neopentyl tosylate. A crude estimate of a ten-fold retarding inductive factor per ring gave a calculated rate enhancement of 5.3×10^3 (31g).



(22)

b. Three β-Phenyl Groups; β,β,β-Triphenylethyl Tosylate. Acetolysis of β,β,β-triphenylethyl tosylate, **23**, is accompanied by a large "raw" rate enhancement of 7.7×10^3 (31g). The same inductive correction for **23** of a factor of 10 per phenyl ring gives an estimated corrected rate enhancement of 7.7×10^6. In formic acid, the "corrected" rate enhancement is persuasively big: 6×10^7 as compared to neopentyl tosylate (67).



(24) (23) (25)

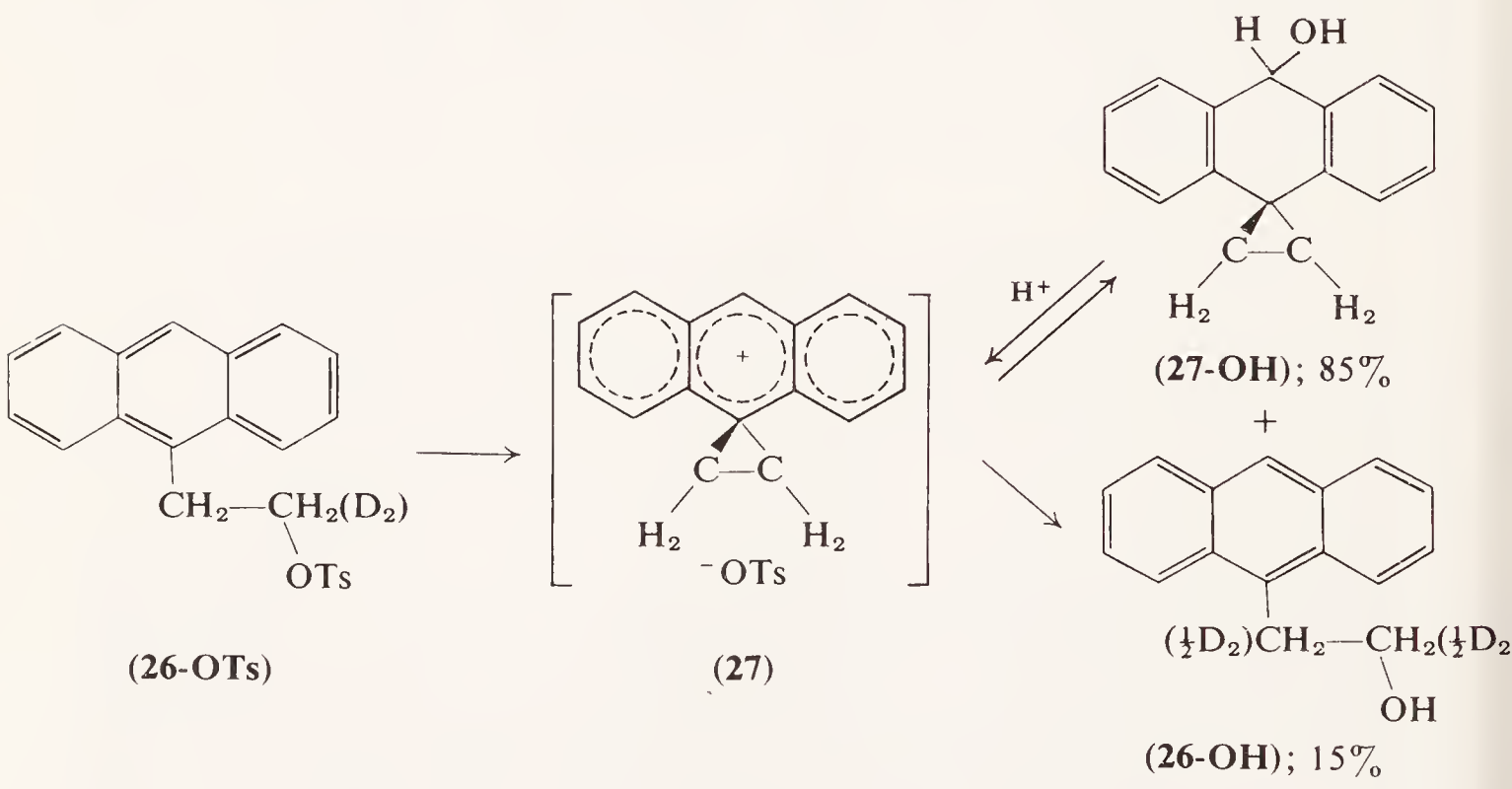
As with nearly all the early systems studied, the large rate enhancements for **23** (and **22**) were originally attributed to the inherent tendency of a neighboring phenyl group to participate in the ionization step (68) although it was suggested also that the available evidence did not absolutely require the bridged phenonium ion intermediate **24** (68b). The direct formation of the highly stabilized benzhydrylic intermediate **25** also would have accounted for the driving force for phenyl migration (68b). Steric arguments were considered also; in his original work, Winstein (31g)

suggested the relief of steric strain in the quaternary β-arylethyl systems as a possible driving force for the migration: ". . . participation may provide a mechanism for relief of steric strain" (31g). Brown (3,52,68c) has always stressed steric factors in this and similar systems; the enormous rate enhancements exhibited by **23** could be due to the release of a considerable degree of ground state strain at the extremely crowded β-carbon atom. Regardless of the precise nature of the driving force, it would seem that the ionization transition state must involve considerable charge delocalization into the migrating aryl ring.

5. Isolable Bridged Intermediates or Bridged Products in the Solvolysis of Primary β-arylalkyl Systems

As a rule, the presence of bridged phenonium ion intermediates in β-arylalkyl solvolyses is inferred indirectly from the available stereochemical and/or kinetic evidence. Only in rare instances has the bridged ion either been isolated or trapped directly as bridged product. For β-arylalkyl systems, each of these situations is realized in but a single example. These are treated in this section.

a. Isolation of a Bridged Product; Solvolysis of β-9-Anthrylethyl Tosylate. Solvolysis in aqueous dioxane of β-9-anthrylethyl tosylate (**26**) gave as the chief product (85%) the spiroalcohol (**27-OH**) (69a). Winstein's remarkable isolation of this "phenonium alcohol" constitutes a rare piece

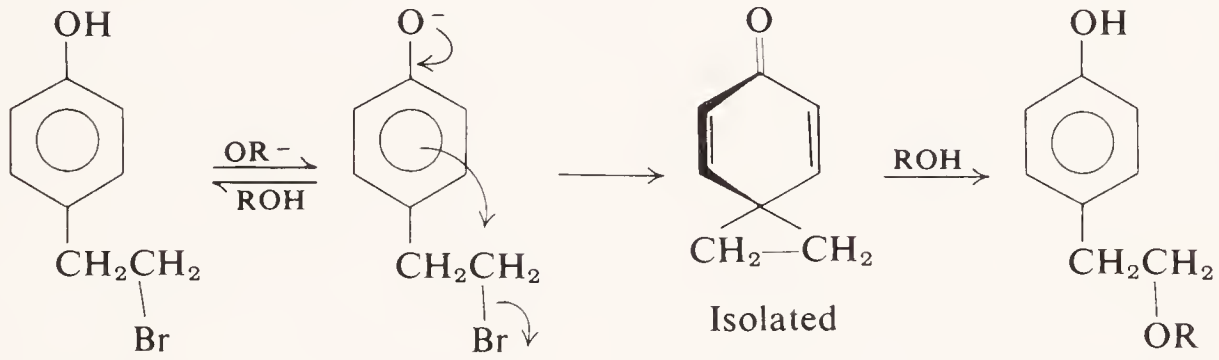


of direct evidence that the bridged anthrylonium ion **27** was an intermediate in the solvolysis of **26-OTs**. The bridged anthrylonium ion apparently also is involved in the formation of the 15% of open

anthrylethanol (**26-OH**). This is evidenced by the complete scrambling of an α-D_2 label (69a) (Table I). Alcohol **27-OH**, the product of kinetic control, was shown to rearrange to the thermodynamically more stable isomer, **26-OH**, on treatment with acid.

In view of the actual isolation of the anthrylonium alcohol (**27-OH**) in the solvolysis of **26**, it is not surprising that the same bridged ion could be generated from the spiroalcohol and observed directly by nmr in a very strong acid medium (69b). [Many other stable β-arylalkyl cations have been studied by nmr in strongly acidic solvents, and, in some of these cases, direct observation of a phenonium bridge has been achieved (70,118). Only a few of these studies are included in the present chapter (Section IV-C-3), since most of this work is reviewed elsewhere in this series (70b).]

b. Isolation of a "Phenonium" Intermediate; β-*p*-Hydroxyphenylethyl Bromide. The first-order rate constant for the ethanolysis or methanolysis of the conjugate base of β-*p*-hydroxyphenylethyl bromide, **28**, is about six powers of 10 faster than that for the solvolysis of β-*p*-anisylethyl bromide (69c), and 10^7 times the rate of the parent phenyl derivative (41). This represents perhaps the largest rate enhancement ever observed for a β-arylethyl



(28-Br) **(28a)** **(29)** **(28-OR)**

system, leaving little doubt about the intermediacy of the "phenonium" species (**29**). This neutral intermediate is formed simply by internal displacement by the negatively charged phenoxide group.

Such anionic displacement recalls some of the early work by Winstein on the solvolysis of α-halocarboxylates. In the latter instance, a neutral, three-membered α-lactone was implicated and later isolated (31b). Such behavior was predicted more than 30 years ago by Hughes and Ingold: "A charged substituent of neutralizing sign . . . may stabilize a pyramidal configuration in the ion, and lead to eventual substitution with retention of form" (71).

In an elegant set of experiments by Winstein, the formation and subsequent destruction of the postulated intermediate spirodienone (**29**) were actually followed spectrophotometrically during the course of methanolysis (69c). The original phenolic ultraviolet absorbance was gradually

replaced by a more intense absorbance at much higher wavelength. This, in turn, was replaced by the phenolic absorbance of the product ether (**28-OR**).

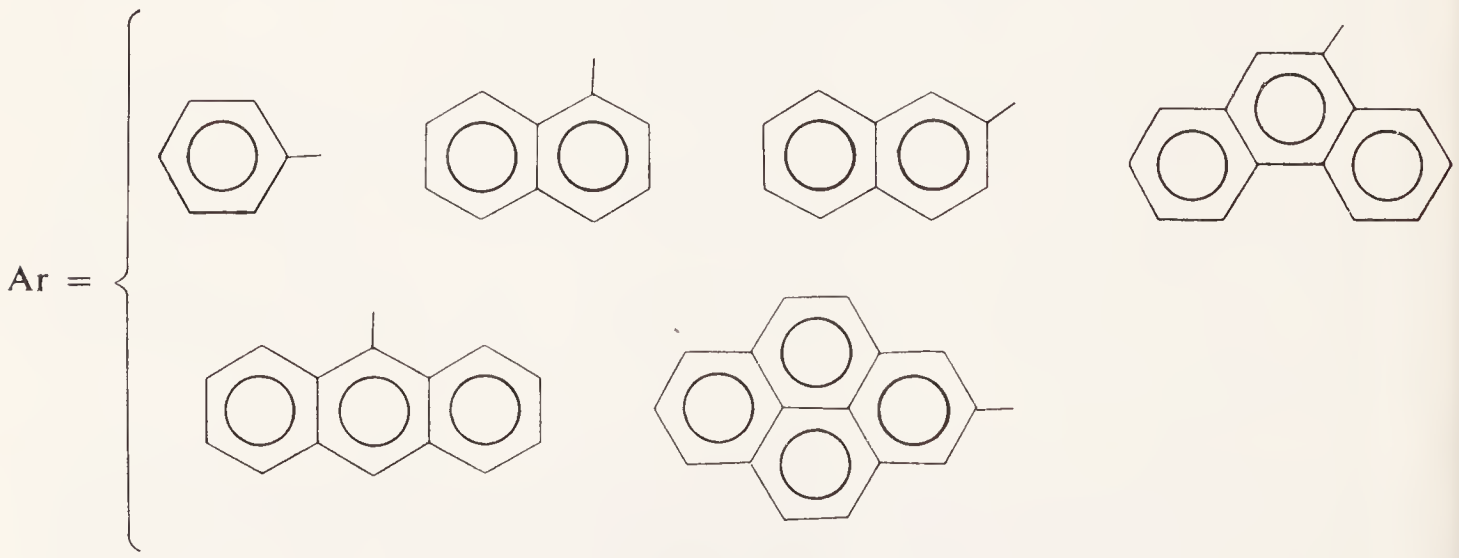
Final, convincing evidence that the intensely absorbing intermediate really was the spirodienone (**29**) was provided by its actual isolation and characterization (infrared, ultraviolet, and nmr spectra), following an extremely carefully worked out reaction and recovery sequence (69c).

Although the only bridged intermediate ever to be isolated and characterized in the solvolysis of a β-arylalkyl system is a neutral molecule, and therefore strictly not a phenonium *ion*, the isolation of spirodienone **29** should be given due recognition as one of the most unusual and interesting accomplishments in phenonium ion chemistry and as a powerful demonstration of β-aryl participation.

6. *MO Correlations of Aryl Participation in Primary Systems*

Polynuclear β-arylethyl systems have been used to advantage in an application, chiefly by Dewar, of MO theory to the detection and assessment of charge delocalization into a participating aryl ring in the ionization step (72,73). In earlier work, Dewar had shown that the formolysis rates of a series of fused polynuclear arylmethyl chlorides could be correlated with the difference in π-binding energy (δE_π) between the ground state of the starting arylmethyl chloride and the corresponding benzylic cation formed in solution during ionization (72b). On the assumption that the inductive effects of the various polynuclear aryl groups were reasonably constant, Dewar proposed that the anchimerically *un*assisted solvolysis rate constants (k_s) for a series of β-arylethyl tosylates **11** would vary negligibly throughout the series and therefore be reasonably independent of δE_π.

The validity of this assumption, at least for primary substrates such as the ones Dewar examined (72a,73), has been experimentally demonstrated



Ar—CH_2CH_2—OTs

(11)

recently. A series of deactively substituted β-phenylethyl tosylates, in which participation was inhibited, gave rate constants that defined a linear Hammett correlation versus the σ constants, with an extremely small ρ value of -0.1 (39b). Such a low ρ value effectively reduces the individual inductive effects of neighboring groups to near zero, undoubtedly reflecting the largely bimolecular nature of the solvolysis of primary derivatives.

Participation by the neighboring aryl group (k_Δ), resulting in charge delocalization into the aryl ring, should yield a series of rate constants proportional to δE_π. The situation is analogous to a Hammett correlation of solvolysis rates for β-arylalkyl substrates: low slopes ($\rho \lesssim 1$) in the absence of aryl participation (k_s) (39), and higher slopes, correlating against σ^+ rather than σ, for anchimerically assisted (k_Δ) solvolysis. (See Table II and pertinent discussion.)

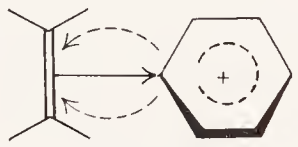
In the original work, Dewar did not distinguish between energy differences (δE_π) in both the arylmethyl and arylethyl systems, and he correlated solvolysis rates for both against the same δE_π term. Dewar depicted aryl participation in **11** either as a π complex  or as a σ complex, which is simply a σ-bridged phenonium ion (**1**). The π complex is isoconjugate with $ArCH_2^+$, but rates involving the σ complex would strictly correlate with the energy difference, $\delta E'_\pi$, between the σ-bridged arenoniun ion and the ground state (72). Since $\delta E'_\pi$ and δE_π are linearly related, Dewar's original results did not distinguish between a σ- or a π-complex intermediate. However, his most recent work (73), to be described shortly, does provide evidence in favor of a π complex, preceded by an unsymmetrical transition state in agreement with the conclusions of Saunders (44), Cram (30b), and Gregoriou (49).

We could conceive of borderline situations in which only the more activated derivatives undergo aryl participation. In such a series, solvolysis should proceed with a variable degree of aryl assistance. Here, a broken plot of rates versus δE_π is to be expected, consisting of a section with near-zero slope (aryl-unassisted; k_s) followed by a section with finite slope (aryl-assisted; k_Δ). Those derivatives which undergo partial aryl participation may be expected to define a curved segment joining the two sections of zero and finite slope. Again, analogy can be drawn with Hammett treatments (36–39) of borderline substrates, where only the more actively substituted derivatives exhibit aryl participation (see Fig. 1).

Dewar in fact found a reasonably linear correlation between the rates of formolysis of the series **11** versus δE_π for all the derivatives tested (72a), although there was a regular upward curvature that might have indicated incomplete aryl participation in the less activated substrates. Acetolysis

of the same series produced a broken plot intersecting at the α-naphthyl derivative. All the derivatives except β-phenylethyl gave a correlation of approximately the same slope as for formolysis. Dewar concluded that all the derivatives except the parent β-phenylethyl system underwent a substantially aryl-assisted acetolysis, and all derivatives including phenylethyl were anchimerically assisted on formolysis (72a). These results agree with previously described data (Section IV-A-1) concerning the behavior of the parent β-phenylethyl system in acetic and formic acids.

Dewar has very recently reported (73) a refinement of his earlier work (72), in which the MO treatments showed significant differences between the responses of the arylmethyl and arylethyl (**11**) systems to the rate correlations. In brief, the transition state interaction between the aryl groups and the methylene carbonium center in the benzylic arylmethyl series was found to be considerably stronger than the transition state interaction between the aryl and ethylene groups in **11**. Dewar reconciled the apparently weak transition state interactions with the obviously large overall effect of the aryl group in the assisted (k_Δ) pathway for **11** in terms of a π complex, which is isoconjugate with a benzylic cation, $Ar–CH_2^+$, as noted previously. In the benzylic cation, the π system of the aromatic group interacts (back-donates) to a vacant *p*-AO of the methylene carbon, whereas in the π complex intervening in the assisted (k_Δ) solvolysis of **11**, the aryl π-system, which interacts with the ethylene moeity via a three-centered dative bond involving an aryl sp^2-AO, must back-donate electrons to a relatively high-energy antibonding MO of the ethylene group, as in **30.**



(30)

Dewar further suggested that the transition state for the aryl-assisted (k_Δ) solvolysis of **11** more closely resembled $Ar–CH_2–X$ rather than $Ar–CH_2^+$, on the basis of a reasonably good first-order perturbation correlation of the rates aginst the self-polarizability of the π electrons in Ar.

Finally, Dewar's work did not give calculated rate enhancements (k_t/k_s; see Section III-B) based on his observed rate constants for the solvolysis of **11**, because he could not determine a purely aryl-unassisted rate (k_s) for his compounds. However, a measure of Fk_Δ, k_s, and k_t/k_s has been provided recently (39b) for the acetolysis of β-phenylethyl tosylate (**11**; Ar = C_6H_5). If we accept Dewar's hypothesis, supported by the low Hammett ρ (39b), that the inductive effects of the polynuclear aryl groups in **11** are reasonably constant, then we can take the k_s value determined

for the parent phenyl derivative (39b) and assume that it is the same for all the other derivatives in Dewar's series (72,73) as well. Thus using Dewar's observed titrimetric rate constants k_t, the rate enhancements k_t/k_s, are readily calculated for the entire series. The results are summarized in Table III. The rate enhancements begin to become relatively significant after the α-naphthyl derivative, which defined the breaking-point in Dewar's theoretical acetolysis correlation (see above).

TABLE III

Rate Enhancements Calculated[a] for Acetolysis of Polynuclear β-Arylethyl Tosylates; Ar—CH_2CH_2—OTs; HOAc, 75°

Ar, in $ArCH_2CH_2OTs$	k_t, sec^{-1}	Ref.	Rate enhancement, k_t/k_s
Phenyl[a]	2.88×10^{-7}	41	1.48
4-Biphenylyl	3.28×10^{-7}	—	1.68
β-Naphthyl	3.17×10^{-7}	—	1.62
α-Naphthyl	3.86×10^{-7}	—	1.98
1-Pyrenyl	1.99×10^{-6}	—	10.2
9-Anthryl	1.16×10^{-5}	69a	59.5

[a] k_s for β-phenylethyl tosylate in acetic acid at 75° is 1.95×10^{-7} calculated from deactivated β-phenylethyl tosylates by Hammett treatment (e.g., Figs. 1*a–c*). See Ref. 39b. We are grateful to Dr. Wallace F. Sliwinski, Princeton University, for writing a computer program for determining the corrected (39b) k_s line.

Experimental agreement with Dewar's theoretical correlation (72,73) has been obtained recently by Ouellette (54), who determined the rates of acetolysis of a series of polynuclear β-arylethylmercuric perchlorates. When this leaving group is used the parent phenyl derivative is known to be substantially anchimerically accelerated (Section IV-A-2) (53); hence, acetolysis of the entire series of polynuclear homologs would be expected to be essentially entirely aryl assisted. Ouellette found an excellent linear correlation between the acetolysis rates of the β-arylethylmercuric perchlorates and those of the corresponding arylmethylmercuric perchlorates (54,74).

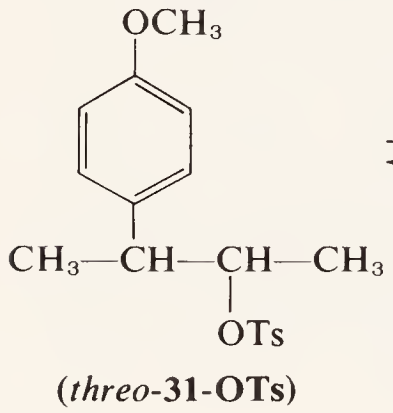
This is just what would be predicted from Dewar's finding (73) that acetolysis of both arylethyl and arylmethyl tosylates are proportional to the same differential energy parameter δE_π. Ouellette's experimental correlation (54) is additional evidence of the extent of β-aryl participation with the unusual mercuric perchlorate leaving group.

B. Kinetics and Rearrangements in Secondary Systems

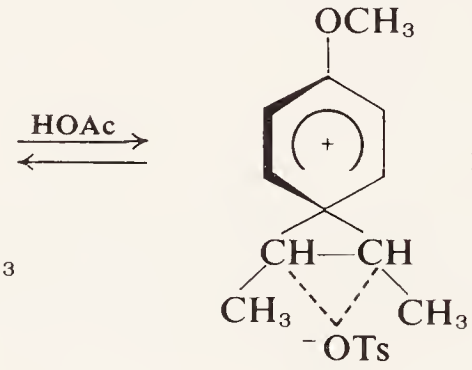
1. The 3-p-Anisyl-2-Butyl System; Some Properties of Bridged Ion Pairs

The use of the activating *p*-anisyl group as a probe for β-aryl participation in the primary β-arylethyl system (**11**) was described in Section IV-A-1. Similarly, Winstein made an extremely thorough study of *p*-methoxyl activation in the *threo*-3-aryl-2-butyl system with the *p*-anisyl neighboring group (14,75,76). Perhaps the most significant result of Winstein's extensive analysis of the *threo*-3-*p*-anisyl-2-butyl system (**31**) was a considerably more detailed understanding of the precise nature of the different types of bridged ion pairs that may intervene in the solvolysis of various substrates with neighboring groups.

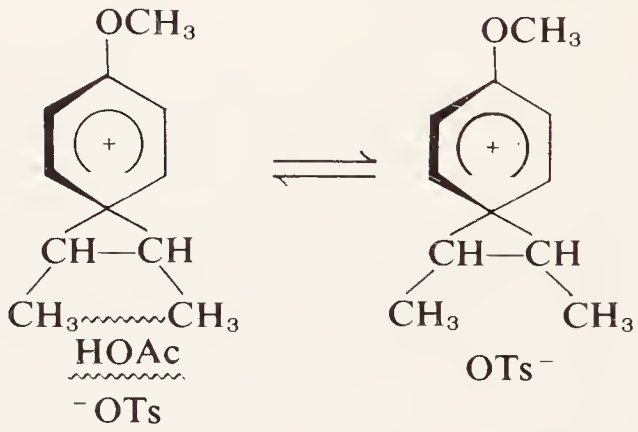
The solvolysis of **31-OTs** was subject to a special lithium perchlorate kinetic salt effect (13c,14,76) and was therefore best formulated as proceeding to solvent-separated and dissociated bridged ion pairs (**33** and **34**), which then either reacted with the solvent to give covalent product or underwent *external* return to covalent starting material (**31-OTs**) (14, 75b,76). This external return is inhibited by $LiClO_4$.



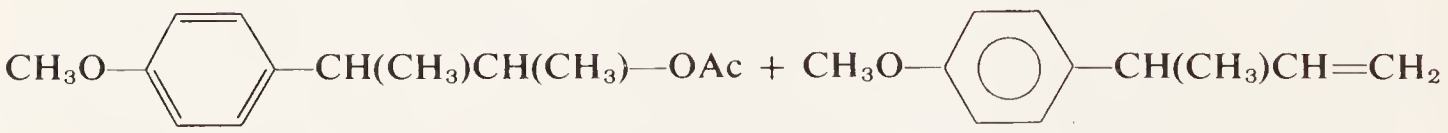
(*threo*-**31-OTs**)



(**32**)



(**33**) (**34**)



(*threo*-**31-OAc**) (**35**)

99.7% 0.3%

In contrast, the available evidence indicates that the parent phenyl system (**2**) ionizes primarily to an "intimate" (12–14) ion pair, similar to **32**, with only partial "leakage" to some form of solvent-separated ion pair (1b). Unlike the activated *p*-anisyl derivative (**31-OTs**), the parent phenyl compound (**2**) was not subject to a special *kinetic* salt effect (75b); therefore, the known return to covalent starting material (1b,12) which accompanies the acetolysis of **2** cannot be formulated primarily as external (see Sections I and III-B-1).*

Some recent key studies by Goering on the acetolysis (k_t), racemization (k_α), and ^{18}O equilibration (k_{eq}) of 2-*endo*-bicyclo[3.2.1] tosylate confirm that a multiplicity of ion-pair types may intervene even in systems, e.g., **2**, where no special *kinetic* salt effect is observed (77). For the acetolysis both of 2-*endo*-bicyclo[3.2.1]octyl-OTs and **2a-OTs**, ^{18}O equilibration is slower than racemization, and $k_{eq}/k_\alpha \sim 0.5$ in both cases. In the bicyclooctyl case, added lithium perchlorate reduced *both* k_α/k_t and k_{eq}/k_α, suggesting that part of the return eliminated by $LiClO_4$ would otherwise have given completely scrambled substrate. Yet neither the bicyclooctyl substrate nor **2a** exhibits a special *kinetic* $LiClO_4$ effect (77).

To account for all these data, Goering postulated for the acetolysis of *threo*-3-phenyl-2-butyl tosylate (**2a-OTs**) a combination of bridged ion pairs exactly analogous to the three (**16–18**) treated by Denney (62) for **13**. A 50/50 blend of the **16** and **18**-types agreed with the observed ^{18}O data, suggesting that return in nonrearranging secondary systems also should give $\leq 50\%$ ^{18}O scrambling (77).

In the acetolysis of the *p*-anisyl derivative (*threo*-**31-OTs**), the nature of the products strongly suggests the sole operation of the aryl-assisted (k_Δ) path. Retention of configuration in the acetate product (**31-OAc**) is complete. No *erythro* acetate, the product of inversion (k_s), was detectable by gas chromatography (14). The extremely small amount of olefin formed from **31-OTs** (only 0.3%) is far less than normally found in systems where open secondary cations or ion pairs are entirely or partially involved. For example, the parent phenyl derivative (**2**) gives as much as 35% olefins in acetic acid (Section I). Of the olefin formed from **31-OTs**, at least 97% was the terminal, nonconjugated isomer (**35**), whereas the more stable, conjugated styrene derivative would have been expected from open 3-*p*-anisyl-2-butyl cations but cannot be formed from the bridged ion pair (**32–34**).

Models show that a hydrogen on the terminal methyl group of a bridged ion such as **32–34** can attain the correct geometry *anti* to the aryl bridge, with some torsional strain, for elimination to the terminal olefin (**35**). On

* A qualitative estimate of the balance of internal versus external return in the parent 3-phenyl-2-butyl system (**2**) can be obtained from Cram's tosylate/brosylate exchange experiments, reported in Section I.

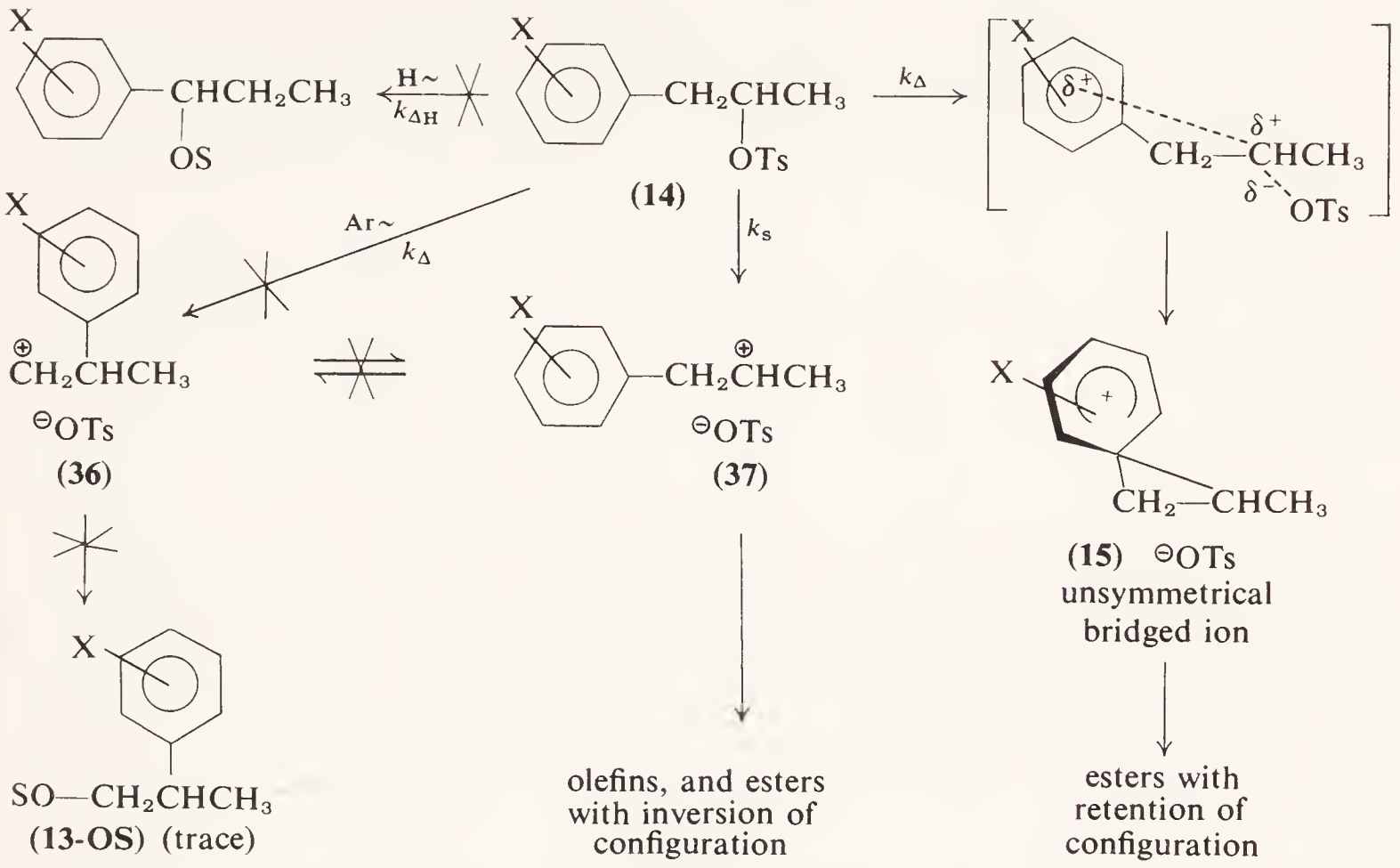
the other hand, the hydrogens of the three-membered phenonium ring cannot possibly attain the correct geometry for elimination to the styrene derivative (1d,15), as pointed out in Section I, page 1355.

From Brown's Hammett analysis (e.g., Fig. 1*c*) of the *threo*-3-aryl-2-butyl series (4,38c), an estimate of the acetolysis rate enhancement is available for **31-OTs**. This value, 10^2 for solvolysis (k_t/k_s) and 4×10^2 for ionization [k_α/k_s, where $k_\alpha/k_t = 4$ (4,14,76)], argues convincingly in favor of substantial *p*-anisyl participation in the rate-determining ionization step.

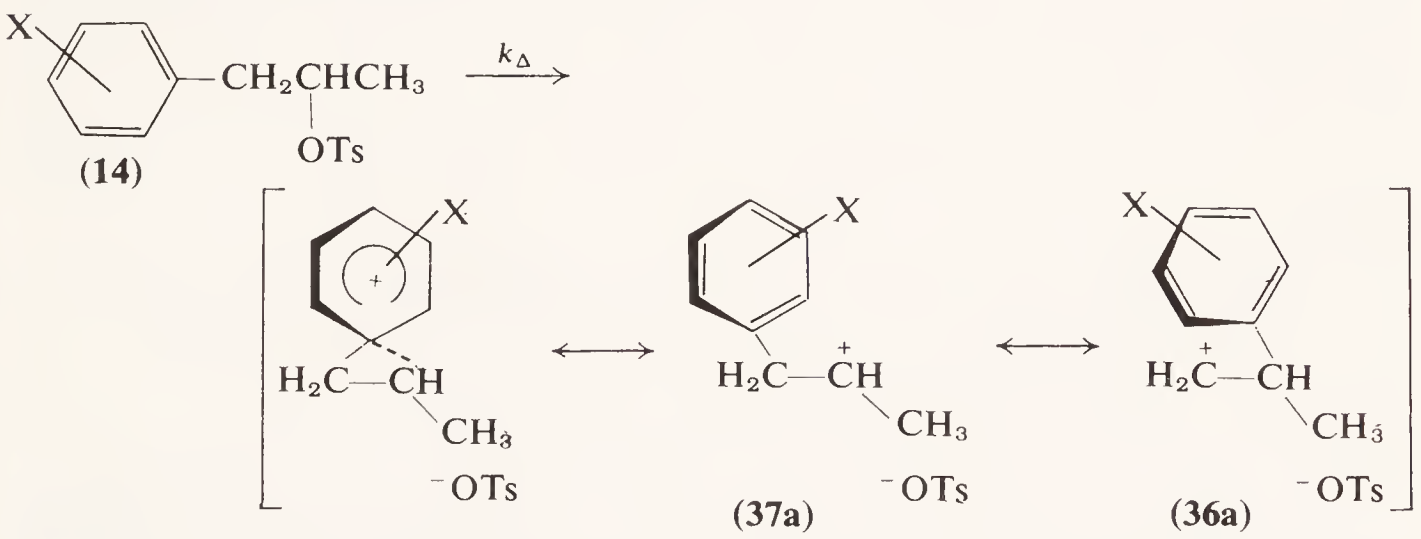
2. *The 1-Aryl-2-Propyl System; Bias Against β-Aryl Participation*

In symmetrical β-arylalkyl systems—e.g., 3-aryl-2-butyl (**2**); β-phenylethyl (**11**)—arguments against σ-bridged intermediates employ equilibrating open or unsymmetrically π-bridged ions to explain the C_α–C_β equivalence observed, especially in the absence of significant rate enhancements (Section II). In β-substituted unsymmetrical β-arylalkyl systems (e.g., **19**, **22**, **23**) where substantial aryl participation often occurs with correspondingly large rate enhancements, it is usually argued that bridged intermediates are bypassed and that a possibly bridged transition state leads directly to the aryl-shifted, usually more stable, rearranged open ion (Sections IV-A-3, 4).

The 1-aryl-2-propyl system (**14**) offers one of the few examples in which any rate enhancement at all must be due to aryl bridging (which may or may not be full σ bridging) rather than to direct aryl migration in or after the rate-determining transition state. Also, any retention of configuration must be attributable to an aryl-bridged intermediate rather than to a pair of equilibrating, open cations. The symmetry properties of **14** rule out both aryl shift and aryl equilibration because the rearranged primary ion (**36**), if formed, would be ca. 16–18 kcal/mole less stable (5,79) than the secondary carbonium ion (**37**). Similarly, equilibration between two species so far apart in energy as the primary (**36**) and secondary (**37**) carbonium ions appears very unlikely. Hydrogen migration ($k_{\Delta H}$) as a source of rate acceleration is unlikely insofar as no hydride-shift (substitution) product is found either in acetic acid (61c,75a,80,81) or formic acid (75a). In trifluoroacetic acid (15), the contribution of hydride shift to the overall observed kinetics must be minimal, since the *maximum* product of hydride shift that could have been formed is only 10%. An isolated yield of unrearranged ester of 90% was found, and only a trace of rearranged ester (**13-OCO$_2$CF$_3$**). The large rate enhancements found in this solvent (15) do not appear solely attributable to a mere maximum 10% hydride shift. Therefore, the 1-aryl-2-propyl substrate (**14**) provides a good model in which to test for aryl participation and bridged arylonium ion formation.

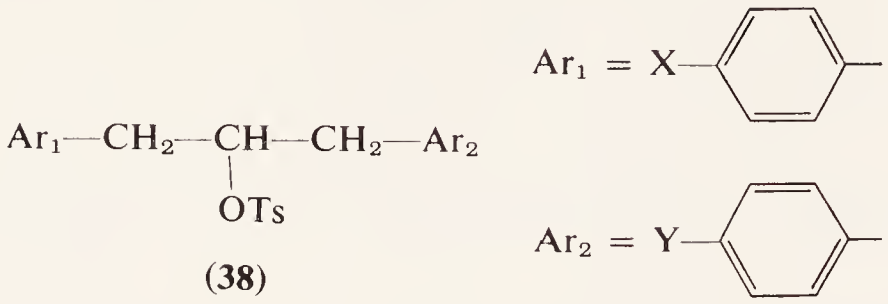


We can expect aryl bridging in **14** to be made difficult for the same reason that equilibration between open ions is altogether ruled out; bridging must be unsymmetrical because distribution of positive charge to a primary center in one of the resonance forms (**36a**) of the phenonium ion is expected to raise the energy of this ion.



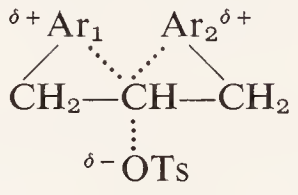
The acetolysis and formolysis of **14** were analyzed kinetically by three different methods, whose results were all in excellent agreement (39a). These included the Hammett and Taft treatments previously described (Section III-B-1; see Figs. 1 and 2), as well as a novel multiple-substitution technique, applied for the first time to acyclic β-arylalkyl systems in this study. This method utilized a series of 1,3-diaryl-2-propyl tosylates (**38**) and a simple algebraic analysis to estimate the magnitudes of the aryl-assisted (k_Δ) and aryl-unassisted (k_s) kinetic pathways. In **38**, both the Ar_1

and Ar_2 groups can exert inductive effects, leading to a multiplicative overall inductive term. In contrast, only one aryl group can participate at any given time without exceeding the maximum allowed pentacovalency



(38)

(82) of the carbonium ion. Therefore, the anchimeric assistance effect of the two aryl groups can only be statistically additive in determining the observed overall accelerative effect. Simultaneous aryl participation by *both* aryl groups, with partial bonding to the leaving group, would involve a transition state (**38a**) approaching hexacovalency (82).



(38a)

By varying Ar_1 and Ar_2, a series of six simultaneous equations of the form of equation 1 were obtained and solved for the various inductive (s_{Ar_1}, s_{Ar_2}) and anchimeric ($\Delta_{Ar_1}, \Delta_{Ar_2}$) parameters both for acetolysis and formolysis (39a).

$$k_{obs} = k_0(s_{Ar_1}s_{Ar_2} + \Delta_{Ar_1}s_{Ar_2} + s_{Ar_1}\Delta_{Ar_2}) \quad (1)$$

where

k_{obs} = observed titrimetric rate constant for **38**
k_0 = rate constant for model compound: 2-propyl tosylate
s_{Ar_1}, s_{Ar_2} = inductive rate retardation relative to k_0
$\Delta_{Ar_1}, \Delta_{Ar_2}$ = anchimeric acceleration relative to k_0.

Rate enhancements determined for the 1-aryl-2-propyl system (**14**) by each of the three kinetic methods are listed in Table IV. The precision of the measurements is evident from these results.

In spite of the electronic bias against participation in **14**, the considerably enhanced acetolysis and formolysis rates of the *p*-anisyl derivative (**14**; X = *p*-CH_3O) suggest substantial aryl participation in the transition state for this substrate. The parent phenyl compound (**14**; X = H) appears to involve only moderate participation in formic acid and very minor aryl bridging in acetic acid, a consequence of the unfavorably

TABLE IV

Determination of Rate Enhancements in 1-Aryl-2-Propyl Tosylates (14)

X	Solvent	Temp., °C	Rate enhancement by method: Hammett (Fig. 1)	Taft (Fig. 2)	Multiple Substitution (eq. 1)
p-CH_3O—	HOAc	100	12	16	13
	HCOOH	75	88	110	105
H—	HOAc	100	1.6	1.6	1.5
	HCOOH	75	4.7	4.5	3.9

biased symmetry. Winstein's earlier product data for the phenyl system (75a) (**14**; X = H), which were interpreted as indicative of a continuous trend in competition between nucleophilic attack by aryl or solvent, are in good agreement with the present kinetic results. Winstein found 85% retention of configuration in formolysis of the parent phenyl derivative and only 35% retention of configuration in acetolysis (75a).

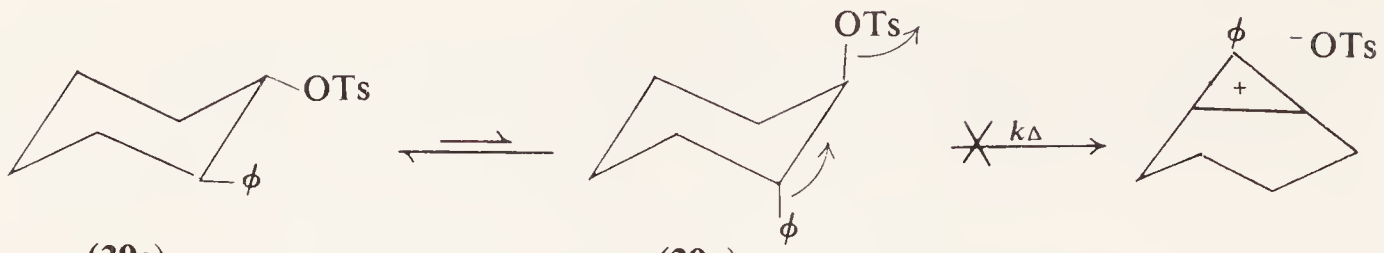
The reduced nucleophilicity and high ionizing power (55) of trifluoroacetic acid are sufficient to bring about very extensive aryl participation even in the parent phenyl derivative (**14**; X = H), in spite of the electronic bias against it. In this solvent, Nordlander determined a solvolysis rate enhancement of 600 (15,34) by a Taft analysis and found 100% retention of configuration in the product trifluoroacetate ester, which was recovered unrearranged in 90% yield. These results leave little doubt that the trifluoroacetolysis of 1-phenyl-2-propyl tosylate proceeds essentially entirely via an unsymmetrically bridged phenonium ion intermediate **15** (15).

A more quantitative description of the rates and products of solvolysis of **14** appears in Section VII.

3. Aryl Participation in Secondary Cyclic Compounds

The question of β-aryl participation in cyclic systems has been studied widely in a variety of specific examples. Most of these are covered in this section.

a. Monocyclic Substrates; 2-Arylcyclohexyl and 2-Arylcyclopentyl Tosylates. No evidence has been found to suggest that a β-phenyl group in the cyclohexyl system provides any anchimeric assistance. In aqueous ethanol, solvolysis of *trans*-2-phenylcyclohexyl tosylate (**39**), where the phenyl ring can adopt the required conformation (**39a**) *anti* to the tosylate, proceeds one-sixtieth as fast as that of the *cis* epimer, in which participation is geometrically prohibited; principally olefinic products result from the

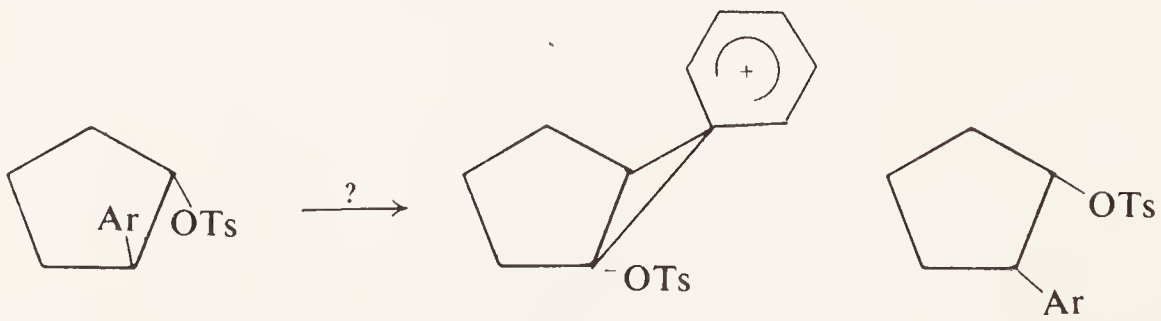


(39e) **(39a)**

solvolysis (83). Acetolysis of *trans*-**39** proceeds at a rate only one-sixteenth that of *cis*-**39** (84). On the assumption (not yet unequivocally proven) that inductive effects of β-neighboring groups are independent of geometry or conformation, the *trans*/*cis* rate ratio for cyclic systems has been used often as a means of canceling inductive effects of β-neighboring groups in order to factor out anchimeric assistance in the *trans* epimer (31,38a,b); i.e., for participating systems, $k_{trans}/k_{cis} \gg 1$. In contrast, since $k_{trans}/k_{cis} \ll 1$ for the ethanolysis and acetolysis of **39**, it would appear that aryl participation is absent in the solvolysis of trans-**39**. It is also possible, however, that the inductive effect of the β-phenyl ring is less conformation-independent than has generally been assumed (31,38a,38b), although available data (38) suggest that the difference in *cis*- and *trans*-2-phenyl inductive effects would not be large enough ($\gtrsim 10$) to offset the small k_{trans}/k_{cis} ratio in **39**. Indeed, the data, in general, appear to indicate that it is the *cis*, and not the *trans*, epimer of **39** that is accelerated, perhaps due to hydrogen participation (86). It has been suggested that the failure of the β-phenyl ring to participate in the solvolysis of *trans*-**39** is attributable to the unfavorably high energy required to place both the phenyl and tosyloxy groups in axial conformations in order to attain the *anti* geometry (*trans*-**39a**) required for phenyl participation (85).

The phosphoric acid-catalyzed dehydration of *trans*-2-phenyl cyclohexanol (*trans*-**39-OH**) was also studied (87), and the possible intermediacy of a bridged ion was considered. However, other studies (1d,14,15) suggest that phenonium ions do not generally lead *directly* to olefins (Sections I; IV-B-1. VII-A-2, pp. 1468ff).

Participation appears minimal also in most five-membered cyclic β-aryl systems. Early results indicated that there was little if any participation in the acetolysis of the *trans*-2-phenylcyclopentyl system (88), and it was proposed that the driving force for such assistance could not overcome the unfavorable bond angles in forming the [3.1.0]bicyclohexylphenonium ion **41**.



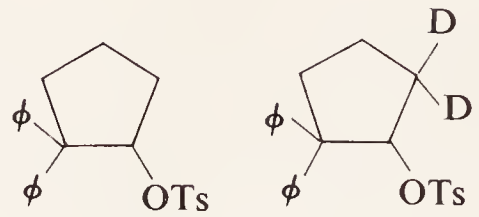
(*trans*-**40**) **(41)** (*cis*-**40**)

In a recent study (38a,b,78,89) of the *cis*- and *trans*-2-arylcyclopentyl series (**40**) Brown has confirmed the conclusion that aryl participation in *trans*-**40** is, for the most part, unimportant. Employing a Hammett treatment (Fig. 1) Brown found that all the aryl derivatives in the *cis* series adhered to a linear relationship on acetolysis when plotted versus the usual σ constants, with a value of $\rho = -1.56$ (Table II), indicating the absence of any charge delocalization into the aromatic nucleus (38a,78). This is not unexpected, since the *cis* phenyl ring is not properly disposed for backside attack on the tosylate-bearing carbon atom.

On the other hand, the aryl ring in the epimeric *trans* series can, with some twisting of the ring (into a distorted half-chair), assume the required *anti* disposition to the leaving group; but here also, with the exception of the *p*-anisyl derivative, all compounds define a linear relationship versus the σ constants, with an even lower ρ value (-1.25) than the *cis* epimers (Table II) (38b).* No anchimeric assistance appears to be involved as a major reaction pathway for all but perhaps the *p*-anisyl compound.* In accord with the rate data, the reaction products are composed mostly of olefins, with very little of the expected product of aryl participation, the *trans* acetate (viz., retention of configuration). For instance, the parent *trans*-2-phenylcyclopentyl tosylate, which falls on the $\sigma\rho$ line* (i.e., no acceleration) yields only 4% of the *trans* acetate. But the *p*-anisyl derivative does give considerable *trans* acetate, to the extent of some 70%, whereas the calculated rate enhancement for this compound is merely a factor of 3 (38b,89). This rate-product discrepancy originally led Brown to consider for this system also a pair of rapidly equilibrating open cations controlling the stereochemistry (38b).* (See also footnote, p. 1359.)

Although one phenyl ring generally appears to furnish little if any anchimeric assistance in the solvolysis of cyclopentyl systems, there is some evidence that aryl assistance does occur in cyclopentyl systems with two β-phenyl rings. Sneen examined the acetolysis of 2,2-diphenylcyclopentyl tosylate (**42**) and its 5,5-dideuterio analog (**43**) and found a β-deuterium isotope effect, k_H/k_D, of 1.18 (90), considerably lower than the β-deuterium isotope effect determined earlier by Streitwieser (91) for the parent deuterated system without the β-phenyl groups ($k_H/k_D = 2.06$). The rate enhancement k_t/k_s for the acetolysis of **42** was 1.26, not corrected for the

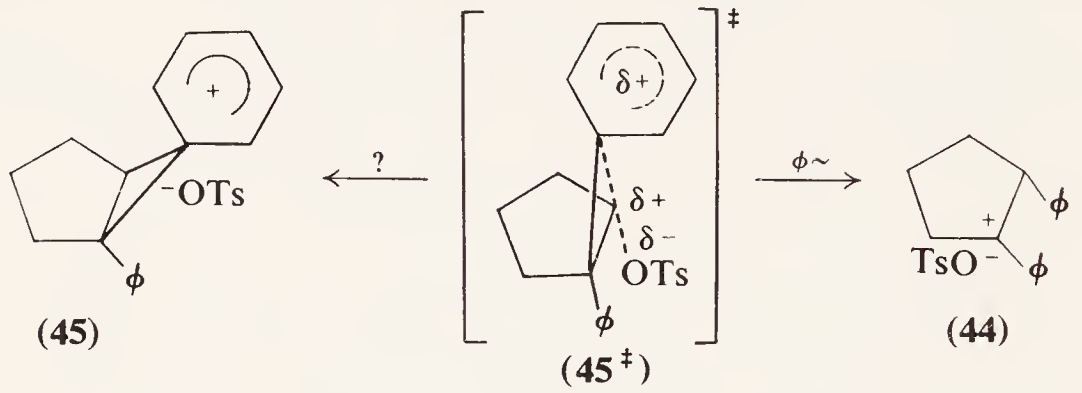
* NOTE ADDED IN PROOF. The full paper (89) describing Brown's study of the *cis*- and *trans*-2-arylcyclopentyl systems contains a considerably more refined treatment than was reported in the preliminary communications (38a,b). In the later work (89), the Hammett correlation of the *trans* series gives a somewhat lower ρ-value (-1.05) than that originally reported (see text) (38b). Also, the later correlation (89) suggests moderate aryl participation for the *p*-tolyl and phenyl groups, in addition to that detected earlier for the *p*-anisyl group. A full discussion of the refined kinetic and product studies in this system is given in Section **VII**.



(42) (43)

inductive effect of the two β-phenyl rings (90). Sneen suggested that, if this rate enhancement were due to relief of steric strain at the β-carbon atom in an open ion, rather than to aryl participation, then the β-deuterium isotope effect would be $k_H/k_D \sim 2$, as found for the model (91). The reduced isotope effect was taken as evidence of phenyl participation in ionization.

However, here, as in other cases of this type (see, e.g., Sections IV-A-3; IV-A-4), the actual driving force for participation may be direct aryl

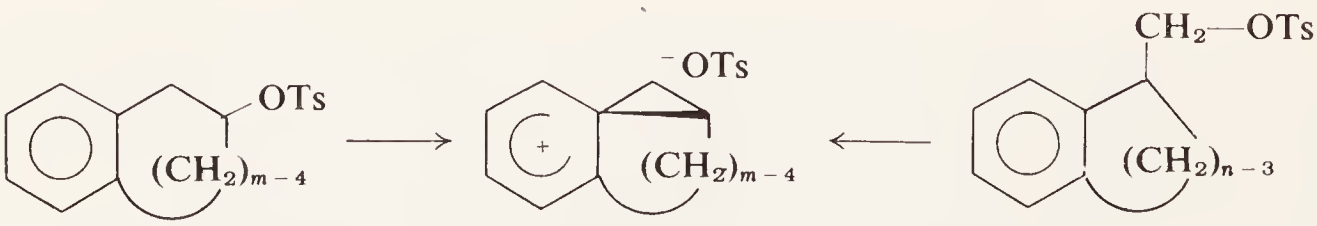


(45) (45‡) (44)

(42)

migration to give the more stable benzylic cation (**44**). The bridged phenonium ion *intermediate* (**45**) may be altogether bypassed. Actually, Sneen's results simply imply that less positive charge is generated at the initial carbonium center in the solvolysis of **42** than in the nonaryl model. Any of the possibilities described previously fulfills this requirement.

b. The 1,2-Benzocyclenyl and Related Systems. In an extremely thorough series of investigations, Huisgen and his co-workers studied the rates and products of solvolysis of the 1,2-benzocyclenyl-4-tosylates (**46**) and of the isomeric 1,2-benzocyclenyl-3-carbinyl tosylates (**48**); both are possible precursors of the same polycyclic phenonium ion (**47**) (92–94).



(46) (47) (48)

$m = 6–9$ $m = 6–9$ $n = m - 1 = 5–8$

The 1,2-benzocyclenyl-4-tosylate series (**46**) is recognizable as the closed-ring benzocyclic analog of 1-phenyl-2-propyl tosylate (**14**), which was discussed in Section IV-B-2. The cyclic substrates (**46**) ought therefore to be subject to the same electronic bias against participation as the open-chain model (**14**) for similar reasons (see Section IV-B-2). Likewise, the 3-carbinyl tosylate (**48**) is the closed-ring benzocyclic analog of the corresponding isomeric open-chain 2-phenyl-1-propyl tosylate (**13**), which was discussed in detail in Section IV-A-3a. Similar behavior is expected here also between the closed-ring (**48**) and open-chain (**13**) systems. Both the rates and products of solvolysis of the 4-tosylates (**46**) and the 3-carbinyl tosylates (**48**) provide evidence for substantial phenyl participation in some, but not all, of the homologs.

Formolysis of the series of 4-tosylates (**46**; $m = 6$–9) showed a pronounced dependence on ring size, increasing by a factor of 10^2 from $m = 6$ to $m = 8$. Table V summarizes the formolysis rate constants for the series,

TABLE V

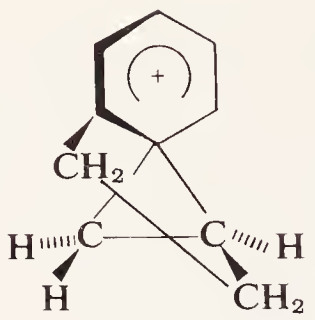
Formolysis Rates (35°) for 1,2-Benzocyclenyl-4-Tosylates (46) and 1,2-Benzocyclenyl-3-carbinyl Tosylates (48)

m in **46**	$k_{46}^{a} \times 10^5$, sec^{-1}	k_{46}/k_{48}	$k_{48}^{b} \times 10^5$, sec^{-1}	n in **48**
6	27.3	10.9	2.51	5
7	152	22.4	6.80	6
8	2250	1250	1.80	7
9	741	4100	0.18	8

[a] Ref. 92b.
[b] Ref. 93b.

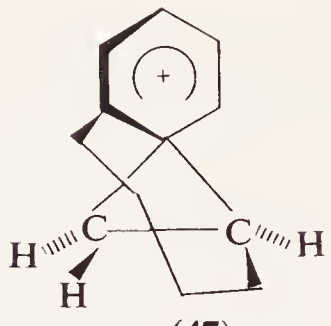
along with the formolysis rate constants for each corresponding isomeric 3-carbinyl tosylate (**48**; $n = 5$–8). The pronounced rate dependence on ring size of the 4-tosylates (**46**) was taken as evidence for increasing phenyl participation along the series as the degree of ring strain in attaining the required perpendicular spirane geometry in the phenonium ion (**47**) decreased by lengthening the polymethylene chain from two units (**47**; $m = 6$) to four units (**47**; $m = 8$).

Therefore, Huisgen suggested that β-aryl participation was predominant in the formolysis of the seven- and eight-membered homologs (**46**; $m = 7, 8$) and might be in operation to a lesser extent in the formolysis of the smallest homolog (**46**; $m = 6$). However, it was pointed out (92b) that



(47)

$m = 6$; strained

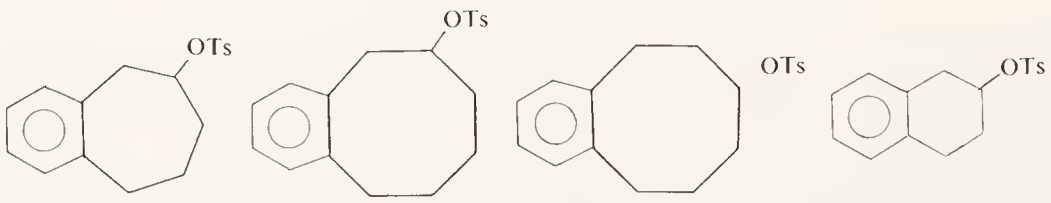


(47)

$m = 8$; less strained

the solvolysis rates of ordinary cycloalkyl sulfonates also increase markedly with increasing ring size (e.g., $k_{\text{cyclooctyl-OTs}}/k_{\text{cyclohexyl-OTs}} = 10^3$; HCOOH; 35°), reaching a pronounced maximum with the cyclodecyl derivative (95), as ring strain and nonbonded interactions are partially alleviated by the departure of the leaving group. But in **46**, the presence of two sp^2 centers in the alkyl ring is expected to reduce considerably the steric constraints responsible for the accelerated rates in the medium-sized, simple saturated cycloalkyl derivatives. Since the importance of this effect is difficult to measure, the fact and amount of β-phenyl participation in the formolysis of the 1,2-benzocyclenyl-4-tosylates (**46**); $m = 7$–9) could not be ascertained without the use of suitable models.

1,2-Benzocyclooctenyl-5-tosylate (**46a**; $m = 8$) was used as a model for a benzocyclenyl system in which there is no phenyl participation (96a). In fact, the formolysis rates of **46** ($m = 7$, 8) were found to be 67 and 10^3 times faster, respectively, than the rate of the model (**46a**; $m = 8$). These observed rate enhancements are actually *too low*, because the rate-retarding inductive effect of the neighboring phenyl ring should decrease



Relative Rate for:	**46**; $m = 7$	**46**; $m = 8$	**46a**; $m = 8$	**46**; $m = 6$	cyclo-octyl-OTs
HCOOH; 35°	67	10^3	1.0	12	4.9×10
HCOOH; 35°	(—)	(0.2)	(0.0002)	(—)	(1.0)
CH_3COOH; 70°	9.5	59	<1.0	<10	—
CH_3COOH; 90°*	—	~0.2	0.0022	—	1.0

* Data for brosyates. OBs:OTs = 3.3 used.

in going from the 4-isomer (**46**) to the 5-isomer (**46a**), in effect increasing the rate of the 5-isomer relative to the expected aryl-unassisted rate of the 4-isomer.

Although the use of the 5-tosylate isomer (**46a**; $m = 8$) provides strong kinetic evidence for an aryl-assisted transition state in the formolysis of the 4-tosylate isomers, (**46**; $m = 7, 8$), the actual situation may not be as simple as implied. The choice of a proper model should always be subjected to the most detailed analysis possible.

If the formolysis of cyclooctyl tosylate is taken as the model rate, very little apparent rate effect is caused by a 3,4-fused benzene ring; the formolysis rate of this derivative, 1,2-benzocyclooctenyl-4-tosylate (**46**; $m = 8$), is only a factor of 5 slower than that of cyclooctyl tosylate (92b). In contrast, a 4,5-fused benzene ring (**46a**; $m = 8$) causes a rate depression of a factor of 5000 relative to cyclooctyl tosylate. It could be argued then that the foregoing rate comparisons with cyclooctyl tosylate as the model are suggestive of steric, rather than anchimeric, rate effects. For instance, the rate of the 4-tosylate isomer (**46**; $m = 8$) could be considered close to "normal" (i.e., cyclooctyl), whereas the rate of the 5-tosylate isomer (**46a**; $m = 8$) is greatly retarded by steric hindrance to ionization or a similar steric effect.

These are very unlikely arguments. In the first place, the formolysis rate of Huisgen's model, the 5-tosylate isomer (**46a**; $m = 8$), is very close to the rates of other model secondary tosylates, e.g., isopropyl, 1-phenyl-2-propyl (**14**; after correction for the known amount of phenyl participation (39b)) and cyclohexyl. Second, recent studies by Closson (96b) of the acetolysis of 1-cyclooctenyl-5-brosylate, which is exactly analogous to Huisgen's 5-tosylate isomer (**46a**; $m = 8$), showed that the rate of the cyclooctenyl derivative was 40 times slower than the acetolysis rate of cyclooctyl brosylate. Yet the acetolysis products from 1-cyclooctenyl-5-tosylate are exclusively rearranged; 95% of the rearranged products are isomeric bicyclo[3.3.0]octyl acetates plus bicyclo[3.3.0]oct-2-ene, all products of *transannular participation* by the double bond. The rate of the cyclooctenyl derivative, although 40 times slower than cyclooctyl, is 10 time *faster* than Huisgen's nonparticipating model, 1,2-benzocyclooctenyl-5-tosylate (**46a**; $m = 8$; after a correction of $k_{OBs}/k_{OTs} = 3.3$). Thus all the available evidence suggests that Huisgen's choice of the 5-tosylate isomer (**46a**) as the model was an appropriate one and that the rate of this compound is a reasonable approximation of the aryl-unassisted rate for the 4-isomers (**46**), although it does not take inductive effects fully into account. In contrast, cyclooctyl tosylate, with a sterically accelerated rate, is a less appropriate model for the formolysis of the 1,2-benzocyclooctenyl-4-tosylates (**46**).

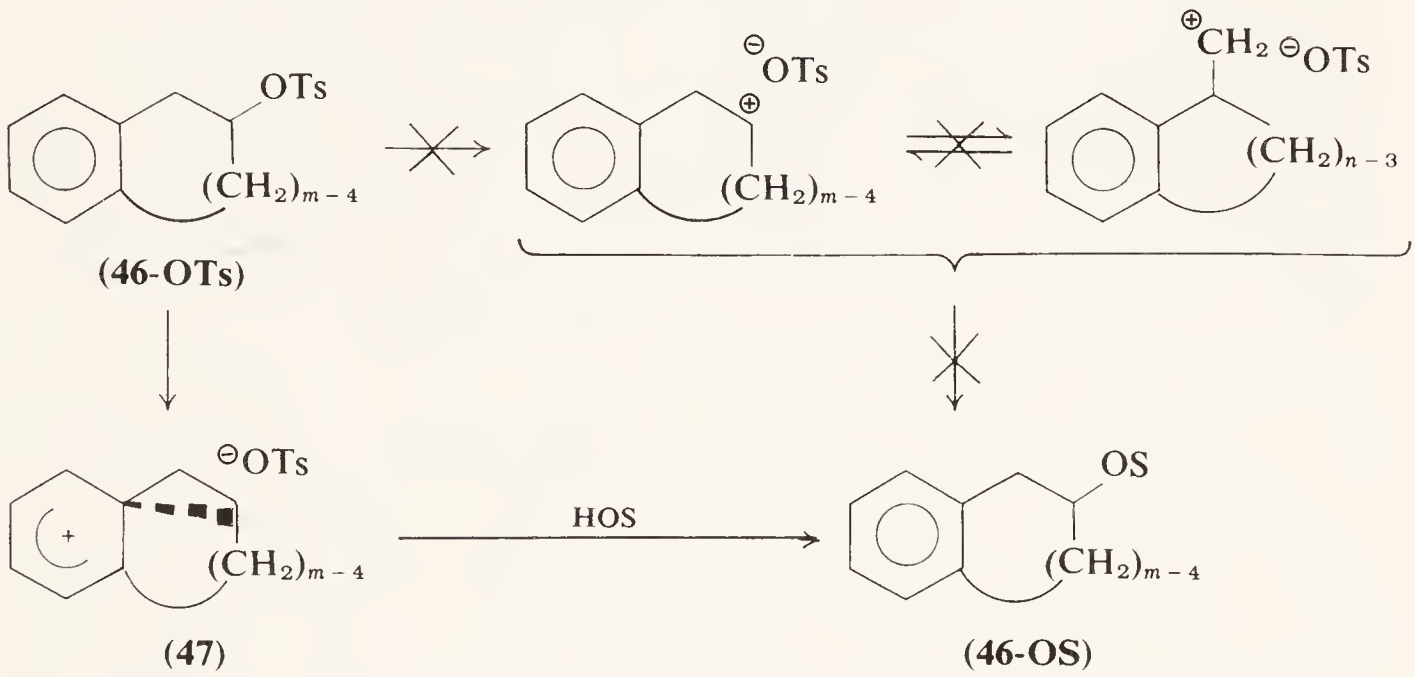
In summary, the kinetic data do reveal substantial phenyl participation in the formolysis of **46** (m = 7–9). Similar comparisons of the acetolysis data for the 4-tosylates (**46**) and the 5-tosylate (**46a**) isomer show that phenyl participation is still occurring in acetic acid, although somewhat reduced in importance, for the seven- and eight-membered homologs (**46**; m = 7, 8).

In accord with the kinetic data, the product data also suggests β-phenyl participation in the transition state and the intermediacy of bridged ions (**47**). (The product data in Huisgen's original work (92,93) were carefully obtained in great detail but nevertheless were compared only qualitatively with the kinetic data. Only these original comparisons are discussed here. In Section VII, quantitative rate/product correlations are given for Huisgen's compounds, with those for other systems.) In formic acid (20°), the seven- and eight-membered 1,2-benzocyclooctenyl-4-tosylates (**46**; m = 7, 8) each gave a 96% yield of formate ester and no olefin. The formate from optically active **46** (m = 7) was produced with *100% retention of configuration* (formate-buffered). Acetolysis of **46** (m = 7 gave only 9% olefin along with 83% acetate; the latter showed 94.5% retention of configuration and 5.5% inversion (unbuffered) or 92% retention and 8% inversion (buffered). The nine-membered 4-tosylate (**46**; m = 9), which formolyzed about 3 times slower than the next lower homolog (**46**; m = 8), gave a slightly lower yield of 4-formate (78%, unbuffered; 86% buffered). This result, obtained at 20°, is contrasted below with the very interesting results obtained in the higher-temperature formolysis (65°) of the corresponding eight-membered 3-carbinyl tosylate (**48**; n = 8).

Although the six-membered 4-tosylate (**46**, m = 6) formolyzes and acetolyzes about ten times faster than the eight-membered 5-tosylate model (**46a**; m = 8), the product data do not agree with a phenonium ion interpretation. Only 25–30% of the corresponding 4-ester (**46-OAc**; **-OCHO**; m = 6) was formed in either solvent, and much olefin (1,2- and 1,4-dihydronaphthalenes) and nonvolatile residue were formed instead. More likely, the data indicate the primary intermediacy of an aryl-unbridged secondary cationoid species that yields olefins and β-tetralyl ester, accompanied by a high degree of hydride shift, yielding 1,2-dihydronaphthalene and α-tetralyl ester. α-Tetralol was found to be completely unstable under the formolysis conditions, giving mostly nonvolatile residue, and Huisgen suggested that α-tetralyl formate should behave similarly. Likewise, 1,2-dihydronaphthalene was unstable under the formolysis conditions, giving 60–86% nonvolatile residue (unbuffered). On the other hand, the expected product of phenyl participation, the β-tetralyl ester, formed only as a minor product, was stable under the formolysis con-

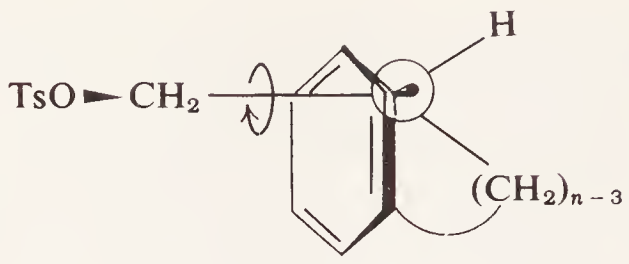
ditions. The evidence from product data against the phenonium ion in this derivative is in accord with the previously noted degree of ring strain required to accommodate the phenonium ion (**47**; $m = 6$).

As was the case with the open-chain analog (**14**; Section IV-B-2), the product and kinetic evidence presented in the preceding discussions, which supports the predominance of β-phenyl participation in the solvolyses of some of the 1,2-benzocyclenyl-4-tosylates (**46**; $m = 7, 8$) is better explained in terms of a discrete, but unsymmetrically bridged, phenonium ion (**47**; $m = 7, 8$). The alternative formulation of a set of rapidly equilibrating aryl-unbridged cations appears much less attractive because of the unlikely equilibration between primary and secondary cations, as discussed in Section IV-B-2.



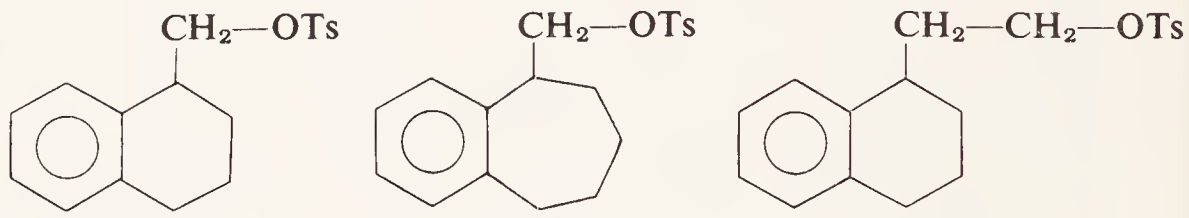
(47) **(46-OS)**

Formolysis rates of the corresponding 1,2-benzocyclenyl-3-carbinyl tosylates (**48**; $n = 5$–8) showed considerably less dependence on ring size (Table V) than did the 4-tosylates (**46**) (93b). This was ascribed to the operation of two opposing effects: first, an accelerative trend along the series **48** ($n = 5$–8) due to the increasing ease of phenonium ion formation with increasing ring size, as already discussed for the isomeric 4-tosylates (**46**) and, second, a decelerative trend along the series **48** ($n = 5$–8) due to increasing torsional strain in achieving the proper axial conformation of the carbinyl tosylate group (**49**) for backside displacement by the benzene ring (93b). Models showed that only in the smallest homolog of the series (**48**; $n = 5$) is the indicated conformation (**49**) easily attainable with minimum strain and with maximum freedom of the carbinyl tosylate group to rotate freely about the carbon–carbon bond axis (see **49**) so that the *anti* disposition of the benzene and tosyloxy groups is achieved. Apparently, the best balance between the ground state conformational retarding effect and the phenonium ion strain effect is attained in the six-membered homolog (**48**; $n = 6$); the formolysis rate of this derivative describes a



(49)

shallow maximum (Table V) in the trend of rates for the series of 3-carbinyl tosylates (**48**). β-Phenyl participation seems to predominate in the formolysis of both the six- and seven-membered homologs (**48**; $n = 6$, 7), as suggested by a comparison of the formolysis rates with that of the homologous α-tetralylethyl tosylate model (**50**; $n = 6$), in which there is no phenyl participation (96a). Both of the 3-carbinyl tosylates (**48**; $n = 6, 7$) formolyzed *more than* 10^2 *times faster* than the model (**50**; $n = 6$). Although the inductive effect of the neighboring phenyl ring should fall off in going from the β position (**48**) to the γ position (**50**), making the observed rate enhancements actually somewhat low, the magnitude of the correction in this case ought to be very small, since inductive effects in primary systems have been found to be very small (39b,72,73).



	(48) $n = 6$	**(48)** $n = 7$	**(50)** $n = 6$
Relative rate			
HCOOH; 65°	4.3×10^2	—	1.0
HCOOH; 70°	—	1.4×10^2	1.0

Since the ring-strain effect in the phenonium ion (**47**) is common both to the series of 4-tosylates (**46**) and 3-carbinyl tosylates (**48**), Huisgen used the rate ratios for the formolysis of each corresponding pair of isomers (e.g., $k_{46;\, m=6}/k_{48;\, n=5}$) to obtain a measure of the conformational restriction to phenyl participation in the 3-carbinyl isomers (**48**) (93b). These ratios are given in Table V. As expected, there is a marked increase with increasing ring size over a range of about 4×10^2.

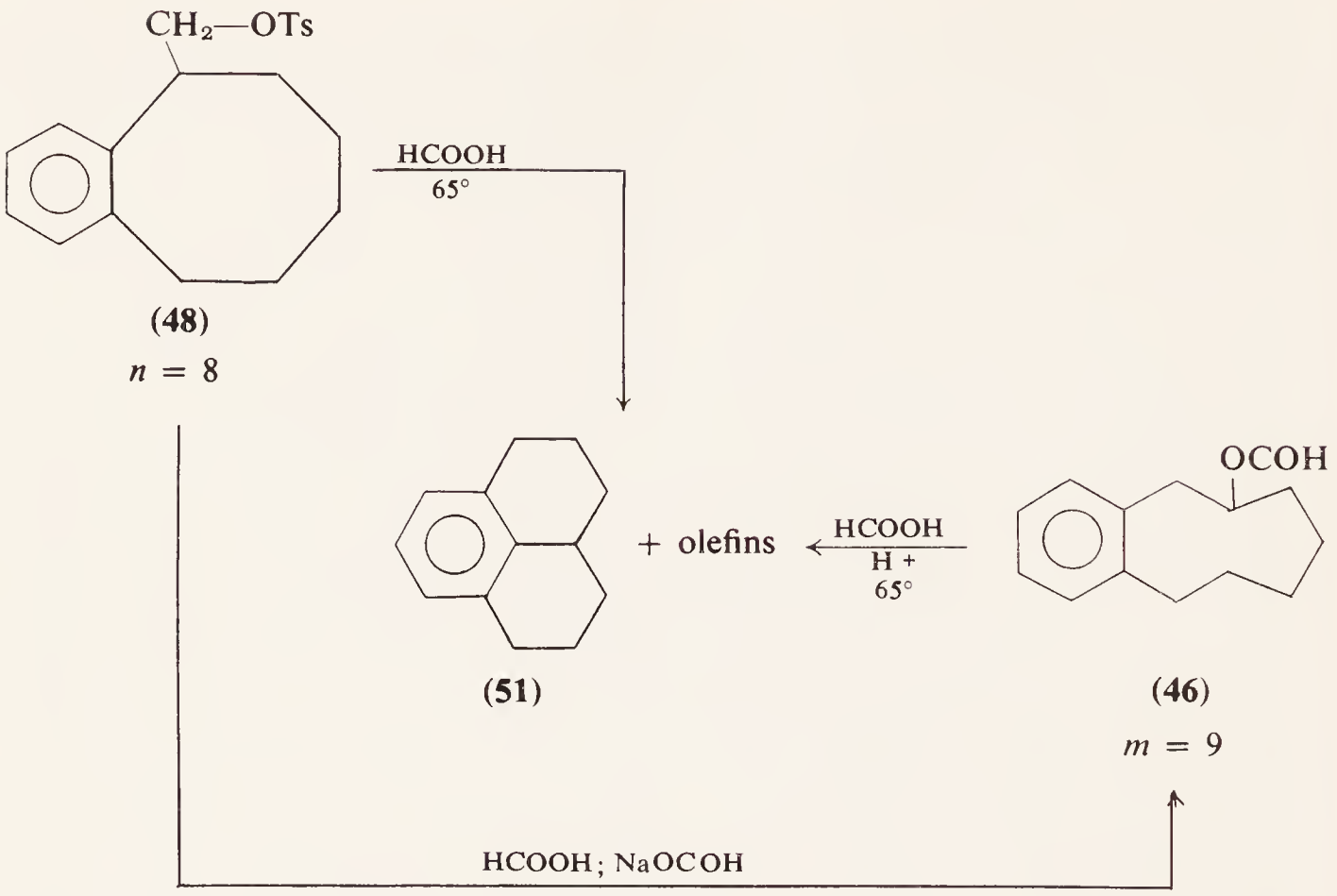
Since the axial conformation (**49**) with maximum rotational freedom is readily attainable in the smallest-ring derivative (**48**; $n = 5$), the rate ratio of 1/10.9 (Table V) found for this substrate relative to the corresponding six-membered 4-tosylate (**46**; $m = 6$) should reflect merely the rate difference between the primary and secondary systems in the absence of extra

conformational factors. In support of this expectation is the fact that the formolysis rate ratio (25°) of the corresponding open-chain secondary model, 1-phenyl-2-propyl tosylate (**14**), to the corresponding open-chain primary model, 2-phenyl-1-propyl tosylate (**13**), is $k_{14}/k_{13} = 9.0$ (41a) close to the value of 10.9 found for $k_{46;\, m=6}/k_{48;\, n=5}$. Therefore, correction of all the k_{46}/k_{48} rate ratios in Table V by a factor of 10.9 provides a more absolute measure of the conformational retardation factor in the formolysis of the higher homologs of the 3-carbinyl tosylates (**48**; $n = 6$–8). This corrected factor ranges from 2 (**48**; $n = 6$) to 3.8×10^2 (**48**; $n = 8$).

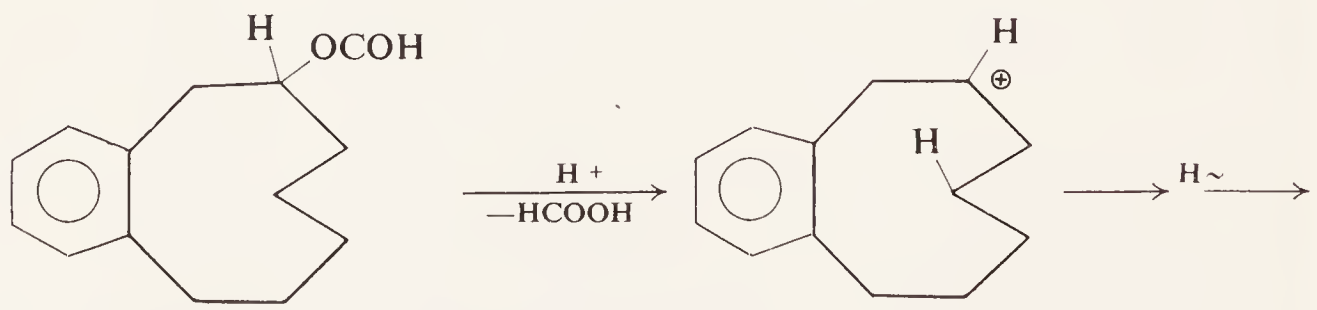
The product data (93a) for the formolysis and hydrolysis (aqueous dioxane) of the 6- and 7-membered 3-carbinyl tosylates (**48**; $n = 6, 7$) are in accord with the kinetic data and support the predominant intervention of bridged phenonium ions. (More quantitative rate/product correlations are provided in Section VII.) Formolysis of both derivatives gave quantitative ring enlargement and led to the corresponding 1,2-benzocyclen-4-yl formate (**46-OCOH**) exclusively. Only 6–7% racemization accompanied the formolysis or acetolysis of **48** ($n = 6$). An indication of the greater ease of phenonium ion formation with the larger ring system (**48**; $n = 7$) is that neither the addition of formate buffer nor the use of the more nucleophilic solvent, aqueous dioxane, reduced the quantitative formation of the ring-enlarged 1,2-benzocycloocten-4-ol (**46-OH**; $m = 8$) with this substrate. On the other hand, formate-buffered formolysis or solvolysis in aqueous dioxane of the lower homolog, α-tetralylcarbinyl tosylate (**48**; $n = 6$), results in about a 10% reduction in the yield of ring-enlarged 1,2-benzocyclohepten-4-ol (**46-OH**; $m = 7$). Here the slightly greater strain in the phenonium ion (**47**; $m = 7$) results in some competition from a direct S_N2-type displacement on the primary 3-carbinyl tosylate either by the formate ion or by the more nucleophilic solvent.

As expected, solvolysis of the five-membered 3-carbinyl tosylate (**48**; $n = 5$) gave a substantially lowered yield of the ring-enlarged β-tetralol (**46-OH**; $m = 6$) and more products of direct rearrangement (via an aryl-bridged transition state) to an aryl-unbridged secondary cyclic cation, which also could have been formed by "leakage" from an unstable, highly strained phenonium ion intermediate (**47**; $m = 6$) (93a).

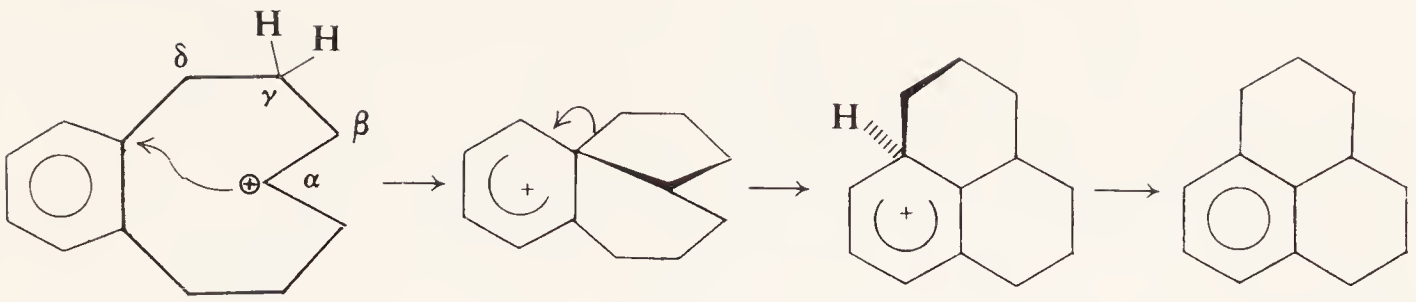
Perhaps the most interesting product study in the 3-carbinyl tosylate series (**48**) was the formolysis of the largest-ring system, 1,2-benzocyclooctenyl-3-carbinyl tosylate (**48**; $n = 8$) (93c), which had to be carried out at higher temperatures (65°) because of its slow rate. Instead of the expected ring-enlarged product, 1,2-benzocyclononen-4-ol (**46-OH**; $m = 9$), unbuffered formolysis (65°) gave a hydrocarbon mixture in 83% yield consisting of a 4/1 ratio of nonolefinic components to olefinic components. The nonolefinic component turned out to be tetrahydroperinaphthane (**51**).



Furthermore, *buffered* formolysis gave *no* tetrahydroperinaphthane (**51**), but instead led to an 81% yield of the normally expected 4-cyclenol after ester hydrolysis. It will be recalled that *either* buffered *or* unbuffered formolysis at lower temperature (20°) of the corresponding 1,2-benzocyclononenyl-4-tosylate (**46**; $m = 9$) gave no tetrahydroperinaphthane (**51**), but instead, 85–90% of the expected 4-alcohol after hydrolysis (**46-OH**; $m = 9$). However, reinvestigation of the unbuffered formolysis of 1,2-benzocyclononenyl-4-tosylate (**46**; $m = 9$) at higher temperatures (65°) indeed resulted in the formation of tetrahydroperinaphthane (**51**) as the major product within 2 hr. Also, the tricyclic hydrocarbon (**51**) was formed in 79% yield upon treatment of 1,2-benzocyclononen-4-ol (**46-OH**; $m = 9$) under the unbuffered formolysis conditions. The following thermodynamically controlled process was proposed to account for the formation of tetrahydroperinaphthane (**51**) from the kinetically controlled ring-enlarged ester product at higher temperatures.



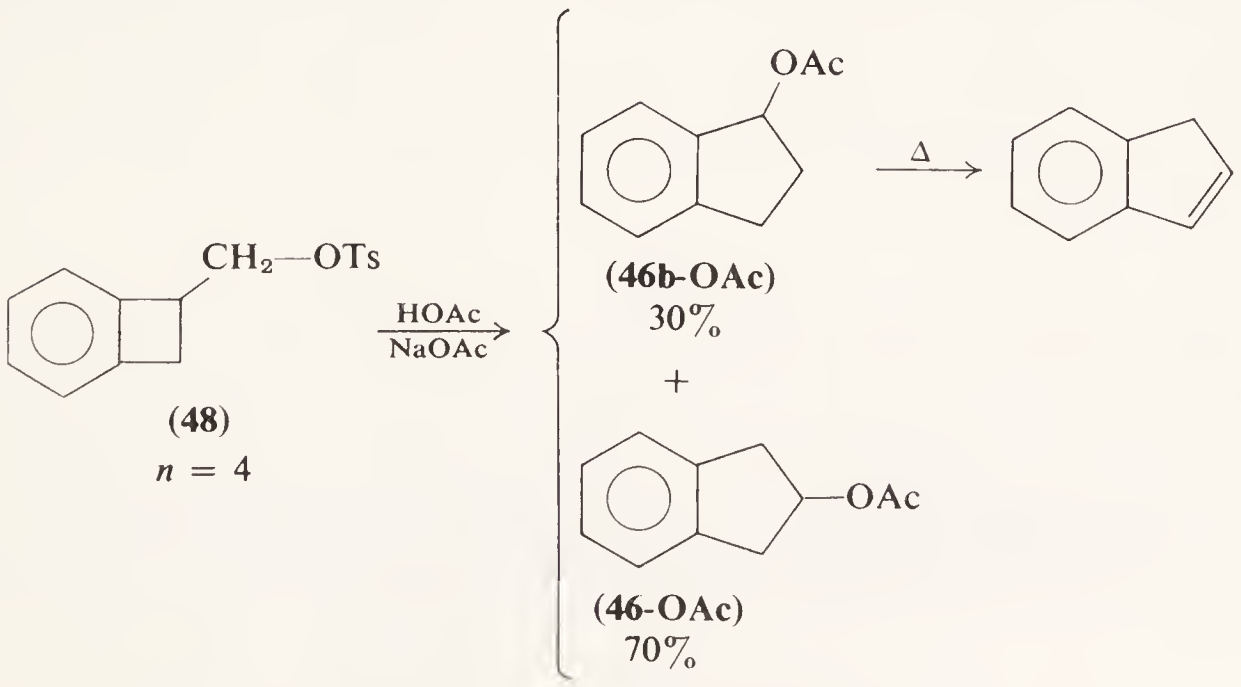
(46-OCOH)
$m = 9$



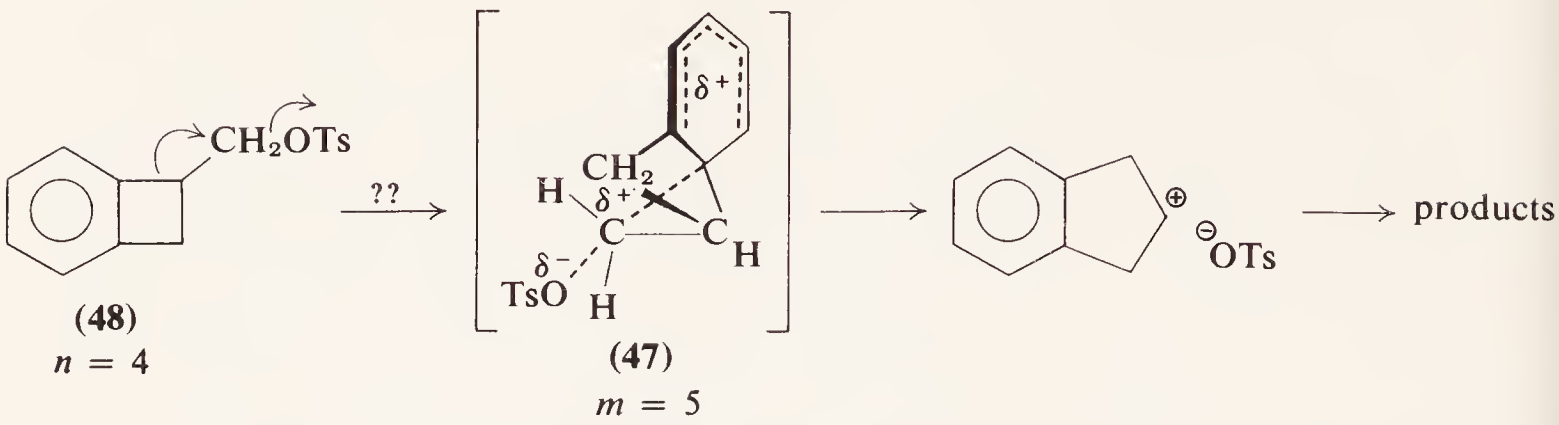
(52) (51)

The transannular δ-phenyl interaction to give the "phenonium ion" with the five-membered spirane bridge (**52**) in the proposed scheme is identical to a process described earlier by Winstein (96a) and termed Ar_4 participation. (Under this terminology, regular β-aryl would be called Ar_2 participation.) Basically, this amounts to an intramolecular Friedel-Crafts-type aromatic alkylation, and the suggested driving force in the present case is the thermodynamically favorable transformation of the strained cyclononyl ring system into the less strained decalyl ring system in **51**. Section VI continues the discussion of the interesting and quantitatively useful phenomenon of Ar_4 participation by remote aryl groups.

Finally, an extension of Huisgen's studies down to the smallest available homolog, 1,2-benzocyclobutenyl-3-carbinyl tosylate (**48**; $n = 4$), has recently been reported by Whitlock and Fuchs (97). As expected, buffered acetolysis at reflux led to quantitative ring-enlargement to the corresponding indanyl ring system (**46**; $m = 5$), yielding initially a product mixture of 70% indan-2-yl acetate (**46-OAc**; $m = 5$), which was stable under the reaction conditions, and 30% indan-1-yl acetate (**46b-OAc**; $m = 5$), which was unstable and gave indene on continued reaction. In the benzocyclobutenylcarbinyl case, the enormous strain required to achieve a perpendicular spirane geometry in a phenonium ion (**47**; $m = 4$) renders such an ion an extremely unlikely intermediate—and not even a particularly good transition state in a direct aryl migration to the 2-indanyl



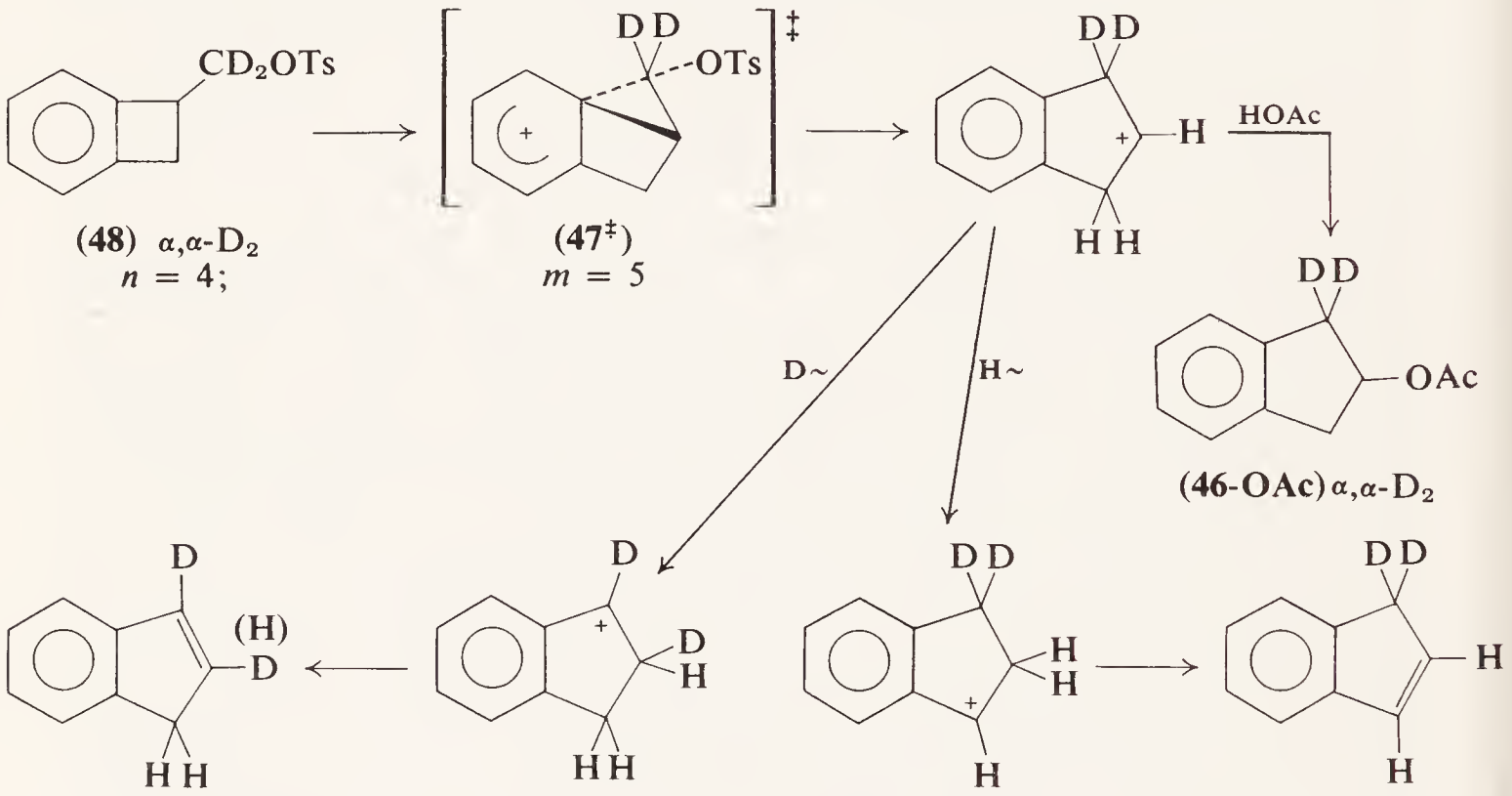
(48)
$n = 4$



(48)
$n = 4$

(47)
$m = 5$

cation. Instead, alkyl migration to give initially the 1-indanyl cation would seem to be the preferred route. Surprisingly, however, solvolysis of labeled 1,2-benzocyclobutenyl-3-carbinyl-α,α-D_2 tosylate and examination of recovered acetate and indene indicated that *aryl* migration was the exclusive route. The scheme proposed for the overall observations is shown.



(48) α,α-D_2
$n = 4$;

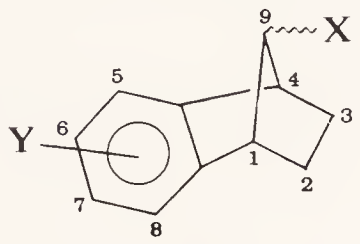
($47^{\ddagger}$)
$m = 5$

(46-OAc) α,α-D_2

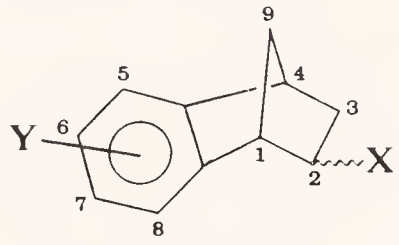
Although the "formal" intermediacy of the bridged ion was considered (97) its intervention is almost certainly ruled out for steric reasons, and the transition state for aryl migration must involve only as much interaction between the carbonium center and the aryl π orbitals as can be achieved in a partially bridged structure that only slightly approaches perpendicularity ($47^{\ddagger}$).

c. Fused Benzopolycyclic Substrates; The anti-9- and exo-2-Benzonorbornenyl Systems. β-Aryl participation can be induced or enhanced by forcing the aryl ring into a conformation most favorable for concerted migration: *anti* to the leaving group and also more or less perpendicular to the plane containing the C_β–C_α–X bonds (e.g., see **49**). Huisgen's work (93) showed that participation is heavily dependent on the ease of attaining

the correct ground state aryl conformation. Optimum aryl conformation and, therefore, maximum overlap between the aryl π orbitals and the developing carbonium *p* orbital, is approached by locking the aryl ring suitably in a rigid, polycyclic system. Detailed studies of several fused benzopolycyclic systems have been reported by Wiley (102), Bartlett (105), Tanida (98,99), Winstein (100), and Brown (101). A review of work up to 1968 has been provided by Tanida (98d). The two most studied systems, *anti*-9- and *exo*-2-benzonorbornenyl, are covered here.

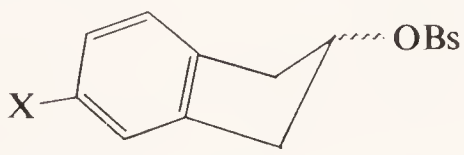


(53)



(54)

The π orbitals of the aryl ring in the *anti*-9-benzonorbornenyl brosylates (*anti*-**53-OBs**) are especially well oriented geometrically for maximum overlap with the developing empty *p* orbital of the carbonium center at the 9-position, and all the available evidence points to very substantial aryl participation in the acetolysis of this series of compounds. For almost the entire series of aryl substituents studied, the sole acetolysis product was the *anti* acetate (*anti*-**53-OAc**), i.e., complete retention of configuration. Not surprisingly, the only exception was the 6-nitro derivative (*anti*-**53-OBs**; Y = 6-NO_2), and even here, predominant retention of configuration was found. The *anti*/*syn* rate ratio of 4.4 for the 6-NO_2 derivative further suggests that participation is not prevented even by the deactivating nitro substituent. The dispersal of the developing positive charge throughout the series into the benzo ring is also reflected by the enormous range of reactivities (98b) found, the rate ratio $k_{6\text{-}CH_3O}/k_{6\text{-}NO_2}$ being 3.9×10^5. As a comparison, the 2-indanyl system (**46**), where an equally favorable interaction with the developing carbonium center is not imposed upon the π-electron system of the aryl ring, shows a corresponding k_{CH_3O}/k_{NO_2} of only a factor of 8.



(46)

X = CH_3O; NO_2

$m = 5$

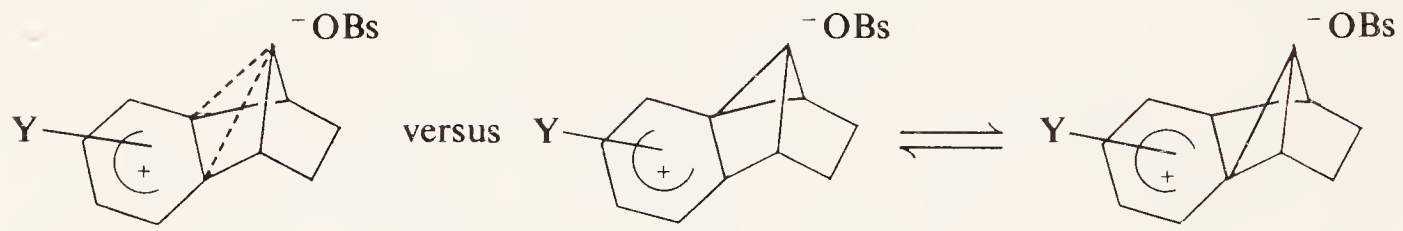
$k_{CH_3O}/k_{NO_2} = 8$; $\rho = -1.1$

The magnitude of the charge delocalization during solvolysis of *anti*-**53** is also defined by the experimentally determined value of -5.10 for

the Hammett ρ^+ (98b,98c); this is the largest such value yet determined for any β-arylalkyl system (see Table II) and falls into the range of ρ^+ values (-4 to -12) normally found for a variety of ordinary aromatic substitution reactions (103). In contrast, an estimated value from the available data for the 2-indanyl system (**46**; $m = 5$) gives $\rho = -1.1$.

It is instructive to examine the manner in which the Hammett correlation of the data for the *anti*-9-benzonorbornenyl system (*anti*-**53**) was carried out, since it contributes to an understanding of the more intimate nature of the transition state.

Tanida found the most satisfactory Hammett fit by plotting the relative rates against the term $(\sigma_m^+ + \sigma_p^+)/2$, which suggests a symmetrical transition state preceding a bridged ion such as **55**, rather than two unsymmetrical transition states leading to unsymmetrically bridged ions such as **56**. The distinction between the symmetrically bridged ion (**55**) and the unsymmetrically bridged ions (**56**) is somewhat different in this particular case because the equilibrating, unsymmetrical ions (**56**) also are fully σ-bridged phenonium ions. It is the symmetrically bridged ion (**55**) that is, in a sense, unlike the other symmetrically bridged ions discussed thus far.* In ion **55**, a Y substituent at the 6- or 7-position is always *homometa* and



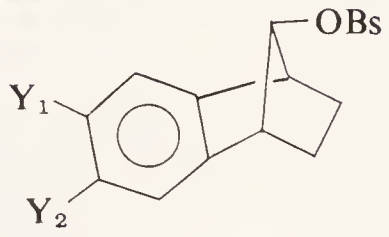
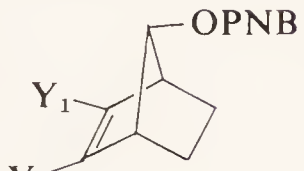
(**55**) (**56**) (**56**)

homopara (98–100) to the positive charge. This conclusion was confirmed by Tanida (98c) through the use of a symmetry technique somewhat similar in principle to the ones used by Schleyer (36,39) in the 1-aryl-2-propyl (**14**) series and in the cyclopropylcarbinyl system (104a), by Bartlett in the β-[3-cyclopentenyl]-ethyl systems (104b), by Gassman (104c) in the *anti*-7-norbornenyl system, and by Shiner with β-deuterium substitution (104d,104e). Acetolysis of the 6,7-dimethoxy and 6,7-dimethyl derivatives of *anti*-**53** yielded rate constants close to the square of those for the monosubstituted homologs (98c). Table VI summarizes the data, together with comparison data from Gassman's study of the *anti*-7-norbornenyl system (104c).

* See also P. D. Bartlett, *Nonclassical Ions*, W. A. Benjamin, New York, 1965, pp. 507ff, for some critical comments on Tanida's (98b) usage of the term "classical ions" to describe the unsymmetrically bridged ions (**56**). This particular situation illustrates well the confusion that can result from the use of the familiar terms "classical/nonclassical ions." We have deliberately avoided the use of these terms in this chapter.

TABLE VI

Kinetic Effect of Multiple Substitution in the anti-9-Benzonorbornenyl and anti-7-Norbornenyl Systems

System	R	Relative rates			
		$Y_1 = Y_2 = H$	$Y_1 = R; Y_2 = H$	$Y_1 = Y_2 = R$[a]	$Y_1 = Y_2 = R$[b]
	CH_3	1.0	5.7	36	32
	CH_3O	1.0	54	3000	2966
	CH_3	1.0	13.3	148	177

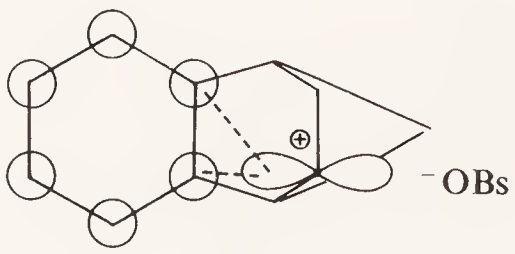
[a] Observed.

[b] Calculated; $(Y_1 = R; Y_2 = H)^2$.

We would have expected the effect of dimethyl or dimethoxyl substitution in the unsymmetrical ions (**56**) to have been closer to a statistical doubling (actually $2x - 1$; see Section IV-B-2) than to the observed multiplicative effect. Furthermore, both the dimethyl and the dimethoxyl derivatives fell on the same Hammett correlation line defined by the monosubstituted derivatives (98c).

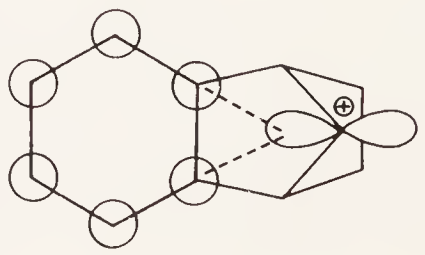
Largely because of its structural relation to the controversial 2-norbornyl system, the 2-benzonorbornenyl series (**54**) has been examined in considerable detail by several groups of investigators (99–102,105,106). These studies have not only helped to elucidate the mechanistic details of the solvolysis of fixed β-arylalkyl systems (**54**), but they have also provided us with a set of experimental tools and results which help to clarify analogous aspects of the solvolytic behavior of the parent 2-norbornyl system. The 2-benzonorbornenyl system (**54**) has an important advantage over the 2-norbornyl (**58**) system. The participating power of the aryl ring can be varied systematically by the introduction of electron-withdrawing or -releasing substituents at the 6- and 7-positions of the aromatic ring. These substituents, remote from the reaction site, can have no significant steric effect on the course of the solvolysis of (**54**), whereas direct substitution on the norbornyl structure (**58**) very often introduces complicating steric factors.

Two basic factors could conceivably enhance β-phenyl ("benzo") participation in the solvolysis of *exo*-2-benzonorbornenyl derivatives (*exo*-**54**). First, the β-phenyl ring is fused into a rigid system to provide close to optimal overlap between the aryl π and the carbonium p orbitals. The size of the Hammett ρ^+ value for acetolysis of *exo*-**54-OBs** (-3.3; see Table II and later discussion) is an indication of the better overlap in *exo*-**54** than in typical symmetrical alicyclic systems ($\rho^+ = -2.4$ for **11** and -2.7 for **2a**). On the other hand, the aryl π-electron density is less symmetrically oriented toward the carbonium center in **54** than it is in the *anti*-9-benzonorbornenyl isomer **53**, which gives a much higher ρ^+ value (-5.10, see above). The second factor that facilitates aryl participation in the *exo*-2-benzonorbornenyl system (*exo*-**54**) is that the alternative aryl-unassisted solvolysis (k_s) of the *exo* epimer cannot compete favorably with aryl participation, since backside solvation (either nucleophilic solvent



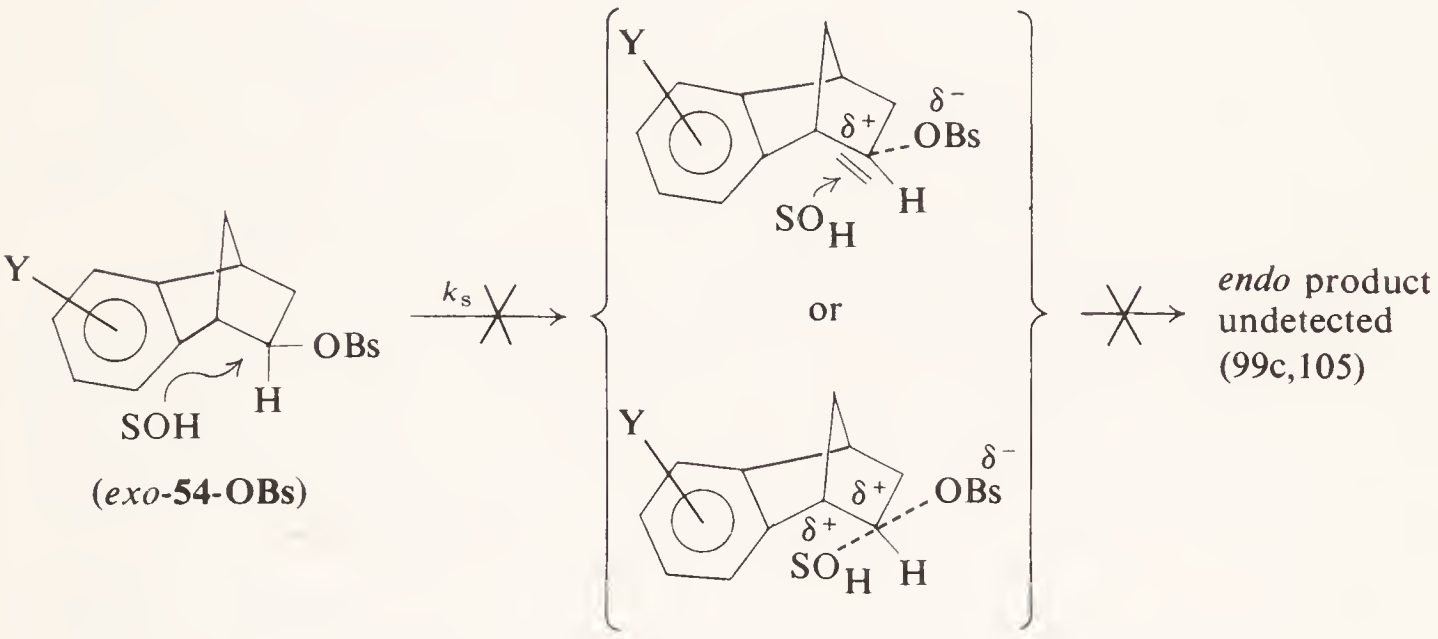
(54)

versus



(53)

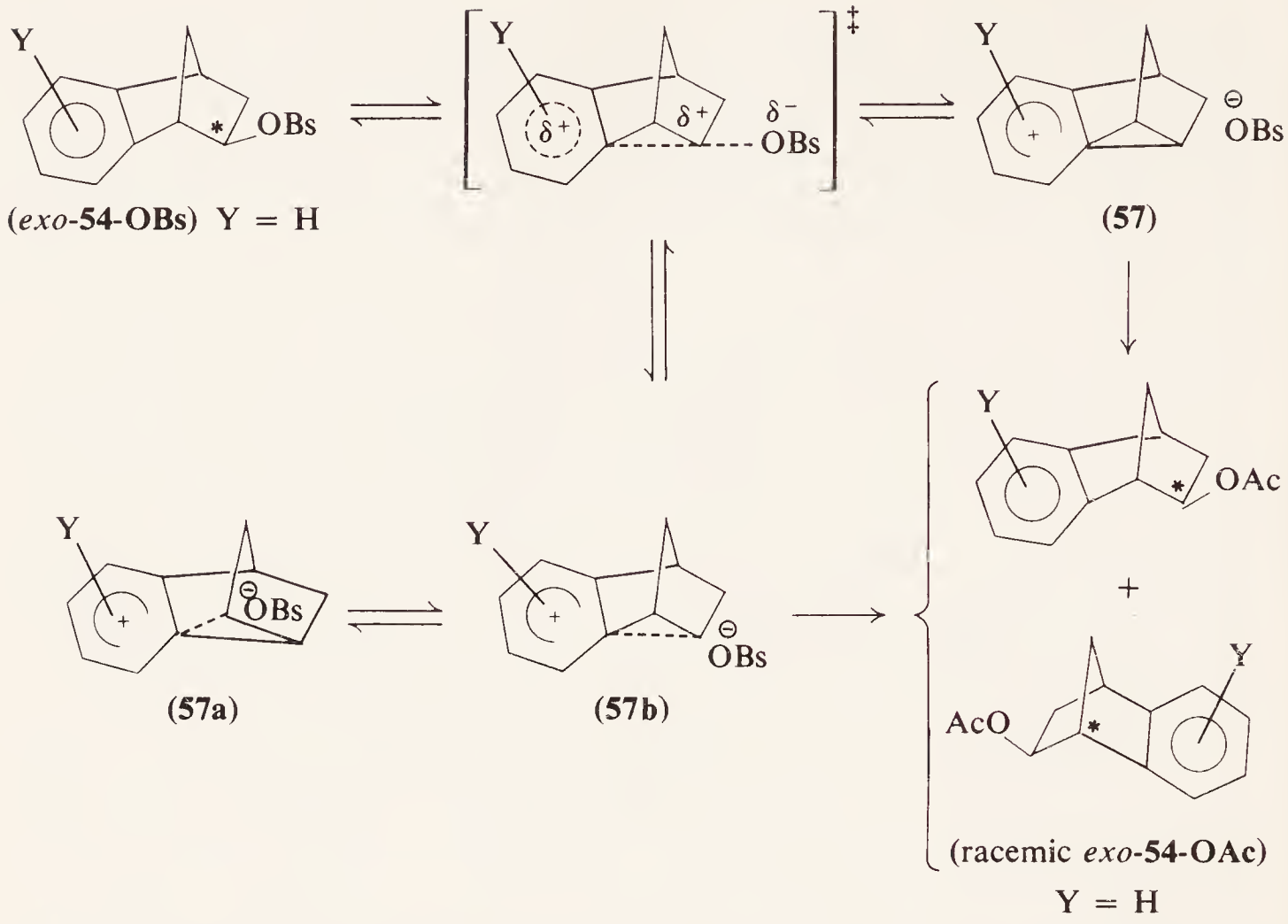
assistance or solvent attack on an aryl-unbridged ion pair; see Sections I, III, V–VII; Refs. 2,12,19,31) of the relatively hindered *endo* side of the molecule is possible only with difficulty. The accumulated data conclusively point to predominant phenyl participation in the solvolysis of the secondary *exo*-2-benzonorbornenyl system (*exo*-**54**) and some of its derivatives.



Participation by the benzo ring in *exo*-**54** is strongly supported by the large *exo*/*endo* rate and product ratios and by the effects of substituents, both on the benzo ring and on the norbornenyl structure, on the rates of the *exo* and *endo* epimers and their derivatives.

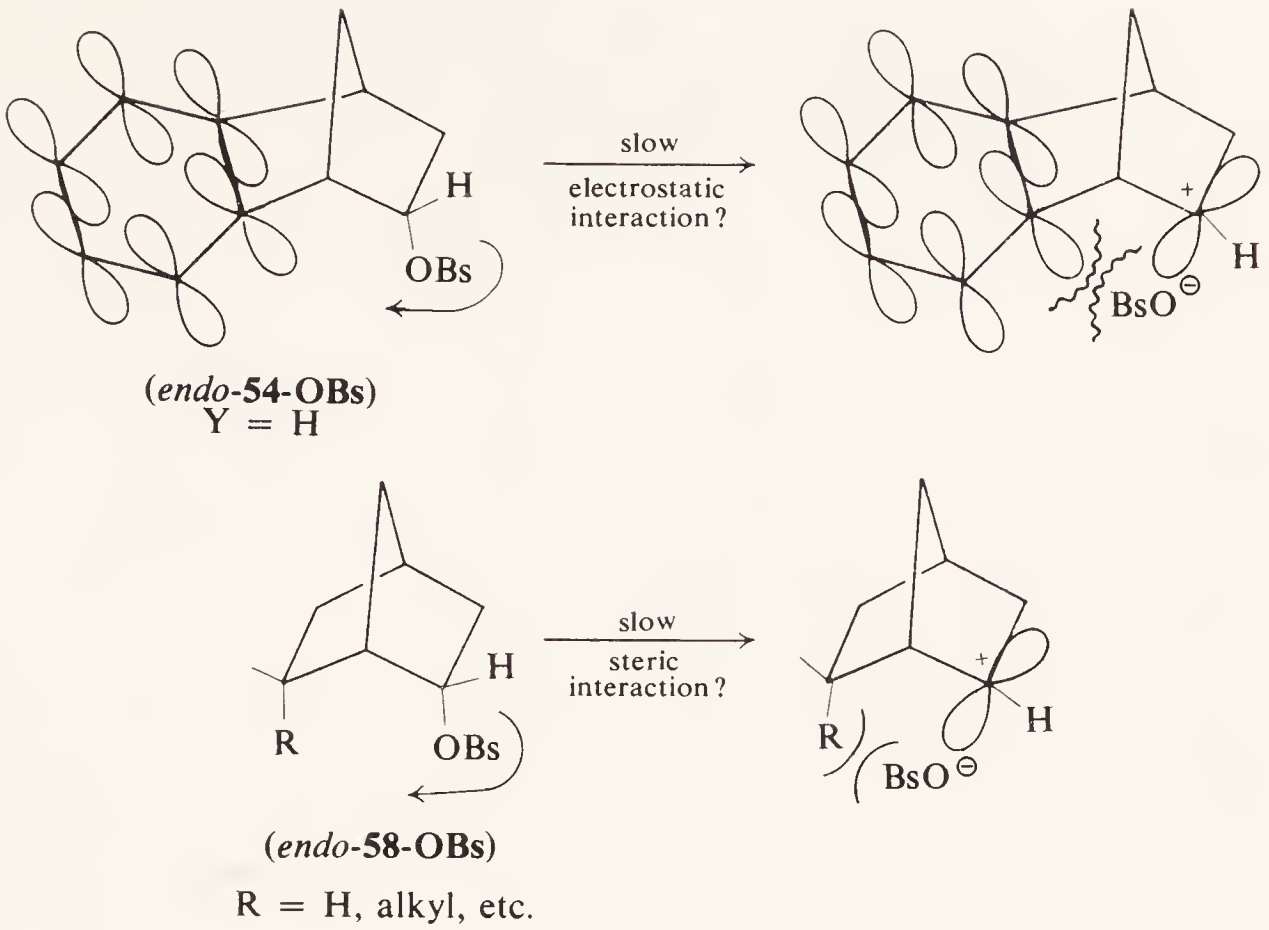
The *exo*/*endo* rate ratio (105) for the acetolysis (25°) of the parent epimeric 2-benzonorbornenyl brosylates (**54-OBs**; Y = H) is 15,000 (101b,105). This was attributed to significant π participation in the *exo* epimer (99,100,102,105) but, of course, not in the *endo*. [The originally reported (105) *exo*/*endo* rate ratio of 7500 at 25° was inaccurate because of an extrapolation error (101b).] The only reported product of acetolysis of either epimer is the *exo*-2-acetate (*exo*-**54-OAc**; Y = H). In other words, the *exo* epimer acetolyzes with ~100% retention and the *endo* epimer with ~100% *inversion* of configuration. Optically active *exo*-2-benzonorbornenyl brosylate (*exo*-**54-OBs**; Y = H) gave acetate product that was 100% racemized (106), further implicating the intermediacy of either a symmetrically bridged ion-pair (**57**) or possibly an equivalent set of equilibrating, unsymmetrically bridged ion pairs (**57a**, **57b**). (The racemization rate k_α is 4.6 times the rate of acetolysis k_t (99b,106b).

It is also possible that a portion of the high (15,000) observed *exo*/*endo* rate ratio in the acetolysis of the 2-benzonorbornenyl brosylates (**54-OBs**; Y = H) could be due to ground or transition state steric effects operating in conjunction with the (postulated) anchimeric effects. Equilibration studies in the closely related norbornenyl and other systems (107b,107c)



have pointed to the comparable ground state stabilities of the *exo* and *endo* epimers of **54-OBs**. With ground state steric effects thus largely ruled out, Brown has supported the position (101) that the solvolysis of *endo*-**54**, as with *endo*-2-norbornyl derivatives, is retarded relative to the *exo* epimer owing to steric hindrance to ionization of the *endo* leaving group as it is forced closer to either the π orbitals of the aromatic ring in *endo*-**54** or to an *endo*-6 substituent in *endo*-2-norbornyl (**58**). The former interaction should perhaps be regarded as an electrostatic effect (i.e., repulsion between the developing negative charge on the leaving group and the π MO of the nearby aromatic nucleus), but the latter interaction is a steric effect (101,107a,107c). (For a full discussion of the question of σ participation versus steric effects in the solvolysis of 2-norbornyl systems, see Chapter 24.)

The actual magnitude of the steric-electrostatic contribution to the observed *exo*/*endo* rate ratio in the acetolysis of the 2-benzonorbornenyl system (**54**; Y = H) can be determined experimentally by eliminating aryl participation in the solvolysis of the *exo* epimer. This can be done in two ways: either the benzo ring can be completely deactivated by one or more electron-withdrawing substituents, or a stronger neighboring group, which can anchimerically accelerate both the *exo* and *endo* epimers without introducing steric effects in either epimer, can be attached. Both of these methods have been applied recently to **54**, and both sets of results are



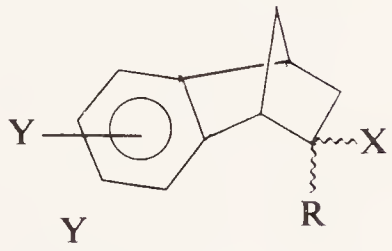
indicative of the relatively small importance of steric effects in the solvolysis of the parent secondary 2-benzonorbornenyl system (**54**; Y = H).

Deactivation of the benzo ring in **54** by 6,7-dinitro substitution causes an enormous reduction in the *exo*/*endo* rate ratio for acetolysis from 15,000 for the parent compound (**54**; Y = H; 25°) to ~4 for the 6,7-dinitro derivative (**54**; Y = 6,7-di-NO_2; relatively temperature independent, e.g., 4.1 at 150° or 180°; 3.7 at 77.6°) (99c). The results of benzo-ring and other substitution on the *exo*/*endo* rate ratio for **54** are summarized in Table VII. For the acetolysis of the parent secondary 2-benzonorbornenyl system (**54**), the *exo*/*endo* rate ratio varies over five powers of 10 as the benzo-ring substituents are changed from 6-CH_3O to 6,7-di-NO_2. Such a large *exo*/*endo* rate ratio variation with changes in remote substituents cannot be explained satisfactorily by steric effects alone.

There is some question of whether the observed *exo*/*endo* rate ratio (3.7–4.1) for the highly deactivated 6,7-dinitro derivative (**54-OBs**; Y = 6,7-di-NO_2) can be used as a direct estimate of steric effects in the anchimerically unassisted solvolysis of the parent unsubstituted 2-benzonorbornenyl system (**54-OBs**; Y = H). Both the *exo* (99b) and *endo* (99c) dinitro derivatives (**54**; Y = 6,7-NO_2) were very thoroughly investigated by Tanida (99), and he concluded, from a detailed rate and product analysis, that about 40% β-aryl participation remained in the acetolysis even of the *exo*-6,7-dinitro derivative in spite of the aromatic deactivation. Also, rate and deuterium scrambling data for the *endo* dinitro derivative were interpreted (99c) in terms of a primarily solvent-assisted (k_s) process

TABLE VII

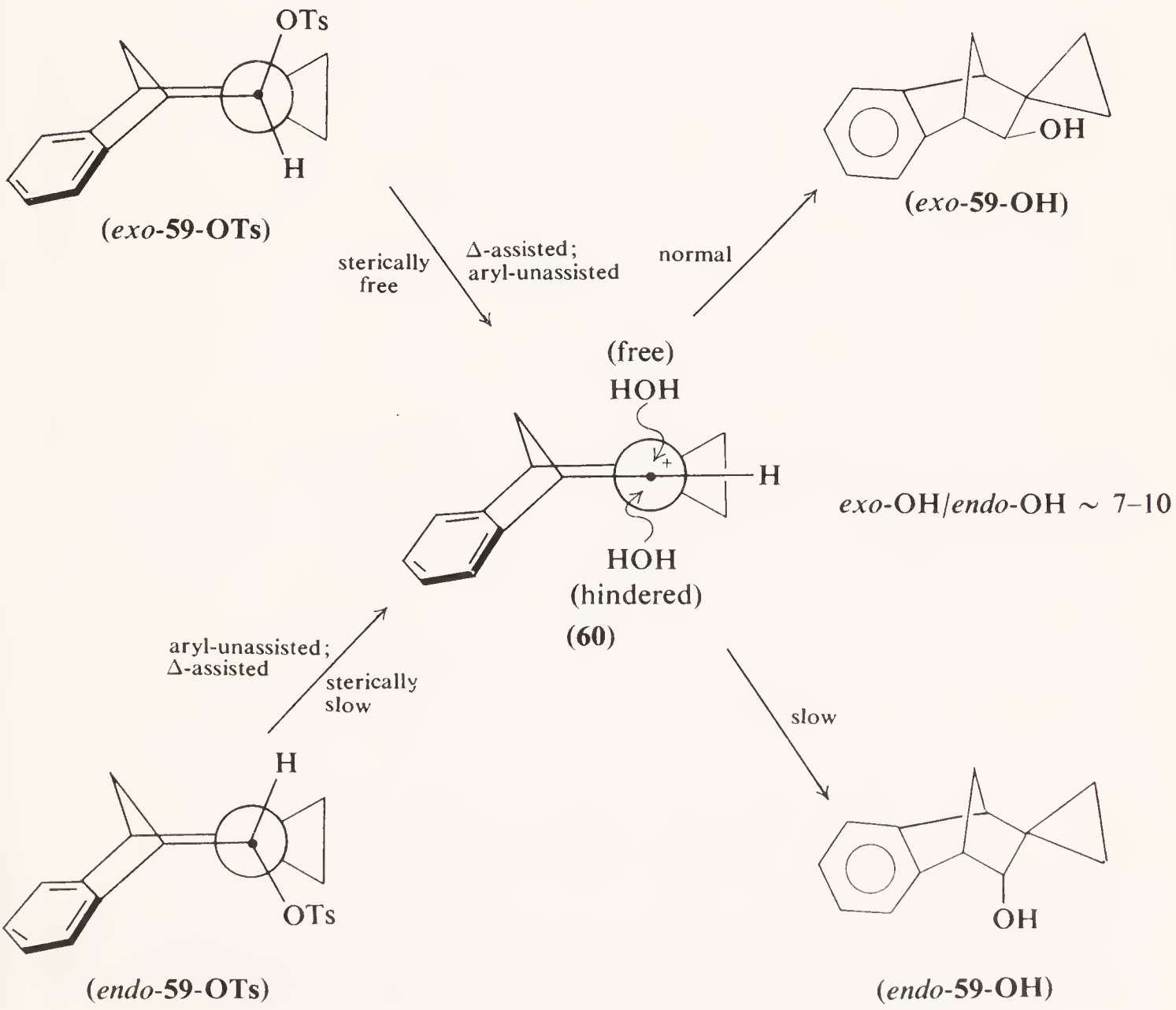
Effect of Substituents on *exo*/*endo* Rate Ratios in 2-Benzonorbornenyl System



Y	R	X	Solvent	k_{exo}/k_{endo}	Ref.
6-CH_3O	H	Cl	HOAc	400,000	99–101
H	H	OBs	HOAc	15,000	101b–101d,105
6,7-di—NO_2	H	OBs	HOAc	4 (Observed)	99b,99c
				2.2 (Calculated "S_N2")	99c
H	CH_3	OPNB	80% aq. acetone	6,500	101d
H	C_6H_5	OPNB	80% aq. acetone	2,900	101c,101d
H; 3-Spirocyclopropyl	H	OTs	80% aq. acetone	12	109a
exo-$Cr(CO)_3$ complex	H	OTs	70% aq. acetone	21	109b

(~68% of the overall observed *endo* rate), which Tanida called an S_N2 process, and ~32% "leakage" to a bridged ion. Also, about one-third of the overall observed rate for the *exo* dinitro epimer was attributed to S_N2-type behavior. Therefore, probably the best measure of steric effects available from Tanida's data (99b,99c) is the derived (99c) k_{S_N2exo}/k_{S_N2endo} ratio, a factor of 2.2 (HOAc; 77.6°). (Whether the reported (99b,c) "S_N2" processes actually are bimolecular solvent displacements is of no real consequence for the present purpose. The reported factor of 2.2 for the "S_N2" *exo/endo* rate ratio simply was determined by excluding all probable rate contributions from aryl bridging.)

A somewhat more straightforward measure of aryl-unassisted steric behavior in the parent 2-benzonorbornenyl system (**54**; Y = H) was provided recently (109a) by using a neighboring cyclopropyl group to "swamp out" participation by the benzo ring. Cyclopropyl is a very powerful neighboring group, and cyclopropyl carbinyl systems solvolyze with extensive participation by the cyclopropyl ring (108). The 2-carbon of 3-spirocyclopropylbenzonorbornen-2-yl tosylate (**59-OTs**) is part of a



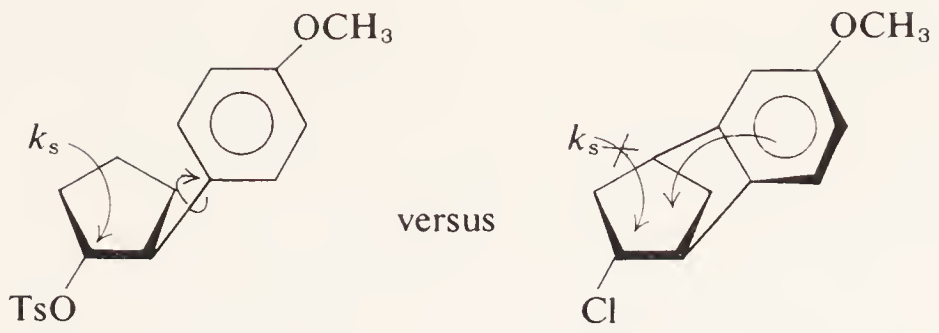
cyclopropylcarbinyl moeity. Since both the *endo*- and *exo*-2-leaving groups in **59** are similarly oriented with respect to the 3-spirocyclopyl group, no unbalancing steric effects are introduced in either epimer. Both epimers of **59** solvolyze to the preferred "bisected" (108) conformation of the cyclopropylcarbinyl cation (**60**), and therefore they should be equally anchimerically assisted by the cyclopropyl group. Presumably the steric factors involved in the generation and solvent capture of the cyclopropyl-stabilized cation (**60**) from either the *exo* or *endo* direction approximate the steric situation that would be encountered in a simple aryl-unbridged 2-benzonorbornenyl cation. (Similarly, a 3-spirocyclopropyl group was used to assess steric factors in the 2-norbornyl system) (107b).

Hydrolysis (80% aqueous acetone) of **59-OTs** resulted in an *exo*/*endo* rate ratio of 12 (109a), in satisfactory agreement with the factor of ~4 (99c) produced by 6,7-dinitro substitution. Compare with 15,000 for the parent system. Significantly, the *exo*/*endo* rate ratio of 12 is in quantitative agreement with the product data. Hydrolysis of the *exo* epimer (*exo*-**59-OTs**) gave an *exo*/*endo* alcohol ratio of 7, and the *endo* epimer gave *exo*-OH/*endo*-OH = 10. (See Sections V–VII.) Thus the combined results of both benzo-ring deactivation (99c) and cyclopropylcarbinyl stabilization (109a) signify the relatively small importance of transition state steric effects in the solvolysis of the 2-benzonorbornenyl (**54**) system. The aryl-*unassisted* rate of *exo* epimer (*exo*-**54-OBs**) is at best only about a factor of 10 faster than the rate of the *endo* epimer (*endo*-**54-OBs**).

The residual *exo*/*endo* rate ratio of 1500 in the acetolysis of 2-benzonorbornenyl derivatives (**54**; Y = H) after factoring out an approximate steric factor of 10 most reasonably must be attributed to aryl participation. There is considerable supporting evidence.

Wiley (102), Winstein (100), Brown (101), and Tanida (99) independently studied the kinetic effects of methoxyl substitution in the benzene ring of **54**. In the *exo* epimer, pronounced rate effects were observed, whereas only minor effects were produced in the *endo* epimer. For example, a 6-methoxy (homopara) substituent (**54-OBs**; Y = 6-CH_3O) enhances the rate of the *exo* epimer by a factor of 150 relative to that of the parent substrate (*exo*-**54**; Y = H) and increases the *exo*/*endo* rate ratio to 4×10^5 in acetic acid. The magnitude of the combined effects of a nearly ideally oriented aryl ring and a decrease in competitive solvent assistance (k_s) can be illustrated by the following comparison between the acetolysis rates of 6-methoxy-2-benzonorbornenyl chloride (**54-Cl**; Y = 6-CH_3O) and its monocyclic counterpart, 2-*p*-anisylcyclopentyl tosylate (**40**; Ar = *p*-$CH_3OC_6H_5$).

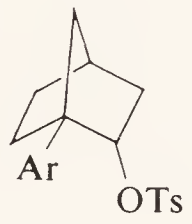
The importance of substituent effects on the epimeric series is also measured by the Hammett ρ values: the *exo* rates are correlated by σ^+ with



(40); Ar = *p*-An
$k_{trans}/k_{cis} = 0.6$

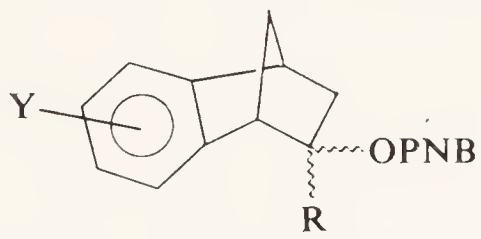
(54); Y = 6-CH_3O
$k_{exo}/k_{endo} = 4 \times 10^5$

a ρ^+ of -3.3 (99,100c,101d) but the *endo* rates correlate with the regular σ constants (99c) with a ρ of -1.3 (see Yukawa-Tsuno values in Table II, *exo*-**54** (99): $\rho = -3.3$, $r = 1.0$; *endo*-**54** (99–101) $\rho = -1.3$, $r = 0$). The obvious implication of these Hammett results is that substantial positive charge is delocalized into the benzo ring during solvolysis of the *exo* epimer, but not the *endo*. An additional reference point against which to compare $\rho^+ = -3.3$ for *exo*-2-benzonorbornenyl brosylates (*exo*-**54-OBs**) is the acetolysis of the closely related series of 1-aryl-*endo*-2-norbornyl tosylates (**61**), in which the β-aryl ring cannot attain the correct *anti* conformation with respect to the *endo*-2 tosylate. This nonparticipating model correlates against the regular σ constants, with $\rho = -1.1$ (37), which is very close to $\rho = -1.3$ for the *endo*-2-benzonorbornenyl brosylates (99c) (*endo*-**54-OBs**).



(61)
$\rho = -1.1$[37]

The tertiary 2-methyl (**62**; R = CH_3) and 2-aryl (**62**; R = aryl) systems have been suggested as models for the steric behavior of aryl-unbridged benzonorbornenyl cations (101), on the assumption that π participation



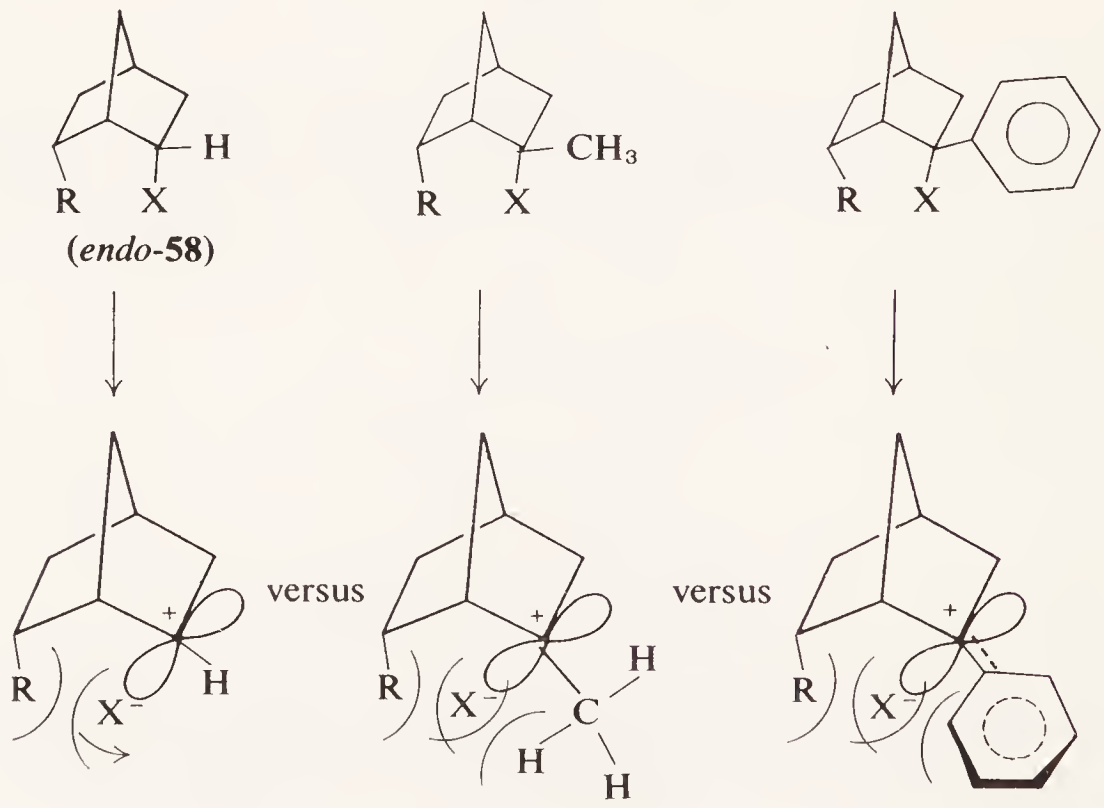
(62)

R(Y = H):	CH_3	C_6H_5
exo/endo:	6500	2900

by the benzo ring is diminished in the more stable tertiary carbonium systems. Yet both of these tertiary substrates also give relatively high *exo/endo* rate ratios: 6500 (100c,101d) for the 2-methyl derivative (**62**;

R = CH_3; Y = H) and 2900 for the 2-aryl derivative (**62**; R = C_6H_5; Y = H) (see also Table VII). These high rate ratios in the tertiary systems are reportedly (101) indicative of major transition state steric effects, and the consequent implication is that aryl participation is not needed to explain the *exo*/*endo* rate ratio of 15,000 for the parent secondary system (**54**; Y = H) (101). Ground state stability differences in the epimeric 2-methyl and 2-aryl derivatives do not appear to be the source of the observed *exo*/*endo* rate ratios for these tertiary systems, since equilibration data on the corresponding 2-methyl- and 2-arylnorbornanols show that both epimers of each derivative are of comparable stability (107c).

In fact, neither the 2-methyl nor the 2-aryl derivative is a suitable steric model for aryl-unassisted behavior in the parent secondary 2-benzonorbornenyl system (**54**). The 2-methyl derivative is an unsuitable model for two reasons. First, contrary to assumption (101) aryl participation cannot be ruled out in the *exo* epimer (*exo*-**62**-OPNB; R = CH_3). There is evidence that anchimeric assistance actually is still occurring in this tertiary substrate, although to a lesser extent than in the parent secondary compound (*exo*-**54**), as measured by substituent effects on the two systems. The rates (50% aqueous acetone; 125°) of the *exo* epimers of the 2-methyl system (*exo*-**62**-OPNB; R = CH_3) are correlated by the σ^+ constants, with a value of $\rho^+ = -1.9$ (see Yukawa-Tsuno values in Table II: $\rho = -1.1$; $r = 1.5$) (100c). Compared with $\rho^+ = -3.3$ (99b) for the parent secondary system (*exo*-**54**), the interaction of the aryl ring with the carbonium center is somewhat weaker in the 2-methyl derivative but still much stronger than in the related, *non*participating model secondary *endo* systems, which correlate against σ: *endo*-2-benzonorbornenyl brosylates [*endo*-**54-OBs**;

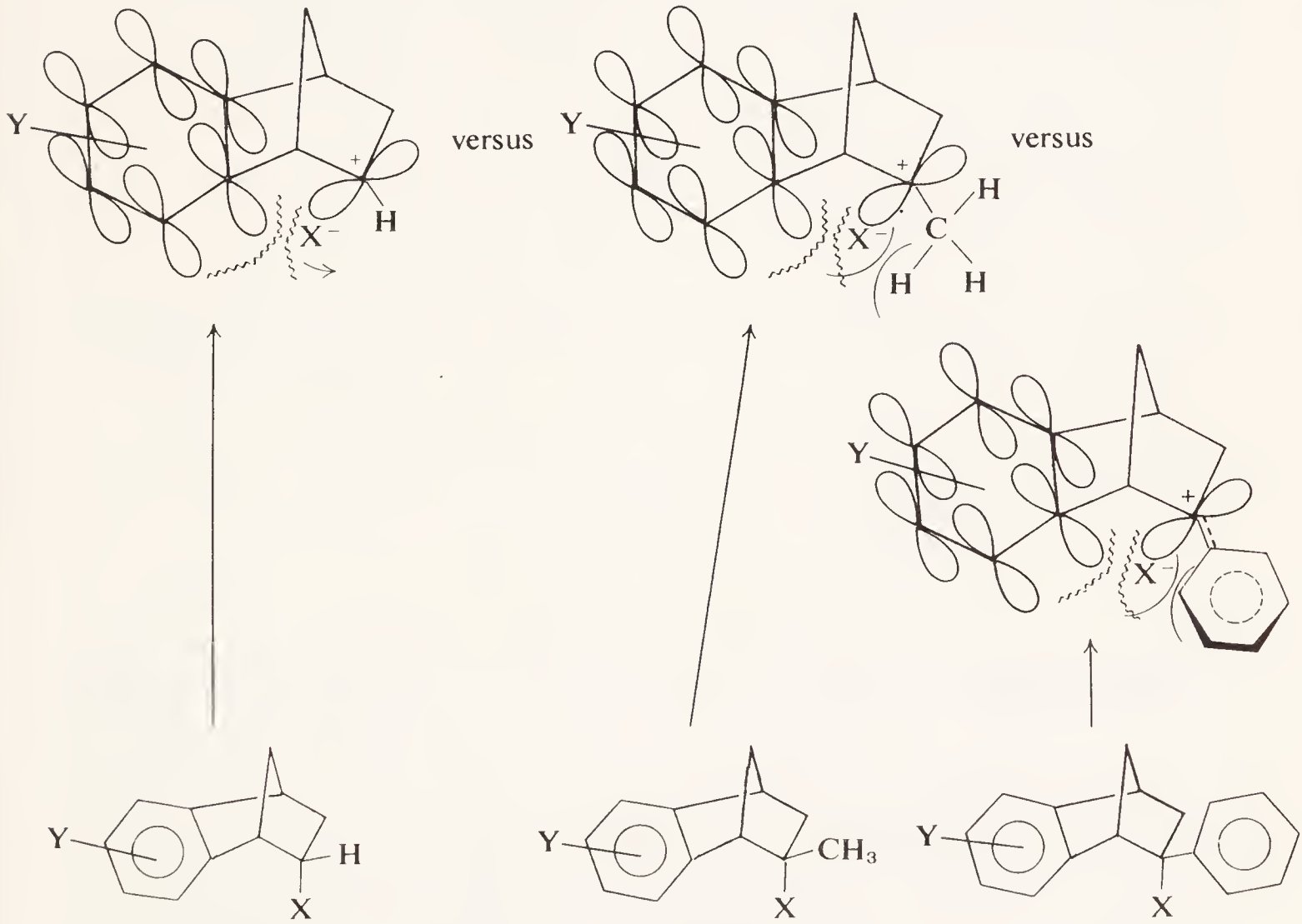


(*endo*-**58**)

$\rho = -1.3$ (99c)] and 1-aryl-*endo*-2-norbornyl tosylates [**61**; $\rho = -1.1$ (37)]. Second, it is possible that transition state steric effects (i.e., steric hindrance to *endo* ionization) are actually *worse* in the 2-methyl or 2-aryl derivatives of either the 2-benzonorbornenyl (**54**) or the 2-norbornyl (**58**) systems than in the corresponding parent secondary compounds. Any freedom of the departing *endo* leaving group to alleviate electrostatic (in **54**) or steric (in **58**) compressions by moving outward in the parent secondary compounds (*endo*-**54** or *endo*-**58**) could conceivably be greatly diminished by the presence of an *exo*-2-methyl substituent, and even more so by an *exo*-2-aryl group.

Since considerable π participation by the benzo ring apparently remains (100c) in the solvolysis of the 2-methyl-*exo* epimer (*exo*-**62**-OPNB; Y = H), the precise relative contributions of anchimeric and steric effects to the observed *exo*/*endo* rate ratio of 6500 (100,101) for this system cannot be established accurately at present. In the 2-aryl derivative (**62**; R = aryl), the contributions of steric and anchimeric effects can be estimated somewhat more reliably.

Benzylic stabilization of an aryl-unbridged carbonium ion by the 2-aryl group in the 2-benzonorbornenyl system is probably sufficient to reduce



(*endo*-**54**)
Y = H

(*endo*-**62**)
Y = H; R = CH_3

(*endo*-**62**)
Y = H; R = C_6H_5

sharply the extent of aryl participation by the benzo ring in the 2-aryl derivative (*exo*-**62**-OPNB; R = C_6H_5; Y = H). The Hammett behavior of this system, based on the available two-point data ($\rho^+ = -0.9$ versus σ^+; $\rho = -2.6$ versus σ) (100d), does not completely rule out the likelihood of benzo-ring participation; but a very weak, at best, interaction with the carbonium center (cf. $\rho^+ = -3.3$ for the secondary and $\rho^+ = -1.9$ for the tertiary 2-methyl substrates) is suggested. Consequently, a major fraction of the observed *exo*/*endo* rate ratio of 2900 for solvolysis of the 2-aryl system should most reasonably be attributed to the increased steric hindrance to ionization in the *endo* epimer caused by the 2-aryl group.

The overall conclusions from the combined data for the 2-benzonorbornenyl system and its tertiary derivatives are summarized in Chart 4. It is almost impossible to avoid the conclusion that β-aryl participation and phenonium ion intermediates (**57** or **57a**, **57b**) play a major role in the solvolysis of the parent *exo*-2-benzonorbornenyl system (*exo*-**54**; Y = H). This is one of the few systems in which a large body of data unanimously and overwhelmingly points to this conclusion.

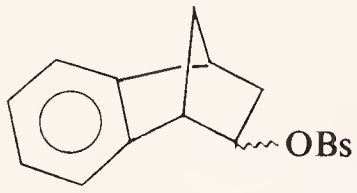
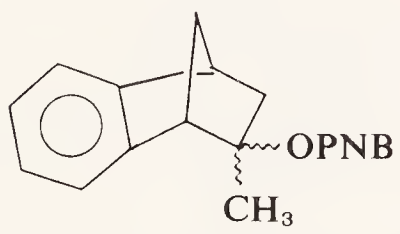
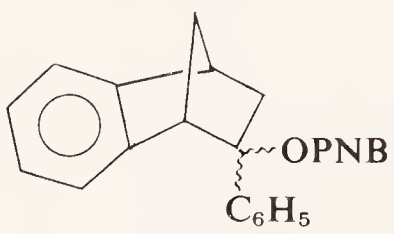
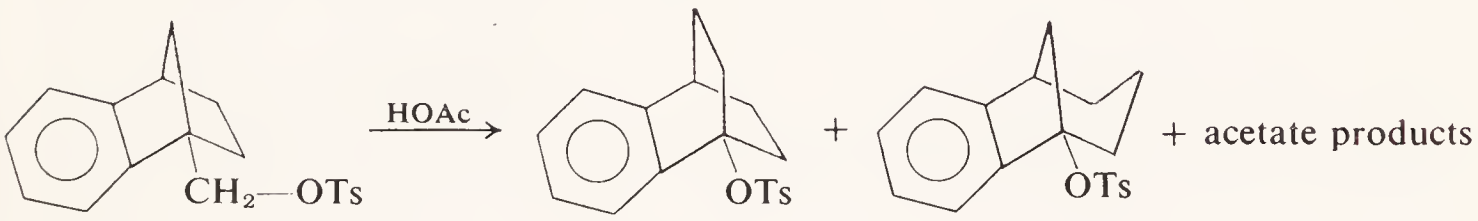
Substrate	k_{exo}/k_{endo}	Contribution to k_{exo}/k_{endo}
Parent secondary 2-benzonorbornenyl brosylates 	15,000	Steric: $\lesssim$10 Aryl participation in *exo*: $\gtrsim$1,500
Tertiary 2-methyl-2-benzonorbornenyl *p*-nitrobenzoates 	6500	Steric and *exo* anchimeric effects of comparable magnitude
Tertiary 2-aryl-2-benzonorbornenyl *p*-nitrobenzoates 	2900	Steric effects predominate; *exo* anchimeric assistance only minor at best

Chart 4. Summary of Solvolytic Behavior of 2-Benzonorbornenyl Systems.

d. Fused Benzopolycyclic Systems with the β-Phenyl Ring Conformationally Locked against Participation. The previous section showed the increased β-aryl participation attainable by locking the β-aryl ring into a conformation favorable for participation, where a more ideal overlap is possible between aryl π and carbonium *p* orbitals. Another type of study has directed attention to the behavior of systems that cannot possibly undergo β-aryl participation, at least not via the usual spirane transition state (and, sometimes, spiro-phenonium ion intermediate) formulated for typical participating systems. In the nonparticipating cases, the β-aryl ring is locked, usually in a rigid polycyclic framework, into the *least* favorable conformation with the *minimum* overlap between aryl π and carbonium *p* orbitals. The following brief review provides some examples.

During the course of a series of investigations into the neophyl rearrangement (see discussion of **19**; Section IV-A-3b), Wilt and co-workers obtained a measure of the inductive effect of a nonparticipating phenyl ring in a neophyl-type system (110). Models show that the phenyl ring in benzonorbornenyl-1-carbinyl tosylate (**63-OTs**) is oriented in the poorest conformation for overlap with the carbonium *p* orbital and cannot achieve the perpendicular conformation required for maximum overlap. The benzonorbornenyl-1-carbinyl system is indeed a neophyl system, with the β,β-dimethyl groups merely incorporated into the norbornenyl skeleton. Therefore, the conformational guarantee of a nonparticipating aryl moeity allows a measure to be taken of the purely inductive (and steric!) effect of the β-aryl group on the solvolysis of this particular neophyl-type system. Of course, it seldom happens that the inductive effect determined for this system may be used as an inductive indicator in other systems or solvents, as discussed in Section III-B.

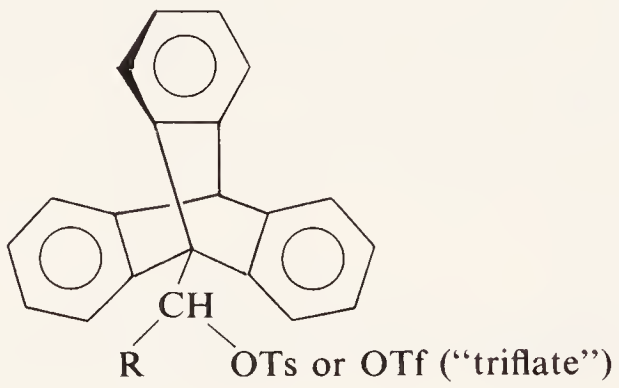


(63-OTs) **(64a)** **(64b)**

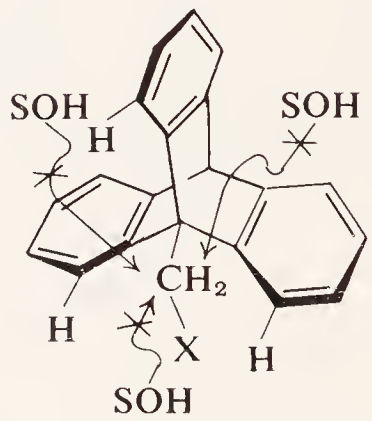
Acetolysis of **63-OTs** was complicated by ~20% return to a relatively inert bridgehead tosylate mixture (111) (**64a, 64b**) via alkyl migration processes. Nevertheless, the initial stage of the solvolysis was used to obtain the reported rate data. Acetolysis of benzonorbornenyl-1-carbinyl tosylate (**63-OTs**) proceeded 50 times slower than the nonaryl model norbornyl-1-carbinyl tosylate (110). An inductive retardation factor of 50 appears to be somewhat high for a β-phenyl ring—actually in this case a β-[*o*-alkylaryl] ring—in the solvolysis of a primary system. Normally,

aryl-unassisted (k_s) solvolyses of primary substrates are characterized by very low Hammett ρ values [~ -0.1 (39b), see Section IV-A-6], leading to very small inductive effects; this is due to the high degree of solvent assistance, essentially bimolecular solvent displacement, in the solvolysis of primary systems. But solvent assistance ought to be considerably diminished sterically in primary systems with quaternary β-carbon atoms, such as neopentyl, norbornyl-1-carbinyl, benzonorbornenyl-1-carbinyl (**63**), and neophyl (**19**). Consequently, the amount of carbonium ion character, and hence the ρ value and resulting inductive effects, would be increased in these systems. In any event, if the reasonable assumption is made that the inductive effects of all groups in the closely related neophyl (**19**) and benzonorbornenyl-1-carbinyl (**63**) systems are essentially similar, an estimate of the rate enhancement (k_t/k_s; see Section III-B) in the acetolysis of the parent neophyl system (**19**) due to β-phenyl participation is available. Neophyl tosylate (**19**) acetolyzes more than 800 times faster than the non-participating model (**63-OTs**; 133°). This large rate enhancement is in excellent agreement with the data presented in Section IV-A-3b, which showed the extent of β-aryl participation in the acetolysis of the neophyl system (**19**).

The cumulative effect of three β-aryl groups that are conformationally restricted from participation is especially interesting. Acetolysis of methyl-9-triptycylcarbinyl tosylate (**65-OTs**; R = CH_3) was immeasurably slow, even at high temperatures (112). The use of the much more reactive



(65)



(66)

trifluoromethanesulfonate ("triflate") leaving group gave rise to measurable acetolysis rates for the primary homolog (112). Assuming a triflate/tosylate ratio of 10^5, the acetolysis of 9-triptycylcarbinyl tosylate (**65-OTs**; R = H) is slower by a factor of 10^7–10^8 than either 1-bicyclo[2.2.2]-octylcarbinyl tosylate or neopentyl tosylate (112,113). This would correspond to an inductive retardation factor of about $10^{2.3}$–$10^{2.7}$ per aryl ring, which is clearly an unrealistically high number for a simple inductive effect in a primary β-arylalkyl system, or even a secondary unhindered

system (see Section III-B). There is little doubt that the inductive effect of the aryl rings in **65-OTs** (R = H) should be substantially stronger than in primary systems which are unhindered at the β-carbon atom; but close examination of **66** suggests an additional, unusual steric factor that may be important in the solvolysis of **65-OTs** (R = H). Solvent assistance (k_s) at the rear of the tosylate-bearing carbon is severely hindered by the aryl *ortho* hydrogens in all possible directions of attack. The "caging-in" effect of these hydrogen atoms and the consequent hindrance of solvent assistance, coupled with the inability of any of the aryl rings to participate in ionization because of their rigid, unfavorable orientation, raise the strong possibility that the acetolysis of 9-triptycylcarbinyl derivatives (**65**; R = H) may approach limiting carbonium ion character more closely than any other *primary* system examined to date. The prospect of approaching limiting behavior in a primary substrate makes the triptycylcarbinyl (**65**; R = H) and related systems extremely interesting candidates for further study. The full implications of limiting and nonlimiting solvolyses with regard to β-aryl participation are discussed in Section VII.

C. Kinetics and Rearrangements in Tertiary Systems

By far the greatest amount of attention in studies of β-arylalkyl systems has centered on primary (Section IV-A) and secondary (Section IV-B) systems. It has long been accepted that the inherent relative stability of most tertiary cations reduces the need for additional stabilization by neighboring-group participation (31,101). Therefore, relatively little attention has been paid to the solvolysis of tertiary β-arylalkyl systems. Their principal utility has been to serve as probable models for anchimerically unassisted behavior, as in Brown's critical evaluations of σ participation in the 2-norbornyl system (**58**) and π participation in the 2-benzonorbornenyl system (**54**).

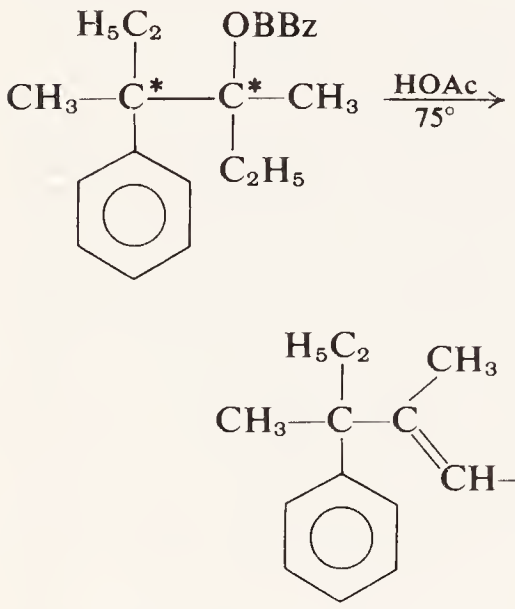
In this section, several acyclic tertiary β-arylalkyl systems are discussed. These substrates serve as calibration points against which to check the often dramatically contrasting behavior of the participating primary and secondary acyclic β-arylalkyl systems.

1. The 3,4-Dimethyl-4-Phenyl-3-hexyl System; Threo–Erythro Interconversions

In Cram's earliest reported work (1a–1e,2,20) concerning the question of phenonium ions as discrete intermediates in the solvolysis of the 3-phenyl-2-butyl (**2**) and related systems, one of the more important pieces of stereochemical evidence cited in support of bridged intermediates was that there was little or no diastereomeric interconversion depending on the solvent in the solvolysis of either the *threo* or *erythro* isomer of the

starting sulfonate ester (see Chart 1a). This characteristic feature is largely lost in the acetolysis and formolysis of the homologous acyclic tertiary system.

In an investigation supported by careful and thorough classical pre-glc product analyses, the solvolyses of the *threo* and *erythro* diastereomers of the tertiary 3,4-dimethyl-4-phenyl-3-hexyl *p*-bromobenzoate esters (**67-OBBz**) were reported (114a). Unlike the solvolysis of the secondary 3-phenyl-2-butyl sulfonates (**2**), which produced primarily acetate and formate ester products along with olefin mixtures, the acetolysis and formolysis of the tertiary 3,4-dimethyl-4-phenyl-3-hexyl system (**67-OBBz**) gave only olefins and no detectable ester products. Equilibration of the olefins under the formolysis conditions and experimental difficulties with product analysis led to less satisfactory results and conclusions in this solvent than in acetic acid. Consequently, only acetolysis data are discussed here. Chart 5 tabulates the acetolysis results for *threo*- (**67a**) and *erythro*-3,4-dimethyl-4-phenyl-3-hexyl (**67b**) *p*-bromobenzoates (114).



threo (**67a-OBBz**): ~68% ~26% 6%

26% racemic; 74% active

erythro (**67b-OBBz**): ~63% ~31% 6%

18% racemic; 82% active

Chart 5. Acetolysis of Diastereomers of 3,4-dimethyl-4-phenyl-3-hexyl *p*-Bromobenzoates.

The most striking differences between the behavior of the tertiary and secondary (3-phenyl-2-butyl) systems are, first, that the optically active *threo* tertiary starting material (**67a-OBBz**) acetolyzes *without* the predominant racemization that characterized the acetolysis of the secondary *threo*-3-phenyl-2-butyl system (**2a**) (see Chart 1a). Instead, the active *threo*

tertiary system gives three times as much optically active as racemic product, exclusive of the minor amount of methyl-migration product found. Clearly, a *meso* phenonium ion (or equivalent set of rapidly equilibrating enantiomeric unbridged or weakly bridged ions) cannot be involved as the product-controlling intermediate in the acetolysis of the tertiary *threo* substrate (**67a-OBBz**).

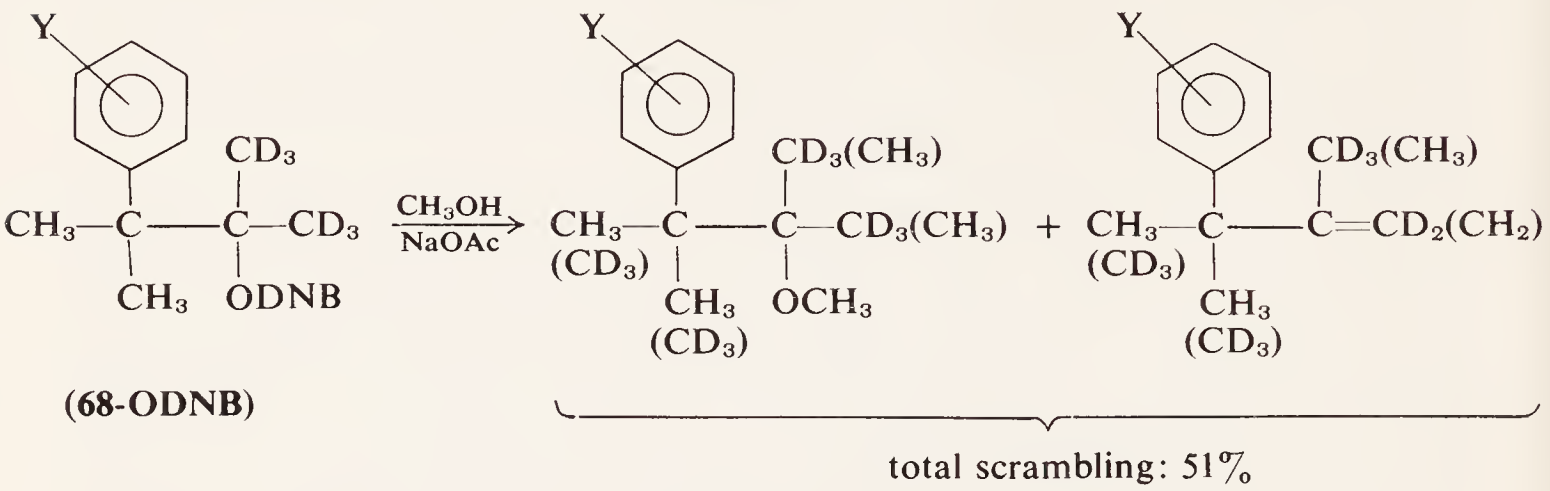
Second, both the *threo* (**67a-OBBz**) and *erythro* (**67b-OBBz**) diastereomers of the tertiary system gave the same three products in similar relative quantities and with similar stereochemistry. This suggests substantial mixing, or crossover, of the intermediate ion pairs derived from either diastereomer. Finally, extensive ($\sim 18\%$) racemization accompanied the acetolysis of the *erythro* tertiary diasteromer (**67b-OBBz**).

The results for the tertiary system (**67-OBBz**) were originally explained (114a) in terms of a combination of nonstereospecific processes, involving primarily aryl-unbridged ion pairs as elimination intermediates, and stereospecific processes (e.g., racemization of *threo*), possibly involving phenonium ion intermediates to some degree. The original report (114) clearly pointed out that no evidence in this data *required* the intermediacy of bridged ions, but neither was there any evidence to rule them out positively as intermediates between the enantiomeric and/or diastereomeric aryl-unbridged ion pairs.

The principal evidence for phenyl rearrangement in either diastereomer of the tertiary system (**67-OBBz**) was the observed racemization (114a). This must represent a lower limit, since the available data (114a), in the absence of C_α–C_β scrambling information, do not permit us to estimate the *total* amount of phenyl migration that may have occurred during the solvolysis of either diastereomer. Aryl migration in the *erythro* series cannot be detected stereochemically because a migration or bridging process will generate the same ion pair enantiomer again (cf. *erythro*-3-phenyl-2-butyl, **2b**, in Section I). The same is true in the *threo* system (**67a-OBBz**) if appreciable crossover into the *erythro* series (**67b**) occurred; in this case the *threo* racemization mechanism, involving a *meso* bridged ion or equivalent set of enantiomeric, unbridged ions, would no longer be available.

Actually, there is good reason to believe that considerable phenyl migration did occur in the reaction of the tertiary systems, over and above that suggested by the degree of racemization observed for the *threo* diastereomer (**67a-OBBz**). For example, buffered methanolysis of the closely related 3,4-dimethyl-3-phenyl-2-butyl dinitrobenzoates (**68-ODNB**; Y = H) resulted in a total of 51% C_α–C_β equilibration in both the ether and olefinic products, as measured by α,α-$(CD_3)_2$ label scrambling (23). At least as much, and probably considerably more, scrambling should

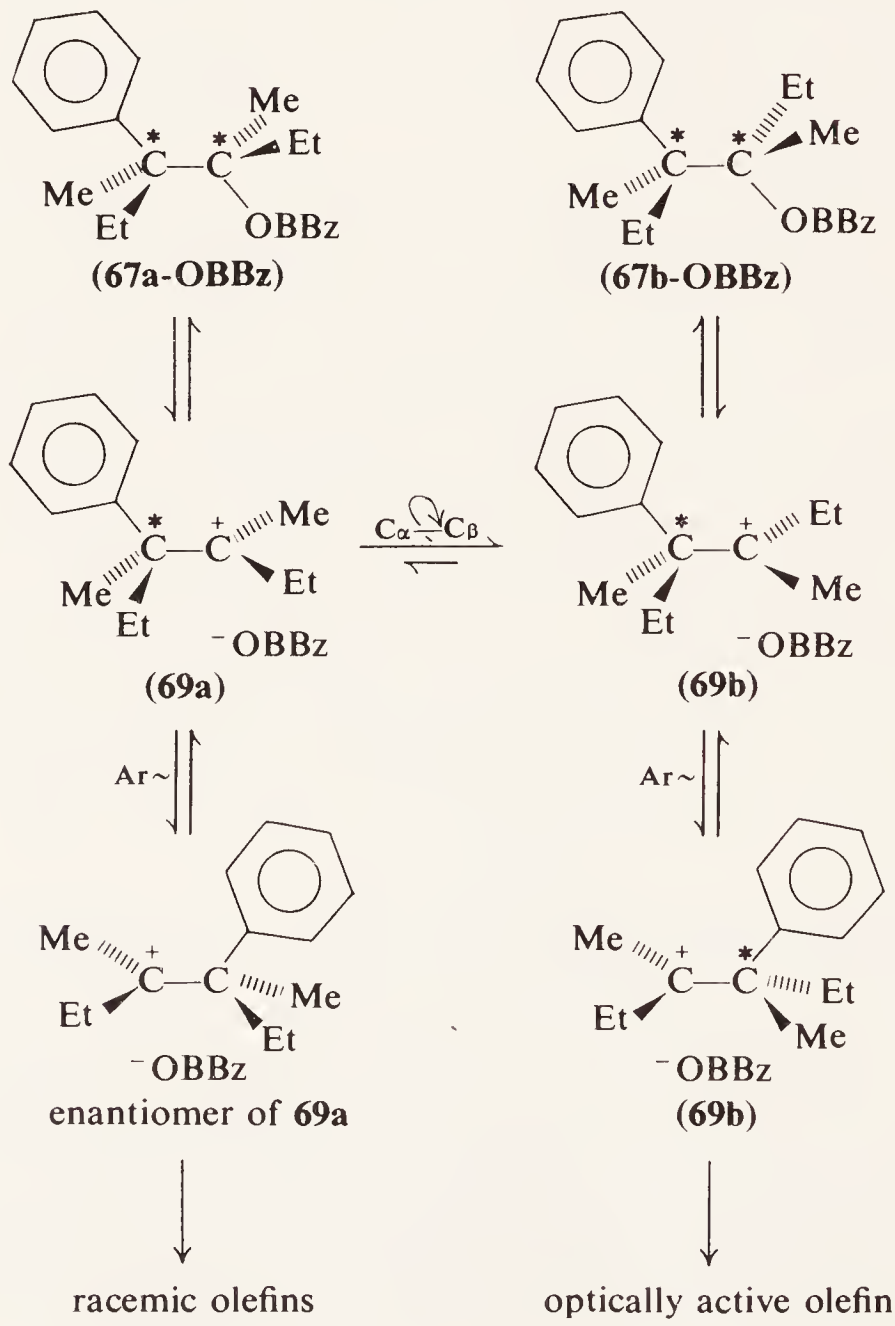
occur in the less nucleophilic solvent, acetic acid, during the acetolysis of the homologous 3,4-dimethyl-4-phenyl-3-hexyl derivatives (**67-OBBz**).



(68-ODNB)

total scrambling: 51%

The most reasonable way of reconciling the high probable amount of aryl migration in the acetolysis of *threo*-**67a-OBBz** with the relatively small degree of racemization observed (114a) (~26%) is to assume a mechanism involving largely aryl-unbridged (or very weakly bridged) ion pairs, which rotate about the C_α–C_β axis and cross over to give



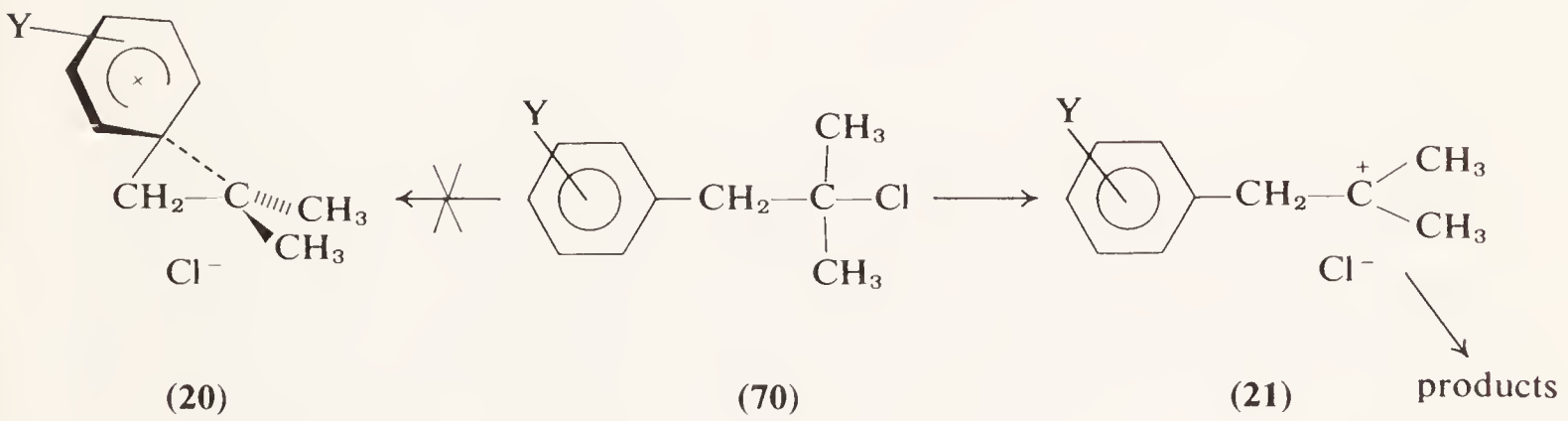
erythro-derived ion pairs at least three times as fast as they undergo aryl migration to give enantiomeric ion pairs (i.e., racemization). In this mechanistic scheme, *threo* material (**67a-OBBz**) ionizes with little or no aryl participation to give essentially an unbridged tertiary ion pair (**69a**), which still maintains optical activity at at least one center. About 75% leakage of these ion pairs to optically active *erythro*-derived conformers (**69b**), followed by extensive phenyl equilibration, would account for the observed retention of optical activity and still permit aryl migration.

The most probable reason for this preference for *erythro*-derived ion pairs (**69b**) over *threo*-derived conformers (**69a**) is the reduction in torsional strain obtained by relief of the partial ethyl–ethyl eclipsing present in the *threo*-derived conformer (**69a**).

Bridged phenonium ions have not been included in the mechanistic scheme as phenyl migration intermediates. The available evidence does not require the intervention of such bridged ions, but their presence as energy minima, though unlikely, cannot be ruled out either. However, the principal conclusion emerges that aryl-*unbridged* ion pairs can best explain the behavior of tertiary β-arylalkyl systems (114a). An exact quantitative description of the various processes involved in the acetolysis of the 3,4-dimethyl-4-phenyl-3-hexyl system (**67**) must await the appropriate label-scrambling data for this particular substrate.

2. The Unsymmetrical 1-Aryl-2-Methyl-2-Propyl System; Substituent Effects on a Tertiary Nonparticipating System

The 1-aryl-2-methyl-2-propyl system (**70**) is potentially the precursor of the same bridged ion (**20**) generated by solvolysis and rearrangement of neophyl tosylates (**19**; Sections IV-A-3-b and IV-B-3-d). In the tertiary system **70**, there is an enormous electronic bias against aryl participation or migration, because positive charge would be distributed from the incipient, relatively stable tertiary carbonium center to the far less stable primary one. Solvolysis of 1-aryl-2-methyl-2-propyl derivatives (**70**) should show little if any evidence of charge delocalization into the β-aryl ring.



(20) **(70)** **(21)**

In agreement with prediction, the rate constants (aqueous ethanol) of a series of ring-substituted 1-aryl-2-methyl-2-propyl chlorides (**70**; Y = *p*-Br, *p*-Cl, *p*-F, H, *p*-Me, *p*-Et, *p*-*i*-Pr) were well correlated with the regular Hammett σ constants with a value of $\rho = -1.11$ (115) (see Table II). Brown (23) reported a ρ value of -0.65 for ethanolysis of **70**, using a series of four activating substituents (**70**; Y = H, *m*,*p*-Me, *p*-MeO). A combination of Brown's data (23), together with those from a later study by Vander Werf (115b) using substrates with deactivating *meta* substituents, gives a composite value of $\rho = -0.93$ over a broader, more reliable range of substituents (116).

The observed ρ value of ~ -1 for this nonparticipating tertiary system (**70**) is very close to that determined for the nonparticipating secondary systems, *endo*-2-benzonorbornenyl brosylates [*endo*-**54-OBs**; $\rho = -1.3$ (99c)] and 1-aryl-*endo*-2-norbornyl tosylates [**61**; $\rho = -1.1$ (37)]. The ρ_s values determined for the anchimerically unassisted (k_s) pathway in a number of partially assisted solvolyses are all very similar also, in the range -0.7 to -1.5 (Table II). The only significantly deviating value is found for the anchimerically unassisted (k_s) solvolysis of *primary* β-arylalkyl systems, and this is extremely small by comparison—only -0.1. These relative σ values suggest similar carbonium ion character in the simple solvolysis of secondary and tertiary systems, and much less carbonium ion character with primary systems. The significance of this observation is discussed in detail in Section VII.

An analysis of the methanolysis products of 1-phenyl-2-methyl-2-propyl chloride (**70**; Y = H) under a wide variety of conditions produced no evidence of any phenyl involvement in terms either of participation or rearrangement (117). The data indicated that solvolysis proceeds primarily in a unimolecular fashion (S_N1 and $E1$) via the tertiary cation (**21**) to give the expected unrearranged substitution product and olefins, the same products as from the solvolysis of the isomeric neophyl system (**19**; see Sections IV-A-3-b and VI-B-3-d), but in different relative amounts because of the different conditions. The $E2$ elimination mechanism apparently became important in the presence of added bases (117).

3. The Symmetrical 2,3-Dimethyl-3-Aryl-2-Butyl System; A Large Rate-Product Discrepancy

Cram's study (114) of the 3,4-dimethyl-4-phenyl-3-hexyl system (**67**) first suggested that phenyl participation and bridged phenonium ion intermediates might not be involved in the solvolysis of symmetrical tertiary acyclic systems. If this were the case, one might expect to find extensive C_α–C_β equilibration *in the absence of major rate effects* in symmetrical tertiary systems undergoing aryl migration. Only one symmetrical tertiary

acyclic system has been subjected to a detailed examination both of the rates and the products of solvolysis, and the results are fully in accord with this prediction.

Brown and Kim examined the behavior of the 2,3-dimethyl-3-aryl-2-butyl system (**68**) in a variety of carbonium ion reactions (23). A plot of the ethanolysis rates of a series of ring-substituted derivatives (**68-Cl**; Y = H, *m*,*p*-CH_3, *p*-CH_3O) versus the regular Hammett σ constants displays an upward curvature typical of systems in which partial aryl participation increases with more activated aryl groups (4,36,38,39) (see Section III-B). The lack of data for deactivating substituents makes the precise magnitude of the deviations (k_Δ) for the participating substrates uncertain; but an estimate of the rate enhancement k_t/k_s for the activated *p*-anisyl derivative (**68-Cl**; Y = *p*-OCH_3) amounts merely to a factor of $\sim$2 relative to the aryl-unassisted rate (k_s) obtained by extrapolation to Brown's (23) crude ρ_s line. The entire range of reactivities observed, only a factor of $k_{CH_3O}/k_H = 8$, indicates at best a weak interaction between the aryl ring and the carbonium center, and even so only in the more activated derivatives. These data correspond to a crude two-point overall ρ value of ~ -3 (versus σ), or a ρ^+ of ~ -1 (versus σ^+), which is comparable to $\rho = -2.6$ or $\rho^+ = -0.9$ for the weakly participating 2-aryl-*exo*-2-benzonorbornenyl system (*exo*-**62**; R = C_6H_5).

In spite of the truly minor kinetic effects observed in the solvolysis of the 2,3-dimethyl-3-aryl-2-butyl chlorides (**68-Cl**), the product distributions in a large number of reaction types indicate variously high degrees of aryl rearrangement. In most of the carbonium ion reactions of **68** that were examined, very substantial C_α–C_β equilibration had occurred, as measured by α,α-$(CD_3)_2$ scrambling (23). More specifically, all but three reactions of the *p*-anisyl derivative resulted in *complete scrambling*. Methanolysis of this derivative (rate enhancement, $k_t/k_s \sim 2$) gave completely scrambled ether plus completely scrambled olefin. The parent, unsubstituted derivative (**68-ODNB**; Y = H), which shows no evidence of any rate enhancement at all on the basis of the available data (23), underwent methanolysis with 51% scrambling!

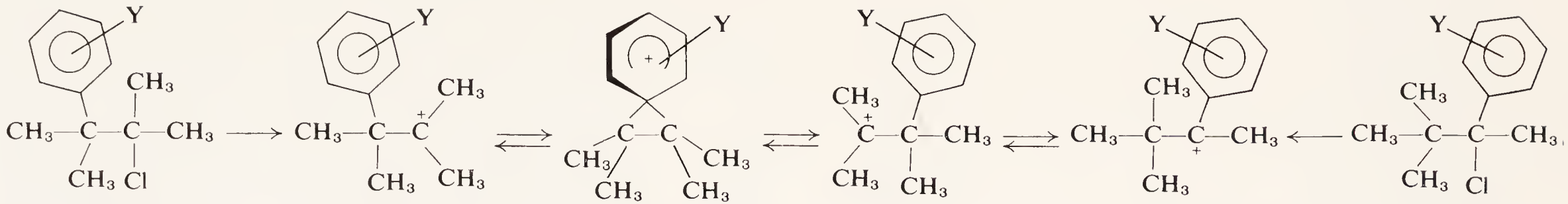
Clearly, there is a genuine, unambiguous rate-product discrepancy here. The kinetic data indicate very weak aryl participation, in accord with prediction for tertiary systems (31), but very extensive or complete aryl migration has occurred. These results argue strongly in favor of the intermediacy of a dynamic pair of rapidly equilibrating unbridged or very weakly bridged ion pairs, formed with little or no aryl participation in the ionization transition state. This conclusion is basically in agreement with that reported by Cram (114) in the initial studies with symmetrical, acyclic tertiary systems.

An interesting series of experiments in superacid media (70) has been reported for the 2,3-dimethyl-3-aryl-2-butyl system (**68**) (118a). Although no evidence was found for more than very weak aryl bridging in this substrate in the usual solvolysis media (23), the use of very strongly ionizing, very poorly nucleophilic solvents led to considerably different results. Under these conditions, where stable, long-lived carbonium ions are not trapped nucleophilically and can be observed directly by spectroscopic methods, thermodynamic factors prevail and the most stable cation usually will be formed, provided a rearrangement mechanism is available. (For a full discussion of the chemistry of stable carbonium ions in superacids, see Ref. 70b.)

A series of ring-substituted 2,3-dimethyl-3-aryl-2-butyl chlorides (**68-Cl**; Y = *p*-CF_3, H, *p*-CH_3, *p*-CH_3O) and the isomeric 3,3-dimethyl-2-aryl-2-butyl chlorides (**71-Cl**; Y = same) were ionized at $-78°$ in the extremely strong Lewis acid system, SbF_5–SO_2. For a given aryl group, both isomers (**68-Cl** and **71-Cl**) ionized to the same ion or mixture of ions, as shown by the identical nmr spectra. Both the spectra and the products from methanol quenching for each pair of isomers showed that the composition of the carbonium ion mixture at equilibrium ($-78°$) was very sensitive to the nature of the aryl ring. The data and conclusions are summarized in Chart 6.

The compositions of the carbonium ion mixtures summarized in Chart 6 were established by detailed interpretation of the observed pmr spectra and comparison with the spectra of appropriate model carbonium ion systems.* The principal feature of the results is that the same ion or mixture of ions is formed from either one of the isomeric tertiary precursors. This shows that the observed ion or ions are the most stable for each particular

* NOTE ADDED IN PROOF. While this chapter was in press a refined reexamination of some of the compounds in series **68-Cl** and **71-Cl** was reported by Olah (118c), employing the more sensitive ^{13}C nmr probe. Although the major trends and conclusions of the earlier work (118a) remain essentially unaltered, some specific aspects were revised. For example, reinterpretation of the spectra of the ions generated from the *p*-tolyl derivative (**68-Cl**; Y = *p*-CH_3) in the light of the new ^{13}C nmr data as well as data obtained on ions frozen out on the nmr time scale at very low temperatures suggest that the methyl-equilibrating benzylic ion (**72**; Y = *p*-CH_3) is the only ion present *in appreciable concentrations* at equilibrium (119), rather than the previously reported mixture of benzylic and phenonium ions (118a). Also, for the *p*-CF_3 derivative, the combined data are said to be more consistent (118c) with the phenonium ion (**73**; Y = *p*-CF_3) as the only ion present *in appreciable concentrations* at equilibrium, rather than the previously reported (118a) mixture of open, isomeric β-arylalkyl ions (**73a**, **73b**; Y = *p*-CF_3). However, the presence of *all* pertinent ions, fully aryl-bridged, partially bridged, unbridged, and benzylic, is acknowledged as best accounting for the observed labile isomer interconversions (118c) as well as the quenching data (118a).



(68-Cl) Y	(73a) % [a]	(73) % [a]	(73b) % [a]	(72) % [a]	(71-Cl) Y
p-CH_3O	~0	~2	~0	~98	*p*-CH_3O
p-CH_3	~0	~60*	~0	~40*	*p*-CH_3
H	~0	>90[b]	~0	<10	H
p-CF_3	~50†	~0†	~50†	~0	*p*-CF_3

Chart 6. Ionization of 2,3-Dimethyl-3-aryl-2-butyl and 3,3-Dimethyl-2-aryl-2-butyl Chlorides in Antimony Pentafluoride–Sulfur Dioxide

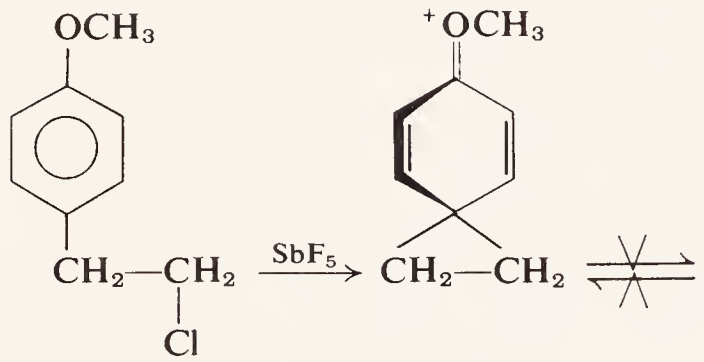
[a] As measured by quantitative analysis of nmr spectra and methanol quenching products.

[b] Possibly an equilibrating mixture of unsymmetrically bridged ions; available evidence (118a), e.g., aromatic deshielding patterns, was interpreted in terms of the symmetrically bridged ion structure (**73**).

* See note added in proof. Reexamination suggests the presence of the benzylic ion (**72**; **Y** = *p*-$\mathbf{CH_3}$) as the major component at equilibrium (118c).

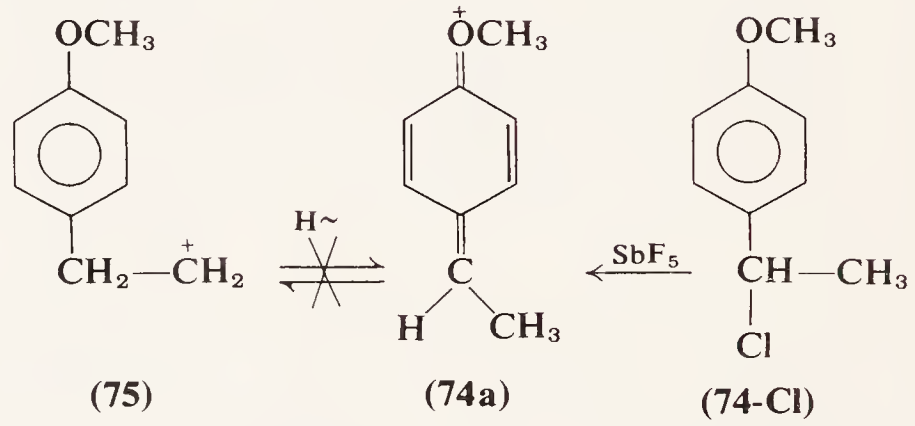
† See note added in proof. Reexamination suggests the presence of the phenonium ion (**73**; **Y** = *p*-$\mathbf{CF_3}$) as the major component at equilibrium (118c).

aryl system. These results contrast with the behavior of the *primary* β-*p*-anisylethyl system (70a), where ionization of β-*p*-anisylethyl chloride (**11-Cl**; Ar = *p*-CH_3O–C_6H_4–) in SbF_5 gave the symmetrically bridged phenonium ion (**12**; Ar = *p*-CH_3O–C_6H_4–), and ionization of the isomeric α-*p*-anisylethyl chloride (**74-Cl**; Ar = *p*-CH_3O–C_6H_4–) gave the corresponding benzylic ion, the two ions being *non*interconvertible.



(11-Cl) Ar = *p*-anisyl

(12) Ar = *p*-anisyl



(75) **(74a)** **(74-Cl)** Ar = *p*-anisyl

The phenonium ion–benzylic ion equilibration must occur via the open β-arylalkyl cation (**73a**, **73b**, **75**) or some form of partially, unsymmetrically bridged species. (See reference 118c and Note added in proof.) This explains the difference in behavior between the tertiary systems (**68-Cl**; **71-Cl**) and the *p*-anisylethyl derivatives (**11-Cl**; **74-Cl**). The relatively stable *tertiary* β-arylalkyl cation (**73a**, **73b**) is readily obtainable in the superacid solvent; but even this highly ionizing medium cannot generate the required high-energy (79) *primary* β-*p*-anisylethyl cation [**75**; ca. 30 kcal less stable than typical tertiary cations (79)] that would permit equilibration between the α-*p*-anisylethyl cation (**74a**) and the ethylene-*p*-anisonium ion (**12**) (120).*

* Very recently reported results with the parent α- and β-phenylethyl systems (**11-Cl**; **74-OH**; Ar = C_6H_5–) confirm the absence of equilibration between the phenonium ion and benzylic ion in primary β-arylalkyl systems (118b). Ionization of β-phenylethyl choride (**11-Cl**; Ar = C_6H_5–) in SbF_5–FSO_2Cl (−78°) does give about 25–33% of the rearranged α-styryl cation in addition to the phenonium ion; but this undoubtedly is attributable to competitive hydrogen *participation* in the ionization process, rather than to a thermodynamic rearrangement involving open β-phenylethyl cations. Complementing this result is the exclusive formation of the α-styryl cation by

The trend in relative populations of the various possible carbonium ions in the tertiary system (**68**, **71**) as the ring substituent is varied (Chart 6) can be illustrated by the energy diagram of Figure 3. The open β-arylalkyl cations (**73a**, **73b**) are least affected by ring substituents (inductive and field effects only).

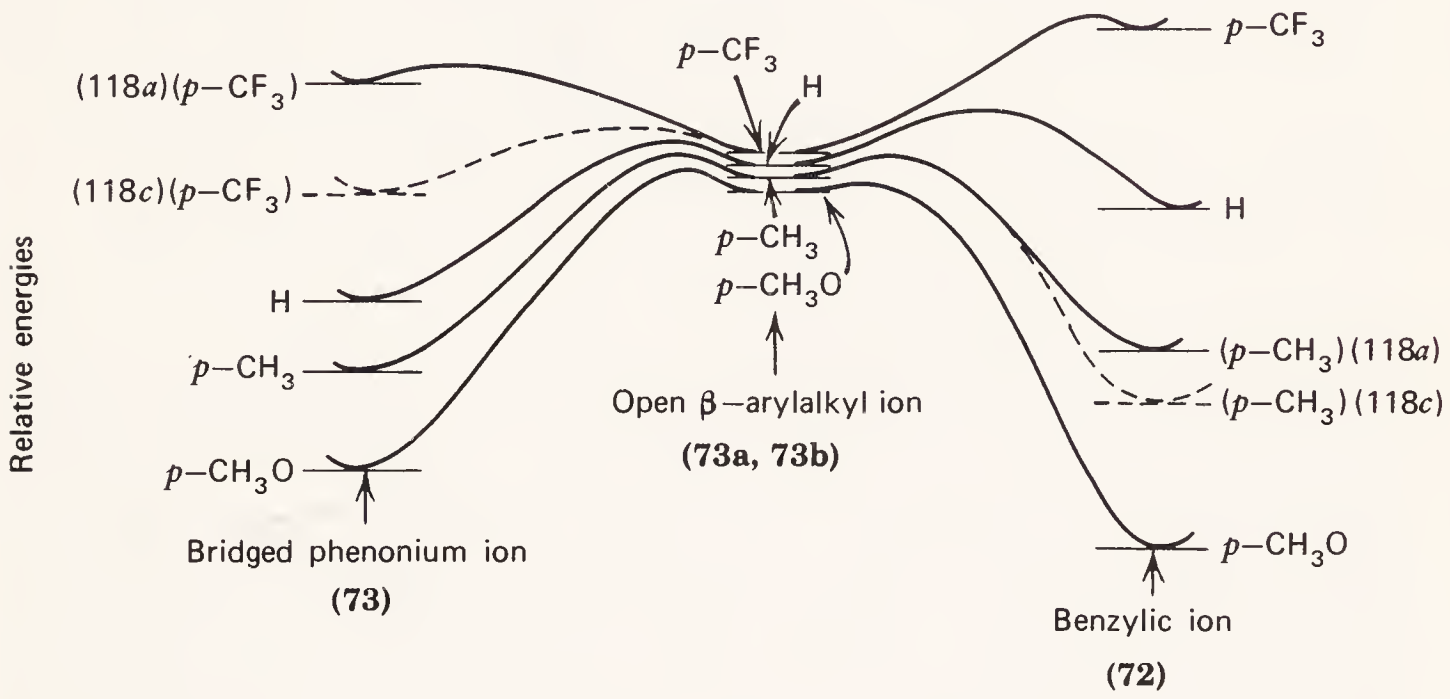


Fig. 3. Relative energies of carbonium ions in the 2,3-dimethyl-3-aryl-2-butyl and 3,3-dimethyl-2-aryl-2-butyl systems (118), in SbF_5–SO_2 medium.

Resonance effects cause the energies of the bridged phenonium ions (**73**) and benzylic ions (**72**) to be much more substituent dependent. In turn, the relative effects of substituents on these ions are governed to an extent by partial delocalization of the positive charge to the cyclopropane carbons in the bridged ions (**73**) on the one hand, and by steric hindrance of resonance in the benzylic cations (**72**) on the other.

The observed equilibrium data for the tertiary series (**68** and **71**) imply that substituent effects and, consequently, energy differences, are greater in the benzylic cations (**72**; Chart 6) than in the phenonium ions (**73**; Chart 6; cf. Fig. 3), although this would not easily have been predictable beforehand. The only aryl group with which there was apparently a predominant concentration of the phenonium ion at equilibrium was the parent phenyl group (**68-Cl**; **71-Cl**; Y = H), and posssibly also the *p*-trifluorotolyl group, as indicated by the recent reexamination (118c). The

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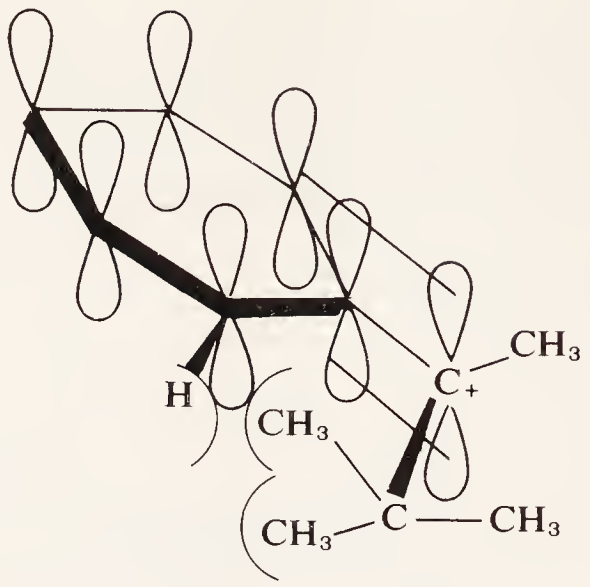
ionization of α-phenylethyl alcohol (**74-OH**; Ar = C_6H_5–). The only possible rearrangement route to the phenonium ion from this precursor *would* involve an open β-phenylethyl cation intermediate, and no phenonium ion is observed.



(72)

assignment of the observed nmr spectrum to that of the static, symmetrical, σ-bridged phenonium ion (**73**; Y = H) was primarily based on the aryl and methyl deshielding patterns; but the evidence, in our opinion, does not *conclusively* rule out the alternative assignment of the spectrum to a pair of equilibrating, unsymmetrically bridged cations, intermediate between **73** and **73a** and **73b**.* This alternative was considered (118a) as a possible explanation for the observed reduction in deshielding of the aromatic protons in the spectrum of the 2,3-dimethyl-3-phenyl-2-butyl cation relative to the model *t*-cumyl cation; however, it was rejected (118a) in favor of the symmetrical phenonium ion, with the reduced positive charge on the aryl group accounted for by the postulated partial delocalization of the charge to the spirocyclopropyl ring (118a). Support for this explanation was claimed (118a) on the basis of comparative data from the spectrum of the ethylene-*p*-anisonium ion (**12**). The aromatic protons of this primary-derived ion are even *less* deshielded than those of the cation derived from the tertiary system; and open or unsymmetrical, partially bridged ions were either ruled out (70a) or are unlikely in the primary system (118a).

This is a somewhat tenuous comparison. It is also very likely that the relative shielding of the aromatic protons in the ethylene-*p*-anisonium ion (**12**) could simply be due to distribution of a substantial fraction of the positive charge from the aryl ring to the methoxyl oxygen atom. This is supported by more recent measurements on the parent ethylene phenonium ion (**12**; Ar = C_6H_5), in which the aromatic protons are deshielded by about *1 full ppm* relative to either the tertiary 2,3-dimethyl-3-phenyl-2-butyl system or to the substituted primary β-anisylethyl system (118b).

The formulation of a rapidly equilibrating pair of unsymmetrically bridged ions instead of a static, symmetrically σ-bridged ion (**73**; Y = H) in the parent 2,3-dimethyl-3-phenyl-2-butyl system (**68**) appears more

* See, however, the further arguments presented in Ref. 118c.

attractive to us for two reasons. First, the continuity in the trends apparent in Chart 6 becomes somewhat more logical if we assume increasing "leakage" of bridged to partially bridged to nonbridged ions in going from the *p*-tolyl to the *p*-trifluorotolyl systems. The relative energy picture in Figure 3 is not altered to any great extent by this modification. Second, and more important, a smoother continuity with Brown's solvolytic results (23) for the parent tertiary phenyl system (**68-Cl** or **-ODNB**; Y = H) is achieved by the alternative formulation of equilibrating, unsymmetrically bridged cations for this system in the superacid medium.

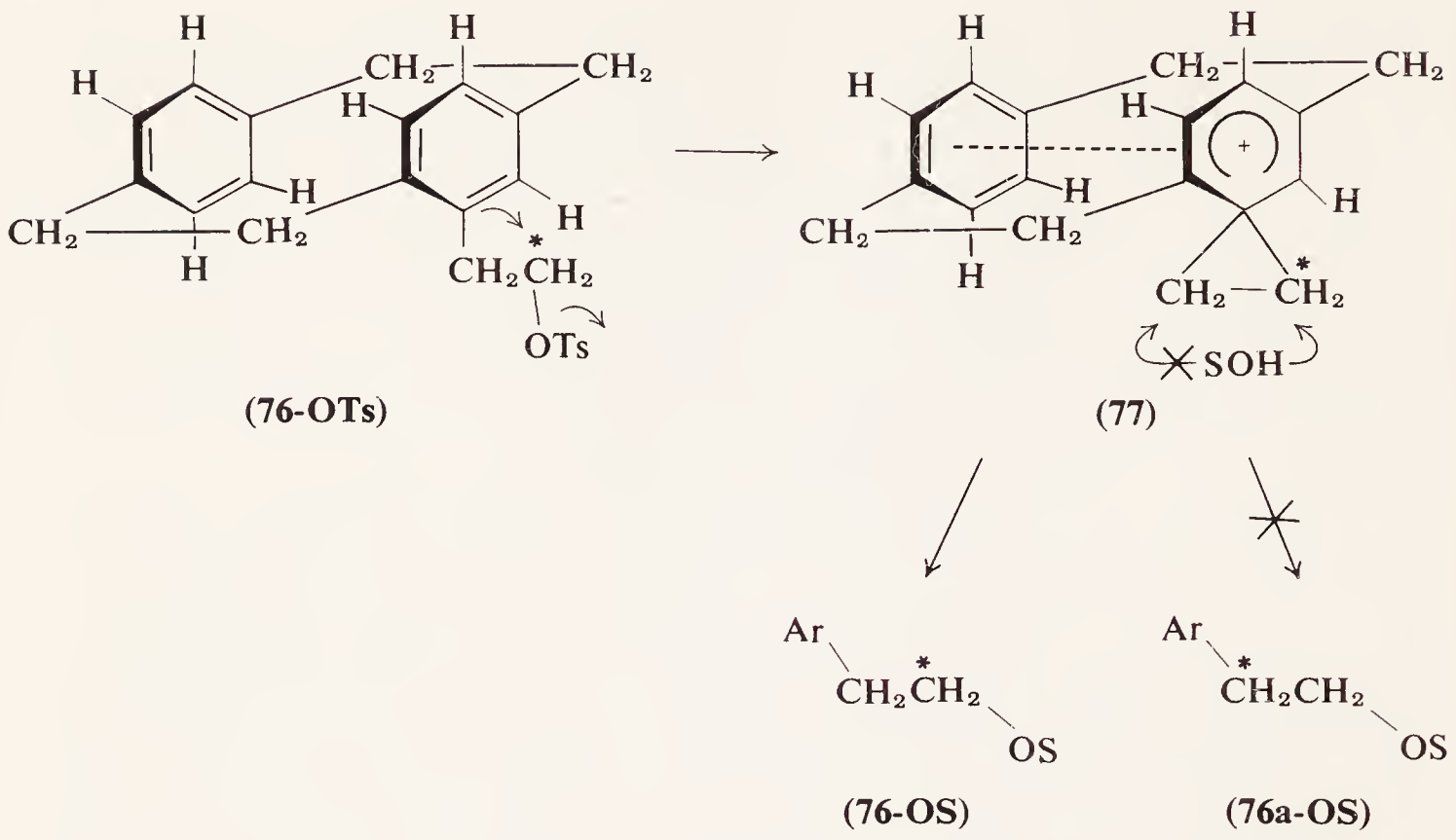
The parent 2,3-dimethyl-3-phenyl-2-butyl system (**68-Cl** or **-ODNB**; Y = H) solvolyzed with extensive (51%) phenyl rearrangement but without any indication of significant phenyl participation or of the intermediacy of any but the most weakly, unsymmetrically bridged ions (23). Tertiary systems, e.g., **68**, are the *least* susceptible to solvent (or neighboring-group) nucleophilicity in solvolysis reactions. (See the fuller discussions on structure and mechanism in Sections V and VII.) Therefore, reduction in solvent nucleophilicity in going from the usual solvolysis solvents to the nonnucleophilic superacid solvents (118) should not appreciably increase the demand for nucleophilic aryl participation or aryl bridging in *tertiary* β-arylalkyl systems, and those tertiary compounds which solvolyze without evidence of significant aryl bridging are not expected to undergo much additional aryl bridging in the strong acid solvents. The only major effect of the nonnucleophilic, highly ionizing medium in such cases is to permit essentially indefinite equilibration between the isomeric open or weakly bridged cations in the absence of any ion-capture processes.

D. The Paracyclophane Group; Consequences of a Three-Dimensional β-Aryl Group

Participation, bridging, migration, or rapid equilibration of planar aryl groups gives rise to rearrangement, scrambling, retention of configuration, or racemization, to various degrees depending on the system and the conditions. When a three-dimensional β-aryl group is present in a β-arylalkyl system, the stereochemical results can be strikingly different. The three-dimensional paracyclophane (PCP) group, extensively studied by Cram (50a,122) is an example.

Kinetic evidence suggests that the acetolysis and formolysis of β-paracyclophanylethyl tosylate (**76-OTs**) are anchimerically assisted. Table VIII shows that acetolysis of β-paracyclophanylethyl tosylate (**76-OTs**) proceeds 18 times faster than the parent β-phenylethyl tosylate (**11**).* Although formolysis rates were not measured (50a), it appears

* If the acetolysis rate of β-paracyclophanylethyl tosylate **76-OTs** is compared with the calculated (39b) aryl-unassisted rate (k_s) for β-phenylethyl tosylate (**11**; Ar = C_6H_5–; $k_s \sim 0.6k_t$), the rate enhancement for **76-OTs** becomes a factor of 30.

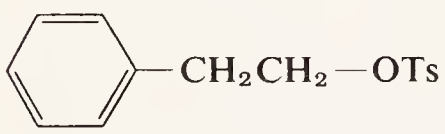
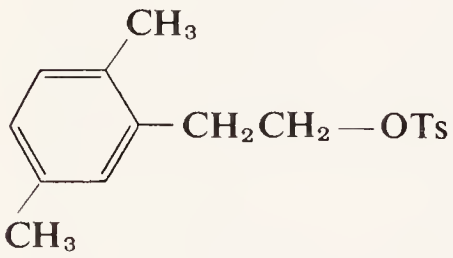
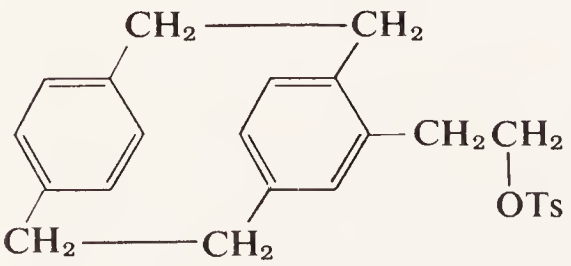


(76-OTs) (77) (76-OS) (76a-OS)

certain that the indicated rate acceleration in acetic acid would be increased in formic acid. The activation entropies, $\Delta S^{\ddagger}$, for **76-OTs** and the β-(2,5-dimethylphenyl)-ethyl tosylate model (Table VIII) in acetic acid are of the same order as that for formolysis of β-phenylethyl tosylate (**11**), where substantial anchimeric assistance has been suggested (41–45) (cf.

TABLE VIII

Solvolysis of β-Paracyclophanylethyl Tosylate and Typical Model Compounds

Substrate	Solvent	Relative rate	$\Delta S^{\ddagger}$, eu
	EtOH	1.0	−20.2
	HOAc	1.0	−17.3
	HCOOH		−9.5
	EtOH	0.65	−21.4
	HOAc	3.1	−11.1
	EtOH	1.6	−18.8
	HOAc	18.0 (30; if compared with k_s only for β-phenylethyl)	−11.7

Section IV-A-1). In contrast, the ethanolysis of **76-OTs** exhibits rates and activation entropies that indicate little or no anchimeric assistance in this solvent (Table VIII).

Surprisingly, acetolysis and formolysis of *a,a*-D_2-labeled β-paracyclophanylethyl tosylate (**76-OTs**; *a,a*-D_2) produced *no label scrambling* in the recovered esters (50a), in spite of the kinetic evidence supporting substantial β-aryl participation in these solvents. This apparent inconsistency has been explained as follows (50a).

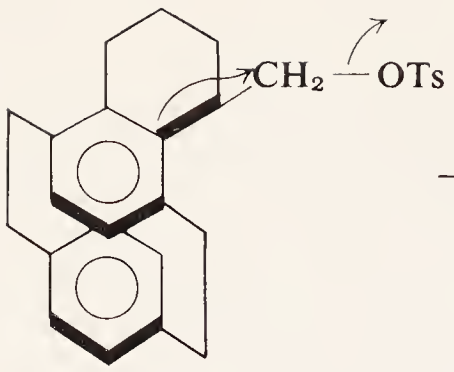
The PCP group most probably attacks the α-carbon atom from the ground state conformation in which steric interaction with the ethylene group is minimized (cf. **76-OTs**). In the resulting paracyclophanonium ion (**77**), solvent attack at the β-carbon of the ethylene bridge is severely hindered sterically by the PCP hydrogen atoms, but the α-carbon is as free toward solvent attack as it would be in a simple phenonium ion. Consequently, the solvent attacks only the α-carbon of the paracyclophanonium ion (**77**), leaving the α,α-D_2 label completely unscrambled.

Recent studies (121) confirm the preference of β-paracyclophanylalkyl derivatives for solvolysis via the so-called *exo* route, as well as the remarkable resistance of the inside (*endo*) carbon atom of a paracyclophanonium ion to solvent attack.

Formolysis of 1,2-paracyclophanocyclohexenyl-*exo*-3-carbinyl tosylate (*exo*-**78-OTs**) proceeded about seven times faster than the *endo* epimer, suggesting a moderately strong preference for *exo* generation of the paracyclophanonium ion (**79a**). Nevertheless, both epimers are very strongly anchimerically accelerated in comparison to a nonparticipating model such as α-tetralylethyl tosylate (93) (**50**; $n = 6$). For example, *exo*- and *endo*-**78-OTs** formolyze 5.2×10^4 and 7.3×10^3 times faster, respectively, than the model (**50**; $n = 6$).

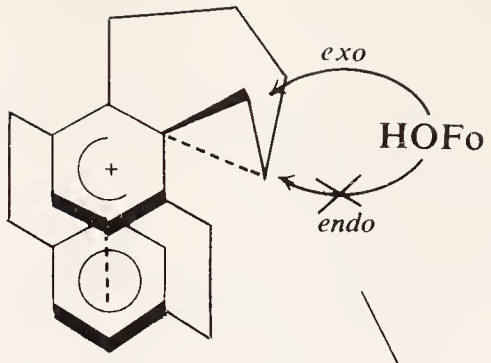
The *endo* epimer (*endo*-**78-OTs**) solvolyzes via the *exo*-paracyclophanonium ion (**79b**). Solvent attack at the *exo* carbon of this unsymmetrically bridged ion is favored both electronically and sterically, and so the expected ring-enlarged seven-membered formate (**80-OFo**) is formed exclusively and in high yield (98%). This result is completely consistent with the results for similar primary β-substituted β-arylethyl systems, e.g., 2-phenyl-1-propyl (**13**) and 1,2-benzocyclenyl-3-carbinyl (**48**; $n = 6, 7$), which both give predominantly rearranged or ring-enlarged secondary products.

The *exo* epimer (*exo*-**78-OTs**) provides a surprising break from this typical behavior. Electronically, the unsymmetrical paracyclophanonium ion (**79a**) from the *exo* epimer should be attacked at the *endo* secondary carbon to give the usual ring-enlarged product, because of the greater positive charge density at this carbon. However, the steric hindrance to

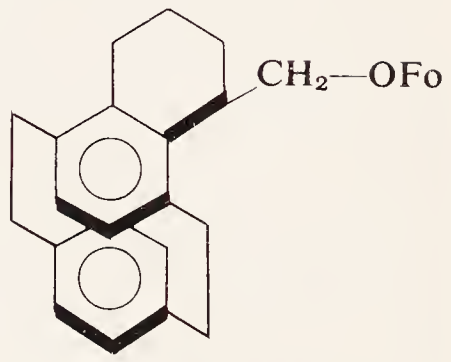


(*exo*-**78-OTs**)
rel. rate = 5.2×10^4

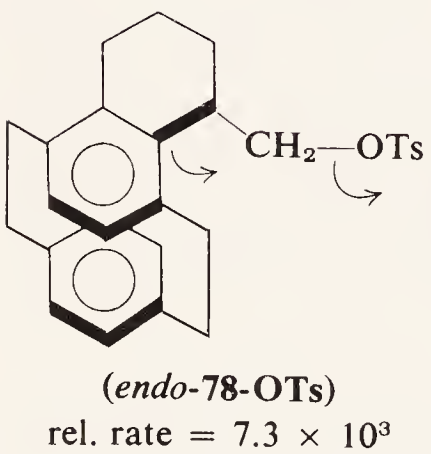
HOFo
"*exo*"
route



(79a)
(*endo*)

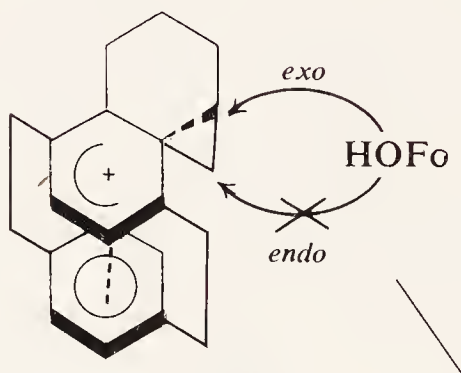


(*exo*-**78-OFo**)

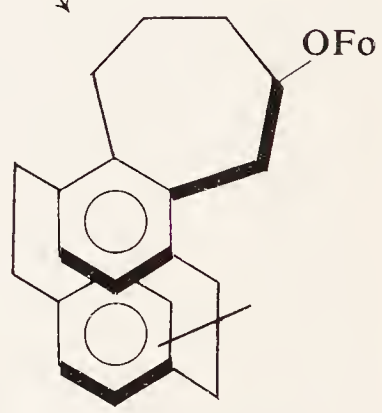


(*endo*-**78-OTs**)
rel. rate = 7.3×10^3

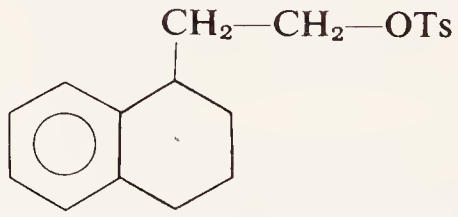
HOFo
"*endo*"
route



(79b)
(*exo*)



(80-OFo)



(50)
$n = 6$; rel. rate = 1.0

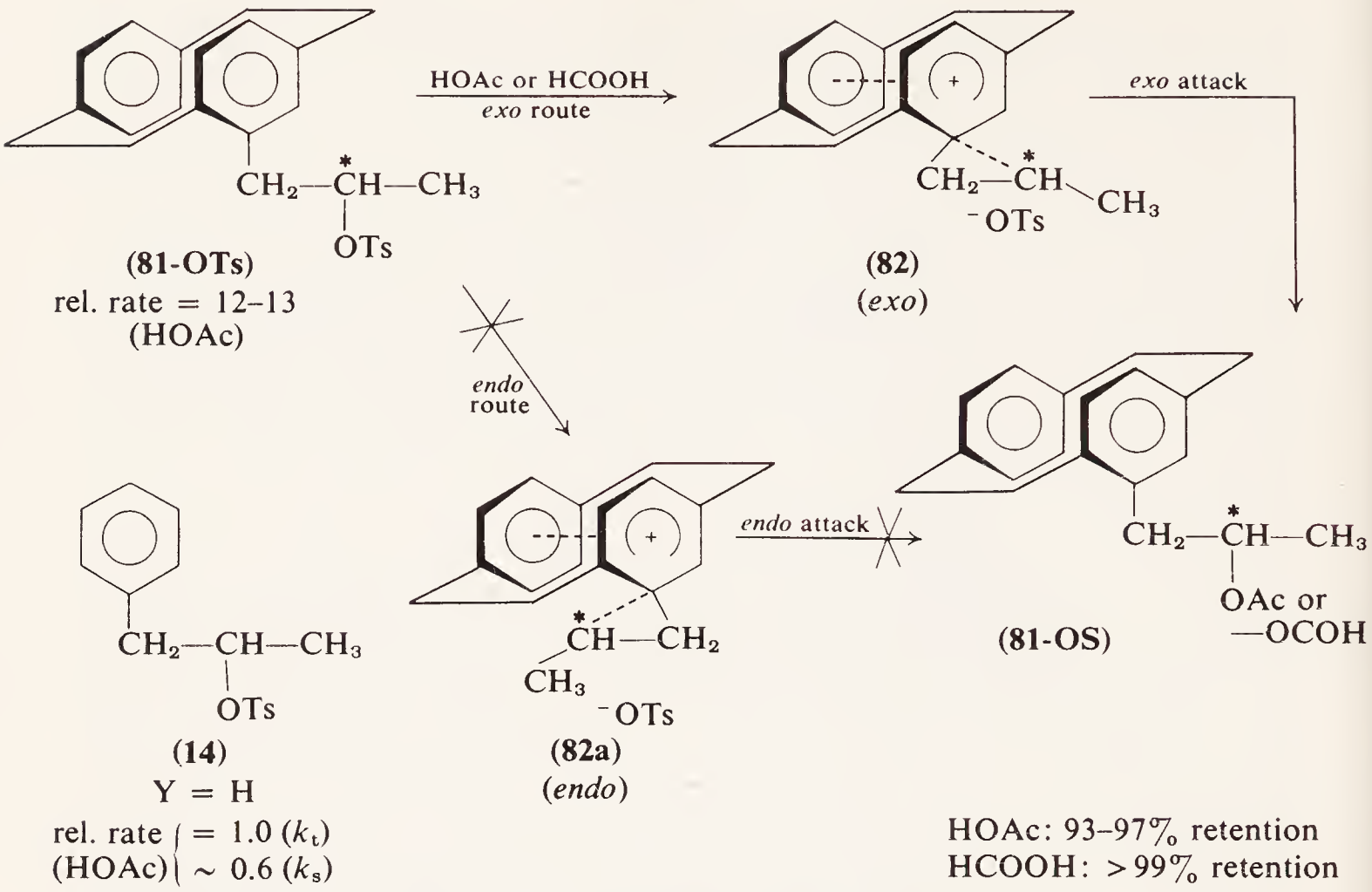
endo solvent attack in paracyclophanonium ions apparently is so great that *exclusive exo* solvent attack is forced to occur instead, and the unprecedented formation in 96% yield of only the *unrearranged, primary formate* (*exo*-**78-OFo**) from the *exo* tosylate is the observed result.

The same modes of β-PCP attack and solvent opening were recently proposed by Cram (122) for the acetolysis and formolysis of 1-paracyclophanyl-2-propyl tosylate (**81-OTs**). The enhanced participating ability of the PCP moiety is able to overcome the electronic bias common to all such 1-aryl-2-propyl structures (cf. **14**; Section IV-B-2, and **46**; Section IV-B-3-b), and appreciable β-aryl participation is reflected in the rate and product data.

Acetolysis of either diastereomer of **81-OTs** gave more than 93% retention of configuration, and formolysis led to essentially complete retention. The considerable increase in aryl product control over the planar-aryl model, 1-phenyl-2-propyl tosylate (**14**; X = H), is apparent; the model (**14**; X = H) acetolyzed with only 35% retention of configuration and formolyzed with 85% retention (see Section IV-B-2). The PCP derivative (**81-OTs**) acetolyzed 12–13 times faster than the 1-phenyl-2-propyl tosylate model (**14**; X = H). If, instead, the aryl-*unassisted* (k_s) acetolysis rate of the model is used as the basis of comparison (36–39) (see discussions on pp. 1372ff and Figs. 1 and 2), then the rate enhancement for the paracyclophanyl derivative (**81-OTs**) becomes about a factor of 20. Quantitative correlation between this rate enhancement and the extent of retention of configuration in acetic acid is provided in Section VII.

By analogy with the convincing results obtained with the epimeric 1,2-paracyclophanocyclohexenyl-3-carbinyl tosylates (**78-OTs**) (121), the *exo* pathway for paracyclophanonium ion (**82**) formation and solvent capture in the solvolysis of 1-paracyclophanyl-2-propyl tosylate (**81-OTs**) appears the most likely, in agreement with Cram's proposal (122). Actually, **81-OTs** should favor the *exo* route to the bridged ion (**82**) even more than the cyclic 3-carbinyl system (**78-OTs**). The *exo* route in the cyclic 3-carbinyl case (**78**) involves β-aryl attack from the less crowded outer face of the PCP group, but the resulting *endo* paracyclophanonium ion (**79a**) has the cycloalkyl group attached at the more crowded *endo* carbon atom. The *exo* route for the 1-paracyclophanyl-2-propyl system (**81-OTs**) also involves the more favorable β-aryl attack from the less crowded outer face of the PCP group; but the resulting *exo* bridged ion (**82**) has the methyl group attached to the less crowded *exo* carbon, so both factors complement each other.

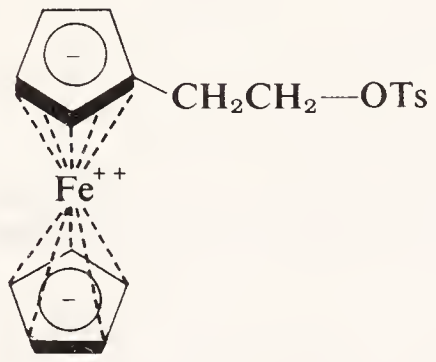
Considering the great amount of time and effort that has been spent on the study of β-arylalkyl systems, we would expect that virtually every possible aryl group would have received some attention at one time or



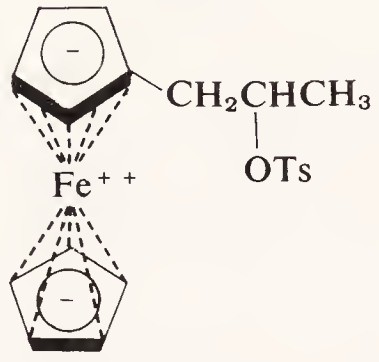
another. Recently the list of β-aryl groups has been extended to another, quite unique, three-dimensional group, ferrocene. Nugent and Richards (50b,121b) have examined the behavior of the ferrocenyl analogs of all the paracyclophanyl derivatives discussed in this section.

Although many apparent parallels are to be found in the relative behavior of the ferrocenyl (FER) and paracyclophanyl (PCP) derivatives of a given system, they differ fundamentally in one basic respect, which is shown later. In all the systems studied, the ferrocene (FER) group proved to be one of the most powerful β-aryl groups in assisting ionization, as indicated by the unusually large rate enhancements observed. For example, β-ferrocenylethyl tosylate (**FER-76-OTs**) (50b) acetolyzes faster than the corresponding β-phenylethyl derivative by a factor of 3×10^3, and 1-ferrocenyl-2-propyl tosylate (**FER-81-OTs**) (50b) acetolyzes faster than the corresponding 1-phenyl-2-propyl tosylate (**14**; Section IV-B-2) by a factor of 1.6×10^2. (These factors become $\sim 5 \times 10^3$ and $\sim 2.7 \times 10^2$, respectively, if the comparisons are made with k_s rather than with k_t for the parent phenyl derivatives.) Similarly, retention of configuration is complete in the acetolysis of 1-ferrocenyl-2-propyl tosylate (**FER-81-OTs**), and stereospecific ferrocenonium ion formation and capture are indicated by the total lack of deuterium scrambling observed in the acetolysis of the clearly participating β-ferrocenylethyl tosylate (50b) (**FER-76-OTs**; rate enhancement $> 10^3$), exactly analogously to the behavior of the corresponding PCP derivatives. However, β-ferrocenylalkyl derivatives

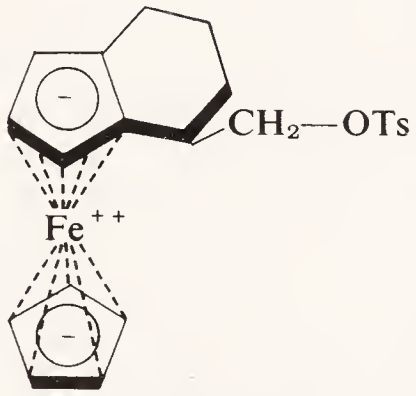
exclusively favor *endo* bridged ion formation and capture, in direct contrast to the PCP derivatives, which exclusively favor *exo* bridged ion formation and capture. This difference was strikingly demonstrated by the kinetics and stereochemistry of the solvolysis of the diastereomeric *exo*- and *endo*-ferrocenocyclohexenyl-1-carbinyl tosylates (*exo*- and *endo*-**FER-78-OTs**) (121b). Of these two epimers, the *endo* compound acetolyzed faster than the *exo* by a factor of 2.8×10^3, whereas *exo* was faster than *endo* by a factor of 7 in the PCP series. Moreover, of the two ferrocenyl epimers, the *exo* derivative underwent quantitative ring enlargement to the ferrocenocyclohepten-2-yl acetate, and the *endo* epimer gave only unrearranged acetate. Just the opposite product pattern was observed for the PCP series.



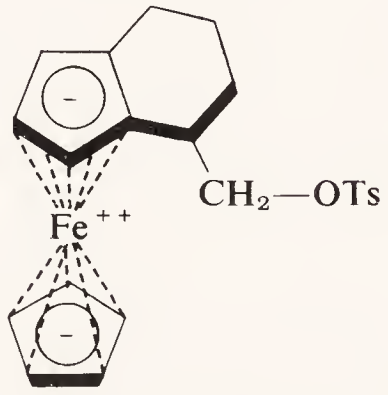
(FER-76-OTs)



(FER-81-OTs)



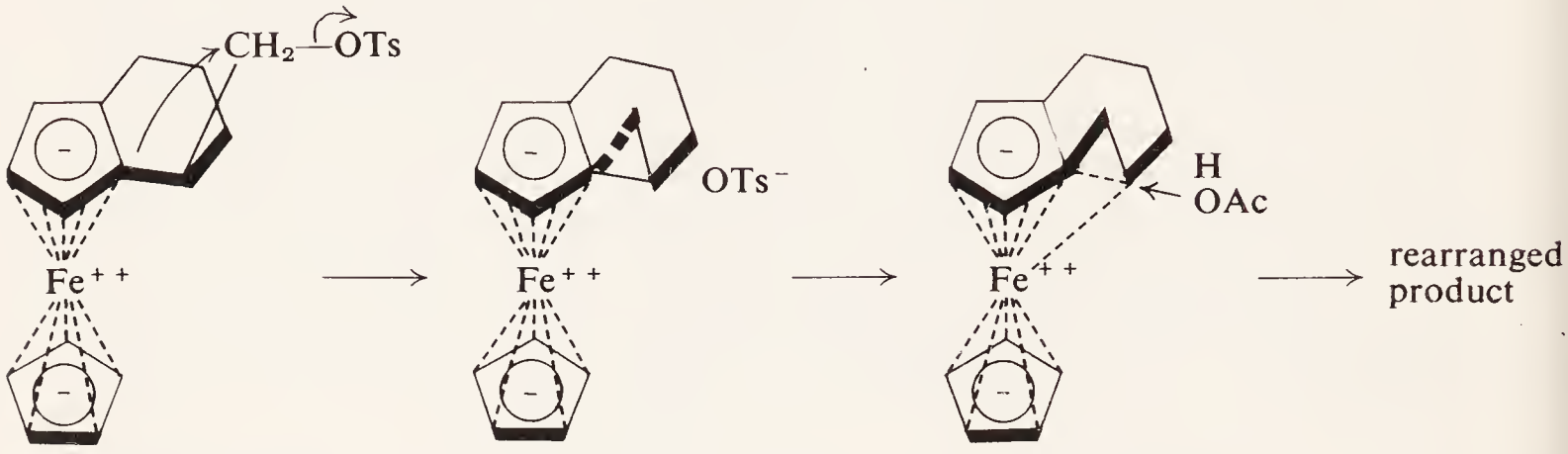
(*exo*-FER-78-OTs)



(*endo*-FER-78-OTs)

Since the steric requirements of the FER and PCP moieties must be very similar, the most likely explanation for these opposite behavior patterns (121b) probably lies in differences between the electronic characteristics of the two groups. Whereas the interannular electron density is much greater than the extraannular electron density in the FER group, the extraannular electron density is said to be somewhat greater in the PCP group (122). Indeed, the preferred intermediates in the FER series (121b) are quite different from the "ordinary" phenonium ions described thus far. In these intermediates, considerable interaction between the carbonium center and the interannular ferrous-cyclopentadienyl bond orbitals and/or the nonbonding iron electrons is postulated (121b). Such an intermediate is readily formed directly from the *endo* tosylate, and captured by

solvent at the *endo* carbon without rearrangement. The initial intermediate from the *exo* tosylate, however, would have to rearrange in order to allow participation by the interannular electrons, and this would result in the observed rearranged product (121b).



(*exo*-FER-78-OTs)

V. THE NATURE OF THE RATE-PRODUCT DISCREPANCY IN THE SOLVOLYSIS OF β-ARYLALKYL SYSTEMS

Three broad categories of behavior in solvolysis reactions of β-arylalkyl systems are outlined in Table IX, with representative examples taken from the compounds reviewed in Sections I–IV.

According to one interpretation [cf. Cram (1a,1b,2) and Winstein (31)] these three types of behavior can be explained in the following manner: β-aryl participation, in primary and secondary systems, is in competition with solvent participation; each is a discrete, independent mechanistic pathway. When β-aryl participation is overwhelmingly stronger than solvent participation, the net kinetic difference (observed rate enhancement) is large, and product control by the aryl group is large (Table IX; group *a*). When solvent participation predominates, there is no rate enhancement and solvent attack controls the products (Table IX, group *b*). When aryl and solvent participation are both large and of comparable magnitude, a relatively small excess of aryl participation produces a small net kinetic effect ($k_\Delta \gtrsim k_s$) but can still control a substantial proportion of the product distribution (Table IX; group *c*).

In an alternative proposal [cf. Brown (3)], the three classes of behavior in Table IX reflect the intermediacy of a continuous spectrum of cationic intermediates and/or transition states. Fully σ-bridged transition states and intermediates lead to large rate and product effects. Open cations, formed with little or no aryl participation in the transition state, lead to minor rate and product effects. The seemingly "anomalous" behavior, large product and apparently small rate effects, was said to be best explained by a dynamic pair of rapidly equilibrating, unbridged ions (when

TABLE IX

Summary of Rate and Product Effects in the Solvolysis of β-Arylalkyl Systems

Group *a*: Those compounds for which both rate enhancements and aryl product control are clearly very large. The intervention of phenonium ions, or at least phenonium transition states, is definitely indicated.

Example	Rate effect	Product effect
1. Acetolysis of *anti*-9-benzonorbornenyl brosylates (**anti-53**)	$\rho^+ = -5.10$ versus σ^+	Complete retention of configuration
2. Alcoholysis of β-(*p*-hydroxyphenyl)ethyl bromide (**28-Br**) as anion (**28a**)	Rate enhancement $\sim 10^7$	Bridged intermediate isolated
3. Acetolysis of neophyl brosylates (**19**)	$\rho^+ \sim -3$ versus σ^+	Complete rearrangement
4. Trifluoroacetolysis of β-phenylethyl tosylate (**11**; Ar = C_6H_5)	Rate enhancement $\sim 10^3$ versus EtOTs	Complete α,α-D_2 scrambling
5. Trifluoroacetolysis of 1-phenyl-2-propyl tosylate (**14**; X = H)	Rate enhancement = 6×10^2 by Taft analysis (Fig. 2)	Complete retention of configuration

Group b: Those compounds for which both rate and product effects are clearly minor and postulation of the intervention of bridged species is not required.

Example	Rate effect	Product effect
1. Ethanolysis of 1-aryl-2-methyl-2-propyl chlorides (**70-Cl**)	$\rho \sim -1$ versus σ	No rearrangement
2. Acetolysis of *trans*-2-phenylcyclopentyl tosylate (*trans*-**40**) Ar = C_6H_5—	No measurable rate enhancement	4% retention of configuration
3. Ethanolysis of β-phenylethyl tosylate (**11**) Ar = C_6H_5	*Slower* than ethyl tosylate	0.6% α,α-D_2 scrambling

(*continued*)

TABLE IX (*Continued*)

Group *c*: Those compounds responsible for much of the problem in interpretation. The product effects appear to be greater than the seemingly modest rate effects, and an apparent rate-product discrepancy complicates postulation of the intervention of bridged species.

Example	Rate effect	Product effect
1. Formolysis of β-phenylethyl tosylate (**11**) Ar = C_6H_5—	Twice as fast as ethyl tosylate	90% α,α-D_2 scrambling
2. Acetolysis of *trans*-2-*p*-anisylcyclopentyl tosylate (*trans*-**40**) Ar = *p*-$CH_3OC_6H_4$	Rate enhancement (k_t/k_s) = 3, by Hammett analysis (cf. Fig. 1)	60–70% retention of configuration
3. Acetolysis of *threo*-3-phenyl-2-butyl brosylate (**2a**)	k_t/k_s = 2.5–4.0, or k_α/k_s = 11–18 (cf. Fig. 1*c*)	95% retention of configuration
4. Formolysis of 1-phenyl-2-propyl tosylate (**14**) X = H	k_t/k_s = 4.5 (cf. Fig. 1*b*)	85% retention of configuration
5. Acetolysis of 1-paracyclophanyl-2-propyl tosylate (**81-OTs**)	12–13 times faster than 1-phenyl-2-propyl tosylate	93–97% retention of configuration
6. Methanolysis of 2,3-dimethyl-3-*p*-anisyl-2-butyl chloride or dinitrobenzoate (**68-Cl** or **-ODNB**; Y = *p*-CH_3O—)	$k_t/k_s \sim 2$ by crude Hammett analysis (Ref. 23)	Complete α,α-$(CD_3)_2$ scrambling

no rate enhancements are observed) or weakly π-bridged ions (when small or moderate rate enhancements are found). Chart 2 summarizes the mode of product control by rapidly equilibrating, unbridged (or weakly bridged) cations.

Tertiary β-arylalkyl systems pose no real problem in interpretation. There is general agreement that the solvolytic behavior of tertiary β-arylalkyl systems is best explained by rapidly equilibrating unbridged or weakly bridged cations, except when strongly electron-releasing groups are present. Winstein long ago suggested that neighboring-group participation should be smallest at tertiary centers (31), and all the evidence reviewed in Section IV-C-1–3 indicates that this is the case.

In contrast, the apparent rate-product discrepancy is less easily established for primary and secondary β-arylalkyl systems than for the tertiary ones. Consequently, it is necessary to develop and apply accurate analyses independently to the rates and to the products of the "borderline" primary and secondary systems (e.g., Table IX; group *c*). The solvent-assistance-versus-aryl assistance (k_s versus k_Δ) interpretation predicts exact, quantitative agreement between the extent of aryl participation as calculated independently from rates and from products; the equilibrating-ions interpretation predicts a lack of quantitative agreement. Such accurate rate-product correlations have been made extremely difficult for β-arylalkyl systems by the relative crudeness and unreliability of the usual partitioning of observed kinetic data into inductive, steric, and anchimeric assistance effects. For several years, however, such quantitative correlations have been available for systems with remote neighboring groups, where inductive and steric effects could be neglected (96a,123). Since the methods used in these and later similar correlations are essential to a discussion of β-arylalkyl substrates, the studies of remotely-substituted arylalkyl systems are summarized first.

VI. EXACT RATE-PRODUCT CORRELATIONS IN δ-ARYLALKYL SYSTEMS

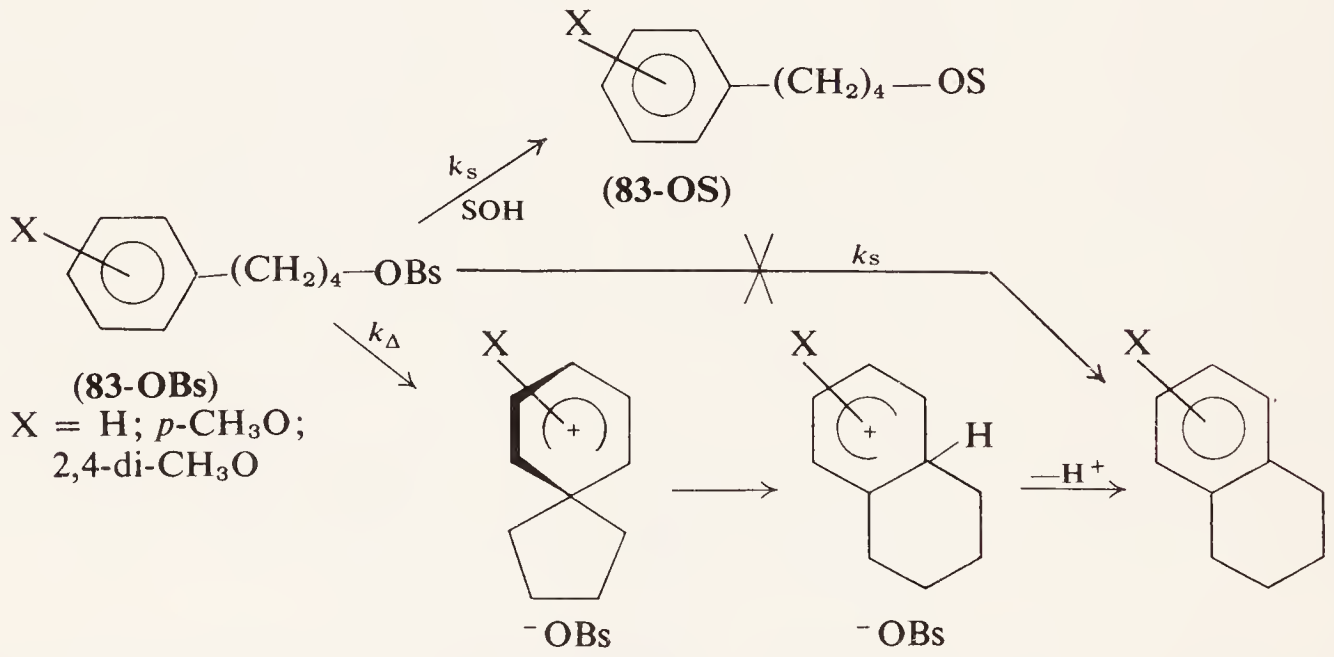
The complicating inductive effects of β-aryl groups are effectively reduced to neglibible proportions by removing the ring far enough from the reaction site. A δ-phenyl ring causes a negligible effect in the rates both of acetolysis and formolysis of 1-butyl brosylate (96a). Since there was no evidence from the products (see below) of δ-aryl participation in the solvolysis of 4-phenyl-1-butyl brosylate (**83-OBs**), and since δ-aryl inductive and field effects are negligible, the rates of **83-OBs** (X = H) can be taken as reasonable approximations of the anchimerically unassisted rates for the methoxy-substituted derivatives (**83-OBs**; X = *p*-CH_3O; 2,4-di-CH_3O).

Returning to Winstein's formulations, the total observed solvolysis rate constant k_t is taken as the sum of the anchimerically assisted reaction k_Δ and the unassisted reaction k_s (31)

$$k_t = k_\Delta + k_s \tag{2}$$

The solvolysis rate of **83-OBs** (X = H) was taken as equal to k_s for the methoxy derivatives; therefore, the observed difference, $k_t - k_s$, in rates for the methoxy derivatives was taken as the anchimerically assisted rate constant k_Δ. (Internal return was neither indicated nor treated in this study).

Detailed analysis of the solvolysis of **83-OBs** is simplified because anchimeric assistance k_Δ and simple solvolysis k_s give characteristically different products. The five-membered "phenonium ion" from the k_Δ route rearranges further and is "trapped" as a tetralin derivative. A similar reaction pathway was observed by Huisgen (93c) in the formolysis of 1,2-benzocyclooctenyl-3-carbinyl tosylate (**48**; $n = 8$) and 1,2-benzocyclononenyl-4-tosylate (**46**; $m = 9$; Section IV-B-3-b).



If the solvolysis of **83-OBs** is truly represented best as a competition between two discrete, independent mechanistic routes, k_s and k_Δ, then the percentage of kinetic aryl participation $k_\Delta/(k_\Delta + k_s) \times 100$ should agree closely with the percentage of tetralin derivative found among the products. The results of the formolysis of the methoxy-substituted derivatives of **83-OBs** appear in the first section of Table X. The rate-product agreement is surprisingly good, supporting the dual-mechanism concept for this particular substrate.

An analysis of rate enhancements relative to the parent phenyl derivative is instructive. These are listed in the fifth column of Table X. They are surprisingly small, only 1.8 in a solvolysis with 54% aryl participation and

10 in a 90% aryl-assisted solvolysis. This suggests that comparisons between rate *enhancements* and product data may be rather misleading. In fact, equation 3 and Figure 4 show that relatively small rate enhancements (k_t/k_s) correspond to relatively high contributions from k_Δ to the total rate (k_Δ/k_t).

$$\frac{(k_t/k_s) - 1}{k_t/k_s} = \frac{k_\Delta}{k_t} \tag{3}$$

According to this relationship, a *seemingly* small rate enhancement of 10 would correspond to a high proportion of anchimeric assistance (10 − 1)/10, or 90%. A genuinely small rate enhancement of only 2 would correspond to 50% of the total reaction being anchimerically assisted! Since these relationships are so simple and direct, it is surprising that "small" rate enhancements of the order of $k_t/k_s \sim 10$ or less have been cited as evidence *against* predominant control by neighboring groups over the rates and stereochemical outcome of many reactions, especially those involving neighboring phenyl groups (3b).*

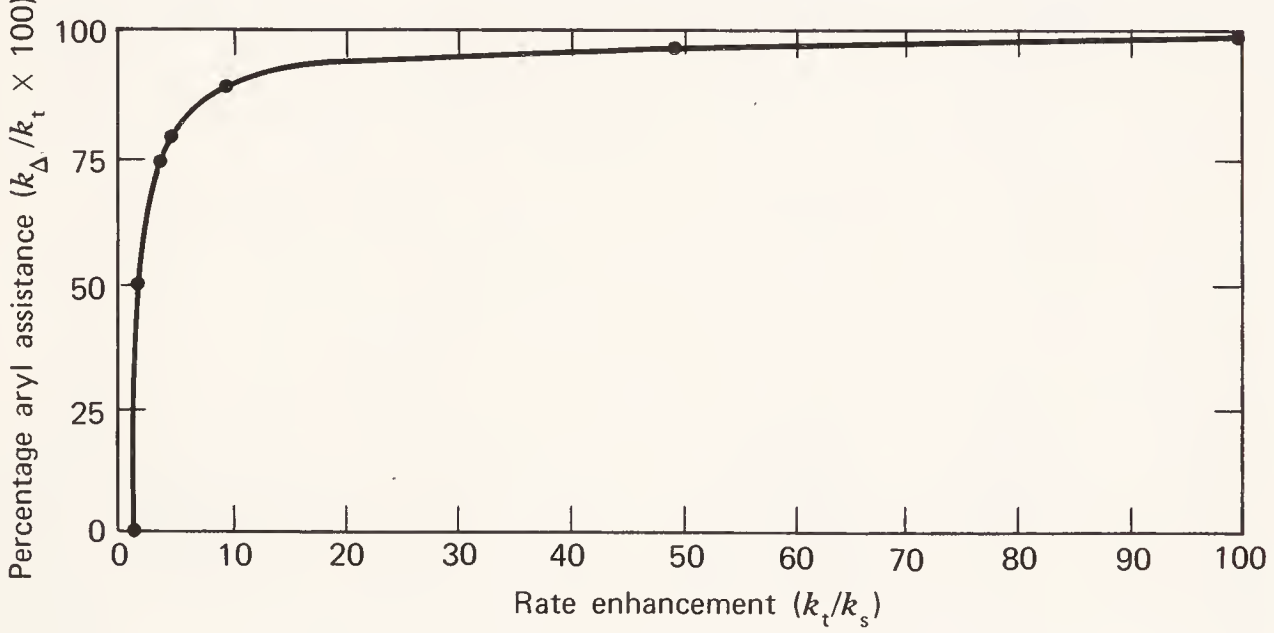
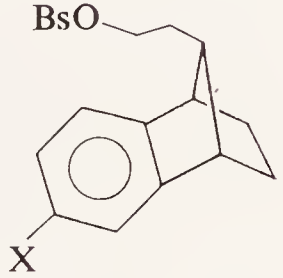


Fig. 4. Rate enhancement versus percentage of aryl assistance.

* Equation 3 describes, actually, an intuitively reasonable situation. The term "rate enhancement," by definition, is a relative rate for an overall process which is faster than some standard reference reaction, in this case the aryl-unassisted reaction k_s, which is placed implicitly at unity. If the rate enhancement is 2, then both k_Δ and k_s must be equal ($k_\Delta = k_s = 1$). If both are first-order processes, and if no other reaction is occurring simultaneously, half of the product will arise by either process. The qualitative comparison of rate enhancements with product data seems to obscure these facts.

TABLE X

Determination of Aryl Participation from Rates and Products for δ-Arylalkyl Systems

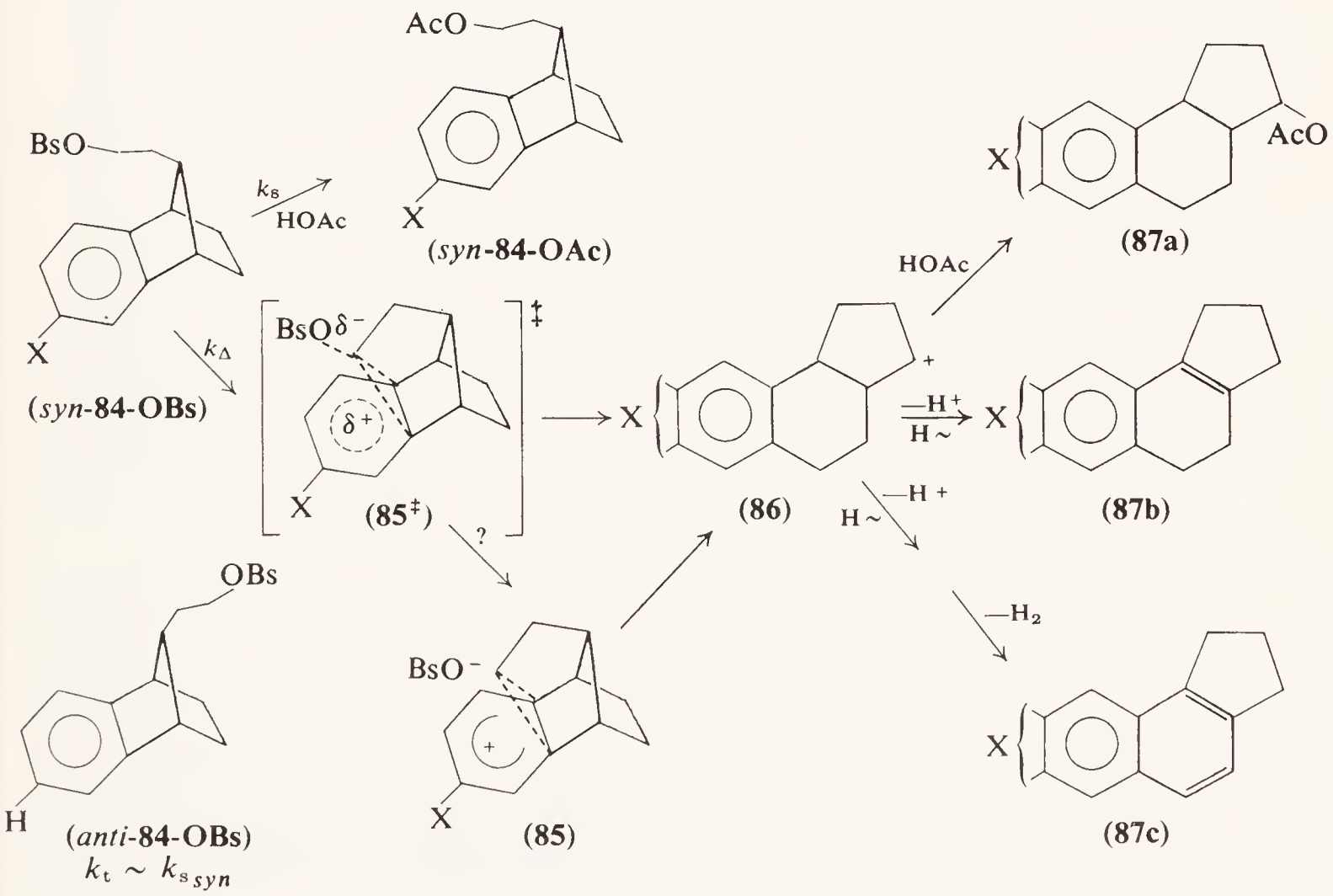
Substrate	Solvent	$(k_\Delta/k_t) \times 100$	Cyclized products, %	Rate enhancement (k_t/k_s)	k_Δ Rel. determined from $(k_t - k_s)$	k_Δ Rel. determined from $k_t \times$ % rearrangement
X—C_6H_4—$(CH_2)_4$—OBs (**83-OBs**)						
X						
p-CH_3O	HCOOH	54	54	1.8[a]	—	—
2,4-$(CH_3O)_2$—	HCOOH	92	91	10[a]	—	—
 (**84-OBs**) (*syn*)						
X						
CH_3O	HOAc	99	97	157[b]	7.58	8.09
H	HOAc	95	86	22[b]	1.00	1.00
F	HOAc	85	66	6.8[b]	0.34	0.29
Cl	HOAc	70	52	3.3[b]	0.12	0.10
NO_2	HOAc	~20	~0	1.3[b]	0.02	0

[a] k_t for (**83-OBs**) X = H, taken as k_s.

[b] k_t for *anti*-**84-OBs**; X = H, taken as k_s.

A more recent example of quantitative rate-product correlations in remotely substituted arylalkyl systems, where inductive corrections are negligible, is provided by Tanida's detailed examination (123a) of a series of benzo-ring-substituted *syn*-9-β-benzonorbornenylethyl brosylates (*syn*-**84-OBs**). Acetolysis of *syn*-**84-OBs** (X = NO_2, Cl, F, H, CH_3O) gave a product mixture comprising unrearranged acetates (*syn*-**84-OAc**), ascribed to aryl-unassisted acetolysis (k_s), and a mixture of benzindenes (**87b**, **87c**) and benzindanyl acetates (**87a**). The rearranged products were presumed to arise via bridged transition states (e.g., **85**‡) and rearranged ions in a k_Δ pathway. The symmetrical transition state (**85**‡) is similar to that proposed for the acetolysis of the closely related *anti*-9-benzonorbornenyl system (*anti*-**53**) (98), but acetolysis of the β-benzonorbornenylethyl system (*syn*-**84-OBs**) need not proceed with the intervention of a symmetrically bridged intermediate ion (**85**), since the transition state (**85**‡) conceivably could collapse directly to the rearranged benzindanyl cation (**86**).

The symmetrical nature of the rate-determining transition state involved in the acetolysis of *syn*-**84-OBs** was suggested by the manner in which the Hammett $\sigma^+\rho^+$ correlation was applied to the derived assisted rate constants (k_Δ). This was best accomplished by plotting log k_Δ terms against the composite term $(\sigma_m{}^+ + \sigma_p{}^+)/2$. The ρ^+ value of -2.88 is consistent with charge delocalization into a bridging aryl ring. (Cf.



$\rho^+ = -3.3$ (99b) for *exo*-2-benzonorbornenyl brosylates (*exo*-**54-OBs**) and other ρ^+ values given in Table II.

Acetolysis of 9-*anti*-β-benzonorbornenylethyl brosylate (*anti*-**84-OBs**; X = H), in which benzo-ring participation is impossible, gave only unrearranged primary acetate (*anti*-**84-OAc**; X = H) (123a). Remote inductive effects can be assumed to be essentially negligible (96a) both in the parent *anti* epimer and in all the *syn* epimers. Therefore, the acetolysis rate of the parent *anti* epimer $k_{t;anti;H}$ can be taken as a reasonable estimate of the aryl-unassisted rate (k_s) for each of the *syn* epimers, and k_Δ for each *syn* epimer is calculated as the difference between the observed rate $k_{t;syn;X}$, and the parent *anti* rate $k_{t;anti;H}$ (123a).

Comparison between the kinetically derived values of k_Δ/k_t with the actual percentages found of rearranged products (**87a**–**87c**) appears in the lower portion of Table X. For most of the derivatives in the series, reasonably good agreement was found between rates and products, further supporting the dual-mechanism interpretation (k_Δ versus k_s) for remotely substituted systems. Some modest discrepancies are apparent in Table X, and these are readily explained.

Figure 4 reveals that 90% of the product control range (k_Δ/k_t) is achieved merely by the first order of magnitude in rate enhancement (k_t/k_s = 1–10). In other words, relatively minor errors in the rate data could lead to relatively large errors in k_Δ/k_t. Consequently, the discrepancies in the comparisons between k_Δ/k_t and the percentage of rearranged products (**87a**–**87c**) in the acetolysis of the *syn*-β-benzonorbornenylethyl system (*syn*-**84-OBs**; Table X) become much smaller when values of k_Δ as calculated both from $k_t - k_s$ and from products are compared instead. These comparisons are given in the last two columns of Table X. The agreement is very good in all cases.

Minor error in k_Δ, and consequently larger error in k_Δ/k_t, as calculated from kinetic data could have arisen from neglect of field effects in the k_s process as the ring substituent was varied. Since the δ-arylalkyl structure is doubled back on itself in *syn*-**84-OBs**, the benzo-ring and the reaction center are fairly close to one another, and field effects may be as important, or more important, than simple inductive effects, although both should be relatively small in a primary system.

Except for the highly activated 6-methoxy derivative (*syn*-**84-OBs**; X = CH_3O), all the rate enhancements (k_t/k_s) are small or modest (Table X; fifth column). This further underscores the ambiguity which could arise from direct, qualitative comparisons of product data with rate *enhancements* rather than quantitative comparisons with the proportion of aryl participation (k_Δ/k_t) derived from the rate data.

The principle of a quantitative rate-product correlation has been

illustrated for remotely substituted arylalkyl systems, supporting the dual mechanism concept of Cram and Winstein. Small rate enhancements are effectively handled by this treatment. The following section examines the applicability of similar treatments to β-arylalkyl systems, where inductive effects must be accurately estimated before k_Δ can be determined.

VII. RATE-PRODUCT CORRELATIONS IN β-ARYLALKYL SYSTEMS

A. Techniques for Estimation of k_s and Fk_Δ in β-Arylalkyl Systems

The discussion in Section VI shows how kinetic and product control by remote aryl rings are experimentally in quantitative agreement regardless of the magnitude of the observed rate enhancement. Two factors made such experimental correlations possible: inductive (or field) and steric effects of remotely situated aryl groups are negligible, so any observed kinetic effect by the aryl group must be due to the intervention of a k_Δ mechanism; and the k_Δ and k_s routes each give characteristically different products (i.e., cyclic versus open products).

Both these advantages are largely lost in the study of β-arylalkyl systems. In general, very small or moderate kinetic effects must be separated into anchimeric and inductive/steric effects of often quite comparable magnitude, and any reliable product analysis requires accurate treatment of rearrangement, scrambling, configurational data, etc., since the k_Δ and k_s routes for β-arylalkyl systems do not give products of differing gross structures, as do the remotely substituted systems. Moreover, rate and product analysis is often complicated by the occurrence of internal return, but this can be handled effectively by several means (Sections I, III, IV). Although reasonably good semiquantitative rate and product comparisons have been available for some time in a few cases (2,21), it is now possible to achieve accurate, more nearly quantitative rate-product correlations in many β-arylalkyl systems with the aid of more reliable methods of kinetic analysis (4,36,39,40,89) (see Figs. 1 and 2). Although more sensitive product-analysis techniques (e.g., glc) have also become available, agreement with the earlier, classical product analyses in several of the key systems is, in many cases, excellent (1a–1e).

1. Kinetic Determinations of k_s and Fk_Δ for β-Arylalkyl Systems

The solvolytic scheme used by Winstein and others to describe the dual-mechanism behavior of β-arylalkyl systems, including internal return, is shown in Figure 5. Usually, titrimetric solvolysis rates are taken as the overall observed rate k_t, but this includes only that fraction F of the aryl-assisted ionization rate k_Δ, which proceeds to product plus acid (HBr, HOTs, HOBs, etc.). Accordingly, equation 2, as used for the δ-arylalkyl

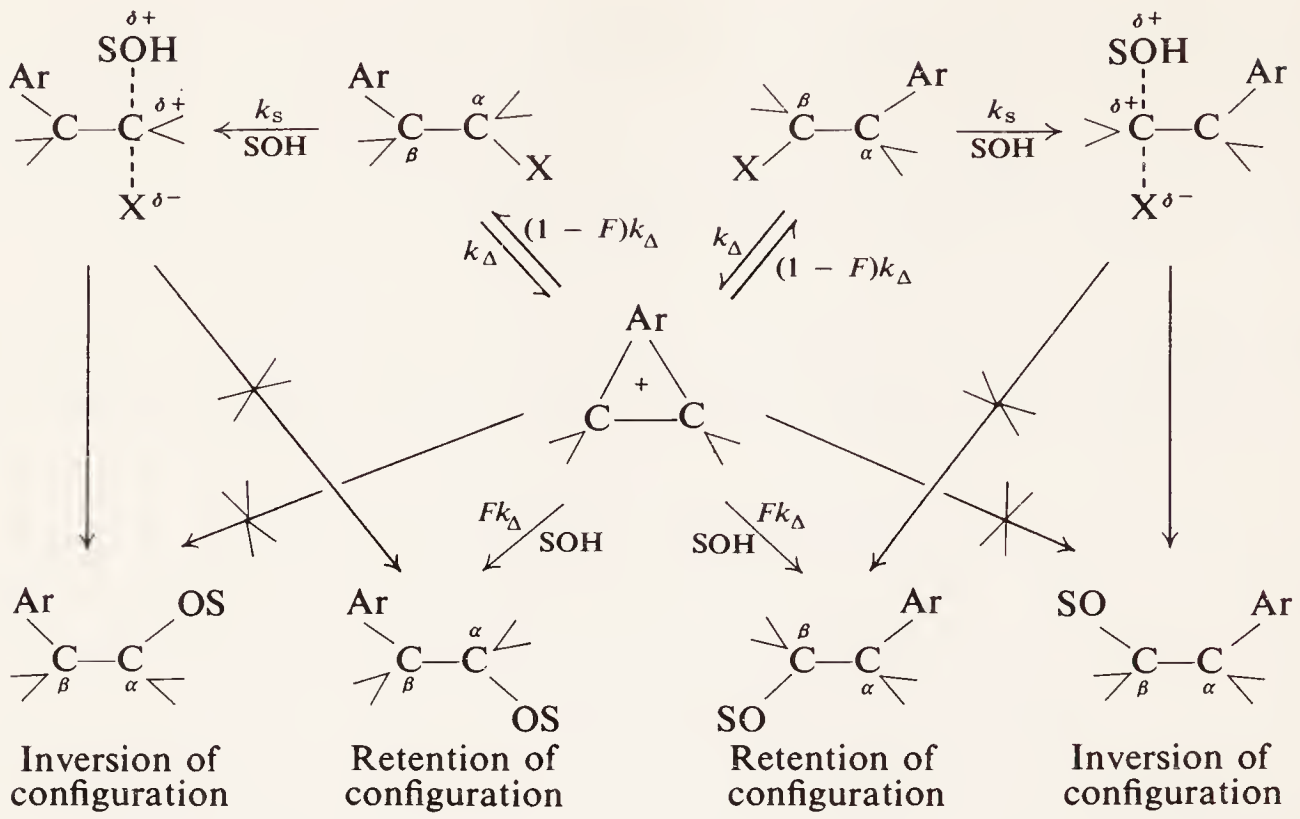


Fig. 5. Detailed description, including internal return, of the dual-mechanism concept of solvolysis of β-arylalkyl systems.

systems (Section VI), must be modified by the additional incorporation of the F factor:

$$k_t = Fk_\Delta + k_s \tag{4}$$

The most commonly used technique for separating k_t into Fk_Δ and k_s has been the Hammett correlation (Section III-B-1), in which the rates of deactivated derivatives (e.g., p-$NO_2C_6H_4$–, etc.) define a k_s correlation line (ρ_s, Fig. 1). Representative ρ_s values for the deactivated substrates of several systems are listed in Table II. It is assumed that these deactivated compounds undergo no aryl participation, so that $k_t \sim k_s$.*

Extrapolation of the Hammett ρ_s line through the σ constants of the activated derivatives, whose positively deviating points indicate the incursion of β-aryl participation, gives the k_s rates for these participating substrates. This procedure was outlined briefly in Section III-B-1, where other accurate methods of determining rate enhancements (k_t/k_s) are discussed. In the present application, k_s as determined by extrapolation is deducted from the observed k_t to calculate Fk_Δ by difference. The parameter $Fk_\Delta/k_t \times 100$ gives the percentage of the total observed reaction (k_t)

* In practice, even the deactivated substrates of a given series undergo a small, almost undetectable amount of aryl participation ($Fk_\Delta \rightarrow 0$ as $k_t/k_s \rightarrow 1.0$). A series of successive approximations in a computer program (39b) has been used to correct the "raw" $k_t \sim k_s$ correlation line for the small amounts of participation in the deactivated substrates.

that proceeds to product via β-aryl participation. This value is then compared with product control by the β-aryl group. Most of the k_s values given in Table XI (Section VII-B) were determined by this method.

2. *Determination of Fk_Δ/k_t from Solvolysis Products*

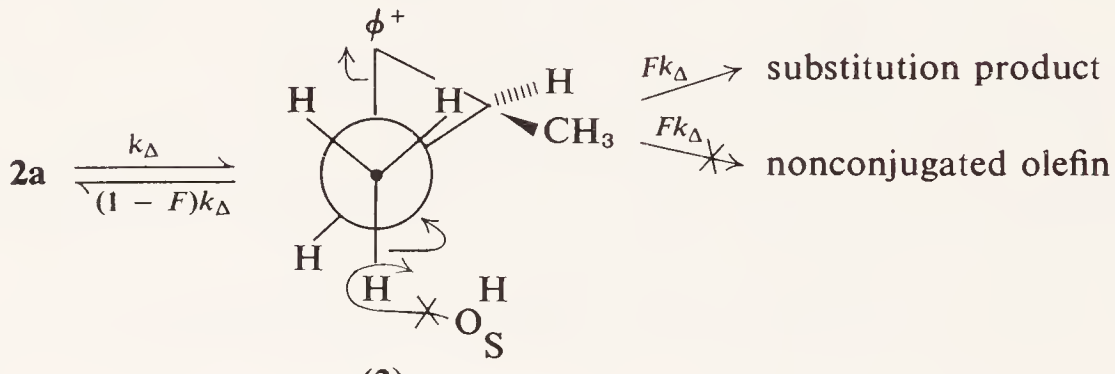
Substitution product (ester, ether, etc.) with retained configuration and/or equilibrated C_α and C_β (in symmetrical systems) is the overwhelmingly favored product of β-aryl participation. The percentage yield of substitution product multiplied by the percentage of retention of configuration or of label scrambling gives, to a first approximation, a measure of the amount of product arising with β-aryl participation, in the absence of internal return. Sometimes, the "percentage retention" in the substitution product has been taken directly as a measure of the amount of participation; this is only correct if the sole product formed is substitution product (39). This is rarely the case, with a few notable exceptions, e.g., β-arylethyl systems, which give little, if any, olefins.

When internal return is known to occur, special considerations must be taken into account when analyzing products for C_α–C_β label scrambling. Examination of Figure 5 shows why this is so. The k_s process can give scrambled product from starting material that has undergone k_Δ ionization and internal return $[(1 - F)k_\Delta]$. Therefore, the relative amount of C_α–C_β-scrambled substitution product is expected to increase during the course of the reaction as the substrate becomes increasingly scrambled. This has been experimentally observed (43), and the net amount of scrambling due only to the Fk_Δ process (Fk_Δ/k_t) has been found simply by extrapolating the observed scrambling in the (substitution) product back to time = 0, before the internal return process has begun to scramble the starting material (43). Only the degree of scrambling extrapolated to time = 0 should be compared with kinetic data when internal return has been demonstrated.

Configurational data, on the other hand, may be treated similarly either in the presence or the absence of internal return. Figure 5 shows that inversion of configuration can only occur via the k_s route, and that retention does not ordinarily occur via the k_s route, regardless of the occurrence of internal return. The reason, of course, is that attack by the counterion on the bridged species to give back substrate $[(1 - F)k_\Delta]$ occurs with inversion of configuration, yielding substrate with unchanged configuration. For systems where scrambling has been shown to increase with time because of internal return (43), no significant variation with reaction time in the amount of retention of configuration in the product has been experimentally observed (124).

The production of olefins must be taken into account appropriately.

There are several points to consider in this area. Conjugated olefins cannot arise directly from bridged ions in an Fk_Δ process because of the unfavorable geometries involved in this elimination (Sections I and IV-B-1). In secondary or tertiary β-arylalkyl systems, nonconjugated olefins conceivably could arise directly from bridged species, but all available evidence suggests that this probably is not favorable in most systems (1d,14,15) (see below). The most likely reason is the added torsional strain introduced by the partial eclipsing in the phenonium ion conformation from which elimination to nonconjugated olefin will occur (assuming a *trans* elimination course) (1d). Scrambling and/or racemization in nonconjugated



(3)

olefin products in excess of that accountable by an aryl-unassisted (k_s) mechanism with internal return [$(1 - F)k_\Delta$] could be suggestive of direct elimination from a symmetrical bridged ion (89).* Such excess racemization was *not* found, e.g., in the nonconjugated olefins produced in the acetolysis of active *threo*-3-phenyl-2-butyl brosylate (**2a**) (1d) (Section I). Little or no olefin is formed in solvolyses that unquestionably involve phenonium ions as the predominant or exclusive *intermediates*. Typical cases are examples 2, 4, and 5 of group *a* in Table IX, as well as the acetolysis of *threo*-3-*p*-anisyl-2-butyl tosylate (*threo*-**31-OTs**; Section IV-B-1).

In view of the available evidence against direct elimination pathways from aryl-bridged intermediates, rate-product correlations are usually performed with the simplifying assumption that very little or no olefins arise via the aryl-assisted solvolysis (Fk_Δ) mechanism. Nevertheless, in any case where direct olefin formation from an aryl-bridged intermediate cation can be validly demonstrated, such olefin must, of course, be included in the product-derived estimate of Fk_Δ/k_t (89).

The possibility of hydride shift is an additional complicating factor. Such shifts may occur with participation during ionization, in which case a third mechanistic path $k_{\Delta H}$ must be included as a component of k_t. Under

* There are some preliminary indications (89) that some direct elimination may occur from an equilibrating mixture of relatively weakly, unsymmetrically bridged ions in the solvolysis of the *trans*-2-arylcyclopentyl system (*trans*-**40**), but this evidence has not yet been confirmed.

these circumstances, any overall observed acceleration will consist of $k_{\Delta Ar} + k_{\Delta H}$. This introduces some uncertainty into any simplified quantitative treatment. There are no data conclusively indicating the operation of a $k_{\Delta H}$ pathway in the individual cases tabulated in Table XI (next section), but some related observations can be made (125). For instance, the 3-cyclohexyl-2-butyl system undergoes substantial hydride shift in acetic acid, with a reasonably high isotope effect; $k_H/k_D = 1.8$–2.0 (125a) (cf. $k_H/k_D = 1.8$–2.2 in 3-methyl-2-butyl system) (125b). On the other hand, the *cis*-2-phenylcyclopentyl system (*cis*-**40**; Ar = C_6H_5) acetolyzes with 85% hydride shift, and yet the kinetic data reveal no substantial deviation from unaccelerated behavior (e.g., $\rho = -1.6$ versus regular σ constants, only slightly higher than standard nonparticipating systems; cf. Table II (38,125c). Unless the data conclusively indicate the operation of a $k_{\Delta H}$ path for any particular system under examination, hydride-shift product, if formed, is most readily handled by inclusion in the k_s mechanism, and overall k_Δ simply ascribed exclusively to aryl participation. The widespread success of the treatment (see Table XI) apparently justifies this assumption.

In summary, product-derived estimates of Fk_Δ/k_t can be taken as the percentage yield of substitution product obtained with retained configuration and/or rearrangement, scrambling, etc.; plus any additional product (nonconjugated olefin, hydride-shift product) *known* to arise either with aryl or hydride participation. To obtain the data for the systems in Table XI, all estimates of Fk_Δ/k_t were made using substitution product data only, except where noted.

B. A Tabulation of Rate-Product Correlations for β-Arylalkyl Systems

Eight series of ring-substituted β-arylalkyl substrates are examined in this section with respect to a comparison between kinetically derived and product-derived values of Fk_Δ/k_t. A considerable variety of structural types is listed in Table XI.

Inspection of Table XI reveals consistently good agreement for *primary* and *secondary* systems between the proportion of Fk_Δ as calculated both from the kinetic and from the product data. This is true for a large number of systems exhibiting rate enhancements (k_t/k_s) ranging over several orders of magnitude. The amount of aryl participation [$(Fk_\Delta/k_t) \times 100$] varies from 10 to 100%. Clearly, we must conclude that an exact, quantitative rate-product correlation is observed for primary and secondary β-arylalkyl substrates, just as predicted by the Winstein-Cram mechanism (Fig. 5): a competition between *two discrete*, *independent pathways*, with rate constants k_s and Fk_Δ. Therefore, the *seemingly* small rate enhancements that are accompanied by *apparently* high degrees of product control,

TABLE XI

Quantitative Comparison between Product-Derived and Rate-Derived Values of Fk_Δ/k_t for Solvolysis of β-Arylalkyl Systems

Substrate	Solvent	Rate enhancement (k_t/k_s)	Ref.	$(Fk_\Delta/k_t) \times 100$ from Rates[a]	Ref.	$(Fk_\Delta/k_t) \times 100$ from Products[b]	Ref.
Primary							
1. β-Arylethyl tosylates (**11-OTs**); $X—C_6H_4—CH_2CH_2—OTs$							
X							
p-Cl	HOAc	1.21	39b	18	39b	9	43
H	HOAc	1.73	39b	42	39b	38	43
p-CH_3	HOAc	5.63	39b	82	39b	82	43
p-CH_3O	HOAc	51.1	39b	98	39b	95	43
2. 1,2-benzocyclenyl-3-carbinyl tosylates (**48-OTs**)							
$n = 6$	HCOOH	430	93	>99	93	~100	93
$n = 7$	HCOOH	140	93	>99	93	~100	93
Secondary							
1. 1-phenyl-2-propyl tosylate (**14-OTs**) X = H							
$C_6H_5—CH_2—CH(OTs)—CH_3$	HOAc	1.6	39a	37	39a,126	25	75a,126
	HCOOH	4.5	39a	76	39a,126	68	75a,126
	CF_3COOH	564	15	>99	15,126	~100	15,126

2. 1-paracyclophanyl-2-propyl tosylate (**81-OTs**)							
PCP—CH_2—CH(OTs)—CH_3	HOAc	~20[c]	122	~95[c]	122	85–90	122
3. *threo*-3-aryl-2-butyl brosylate (**2a** and derivatives); X—C_6H_4—$CH(CH_3)CH(CH_3)$—OBs							
X							
p-Cl	HOAc	1.6	4,38c	37	4,38c	39	4,38c
H	HOAc	3.0	4,38c,40	66	4,38c,40	59	2,4,38c
m-CH_3	HOAc	3.7	4,38c	73	4,38c	68	4,38c
p-CH_3	HOAc	7.6	4,38c	87	4,38c	88	4,38c
p-CH_3O	HOAc	71	4,38c	99	4,38c	~100	4,14,38c
4. 1,2-benzocyclenyl-4-tosylates (**46-OTs**)							
m = 7	HOAc	9.5[d]	92	89	92	78–80	92
	HCOOH	67[d]	92	98	92	96	92
m = 8	HCOOH	1000[d]	92	>99	92	96[e]	92
5. *trans*-2-arylcyclopentyl tosylate; (*trans*-**40**); *trans*-2-XC_6H_4-*cyclo*-C_5H_8—OTs							
X							
H	HOAc	1.3	38b,89	22	38b,89	7[f]	38b,89
m-CH_3	HOAc	1.3	38b,89	22	38b,89	4	38b,89
p-CH_3	HOAc	1.4	38b,89	25	38b,89	26[f]	38b,89
p-CH_3O	HOAc	3.2	38b,89	69	38b,89	83[f]	38b,89

(*continued*)

TABLE XI (*Continued*)

Substrate	Solvent	Rate enhancement (k_t/k_s)	Ref.	$(Fk_\Delta/k_t) \times 100$ from Rates[a]	Ref.	Products[b]	Ref.
Tertiary							
1. 2,3-dimethyl-3-aryl-2-butyl chloride or dinitrobenzoate (**68-Cl** or **-ODNB**)							
$X—C_6H_4—C(CH_3)_2C(CH_3)_2—\begin{cases}Cl\\ODNB\end{cases}$							
X							
H	EtOH[g]	1.0	23	~0	23	50	23
p-CH_3O	EtOH[g]	2.0	23	50	23	~100	23

[a] Methods of kinetic analysis summarized in Section VII-A-1.
[b] Methods of product analysis summarized in Section VII-A-2.
[c] k_s for acetolysis of 1-phenyl-2-propyl tosylate (**14-OTs**; X = H) at 100° used as aryl-unassisted reference rate.
[d] k_t for 1,2-benzocyclooctenyl-5-tosylate (**46a**; $m = 8$) used as aryl-unassisted reference rate.
[e] 100% retention of configuration based on $m = 7$, which gave 100% retention but formolyzed 15 times slower.
[f] Includes portions of nonconjugated olefins estimated to arise via Fk_Δ mechanism (89).
[g] Preparative solvolyses run in methanol.

first noted by Cram (1a), are more satisfactorily explained by this mechanistic concept than by the postulation of an equilibration between open or weakly bridged cations (Section V). In contrast, the data available for *tertiary* systems (Table XI), although limited, suggest that the extensive rearrangement that accompanies the small rate enhancements in these systems *cannot* be handled adequately by the dual-mechanism concept. The large rate-product discrepancy, already qualitatively evident even from a superficial analysis of tertiary substrates (e.g., cf. discussion of **68**, Section IV-C-3) is confirmed by a more quantitative treatment (Table XI). This supports the previous conclusion that such tertiary β-arylalkyl systems are best described in terms of the Brown (3) picture of rapidly equilibrating unbridged or weakly bridged cations, except possibly for highly activated substrates.

In summary, *two* types of behavior emerge from quantitative rate-product analysis of the solvolysis of β-arylalkyl systems. The principal distinguishing feature is the presence or absence of *open* cations, i.e., carbonium ions formed *without* backside nucleophilic participation either from the solvent (k_s) or from a neighboring group (k_Δ), as solvolysis intermediates. Such *open* cations must be ruled out in the solvolysis of *primary* and *secondary* (nonbenzyl) β-arylalkyl systems; these substrates show no evidence of crossover or "leakage" between the aryl-assisted (Fk_Δ) and solvent-assisted (k_s) mechanistic pathways (Table XI). "Leakage" is inconsistent with a mechanistic picture comprising discrete k_s and Fk_Δ routes; the transition states and intermediates in each pathway are strongly bonded at the backside of the carbonium center, either to the solvent (k_s) or to the aryl group (Fk_Δ). In the solvolysis of *primary* and *secondary* β-arylalkyl systems in the usual solvents, nucleophilically *un*solvated ("open") cations or ion pairs apparently are energetically unattainable.*

* The possibility of the intervention of a *tight* ion pair (16,17), formed in the first step at a rate competitive with the rates of subsequent attack either by solvent (k_s') or aryl group (k_Δ'), recently has been considered (4b) as an attractive alternative to the direct, competitive attack of solvent (k_s) and aryl group (k_Δ) on covalent starting material for *secondary* substrates. This situation and the resulting steady state kinetics (4b) are identical to those presented by Sneen (16) for the competitive reaction of a substrate either with solvent or with *external* nucleophile, e.g., added azide ion (16). Such a solvolysis scheme for β-arylalkyl systems is operationally indistinguishable from the original Cram-Winstein description of direct, competitive k_s and k_Δ reaction of covalent starting material (Fig. 5). Actually, the initial *tight* ion pair formulated in the alternative schemes (16,17,4b) is not easily distinguished conceptually from covalent starting material with a slightly weakened or lengthened bond to the leaving group. Such a tight ion pair is quite different from the carbonium ions or ion pairs described by Winstein for a limiting, unimolecular solvolysis (127). In *either* the direct k_s– versus $-k_\Delta$ or the tight-ion-pair interpretation (4b), the *overall* solvent-assisted and aryl-assisted paths both must involve strong backside bonding in order to prevent crossover.

On the other hand, nucleophilic solvent displacements on tertiary (and hindered secondary) substrates is sterically very unlikely. For these systems, in the absence of anchimeric assistance, an essentially unimolecular solvolysis is predicted, approaching an idealized, limiting (**lim**) process with rate constant designated k_c (127). In Winstein's k_c process (127), open, nucleophilically *un*solvated carbonium ions or ion pairs should intervene. Recent studies on the solvolysis of tertiary bridgehead substrates confirm the validity of *t*-butyl and related tertiary systems as models for limiting (127) carbonium ion behavior (128).

Therefore, since there is no competing solvent-assisted (k_s) pathway in tertiary β-arylalkyl systems to mask any significant accelerative effect by the aryl group, *any* rate enhancement observed in the solvolysis of tertiary β-arylalkyl systems *must* be an essentially complete measure of aryl participation. (For tertiary β-arylalkyl substrates, net rate enhancement due to aryl participation is given by k_t/k_c). Under these circumstances, small rate enhancements *do* mean weak aryl participation! "Leakage" between aryl-unbridged or weakly bridged carbonium ions or ion pairs should occur readily during the solvolysis of most tertiary β-arylalkyl systems (Fig. 6), and the available data appear to confirm this prediction (Table XI).

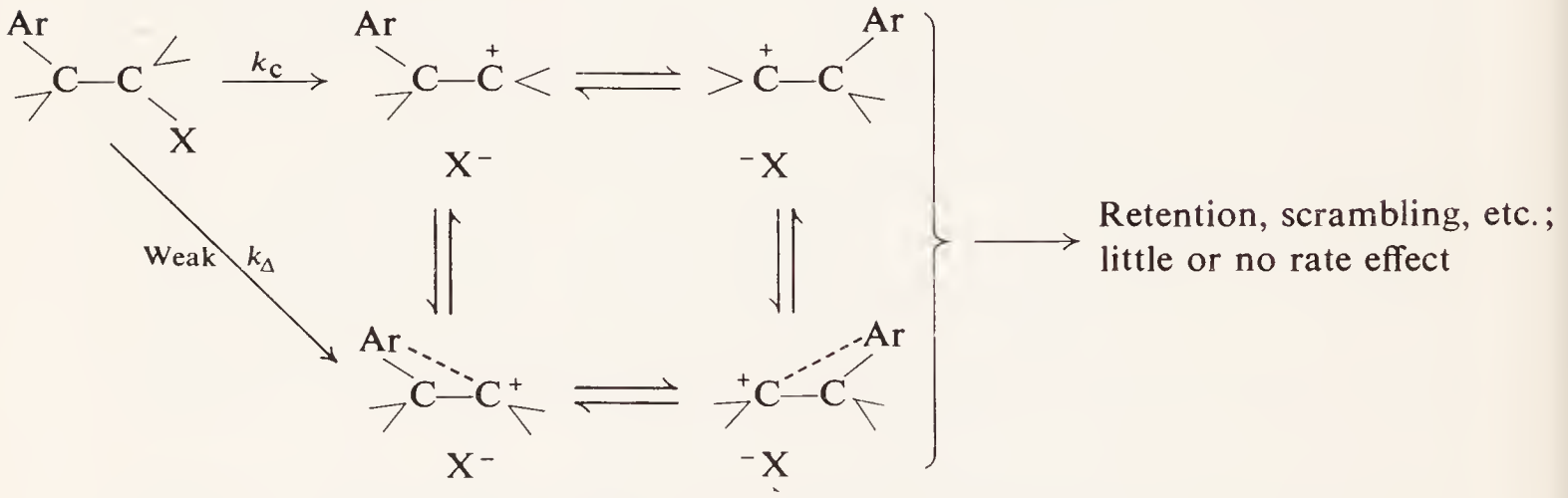


Figure 6. Description of crossover or "leakage" between k_c and k_Δ pathways.

VIII. CONCLUSION

Resolution of the rate-product problem for a large number of β-arylalkyl systems begins to close the long phenonium ion debate (2,3). The description of *primary* β-arylalkyl systems in terms of a competition between discrete k_s and Fk_Δ pathways never posed an interpretative problem, for primary systems have long been considered to solvolyze via direct solvent displacement in an S_N2 or S_N2-like fashion. Also, the description of tertiary β-arylalkyl systems in terms of a nondiscrete blend of k_c and k_Δ processes is consistent with the demonstrated limiting character of the solvolysis of simple tertiary systems.

The conclusion from the data in Table XI that *secondary* β-arylalkyl systems solvolyze in a manner grossly similar to the primary ones, via a competition between discrete solvent-assisted (k_s) and aryl-assisted (k_Δ) mechanisms, has broader consequences on the general theory of the solvolysis of secondary systems. For the past 20 years, Cram (1a–1e,2,21, 122) and Winstein (12,14,31,75a,61c) have independently and consistently formulated the solvolysis of secondary (nonbenzyl) β-arylalkyl systems as aryl-versus-solvent participation (Section V). Although Cram's stereochemical studies have always suggested strongly that aryl and solvent were in nucleophilic competition with each other in secondary β-arylalkyl systems, unambiguous experimental confirmations of this interpretation, especially including quantitative rate-product correlations (Table XI), were not provided until 1967 and thereafter (4,21a,39a,61c,89,126). Now, if the aryl-unassisted solvolysis (k_s) of secondary β-arylalkyl substrates is strongly solvent assisted, as indeed is demanded by the rate-product correlations in Table XI, *then the solvolysis of simple, unhindered secondary systems, without neighboring groups, must also be significantly accelerated by nucleophilic solvent participation.* How does this conclusion fit in with the general literature concerning the solvolysis of simple secondary systems?

Unfortunately, for the past 30 years, the solvolysis literature for *simple* secondary systems has presented a surprisingly inconsistent, confusing picture.* A general breakdown into three major periods of research is convenient. In the earliest work, Ingold (129) and his associates treated secondary systems as "borderline" between extreme unimolecular (S_N1) and bimolecular (S_N2) behavior; tendency toward either extreme was heavily dependent on substrate structure, solvent, etc. (129). Typical marginal behavior was described either by considering a blend of concurrent S_N1 and S_N2 pathways or, preferably (129), by assuming intermediate mechanisms. Later, Winstein suggested that, although the acetolysis and formolysis of simple secondary derivatives approached the limiting (**lim**; S_N1) category (31a–31c, 127a, 127b), nucleophilic solvent participation became important in the more nucleophilic alcohol solvents. This seems to be inconsistent with his simultaneous and subsequent interpretations involving solvent-assisted (k_s) mechanisms for the *acetolysis* and *formolysis* of secondary β-arylalkyl systems. Nevertheless, Winstein never subsequently was more explicit with regard to the extent of nucleophilic solvent participation to be expected in the acetolysis and formolysis either of simple secondary systems or of secondary β-arylalkyl substrates in the absence of an aryl-assisted k_Δ mechanism. Most recently, the solvolytic

* For a very complete bibliography of the solvolysis literature pertinent to secondary systems up to 1970, see Refs. 19 and 128.

behavior of unhindered secondary systems was explained in terms of *tight* and solvent-separated ion pairs (16,17,130), formed without significant solvent assistance in the initial ionization step to the tight ion pair (130). Such *tight* ion pairs were distinguished from the "looser" ion pairs or carbonium ions, which were postulated for the *limiting* solvolysis of tertiary or benzylic secondary systems (16b), so these more recent interpretations of the behavior of simple secondary systems (16,17,130) differ substantially from Winstein's earlier (31a–31c,127a,127b) interpretations of the solvolysis of such systems.

However, it was not until 1970 that the extent of nucleophilic solvent participation in the *overall solvolytic process* for simple, unhindered, nonbenzylic secondary substrates was finally assessed quantitatively. Using suitable models for unambiguous limiting or near-limiting behavior, Schleyer and co-workers (19a–19e) showed that *the solvolysis of simple secondary derivatives occurs with significant overall* nucleophilic solvent participation in all but the least nucleophilic solvents.* Typically, such nucleophilic solvent acceleration, relative to the hypothetical unaccelerated process (k_s/k_c) (127a,127b) in the acetolysis or formolysis of isopropyl tosylate, is estimated to be 10^3 or higher. This degree of nucleophilic solvent participation in the acetolysis and formolysis of simple secondary systems is consistent with the lack of significant crossover or "leakage" as revealed by the rate-product correlations in Table XI, and it independently confirms the conclusion that the solvolysis of secondary as well as primary β-arylalkyl systems is best interpreted in terms of solvent assistance (k_s) versus aryl assistance (k_Δ) (1a–1e,2,12,14,21,39,61c,89,122,126).† (Solvent assistance in primary systems is unquestionably stronger than in unhindered nonbenzylic secondary compounds (4b), but *both* are extensive enough to require k_s versus k_Δ interpretations for neighboring groups.)

The original 1949 (1a–1e) conclusions regarding the acetolysis and formolysis of 3-phenyl-2-butyl brosylate (**2a**, **2b**) remain essentially unaltered after surviving an exhaustive, probing investigation for more than two decades. But a significant outcome of all the phenonium ion research

* The relative partitioning of the observed nucleophilic solvent participation (19a–19e) between the initial formation and subsequent capture of any tight ion pair (16,17,130) that may intervene has not yet been established from the presently available data (19a–19e). See, however, Ref. 130 for some key observations in this area.

† NOTE ADDED IN PROOF. An alternate mechanistic scheme that reconciles the observed rate-product correlations for secondary β-arylalkyl systems with the rate-limiting formation of a π-bridged intimate ion pair has recently been suggested (B. G. Ramsey and N. K. Das, *J. Am. Chem. Soc.*, **94**, 4233 (1972). This scheme resembles the tight-ion-pair mechanism proposed by Brown and Kim (4b), but differs in the relative rates suggested for the various steps of an otherwise very similar overall process.

that has been published since 1949 is a substantial refinement in our understanding of the more general theory of solvolysis.

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