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In Memory of H. L. Meerwein

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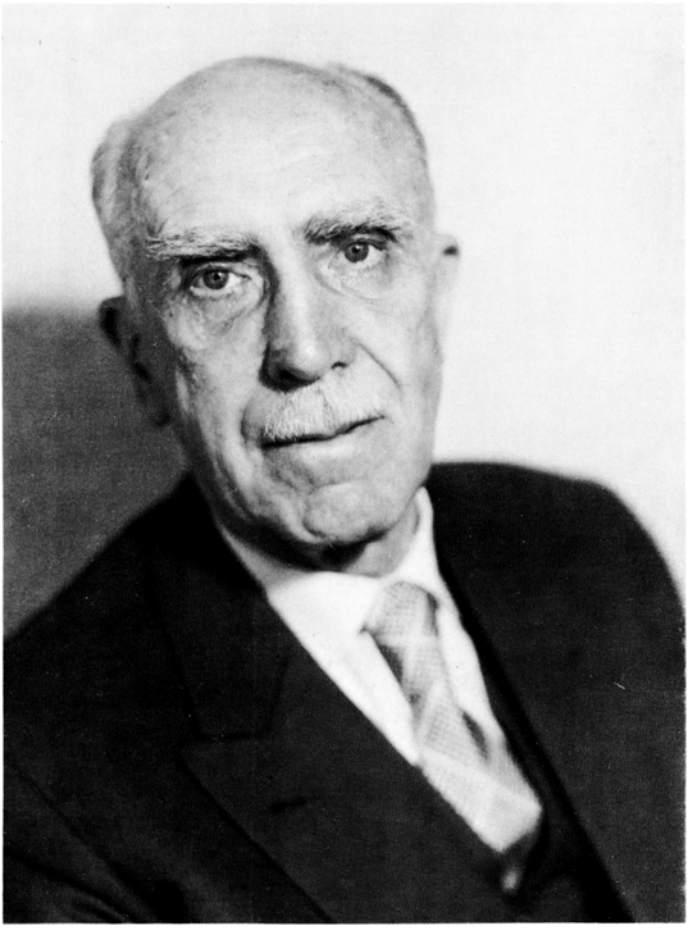

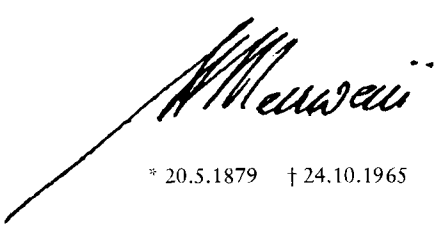

* 20.5.1879 † 24.10.1965

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Fortschritte der Chemischen Forschung

In Memory of H. L. Meerwein

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This series presents critical reviews of the present position and future trends in modern chemical research. It is addressed to all research and industrial chemists who wish to keep abreast of advances in their subject.

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Meerwein and Equilibrating Carbocations

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Fifty-seven years ago, Hans Meerwein published a paper, "Über die Gleichgewichts-Isomerie zwischen Bornylchlorid, Isobornylchlorid and Camphen-chlorhydrat[1]", which had immense consequences for the development of physical organic chemistry. The paper contains the first proposal of carbonium ions as intermediates in molecular rearrangements. It also provided the basis for the later proposal of a nonclassical ion as an intermediate[2], in place of the pair of rapidly equilibrating classical cations utilized by Meerwein[1]. Consequently, this publication opened the door to major research efforts by numerous chemists throughout the world. It is the purpose of this review to discuss the question of whether it is the Meerwein concept of equilibrating cations or the Wilson proposal of a mesomeric nonclassical cation that best accounts for the fascinating behavior of 2-norbornyl cations.

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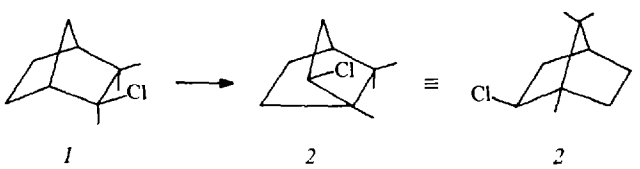
Origins

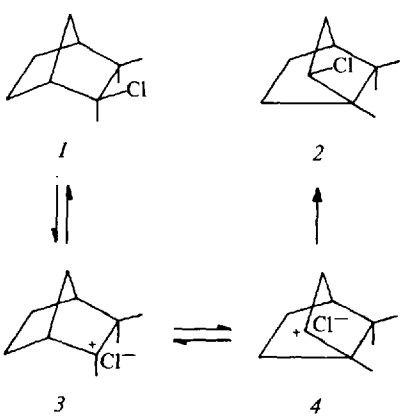
The exceptionally facile rearrangements of terpenes containing norbornyl nuclei[3] long plagued organic chemists attempting to assign structures to terpenes related to camphene. It was a major triumph in 1899 when Wagner recognized the nature of rearrangements of the borneol-camphene type and their relationship to the pinacol-tetra-methylethylene rearrangement[4].

In 1902 Semmler observed the formation of tricyclanes in the reaction products from the Wagner rearrangements of terpenes[5]. A tricyclane mechanism was later proposed by Ruzicka to account for the Wagner rearrangement. However, Ruzicka failed to recognize that the process involes the formation of ionic intermediates.

It was Meerwein, who, in 1922, first recognized that the facile rearrangement of camphene hydrochloride (*1*) into isobornyl chloride (*2*) (1) involves a prior conversion into the corresponding ions or ion-pairs[1] (2). This appears to be the first



1 *2* *2* (1)



1 *2* (2)

3 *4*

proposal of carbonium ions or ion-pairs (*3*, *4*) as intermediates in such molecular transformation (2). Such transformations, long known as Wagner-Meerwein rearrangements, have fascinated organic chemists and have provided for many years a major area for research.

In 1939, in the course of a discussion of the camphene hydrochloride-isobornyl chloride rearrangement, it was suggested by C. L. Wilson that such a rapidly equilibrating pair of cations (*3* ⇌ *4*) might exist instead as the mesomeric species *5*[2]. Previously *5* would have been considered to be the transition state separating *3* and *4*. In effect, the proposal was that this transition state might be sufficiently stable so

as to become a minimum in the reaction path, doing away with the need to consider the equilibrating classical structures, *3* and *4*.

5

The Nonclassical Ion Era

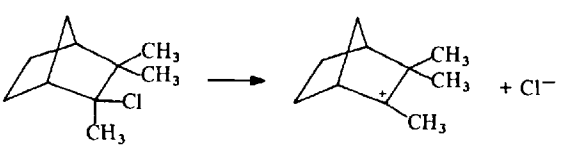
Wilson's suggestion was largely ignored for some ten years. However, in the early 1950's the study of carbonium ions became active[7]. σ-Bridged structures were proposed for the 2-norbornyl[8] and the cyclopropylcarbinyl[9] cations. These caught the fancy of the chemical public. The concept was widely adopted and used. Indeed, it would appear that nonclassical structures were at least considered for every known aliphatic, alicyclic, and bicyclic carbonium ion known to man with the possible exception of the methyl cation[10].

The concept proved to be highly popular. There were few skeptical questions raised. Consequently, the theory underwent rapid elaboration. Many new structures were proposed, some of exceptional complexity. This might be termed the "rococo period" of carbonium ion structures[10, 11].

Space does not permit a detailed discussion of the entire topic. Fortunately, a full discussion has recently appeared[11]. Consequently, the present review will consider only the 2-norbornyl system. Is it better represented as an equilibrating pair of classical cations equivalent to the Meerwein proposal[1], or is it better represented as a σ-bridged species equivalent to the Wilson proposal[2]?

The Problem

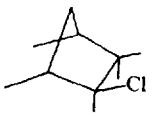
Ingold observed that the rate of solvolysis of camphene hydrochloride (6,000) was greatly enhanced relative to that for *tert*-butyl chloride (1.00)[12]. He argued that such a huge rate increase, 6,000, could not be, in his opinion, compatible with the relief of steric strain[13] accompanying the departure of the chloride ion from its highly congested environment. Consequently, he proposed that ionization was facilitated by the formation of a stabilized mesomeric cation *5*.



(3)

1 *3*

In such comparisons, it is important to use suitable models. Possibly *tert*-butyl chloride is not an appropriate model for camphene hydrochloride. A more suitable model would doubtless be the pentamethylcyclopentyl chloride *6* realized by opening the 5,6-ethano bridge of *1*.



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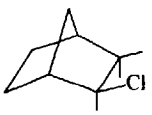
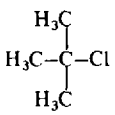
This structure has not yet been synthesized. However, many of the other methyl-substituted 1-methylcyclopentyl chlorides have been prepared and their rates of ethanolysis at 25 °C determined[14] (4).



1
13,600

7
2,380



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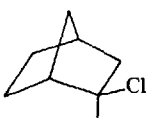

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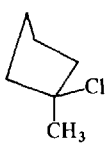
355

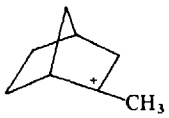


9
66

The results (4) do not support the conclusion that the rates for the norbornyl derivatives exhibit major enhancements. For example, the rate of solvolysis of camphene hydrochloride (*1*) is faster than that of the tetramethylcyclopentyl chloride (*7*) by a factor of only 5.7. Such a factor is far too small to argue for a major new stabilizing phenomenon in the ion from *1*. Removal of the gem-dimethyl substituents decreases the rate from 13,600 for *1* to 355 for *8*. A similar effect is observed in the cyclopentyl derivatives, *7* and *9*. These changes in reactivity are far more compatible with relief of steric strain[13] than with resonance stabilization of the cations[12].

At the present time, many supporters of the nonclassical position, such as Professor Paul von R. Schleyer, now accept the classical formulation of tertiary 2-norbornyl cations[11], such as 2,3,3-trimethyl-2-norbornyl cation (*3*) and the

2-methyl-2-norbornyl cation (*10*). This position supports the Meerwein interpretation (*2*) over that of Wilson (*5*).



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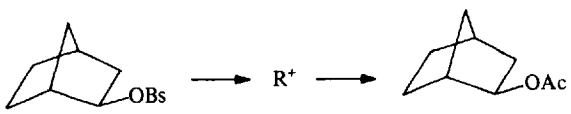
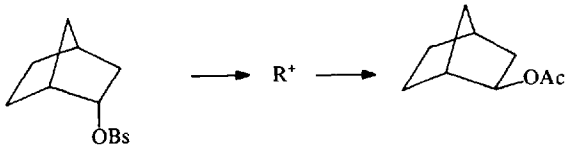
However, it is now argued that the secondary 2-norbornyl cations are different. Here it is proposed that true σ-bridged cations must be involved.

In 1952 Winstein reported a detailed study of the solvolysis of *exo*- and *endo*-norbornyl brosylates and observed fascinating phenomena which he interpreted in terms of a symmetrical σ-bridged norbornyl intermediate[8]. Thus the *exo* isomer (*11*) underwent acetolysis (5) at a rate 350 times that of the *endo* isomer (*13*) (6).



11 *12* (5)



13 *14* (6)

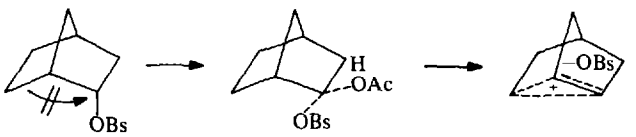
The optically active *exo*-norbornyl brosylate (*11*) yielded inactive *exo*-norbornyl acetate (*12*). However, the optically active *endo*-norbornyl brosylate yielded *exo*-norbornyl acetate retaining 7 to 8% of the original activity.

For the *endo* isomer, titrimetric rates equalled the polarimetric rates in the three solvents examined: acetic acid, aqueous acetone, and aqueous dioxane. However, for the *exo* isomer the polarimetric rate was greater than the titrimetric rates by factors of 1.40 in 75% aqueous acetone to 3.46 in acetic acid (later increased to 4.6, but without experimental data[15]). If the *exo* rate is corrected by this factor, the value becomes 1600 times that for the *endo* isomer.

Winstein proposed that the much faster rate for the solvolysis of the *exo*-norbornyl brosylate (*11*) was the result of participation by the 1,6-bonding pair in the transition state, leading to the formation of a σ-bridged (nonclassical) cation intermediate (*15*) (7). The nonclassical cation *15* possesses a plane of symmetry. Consequently, the acetate product, *12*, must be optically inactive.

11 *15* *12* (7)

The *endo* isomer is postulated to be stereoelectronically unfavorable for such participation. Consequently, ionization proceeds with weak solvent participation (8) to give an intermediate (*16*) which largely (92 to 93%) is converted into the nonclassical species (*15*) before it reacts with solvent to form product (*12*). According to this interpretation, only a small amount (7 to 8%) of the intermediate *16* is converted into the optically active *exo*-norbornyl acetate prior to conversion to *15*.



13 *16* *15* (8)

Winstein's original position was not as dogmatically in favor of the nonclassical structure as it was later interpreted. Thus, in the original publication[8] he stated: "*...racemization alone could be due to a dynamic equilibration between two one-sided cationic species VII and X. Further qualification regarding these species and*

VII X

their reactions would be necessary to account for ... the essentially exclusive formation of exo product and the enhanced solvolysis rate of the exo-p-bromobenzenesulfonate."

Transition State or Intermediate

As was pointed out earlier, rearrangements in bicyclic systems of the norbornyl type are extraordinarily facile[4], involving cationic intermediates[1]. If σ-bridged species are not involved, the barriers for such interconversions must be very low. If the rate of interconversion of such ions or ion pairs is to be fast relative to the rate of their capture by solvent, the barrier to interconversion must indeed be low, not greater than a few kcal mol^{-1}.

In essence, the nonclassical proposal is that those electronic effects which serve to lower the barrier for the interconversion of two cations (Fig. 1) could further stabilize this species so that it produces a symmetrical species sufficiently stable that there is no longer any need to consider the original equilibrating unsymmetrical cations.

This is a fascinating hypothesis. It possesses the advantages of simplicity in replacing two or more equilibrating classical cations by a single σ-bridged species.

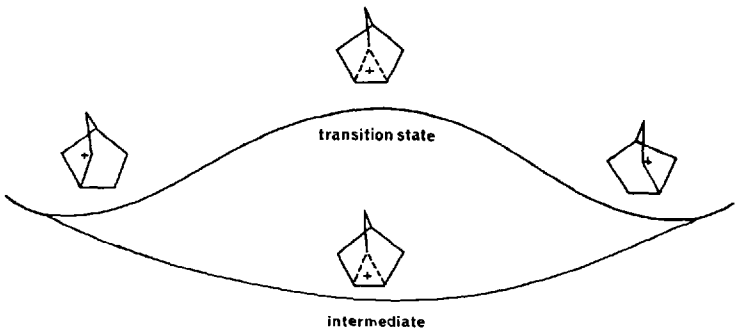


Fig. 1. Proposed transformations of the relatively stable transition state responsible for the rapid equilibration of 2-norbornyl cations into a stabilized symmetrical intermediate sufficiently stable as to make unnecessary further consideration of the unsymmetrical 2-norbornyl cations as intermediates

However, chemistry is still an experimental science--no matter how reasonable and attractive such a proposal may appear, it is still necessary to subject such proposals to experimental test. Indeed, as was pointed out earlier, the similar proposal by Wilson to replace the two isomeric cations of Meerwein, *3* and *4*, by the single mesomeric species *5*, is no longer with us[11]. Let us examine the evidence which has been accumulated with respect to the 2-norbornyl cation.

Equilibrating Carbocations

Some time ago a major anomaly in carbonium ion chemistry was pointed out[16]. Systematic lowering of the potential barrier separating two symmetrical carbocations (9) would be expected to result in three distinct classes of such carbocations:

(9)

(a) essentially static classical carbocations which can be formed and converted into products without significant equilibration;
(b) equilibrating carbocations which undergo rapid equilibration in the time interval between formation and conversion into products; and
(c) bridged species where the potential barrier has disappeared so that resonance now occurs involving the two structures.

At the time that paper was published (1965), practically all systems examined had been assigned to the first and third of these classes, with the intermediate class being almost unpopulated. It was puzzling why there was this apparent discontinuity in the potential barriers separating such pairs of symmetrical cations (9).

Since that time the situation has been greatly changed. Numerous equilibrating carbocations have been identified in solvolysis, such as 3-phenyl-2,3-dimethyl-2-butyl[17], 1,2-di-*p*-anisyl-2-norbornyl[18], 1,2-dimethyl-2-norbornyl[19], etc.

In recent years the pioneering work of Olah, Saunders, Brouwer, and Hogeveen has made possible the direct spectroscopic observation of many carbocations[20]. One remarkable development from such studies has been the conclusion that many carbocations, such as 2,3,3-trimethyl-2-butyl, which can be captured in solvolysis without equilibration[17], undergo very rapid equilibration under stable ion conditions. Such equilibration often cannot be frozen out even at temperatures as low as −150 °C. Under such stable ion conditions it appears that rapid equilibration is the norm.

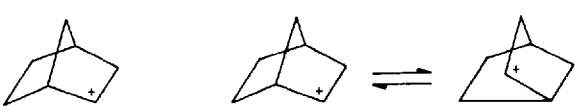
Indeed, many examples are now known of such rapidly equilibrating carbocations under stable ion conditions (see Table 13.1, Ref.[11]). The question to be resolved is whether the behavior of the 2-norbornyl cation under solvolytic conditions is best interpreted in terms of such a pair of rapidly equilibrating classical carbocations or ionpairs, or as the stabilized σ-bridged species.

Proposed Nonclassical "Structures"

Numerous "structures" have been proposed for 2-norbornyl. It is indeed rare for a single species to be so honored. It is appropriate to review the many "structures" which have been proposed before considering in detail the experimental observations we must use to reach a decision as to the most favorable representation.

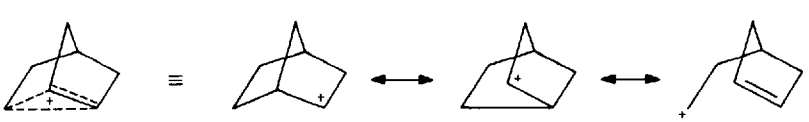
First, there is the classical static structure *17*. It should be clear that this structure will involve the usual electronic readjustments under the influence of the electron deficiency, electronic readjustments which will reflect inductive, inductomeric, field, and hyperconjugative influences.

Clearly this cannot be the structure of the 2-norbornyl cation. It does not possess a plane of symmetry and should therefore be formed and transformed into optically active products. Solvolysis of the optically active brosylate leads to inactive product. A rapidly equilibrating pair of ions or ion pairs (*18*) possesses such a plane of symmetry and constitutes a possible structure for the 2-norbornyl intermediate[8].



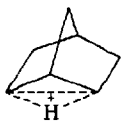
17 *18*

Winstein proposed that the transition state for such an equilibrating pair might be sufficiently stable so as to replace the classical structure[8]. He represented this structure *19* as a resonance hybrid of three canonical structures (*19'* ⟷ *19''* ⟷ *19'''*).



19 *19'* *19''* *19'''*

He also considered the edge-protonated species[8] *20*, while Roberts proposed the face-centered species[22] *21*. On the other hand, Olah has favored a formulation as a corner protonated nortricyclene[23] *22*, deleting the dashed double-bond of Winstein in *19*.



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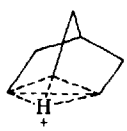

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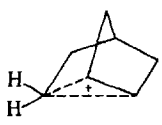
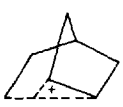


22

More recently Olah has favored still another formulation[24] *23*. Dewar has preferred the formulation as a π-complex[25] *24*. Finally, Traylor has supported a formulation of the 2-norbornyl cation as involving vertical stabilization by the C_1–C_6 bonding pair, but without σ-bridging or movement of the atoms[26] (*25*).



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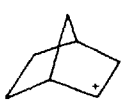


25

The question is -- how can we decide between the formulation of the 2-norbornyl cation as a rapidly equilibrating pair of classical carbocations *18*, and the various nonclassical formulations, *19–25*?

Do the High *exo*:*endo* Rate Ratios Require σ-Bridged Cations?

The racemization of optically active 2-norbornyl derivatives in the course of solvolysis can be accounted for, as Winstein himself appreciated[8], either in terms of a rapidly equilibrating pair of classical carbocations (*18*) or in terms of the formation of a symmetrical nonclassical species (*19–25*). Consequently, the problem cannot be resolved solely on the basis of such racemization.

The high *exo*:*endo* rate ratio exhibited by 2-norbornyl is a remarkable phenomenon, perhaps the least ambiguous characteristic of the 2-norbornyl system on which to base a decision. The precise problem of the 2-norbornyl solvolysis is defined by the energetics of the system as revealed by the energy diagram introduced by Goering and Schewene[27] (Fig. 2).

The rate of acetolysis of *exo*-norbornyl brosylate is 350 times that for the corresponding endo derivative[8]. If the data are corrected for internal return in the *exo* isomer, then the *exo*:*endo* rate of 1600 corresponds to a difference in the free energy of activation of 4.5 kcal mol^{-1}. The strain in *endo*-norbornyl arenesulfonates is estimated to be 1.3 kcal mol^{-1} [28]. This leads to a difference in the energies of the two transition states of 5.8 kcal mol^{-1} (Fig. 2).

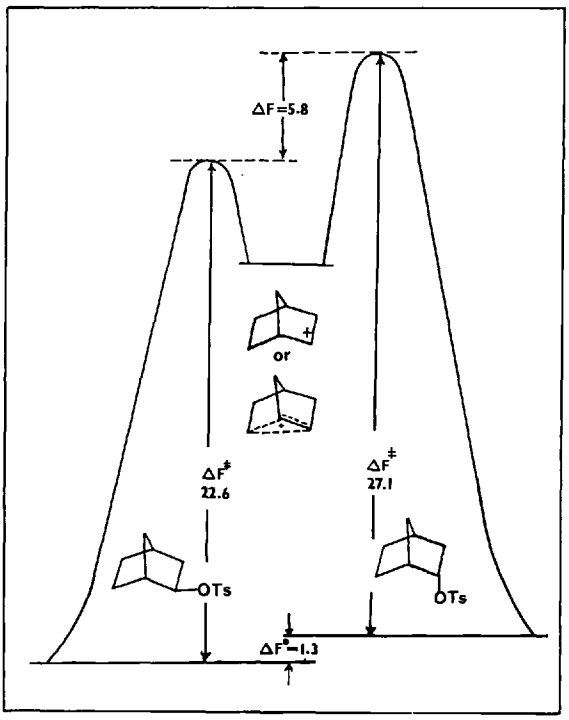
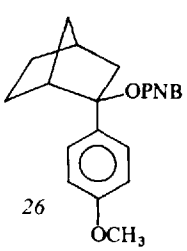


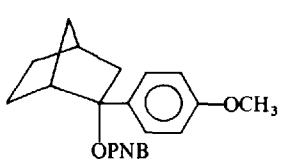
Fig. 2. Free energy diagram for the acetolysis of *exo*- and *endo*-norbornyl tosylates

The problem we are facing is that of defining just what factor or factors are responsible for the difference in energies of the two transition states. Is the *exo* transition state stabilized by σ-bridging? Or is it the *endo* transition state that is anomalous – destabilized by some factor, such as steric hindrance to "ionization"?

The approach we adopted was to examine the *exo:endo* rate ratios of highly stabilized tertiary 2-norbornyl derivatives. There is general agreement that such highly stabilized tertiary 2-norbornyl derivatives cannot involve σ-bridging[29, 30]. Yet the solvolyses of the 2-*p*-anisyl-2-norbornyl *p*-nitrobenzoate (*26*, *27*) in 80% acetone at 25 °C reveal an *exo:endo* rate ratio (RR) of 284[31]!



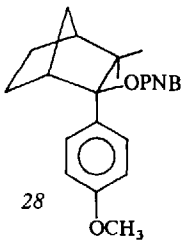
26



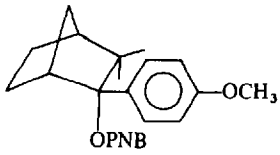
27

RR(25°C)	284	1.00

The corresponding camphenilyl derivatives (*28*, *29*) reveal an even higher *exo:endo* rate ratio[31].



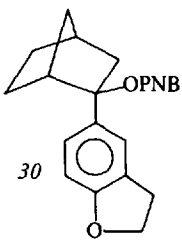
28



29

RR(25°C)	44,000	1.00

The 5-coumaranyl group (σ+ −0.984) is considerably more electron releasing than the *p*-anisyl group (σ+ −0.778)[32]. Yet even these exceptionally stabilized derivatives (*30*, *31*) reveal a high *exo*:*endo* rate ratio[33].



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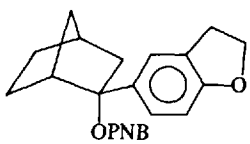


31

RR(25°C)	240	1.00

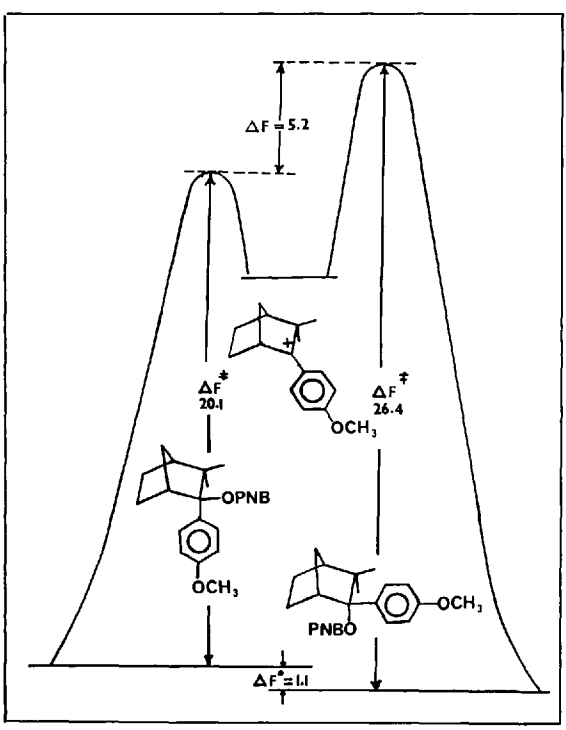


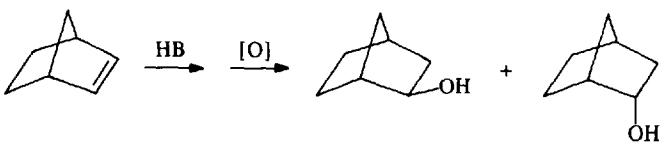
Fig. 3. Free energy diagram for the solvolysis of the 2-p-anisylcamphenilyl p-nitrobenzoates in 80% acetone at 25 °C

The Goering-Schewene diagrams for these stabilized derivatives (Fig. 3) are quite similar to that of the parent derivative (Fig. 2).

The conclusion appears clear–high *exo:endo* rate ratios can be realized in systems which cannot involve σ-bridging.

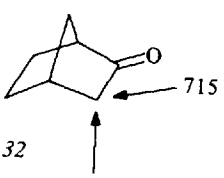
Steric Effects in U-Shaped Systems

The norbornyl system is a rigid three-dimensional structure with the *exo* face more exposed than the *endo*. Such U-shaped molecules invariably exhibit a steric preference for reaction at the more exposed *exo* face than at the more hindered *endo* face.



99.5% 0.5% (10)

Thus hydroboration-oxidation of norbornene yields 99.5% *exo*[34] (10). Similarly, the base-catalyzed deuterium exchange of norcamphor gives an *exo:endo* ratio of 715[35] (*32*). It is now suggested that ionization in such U-shaped structures likewise



32

1.00

exhibits a preference for departure of the leaving group from the *exo* face, rather than from the *endo* face. Indeed, consideration of molecular models for hypothetical ion-pairs for two possible reaction paths for the ionization of *endo*-norbornyl chloride reveals major steric difficulties (Fig. 4).

This concept was tested by examining the stereoselectivities exhibited by three different bicyclic systems (*33–35*) of gradually increasing U-shaped character and rigidity[36]. For all reactions examined, *33* exhibited the smallest preference for *exo:endo*, *34* next, and *35* the greatest. The same pattern is revealed in the solvolysis of the tertiary derivatives (*36*, *37*) (11)[37]. The similarity in the Goering-Schewene

33 *34* *35*

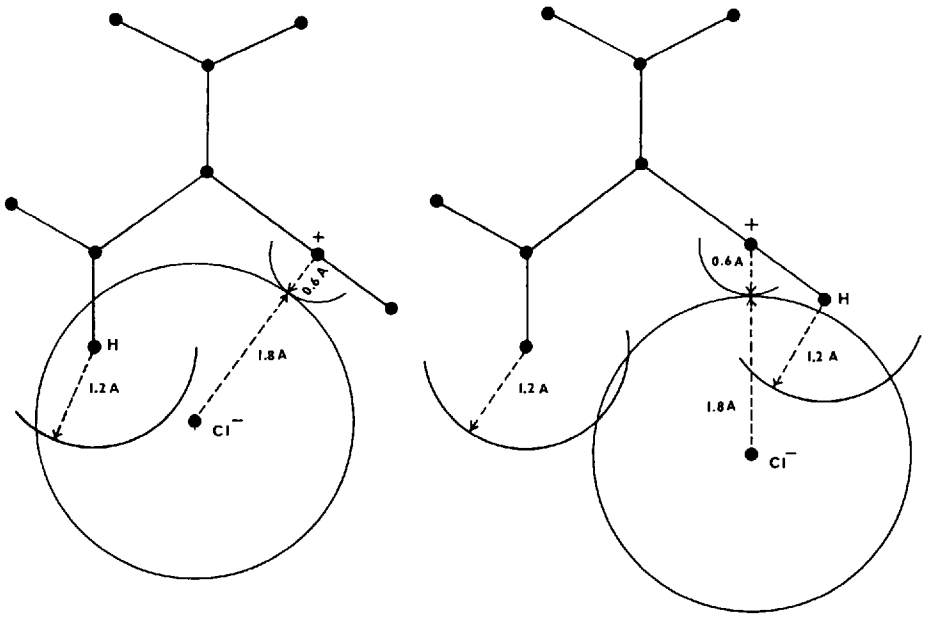


Fig. 4. Molecular models for the hypothetical intimate ion pairs from the two postulated reaction paths

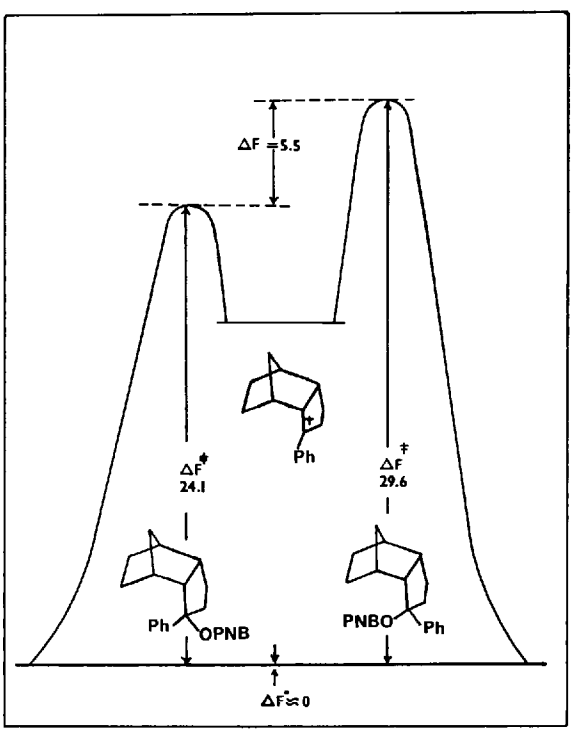
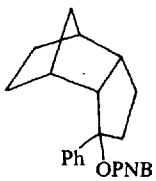
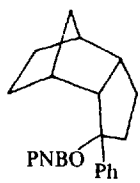


Fig. 5. Free energy diagram for the solvolysis of the 8-phenyl-*endo*-5,6-trimethylene-8-norbornyl p-nitrobenzoates in 80% acetone at 25 °C

diagram for *36* and *37* (Fig. 5) with that for 2-norbornyl (Fig. 2) and 2-*p*-anisyl-camphenilyl (Fig. 3) is evident.





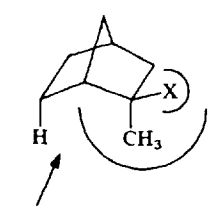
(11)

	36	*37*
RR(25°C)	11,000	1.00

Factor Responsible for the High *exo*:*endo* Rate Ratio in Secondary 2-Norbornyl

The marked similarity in the Goering-Schewene diagrams for secondary 2-norbornyl (Fig. 2) and tertiary 2-norbornyl (Fig. 3) is persuasive of the interpretation that similar physical origins must be involved in both systems. However, when the question was posed, "Is it reasonable to propose two very different explanations for phenomena which appear so similar?", Professor Paul von R. Schleyer answered, "Yes, it certainly is." Indeed, over the years a number of workers have taken this position that the origins of the high *exo*:*endo* rate ratios in secondary and tertiary 2-norbornyl derivatives are different. It is appropriate then to consider the various proposals.

Proposal No. 1. It was originally proposed back in 1966 that steric effects in the tertiary 2-methyl-2-norbornyl derivatives would be very large, with the steric requirements of the methyl substituent far exceeding those for the acyloxy group. On this basis large steric strains were postulated for the *endo*-methyl substituent (*38*). It was proposed that such strain would be relieved during ionization[38].



38

On this basis, the high *exo*:*endo* rate ratio in secondary 2-norbornyl was attributed to an enhanced *exo* rate, resulting from carbon participation, with a normal *endo* rate, whereas the high *exo*:*endo* rate ratio in tertiary 2-norbornyl was attributed to an enhanced *exo* rate, resulting from relief of steric strain, with a normal *endo* rate.

This proposal requires that 2-methyl-*endo*-norbornanol be far more stable than 2-methyl-*exo*-norbornanol. However, equilibration experiments soon revealed that the two isomers possess comparable stabilities[39].

Proposal No. 2. It was next proposed that the solvolysis of *endo*-norbornyl tosylate is enhanced by large solvent participation comparable in magnitude to carbon participation in the *exo* isomer. Thus, one of the two interpretations considered, referring to the 2-Me/2-H reactivity ratios, was that, "These $\approx 10^5$ values can be rationalized by the postulation of anchimeric assistance in the *exo* and solvent assistance in the *endo* secondary cases"[40]. This position was adopted and fully discussed by J. M. Harris and S. P. McManus in their interesting attempt to extrapolate from tertiary to secondary 2-norbornyl rates[41].

However, both J. M. Harris and we, in independent studies, have now concluded that solvent participation is not a significant factor in the solvolysis of *endo*-norbornyl tosylate in solvents of moderate or low nucleophilicities[42, 43]. Consequently, we can no longer account for the similarity in the behavior of secondary and tertiary 2-norbornyl derivatives in terms of the fortuitous presence of comparable solvent participation in *endo*-norbornyl and carbon participation in *exo*-norbornyl, both of which vanish in the tertiaries, resulting in essentially constant tertiary/secondary rate ratios[40, 41].

Proposal No. 3. In *"the nonclassical ion problem"*, Professor Paul von R. Schleyer has advanced a new interpretation[11]. He postulates carbon participation in secondary *exo*-norbornyl and comparable steric hindrance to ionization in the tertiary *endo*-norbornyl derivatives. However, he argues that such steric hindrance to ionization should not be important in the secondary 2-norbornyl system, since the smaller 2-H should provide far less steric hindrance to the departure of the *endo* anion than the larger 2-R[44].

In fact, a careful consideration of the molecular models (Fig. 4) reveals that even 2-H can serve to trap the anion in the *endo* cavity[45]. In addition, the ion-pair, which is presumably the first intermediate in such solvolyses, should be far tighter for the secondary system than the stabler tertiary system. This factor may serve to compensate for the smaller size of 2-H.

However, there appears to be little point to a discussion of this proposal on theoretical grounds, when experimental data are available to settle the question. The Goering-Schewene diagram (Fig. 2) establishes that the two transition states differ in energy by 5.8 kcal mol^{-1}. If this is the result of nonclassical stabilization of the *exo* transition state, the fully developed nonclassical cation should be more stable than the classical ion by a quantity significantly larger than 5.8 kcal mol^{-1}. Let us estimate this stabilization energy conservatively to be ≥ 7 kcal mol^{-1}.

The recent determination of the calorimetric heats of ionization of representative alkyl chlorides in SO_2ClF fails to reveal stabilization of this magnitude in the 2-norbornyl system[46]. For example, the calorimetric heat of ionization of 2-propyl chloride (-15.3 ± 0.9 kcal mol^{-1}) is less than that of *tert*-butyl chloride (-25.4 ± 0.8) by some 10.1 kcal mol^{-1}. On the other hand, the value for *exo*-norbornyl chloride (-23.6 ± 0.8) is less than that of 2-methyl-*exo*-norbornyl chloride (-3.15 ± 1.5) by some 7.4 kcal mol^{-1}. Similarly, the difference between 2-propyl chloride and 2-phenyl-2-propyl chloride (-30.3 ± 0.3) is 15.0 ± 1.2 kcal mol^{-1}, whereas the

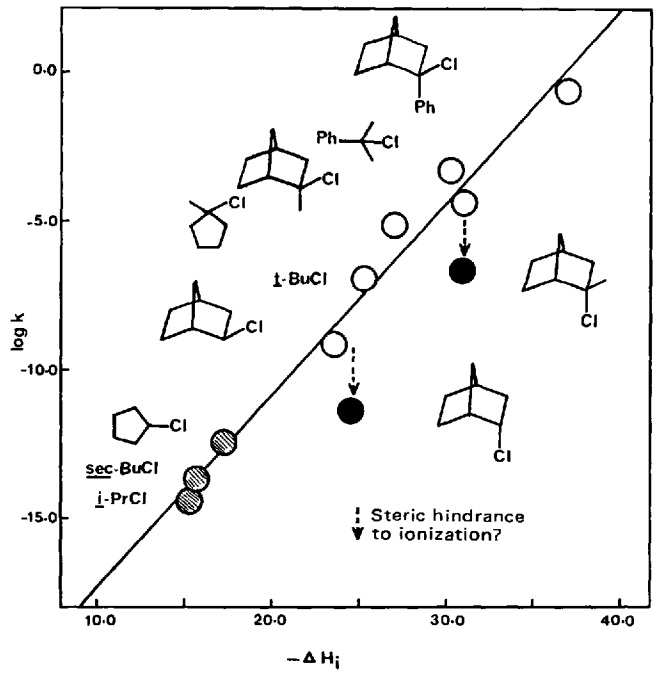


Fig. 6. Linear free energy plot of the rates of ionization of alkyl chlorides (shaded points are corrected to achieve limiting values) versus the calorimetric heats of ionization in SO_2ClF

difference between *exo*-norbornyl chloride and 2-phenyl-*exo*-norbornyl chloride (-37.0 ± 1.2) is 13.4 ± 2.1 kcal mol^{-1}.

This change in the secondary-tertiary energy difference for simple alkyl derivatives and the corresponding 2-norbornyl compounds, 2.7 kcal mol^{-1} for the methyl and 1.6 kcal mol^{-1} for the phenyl derivatives, are far from the value, ≥ 7 kcal mol^{-1}, required by the Goering-Schewene diagram.

It is of interest to plot the heats of ionization against the free energies of ionization under limiting conditions[46]. The values for the *endo* isomers were calculated by correcting the data for the *exo* isomers by the small difference in the ground state energies. The plot (Fig. 6) reveals that both the secondary and the tertiary 2-norbornyl chlorides fall below the line. This is not the behavior to be anticipated on the basis of the present Schleyer proposal[44].

A detailed search for nonclassical resonance energy by determining the Me/H rate ratios at positions 1- and 2- in the 2-norbornyl system likewise failed to uncover any evidence for its presence[47].

Conclusion

Irrespective of the final decision as to the nature of the secondary 2-norbornyl cation, it is now evident that tertiary 2-methyl- and 2-phenyl-2-norbornyl cation are

now accepted as being essentially classical under solvolytic conditions[44]. It follows that the tertiary cation from camphene hydrochloride (*3*) must also be classical. Thus the decision has been that the original Meerwein interpretation[1] of the camphene hydrochloride-isobornyl chloride rearrangement holds and we need no longer include the Wilson nonclassical species[2] *5* in our considerations of this reaction.

The original Meerwein publication[1] has indeed exerted truly major influence on the development of chemical thought and research.

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From Boron Trifluoride to Antimony Pentafluoride in Search of Stable Carbocations

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Table of Contents

I. Introduction

1. Personal Recollections of Hans Meerwein

Hans Meerwein was and always will be one of my heroes in chemistry. He introduced, ahead of Ingold and Robinson, the age of physical measurements into organic chemistry. At the same time his major aims always remained to find new methods and reactions of general synthetic utility. By his choice he was not interested in the synthesis of complex, large molecules, but in fundamental reactions and methods. He disliked narrow categories. He never considered himself to be a "physical organic" or "synthetic" chemist. He simply was a master chemist.

My first contact with Meerwein was in 1954 when I received, while still working in isolated Hungary, a letter from him. He had read a paper of ours, and offered useful comments, even pointing out that we had missed a relevant reference. We subsequently kept up correspondence. He continued to be interested in our early efforts to obtain long lived carbocations from alkyl (and acyl) fluorides in liquid boron trifluoride (and other Lewis acid halides) at low temperature, as well as via metathetic reactions of organic halides with silver tetrafluoroborate (a reagent we introduced in 1955 for the ionization of bromocyclohexadienes to form benzenium ions and which Meerwein developed to a wide utility akylation method).

It was in 1959 when I was first able to meet Meerwein personally during a visit to Marburg. He was at the time 79 but I would have thought him to be 20 years younger. He was not onyl extremely interested and up-to-date in chemistry, full with exciting, inventive ideas, but was even busy at the laboratory bench! His undiminished interest in chemistry and productivity well into his eighties is by now legendary. He maintained to the last an amazing knowledge and love of chemistry. He will always remain a shining example and great inspiration for future generations of chemists. It was indeed a great privilege to have visited him on a number of subsequent occasions, the last in the summer of 1965, shortly before his death. It was particularly rewarding for me to be able to give in his presence at that occasion a comprehensive report of our work on stable carbocations in antimony pentafluoride containing superacids. Meerwein actively participated in the discussion and his generous concluding remarks at the end of the Colloquium were that the search for carbocations, including the elusive alkyl cations, which started with boron trifluoride came to a successful end with antimony pentafluoride. This is then, in Meerwein's words, the topic which I will be reviewing dedicated to the memory of the pioneer and master of ionic organic chemistry.

2. General Concepts of Carbocations

Electrophilic reactions are generally considered[1] to proceed through cationic (i. e., *carbocationic*) intermediates. The general concept[1–3] of *carbocations* encompasses all cations of carbon containing compounds which sometimes were differentiated into two limiting classes: trivalent ("classical") carbenium ions and five or higher coordinated ("non-classical") carbonium ions. Whereas the differentiation of limiting

trivalent carbenium, and pentacoordinated carbonium ions serves a useful purpose to establish the significant differences between these ions, it is also clear that in most specific systems there exists a continuum of charge delocalization. In fact in all carbocations (even in the parent CH_3^+) there is a continuum of the degree of charge delocalization, and thus to think in limiting terms is rather meaningless. Participation by neighboring groups can not only be by *n*- and π-donors, as most generally recognized, but also by σ-ligands. There is in principle no difference between these. σ-Participation in properly oriented systems is not only possible, but it is unavoidable. The only question is its degree, and not whether it exists[4].

As is well known, trivalent carbenium ions play an important role in electrophilic reactions of π- and *n*-donor systems. Similarly, pentacoordinated carbonium ions are the key to electrophilic reactions of σ-donor systems (single bonds). The ability of single bonds to act as σ-donor lies in their ability to form carbonium ions via triangular two electron, three-center bond formation. Consequently, there seems to be in principle no difference between the electrophilic reactions of π- and σ-bonds except that the former react more easily even with weak electrophiles, whereas the latter necessitate more severe conditions. The role of carbocations in electrophilic reactions of π- and σ-donor systems is well recognized!

The concept of carbocations (the logical and now IUPAC recommended name for all cationic carbon compounds since the negative ions are called *carbanions*), with exception of the early isolation of highly stabilized triarylmethyl cation salts, grew to maturity through kinetic, sterochemical and product studies of a wide variety of reactions, especially unimolecular nucleophilic substitutions and eliminations. Leading investigators like Meerwein, Ingold, Hughes, Whitmore, Bartlett, Nenitzescu, Winstein, and others have contributed fundamentally to the development of modern carbocation theory[2], *e. g.*, the concept of elctron deficient cationic intermediates. Direct observation of stable, long-lived carbenium ions, generally in highly acidic (superacid) solvent systems has become possible only in recent years[1].

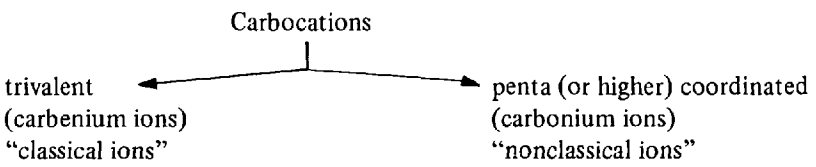
Based on our continuing study of carbocations by direct observation of long-lived species, it became increasingly apparent that the carbocation concept is much wider than previously realized, and necessitated a general definition[1]. Therefore, such a definition was offered *based on the realization that two distinct, limiting classes of carbocations exist:*

a) *Trivalent ("classical") carbenium ions* contain an sp^2-hybridized *electron deficient* carbon atom, which tends to be planar in the absence of constraining skeletal rigidity or steric interference. (It should be noted that sp-hybridized, linear oxocarbonium ions and vinyl cations also show substantial electron deficiency on carbon). The carbenium carbon contains six valence electrons, thus is highly electron deficient. The structure of trivalent carbocations can always be adequately described by using two-electron two-center bonds (Lewis valence bond structures).

b) The bonding nature of *penta- (or higher) coordinated ("nonclassical") carbonium ions*, which contain five or (higher) coordinated carbon atoms, cannot be described by two-electron single bonds alone, but also necessitates the use of two-electron, three (or multi) center bond(s). The carbocation center is always surrounded by eight electrons, although two (or more) of them are involved in multi-

center bonds, and the ions overall are electron deficient (due to electron sharing of two binding electrons between three (or more) centers.

Lewis's concept that a chemical bond consists of a pair of electron shared between two atoms became the foundation of structural chemistry and chemists still tend to brand some compounds as anomalous compounds whose structures cannot be depicted in terms of such bonds alone. Carbocations with too few electrons to allow a pair for each "bond", came to be referred to as "nonclassical", a label still used even though it is now recognized that, like any other substances, they adopt the structures appropriate for the number of electrons they contain.



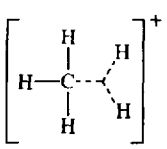
Expansion of the carbon octet via 3d-orbital participation does not seem possible; there can be only eight valence electrons in the outer shell of carbon[5]. Thus, the covalency of carbon cannot exceed four. Penta- (or high)-coordination implies a species with five (or more) ligands within reasonable bonding distance from the central atoms[6]. The transition states long ago suggested for S_N2 and S_E2 reactions may represent such cases. However, the direct observation of stable penta- (or higher) coordinated species in solution was not reported until recent studies of long-lived "nonclassical" ions in superacid solvent systems. Moreover, S_E2 substitution reactions have been, in the past, mainly restricted to organometallic compounds, *i. e.*, organmercurials[7].

Neighboring group interactions with the vacant *p*-orbital of the carbenium ion center can contribute to ion stabilization via charge delocalization. Such phenomena can involve atoms with unshared electron pairs (*n*-donors) C–H and C–C hyperconjugation, bent σ-bonds (as in cyclopropylcarbenium ions) and π-electron systems (direct conjugative or allylic stabilization). Thus trivalent carbenium ions can show varying degrees of delocalization without becoming pentacoordinated carbonium ions. The limiting classes defined do not exclude varying degrees of delocalization, but in fact imply a spectrum of carbocation structures.

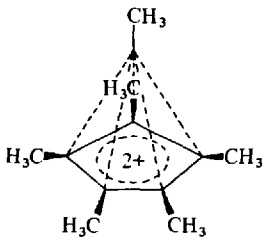
In contrast to the rather well-defined trivalent ("classical") carbenium ions, "nonclassical ions"[8] have been more loosely defined. In recent years, a lively controversy has centered on the classical-nonclassical carbonium ion problem[9]. The extensive use of "dotted lines" in writing carbonium ion structures has been (rightly) criticized by Brown[9d], who carried, however, the criticism to question the existence of any σ-delocalized (nonclassical) ion. For these ions, if they exist, he stated " . . . a new bonding concept not yet established in carbon structures is required."

Clear, unequivocal experimental evidence has by now been obtained for nonclassical ions such as the norbornyl cation[10]. The bonding concept required to define "nonclassical ions" is simply to consider them as penta- (or higher coordi-

nated) carbonium ions, of which CH_5^+ (the methonium ion-carbonium ion) is the parent, as CH_3^+ (methenium ion, methyl cation, carbenium ion) is the parent for trivalent carbenium ions. An example of a hexacoordinated carbonium ion is the pyramidal dication of Hogeveen's[11].



Pentacoordinated



Hexacoordinated

Concerning the carbocation concept, it is regrettable that in the Anglo-Saxon literature the general usage for a long time named the trivalent, planar ions of the CH_3^+ type as *carbonium ions*. If the name is considered analogous to other *onium ions* (ammonium, sulfonium, phosphonium ions, etc.), then it should relate to the higher valency state carbocation. The higher valency state carbocations, however, clearly are not the trivalent but the *penta (or higher) coordinated cations*. The German and French literatures indeed frequently use the "carbenium ion" naming for the trivalent cations. If we consider these latter ions as protonated carbenes, the naming is indeed correct[12]. It should be pointed out, however, that the "carbenium ion" naming depicts only trivalent ions and thus should not be a general name for *all* carbocations. IUPAC's Organic Chemistry Division recently reviewed the nomenclature of physical organic chemistry, and recommends the use of the "carbocation" for naming all positive ions of carbons. "Carbenium" or "carbonium ion" naming, similar to the "carbinol" naming of alcohols, is discouraged.

3. Development of the Carbocation Concept: Kinetic and Stereochemical Studies

One of the most audacious and fruitful ideas born in organic chemistry was the suggestion that carbocations might be intermediates in the course of reactions that start from nonionic reactants and lead to nonionic covalent products. It was Hans Meerwein[13] who in 1922, while studying the kinetics of the rearrangement of camphene hydrochloride to isobornyl chloride reported the important observation that the reaction rate increased in a general way with the dielectric constant of the solvent. Further, he found that metallic chlorides – such as $SbCl_5$, $SnCl_4$, $FeCl_3$, $AlCl_3$, and $SbCl_3$ (but not BCl_3 or $SiCl_4$), as well as dry HCl – which promote the ionization of triphenylmethyl chloride by formation of ionized complexes, considerably accelerate the rearrangement of camphene hydrochloride. Meerwein concluded that the conversion of camphene hydrochloride to isobornyl chloride actually does not proceed by way of migration of the chlorine atom but by a rearrangement of a cationic intermediate. Thus, the modern concept of carbocation intermediates was born.

Ingold, Hughes, and their collaborators in England, starting in the late 1920's carried out detailed kinetic investigations on what later became known as nucleophilic substitution at saturated carbon and polar elimination reactions[14]. The well-known work relating to S_N1 and later E1 reactions established the carbocation concept in these reactions. Whitmore[15], in a series of papers which began in 1932, generalized Meerwein's rearrangement theory to many organic chemical reactions.

Kinetic and stereochemical evidence helped to establish carbocation intermediates in organic reactions. These species, however, were generally too short lived and could not be directly observed by physical means.

II. Observation of Stable, Long Lived Carbocations

The transient nature of carbocations arises from their extreme reactivity with nucleophiles. The use of low nucleophilicity gegenions, particularly tetrafluoroborates (BF_4^-) enabled Meerwein in the forties to prepare a series of oxonium and carboxonium ion salts, such as $R_3O^+BF_4^-$ and $HC(OR)_2^+$ respectively. These Meerwein salts are effective alkylating agents, and transfer alkyl cations in S_N2 type reactions. However, simple alkyl cation salts ($R^+BF_4^-$) were not obtained in Meerwein's studies. The first acyl tetrafluoroborate, i. e. acetylium tetrafluoroborate was obtained by Seel[16] in 1943 by reacting acetyl fluoride with boron trifluoride at low temperature.

$$CH_3COF + BF_3 \rightleftharpoons CH_3CO^+BF_4^-$$

In the early fifties we started a study of the intermediates of Friedel-Crafts reactions and inter alia carried out a systematic investigation of acyl fluoride-boron trifluoride complexes. We were also to observe a series of donor-acceptor complexes as well as stable acyl cations. Subsequently the investigations were also extended to other Lewis acid halides. In the course of these studies we also increasingly became interested in alkyl halide-Lewis acid halide complexes. The study of alkyl fluoride-boron trifluoride complexes by electric conductivity measurements indicated the formation of ionic complexes in the case of tertiary butyl and isopropyl fluorides at low temperature, whereas methyl and ethyl fluoride ions formed molecular coordination complexes. It was, the nucleophilicity of the system which prevented in isolating or to otherwise characterize alkyl cation salts. It was for this reason that we initiated a systematic study of more suitable acid and low nucleophilicity solvent systems. This resulted in the discovery of superacidic systems and very weakly nucleophilic solvents, which finally allowed to obtain alkyl cations as stable, long lived species[1]. Subsequently, a wide range of practically all conceivable carbocations became readily available for structural and chemical studies[1, 2].

A. Trivalent Carbocations

5. Alkyl Cations

a. Early Unsuccessful Attempts. Simple alkyl cations were considered until the early sixties only as transient species[2]. Their existence has been inferred from the study of the course of certain reactions. No reliable physical measurements, other than electron impact measurements of the simple alkyl cations were known. The formation of gaseous organic cations under electron bombardment of alkanes, haloalkanes, and other precursors has been widely investigated in mass spectrometric studies[17]. No similar direct observation of carbocations in solution was achieved.

The observation of alkyl cations like that of tert-butyl cation (trimethylcarbenium ion). $(CH_3)_3C^+$ *1* or the isopropyl cation (dimethylcarbenium ion), $(CH_3)_2CH^+$ *2* thus was a longstanding challenge. The existence of alkyl cations in systems containing alkyl halides and Lewis acid halides has been inferred from a variety of observations, such as vapor pressure depressions of CH_3Cl and C_2H_5Cl in the presence of gallium chloride[18]; conductivity of aluminium chloride in alkyl chlorides[19] and of alkyl fluorides in boron trifluoride[20]; as well as the effect of ethyl bromide on the dipole moment of aluminium bromide[21]. However, in no case had well-defined, stable alkyl cation complexes been established even at very low temperatures.

Electronic spectra of alcohols and olefins in strong proton acids (H_2SO_4) were obtained by Rosenbaum and Symons[22]. They observed, for a number of simple aliphatic alcohols and olefins, absorption maximums around 290 nanometers and ascribed this absorption to the corresponding alkyl cations.

Finch and Symons[23], on reinvestigation of the absorption of aliphatic alcohols and olefins in sulfuric acid solution, showed that the condensation products formed with acetic acid (used as solvent for the precursor alcohols and olefins) were responsible for the spectra, not the simple alkyl cations. Moreover, protonated mesityl oxide was identified as the absorbing species in the system of isobutylene, acetic acid, ans sulfuric acid.

Deno and his co-workers[24] carried out an extensive study of the fate of alkyl cations in undiluted H_2SO_4 and oleum produces equal amounts of a saturated hydrocarbon mixture (C_4 to C_{18}) insoluble in H_2SO_4 and a mixture of cyclopentenyl cations (C_9 to C_{20}) in the H_2SO_4 layer. These cations exhibit strong ultraviolet adsorption around 300 nm.

It must therefore be concluded that earlier attempts to prove the existence of stable, well-defined alkyl cations were unsuccessful in experiments using sulfuric acid solutions and inconclusive in the interaction of alkyl halides with Lewis acid halides. Proton elimination reactions or dialkyl halonium ion formation may have affected conductivity studies.

b. Preparation from Alkyl Fluorides in Antimony Pentafluoride Solution. In 1962 we first directly observed stable alkyl cations in solution[25–27]. We obtained the *t*-butyl cation *1* (trimethylcarbenium ion) when *t*-butyl fluoride was dissolved in excess antimony pentafluoride, which served both as Lewis acid and solvent. Later

the counter ion was found to be, under these conditions, primarily the dimeric $Sb_2F_{11}^-$ anion[28]; whereas in SbF_5–SO_2 or SbF_5–SO_2ClF solutions, SbF_6^- and $Sb_2F_{11}^-$ are both formed.

$$(CH_3)_3CF + (SbF_5)_2 \rightarrow \underset{1}{(CH_3)_3C^+}Sb_2F_{11}^-$$

The possibility of obtaining stable alkyl fluoroantimonate salts from alkyl fluorides (and subsequently other halides) in antimony pentafluoride solution (neat or diluted with sulfur dioxide, sulfuryl chloride fluoride, or sulfuryl fluoride) or in other superacids[29] such as FSO_3H–SbF_5 (Magic Acid^R,[30] HF–SbF_5 (fluoroantimonic acid), HF–TaF_5 (fluorotantalic acid) and the like was evaluated in detail, extending studies to all isomeric C_3 to C_8 alkyl halides, as well to a number of higher homologs[31–32].

Propyl, butyl, and pentyl fluorides with antimony pentafluoride gave the isopropyl, t-butyl and t-amyl cations (as their fluoroantimonate salts) *2*, *1* and *3*.

$$C_3H_7F + (SbF_5)_2 \rightarrow \underset{2}{CH_3C^+HCH_3}\ Sb_2F_{11}^-$$

$$C_4H_9F + (SbF_5)_2 \rightarrow \underset{1}{CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C^+}}{-}CH_3}\ Sb_2F_{11}^-$$

$$C_5H_{11}F + (SbF_5)_2 \rightarrow \underset{3}{CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C^+}}{-}CH_2CH_3}\ Sb_2F_{11}^-$$

The secondary butyl and amyl cations can be observed only at very low temperatures and they rearrange readily to the more stable tertiary ions.

Generally, the most stable tertiary or secondary carbocations are observed from any of the isomeric alkyl fluorides in superacidic solvent system.

c. Nuclear Magnetic Resonance Spectra. One of the most powerful tools in the study of carbocations is nuclear magnetic resonance spectroscopy. The main feature

Table 1. Characteristic PMR[a] Parameters of alkyl cations in SbF_5–SO_2ClF solution at $-70°$

Ion		δ_{1H}					
		CH^+	J_{+CH}	J_{+CCH}	α-CH_2	α-CH_3	β-CH_3
$(CH_3)_2CH^+$	*2*	13	169	3.3		4.5	
$(CH_3)_3C^+$	*1*			3.6		4.15	
$(CH_3)_2C^+CH_2CH_3$	*3*				4.5	4.1	1.94
$CH_3C^+(CH_2CH_3)_2$	*4*				4.44	4.16	1.87

[a] Chemical shifts are in ppm from external capillary TMS. Coupling constants are in Hzs.

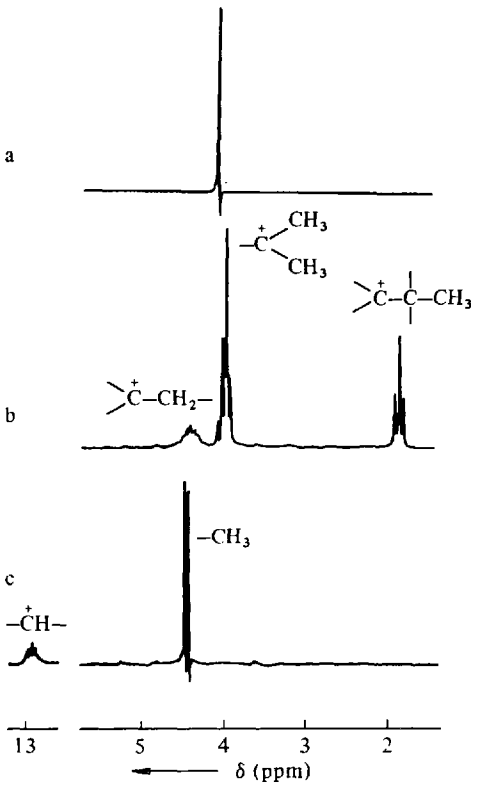


Fig. 1. ^{1}H-NMR spectra of: a) the *tert*-butyl cation (*2*) [trimethylcarbenium ion, $(CH_3)_3C^+$]; b) the *tert*-amyl cation (*3*) [dimethylethylcarbenium ion, $(CH_3)_2C^+-C_2H_5$]; c) the isopropyl cation (*1*) [dimethylcarbenium ion, $(CH_3)_2C^+H$ ium ion, $(CH_3)_2C^+H$]. (60 MHz, SbF_5-SO_2ClF solution. −60 °C)

of the proton NMR spectra of alkyl fluorides in antimony pentafluoride is the substantial deshielding of the protons in the carbocations as compared with the starting alkyl fluorides (Fig. 1 and Table 1).

In Order to prove that stable alkyl cations, and not exchanging donoracceptor complexes were obtained, we also investigated the ^{13}C nuclear magnetic resonance of the potentially electropositive carbenium carbon atom in alkyl cations[31–32].

The $^{13+}$C shift in the *t*-butyl cation $(CH_3)_3{}^{13+}C$ *1* in SO_2ClF-SbF_5 solution at −20 ° is at $\delta_{^{13}C}$ 335.2 (all CMR shifts are from ^{13}C TMS) with a long-range coupling to the methyl protons of 3.6 Hertz.

The $^{13+}$C shift in the isopropyl cation *2* under identical conditions, is $\delta_{^{13}C}$ 320.6 with a long-range coupling to the methyl protons of 3.3 hertz. The direct ^{13}C–H coupling is 169 hertz (indicating sp^2 hybridization of the carbenium carbon atom), while the long-range, proton-proton coupling constant is 6.0 Hertz (see Fig. 1).

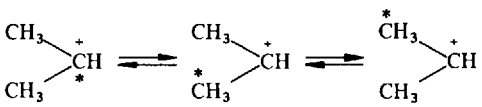
Substitution of the methyl group in the *t*-butyl cation by hydrogen thus causes an upfield shift of 10.4 ppm. Although the CMR shift of the carbocation center of the *t*-butyl cation is more deshielded than that of the isopropyl cation (by about 10 ppm), this can be explained by the methyl substituent effect, which may amount to 22 ppm. The tertiary butyl cation thus is more delocalized and stable than the secondary isopropyl.

The $^{13}C^{+}$ shift in the *t*-amyl cation $C_2H_5C^{+}(CH_3)_2$ *3* is at $\delta^{13}C$ 335.4 which is similar to that of *t*-butyl cation. The shift difference is much smaller than the 17 ppm found in the case of the related alkanes, although the shift observed is in the same direction. The ^{13}C NMR chemical shifts and coupling constants J_{C-H} of C_3–C_8 alkyl cations *1–13* are shown in Tables 2 and 3[32].

It is difficult to interpret these large deshieldings in any way other than as a direct proof that
(i) the state of hybridization of the carbon atoms involved in the carbenium ions is sp^2; and
(ii) at the same time, the carbon atom carries a substantial positive charge.

Table 1 summarizes the ^{1}H and ^{13}C NMR parameters for the carbocations center in a series of selected secondary and tertiary carbenium ions. Data are characterized by substantial deshielded chemical shifts with coupling constant (J_{CH}) that indicate sp^2-hybridization.

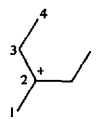
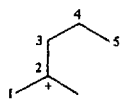
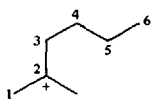
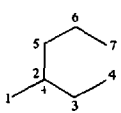
When the isopropyl cation *2* was generated from 2-chloropropane with 50 percent ^{13}C enrichment of C–2 in SO_2ClF–SbF_5 at 60 °C, equilibration of the ^{13}C lable occurred with a half-life of 1 hour. After several hours, the ^{13}C was distributed equally among the three carbons. This observation suggests involvement of protonated cyclopropanes in the carbon scrambling process (see subsequent discussion). Similar scrambling was observed in the secondary butyl *14* (*sec*-butyl) and *t*-amyl cations *4* (Saunders)[33].

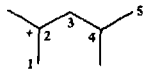
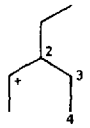
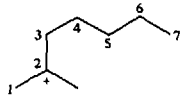
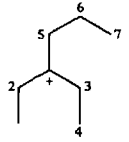
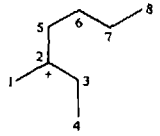
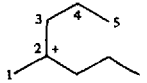


d. Infrared and Raman Spectra. Infrared and Raman spectra of the stable alkyl carbocations were also observed[26, 34] and are in complete agreement with the carbenium structure of the ions. Infrared spectra of these ions and of their deuterated analogs correspond to the spectra predicted by calculations based on molecular models and force constants. Thus, vibrational spectra can also be used in the identification of stable carbenium ions.

Laser Raman spectroscopy, particularly with helium-neon lasers, is another powerful tool in the study of carbocations. Because Raman spectra give valuable information on symmetry, these spectra help to establish, in detail, structures of the ions and their configurations. The Raman spectroscopic data provide strong evidence that the *t*-butyl cation *1* in magic acid[30] solution prefers a conformation leading to overall C_{3v} point group symmetry (Table 4 and Fig. 2). Thus the $C^{+}(CH_3)_3$ ion exists in these solutions with a planar $C^{+}(C_3)$ carbon skeleton and with one hydrogen atom of each CH_3 group above the C^{+}–C_3 plane. The other two hydrogen atoms are arranged symmetrically below the $C^{+}C_3$ plane to the right and left of the C_3 axis. Raman spectra observed for the *t*-amyl cation, the pentamethylethyl cation, and the tetramethylethyl cation also show similar structure. The Raman spectroscopic studies thus provide, in addition to ^{13}C NMR data, direct evidence for the planar carbenium center of alkyl cations.

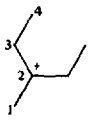
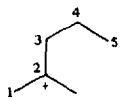
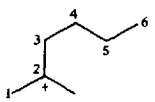
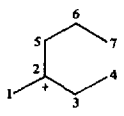
Table 2. ^{13}C chemical shifts of the static C_3 to C_8 alkyl cations

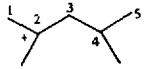
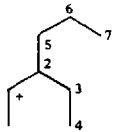
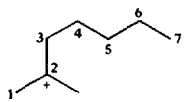
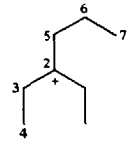
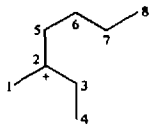
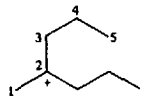
Cation		1[a]	2	3	4	5	6	7	8
	2	51.5 (q)	320.6 (s)						
	1	47.5 (q)	335.2 (s)						
	3	44.6 (q)	335.4 (s)	57.5 (t)	9.3 (q)				
	4	41.9 (q)	336.4	54.5 (t)	8.9 (q)				
	5	45.0 (q)	333.4	64.4 (t)	20.9 (t)	12.6 (q)			
	6	44.9 (q)	332.9 (s)	62.8 (t)	29.3 (t)	22.6 (t)	13.0 (q)		
	7	42.1 (q)	334.7 (s)	55.1 (t)	9.1 (q)	61.6 (t)	20.2 (t)	12.5 (q)	

	8	45.4 (q)	332.1 (s)	70.1 (t)	31.4 (d)	21.7 (q)			
	9		336.8 (s)	51.8 (t)	8.6 (q)				
	10	44.6 (q)	332.5 (s)	62.7 (t)	27.4 (t)	31.1 (t)	22.3 (t)	13.1 (q)	
	11		334.7 (s)	51.6 (t)	8.1 (q)	58.8 (t)	18.3 (t)	11.6 (q)	
	12	42.0 (q)	334.3 (s)	54.7 (t)	8.7 (q)	59.7 (t)	28.5 (t)	22.0 (t)	12.9 (q)
	13	42.1 (q)	332.8 (s)	61.9 (t)	19.7 (t)	12.1 (q)			

[a] All chemical shifts are measured from external Me_4Si.

Table 3. ^{13}C J_{C-H} coupling constants of the static C_3 to C_8 alkyl cations

	1	2	3	4	5	6	7	8
	131.7[a]	171.3						
	130.8							
	131.8		127.4	130.8				
	131.7		124.8	129.6				
	132.1		126.6	131.8	129.1			
	131.4		126.7	131.4	127 5	126.2		
	131.5		124.0	128.8	119.2	126.2	123.9	

	131.6	124.7	137.2	124.1			
		123.2	129.8				
	131.4	127.2	~131	~131	133.1	126.4	
		121.6	130.3	121.1	125.6	124.3	
	132.5	~122	129.2	122.4			127.0
	132.0	126.2	132.5	129.5			

[a] All values are measured in hertz.

Table 4. Raman and IR frequencies of the *tert*-butyl cation and [D_9]-*tert*-butyl cation and their correlation with those of $(CH_3)_3B$ and $(CD_3)_3B$

Species	Frequency of vibration [cm^{-1}]											
	$\nu_1, \nu_{12}, \nu_7, \nu_{19}$	ν_2, ν_{13}	ν_{21}	ν_{14}	ν_{15}	ν_{17}	ν_5	ν_{16}	ν_6	ν_9	ν_{10}	ν_{18}
$(CH_3)_3C^{\oplus}$ *(2)*	2947	2850		1450		1295			667		347	306
$(CH_3)_3B$	2975	2875	1060	1440	1300	1150	906	866	675	973 (486?)	336[a]	320
$(CD_3)C^{\oplus}$	2187	2090		1075		980			720		347	300
$(CD)_3B$	2230	2185		1033	1018	1205			620	870	(289)[b]	(276)[b]

[a] IR frequency. [b] Calculated.

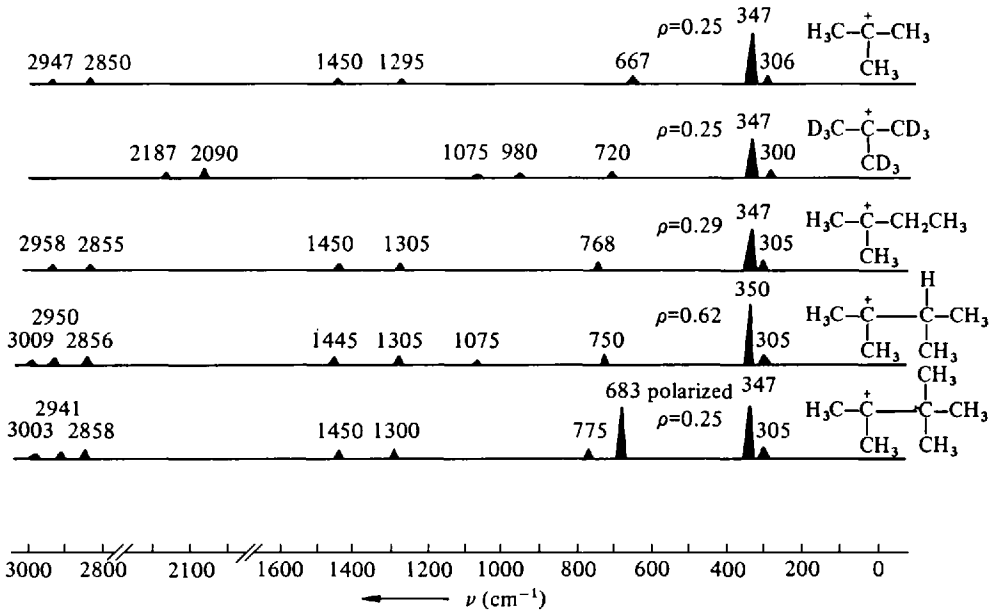


Fig. 2. Schematic representation of Raman spectra of alkyl cations

Evidence for planarity or near planarity of the sp^2 center of trivalent alkyl cations thus comes from the combined results of NMR (^1H and ^{13}C) IR, and Raman spectroscopy[31–32, 34].

e. Electronic Spectra. The observations of stable alkyl cations in antimony pentafluoride solutions also opened up the possibility of investigating the electronic spectra of these solutions. We have reported[35] that solutions of alkyl cations in FSO_3H–SbF_5 solution at –60 °C showed no absorption maxima above 210 nm. In view of this observation, it was resolved that previous claims relating to a 290 nm absorption of alcohols and olefins in sulfuric acid solution were due to condensation products or cyclic allylic ions and not to the simple alkyl cations[36].

f. X-Ray Photoelectron (ESCA) Spectra. X-Ray photoelectron spectroscopy (ESCA)[37] is an extremely useful method for the investigation of carbocations[38]. Within such molecules the formal charge is generally unequally shared by different atoms. Consequently, the core electrons of these atoms are differently screened and show increasing binding energies with increasing positive charge localization. In the latter cases the energy differences are large enough to give rise to separate K-shell photoelectron lines.

In contrast measurements of carbon 1s electron binding energies in several hydrocarbons yielded a rather narrow range of chemical shifts. For instance, one cannot make a distinction between the carbon atoms of neopentane and those of benzene because their 1s binding energies are virtually the same (290.4 eV). Ethane

(290.6), ethylene (290.7), and acetylene (291.2 eV) carbon 1s binding energy differences are also very small. These results are in agreement with theoretical expectations. Core electrons are barely affected unless their screening against nuclear attraction is modified by a significant change in the outer (valence) electron shell. In other words, core electron binding energies are mainly dependent on the formal charge of the corresponding atom and on the electronegativity of attached atoms or groups of atoms. The fact that such factors are minimal in hydrocarbons accounts for the small differences described above.

Electron spectra of carbenium ions were obtained in frozen superacid solutions or as isolated salts, generally in a 1 : 1 (v/v) SbF_5–SO_2 solution. Sulfur dioxide was subsequently removed by the usual freeze-thaw procedure. A thin layer of the viscous SbF_5 solution was deposited on the precooled sample holder, in a dry nitrogen atmosphere. The spectra are recorded at liquid nitrogen temperature[38].

The binding energies E_b (defined as differences between the Fermi level and the 1s atomic level energies) are given by the equation

$$E_b = E_{h\nu} = E_k - \phi_s$$

where $E_{h\nu}$ is the energy (1485.6 eV) of the exciting radiation (Al Kα X-rays), E_k is the measured kinetic energy of the photoejected electron, and ϕ_s is the spectrometer work function (the energy necessary to bring the electron from the Fermi level to the free-electron level). The photoelectron spectrum of *tert*-butyl cation *1* is shown in Fig. 3.

The lower traces in Fig. 3 represent the result given by a curve resolver. The peak area ratio is 1 : 3.

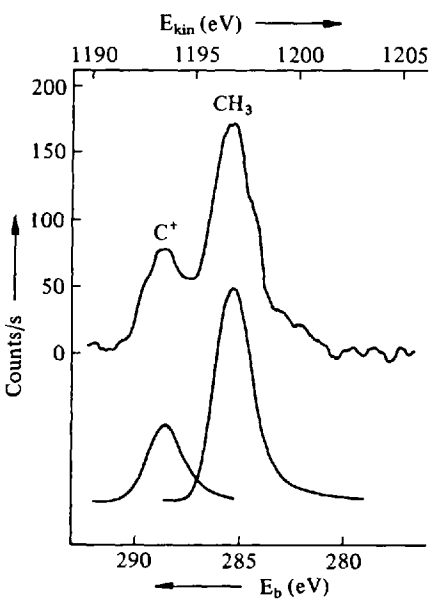


Fig. 3. Carbon 1s photoelectron spectrum of *tert*-butyl cation *1*

The experimental carbon 1s binding energy difference (3.9 eV) between the carbenium ion center and the remaining three carbon atoms is in the limit of that predicted by *ab initio* calculation (4.45 eV). Comparable results were obtained for the *t*-amyl cation ($dE_{b+}{}_{C-C} = 4 \pm 0.2$ eV).

g. Preparation from Other Precursors. Alkyl cations can be formed not only from halide precursors (the earlier investigation of generation from alkyl fluorides was later extended to alkyl chlorides, bromides, and even iodides), but also from olefins in superacids like $HF-SbF_5$[37, 38].

$$RCH=CH_2 \xrightarrow[HF-SbF_5]{FSO_3H-SbF_5} \overset{+}{R}CH-CH_3$$

Tertiary and reactive secondary alcohols in superacids like FSO_3H-SbF_5 ("magic acid"[R 30]),[36] FSO_3H, and $SbF_5-SO_2-(SO_2ClF)$ also ionize to the corresponding carbocations[41]. The generation of alkyl cations from alcohols indicates the great advantages of increasing acidity and of using acid systems with low freezing points. Deno showed that the use of sulfuric acid and oleum results in formation of cyclized allylic ions from simple aliphatic alcohols[24]. With the use of extremely strong acid, FSO_3H-SbF_5, tertiary and many secondary alcohols can be ionized to the corresponding alkyl cations.

$$(CH_3)_3C-OH \xrightarrow[-H_2O]{FSO_3H-SbF_5} (CH_3)_3C^+$$
1

Primary and less reactive secondary alcohols are protonated in FSO_3H-SbF_5 solution at low temperatures (−60 °) and show very slow exchange rates[42].

$$CH_3CH_2CH_2OH \longrightarrow CH_3CH_2CH_2\overset{+}{O}H_2$$

$$CH_3\underset{\underset{OH}{|}}{CH}CH_3 \longrightarrow CH_3\underset{\underset{+OH_2}{|}}{CH}CH_3$$

Temperature-dependence studies of the NMR spectra of protonated alcohols allow the kinetics of dehydration to be followed[43].

$$CH_2CH_2CH_2CH_2OH \xrightarrow[-60°]{FSO_3H-SbF_5-SO_2} CH_2CH_2CH_2CH_2\overset{+}{O}H_2$$

$$CH_2CH_2CH_2CH_2\overset{+}{O}H_2 \xrightarrow[-H_3O^+]{\Delta,\ H^+} [CH_2CH_2CH_2CH_2^+]$$

$$[CH_2CH_2CH_2CH_2^+] \longrightarrow \text{rearrangement} \longrightarrow (CH_3)_3C^+$$
1

Antimony pentafluoride itself (neat or in SO_2 of SO_2ClF solution) ionizes alcohols to form alkyl carbocations.

$$R{-}OH + SbF_5 \rightarrow R^+SbF_5OH^-$$

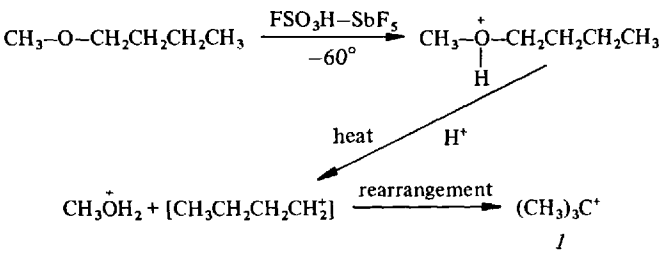
To overcome difficulties and achieve ionization of primary (and less reactive secondary) alcohols at low temperatures, we found, in some cases, that it is advantageous to transfer them with thionyl halides or carbonyl halides to the corresponding haloformates or halosulfites. These in turn ionize readily in $SbF_5{-}SO_2$ solution and lose CO_2 or SO_2 [39, 44].

$$ROH \xrightarrow{COX_2} R{-}O{-}\overset{\overset{O}{\|}}{C}{-}X \xrightarrow{SbF_5{-}SO_2} R^+SbF_5X^- + CO_2$$

$$ROH \xrightarrow{SOX_2} R{-}O{-}\overset{\overset{O}{\|}}{S}{-}X \xrightarrow{SbF_5{-}SO_2} R^+SbF_5X^- + SO_2$$

$X = Cl, F$

Aliphatic ethers are protonated in strong acids, and, at low temperatures, the exchange rates of the acidic proton are slow enough to permit direct observation by NMR spectroscopy [45]. Temperature dependent NMR spectral studies allow one to follow the kinetics of ether cleavage to form alkyl reactions.



1

Protonation and ionization of mercaptans (thiols) and sulfides were similarly studied [46].

Superacids such as $FSO_3H{-}SbF_5$ act as very effective hydrogen abstracting agents, allowing the generation of carbocations from saturated hydrocarbons [47].

$$\underset{\underset{CH_3}{|}}{CH_3CHCH_3} \xrightarrow[SO_2ClF]{FSO_3H{-}SbF_5} (CH_3)_3C^+ + H_2$$

1

Alkyl cations can also be generated by decarbonylation of tertiary acylium ions, like the Pivaloyl cation *15* [27].

$$(CH_3)_3CCOF + SbF_5 \longrightarrow (CH_3)_3CCO^+SbF_6^- \xrightarrow{heat} (CH_3)_3C^+SbF_6^- + CO$$

15 *1*

This reaction corresponds to the reverse of the Koch-Haaf acid synthesis, which is known to involve carbocation intermediates. Indeed the reaction of the tertiary butyl cation with carbon monoxide gives the pivaloyl cation[27, 48].

Thiols and thioesters (sulfides) can also be used, similarly to their oxygen analogs, as precursors for alkyl cations[49]. Ionization with SbF_5 type superacids generally necessitates somewhat more forcing conditions (higher temperatures). Alkyl thiolhaloformates also form alkyl cations via fragmentative ionization[50].

$$R{-}SH \xrightarrow[HF{-}SbF_5,FSO_3H{-}SbF_5]{SbF_5\ or} R^+SbF_5SH^-$$

$$RSOCCl(F) \xrightarrow{SbF_5-SO_2ClF} R^+SbF_5Cl(F) + COS$$

Amines also can be used as precursors for the generation of alkyl cations. The classic method of deaminative formation of carbocations involves some type of diazotization reaction producing an equimolar amount of water.

$$R{-}NH_2 \xrightarrow[-H_2O]{HNO_2} [RN_2^+] \longrightarrow R^+ + N_2$$

Newer methods overcome this difficulty. The corresponding sulfinylamine or isocyanate is prepared and then reacted with stable nitrosonium salts to give the corresponding carbocation[51].

$$RNH_2 \xrightarrow{SOCl_2} RNSO + NO^+SbF_6^- \longrightarrow R^+SbF_6^- + N_2 + SO_2$$

$$RNH_2 \xrightarrow{COCl_2} RNCO + NO^+SbF_6^- \longrightarrow R^+SbF_6^- + N_2 + CO_2$$

h. Observation in Different Superacids. Whereas antimony pentafluoride containing superacids (such as $HF{-}SbF_5$, $FSO_3H{-}SbF_5$, $CF_3SO_3H{-}SbF_5$, etc.) are the preferred solvents for obtaining alkylcations, other superacids such as $HF{-}BF_3$, $HF{-}TaF_5$, etc. can also be on occasions used successfully. The stability of carbocations in these solvents is generally somewhat lower.

6. Cyclopropylmethyl Cations

Solvolysis studies of Roberts[52] and Hart[53] showed both the unusual stability of cyclopropylmethyl cations and the ease with which such ions rearrange. Cyclopropyl groups have a strong stabilizing effect on neighboring carbocation center by delocalizing charge through bent σ-bonds. The direct observation[54] of a veriety of cyclopropylmethyl cations in cyclic, acylic and polycyclic systems by NMR spectroscopy provides one of the clearest examples of delocalization of positive charge into a saturated system.

The first cyclopropylmethyl cation directly observed was the tricyclopropylmethyl cation *16* by Deno[54]. Its ^1H NMR spectrum in H_2SO_4 consists of a single sharp line at δ 2.26. In the 300 MHz ^1H NMR spectrum in SO_2ClF/SbF_5 solution,

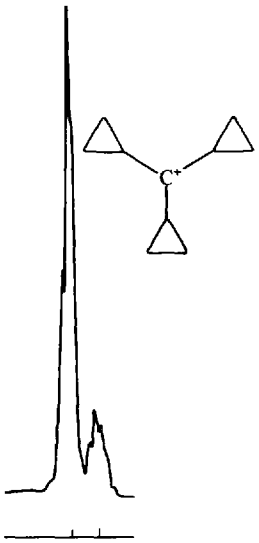


Fig. 4. ^{1}H-NMR spectrum (300 MHz) of the tricyclopropylcarbenium ion in $HSO_3F-SbF_5-SO_2ClF$ at $-60°$

however, the methine and methylene protons are well resolved[55] (Fig. 4). Since then a wide variety of cyclopropylmethyl cations have been prepared and studied by ^{13}C and ^{1}H NMR spectroscopy[56, 57]. These studies have lead to the conclusion that cyclopropylmethyl cations adopt bisected geometry and are static in nature with varying charge delocalization into the cyclopropane ring. Most interesting of these ions is the dimethylcyclopropylmethyl cation *17* (Fig. 5). The methyl groups

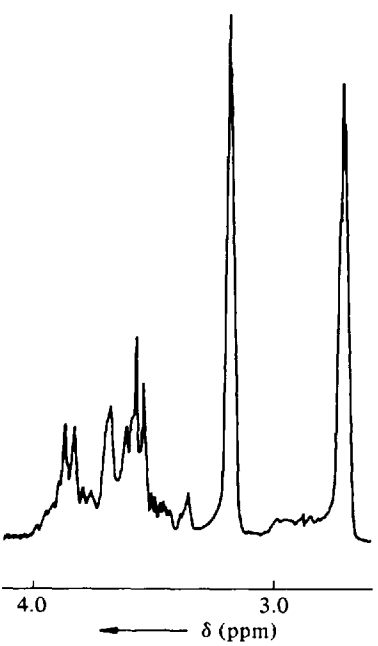


Fig. 5. 100-MHz ^{1}H-NMR spectrum of the dimethylcyclopropylcarbenium ion (*14*)

are non-equivalent and show a shift difference of 0.54 ppm. The energy difference between bisected and eclipsed structures[17] is estimated to be 13.7 kcal/mole[58] (by temperature dependent NMR studies) and is quite close to 12.3 kcal/mole energy obtained by molecular orbital calculations at the minimal basis set STO – 3G level[59].

eclipsed bisected

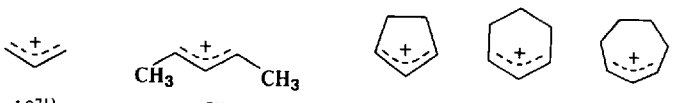
17

A wide range of studies[55, 60–62] have indicated that a cyclopropyl group is equal or more effective than a phenyl group in stabilizing an adjacent carbocation center.

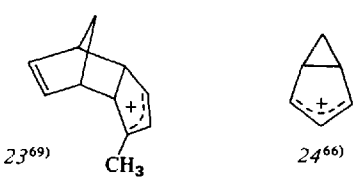
In contrast to "classical" tertiary and secondary cyclopropylmethyl cations (showing substantial charge delocalization into the cyclopropane ring but maintaining its identity) primary cyclopropylmethyl cations in contrast show compeltely σ-delocalized non-classical carbonium ion character (see subsequent discussion).

7. Alkenyl Cations

Many alkenyl cations have now been directly observed particularly by Deno and Richey[24, 63], Sorenson[64], Olah[65–69], and Carpenter[70]. Deno has reviewed the chemistry of these ions[71]. Allylic cations particularly show great stability with generally insignificant 1,3-overlap, exempt of cyclobutenyl cations[72]. Representative observed alkenyl cations are:

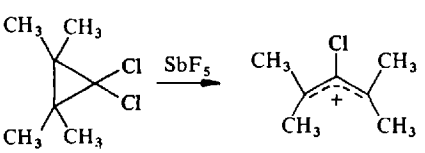


18[71] *19*[71] *20*[66] *21*[66] *22*[66]



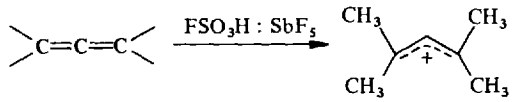
23[69] *24*[66]

The formation of allyl cations from halocyclopropanes via ring opening of the unstable cyclopropyl cations has been also investigated[73–76].



25[73]

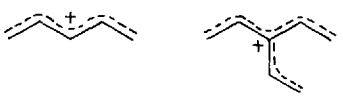
Protonation of allenes also leads to allyl cations, allowing to obtain ions which are otherwise difficult to obtain from allylic precursors[77–78].



26[77]

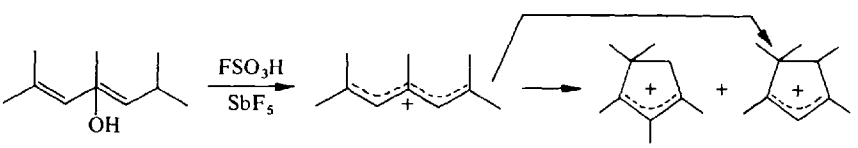
8. Alkadienyl and Polyenylic Cations

Deno, Richey and their co-workers[24] have observed a substantial number of alkadienyl cations. Sorensen[79] has observed divinyl and trivinyl cations *27* and *28*.



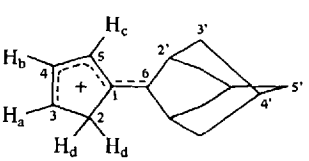
27[79] *28*[79]

Alkadienyl cations show great tendency to cyclize and these reactions have been followed by NMR[80]. More recently several novel fulvenes have been protonated to

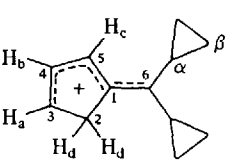


29[80]

their corresponding dienylcations[81] (*30*, *31*, etc.)



30[81]



31[81]

9. Arenium Ions

Cycloalkadienyl cations, particularly cyclohexadienyl cations (benzenium ions) the intermediate of electrophilic aromatic substitution frequently show remarkable stability. Protonated arenes can be readily obtained from aromatic hydrocarbons with strong acids[82–84] and advantageously studied by ^{1}H or ^{13}C NMR spectroscopy[85, 86]. Olah et al. even prepared and studied the parent benzenium ion $C_6H_7^+$ [86]. Representative PMR spectra of benzenium ion[86] *34* and napthalenium ion[88] *35* are shown in Figs. *6* and *7*. Anthracenium ions[89] as well as the isomeric

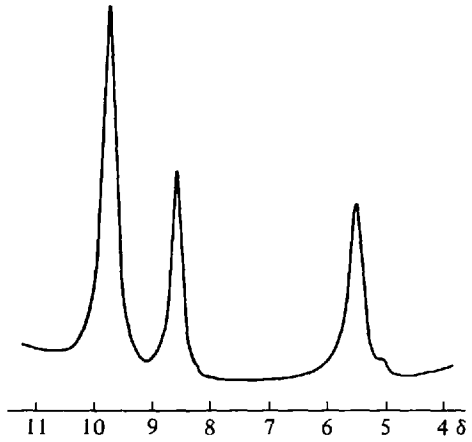


Fig. 6. The 270-MHz FT ^{1}H-NMR spectrum of the "static" benzenium ion in SbF_5-FSO_3H–SO_2ClF–SO_2F_2 solution at −140 °C

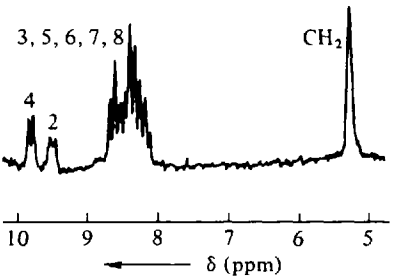


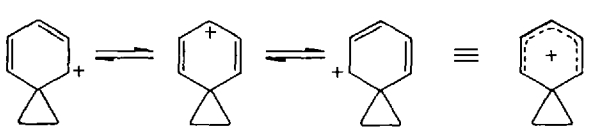
Fig. 7. 100-MHz ^{1}H-NMR spectrum of the naphthalenium ion (*31*) at −90 °C

mono-, di-, tri-, tetra- and pentaalkylbenzenium and halobenzenium ions have been observed[88–89]. Alkylation, nitration, halogenation etc. of hexamethyl benzene gives the related ions. Doering and Saunders prepared the very stable heptamethylbenzenium ion[87] *32*.

Ethylenarenium Ions

The classical-nonclassical ion controversy also frequently included the question of the so-called "ethylenephenonium" ions.

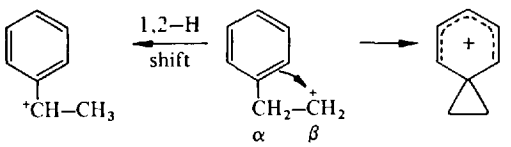
Cram's original studies[90] established, based on kinetic and stereochemical evidence, the nonclassical bridged ion nature of β-phenylethyl cations in solvolytic systems. Spectroscopic studies (particularly PMR and CMR[91a]) of a series of stable long-lived ions proved the symmetrically bridged structure, and at the same time showed that these ions do *not* contain a pentacoordinated carbocation center (thus are not "nonclassical ions"). They are spiro (2,5)-octadienyl cations (spirocyclopropylbenzenium ions), in other words cyclopropylmethyl cations in which the carbocation center belongs to a cyclohexadienyl cation (benzenium ion).



33

The nature of the spiro carbon atom is of particular importance in defining the carbocation nature of the ions. CMR spectroscopic studies clearly established the aliphatic tetrahedral nature of this carbon, thus ruling out a "nonclassical" pentacoordinated carbocation.

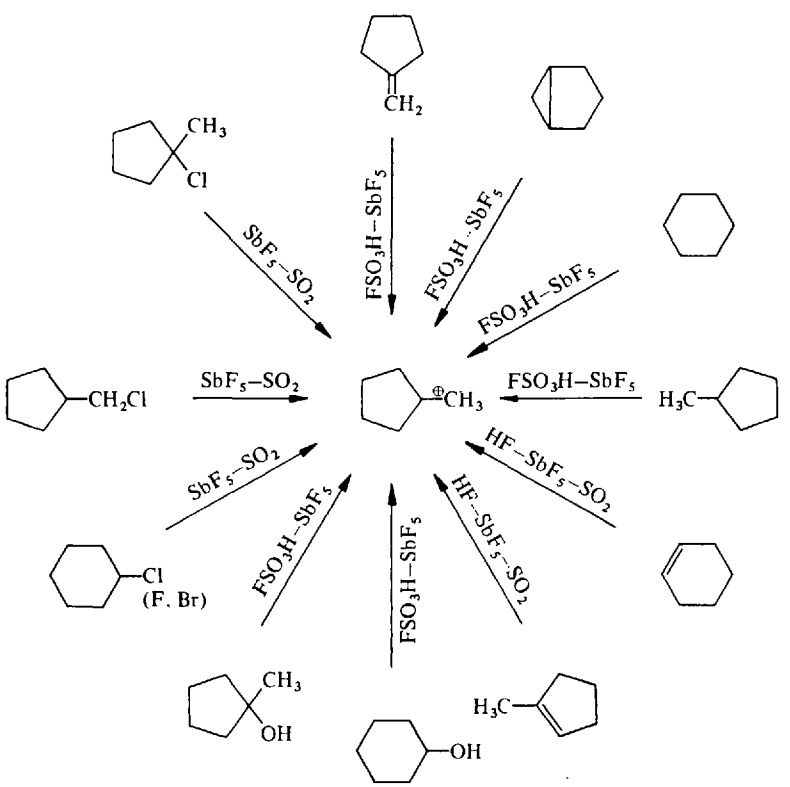
The formation of the ethylenebenzenium ion *33* from β-phenylethyl precursors can be depicted as cyclialkylation of the aromatic π-systems and not of the $C_{AR} - C_{\alpha}$



bond which would give the tetracoordinated ethylenephenonium ion Rearrangement of the β-phenylethyl to α-phenylethyl (styryl ions) on the other hand takes place through a regular 1,2-hydrogen shift. Rearrangement and equilibria of ions formed from side chain substituted β-phenylethylchlorides have also been explored[91d].

10. Cycloalkyl Cations

Tertiary cycloalkylcations, such as the 1-methyl-1-cyclopentyl cation *36* show high stability in strong acid solutions. This ion can be obtained from a variety of precursors[92] (Fig. 8).



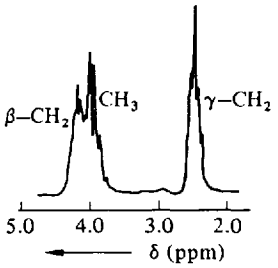


Fig. 8. 60-MHz ^{1}H-NMR spectrum of the 1-methyl-1-cyclopentyl cation at −60 °C

It is worthwhile to mention that not only cyclopentyl but also the cyclohexyl type precursors gives the 1-methylcyclopentyl cation *36*. This indicates that the cyclopentyl cation has higher stability, which causes isomerization of the secondary cyclohexyl cation to the tertiary methylcyclopentyl ion.

The cyclopentyl cation *37* shows in its proton magnetic resonance spectrum in SbF_5–SO_2ClF solution, even at −150 °, only a single absorption line at δ 4.68[40, 90]. This observation indicates a completely degenerate ion with a low barrier to the secondary-secondary hydride shift (see subsequent discussion). Sorensen et al.[93] have prepared a variety of tertiary cycloalkyl cations of different ring sizes n = 4 (small ring), n = 5–7 (common rings), n = 8–11 (medium rings), and n = 12–20 (large rings). These ions were in general found to undergo ring expansion or contraction reactions, often in multiple or repetitive steps, as shown in the following sequence.

4^+–Pr → 5^+–Et + 6^+–Me
5^+–Et → 6^+–Me
7^+–Pr → 6^+–But
8^+–Et → 6^+–Pr
9^+–Me → 8^+–Et + 7^+–Pr + 6^+–Bu
10^+–Me → 6^+–Pen
10^+–Et ⇄ 11^+–Me
11^+–Me ⇄ 10^+–Et ⇄ 6^+–Hex
10^+–Pr → 12^+–Me + 6^+–Hept
11^+–Et → 12^+–Me + 10^+–Pr
12^+–Pr → 13^+–Et
13^+–Et → 14^+–Me
14^+–Et ⇄ 15^+–Me
12^+–R → ring expansions

The parent secondary cyclobutyl cation *38* undergoes immediate rearrangement via σ-bond delocalization into the equilibrating non-classical bicyclobutonium ion like system[94, 95] (see subsequent discussion of non-classical ions). Similar behaviour is also observed for the 1-methylcyclobutyl cation[94, 94–98] *39*. The 1-phenylcyclobutyl cation *40* on the other hand is a classical tertiary carbocation[94].

11. Bridgehead Carbocations

Bredt's rule in its original form[99] excluded the possibility of carbocation formation at bridgehead positions of cycloalkanes. Indeed, bridgehead halides, such as apocamphylchloride, proved extremely unreactive under hydrolysis conditions[100]. However, 1-bromoadamantane very readily gives the bridgehead carboxylic acid under the usual conditions of Koch-Haaf acid synthesis[101]. 1-Fluoroadamantane is ionized in SbF_5 to give the stable bridgehead adamantyl cation *41*[102, 103].

The PMR spectrum of the adamantyl cation in SbF_5 solution at 25 ° consists of resonances at δ 5.40, δ 4.52 and δ 2.67 with peak areas of 3 : 6 : 6 (Fig. 9). The CMR spectrum (Fig. 9b) shows the γ-carbons more deshielded than the β-s, indicating strong C–C bond hyperconjugation with the empty p-orbital.

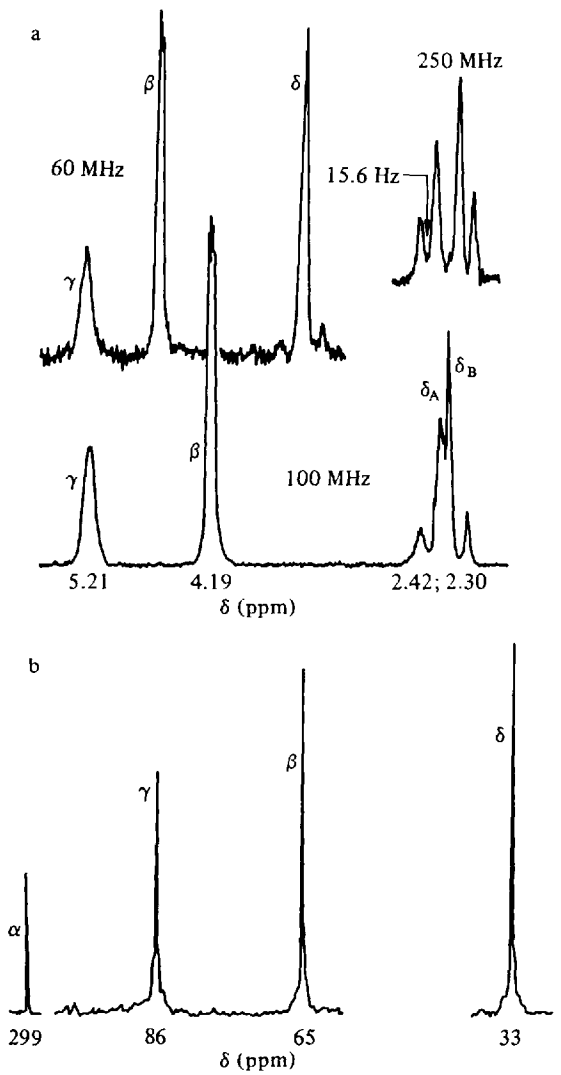
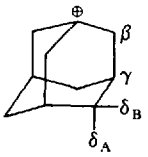
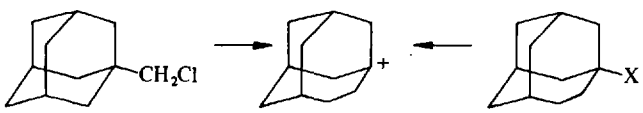


Fig. 9. a) ^{1}-NMR spectrum of the 1-adamantyl cation at 60 MHz, 100 MHz, and 250 MHz; b) Fourier-transform ^{13}C-NMR of the 1-adamantyl cation (in FSO_3H–SbF_5)



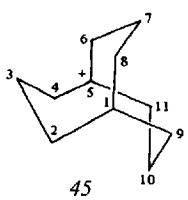
41

Methyl substituted adamantyl cations have also been studied[103]. The bridgehead homoadamantyl cation *42* has been obtained[104] from both adamantylcarbinyl and homoadamantyl precursors. Bridgehead bicyclo [4.4.0] decyl, bicyclo [4.3.0] nonyl



42 X = OH, Br or H

and bicyclo [3.3.0] octyl cations *43*, *44*, and *45* are found to be equilibrating ions[105]. More recently bridgehead bicyclo [3.3.3]-nonyl cation *46* has been prepared and studied[106] by ^{1}H and ^{13}C NMR spectroscopy.

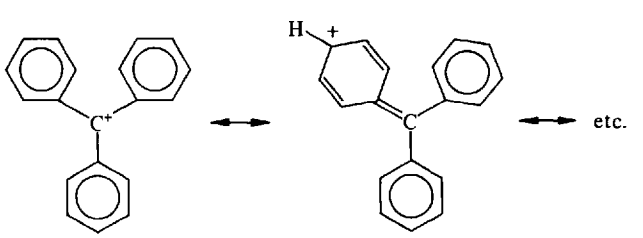


45

The bridgehead congressane (diamantane) cation *46* has also been observed[103]. Although the bridgehead 1-norbornyl cation was not directly observed, 1-chloronorbornane yields the stable 2-norbornyl cation in SbF_5-SO_2 solution[107]. Thus, ionization to the bridgehead carbonium ion must be followed by a fast shift of hydrogen from C-1 to C-2, the driving force for which is obviously the tendency to relieve strain in the carbenium ion.

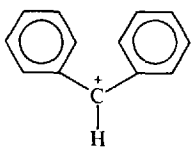
12. Aryl- and Alkylarylmethyl Cations

The first stable long-lived carbocation observed was the triphenylmethyl cation[108–110] *47*.



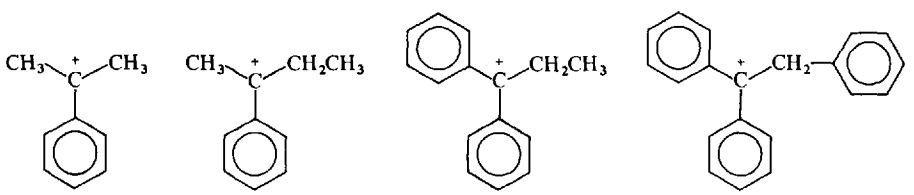
47

This ion is still the best-investigated carbocation[2] and its propeller-shaped structure is well proved. Strong contribution from para (and ortho) quinonoidal resonance forms in the ion make it probable that these reactive secondary forms are responsible for much of the reactivity of the ion. Diphenylmethyl cations (benzhydryl cations) are considerably less stable than their tertiary analogs. Although ultraviolet spectra in dilute sulfuric acid solutions have been obtained[111], only recently has the benzhydryl ion *48* been observed in higher concentrations in acid solutions [$ClSO_3H$[112], FSO_3H[113], and FSO_3H–SbF_5][114].



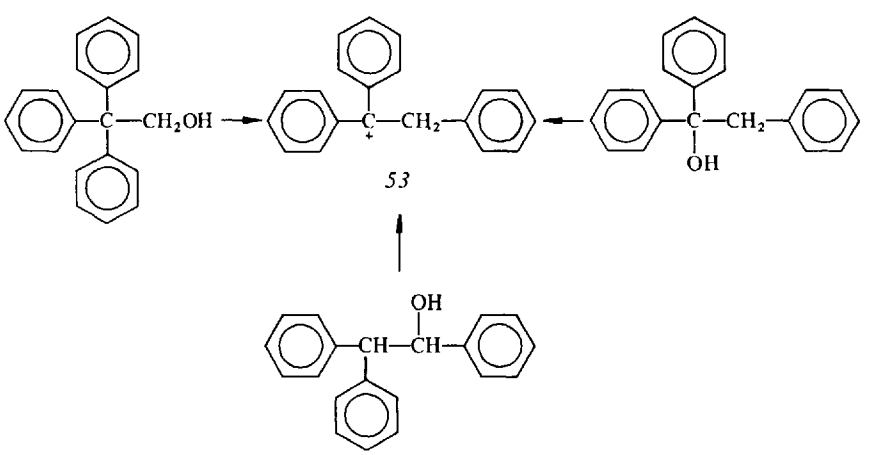
48

Mono- and dialkylarylmethyl cations can be readily obtained from the corresponding alcohols, olefins, or halides in strong acid solution, such as H_2SO_4[111], FSO_3H–SbF_5[114], $ClSO_3H$ and FSO_3H[112], and oleum[113]. Representative alkylarylmethyl cations are:



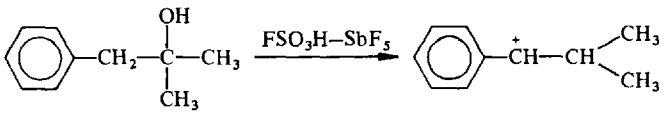
49 *50* *51* *52*

Because of the high stability of the tertiary ions, these are preferentially formed in the strong acid systems from both tertiary, secondary, and even primary precursors[115].



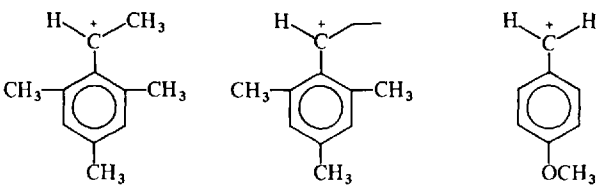
53

If, however, the tertiary carbocation is not benzylic, rearrangement to a secondary, benzylic ion can be observed:



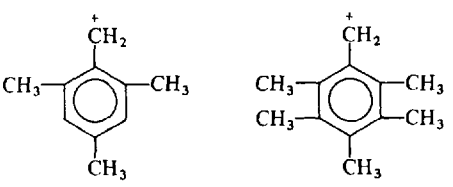
54

With suitable substituent groups (which also prevent transalkylations) secondary styryl cations were found as stable, long-lived ions[116, 117].

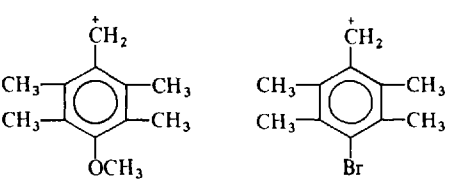


55 *56* *57*

Although the unsubstituted benzyl cation is still elusive, many substituted derivatives have been observed[116].

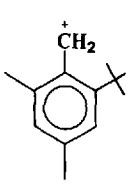


58 *59*



60 *61*

In a cation such as the (2,4-dimethyl-6-t-butyl) benzyl cation *62* a high rotational barrier around sp^2-hybridized carbon atom is observed. The methylene protons are found magnetically non-equivalent in the ^1H NMR spectrum[118].

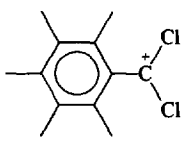


62

No rearrangement of benzyl cations in acid solution to tropylium ions has been found, although this rearrangement is claimed in the gas phase (mass spectroscopy).

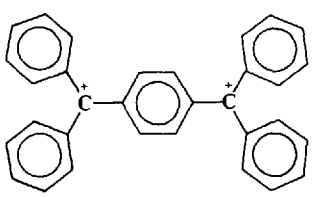
13. Carbodications

Early reports[119] that a carbodication had been observed from pentamethyltrichloromethyl benzene turned out to be incorrect. The species obtained was the dichloropentamethylbenzyl cation *63*[120–122].

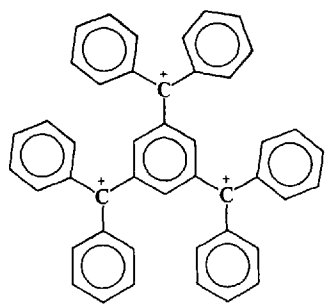


63

If two carbocation centers are separated by a phenyl ring, a variety of carbodi- and tri-cations can be obtained[123, 124].

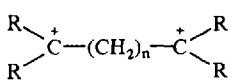


64



65

Separation of the two carbocation centers by at least two methylene groups in open chain carbodications also enables these ions to be obtained as stable species in superacidic systems[125].

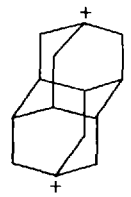


66

$n \geq 2$ stable

A comprehensive NMR spectroscopic study[126], of a series of acyclic carbodications was carried out. Carbodications were also observed in more rigid systems, such as the apical, apical congressane dication *67*[103], bicyclo [2.2.2] octyl dication *68*[127] and bicyclo [3.3.3] nonyl dication *69*[106] (manxyl dication – Fig. 10).

Many aromatic stabilized dications have been prepared and characterized by NMR spectroscopy (see subsequent discussion).



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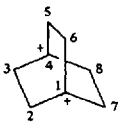

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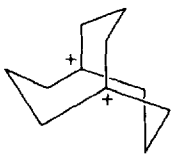

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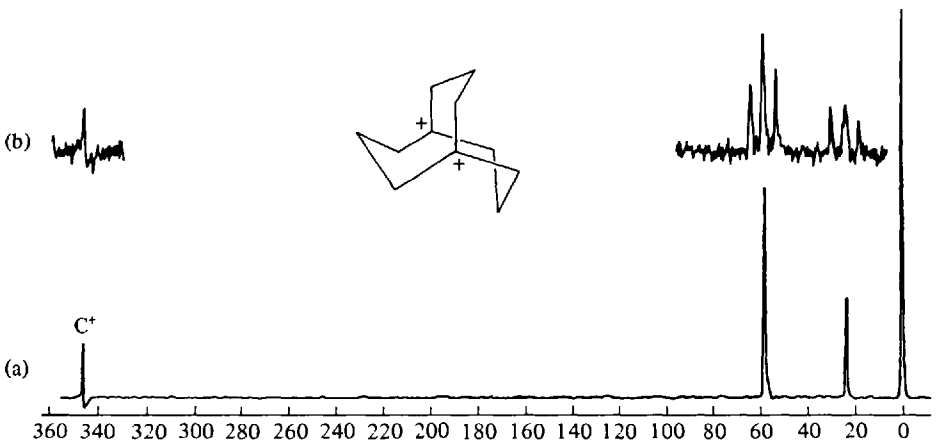
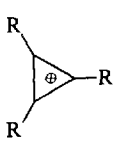


Fig. 10A. The 25 MHz ^{13}C-NMR spectrum of the bicyclo[3.3.3]nonyldication *69* in SbF_5SO_2ClF solution

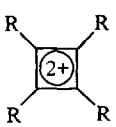
14. Aromatically Stabilized Carbocations

If a carbocation at the same time is also a Huckeloid (4n+2) π aromatic system, resonance can cause substantial stabilization. There were numerous aromatically stabilized Huckeloid systems[128–135] generated in superacidic media in recent years and characterized by NMR spectroscopy. Some of the best known examples are the following.

70[128]

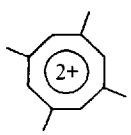


71[129]

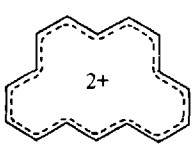


72[130]

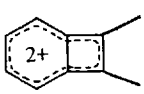
73[72]



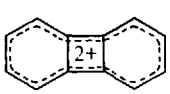
74[131]



75[132]



76[133]



77[134]

78[135]

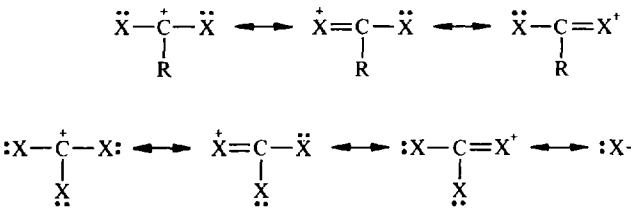
15. Heteroatom-Stabilized Carbocations

In contrast to hydrocarbon cations, heteroatom-substituted carbocations are strongly stabilized by electron donation from the unshared electron pairs of the heteroatoms adjacent to the carbocation center:

$R_2\overset{+}{C}-X \qquad R_2C=\overset{+}{X}$

X=Br or NR_2, SR, F, Cl

The stabilizing effect is enhanced when two, or even three, electron-donating heteroatoms coordinate with the electron-deficient carbon atom.



16. Halogen as Heteroatom

In 1965 with Comisarow and Cupas we reported the first fluoromethyl cation[136]. Since then a large variety of fluorine substituted carbocations have been prepared. Fluorine has a particular ability to stabilize carbocations via back coordination of its unshared electron pairs into the vacant p orbital of the carbocationic carbon atom. ^{19}F NMR spectroscopy is a particularly efficient tool for the structural investigations of these ions[137]. The 2-fluoro-2-propyl and 1-phenylfluoroethyl cations *79* and *80* are representative examples of the many reported similar ions[138].

79 *80*

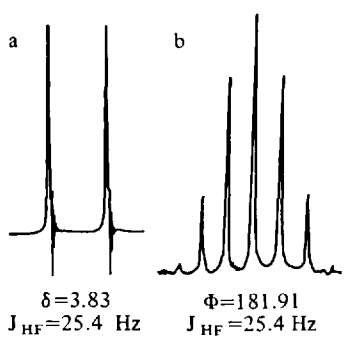
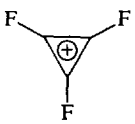


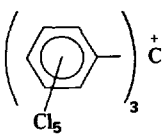
Fig. 10B. a) ^1H-NMR spectrum of the dimethylfluorocarbenium ion at 60 MHz: J_{HF} = 25.4 Hz; b) ^{19}F-NMR spectrum of the same ion at 56.4 MHz: J_{HF} = 25.4 Hz

Trifluormethyl[139] and perfluorophenyl substituted carbocations have also been prepared and studied[140, 141]. Because of the relatively large fluorine chemical shifts, anisotropy and ring current effect play a relatively much smaller role than they do in the case of proton shifts. Therefore, a better correlation of charge distribution with chemical shifts can be obtained. The trifluorocyclopropenium ion *81* was also reported[142].



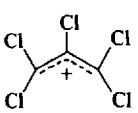
81

A series of chloromethyl cations were observed, including phenyldichloromethyl cations[120–122, 143], and perchlorotriphenylmethyl ion *82*[144].



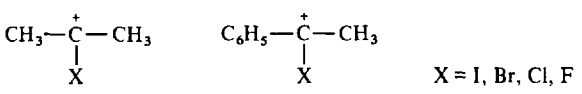
82

West has characterized the perchloroallyl cation *83*. A series of chloro-, as well as



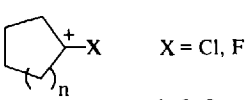
83

bromo- and iodomethyl cations have been observed and the general stabilizing effect of halogen attached to carbocation center has been demonstrated[146]. With Halpern and Mo we were able to study these effects in detail using ^{13}C NMR spectroscopy[147].



84 *85*

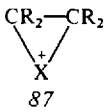
X = I, Br, Cl, F



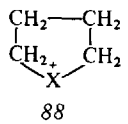
n = 1, 2, 3

86

Three and five-membered ring halonium ions were obtained in our work with Bollinger[148] and studied with Peterson[149]. Illustrative is the propylenebromonium ion whose PMR spectrum is shown in Fig. 11.



87



88

X=I, Br, Cl
R=H or alkyl

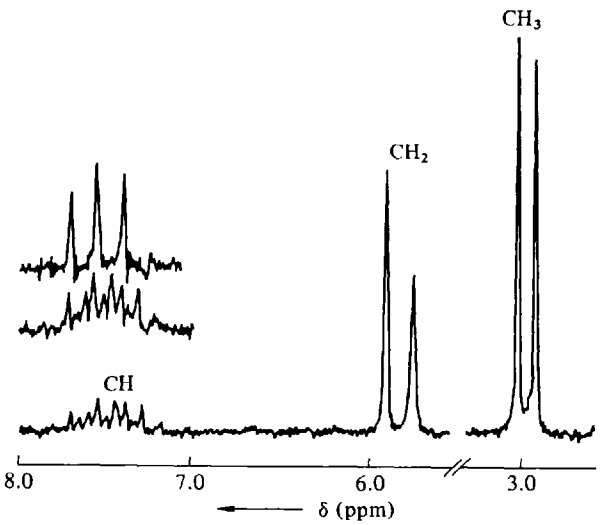


Fig. 11. ^{1}H-NMR spectrum (at 60 MHz) of the propylenebromonium ion; Left: signal of methine protons decoupled

Not only ring halonium ions, but also a series of open chain dialkylhalonium ions were obtained in our work with DeMember[150], such as the following

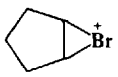
$CH_3\overset{+}{I}CH_3$
$CH_3\overset{+}{Br}CH_3$
$CH_3\overset{+}{Cl}CH_3$
$(CH_3CH_2)_2Br^+$
$(CH_3CH_2)_2Cl^+$
$(CH_3CH_2)_2I^+$
$CH_3\overset{+}{I}CH_2CH_3$
$CH_3\overset{+}{Br}CH_2CH_3$
$CH_3\overset{+}{Cl}CH_2CH_3$

$[(CH_3)_2CH]_2Br^+$
$[(CH_3)_2CH]_2Cl^+$
$[(CH_3)_2CH]_2I^+$
$CH_3\overset{+}{C}ICH(CH_3)_2$
$[CH_3(CH_2)_2]_2I^+$
$[CH_3(CH_2)_2]_2Br^+$

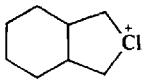
90–105

Dialkylhalonium fluoroantimonate salts can be isolated as crystalline salts and are versatile, very reactive alkylating agents. As the differing halogen atoms effect a range of selectivity, they were found to be more versatile than trialkyloxonium salts.

Several bicyclic halonium ions also have been prepared and studied[151].



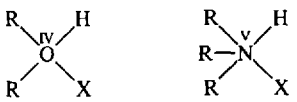
106[151]



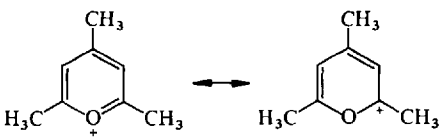
107[151]

17. Oxygen as Heteroatom

Crystalline addition compounds of alcohols, ethers, aldehydes, and ketones with Brönsted and Lewis acids have been known since the middle of the last century. They were long considered unstable "molecular compounds"[152]. Collie and Tickle[153] were the first to assign "oxonium salt" character to the acid complexes as containing a tetravalent oxygen, analogous to the ammonium salts in which nitrogen at that time was assumed to be pentavalent:



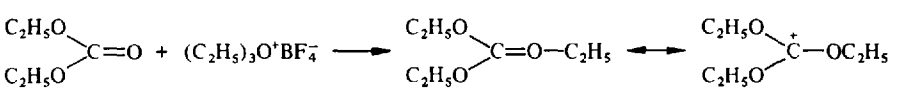
The ionic structure of the pyrylium salts were clearly stated by Hantzsch as early as 1922[154].



108

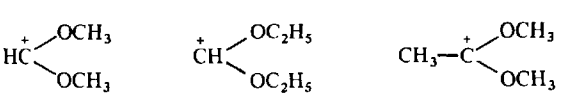
In pyrylium salts there is contribution from carbocation structures, a fact apparent in the behavior toward strong nucleophiles leading to phenols.

a) Alkoxy- and Hydroxylated Carbocations: Resonance, similar to that in pyrilium salts was shown[155] to exist between tri- and dialkyloxonium and carboxonium ion forms in alkylated ketones, esters and lactones which were obtained via trimethyl or triethyloxonium fluoroborates.



109

Taft and Ramsey[156] used ^1H NMR spectroscopy to investigate the nature of a series of secondary and tertiary carboxonium ions.



110 *111* *112*

With Bollinger[157] we obtained primary carboxonium ions such as methoxy- and phenoxymethyl cations and their halogenated derivatives

$CH_3\overset{+}{O}CH_2 \leftrightarrow CH_3\overset{+}{O}=CH_2$ *113*

$CH_3\overset{+}{O}CHCl \leftrightarrow CH_3\overset{+}{O}=CHCl$ *114*

$ClCH_2\overset{+}{O}CH_2 \leftrightarrow ClCH_2\overset{+}{O}=CH_2$ *115*

$CH_3-\overset{+}{O}CHF \leftrightarrow CH_3\overset{+}{O}=CHF$ *116*

$C_6H_5\overset{+}{O}CH_2 \leftrightarrow C_6H_5\overset{+}{O}=CH_2$ *117*

Acidic oxonium ions can be readily obtained and studied in superacidic media. With Sommer and Namanworth[43] we showed that primary and secondary alcohols are protonated in FSO_3H–SbF_5(SO_2, SO_2ClF) solution at –60 °, giving well-resolved spectra of the alkyloxonium ions.

$$R-OH \xrightarrow[-60^\circ]{SbF_5-FSO_3H(SO_2,\ SO_2ClF} R\overset{+}{O}H_2$$

At higher temperature they cleave to alkyl cations; the kinetics of these cleavage reactions could be followed by NMR spectroscopy.

$$R\overset{+}{O}H_2 \xrightarrow[H^+]{heat} R^+ + H_3O^+$$

Tertiary alcohols (with the exception of the ones containing strong electron withdrawing groups, such as CF_3) generally dehydrate very fast in the acid media, and the intermediate protonated species cannot be observed, even at low temperatures before cleavage.

Ethers also protonate in superacid media[45] to give dialkyloxonium ions.

$$R_2O \xrightarrow[-60^\circ]{FSO_3H-SbF_5-SO_2} R_2\overset{+}{O}H$$

Again cleavage reactions can be followed by NMR spectroscopy as in the case of methyl *n*-butyl ether

$$CH_3\overset{+}{O}CH_2CH_2CH_2CH_3 \xrightarrow{heat} CH_3\overset{+}{O}H_2 + [CH_3CH_2CH_2CH_2^+] \longrightarrow (CH_3)_3C^+$$

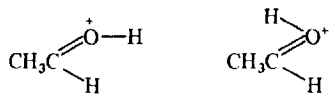
1

Aldehydes and ketones protonate on the carbonyl oxygen atom, and in superacid media at low temperatures to the corresponding carboxonium ions which can be directly observed[158–162].

$$RCHO \xrightarrow{FSO_3H-SbF_5-SO_2} RCH=\overset{+}{O}H$$

$$R_2CO \longrightarrow R_2C=\overset{+}{O}H$$

Even protonated formaldehyde was observed. Protonated acetaldehyde was observed in two isomeric forms, the proton on oxygen being *syn* or *anti* to the methine proton:



syn *anti*

80 percent 20 percent

118

The hydroxymethyl cation forms of protonated ketones and aldehydes contribute to the resonance hybrid. Based on ^{13}C NMR studies[162, 163a], the degree of contribution of the hydroxymethyl cation forms can be quite accurately estimated.

Alkylated carboxonium ions have also been prepared by direct electrophilic oxygenations of alkanes, alcohols, etc. by ozone or hydrogen peroxide in superacidic media[164].

$$(CH_3)_3CH \xrightarrow[FSO_3H\text{–}SbF_5]{H_2O_2 \text{ or } O_3} [(CH_3)_3CO^+] \longrightarrow (CH_3)_2\overset{+}{C}{=}OCH_3$$

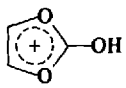
Smith et al. have isolated a series of cyclic carboxonium salts (such as *119–121*) by acylation of alkenes.

119

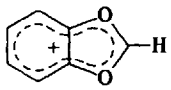
120

121

^{13}C NMR spectral investigations have been extended[163b] to the study of heteroaromatic stabilized 6 π,3-dioxolium and 10 π benzo-1,3-dioxolium ions *122* and *123*.

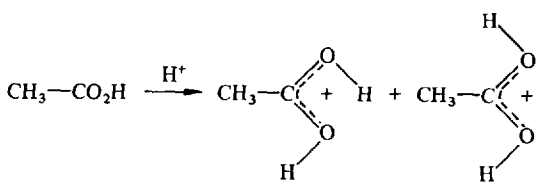


122



123

Carboxylic acids are protonated in superacid media, such as FSO_3H–SbF_5–SO_2, HF–SbF_5, or HF–BF_3[166]. The NMR spectrum of acetic acid in such media at low temperature shows two OH resonances indicating
(i) that carbonyl protonation is favored and
(ii) that hindered rotation about the resultant COH bonds is present.
The predominant conformer observed is the *syn, anti,* although about 5 percent of the *syn, syn* isomer has also been seen.

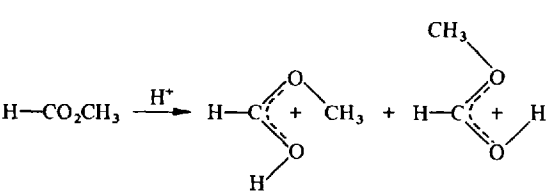


syn, anti 95% *syn, syn* 5%

124

These isomers can be readily identified from the magnitudes of the vicinal coupling constants; thus in the *syn, anti* isomer, the methine proton is a doublet of doublets (J_{HH} = 15 and 3.5 hertz) while in *syn, syn* isomer a triplet is observed (J_{HH} = 3.5 hertz). No evidence for the *anti, anti* isomer has been found in either protonated carboxylic acids, esters, or their analogs.

Esters behave in an analogous fashion, with carbonyl protonation being predominant. Thus protonated methyl formate is present in FSO_3H–SbF_5–SO_2 solution as two isomers in a ratio of 90% to 10%[167].



90% 10%

126

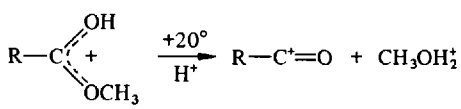
By raising the temperature of solutions of protonated carboxylic acids and esters, unimolecular cleavage reactions are observed. These reactions can be considered within the framework of the two unimolecular reaction pathways for acid-

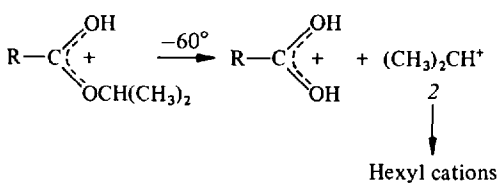
catalyzed hydrolyses of esters, either involving alkyl- or alkyl-oxygen cleavage. The advantage of studies of these reactions in superacid media, as compared to solvolytic conditions, is that the cleavage step can be isolated and studied in detail because the cleavage products generally do not undergo any further reaction.

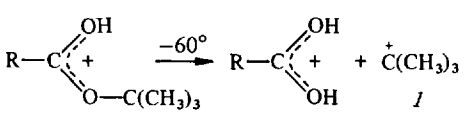
For example, in the case of protonated acetic acid in FSO_3H–SbF_5–SO_2 solution, a reaction analogous to the rate-determining step in the unimolecular cleavage of esters is observed leading to the acyl cation and oxonium (hydronium) ion.

$$R\text{–}CO_2H_2^+ \xrightarrow[H^+]{-20^\circ} R\text{–}C^+ = O + H_3O^+$$

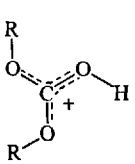
Unimolecular cleavage in this case, corresponds to dehydration of the acid, but in the case of protonated esters the cleavage pathway depends on the nature of the alkoxy group.



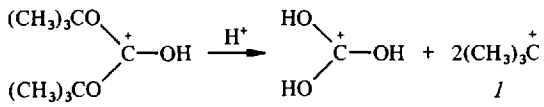




Dialkyl carbonates have been studied in FSO_3H–SbF_5 solution and have been shown to be protonated on the carbonyl group giving the dialkoxyhydroxy methyl cation[168].

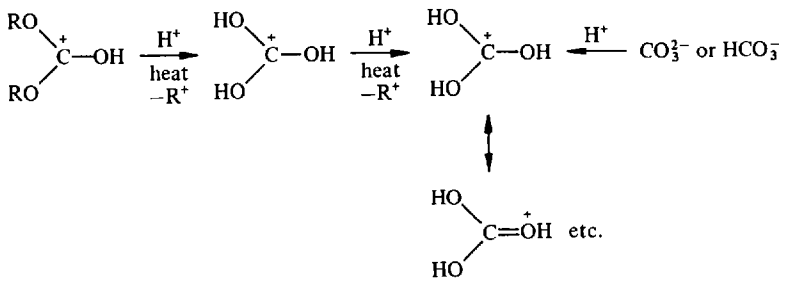


Di-*t*-butyl carbonate cleaves immediately at −80 ° with alkyl-oxygen fission, giving the *t*-butyl cation *1* and protonated carbonic acid. The structure of the latter has been established from the ^{13}C NMR spectrum of the central carbon atom which shows a 4.5 hertz quartet, being coupled to three equivalent hydroxyl protons[168].



27

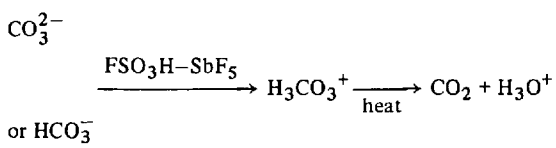
Di-isopropyl and diethyl carbonate cleave at a higher temperature, also via alkyl-oxygen cleavage, with initial formation of protonated alkyl hydrogen carbonates. The alkyl hydrogen carbonates can also be formed by protonation of their sodium salts.



127

Protonated carbonic acid can also be obtained by dissolving inorganic carbonates and hydrogen carbonates in FSO_3H–SbF_5 at −80 °. It is stable in solution to about 0 °, where it decomposes to the hydronium ion and carbon dioxide.

It is worthwhile to point out the close similarity of protonated carbonic acid (trihydroxymethyl cation) with the guanidinium ion, its triaza-analog. Both are highly resonance stabilized through their onium forms.



The observation of protonated carbonic acid as a stable chemical entity with substantial resonance stabilization may have also implications in our understanding of some of the more fundamental biological carboxylation processes. Obviously the in vitro observation in specific, highly acidic solvent systems cannot be simply extrapolated to different environments (biological systems). However, it is possible that on the active receptor sites of enzyme systems (for example, those of the carbonic anhydrase type) local hydrogen ion concentration may be very high, as compared with the overall "biological pH." In addition, on the receptor sites a very favorable geometric configuration may help to stabilize the active species, a factor which cannot be reproduced in model systems in vitro.

b) Acylium Ions (Acyl Cations). Seel observed in 1943 the first stable acyl cation[16]. Acetyl fluoride with boron trifluoride gave a complex (decomposition point 20 °) which was characterized as the acetyl tetrafluoroborate salt

$$CH_3COF + BF_3 \longrightarrow CH_3CO^+BF_4^-$$

128

The identification was based on analytical data and chemical behavior. Only in the 1950's were physical methods like infrared and NMR spectroscopy were applied, making further characterizations of the complex possible. Since 1954, a series of other acyl and substituted acyl cations have been isolated and identified[169–171]. The hexafluoroantimonate and hexafluoroarsenate complexes were found particularly stable[171]. Deno and his co-workers investigated solutions of carboxylic acids in sulfuric acid and oleum[172]. They observed protonation at lower acid concentrations and dehydration, giving acyl cations at higher acidities.

$$RCOOH \xrightarrow{H_2SO_4} RCOOH_2^+ \xrightarrow{\text{oleum}} RCO^+ + H_3O^+$$

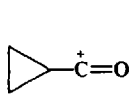
The investigation of acyl cations in subsequent work is substantially helped by NMR. Not only ^1H, but also ^2H, ^{13}C, and ^{19}F resonance studies established the structure of these ions[171–174]. These investigations, based on ^{13}C and proton resonance, showed that acyl cations, such as the CH_3CO^+ ion, are not simple oxonium ions (acylonium complexes), but are resonance hybrids of the oxonium ion, acyl cation and the ketene-like non-bonded mesomeric forms

$$CH_3-C\equiv O^+ \longleftrightarrow CH_3-\overset{+}{C}=O \longleftrightarrow CH_2=C=O \quad (\overset{+}{H})$$

128

The X-ray crystallography study of the $CH_3CO^+SbF_6^-$ complex[175] substantiated this suggestion and provided convincing evidence for the linear structure of the crystalline complex.

Investigation of acyl cations has been extended to be study of cycloacylium ions[176], diacylium ions (diacyl cations)[177], and unsaturated acylium ions[178].



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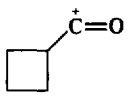

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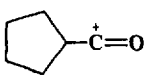

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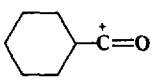


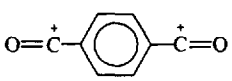
132

$O=\overset{+}{C}(CH_2)_3\overset{+}{C}=O$

133

$O=\overset{+}{C}(CH_2)_4\overset{+}{C}=O$

134



135

$CH_2=C(CH_3)-\overset{+}{C}=O$

136

$CH_2=CH\overset{+}{C}=O$

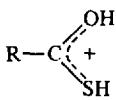
137

$CH_3CH=C(CH_3)\overset{+}{C}=O$

138

18. Sulfur as Heteroatom

Thiols and sulfides are protonated on sulfur in superacid media and give mono- and dialkylsulfonium ions, respectively[49]. Thiocarboxylic acids, S-alkyl esters, thioesters, dithioesters and thiocarbonates in similar media also form stable protonated ions[179] such as



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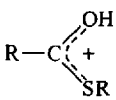

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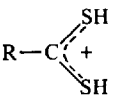

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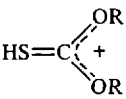
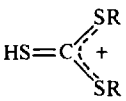


142

R = CH_3, C_2H_5



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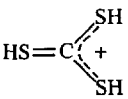
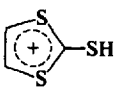


144

sulfur stabilized heteroatomatic species such as *145* and *146* are also known[163b].



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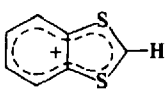


146

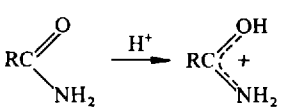
S-methylated and O-methylated dimethyl sulfoxides *147* and *148* have been very extensively studied[180].

$(CH_3)\overset{+}{S}=O$ *147*

$(CH_3)_2-S=\overset{+}{O}CH_3$ *148*

19. Nitrogen as Heteroatom

Amides and protonated, in superacid media at low temperatures, on the carbonyl oxygen atom, as shown first by Gillespie[181].

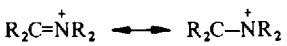


149

It was claimed that protonation of ethyl N,N-diisopropylcarbamate, a hindered amide, takes place on nitrogen, and not on oxygen[182]. A reinvestigation, however, established, that at low temperature first O-protonation is taking place (kinetic control) with the O-protonated amide subsequently rearranging to the more stable N-protonated form (thermodynamic control)[183].

The possibility of observing the protonated amide linkage in strong acid media has particular relevance in the study of peptides and proteins[184, 185].

Since nitrogen is a better electron donor than oxygen, the contribution of aminomethyl cation structures in acid salts of imines, amidines, and guanidines is small[186].



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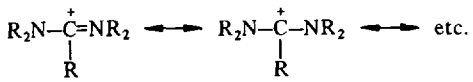

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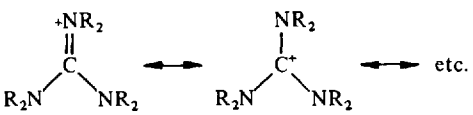
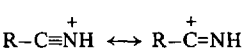


152

In protonated nitriles, however, the contribution from the iminomethyl cation resonance form is important[187, 188].



153

Recently protonated dialkylnitrosamines have been studied[189] to elucidate alkylating and aminoalkylating ability which due to the carcinogenic activity of nitrosamines is of potential biological significance. Ambident carbocationic nature of iminium ions and its relevance to aminoalkylating ability has also been explored[190]. An in vitro path of nitrosamine formations from amines with nitrates has been demonstrated[191].

In search of the still elusive nitrenium ions protonation of benzoquinone monoximes was studied[192]. Ions such as the triazomethyl cation have also been reported[193]. The field of protonated heteroaliphatic compounds has been reviewed[178a, 178b].

III. Five and Higher Coordinated (Non-Classical) Carbocations

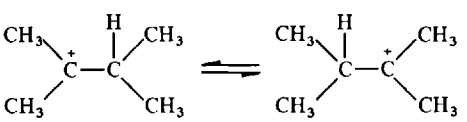
Some carbocations show great tendency to undergo fast degenerate rearrangements, leading through intramolecular hydrogen or alkyl shifts to the related identical structures[2]. The question arises, whether these processes are equilibrations between the limiting trivalent carbocations ("classical ion intermediates") separated by low energy level transition states or whether intermediate hydrogen or alkyl bridged

carbocations are involved. Extensive discussion of the kinetic and sterochemical results in these systems was made and it is not considered part of this review to recapitulate the arguments. The reader is referred to reviews[2] and the original literature.

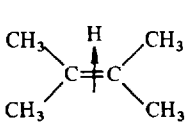
As direct observation of long-lived carbocations, in superacidic media, became possible in recent years it was logical to extend the developed spectroscopic and chemical methods to the study of equilibrating and/or bridged carbocations. Differentiation between these possibilities is difficult when using the ^{1}H NMR method for the study of these ions. On the slow NMR time scale the proton spectra of rapidly equilibrating or bridged ions can be expected to be quite similar. Carbon-13 NMR spectroscopy can be used, however, advantageously[31, 194] to investigate the structure of carbocations in which the possibility exists for degenerate rearrangements to occur which are fast with respect to the NMR time-scale and which lead to average shifts and coupling constants.

20. Equilibrating Alkyl Cations

An example of rapidly equilibrating alkyl cations is the tetramethylethyl cation *154*. It shows a PMR spectrum, in which all four methyl groups are equivalent and thus does not allow a clear distinction to be made between a rapidly equilibrating pair of ions or a static hydrogen bridged ion (which may be formulated either as a π-complex *155* or alkenomium ion *156*).

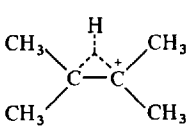


154



π–complex

155



alkenonium ion

156

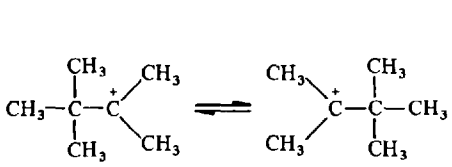
The ^{13}C shift observed for the two central carbons in this ion is $\delta_{^{13}C}$ 197.2 and the proton coupled spectrum consists of a doublet (J_{CH} = 65 Hz)[28]. If the ion is a rapidly equilibrating pair of ions, the observed shift will be the average of the shifts at the two sites. A good model for estimating these shifts is the methyl ^{13}C shift and the central ^{13}C shift in the *t*-butyl cation. The average of these shifts is $\delta_{^{13}C}$ 187.6. The effect of the two additional methyl groups would be expected to deshield slightly both shifts from those in the model compound, and thus the predicted and observed shift for the rapidly equilibrating pair of ions are in excellent agreement. The coupling constant can also be estimated, again using the *t*-butyl cation as a

model compound, from the direct and long range C–H coupling constants. The average of these values (assuming the long-range coupling to be negative as is usual in three-bond CCH coupling) is 64 Hz, again in excellent agreement with the observed value. The agreement of both the coupling constant and chemical shift with those predicted for the rapidly equilibrating ion are so good as to leave little doubt as to the nature of this ion. Laser Raman spectroscopy study of the ion also confirms this conclusion. Whereas NMR study of rapidly equilibrating ions is thus possible, clearly the relatively slow time-scale of the NMR experiment does not allow direct, separate observations of individual molecules, but gives information through analysis of *average* chemical shift and coupling constants of the equilibrating species. Thus clearly the need arises to apply physical methods to the study of these ions, the time scale of which is such, that it will not be affected by even the fastest chemical equilibrating processes.

We consequently undertook the infrared and Raman[26, 34] spectroscopic study of the tetramethylethyl cation *154* and for comparisons a series of alkyl cations with known "static" structure, such as the *t*-butyl, *t*-amyl, and isopropyl cations *1*, *3* and *2*. The nearly identical spectra of the ions and the evident planarity (or close to planarity) of the carbocation centers suggest that the tetramethylethyl cation is "classical", similar to the static ions used for comparison.

Finally perhaps the most decisive physical method yet applied to the study of carbocations in the condensed state is that of X-ray photoelectron spectroscopy (ESCA) which allows to differentiate equilibrating trivalent carbocations from bridged ions[38]. This method allows direct measurement of carbon 1 s electron binding energies. As the charge distribution within carbocations causes increasing binding energies with increasing positive charge localization, highly electron deficient classical alkyl and cycloalkyl cation centers (such as in the *t*-butyl and *t*-amyl cations) show about 4 eV 1 s binding energy differences from the remaining less electron positive carbon atoms. In five coordinated bridged carbocations (see subsequent discussion of the norbornyl cation) there is no such highly electron deficient carbon center indicated by the photoelectron spectra. The ESCA spectrum of the tetramethylethyl cation *154* shows an identical separation (1s E_b energies) between C^+ and C as in the *t*-amyl cation *3* (~4.2 eV). As the photoelectron spectra represent observation of the ejected core electron from a single species, no time scale limitation related to possible chemical equilibration phenomena can exist. The photoelectron spectra thus indicate that the ion studied is a classical carbocation and not a bridged tetramethyletheneprotonium ion *156* (which corresponds to the transition state of the equilibration process or may also be a high lying intermediate).

An example of an equilibrating or methyl bridged ion is the *pentamethylethyl cation (triptyl cation 157*. The proton NMR spectrum consist of a single resonance at δ 2.90[47]. This chemical shift was considered indicative of a rapidly equilibrating structure rather than the bridged structure although the fact that only a single proton resonance is observed does not enable these structures to be distinguished since in the methyl bridged carbocation equilibration of the methyls via the two classical ions as intermediates would be expected to occur. As in the case of the tetramethylethyl cation *154* the ^{13}C NMR spectral data can give additional evidence for the structure[31].



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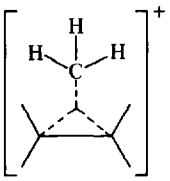
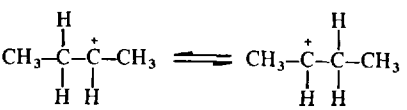


158

The average ^{13}C shift for C_2 and C_3 was found to be $\delta_{C_{13}}$ 205.3 ppm cosistent only with the rapidly equilibrating structure. The norbornyl cation (vide infra) provides an experimentally observed model for the methyl bridged ion (the bridged carbon showing a CMR shift of 21.8) which would on this basis be expected to give a shift of 100 ppm more shielded than that actually observed. Since this ion is equilibrating, the observed coupling will be the average of the two and three bond proton-carbon coupling constants. The two bond coupling constant in *t*-butyl cation is 6.5 Hz and a similar value would be expected in this ion. For the observed coupling constant to be zero, the three bond coupling must therefore have the same magnitude but opposite sign. Although the signs for only a few such couplings have been determined, such a sign alternation has been reported by Karabatsos, the two bond coupling being negative and the three bond coupling positive.

The proton spectrum of the *sec-butyl cation* at $-120\,^{\circ}$ consists of two resonances at δ 3.2 and δ 6.7 of relative area 2 : 1[195]. This is a result of a degenerate 1,2 hydride shift which at this temperature is fast with respect to the NMR timescale.



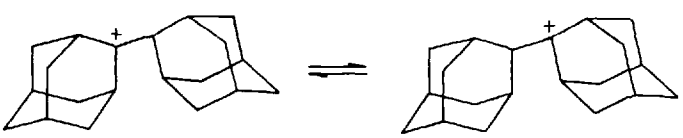
159

The ^{13}C spectrum of the two central carbons was found to be a quartet at $\delta_{^{13}C}$ 172.6, with a carbon-hydrogen coupling constant of 70 ± 2 Hz[31]. Using the shifts observed in the tetramethylethyl and pentamethylethyl cations *154* and *157* as models for the effect of methyl substitution in equilibrating ion (8 ppm) leads to a predicted shift of $\delta_{^{13}C}$ 181. Using the isopropyl cation as a model gives an estimated coupling constant of 72 Hz. As in the two previous examples the ^{13}C evidence demonstrates that the sec butyl cation *159* is an equilibrating "classical" carbocation although some contribution by the bridged "non-classical" cation seems possible.

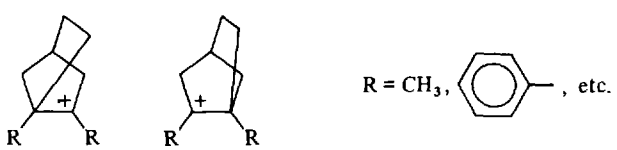
Recently with Donovan we have determined[32] the methyl substituent effect α, β, ν and δ to the carbocation center in C_3 to C_8 alkyl cations. From these values it was possible to estimate the ^{13}C NMR shifts of tertiary-tertiary and secondary-secondary equilibrating ions. The results agreed well with experimentally obtained values in the case of tertiary-tertiary equilibrating ions, but with secondary-secondary equilibrating systems major deviations were observed. This indicates the contribution of partial hydrogen bridged structures in secondary-secondary equilibrating ion such as *159*.

Saunders et al. have reported isotope induced splitting of shifts in the proton NMR spectra of tetramethylethyl[196] and pentamethylethyl cations[197] *154* and *157* where deuterium in the methyl groups perturb the equilibria. The observed splittings clearly reinforce the classical nature of these ions. This ingenious isotopic perturbation of resonance technique has been extended[197] to ^{13}C NMR spectroscopy where the larger-chemical shifts observed enhances the sensitivity. From these splittings it is possible to differentiate a equilibrating classical ion from a non-classical one.

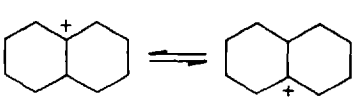
The proton spectrum of *cyclopentyl cation 37* in SbF_5–SO_2–ClF solution at −70 °, as mentioned previously, consists of a singlet at δ 4.68. The ^{13}C satellites from this peak show a J_{CH} coupling constant of 28.5 Hz and have an intensity five times that normally observed. This is a result of the degenerate rearrangements that occur in this ion which, on the NMR time-scale, leading to complete equilibration of the nine protons around the five carbon atoms. The ^{13}C spectrum is a 10 line multiplet at $\delta_{^{13}C}$ 98.4 with a coupling of 28.5 Hz[31]. (Fig. 12). Again ESCA study[38] of the ion shows the presence of a secondary carbocation center separated by ~ 4.8 eV from the additional carbon atoms. There is by now a whole host of equilibrating classical and partially bridged ions reported in the literature [199–201]. Some of the representative examples are:



160[199]



161[200]

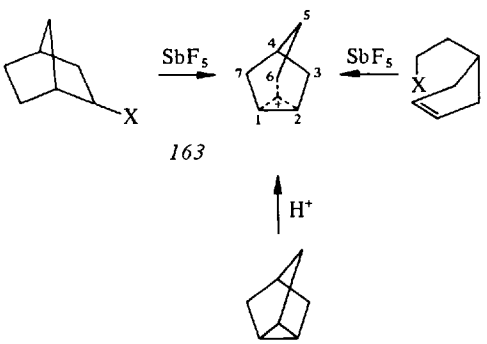


162[105]

21. Norbornyl Cations

Consideration of the cyclopentyl cation is leading us to the discussion of one of the most controversial of all carbocations, the *norbornyl cation, 163* around which the structure the much publicized classical-nonclassical controversy of "carbonium ions" mainly centered in recent years[9].

The methods that we worked out in the early 1960's to generate and observe stable carbocations in low nucleophilicity solutions[2] were successfully applied to direct observation of the norbornyl cation. Preparation of the ion by the "σ route" from 2-norbornyl halides, by the "π route" from β-Δ^3-cyclopentenylethyl halides, and by the protonation of nortricyclene all led to the same norbornyl cation.



163

The method of choice for preparation of the norbornyl cation (giving the best resolved NMR spectra, free of dinorbornylhalonium ion equilibration), is from *exo*-2-fluoronorbornane in SbF_5–SO_2 (or SO_2ClF) solution. With Saunders and Schleyer in a joint effort we first investigated the 2-norbornyl cation in 1964[202] and observed its ^1H NMR spectrum, having prepared the ion from *exo*-2-fluoronorbornane in SbF_5–SO_2. At room temperature the ^1H NMR spectrum consisted of a single broad band at δ 3.75 (Fig. 12) due to scrambling of all hydrogen atoms. The contrast between this single band and the complex spectrum of the progenitor, 2-*exo*-fluoronorbornane, is striking. The equilibration of the hydrogen atoms is caused by fast 3,2- and 6,1,2-hydrogen shifts and by Wagner-Meerwein rearrangement.

Similarly at room temperature the ^{13}C spectrum of the ion shows a single broad absorption line centered at $\delta_{^{13}C}$ 59.8 (from external Me_4Si to which all shifts are related). When the temperature was lowered to −70 °C the ^1H NMR spectrum of the

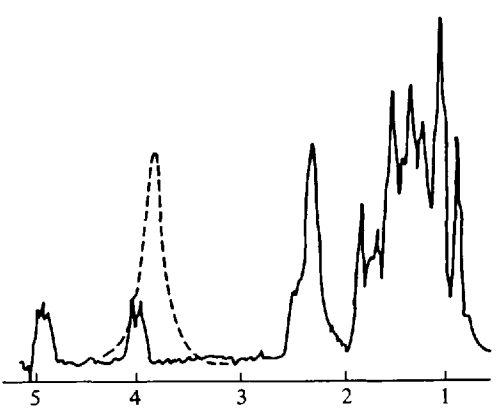


Fig. 12. ^1H NMR spectrum (60 MHz) of the norbornyl cation at 35 °C (dotted line) and the precursor 2-*exo*-fluoronorborane (full line)

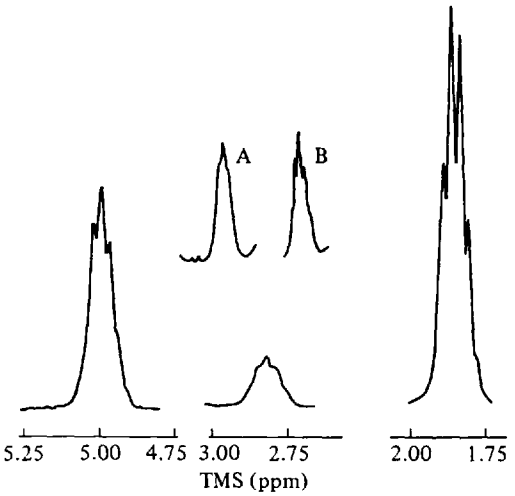


Fig. 13. ^{1}H-NMR spectrum (100 MHz) of the norbornyl cation in SbF_5–SO_2 solution at −80 °C. The insert shows the effect of irradiating the low-field septuplet on the one-proton peak at δ 2.82. A is the spectrum without irradiation and B is with irradiation

2-norbornyl cation resolved into three peaks with relative areas 4 : 1 : 6 (Fig. 13). The spectrum did not change when the temperature was further lowered to −120 °C[10]. Jensen and Beck obtained in $GaBr_3$–SO_2 similar spectra of good resolution[203].

The spectrum was interpreted as evidence that the 3,2-hydrogen shift was frozen out, but the 6,1,2-hydrogen shift and the Wagner-Meerwein rearrangement are still fast even at the low temperature used (−120 °C). The rate of the slow 3,2-hydrogen shift was established from temperature-dependence studies, by comparing experimental spectra with those calculated for different rates. The activation energy of this shift is 10.8 ± 0.6 kcal/mol, with $A = 10^{12.3}$ sec^{-1} [27].

When the ion is prepared at −78 °C in FSO_3D–SbF_5–SO_2 solution from nortricyclane, only one deuterium atom is incorporated, and in the ^{1}H NMR spectrum the relative area of the low-field peak is reduced from 4 to 3. No further inter- or intramolecular scrambling of the deuterium is observed during 1 h at −78 °.

Preparation of the norbornyl cation by protonating nortricyclane, or from reaction of norbornyl fluoride or alcohol with SbF_5, precludes equilibration involving dinorbornylhalonium ions, but that complication can occur under certain conditions between norbornyl chloride or bromide and the norbornyl cation. We have studied equilibration of the norbornyl cation with excess norbornyl halides through the dinorbornylhalonium ions, and described its characteristics.

Subsequently we succeeded in "freezing out". on the NMR time scale, the fast 6,2-hydrogen shift[10]. Using a mixed SbF_5–SO_2ClF–SO_2F_2 solvent system, we could observe the 100-MHz spectrum at temperatures down to −156 °C. At −120 °C, the spectrum was identical to that described at −78 °C, but between −128 and −150 °C significant changes in the spectrum occurred. The low-field peak due to the four equilibrating "protonated cyclopropane" ring protons broadened and then separated into two resonances, each of relative area two, at δ 3.05 and 6.59. The high-field resonance due to the six methylene protons broadened, developing a shoulder at δ 1.70. The peak at δ 2.82 due to the bridgehead proton remained un-

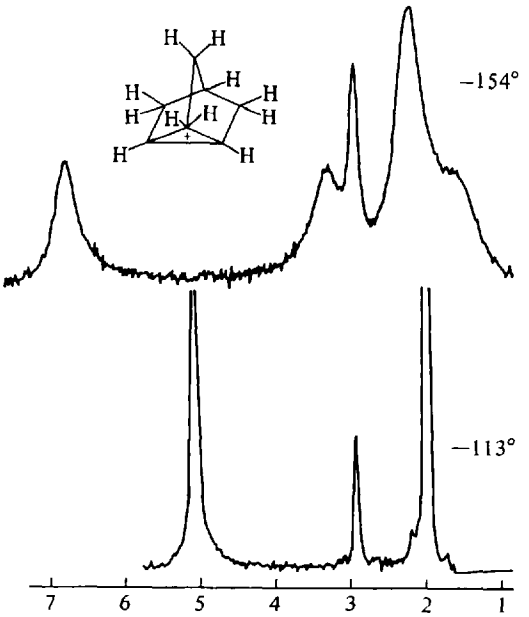


Fig. 14. ^{1}H-NMR spectra (100 MHz) of the "norbornyl cation" in SbF_5–SO_2ClF–SO_2F_2 solution at temperatures between −113 and −154 °C

changed (Fig. 14). The temperature dependence of the low field resonance was used to calculate rate constants; the activation energy was 5.9 ± 0.2 kcal/mol^{-1} and the pre-exponential factor $10^{12.7}$ sec^{-1}.

These observations could be consistent with either of two interpretations:
(a) that the ion is classical and that the temperature dependence corresponds to the "freezing out" of the 6,1,2-hydrogen shift, the Wagner-Meerwein rearrangement still being fast at −156 °, or
(b) that the ion is nonclassical, all rearrangements have been "frozen out", the structure of the ion being that of the methylene bridged pentacoordinated ion.

In order to differentiate between these two possibilities the Raman and ^{13}C NMR spectra of the ion were studied[10]. As Raman spectroscopy is a fast physical method (assuming that vibrational transition rates are faster than any of the hydrogen or alkyl shifts) and the question of possible equilibration versus bridged ion is unimportant. The previously discussed technique of average ^{13}C NMR shifts should be also applicable in this case to differentiate a static nonclassical bridged ion from rapidly equilibrating classical carbenium ions.

The Raman spectroscopy study of the stable norbornyl cation was carried out using a He-Ne laser. In the C–C stretching frequency region there is only one strong line at 972 cm^{-1} (ρ = 0.35). The C-H stretching frequency region shows five lines, one of which is at 3110 cm^{-1}. The skeletal vibrations of the ion and comparison with model compounds suggest a structure closely related to nortricyclene, but not to norbornane, e. g. the bridged ion of protonated nortricyclene nature.

Carbon-13 spectroscopy provides even more convincing evidence for the structure of the norbornyl cation. Using first (with White) the INDOR method[10] and later (with Liang) the fast Fourier transformation method[10], we obtained the com-

plete ^{13}C NMR spectrum, with all the coupling constants and multiplicities both at −70 °C under conditions of rapid equilibration of the norbornyl cation, and at −150 °C as the static "frozen out" ion. The results are summarized in Table 5.

The proton-decoupled FT ^{13}C NMR spectrum of the ion at −70 °C consists of three carbon resonances at δ_{13C} 92, 37.7 and 31.3, for equilibrating C.1, C.2, C.6, bridgehead C.4, and equivalent methylene carbons (C.3, C.5, and C.7), respectively. (Assignments were made by the off-resonance ^{13}C NMR spectrum.) The most deshielded carbon resonance (δ_{13C} 92) shows a quintet indicating that each of the cyclopropane-like ring carbons couples with four equivalent protons, while the bridgehead carbon resonance and the methylene carbon resonance are a doublet and triplet, as they are coupled with one and two protons, respectively. At lower temperatures (−150 °C) this resonance is separated into two components at δ_{13C} 125.3 (for C.1 and C.2) and 22.4 (for C.6). The bridgehead carbon (C.4) resonance is slightly moved to higher field at δ_{13C} 33.4. The methylene resonance is also separated into two component at δ_{13C} 48 (for C.3 and C.7) and 28 (for C.5). The C-H coupling constants (J_{CH}, in Hz) given in Table 5 were obtained directly from the proton-coupled ^{13}C NMR spectrum. The pentacoordinated bridging methylene carbon atom is not deshielded (δ_{13C} 22.4), whereas the tetracoordinated carbons to which bridging takes place (and which consequently carry more positive charge) show more deshielding (δ_{13C} 125.3), but are still much more shielded than expected for an equilibrating classical ion.

In the proton-coupled ^{13}C NMR spectrum of the norbornyl ion no coupling was observed between the methylene hydrogens at the pentacoordinated carbon (C.6) and the cyclopropane-like carbons (C.1 and C.2). This is expected from the nonclassical structure since the two-electron, three-center bonds are longer and weaker than normal $C_{sp}3–C_{sp}2$ bonds.

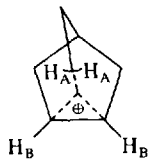
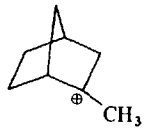
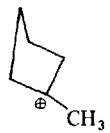
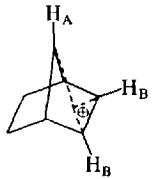
The ^{13}C NMR spectra show that the norbornyl cation is a nonclassical carbonium ion with a pentacoordinated bridging carbon atom. The magnitude of $J_{C.6-H}$ = 145.8 Hz in the 2-norbornyl cation is smaller than those for $J_{C.1-H}$ in the 7-nonbornenyl and 7-norbornadienylions *164* and *165* (218.9 and 216.4 Mz. respectively)[10]. This is expected as the strained C.7 carbons in the latter have higher s character in the C–H bonds than has C–6 in the former (for an sp^3 carbon J_{CH} is about 125 Hz, corresponding to 25% s character). An increase of s character associated with the C–H bond is expected to increase the C–H coupling constant. Both ^1H and ^{13}C NMR spectra indicate that the bridging pentacoordinated methylene carbon C.6 in the norbornyl ion is tetrahedral in nature and carries little positive charge.

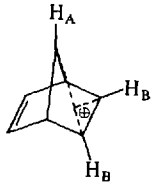
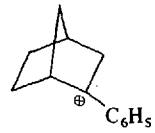
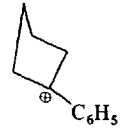
164

165

In a ESCA study with Mateescu and Riemenschneider[38] we also succeeded to observe the ESCA spectrum of the norbornyl cation and compared it with that of the 2-methylnorbornyl cation and other trivalent carbenium ions, such as the cyclopentyl and methylcyclopentyl cations. The 1s electron spectrum of the norbornyl

Table 5. Comparison of the NMR parameters of the carbocation centers

Ion	Carbocation δ [ppm]	J_{CH}[Hz]	δ_{13C}[ppm]	Ion	Carbocation solvent T[°C]	δ_{13C}[ppm]
	H_A = 3.05 H_B = 6.59	H_A = 145.8 H_B = 184.5	C_A = 22.4 C_B = 125.3		FSO_3–H–SbF_5–SO_2 –80	C–1 = 80.8 (J = 169.5 Hz) C^+–2 = 271.1
					SbF_5–SO_2 –60	C^+–1 = 335.8
	H_A = 3.25 H_B = 7.04	H_A = 218.9 H_B = 193.8	C_A = 34.0 C_B = 125.9	$(CH_3)_3C^{\oplus}$	SbF_5–SO_2ClF –60	C^+ = 335.2
				$(CH_3)_2CH^{\oplus}$	SbF_5–SO_2ClF –60	C^+ = 320.6

	$H_A = 3.24$ $H_B = 7.48$	$H_A = 216.4$ $H_B = 192.3$	$C_A = 36.2$ $C_B = 114.9$		FSO_3H −35	C−1 = 59.8 (J = 158.4 Hz) C^+−2 = 257.3
					FSO_3H −20	C^+−1 = 268.4
				$(CH_3)_2\overset{+}{C}C_6H_5$	FSO_3H–SbF_5–SO_2 −60	C^+ = 254.9

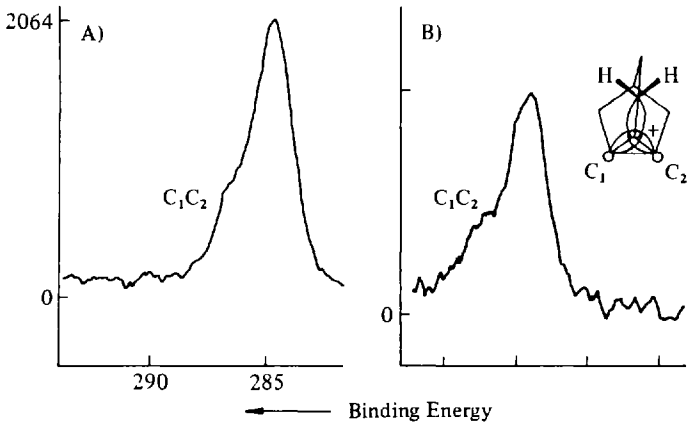


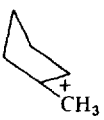
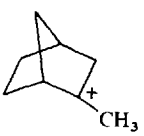
Fig. 15. Carbon 1s photoelectron spectrum of the norbornyl cation: (A) 100-V, (B) 30-V analyzer energy

cation (Fig. 15) shows no high binding energy carbenium center and a maximum separation of less than 1.5 eV between the two "cyclopropyl" type carbons, to which bridging takes place from the other carbon atoms (including the penta-coordinated bridging carbon). The 2-methylnorbornyl cation in contrast shows a high binding energy carbenium center, slightly delocalized, as indicated by the δE_b ~3.7 eV sparation from the other carbon atoms, as do other trivalent carbenium ions. ESCA shift differences are summarized in Table 6.

Since in electron spectroscopy the time scale of the measured ionization processes is on the order of 10^{-16} sec, definite ionic species are characterized, regardless on their possible intra- and intermolecular interactions (e. g., Wagner-Meerwein rearrangements, hydride shifts, proton exchange, etc.). Thus, electron spectroscopy gives an undisputible, direct answer to the long debated question of the "non-classical" nature of the norbornyl cation independent of any possible equilibration process.

The bridging methylene carbon in the norbornyl ion is pentacoordinated. It is bound to the hydrogen atom and a carbon atom by two-electron single bonds. The remaining sp^3 orbital is involved in two-electron three-center bond with C_1 and C_2. It should be pointed, however, that if a highly σ-delocalized but somewhat unsymmetrical non-classical ion would be in a degenerate equilibration process through the completely symmetrical non-classical ion (such as *163*) for all practial purposes such systems would show symmetrical nature in the NMR or even ESCA spectra. Thus, the double energy minima would be indistuinguishable from a single minimum, as the interconversions would take place through a very low energy barrier, i. e. < 2 kcal/mole. The question is not the possible equilibration between classical ions vs. the symmetrical bridged nonclassical ion, which is ruled out by direct, spectroscopic studies of the long lived ion, but of possibly still equilibrating nonclassical σ-delocalized, but somewhat unsymmetrical ions (double minima) vs. the symmetrical nonclassical ion (single minimum). These are becoming by necessity indistinguishable by usual studies. It is important to recognize that σ-delocalized nonclassical

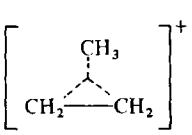
Table 6. Binding energy differences of carbocation centers from neighboring carbon atoms (dE_{B^+C-C})

Ion	dE_{B^+C-C}	Approximate relative C^+/C intensity
$(CH_3)_3C^+$	3.9 ± 0.2	1/3
	4.2 ± 0.2	1/5
	3.7 ± 0.2	1/7
	4.8 ± 0.5	1/4
	1.5 ± 0.2	2/5

ions are not necessarily only static symmetrically bridged species, contrary to claims made to this effect[9f, h].

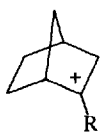
Other examples of directly observed long-lived norbornyl ions in which the tetra- and/or pentacoordinated carbons were identified by NMR spectroscopy are the 7-norbornenyl and 7-norbornadienyl cations[10, 204–209] *164* and *165*.

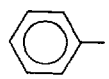
The carbonium centers in the norbornyl cation, 7-norbornenyl cation and 7-norbornadienyl cation[10, 207] are similar and related to the ethenemethonium ion, *166* although strain differences in the ions are obviously significant. All contain a  two electron three-center bond. The bridging carbon atoms are pentacoordinated, whereas the carbons to which they bridge are tetracoordinated carbenium atoms.



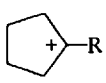
166

It is also instructful to discuss studies on 2-methyl- and 2-phenyl-2-norbornyl catons, *167* and *168*, both of which have been investigated by proton[10, 210] and carbon-13 [211] NMR spectroscopy. The 2-methyl-2-norbornyl cation can be characterized as a partially σ-bond (i. e., C.1–C.6) delocalized carbenium ion, while the 2-phenyl-2-norbornyl cation exhibits the properties of a classical carbenium ion with no significant σ delocalization (of course the positive charge is extensively delocali-



	R
167	CH_3
168	

zed into the phenyl π system). These conclusions are particularly supported by comparing C.1 and C.2 carbon resonances in these two ions; the ^{13}C NMR shifts are shown in Table 2 along with their assignments. The difference in C.2 carbon resonances in the two ions is $\Delta\delta_{13_C} = 271.1 - 257.3 = 13.8$, while the same difference between the related model cyclopentyl cations is 57.8. Also the carbon shift at the carbocationic center in the 2-methyl-2-norbornyl cation is about 64 ppm less de-



R	$\delta\ ^{13}C^+$
CH_3	335.8
C_6H_5	278.0

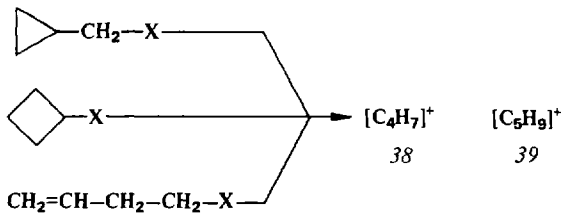
shielded than that in the 1-methyl-1-cyclopentyl cation, while the carbon shifts are comparable in the corresponding phenyl substituted ions. These model ions are evidently classical carbenium ions without significant σ-bond delocalization. The discrepancy observed in explained in terms of partial σ-bond delocalization through the C.1–C.6 bond toward the empty 2p orbital at C.2 in the 2-methyl-2-norbornyl cation. Such delocalization is, however, much more profound in the parent, unsubstituted 2-norbornyl cation.

Farnum and Wolf[211b] studied the relationship between ^1H NMR shifts and substituent effect in a series of substituted 2-aryl-2-norbornyl cations. With substituents increasingly more electron withdrawing, the "onset" of C.1–C.6 σ bond-delocalization or nonclassical stabilization was observed, due to increasing electron demand compared to the parent 2-phenyl-2-norbornyl cation, by a gradual and clear change of the NMR patterns. This effect has been recently studied with Prakash and Liang more thoroughly by ^{13}C NMR spectroscopy[212], as well as by Farnum[213]. It can be concluded that the original views of Winstein[208] on the nonclassical nature of the norbornyl cation, based on kinetic and stereochemical results, were fully substantiated through the direct spectroscopic studies of the long-lived ion[10], which helped to develop our general understanding of carbonium ions, as distinct and well differentiated species from trivalent carbenium ions.

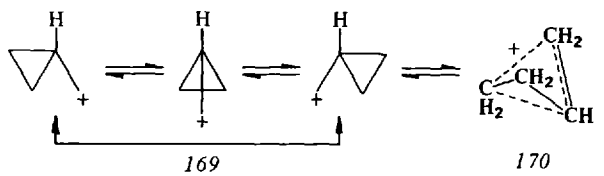
22. Cyclopropylmethyl and Cyclobutyl Cations

Extensive experimental and theoretical work has been devoted to study the nature of cationic intermediates involved in cyclopropylmethyl, cyclobutyl and homoallylic

interconversions under both solvolytic and stable carbocationic conditions[2, 91, 214–215]. The non-classical nature of parent cyclopropylmethyl and 1-methylcyclopropylmethyl cations *38* and *39* is now firmly established[94–97].



Ion *38* (Fig. 16) could be generated both from cyclobutyl and cyclopropylmethyl precursors. At lowest temperatures studied (= 140 °), ion *38* is still an equilibrating mixture of bisected σ-delocalized cyclopropylcarbinyl cations *169* and the bicyclobutonium ion *170*.



From the comparison of calculated NMR shifts, the low lying species is considered to be bicyclobutonium ion *170*[95]. However, in the case of $C_5H_9^+$ *39*, the low lying species are the methylbicyclobutonium ions *171* with no contribution from either

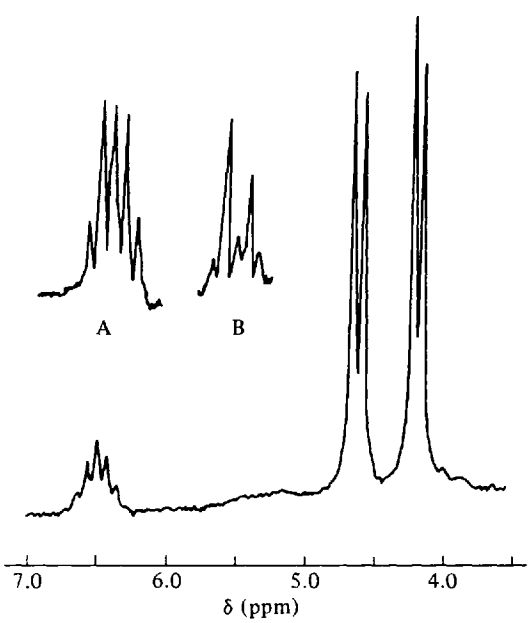
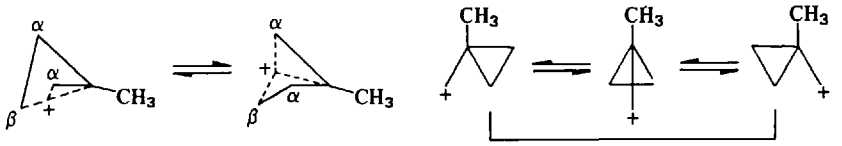
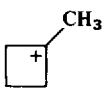


Fig. 16. 100-MHz pmr spectrum of of the cyclopropylcarbinyl cation in SbF_5–SO_2ClF solution at −80°: (A) 60 MHz spectrum of CH-region; (B) 60 MHz spectrum of the CH-region of ion obtained from a α,α-dideuteriocyclopropylcarbinyl precursor

the bisected σ-delocalized 1-methylcyclopropylmethyl cation *172* or the 1-methylcyclobutyl cation *173*, even at the lowest temperature studied (= −158 °)[97]. The observation of the highly shielded β-methylene carbon at $\delta^{13}C$ −2.83 is particularly convincing evidence for the non-classical bicyclobutonium structures.



171 *172*



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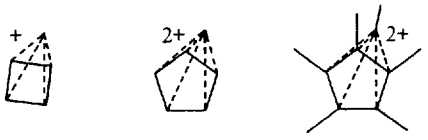
23. Miscellaneous Non-Classical Ions

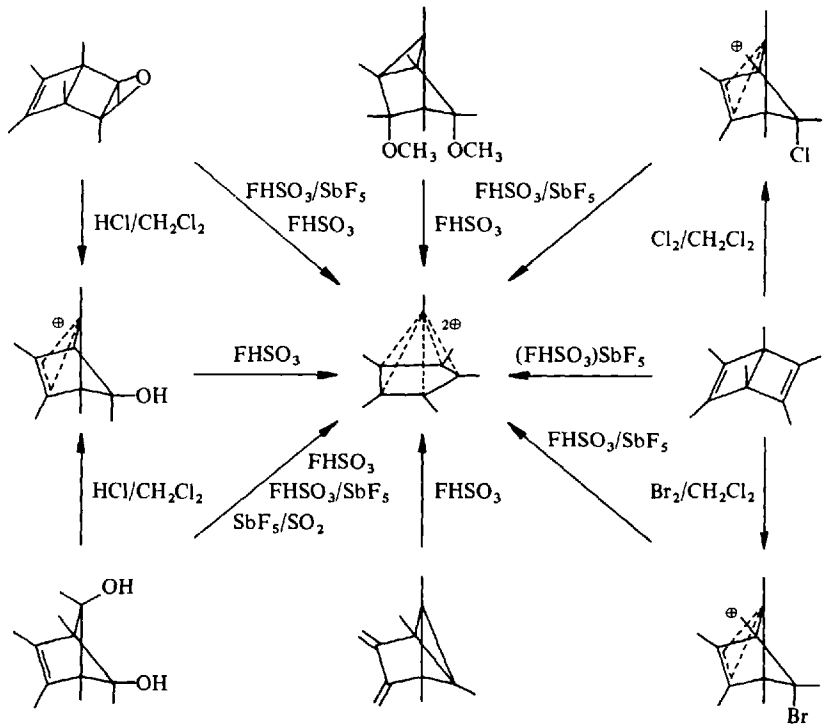
a. Pyramidal Cations. Interest is increasing in the preparation, chemistry, and unusual bonding properties of pyramidal carbocations, fascinating newcomers to the non-classical ion group[11, 216–224]. Representatives of two possible types of these ions, $(CH)_5^+$, and $(CH)_6^{2+}$ have already entered the literature. The parent $(CH)_5^+$ ion has been the subject of a number of calculations[216], and a methyl substituted derivative has been prepared[217]. Preparative work on several substituted homo-[218] and bishomo-$(CH)_5^+$ cations[219] has also been reported.



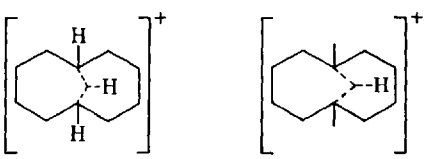
$(CH)_5^+$ $(CH)_6^{2+}$ $C(CH_3)_6^{2+}$

174 *175* *176*

The hexamethyl derivative $(CCH_3)_6^{2+}$ a pyramidal dication *176* has been prepared by Hogeven in superacidic solutions from a variety of precursors[220]. A number of arguments, including NMR spectroscopic evidence and the chemical reactivity justify expression of a strong preference for the nonclassical structure, rather than a rapidly equilibrating system of classical ions (see Fig. 18)[221]. The latter would be expected to show no absorption characteristic of a cyclopropylmethyl system. No such absorption was, however, observed[11]. The nonclassical structure was also substantiated by *ab initio* quantum mechanical calculations on the parent ion[223].



b. Hydrogen Bridged Cyclodecyl Cations. Sorensen et al.[225] have recently demonstrated that at very low temperature cyclododecyl cations *177* exists with static, frozen out, 1,6-μ-hydride structure *178*. Similar behaviour was also observed for 1,6-dimethyl analog *179*.

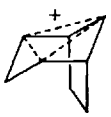


178 *179*

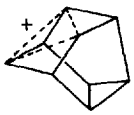
The bridging hydrogen in ion *178* is observed at a unusually high field of δ –6.85 as compared to the adjacent methine protons (δ 6.80).

c. Trishomocyclopropenium and Analogous Ions. Following Winstein's proposal[226] of the formation of the trishomocyclopropenium ion *180* in the solvolysis of *cis*-bicyclo [3.1.0] hexyltosylate, extensive effort was directed towards its generation under stable ion conditions[227]. Masamune et al.[228] were successful in generating ion *180* and its ethanobridged analog *181* from the corresponding *cis*-3-chlorobicyclo [3.1.0] hexane and 8-chlorotricyclo [3.2.1.$0^{2,4}$]octane precursors in superacidic media. The ^{13}C NMR shifts of charged center is unusually shielded indicating

180



181



182

the non-classical nature of these ions. After unsuccessful earlier attempts ion *180* has also been prepared recently[229] from bicyclo[3.1.0]hexan-3-ol[228]. Another trishomoaromatic ion analog of *180* is the 9-pentacyclo[4.3.0.0^{2,4}.0^{2,8}.0^{5,7}]nonyl cation *182*. Coate's[230] ion *182* also has three fold symmetry and its ^{13}C NMR spectrum shows highly shielded shifts for the charged carbons.

IV. Significance and Future Outlook

With the advent of superacidic Lewis acid halide (such as SbF_5, and TaF_5) and Bronsted acid (such as HF–SbF_5, FSO_3H–SbF_5) systems, a new vista of chemistry has emerged. With methods developed in our laboratories in the early sixties it is possible now to generate as stable long lived species practically any type of carbocations and study their structure and chemical reactivity. These studies also helped in the understanding of the nature of electrophilic reactions and their intetmediates. Trivalent carbocations (classical ions) as well penta (or higher coordinated) carbocations are now well established. The concept of pentacoordinated carbocation formation via electron sharing of single bonds with electrophilic reagents in three-center bond formation promises to open up an important new area of chemistry.

Trivalent carbocations as recognized in the pioneering work of Meerwein, Ingold and Whitmore, play an important role in acid-catalyzed hydrocarbon transformation reactions (isomerization, alkylation, cyclization, polymerization, etc.), as well in a large variety of electrophilic reactions including those of the generalized Friedel-Crafts type (generally with n- or π-donor reagents).

On the other hand pentacoordinated carbocations play an equally important role in electrophilic reactions of σ-donor saturated systems.

The realization of the electron donor ability of shared (bonded) electron pairs (single bonds) could one day rank equal in importance with G. N. Lewis' realization of the importance of the electron donor unshared (non-bonded) electron paris. We can now not only explain the reactivity of saturated hydrocarbons and in general single bonds in electrophilic reactions, but indeed use this understanding to explore new areas of carbocation chemistry.

The generalized concept of carbocations and electrophilic reactions indicates that the initial interactions of electrophiles with π-donor systems (olefins, acetylenes, aromatics) involves three-centered bond carbonium ion formation. The π-bond provides the bonding electron pair which interacts with the empty orbital of the electrophile. Thus in principle there is no difference between the electrophilic reactivity of

σ- and π-bonded systems. Electrophilic reactions thus take place at the involved bonds and only in cases where non-bonded electron pairs are present, at individual atoms.

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Wagner-Meerwein Rearrangements in Long-lived Polymethyl Substituted Bicyclo[3.2.0]heptadienyl Cations

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In memory of Professor H. L. Meerwein, on the occasion of his hundredth birthday

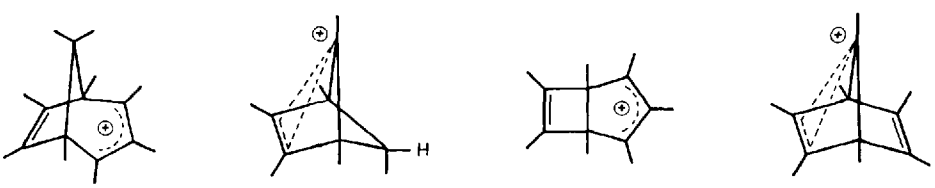
Table of Contents

I. Introduction

The importance of carbonium ions as reactive intermediates in organic chemistry is well known, from both synthetic and theoretical points of view, and is brought out in an excellent review[1]. In nature the formation of many important compounds proceeds via carbonium ion like intermediates (e.g. polyene cyclizations[2]) and via skeletal rearrangements within these species (e.g. terpene rearrangements[3]). The industrial usefulness of carbonium ions is evident from many acid-catalyzed processes (e.g. isomerization[4], Koch-reaction[5]). During the last one and a half decades the use of very strong acids (FSO_3H, $HF-SbF_5$ and FSO_3H-SbF_5) and the application of ^1H and ^{13}C NMR spectroscopy at low temperatures have made it possible to generate and to investigate carbonium ions under conditions of long life time, affording a wealth of new and quantitative information.

Interesting facets of the chemistry of carbonium ions (especially those referred to as "nonclassical" ions, a term first used by Roberts[6]) deal with both the bonding within these ions and the rearrangements they can undergo. With respect to bonding, the long-standing controversy over the norbornyl cation[7] and the recent results in pyramidal mono[8]- and dications[9] are illustrative. In these cases the coordination number of carbon is found to be higher (five or even six) than the usual four. The tendency of carbonium ions to undergo skeletal rearrangements was first proposed by Wagner in 1899[10] and further explored by Meerwein in the beginning of this century[11] in the camphenehydrochloride-isobornylchloride rearrangement. Since that time numerous examples of so-called Wagner-Meerwein shifts have been found, under both solvolytic and superacidic conditions. Especially fascinating Wagner-Meerwein shifts are found within polycyclic carbonium ions, resulting in degenerate and nondegenerate isomerizations.

Stimulated by the recently reported intriguing properties of and interconversions in polymethylbicyclo[3.2.1]octadienyl (e.g. *1*)[12] and -[2.1.1]hexenyl (e.g. *2*)[9a] cations, we investigated a class of carbonium ions which are intermediate between these types with respect to the number of skeletal carbon atoms – 7 instead of 8 and 6, respectively –, namely the polymethylbicyclo[3.2.0]- and -[2.2.1]heptadienyl cations, *e.g. 3* and *4* respectively.



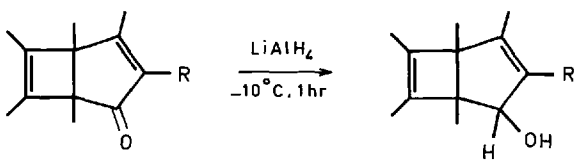
1 2 3 4

In addition the work of Winstein and co-workers on the parent 7-norbornadienyl cation[13] has been an impetus for the present investigation. In this chapter an account is given of the spectroscopic properties of the bicyclo[3.2.0]- and -[2.2.1]-

heptadienyl cations, their degenerate and nondegenerate rearrangements (visualized by spectroscopic and labeling techniques) and the influence of several substituents upon stability and rearrangements in this class of carbonium ions[14].

II. Synthesis of Carbonium Ion Precursors

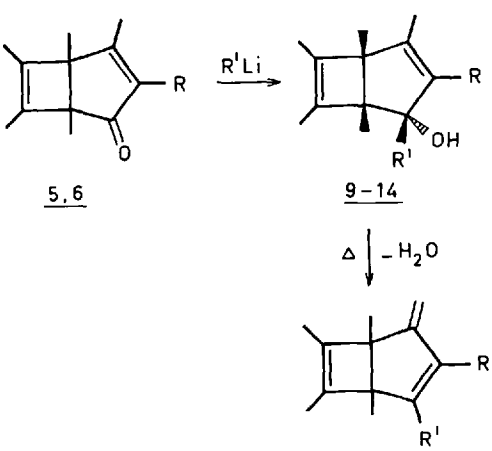
In general bicyclo[3.2.0]heptadienols were used as starting materials for preparing the desired carbonium ions. Reduction of the ketones *5*[15] and *6*[16] with $LiAlH_4$ at −10 °C gave in about 70% yield crystalline mixtures of diastereomeric secondary alcohols *7* and *8*, respectively (Scheme 1).



5 (R=CH_3)
6 (R=H)
7 (R=CH_3)
8 (R=H)

Scheme 1

The tertiary alcohols *9–14* were obtained upon treatment of the ketones *5*[15] and *6*[16] with alkyllithium reagents (Scheme 2).



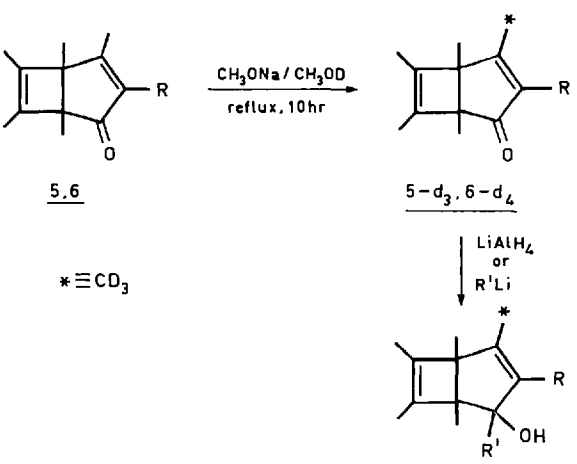
5, 6 — 9–14 — 15–20

	R	R'
5	CH_3	—
6	H	—
9, 15	CH_3	CH_3
10, 16	H	CH_3
11, 17	CH_3	t-C_4H_9
12, 18	H	t-C_4H_9
13, 19	CH_3	c-C_3H_5
14, 20	H	c-C_3H_5

Scheme 2

While alcohols *9* and *10* appeared to be stable crystalline compounds, the alcohols with a bulky R′ group (*11–14*) dehydrated under rather mild conditions (after a few days at 0 °C or during distillation at 50 °C and 0.005 mm Hg) to the corresponding trienes (*17–20*). This dehydration is in line with the observation of Sorensen with analogous cyclopentenyl alcohols[17]. A reason for the easy dehydration may be steric strain between the bulky R′ group and the neighbouring bridgehead methyl group. This argument is strenghtened by the observed deshielded absorption

at δ 1.30 ppm in alcohol *12* of one of the bridgehead methyl groups, normally found between δ 0.90 and δ 1.10; presumably the deshielding is due to a Van der Waals shift[18]. From these observations we conclude that attack of the alkyllithium reagents takes place from the *exo*-face, resulting in the *endo*-alcohols[13, 19]. For the generation of labeled carbonium ions the deuterated alcohols *7*-d_3, *8*-d_4, *9*-d_6, *10*-d_7, *11*-d_3 and *12*-d_4 were synthesized starting from ketones *5*-d_3 and *6*-d_4 upon treatment with $LiAlH_4$, CD_3Li or t-BuLi. Ketones *5*-d_3 and *6*-d_4 were obtained by H-D exchange of the unlabeled ketones in CH_3OD/CH_3ONa (Scheme 3).



	R	R'
5	CH_3	—
6	H	—
5-d_3	CH_3	—
6-d_4	D	—
7-d_3	CH_3	H
8-d_4	D	H
9-d_6	CH_3	CD_3
10-d_7	D	CD_3
11-d_3	CH_3	t-C_4H_9
12-d_4	D	t-C_4H_9

Scheme 3

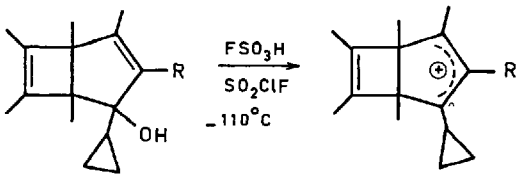
III. Generation and Spectroscopic Observation of Carbonium Ions

A. Generation

From solvolytic studies Hart inferred in 1959 the extreme stabilizing effect of a cyclopropyl group on an adjacent positively charged center[20]. In the early 60's Deno[21] and Olah[22] reported the first spectroscopic data of long-lived cyclopropyl substituted carbonium ions.

Upon ionization of the cyclopropyl substituted alcohols *13* and *14* in FSO_3H/SO_2ClF at −110 °C the corresponding [3.2.0] ions *21* and *22* were formed, respectively (Scheme 4). These ions appeared to be so stable, that after warming the solution to −20 °C no changes in the NMR spectra were observed; even after several hours at this temperature no rearrangements occurred.

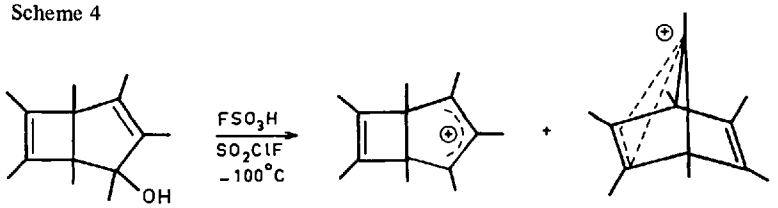
Replacement of the cyclopropyl group by a methyl group changed the behaviour of the primarily formed carbonium ions. The permethylated ions *23* and *24* have been obtained as a mixture in a ratio of about 2 : 1 upon dissolving alcohol *9* in FSO_3H/SO_2ClF at −100 °C (Scheme 5).



13 (R=CH_3)
14 (R=H)

21 (R=CH_3)
22 (R=H)

Scheme 4



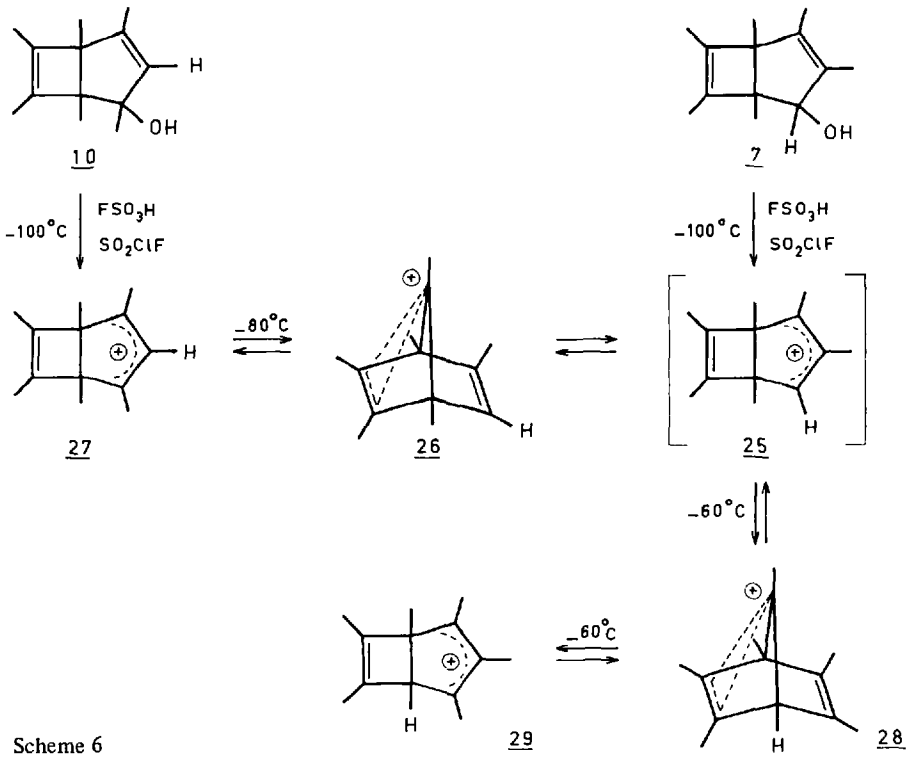
9 23 24

Scheme 5

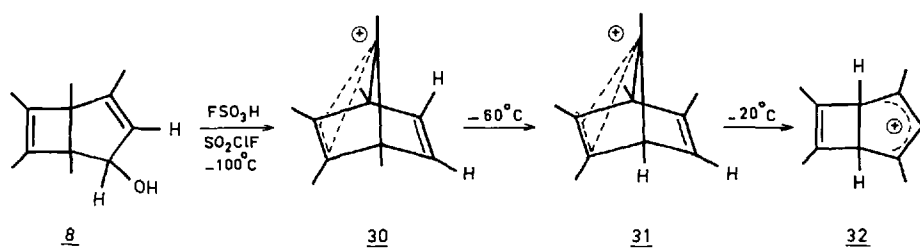
In contrast to the cyclopropyl substituted ions *21* and *22* the permethylated [3.2.0]-cation *23* undergoes a rearrangement to the [2.2.1] isomer. An analogous rearrangement in *21* – the mechanism of which will be discussed in the next section-would give a [2.2.1] ion, with the cyclopropyl group at the "unbound" double bond or at the bridgehead carbon atom and these positions are less favourable, with respect to the allylic position.

Rearrangements were also found with the hexamethylated bicyclic carbonium ions. The initially generated carbonium ions isomerized to thermodynamically more stable isomers. Solutions of both *7* and *10* in FSO_3H/SO_2ClF (prepared below −100 °C) appeared to behave identically, except for the primarily formed carbonium ions. In the case of compound *7* it was impossible to detect ion *25*, but immediate formation of ion *26* (even at −100 °C) was observed. However, starting with compound *10* a mixture of ions *26* and *27* was obtained at −100 °C which upon warming to −80 °C afforded exclusively ion *26*. Our explanation for this behaviour is based on the fact that in *27* the positive charge is delocalized over two tertiary allylic carbon atoms and in *25* over a tertiary and a secondary allylic carbon atom. Warming the solution of *26* to −60 °C resulted in the formation of ion *28*, which at the same temperature started to rearrange into ion *29;* at −20 °C ion *28* was still present to the extent of about 10% (Scheme 6).

The same sequence of temperature-dependent rearrangements to thermodynamically more stabilized ions under kinetically-controlled conditions is observed in the pentamethylated carbonium ions. Upon ionization of *8* in FSO_3H/SO_2ClF at −100 °C, a carbonium ion was generated to which we assign structure *30*. Warming up this solution to −60 °C caused an irreversible rearrangement of ion *30* into ion *31*, which has additional stabilization due to mono-alkyl substitution at the double bond. The thermodynamically most stable ion *32*, in which the double bond is fully alkyl-substituted, was finally formed when the solution of *31* was warmed to −20 °C (Scheme 7).



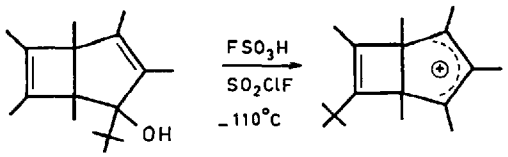
Scheme 6



Scheme 7

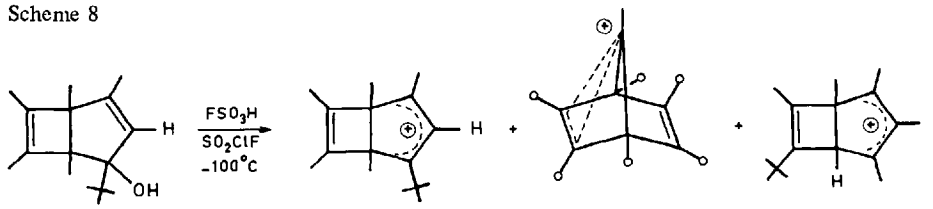
The alcohols *11* and *12*, substituted at C-4 with a tert-butyl group, showed after ionization in FSO_3H/SO_2ClF at −110 °C a rearrangement to bicyclo[3.2.0]heptadienyl cations, with the tert-butyl group at the double bond in the four-membered ring. Compound *11* afforded immediately ion *33* (Scheme 8), no other ions being observed within the measured temperature-range (−110 °C to −20 °C).

In contrast, after ionization of *12* in FSO_3H/SO_2ClF at −100 °C a mixture of at least three ions was obtained (Scheme 9). One of these is carbonium ion *34*, which is nearly exclusively formed upon warming the solution to −40 °C. From the complex spectroscopic data obtained between −100 °C and −40 °C the conclusion is tentatively derived that ion *35* (the ion expected to be formed initially upon ionization of *12)* and a [2.2.1]carbonium ion (one of the isomers of *36*) constitute the remaining species in this mixture (vide infra).



11 33

Scheme 8



12 35 36 34

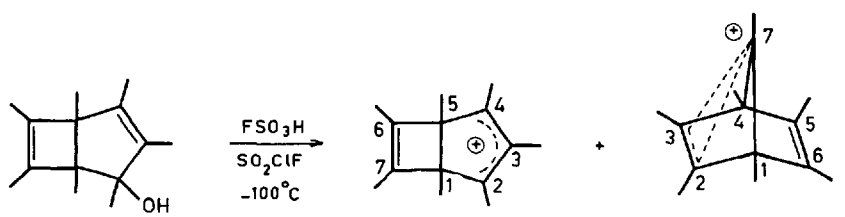
—○ ≡ H, t-C_4H_9 and four CH_3

Scheme 9

B. Spectroscopic Observation

The assignments of the structures of the carbonium ions are based upon both ^1H and ^{13}C NMR spectroscopic evidence, as summarized in Tables 1 and 2[23] (pp. 99–101), and in some cases also on quenching reactions.

Relevant literature NMR data on substituted allylic cations are found in Ref.[25–27], on norbornadienyl and bicyclo[2.1.1]hexenyl cations in Ref.[13, 28] and on several types of nonclassical ions in Ref.[29]. Characteristic absorptions in the NMR spectra for the polymethylated bicyclo[3.2.0]- and -[2.2.1]heptadienyl cations are exemplified in Fig. 1 for the mixture of the permethylated[3.2.0]- and -[2.2.1] isomers *23* and *24*.



9 23 24

^1H NMR	23	C-2,4 methyl	δ 2.75
		C-3 methyl	δ 2.09
	24	C-7 methyl	δ 1.30
^{13}C NMR	23	C-2,4 methyl	δ 22.1
		C-2,4 ring C	δ 237.1
	24	C-7 methyl	δ 1.7

Fig. 1. Characteristic NMR absorptions of polymethylated bicyclo[3.2.0]- and [2.2.1]heptadienyl cations

Remarkable are the high-field absorptions of the top-methyl of the [2.2.1]ion *24* in both ^{1}H and ^{13}C NMR spectra, as well as the extremely low-field absorption in the ^{13}C spectra of the allylic carbon atoms 2 and 4 in the [3.2.0] ion *23*. An example of the ^{1}H and ^{13}C NMR spectra is presented in Fig. 2 for the mixture of ions *23* and *24*.

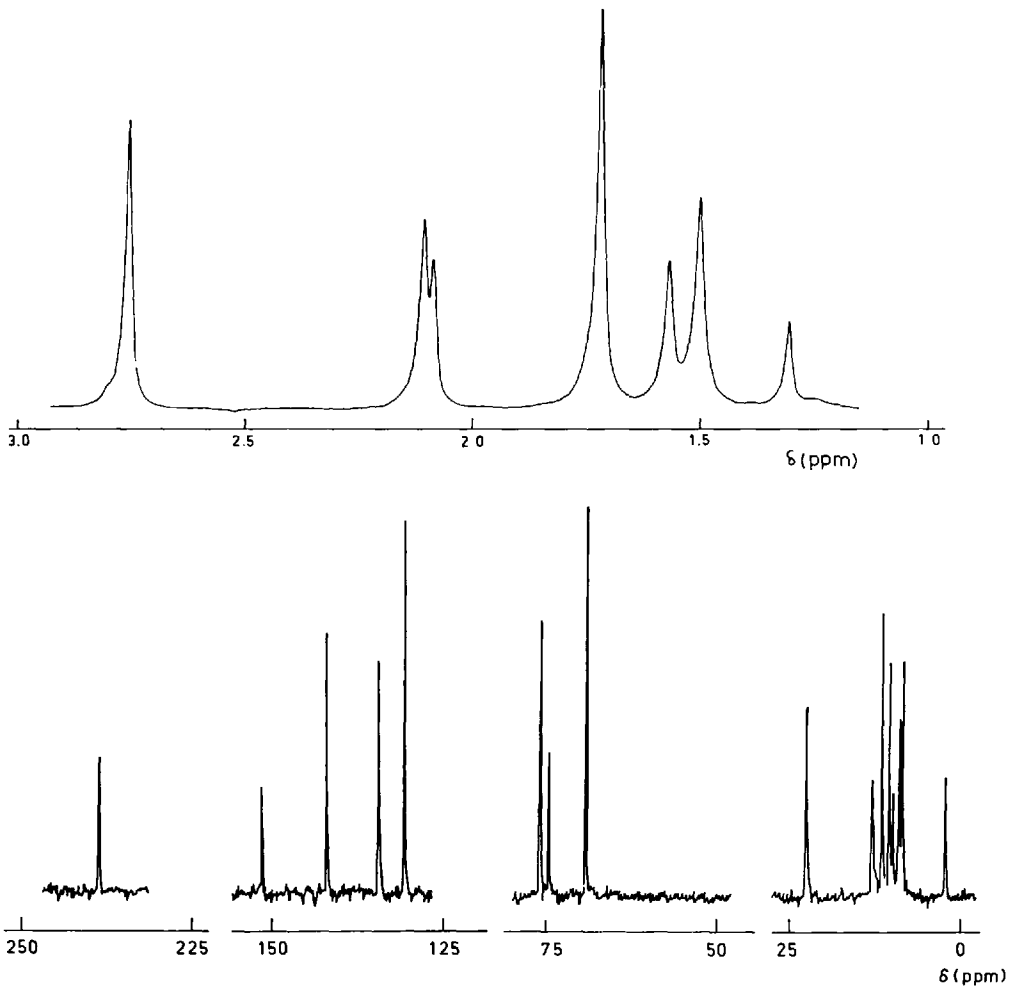
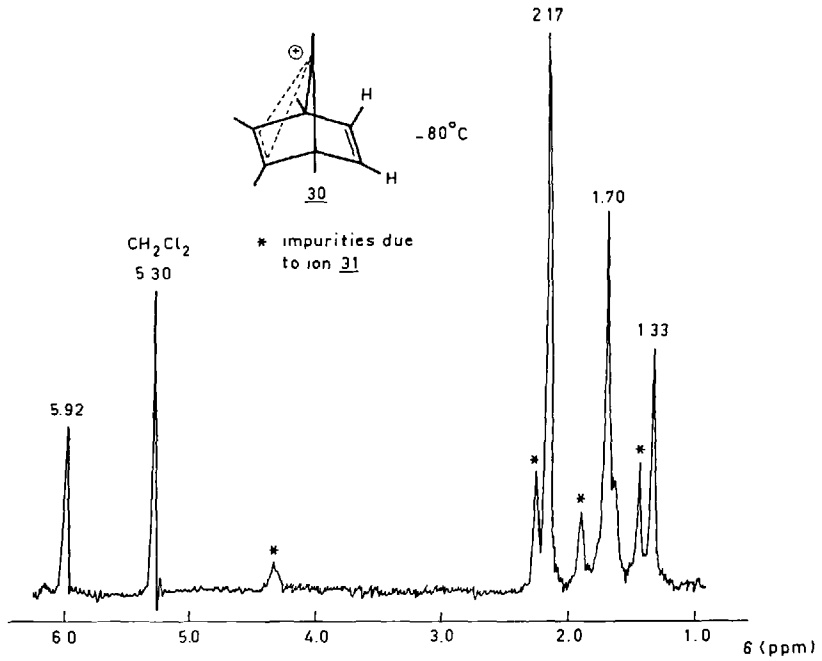


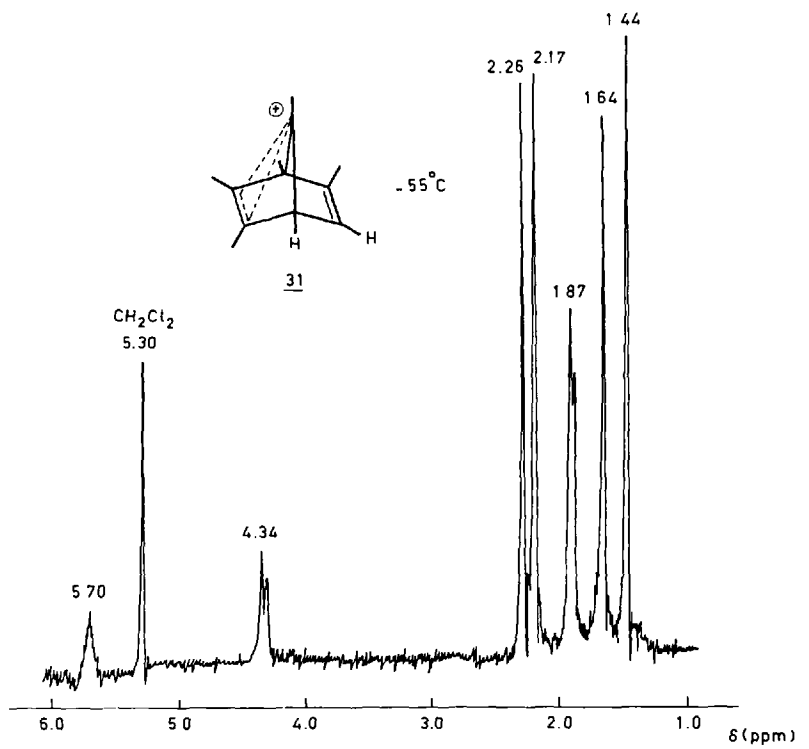
Fig. 2. ^{1}H (top) and ^{13}C (bottom) NMR spectra of the mixture of ions *23* and *24* (ratio 2:1) at −70° and −100 °C, respectively

The irreversible rearrangements of certain carbonium ions were monitored by scanning the NMR spectra at various NMR probe temperatures. A representative example of ^{1}H NMR spectra of such a sequence of rearrangements is reported for the pentamethyl substituted carbonium ions (Fig. 3).

The evidence for the occurrence of ion *35* is the following: ^{1}H NMR absorption at δ 6.23 and ^{13}C NMR absorptions at δ 237.9, 237.6, 167.7 and 23.9, charac-


2.17
1.70
1.33
5.92
CH_2Cl_2
5.30
-80°C
30
* impurities due to ion 31
6.0
5.0
4.0
3.0
2.0
1.0
δ (ppm)

3a


1.44
2.26
2.17
1.64
1.87
4.34
5.70
CH_2Cl_2
5.30
-55°C
31
6.0
5.0
4.0
3.0
2.0
1.0
δ (ppm)

3b

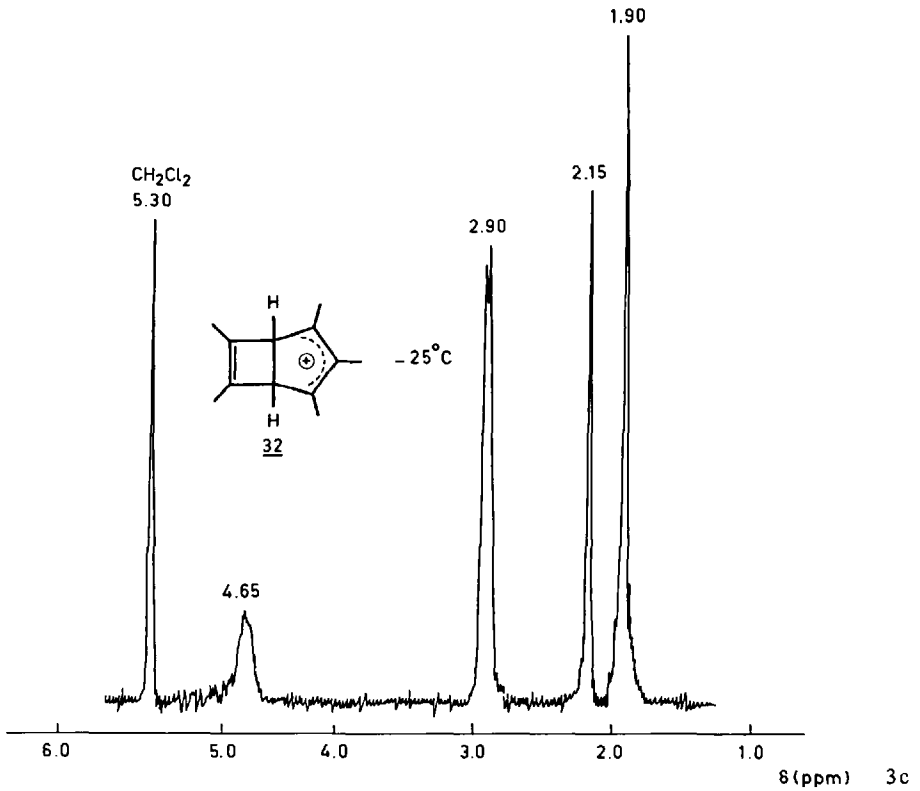


Fig. 3. Temperature-dependent ^1H NMR spectra of alcohol *8* in FSO_3H/SO_2ClF

teristic of mono-methyl substituted allylic cations. The only evidence for the presence of ion *36* in this mixture is the ^1H NMR absorption at δ 5.57 and the ^{13}C NMR absorption at δ 1.8 (top-methyl group). The occurrence of at least three ions in the mixture derived from alcohol *12* at temperatures below −75 °C is clearly indicated by the observation of three tert-butyl signals in the ^{13}C NMR spectra (δ 36.6 and 28.4; δ 36.2 and 28.0; δ 33.0 and 27.6). At higher temperatures only ion *34* is observed.

In two cases the cations were quenched by methoxide ion in methanol in order to obtain additional affirmation of the structure. The products obtained were consistent with the proposed structures of the precursor cations as presented in Scheme 10 (p. 102).

IV. Mechanisms of the Rearrangements

The mechanisms of the interconversions within these classes of ions mainly involve 1,2 Wagner-Meerwein shifts, interchanging [3.2.0] and [2.2.1] skeletons. If these

Table 1. ^{1}H NMR[1]) and ^{13}C NMR[2]) chemical shifts of polymethyl substituted bicyclo[3.2.0]heptadienyl cations

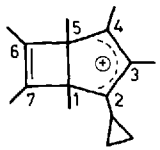
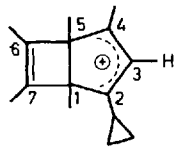
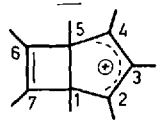
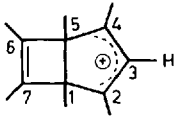
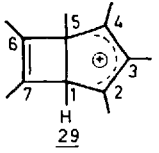
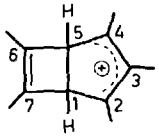
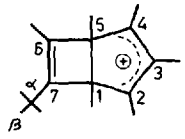
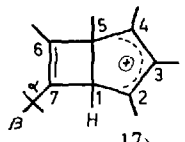
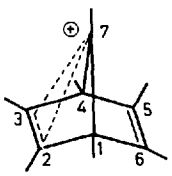
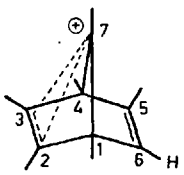
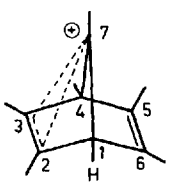
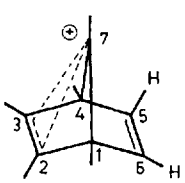
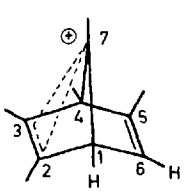
		C-1,5	C-2,4	C-6,7	C-3
 21	^{1}H NMR	1.41/1.45	2.15-2.50(c-Pr); 2.55(CH_3)[3])	1.72	2.06
	^{13}C NMR, CH_3	8.5/9.7	–; 19.9	13.6/12.6/10.3	
	^{13}C NMR, ring-C	73.0/72.2	240.1(C-2); 220.7(C-4)[3])	147.8/143.3/141.7	
	^{13}C NMR, c-Pr		28.5[4])(C_α); 25.8[5])(C_β)/22.7[5])(C_β)		
 22	^{1}H NMR	1.37/1.52	2.20–2.55(c-Pr); 2.55(CH_3)[3])	1.68	6.70
	^{13}C NMR, CH_3	8.2/8.5	–; 21.6	12.2/12.5	–
	^{13}C NMR, ring-C	74.9/73.0	247.8(C-2); 223.1(C-4)[3])	142.8/141.5	131.4[6])
	^{13}C NMR, c-Pr		32.3[7])(C_β)/31.8[8])(C_β); 28.0[9])(C_α)		
 23	^{1}H NMR	1.53	2.75	1.76	2.09[10])
	^{13}C NMR, CH_3	8.2	22.1[11])	10.0[11])	12.4
	^{13}C NMR, ring-C	75.6	237.1	141.2	150.9
 27	^{1}H NMR	1.70	2.92	1.87	7.31
	^{13}C NMR, CH_3	8.0	24.1[11])	11.0[11])	–
	^{13}C NMR, ring-C	76.6	241.4	141.1	[12])
 29	^{1}H NMR	4.35(H); 1.68(CH_3)	2.90(C-2); 2.80(C-4)[13])	1.90/1.83	2.16
	^{13}C NMR, CH_3	–; 8.6	23.4/22.0[11])	11.6/10.1[11])	13.7
	^{13}C NMR, ring-C	74.7(C-1)[14]); 72.4	236.6/233.9	141.1/139.0	153.2

Table 1 (continued)

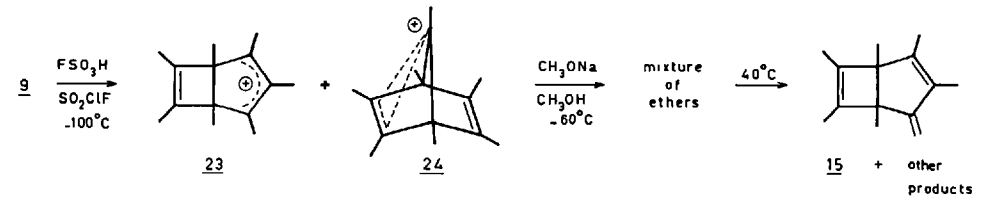
		C-1,5	C-2,4	C-6,7	C-3
 32	^{1}H NMR	4.65	2.90[15])	1.90	2.15
	^{13}C NMR, CH_3	–	23.6[11])	11.8[11])	10.4
	^{13}C NMR, ring-C	68.5	234.5	139.5	155.8
 33	^{1}H NMR	1.60/1.53	2.95(C-2); 2.88(C-4)[16])	1.91(CH_3); 1.16(t-C_4H_9)	2.16
	^{13}C NMR, CH_3	9.8/10.1	23.9/22.2	13.7/14.9	
	^{13}C NMR, ring-C	77.2/76.7	238.1/236.6	154.5/142.5/137.5	
	^{13}C NMR, t-Bu			36.9(C_α); 29.0(C_β)	
 34 [17])	^{1}H NMR	4.35(H); 1.58(CH_3)	2.97(C-2); 2.78(C-4)[16])	1.92(CH_3); 1.17(t-C_4H_9)	2.12
	^{13}C NMR, CH_3	9.7	24.8/21.8	14.4/10.3	
	^{13}C NMR, ring-C	74.1/71.9	234.8/233.8	154.0/150.8/135.8	
	^{13}C NMR, t-Bu			36.6(C_α); 28.4(C_β)	

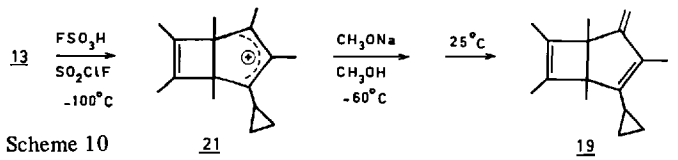
[1]) measured relative to internal CH_2Cl_2 (δ = 5.30).
[2]) measured relative to internal CD_2Cl_2 (δ = 53.16).
[3]) note 30[a].
[4]) doublet with J 172 Hz.
[5]) triplet with J 169 Hz.
[6]) doublet with J 175 Hz.
[7]) triplet with J 170 Hz.
[8]) triplet with J 171 Hz.
[9]) doublet with J 181 Hz.
[10]) note 30[b].
[11]) note 30[c].
[12]) not observed.
[13]) note 30[d].
[14]) doublet with J 162 Hz.
[15]) note 30[e].
[16]) note 30[f].
[17]) note 30[g].

Table 2. ^{1}H NMR[1]) and ^{13}C NMR[2]) chemical shifts of polymethyl substituted bicyclo[2.2.1]heptadienyl cations

		C-1,4	C-2,3	C-5,6	C-7
 24	^{1}H NMR	1.59	2.11[3])	1.76	1.29
	^{13}C NMR, CH_3	8.6	9.5	11.0	1.7
	^{13}C NMR, ring-C	69.2	133.6	129.9	74.4
 26	^{1}H NMR	1.71	2.21	1.95(CH_3); 5.55(H)	1.42
	^{13}C NMR, CH_3	10.6/8.6	11.2	12.1	2.0
	^{13}C NMR, ring-C	69.7/67.0	133.8/133.0	139.1/123.1	75.4
 28	^{1}H NMR	[4]); 4.20 (H)	2.34/[4])	[4])	1.50
	^{13}C NMR, CH_3	8.1	10.9/10.5	14.7/14.0	4.5
	^{13}C NMR, ring-C	72.9/70.8	139.7/138.5	130.2/127.6	66.7
 30	^{1}H NMR	1.70	2.17	5.92	1.33
	^{13}C NMR, CH_3	9.9	10.9		1.6
	^{13}C NMR, ring-C	68.8	133.0	129.8	75.4
 31	^{1}H NMR	4.34(H); 1.64(CH_3)	2.17/2.26	5.70(H) 1.87[5])(CH_3)	1.44
	^{13}C NMR, CH_3	8.6	11.2/12.3	14.6	4.7
	^{13}C NMR, ring-C	75.0/71.1	140.5/135.0	130.8/118.7	63.2

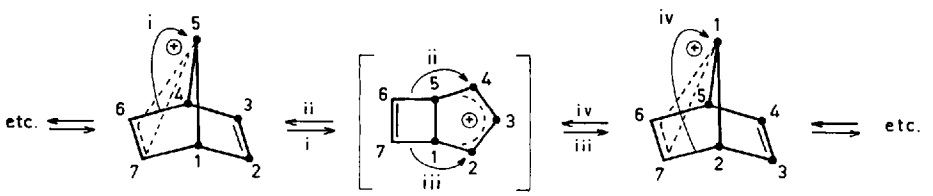
[1]) Measured relative to internal CH_2Cl_2 (δ = 5.30).
[2]) Measured relative to internal CD_2Cl_2 (δ = 53.16).
[3]) Note 30[b].
[4]) Not observed, ion *28* has only been observed as minor component in mixtures with ions *26* and/or *29*.
[5]) Doublet with J 1.4 Hz, due to longe-range coupling with the hydrogen atom at C-5.





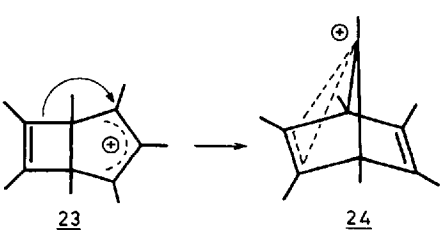
Scheme 10

shifts occur sequentially, then the overall process involves a stepwise circumambulatory motion of five carbon atoms (viz. C-1,2,3,4,5 in e.g. *37*) with respect to the remaining two carbon atoms (C-6,7 in *37*); this has been observed by Winstein[13] in the case of the 7-norbornadienyl cation (Scheme 11).



Scheme 11 37

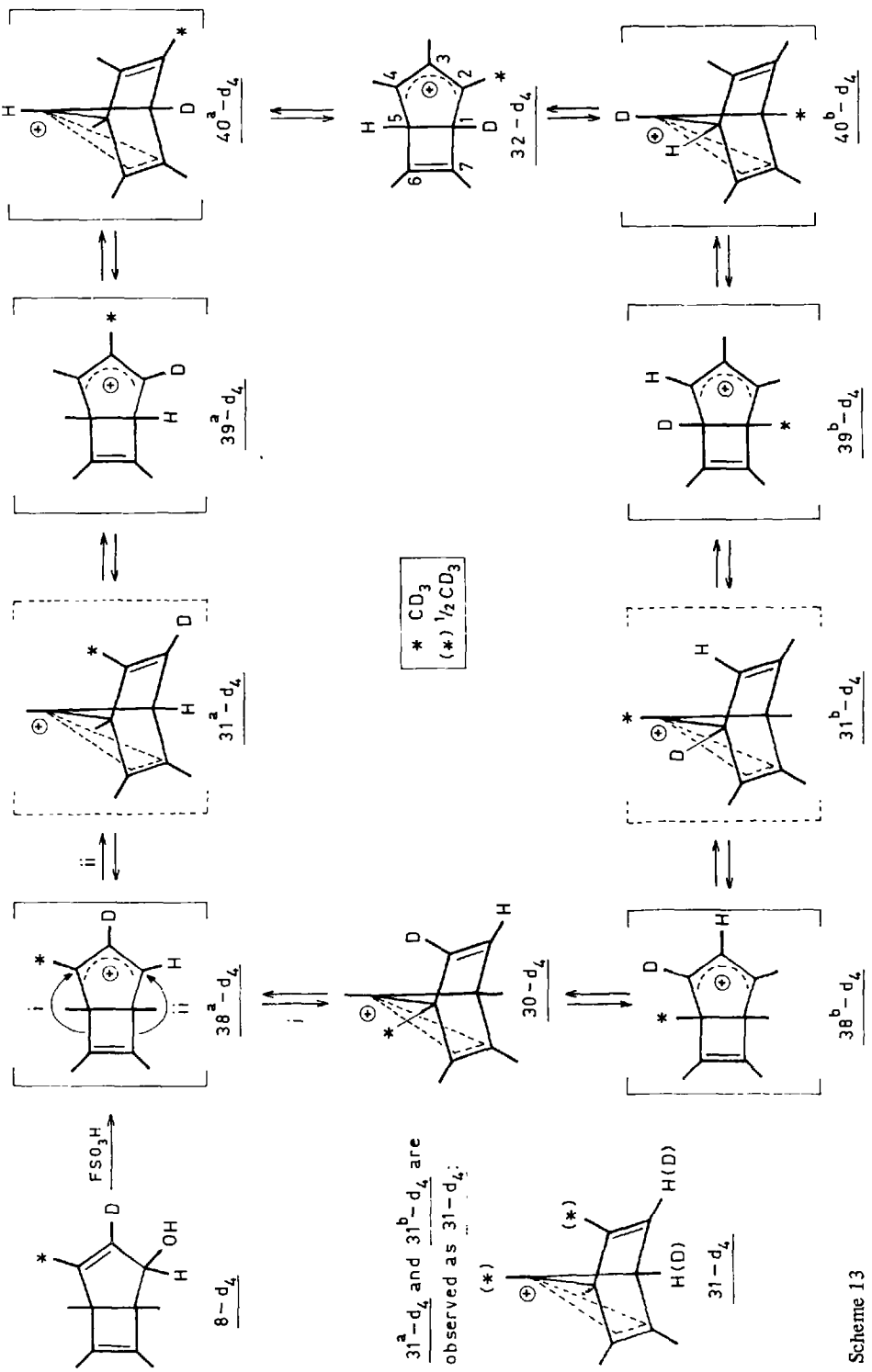
The formation of *24* from *23* can be explained by this mechanism (Scheme 12).



Scheme 12

In the pentamethyl substituted carbonium ions this process readily explains the experimentally observed sequence of cations *30* → *31* → *32*. The two hydrogen atoms in these carbonium ions appeared to be good labels for testing the mechanism. Additional confirmation was obtained by the use of the labeled alcohol *8*-d_4, from which upon ionization in FSO_3H/SO_2ClF the ions *30*-d_4, *31*-d_4 and *32*-d_4 were consecutively obtained (Scheme 13).

The ions *30*-d_4, *31*-d_4 and *32*-d_4[30e] showed the correct areas for the ^1H NMR signals, which confirms the proposed mechanistic sequence. Remarkably, none of the intermediate carbonium ions which have a hydrogen at a positively charged carbon atom is observed (*38*, *39*, *40*, nor their deuterated analogues). An explanation for


FSO3H
8-d4
38a-d4
31a-d4
39a-d4
40a-d4
32-d4
40b-d4
39b-d4
31b-d4
38b-d4
30-d4
* CD3
(*) 1/2 CD3
31a-d4 and 31b-d4 are observed as 31-d4:
31-d4

Scheme 13

the kinetic formation of ion *30* in preference to ion *31* is the stabilizing effect of three methyl groups on the positive charge in the transition state *A*, that belongs to the conversion *38* → *30* (path i) as compared to that of two methyl groups in the transition state *B* for the conversion *38* → *31* (path ii). The effect of the number of methyl groups on the stability of protonated cyclopropane rings has recently been summarized by Brouwer and Hogeveen[31]. Saunders has estimated a stabilization energy of 5 kcal/mole for each methyl group, attached to a protonated cyclopropane ring[32]. The difference in thermodynamic stability between ions *30* and *31* is due to the different number of alkyl substituents at the C=C bond whereas the difference between ions *31* and *32* resides not only in that factor, but also in the different geometry and, as a consequence, the different strain of the [2.2.1] vs. the [3.2.0] carbon skeleton[33, 34]. The results are illustrated schematically in a free-enthalpy diagram (Fig. 4)[35].

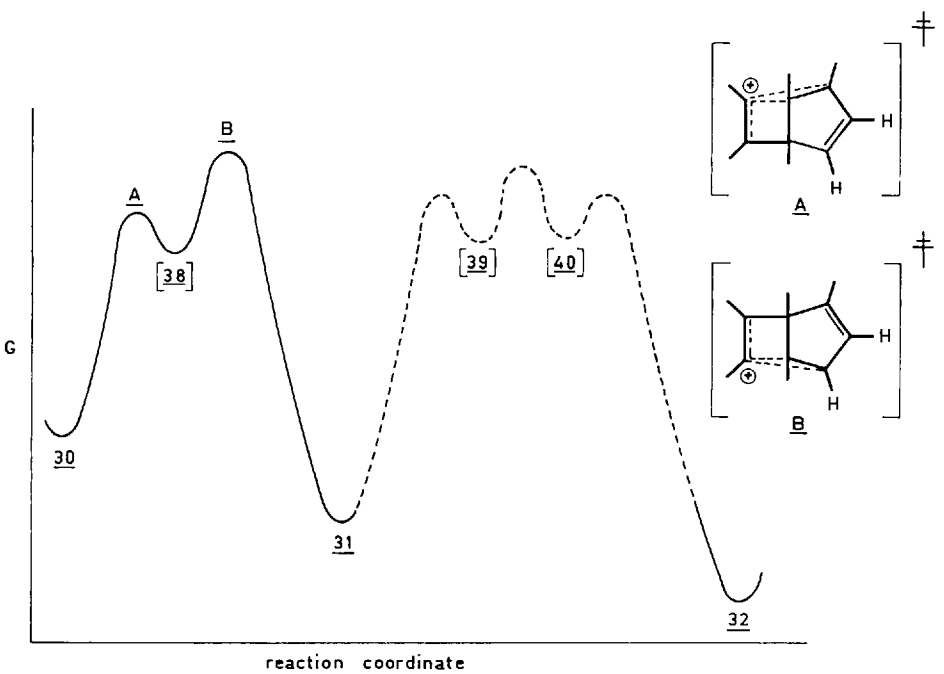
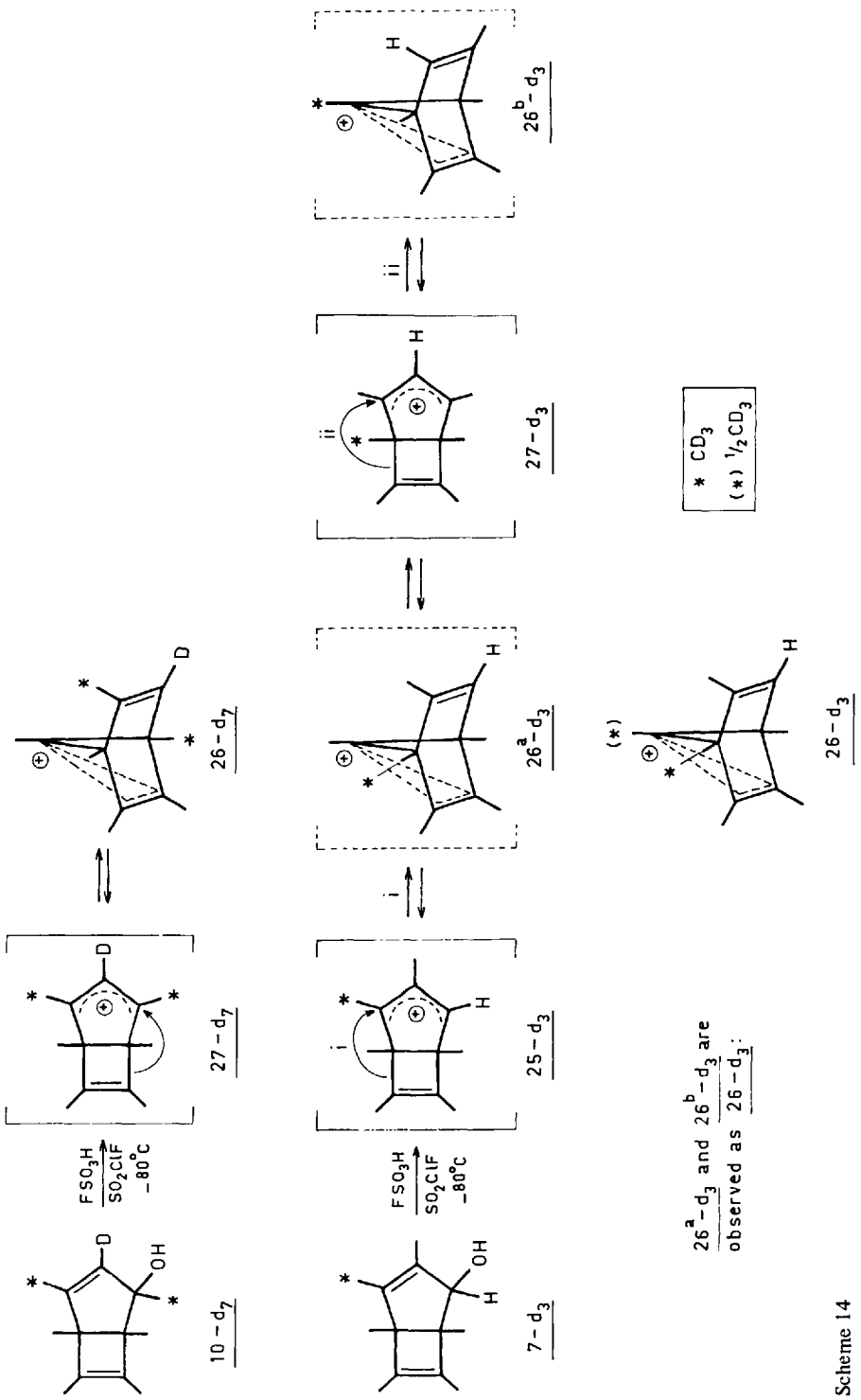


Fig. 4. Free-enthalpy diagram for the interconversions of pentamethylbicyclo[3.2.0]- and [2.2.1]heptadienyl cations

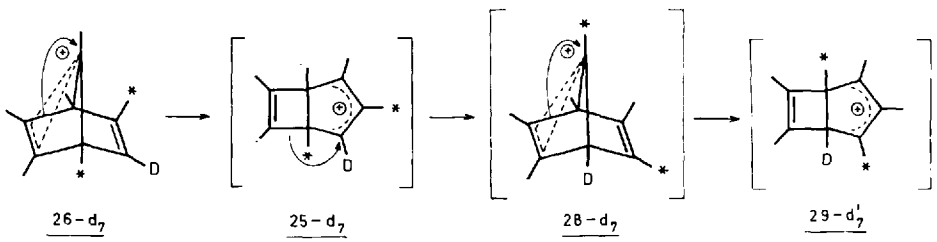
Also in the hexamethyl substituted ions an analogous serie of consecutive 1,2 Wagner-Meerwein shifts gives rise to the observed carbonium ions, as is shown in Scheme 6. In order to confirm this mechanism some experiments were carried out with the deuterated compounds *10*-d_7 and *7*-d_3, which on treatment with FSO_3H/SO_2ClF at −80 °C gave the ions *26*-d_7 and *26*-d_3, respectively; the ^1H NMR spectra of these ions showed the expected areas for the absorption signals (see Scheme 14).

Upon warming solutions of *26*-d_7 or *26*-d_3 to −40 °C these ions rearranged to bicyclic[3.2.0]cations in which the CD_3 label(s) is (are) randomly distributed. On


FSO3H
SO2ClF
−80°C
10 − d7
27 − d7
26 − d7
i
ii
7 − d3
25 − d3
26a − d3
27 − d3
26b − d3
(*)
26 − d3
* CD3
(*) ½CD3
26a − d3 and 26b − d3 are
observed as 26 − d3:

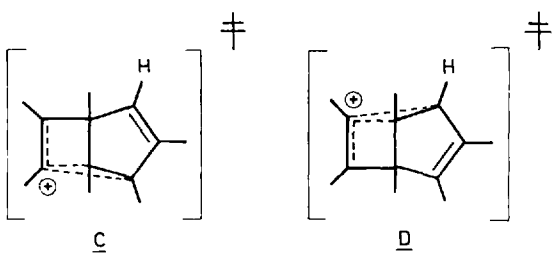
Scheme 14

basis of only 1,2 Wagner-Meerwein shifts, however, one would have expected those labels to end up at distinct positions, for example, ion *26-d*$_7$ would exclusively convert to *29-d'*$_7$ (Scheme 15).



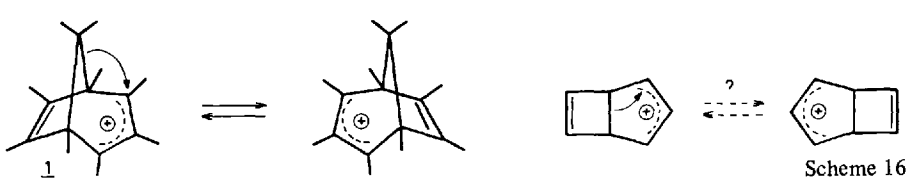
Scheme 15

The same arguments as used in the case of the pentamethyl substituted species (see Fig. 4) play a role in the understanding of the kinetic preference for the formation of ion *26* rather than ion *28* from *25*. It should be pointed out that the transition state *C* (for the conversion *25* → *26*) is more stabilized than transition state *D* (for conversion *25* → *28*) because of the presence of an additional methyl group (rather than a hydrogen atom) in the positively charged cyclopropane-like structure[31, 32, 35].



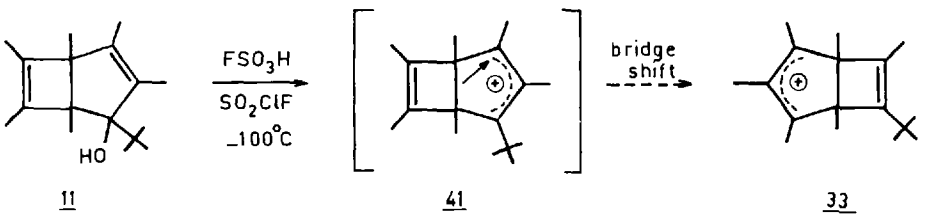
At higher temperatures (−60 °C) the Wagner-Meerwein shifts become thermodynamically controlled and, as a consequence, ions *28* and *29* are formed (Scheme 6). These ions contain carbon-carbon double bonds with a maximum number of alkyl substituents.

The formation of the [3.2.0] cations *33* and *34*, substituted at the carbon-carbon double bond in the four-membered ring with a tert-butyl group, cannot be explained by a circumambulatory process of the type described above, since by such a process the tert-butyl group, originally located at the five-membered ring, would have stayed at that ring. It is therefore assumed that another process must be responsible for the observation that the tert-butyl group is found at C-7. In analogy with the bridge-shift which Hart and Kuzuya[36] observed in polymethylbicyclo-[3.2.1]octadienyl cations (e.g. *1*) we were tempted to consider such a 1,2 bridge-shift also in the [3.2.0] cations (Scheme 16).



Scheme 16

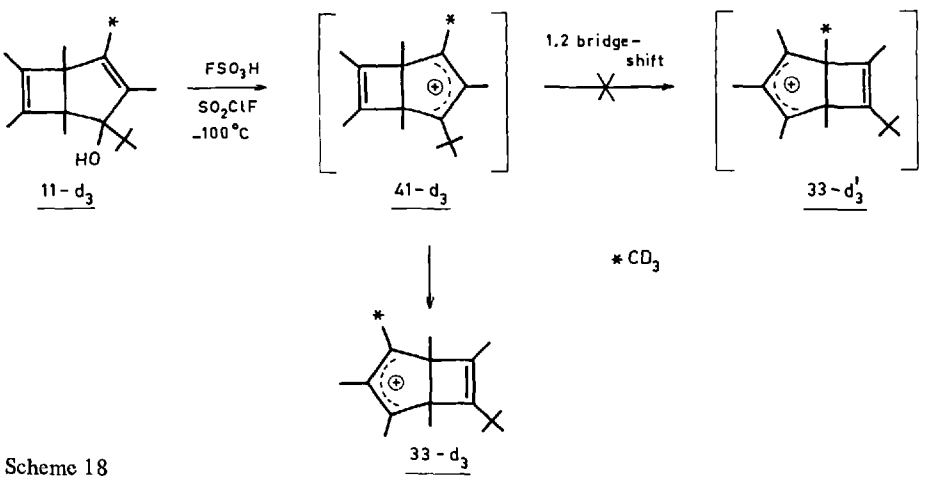
Such a 1,2 bridge-shift can indeed explain the formation of the observed [3.2.0] ion *33* from the primarily formed ion *41* (Scheme 17)[37].



11 41 33

Scheme 17

A confirmation of this mechanism was searched for by a tracer experiment with alcohol *11-d*$_3$, which upon ionization in FSO_3H/SO_2ClF was expected to yield via the intermediate cation *41-d*$_3$ the cation *33-d'*$_3$, in which the CD_3 group is located at the bridgehead position. However, the species observed was carbonium ion *33-d*$_3$ (!), the ^1H NMR spectrum of which lacked the signal due to the indicated allylic methyl group (Scheme 18).



Scheme 18

The absence of a 1,2 bridge-shift in these [3.2.0]cations is in accordance with the principle of orbital orientation control, which was first introduced for long-lived carbonium ions by both Brouwer and Hogeveen[38] and, by von Schleyer and co-workers[39] in 1970. This principle implies that in a carbonium ion in which a shift or a rearrangement takes place, the interacting orbitals (the vacant p-orbital of the electron-deficient carbon and the σ-orbital carrying the migrating atom or group) must have a zero or small dihedral angle, to get a maximum overlap in the transition state. In the bicyclo[3.2.0]heptadienyl cations these orbitals, to wit the σ-orbital at the C1-C5 bridge and a terminal p-orbital at the allylic moiety, are perpendicular, as depicted in Fig. 5. (The Newman projection is along the C4-C5 bond).

This stereochemical argument rationalized therefore the absence of a bridge-shift in this class of cations (e.g. *41*).

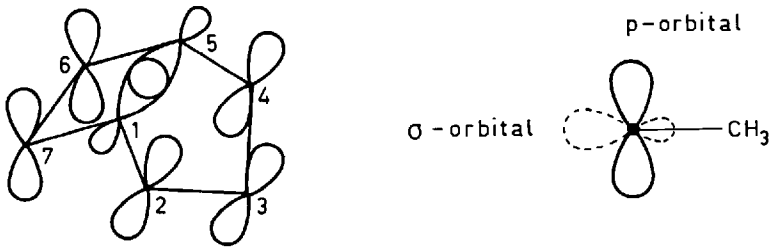
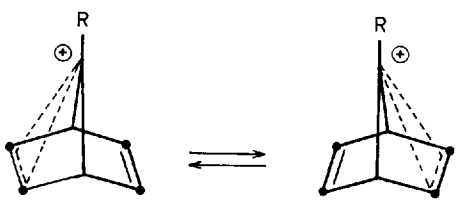


Fig. 5. Newman projection (along C4-C5 bond) of the orbitals in [3.2.0]cations

In order to explain the above mentioned observations within [3.2.0] cations, we propose the formation of *33* and *34* to proceed via an intermediate [2.2.1]cation, in which a bridge-flip takes place. Such a bridge-flip has been proposed by Winstein for several 7-substituted norbornadienyl cations, interchanging the "bound" and "unbound" vinyl group (Scheme 19). In the parent 7-norbornadienyl cation he



Scheme 19

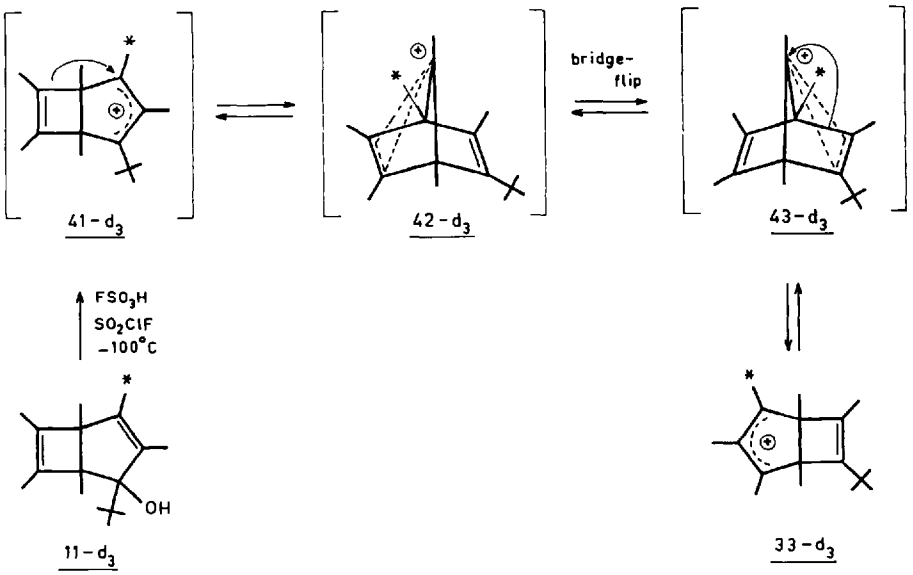
found a similar exchange between those vinyl groups; it was, however, impossible in this case to exclude other mechanisms for this isomerization (vide infra)[13].

In our case, the bridge-flip fits in well with the findings for the tert-butyl substituted [3.2.0]carbonium ions. The results of the experiments with the deuterated alcohols *11*-d_3 and *12*-d_4 are in agreement with such a process. Upon ionization in FSO_3H/SO_2ClF alcohol *11*-d_3 will initially give ion *41*-d_3 which can, in principle, undergo two 1,2 Wagner-Meerwein shifts to a [2.2.1]carbonium ion. Because three methyl groups stabilize the positive charge in the transition state better than two methyl groups and one tert-butyl group (vide infra)[40], cation *41*-d_3 will rearrange preferantially to the bicyclo[3.2.0] cation *42*-d_3 as indicated in scheme 20. A bridge-flip of ion *42*-d_3 to give *43*-d_3, followed by a 1,2 Wagner-Meerwein shift (involving the most stabilized transition state) affords ion *33*-d_3, which is indeed the species observed (Scheme 20).

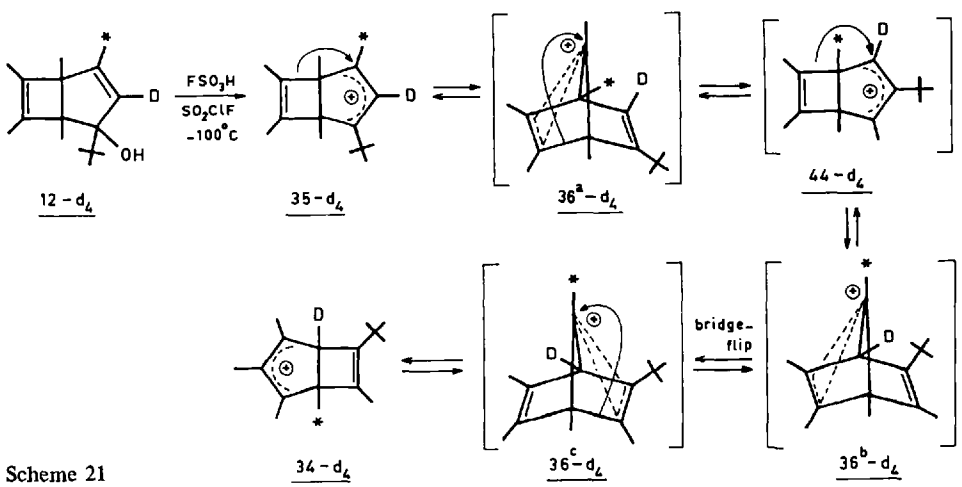
The fact that we obtain ion *34*-d_4 after ionization of alcohol *12*-d_4 is in line with the proposed mechanism. As shown in Scheme 21 some additional 1,2 Wagner-Meerwein shifts are necessary to account for the observed ion. This is reasonable because ion *36*^{a}-d_4 is destabilized relative to ion *42*-d_3 by the lack of a methyl substituent on the double bond.

Both ions *33*-d_3 and *34*-d_4 show in the ^1H NMR spectra the correct areas for the various absorptions.

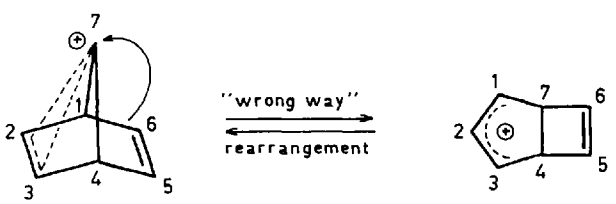
However, it should be mentioned that just as in the case of the parent 7-norbornadienyl cation, it is difficult to rule out rigorously other processes within these [2.2.1] cations. "Wrong way" ring contractions and expansions (in Winsteins ter-



Scheme 20

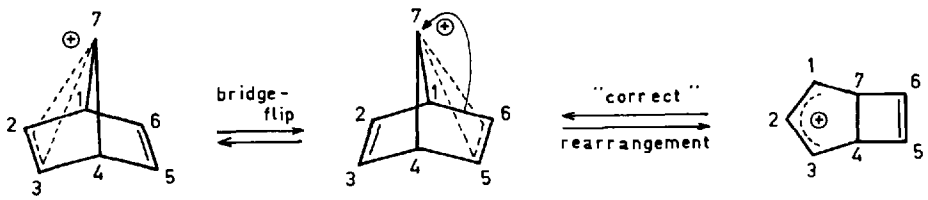


Scheme 21



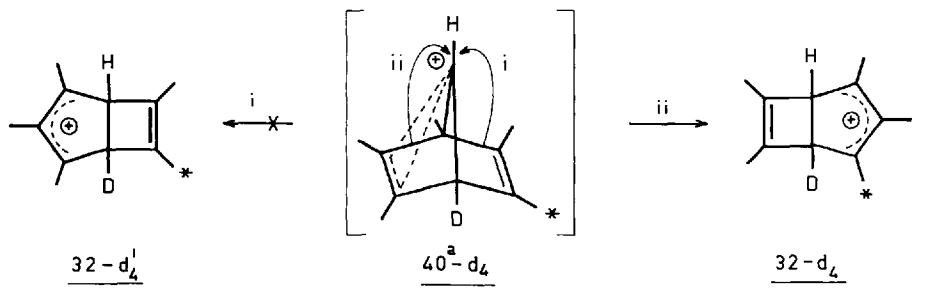
Scheme 22

minology[13]), as depicted in Scheme 22, are indistinguishable from a combination of a bridge-flip and a "correct" rearrangement between the [3.2.0] and the [2.2.1] isomers (Scheme 23).



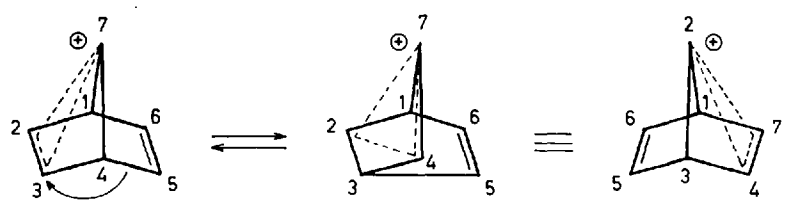
Scheme 23

There is, however, an experiment, which makes such a "wrong way" rearrangement in the [2.2.1] cation unlikely: cation *40*^{a}-d_4, which is a supposed intermediate in the rearrangement of *31*^{a}-d_4 to *32*-d_4 (Scheme 13), gives exclusively cation *32*-d_4 and no (or at least less than 5%) "wrong way" product *32*-d_4' (Scheme 24).



Scheme 24

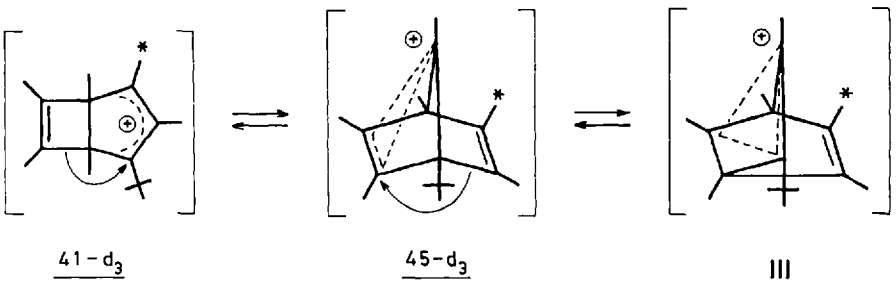
A second mechanism, which can account for the results obtained for the 7-norbornadienyl cation[13] is reported in Scheme 25.



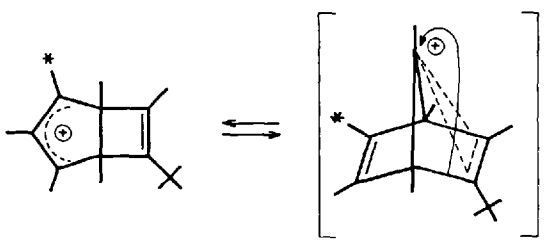
Scheme 25

Such a process, in combination with "correct" interconversions between [2.2.1]- and [3.2.0] skeletons, can explain the formation of ion *33*-d_3 from *41*-d_3 (Scheme 26).

It is, however, impossible to explain by this mechanism the formation of *34*-d_4 from *35*-d_4; rather *34*-d_4' would have been expected as the product ion (Scheme 27). Moreover, in both Schemes 26 and 27 transition states are involved with relatively unfavorable substitution patterns for the protonated cyclopropane-like structures. A third alternative mechanism suggested by Winstein[13] comprises a process-homologous to that postulated by Hogeveen and Volger[41] for scrambling in hexamethyl-

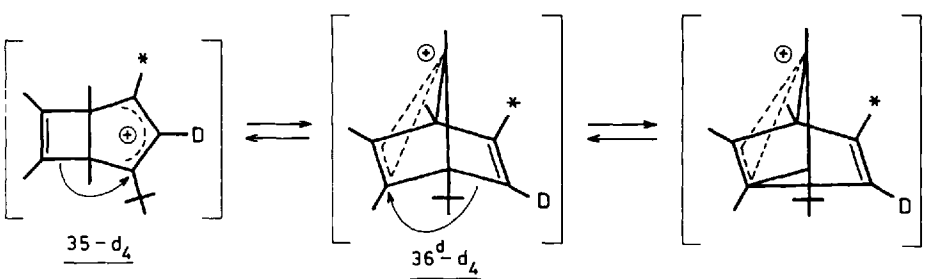


41 – d_3 45 – d_3 III

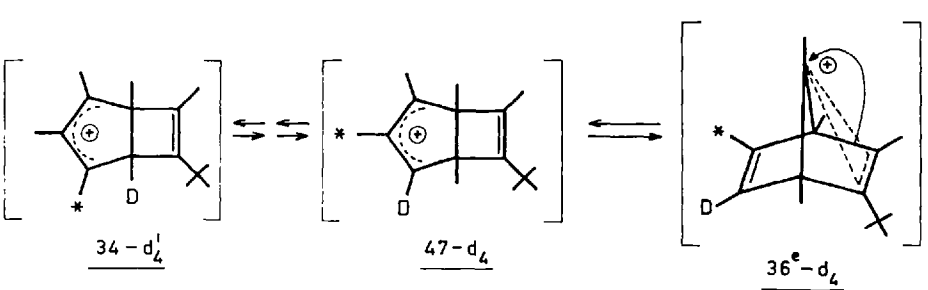


33 – d_3 46 – d_3

Scheme 26



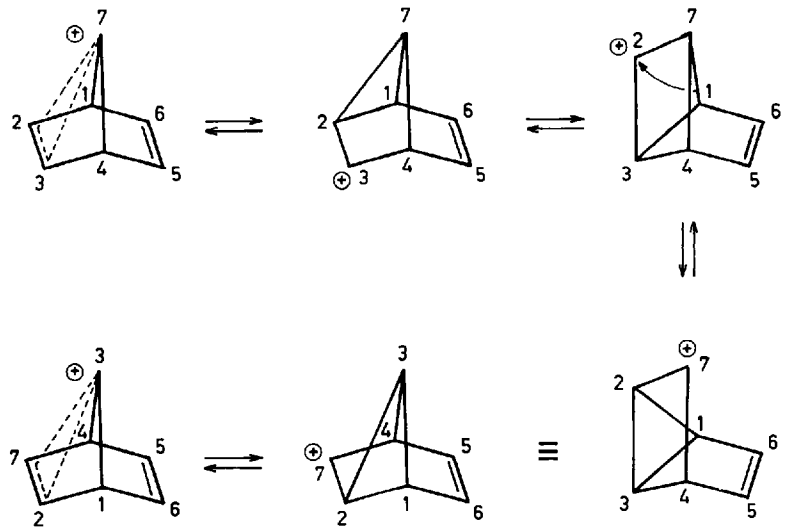
35 – d_4 36^{d} – d_4 III



34 – d_4^{1} 47 – d_4 36^{e} – d_4

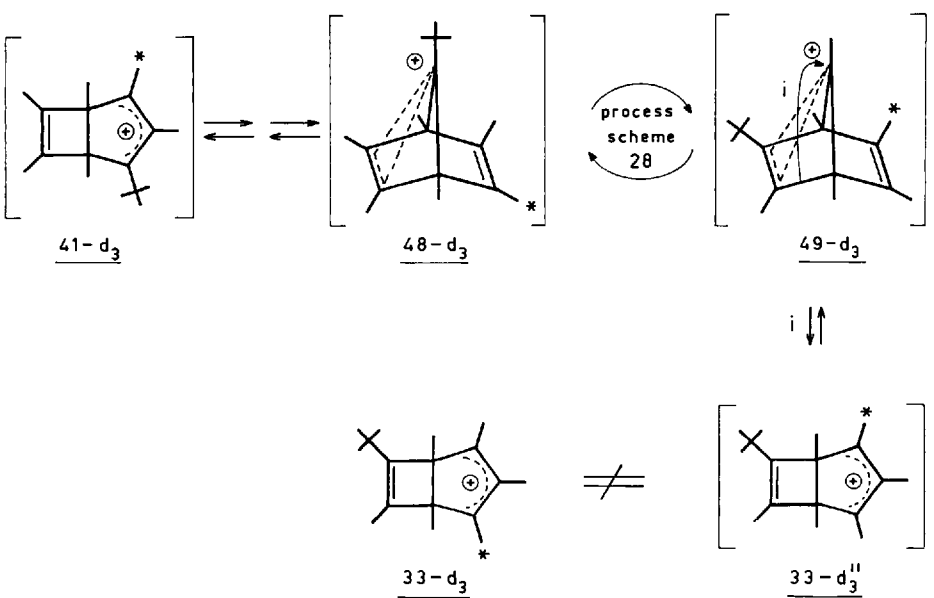
Scheme 27

bicyclo[2.1.1]hexenyl cations – which scrambles the "bound" vinyl carbon atoms and the top-carbon atom (Scheme 28).



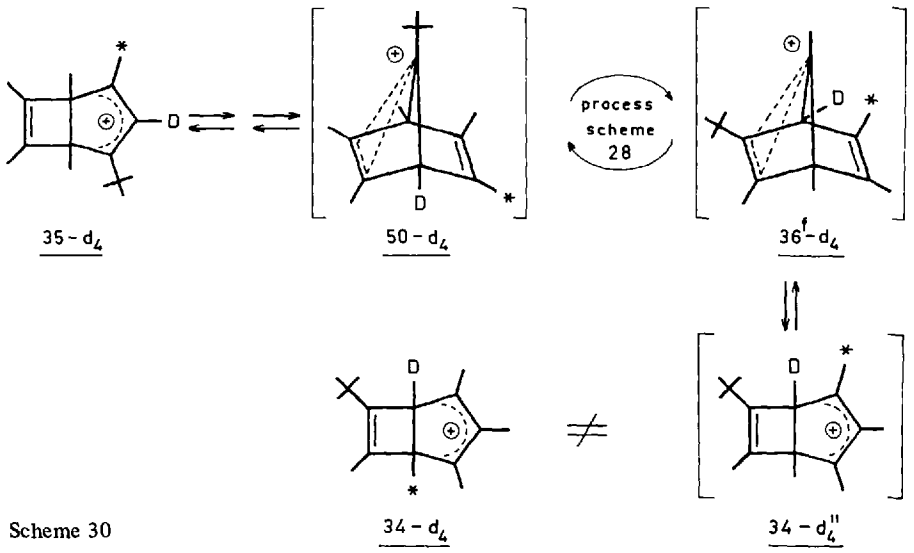
Scheme 28

On the basis of this mechanism one would anticipate that ion *41*-d_3 would converts into *33*-d_3''; however the product observed is the isomeric species *33*-d_3 (Scheme 29).



Scheme 29

A similar discrepancy is found in the rearrangements of ion *35*-d_4 (Scheme 30).



35-d_4 50-d_4 36^{I}-d_4

34-d_4 34-d_4^{II}

Scheme 30

It is worth pointing out that similar shifts in bicyclo[2.2.1]ions, isomeric with *48*-d_3 (Scheme 29) and *50*-d_4 (Scheme 30), followed by skeletal rearrangement of [2.2.1] and [3.2.0] structures, also leads to wrongly substituted bicyclo[3.2.0]ions.

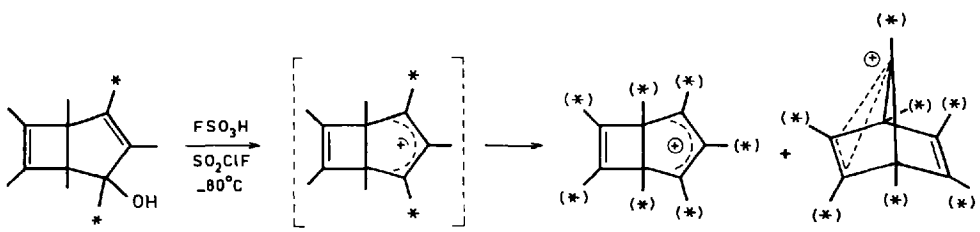
In conclusion, a mechanism involving a bridge-flip process in [2.2.1] cations is considered to be the most likely one, in order to explain the experimental results, described above.

V. On the Question of Methyl Scrambling in Bicyclo[3.2.0]heptadienyl Cations

The processes discussed in the preceeding section, lead to several degenerate isomerizations with certain bicyclo[3.2.0]heptadienyl cations. These degenerate processes have been visualized by means of line-broadening in the ^{1}H NMR spectra and/or by labeling experiments.

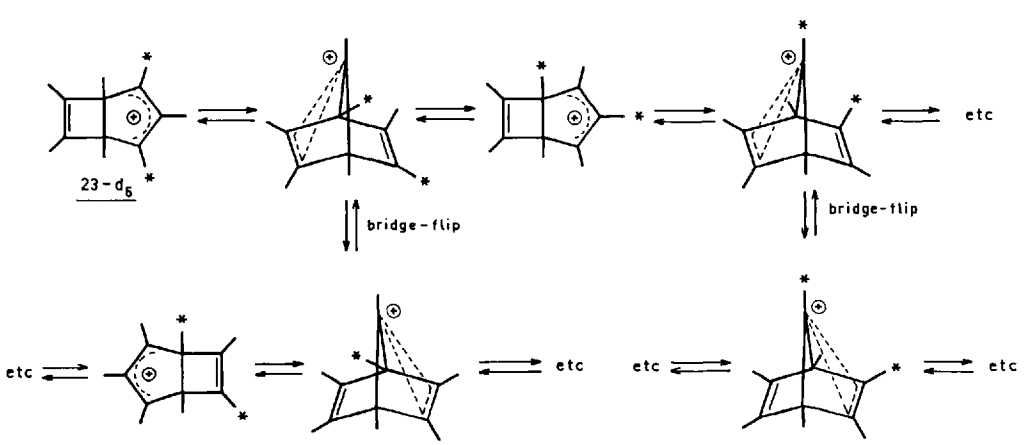
The ^{1}H NMR spectra of the mixture of the permethylated [3.2.0]- and [2.2.1]-isomeric ions *23* and *24* show upon warming above −50 °C a (reversible) line-broadening process. Owing to the solvent system used (FSO_3H/SO_2ClF) no measurements at temperatures above −10 °C have been performed and, as a consequence, the rapid exchange region has not been studied. First-order rate constants for disappearance of a methyl group from a given site were calculated using the slow-exchange approximation[42]. From the line-width of the signals at δ 2.75 (methyl groups at C-2 and C-4 in ion *23*) and δ 1.30 (methyl group at C-7 in ion *24*), (the other signals showed chemical shift differences too small for such measurements) the rate constants at −42 °C were calculated to be 4.7 sec^{-1} ($\Delta G^{\ddagger}$ = 12.7 kcal/mole) and 11.8 sec^{-1} ($\Delta G^{\ddagger}$ = 12.2 kcal/mole), respectively. Within the limits of accuracy of the measure-

ments the ratio of these rate constants equals the 2:1 ratio, in which the ions *23* and *24* occur. The line-broadening is ascribed to the interconversion process between the [3.2.0]- and [2.2.1] isomers. This interconversion process would lead to a "five-methyl" scrambling, analogous to the parent system *37*. On preparation at −80 °C of the mixture of ions from labeled alcohol *9-d_6* and immediate (within about 5 min) scanning of the ^{1}H NMR spectrum it was found that the signal at δ 2.75 showed a reduced intensity, due to the expected deuterium labeling in the primarily formed ion *23-d_6*. After twenty minutes at that temperature a random distribution of the CD_3-labels over all seven positions was observed (Scheme 31), the ^{1}H NMR spectrum being indistinguishable from that of the unlabeled isomers.



Scheme 31

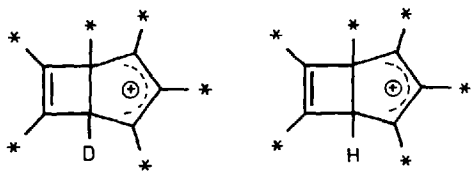
A deprotonation-reprotonation mechanism plays no role, because the use of FSO_3D in stead of FSO_3H does not change the intensity of the absorptions in the spectrum. The observed "seven-methyl" scrambling is assumed to be due to interconversions between [3.2.0]- and [2.2.1] isomers, and to a bridge-flip in a [2.2.1] ion (see Scheme 32).



Scheme 32

On comparing the line-broadening data (−26° to −50 °C) extrapolated to −80 °C, with the time, needed for complete scrambling at that temperature, it may be concluded that both observations are due to the same process.

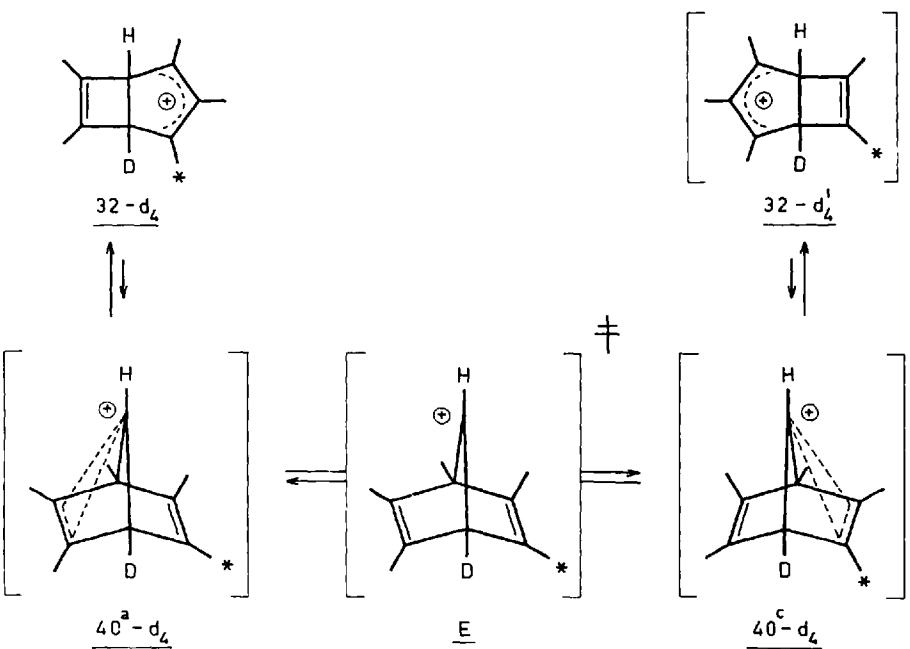
In contrast to the heptamethylated ions *23* and *24*, the pentamethylated ion *32-d*$_4$ does not show any scrambling of the methyl groups under the conditions investigated (1 day at −20 °C). The hexamethylated ion *29* occupies an intermediate position in this respect, showing a distribution of the CD_3-labels over all six methyl positions of ions *29-d*$_7$ and *29-d*$_3$ during their formation at −40 °C (vide supra), but no line-broadening below −10 °C.



29 – d_7 * $^1/_3$ CD_3

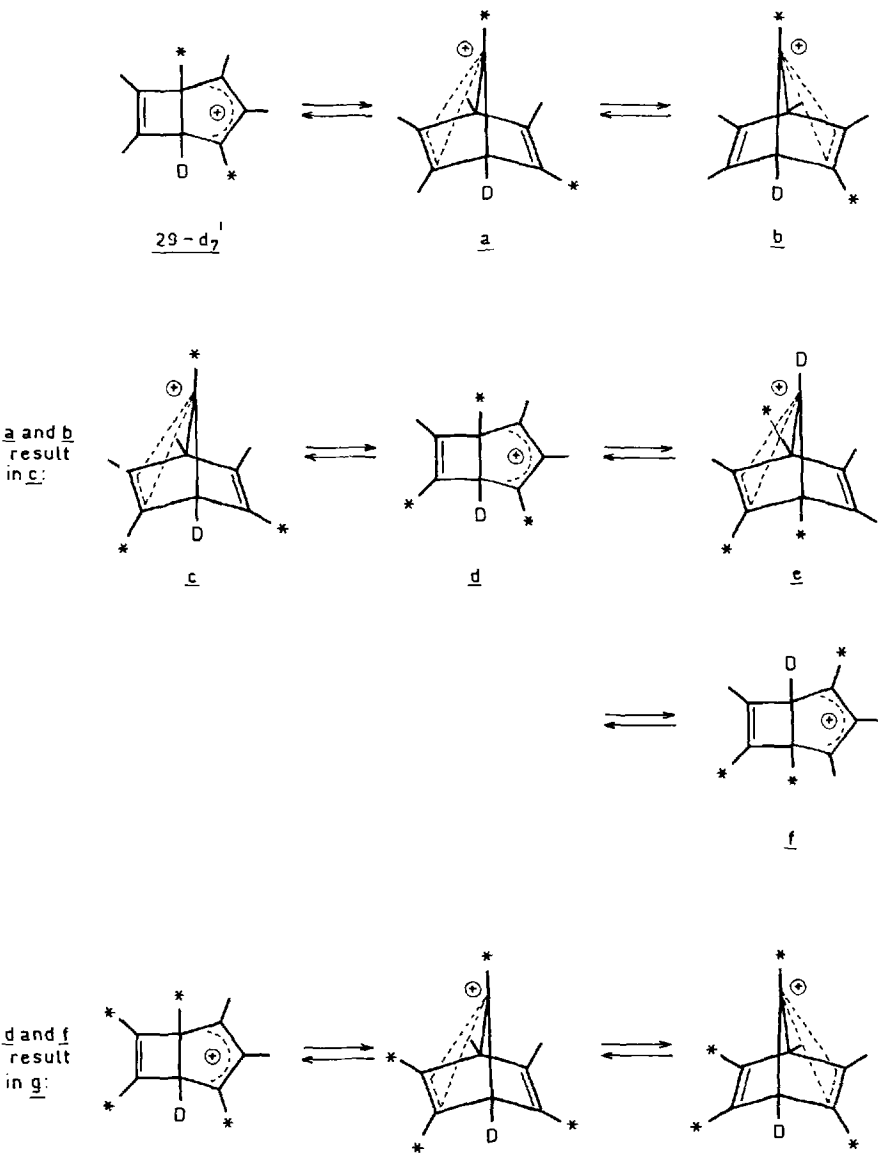
29 – d_3 * $^1/_6$ CD_3

A possible explanation for this difference in behaviour between the penta- and hexamethyl-substituted ions may be that polymethylbicyclo[2.2.1]cations with a hydrogen atom substituted at the top-carbon atom do not undergo the bridge-flip. This is comprehensible if the transition state for the bridge-flip resembles a relatively unstable secondary cation (e.g. *E*, Scheme 33). This is exemplified in Scheme 33 for cation *32-d*$_4$ in which no scrambling of the CD_3-label is found.

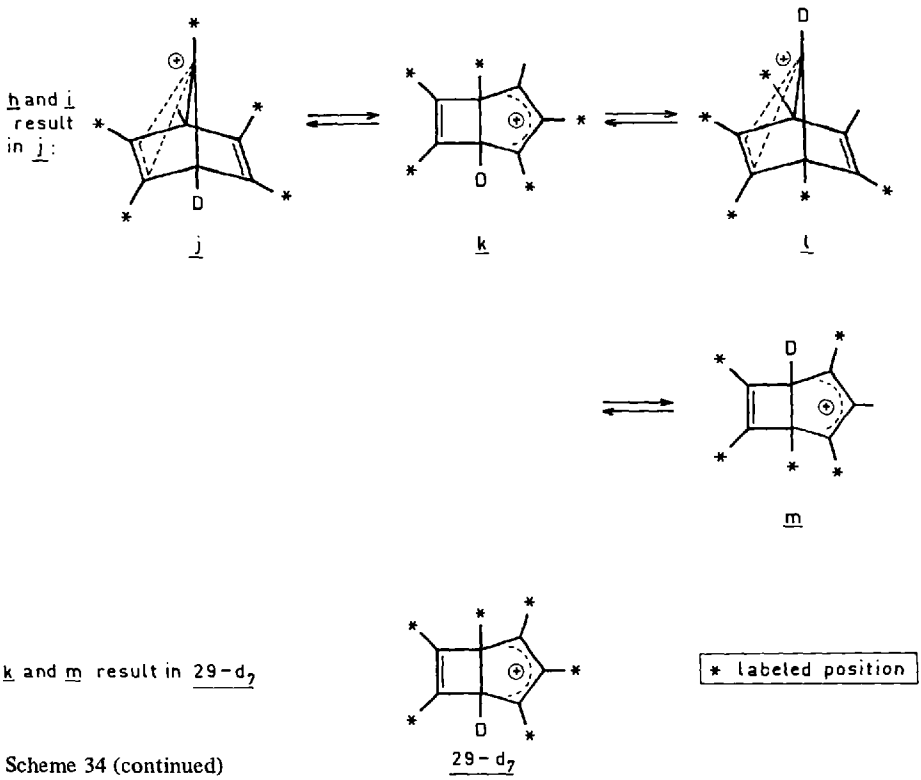


Scheme 33

Upon rearrangement of the observed ion *26-d*$_7$ (formed according to Scheme 14) one predicts, on the basis of 1,2 Wagner-Meerwein shifts, ion *29-d*$_7$' to be formed, as presented in the preceeding section (Scheme 15). At −40 °C, however, complete scrambling of the CD_3-labels is found in *29-d*$_7$. A possible pathway from *29-d*$_7$' to *29-d*$_7$ – based on previously discussed rearrangements, including a bridge-flip in a [2.2.1] cation bearing a methyl group at the top-carbon atom – is depicted in detail in Scheme 34[43].

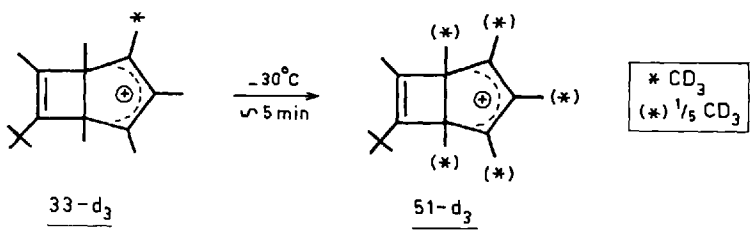


Scheme 34



Scheme 34 (continued)

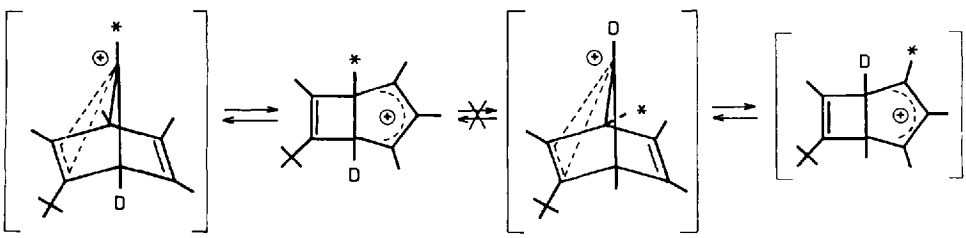
The behaviour of the labeled ions *33-d*$_3$ and *34-d*$_4$ is in agreement with the mechanisms described above. Ion *33-d*$_3$ shows upon warming from –50 °C to –30 °C a scrambling of the CD_3-label amongst the five methyl positions at the five-membered ring (Scheme 35)[44]. This is due to the "five-carbon" scrambling mechanism, as given in Scheme 11. The intermediate [2.2.1] cations in this scrambling process may



Scheme 35

undergo a bridge-flip, but, because this finally will lead to less favorable [3.2.0] isomers, substituted with the tert-butyl group in the five-membered ring, this process plays no role. In contrast to ion *33-d*$_3$, ion *34-d*$_4$ shows no scrambling of the CD_3-label below –10 °C during a few hours. A 1,2 Wagner-Meerwein shift in

34-d_4 will lead to either *36^c-d_4* or *52-d_4*. Although the former ion may undergo a bridge-flip, this process turns out to be a dead end, analogous to the reasoning for cation *33-d_3*. The latter ion *52-d_4* is probably not formed at all (at least not in a sufficient amount), because in that case also a rearrangement of *52-d_4* to *34-d_4'''* would have been observed, which is not the case (Scheme 36).

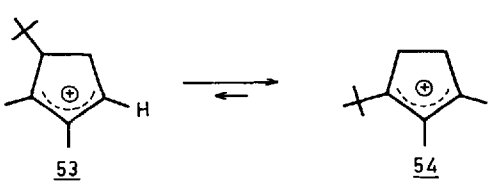


Scheme 36

VI. Substituent Effects

The effect of several alkyl groups upon the stabilization of carbocationic centers has been investigated intensively. Most results have been obtained by solvolytic rate comparisons[1, 45]; experimental data obtained with longlived carbonium ions as far as relevant to the present study are compared below.

H vs. alkyl. Secondary carbonium ions derived from the substrates described in this chapter have not been observed, even at temperatures as low as −110 °C. Rapid rearrangements to tertiary cations occur, in agreement with the fact that there is a considerable energy difference between secondary and tertiary cations. In alkyl cations the difference amounts to 11–15 kcal/mole[46], while Sorensen[17] and Brouwer[47] in their studies of delocalized allylic cations found differences of $\geqq$ 4.6 and 5.3 kcal/mole, respectively. For example, it has not been possible to observe[17] ion *53*, and on that basis a minimum value of 120 has been derived for the equilibrium constant of 53 $\rightleftarrows$ 54 (Scheme 37).



Scheme 37

This is consistent with the rearrangements of ions *25*, *38*, *39* and *44-d_4* (which are analogous to *53*) to the corresponding cations *29*, *32* and *34-d_4*, which are peralkyl substituted at the allylic moiety (compare *54*).

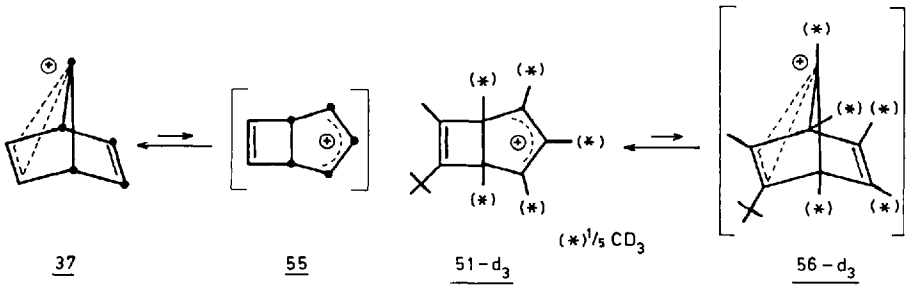
Methyl vs. tert-butyl. Ranganayakulu and Sorensen studied the stabilizing ability of alkyl groups on tetraalkylcyclopentenyl cations under stable ion conditions[17]; they were unable to find experimental evidence for a steric origin of the Baker-Nathan order[48, 49] for alkyl groups {stabilizing power: $CH_3 > CH_2CH_3 > CH(CH_3)_2 > C(CH_3)_3$}. The only explanation is the well documented concept of hyperconjugation[45, 49]. In our systems we have also found that a methyl group is better able than a tert-butyl group to stabilize an allylic carbonium ion[50]. Hyperconjugation is the preferred explanation for the observed rearrangement of *41* to *33* and of *35* to *34* (Schemes 20 and 21), because molecular models of the carbonium ions show no clear steric origin for these rearrangements. While different alkyl substituents do, very remarkably, not exhibit a substantial difference in stabilizing power within alkyl cations (e.g. t-hexyl and t-heptyl cations[51–53]), the present study constitutes an additional example of the Baker-Nathan order to be a very useful concept in certain classes of delocalized carbonium ions. This has also been found by Arnett and Larssen[54] in the case of alkylbenzenium ions, using calorimetric heats of protonation of different polyalkylbenzenes (alkyl = CH_3, C_2H_5, i-C_3H_7 and t-C_4H_9). If the charge is too much delocalized, for example in the 9-ethyl-10-methylanthracenium ion, no significant differences are found (as reported by Brouwer)[55].

Methyl vs. cyclopropyl. The extreme stabilizing power of a cyclopropyl group in comparison with a methyl group is reflected in the behaviour of the ions *21* and *22*, as compared to that of *23* and *27*. While the cyclopropyl substituted ions *21* and *22* remain stable up to −20 °C, ions *23* and *27* rearrange already at −100 °C. Recently Brown[56–58] has compared methyl and cyclopropyl substituted cations using rate studies, and in agreement with equilibrium data[27] he has confirmed the stabilizing power of a cyclopropyl group to be greater than that of a methyl group. Using a correlation between ^{13}C chemical shift and the electron density in carbonium ions Olah has reached the same conclusion[59, 60].

The present study confirms the ability of substituents to stabilize a positive charge to follow the order hydrogen < tert-butyl < methyl < cyclopropyl.

VII. Comparison with other Work

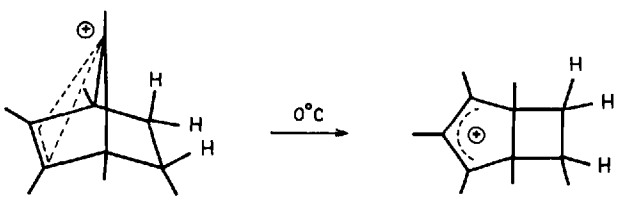
One of the most striking differences between Winstein's and our work is the fact that the bicyclo[3.2.0] cations, reported in this chapter, are observable[61]. Although the [2.2.1] isomers have been observed in some cases, the thermodynamically more stable ions always turned out to have the [3.2.0] skeleton. The difference is nicely demonstrated in the "five-carbon" scrambling process. Winstein assumed a [3.2.0] cation *55* to be involved as an intermediate in the scrambling of the *observed* ion *37*[13], (see also Scheme 11), whereas we assume that a [2.2.1] cation *56-d*$_3$ is an intermediate in the scrambling of the *observed* [3.2.0] carbon *51-d*$_3$ (Scheme 38). The position of the equilibrium is not dependent on the presence of the C=C double



37 55 51-d_3 56-d_3

Scheme 38

bond in the four-membered ring, as shown by the previous reported conversion *57* → *58*[33] (Scheme 39). The thermodynamic stability of polymethylcyclopentenyl



57 58

Scheme 39

cations[47] is obviously so large that the inherent increase in strain by forming a fused cyclobutane (cyclobutene) ring is overcompensated[33, 34]. This fits in with an early observation by Deno et al.[62] that polyalkyl cyclopentenyl cations are frequently observed in acid-catalyzed processes, which has led him to propose the name "ubi" cations for these species.

It is of interest that Goldstein and Hoffmann[63] in their paper "Symmetry, Topology and Aromaticity", have described a method to predict "the preferred directions of numerous isoconjugate rearrangements that interconvert typologies". As an illustration of their theory they refer to Winstein's work on the transformation of the destabilized pericyclic bicyclo[3.2.0]heptadienyl cation *55* to the stabilized longicyclic bicyclo[2.2.1]heptadienyl cation *37*. In the authors' opinion[63] their paper is "intended as a further guide to the experimentalist, warning him of the opportunities and pitfalls of topological interconversions. How useful this will be remains to be established". The present examples clearly show that the balance between the topological [3.2.0] and [2.2.1] systems is rather delicate and obviously strongly dependent upon substituents. The same may be equally true for other topological interconversions, a hypothesis which needs to be examined experimentally.

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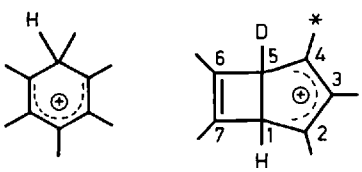
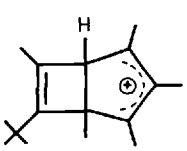
c) In preliminary communications[14] the ^{13}C resonance due to the methyl groups at C-2,4 and C-6,7 in [3.2.0] cations were assigned in reverse order, and should be interchanged
d) These assignments are based upon comparison with the corresponding absorptions of ions *23* and *32*
e) In ion *32* the CH_3 signal at δ 2.90 is observed as a doublet (J = 1.4 Hz). This is due to a coupling between the bridgehead hydrogen at C-1 (or C-5) and the CH_3 group at C-4 (or C-2), and not to a coupling between the hydrogen at C-1 (or C-5) and the CH_3 group at C-2 (or C-4). It is substantiated by the fact that in ion *32-d*$_4$ there is no such coupling. Presumably this coupling is an anlogous to the para coupling found in the hexamethylbenzenium ion *i*, in which $J_{H,CH_3\text{-para}}$ = 2 Hz. See Ref.[1], Vol. II, p. 866



i 32 – d$_4$

f) These assignments are based on the assumption that the tert-butyl group at C-7 has a stronger effect on the methyl group at C-2 than on that at C-4; Compare the absorption of the C-2,4 methyl groups in ion *23* (δ = 2.75)
g) Within this class of carbonium ions it is normally observed that substituents retain their relative order during the rearrangements; therefor cation *34* is substituted as indicated and does not have the structure *ii*



ii

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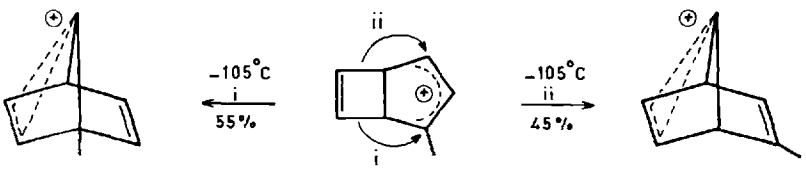
35. Compare for a similar, although less extreme observation the rearrangement of ion *59*, resulting in ions *60* and *61*, as reported by Winstein and co-workers[13]



60 59 61

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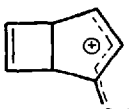
60. With regard to that correlation a controversy exists between Brown and Olah, which focusses upon the opposite conclusion they obtain with cyclopropyl and phenyl substituted carbonium ions. While Brown in his solvolytic study finds the order to be phenyl < cyclopropyl[57], Olah reports the opposite order, based upon ^{13}C chemical shifts[30a]
61. The only alkyl substituted [3.2.0] isomer that Winstein ever observed was cation *59*[35], which rearranged at −105 °C to the [2.2.1] cations *60* and *61*. Besides *59* he also reported cation *62*, having a [3.2.0] skeleton[13]



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Rearrangements of Carbocations
Stereochemistry and Mechanism

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In memory of Professor H. L. Meerwein, on the occasion of his hundredth birthday

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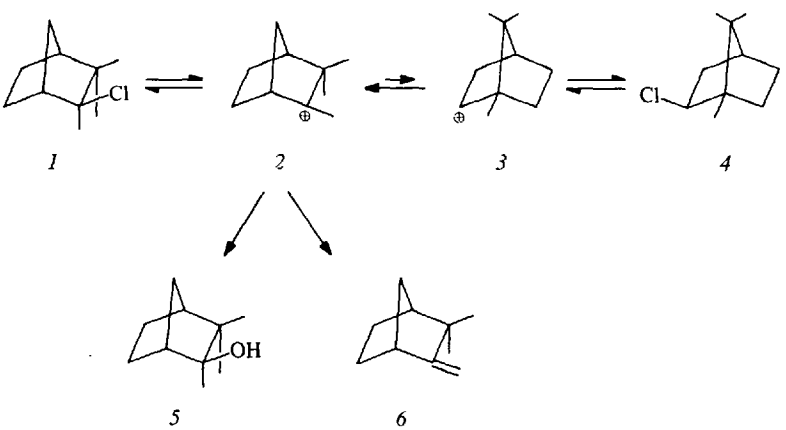
1 Introduction

Molecular rearrangements have attracted the attention of organic chemists for more than a century. At first rearrangements appeared to undermine the foundations of structural chemistry. An expanding appreciation of rearrangement mechanisms, however, has led to a deeper understanding of many problems ranging from valence theory to biosynthesis.

The intermediacy of carbocations in molecular rearrangements was first suggested by Meerwein and van Emster[1] in 1922. These authors studied the conversion of camphene hydrochloride (*1*) into isobornyl chloride (*4*), discovered by Wagner[2] in 1899. They observed that the reaction rate was increased by polar solvents and by catalysts of the Friedel-Crafts type. The same solvents and catalysts were known to promote the ionization of triphenylmethyl chloride, producing the well established triphenylcarbenium ion[3]. Meerwein concluded that ". . . the rearrangement takes place only after preceding ionization. The conversion of camphene hydrochloride to isobornyl chloride actually does not consist of a migration of the chlorine atom but of a rearrangement of the cation."



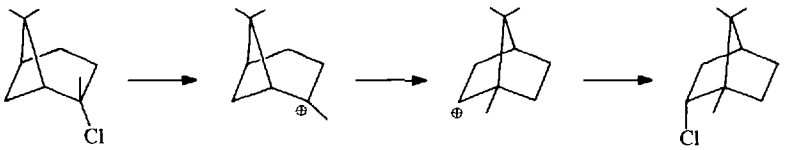
1 *2* *3* *4*

5 *6*

Analogous rearrangements in acyclic systems were extensively studied by Whitmore and his school[4]. Whitmore was the first to appreciate that a variety of seemingly unrelated rearrangements (the Demjanov, Lossen, Curtius, and Beckmann reactions as well as the Wagner-Meerwein and pinacol-pinacolone rearrangements) all involved electron-deficient intermediates with a sextet of electrons. His studies soon revealed that carbocations normally rearrange in the direction of increasing stability, e.g., secondary → tertiary. The conversion of tertiary camphene hydrochloride (*1*) into secondary isobornyl chloride (*4*) is due to the greater thermodynamic stability of (*4*), combined with reversible ionization. Under conditions of irreversible capture, e.g., buffered hydrolysis of either (*1*) or (*4*), the products, (*5*) and (*6*) are derived from the tertiary cation (*2*)[1].

Theoretical reasons and the analogy with boron suggest the trigonal planar structure of carbocations which has recently been confirmed by spectroscopy in superac-

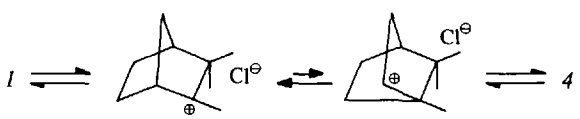
ids[5]. Hughes, Ingold, and their school related kinetic and stereochemical evidence in their ingenious theory of nucleophilic substitution[6]. They stated: "Mechanism S_N1, proceeding through a carbonium ion, involves racemization, together, in general, with an excess of inversion unless a configuration-holding group is present, when



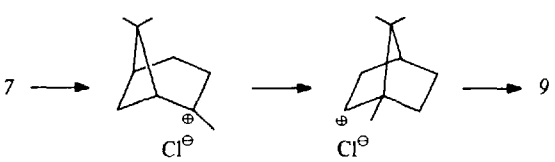
7 *8* *3* *9*

configuration is predominantly retained". The stereochemistry of the Wagner-Meerwein rearrangement, (*1*) → (*4*), is in obvious contrast to Ingold's "S_N1 rule" as it proceeds with complete inversion of configuration. The formation of (*4*) from (*1*) cannot be attributed to preferential *exo* attack of chloride on the bornyl cation (*3*) because the related isomerization of pinene hydrochloride (*7*) produces the *endo* isomer, bornyl chloride (*9*)[1,7]. The intermediacy of a "free" bornyl cation (*3*) should lead to the same product (s) in both reactions.

A possible explanation of the stereospecificity observed in the rearrangements of (*1*) and (*7*) is ion pairing. If chloride retains its orientation relative to the plane of the carbocation throughout the rearrangement, distinct intermediates, (*3a*) and (*3b*), are involved and the correct product stereochemistry is predicted. Conditions which pro-



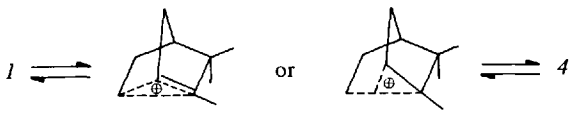
3a



3b

mote dissociation (e.g., increasing ionic strength of the solvent, better leaving groups) should remove the stereospecificity induced by ion pairing. However, the rearrangements of isobornyl and pinanyl substrates appear to be rather insensitive to such variations[8].

The concept of bridged ions provides an alternative explanation of stereospecificity. The equilibrating pair of carbocations, (*2*) $\rightleftarrows$ (*3*), is replaced by a σ-delocalized ("nonclassical") intermediate (*10*). A two-electron, three-center bond is characteristic of (*10*). Other compounds have structures which indicate delocalized σ bonds. Well known examples are diborane and the dimer of trimethylaluminum. Because of



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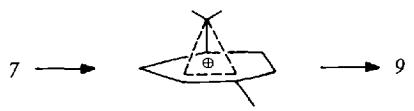

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the partial covalency between C–6, C–1 and C–2, nucleophilic attack at C–1 or C–2 is expected to occur with inversion of configuration.

Analogously the isomeric bridged ion (*11*) involved in the rearrangement of (*7*) gives rise to *endo* product. The concept of bridged ions, first suggested by Wilson[9], has been supported by Winstein[10] and Olah[11], but has been strongly repudiated by H. C. Brown[12]. Some of their arguments will be considered in subsequent sections of this review.

The case history of the Wagner-Meerwein rearrangement may serve as a guideline to an extensive discussion of mechanism and stereochemistry of cationic 1,2 shifts. First principles may be derived from the behavior of free carbocations as they occur in the gas phase (Section 2) and in solvents of extremely low nucleophilicity ("superacids") (Section 3). While such conditions provide valuable information on energetics and some insight into mechanism, they virtually exclude stereochemical studies.

Stereochemistry develops in nucleophilic solvents where carbocations are short-lived intermediates. Any observation of stereospecificity excludes the intervention of achiral carbocations. Chirality may be conferred on otherwise planar carbocations by their environment. Ion pairing is the best known example of asymmetric solvation (Section 4). Incorporation of a carbocation in micelles has recently been recognized as another way of controlling its stereochemistry (Section 5).

In most cases inherent properties of the reacting system are found to be more important than external factors. Rearrangement may occur before the carbocation has reached conformational equilibrium. Conformational control (Section 6) leads to a variable degree of inversion at the migration terminus, depending on the relative rates of rotation and rearrangement. Complete inversion at the migration terminus results from participation of the migrating group in the process of ionization (anchimeric assistance, Section 7). Neighboring group participation involves a bridged transition state but does not necessarily imply a bridged intermediate. Bridged ions may also form after rate-determining ionization. Anchimeric assistance is neither essential nor sufficient for bridging although both effects are often associated (Section 7). The spectrum of bridged ions extends from the well-defined electron-sufficient species which allow a bridged representation with normal single bonds (e.g., bromonium ions, phenonium ions) to the controversial electron-deficient structures which require σ-delocalization (Section 7).

2 Carbocations in the Gas Phase

2.1 Thermodynamic Aspects

Ionization reactions in solution inevitably involve solvated ions; the carbocation and its counter-ion are stabilized by interaction with the solvent. In order to assess the thermodynamic stability of carbocations free of complications by intermolecular solvent-ion forces, one is essentially limited to gas phase studies[13–15].

Direct measurements of the activation energies involved in breaking a bond heterolytically into ions are made impossible by the fact that the thermally induced homolysis requires much less energy. It is then necessary to determine the heats of formation of the positive and negative ions individually *via* ionization or appearance potential and electron affinity.

The ionization potential (IP) of a molecule or radical is defined as the minimum energy required to remove an electron.

$$R\cdot \longrightarrow R^+ + e^-$$

$$IP = \Delta H_f^\circ(R^+) - \Delta H_f^\circ(R\cdot), \text{ with } \Delta H_f^\circ(e^-) = 0$$

Because each molecular-orbital level has associated vibrational levels, the lowest measurable ionization potential is strictly the energy required to remove an electron from the highest occupied orbital in the $v = 0$ state to give an ion in the $v = 0$ state. Such an ionization potential has been called adiabatic and can usually be determined by methods such as ultraviolet[16], photoionization[17], and photo-electron spectroscopy. These adiabatic ionization potentials are distinguished from the so-called vertical ionization potentials which correspond to ionization to an ion with the same internuclear distances and bond angles as the radical. According to the Franck-Condon principle this is the most probable ionization process occurring on electron impact in the mass spectrometer. Vertical ionization involves a somewhat larger energy than adiabatic ionization which is the process to be related to thermochemical data. However, the comparison of photoionization and recent electron impact data suggests that this effect is within the present limits of experimental error (Table 1).

Table 1. Ionization potentials of simple alkyl radicals

	Ionization Potentials (eV)[1]				ΔH_f (kcal/mol)	
	UV[16]	PI[17]	RPD[19]	EI[18]	$\Delta H_f(R\cdot)$	$\Delta H_f(R^+)$
CH_3	9.84	9.82	9.80; 9.87	9.84	34.0	261
CH_3CH_2		8.4	8.25; 8.34	8.38	25.7	219
$CH_3CH_2CH_2$		8.1	8.15; 8.13	8.10	20.8	208
$(CH_3)_2CH$		7.5	7.52; 7.57	7.55	17.8	192
$CH_3CH_2CH_2CH_2$			8.01	8.01	16.0	201
$(CH_3)_2CHCH_2$				8.01	14.0	199
$CH_3CH_2(CH_3)CH$				7.41	12.4	183
$(CH_3)_3C$				6.93	6.8	167

[1] 1 eV = 23.0609 kcal/mol.

Earlier estimates of ionization potentials obtained with conventional mass spectrometric ion sources were beset with difficulties caused by the relatively wide energy spread (0.5–1 eV) in the thermally produced electron beam. Refinements of the electron-impact method, such as use of an energy-resolved electron beam from a double-hemispherical electrostatic monochromator[18] or the "retarding potential difference" (RPD) method[19] afforded values which are in good agreement with photoionization and spectroscopic data.

The appearance potential (AP) of a fragment ion is the energy required to produce the ion and its accompanying neutral fragment from the molecule.

$$R{-}X + e^- \longrightarrow R^+ + X\cdot + 2\,e^-$$

$$AP(R^+) = \Delta H_f^\circ(R^+) + \Delta H_f^\circ(X\cdot) - \Delta H_f^\circ(RX)$$

The energy necessary to produce the carbocation R^+ from a molecule RX exceeds the ionization potential of the radical $R\cdot$ by the bond dissociation energy of RX.

$$AP(R^+) \geqslant IP(R\cdot) + D(R{-}X)$$

The inequality sign is written because the products of the reaction may contain excess energy; i.e. vertical and adiabatic potentials may not be the same. The process of fragmentation involves first ionizing the molecule and then adding sufficient further energy to cause the appearance of the fragment ion. Skeletal rearrangements may occur at the stage of the molecular ion, and give rise to fragments not directly related in structure to their precursor. E.g., the ionization of both *n*-propyl and isopropyl halides affords appearance potentials characteristic of the isopropyl cation. Data relevant to the *n*-propyl cation are obtained by ionization of *n*-propyl radicals, generated by pyrolysis of *n*-propyl nitrite[18]. Such rearrangement is quite common, and is a compelling reason for exercising caution in the interpretation of appearance potential measurements.

Recent advances in the study of ion-molecule reactions have opened another approach to the determination of relative carbocation stabilities. The halide transfer

Table 2. Heats of formation, hydride and bromide affinities of secondary and tertiary carbocations[20,21]

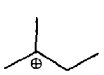
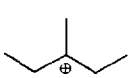
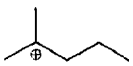
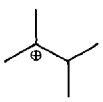
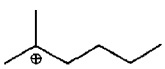
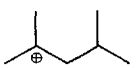
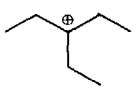
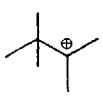
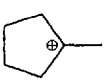
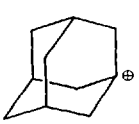
R^+	$\Delta H_f(RH)$ kcal/mol	$\Delta H_f(R^+)$ kcal/mol	$D(R^+{-}H^-)$ [1] kcal/mol	$D(R^+{-}Br^-)$ kcal/mol
	−32.07	169.1 [2]	235.9	148.7
	−36.73	161.1	232.5	
	−41.11	155.3	231.1	

Table 2 (continued)

R^+	$\Delta H_f(RH)$ kcal/mol	$\Delta H_f(R^+)$ kcal/mol	$D(R^+-H^-)$ [1] kcal/mol	$D(R^+-Br^-)$ kcal/mol
	−41.75	155.6	232.1	
	−42.59	153.2	230.5	
	−46.52	151.5	232.7	
	−48.20	148.4	231.3	
	−45.25	150.6	230.5	
	−48.87	144.5	228.1	
	−25.27	169.3	229.3	
	−19.6	174	228.4	
				137.9
	−25.02	192 [2]	251.7	162.9
	−18.46	192.6	245.8	161.3
	−12.42	187.3	234.4	146.8

[1]) $D(R^+-H^-) = \Delta H_f(R^\oplus) + \Delta H_f(H^-) - \Delta H_f(RH)$; $\Delta H_f(H^-) = 34.7$ kcal/mol.
[2]) Arbitrary standard; values obtained from IP data[18].

$$R'-X + R^+ \rightleftharpoons R'^+ + R-X$$

equilibria have been investigated, using trapped ion cyclotron resonance techniques[20]. This work is largely concerned with hetero-substituted carbocations, but also includes aliphatic and alicyclic species (Table 2). The hydride transfer equilibria

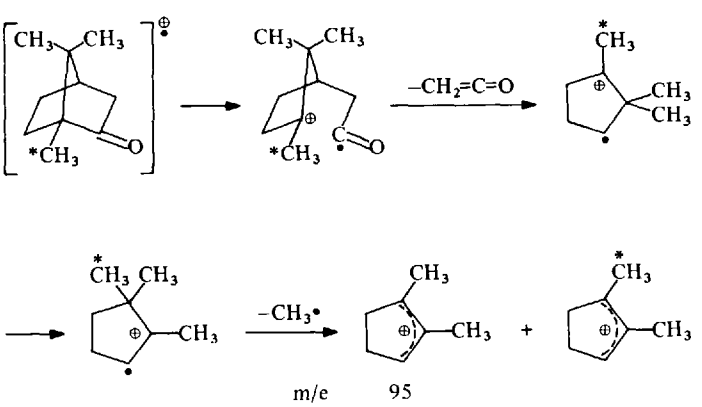
$$R'-H + R^+ \rightleftharpoons R'^+ + R-H$$

were established by pulsed, high-pressure mass spectrometry, and their temperature variations used to obtain the enthalpies of formation of various alkyl and cycloalkyl cations[21]. These studies reveal differences in ΔH_f up to 5 kcal/mol among the isomeric tertiary $C_7H_{15}^+$ ions and suggest an abnormal stability of the norbornyl cation. The stabilities of isomeric cations may be compared by simple inspection of their heats of formation. For cations of different molecular weight it is customary to refer to the corresponding hydrocarbons and compare the calculated heats of reaction of the hypothetical heterolysis $RH \rightarrow R^+ + H^-$. On that basis, secondary and tertiary carbocations differ by *ca.* 16 kcal/mol whereas the norbornyl cation is only 6 kcal/mol above 2-methylnorbornyl (Table 2).

2.2 Rearrangements

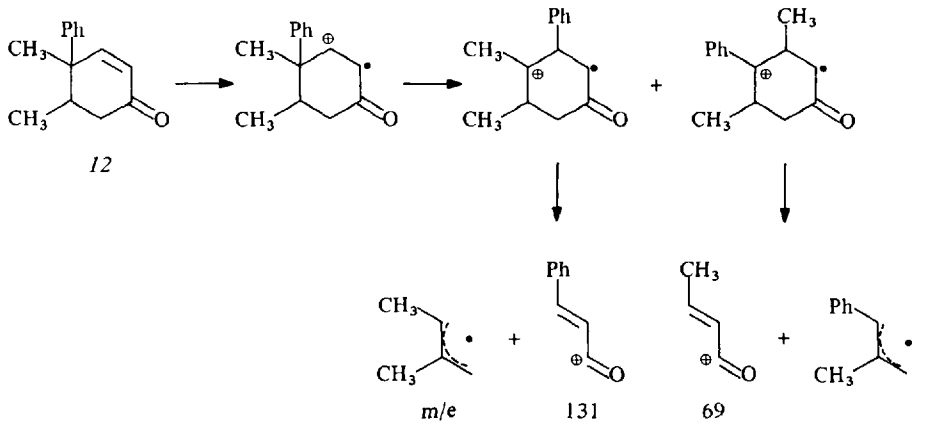
Mass spectrometry and related techniques offer the opportunity of studying the rearrangement of carbocations in the gas phase. Such studies are highly desirable for comparison with the behavior of carbocations in solution. They are seriously hampered, however, by the difficulty of obtaining structural information on gaseous organic ions.

Many rearrangements have been invoked to explain the fragmentation pattern of molecular ions[22]. (It should be remembered that the fragmenting species are radical cations. Their radical functionality may open to them reaction paths which are not available to simple carbocations). Only a few illustrative examples of well-established alkyl and aryl shifts are given here. The mass spectrum of camphor displays the base peak at m/e 95, corresponding to the loss of ketene and a methyl radical. As shown



by isotopic labelling, 50% of C–10 is lost in this process[23]. This observation has been explained by assuming a methyl shift in the fragment arising by loss of ketene.

4,4,5-Trisubstituted cyclohexen-2-ones produce fragments which are indicative of an alkyl (aryl) shift to the 3-position. The relative intensities of the peaks m/e = 69 and 131 in the case of (*12*) suggest a preference for phenyl migration[22,24].



The molecular ions derived from epoxides undergo reorganizations related to the pinacol rearrangement[25].

Ion-molecule reactions have been employed in the structural characterization of gaseous organic ions, especially utilizing ion cyclotron resonance (ICR) spectrometry. E.g., equilibrium constants have been measured for proton transfer reactions between protonated methanol or protonated formic acid with a variety of hydrocarbons[26]. These studies show that protonated cyclopropane and methylcyclopropane have heats of formation different from those of the propyl and butyl ions, indicating that the ring structure of these ions is retained. Determination of the proton affinity of cyclopropene reveals that the $C_3H_5^+$ ion formed has a heat of formation of 238 kcal/mol[27]. This value is not consistent with the heat of formation of allyl cation (226 kcal/mol) and suggest that the allyl cation is not readily formed by protonation and concomitant opening of the cyclopropyl ring. Either a cyclopropyl cation is formed in the initial proton transfer, or the proton transfer must occur with a 12 kcal/mol barrier to allyl cation formation.

In a different experimental approach, ICR spectroscopy was used to examine proton-deuteron transfer from specifically labeled propyl ions, generated from the corresponding bromides[28]. It was found that *sec*-propyl ions undergo little (< 20%) isomerization in the time required for ICR reactions (ca. 10^{-3} sec) whereas most (80–100%) *n*-propyl ions isomerize to *sec*-$C_3H_7^+$. The results of proton transfer from and hydride transfer to specifically deuterated ethyl cations can only be accounted for by a statistical scrambling of the hydrogen atoms[29]. These studies show that 1,2 hydrogen shifts in the ethyl cation occur with a high rate, in contrast to solution chemistry where little, if any, scrambling of hydrogen is observed. It appears that the ethyl cation is bypassed in the solvolysis and deamination of ethyl derivatives.

Collisional activation (CA) spectrometry is another valuable tool for the structural identification of gaseous ions[30]. Collisional activation produces a fragmentation pattern of long-lived ions in much the same way as conventional mass spectrometry yields fragments of the short-lived ions decomposing in the ion source. CA spectra are particularly well suited for the comparison of ions from different precursors.

The CA spectra of gaseous ions formed by the protonation of cyclopropane and propene confirm that the isomerization of protonated cyclopropane to *sec*-propyl cation occurs in less than 10^{-5} sec[31]. On the other hand, the isomerization is slow in comparison to the 10^{-7} to 10^{-8} sec-between collisions in the high pressure studies mentioned above[26]. The apparent low activation energy suggests that the isomerization of protonated cyclopropane does not proceed by way of the *n*-propyl cation.

The CA spectra of *sec*- and *tert*-butyl ions (generated by electron ionization of the corresponding bromides) are consistent with minimal isomerization in *ca.* 10^{-6} sec. The CA spectrum of the isobutyl cation, however, corresponds to 75% ($\pm$ 20%) *sec*-butyl and 25% *tert*-butyl[32]. The predominant formation of *sec*-butyl ions is in contrast to the preferred solution isomerization of isobutyl to *tert*-butyl cations.

Considerable attention has been focused on gaseous $C_7H_7^+$ ions since the proposal by Meyerson[33] that both cycloheptatriene and toluene give the tropylium ion as the most abundant ion in their mass spectra. Extensive hydrogen scrambling occurs in the fragmentation of $C_7H_7^+$ ions from benzylic precursors[34]. Investigation of the nondecomposing $C_7H_7^+$ ions by CA spectroscopy showed, however, that benzyl and tropylium ions of low internal energies are stable[35]. $C_7H_7^+$ ions, formed from various precursors in an ICR spectrometer, were resolved into two populations of markedly different reactivity[36, 37]. The benzyl structure was assigned to the reactive $C_7H_7^+$ population on the basis of their reactions with labeled toluene[36]. The unreactive $C_7H_7^+$ ions were assigned the tropylium structure. The relative abundance of the unreactive tropylium ions decreases with decreasing energy of the ionizing electrons[37]. This is interpreted to mean that rearrangement to the seven-membered ring structure occurs with ions of high internal energy. Rate constants for the hydride transfer to the benzyl cation from various hydrocarbons

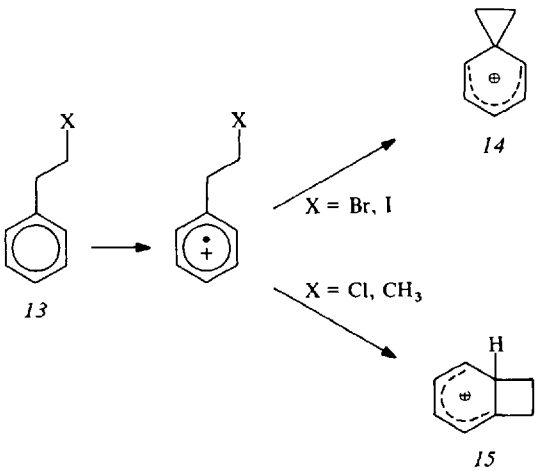
$$C_6H_5CH_2^+ + R{-}H \longrightarrow R^+ + C_6H_5CH_3$$

lead to an estimate for $\Delta H_f^\circ(C_6H_5CH_2^+) = 219 \pm 2$ kcal/mol[37]. Both ΔH° (0.03 kcal/mol) and ΔS° (–0.5 e.v.), measured by ICR for the halide transfer equilibrium are consistent with the notion that the $C_7H_7^+$ ion formed is the benzyl

$$C_7H_7^+ + (CH_3)_3C{-}Cl \longrightarrow (CH_3)_3C^+ + C_6H_5CH_2Cl$$

cation and not the thermodynamically favored tropylium ion[38].

Evidence for anchimeric assistance in gas phase ionization is provided by β-phenylethyl bromide and iodide (*13*, X=Br, I) which yield ethylenebenzenium ions (*14*) at low ionizing electron energy[39]. The CA spectrum of (*14*) is unique in showing the highest loss of CH_2 of any of the $C_8H_9^+$ isomers studied; the CA spectra of $\alpha{-}^{13}C$ and $\beta{-}^{13}C$ derivatives are identical within experimental error. In contrast,



13 14 15

β-phenylethyl chloride (*13*, X=Cl) and *n*-propylbenzene (*13*, X=CH_3) appear to yield protonated benzocyclobutene (*15*); their CA spectra agree closely with that obtained by the ion source protonation of benzocyclobutene[40].

In conclusion, elaborate mass spectrometric techniques provide sufficient structural information to delineate the prominent reorganizations of gaseous organic ions. If highly energetic ions are eliminated the gas phase chemistry of carbocations conforms qualitatively, at least, with that observed in solution. It appears that the potential of carbocations for rearrangement is not profoundly altered by solvation. Moreover, the behavior of "isolated" gaseous ions demonstrates that ionization and rearrangement may occur in discrete steps as well as in concert.

3 Carbocations in Superacids

In 1937, Meerwein recognized the decisive role of weakly nucleophilic, complex anions in stabilizing organic cations[41]. A series of progressively less stable cations has since then been prepared. In 1962, Olah reported the first direct observation of stable alkyl cations in solution[5,42]. He showed that an excellent medium for the stabilization of carbocations could be formed from a mixture of antimony pentachloride with fluorosulfonic acid, and diluted if necessary with liquid SO_2 or sulfonyl chlorofluoride, SO_2ClF. These mixtures are the most highly acidic media known and are often referred to as "superacids".

Tertiary carbocations may be conveniently prepared in such media from alkyl halides, alcohols, and alkenes. Secondary cations can be observed at low temperatures, but they rearrange readily to more stable tertiary ions. For such cases, special techniques of mixing the reactants, e.g. cocondensation on a cold surface ("molecular beam technique"), have been developed[43]. Attempts to prepare primary ions in the same manner have not been successful. Methyl and ethyl fluorides exchange halogen but do not generate observable concentrations of cations. All other simple

primary halides give ions resulting from isomerization to more stable secondary or tertiary species.

The following evidence indicates that carbocations are the principal species present in these solutions:

(1) The large downfield shifts in the ^{1}H and ^{13}CNMR spectra, relative to those of the starting halides, are consistent with a full positive charge on carbon.

(2) The coupling between H and F, which was present in the starting fluorides, disappears.

(3) Large ^{13}C–H coupling constants (169 Hz in the isopropyl cation[44]) indicate sp^2 hybridization of the carbenium carbon atom.

3.1 Structural Aspects

3.1.1 Alkyl Cations

Table 3 lists the parameters of the ^{1}H and ^{13}C–NMR spectra of some alkyl cations. The ^{13}C–NMR resonances of the carbons bearing positive charge are shifted by 300 ppm to lower field, relative to the parent hydrocarbons. The effect of charge on chemical shift falls off rapidly with distance. *Ab initio* calculations (STO–3G) have been reported that show an increase in positive charge on the central carbon on going from the isopropyl to the *t*-butyl to the *t*-amyl cation[45]. Table 3 reveals a parallel behavior of ^{13}C–NMR shifts.

Infrared and Raman spectra of the alkyl cations were also recorded[46] and are in agreement with the carbenium structure of these ions. Raman spectra provide strong evidence that the *t*-butyl cation possesses a planar carbon skeleton with one hydrogen atom of each CH_3 group above the plane of the carbon atoms (C_{3v} point group symmetry).

ESCA spectroscopy is another useful method for the investigation of carbocations[47]. Whereas the carbon 1s electron binding energy differences of hydrocar-

Table 3. NMR data for some carbocations in SbF_5-SO_2ClF solution at −70 °C (in ppm from TMS)

	^{1}HNMR			^{13}CNMR	
	$^{+}$CH	α-CH_3	β-CH_3	C^{+}	α-CH_3
$(CH_3)_2CH^{+}$	13	4.5		319.6	61.8
$(CH_3)_3C^{+}$		4.15		330.0	48.3
$(CH_3)_2C^{+}C_2H_5$		4.1	1.94	333.8	44.5
$CH_3C^{+}(C_2H_5)_2$		4.16	1.87	334.0	43.8
$PhCH^{+}CH_3$	10.5	3.73		229.8	27.2
$PhC^{+}(CH_3)_2$		3.60		255.5	35.8
Ph_2CH^{+}	9.8			201.5	
Ph_3C^{+}				212.7	

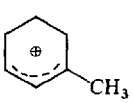
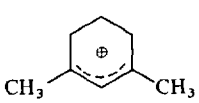
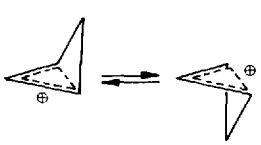
bons are well below the resolution of ESCA instruments, the large positive charge on carbocationic centers gives rise to separate 1s-level photoelectron lines. The ESCA spectrum of the *t*-butyl cation exhibits two peaks with a separation of 4 ± 0.2 eV and a peak area ratio of 1:3. Comparable results were obtained on a series of other alkyl cations.

3.1.2 Charge Delocalization

The NMR spectra of benzylic carbocations show that the chemical shifts reflect the lowered positive charge density expected at the carbenium ion center (Table 3). The difference in ^{13}CNMR shift between the dimethyl- and the diphenylcarbenium ion is about 120 ppm. There appears to be little increased delocalization due to substitution by three phenyl groups at a carbenium ion center relative to only two phenyl groups.

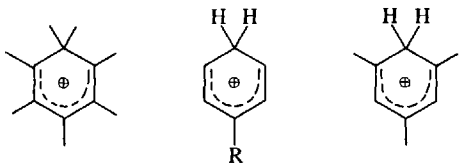
The ^{13}C–NMR spectra of most alkenyl and cycloalkenyl cations (Table 4) indicate little 1.3-interaction[48]. The deshielding of C–2 relative to reference olefins

Table 4. ^{13}C-NMR data for some alkenyl and cycloalkenyl cations (δ in ppm from TMS)

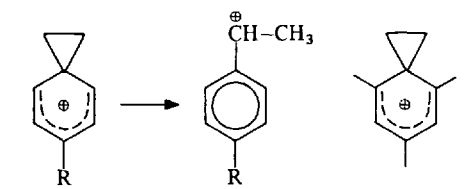
	C-1	C-2	C-3	CH_3
$CH_3CH{=}CH{=}CHCH_3^{\oplus}$	231.3	147.0	231.3	29.8
$(CH_3)_2C{=}CH{=}CH_2^{\oplus}$	268.2	146.7	174.0	19.3
$(CH_3)_2C{=}CH{=}C(CH_3)_2^{\oplus}$	235.6	143.0	235.6	
	235.6	146.6	235.6	
	247.1	140.5	205.9	42.7
	228.5	138.7	228.5	33.6
	218.6	137.6	218.6	
	133.5	187.6	133.5	

may readily be explained as due to the inductive effect of the neighboring carbon atoms. A notable exception is the cyclobutenyl cation which exhibits strong 1,3 overlap and aromatic delocalization (homocyclopropenium ion)[49]. Complete line shape analysis of the 270 MHz ^{1}H–NMR spectra gave a value for $\Delta G^{\ddagger} = 8.4$ kcal/mol for the ring flipping process. The large chemical shift differences between the terminal carbons in unsymmetrically substituted alkenyl and cycloalkenyl cations indicate that significant positive charge has moved toward the tertiary carbon.

Protonation and alkylation of arenes afford cyclohexadienyl cations (arenium ions) which are also of importance in electrophilic aromatic substitution. The heptamethylbenzenium ion (*16*) is a very stable species[50], but even the parent benzenium ion (*17a*) has been observed as have most of its alkyl, halo, and alkoxy derivatives[51]. The benzenium ion (*17a*) undergoes a rapid degenerate rearrangement which equilibrates the seven protons over six carbons. Data for the monosubstituted benzenium ions show that (*17*) is the most stable of the possible isomeric forms. Positive charge



16 *17a* R = H, *b* R = CH_3, *c* R = OCH_3 *18*



19a R = H, *b* R = CH_3, *c* R = OCH_3 *20* *21*

Table 5. NMR data for some arenium ions (δ in ppm from TMS)

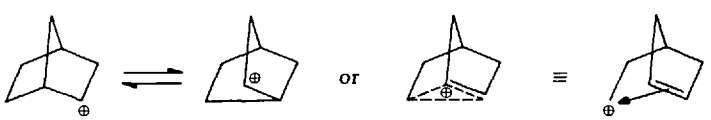
	H-2,6	H-3,5	C-1	C-2,6	C-3,5	C-4	CH_2
17b	9.43	8.49	49.5	181.2	139.4	201.9	
17c	8.85	7.82	42.6	176.6	129.6	193.6	
				169.6	123.6		
18		7.7	56.0	196.9	135.9	196.9	
19a	9	8.2	68.8	171.8	133.4	155.4	60.7
19b	8.36	8.05	64.6	174.6	138.6	185.6	54.6
19c	8.12	7.47	49.2	171.2	121.0	183.1	41.2
21		7.7	61.6	185.6	136.6	175.6	51.6

as indicated by ^{13}C–NMR shifts (Table 5) is predominantly on C–2, C–4, and C–6 while C–3 and C–5 show little deshielding in going from the neutral arene to the corresponding arenium ion. The chemical shift of C–1 is clearly that of an sp^3 and not an sp^2 carbon. Methyl substitution at C–2 and C–6 (*18*) causes substantial deshielding of these carbons at the expense of C–4.

Ethylenearenium ions (*19*) are of special interest with regard to the nature of β-phenylethyl cations in solvolytic systems (cf. Section 7.3). The stable, long-lived ions obtained from β-arylethyl chlorides in superacids were shown by NMR to be spiro [2.5] octadienyl cations (*19*); i.e. cyclopropylmethyl cations in which the carbenium ion center belongs to a cyclohexadienyl cation[52]. The cyclohexadienyl ring portion of the ions shows charge distribution similar to that of the analogous arenium ions. The tetrahedral nature of the spiro carbon is clearly established. Upon standing at -78°C, (*19a*) rearranges irreversibly to form the 1-phenylethyl cation (*20a*) (E_a=13 kcal/mol).

3.1.3 Rapidly Equilibrating or σ-Delocalized Carbocations?

Some carbocations undergo fast degenerate rearrangements through intramolecular hydrogen or alkyl shifts. The degeneracy may be due to equilibrations of localized ("classical") cations separated by low barriers of activation. Alternatively, static hydrogen or alkyl bridged ("nonclassical") cations may be involved. The bridged ions can be described in terms of two-electron, three-center bonds (σ-delocalization)[9–11] or in terms of complex interaction of carbocations with π donor systems[53]. The norbornyl cation (*22*) is the most disputed case of a possibly alkyl bridged ion, and the 5-norbornen-2-yl cation (*23*) belongs to the vinyl bridged or cyclopropylcarbinyl category. The NMR spectra of these ions show that C–1,2 of (*22*) and C–5 of (*23*) are the carbon atoms bearing most of the positive charge.



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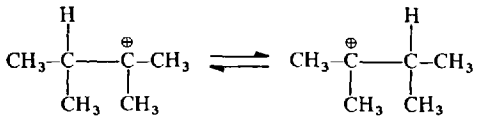
Differentiation between bridged and rapidly equilibrating ions by NMR spectroscopy is difficult. Equilibration is expected to give chemical shifts which are the average of positively charged and uncharged carbon atoms. Upfield deviations from the average may be attributed to charge delocalization by bridging. Of course, this argument depends critically on the choice of a model for calculating the average.

For the dimethylisopropylcarbenium ion (*24*) the ^{13}C–NMR shift for the two central carbons is 198.0 ppm[54]. A good model for estimating this shift is the *t*-butyl



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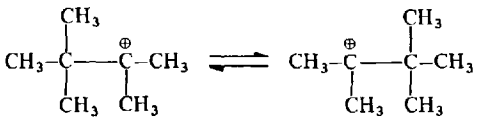

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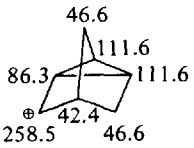
cation; the average value of the methyl group and of the central C^+ atom is 188.4. The effect of the two additional methyl groups in (*24*) should cause additional deshielding of both shifts compared with those in the *t*-butyl cation. Thus, the observed shift is in accord with expectation for a rapidly equilibrating ion. Similar agreement is reached for the *t*-butyldimethyl carbenium ion (*25*) where the ^{13}C–NMR shift of the central carbon atoms is 206.1 ppm.

For the norbornyl cation (*22*), on the other hand, the average ^{13}C chemical shift for C–1,2 was found at 126.1 ppm (at -150°C where all other rearrangements except for the degenerate alkyl shift are "frozen out")[55]. Thus, C–1,2 absorb by ca. 80 ppm further upfield that the corresponding carbons of the equilibrating ion (*25*). A similar discrepancy (85 ppm) is estimated on the basis of isopropyl cation and C–1 of norbornane as a model. Some doubt, however, remains whether these acyclic ions are good approximations of the hypothetical 2-norbornyl cation.

In principle, the problem of equilibrating *vs.* bridged ions could be readily solved by ESCA spectroscopy. Since ESCA spectra observe the energy of core electrons ejected from a single species, no time scale limitations due to chemical equilibration can exist. One would expect a classical (equilibrating) ion to exhibit two peaks with an area ratio of 6:1 and the bridged ion to show two peaks with a 5:2 ratio. The experimental spectra[55], however, show severe overlap of the two peaks, and the results of deconvolution have been a matter of dispute[55–57]. Another argument in favor of delocalization, the smaller separation of the two signals in the ESCA spectrum of (*22*) (<1.5 eV) compared with that of *t*-butyl cation (4 eV), has not been universally accepted. ESCA spectra have been computed for the classical and bridged norbornyl cations on the basis of calculated charge distributions[57]. The observed spectrum was found similar to that calculated for the classical structure by MINDO/3[57a], but the opposite conclusion was drawn[57c] from *ab initio* (4–31 G) calculations[57b].

It appears that spectroscopic studies in superacids will not conclude the nonclassical ion controversy. Nevertheless the NMR spectra of equilibrating and (or) delocalized cations provide useful information on charge distribution in such species[58]. The ^{13}C–NMR shifts given in formulas (*23*)–(*33*) indicate that positive charge resides largely at C–3 of the nortricyclyl cation (*23*)[59] whereas it is highly delocalized in the 7-norbornenyl (*26*) and 7-norbornadienyl cations (*27*)[42]. The



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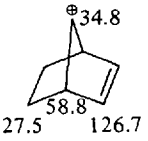

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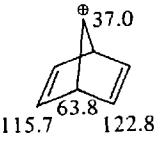

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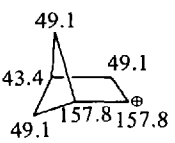

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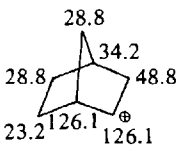

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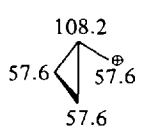
different chemical shifts of C–2,3 and C–5,6 reveal the unsymmetrical structure of (*27*), with the bridge bent toward one of the olefinic bonds. The bicyclo [2.2.1] hexyl cation (*28*) is a lower homolog of the norbornyl cation (*22*); all three CH_2 groups are equivalent at -110°C and the chemical shifts compare reasonably well with those of (*22*)[60].

Isotopic perturbation has been advanced as a novel tool for distinguishing between a symmetrical, delocalized structure of (*28*) and a pair of rapidly equilibrating ions[60a]. The ^{13}C–NMR spectrum of 2–D–(*28*) displays a relative isotopic splitting, $\delta/\Delta = 0.0058$, of the downfield carbon resonance. This value is an order of magnitude smaller than the relative isotopic splittings observed with equilibrating systems, e.g. 1,2-dimethylcyclopentyl cation ($\delta/\Delta = 0.085$). Comparably small values are found for isotopic perturbation of resonance in allylic systems, e.g. cyclohexenyl cation ($\delta/\Delta = 0.0035$). The relative splitting suggests that the structure of (*28*) is extensively σ-delocalized.

All cyclopropylcarbinyl cations show some charge delocalization into the three-membered ring, but only the primary system (*29*) is unique in its chemical shifts which suggest a delocalized structure[61]. The C–1–H coupling constants, however, do not support this conclusion. The non-equivalence of the methyl groups establishes the bisected geometry of (*31*), with slow rotation about the exocyclic C–C bond. The



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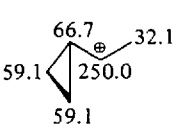

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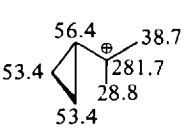

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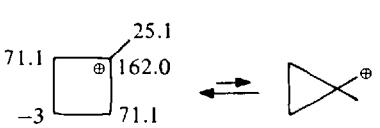

32 *33*

1-methylcyclopropyl-carbinyl cation (*33*) is thought to exist in a dynamic equilibrium with the 1-methylcyclobutyl cation (*32*), leading to equivalence of the three methylene groups[62a]. The (*32*) $\rightleftarrows$ (*33*) interconversion is frozen out at low temperatures. At -100°C the maximum population of (*33*) is less than 0.5%. In order to rationalize the very unusual $^{13}C^{+}$ chemical shift in (*32*), the possibility of sp^3 hybridization for this cationic center has been considered[62b].

3.2 Rearrangements

1,2-Alkyl and hydrogen shifts are normally fast on the NMR time scale down to -150°C. Selected degenerate rearrangements have been discussed in the preceding paragraph. Additional examples include the 2-butyl cation (*34*), in which the secondary-secondary hydrogen shift is faster than 10^4 sec^{-1} at −130°C ($\Delta G^{\neq} < 5.5$ kcal/

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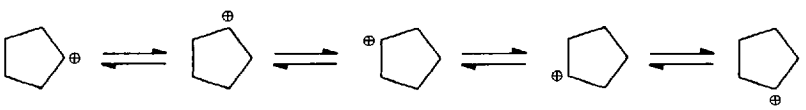

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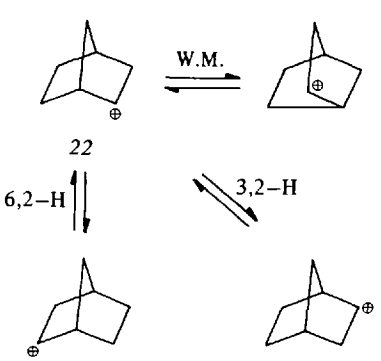
mol)[63], and the cyclopentyl cation (*35*) which shows a single ^1H–NMR line at -70°C as a result of complete scrambling of the nine hydrogens among the five carbons[64].

Superacids offer the chance of observing rearrangements that involve higher activation barriers[65–67]. At room temperature, the ^1H and ^{13}C–NMR spectra of the norbornyl cation (*22*) consist of single broad bands[11,42]. The equilibration is caused by fast 3,2 and 6,2-hydrogen shifts, and by Wagner-Meerwein rearrangement. The 3,2-hydrogen shift is frozen out by lowering the temperature to −70°C. From temperature-dependence studies the activation energy of this shift was established, E_a = 10.8±0.6 kcal/mol. The 3,2-shift is exceptionally slow, as compared with (*34*) or



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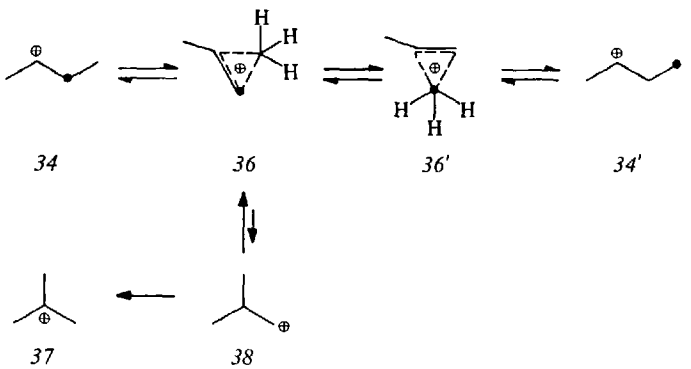
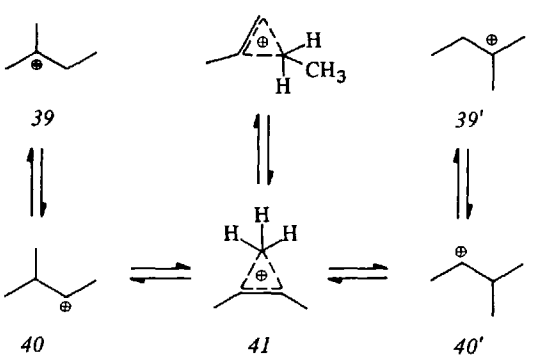
(*35*), which has been attributed to the diminished positive charge density at C–2. The spectrum of (*22*) remains unchanged between –70 and –120°C, but between –128 and –156°C the 6,2-hydrogen shift is frozen out (E_a=5.9±0.2 kcal/mol). The same order of rates (Wagner-Meerwein >6,2–H >3,2–H) is observed in solvolytic systems, but the differences in E_a appear to be much smaller (Section 7.6.2.5).

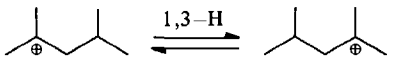
The 2-butyl cation (*34*) also exhibits energetically more demanding rearrangements in addition to its very rapid degenerate 2,3–H shift. A process which scrambles all the protons in (*34*) was studied by line-shape analysis of the ^{1}H–NMR spectrum at temperatures from –100 to –40°C (E_a=7.5±0.1 kcal/mol)[63, 66]. The most probable mechanism involves reversible formation of a corner-protonated methylcyclopropane (*36*) which undergoes degenerate corner-to-corner proton shifts. At higher temperatures the 2-butyl cation (*34*) rearranges to *t*-butyl cation (*37*) with an



activation energy of *ca.* 18 kcal/mol. This process probably proceeds through structures close to the primary isobutyl cation (*38*). The heat of reaction of the (*34*) → (*37*) transformation was measured by dynamic calorimetry, ΔH=14.5±0.5 kcal/mol[68]. The close correspondence between the values observed in superacid solution and in the gas phase (Table 1) indicates that the degree of electrostatic solvation varies little between isomeric carbocations.

The *t*-amyl cation (*39*) exchanges the two types of methyl groups (E_a=13.2 kcal/mol) and, at higher temperatures, the two methylene protons with the nine methyl protons (E_a=18.8 kcal/mol)[44,69,70]. Most of the former activation energy may be attributed to the formation of the secondary 3-methyl-2-butyl cation (*40*). The more





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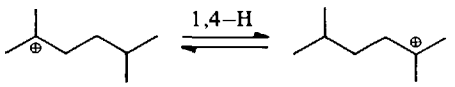

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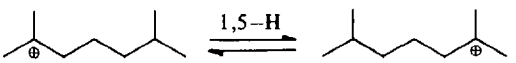

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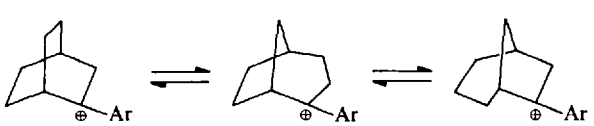
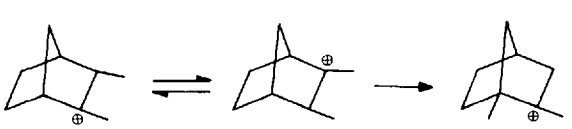
extensive redistribution is accounted for by corner-to-corner proton shifts in the protonated cyclopropane (*41*). Similar results have been obtained with methylcyclopentyl, *t*-hexyl and *t*-heptyl cations[65,66]. These studies establish upper limits for the energy differences between "classical" and bridged acyclic cations.

The NMR spectrum of 2,4-dimethyl-2-pentyl cation (*42*) in the temperature range from -110 to -70°C indicates rapid exchange of the nonequivalent methyl groups (E_a=8.5 kcal/mol)[71]. As the signal of the methylene protons remains unaffected, a direct 1,3 shift of hydrogen is the most plausible mechanism. Similar degenerate 1,4- and 1,5-hydrogen shifts have been shown to occur in (*43*) and (*44*), respectively. The relative rates decrease in the order 1,5>1,3>1,4–H shift.

Many rearrangements of bicyclic cations in superacids have been reported which are not observable under solvolytic or acidcatalyzed conditions. The equilibration of the arylbicyclooctyl cations (*45*)–(*47*)[72] and the rearrangement of the rapidly equilibrating 2,3-dimethyl-2-norbornyl cation (*48*) into the more stable 1,2-dimethyl-2-norbornyl cation (*49*)[73] may serve as examples. These transformations are thought



45 *46* *47*



48 *49*

to proceed by several steps involving tertiary→secondary Wagner-Meerwein rearrangements in combination with 6,2- and 3,2-H shifts. Elaborate studies of the camphene, fenchene and santene cation systems have led to valuable generalizations concerning

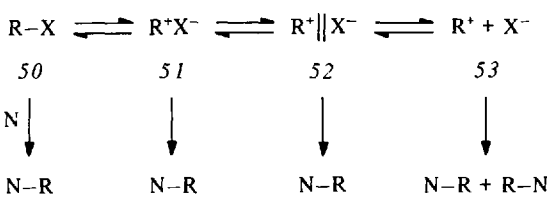
the energy requirements of the individual steps which enable one to predict the most favored reaction path[67, 74].

In summary, the observation of carbocations in superacids has provided a wealth of previously inaccessible information on structure and reactivity. The infinite lifetime of the cations precludes, of course, any stereochemical studies. On a scale of activation energies, the rearrangements studied in superacids overlap in part with those observed in more nucleophilic solvents and extend toward higher energy barriers.

4 Ion Pairs

4.1 Winstein's Ion Pair Scheme

The formation of ion pairs in solvolysis reactions is now well documented[75]. The separation of the charged species during heterolytic bond cleavage is not a continuous process but proceeds through a series of progressively more dissociated intermediates: an "intimate" or "internal" ion pair (*51*), a "solvent separated" or "external" ion pair (*52*), and the dissociated carbocation and counterion (*53*). Attack by a nucleophile may occur on the complete spectrum of cationic intermediates and on neutral substrate.



Evidence supporting this scheme will be summarized briefly. The common ion rate depression (mass law effect) is diagnostic for the regeneration of neutral substrate, RX, from dissociated ions (*53*). If the recombination rate is increased by a salt, MX, it is apparent that the X^- anions formed by ionization of RX and those corresponding to the added MX are chemically indinstinguishable. Thus ionization of RX in such cases must afford dissociated ions with little or no interaction between R^+ and X^-.

In addition to the kinetic effect, an exchange process could also be observed if the reaction medium contains isotopically labeled MX*. Whenever a common ion rate depression has been observed, it has also been possible to demonstrate exchange. With some substrates, however, exchange has been found in the absence of a mass law effect. In such cases it is likely that dissociated ions are not involved. Solvolysis and exchange are thought to take place via attack on the solvent-separated ion pair (*52*).

With optically active substrates (X attached to a chiral carbon atom), racemization may be taken as a measure of ionization. Whenever the rate of racemization, k_α,

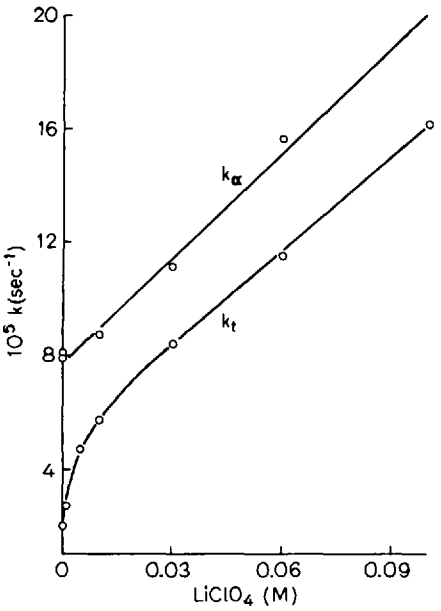


Fig. 1. Effect of added $LiClO_4$ on k_α and k_t in solvolysis of *threo*-3-p-anisyl-2-butyl brosylate in acetic acid. [Reproduced from Winstein, S., Robinson, G. C.: J. Am. Chem. Soc. *80*, 169 (1958).]

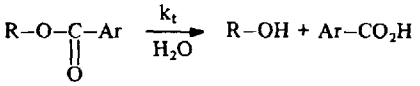
Table 6. Oxygen scrambling and racemization results for p-substituted benzhydryl p-nitrobenzoates (*54*)[76]

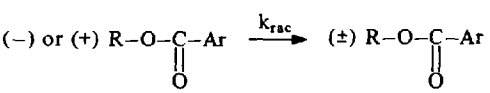
X	Temp. (°C)	rel. k_t	k_{eq}/k_t	k_{rac}/k_{eq}
Cl	99.6	1	2.4	0.35
H	99.5	2	2.9	–
CH_3	99.5	22	2.9	0.60
	48.8		3.0[1])	0.17[1])
OCH_3	99.5	2500	–	–
	48.8		2.4	0.28

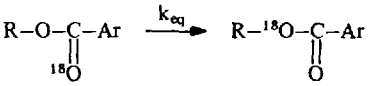
[1]) Extrapolated value.

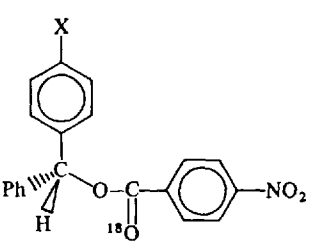
exceeds the titrimetric rate of solvolysis, k_t, return from ion pairs to neutral substrate is indicated. The addition of noncommon-ion salts (e.g., $LiClO_4$) will increase the ionic strength of a solvolysis medium and cause a rate acceleration. In some cases a steep nonlinear increase of k_t was produced with small amounts of $LiClO_4$ ("special salt effect") whereas k_α was found to depend linearly on [$LiClO_4$] (Fig. 1). The different response of k_α and k_t to noncommon-ion salts led Winstein and his coworkers to postulate the intermediacy of two different kinds of ion pair. Lithium perchlorate is thought to remove return from the solvent-separated ion pair (*52*) by formation of $R^+ \| ClO_4^-$ but does not affect internal return from the intimate ion pair (*51*).

Another powerful tool for the detection of internal return is ^{18}O equilibration in appropriately labeled benzoate and sulfonate esters. Goering and co-workers have determined k_t, k_{eq}, and k_{rac} for a series of benzhydryl p-nitrobenzoates (*54*) with *para* substituents ranging from chloro to methoxy (Table 6)[76]. Whereas k_t varied by more than 10^3, k_{eq}/k_t remained essentially constant. $k_{rac}/k_{eq}<1$ reveals internal return with retention of configuration. The slight increase in k_{rac}/k_{eq} with increasing reactivity indicates a weakening of the attractive forces in the ion pair. When sodium azide was added to the solvolysis of (*54a*), k_{rac} dropped to zero. With (*54b*) and (*54c*), however, the addition of sodium azide resulted in only slight decreases in k_{rac}. Furthermore, (*54b*) yielded retained alcohol and inverted azide products. These observations were interpreted in terms of the ion pairs (*51*) and (*52*) of which only (*52*) is captured by azide.

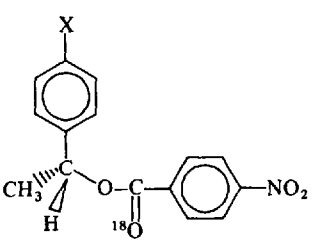








54a X = Cl
b X = CH_3
c X = OCH_3



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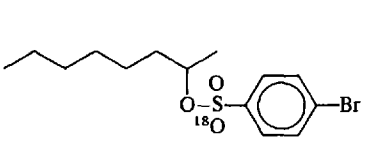

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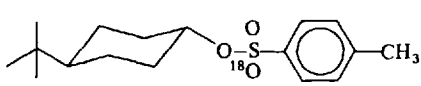

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The stereochemistry of ion pair return for 1-phenylethyl *p*-nitrobenzoates (*55*) also depends on the lifetime of the intermediate ion pair[77]. In accord with these views the unreactive secondary sulfonates (*56*) and (*57*) show small ratios of k_{eq}/k_t (Table 7)[78]. The inversion of stereochemistry upon solvolysis of (*56*) and (*57*)[79] indicates that the reactions proceed largely by intimate ion pairs.

Table 7. Oxygen equilibration data, k_{eq}/k_t, for alkyl arenesulfonates[78]

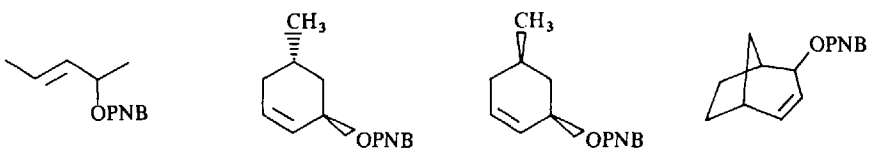
Solvent	k_{eq}/k_t	(56)	(57)
CH_3OH		0.011	–
CH_3CO_2H		0.066	0.041
HCO_2H		0.088	0.030
CF_3CO_2H-CF_3CO_2Na		0.248	0.082

This brief account of nonrearranging systems demonstrates that ion pairs are potentially chiral intermediates of limited configurational stability. It will be of considerable interest to examine the effects of ion pairing on the rearrangements of carbocations.

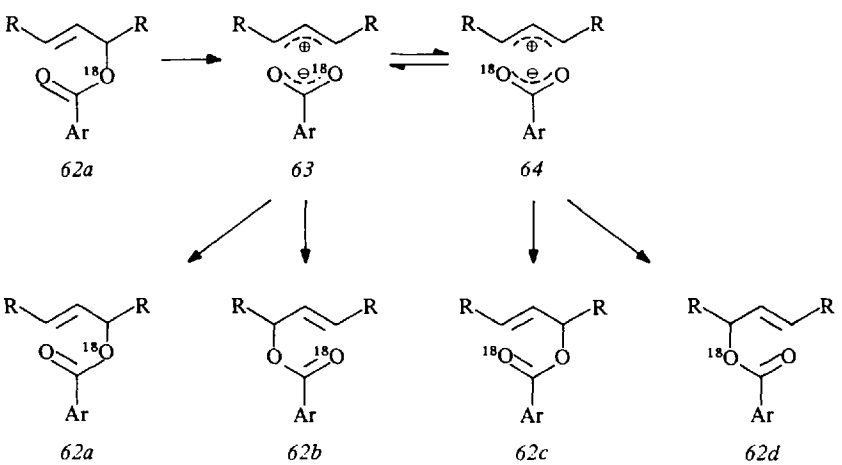
4.2 Rearrangements within Ion Pairs

4.2.2 Wagner-Meerwein Rearrangements

Goering and his associates studied the solvolysis of several allylic p-nitrobenzoates which can give symmetrical allyl cations, (*58*)–(*61*)[80-82]. For all four systems, the rate of racemization, k_α, was found to be greater than k_t. External return was not involved. In the cyclic systems (*59*) and (*60*) geometrical purity was preserved during



58 *59* *60* *61*



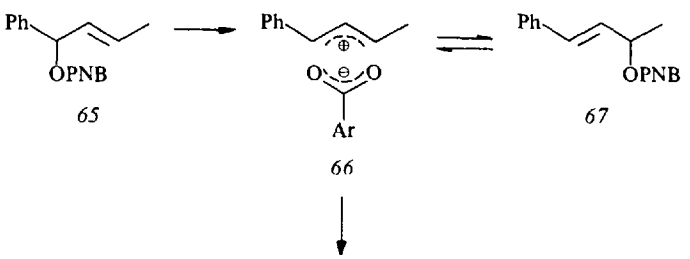
62a *63* *64*

62a *62b* *62c* *62d*

solvolysis, i.e. (*59*) and (*60*) did not interconvert[80]. Originally these results were taken to mean that in allylic systems ion pair return in general is stereospecific in that the anion remains on the side of the planar cation from which it departed. Later it was recognized that conformational factors might be responsible for the stereospecificity observed in the 5-methyl-2-cyclohexenyl system[83]. Ion pair return associated with solvolysis of (*61*) and its endo isomer resulted in considerable interconversion of geometric isomers[81]. In this bicyclic system the cyclohexenyl cation is conformationally rigid. Thus, unlike in the 5-methyl-2-cyclohexenyl system, intermediates derived from the geometric isomers cannot differ conformationally.

For (*58*) and (*60*) k_{eq} was found to equal k_{rac}[80, 82]. Thus it appears that internal return in allylic systems results in racemization and complete oxygen equilibration. However, this result is also consistent with an ion pair (*63*) which retains coordination of the ether oxygen to the carbon atom from which it departed. (*63*) would produce an equimolar mixture of (*62a*) and (*62b*). Determination of the ^{18}O distributions of both recovered enantiomers from the solvolysis of (*60*) revealed identical scrambling, i.e. rapid interconversion of ion pairs (*63*) and (*64*)[82]. With (*58*), however, predominant product formation from (*63*) was indicated by excess carbonyl-^{18}O in the inverted ester and excess ether-^{18}O in the ester of retained configuration[80].

The asymmetric α-phenyl-γ-methylallyl p-nitrobenzoate (*65*) undergoes simultaneous solvolysis and isomeric rearrangement to the α-methyl-γ-phenylallyl isomer (*67*)[84]. The latter is *ca.* 300 times less reactive than (*65*) and accumulates. At higher temperatures (*67*) solvolyzes without rearrangement. In this case return results in reformation of (*67*); the much more reactive (*65*) cannot accumulate under conditions for the solvolysis of (*67*). Two independent measures of ion pair return are available in this system: k_{eq}/k_t, determined with ^{18}O-labeled (*67*), was found nearly as large as the ratio of (*67*) to solvolysis products observed with (*65*). This means that return from ion pair (*66*) to regenerate (*67*) results in almost complete oxygen equilibration. The amount of carboxyl-oxygen scrambling for the (*65*) → (*67*) isomerization was also found to be essentially complete.

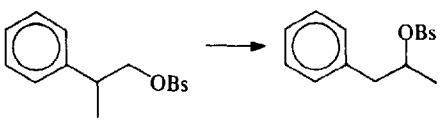


Ion pair return from (*66*) results in partial loss of enantiomeric purity[85]. The amount lost starting with (*67*) was determined from the k_{rac}/k_{eq} ratio and the amount lost starting with (*65*) was determined from the enantiomeric purity of (*67*) produced in the solvolysis of optically active (*65*). Within experimental error the stereochemistry of return is the same starting from either (*65*) or (*67*), e.g. 65% racemization in 90% aqueous acetone. About one third of the return involves rebond-

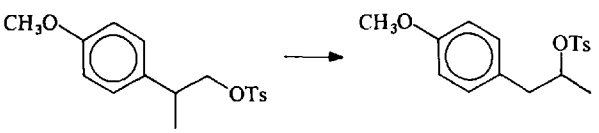
ing of the anion on the opposite side of the planar allyl cation from which it departed. The amount of racemization associated with the return decreases as the water content of the solvent increases. The more capturable ion pairs racemize more readily. Attack of water on chiral ion pairs might give optically active alcohols, but unfortunately the stereochemistry of the solvolysis products has not been reported.

4.2.2 Wagner-Meerwein Rearrangements

The ^{18}O-equilibration technique was applied to several systems which undergo 1,2 alkyl or aryl shifts. The first study with a labeled sulfonate was carried out by Denney and Goldstein[86] who rearranged (*68*) to (*69*) (25% scrambling of ether-^{18}O) and



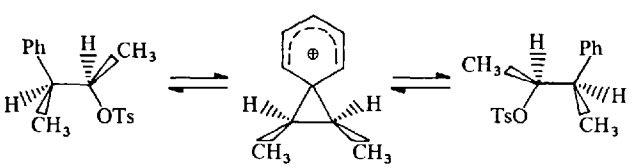
68 *69*



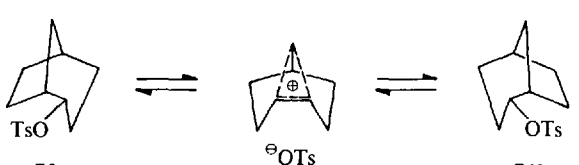
70 *71*

(*70*) to (*71*) (complete equilibration of ^{18}O). The solvolysis of (*70*) appears to involve an intermediate which is more dissociated than that from the phenyl derivative (*68*). This conclusion is supported by the observation of a special salt effect for (*70*) but not for (*68*).

In these early studies equilibration was not correlated with an independent measure of ion pair return. If initial ionization leads to an ion pair whose cationic fragment is either an achiral bridged species or a rapidly equilibrating pair of enantiomers,



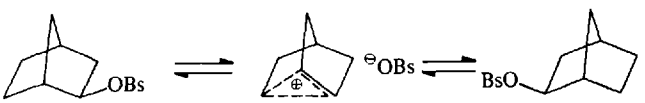
72a *72b*



73a *73b*

then the argumentation developed for allylic systems may be applied analogously. Goering and Thies[87] have studied ^{18}O-scrambling in the solvolysis of (*72*) and (*73*). Both compounds can give achiral ion pairs and in each case k_{rac} was observed to be twice as large as k_{eq}. Therefore at least 50% of the ion pair return occurs without oxygen equilibration. Resolution of the enantiomers (*72a*) and (*72b*) revealed that the same amount of equilibration occurs when the anion rebonds to the original carbon atom as for return with rearrangement. From the effect of lithium perchlorate on ^{18}O-scrambling in related systems it was concluded that $k_{eq}/k_{rac} = 0.5$ is characteristic of internal return from sulfonate ion pairs whereas external return involves complete equilibration[88].

The solvolysis of optically active *exo*-2-norbornyl brosylate (*74*) affords completely racemic products. The rate of racemization exceeds the rate of solvolysis, indicating return from an achiral ion pair[89]. Products of return to isomeric cations were isolated from the solvolysis of many substituted norbornyl sulfonates; some



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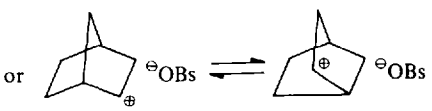
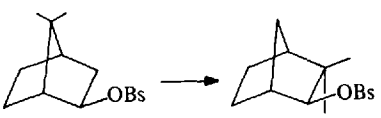
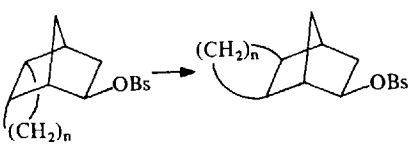
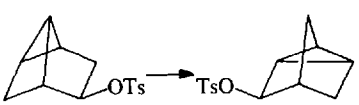




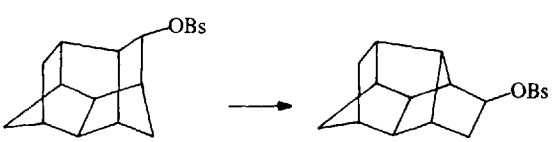
75[90]



76 n=1[91], 2[92], 3[93]



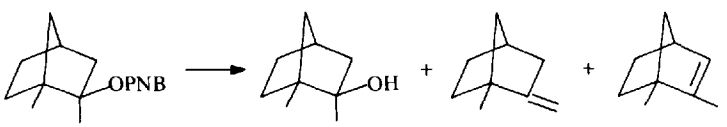
77[94]



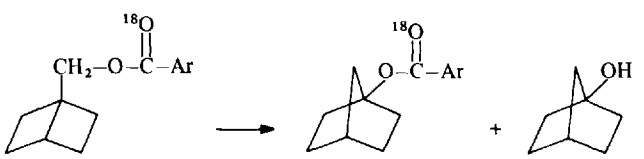
78[95]

recent examples are given by formulas (*75*) to (*78*)[90-95]. These rearrangements appear to be stereospecific, no *endo* products were found. The stereospecificity may be attributed to the bridged structure of the norbornyl cation[11] or, alternatively, to the *exo* preference exhibited by the U-shaped norbornane skeleton[12].

In contrast to (*74*), optically active 1,2-dimethyl-2-norbornyl p-nitrobenzoate (*79*) gives active products; the S_N1 product (*80*) is formed with *ca.* 9% and the E1 product (*81*) with *ca.* 63% retention of configuration[96]. Interconversion of enantiomeric 1,2-dimethylnorbornyl cations apparently competes with the product forming steps. The different optical purities of (*80*) and (*81*) show that they are derived from different intermediates. The authors suggest that most, or all, of the E1 product is formed from an intimate ion pair and that the S_N1 product is formed from a solvent-separated ion pair or a dissociated carbocation. Solvolysis is accompanied by ion pair return which results in racemization of (*79*) and equilibration of ^{18}O-labeled (*79*). The rate of racemization exceeds that of scrambling of ^{18}O by a factor of *ca.* 2. Substrate re-formed by ion pair return must be at least as optically active as the E1 product (*81*). Therefore, k_{rac} and k_{eq} correspond to upper limits of 37% and 20% of the total return, respectively. Scrambling of ^{18}O detects only a small fraction of the total ion pair return in the solvolysis of (*79*).



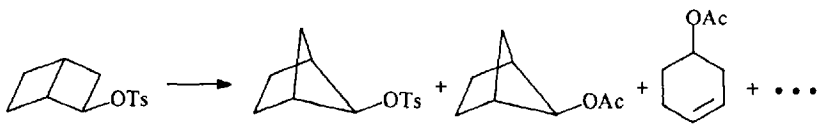
79 *80* *81*



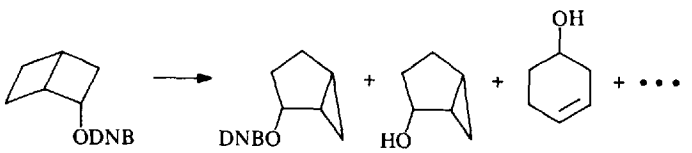
82 *83* *84*

There is an obvious relationship between the stability of the ion pair intermediates and the amount of ^{18}O equilibration associated with their return. It is not surprising, therefore, that the solvolysis of labeled neopentyl tosylate was not accompanied by ^{18}O scrambling in recovered starting material[97]. The stage of primary ion pair is most probably by-passed in the solvolysis of neopentyl derivatives (i.e., migration and ionization are concerted). Even if a primary ion pair were formed, return would not compete with rearrangement. The strained primary p-nitrobenzoate (*82*) afforded 81% of the rearranged ester (*83*) with no detectable ^{18}O equilibration[98]. Nevertheless 19% of 1-norbornanol (*84*) were formed the oxygen of which is derived from the solvent. The origin of (*84*) presents an unresolved problem. An ion pair which is tight enough to preclude oxygen equilibration is not likely to be captured by water. On the other hand, the formation of a more dissociated species (which does not return) is also unlikely in view of the instability of the 1-norbornyl cation.

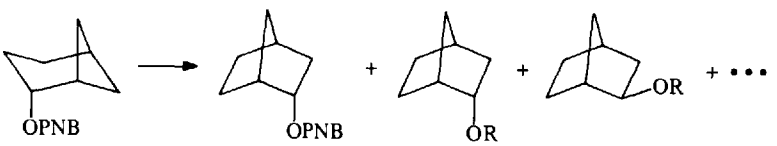
Compounds (*85*)–(*88*)[99–102] represent some more substrates which afford rearranged ion pair return products in an apparently stereospecific manner, with inversion at the origin of the 1,2 alkyl shift. Formation of *endo*-2-norbornyl p-nitrobenzoate from (*87*) is noteworthy because ion pair return occurs contrary to the "natural" *exo* preference of the norbornyl cation[101]. The stereochemistry of return may be explained in terms of bridged carbocations. Alternatively the anion may rebond to the same side of the carbon framework from which it departed. Although return to the opposite side was clearly established with allyl cations (Section 4.2.1), reorien-



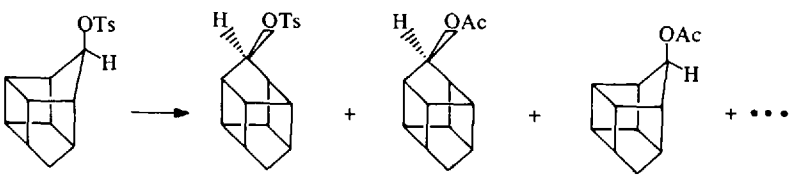
85[99]



86[100]



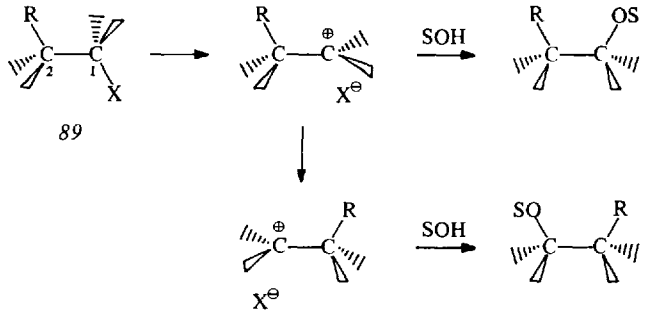
87[101]



88[102]

tation of the anion is less likely in the present systems. The tightness of ion pairs undoubtedly increases with decreasing stability of the carbocation (cf. the account of ^{18}O equilibration given above). However, the configurations of the major solvolysis products from (*85*)–(*88*) conform to those of the return products. The analogous stereochemistry of products derived from various stages of the ionization process speaks in favor of bridged ions.

In the absence of bridging attack by solvent on a rearranging ion pair should lead to retention of configuration at the migration origin. The migrating group (R) and the departing anion (X) will assume *anti* positions, cf. (*89*), to allow for anchimeric



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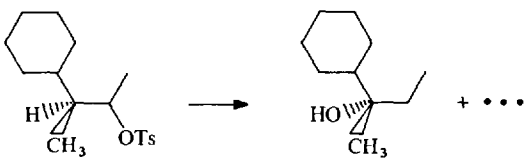

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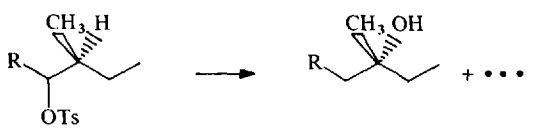
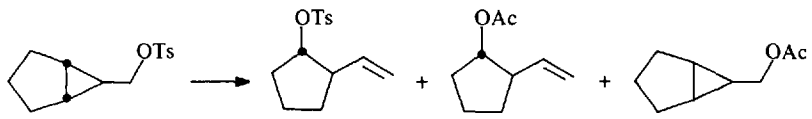


91

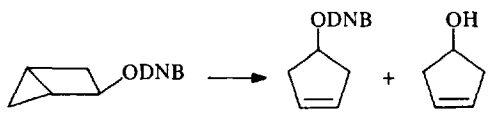
assistance or conformational control (Section 6). Shielding of one side of the carbon framework by the anion leaves the other side exposed to solvent. The expected result is inversion at the migration terminus (C–1) and retention at the migration origin (C–2). Whereas inversion at C–1 is the rule [cf. (*56*) and (*57*)[79]], retention at C–2 was found only in 1,2 hydrogen shifts. The tertiary alcohols obtained from the solvolysis of 3-cyclohexyl-2-butyl tosylate (*90*)[103] and of various 3-methyl-4-alkyl tosylates (*91*)[104] were formed with *ca.* 50% retention of configuration. Less retention was found in the presence of lithium perchlorate[104]. This "salt effect" supports the idea that the stereochemistry is controlled by ion pairing. Retention of configuration at the migration origin has rarely, if ever, been observed in alkyl or aryl shifts. Either these groups migrate by a different mechanism (*via* bridged ions) or shielding by the migrating alkyl predominates over shielding by the counterion.

4.2.3 Rearrangements to Remote Positions

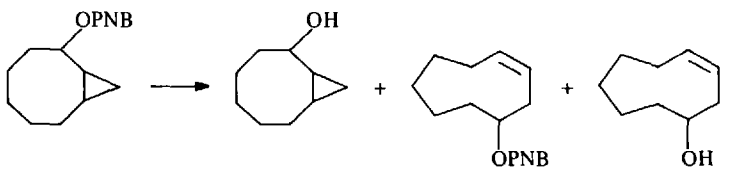
Ion pair return to positions more remote than the adjacent carbon is quite common with homoallyl-cyclopropylcarbinyl cations, cf. compounds (*92*)–(*94*)[105–107]. Even the vinyl tosylate (*96*) is produced from either of the allenic isomers (*95*) and (*97*)[108]. In contrast, 5-norbornen-2-yl brosylate (*98*) does not yield any nortricyclyl brosylate (*99*) although scrambling of a deuterium label, (*98a*) $\rightleftarrows$ (*98b*), is *ca.* 12 times faster than solvolysis[109].



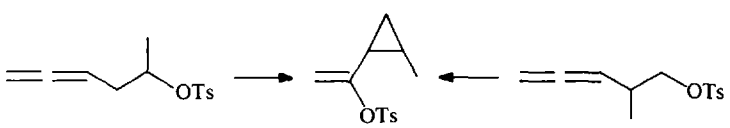
92[105]



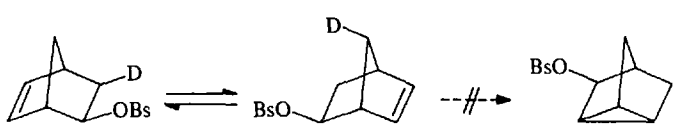
93[106]



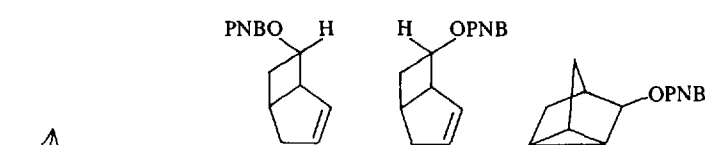
94[107]



95 *96* *97*



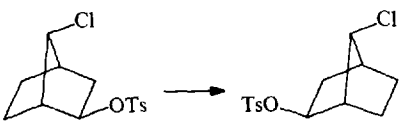
98a *98b* *99*



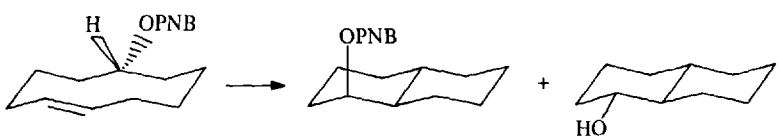
100	96.0	1.9	2.1
101	60.4	39.6	trace

The tricyclo [3.2.0.0^{2,7}] hept-3-yl p-nitrobenzoates (*100*) and (*101*) provide interesting stereochemical aspects [110]. Hydrolysis of either epimer proceeded with 9-11% ion pair return to unreactive esters. Whereas the hydrolysis product distribution was essentially the same from either epimer, the ion pair return product distributions were different. (*100*) and (*101*) apparently ionize to separate ion pairs, but return is much less stereospecific than with the Wagner-Meerwein related pairs discussed above.

Ion pair return to products resulting from a 1,3 hydrogen shift was observed concurrently with acetolysis of 7-chloro-2-norbornyl tosylates[111]. The *syn-exo* tosylate (*102*) is converted into the *anti-exo* isomer (*103*) but the reverse reaction could not be detected.



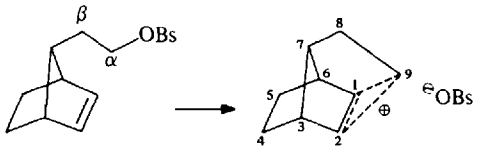
102 *103*



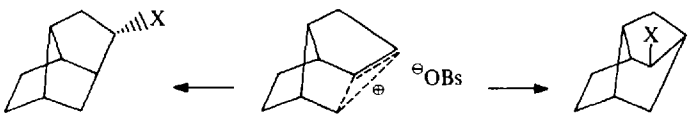
104 *105* *106*

Goering has examined the steric course of the rearrangement of *trans*-cyclodec-5-enyl p-nitrobenzoate (*104*) into 1-decalyl p-nitrobenzoate (*105*), and also measured the extent of ^{18}O scrambling[112]. Working with (*104*) of known absolute configuration inversion of stereochemistry at C–1 was demonstrated. The configuration of (*105*) corresponds to *cis* addition of carbon and p-nitrobenzoate to the double bond. The solvolysis product (*106*) has the opposite configuration at the hydroxyl bearing carbon, in accord with the views presented in Section 4.2.2. Despite the long distance that the p-nitrobenzoate anion has to migrate, there is only 70% equilibration of the oxygens as demonstrated with ether and carbonyl ^{18}O-labeled (*104*).

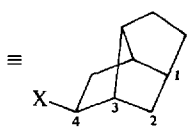
Multiple cation automerizations in tight ion pairs have been studied with π-route generated 2-brexyl cations (*108*). The solvolysis of β-(*syn*-7-norbornenyl) ethyl brosylate (*107*) leads to a mixture of *exo*-4-brexyl (*110*) and *exo*-2-brendyl derivatives (*111*)[113]. These results are rationalized by a hydrogen shift which converts the initially formed 2-brexyl ion pair (*108*) to the product forming intermediate (*109*). Studies with either α- or β-labeled (*107*) revealed that the initial 2-brexyl-cation (*108*) undergoes Wagner-Meerwein automerizations (*108a, b, c*) prior to hydrogen migration[114]. Significantly, returned 2-brendyl brosylate (*111*-OBs) showed virtually the same distribution of labels as *exo*-2-brendyl acetate (*111*-OAc). Thus, reorientation and return of the anion competes quite effectively with attack by solvent during acetolysis. Most of the products arise by a hydrogen shift from C–9 in the initial ion pair (*108a*). The authors suggest that the counterion in the initial ion pair (*108a*)



107 *108*



109



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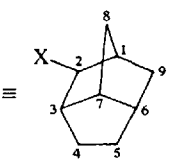

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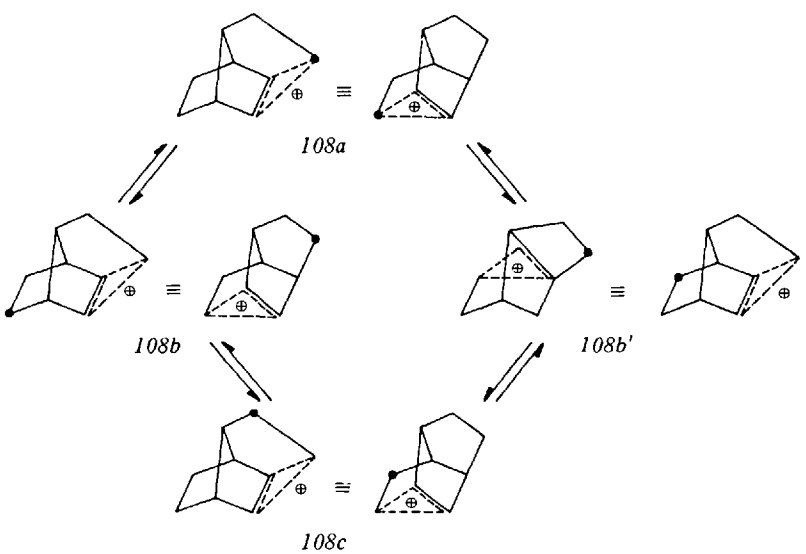


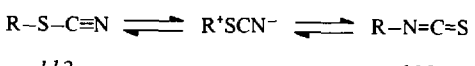
108a *108b* *108b'* *108c*

retards the rate of rearrangements which increase the effective charge separation (e.g., Wagner-Meerwein automerization) and enhances the rate of any process which decreases the net charge in the ion pair [e.g., (*108*) → (*109*)]. It remains to be seen whether the regiodirective effect of the counterion is of general importance.

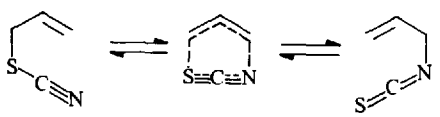
4.2.4 Ambident Anions

An ambident anion is one with different kinds of atoms which may become attached to a carbocation. Isomerization of the anionic portion permits detection of ion pair return in close analogy to the equilibration of ^{18}O labeled benzoate or sulfonate esters. The isomerization of thiocyanates (*112*) to isothiocyanates (*113*) is the most studied of these ambident rearrangements[115, 116]. In some respects these reactions differ from the return processes of carboxylate or sulfonate ion pairs:

(a) Common ion exchange is enhanced, and sometimes even proceeds by attack on covalent substrate, due to the high nucleophilicity of the thiocyanate anion.



112 *113*

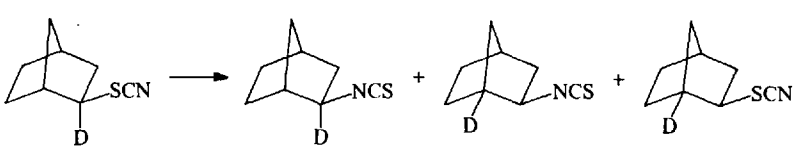


114

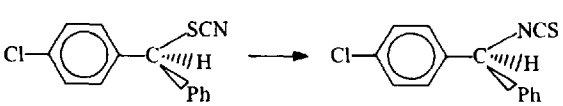
(b) A concerted, electrocyclic mechanism is available for the isomerization of allylic thiocyanates (*114*).

(c) In the recombination of carbocations with thiocyanate attack on sulfur is kinetically favored. However, isothiocyanates accumulate because isothiocyanate is a very poor leaving group. Only those isothiocyanates dissociate which can give rise to particularly stable carbocations.

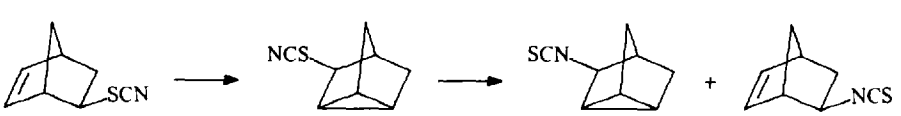
2-*exo*-Norbornyl thiocyanate (*115*) gave only 2-*exo*-norbornyl products. Deuterium labeling showed that isothiocyanates (*116a*) and (*116b*) were formed in equal



115 *116a* *116b*



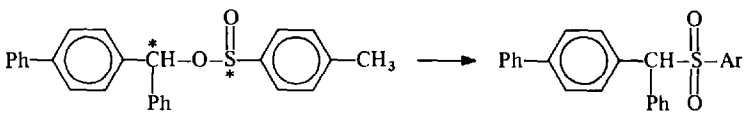
117 *118*



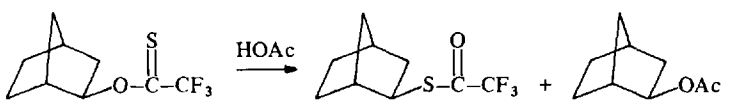
119

amounts, but no 6,2- or 3,2- hydrogen shifts were observed[117]. Optically active (*115*) was rapidly racemized (k_α/k_{is} = 2.85) and the isothiocyanate (*116*) formed was racemic. The rapid racemization of the norbornylthiocyanate ion pair contrasts with the rearrangement of chiral p-chlorobenzhydryl thiocyanate (*117*) which gave the corresponding isothiocyanate (*118*) with 61% retention of configuration[118]. The rearrangement of 5-norbornen-2-yl thiocyanate (*119*) afforded nortricyclyl derivatives[119]; this type of return was not observed in the solvolysis of the corresponding brosylate (*98*) [109]. No tricyclic products were obtained from 7-norbornenyl and 7-norbornadienyl thiocyanates[120].

The rearrangement of sulfinate esters to sulfones has also been investigated. Detailed understanding of the mechanism results from the acetolysis of chiral (asymmetric sulfur and carbon) p-phenylbenzhydryl p-toluenesulfinate (*120*)[121]. Fava found that (*120*) undergoes epimerization at sulfur with complete retention at carbon. Sulfone (*121*) was formed in 33% optical purity, together with a small amount of racemic acetate. It appears that epimerization at sulfur is due to return from the intimate ion pair whereas sulfone (*121*) can form from both intimate and solvent-separated ion pairs.



120 *121*



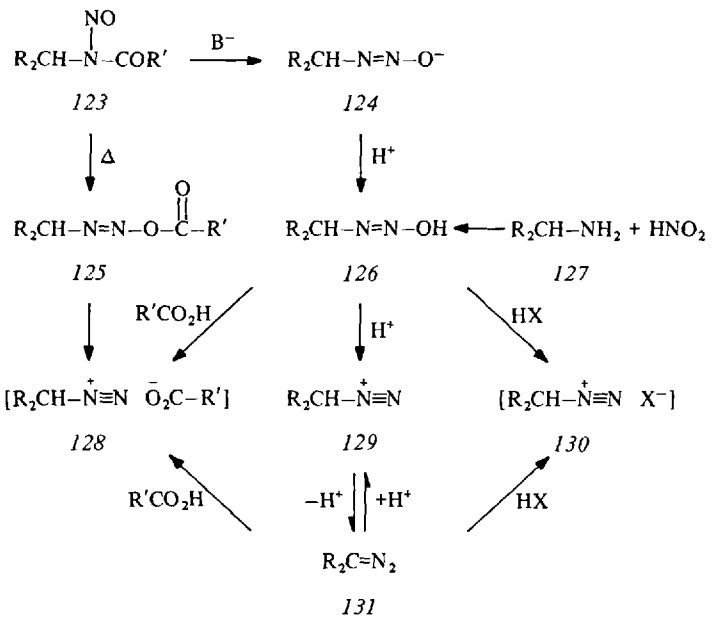
122

The isomerization of thioncarboxylates to thiolcarboxylates has been less extensively studied, but also served to demonstrate the formation of a symmetrical (or rapidly equilibrating) intermediate from the norbornyl derivative (*122*). Acetolysis of optically active (*122*) gave $k_\alpha = k_t$, i.e., there is no ion pair return to (*122*). The products were racemic and a deuterium label at C–2 of (*122*) was equally distributed among C–1 and C–2 of the products[122].

4.3 Ion Pairs from Diazonium Ions

Diazonium ions, with the exception of aryl examples, readily undergo loss of a nitrogen molecule to generate carbocations[123–126]. Some of the different ways in which diazonium ions may be formed are listed below.

a) The deamination (diazotization) of primary alkylamines (*127*); [127]
b) the reaction of diazoalkanes (*131*) with acids; [128]
c) the thermal rearrangement of N-alkyl-N-nitrosoamides (*123*); [129]
d) the solvolysis of alkanediazotates (*124*);[125].



In polar (aqueous) solvents all of these reaction pathways merge to give a common product-forming intermediate[130] which may be regarded as the solvated diazonium ion (*129*). Reactions of diazoalkanes (*131*) with acids and decompositions of N-nitroso-N-alkylamines (*123*) are readily carried out in non-polar solvents and are well suited for the generation of ion pairs. Under special conditions ion pairs may intervence even in the nitrous acid deamination of amines (*127*) and in the solvolysis of alkanediazotates (*124*). When a diazonium ion pair collapses the carbocation and its counterion are initially separated by nitrogen. However, ion pairs generated from diazonium ions behave very much like those arising from the direct heterolysis of a C–X bond. Evidence supporting this statement will be discussed in the following paragraphs.

4.3.1 Protonation of Diazoalkanes

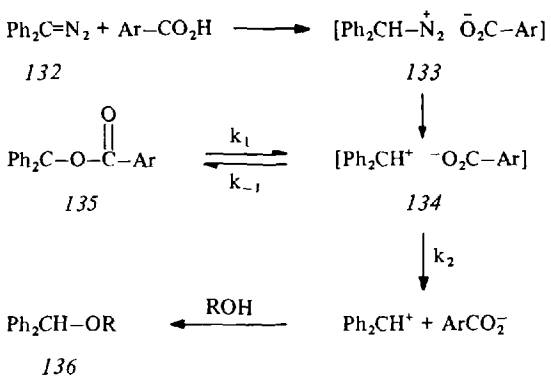
The most detailed comparison of ion pairs from diazonium ion and ester precursors has been made in the reaction of diphenyldiazomethane (*132*) with benzoic acids and in the solvolysis of benzhydryl benzoates (*135*)[131]. If the diphenyldiazomethane reaction is carried out at sufficiently low temperatures for the ester formed not to undergo subsequent ionization, the fraction of (*135*) in the total products corresponds to the ratio $k_{-1}/(k_{-1}+k_2)$. The same ratio in the ester solvolysis is given by $k_{eq}/(k_{eq}+k_t)$ of ^{18}O-labeled (*135*). The results for the two reactions are quite close (Table 8). The small discrepancy may be due to the fact that k_{eq} provides too low a measure of ion pair return from (*134*), some return occuring without equilibration.

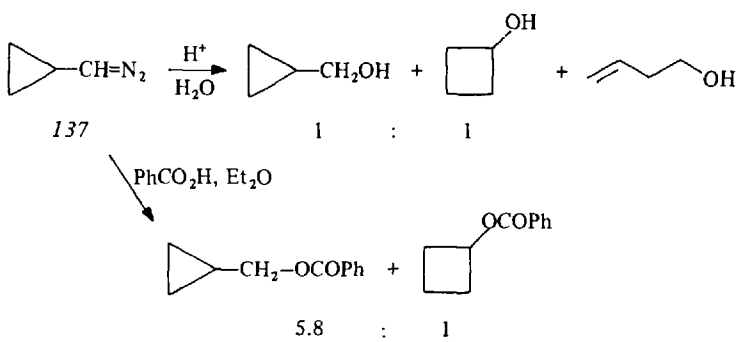
Rearrangements which proceed readily with solvated diazonium ions are often minimized by ion pairing. For example, the reaction of 1-diazopropane with benzoic acid in benzene gives nearly pure 1-propyl benzoate, but the action of aqueous per-

Table 8. Percent return for the reactions of (*132*) and (*135*)

	Ar = Ph EtOH, 110 °C	Ar = 4-NO_2–C_6H_4 90% aq. acetone 118.6 °C
Solvolysis of (*135*)	47	74.5
(*132*) + $ArCO_2H$	56[1])	82[1])

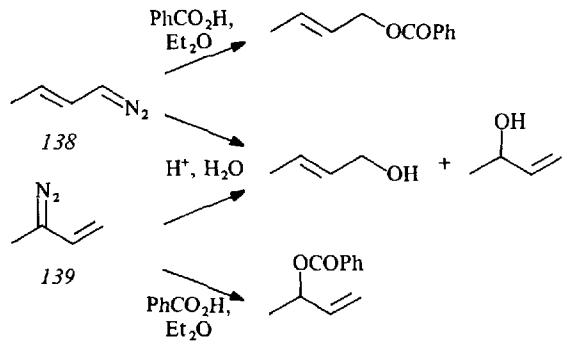
[1]) Data extrapolated from lower temperature.

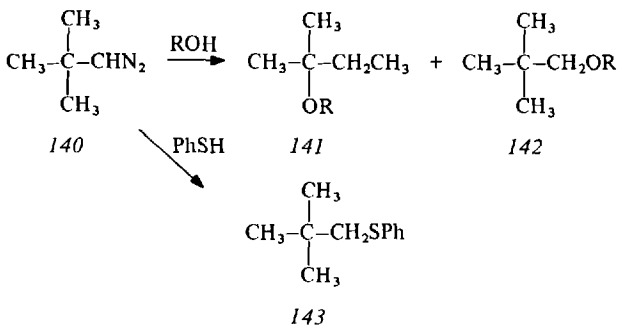




chloric acid on 1-diazopropane gives a propanol mixture containing 28% of 2-propanol[130]. Protolysis of cyclopropyldiazomethane (*137*) in water gives cyclopropylmethanol and cyclobutanol in a 1:1 ratio, along with a small amount of 3-buten-1-ol. However, reaction of (*137*) with etheral benzoic acid proceeds with much less skeletal rearrangement (cyclopropylmethyl: cyclobutyl = 5.8)[132].

For the reactions of the isomeric diazobutenes (*138*) and (*139*) with benzoic acid in ether solution the principal product isolated is in each case the unrearranged butenyl benzoate[133]. Under these conditions a benzoate anion is specifically associated with the carbon atom from which the nitrogen is lost. On the other hand, in the reaction with perchloric acid in aqueous solution each isomer yields a similar mixture of alcohols.



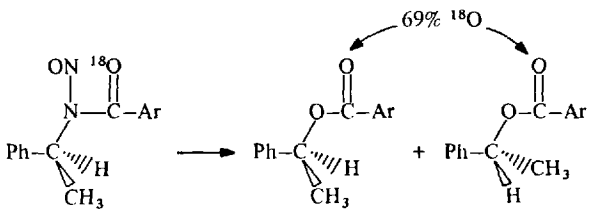


The amount of rearrangement depends not only on the nature of the solvent but also on the nucleophilicity of the counterion of the $RN_2\ ^+X^-$ pair. Diazoneopentane (*140*) in hydrocarbon solvents reacts with methanol, phenol, and carboxylic acids to give largely rearranged t-amyl products (*141*), along with small amounts (2-20%) of neopentyl derivatives (*142*)[134]. The reaction of (*140*) with thiophenol, however, affords nearly pure (99.8%) neopentyl phenyl sulfide (*143*). Presumably, the thiophenolate anion displaces nitrogen within the ion pair before rearrangement can occur.

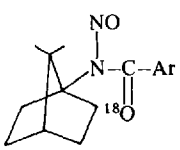
4.3.2 Thermolysis of *N*-Nitrosoamides

The first step in the decomposition of nitrosoamides (*123*) is formation of the diazo ester (*125*) which fragments to a diazonium ion pair (*128*)[129]. The ion pairs thus produced differ from those obtained in the reaction of diazoalkanes with acids. The ratio of ester to ether formed in the decomposition of *N*-nitroso-*N*-benzhydrylbenzamides in alcohol is lower than that found in the reaction of diphenyldiazomethane (*132*) with acids, and in the solvolysis of benzhydryl benzoate (*135*)[135, 136]. This effect has been attributed to the intervention of *trans*-diazo ester in the decomposition of (*125*) which leads to a greater distance between carbocation and carboxylate anion. In the diazoalkane reaction attack of the acid occurs at the electron-rich carbon atom to generate the carboxylate in the immediate vicinity of the incipient carbocation.

The decomposition of nitrosoamides is especially suited to the formation of optically active diazonium ions with specifically oriented counterions. Internal return of the carboxylate proceeds invariably with predominant retention of configuration[129]. The configuration of "external" products ranges from retention to inversion, depending on the nature of the solvent[130, 137]. The thermolysis of optically active *N*-nitroso-*N*-(1-phenylethyl) naphthamide (*144*) was studied with ^{18}O in the carbonyl position[137]. The ester (*145*) was formed with 72% retention of configuration and 38% racemization. Surprisingly, the ^{18}O distribution was identical in the optically active and racemic fractions, 69% of the excess ^{18}O was found in the carbonyl group of (*145*). The ions must be free for a finite period of time as some mixing of the label



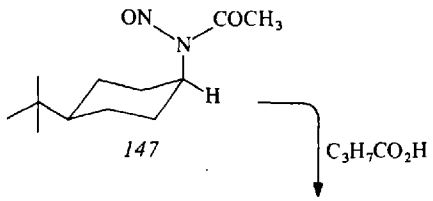
(*S*)–*144* (*S*)–*145* (81%) (*R*)–*145* (19%)



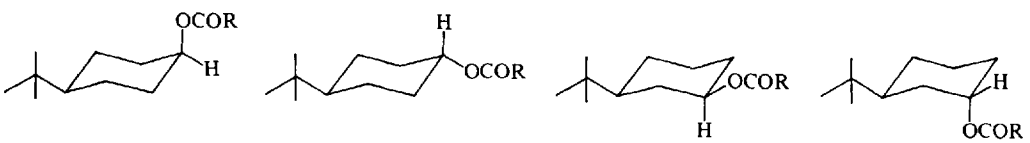
146

occurs; on the other hand the steps leading to the ester are fast enough to compete successfully with randomization of the oxygens. In contrast to (*144*), complete equilibration of ^{18}O was observed in the ester derived from the bridgehead nitrosoamide (*146*)[137]. Since a bridgehead carbocation would be expected to be shorter lived than an α-phenylethyl cation, equilibration of the label is most likely to occur at the diazonium ion stage.

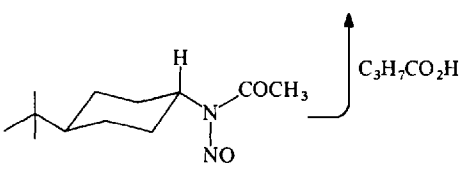
In spite of their tightness, ion pairs generated from nitrosoamides may undergo rearrangement. The stereochemical course of a 1,2 hydrogen shift has been studied in the butyrolysis of the *cis*-4-tert-butylcyclohexylamine derivative (*147*) which allows for dissection of "internal" (R=CH_3) and "external" products (R=n-Pr)[138]. The ratio of internal to external substitution at the rearranged position (2.8:1.1) is somewhat smaller than the corresponding value at the unrearranged position (7.8:1.7). The internal nucleophile favors a "least motion" attack at both sites: axial at C-4, and equatorial at C-3. The external nucleophile shows a rather weak stereochemical preference, opposite to that of the internal return. The *trans*-nitrosoamide (*148*) does not produce significant amounts of rearranged products. Clearly, the 1,2 hydrogen shift has stringent stereochemical requirements, and the counterion does not greatly



R = CH_3	7.2	0.6	2.7	0.1
R = C_3H_7	0.7	1.0	0.3	0.8



R = CH_3	4.9	33.9	0.2	0.1
R = C_3H_7	6.7	27.0	0.1	0.2

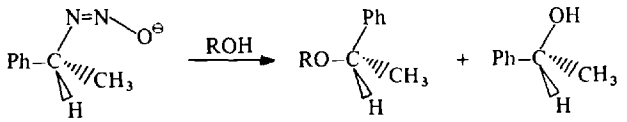


change its stereochemical relationship with the cation in the time required for migration of hydrogen.

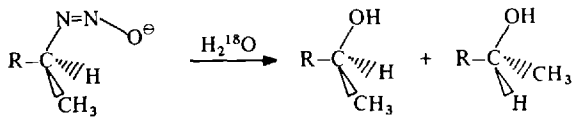
4.3.3 Acidolysis of Diazotates

Alkanediazotates (*124*) are formed by base-induced deacylation of nitrosoamides (*123*) and can be isolated from aprotic solvents in the form of their alkali metal salts[139]. This procedure affords the *Z* isomers, as confirmed by X-ray analysis[140]. The *E* isomers are accessible from alkylhydrazines, isoamyl nitrite, and base[141]. Diazotates are the conjugate bases of diazohydroxides (diazotic acids) (*126*). At the stage of the diazohydroxide the protonation of a diazotate would be expected to merge with the nitrous acid deamination of a primary amine. However, diazotate salts can be decomposed under a wide variety of conditions, including addition of one equivalent of a proton donor in an aprotic solvent. The protonation of diazotates provides a unique source of diazonium hydroxide ion pairs which, by loss of nitrogen generate the correspondingly paired carbocations.

In the alcoholysis of 1-phenylethanediazotate (*149*), reaction with the external nucleophile affords 1-alkoxy-1-phenylethane (*150*) (44-64%) whereas return of the hydroxide ion gives 1-phenylethanol (*151*) (18-29%). When optically active (*149*) is employed, the ether (*150*) is formed with predominant inversion and the alcohol (*151*) with high retention of configuration[142, 143]. The data on solvent and salt effects suggest that both products arise from an ion pair. Similar results have been



Z–149 *150* *151*



152
R = n–C_6H_{13}

40.4% yield
34% ^{18}O

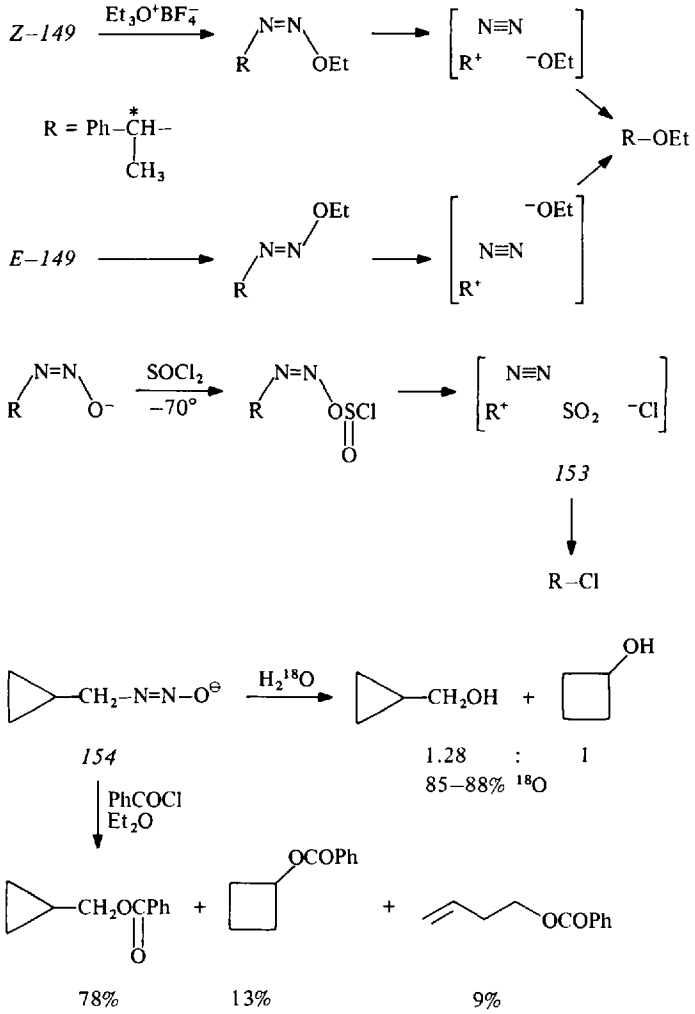
59.6% yield
72% ^{18}O

obtained in the ammonolysis[144] and hydrazinolysis[145] of (*149*); the ethanolysis and ethanthiolysis of 2-octanediazotate (*152*) conform to the same mechanistic pattern[146]. A more sophisticated approach involves hydrolysis of optically active (*152*) in ether with $H_2{}^{18}O$ [147]. The incorporation of ^{18}O leads preferentially to inverted 2-octanol whereas ^{16}O (the diazotate oxygen) predominates in the 2-octanol of retained configuration. A homogeneous medium and complexation of the counterion increase the incorporation of ^{18}O and the contribution of the inversion pathway[148].

The decomposition of diazotates may also be induced by Lewis acids. Solution of (*152*) in hexamethylphosphoric triamide are slowly decomposed by excess lithium azide or lithium chloride with the formation of inverted 2-octyl azide and chloride, respectively, along with retained 2-octanol[149]. Diazotates are readily decomposed by acylation. Although the intermediate diazoesters (*125*) should be identical with those generated by thermolysis of nitrosoamides, differences in stereochemistry and product distribution were noticed which may be due to the heterogeneity of the diazotate system[149–151].

The alkylation of 1-phenylethanediazotate with triethyloxonium fluoborate is of considerable interest as it has been applied to both the *Z* and *E* isomers[142, 152]. Although both precursors give 1-ethoxy-l-phenylethane with retention of configuration, the stereospecificity is much greater with *Z*– than with *E*– (*149*). This is compatible with the greater C–O separation in the ion pair generated from *E*– (*149*), allowing for more cation rotation. Another means of increasing the distance between the carbocation and its counterion is treatment of a diazotate with thionyl chloride[153]. This process has been termed "extended deamination" because in the ion pair (*153*) the carbocation and chloride anion are separated by two neutral fragments rather than one. The alkyl chlorides are produced with decreased retention of configuration, and in moderate yields.

The potential of diazotate reactions for the generation of "tailor-made" ion pairs is obvious. Unfortunately, this method has not yet been extensively applied to rearranging systems. The only recorded example is cyclopropylmethanediazotate (*154*) which gave cyclopropylmethanol and cyclobutanol on hydrolysis in nearly the same ratio as does nitrous acid deamination of the corresponding amine[154]. The basic hydrolysis of deuterium labeled (*154*) with $H_2{}^{18}O$ afforded cyclopropylmetha-

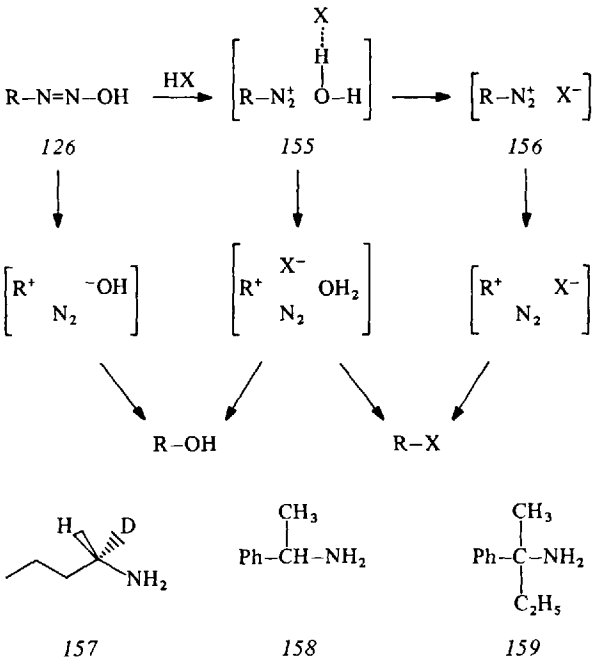


nol with little ^{16}O return and extensive scrambling of the deuterium. Less rearrangement was observed on acylation of (*154*) which gave esters of cyclopropylmethanol as the major products. It has been argued that the stability of cyclopropylcarbenium ions tends to suppress ion pair phenomena.

4.3.4 Nitrous Acid Deaminations

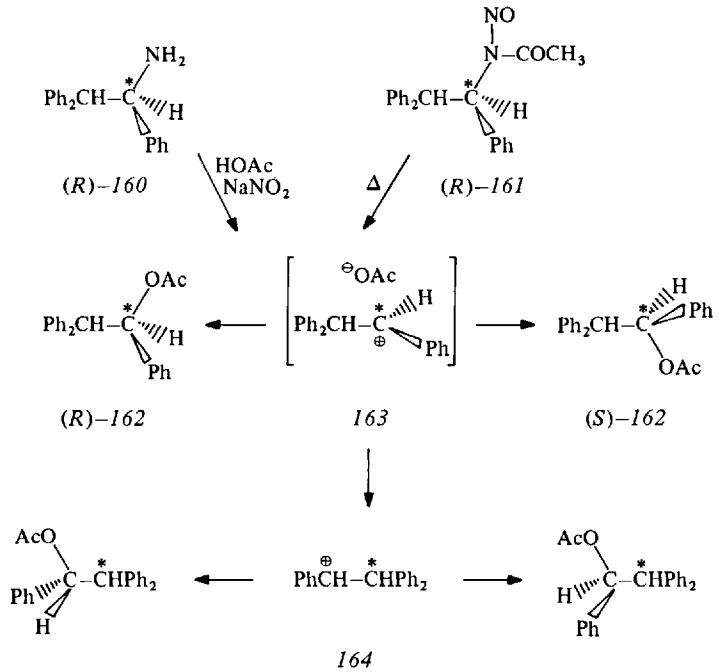
Proceeding via diazohydroxide (*126*), the nitrous acid deamination is subject, in principle, to the ramifications discussed in Section 4.3.3. In aqueous nitrous acid reactions the role of the counterion is poorly defined. Secondary alkylamines give alcohols with predominant inversion of configuration[155]. An ^{18}O study on the deamination of cyclohexylamine has shown that most of the oxygen atoms of the alcohol are derived from the solvent[156].

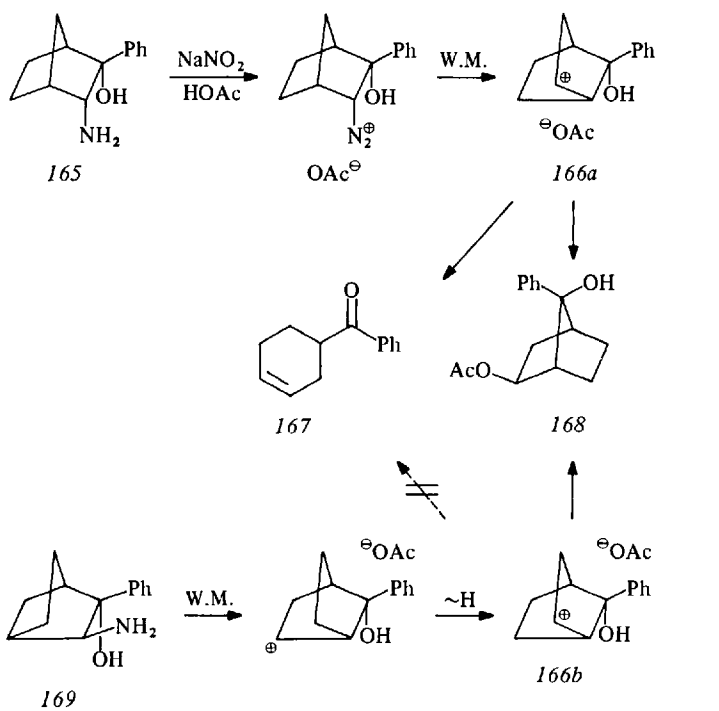
In acetic acid, however, nitrous acid deamination resembles in many respects the acidolysis of alkanediazotates and the thermolysis of nitrosoamides. Alcohols are formed in low yield but with high retention of configuration[129, 130, 157, 158]. The fraction of alcohol increases with increasing stability of the carbocation, suggesting that exchange of acetate for hydroxide occurs at the stage of the diazonium ion, (*126*) → (*155*) → (*156*). The stereochemistry of the acetates ranges from 68% net in-



version with n-butylamine (*157*)[159] to 8% and 22% net retention with 1-phenylethylamine (*158*)[130] and 1-methyl-1-phenylpropylamine (*159*)[157], respectively. The acetates are products of several reaction paths among which displacement at the diazonium ion (pair) is prominent with (*157*) whereas ion pair collapse contributes significantly in the case of (*158*) and (*159*).

Although many rearrangements have been observed during nitrous acid deaminations in acetic acid, the effects of ion pairing have rarely been considered. Optically active 1,2,2,-triphenylethylamine (*160*) yielded 1,2,2,-triphenylethyl acetate (*162*) with 40% net retention of configuration. Resolution of (*162*) from ^{14}C-labeled reactant showed that formation of the retained product proceeded with less rearrangement (1,2-phenyl shift) than formation of the inverted product[160]. These results are reasonably attributed to internal return of the initial ion pair (*163*), with predominant retention of configuration, but they do not specify the orientation of acetate with respect to the rearranged carbocation (*164*). The effects of ion pairing were more pronounced but qualitatively similar in the decomposition of the nitrosoamide (*161*). It was also established, by the use of acetyl-labeled (*161*), that (*R*)–(*162*) was formed predominantly by cation-anion collapse of (*163*) whereas (*S*)–(*162*) was form-

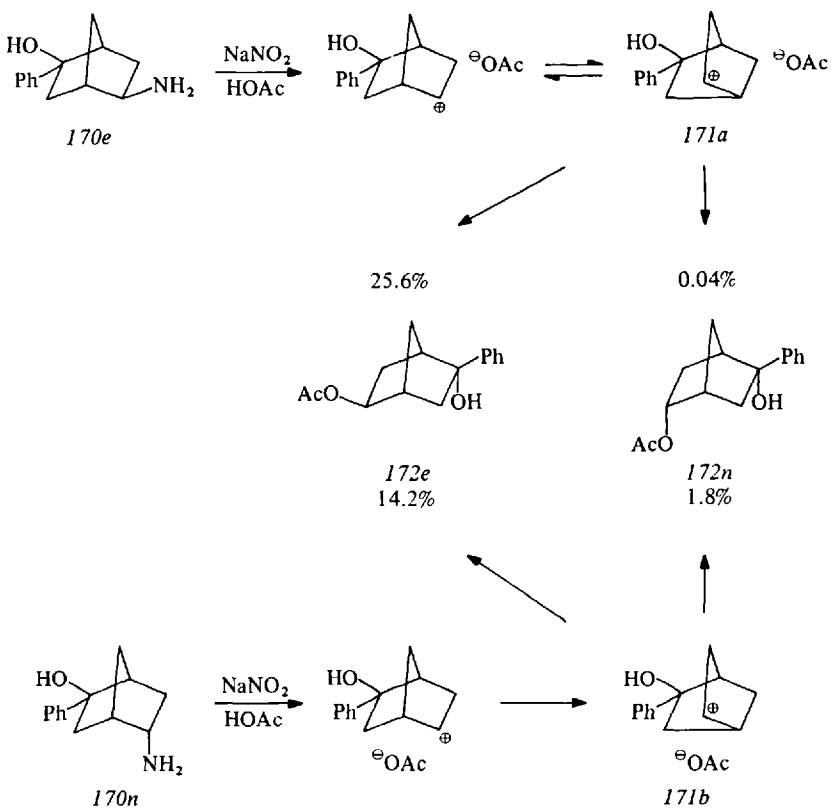

NO
N–COCH3
Ph2CH–C*–H
NH2
Ph
(R)–160
HOAc
NaNO2
Δ
(R)–161
⊖OAc
OAc
(R)–162
163
(S)–162
AcO
CHPh2
PhCH–CHPh2
164


Ph
OH
NH2
NaNO2
HOAc
W.M.
⊖OAc
165
OAc⊖
166a
O
Ph
167
AcO
168
~H
166b
169

ed principally through reaction of the carbocation with unlabeled acetate from the solvent[160].

The reactivity of cation (*166*), formed by deamination and rearrangements of the amines (*165*) and (*169*), was found to depend on its genesis[161]. Two products, (*167*) and (*168*), were obtained in comparable amounts if (*165*) was the precursor of (*166*) whereas the reaction sequence starting from (*169*) produced (*168*) only. The differences in reactivity were ascribed to different orientations of the acetate counterion in the ion pairs (*166a*) and (*166b*). The anion in (*166b*) is situated for easy *exo* collapse to product (*168*). The acetate in (*166a*) is not available for internal return; here reaction with the solvent is necessary to give (*168*), and ring opening becomes competitive.

The different *exo/endo* ratios of the rearranged product (*172*) from the deamination of the stereoisomeric amines (*170e*) and (*170n*) were similarly explained in

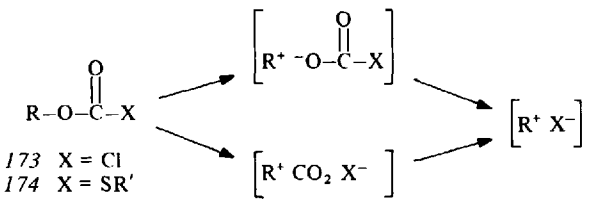


terms of orientation of the counterion in the ion pairs (*171a*) and (*171b*)[162]. These results led Collins to emphasize the important role of ion pairs in "memory effects" (i.e. genesis-dependent product distribution from seemingly identical cations)[163]. Alternative explanations have been advanced[164] (Section 6.4) which cannot be dismissed on the basis of the presently available data.

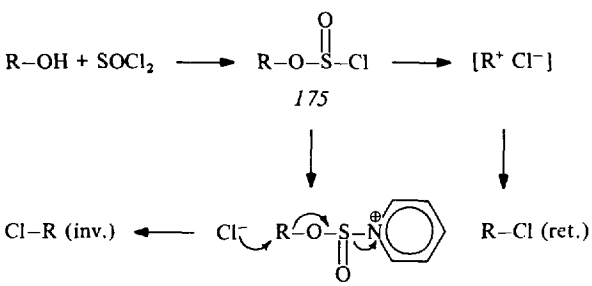
4.4 Ion Pairs from Other Sources

4.4.1 Decomposition of Chloroformates and Chlorosulfinates

An ion pair mechanism for the decomposition of chloroformates (*173*) is supported by the following experimental results: The decomposition rates increase with increasing stability of the carbocation and with increasing ionizing power of the solvent; alkyl chlorides are formed with predominant retention of configuration[165, 166]. Carbonyl–^{18}O does not equilibrate with the ether oxygen of chloroformates[167] although such equilibration has been observed with thiocarbonates (*174*)[168]. Even



173 X = Cl
174 X = SR'



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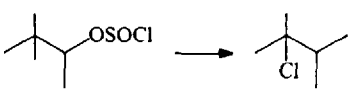
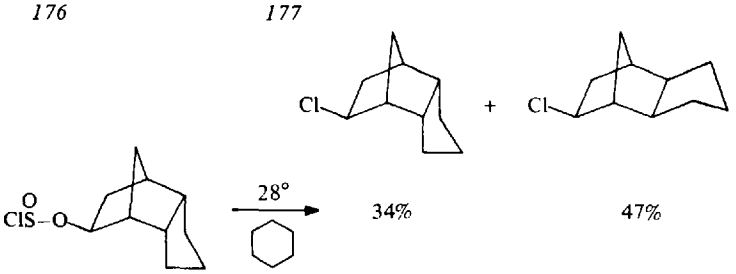
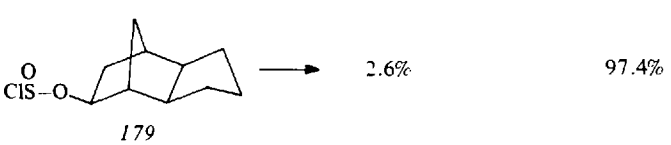


176 *177*



178



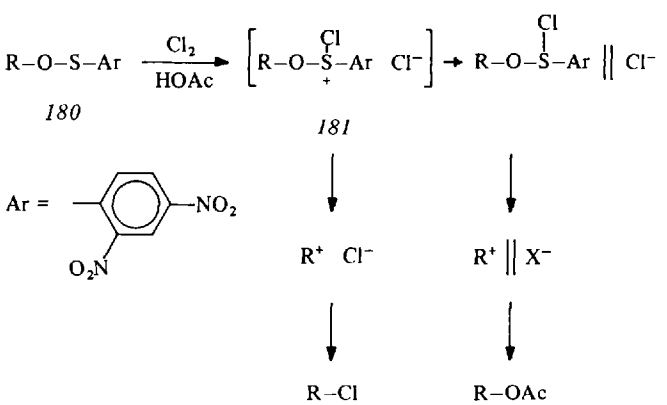
179

the slowly reacting primary chloroformates produce extensively rearranged products, e.g. *n*-butyl chloroformate gives 7% 1-chlorobutane, 27% 2-chlorobutane, 44% 1-butene, and 22% 2-butene[169]. Sequential cleavage of alkyl-oxygen and carbonyl-x-bonds has been favored, but simultaneous cleavage also remains a possibility[168, 170].

Thionyl chloride is the classical reagent for the preparation of alkyl chlorides from alcohols with retention of configuration. This reaction is known to proceed via alkyl chlorosulfinates (*175*) which decompose by an ion pair mechanism, but may be diverted to an S_N2 displacement path by addition of pyridine[171]. Wagner-Meerwein rearrangements have been observed in the course of alkylchlorosulfinate decomposition, e.g. (*176*) → (*177*)[172]. The behavior of the isomeric chlorosulfinates (*178*) and (*179*) is consistent with competitive ion pair collapse and 1,2-alkyl shift[173].

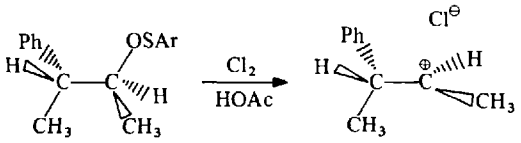
4.4.2 Chlorinolysis of Alkylsulfenates

The chlorination of an alkyl 2,4-dinitrobenzenesulfenate (*180*) in acetic acid leads to an intimate sulfoxonium ion pair (*181*) which may lose a sulfinyl chloride fragment before or after solvation[174-177]. The chloride-acetate ratio decreases sharply in the presence of added lithium perchlorate, a manifestation of a special salt effect. Since

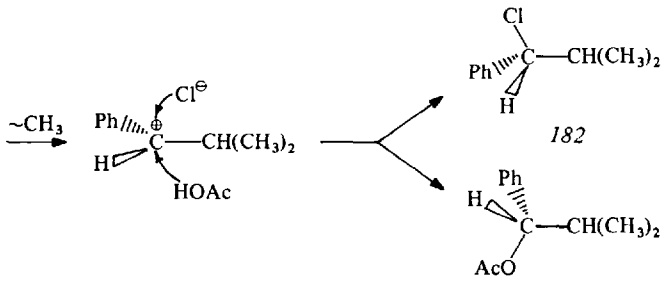


perchlorate anion exerts its influence by enhancing the proportion of solvent-separated ion pairs, the decrease in chloride-acetate ratio indicates that alkyl chloride is mainly a product of intimate ion pairing. In accord with these views, the optically active 1-phenylethyl compound afforded chloride with predominant retention of configuration[174].

The chlorinolysis of ^{14}C-labeled and optically active *threo*- and *erythro*-3-phenyl-2-butyl arenesulfenates (*181*) has been investigated[175]. Phenyl, methyl, and hydrogen migration occur. With respect to migratory aptitudes and *erythro-threo*-leakage, the reaction takes a position intermediate between diazonium ion decomposition and tosylate solvolysis (see Section 6.2). The stereochemistry at the origin of the methyl shift is remarkable: the chloride (*182*) is formed with inversion of configuration, and the acetate (*183*) with predominant retention. Obviously the rearrangement proceeds within the intimate ion pair and the chloride counterion continues to



threo–181

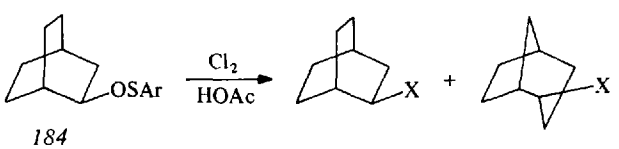


182

183

exert its stereochemical control after the rearrangement. We arrived at similar conclusions regarding 1,2 hydrogen shifts in Section 4.2.2.

Bicyclo [2.2.2] octyl arenesulfenate (*184*) affords mixtures of bicyclo [2.2.2] octyl and bicyclo [3.2.1] octyl chlorides and acetates[176]. The chloride-acetate ratio depends strongly on the amount of added lithium perchlorate, but the ratio of [2.2.2] to [3.2.1] is similar for chlorides and acetates and is not appreciably changed by the presence of lithium perchlorate. The chlorinolysis of deuterium-labeled cyclooctyl (*185*) and cyclodecyl (*186*) arenesulfenates has been studied to compare



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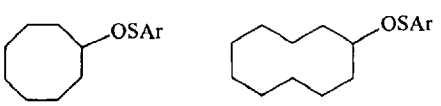


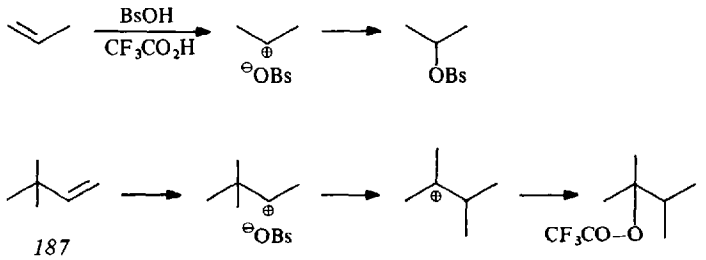
185 *186*

the transannular hydrogen shifts occuring in different intermediate ion pairs[177]. The deuterium scrambling in the chloride and acetate products implies that transannular hydrogen shifts occur to nearly the same extent in both intimate and solvent-separated ion pairs.

4.4.3 Acid Addition to Alkenes

Several mechanistic possibilities have been recognized by which acid addition to olefins may proceed[178, 179]. In many cases tight ion pairs appear to be involved. The

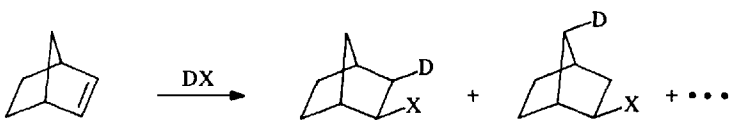
ion pair mechanism accounts for the observation of predominant *cis* addition in nonpolar solvents and predominant *trans* addition in highly ionizing solvents[179]. p-Bromobenzenesulfonic acid in trifluoroacetic acid reacts with propene to give 2-propyl brosylate exclusively, whereas under the same conditions t-butylethylene (*187*) gives only rearranged trifluoroacetate[180]. It was suggested that both of these



187

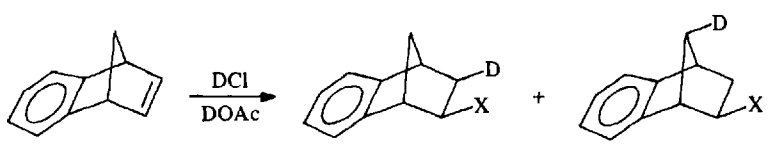
reactions produced intimate ion pairs. Return of the 2-propyl brosylate pair was rapid relative to other processes whereas the pinacolyl brosylate pair reacted by methyl migration exclusively.

The addition of deuterium chloride to norbornene (*188*) gives *exo*-2-norbornyl chloride (*189*, X=Cl) containing more deuterium in the *exo*-3 than in the *syn*-7 position[181]. Even the addition of deuteriotrifluoroacetic acid to (*188*) produces an excess of *exo*-3-D-*exo*-norbornyl trifluoroacetate (*189a*, X=CF_3CO_2)[182]. The reac-



188 *189a* *189b*

DCl	57%	41%
CF_3CO_2H	35%	26%



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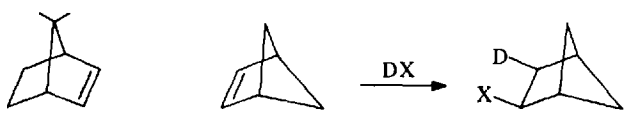
X = Cl	50.3%	49.7%
X = OAc	58.8%	41.2%



191 *192*

tion of deuterium chloride in deuterioacetic acid with benzonorbornene (*190*) leads to complete scrambling of deuterium between positions 3 and 7 in the chloride, but less than complete scrambling in the acetate[183]. The results have been interpreted on the basis of rearranging classical ions (which fail to give *trans* products on steric grounds)[181, 182] or by a mechanism involving symmetrical carbocations in competition with molecular *cis* addition of acid[183]. 7,7-Dimethylnorbornene (*191*) has been proposed as a diagnostic tool to test for cyclic molecular addition. Typical cyclic additions such as epoxidation, hydroboration, and the addition of benzenesulfenyl chloride involve attack on (*191*) from the *endo* side[184]. Addition of acids to (*191*), however, proceeds with *exo, cis* stereochemistry, apparently unperturbed by the 7-methyl groups[182]. Molecular addition was therefore considered to be insignificant. On the other hand, addition of deuterium chloride and deuterioacetic acid to bicyclo [2.2.1] hexene (*192*) affords unrearranged *cis* products[185]. No "inherent" *exo* preference precludes *trans* addition to (*192*) in a stepwise process, the cation derived from (*192*) being symmetrical. The results with (*192*) support molecular addition of acid to an alkene which is closely related to norbornene.

Due to its complexity, the addition of acids to alkenes does not encourage straightforward mechanistic conclusions. The studies with norbornene appear to add a new dimension to the nonclassical ion controversy.

5 Micellar Effects

5.1 Properties of Micelles in Aqueous Solution[186]

Micelles are molecular aggregates formed in solutions of amphiphiles – molecules in which a lipophilic "tail" is joined to a hydrophilic head-group. At low concentrations in water, amphiphiles exist mostly as monomers. At higher concentrations, they form more or less spherical aggregates with the polar groups on the surface and the hydrocarbon chains forming a core (Fig. 2). The size of micelles depends on the balance of attractive forces between the non-polar portions and repulsive forces between the head-groups. Micelles of ionic amphiphiles have aggregation numbers ranging from 10 to 100; their interiors resemble those of liquid hydrocarbon droplets.

The concentration above which micelles form is called the critical micelle concentration (CMC). Experimentally, the CMC is found by plotting a graph of a suitable physical property as a function of concentration. A change of slope marks the CMC. Many physical properties have been used[187], including interfacial tension, electrical conductivity, and light scattering. The sharpness of the break in physical properties depends on the nature of the micelle and the method of CMC determination. The choice of CMC is never unambiguous. Some parameters affecting the value of the CMC are briefly summarized: The longer the total carbon chain length of the monomeric amphiphile, the lower the CMC becomes. Additional polar groups, C=C double bonds, and chain branching tend to increase the CMC, but changes in the hydrophilic part of the amphiphile generally have insignificant effects. The CMC is also affected by temperature, pressure, and by the addition of both ionic and nonionic solutes.

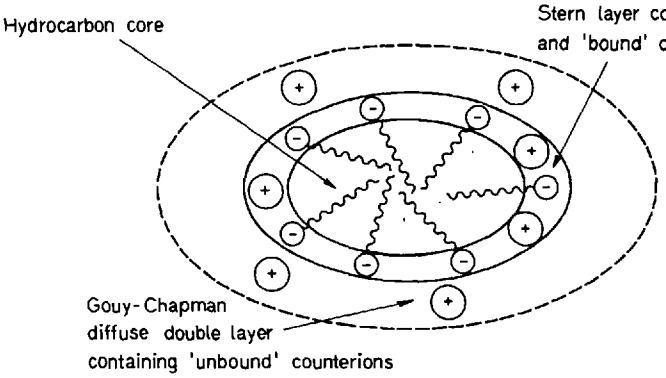


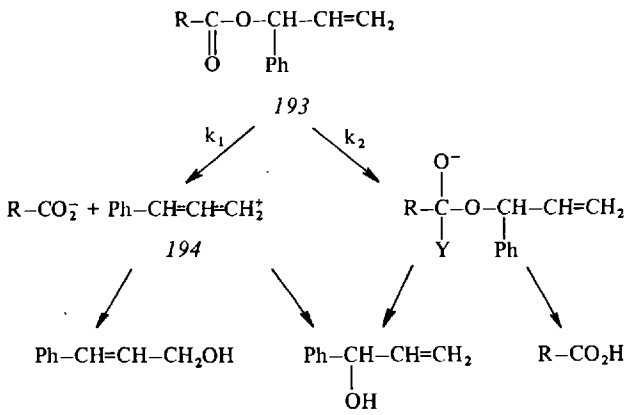
Fig. 2. Cross-section of an idealized anionic micelle. [Reproduced from Fisher, R. L., Oakenfull, D. G.: Chem. Soc. Rev. *6*, 25 (1977).]

Above the CMC, monomers and micelles exist in dynamic equilibrium. The kinetics of micelle dissociation have been measured by the methods used to study fast chemical reactions. Transient methods, such as pressure jump and temperature jump, give relaxation times ranging from 10^{-2} to 10^{-5} s, while steady-state methods, such as NMR, ESR, and ultrasonic absorption, always give values less than 10^{-5} s. Trying to reconcile these discrepancies, Muller suggested that transient methods follow the slow complete breakdown of micelles whereas steady-state methods observe the fast exchange of amphiphiles between micelles and solution[188]. Accordingly, molecules are thought to have a mean residence time in a micelle of about 10^{-5} s.

Further aspects of micellation which are relevant to the subsequent discussion include premicellar aggregation and water penetration. Premicellar formation of dimers, trimers, and smaller aggregates might affect the reactivity of amphiphiles well below the CMC. Although some earlier observations supported the formation of small aggregates, there is now no compelling evidence for premicellar aggregation. The extent to which water from the extensively hydrated micellar surface penetrates the hydrocarbon core is not readily evaluated. Water is considered, at present, to penetrate into micelles only up to distances of approximately three to six carbon atoms. The interior of the micelle has generally been inferred to be hydrocarbon-like from ESR and NMR spectroscopy and from the utilization of fluorescent probes.

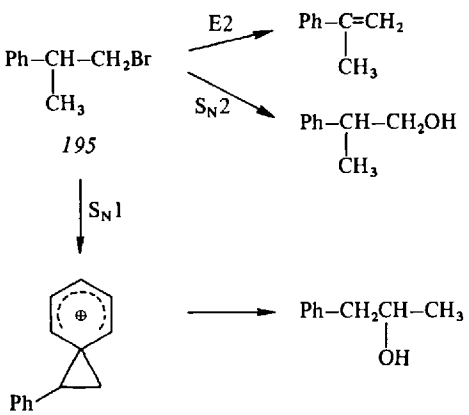
5.2 Micellar Effects on Nucleophilic Substitution Reactions

Most of the work concerned with micellar catalysis of nucleophilic substitution refers to reactions of the $A_{AC}2$ and S_N2 types and will not be reviewed here. To date only a few systems have been examined in which a micellar medium affects the partitioning of solvolytic reactions between unimolecular and bimolecular mechanisms. The effects of cationic (hexadecyltrimethylammonium bromide = CTAB) and anionic (sodium lauryl sulfate = NaLS) micelles on competitive S_N1 and S_N2 reactions of α-phenylallyl butanoate (*193*) have been investigated[189]. The rate of formation of the phenylallyl cation (*194*) is retarded by both surfactants probably as a consequence of the decreased polarity of the micellar pseudo phase. The bimolec-



ular nucleophilic reaction with water is also inhibited which can be attributed to the lower effective activity of water in the micellar region as compared to the bulk solution. The rate of nucleophilic attack by hydroxide ion on (*193*) is increased by cationic CTAB and retarded by anionic NaLS, as has been found for many other reactions of neutral substrates with anions. By simple electrostatics, the cationic micellar surface attracts hydroxide ions whereas the anionic one repels them.

Competitive S_N1, S_N2, and E2 reactions of 1-bromo-2-phenylpropane (*195*) have also been investigated in the absence and presence of cationic surfactants[190].



Again the unimolecular solvolysis which involves formation of a phenonium ion is retarded by incorporation of (*195*) in cationic micelles whereas the bimolecular reactions are catalyzed.

Micellar control of the stereochemistry of nucleophilic substitution reactions was first recognized in the nitrous acid deamination of 2-aminooctane[191]. Below the CMC of 2-octylammonium perchlorate, 2-octanol is formed with the inversion stereochemistry normally expected in the deamination of a 2-aminoalkane. With increasing concentration the percentage of inversion decreases to zero, after which retention of configuration occurs. The observed stereochemistry was demonstrated to

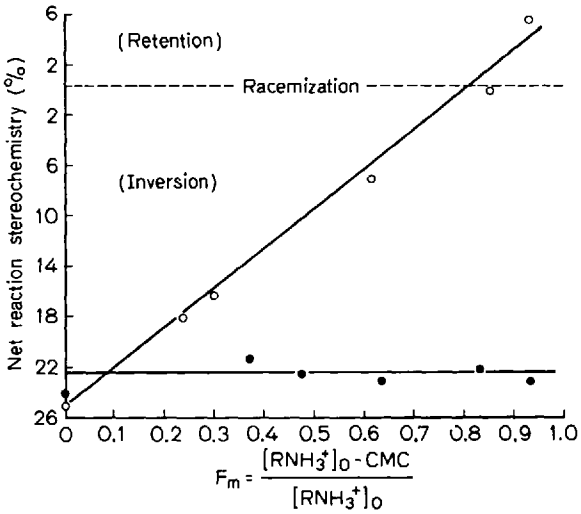
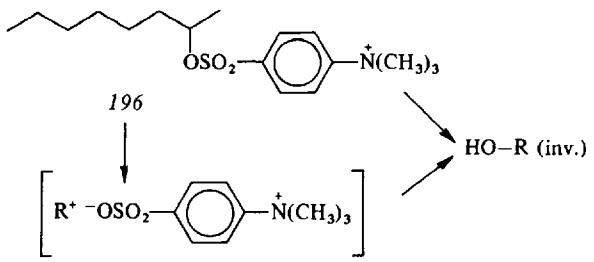


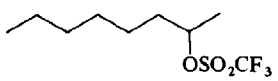
Fig. 3. The stereochemical course of the 2-aminooctane → 2-octanol transformation with 1.6 *M* $NaNO_2$, 25 °C, pH 4, *vs.* Fm. Open circles correspond to runs in $HClO_4$; solid circles correspond to runs in HCl. [Reproduced from Moss, R. A., Talkowski, C. J., Reger, D. W., Powell, C. E.: J. Am. Chem. Soc. *95*, 5215 (1973).]

be weight-averaged deamination occurring in the micellar and aqueous pseudo phases by obtaining a linear plot of stereochemistry *vs.* the initial extent of micellation, *Fm* (Fig. 3). Further support of micellar control comes from the deamination of 2-octylamine, well below its CMC, in the presence of cationic surfactants, to give 2-octanol with net retention of configuration.

The stereochemical effects of micellation are highly dependent on the nature of the counterions. No stereochemical changes are seen in micellar deamination conducted in the presence of bromide, chloride, or acetate counterions. Perchlorate, fluoroborate, or alkyl (aryl) sulfonate counterions are required for micellar control of stereochemistry. Strongly hydrated ions such as bromide, chloride, and acetate are thought to be weakly associated with alkylammonium micelles, and to provide a highly aqueous Stern layer. On the other hand, the poorly hydrated counterions (ClO_4^-, BF_4^-, RSO_3^-) are strongly bound and afford denser, less aqueous micelles. In terms of this interpretation, the micellar stereochemical control is due to the variation of solvent polarity at the site of reaction. It is known that homogeneous deamination reactions give increasing retention as the medium is altered from water to less polar solvents.

The increasing retention observed in micelle-perchlorate deaminations might alternatively be attributed to a "double-inversion" process. The tightly bound perchlorate might displace nitrogen with inversion to give an alkyl perchlorate which undergoes rapid, inverting hydrolysis. Evidence supporting a double-inversion process was obtained in the solvolysis of 2-octyl p-trimethylammonium benzenesulfonate (*196*)[192]. Cationic micelles (either of the reactant itself or CTAB) did not change the rate of hydrolysis nor did they affect the stereochemistry (100% inversion). However, anionic micelles strongly inhibited the solvolysis reaction and modified the stereochemistry to a value as low as 54% inversion (NaLS). The stereochemical changes were shown to arise from direct attack of the surfactant head group upon (*196*), leading to a short-lived covalent dialkyl sulfate intermediate.





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On the other hand, when optically active 2-octyl triflate (*197*) was hydrolyzed in the solubilized state with surfactant concentrations greater than their CMC, the stereochemical course changed to net retention (*ca.* 48% for CTAB, and *ca.* 27% for NaLS)[193]. The rate constants, very much lower than those in the absence of micelles, indicate that the reaction proceeded in the micelles. The different behavior of (*196*) and (*197*), particularly in the presence of cationic micelles (CTAB), may be due to the greater efficiency of triflates in producing carbocations. The comparison of (*196*) and (*197*) then suggests that the solvation model of micellar stereochemical control applies to unassisted solvolyses whereas the double inversion mechanism operates with leaving groups which invite participation of a nucleophile.

5.3 Micellar Effects on Rearrangements

The stereochemistry at the origin of deaminatively induced 1,2-hydrogen shifts was found to be strongly affected by aggregation of the alkylammonium ions in micelles [194]. With a series of 4-amino-3-methylalkanes (*198*) retention at C–3 predominated in dilute solution, in analogy with the corresponding tosylates (*91*), (Section 4.2.2). Above the cmc, however, the stereochemistry moved toward racemization and crossed over to ca. 7% inversion. Although the cmc's of the various amines differ substantially, the stereochemical results come very close if plotted against *F*m (Fig. 4). Compared with the direct displacement at 2-octanediazonium ions[191], the transformation (*198*) → (*199*) is subject to a micellar effect of similar magnitude but of opposite sign.

The inverse relationship between the micellar effects on direct displacement and hydrogen shift has been confirmed with esters of isoleucine (*200*)[194] (Fig. 5). Apparently the two competing reactions are controlled by the preferential mode of solvent approach on conformation (*203*) of the diazonium ion, with migrating hydrogen and leaving group antiperiplanar. In dilute solution the solvent approach is preferentially

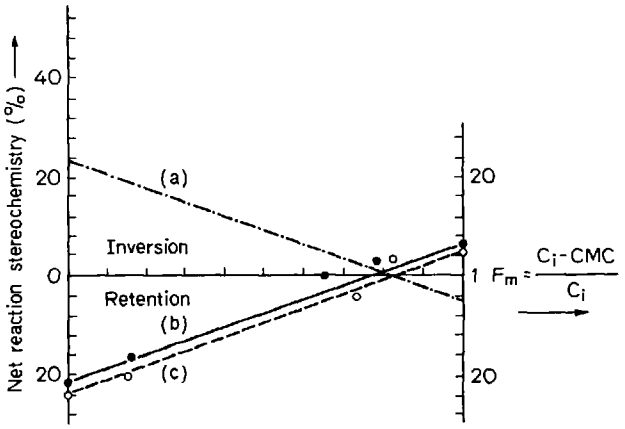


Fig. 4. The stereochemical course of the 2-aminooctane → 2-octanol (a), (*198a*) → (*199a*) (b), and (*198d*) → (*199d*) (c) transformations, with 1.6 *M* $NaNO_2$, 25 °C, $HClO_4$(pH 3.5–4), *vs.* Fm. [Reproduced from Kirmse, W., Rauleder, G., Ratajczak, H. J.: J. Am. Chem. Soc. *97*, 4141 (1975).]

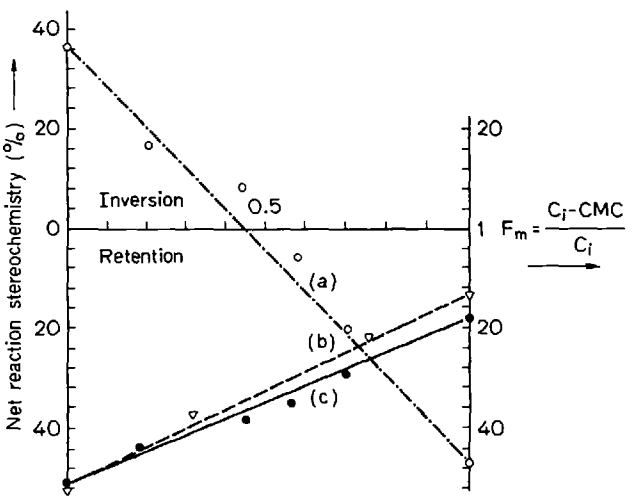
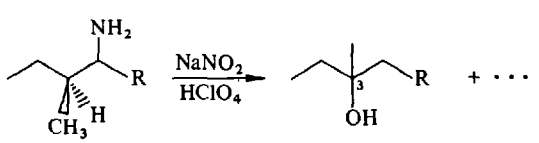
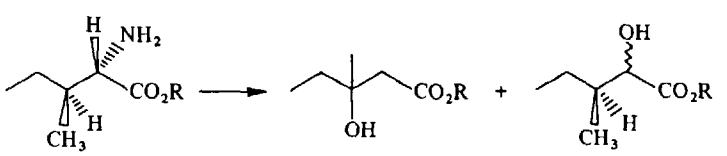


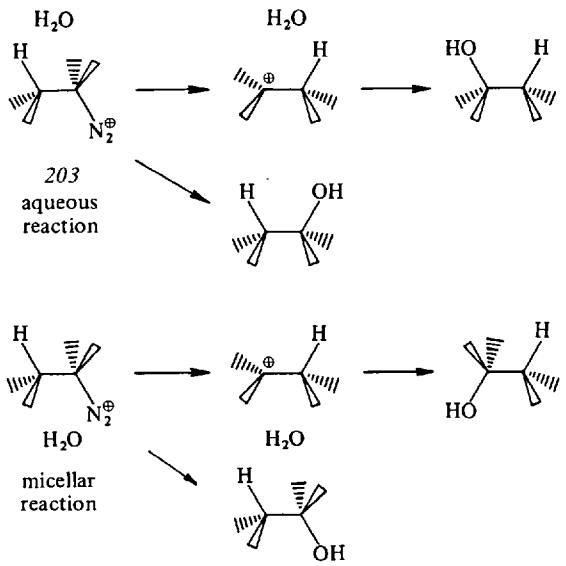
Fig. 5. The stereochemical course of the transformations (*200a*)→(*202a*) (a), (*200a*)→(*201a*) (b), and (*200b*)→(*201b*) (c), *vs.* Fm. [Reproduced from Kirmse, W., Rauleder, G., Ratajczak, H. J.: J. Am. Chem. Soc. *97*, 4141 (1975).]



198a R = C_2H_5 *199*
b n–C_4H_9
c n–C_6H_{13}
d $CH_2CH_2CH(CH_3)_2$



200a R = CH_3 *201* *202*
b n–C_6H_{13}



from the rear to give inverting solvolysis and retention at the migration origin. Incorporation of the diazonium ions in micelles favors frontside return to the diazonium site and inversion at the neighboring carbon.

No comparable micellar effects have been observed in 1,2-alkyl shifts which proceed with inversion of configuration above and below the cmc[195]. A slight increase in racemization above the cmc may be attributed to delayed nucleophilic capture of the carbocations in the less aqueous micellar environment.

6 Conformational Control

6.1 Fundamental Concepts

A reaction is conformationally controlled if the distribution of products and (or) their stereochemistry depends on the preferred conformation of the reactant. Consider two diastereomerically different conformers, C_1 and C_2, which must give rise to different products (or product distributions), P_1 and P_2.

$$P_1 \xleftarrow{k_1} C_1 \underset{k_{-c}}{\overset{k_c}{\rightleftharpoons}} C_2 \xrightarrow{k_2} P_2$$

The outcome of this reaction depends on the relative magnitude of the various rate constants (activation barriers). If the conformational equilibration is rapid compared with product formation, essentially all of the reaction will be channelled through the more reactive conformer (Fig. 6a). For that reason the relative population of the conformers is irrelevant in the reactions of conformationally "mobile" systems

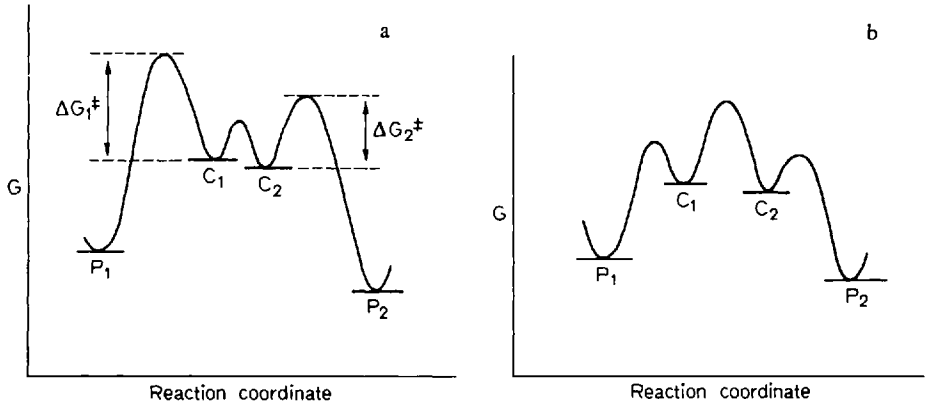


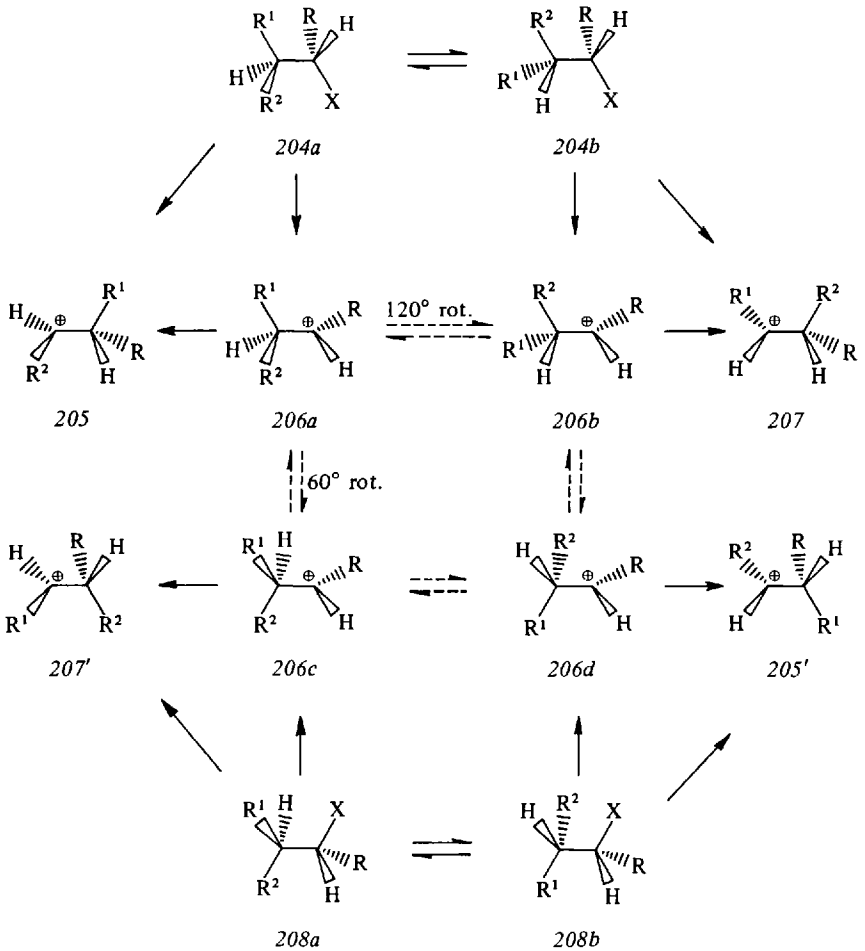
Fig. 6. Reaction profiles of carbocation conformers, C_1, C_2. a) Rapid equilibration; b) conformational control

($\Delta G_c^{\ddagger} < 5$ kcal/mole, $\Delta G_{1,2}^{\ddagger} > 10$ kcal/mole). If the rate of reaction is fast with respect to conformational equilibration the relative populations of the conformers will be of major importance (Fig. 6b). This situation is often encountered with conformationally "rigid" systems (e.g., polycyclic compounds). Obviously, conformational control can also be brought about by increasing the rate of reaction. We have seen (Section 3) that some 1,2 shifts in carbocations are extremely fast ($\Delta G^{\ddagger} < 5$ kcal/mole). We expect, therefore, that rearrangements of carbocations may be competitive, at least, with conformational equilibration even in acyclic systems.

Similar arguments apply to the ionization step of a Wagner-Meerwein rearrangement. A good leaving group X (e.g., N_2) responds little to variations of the molecular environment ($k_1 \simeq k_2$). Different conformers of the precursor (*204a, b*) generate different conformers of the carbocation (*206a, b*) which subsequently undergo 1,2 shifts of either R^1 or R^2 (we neglect hydrogen shifts for the sake of simplicity). Barring rotation about the central C–C bond only those groups migrate which are properly aligned with the vacant p orbital, i.e. R^1 in (*206a*) and R^2 in (*206b*). The energy profile corresponds to Fig. 6b. The ratio of the rearranged carbocations (*205*) and (*207*), and of any products derived therefrom, is determined by the relative populations of the conformers (*204a*) and (*204b*). The migration terminus is inverted.

A 60° (180°, 300°) rotation about the C–C bond affords the conformers (*206c*) and (*206d*) which are not directly accessible from (*204*) but may be generated from the diastereomeric precursor (*208*). Such a rotation is readily detected as it leads to enantiomeric products, (*206c*) → (*207'*) and (*206d*) → (*205'*). Complete conformational equilibration of the carbocation (*206*) results in racemization at the migration terminus and affords identical product mixtures from the diastereomeric precursors (*204*) and (*208*). The stability of the carbocation (*206*) is an important factor in determining the relative rates of rotation and rearrangement.

Very likely (*204a*) and (*208a*) represent the most stable conformations of (*204*) and (*208*), respectively (only two gauche interactions). In the conformationally controlled reaction of (*204*) R^1 migrates in preference to R^2 while the reverse holds for

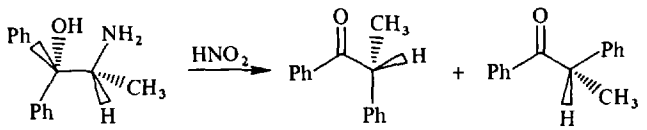


(*208*). The observation of different migratory aptitudes with diastereomeric precursors is the most conclusive criterion of conformational control.

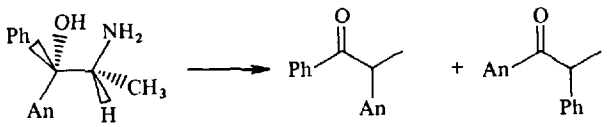
If the C–X bond ionizes more reluctantly (e.g., X=Br, OSO_2Ar), part of the required activation is often provided by participation of the migrating group (cf. Section 7). Anchimerically assisted ionization bypasses carbocation (*206*) and leads immediately to the rearranged carbocations (*205*) and (*207*) (alternatively, bridged ions may be formed). The stereochemistry, inversion at the migration terminus, is essentially the same for anchimerically assisted and conformationally controlled reactions. The two mechanisms are distinguished, however, by different migratory aptitudes. The ability of the migrating group to act as an internal nucleophile and to disperse positive charge is essential in the assisted ionization. If the nucleophilicity of R^1 exceeds that of R^2, both of the diastereomers (*204*) and (*208*) will react with preferential migration of R^1. The energy profile corresponds to Fig. 6a. The experimental verification of these concepts will be reviewed in the following paragraphs.

6.2 Acyclic Systems

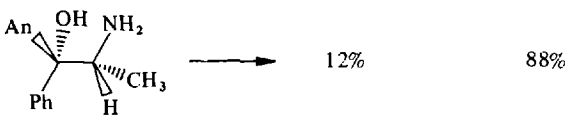
The pinacolic deamination of 2-amino-1,1-diaryl-1-propanols provides a convincing case for conformational control. Optically active 2-amino-1,1-diphenyl-1-propanol (*209*) affords α-phenylpropiophenone (*210*) with 88% inversion plus 12% retention (76% inversion plus 24% racemization) at the terminus of phenyl migration[196]. The diastereomer (*211*) of 2-amino-1-anisyl-1-phenyl-1-propanol reacts with preferential



209 88% *210* 12%



and enantiomer *211* — *212* 94% — *213* 6%



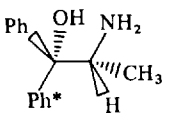
12% 88%

and enantiomer *214* — An = CH_3O–C$_6$H$_4$–

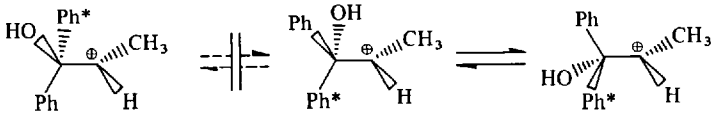
anisyl migration whereas phenyl migration predominates with diastereomer (*214*)[197]. Clearly, the nucleophilicity of the aryl group is not the factor controlling the migratory aptitude (in anchimerically assisted reactions, anisyl is superior to phenyl, cf. Section 7). The product ratios are readily explained by conformational control if the most stable conformers are those shown (gauche orientation of OH and NH_2, stabilized by intramolecular hydrogen bonding).

Intimate details about the mechanism of aryl migration were uncovered by Collins et al.[198] who prepared (*209*) specifically labeled with ^{14}C in one of the phenyl groups. Resolution of (*210*) obtained from the deamination of (*209a*) revealed that the inverted product had been formed exclusively by migration of the labeled phenyl group whereas the product of retained configuration was formed exclusively by migration of the unlabeled phenyl group. These results suggest that the lifetime of the carbocation (*215*) permits some 60° rotation, but does not permit 120° rotation which would lead to migration of unlabeled phenyl with inversion (or of the labeled phenyl with retention).

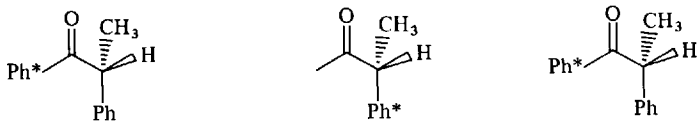
The first-formed carbocation from the deamination of 2-amino-1,2-diaryl-1-propanols (*216*) is stabilized by resonance and longer lived than cation (*215*). *Erythro*-(*216*) yields more ketone (*217*) of retained configuration than does (*209*), as would be expected when the intermediate cation rotates more freely. The ratio of retention



209a

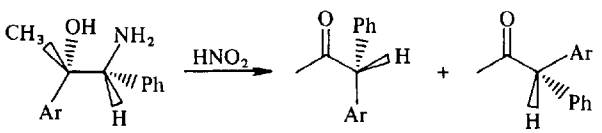


215

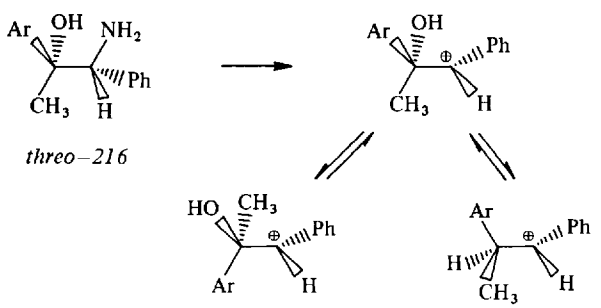


not observed | 88% | 12%

210a



	erythro–216	*217*	*217'*
Ar =	C_6H_5	73.5%	26.5%
	$p\text{–}CH_3C_6H_4$	74%	26%
	$p\text{–}CH_3OC_6H_4$	77%	23%

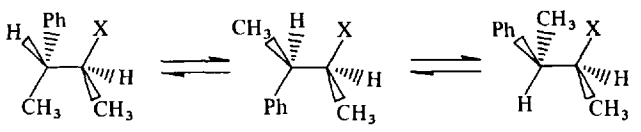


threo–216

	217	*217'*
Ar = $p\text{–}CH_3C_6H_4$	43%	57%
$p\text{–}CH_3OC_6H_4$	41%	59%

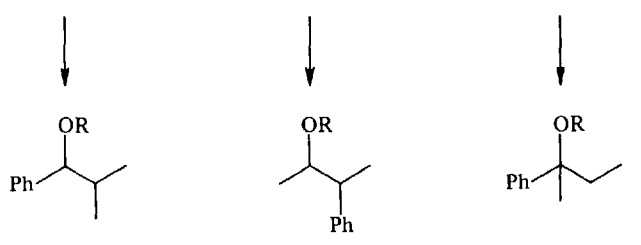
to inversion was found to be independent, however, of the nature of the aryl group (stereochemical analysis in the case of Ar=C_6H_5 was achieved by means of an elegant ^{14}C labeling technique)[199]. Conformational control is virtually absent in the deamination of *threo*-(*216*). In the most stable conformer of *threo*-(*216*) the aryl group is not properly aligned with the vacant p-orbital of the incipient carbocation; aryl migration may occur only after rotation. It is difficult to comment on the slight excess of retention over inversion[199]. It may reflect a preference for 60° rotation over 120° rotation, but even in a completely equilibrated carbocation the transition state leading to retention may be favored because the bulky phenyl and methyl groups are *trans* to each other. Methyl does not migrate in the deamination of *threo*-(*216*), in spite of its favorable orientation.

The deamination reactions of the hydroxyamines (*209*), (*211*) and (*216*) were explained on the basis of a single, particularly stable conformation. The complete spectrum of conformers appears to contribute to the reactions of 3-phenyl-2-butyl derivatives which have been studied with a variety of leaving groups, cf. (*218*)–(*221*).

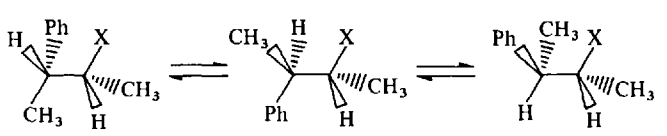


a *b* *c*

threo–218–221



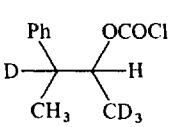
222 *223* *224*



a *b* *c*

erythro–218–221

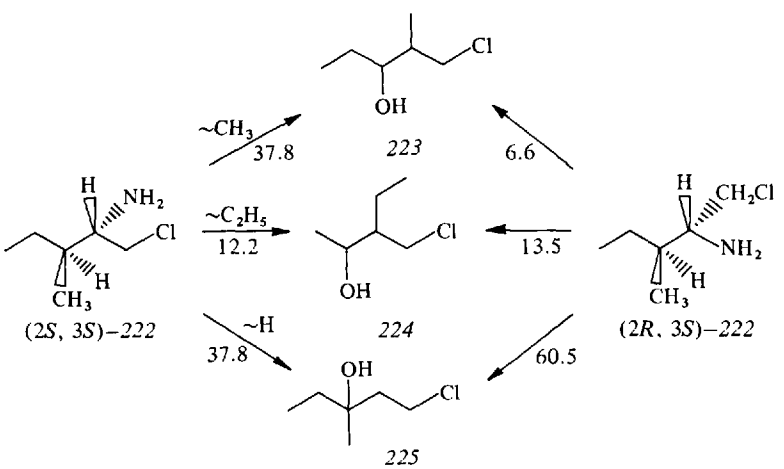
218 X = NH_2
219 OCOCl
220 Cl
221 OTs



219D

3-Phenyl-2-butyl products (*223*) are formed by phenyl migration and by simple substitution. The amount of phenyl migration in the deamination of (*218*)[200] and in the solvolyses of (*220*)[201] and (*221*)[202] has been estimated by assuming the intervention of phenonium ions (cf. Section 7.3.) which produce optically active *erythro*-(*223*) and racemic *threo*-(*223*). More direct data have been obtained by means of deuterium-labeled (*219*-D) in the silver-promoted dehalodecarboxylation of chloroformate (*219*)[201]. The *threo*-amine and *threo*-chloroformate favor methyl migration, hydrogen and phenyl shifts occurring to lesser extents. The migratory aptitudes correspond to the expected order of conformer stabilities, (*a*)>(*b*)>(*c*). In the *erythro* series the order of stabilities is reversed, (*b*)>(*c*)>(*a*), resulting in phenyl participation as the major process. Methyl migration decreases from 32% in *threo*-(*218*) to 6% in *erythro*-(*218*), and from 45% in *threo*-(*219*) to 8% in *erythro*-(*219*). No methyl shift was observed with (*220*) and (*221*); phenyl participation dominates with both of their diastereomers. Anchimeric assistance in the solvolyses of (*220*) and (*221*), in contrast to conformational control with (*218*) and (*219*), nicely illustrates the effect of the leaving group.

The deamination of the diastereomeric 2-amino-1-chloro-3-methylpentanes (*222*)[203] provides data on a purely aliphatic system. Although hydrogen migrates preferentially the ratio of methyl and ethyl shifts depends strongly on the choice of



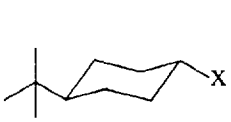
diastereomer. Dominant methyl migration in (2*S*, 3*S*)–(*222*) and the preference for ethyl migration in (2*R*, 3*S*)–(*222*) support conformational control, with major contributions from the most stable conformers. Inversion at the terminus of methyl migration decreases from 90% with (2*S*, 3*S*)–(*222*) to 72% with (2*R*, 3*S*)–(*222*), as expected. The opposite trend for ethyl migration is not observed, however (see Section 7.6.1.4 for an explanation).

6.3 Cyclohexane Derivatives

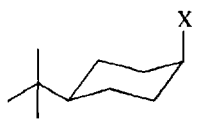
The conformational energies of many acyclic compounds are not precisely known. Cyclohexane derivatives would be expected to represent a much simpler case. They

offer the additional advantage that bulky groups, such as *t*-butyl, "freeze" the ground state into a known and homogeneous conformation.

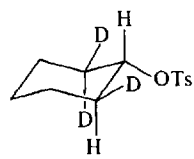
Equatorial cyclohexylamines give retained (equatorial) substitution products and little elimination; axial amino groups give extensive elimination and a small yield of predominantly inverted (equatorial) substitution product[204–208]. Similar situations obtain with 1- and 2-aminodecalins[209, 210], and with various aminocholestanes[211, 212]. Very thorough studies have been carried out on the deamination of the epimeric 4-t-butylcyclohexylamines (*226*)[138, 205–208], the silver-assisted dehalodecarboxylation of the analogous chloroformates (*227*)[201], and the solvolysis of the corresponding p-nitrobenzenesulfonates (*228*)[213]. Although ion pairs play an important role in some of the deamination reactions (cf. Section 4.3.2), *cis*- and *trans*-(*226*) clearly



trans



cis

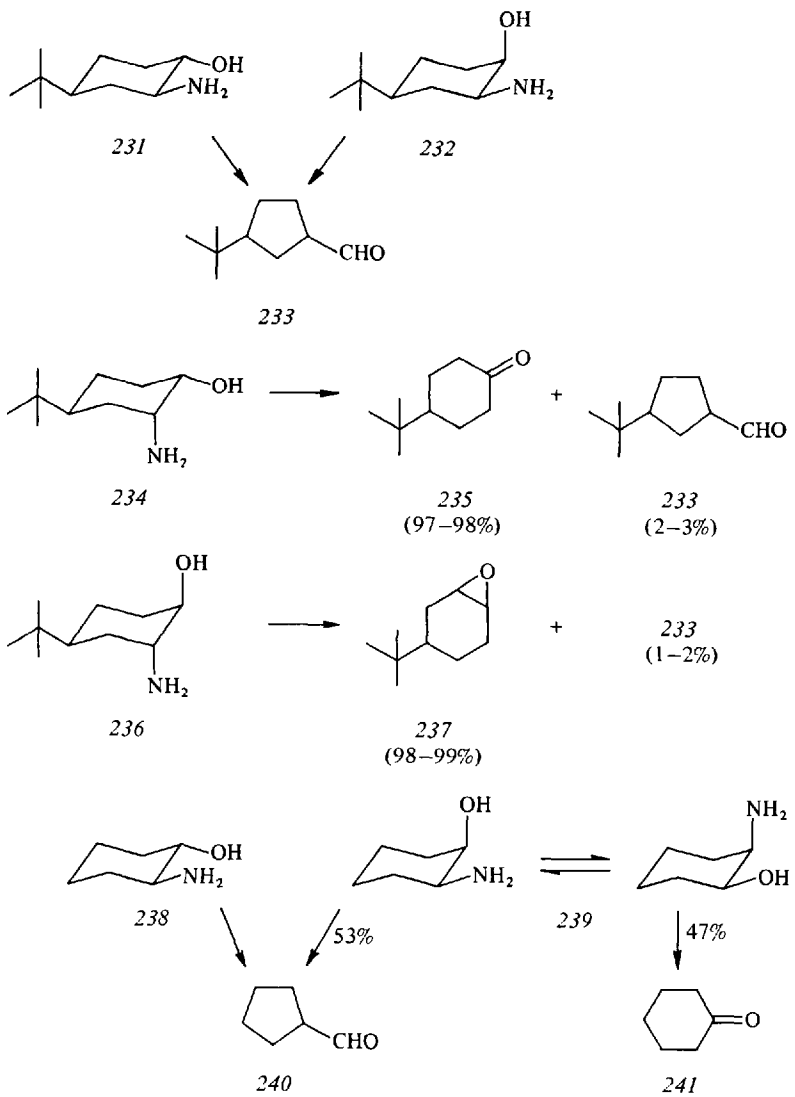


230

226 X = NH_2
227 OCOCl
228 $OSO_2C_6H_4NO_2$
229 OSO_2CF_3

follow different reaction paths with respect to substitution and rearrangement. There can be almost no crossover between the intermediates from the diastereomeric precursors[138]. The massive amount of hydrogen shift (35%) observed with *cis*-(*226*) is in contrast to the very small amount (2%) which occurs in the deamination of *trans*-(*226*). No hydrogen *trans* to the leaving group, suitably positioned for overlap with the p orbital of the incipient cation, is available in *trans*-(*226*). The conformationally controlled reactions of (*226*) and (*227*) are in contrast to the results of the solvolysis of (*228*), both diastereomers of which give predominantly elimination, inverted products of substitution, and similar amounts of 1,2 hydrogen shift. The reaction mechanism of the diastereomeric triflates (*229*)[214] appears to be substantially identical to that of the arenesulfonates (*228*). The product distribution from the conformationally mobile, deuterium-labeled tosylate (*230*)[215] closely resembles that from *trans*-(*228*) (OSO_2Ar equatorial).

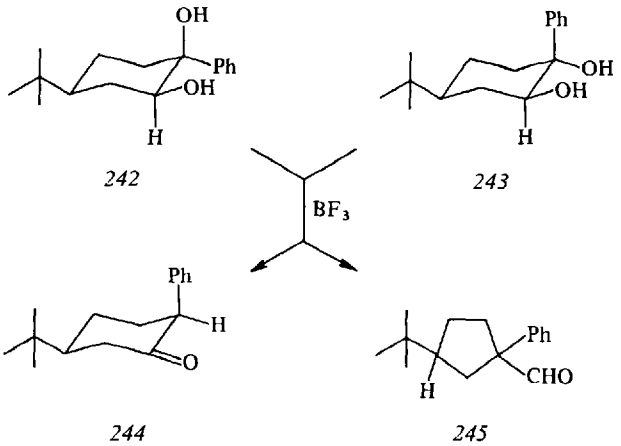
The deamination of the four conformationally rigid 2-amino-4-t-butylcyclohexanols is highly stereoselective[216]. From the two amino alcohols (*231*) and (*232*), where the amino group is equatorial, only the expected aldehyde (*233*) is obtained. With (*234*) and (*236*), where the amino group is axial, the yields are lower (~75%) as a result of glycol formation, but the ketone (*235*) and epoxide (*237*) are the respective rearrangement products. Small amounts of aldehyde (*233*) indicate that some stereochemical leakage is occurring. The deamination of the conformationally mobile *cis*-2-aminocyclohexanol (*239*) affords a mixture (53:47) of ring contracted aldehyde (*240*) and cyclohexanone (*241*). When the diazonium ion is axial, hydrogen migration is favored; when it is equatorial, alkyl migration (ring contraction) occurs. The product ratio does not reflect the estimated position of the conformational equilibrium (NH_2 equatorial/NH_2 axial = 3). Conformational reequilibration presumably occurs



at some intermediate stage of the diazotization process. With *trans*-2-aminocyclohexanol (*238*) only ring contraction occurs, as would be expected of the dominant diequatorial conformer.

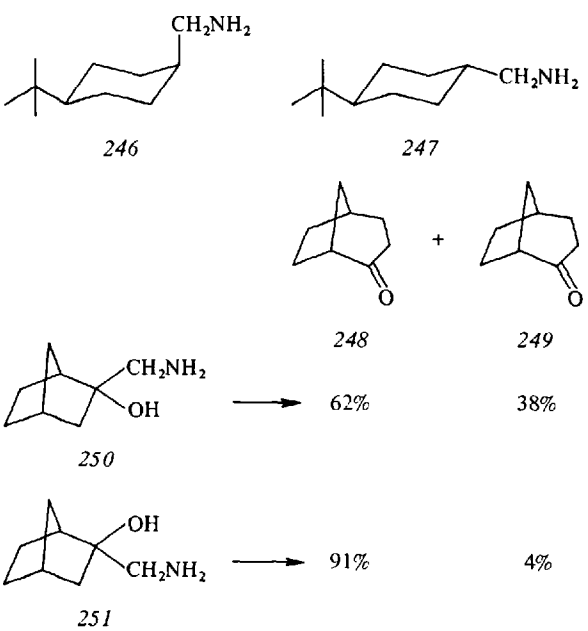
In contrast to the deamination of 2-aminocyclohexanols the related glycols (*242*) and (*243*) give the same products, (*244*) and (*245*), in the same ratio (9:1) when they undergo acid-catalyzed pinacol rearrangement[216]. ^{18}O exchange and kinetic isotope effects indicate a reversible C–O heterolysis, followed by alkyl or hydrogen migration, in the acid-catalyzed dehydration of aryl glycols[217]. These pinacol rearrangements exemplify the intermediacy of completely equilibrated carbocations.

Brief reference is made to other cyclic systems where conformational control is less clearly established. The dramatically different product distributions from the



242 *243* *244* *245*

deamination of *cis*- and *trans*-3-alkylcyclobutylamines have been explained in terms of the puckered structure of the cyclobutane ring[218]. The corresponding tosylates are thought to solvolyze via cyclopropylmethyl cations[219,220]. The attainment of specific conformations is essential for transannular hydrogen shifts to occur in medium-sized rings[221]. Conformational effects are clearly important in the ring expansion reactions of cyclohexylmethylamines. The deamination of (*246*) affords 46% of cycloheptane derivatives (alcohol and alkene) whereas (*247*) gives only 10%[222]. The semipinacolic ring expansions of (*250*) and (*251*) produce bicyclo [3.2.1] octan-2-one (*248*) and bicyclo [3.2.1] octan-3-one (*249*) in widely different ratios[223,224]. The intervention of short lived primary carbocations in these rearrangements is questionable and concerted reactions of the primary diazonium ions are a distinct possibility.



246 *247* *248* *249* *250* *251*

6.4 Bicyclic Systems ("Memory Effects")

In the ring expansion route to bicyclic carbocations, the nature of the product forming intermediate depends markedly on the stereochemistry of the reactant. The prototypical cases are derived from the *endo*- and *exo*-2-norbornylmethylamines (*254*, *257*) which give distinctly different product distributions on nitrous acid deamination (Table 9)[225]. The major product from the optically active *endo*-amine (*254*) is largely racemic *endo*-bicyclo [3.2.1] octan-2-ol (*253*) whereas the *exo*-amine (*257*)

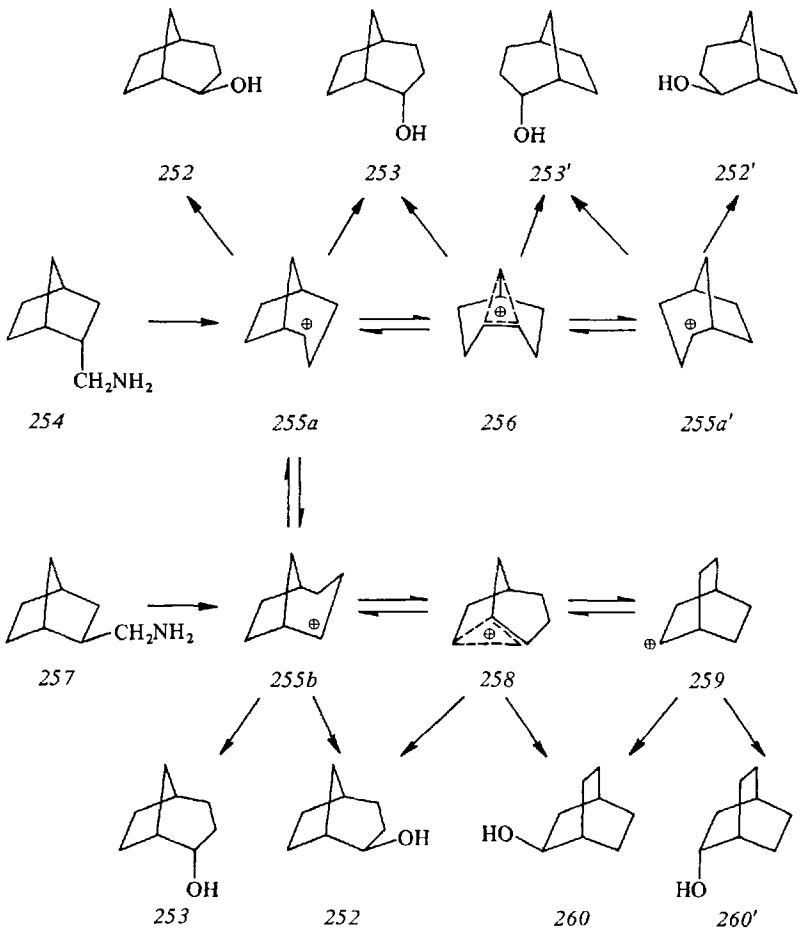
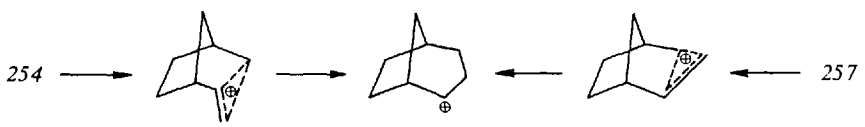


Table 9. Products from the deamination of *endo*- and *exo*-2-norbornylmethylamines in $HOAc/H_2O$

Amine	(*252*)	(*252'*)	(*253*)	(*253'*)	(*260*)	(*260'*)
(*254*)	4.5	4.5	44–47	36–38	7	
(*257*)[1])	36	1	3		32	9

[1]) 19% of Bicyclo[3.2.1]octan-3-ol were also obtained.

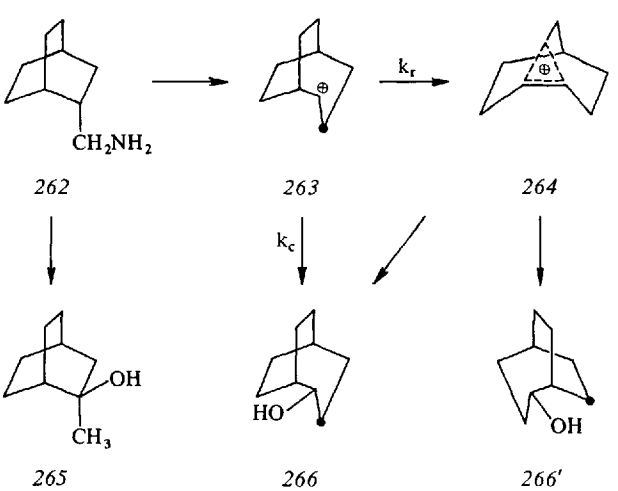
affords comparable quantities of optically active *exo*-bicyclo [3.2.1] octan-2-ol (*252*) and bicyclo [2.2.2] octan-2-ol (*260*). Berson explains his results in terms of conformationally isomeric chair and boat cyclohexyl cations (*255a, b*). Interconversion of these conformers must be slow relative to the rates of second rearrangement steps, (*255a*) → (*256*) by migration of C–8, and (*255b*) → (*258*) by migration of C–7. The specificities of these second rearrangements have been called "memory effects". The formation of some (*260*) from (*254*), and of some (*253*) from (*257*), indicates that a slow leak, possibly the chair-boat interconversion (*255a*) ⇄ (*255b*), connects the *endo*- and *exo*-derived systems. Alternative explanations of the "memory effects" are in terms of bridged ions and ion pairs. Bridged ions (*261a, b*) might replace the conformational isomers (*255a, b*), and leakage to the open ion (*255*) would account for incomplete stereospecificity. This idea has been rejected because the three-center orbitals of (*261a, b*) are not properly oriented for overlap with the C–1–C–8 and C–1–C–7 bonds, respectively[225]. Stereochemical control by the counter-ion was



261a *255* *261b*

recently emphasized by Collins[163]. Berson did not attribute an important role to ion pairing since variations of the solvent and of the leaving group had only a small effect (e.g., the deamination of (*254*) resembles the acetolysis of the corresponding brosylate)[225]. Therefore, further examples of "memory effects" will be discussed on the basis of Berson's conformational hypothesis[164].

The products from the deamination of bicyclo [2.2.2] octyl-2-methylamine (*262*) include the tertiary alcohol (*265*) resulting from a hydrogen shift and bicyclo [3.2.2] nonan-2-ol (*266*) from the migration of C–3[226]. The insertion of a single methylene group converting (*255*) to (*263*) results in a 30- to 60-fold decrease in the relative rates of rearrangement to solvent capture (k_r/k_c), as shown by the high

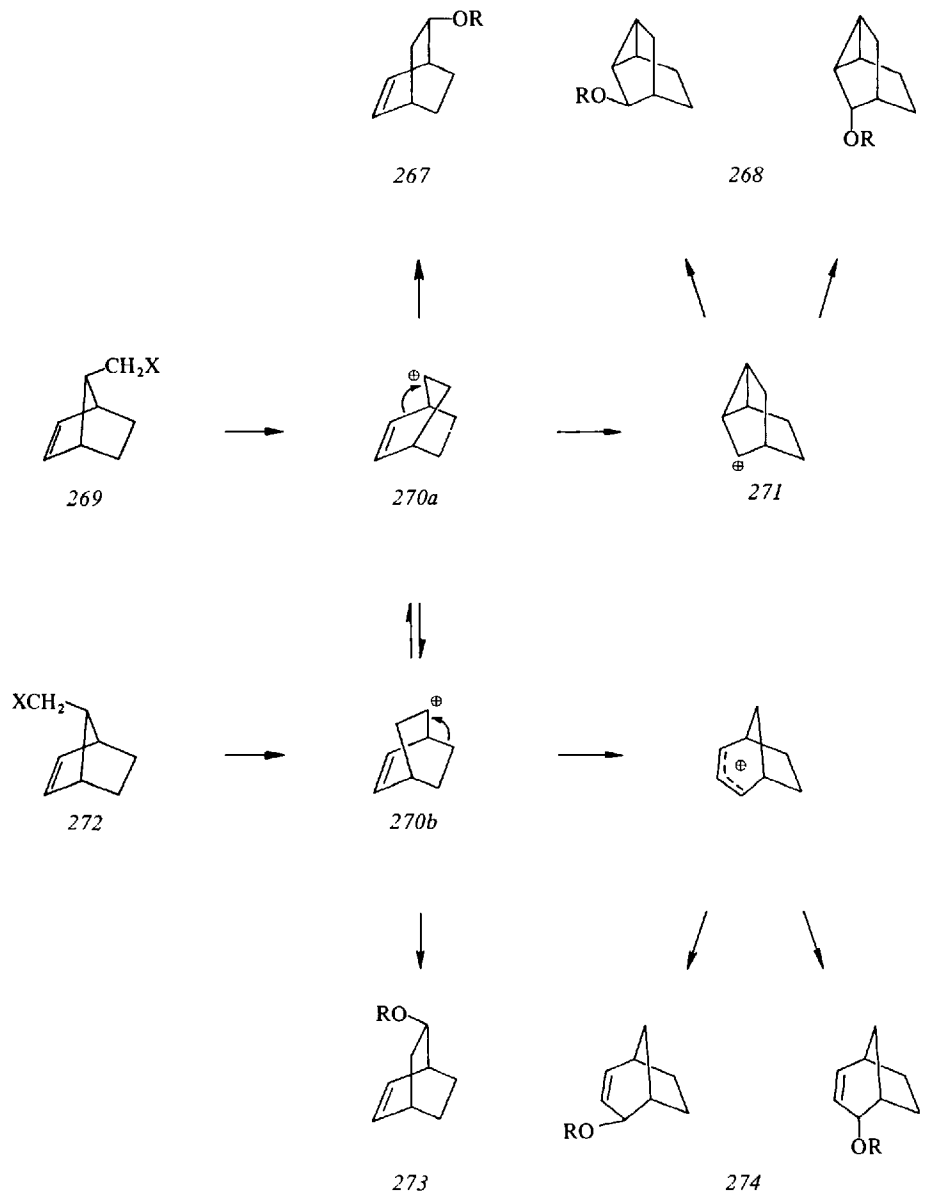


262 *263* *264*

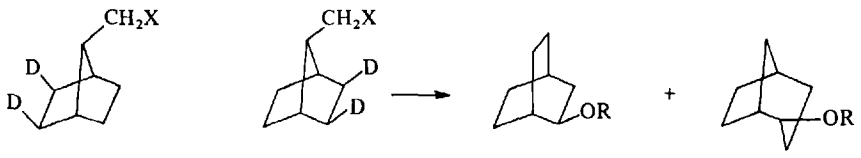
265 *266* *266'*

optical purity of (*266*) and the distribution of a tritium label (91% at C–3). The dramatic effect of the additional ring members was attributed to unfavorable orbital overlap in (*264*) as compared to (*256*).

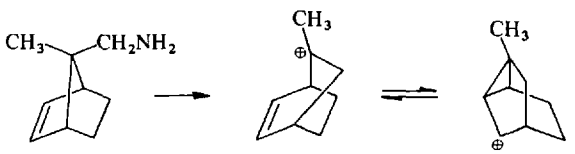
A definite barrier to conformational isomerization is readily imagined in the case of ions (*255*) and (*263*). Much smaller conformational barriers would be expected to separate the bicyclo [2.2.2] octenyl cations (*270a*) and (*270b*). Nevertheless the distribution of products obtained from the ring expansions of *anti*- and *syn*-2-norbornenyl-7-methylamines, (*269*) and (*272*), demonstrate the existence of a memory



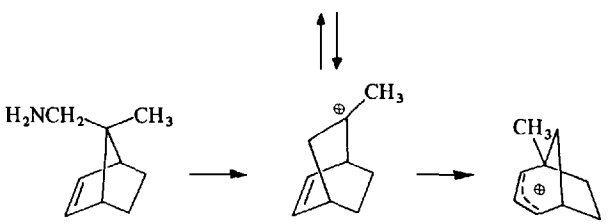
effect[227]. Each ring expansion passes first over a separate "twisted" cation which undergoes specific further bond rearrangement in competition with symmetrization. The ratio of products (*267*)+(*268*)/(*273*)+(*274*) from (*269*) was found as high as 40 in the deamination reaction (X=NH_2), and somewhat lower in solvolyses (X=Br, ONs).



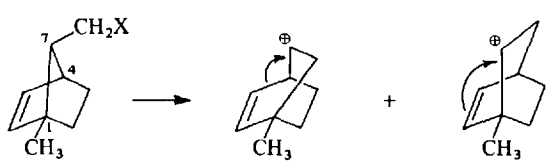
275 *276* *277* *278*



279 *280a* *281*



282 *280b* *283*



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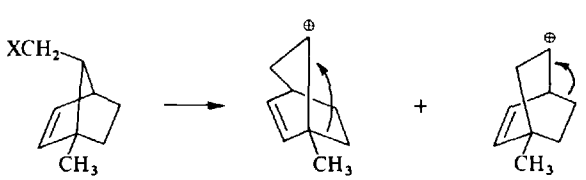

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The *syn*-isomer (*272*) is less specific in its secondary rearrangements; alkyl migration in (*270b*) would be expected to trap the twisted cation less efficiently than double bond participation in (*270a*).

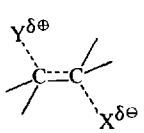
Ring expansions of stereospecifically labeled *anti*- and *syn*- [2,3-D_2]-7-norbornylmethylderivatives, (*275*) and (*276*), lead to bicyclo [2.2.2] oct-2-yl (*277*) and *exo*-bicyclo [3.2.1] oct-2-yl derivatives (*278*)[228]. The distribution of the deuterium label in (*278*) demonstrates the existence of a memory effect in the second rearrangement step. Migration of the bridge which was originally *anti* to the 7–CH_2X group is favored by a factor of ca. 6 in the room temperature deamination reactions, and by a factor of ca. 2 in the solvolytic reactions at 120°C.

A methyl substituent at C–7 would be expected to facilitate conformational equilibration of the once rearranged cations (*280a*) and (*280b*) which are now tertiary. In fact, (*279*) and (*282*) give very similar product distributions on nitrous acid deamination, but this is due, at least in part, to extensive crossover from ion (*281*) to ion (*283*)[228]. The memory effect is magnified by methyl substitution at C–1, as in (*284*), (*285*)[229], and their saturated analogs[230]. Both the 1,7 and the 4,7 bond migrate in the initial rearrangement. In the former case, the methyl substituent provides additional driving force to the second rearrangement and produces a large enhancement of selectivity.

7 Bridged Ions. Anchimeric Assistance

7.1 Terms and Definitions

The driving force behind all reactions of carbocations is the need to provide electrons to the electron-deficient carbon. When an electron-deficient carbon is generated, a near-by group may help to relieve this deficiency. It may release electrons through the molecular framework, inductively, by resonance, or by hyperconjugation. Alternatively, a group adjacent to the leaving group may act as an intramolecular nucleophile by becoming bonded to the electron-deficient site. The nucleophilic assistance of a neighboring group to departure of a leaving group is called neighboring group participation or anchimeric assistance. As defined by Traylor[231], a substituent Y provides vertical stabilization if Y does not change its geometry or its distance from



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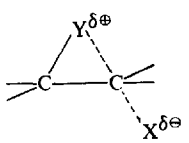

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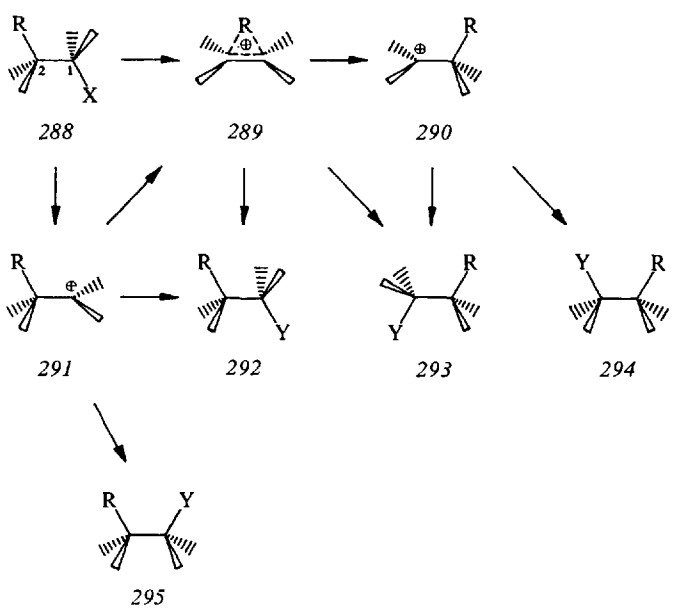
the positively charged carbon as the transition state is approached (*286*) and non-vertical stabilization if the substituent Y changes its geometry or its distance from the reaction site (*287*). Anchimerically assisted reactions proceed through bridged transition states.

In nucleophilic participation the electrons of the neighboring group that become bonded to the reaction center may be nonbonding electrons, π electrons, or σ electrons. Participation by oxygen, sulfur, and nitrogen groups is closely analogous to intermolecular nucleophilic substitution. A recent comprehensive review[232] is available. We shall not discuss n participation as it is but loosely related to the subject of Wagner-Meerwein rearrangements. Our major concern is participating carbon and, eventually, hydrogen.

If the migrating group does provide anchimeric assistance, certain consequences should follow. One is kinetic: The rate should be faster than the rate of an exactly analogous, but unassisted, reaction. Another is stereochemical: The migration terminus should be inverted by the rearrangement. There are obvious problems in the experimental evaluation of these criteria. Rate acceleration is often difficult to ascertain because the rate of the non-assisted reaction cannot be reliably predicted (cf. Section 7.2.). Inversion of the migration terminus may also be a result of ion pairing (Section 4.) or of conformational control (Section 6.). Combined kinetic and stereochemical evidence provides the most powerful support for anchimeric assistance.

A related, but distinct, question is whether there is an energy minimum on the reaction path of an anchimerically assisted reaction, i.e., whether there is a bridged intermediate. A variety of energy profiles must be considered for the rearrangement of (*288*):

(a) The bridged structure (*289*) is higher in energy than either of the open ions (*290*) and (*291*). In that case (*289*) represents the transition state for the interconversion of (*290*) and (*291*). Very likely the activation energy for generating (*291*) from covalent substrate (*288*) will be smaller than the energy difference between (*288*) and (*289*); i.e., the ionization of (*288*) is unassisted (Fig. 7a). Products are derived from (*290*) and (*291*).



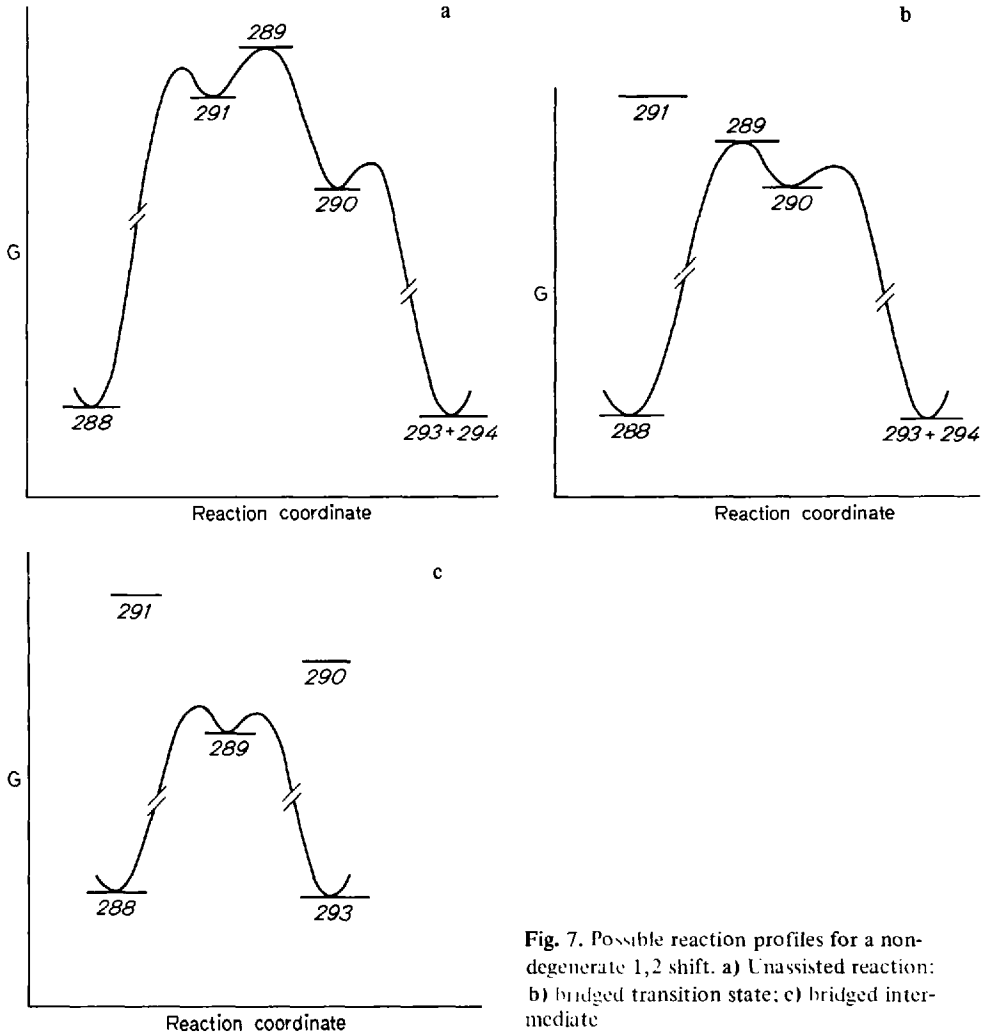


Fig. 7. Possible reaction profiles for a non-degenerate 1,2 shift. a) Unassisted reaction; b) bridged transition state; c) bridged intermediate

(b) The relative energies of the cationic species are in the order (*291*) > (*289*) > (*290*). Now it becomes attractive to bypass (*291*) in the ionization of (*288*) by participation of the migrating group R (Fig. 7b). Products are derived from (*290*) only. Anchimeric assistance depends strongly, however, on the leaving group X. With readily ionizing substrates, such as aliphatic diazonium ions, (*291*) may still intervene.

(c) The bridged ion (*289*) is more stable than either of the open ions (*290*) and (*291*). In that case the reaction is anchimerically assisted and involves (*289*) as the only intermediate, from which all products are derived (Fig. 7c).

The energy profiles of Figs. 7a and 7b may be more complex if (*289*) represents a shallow energy minimum rather than a maximum. As an intermediate, albeit of high energy, (*289*) might contribute to product formation even in unassisted reactions, depending on the relative rates of conversion to (*290*) and solvent attack. It is

advisable to defer this subtle question and to discuss the consequences of bridging in terms of Fig. 7.

Lowering the energy of (*289*) relative to that of (*290*) and (*291*) leads to a decrease in activation energy of the rate determining step (Fig. 7). Rate acceleration does not differentiate, however, between a bridged transition state (Fig. 7b) and a bridged intermediate (Fig. 7c). For the unequivocal identification of a bridged intermediate the transition state of the ionization step must be lower in energy than the most stable open cation (*290*). Although straightforward in principle, this criterion

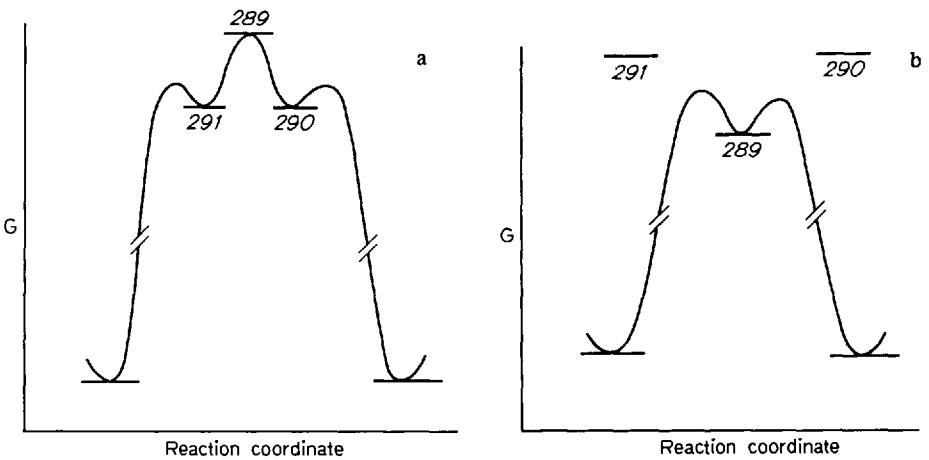


Fig. 8. Possible reaction profiles for a degenerate 1,2 shift. **a)** Unassisted; **b)** assisted, with bridged intermediate

can rarely be applied in practice because of difficulties in estimating the energy of a solvated carbocation. The disturbing case of Fig. 7b is eliminated if the ions (*290*) and (*291*) have the same energy. For a degenerate rearrangement only two alternatives remain (Fig. 8). Anchimeric assistance in a degenerate rearrangement strongly supports a bridged intermediate.

The stereochemical consequences of bridging are more prone to experimental scrutiny. Bridged and open ions are often distinguished by elements of symmetry present in one but not in the other. The predicted stereochemistry for the limiting cases of Fig. 7 follows:

(a) Unassisted reaction: Products of substitution (*292*, *295*) and of rearrangement (*293*, *294*) are formed, both with (partial) racemization.

(b) Bridged transition state: Only rearranged products are observed, with complete inversion at the migration terminus but undefined stereochemistry at the migration origin (*293*, *294*).

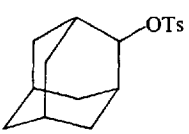
(c) Bridged intermediate: Substitution proceeds with complete retention of configuration (*292*); rearrangement involves complete inversion at both the migration terminus and migration origin.

7.2 Kinetic Methods

Some difficulties encountered in ascertaining anchimeric assistance have been mentioned in the preceding section. It will be appropriate to review the methods which have been developed to overcome these difficulties before kinetic criteria are applied to specific systems.

7.2.1 Relative Rates

It is convenient to designate solvolytic processes by three rate constants, k_Δ (anchimerically assisted), k_s (nucleophilically solvent assisted), and k_c (unassisted). More nucleophilic solvents, such as aqueous alcohols or acetic acid, can attack substrate in S_N2-type processes. In order to test the generality of nucleophilic solvent participation Schleyer and his associates carried out detailed studies of secondary systems without participating groups[233]. 2-Adamantyl tosylate (*296*) was selected as a model for S_N1 behavior because the adamantyl structure protects the backside of the developing cation from nucleophilic attack. Extensive experimental evidence has been adduced that the solvolysis of (*296*) involves a true k_c process; e.g. the addition of sodium azide, a powerful nucleophile, causes only minor changes in the rates and products[234]. (*296*) was then used as a reference standard against which solvent



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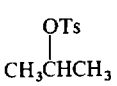

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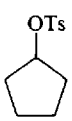

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assistance for other systems could be compared. A linear correlation of log k_{RX} with log k (*296*) for all solvents indicates limiting behavior of RX. This relationship is clearly not obeyed by simple secondary substrates such as 2-propyl tosylate (*297*) or cyclopentyl tosylate (*298*). There is good evidence that secondary tosylates approach limiting behavior in trifluoroacetic acid or hexafluoroisopropanol (Fig. 9). In acetic acid, (*297*) appears to be nucleophilically assisted by a factor of 470 whereas the more hindered (*298*) is assisted by a factor of 105[233].

Solvent participation often competes very successfully against neighboring group participation with the result that rate enhancements in comparison with model compounds are inconclusive. Thus, the $PhCH_2CH_2OTs/CH_3CH_2OTs$ rate ratio varies from 0.2 in 50% ethanol, through 0.35 in acetic acid and 2.7 in formic acid, to 1770 in trifluoroacetic acid[235]. Only the last value reveals the true participating ability of the phenyl group.

Even if solvent participation is excluded by the use of "limiting solvents" the problem of comparable models remains. When the neighboring group is close to the reaction center, polar and steric effects generally become important. In such cases the Taft equation[236], $\log k/k_0 = \rho^*\sigma^*$, can be applied with reasonable success in estimating rates of non-participating systems. The titrimetric rate constants for the acetolysis of secondary alkyl tosylates fall on the same line when plotted against σ^* (Fig.

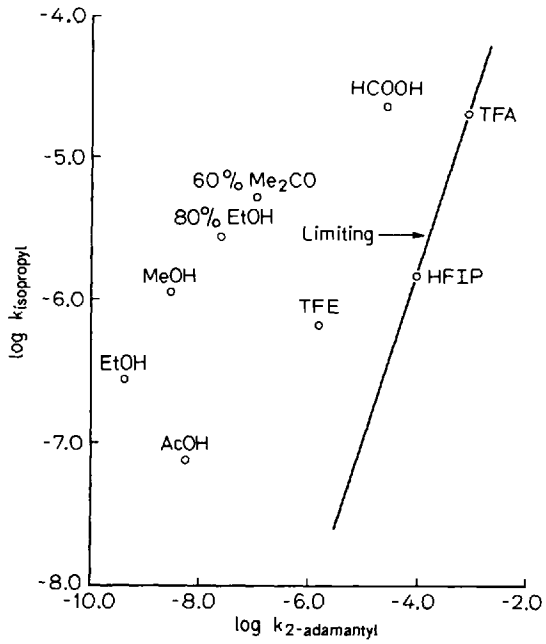


Fig. 9. Absence of a free-energy correlation for the solvolysis of isopropyl tosylate in representative solvents. [Reproduced from Brown, H. C.: The nonclassical ion problem. New York: Plenum Press 1977.]

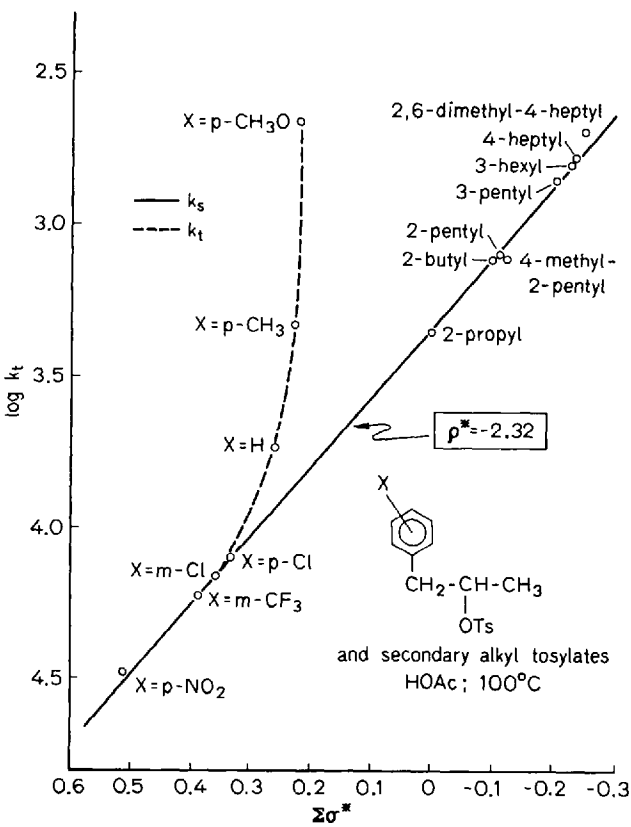


Fig. 10. Taft treatment of the acetolysis of secondary alkyl and 1-aryl-2-propyl tosylates. [Lancelot, C. J., Cram, D. Y., Schleyer, P. v. R., in: Carbonium ions. Olah, G. A. and Schleyer, P. v. R. (eds.). New York: Wiley 1972, Vol. III, p. 1347.]

10)[237]. The slope of this line is ρ^* for the solvent assisted reaction (k_s). Anchimeric assistance (k_Δ) is indicated by positive deviation from the line.

Application of the Taft treatment to cyclic and bicyclic systems suffers from the availability of σ^* values only for noncyclic substrates. The Foote-Schleyer correlation[238, 239] was proposed as a means for estimating acetolysis rates of cyclic substrates:

$$\log k_{rel} = \frac{1715 - \nu_{CO}}{8} + 1{,}32 \sum_i (1 + 3 \cdot \cos \phi_i) + \text{inductive terms} + \frac{GS_{strain} + TS_{strain}}{1{,}36}$$

This correlation utilizes the infrared carbonyl frequency of the ketone related to the secondary tosylate under investigation as a measure of angle strain contributing to the solvolysis rate. Torsional effects are accounted for by the second term. The third term corrects for the inductive effects of substituents. The last term represents the effect of nonbonded strain in the ground state (GS) and transition state (TS). However, since the latter quantity is difficult to calculate, TS $\simeq$ O has generally been assumed. As a consequence, serious discrepancies were observed with highly crowded systems[240]. The Foote-Schleyer equation predicts the acetolysis rates of "normal" substrates with remarkable success. It is, however, bothersome to find k_c and k_s substrates correlated by the same line. This reservation also applies to other empirical methods[241] which predict rates of acetolysis better than those of formolysis and trifluoroacetolysis.

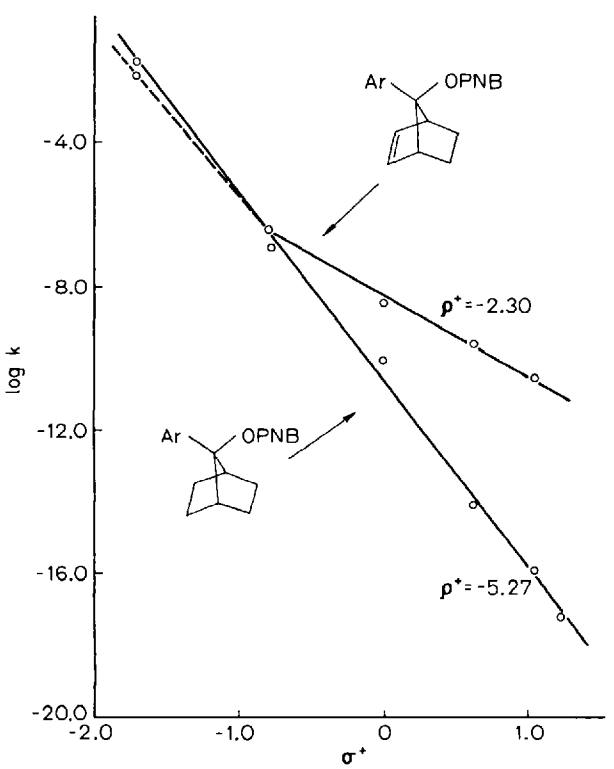
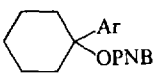


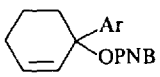
Fig. 11. Effect of increasing electron demand on the rates of solvolysis of 7-arylnorbornyl (*303*) and 7-aryl-*anti*-norbornenyl p-nitrobenzoates (*304*). [Reproduced from Brown, H. C.: The nonclassical ion problem. New York: Plenum Press 1977.]

7.2.2 Effect of Increasing Electron Demand

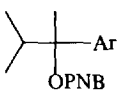
The importance of neighboring group participation should diminish as an incipient cation is stabilized by structure modification. The method is generally applied to a series of tertiary, aryl p-nitrobenzoates. By varying the substituents on the aryl ring, the sensitivity of the reaction to the substituents is revealed in the slope (ρ^+) of a Hammett-Brown plot of log k vs. σ^+. A very negative ρ^+ indicates that the incipient carbocation has high electron demand. Less negative values of ρ^+ are often symptomatic of carbocations whose electron demand is diminished by neighboring group participation. A break in the Hammett-Brown plot marks the onset of participation (Fig. 11)[242].



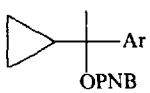
299
ρ^+ −4.60



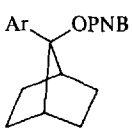
300
−2.52



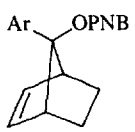
301
ρ^+ −4.76



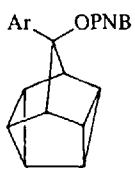
302
−2.78



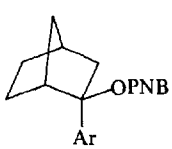
303
ρ^+ −5.27



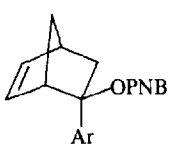
304
−2.30



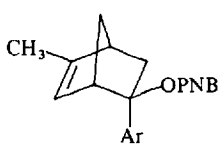
305
−2.05



306
ρ^+ −3.82



307
−4.21



308
−3.27

The pairs of p-nitrobenzoates, (*299*)/(*300*)[243] and (*301*)/(*302*)[244] confirm electron release to the carbocation by conjugation with double bonds and cyclopropane rings, respectively. The comparison of (*303*) with (*304*)[242] and (*305*)[245] demonstrates the analogous effect of double bond and cyclopropane participation in

the solvolyses of 7-norbornyl p-nitrobenzoates. The data for (*306*) and (*307*)[246] reveal that there is much less, if any, double bond participation in the solvolysis of (*307*). Anchimeric assistance is enhanced by methyl substitution at the double bond, as in (*308*)[247].

A theoretical method for estimating ρ^+ has been developed on the basis of perturbation theory and MINDO/3 calculations[248]. The agreement between theory and experiment establishes that the key factors governing the electron demand of a carbocation are the delocalization and energy of the cation's LUMO.

Attempts have been made to extend the Hammett-Brown treatment to other substrates. A linear free energy relationship $\log (k/k_o) = \rho\gamma^+$ was defined[249]. The group constants, γ^+, are characteristic of the ability of the group to stabilize an adjacent cationic center. These group constants are set equal to σ^+ for the aryl substituents. A constant for hydrogen, $\gamma^+_H = 2.53$ was obtained by extrapolating the data for (*303*) to the secondary derivative[249]. This constant correlates some secondary bicyclic tosylates remarkably well but fails with others, such as (*305*). In a similar way, $\gamma^+_{CH_3} = 0.77$ was determined and applied in correlating rates of solvolysis of tertiary methyl derivatives with the analogous tertiary benzyl derivatives[250, 251]. Correlations were excellent except when unusual steric effects cause a deviation. Moreover, $\gamma^+_{CH_3}$ appears to be solvent dependent[251].

In concluding this section, it should be emphasized that the tool of increasing electron demand is a rather coarse one. All the aryl groups, even $3,5\text{-}(CF_3)_2C_6H_3$, are π donors and stabilize an adjacent positive charge. Consequently, participation will be detected only in systems where anchimeric assistance is very large in magnitude. On the other hand, anchimeric assistance need not be of large magnitude to be significant. For example, a k_Δ/k_s ratio of only 10 implies that more than 90% of the reaction proceed through the anchimerically assisted pathway.

7.2.3 Kinetic Isotope Effects

Primary and secondary kinetic isotope effects are of general importance in the study of neighboring group participation. Isotopic substitution α to the incipient carbocation produces a secondary isotope effect whereas β and γ substituents may give rise to both primary and secondary effects. For example, if the rate determining step of a solvolytic reaction involves a hydrogen shift or elimination, primary deuterium isotope effects are clearly implicated.

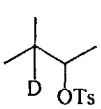
Secondary kinetic isotope effects provide one of the most subtle probes of reaction mechanism currently available as the perturbation of the system under study is small. Unfortunately, the interpretation of isotope effects is far from straightforward. There is no general agreement about the mechanistic significance of α-deuterium isotope effects in solvolytic reactions. The interpretation of more remote deuterium isotope effects appears to be even more complex.

According to Shiner[252] an α-deuterium isotope effect close to unity indicates a classical S_N2 reaction. However, recent reports[253–255] suggest that α-deuterium isotope effects up to 1.15 are consistent with displacement on covalent substrate. There is a linear relationship between the magnitude of nucleophilic solvent assistance

and the α-deuterium isotope effect for solvolyses of 2-propyl brosylate[233] (e.g., k_H/k_D = 1.114 in 50% ethanol/water[256]; k_H/k_D = 1.22 in trifluoroacetic acid[257]). As might be expected, the α-deuterium isotope effect for 2-adamantyl tosylate (*296*) is independent of solvent[258], k_H/k_D = 1.23 (sometimes referred to as the maximum or limiting value of α-deuterium isotope effects). For pinacolyl brosylate (*313*), k_H/k_D is likewise solvent independent, but only 1.15[256], contrary to the original interpretation[252, 256] it appears now[233] that such a change in α-deuterium isotope effect does not require different mechanisms. α-Deuterium isotope effects depend on the structure of the alkyl group, a fact which devalues their importance in the assignment of participation.

Hyperconjugation seems to be the major cause of secondary β-deuterium isotope effects. A linear free energy relationship between the CH_3/H rate effect and the CH_3/CD_3 isotope effect supports this conclusion[259]. The magnitude of a secondary β-deuterium isotope effect varies with the conformation of the transition state[252]. An empirical method has been developed which allows the estimation of secondary β-deuterium isotope effects as a function of the dihedral angle between the β–C–D bonds and the empty p orbital[260]. The maximum k_H/k_D (dihedral angle of 0°) is *ca.* 1.3.

The β-deuterium isotope effect of 3-methyl-2-butyl tosylate (*309*), k_H/k_D = 2.14–2.24, is much greater than the value expected for a secondary β–D effect[261]. These results, combined with product data, implicate neighboring hydrogen participation. The β–D effects on 3-pentyl brosylate (*310*) are cumulative, 1.317 for 2,2–D_2, 1.736 ≃ $(1.317)^2$ for 2,2,4,4–D_4[262]. This type of behavior, in which all deuteriums have an equal effect, is consistent with the hyperconjugative origin of β-deuterium isotope effects. In contrast, the β–D effects on the solvolysis of 2,4-dimethyl-3-pentyl brosylate (*311*) are noncumulative[262]; this type of behavior indicates hydrogen participation. β-Deuterium isotope effects in cyclopentyl brosylates are cumulative[263] whereas those in cyclohexyl tosylates are not[264]; major amounts of hydrogen shift are observed in the latter reaction.



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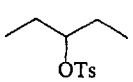

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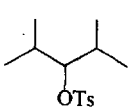

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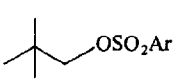

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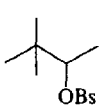

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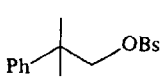

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Attempts to detect methyl participation in the solvolyses of neopentyl arenesulfonates (*312*) and pinacolyl brosylate (*313*) by means of γ-deuterium isotope effects have been inconclusive. Both compounds showed no significant kinetic isotope effect but nevertheless a distinct preference for CH_3 over CD_3 to migrate[265]. These data

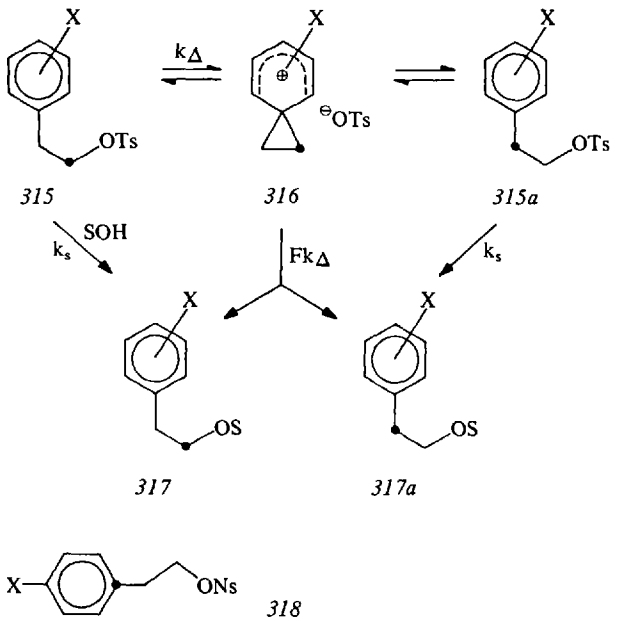
were interpreted as evidence for rate-limiting ionization without anchimeric assistance. Alternatively, the absence of a kinetic γ-deuterium isotope effect would be consistent with methyl participation if a regular effect of the migrating group is cancelled by an inverse effect of the two non-migrating groups[75]. In fact, the γ–D isotope effects of non-migrating methyl groups are inverse, k_{CH_3}/k_{CD_3} 0.90–0.95. Some support for methyl participation in the solvolysis of (*312*) comes from a study of γ-carbon kinetic isotope effects[266]. The effect for (*312*), k_{12}/k_{14} = 1.050, was even greater than that for the definitely aryl-assisted[237] neophyl brosylate (*314*), k_{12}/k_{14} = 1.023 (^{14}C at C–1 of the phenyl group).

7.3 Aryl Participation. Phenonium Ions

Arenes are known to undergo electrophilic substitution with variable ease, depending on the nature of the substituents. Aryl participation is the intramolecular analog of Friedel-Crafts alkylation. The phenonium ion (ethylenebenzenium ion) is a special example of the σ complex found in electrophilic aromatic substitution. Phenonium ions have been thoroughly studied in superacids (Section 3.1.2). The intervention of phenonium ions in solvolytic reactions has been controversial for some time, due to an apparent rate-product discrepancy[267]. This problem was later resolved by the understanding that solvent participation in the solvolysis of secondary tosylates can be large[233, 234] (Section 7.2.1.). To-day phenonium ions represent a well established class of bridged ions which provide valuable information on the reactivity of such species.

7.3.1 Primary Systems

The 2-arylethyl system (*315*) has received detailed scrutiny from many workers. Departure of the leaving group from a primary carbon eliminates unassisted ionization (k_c). The probability of anchimeric assistance (k_Δ) is increased, but nucleophilic solvent participation (k_s) is also accentuated. Ion pair return from (*316*) is revealed by scrambling of a ^{14}C label in the starting material[268]. Therefore, the titrimetric rate constant is given by $k_t=k_s+Fk_\Delta$, F representing the fraction of phenonium ion (*316*) which goes on to product. The dissection of k_t into k_s and Fk_Δ has been achieved by a combination of rate data and product data. (It must be taken into account that the k_s process can give scrambled product from starting material that has undergone k_Δ ionization and internal return. The net amount of scrambling due to the Fk_Δ process has been obtained by extrapolating the observed scrambling in the product (*317*) back to time = 0). The dissection has also been accomplished using rate data alone[269]. A Hammett plot was constructed from the acetolysis data for a series of β-arylethyl tosylates (Fig. 12). k_s was obtained by a computer program which iteratively corrects for the small Fk_Δ contributions found with deactivated substrates. The close agreement between rate and product data (Table 10) provides direct evidence for discrete solvent-assisted (k_s) and aryl-assisted (Fk_Δ) pathways. Electron-donating substituents X increase the percentage of aryl participation. This



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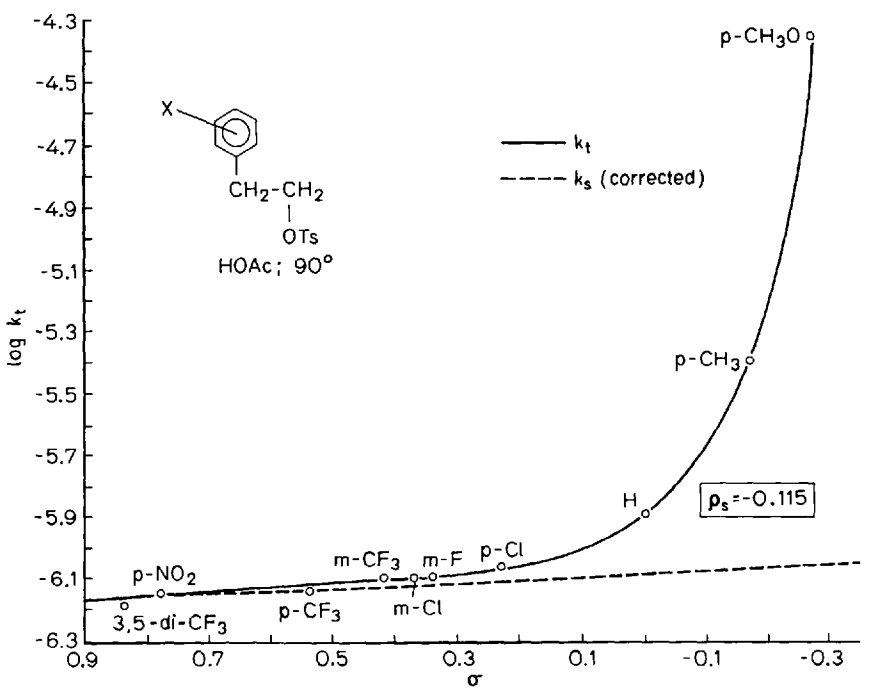


Fig. 12. Hammett treatment of the acetolysis of β-arylethyl tosylates. [Reproduced from Harris, J. M., Schadt, F. L., Schleyer, P. v. R., Lancelot, C. J.: J. Am. Chem. Soc. *91*, 7508 (1969).]

Table 10. Rate-product correlation for the acetolysis of 2-arylethyl tosylates (*315*) at 115°

X	k_t/k_s	% Rearr. (t = 0)	$Fk_\Delta/k_t \cdot 100$ from rates	products
p-Cl	1.21	4.4	18	9
H	1.73	14.6	42	38
p-CH_3	5.63	35.8	82	82
p-OCH_3	51.1	43.4	98	95

Table 11. Comparison of scrambling and stereochemistry in 2-phenylethyl solvolysis

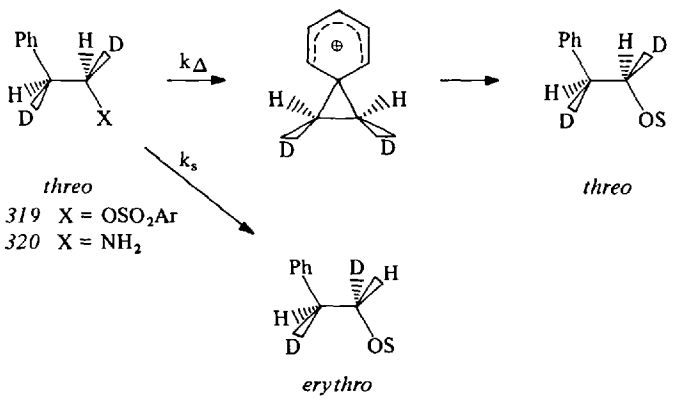
	% Rearr.	% Retention of stereochemistry
(*319*), CH_3CO_2H	6.5[1])	13
(*319*), HCO_2H	43.5	81
(*319*), CF_3CO_2H	50	98
(*320*), HNO_2, H_2O	27	52

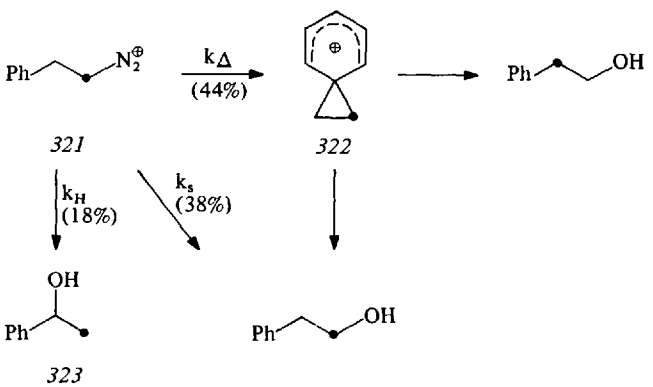
[1]) Buffered acetolysis, in contrast to Table 10. The presence of nucleophilic acetate ion increases k_s and decreases k_Δ.

is also seen from the kinetic isotope effects, k_{12}/k_{14} in the acetolysis of 2-arylethyl p-nitrobenzenesulfonates (*318*) which increase from 1.002 for X=H to 1.028 for X=OCH_3[270]. The k_s pathway (which contributes substantially in acetic acid) is virtually eliminated in weakly nucleophilic solvents. Thus, solvolysis of (*315*) in trifluoroacetic acid[271] and in trifluoroethanol[272] proceeded with complete scrambling of the label.

The stereochemistry of the solvolysis of 2-phenylethyl derivatives was determined with the aid of deuterium labels[273]. Diastereomerically pure (*319*) afforded product in which the extent of retention of diastereomeric configuration was twice the extent of label rearrangement in the solvolysis of (*315*), X=H (Table 11). This relation, which is uniquely required by a symmetric phenonium ion, also holds for the deamination of the corresponding amine (*320*)[274]. The 2-phenylethanediazonium ion (*321*) displays hydrogen shift to give 1-phenylethanol (*323*) in addition to the k_Δ and k_s pathways[275]. The position of the label in (*323*) – exclusively at C–2 – reveals that (*323*) does not originate from the phenonium ion (*322*). Conversion of (*322*) to the 1-phenylethyl cation proceeds slowly in superacids, E_a = 13 kcal/mole[52].

Among the many 2-arylethyl tosylates which have been studied the 1-azulyl- and 9-anthryl systems are distinguished by large rate accelerations. (*324*) solvolyzes 94000 times faster than (*315*), X=H, without ion pair return, and with complete scrambling of a label over C–1 and C–2[276]. Solvolysis of (*325*) in aqueous dioxane gave as the major product the spiro alcohol (*326*) which constitutes direct evidence

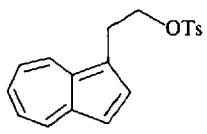




for a bridged intermediate[277]. The related spirodienone (*328*) was isolated from the alcoholysis of the conjugate base of 2-(4-hydroxyphenyl) ethyl bromide (*327*)[278]. The rate of this process exceeds that of the parent phenyl compound by a factor of 10^7.

One alkyl group at C–2 of (*315*) does not alter the mechanism of aryl participation. In the acetolysis of 2-phenyl-1-propyl brosylate (*329*) the rearranged product of internal return, (*331*), accumulates and can be isolated[279]. No rearranged products of return, (*329*), or solvolysis, (*332*), were obtained from (*331*). It may be concluded that the unsymmetrical phenonium ion (*330*) is attacked by nucleophiles at the methyl substituted site only. The formation of (*332*) from (*329*) must then be attributed to the k_s process. Stereochemical support for a bridged intermediate comes from the deamination of the amines (*334*) which produces products of phenyl migration (*335*) with virtually complete inversion of configuration[280, 281]. The lack of a sequential hydrogen shift to give (*337*) and products derived therefrom is additional evidence against the intervention of open cations (*336*)[281].

Further stabilization of a positive charge at C–2 leads to a reaction profile as shown in Fig. 7b. The first intermediate following the aryl-bridged transition state is no longer a phenonium ion but the more stable rearranged carbocation. This change in mechanism is brought about by two alkyl groups or one alkoxy substituent. Aceto-



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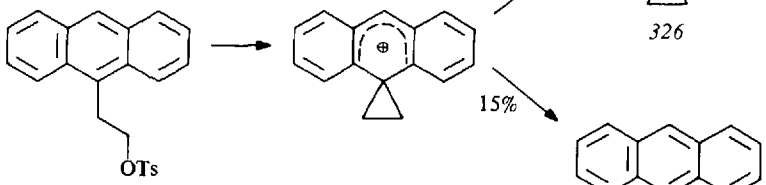
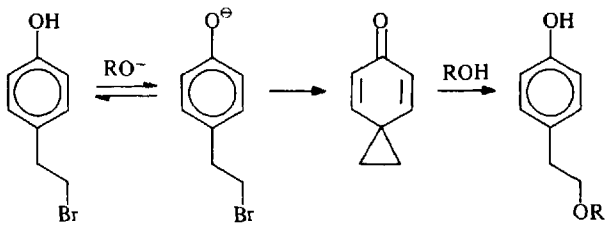
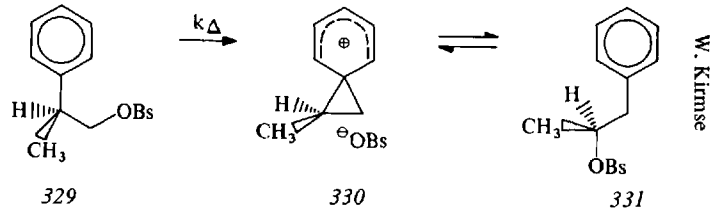


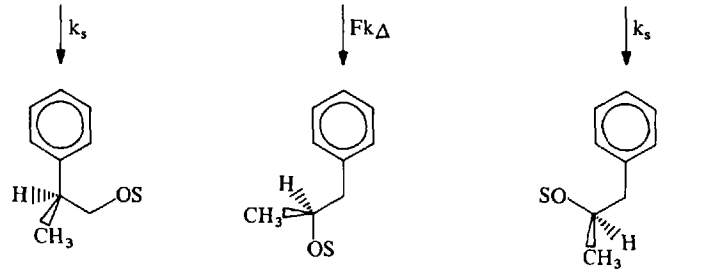
325 *326*



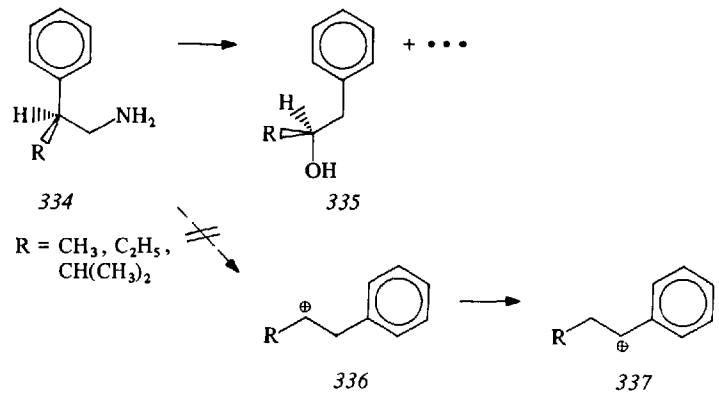
327 *328*



329 *330* *331*

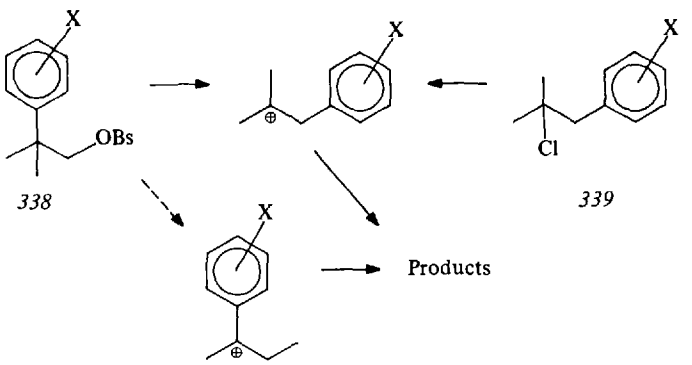


332 *333* *333'*

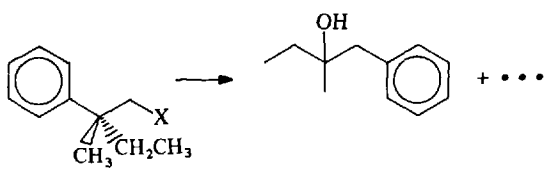


334 *335* *336* *337*

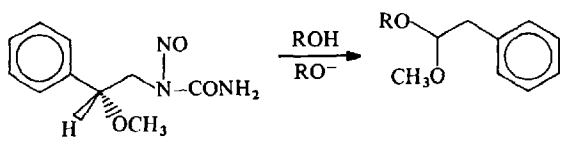
lysis of 2-aryl-2-methyl-1-propyl (neophyl) brosylates (*338*) results completely in rearranged products[283, 284] ($k_t=k_\Delta$). Methyl migration is a very minor reaction path with (*338*), X=H (0.3%)[284] but increases to 25% with (*338*), X=p–NO_2 [285]. A Hammett correlation of log k_t vs. σ^+ was obtained with a large negative ρ^+ of -3[283] which indicates considerable charge delocalization into the aryl ring in the rate-determining step. (Non-participating systems correlate against σ, with less negative slopes, $\rho \leq 1$). Moreover, log k_t of (*338*) correlates linearly with log (Fk_Δ) of (*315*)[285]. The observed slopes, 1.05 ± 0.14, are remarkably independent of solvent and suggest a similar degree of aryl participation in the transition state. The carbon kinetic isotope effect, $k_{12}/k_{14} = 1.023$ (phenyl-1-^{14}C) supports this conclusion[266].



338 *339*



340 X = OSO_2CH_3 *342*
341 X = NH_2

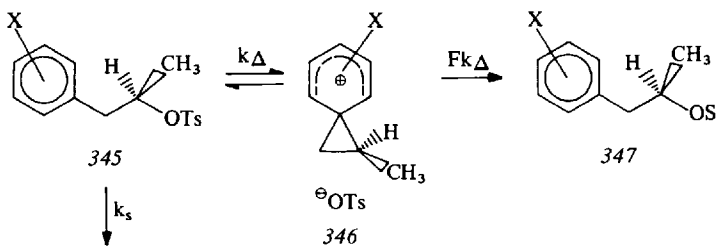


343 *344*

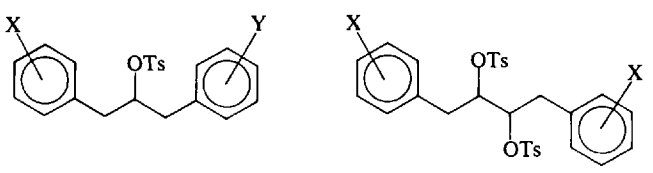
A bridged intermediate appears unlikely in the acetolysis of (*338*) since the solvolysis of the tertiary system (*339*) goes with neither aryl participation nor phenonium intermediates (cf. Section 7.3.3.). More direct evidence comes from the solvolysis of the chiral 2-methyl-2-phenyl-1-butyl system. Both the mesylate (*340*) and the amine (*341*) afford the product of phenyl migration, (*342*), with substantial racemization[285]. Similarly, the alkaline deamination of (*343*) yields largely racemic acetals (*344*)[286]. These stereochemical results clearly demonstrate the limits of phenonium ion intervention.

7.3.2 Secondary Systems

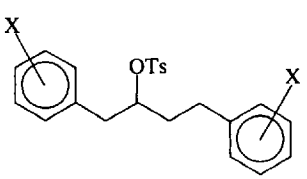
1-Aryl-2-propyl tosylates (*345*) solvolyze without rearrangement[279]. Therefore, any rate enhancement, and any retention of configuration, must be due to aryl bridging, (*346*). Fk_Δ was extracted from Hammett plots which are in qualitative agreement with those of primary systems (Fig. 12)[287]. In addition, a multiple substitution technique was applied which utilized a series of 1,3-diaryl-2-propyl tosylates (*348*).



345 *346* *347* *347'*



348 *349*



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In (*348*), both aryl groups can exert inductive effects but only one aryl group can participate. Therefore, the inductive term is multiplicative whereas the anchimeric assistance effect is statistically additive. The Fk_Δ values obtained from algebraic analysis of this system agree with those from the Hammett plot and correlate nicely with product data[279, 288, 289] (Table 12). The effects of added sodium azide on rates and products also reflect the relative contribution of the k_s pathway [290]. The higher the proportion of nucleophilic solvent assistance, the greater are both the rate enhancement due to added azide and the percentage of azide product. Enhanced aryl participation can be achieved by placing an electronwithdrawing

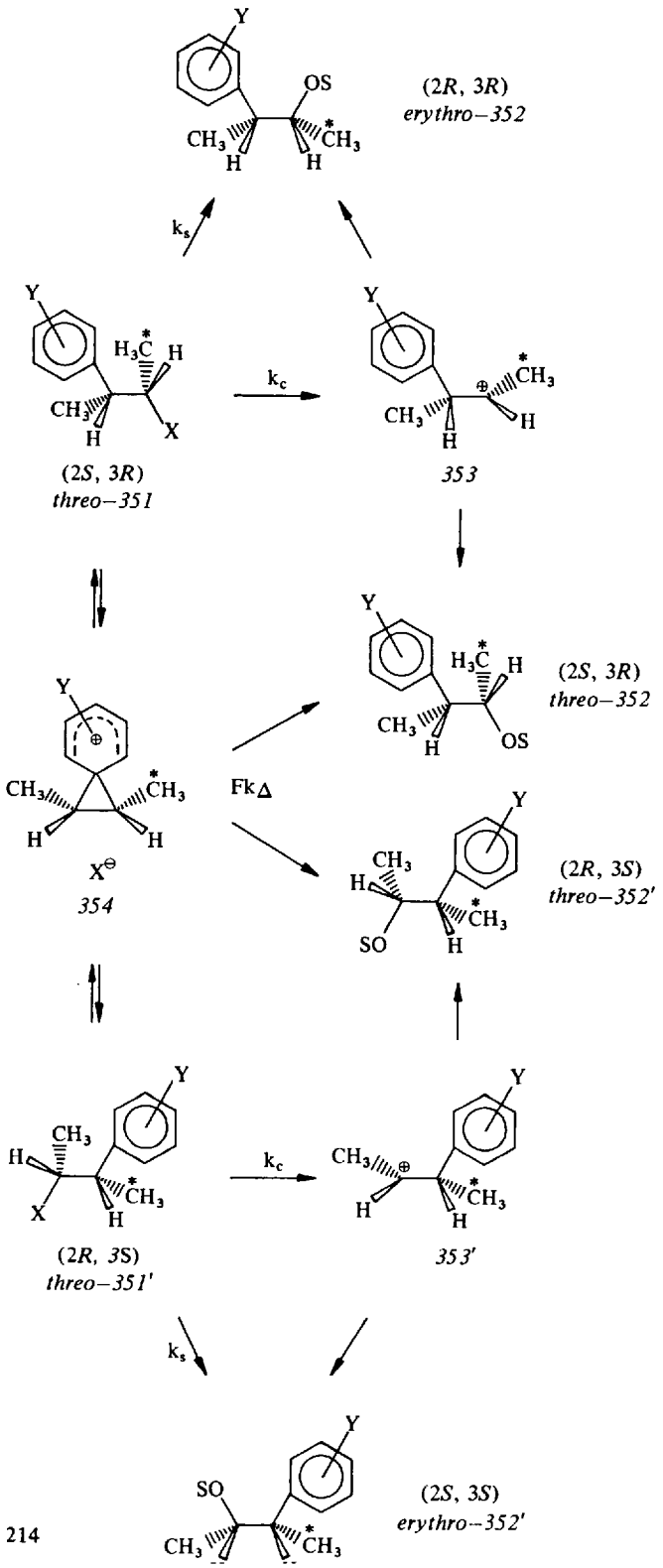
Table 12. Rate-product correlation for the solvolysis of 1-phenyl-2-propyl tosylate (*345*)

Solvent	k_t/k_s	% Inv.	% Ret.	100 Fk_Δ/k_t from rates	products
C_2H_5OH	1.08	93	7	7	7
CH_3CO_2H	1.6	65	35	37	35
HCO_2H	4.5	15	85	76	85
CF_3CO_2H	564	0	100	99.8	100

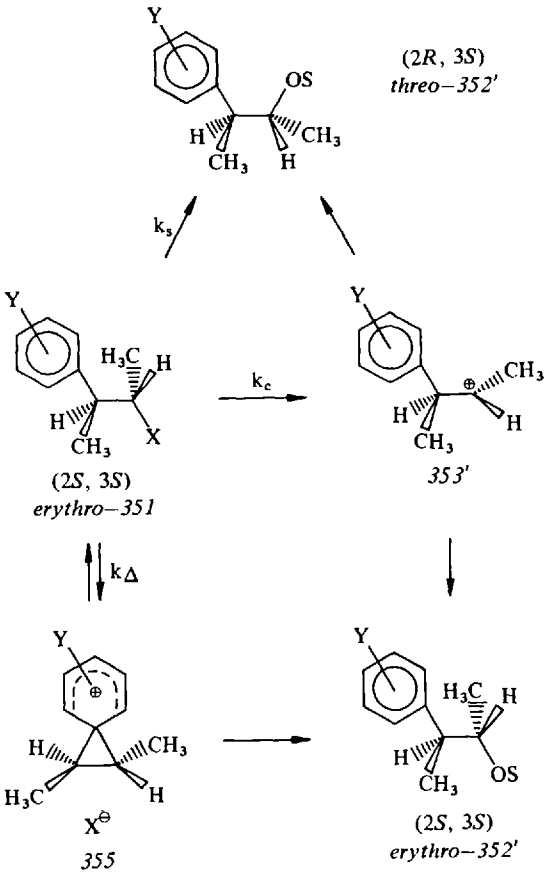
substituent vicinal to the leaving group, such as the second tosylate group in (*349*). Comparison with (*350*) shows that aryl participation increases from 66 to 99% for p–CH_3, from 35 to 94% for H, and from 0 to 68% for p–Cl[291] (values derived from the Hammett plots; (*350*) corresponds closely to (*345*)). Historically, Cram's exhaustive study of the 3-phenyl-2-butyl system (*351*) was the first account of aryl participation and phenonium ion intermediates[292]. The most striking result in the acetolysis of optically pure *threo*- and *erythro*- (*351*), X=OTs, is that the *threo*-tosylate gave 96 percent racemic *threo*-acetate (*352*) (plus olefins), whereas the *erythro*-tosylate gave 98% optically active *erythro*-acetate (Table 13). Phenyl migration was demonstrated by acetolysis of optically pure diastereoisomers which had been labeled at C–1 with ^{14}C. The racemic *threo* product from (2*S*, 3*R*)–(*351*) was reresolved; the (2*S*, 3*R*) enantiomer was found to have all the radioactive label at C–1 and the (2*R*, 3*S*) enantiomer at C–4. These results are consistent with the intervention of the achiral phenonium ion (*354*) in the solvolysis of *threo*- (*351*), and of the chiral phenonium ion (*355*) in the solvolysis of *erythro*- (*351*).

Table 13. Products of solvolysis of 3-phenyl-2-butyl derivatives (*351*)

X	Y	Solvent	(*352*) % Yield	*Threo*-(*352*) active	rac.	*Erythro*-(*352*) active	rac.
OTs	H						
Threo		CH_3CO_2H	53	0.6	94	1.2	4.8
Erythro		CH_3CO_2H	68	2	0	98	0
Threo		HCO_2H	70		>99		
Erythro		HCO_2H		<0.5		>99	
OTs	OCH_3						
Threo		CH_3CO_2H	99.7		100		
OTs	NO_2						
Threo		CH_3CO_2H	13	7		93	
Erythro		CH_3CO_2H	9	90		10	
Threo		HCO_2H	11	30		70	
Erythro		HCO_2H	9	63		37	
N_2^+	H						
Threo		H_2O	44	14	43	32	11
Erythro		H_2O	74	8	0	92	0


(2R, 3R)
erythro–352
(2S, 3R)
threo–351
353
(2S, 3R)
threo–352
354
(2R, 3S)
threo–352'
(2R, 3S)
threo–351'
353'
(2S, 3S)
erythro–352'

Ion pair return from (*354*), X=OTs, results in racemization of *threo*-(*351*) which is about 4 times faster than acetolysis; i.e. only 20% of the products come from optically active *threo*-(*351*) and 80% come from racemic tosylate. These proportions are in quantitative agreement with those determined from kinetic studies[293]. Ion pair



return must be taken into account when we estimate the fraction of products which do not arise from the phenonium ion (*354*). *Threo*-(*351*) affords 0.6% of optically active *threo*-acetate. Since the starting tosylate was 80% racemized, about 2.4% of racemic *threo*-acetate must have arisen from the same mechanistic pathway that gave the 0.6% active *threo*-acetate; i.e. about 3% of the *threo*-acetate are not derived from (*354*). Unassisted ionization (k_c) reasonable accounts for the active *threo*-acetate, and also for a fraction of the olefins[292, 294]. *Erythro*-acetate (*352*) may arise by the k_c and k_s processes.

Aryl participation is enhanced by less nucleophilic solvents (cf. formolysis of (*351*), Y=H, Table 13) and by increasing the donor capacity of the aryl group. *Threo*-(*351*), Y=OCH_3, X=OTs, gave *threo* acetate to the virtual exclusion of any other products; no *erythro* acetate was detectable by gas chromatography[295]. On the other hand, a nitro group accentuates the k_s pathway. (*351*), Y=NO_2, X=OTs was found

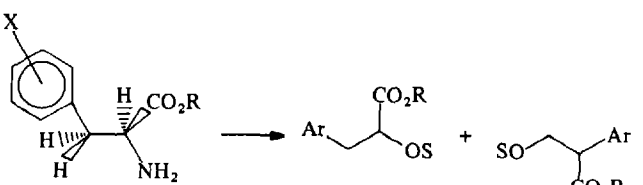
Table 14. Rate-product correlation for the acetolysis of *threo*-2-aryl-2-butyl brosylates (*351*)

Y	k_t/k_s	$100\ Fk_\Delta/k_t$	% *Threo*-acetate
p-NO_2	1.0	0	1
p-Cl	1.6	37	39
H	3.0	66	59
m-CH_3	3.7	73	68
p-CH_3	7.6	87	88
p-OCH_3	71	99	100

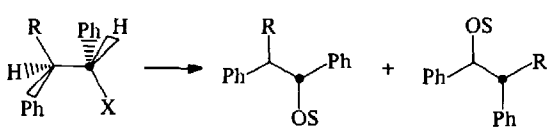
to acetolyze with predominant inversion, i.e. *threo*- (*351*) → *erythro*- (*352*), and *erythro*- (*351*) → *threo*- (*352*) (Table 13)[296]. An excellent product-rate correlation was obtained for a series of substituted *threo*-2-phenyl-2-butyl brosylates, (*351*), X=OBs, (Table 14)[297].

The deamination of 3-phenyl-2-butylamines, (*351*), X=NH_2, differs strongly from the solvolysis of the corresponding tosylates (Table 13)[200]. As pointed out previously, these reactions are conformationally controlled (Section 6.2). With the *erythro* diastereomer, the *trans* orientation of phenyl and amino (diazonium) groups is conformationally favored. A high yield of optically active *erythro* product results. With the *threo* diastereomer, phenyl participation is conformationally disfavored. *Threo* and *erythro* products are obtained in comparable quantities, and with partial racemization, indicating the dominance of the k_c pathway.

The factors which control aryl participation in the decomposition of secondary diazonium ions are illustrated by the nitrous acid deamination of ethyl 2-amino-3-arylpropionates (*356*)[298]. Both the retention of configuration in non-rearranged product (*357*) and the relative yield of rearranged product (*358*) increase in the order $O_2N < H < OCH_3$ for phenyl substitution, and in the order $H_2O < CH_3CO_2H < CF_3CO_2H$ for the solvent.



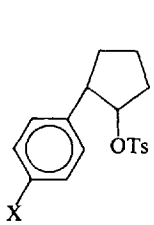
356 *357* *358*



357 R = Ph, X = OTs *361* *362*
358 Ph NH_2
359 H NH_2
360 CH_3 NH_2

Further stabilization of a positive charge at the migration terminus removes the need for aryl participation even in tosylate solvolysis. Appropriately labeled 1,2,2-triphenylethyl tosylate (*357*) undergoes acetolysis with equilibration of the phenyl groups but with only a slight preference of retention over inversion (1.2–1.4)[299]. Deamination of 1,2,2-triphenylethylamine (*358*) yields analogous results, with a slightly higher degree of retention of configuration[300]. The degenerate phenyl shift in the deamination of (*358*) is remarkable as 1,2-diphenylethylamine (*359*) and 1,2-diphenylpropylamine (*360*) do not react with analogous shifts of hydrogen and methyl, respectively[301]. Although phenonium ions are no longer intermediates in the 1,2,2-triphenylethyl system they still represent energetically favorable transition states (cf. the reaction profile shown in Fig. 7a).

The following paragraphs review some cyclic systems with geometrical contraints on aryl participation. In *cis*-2-arylcyclopentyl tosylates (*363*) the aryl group is not properly disposed for backside attack on the tosylate-bearing carbon atom. The acetolysis of (*363*) gives rise predominantly to elimination and small amounts of inverted acetate; the rate constants correlate with the regular σ constants[302]. On the other hand, the aryl ring in the epimeric *trans* series (*364*) can, with some twisting of the ring, assume the required *anti* orientation to the leaving group. The solvolysis products of (*364*) vary from almost complete retention (98% for 4–OCH_3) to complete inversion (100% for 4–NO_2). The curved Hammett plot also suggests participation of the electron-rich aryl groups[302].



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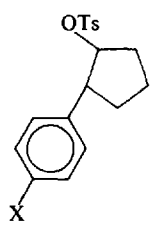

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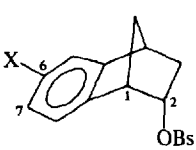

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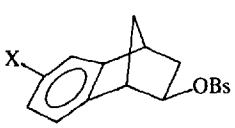
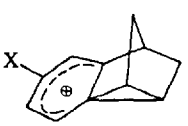


366

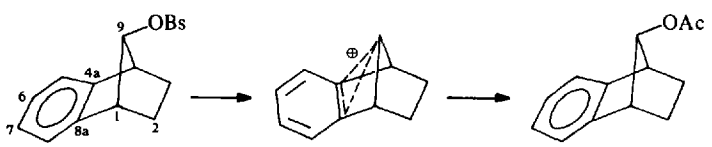


367

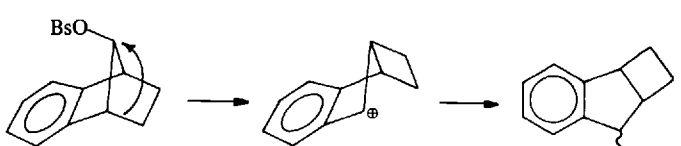
Aryl participation is greatly enhanced in *exo*-2-benzonorbornenyl tosylate (*366*) which differs from (*364*) by an additional C–C bond. The phenyl ring is now fused into a rigid system to provide close to maximal overlap between the aryl π and carbenium p orbitals. The aryl group cannot provide anchimeric assistance to the ionization of the *endo* epimer (*365*). The *exo/endo* rate ratio for the acetolysis of the parent brosylates, X=H, is 15000[303, 304] (62000 if polarimetric rates are used instead of k_t[305]). A 6-methoxy group in (*366*) increases the rate by a factor of 150, and the *exo/endo* rate ratio by a factor of 60[303, 306]. A 7-methoxy group has no

significant effect[306, 307]. Deactivation of the benzo ring in (*366*) by 6,7-dinitro substitution causes an enormous reduction in the *exo/endo* rate ratio to ca. 4[308]. The substituent effect is clearly inconsistent with a purely steric explanation of *exo/endo* rate ratios. Acetolysis of both epimers of the parent brosylate, X=H, affords only *exo* acetate. Optically active substrates solvolyze with complete racemization[305]. These observations are consistent with the bridged phenonium ion (*367*) as the product-forming intermediate. The 6,7-dinitro derivative, however, gives rise to about equal amounts of *exo* and *endo* acetates, and if optically active substrate is used, the products are not completely racemic[308].

All the available evidence points to very substantial aryl participation in the *anti*-9-benzonorbornenyl system (*368*)[309]. The sole reaction product is the *anti* acetate (*370*). The experimentally determined value of -5.10 for the Hammett ρ^+ is the largest yet observed for any 2-arylalkyl system. The structure of the intermediate (or transition state) (*369*) must be different from the phenonium ions considered until now. In the symmetrically 6,7-disubstituted system the effect of the two groups is the square of that of a single group, i.e. two carbons of the aryl ring (C–4a and C–8a) assist in the formation of the carbocation (edge participation). The aryl group behaves like a double bond (Section 7.4), but less efficiently[310]. Structure (*369*)



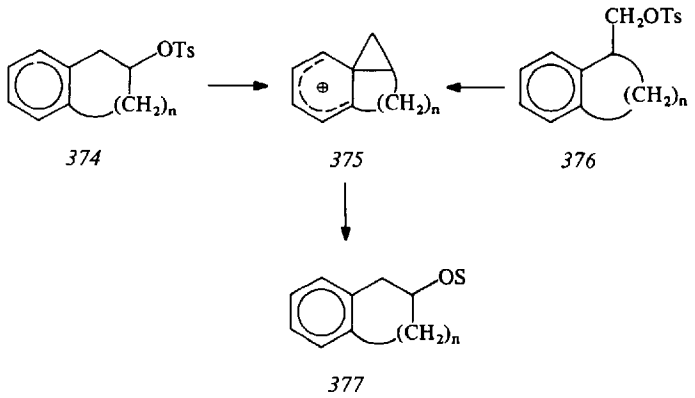
368 *369* *370*



371 *372* *373*

may be classified as a bishomobenzocyclopropenium ion rather than a phenonium ion. The unassisted solvolysis of *syn*-9-benzonorbornenyl brosylate (*371*) involves an alkyl shift to give (*373*). Increasing ring strain is compensated by the benzylic resonance of the rearranged carbocation (*372*). The behavior of (*368*) and (*371*) contrasts with the 2-benzonorbornenyl series where both epimers react by way of the phenonium ion (*367*), despite the lack of anchimeric assistance in the ionization of (*365*).

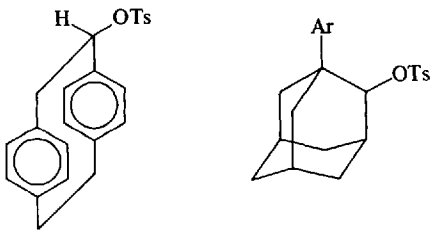
The tosylates (*374*) and (*376*) are both possible precursors of the spirocyclic phenonium ion (*375*). The degree of strain required to accomodate the phenonium ion is clearly dependent on ring size. Rate and product studies – including the stereochemistry of (*377*) from optically active precursors – suggest intervention of (*375*) with $n \geq 3$[311]. With n=2, all evidence is against a phenonium ion intermediate.



374 *375* *376* *377*

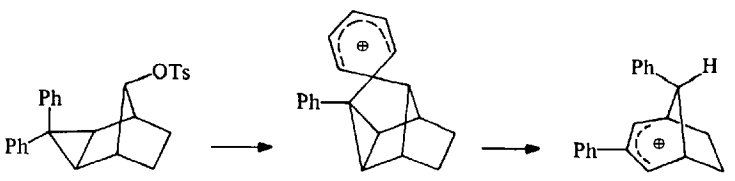
Nevertheless even the smallest available homolog, (*376*, n=1), solvolyzes with predominant phenyl (rather than alkyl) migration[312].

Aryl participation in the [2.2] paracyclophane system (*378*) requires distortion of this already highly strained molecule. Yet solvolysis proceeds with complete re-

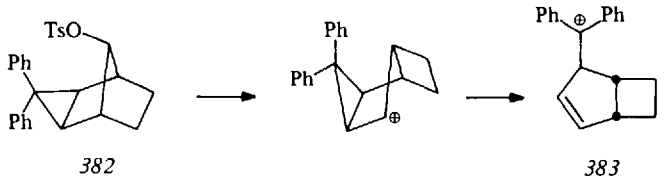


378 *379*

tention of configuration, and acetolysis rates are about 100 times faster than those of aliphatic secondary tosylates[313]. As might be expected, no significant aryl participation was observed in the solvolysis of 1-aryl-2-adamantyl tosylates (*379*)[314].



380 *381*



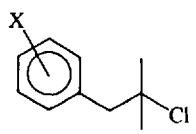
382 *383*

A remarkable transannular phenyl migration occurs in the tricyclic system (*380*) which hydrolyzes to products derived from the allylic cation (*381*)[315]. Aryl-assisted ionization gives rise to a cyclopropyl cation which undergoes ring opening to (*381*). Alkyl shift predominates in the epimeric tosylate (*382*) although some leakage toward (*381*) is also found.

7.3.3 Tertiary Systems

The 1-aryl-2-methyl-2-propyl system (*384*) serves as a model for anchimerically unassisted behavior. The rate constants are well correlated with the regular Hammett σ constants; a value of ρ close to -1 indicates little if any charge delocalization into the aryl ring[297, 316]. No rearranged products are found[317].

Methanolysis of the labeled 2,3-dimethyl-3-phenyl-2-butyl chloride (*385*), X=H, proceeds with 49% scrambling *via* phenyl migration[297]. The p-chloro compound



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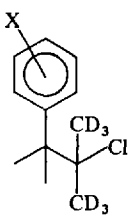

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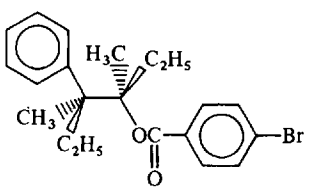
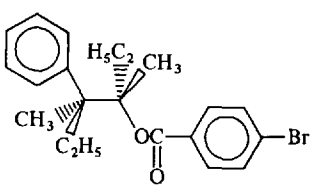


threo–386



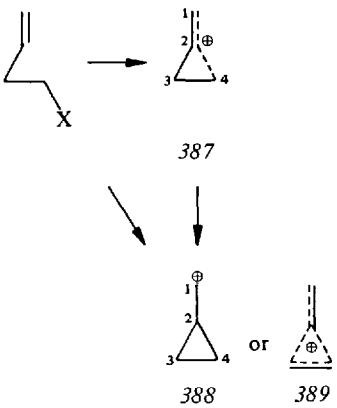
erythro–386

shows only 19% rearrangement. Scrambling increases with the introduction of activating groups: X=CH_3, 97%; X=OCH_3, 100%. In spite of complete scrambling the rate enhancement for the p-anisyl derivative amounts merely to a factor of *ca.* 2. The product-rate discrepancy argues strongly in favor of a pair of equilibrating tertiary ions, formed with little or no aryl participation.

Stereochemical results from the acetolysis of the chiral 3,4-dimethyl-4-phenyl-3-hexyl p-bromobenzoates (*386*) support this conclusion[318]. The product distributions from *threo*- and *erythro*- (*386*) are very similar. In contrast to the 3-phenyl-2-butyl system (*352*), *threo*- (*386*) acetolyzes without predominant racemization but gives three times as much optically active as racemic product (olefins only). A meso phenonium ion cannot intervene in the solvolysis of *threo*- (*386*).

7.4 Participation by Double Bonds. Homoallylic and Homoaromatic Cations

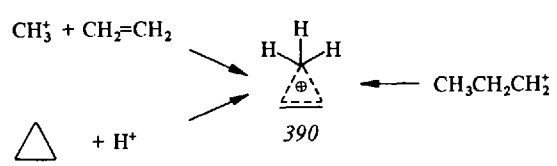
Interaction between double bonds and incipient carbocations may occur in an unsymmetrical fashion ("end-on") to give homoallylic cations (*387*) and/or cyclopropylcarbinyl cations (*388*). The relationship of (*387*) with the conjugated allyl cation is obvious. As suggested by Winstein[319], homoconjugation involves electron delocalization across intervening carbon atoms. In contrast to (*387*), cyclopropylcarbinyl cations (*388*) are readily obtained in superacids. Their spectra indicate substantial charge delocalization into the three-membered ring (Section 3.1.3). A "dotted line"



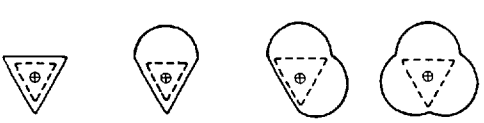
387 *388* *389*

representation (*389*) is preferred by some authors. The equivalence of carbons 3 and 4 distinguishes the cyclopropylcarbinyl cation (*388*)/(*389*) from the homoallylic cation (*387*). The homoallylic structure (*387*) places no partial positive charge on C–3. It remains to be seen whether (*387*) represents an energy minimum or merely a transition state on the reaction path to (*388*). Cyclopropylcarbinyl cations are treated more explicitly in Section 7.5.. The type of π-participation just described may be extended to triple bonds[320].

Alternatively, double bonds and carbocations may interact in a more symmetrical fashion ("side-on") to generate a three-center, two-electron bond (*390*). Closely



390



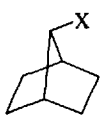
Monohomo Bishomo Trishomo

391 *392*

related, if not identical species are produced by protonation of cyclopropanes, and in 1,2 alkyl shifts. Depending on its genesis, (*390*) has been viewed as a π complex, protonated cyclopropane, or as an alkyl-bridged ("nonclassical") carbocation. The role of (*390*) as an intermediate is discussed in Section 7.6. Some special cases of (*390*) may be classified as bishomocyclopropenium ions (*391*). Winstein's concept of homoaromaticity[319] suggests that part of the cyclic delocalization of the aromatic cyclopropenium ion is retained when the σ skeleton is interrupted on one, two, or three sides. Designations such as mono-, bis-, and tris-homoaromatic refer to the number of sides where the σ backbone is removed or lengthened and not to the number of carbon atoms inserted on any particular side. The efficiency of homoaromatic stabilization depends critically on the ability of the σ framework to ensure the appropriate distance and orientation of the p orbitals.

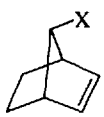
7.4.1 The 2-Norbornen-7-yl Cation and Related Systems

7-Norbornyl esters (*393*) solvolyze very slowly, probably because of angle strain and eclipsing in the 7-norbornyl cation. The presence of a double bond *anti* to the 7-sub-



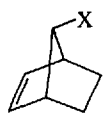
393

$k_{rel.}$ 1



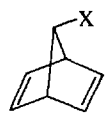
394

10^4



395

10^{11}

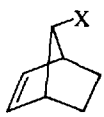


396

10^{14}

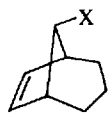
397

$\frac{k_{unsat.}}{k_{sat.}}$ $5 \cdot 10^{16}$



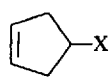
395

10^{11}



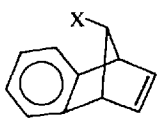
398

$2 \cdot 10^5$

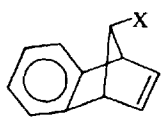


399

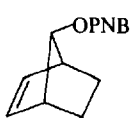
0.12



400

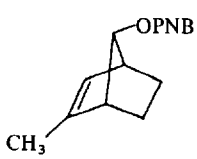


401



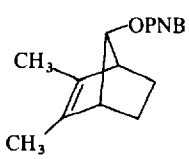
395a

$k_{rel.}$ 1



402

13.3



403

148

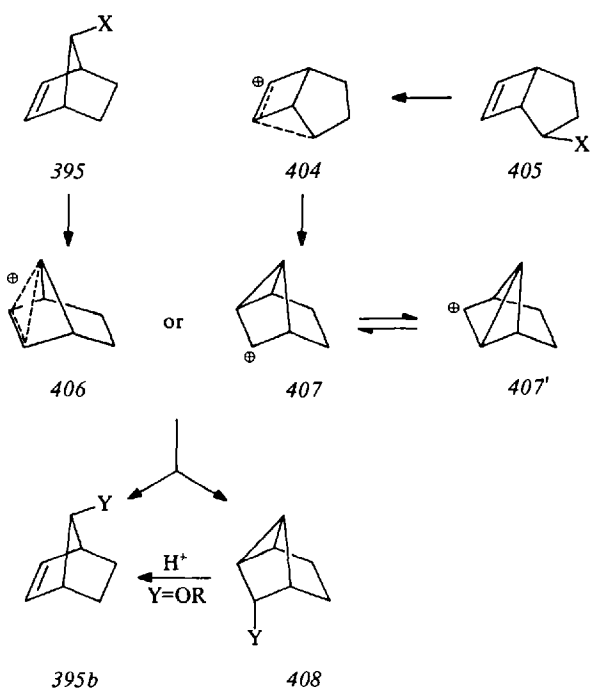
stituent enormously enhances the rate of solvolysis of (*395*)[321]. The *anti/syn* rate ratio, (*395*)/(*394*), is also large. Participation of the double bond in the solvolysis of (*395*) is confirmed by the tool of increasing electron demand (Section 7.2.2)[242, 243].

The effect of structural variations is demonstrated by comparing the rates of the unsaturated compounds (*397*)–(*399*) with those of their saturated analogs. Anchimeric assistance decreases in the order (*397*)[322] > (*395*) > (*398*)[323] > (*399*)[324]. Both the rate ratios[324] and the tool of increasing electron demand[325] suggest the absence of significant 1,3-interaction in (*399*). In the lower homologs of the bicycloalkenes the five-membered ring is more puckered than in the higher homologs, and backside participation by the double bond is facilitated.

The π electrons of an alkene are higher in energy and, therefore, more efficient in assisting ionization than those of an aryl group. The solvolytic rates of (*400*) are enhanced over those of (*401*) by factors of 10^3 (X=Cl) and $4 \cdot 10^4$ (X=Br)[310].

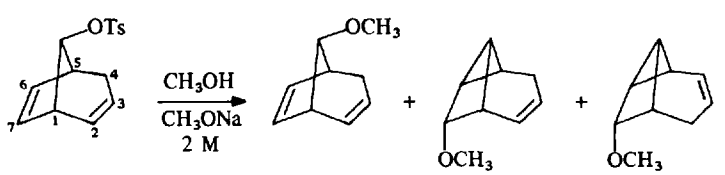
The transition state of the assisted ionization of 2-norbornen-7-yl p-nitrobenzoate (*395a*) has been explored by comparison with the 2-methyl and 2,3-dimethyl derivatives, (*402*) and (*403*), respectively[326]. If participation stemmed from one end of the double bond, then the rate effect of 2,3-dimethyl substitution should double that of a 2-methyl group (statistical effect). The cumulative effect which was actually observed is evidence for the symmetrical nature of the transition state. Caution must be exercized, however, in extrapolating the symmetrical effects in the transition state to postulate a symmetrical carbocation.

Structures which have been proposed for the 2-norbornen-7-yl cation include the symmetrical bishomocyclopropenium ion (*406*) (Winstein)[321] and the rapidly equilibrating pair of tricyclic cations (*407*) ⇄ (*407'*) (H.C. Brown)[327]. The products de-

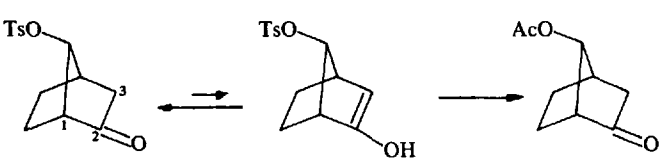


rived from the 2-norbornen-7-yl cation under conditions of thermodynamic control are *anti*-7-norbornenyl derivatives (*395b*). Under conditions of kinetic control, and with strong nucleophiles, tricyclic products (*408*) are also obtained, e.g. (*408*), Y=OCH_3 with methoxide[328], and (*408*), Y=H, with sodium borohydride[327]. The product ratios do not depend on the genesis of the 2-norbornen-7-yl cation, whether by solvolytic[328] or deaminative routes[329], or from the bicyclo [3.2.0] heptenyl system (*405*)[329–331]. The proportion of (*408*), Y=OCH_3, increases strongly, however, with increasing concentration of methoxide[328]. In buffered methanol, in which (*408*), Y=OCH_3, is fully stable, only 0.3% of this material is formed whereas in 4 M methoxide 50% of the tricyclic ether obtains.

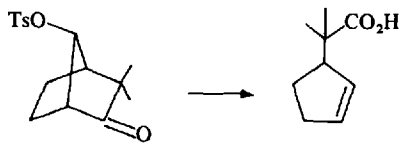
The nature and ratio of the products does not provide definitive answers as to the structure of the intermediate cation. The highly strained tricyclic ether (*408*), Y=OCH_3, and alcohol, Y=OH[332] rearrange readily to 7-norbornenyl derivatives (*395b*) on acid catalysis. Large amounts of (*395b*) are formed, however, under conditions where (*408*) is perfectly stable. These results are interpreted without difficulty in terms of the bridged cation (*406*), but they are also compatible with the cyclopropylcarbinyl formulation (*407*) if some delocalization of positive charge to C–7 is implicated, cf. (*388*) and (*389*). Even with such delocalization each individual molecule of (*407*) is still distinguished from (*406*) by its chirality. The ^{13}C-NMR spectrum of the 2-norbornen-7-yl cation (Section 3.1.3.) reveals C_2 symmetry. If the cyclopropylcarbinyl structure is correct, the equilibration (*407*) $\rightleftarrows$ (*407'*) must be rapid on the NMR time scale. The ^{13}C chemical shifts indicate more positive charge at C–2,3 than at C–7, a result which is consistent with both structural hypotheses. The variation of product ratio with the attacking nucleophile has been interpreted in terms of "early" and "late" transition states[328]. A good nucleophile ("early" transition state) attacks the site of greatest positive charge to give predominantly (*408*) whereas a poor nucleophile ("late" transition state) produces the energetically more favorable product (*395b*). The exclusive *endo* stereochemistry of (*408*) is a logical consequence of the bridged structure (*406*) but is most difficult to explain in terms of (*407*). The reason Brown has given in such cases is that the rapid bond shifts (*407*) $\rightleftarrows$ (*407'*) prevent attack of solvent from the *exo* side (the "windshield wiper effect").



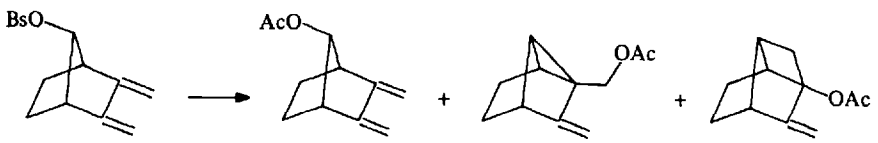
409 85 8 4%



410 *411* *412*



413



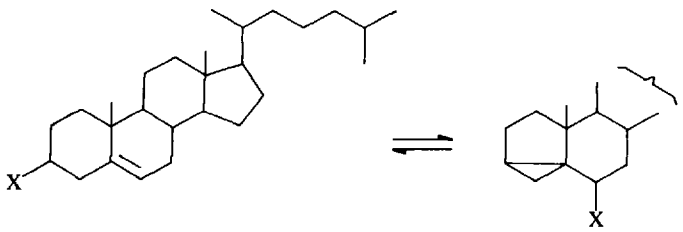
414

The cations intervening in the solvolysis of 7-norbornadienyl esters (*396*)[321, 327, 333] and of bicyclo [3.2.1] octa-2,6-dien-8-yl tosylate (*409*)[334] pose similar structural problems. Both systems afford tricyclic products in the presence of strong nucleophiles. The interesting degenerate rearrangements and bride-flipping processes of 7-norbornadienyl cations in superacids[335] are outside the scope of this review. π-Participation in 2-norbornen-7-yl systems is so effective that the ketone (*410*) solvolyzes *via* its enol (*411*) to give the ketoacetate (*412*) with retention of configuration[336]. Acetolysis of (*410*) is 10^4 times faster than that of its epimer, and 10^7 times faster than that of 7-norbornyl tosylate (*393*), X=OTs. Intervention of the enol (*411*) is clearly demonstrated by the incorporation of deuterium at C–3 during acetolysis in CH_3CO_2D. The enol mechanism is eliminated by 3,3-dimethyl substitution. The solvolysis of (*413*) is unassisted and proceeds with fragmentation[337].

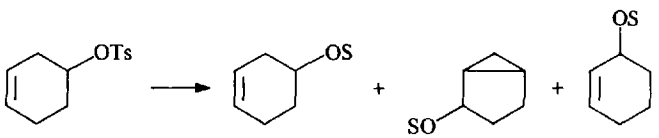
2,3-Dimethylene-*anti*-7-norbornyl brosylate (*414*) is another interesting substrate to compare with (*395*). Although C–2 and C–3 are sp^2 hybridized in both (*395*) and (*414*) the electron distributions differ strongly. The diene HOMO of (*414*) has minimum electron density between C–2 and C–3; therefore, homoaromatic participation cannot occur. The rate of acetolysis of (*414*) is slower by a factor of 10^7 than that of (*395*); the products point to homoallylic participation of one double bond[338]. (*414*) actually belongs to the category of compounds to be discussed in the following paragraph.

7.4.2 The 5-Norbornen-2-yl Cation and Related Systems

Homoallylic participation was first invoked by Shoppee to account for the high rates and the stereospecificity of 3β–(*415*) and i-cholesteryl (*416*) interconversions[339]. The double bond in (*415*) is clearly restricted to participation by one end. We cannot distinguish, however, between a homoallylic and a cyclopropylcarbinyl cation as the intermediate [cf. (*387*) and (*388*)] because both would be chiral. The same limitations apply to the 3-cyclohexenyl system. The tosylate (*417*) acetolyzes slightly more slowly than cyclohexyl tosylate[340]. The products include the acetate (*418*) corresponding to the starting material, the bicyclic acetate (*419*), and (*420*) as a result of hydro-



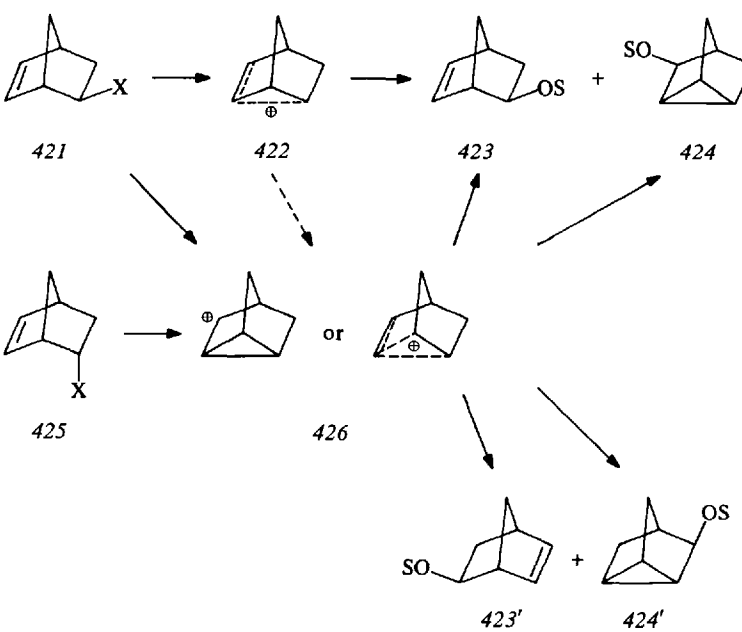
415 *416*



417 *418* *419* *420*

gen shift[341]. Starting with optically active (*417*), the stereochemistry of (*418*) varies from 100% inversion in aqueous dioxane to 100% retention in hexafluoroisopropanol[340]. Inversion is taken to indicate solvent displacement (k_s), and retention to indicate homoallylic assistance (k_Δ).

The 5-norbornen-2-yl system (*421*) is relatively well understood. Homoallylic participation is weak so that the double bond actually causes a rate retardation[342]. Participation is not detected by the tool of increasing electron demand (Section 7.2.2.)[244,266]. Yet the *exo*-tosylate (*421*), X=OTs, acetolyzes 7000 times faster than the *endo*-tosylate (*425*), X=OTs, to give the tricyclic acetate (*424*) as the principal product (ca. 90%)[343]. The hypothetical homoallylic intermediate (*422*) is

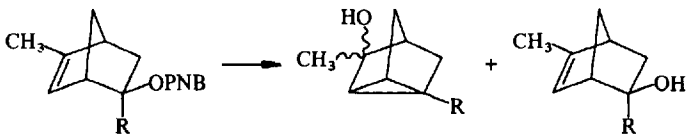


421 *422* *423* *424*

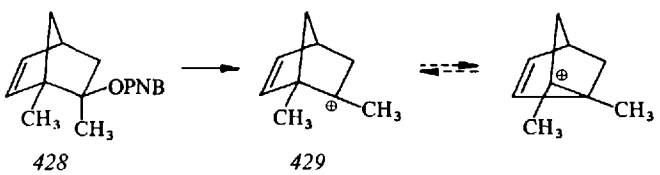
425 *426*

423' *424'*

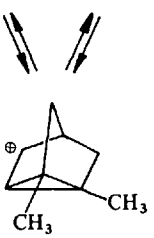
distinguished from the cyclopropylcarbinyl (=nortricyclyl) cation (*426*) by its chirality. Partial retention of configuration (or incomplete scrambling of a label) in the norbornenyl products, i.e., an excess of (*423*) over (*423'*), has been observed in some solvolytic[344,345] and deaminative studies[346], though not in others[343,347]. These results may be due to solvent displacement (k_s) and provide no conclusive evidence

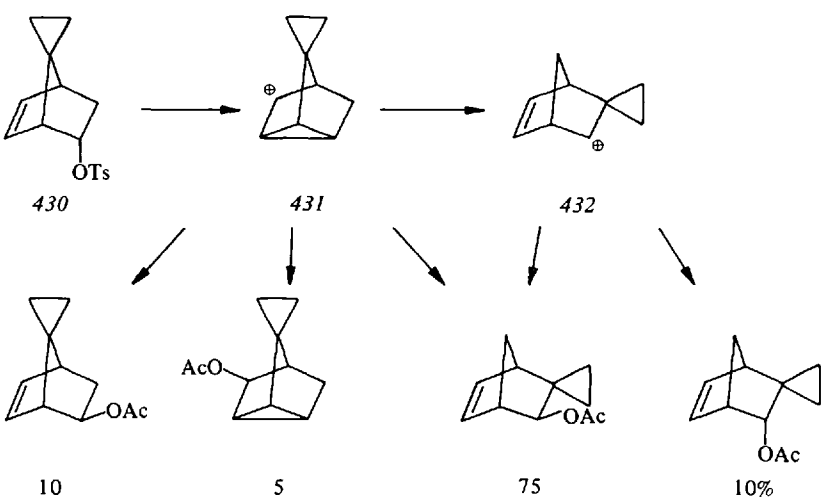


427 R = CH_3 > 98 < 2%
R = Ph 82 18%



428 *429*





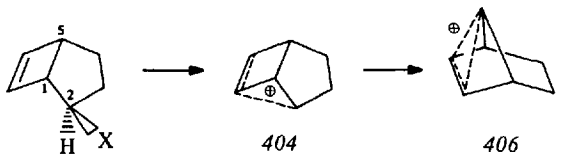
430 *431* *432*

10 5 75 10%

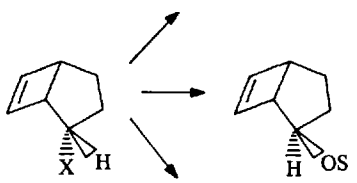
for (*422*). The nortricyclyl products (*424*) are definitely racemic and must arise from (*426*)[346,347].

The introduction of a methyl group at C–5 of the 5-norbornen-2-yl system brings about significant enhancement of the relative rate, of the *exo*/*endo* rate ratio, and of the proportion of tricyclic products[247]. Anchimeric assistance in (*427*) is detected by the tool of increasing electron demand[247]. Methyl substituents at C–1 and/or C–2 exert the opposite effect[246,346,347]. The optically active 1,2-dimethyl-5-norbornen-2-yl p-nitrobenzoate (*428*) solvolyzes with partial retention of configuration[347]. Presumably the first intermediate formed from (*428*) is tertiary carbocation (*429*). The products derived from (*430*) suggest predominance of the cyclopropylcarbinyl cation (*432*) over its isomer (*431*)[348].

The bicyclo [3.2.0] hept-6-en-2-yl system (*405*) is an isomer of (*421*), with similar disposition of the double bond. The *exo*-tosylate (*405*), X=OTs, solvolyzes

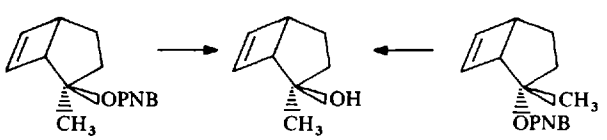


405 *404* *406*

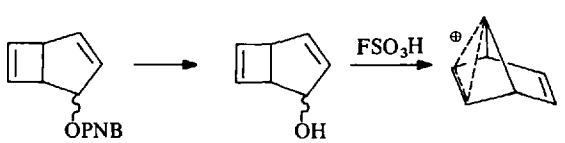


433 *434*

435



436 *437* *438*



439 *440* *441*

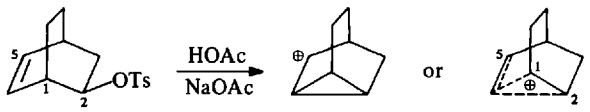
88% *exo*, 12% *endo*

with π participation to give the 2-norbornen-7-yl cation (*406*) and products derived therefrom[330,331]. There is no evidence that the homoallylic ion (*404*) represents an energy minimum on the reaction path from (*405*) to (*406*). The *exo*/*endo* rate ratio is 2400 in aqueous acetone[330], and 3500 in acetic acid[331]. The *endo* isomer (*433*) partitions between solvent displacement to yield (*434*) and unassisted ionization leading to 7-norbornenyl products[331,349]. Migration of the 1,5 bond to give the allylic cation (*435*) was observed as a minor process in the decomposition of the diazonium ion (*433*), X=N_2^+[329]. Anchimeric assistance in (*405*) is virtually eliminated by the introduction of a methyl group at C–2, or of an additional double bond. The *exo*/*endo* rate ratio of (*436*)/(*438*) is only 2.8; both isomers produce *exo* alcohol (*437*) without rearrangement[331]. Similarly, *exo*- and *endo*- (*439*) afford identical mixtures of *exo*- and *endo*- (*440*)[350], illustrating the predominance of allylic conjugation over homoallylic participation. Transformation of (*440*) into the 7-norbornadienyl cation (*441*) is achieved in fluorosulfonic acid[350]. As mentioned earlier (Section 3.2), superacids offer the chance of observing rearrangements which involve higher activation barriers.

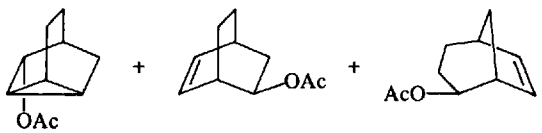
Some homologs of the 5-norbornen-2-yl system (*421*) deserve comment. The double bond in *exo*-bicyclo [2.2.2] oct-5-en-2-yl tosylate (*442*) provides a rate enhancement of at least $4 \cdot 10^5$ over the saturated compound[351]. Solvent attack at carbons 1, 2, and 5 of the cyclopropylcarbinyl cation (*443*) occurs in similar proportions as with (*426*). The tricyclic acetate (*444*) is formed with distinct stereochemical preference because (*443*) is asymmetric, in contrast to (*426*). The *endo*-tosylate (*447*) appears to ionize directly to the allylic cation (*448*)[352]. A similar rearrangement in the 5-norbornen-2-yl system would create prohibitive strain (formation of a cyclobutane ring); it is not observed with (*425*), X=OTs,[335] and contributes to a minor extent with (*425*), X=N_2^+[354]. *anti*-Bicyclo [3.2.1] oct-2-en-8-yl tosylate (*449*) undergoes acetolysis ca. 10^5 times faster than the corresponding *syn*-tosylate, thereby providing strong evidence for homoallylic participation[355]. The intermediate cation (*450*) does not afford tricyclic products but is attacked at C–8 and C–1 to give (*451*) and (*452*), respectively. The presence of the diene (*453*) among the products indicates migration of C–7 from C–1 to C–8. The product spectrum clearly distinguishes the homoallylic participation in (*449*) from the homoaromatic participation in (*395*). The hydrolysis of bicyclo [3.2.1] oct-2-en-7-yl 3,5-dinitrobenzoate (*454*)[356] proceeds in close analogy to that of (*421*). A deuterium label at C–7 of (*454*) is evenly distributed between C–1 and C–7 of the products; optically active (*454*) yields racemic alcohols.

7.4.3 Acyclic Systems

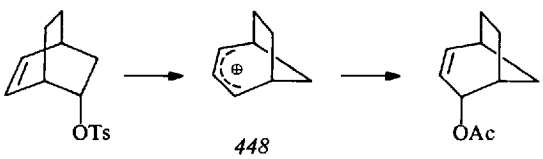
In Section 7.4.1 we have been concerned with double bonds predisposed for symmetrical (homoaromatic) participation whereas Section 7.4.2 was devoted to systems where only one end of the double bond is accessible to the incipient carbocation. 3-Buten-1-yl substrates (*455*) cannot approach a symmetrical transition state, but two homoallylic interactions are possible: (*387*), leading toward a cyclopropylcarbinyl cation (*388*), and (*456*), leading toward a cyclobutyl cation (*458*). Structure (*387*) implies strong interaction between C–1 and C–3 with little or no overlap be-



442 *443*

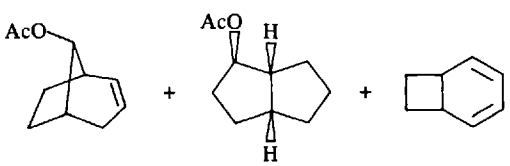


444 (90%) *445* (7%) *446* (3%)

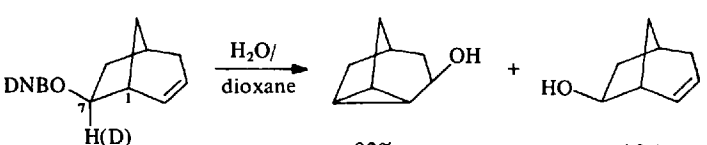


447 *448*

449 *450*

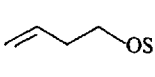
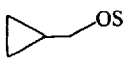
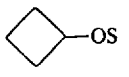
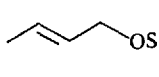
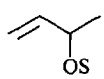


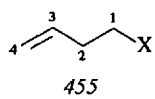
451 *452* *453*



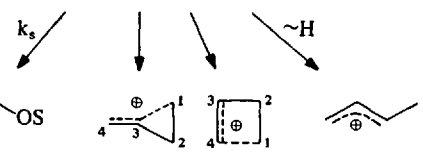
454 82% 18%

Table 15. Product distribution in the solvolysis of 3-buten-1-yl-derivatives

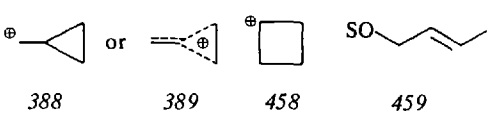
X	HOS	 (455a)	 (461)	 (462)	 (459)	 (460)
OTs	HOAc	80	12	8	–	–
N_2^+	H_2O	44	15	13	7	21
N_2^+	CH_3OH	80	3	5	2	10



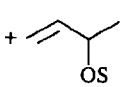
455



455a 387 456 457



388 389 458 459



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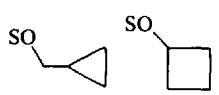

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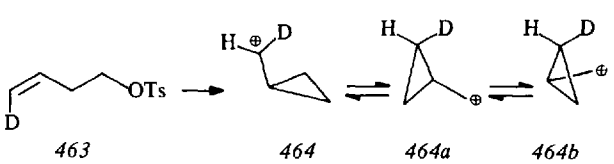
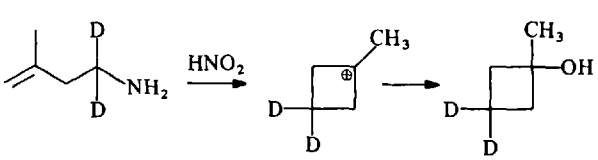


463 464 464a 464b



465

tween C–1 and C–4; the reverse holds for (*456*). For some time (*387*) and (*456*) were viewed as resonance structures of a single intermediate, the bicyclobutonium ion (Section 7.5.2). It appears now that (*387*) and (*456*) are better regarded as transition states leading to the distinct although interconvertible ions (*388*) and (*458*).

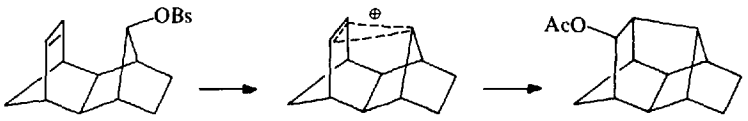
The yield of cyclic products from 3-buten-1-yl precursors is low (Table 15) because (*455*) is prone to competing processes. S_N2– type displacement predominates, (*455a*) being formed without redistribution of a label[357,358]. Hydrogen shift occurs in deamination reactions of (*455*), X=N_2^+, to give the methylallylcation (*457*)[357,359]. The conversion of (*455*) to (*461*) was studied by means of a deuterium label. The acetolysis of (*463*) produced cyclopropylcarbinyl acetate with essentially statistical distribution of the deuterium between the methylene groups, and with 68–80% of the ring deuterium *cis* to the carbinyl group[358]. Assisted ionization leads selectively to a cyclopropylcarbinyl cation (*464*) in which the deuterium lies over the cyclopropane ring. The stereospecificity of the cyclopropylcarbinyl rearrangement (*464*) $\rightleftarrows$ (*464a*) $\rightleftarrows$ (*464b*) is well known (Section 7.5).

Methyl, phenyl, and cyclopropyl substituents at C–4 of (*455*) promote the formation of cyclopropylcarbinyl products by stabilizing the intermediate (*388*)[360]. Rate enhancement over the saturated analogs is observed with the "activated" double bonds but not with the parent (*455*)[361]. A 3-methyl group, on the other hand, stabilizes the cyclobutyl cation (*458*). The fate of the deuterium label in (*465*) shows that ring closure proceeds directly to a 1-methylcyclobutyl cation[362].

7.4.4 Remote Double Bonds

The term "remote" is used here in a formal sense for double bonds which are separated from the incipient carbocation by more than one carbon atom. The number of intervening carbon atoms can be made greater with little or no sacrifice in effectiveness if a well-oriented, rigid structure is maintained. Notable examples are the "birdcage" cations arising from the tetracyclic systems (*466*)[363] and (*467*)[364]. The brosylate (*466*) acetolyzes at a rate of ca. 10^{10} relative to that of 7-norbornyl (*393*). Derivatives of structure (*467*) are even more reactive than the corresponding *anti*-7-norbornenyl derivatives (*395*) by a factor of approximately 10. The cyclopropyl triflate (*468*) undergoes acetolysis 81 times faster than the saturated analog (*472*)[365]. π-Participation in (*468*) affords the rapidly equilibrating (or mesomeric) pair of tetracyclic cations, (*470*) and (*471*), whereas (*472*) produces the allylic cation (*473*). Even the cyclopropane-diazonium ions (*469*)[366,367] and (*474*)[368] decompose with participation by the double bond. The hydrolysis of bicyclo [4.3.1] dec-6-en-1-yl p-nitrobenzoate (*475*) is accelerated by a factor of 120 and affords, inter alia, the tricyclic alcohols (*476*)[369]. A related case of transannular participation, leading to ion pair return, was observed with 5-cyclodecen-1-yl p-nitrobenzoate (*104*)[112] (Section 4.2.3).

π-Assistance generally becomes less effective when the double bond is merely able to participate than when it is forced into a favorable position by a rigid structure. Among the alkenyl sulfonates (*477*) only the 5-hexenyl ester (n=3) affords a modest yield (10–60%) of cyclohexane derivatives, with little rate acceleration[370,371]. 2-(3-Cyclopenten-1-yl) ethyl nosylate (*478*), R=H, solvolyzes faster than the saturat-



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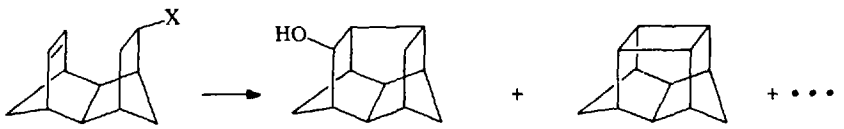

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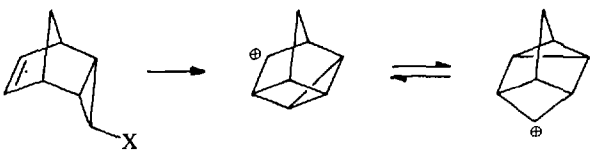
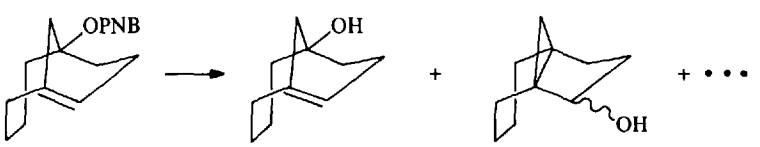


468 X = OSO_2CF_3 *470* *471*
469 X = N_2^+

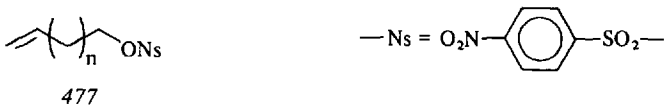
472 *473* *474*



475 *476*

ed analog by 1–3 orders of magnitude, depending on the solvent[372,373]. The reaction affords exclusively *exo*-2-norbornyl products (*479*). The effects of methyl[374] and phenyl substitution[374] (one or both R=CH_3, Ph) on rate suggest a symmetrical transition state. Chain extension lowers k_Δ : the acetolysis of (*480*), R=CH_3, produces some bicyclic products whereas that of (*480*), R=H, proceeds exclusively by S_N2-type displacement[376]. Participation occurs more readily in 4-cyclohepten-1-ylmethyl nosylate (*481*)[377] and in 4-cycloocten-1-ylmethyl tosylate (*482*)[378] than in the 3-cyclohexen-1-ylmethyl system. Even the strongly "activated" double bond in (*483*) produces only a 12% yield of norbornyl derivative (*484*)[379].

The problem of adjusting the distance between the reacting center and the π orbital is also seen in the virtually unassisted acetolysis of (*485*)[380] in contrast to



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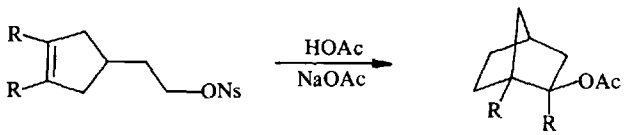
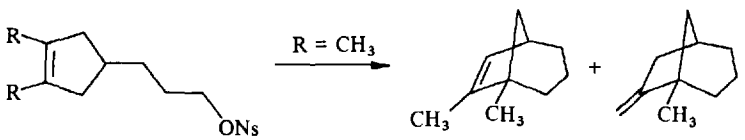
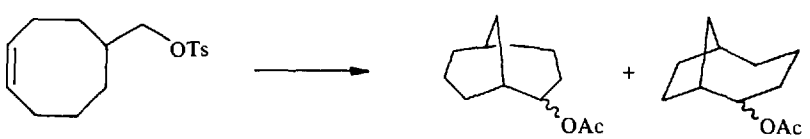


478 *479*



480 32% 25%

481



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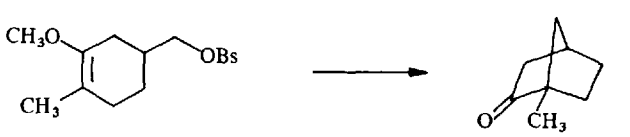
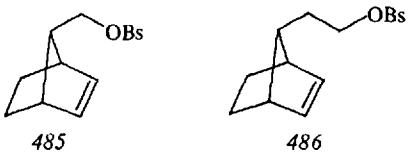


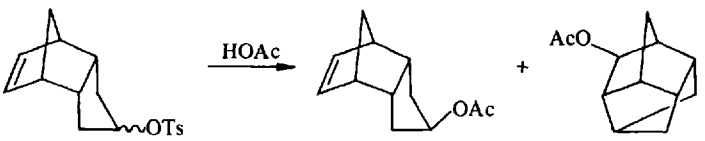
483 *484*

the very fast rate of (*486*) ($2 \cdot 10^5$ compared to either the saturated analog or the *anti* epimer)[381]. The products formed in the acetolysis of (*486*) are controlled by ion pairing[114] (Section 4.2.3). Stereochemical factors in a "borderline case" of π-assistance are illustrated by the epimers of (*487*)[382]. Although the *exo*/*endo* rate ratio is 0.62, the products reveal more participation in the *exo* than in the *endo* isomer.

Participation by remote double bonds has often been adressed as the π route to σ-bridged ("nonclassical") cations. Detailed examination of the intermediates is deferred to Section 7.6 where the generation of such species from other sources is discussed.



485 *486*

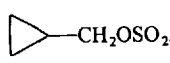


487 exo <5 >95%
endo 70 30%

7.5 Cyclopropane Participation

7.5.1 Cyclopropylcarbinyl Cations

The rates of solvolysis of cyclopropylcarbinyl derivatives are strongly enhanced. Thus, the ethanolysis of cyclopropylcarbinyl benzenesulfonate (*488*), Ar=Phenyl, is 500 times as fast as that of ethyl benzenesulfonate (*489*)[383]. The rate acceleration of (*488*), Ar=β-Naphthyl, is 1220 in methanol, and 139000 in acetic acid[384]. Electron supply by the cyclopropyl group increases with increasing electron demand at the cationic center. The ρ^+ value for the cyclopropyl derivatives (*491*), -2.78, is consider-



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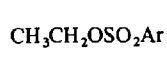

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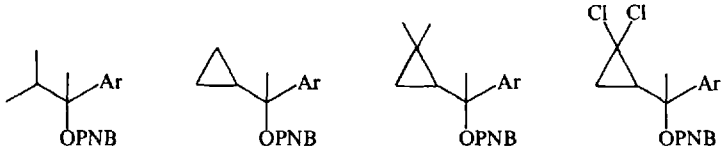
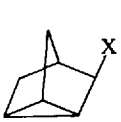


490 *491* *492* *493*
ρ^+ −4.76 −2.78 −2.06 −4.99

ably less negative than the value for the isopropyl derivative (*490*), -4.76[385, 386]. The introduction of methyl groups into the cyclopropane ring increases the electron supply whereas chlorine substituents have the opposite effect[386]. Solvolytic rates indicate that cyclopropyl stabilizes a carbocation more effectively than phenyl[387]. On the other hand, ^{13}C–NMR chemical shifts under stable ion conditions suggest comparable charge delocalizing abilities of cyclopropyl and phenyl[388].

Maximum acceleration occurs when the vacant p orbital is parallel to the plane of the cyclopropane ring. For example, 3-nortricyclyl derivatives (*494*) are more reactive than 7-norbornyl by a factor of $6 \cdot 10^8$ [385,389]. 8,9-Dehydro-2-adamantyl p-nitrobenzoate (*495*) solvolyzes $2 \cdot 10^8$ times faster than the 2-adamantyl analog[390]. The cyclopropylcarbinyl cations from (*494*) and (*495*) are forced into a bisected conformation. The rigid framework of (*494*) and (*495*) does not permit significant changes in geometry on ionization, i.e., the cyclopropane ring provides "vertical stabilization"[231] or "σ conjugation"[386]. The other extreme is represented by spiro [cyclopropane-1,2'-adamantyl] chloride (*498*) which solvolyzes 10^3 times more slowly than 1-adamantyl chloride[391]. The carbocation formed from (*498*) has its empty p orbital perpendicular to the cyclopropane ring. The tosylates (*496*) and (*497*) feature intermediate geometries with angles of *ca.* 30° and *ca.* 60°; they show rate enhancements of $4 \cdot 10^5$ and $4 \cdot 10^3$, respectively[392]. In the trishomobarrelene chloride (*499*)



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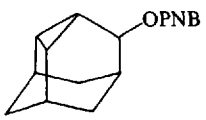

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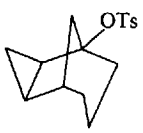

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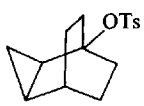

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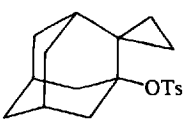

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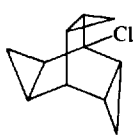

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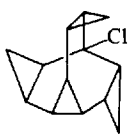

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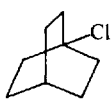
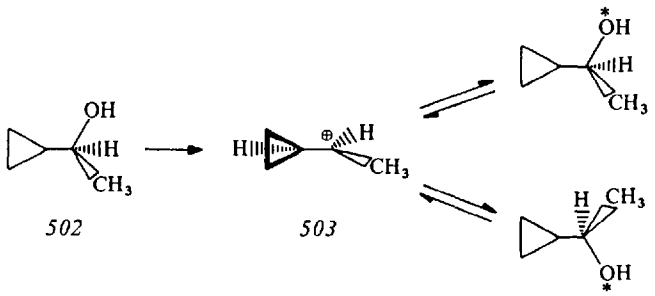


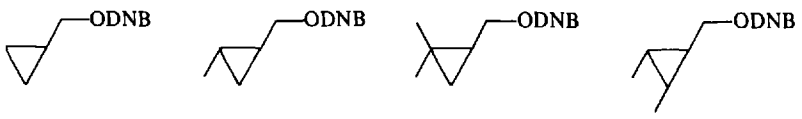
501

and in the trishomobullvalene chloride (*500*) the angles are about 60°; simultaneous interaction with three cyclopropane rings, however, leads to rates of 10^{10} and more, relative to 1-chlorobicyclo [2.2.2] octane (*501*)[393]. Stable bridgehead carbocations were obtained from (*499*) and (*500*) in SbF_5/SO_2ClF[394]. Optically active precursors afford cations of extremely high specific rotations[395].

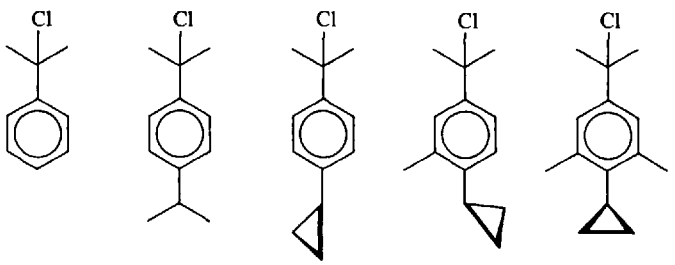
The bisected conformation is also favored in less rigid cyclopropylcarbinyl systems. The acid catalyzed racemization of 1-cyclopropylethanol (*502*) has about the same rate as that of oxygen exchange, a result which is readily rationalized in terms of the bisected cation (*503*)[396]. Methyl substituents accelerate the rate of cyclopropylcarbinyl 3,5-dinitrobenzoates (*505*)–(*507*) by an amount dependent only on the number of substituents and not on their position[397]. These data require the simultaneous participation of two cyclopropane carbons in a symmetrical transition state. The bisected structure applies even to the 4-cyclopropylcumyl chlorides (*510*)–(*512*). The cyclopropyl substituent is less effective than isopropyl in stabilizing a positive charge if it is forced into a parallel conformation (*512*) by two *m*-methyl groups[398] (the relative rates have been corrected for the rate enhancing effect of *m*-methyl). The NMR spectra of cyclopropylcarbinyl cations in superacids reveal them to exist in the bisected conformation, and indicate substantial charge delocalization into the three-membered ring (Section 3.1.3).



502 *503*

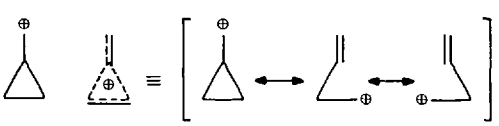


	504	*505*	*506*	*507*
$k_{rel.}$	1	11	92	114



	508	*509*	*510*	*511*	*512*
$k_{rel.}$	1	18	157	86	9

Although the structure of the cyclopropylcarbinyl cation is not controversial, there is some disagreement whether this species should be considered to be "classical" or "nonclassical"[399]. σ-Bridging is clearly not involved. Yet the classical representation (*388*) is unsatisfactory in view of the abundant evidence for conjugation. The

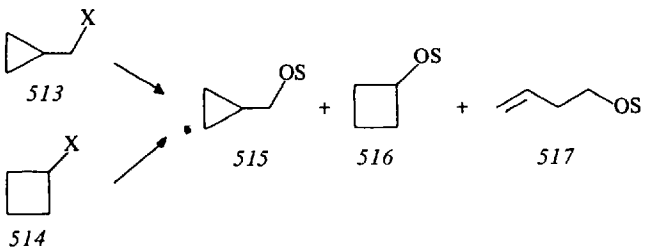


388 *389* *389a* *389b* *389c*

"dotted line" formulation (*389*), an equivalent of the resonance hybrid (*389a,b,c*), accounts well for charge delocalization into the cyclopropane ring. Structure (*389*) also conforms to other views "nonclassical" ions: it may be regarded as a π complex (vinyl cation + alkene), or as a protonated methylenecyclopropane.

7.5.2 Rearrangements of Cyclopropylcarbinyl Derivatives[360,400]

The solvolysis of both cyclopropylcarbinyl and cyclobutyl derivatives proceeds with rearrangement to give mixtures of cyclopropylcarbinyl (*515*), cyclobutyl (*516*), and allylcarbinyl derivatives (*517*)[401,402]. Under certain conditions the product distributions are very similar, starting from either (*513*) or (*514*) (Table 16). These data



518

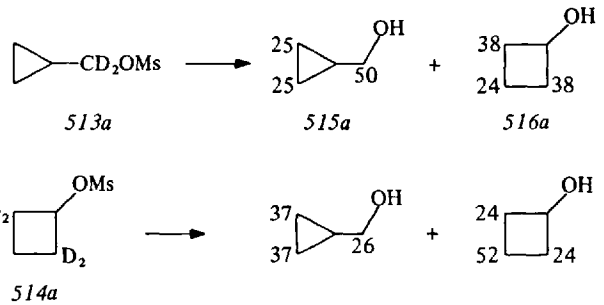
led to the proposal that all products are derived from a common intermediate, the bicyclobutonium ion (*518*)[401]. More nucleophilic solvents, however, afford a larger proportion of unrearranged product[384,403]. The effect of solvent nucleophilicity on product composition suggests that the cyclopropylcarbinyl and the cyclobutyl products are formed *via* different ions.

The solvolysis of either (*513*) or (*514*) is associated with partial equilibration of the three methylene groups[404,405]. When the starting material is the cyclopropylcarbinyl methanesulfonate (*513a*), the label scrambling is less complete in the cyclopropylcarbinol than in the cyclobutanol. Cyclobutyl methanesulfonate (*514a*) gives less scrambling in the cyclobutanol than in the cyclopropylcarbinol[405]. It appears that the first formed ions are similar in structure to the starting material, and may be captured by solvent.

The stereochemistry of the rearrangment has been determined[406]. A derivative of the parent system, (*513b*), deuterated except for one position, was hydrolyzed to give products (*515b*)–(*517b*) with hydrogen at the indicated positions. The inter-

Table 16. Products from S_N1 reactions of cyclopropylcarbinyl and cyclobutyl derivatives

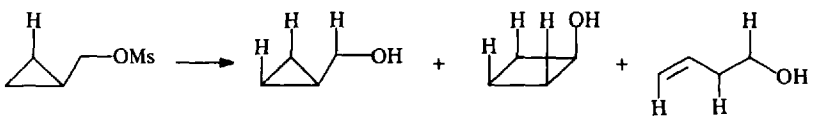
Precursor		(*513*)			(*514*)		
HOS	X	(*515*)	(*516*)	(*517*)	(*515*)	(*516*)	(*517*)
H_2O	N_2^+	56	40	4	52	44	4
HOAc	β-ONs	56	37	7	53	40	7
CH_3OH	β-ONs	66	31	3	48	47	5



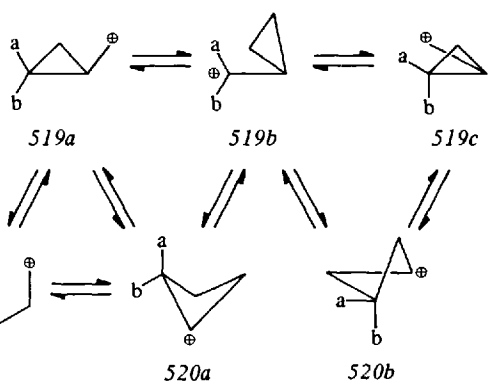
513a *515a* *516a*

514a

[figures indicate the distribution of label, CD_2 in *513a*, CH_2 in *514a*]



513b *515b* *516b* *517b*

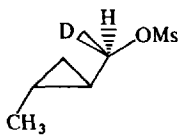


519a *519b* *519c*

520a *520b*

conversion of the methylene groups must occur with inversion at the migrating carbon, (*519a*) $\rightleftarrows$ (*519b*) $\rightleftarrows$ (*519c*). This stereochemistry is consistent with the NMR spectrum of the cyclopropylcarbinyl cation in which *cis*- and *trans*-methylene hydrogens retain their identity even though the three methylene groups are equivalent[61]. Alternatively, the rearrangement might proceed *via* a puckered cyclobutyl cation (*520*). This reaction path would also account for the stereospecific formation of (*516b*). The 3-buten-1-ol (*517b*) could arise from ring opening of the cyclobutyl cation (*520*) as well as from that of the cyclopropylcarbinyl cation (*519*). Concerted ring opening and attack by a nucleophile is more likely than intervention of a primary allylcarbinyl cation.

The stereochemistry just described also applies to the transformations of optically active (*521*) which ionizes to give two distinct bisected cyclopropylcarbinyl cations in a 3:1 ratio[407]. The tertiary cyclopropylcarbinyl derivative (*522*), on the other hand, solvolyzes without equilibration of the $C(CH_3)_2$ groups[408]. A cyclopropylcarbinyl rearrangement with inversion at the migrating carbon is also necessary for



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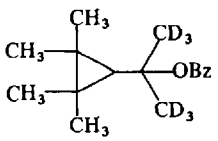

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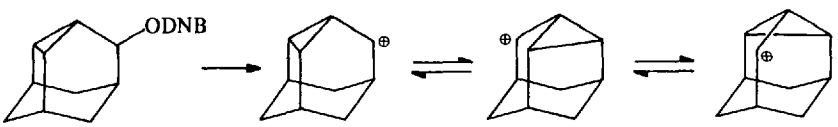
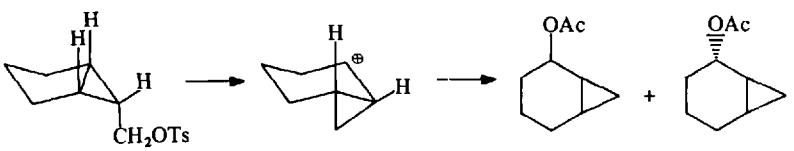
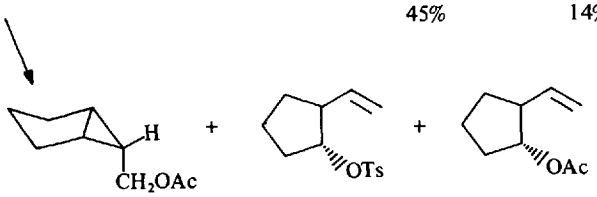


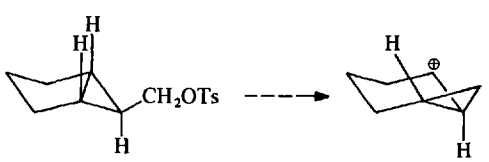
495 *523a* *523b* *523c*



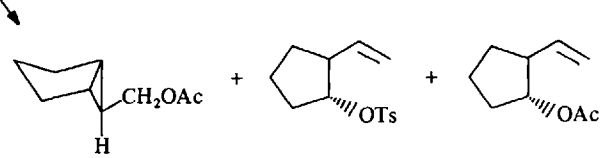
524 *525* *526a* 45% *526b* 14%



3% 6% 14%



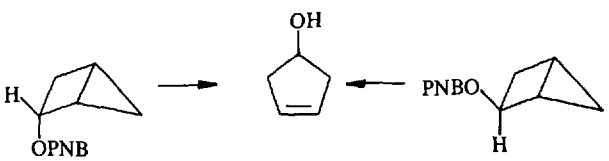
527 *528*



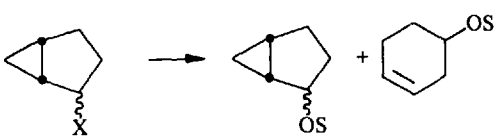
25% 50% 25%

the label-scrambling process observed in the 8,9-dehydro-2-adamantyl cation (*523*)[390]. The same stereochemical course explains the products derived from the bicyclo [3.1.0] hex-6-ylmethyl tosylates (*524*) and (*527*)[409]. The *endo* isomer (*524*) rearranges to the *cis*-fused 2-norcaranyl cation (*525*) and affords the acetates (*526*) as the major products. With the *exo* isomer (*527*) the same rearrangement does not occur because it would lead to the highly strained *trans*-fused ion (*528*).

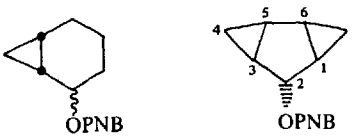
The series of 2-bicyclo [n.1.0] alkyl cations shows remarkable variations in reactivity and stereoselectivity. The bicyclo [2.1.0] pentane derivatives (*529*) and (*530*) have an unusually large *cis*/*trans* rate ratio of 10^7. In the *cis* isomer (*529*) ionization is thought to occur in concert with ring opening[210]. Outward disrotation of H–1 and H–4 leads to maximum overlap between the orbitals of the bond being broken and the backside of the developing vacant p orbital. A concerted reaction path is not available to the *trans* isomer (*530*) because the bridgehead hydrogens would have to move inward (toward each other). The bicyclopentyl system is one of the rare cases where quantitative cyclopropylcarbinyl→allylcarbinyl rearrangement occurs, due to



529 *530*



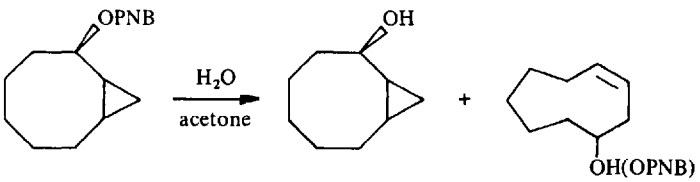
531 *trans*/*cis* ~2



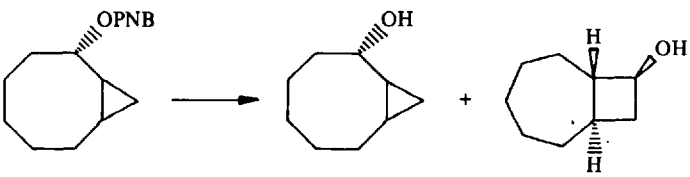
532 *533*

relief of ring strain. The tendency for such rearrangement decreases with increasing ring size. The *cis*- and *trans*-bicyclo [3.1.0] hex-2-yl derivatives (*531*) react at essentially the same rate and afford similar product mixtures[411,412]. Bicyclo [4.1.0] hept-2-yl (*532*)[413] and tricyclo [4.1.0.$0^{3,5}$] hept-2-yl derivatives (*533*)[414] solvolyze without rearrangement. With (*532*) the *cis*/*trans* product ratio is 3–4 from each of the epimeric starting materials. The absence of degenerate cyclopropylcarbinyl rearrangements has been established for both (*532*) and (*533*) by means of a deuterium label.

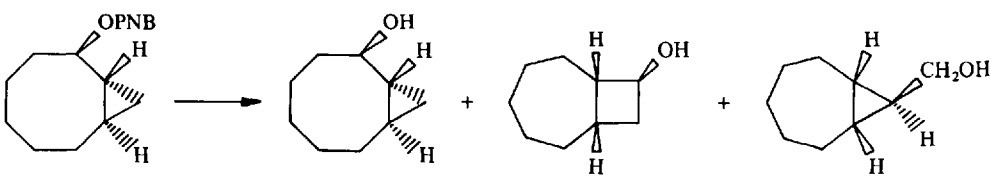
All available evidence indicates that a single carbocation is formed from both stereoisomers of (*531*), n=3, and (*532*), n=4. When n is larger, distinct cationic inter-



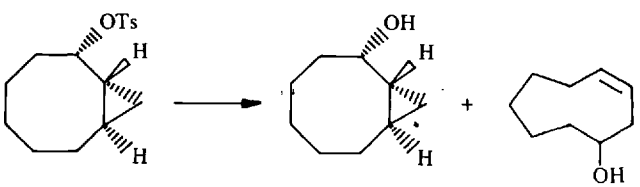
534 *535* (61%) *536* (23% + 16%)



537 *538* (96%) *539* (4%)



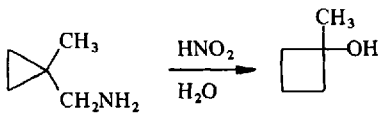
540 *541* (82%) *542* (7%) *543* (5%)



544 *545* (39%) *536* (60%)

mediates are apparently produced from epimeric precursors. The bicyclo [6.1.0] non-2-yl case is particularly instructive because there is essentially no crossover in products with any of the four isomers (*534*), (*537*)[415], (*540*), and (*544*)[416,417]. These results require unsymmetrical cyclopropylcarbinyl cations, separated by energy barriers which correspond to conformational changes in the cyclooctane ring. Degenerate cyclopropylcarbinyl rearrangement occurs only in the solvolysis of (*540*), as shown by scrambling of a deuterium label at C–2[416]. The major product in each case is the alcohol corresponding to the reactant. The minor products are also formed stereospecifically. Thus (*537*) gives the *trans*-fused bicyclo [5.2.0] nonan-8-ol (*539*), whereas (*540*) gives the *cis*-fused isomer (*542*). *cis*-Cyclononen-4-ol (*536*) arises only from (*534*) and (*544*). The stereochemistry of all these transformations is that described for the simple acyclic case, (*519a*). Similar observations have been made in the bicyclo [5.1.0] octyl[418] and bicyclo [7.1.0] decyl series[419].

Product formation from cyclopropylcarbinyl derivatives is often controlled by stabilization of the positive charge in the various cationic intermediates. Methyl or



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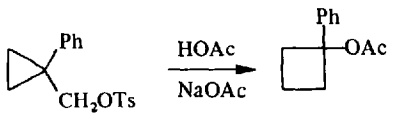

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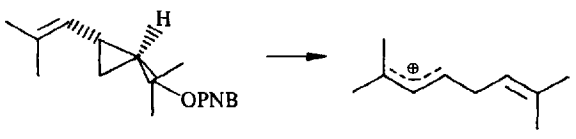
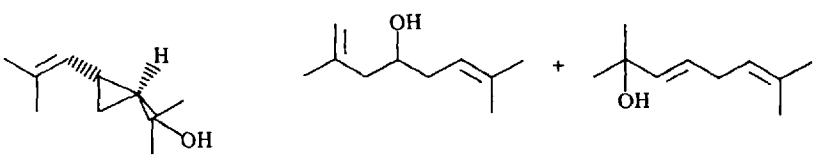
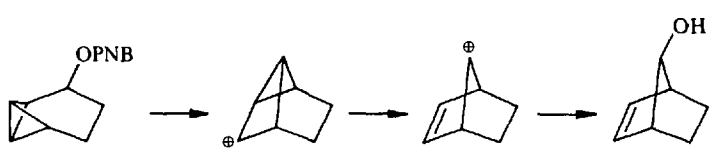


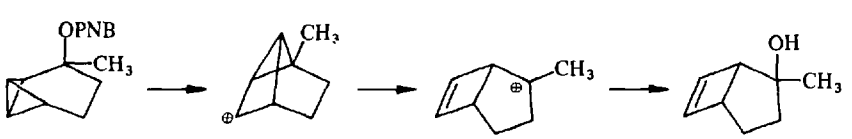
548 549



2% 38% 60%



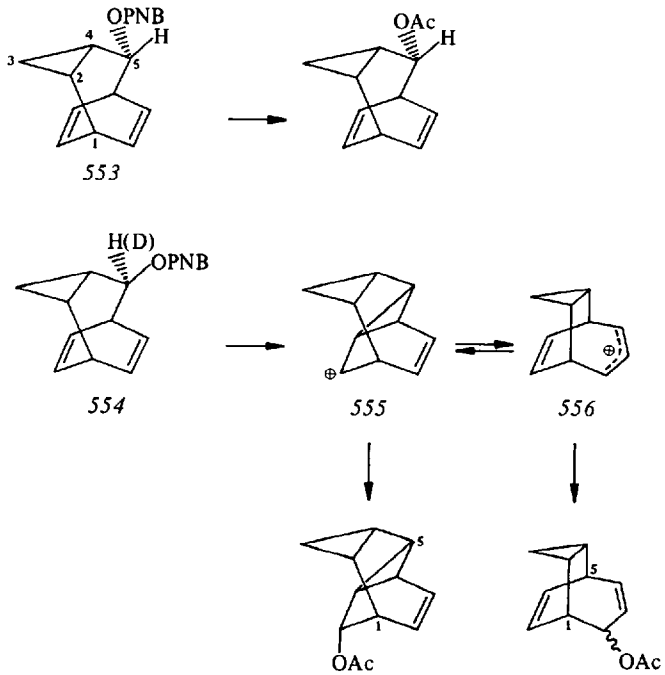
550



551 552

phenyl groups at C–1 of the cyclopropane ring induce the formation of cyclobutyl derivatives, cf. (*546*)[420,421] and (*547*)[403]. Allylcarbinyl products dominate in the hydrolysis of (*548*)[422] because the cation (*549*) is stabilized by allylic resonance. Hydrolysis of tricyclo [4.1.0.$0^{2,7}$] hept-3-yl p-nitrobenzoate (*550*), assisted by release of ring strain, affords 2-norbornen-7-ol, whereas the 3-methyl analog (*551*) gives *exo*-2-methylbicyclo [3.2.0] hept-6-en-2-ol (*552*) rather than 1-methyl-2-norbornen-7-ol[423].

If cyclopropyl competes with other neighboring groups, steric factors may assume a major role in controlling the reaction course. The epimeric tricyclo [4.2.2.$0^{2,4}$] deca-7, 9-dien-5-yl p-nitrobenzoates (*553*) and (*554*) solvolyze without any crossover in products[424]. The exclusive formation of retained acetate from (*553*) suggest cy-



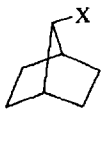
553

554 *555* *556*

clopropyl conjugation. Ionization of (*553*) produces a vacant p orbital in optimum steric relationship for cyclopropyl interaction. The geometry of (*554*) is much less favorable for cyclopropyl-assisted ionization. Charge is delocalized by participation of the homoallylic π bond. Deuterium distribution between C–1 and C–5 during the solvolysis of 5-D- (*554*) requires rapid equilibration of the tetracyclic intermediate (*555*) with the tricyclic allylic cation (*556*).

7.5.3 π σ -Participation

The strained carbon-carbon bonds of the cyclopropane ring provide a transition from the electron-rich alkenes to the much more tightly held σ electrons of the carbon-carbon single bond. Anchimeric assistance to ionization by a properly situated cyclopropane ring can be as large or larger than that by a similarly situated double bond, cf. (*395*) and (*557*)[425,426]. The relatively small rate acceleration of the analogous cyclobutane derivative (*558*)[427] indicates that the assistance to ionization in (*557*) stems from the partial π character of the cyclopropane bonds. Therefore, the term π σ participation has been coined (H. C. Brown)[399]. Compound (*557*) provides the correct geometry for interaction of the Walsh orbitals with the backside of the devel-

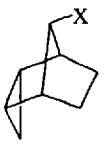


393

$k_{rel.}$ 1

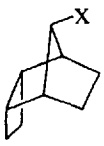
395

10^{11}



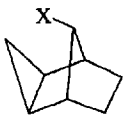
557

10^{14}



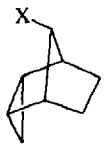
558

10^{4}



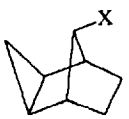
559

$k_{rel.}$ 10^{6}



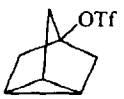
560

10^{3}



561

10^{2}



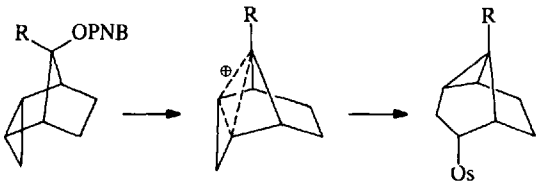
562

oping vacant p orbital at C–8, in contrast to its stereoisomers (*559*)–(*561*). The case of (*561*) confirms that the cyclopropane ring donates electrons with an edge but not with its face. The same principle is illustrated by the extremely inert 1-nortricyclyl triflate (*562*) which requires a temperature of 255°C for solvolysis[428,429].

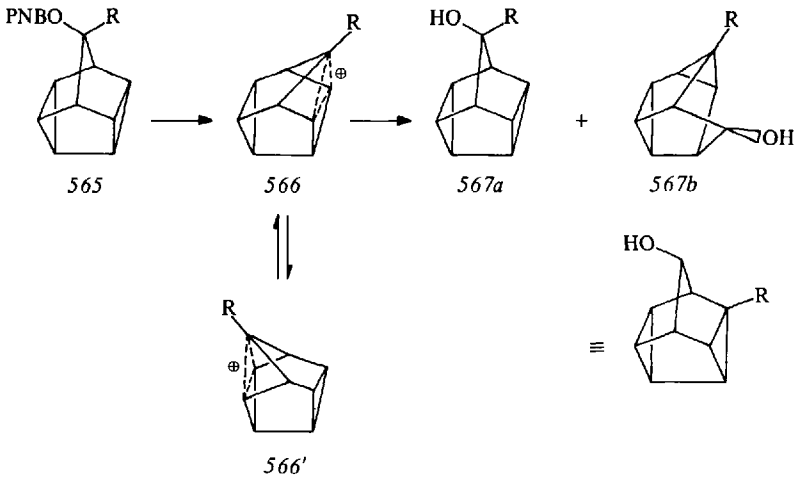
The ionization of (*557a*) proceeds with rearrangement to give (*564*)[425,426]. The stereochemistry of product formation is consistent with an intermediate trishomocyclopropenium ion (*563*). Whereas a p-anisyl group in the 7-position of (*395*) is capable of swamping the π-participation by the double bond, it does not entirely eliminate π σ-participation: (*557b*) hydrolyzes 4000 times faster than the 7-norbornyl analog to give (*564b*)[242].

It might be argued that the rearrangement of (*557*) provides driving force for ionization. However, the rate enhancement of (*565*), ca. 10^{12} *vs.* 7-norbornyl, cannot be attributed to the formation of a rearranged ion of lower strain energy[430]. In this system, the rearrangements are degenerate. Label scrambling (R=D) among just three positions is consistent with the C_{3v} symmetry of the bridged ion (*566*), but excludes a set of rapidly equilibrating ions. In the first stage of rapid equilibrium, scrambling among five positions should occur, and ultimately all nine CH groups should become equilibrated. The stable ion (*566*) in superacids also shows C_{3v} symmetry[431]. The "bridge-flipping" process, (*566*) $\rightleftarrows$ (*566'*), has an immeasurably large barrier for R=H, $\Delta G^{\neq}$= 13 kcal/mol (–8°C) for R=CH_3, and $\Delta G^{\neq}$<10 kcal/mol (–75°C) for R=Ph. The "tool of increasing electron demand" (Section 7.2.2) applied to (*565*) gives ρ^{+}-2.05, *vs.* ρ^{+}-5.27 for 7-norbornyl[245, 432]. A comparison of (*566*) with the radical cations of related olefins strongly indicates that the exceptional stability of (*566*) must be due to bridging rather than to vertical stabilization[433]. In summary, (*565*) provides a well documented case of π σ-participation, leading to the bridged, trishomocyclopropenium ion (*566*).

Exo, anti-tricyclo [3.1.1.$0^{2,4}$] hept-6-yl p-nitrobenzoate (*568*) hydrolyzes approximately ten times slower than (*557a*) to give (*570*) and the corresponding p-nitrobenzoate (*571*)[434,435]. The predominant product from the acetolysis of (*572*) is



557a R = H *563* *564*
557b R = p–Anisyl

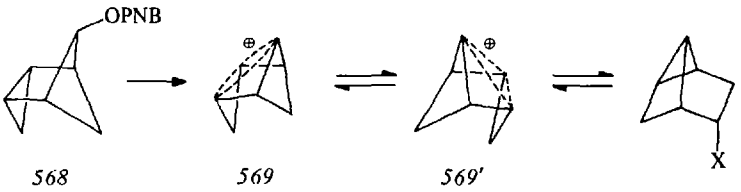


565 *566* *567a* *567b*

566'

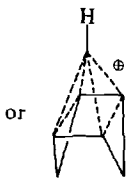
the unrearranged acetate (*573*)[436]. Both reactions involve the same intermediate, a rapidly equilibrating pair of trishomocyclopropenium ions, (*569*) $\rightleftarrows$ (*569'*), or a single ion of C_{2v} symmetry, (*574*). The apparent C_{2v} symmetry is revealed by scrambling of a deuterium label among four of the five CH groups during solvolysis of both (*568*)[473] and (*572*)[436]. Moreover, the ^{13}C–NMR spectrum of (*574*) at -100°C shows three signals[437]. At - 80°C rearrangement of (*574*) to the nortricyclyl cation (*426*) occurs. The nortricyclyl cation is also produced from the *exo*-tosylate (*575*). A small amount of leakage to (*426*) was observed in the solvolysis of (*572*).

Bridged analogs of (*569*), or (*574*), are accessible from (*576*) and (*577*). The tricyclo [3.3.0.$0^{2,8}$.$0^{3,6}$] oct-4-yl system (*576*) is 10^3 times less reactive than (*568*)[438]. The methylene bridge in (*576*) must increase the strain energy associated with the movement of the two equivalent cyclopropane carbons (C–1 and C–2) toward the incipient carbocation at C–4, thus destabilizing the transition state and the resulting trishomocyclopropenium cation. The sole product formed in the acetolysis of (*577*) is the corresponding acetate (*579*)[439]. A deuterium label at C–2 of the starting material is distributed between C–1, C–2, C–7, and C–8 of the product. The deuterium scrambling is consistent with the intervention of either the pyramidal carbocation (*578*) or two rapidly equilibrating trishomocyclopropenium ions. The apex of the pyramidal cation is C–9 of (*577*). The proton and carbon-13 spectral data of (*578*) are consistent with the static pyramidal structure[439]. The homologous system (*580*) cannot give rise to an intermediate of C_{2v} symmetry. The hydro-



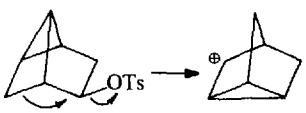
568 *569* *569'*

570 X = OH
571 OPNB
572 OTs
573 OAc

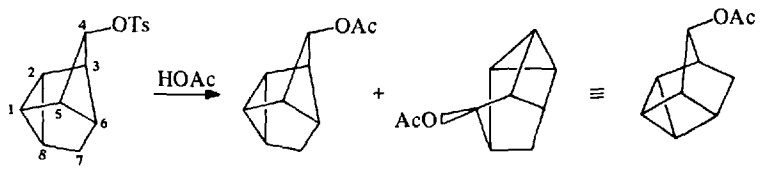


574

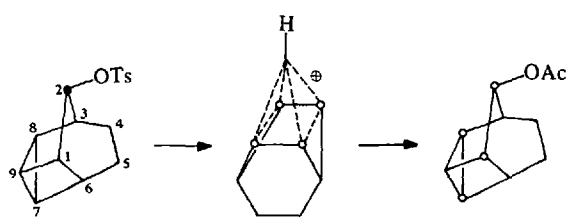
–80°C



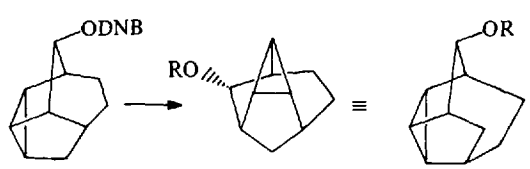
575 *426*



576 60% 40%



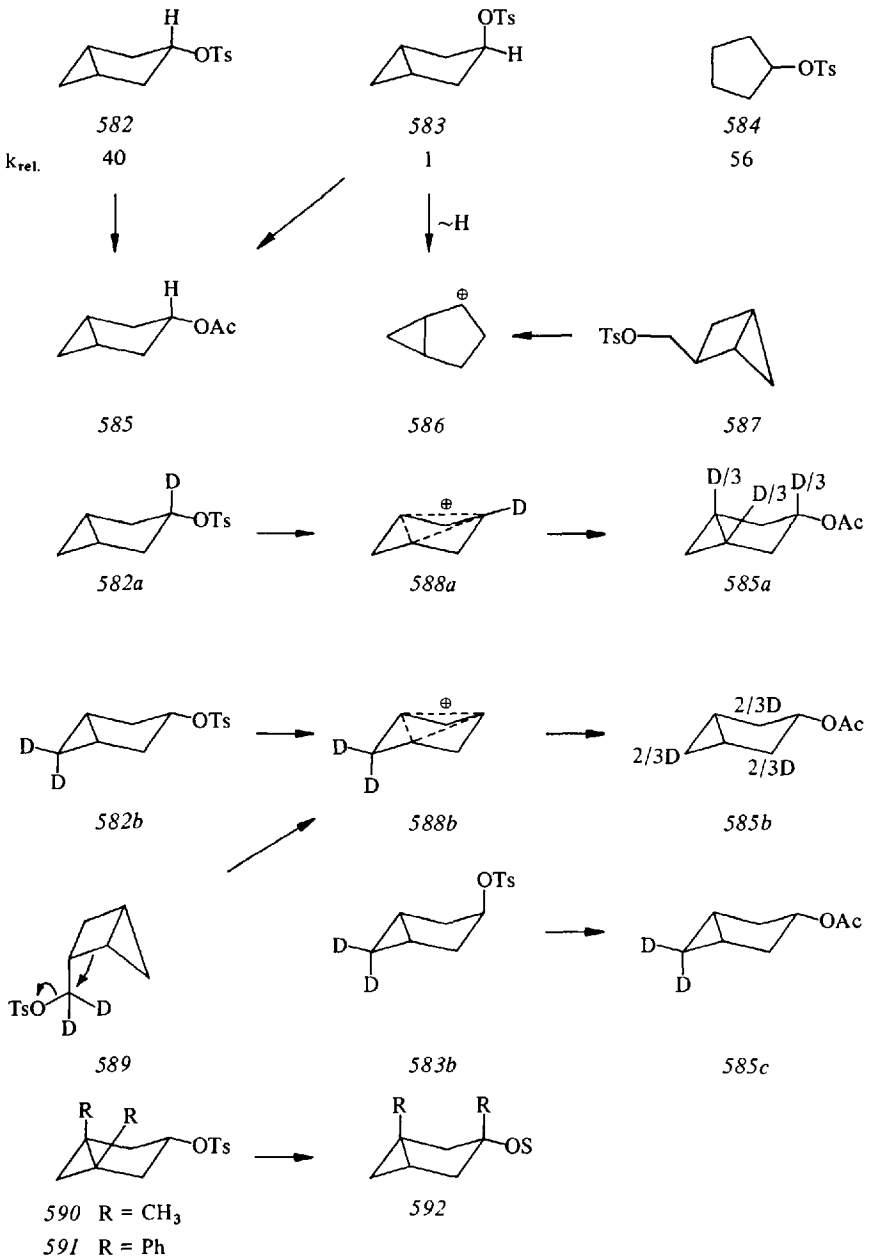
577 *578* *579*



580 *581*

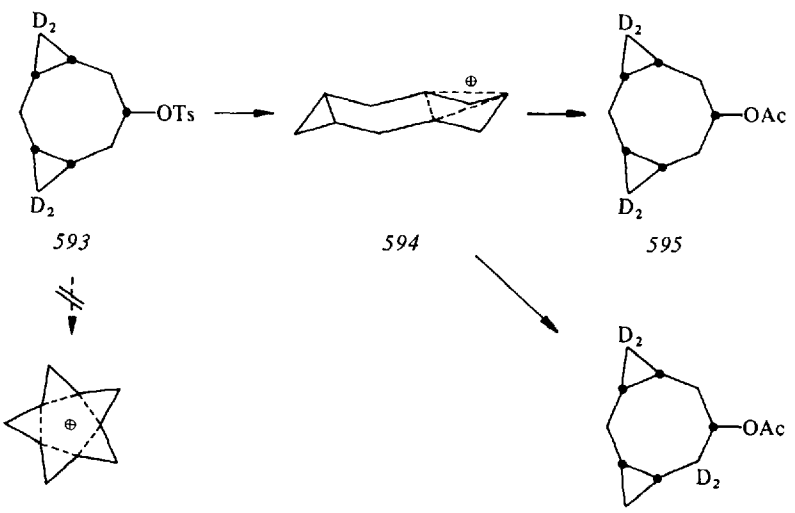
lysis of (*580*) proceeds with virtually complete rearrangement to give (*581*)[440]. The rate of ionization is comparable to that of (*477a*) (10^{14}–10^{15} *vs.* 7-norbornyl).

The effect of cyclopropane participation in the solvolysis of *cis*-bicyclo [3. 1. 0] hex-3-yl tosylate (*582*) is much less dramatic than in the rigid systems mentioned above[441]. The rate of acetolysis of (*582*) is not increased over that cyclopentyl tosylate (*584*), although (*582*) solvolyzes 40 times faster than the *trans* isomer (*583*).



On the other hand, the products do support the involvement of the cyclopropane ring. The exclusive product of solvolysis of (*582*) is the *cis*-acetate (*585*). The solvolysis of (*583*) gives several products, some of which are derived from a 1,2 hydrogen shift *via* cation (*586*). Scrambling of deuterium among positions 1, 3, and 5 in the solvolysis of (*582a*), and among positions 2, 4, and 6 in the solvolysis of (*582b*), is consistent with the intervention of the trishomocyclopropenium ion (*588*). The same intermediate is generated from (*589*) in a conformationally controlled ring expansion; the isomeric precursor (*587*) gives products derived from ion (*586*)[442]. No distribution of deuterium is observed in the conversion of *trans*-tosylate (*583b*) to *cis*-acetate (*585c*)[441]. The C_{3v} symmetry of the intermediate (*588*) is removed by introducing substituents at C–1,5. Kinetic control favors tertiary rather than secondary products in the solvolysis of (*590*)[441] and of (*591*)[443]. The rate of solvolysis of (*590*) is accelerated by a factor of only 7 over that of (*582*), whereas (*591*) is less reactive than (*582*). The observation by NMR of the trishomocyclopropenium ion (*588*) under stable ion conditions was claimed by one group[444], but was questioned by others [445].

In the tricyclo [7.1.0.0^{5,7}] dec-3-yl system (*593*) either one or both cyclopropane rings could conceivably become involved with the incipient carbocation.

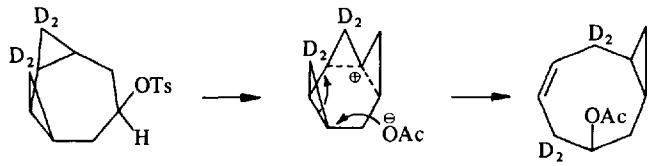


593 *594* *595*

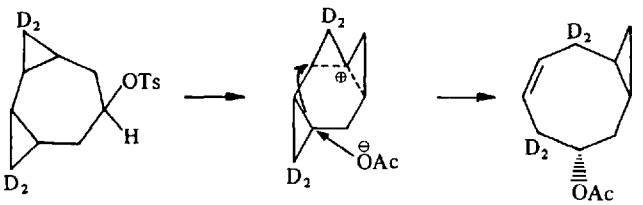
596

Scrambling of deuterium in (*595*), the major product of acetolysis, clearly indicates participation of only one cyclopropane ring[446]. The trishomocyclopropenium intermediate (*594*) is preferred to the pentahomocyclopentadienylium ion (*596*), in accordance with Winstein's concept of homoaromaticity[319].

The related tricyclo [6.1.0.0^{5,7}] non-3-yl systems behaves differently[447]. Acetolysis of tosylate (*597*) results in a deepseated reorganization involving rupture of both original cyclopropane rings. Acetolysis of the isomeric tosylate (*600*) reveals an identical rearrangement; however, the stereochemical outcome is opposite. Interaction of the cyclopropane ring *cis* to the leaving group with the developing cationic



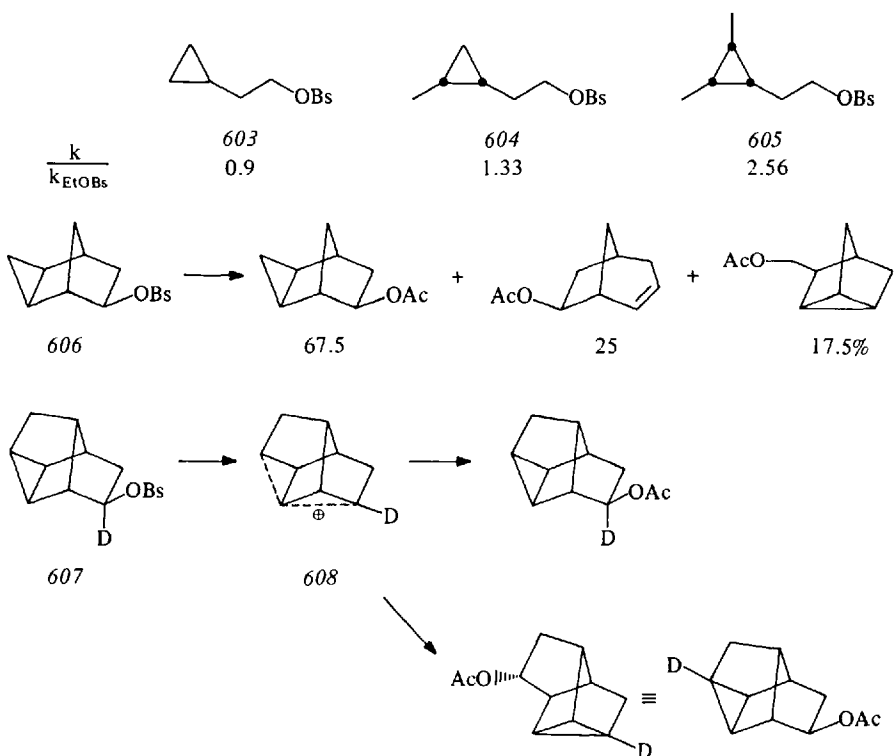
597 *598* *599*

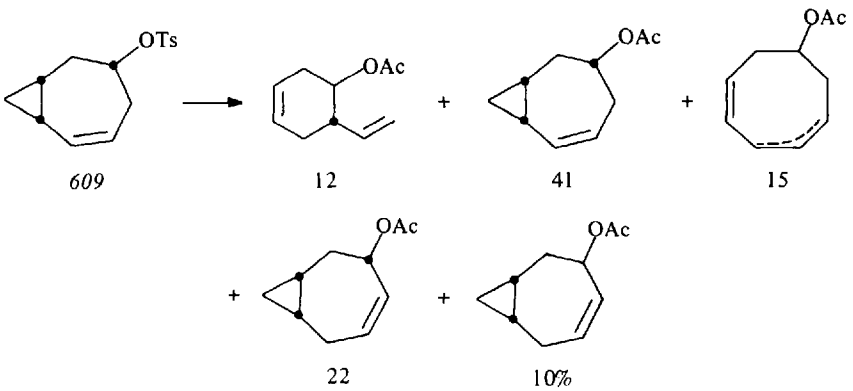


600 *601* *602*

center, visualized by the bishomoallylic structures (*598*) and (*601*), would account for the observed formation of acetates (*599*) and (*602*). Much less cyclopropane participation appears to be involved in the decomposition of the corresponding diazonium ions[447].

The geometry of (*597*), in contrast to the more flexible (*593*), enforces unsymmetrical, bishomoallylic participation of the cyclopropane ring. As was observed with double bonds, this type of participation is less effective than the symmetrical, tris-





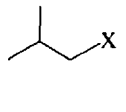
homoaromatic approach. No significant anchimeric assistance has been found in the solvolyses of 2-cyclopropylethyl brosylate (*603*) and its methyl substituted derivatives (*604*) and (*605*)[448]. *exo, exo*-Tricyclo [3.2.1.$0^{2,4}$] oct-6-yl brosylate (*606*) acetolyzes more slowly than *exo*-2-norbornyl brosylate, but the mixture of acetates produced indicates involvement of the cyclopropane ring[91]. A degenerate rearrangement, associated with complete retention of configuration, suggests the intermediacy of the bishomoallylic cation (*608*) in the solvolysis of (*607*)[449]. Competitive participation of a double bond and a cyclopropane ring has been studied in the solvolysis of *cis*-bicyclo [5.1.0] oct-5-en-3-yl tosylate (*609*)[450]. Analysis of the complex product mixture indicates that about 80% of the reaction occurs by double bond participation, although it is the less stable conformer of (*609*) in which the double bond is suitably disposed. More information on the long-range interaction of cyclopropane rings with carbocations may be found in a comprehensive review[451].

7.6 Alkyl Participation. Protonated Cyclopropanes. ("Nonclassical" Carbocations)

7.6.1 Acyclic Systems

Alkyl-bridged ions may be generated as potential intermediates in 1,2-alkyl shifts ("σ route"), by double bond participation ("π route"), and by protonation of cyclopropanes. In the acylic series, kinetic methods are not very useful for detecting alkyl participation. The solvolyses of alkyl sulfonates proceed with 1,2-alkyl shifts only in the case of neopentyl-type substrates, (*612*) and (*613*). Isobutyl (*610*) and 3-methyl-2-butyl sulfonates (*611*) prefer solvolytic displacement and 1,2-H shifts. Alkyl shifts in (*610*) and (*611*) are induced only by deamination ($X=N_2^+$) and related reactions which are not amenable to kinetic studies.

7.6.1.1. Anchimeric Assistance by Alkyl Groups? The formolysis of neopentyl tosylate (*612*, X=OTs) is as rapid as that of ethyl tosylate whereas the rate of trifluoroacetolysis is enhanced by a factor of 160. These data have been taken as evidence



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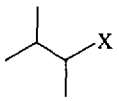

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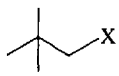

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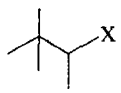

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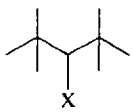

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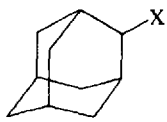
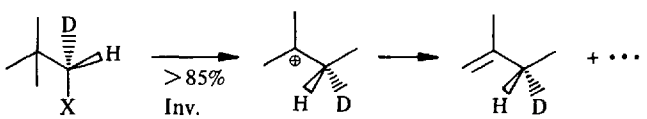


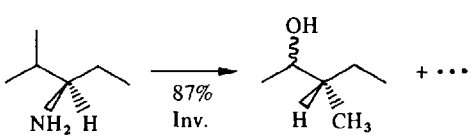
615

for concerted ionization and rearrangment[452]. On the other hand, the insignificant isotope effect observed with γ-deuterated derivatives of (*612*) and (*613*) suggests that methyl migration occurs after the ionization step[265] (Section 7.2.3). The (*614*)/(*615*) rate ratio (ca. 10^3) is remarkably independent of leaving group and solvent; i.e., the solvolysis of (*614*) is not solvent-assisted[453]. The enhanced reactivity of (*614*) has been attributed to methyl participation, steric ("B strain") and inductive factors. Even if alkyl participation in the ionization of (*612*) and (*613*) were definitely established, alkyl-bridged intermediates are not likely. Concerted ionization and rearrangement would be expected to lead directly to a tertiary cation, in analogy with the neophyl system (*338*) (Section 7.3.1) (see Fig. 7b for the appropriate reaction profile).

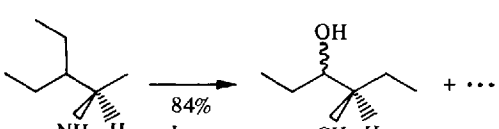
Methyl migration in the solvolysis (X=OTs)[454], deamination ($X=N_2^+$)[455], and deoxidation (X=OCX)[456] of chiral neopentyl derivatives (*612a*) proceeds with >85% inversion at the migration terminus. The stereochemical results, somewhat obscured by uncertainties about the maximum rotation of (*616*), are consistent with



612a *616*



617 *618*

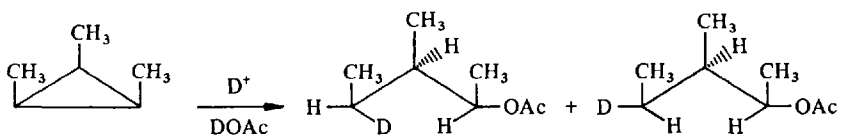


619 *620*

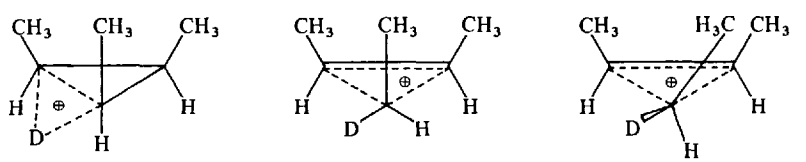
– but do not require – concerted ionization and rearrangement. Deamintively induced methyl migration to a secondary carbon, (*617*) → (*618*), involves 87% inversion (13% racemization)[457]. The analogous ethyl shift, (*619*) → (*620*), is 84% stereospecific. The incomplete inversion at the migration terminus observed with (*617*) and (*619*) is most reasonably explained in terms of conformational control (Section 6). Different enantiomeric purities of *erythro*-(*618*) (97%) and *threo*-(*618*) (72%) support this interpretation.

7.6.1.2 Protonation of Cyclopropanes. Unassisted ionization does not preclude the subsequent formation of alkyl-bridged ions. Evidence for σ-delocalization must then be derived from the product-forming step of the rearrangement. Useful information on this point may be obtained from the electrophilic ring opening of cyclopropanes. Several comprehensive reviews on protonated cyclopropanes are available[66,458–460]. Some observations pertinent to the present discussion will be summarized:

a) Stereochemistry: The ring opening of protonated cyclopropanes proceeds with 95% or greater inversion by the nucleophile[461]. The electrophile has been shown to enter with predominant retention of configuration in the majority of the cases; e.g., the attack of D^+ on *cis*-1,2,3-trimethylcyclopropane (*621*) proceeds with 68% retention to give (*622a*) and 32% inversion to give (*622b*)[461]. The results are



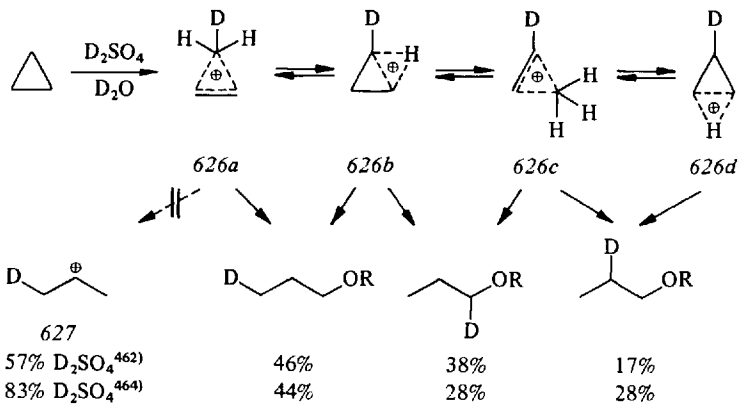
621 *622a* *622b*



623 *624* *625*

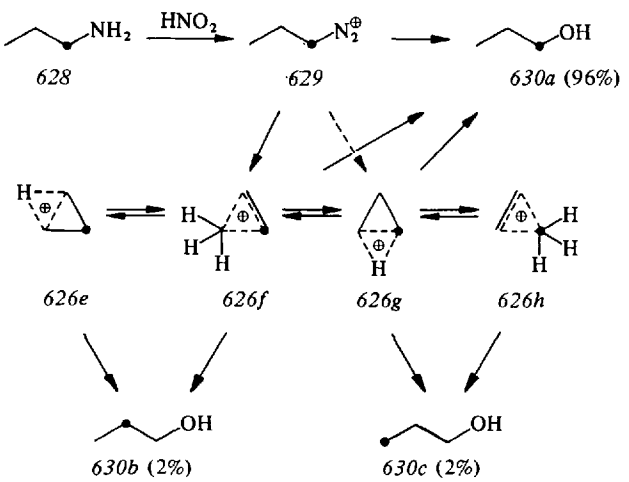
inconsistent with an edge-protonated cyclopropane (*623*), leading to complete retention, but also exclude a symmetrical corner-protonated cyclopropane (*624*). The stereochemistry of electrophilic attack on (*621*) is best interpreted in terms of an unsymmetrical corner-protonated cyclopropane (*625*), approaching the geometry of a trigonal bipyramid.

b) Rearrangements: The treatment of cyclopropane with sulfuric acid gives rise to 1-propyl hydrogensulfate and 1-propanol, but does not produce 2-propanol[462]. Protonated cyclopropane (*626*) does not rearrange to the 2-propyl cation (*627*). In that respect (*626*) parallels the behavior of the phenonium ion (*322*) which does not afford 1-phenylethanol (*323*) (Section 7.3.1). The distribution of deuterium in 1-propanol, obtained from cyclopropane and D_2SO_4, indicates a degenerate rearrange-



ment of (*626*) prior to hydrolysis. The isotope scrambling data[462–464] do not permit a clear distinction between edge- and corner-protonated cyclopropanes.

Protonated cyclopropanes have been implicated in many rearrangements of carbocations in superacids[66] (Section 3.2). The report that protonated cyclopropanes in SbF_5/FSO_3H generally possess a single exchangeable proton[456] is compatible with either the edge or an unsymmetrical corner-protonated formulation. In aqueous solution, deprotonation of protonated cyclopropanes must be essentially irreversible.

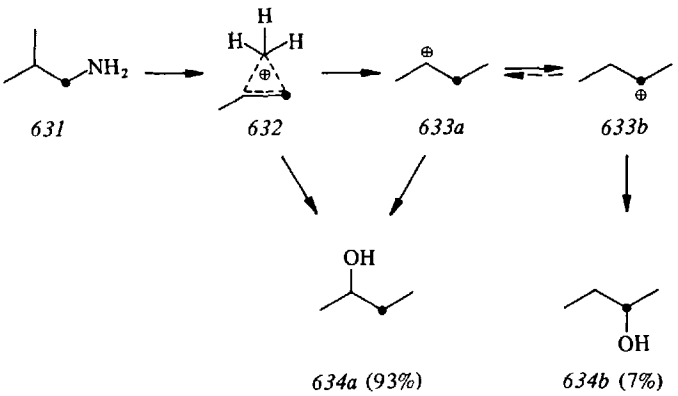


Nevertheless intramolecular proton shifts are competive with deprotonation under these conditions. The hydrocarbon products from the nitrous acid deamination of 1-propylamine (*628*) consist of 10% cyclopropane and 90% propene. The 1-propanol (*630*) obtained from labeled (*628*) arises mainly by solvolytic displacement leading to isotopically unrearranged (*630a*) and partly from protonated cyclopropane with isotopic scrambling[466].

The rearrangements associated with the deamination of 1-propylamine (*628*) are indicative of protonated cyclopropane but do not require the intervention of the

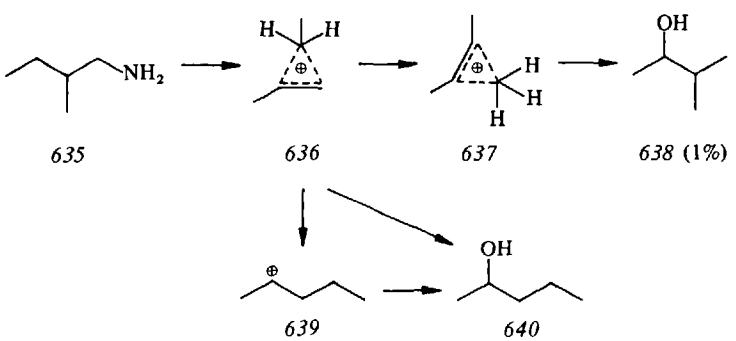
methyl-bridged ions (*626f*) and (*626h*). Formation of the edge-protonated species (*626g*) in the course of a 1,3-hydrogen shift, and its equilibration with (*626e*), would suffice to explain the isotopic scrambling. It remains to be seen whether the characteristics of protonated cyclopropanes may be recognized in systems undergoing 1,2-alkyl shifts.

7.6.1.3 Alkyl Shifts from Secondary to Primary Carbon. The deamination of isobutylamine (*631*) produces a small amount of methylcyclopropane (3% of the hydrocarbon fraction from deamination in aqueous acetic acid, up to 15% in aprotic solvents)[467]. The methylcyclopropane may eventually arise from the deprotonation of (*632*). The intervention of the open 2-butyl cation (*633*) is clearly indicated by the



631 *632* *633a* *633b*

634a (93%) *634b* (7%)

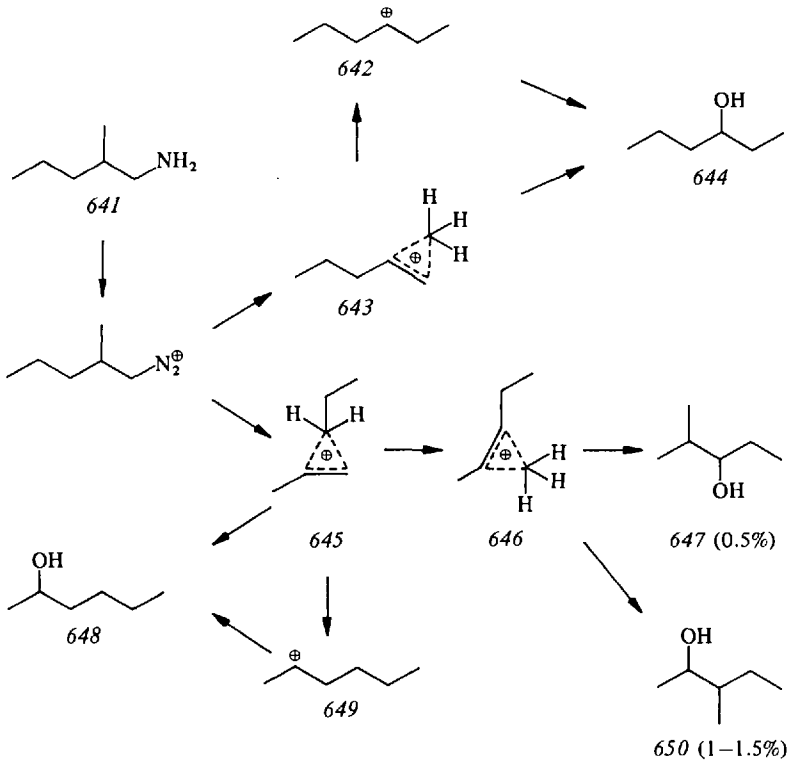


635 *636* *637* *638* (1%)

639 *640*

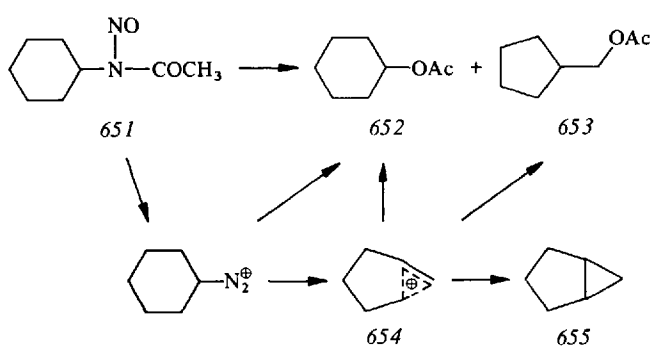
formation of 7% of isotope-rearranged 2-butanol (*634b*) from labeled (*631*)[468]. The rearranged 2-butyl cation (*633b*) is readily derived from (*633a*) by a 1,2 shift of hydrogen, but cannot arise directly from the protonated cyclopropane (*632*).

Additional evidence for open secondary cations comes from the stereochemistry of 1,2-alkyl shifts from a secondary to a primary carbon. The ethyl shift induced by diazotization of 2-methyl-butylamine (*635*) gives 2-pentanol (*640*) with 54% inversion of configuration[469]. 69% inversion was observed in the formation of 3-hexanol (*644*) from 2-methylpentylamine (*641*) by a 1,2-methyl shift while the 1,2-propyl shift leading from (*641*) to 2-hexanol (*648*) proceeds with 65% inversion[457]. (These



data refer to deaminations below the critical micelle concentration). The inverted fraction of the alcohols may arise from the alkyl-bridged ions (*636*), (*643*), and (*645*), respectively, which would also account for the minor reaction products (*638*), (*647*), and (*650*). In contrast to (*638*) and (*647*), (*650*) cannot be formed by a direct 1,3-hydrogen shift and is most reasonably explained by the interconversion of protonated cyclopropanes, (*645*) → (*646*). For the sake of simplicity only corner-protonated cyclopropanes are shown; edge-protonated species would also be adequate.

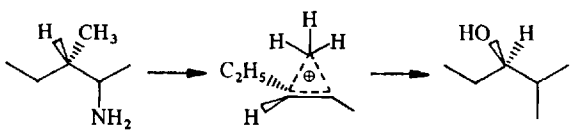
These studies indicate that protonated cyclopropanes, if formed in the course of 1,2-alkyl shifts from secondary to primary carbon, are unstable with respect to open secondary alkyl cations. The bridged ions cannot be entirely disregarded as interme-



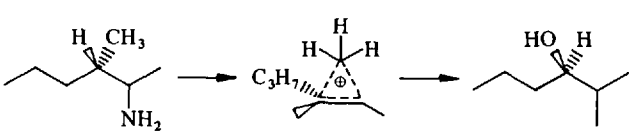
diates, however, because they account for some observations which are otherwise difficult to explain. In addition to those already mentioned the formation of small quantities (<1%) of primary products from secondary diazonium ions is noteworthy [470]. Acetolysis of *N*-nitroso-*N*-cyclohexylacetamide (*651*) gives a substitution product consisting of cyclohexyl acetate (*652*) and cyclopentylmethyl acetate (*653*) (99.05:0.95). Similar results have been obtained with 2-butyl and 3-pentyldiazonium ions generated from the corresponding nitrosoamides[470]. Equilibration of secondary and primary carbocations would appear unrealistic in view of the large difference in energy (17–19 kcal/mol in superacids[63,66]). Protonated cyclopropanes, e.g. (*654*), economically explain the formation of (*653*) as well as that of bicyclo [3.1.0] hexane (*655*)[471] from cyclohexanediazonium ions.

7.6.1.4. Alkyl Shifts from Secondary to Secondary Carbon. Corner-protonated cyclopropanes should be stabilized by alkyl substituents at the non-protonated corners. In terms of simple resonance theory, a hybrid of two secondary cations is lower in energy than a hybrid of secondary and primary cations. Therefore, bridged cations are more likely to intervene in 1,2-alkyl shifts between secondary carbons than in the $2^{\circ} \rightarrow 1^{\circ}$ rearrangements discussed above.

The methyl shifts induced by deamination of 1,2-dimethylbutylamine (*656*)[457] and of 1,2-dimethylpentylamine (*658*)[472] proceed with >98% inversion at the migration origin, in contrast to the low stereospecificity (69%) of the (*641*) → (*644*)



656 *646* *657*



658 *659* *660*

transformation. Whereas a proton shift converting the protonated cyclopropane (*645*) to its isomer (*646*) is indicated by the formation of (*647*) and (*650*) from (*641*), the reverse reaction does not take place: no trace of 2-pentanol (*648*) is obtained from the deamination of (*656*). These observations support the greater stability of (*646*), compared with (*645*).

The stereochemical control exerted by migrating methyl in the deamination of 1-ethyl-2-methylbutylamine (*661*) is also informative[457]. Since the decomposition of the diazonium ion is unassisted, only 28% of the 4-methyl-3-hexanol arises by a 1,2-methyl shift (concerted ionization leading directly to the methyl-bridged ion (*662*) would require 50%). An excess of (3*S*, 4*S*)–(*664*) over (3*R*, 4*R*)–(*664*) is obtained (72:28) and substantial crossover from *threo*-amine to *erythro*-alcohol occurs. The *erythro*-alcohol, however, is enantiomerically pure (3*R*, 4*S*)–(*664*). Although the

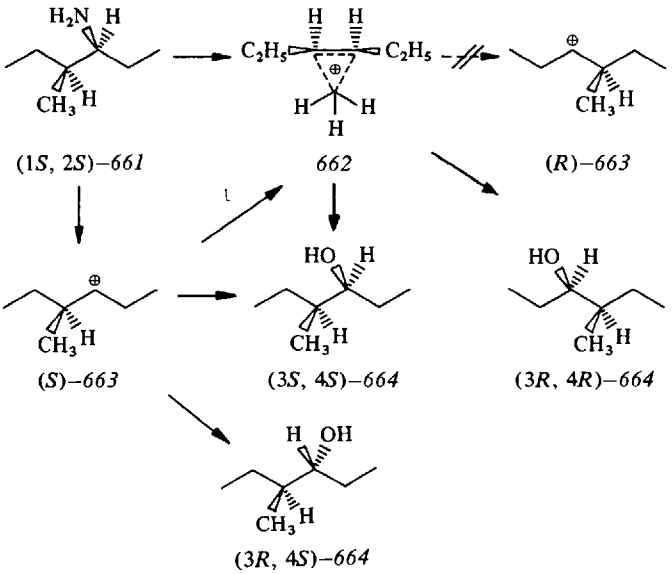
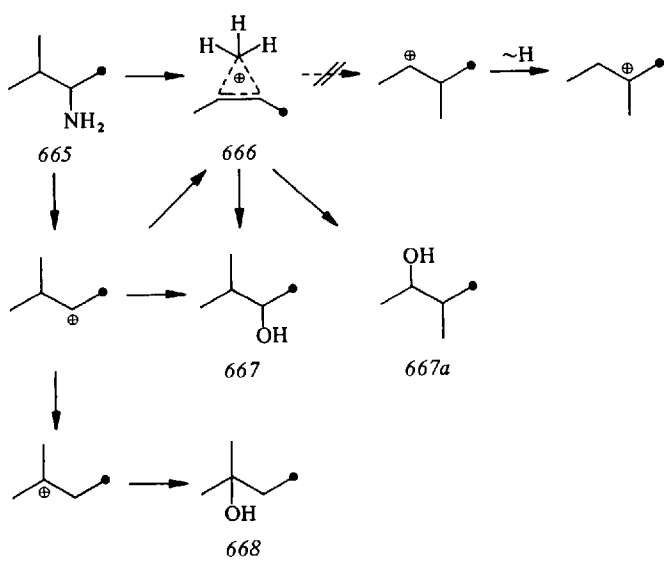


Table 17. Products derived by interconversion of protonated cyclopropanes

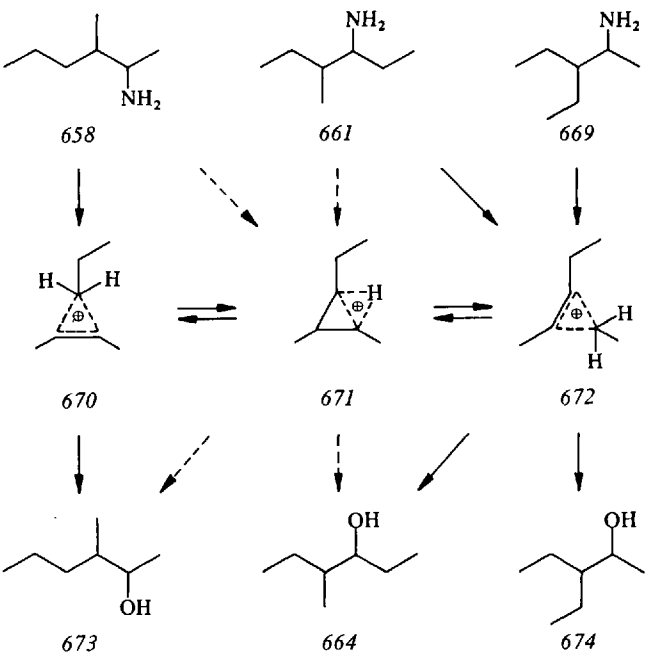
Precursor	*Threo*-(673)			*Erythro*-(673)		
	% y.	% e.e.	config.	% y.	% e.e.	config.
(1*S*, 2*S*)-(*661*)	1.0	100	(2*R*, 3*R*)	1.5	61	(2*S*, 3*R*)
(1*R*, 2*S*)-(*661*)	1.6	100	(2*R*, 3*R*)	0.3	62	(2*S*, 3*R*)
(*R*)-(*669*)	5.7	86	(2*S*, 3*S*)	2.3	23	(2*R*, 3*S*)



open ion (*S*)–(*663*) clearly intervenes, its enantiomer (*R*)–(*663*) does not. Obviously the methyl-bridged ion (*662*), once formed, does not reopen to a classical carbocation.

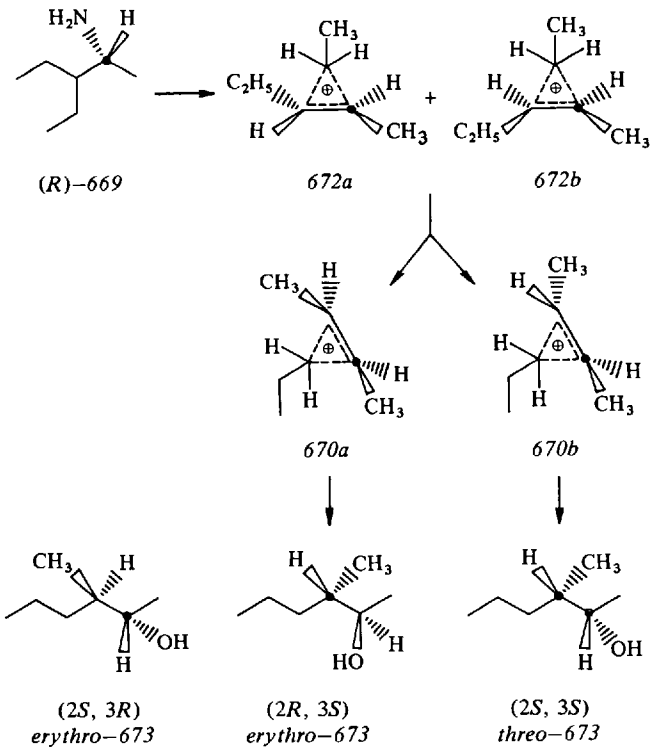
Analogous conclusions must be drawn from the deamination of labeled 1,2-dimethylpropylamine (*665*)[473,474]. Although *ca.* 30% of the 3-methyl-2-butanol is methyl-shifted (*667a*), the 2-methyl-2-butanol (*668*) carries its label exclusively at C–4. Reopening of the methyl-bridged ion (*666*), followed by a 1,2-hydrogen shift, would lead to C-1-labeled 2-methyl-2-butanol.

The methyl-bridged ions discussed so far have no reasonable chance for intramolecular proton shifts because the resultant isomers would be higher in energy, e.g. (*646*) ↛ (*645*). With ethyl-bridged ions, however, such proton shifts are nearly isoenergetic. Products attributable to the rearrangement of protonated cyclopropanes



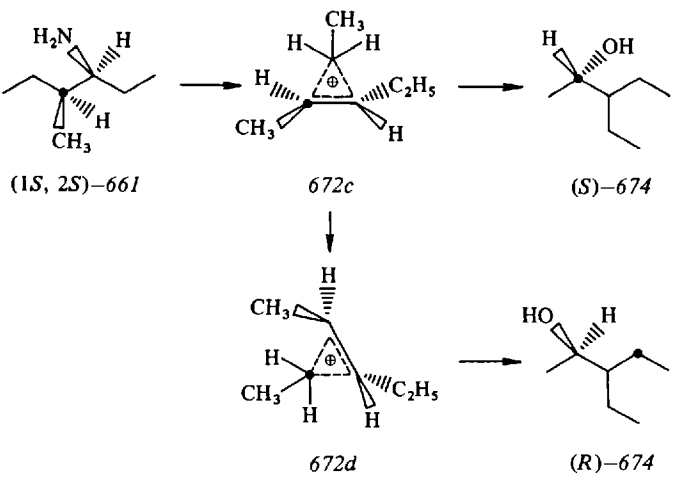
have been observed in the deaminations of (*658*), (*661*), and (*669*)[457,472]. Some of these products might also arise by direct 1,3-hydrogen shifts, e.g. (*664*) from (*658*), but others cannot originate in such a way, e.g. (*673*) from (*669*).

The intervention of protonated cyclopropanes reasonably explains the stereochemistry of the products and the distribution of a label. Proton shifts within the ethyl-bridged ion (*672*) produce the isomers (*670a*) and (*670b*) in which the non-protonated corners are equivalent or nearly so. The chiral ion (*670b*) should afford optically active *threo*- (*673*) whereas racemic *erythro*- (*673*) is expected from the achiral ion (*670a*). The experimental results (Table 17) come close to expectation, although some 20% excess of (2*R*, 3*S*)–(*673*) over (2*S*, 3*R*)–(*673*) was found[457]. Either (*670a*) is not fully symmetrical – cf. (*621*) → (*622*), Section 7.6.1.2 – or the edge-protonated species (*671*) contributes to the formation of (*673*). The distribution of a label, originally at C–1 of (*669*), between C–2 and C–3 of (*673*) (58:42) conforms with the stereochemical results. Alternative mechanisms involving open ions predict

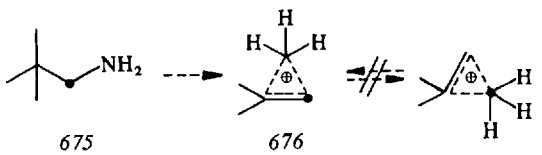


identical enantiomeric purities of *threo*- and *erythro*-(*673*), and complete recovery of the label at C–3 of (*673*).

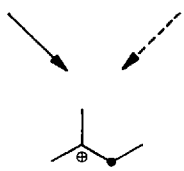
Proton shifts within protonated cyclopropanes also explain the rather low stereospecificity at the origin of 1,2-ethyl shifts. (1*S*, 2*S*)–(*661*) gives 3-ethyl-2-pentanol (*674*) with 54% inversion and with substantial redistribution of a label, as required by the conversion of the protonated cyclopropane (*672c*) to its enantiomer (*672d*)[457,472].



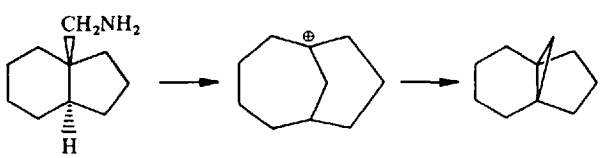
7.6.1.5 Alkyl Shifts from Tertiary to Primary or Secondary Carbon. As mentioned above (Section 7.6.1.1). protonated *gem.*-dialkylcyclopropanes, e.g. (*676*), are expected to be unstable with respect to tertiary carbocations, e.g. (*677*). The deamination of neopentylamine (*675*) proceeds without scrambling of a ^{13}C label[475] and does not produce significant quantities of 1,1-dimethylcyclopropane. In contrast, (*678*) afforded 74% of tricyclo [4.3.1.$0^{1,6}$] decane (*680*) in its reaction with nitrous acid[476]. The instability of the bridgehead carbocation (*679*) probably facilitates the



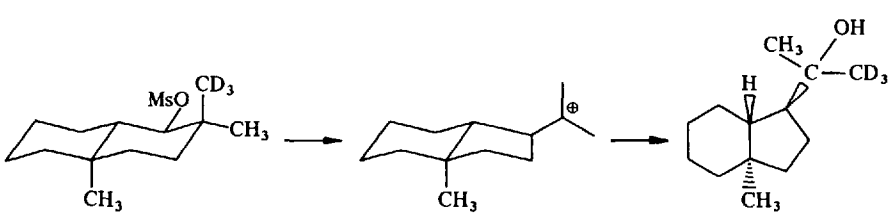
675 *676*



677



678 *679* *680*



681 *682* *683*

formation of a (protonated) cyclopropane. The only stereochemical study available reports that the decalin derivative (*681*) undergoes ring contraction to (*683*) with complete scrambling of the CD_3 group (the methyl groups in (*683*) are diastereotopic and, therefore, distinguishable)[477]. The intervention of the open, tertiary carbocation (*682*) is clearly indicated.

7.6.2 The 2-Norbornyl Cation

"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." (G. D. Sargent)[478]. In retrospect it appears unfortunate that the "nonclassical ion controversy" has concentrated so much on the 2-norbornyl cation. The dissenting parties have recently restated their positions in considerable detail[10–12, 399]. A brief survey will suffice here to show why the structure of the 2-norbornyl cation has resisted unambiguous identification. The following points have been made in discussing the proposal of σ-delocalization:

7.6.2.1 Exceptionally Fast Rates? The "fast" rate of ethanolysis of camphene hydrochloride (*1*), 13600 times faster than that of t-butylchloride[479], was attributed to anchimeric assistance[480]. However, (*1*) solvolyzes only 5,7 times faster than 1,2,2,5,5-tetramethylcyclopentyl chloride (*684*), and only 2,5 times faster than 1,2,2,5,5-pentamethylcyclopentyl chloride (*685*)[479]. Thus, relief of steric strain is probably sufficient to explain the reactivity of (*1*).

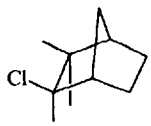
Exo-2-norbornyl brosylate (*74*) acetolyzes 517 times faster than cyclohexyl brosylate (*686*), but only 16 times faster than cyclopentyl brosylate (*687*)[481]. In trifluoroacetic acid the (*74*): (*687*) rate ratio is 172[482]. The difficulty with such comparisons is that neither model is identical to (*74*) with respect to angle strain, torsional strain, and nonbonded repulsions. In terms of the Schleyer-Foote correlation (Section 7.2.1), which takes into account all of these effects, the acetolysis of (*74*) is accelerated by a factor of 2000.

Anchimeric assistance in (*74*) is not detected by the tool of increasing electron demand[246]. The ρ^+ value of 2-aryl-2-*exo*-norbornyl p-nitrobenzoates (*306*) agrees with that of the corresponding cyclopentyl derivatives (*689*) although it deviates considerably from cyclohexyl (*690*) and 3-methyl-2-butyl (*301*) models. Analysis of the Hammett-Brown correlations must take into account that all aryl groups would be capable of leveling a small amout of σ participation.

The correlation, $\log k/k_0 = \rho\gamma^+$, has been extended to (*74*) using $\gamma^+ = 2.53$ for hydrogen, a value derived from rate data on allegedly unassisted systems[249] (Section 7.2.2). With the incursion of major participation in the secondary, but not in the tertiary derivatives, positive deviations for the secondary should be expected. The 2-norbornyl derivatives reveal an excellent correlation, indicating that the solvolysis of (*74*) is unassisted[483]. Unfortunately, the method is not very reliable because of the OBs-OPNB conversions involved. Serious dicrepancies with some secondary systems have been noticed[484].

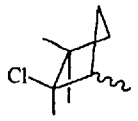
The rates of 1-substituted norbornyl derivatives (*691*) (X=CN, CO_2CH_3, CH_2OH) have been correlated by the Hammett-Taft equation[485]. In that case, extrapolation to X=H indicates a rate enhancement of (*74*) by a factor of 100.

We may summarize that the rate data are inconclusive and that the amount of anchimeric assistance involved in the ionization of (*74*) (if any) is small.



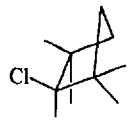
1

$k_{rel.}$ 1.0



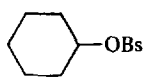
684

0.17



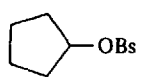
685

0.40



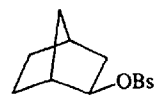
686

$k_{rel.}$ 1.0



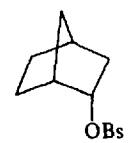
687

32



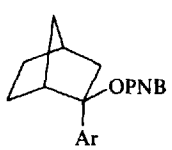
74

517



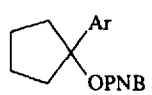
688

1.47



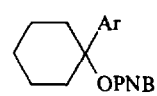
306

ρ^+ −3.82



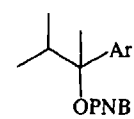
689

−3.82



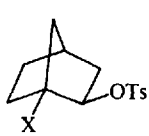
690

−4.60



301

−4.76



691

692

7.6.2.2 High Exo : Endo Rate and Product Ratios. Exo-2-norbornyl brosylate (*74*) undergoes acetolysis at a rate 350 times greater than that of the *endo* isomer (*688*)[10]. If polarimetric rather than titrimetric rate constants are used, the *exo* : *endo* rate ratio is 1550. Both *exo* and *endo* starting material give >99.9% *exo* product. If the leaving group and the nucleophile are identical, the product forming step is the microscopic reverse of ionization. The acid-catalyzed equilibration of *exo*- and *endo*-2-norbornyl acetates, (*693*) $\rightleftarrows$ (*694*), represents such a case. The reaction profile shown in Fig. 13 has been established and is commonly referred to as the Goering-Schewene diagram[486]. In the solvolysis of (*74*) and (*688*) product formation is not the exact reverse of ionization, yet a free energy diagram very similar to Fig. 13 may be constructed. Even the carbonylation-decarbonylation equilibrium of the 2-norbornyl cation in superacids, (*693*) $\rightleftarrows$ (*22*) $\rightleftarrows$ (*694*), $X{=}CO^+$, conforms to the same pattern[487], indicating that the *exo* preference of (*22*) is independent of solvation.

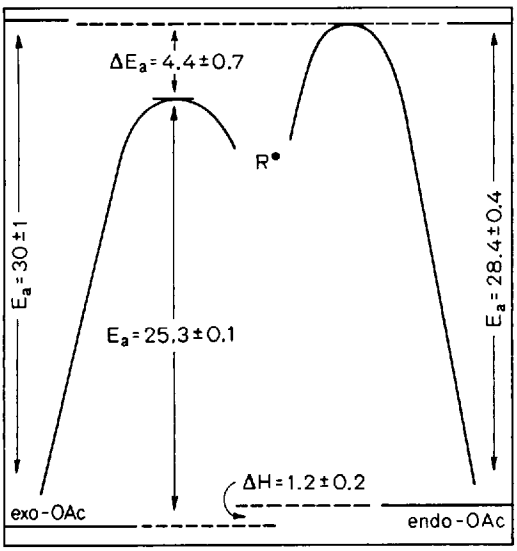
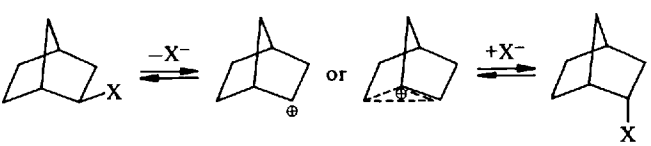
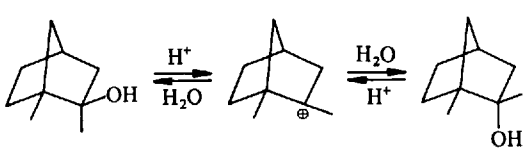


Fig. 13. Apparent activation energies (E_a) for acid-catalyzed reactions of *exo*- and *endo*-2-norbornyl acetate and ΔH for equilibration. [Reproduced from Goering, H. L., Schewene, C. B.: J. Am. Chem. Soc. *87*, 3516 (1965).]



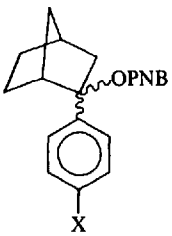
693 *22* *694*



695 *696*

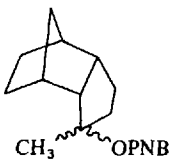
High *exo* : *endo* rate and product ratios have been alternatively attributed to the bridged structure of the 2-norbornyl cation[10,11] and to steric effects[12,399]. The supporters of σ delocalization insist that the *exo* rates are exceptionally high while the advocates of steric hindrance claim that the *endo* rates are exceptionally slow. All attempts to escape from this dilemma by assessing rates on an absolute basis have more or less failed (Section 7.6.2.1). An *exo* preference is found in essentially all reactions of the norbornane system[8], including free radical additions and the decomposition of peresters[488]. Thus, it is not the direction but only the magnitude of the effect which is subject to interpretation.

The following evidence has been cited in favor of steric effects: Stabilizing substituents at C–2, including p-anisyl, do not affect the *exo* : *endo* rate ratios significantly although they should swamp σ participation[489]. The failure to observe increasing electron demand in (*697*) is in accord with the steric interpretation[490]. The



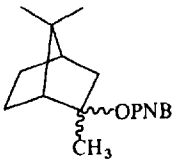
697

X =		
OCH_3	exo	284
	endo	232
CH_3		127
H		127
CF_3		187



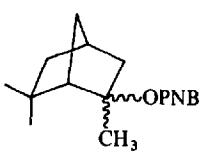
698

exo	4300
endo	



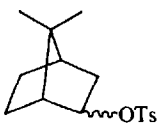
699

6.1



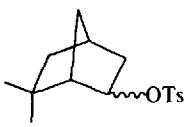
700

exo	$3.6 \cdot 10^6$
endo	



701

4100



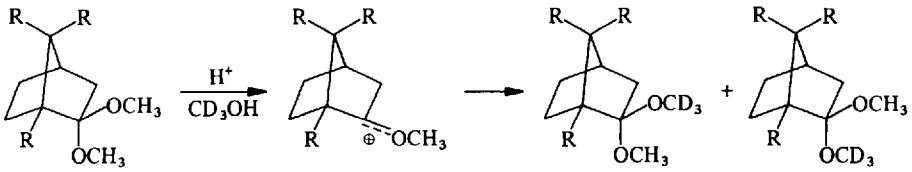
702

206

energy diagram for the acid-catalyzed equilibration of the 1,2-dimethyl-2-norbornanols, (*695*) ⇄ (*696*), is similar to that for 2-norbornanol[491]. Steric hindrance is evident in other U-shaped systems, e.g. (*698*)[492], where σ delocalization is less likely. The introduction of *gem*-dimethyl into the 7-position decreases the *exo* : *endo* rate ratio in (*699*) while the opposite effect results from 6,6-dimethyl substitution in (*700*)[493].

These observations clearly demonstrate the dominance of steric effects in tertiary norbornyl derivatives but do not necessarily apply to secondary systems. The different response to *gem*-dimethyl substitution in (*701*)[90] and (*702*)[494] as compared with (*699*) and (*700*) is a disturbing feature.

The following experimental results support the concept of bridged ions: The acid-catalyzed exchange of methoxy groups in norbornanone ketals (*703*) and (*704*) exhibits remarkably low *exo* : *endo* ratios[495]. The stabilized intermediate (*705*) is thought to define the behavior of 2-norbornyl cations in the absence of σ delocalization. These results stand in stark contrast with Brown's data on (*697*). Destabilization of a positive charge at C–1 should also minimize σ delocalization. In fact, the cyano group in (*706*) lowers the *exo* : *endo* rate ratio to *ca.* 3[496,497]. 6-Methoxycarbonyl-2-norbornyl tosylate (*707*)[498] and 2-tosyloxy-7-norbornanone (*708*)[499] may belong to the same category, although the product ratios from *endo*-(*708*) indicate some solvent participation. If a substituent is present in the 3-position which can delocalize positive charge, the reduced need for σ participation should likewise decrease the *exo* : *endo* ratio. In the allylic system (*709*)[500] the acetolysis rate ratio is

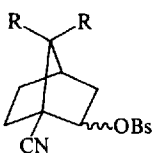


703 R = H
704 R = CH_3

705

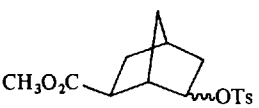
16
0.1

1
1



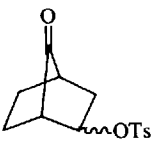
706

exo 3 (R = H)
endo 2.8 (R = CH_3)



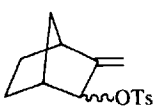
707

0.4



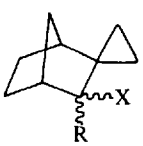
708

0.17



709

exo 3.9
endo

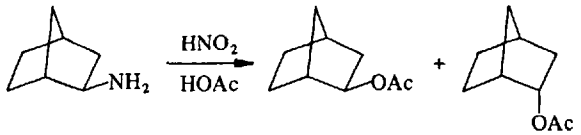


710

2.6 (R = H)
831 (R = CH_3)

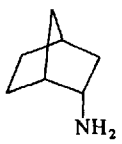
down to 3.9; in the cyclopropyl substituted molecule (*710*) (R=H)[501] it is down to 2.6. Remarkably, the decrease in *exo : endo* rate ratio is observed only for the secondary system (*710*), R=H, but not for the tertiary system (*710*), R=CH_3[502]. This result suggests that high tertiary *exo* : *endo* ratios are steric in origin while those of secondary substrates may be due to σ delocalization.

The nitrous acid deaminations of *exo*- and *endo*-2-norbornylamine afford substantial amounts of *endo* products, in contrast to the solvolysis of the corresponding tosylates[503,504]. The *endo* amine (*714*) yields about twice as much *endo* acetate (*713*) as does the *exo* amine (*711*)[504]. The effect of the diazonium precursor is even more dramatic in the deamination of (*715*)[505] which produces acetates (*718*) and (*719*) in an *exo* : *endo* ratio of *ca.* 0.15. No *endo* acetate (*718*) is found in the acetolysis of the corresponding tosylate ! (Additional products are formed by hydrogen shifts, see Section 7.6.2.5). As was noticed with acyclic systems, the decomposition of secondary diazonium ions is normally unassisted, but bridged ions may form subsequently. The norbornandediazonium ions conform to this pattern: the product (*720*), derived from (*715*) by Wagner-Meerwein rearrangement, is exclusively *exo*.



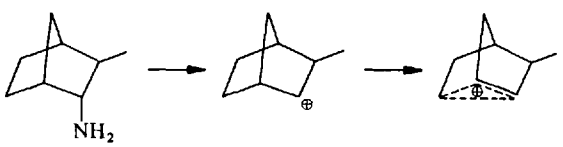
711 *712* *713*

98 2%

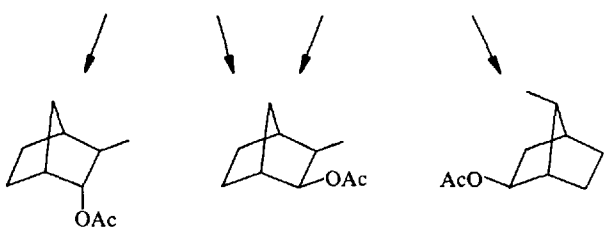


714

95 5%



715 *716* *717*



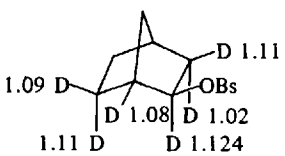
718 *719* *720*

28.4 4.3 46.4%

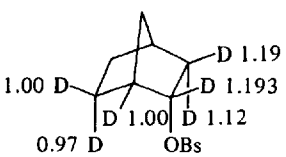
In summary, the interpretation of *exo* : *endo* ratios is obscured by the inherent preference of the norbornane skeleton for *exo* attack. The stereochemistry of tertiary 2-norbornyl cations appears to be governed by steric factors. There is substantial evidence, however, that bridging contributes to the selectivity of secondary norbornyl cations.

7.6.2.3 Secondary Deuterium Kinetic Isotope Effects. Deuterium substitution has been employed to probe for bridging in the transition state of 2-norbornyl brosylate solvolyses. The secondary α-, β-, and γ-deuterium kinetic isotope effects for *exo*- and *endo*-norbornyl brosylate are shown in formulas (*721*) and (*722*), respectively. The overall pattern for the *endo*-compounds (*722*), with an α-effect close to the limiting value (1.22, cf. Section 7.2.3)[506], with nil effect of C(1)–D[507], a modest

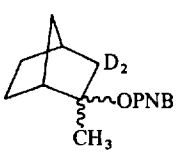
effect due to *endo*-C(3)–D, and a substantial effect due to *exo*-C(3)–D[506], is entirely compatible with unassisted ionization. The distinctive pattern of the *exo*-isomer (*721*) is not easily reconciled with such a mechanism. γ-Deuterium isotope effects in general are unity or slightly inverse. The abnormal value of 1.10 observed for (*721*) [508, 509] may originate in vibrational changes in the C(6)–H(D) bonds during ionization. The near identity of k_H/k_D for *exo*- and *endo*-C(6)–H(D) is in accord with the equivalence of these protons in the bridged ion. The combination of a depressed α-effect[506] and an enhanced C(1)–D effect[507], as well as the low C(3)–D effects [506], are all consistent with charge delocalization away from C(2) in the transition state for ionization.



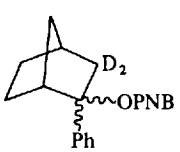
721



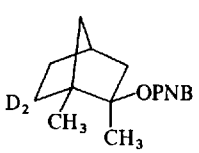
722



723



724



725

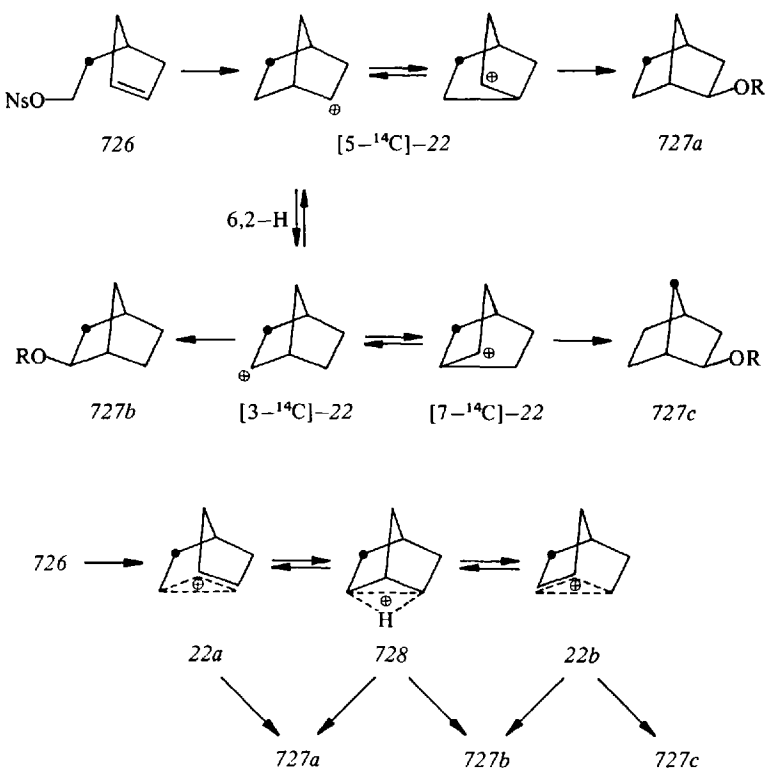
		723	*724*	*725*
k_H	*exo*	1.33	1.18	1.02
k_D	*endo*	1.31	1.15	

These conclusions are supported by data on the tertiary 2-norbornyl esters (*723*) [510] and (*724*)[511] in which the C(3)–D_2 effect is nearly independent of configuration. The k_H/k_D of (*724*) is much smaller than that of (*723*), due to charge delocalization into the phenyl ring. 6,6-Dideuteration has a negligible effect on the solvolysis rate of 1,2-dimethyl-2-norbornyl p-nitrobenzoate (*725*)[512]. Although the interpretation of secondary deuterium isotope effects is often difficult, comparison of the various norbornyl derivatives discussed here has uniformly been claimed to support alkyl participation.

7.6.2.4 Symmetry. Solvolysis of optically active *exo*-2-norbornyl brosylate (*74*) yields racemic *exo*-norbornyl derivatives[10,513]. The rate of racemization exceeds the titrimetric rate by a factor of 1.40 in 75% acetone, 2.94 in ethanol, and 3.46 in acetic acid[10] (later revised to 4.6[513]). This is attributed to recapture of the anion by the racemic cation. Solvolysis of optically active *endo*-norbornyl brosylate (*688*) yields *exo*-norbornyl products with a small amount of retained activity (13% in 75% acetone, 7% in acetic acid, and 3% in formic acid)[10,513]. Solvent attack with inversion on (*688*), or the corresponding tight ion pair, must be involved.

The formation of racemic products may be attributed to σ delocalization, the bridged ion being achiral, or to rapid Wagner-Meerwein rearrangement of the "classical" 2-norbornyl cation. 6,2- and 3,2 hydrogen shifts (Section 7.6.2.5) also contribute to racemization. Attempts to capture unsymmetrical 2-norbornyl cations by internal return, empolying ambident anions, have failed (Section 4.2.4). The deamination of optically active 2-norbornylamines, however, proceeds with partial retention of optical purity[503,504]. The *exo*-acetate (*712*) from *exo*-amine (*711*) revealed $11 \pm 2\%$ optical activity. The *exo*-acetate (*712*) from *endo*-amine (*714*) was 18% optically pure whereas the *endo*-acetate (*713*) was formed with $85 \pm 12\%$ retention of configuration. These results may in part be due to the unassisted decomposition of 2-norbornanediazonium ions th give localized 2-norbornyl cations. Since the product distributions and the stereochemical results from (*711*) and (*714*) are different, solvolytic displacement and/or ion pairing must also be involved. Unfortunately, the deaminations were performed in acetic acid which maximizes ion pairing (Section 4.3.4.).

Unsymmetrical 2-norbornyl cations apparently arise by 6,2- and 3,2-hydrogen shifts. Solvolysis of the labeled 2- (3-cyclopentenyl) ethyl p-nitrobenzenesulfonate (*726*) (π route to the norbornyl cation) yields unequal amounts of the products (*727b*) and (*727c*)[514,515]. This result is incompatible with the bridged ion (*22b*) as the only source of (*727b*) and (*727c*). It was pointed out that the formation of an excess of (*727b*) over (*727c*) is consistent with the intervention of the open ion 3–



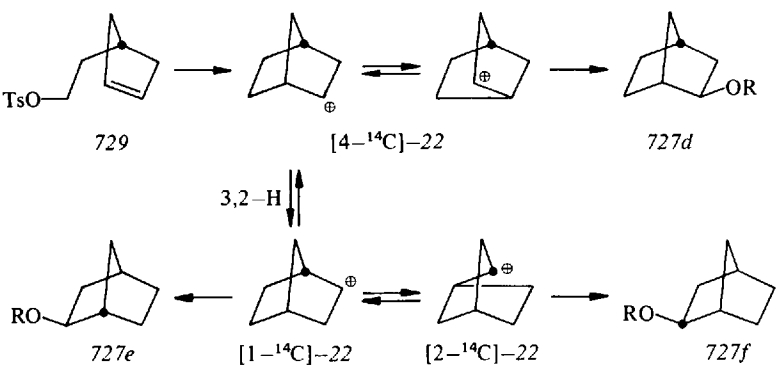
726 [5–^{14}C]–*22* *727a*

727b [3–^{14}C]–*22* [7–^{14}C]–*22* *727c*

726 *22a* *728* *22b* *727a* *727b* *727c*

^{14}C–(*22*) which is captured competitively with its Wagner-Meerwein conversion into 7–^{14}C–(*22*)[516]. The (*727b*):(*727c*) ratios in different solvents (1.52 in acetic acid[514], 1.18 in buffered acetic acid, and 1.05 in buffered aqueous acetone[515]) do not conform with this mechanism and are ignored by the partisans of classicism[399]. Nucleophilic capture of 3–^{14}C–(*22*) in competition with rearrangement should lead to an increase in the (*727b*):(*727c*) ratio with increasing nucleophilicity of the solvent. The alternative explanation[515], capture of the edge-protonated nortricyclene (*728*), is in better accord with the solvent effect: the contribution of (*728*) is expected to decrease with decreasing acidity of the solvent.

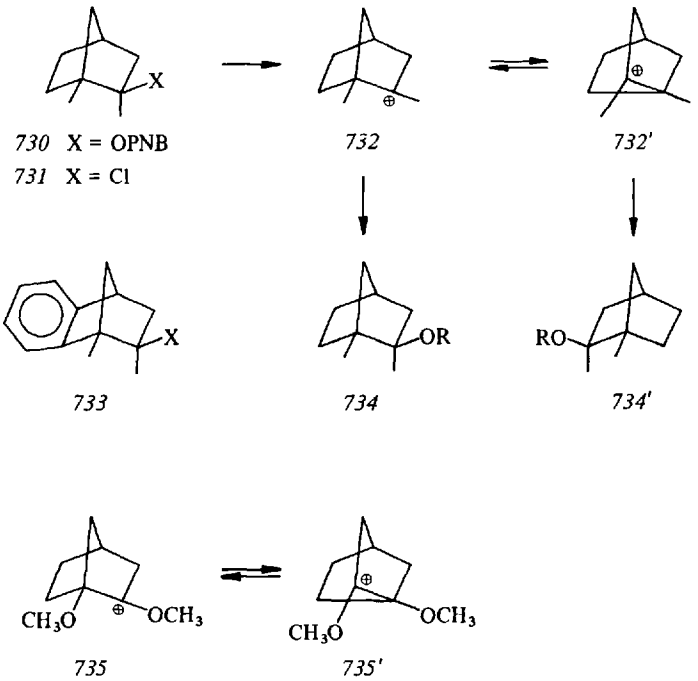
Unequal distribution of a label was also observed in the acetolysis of (*729*)[517]. In this case the unsymmetrical norbornyl cation arises from a 3,2–H shift; all other rearrangements leave the label at C–4. The excess of (*727e*) (0.52%) over (*727f*) (0.33%) was explained by capture of the first formed ion 1–^{14}C–(*22*) prior to complete equilibration. The product mixture (*727d-f*) was reconverted to the tosylate and reacetolyzed. After four cycles (*727e*) had increased to 1.52% and (*727f*) to 0.52%. This is a strange result which casts some doubt on the validity of the experi-



ment. The acetolysis of a mixture of (*727e*) and (*727f*), R=Ts, must lead to an even distribution of the label between C–1 and C–2. Consequently, repeated acetolysis should decrease the (*727e*):(*727f*) ratio while the sum of these products increases.

The addition of protic acids to norbornene leads to incomplete scrambling of a label (Section 4.4.3). The mechanism of these additions is not sufficiently understood to allow straightforward interpretations.

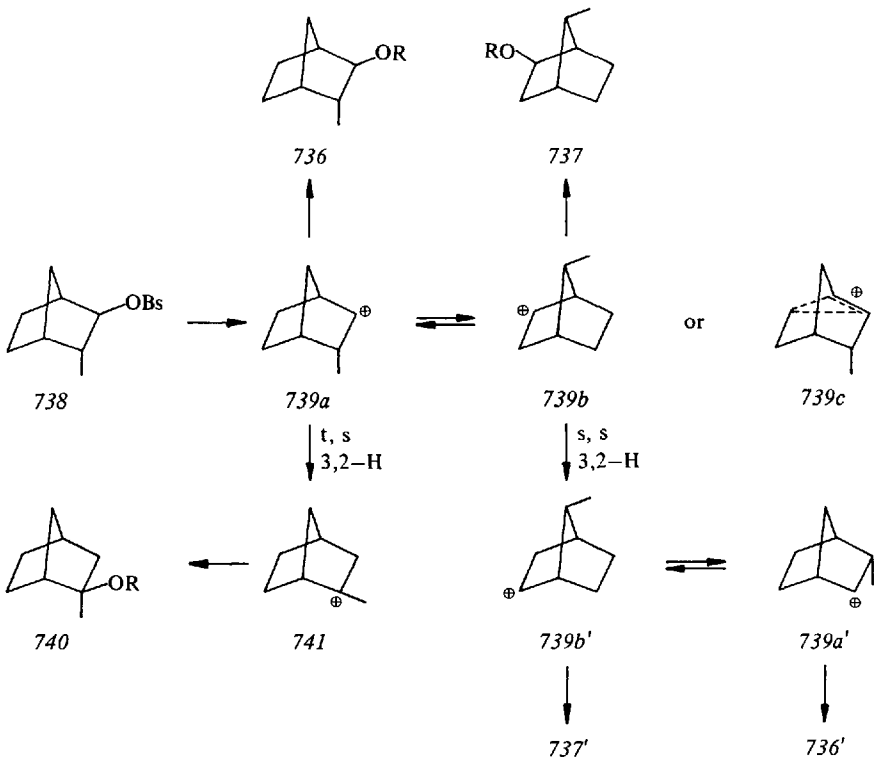
The tertiary 1,2-dimethyl-2-norbornyl cation (*732*) is clearly unsymmetrical. Solvolyses of the p-nitrobenzoate (*730*)[96] and of the chloride (*731*)[518] proceed with partial retention of configuration, i.e., an excess of (*734*) over its enantiomer (*734'*) is produced (57.5:42.5 with (*731*) in methanol-lutidine). Similar results were obtained with 1,2-dimethyl-5-norbornen-2-yl p-nitrobenzoate (*428*)[347] and the 5,6-benzo derivatives (*733*)[519], in spite of eventual π participation. The 1,2-dimethoxy-2-norbornyl cation (*735*) is unsymmetrical even under stable ion conditions[520]. The low temperature NMR shows distinct signals for the two methoxy groups, coalescence occurring at +7°C.



In summary, 2-norbornyl cations, generated by solvolysis of *exo*-2-norbornyl halides of sulfonates, behave as symmetrical (achiral) intermediates. Other modes of generation (deamination, hydrogen shifts, addition of HX to norbornene) lead to partial asymmetry, excluding the bridged norbornyl cation as the only intermediate. Although "classical" 2-norbornyl cations may intervene in some of these reactions, no unequivocal identification has been achieved and alternative interpretations are possible.

7.6.2.5 Hydrogen Shifts. Solvolyses of ^{14}C- and ^{3}H-labeled 2-norbornyl brosylates[521,522] as well as that of (*726*)[514,515] have demonstrated that the 2-norbornyl cation undergoes hydrogen shifts in addition to Wagner-Meerwein rearrangement. Mathematical analysis of the isotopic data[516] reveals that only in the formolysis of (*74*) and of (*726*) there appears to be definite evidence for the 3,2–H shift. The buffered acetolysis of (*729*)[517] provides a ratio of *ca.* 115 of the rates of solvent attack and 3,2–H shift (k_S/k_H). The acetolysis of optically active 3-*endo*-methyl-*exo*-2-norbornyl brosylate (*738*) allows to compare the rates of tertiary, secondary and secondary, secondary 3,2–H shifts relative to solvent capture[523]. (6,2–H shifts have been omitted for the sake of clarity). The tertiary, secondary 3,2–H shift, (*739a*) → (*741*), is at least 14 times faster than the secondary, secondary shift, (*739b*) → (*739b'*), which leads to racemization. The competition ratio between solvent capture and the secondary, secondary H-shift is at least 122, in good agreement with the value from isotopic data.

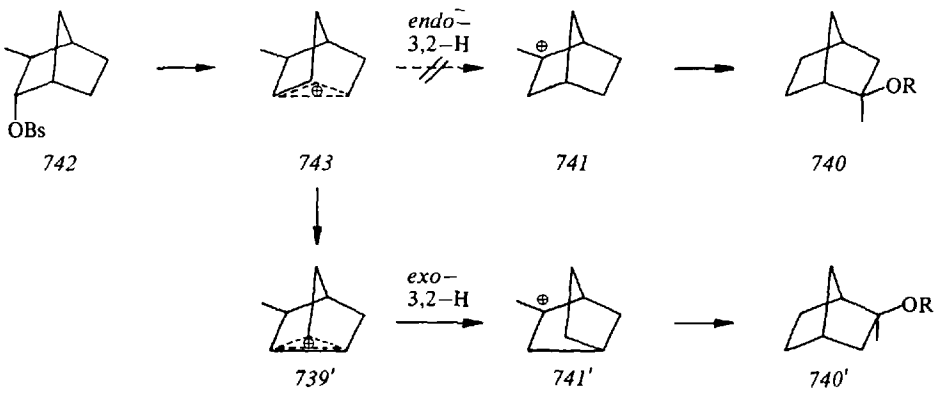
The configuration and optical purity of the tertiary product (*740*) from (*738*) show that it arises entirely by direct *exo* vicinal hydrogen shift in cation (*739*)[523].

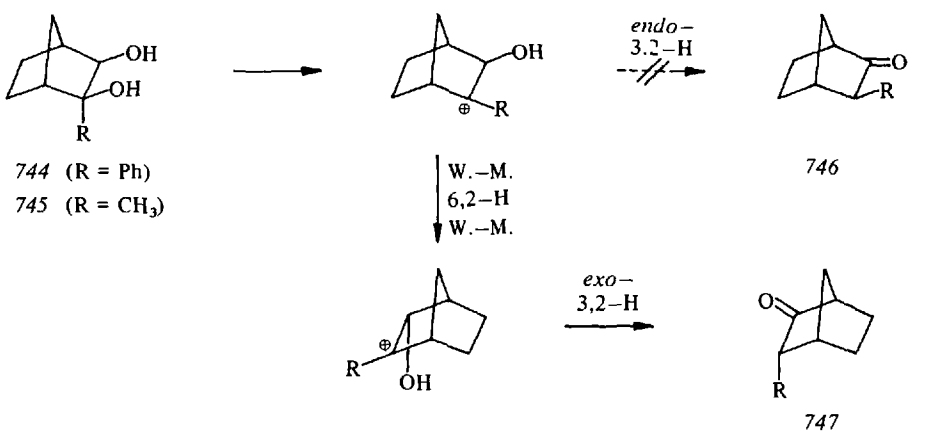


The cation (*743*) generated from optically active 3-*exo*-methyl-2-*endo*-norbornyl brosylate (*742*) scrupulously avoids rearrangement to the tertiary cation (*741*) by *endo*-3,2-H shift[524]. The small amount of tertiary acetate (*740'*) arises by a more circuitous route involving 6,2–H shift to give (*739'*), followed by *exo*-3,2-H shift leading to (*741'*). The latter route is at least 100 times as efficient as the direct one relative to solvent capture. The pinacolic rearrangements of the diols (*744*)[525] and (*745*)[524] produce the ketones (*747*) rather than (*746*). The preference for *exo, exo* over *endo, endo-3,2*-H shifts is estimated to be $\geq$ 200 for (*744*), and at least 3300 in the case of (*745*). A strong *exo, exo* preference has also been established for 3,2-methyl shifts[526,527].

In 3,2 shifts the migrating group acts as an internal nucleophile. The controversial arguments concerning high *exo* : *endo* product ratios (Section 7.6.2.2) also apply to the stereospecificity of 3,2 shifts. The invariance in *exo* preference as a function of cation stability casts some doubt on the explanation of this phenomenon in terms of σ delocalization[524].

6,2–H shifts compete effectively with capture by solvent. For the parent 2-norbornyl cation the k_S/k_H ratio is *ca.* 1 in formic acid, *ca.* 2 in acetic acid, and *ca.* 6 in aqueous acetone[506,516]. The decomposition of 2-norbornanediazonium ions in aqueous sodium hydroxide, however, proceeds with less than 4% 6,2–H shift[528]. Tertiary, secondary shifts, e.g. (*749*) $\rightarrow$ (*750*)[505], occur more readily than secondary, secondary shifts do. Steric effects also play some role: there is more 6,2–H

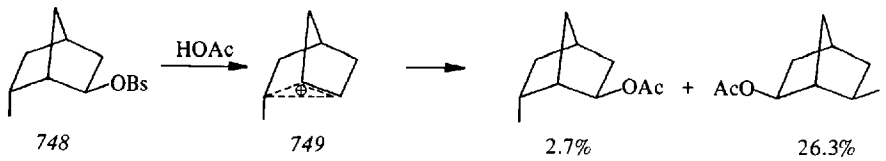




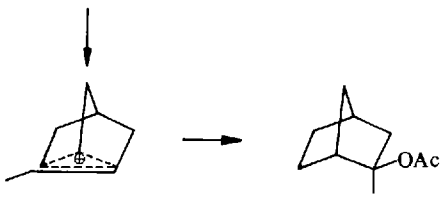
shift in the solvolysis of (*751*) to give (*754*) than in the reverse reaction, (*755*) → (*752*) + (*753*)[90]. The *syn*-7-chloro-*exo*-2-norbornyl tosylate (*756*) gives more *anti* product (*758*) by 6,2–H shift than its epimer (*759*) affords *syn* product (*757*)[529, 530].

The stereochemistry of 6,2–H shifts is *endo, endo*. Treatment of acid (*760*) with 50% sulfuric acid results in formation of lactone (*761*), contaminated by less than 3% of the 2–H species which would arise by 6,2 shift of *exo*-D[531]. The pinacolic rearrangement of labeled diol (*744a*) produces ketone (*747a*) by way of an *endo, endo* 6,2–D shift[532].

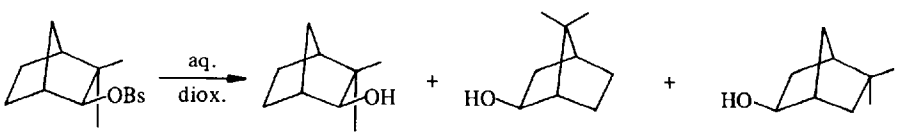
Additional information comes from the solvolyses of tosylates (*765*) and (*769*)[533]. The bridged ion (*766*) (or the equivalent pair of open ions) undergoes 6,1–D shift in strong preference to 6,2–H shift (ca. 40:1). The regioselectivity of hydrogen shift parallels that of attack by external nucleophiles which gives (*762*) rather than vicinal diol. The deuterium distribution in the products (*771*) and (*772*) reveals that even a sequence of 6,1–D and 6,2–H shifts, (*766*) → (*768*) → (*770b*), is more effective in producing (*770*) than the direct 6,2–H shift, (*766*) → (*770a*). Significantly, the



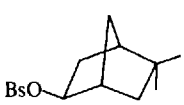
748 *749* 2.7% 26.3%



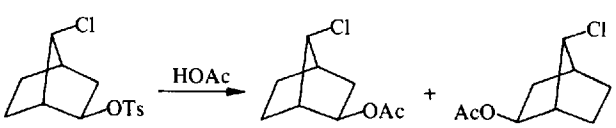
750 68%



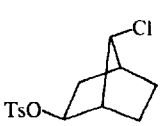
751 *752* 10.5 *753* 71.5 *754* 18.0%



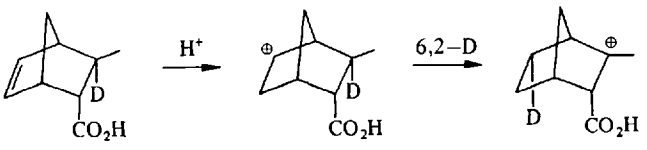
755 2.0 12.5 85.5%



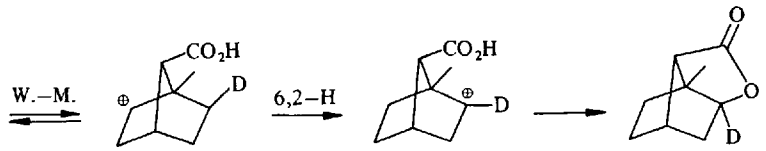
756 *757* 45 *758* 42%



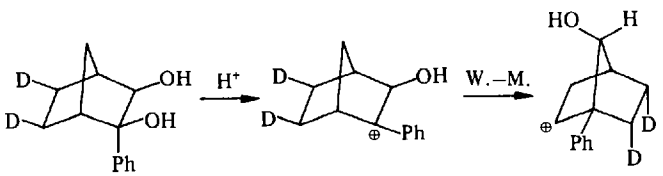
759 14 70%



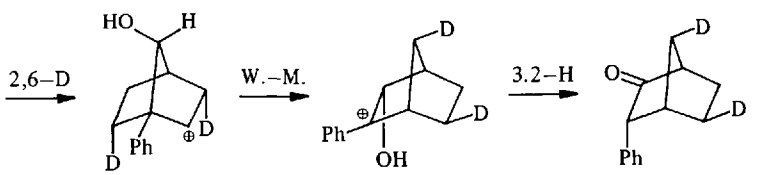
760



761



744a

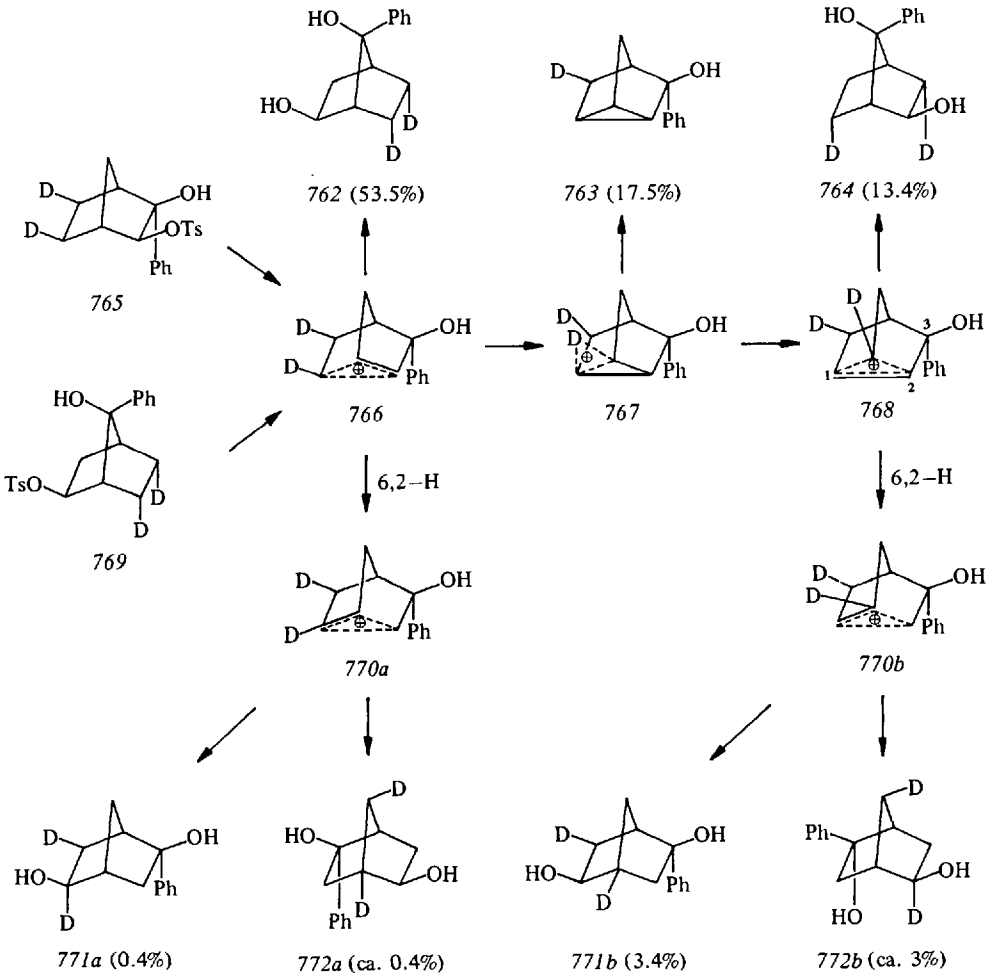


747a

nortricyclene (*763*) is monodeuterated, i.e., elimination proceeds with loss of the migrating deuterium. Elimination certainly contributes to the decreasing importance of 6,2–H shifts with increasing basicity of the solvent.

All data which are available on 6,2 (6,1) -H shifts are nicely compatible with an interconversion of corner-protonated nortricyclenes (bridged 2-norbornyl cations) *via* edge-protonated nortricyclenes.

7.6.2.6 Norpinyl-Norbornyl Interconversions. All routes to the 2-norbornyl cation discussed so far gave high *exo : endo* product ratios. The rearrangement of 2-norpinyl (bicyclo [3.1.1] heptyl) precursors is an exception to this rule. Both the solvolysis of the p-nitrobenzoate (*87*) and the decomposition of the diazonium ion (*774*) give substantial amounts of *endo*-2-norbornyl products[101]. The lowest *exo* : *endo* ratio (0.15) is found for the 2-norbornyl p-nitrobenzoate formed by ion pair return. The *exo : endo* ratios of the solvolytic products increase with decreasing nucleophilicity of the solvent. The *endo*-2-norbornyl products are thought to derive from the



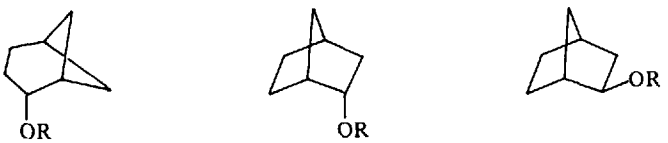
bridged ion (*775*) which may be captured prior to its conversion into (*22*). The data are incompatible with recent MINDO/3 calculations which predict (*775*) to be the most stable form of the 2-norbornyl cation[57].

The symmetry of the norpinane system conceals the stereochemistry at the terminus of the alkyl shift. The acid-catalyzed rearrangements of the isomeric 6,6-dimethylnorpinan-2-ols (nopinols) (*776*) and (*782*) reveal complete inversion of configuration[534,535]. The initially formed cations (*779*) and (*784*) do not interconvert although both rearrange to the dimethylnorbornyl cations (*780*) and (*781*). Fragmentation to give the 3-cyclohexenyldimethylcarbenium ion (*778*) occurs with (*779*) but not with (*784*). The dehydration of the norpinols, and the deamination of (*783*), constitute exceptional cases of 1,2 alkyl shifts which are stereospecific at the migration terminus but nonstereospecific at the migration origin. This unusual stereochemistry is probably due to the relief of cyclobutane ring strain.

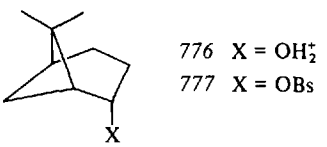
87 X = OPNB
774 X = N_2^+

775

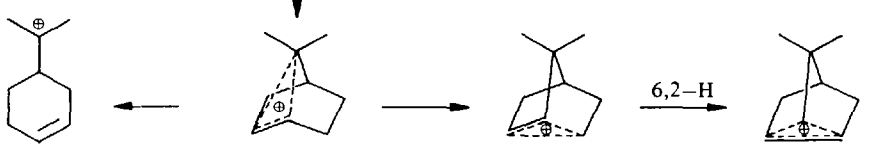
22



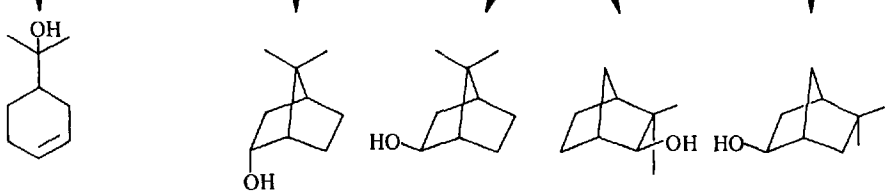
R = PNB (ion pair return)	87	13
C_2H_5	54	46
H	43	57
CH_2CF_3	17	83



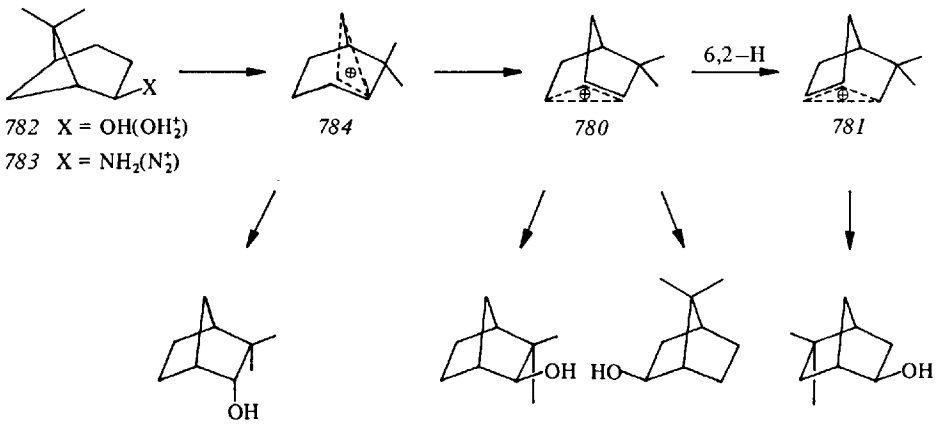
776 X = OH_2^+
777 X = OBs



778 *779* *780* *781*



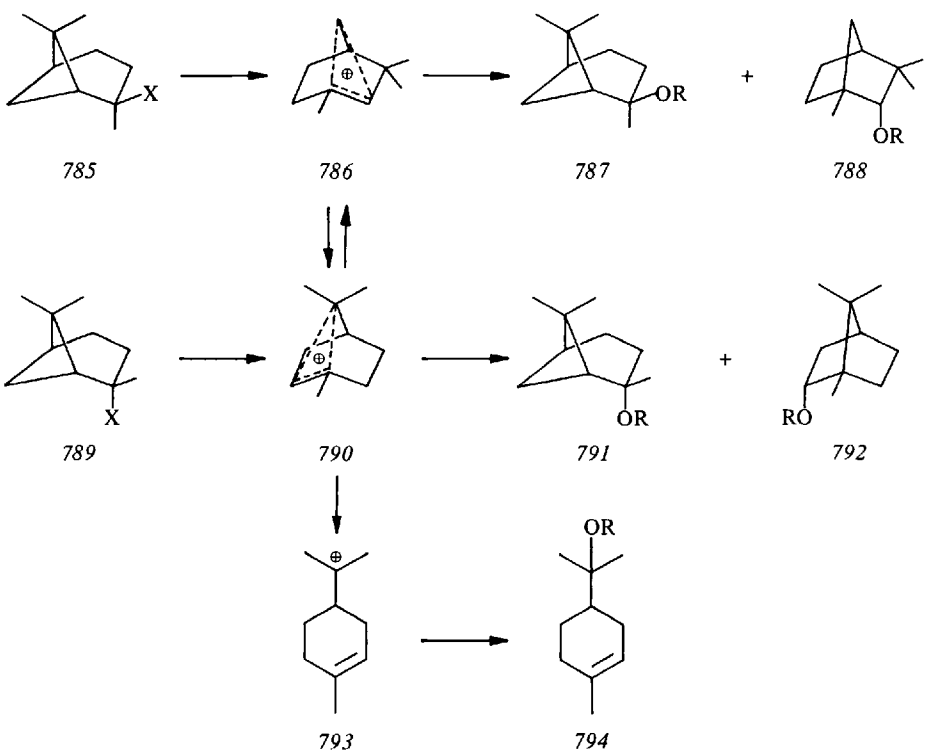
776	37	27	20	5	11%[534]
	37	22	25	4	12%[535]
777	37	10	37	6	9%[534]



782 X = $OH(OH_2^+)$
783 X = $NH_2(N_2^+)$

784 *780* *781*

782	59	4	26	11%[534]
	52	4	35	9%[535]
783	39	7	34	13%[535]



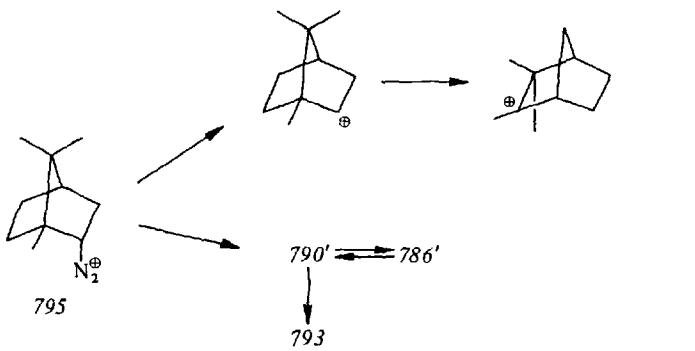
785 *786* *787* *788*

789 *790* *791* *792*

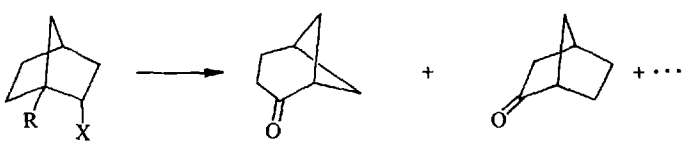
793 *794*

The norpinyl system returns to "normal" behavior on introduction of a stabilizing methyl group at C–2. Each of the 2-pinanol p-nitrobenzoates, (*785*) and (*789*), X=OPNB, produces mixtures of the epimeric 2-pinanyl derivatives (*787*) and (*791*) [536]. Substantial crossover between cations (*786*) and (*790*) occurs, probably by way of the open, tertiary 2-pinanyl cation. On the other hand, the fenchyl (*788*) and bornyl (*792*) products are exclusively *endo*[536,537], i.e., (*786*) and (*790*) do not rearrange to fenchyl and bornyl cations, respectively. Analogous results have been obtained in the acid-catalyzed rearrangement of the 2-pinanols (X=OH)[538,539] and in the Lewis-acid catalyzed rearrangement of the corresponding chlorides (X=Cl) [1,7] (see loc.cit.[540] for a review).

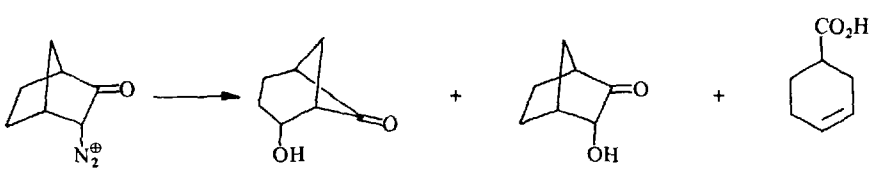
The enhanced stability of (*786*) is also indicated by the observation that some (*790'*) ⇄ (*786'*) is formed in the decomposition of *endo*-2-bornanediazonium ions



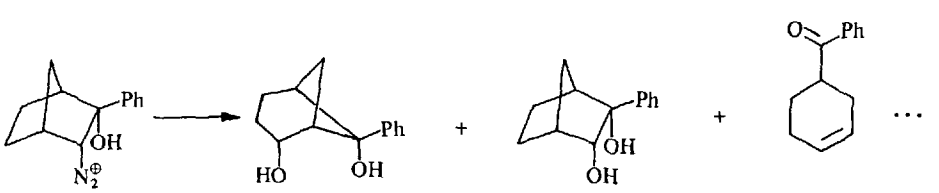
795



796 R = OCH_3, X = OTs
R = OH, OCH_3, NH_2, NHAc; X = N_2^+



797



798

(*795*)[541–543]. 2-Pinanyl derivatives, (*787'*) and (*791'*), were isolated only from alkaline deaminations[543] whereas products derived from the α-terpinyl cation (*793*) dominated under acidic conditions[541,542]. An analogous rearrangement does not occur with *endo*-2-norbornyl precursors, but can be enforced by electron-donating groups at C–1[544,545] or by destabilizing substituents at C–3[546,547]. Formulas (*796*)–(*798*) represent some examples.

The reactions discussed in this Section are difficult to explain without invoking bridged intermediates. The stereospecific rearrangement of the nopinols, (*776*) and (*782*), as well as formation of the highly strained norpinyl products from norbornyl precursors, would seem to require alkyl-assisted ionization.

7.6.2.7. Resumé. Alkyl participation in the solvolysis of *exo*-2-norbornyl derivatives is not unambiguously detected by rate measurements. Neither monocyclic analogs nor the corresponding *endo*-2-norbornyl compounds appear to be good models for comparison. Secondary deuterium kinetic isotope effects, however, point to distinct ionization mechanisms of *exo*- and *endo*-norbornyl derivatives.

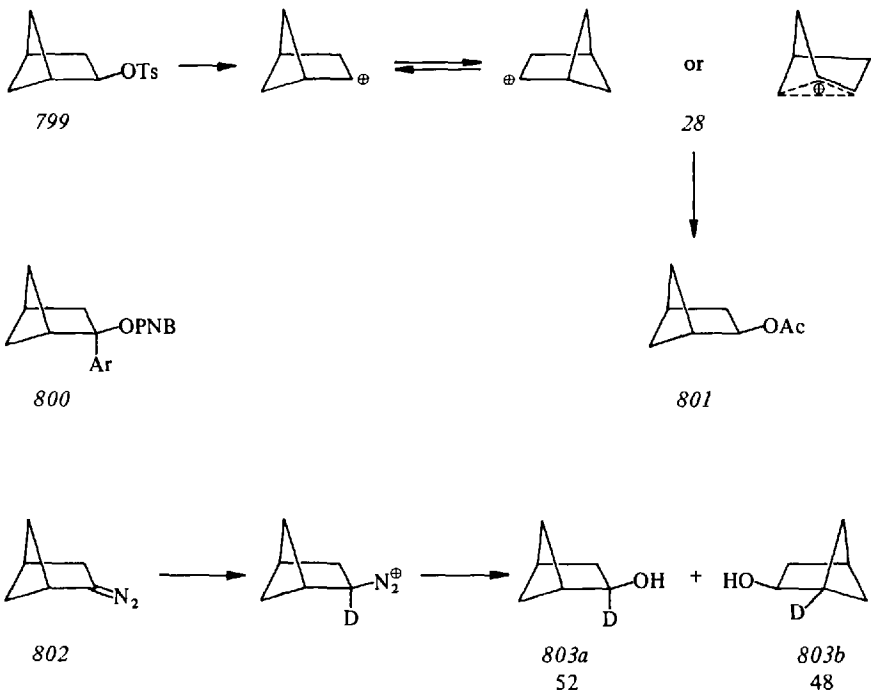
2-Norbornyl cations meet important criteria of bridging (stereochemistry, hydrogen shifts within the protonated cyclopropane). The significance of high *exo* : *endo* product ratios remains a matter of dispute. Model compounds designed for estimating such ratios in the absence of bridging have led to grossly divergent results. Whatever the final solution of this problem may be, bridging remains the most rational explanation of the dramatically different *exo* : *endo* product ratios from norbornyl and norpinyl precursors.

The energy difference between open and bridged 2-norbornyl cations is probably small[57]. Both intermediates may occur in succession, particularly if generated by strongly exothermal reactions. Capture of unsymmetrical 2-norbornyl cations in such reactions does not disprove the existence of the bridged, symmetrical species.

The rearrangements of the 2-norbornyl cation are unexceptional. All 1,2-alkyl shifts, even those in acyclic systems (Section 7.6.1) conform to essentially the same pattern. Individual differences exist in the rates of alkyl shift, relative to the rates of capture by solvent. In that respect the 2-norbornyl cation is superior to acyclic analogs because it can approach the geometry of corner-protonated nortricyclene with only small distortions of the nuclear positions. (A more sophisticated treatment in terms of relaxation theory has been published[548].) Other bicyclic and polycyclic systems provide similarly favorable conditions for 1,2-alkyl shifts. Some of them will be discussed in the following Sections.

7.6.3 Other Bicyclic and Polycyclic Systems

7.6.3.1 The 2-Bicyclo[2.1.1]hexyl Cation. The nature of the 2-bicyclo [2.1.1] hexyl cation (*28*) is of special interest in view of its relationship to the 2-norbornyl cation. MINDO/3 calculations indicate that the strain in (*28*) makes this an especially favorable case for σ delocalization[549]. ^{1}H– and ^{13}C–NMR reveal rapid degenerate rearrangements in superacid media which cannot be frozen out[60] (Section 3.1.3). 2-Bicyclo [2.1.1] hexyl tosylate (*799*) acetolyzes to give the corresponding acetate (*801*). Application of the Schleyer-Foote correlation (Section 7.2.1) assigns the



799 *28* *800* *801* *802* *803a* 52 *803b* 48

tosylate (799) an acceleration of *ca.* 800[550]. Application of the tool of increasing electron demand (Section 7.2.2) does not support the presence of strong σ participation: solvolysis of 2-aryl-2-bicyclo [2.1.1] hexyl p-nitrobenzoates (*800*) provides a value for ρ^+ of -4.31. Moreover, extrapolation of the data from (*800*) to the parent secondary tosylate fails to reveal a significant rate enhancement of (*799*)[551]. (See Section 7.6.2.1 for a critical evaluation of this method). The (*799*) → (*801*) transformation has apparently not been scrutinized for a degenerate rearragement, but the deuteriolysis of 2-diazobicyclo [2.1.1] hexane (*802*) leads to an approximately even distribution of deuterium between positions 1 and 2 of 2-bicyclo [2.1.1] hexanol (*803*)[552].

5,5-Dimethyl-2β-bicyclo [2.1.1] hexyl tosylate (*804*) solvolyzes with partial return to the isomeric tosylate (*808*) which is less reactive than (*804*)[553]. The products, (*805*)–(*807*) and (*809*), do not define the stereochemistry at the migration origin and reveal incomplete stereospecificity at the migration terminus – in contrast to the homolog (*782*). The 1,5,5-trimethyl compound (*810*) reacts 560 times faster than (*799*) to give predominantly the fragmentation product (*811*) and a trace of retained acetate (*812*)[554]. Surprisingly, no tertiary acetate (*813*) is found. The discrepancies between related bicyclo [2.1.1] hexyl and bicyclo [2.2.1] heptyl systems invite further studies.

7.6.3.2 Bicyclooctyl Cations. Solvolyses of *endo*-2-bicyclo[3.2.1]octyl tosylate (*73*)[555] and 4-cycloheptenylcarbinyl brosylate (*481*)[377,555] give similar product mixtures consisting primarily of *endo*-2-bicyclo [3.2.1] octanol or its acetate (*819*)

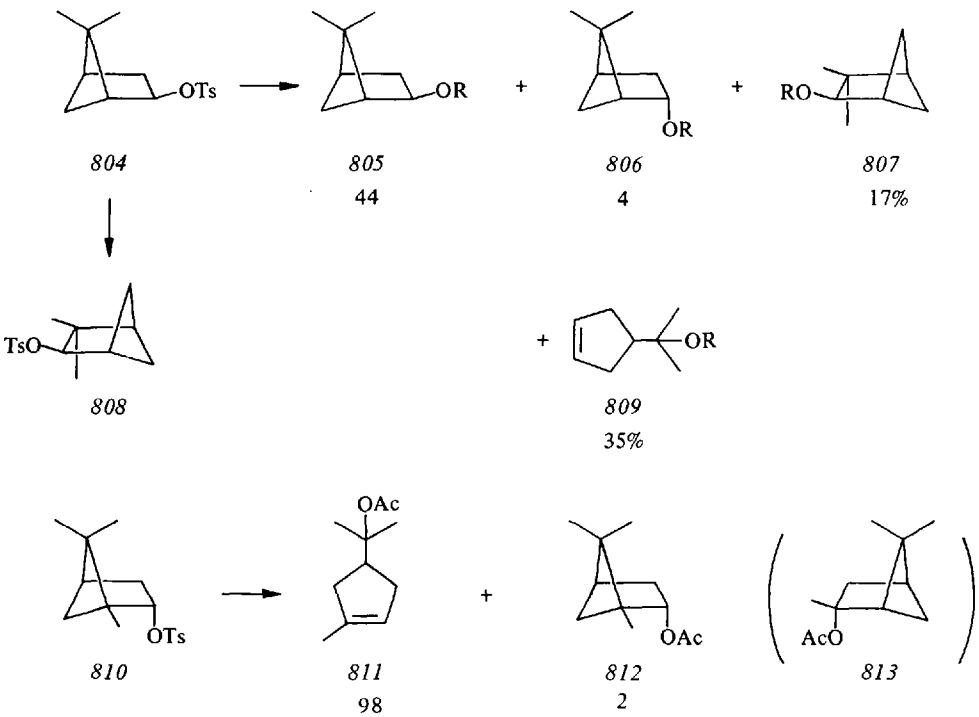
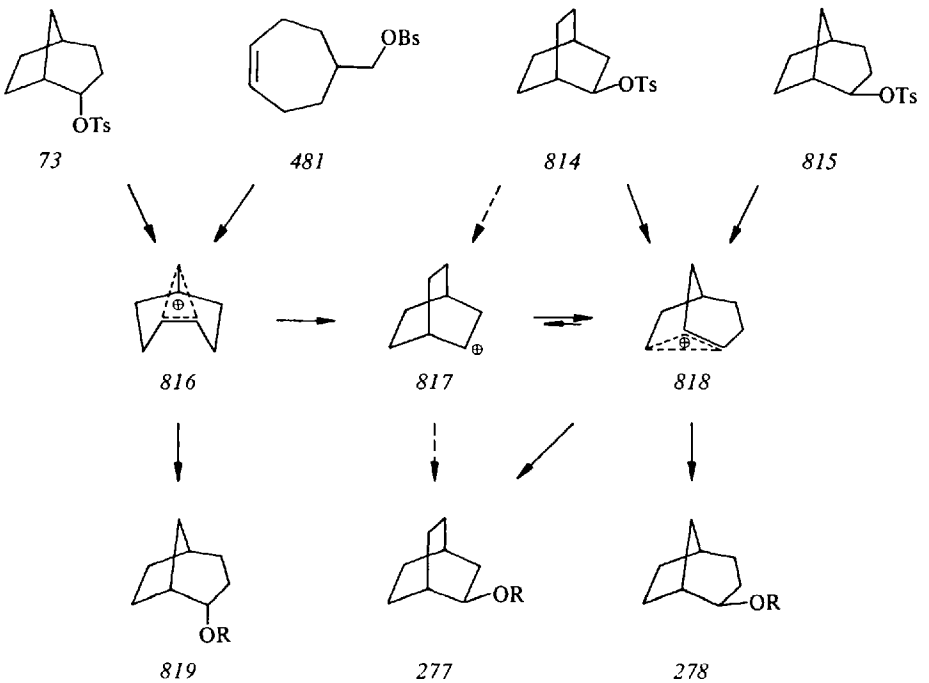


Table 18. Product distributions from the solvolysis of bicyclooctyl tosylates

Tosylate	(*819*)	(*277*)	(*278*)	(*823*)
	Acetolysis (R = Ac)			
(*73*)	89.4	4.0	6.6	–
(*481*)	93.6	3.0	3.4	–
(*814*)	0.4	53.4	46.2	–
(*815*)	0.6	53.9	45.5	–
(*820*)	–	44	40	16
(*822*)	–	21	19	60
	80% Acetone (R = H)			
(*73*)	94.9	1.0	4.1	–
(*481*)	97.5	1.1	1.4	–
(*814*)	–	57.2	42.8	–
(*815*)	–	56.7	43.3	–

(Table 18). The solvolyses of (*73*) are accompanied by ion pair return which leads to interconversion of the enantiomers of the unsolvolyzed ester[555] and to ^{18}O scrambling within the sulfonate group[87] (Section 4.2.2). Evidently (*73*) and (*481*) give rise to the same carbocation (*816*) by the σ and π routes, respectively. The minor amount of (*277*) and (*278*) in the product mixture is thought to result from isomer-



ization of (*816*) to (*818*). Solvolytic displacement on (*73*) or the ion pair may contribute to the formation of (*278*) from (*73*).

Solvolyses of 2-bicyclo [2.2.2] octyl tosylate (*814*) and *exo*-2-bicyclo [3.2.1] octyl tosylate (*815*) give mixtures of (*277*) and (*278*) having the same composition (Table 18)[555]. These results are compatible with the view that (*814*) and (*815*) give rise to the same bridged ion (*818*). The products derived from optically active tosylates, however, are partially racemic[555]. In all cases the [2.2.2] isomer (*277*) is less

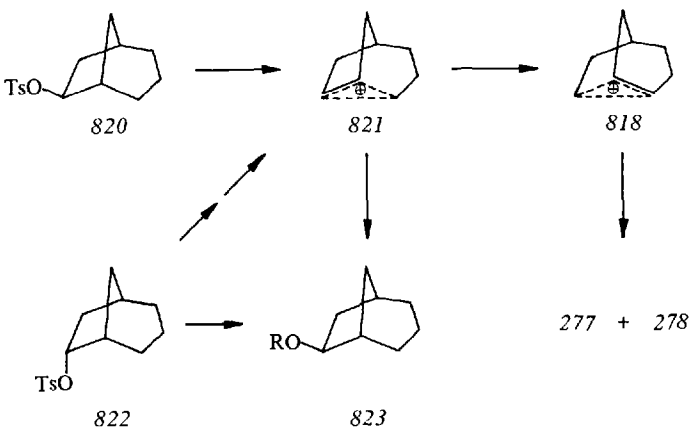
Table 19. Optical purities of solvolysis products derived from optically active tosylates (*814*) and (*815*)

Tosylate	(*277*)	(*278*)
	Acetolysis (R = Ac), 49 °C	
(*814*)	47(53)[1])	63(72)
(*815*)	52(59)	68(77)
	80% Acetone (R = H), 49 °C	
(*814*)	73(78)	87(93)
(*815*)	78(83)	88(94)

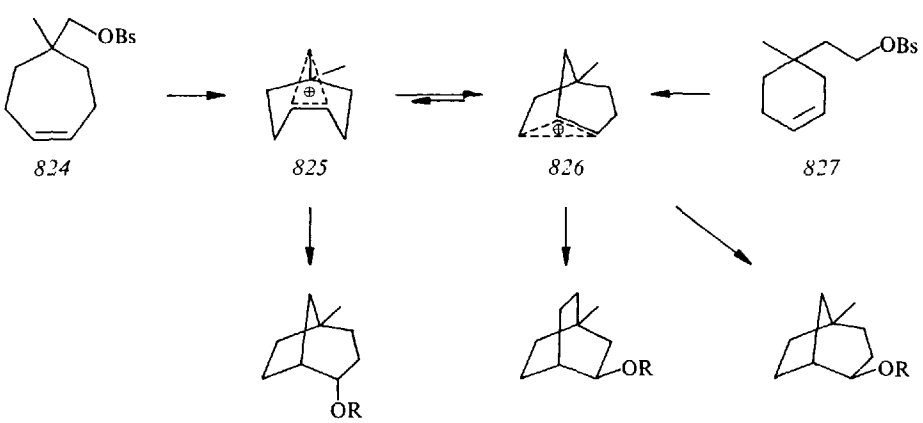
[1]) The first value is relative to the initial optical purity of the substrate and the value in parentheses is relative to the average optical purity of the substrate (i.e. corrected for ion pair return).

optically pure than the *exo*-[3.2.1] isomer (*278*) (Table 19). Acetolysis gives products of lower optical purity than solvolysis in 80% acetone. The partial loss of configuration is thought to result from a reversible opening of the bridged ion (*818*) to the achiral bicyclo [2.2.2] octyl cation (*817*). The latter intermediate would also explain the excess racemic (*277*) in the product. 6,2–H shifts, converting (*818*) to its enantiomer, have not been investigated with tosylates (*814*) and (*815*). There is evidence, however, that 6,2–H shifts are not involved in the ring expansion route to the bicyclooctyl system[228] (Section 6.4.).

Hydrogen shifts do occur in the solvolysis of *exo*- and *endo*-6-bicyclo [3.2.1] octyl tosylates, (*820*) and (*822*)[556]. Both substrates produce *exo*-6-bicyclo [3.2.1]



octyl acetate (*823*) and substantial amounts of (*277*) and (*278*) (Table 18). The different ratios of (*823*):(*277*) + (*278*) may be attributed to solvolytic displacement on (*822*) or the corresponding ion pair. The solvolytic behavior of (*820*) and (*822*) resembles that of the epimeric 2-norbornyl brosylates except that the 6,2–H shift is nondegenerate.



824	83	6	5%
827	1	55	41%

The 5-methyl derivatives of (*816*) and (*818*) have been generated by the π route from (*824*) and (*827*), respectively[557]. The results are very similar to those of the parent system. Again, there is more leakage from (*825*) to (*826*) than in the reverse direction.

7.6.3.3 Bicyclononyl Cations. The exploration of the bicyclononyl system is far from complete, but some interesting results have been reported (Table 20). Ionization of 2-bicyclo [3.2.2] nonyl derivatives (*828*) is associated with a degenerate Wagner-Meerwein rearrangement although full equivalence of C–1 and C–2 is not achieved[552]. A deuterium label, initially at C–2, is distributed between C–2 and C–1 in a 1.5:1 ratio. The cation (*830*) (or its "classical" equivalent) undergoes extensive 6,2–H shift to give (*831*)[552,558]. The reaction of (*831*) with nucleophiles yields predominantly (*833*), only minor amounts of (*829*) being obtained. The virtually stereospecific reaction of (*831*), whether generated from (*828*) or from (*829*)[559], indicates little leakage to the open ions (*832*) and (*835*).

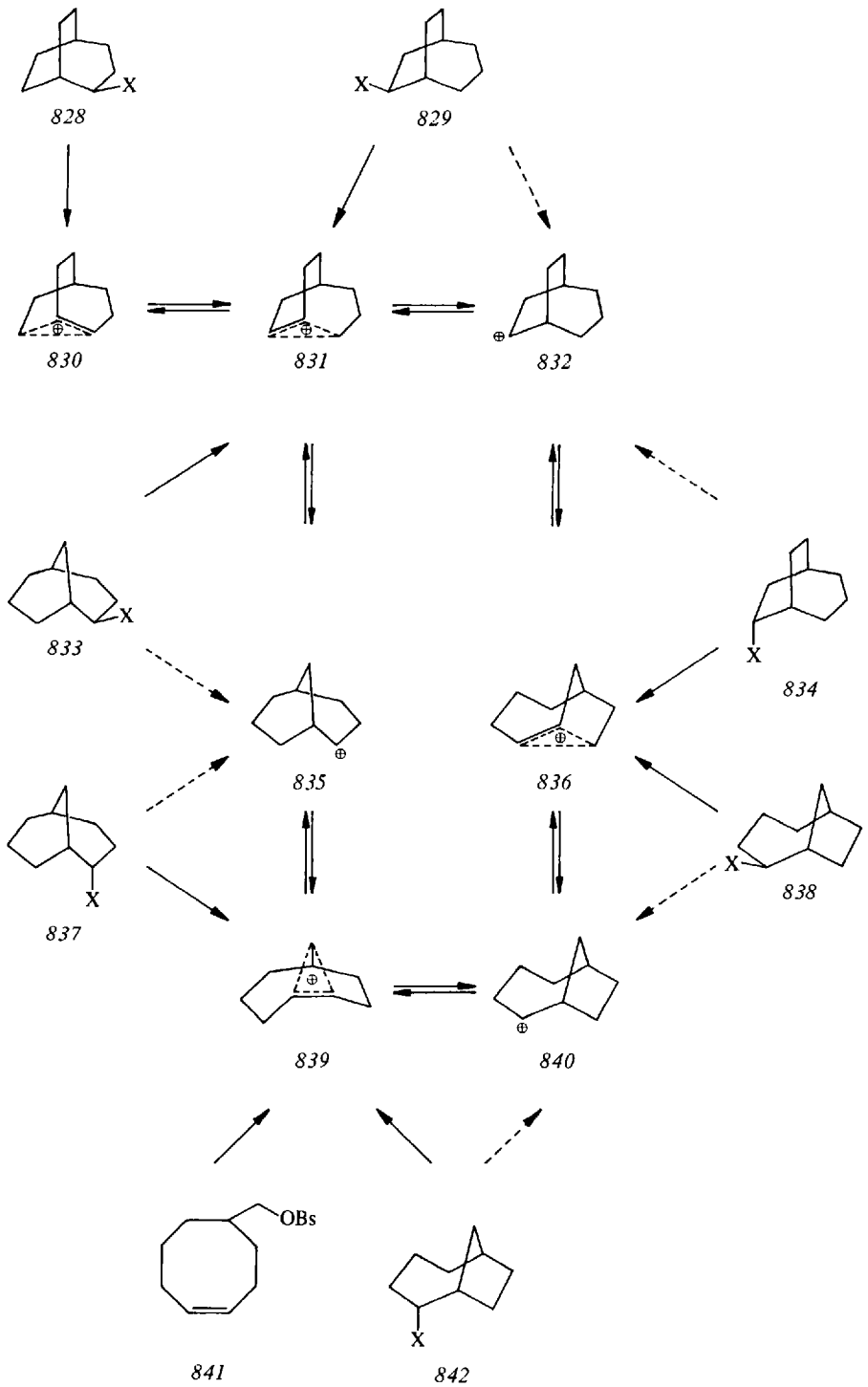
Some crossover is observed in the opposite direction, (*839*) → (*831*). The solvolyses of both *endo*-2-bicyclo [3.3.1] nonyl tosylate (*837*)[560] and 4-cyclooctenylcarbinyl brosylate (*841*)[560,561] give significant amounts of *exo*-2-bicyclo [3.3.1] nonyl products (*833*). These results parallel those in the bicyclooctyl series (Section 7.6.3.2.). An equilibrating mixture of (*838*) and (*842*), X=N_2^+, generates (*836*) and (*839*) in comparable quantities[552]. (*836*) produces *exo*-2-bicyclo [4.2.1] nonanol (*838*), X=OH, in strong preference to *endo*-6-bicyclo [3.2.2] nonanol (*834*). The stereochemistry is consistent with the dominance of bridged over localized ions; the preferred formation of (*833*) and (*837*), whenever possible, reflects the small strain energy of bicyclo [3.3.1] nonane[562,563].

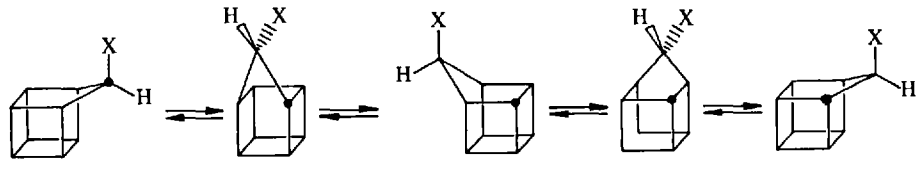
7.6.3.4 Homocubyl and Bishomocubyl Cations. The 9-homocubyl cation (*844*) is of interest because of its potential degeneracy. A label at C–9 will be scrambled around only one five-membered ring of (*843*) in an anchimerically assisted process involving bridged ions. A nonstereospecific reaction path, involving the open ion (*844*), would allow distribution of the label to all nine carbons. Such complete degeneracy appears to prevail in the formolysis of 9-homocubyl tosylate[564]. On the other hand,

Table 20. Products from bicyclononyl cations[1])

Substrate	Products X	(*828*)	(*829*)	(*834*)	(*833*)	(*837*)	(*838*)	(*842*)
(*828*)-OTs	OAc	32	3	–	50	1	–	–
(*828*)-N_2^+	OH	50	3	–	44	0.5	–	–
(*829*)-N_2^+	OH	–	28	–	72	–	–	–
(*834*)-N_2^+	OH	–	–	–	–	–	97	–
(*837*)-OTs	OH	–	–	–	16	78	16	
(*841*)-OTs	OAc	–	–	–	6	82	11	
(*838*) + (*842*) $-N_2^+$	OH	–	–	3	1	51	41	4

[1]) Products arising from vicinal H shifts and unidentified products have been omitted.


X
828
X
829
830
831
832
X
833
X
834
835
836
X
837
X
838
839
840
OBs
841
X
842



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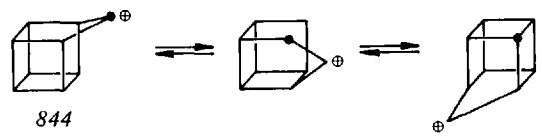
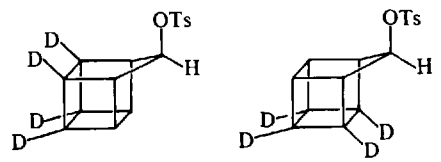
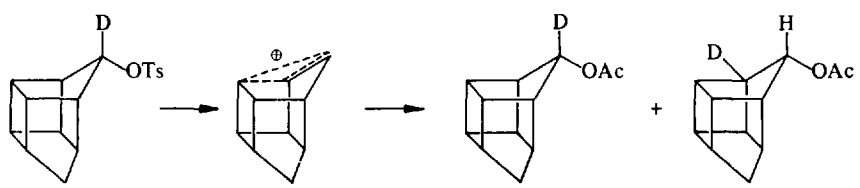


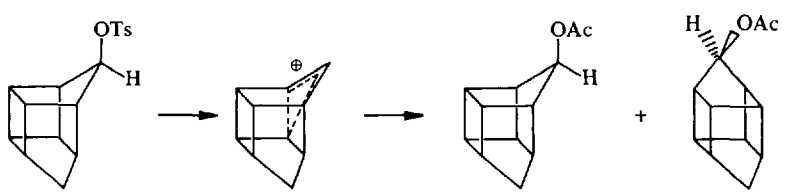
844



845a *845b*

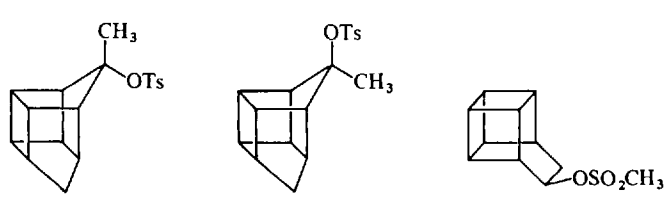


846 *847* *848a* *848b*



849 *850* *851* *852*

15 85



853 *854* *855*

the acetolyses of (*845a*) and (*845b*) proceed by a stereospecific mechanism[565]. The acetate formed from (*845a*) showed twice as much deuterium at C–9 as the acetate formed from an equimolar mixture of (*845a*) and (*845b*). Obviously, no deuterium is distributed to C–9 in the solvolysis of (*845b*); the open ion (*844*) does not intervene.

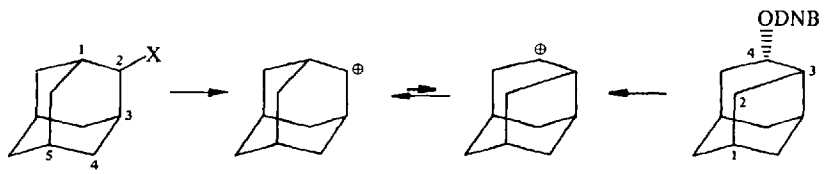
The bishomocubyl systems (*846*) and (*849*) have also been studied. Solvolysis of the *syn* tosylate (*846*) gives almost exclusively the *syn* acetate (*848*)[566], but with 50:50 scrambling of a deuterium label[567]. Acetolysis of the *anti* tosylate (*849*) gives mainly the rearranged acetate (*852*) accompanied by 15% of the unrearranged acetate (*851*). The simplest and most consistent explanation for the stereochemical results is the intermediacy of the bridged ions (*847*) and (*850*), respectively. In contrast to the secondary systems, the tertiary tosylates (*853*) and (*854*) give approximately the same mixture of *syn* and *anti* products[568]. The nearly equal acetate distribution from the isomeric tosylates (*853*) and (*854*) indicates that no inherent steric or strain effect is present in this system which could account for the high degree of stereospecificity observed with the secondary tosylates (*846*) and (*849*).

Sequential rearrangements have been observed in the acetolysis of 1'-bishomocubyl methanesulfonate (*855*) which produce, inter alia, acetates (*848*), (*851*), and (*852*)[569]. 61% of (*855*) undergo rearrangement with internal return to slower solvolyzing mesylates. The stereochemistry of the internal-returned mesylates suggests ionization to bridged-ion pairs, followed by frontside collapse.

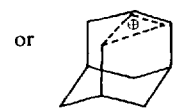
7.6.3.5 Adamantyl and Homoadamantyl Cations. The 2-adamantyl system is exceptional among *sec*-alkyl substrates since it solvolyzes without nucleophilic solvent participation (Section 7.2.1). The extent of anchimeric assistance is more difficult to evaluate. Some evidence is consistent with a weakly bridged intermediate:
(i) the formation of a small amount of 4-*exo*-protoadamantyl products (*863*) (0.4% from the tosylate (*856*)[570,571], 4% from the diazonium ion (*857*)[570], but no detectable amount of the *endo* epimer (*868*);
(ii) the predominant (64 to 84%) retention of configuration during solvolysis of the two 5-methyladamantyl derivatives (*864*) and (*865*)[572]. 4-*exo*-Protoadamantyl 3,5-dinitrobenzoate (*860*) rearranges readily to give 2-adamantyl products[571]. Starting with 4–D–(*860*), the label is found exclusively at C–1 of (*862*). In contrast, 4-*endo*-protoadamantyl tosylate (*866*) produces 4-*endo*-protoadamantyl as well as 2-adamantyl derivatives[571]. The distribution of a deuterium label shows that a degenerate protoadamantyl rearrangement precedes leakage to the adamantyl system.

Obviously the epimeric 4-protoadamantyl precursors, (*860*) and (*866*), do not react by way of a common 4-protoadamantyl cation (*859*). Assisted ionization with rearrangement, leading directly to the 2-adamantyl cation (*858*), would explain the enhanced reactivity of (*860*) (*exo* : *endo* = 10^4). Even if the intermediate is bridged, the bridging should be weak and it must be unsymmetrical. The carbon skeleton of (*858*) is much more stable than that of (*859*); any tendency of the 2-adamantyl cation to bridge must be offset, at least in part, by an increase in ring strain. The obvious way to improve this situation is to stabilize (*859*), or to destabilize (*858*).

Alkyl substituents at C–1 of 2-adamantyl tosylate greatly increase the yield of 4-*exo*-protoadamantyl solvolysis products[573]. 1-Methyl-2-adamantyl tosylate (*869*) and 4-methyl-4-*exo*-protoadamantyl dinitrobenzoate (*871*) give approximately the

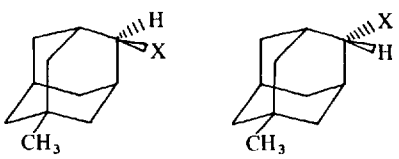


856 X = OTs *858* *859* *860*
857 X = N_2^+

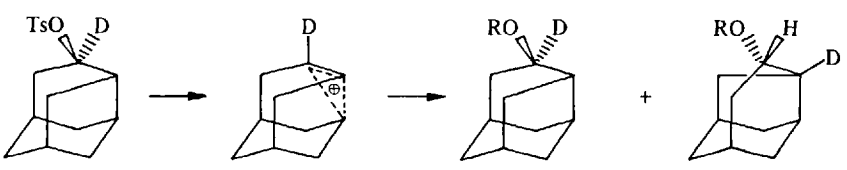


861

862 *863*



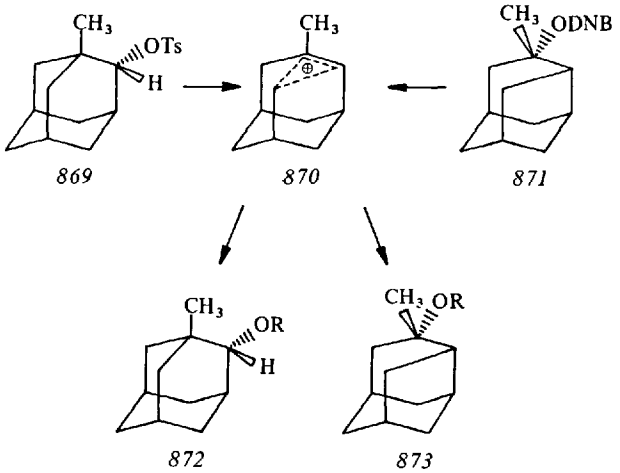
864 *865*

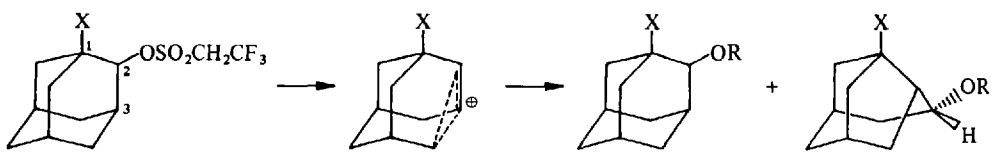


866 *867* *868a* *868b*

858 or *861*

same mixture of (*872*) and (*873*) (*ca.* 2.7.:1)[574]. Moreover, the solvolysis of optically active (*869*) in 50% aqueous acetone proceeds with 90% retention of configuration[575]. The solvolysis rate enhancement produced by successive methyl substitution along the tosylate series, 2-adamantyl (1.0), 1-methyl-2-adamantyl (14–21), 1,3-dimethyl-2-adamantyl (38–70) is approximately additive rather than multiplicative [576]. The data suggest that σ delocalization accounts for the observed behavior, and that ionization of (*869*) and (*871*) leads directly to a common bridged ion (*870*).



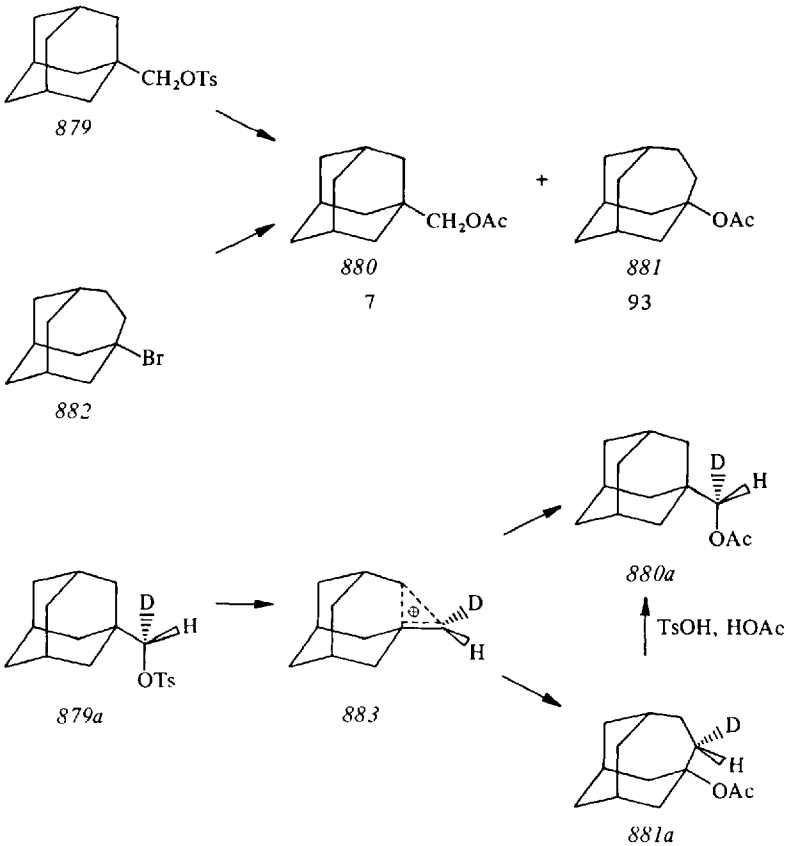


874 X = CO_2CH_3
875 X = CN

876 *877* *878*

1-Methoxycarbonyl-2-adamantyl tresylate (*874*) affords 6% of the protoadamantyl derivative (*878*) although its rate of solvolysis is only $8 \cdot 10^{-3}$ relative to 2-adamantyl tresylate[577]. An even stronger effect was observed with the 1-cyano compound (*875*):38% of (*878*), relative rate $4.2 \cdot 10^{-5}$. In these cases delocalization is enhanced by inductive destabilization of the 2-adamantyl cation. The apparent absence of a rate-product correlation is not a valid argument against bridging[577]. No rate-product correlation is to be expected unless solvent assistance (k_S) competes against anchimeric assistance (k_Δ)[575]. In the 2-adamantyl system solvent assistance is not possible because of the crowding involved (Section 7.2.1).

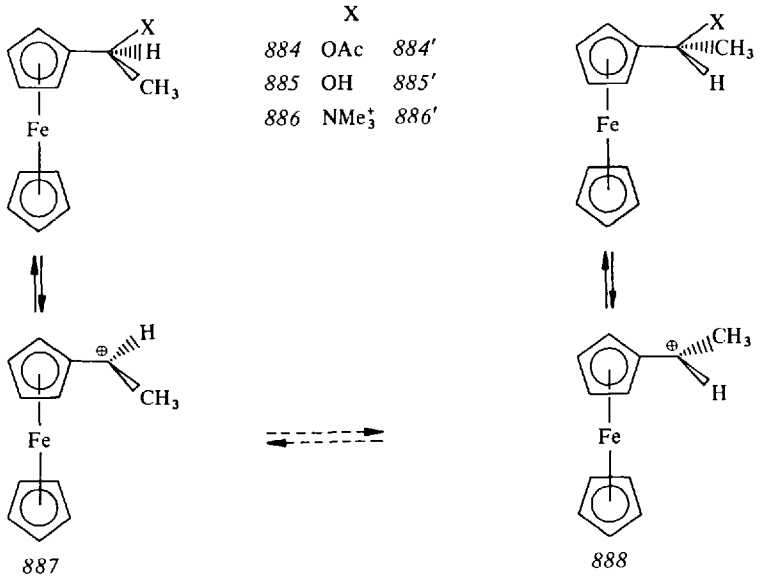
1-Adamantylcarbinyl and 3-homoadamantyl systems are interconvertible. Acetolysis of both 1-adamantylcarbinyl tosylate (*879*) and 3-homoadamantyl bromide (*882*) give the same mixture of acetates (*880*) and (*881*) by kinetic control[578]. Catalytic amounts of toluenesulfonic acid in acetic acid rearrange (*881*) to the thermodynamically more stable (*880*). Thus, in the 1-adamantylcarbinyl→3-homoadamantyl transformation, increasing stabilization of positive charge is offset by increasing ring strain. This situation provides a chance for bridging which is absent in acyclic neopentyl systems. Acetolysis of the chiral tosylate (*879a*) affords acetate (*880a*) with complete retention of configuration[579]. The major acetolysis product (*881a*) produces exclusively (*880a*) on acid-catalyzed isomerization. The conservation of optical integrity strongly implicates the bridged ion (*883*) as the intermediate in these reactions.

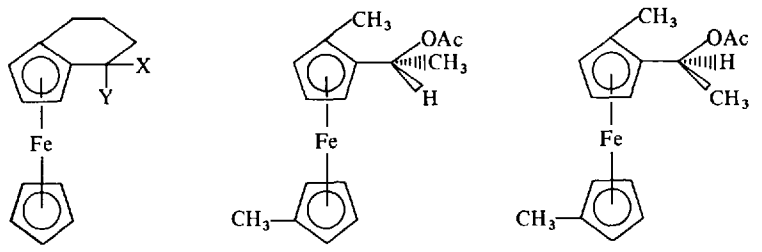


7.7 Metal Participation

7.7.1 π-Complexed Organometal Systems[580]

During the development of the chemistry of ferrocene, it soon became apparent that the ferrocenyl group possesses a remarkable electron-releasing capacity[581]. 1-Ferrocenylethyl acetate (*884*) solvolyzes in 80% acetone 6–7 times faster than triphenylmethyl acetate[582]. The analogous derivatives of ruthenocene and osmocene undergo solvolysis even more rapidly; the relative rates are Fe:Ru:Os = 1:1.36:5.37[583]. *Exo*- and *endo*-α-acetoxy-1,2-tetramethyleneferrocene, (*889*) and (*890*), respectively, produce the same *exo*-alcohol (*891*), but (*889*) reacts $2 \cdot 10^3$ times faster than (*890*)[584]. Hydrolysis of the diastereomeric acetates (*892*) and (*893*) proceeds by an S_N1 mechanism with complete retention of configuration[584]. The trimethylammonium group of optically active (*886*) is replaced by various nucleophiles without any loss of stereochemical integrity[585]. When the enantiomeric alcohols (*885*) and (*885'*) are dissolved in acidic solvents (e.g., trifluoroacetic acid, 60% aqueous H_2SO_4), optically active solutions of the cations (*887*) and (*888*), respectively, are produced[586]. From the rates of racemization the activation energy of rotation around the exocy-



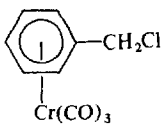


	X	Y
889	OAc	H
890	H	OAc
891	OH	H

clic bond was estimated, E_a=21.2 kcal/mol. The barrier to rotation for a tertiary ferrocenylalkylium ion is lower (ca. 16 kcal/mol) but still sufficient to allow preferential *exo* protonation of alkenylferrocenes in trifluoroacetic acid, followed by preferential *exo*-deprotonation on reaction with base[587].

Analogous results have been obtained with other carbocyclic and acyclic metal complexes attached to a carbocation. Benzyl chloridechromium tricarbonyl (*894*) solvolyzes by an S_N1 mechanism, 10^5 times faster than does benzyl chloride itself[588]. The solvolysis of chloromethylcyclobutadiene-iron tricarbonyl (*895*) is accelerated by a factor of 10^8, relative to benzyl chloride[589]. In the dinitrobenzoate esters of the diastereomeric *trans, trans*-4-methyl-3,5-heptadien-2-ol-iron tricarbonyls, (*896*) and (*897*), the departure of the leaving group is *exo* to the iron atom and the products exhibit retention of the original configuration[590].

The electronic interaction resulting in the observed stability and stereospecificity is still a matter of controversy. One proposal is direct metal participation, involving a



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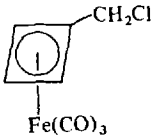

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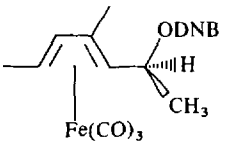

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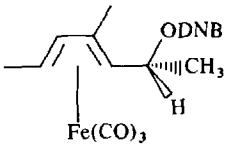

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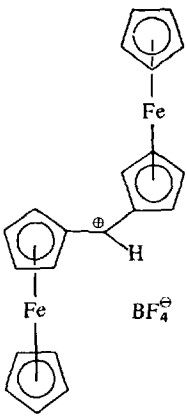

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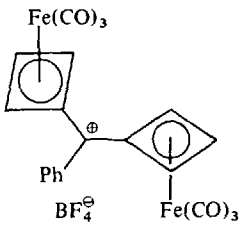
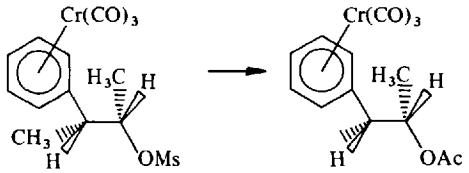


899

(partial) metal-C_{exo}bond[581,584,591,592]. Other authors advocate electron donation from the metal to the cationic center by a hyperconjugative mechanism[593,594]. The X-ray structural data of *bis*-ferrocenylcarbenium fluoroborate (*898*) reveal that the exocyclic carbon is displaced from each of the cyclopentadienyl planes toward one of the iron atoms by ca. 20°. However, the iron-exocyclic carbon distance is still large (2.78 Å) and not indicative of strong interaction[595]. In the phenyl-*bis*-cyclobutadienyl-iron tricarbonyl carbenium ion (*899*) the exocyclic carbon lies very nearly in the plane of each cyclobutadiene ring[589]. The structural data do not fully resolve the problem of anchimeric *vs.* hyperconjugative effects.

An important question has yet to be answered: are π-complexed organometal systems capable of controlling the stereochemistry of 1,2 shifts ? The π-(arene) chromium tricarbonyl complexes of *threo*- and *erythro*-3-phenyl-2-butyl mesylates, (*900*) and (*901*), and of *erythro*-2-phenyl-3-pentyl mesylate (*902*) have been aceto-



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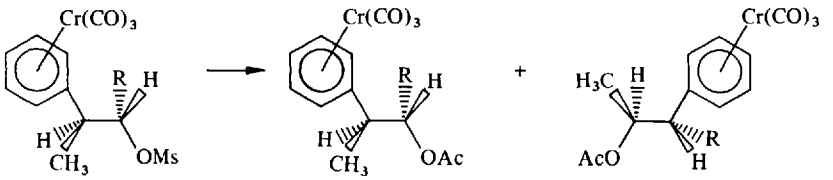


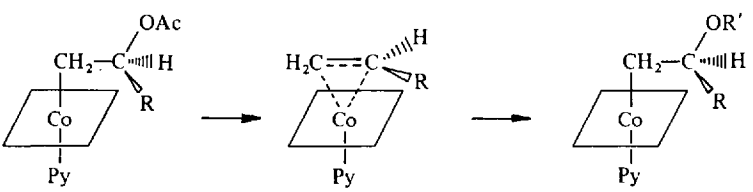
901 R = CH_3 15 1

902 R = C_2H_5

lyzed and the products compared with those of the noncomplexed compounds[596]. π-Complexation prevents racemization but also inhibits phenyl and hydrogen migration. Thus, the ratio of unrearranged to rearranged *erythro* acetate from (*902*) is 15 whereas it is 0.9 with the uncomplexed compound. Further studies on 1,2 shifts in the side chain of π-complexed organometal systems are clearly desirable.

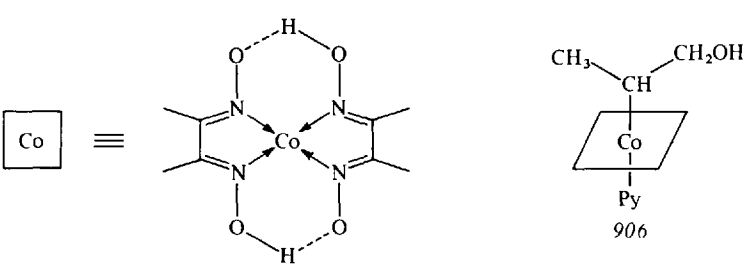
7.7.2 σ-Bonded Organometal Systems

The alcoholysis of 2-acetoxyalkyl (pyridine) cobaloximes (*903*) gives the corresponding ethers (*905*) (R′=CH_3, C_2H_5, CH_2Ph) with remarkable ease[597]. The reactions



903 *904* *905*

a: R = H; *b*: R = CH_3; *c*: R = OR″



906

follow first order kinetics at a rate comparable to the rate of solvolysis of trityl acetate. Solvolysis of the chiral acetate (*903b*) proceeds with complete retention of configuration[598]. Deuterium[598] or ^{13}C labels[599] in the β position of (*903a*) are equally distributed between C–1 and C–2 of (*905a*). The intermediate in these reactions can be envisaged as an olefinic π-complex of cobalt (*904*). Further evidence for olefin π complexes of trivalent cobalt comes from the reaction of cobaloximes and vinyl ethers which gives the corresponding σ-bonded cobalt acetals (*905c*)[599]. β-Hydroxy-isopropyl (pyridine) cobaloxime (*906*) rearranges to (*905b*), R'=H, under acid conditions[600]. Pinacolic rearrangements[601] as well as 1,2 shifts of alkoxycarbonyl[602,603] and alkylthiocarbonyl groups[604] have been observed in the course of photochemical or thermal detachment of ligands from cobaloximes and cobalamines. These studies provide nonenzymic models for Vitamin B_{12} which is an obligatory cofactor in at least three carbon-skeleton rearrangement reactions[605,606]. Extension of the models to include the stereochemistry of metal-mediated 1,2 shifts is being pursued.

8 Epilogue

The coverage of this review has been restricted to those rearrangements of carbocations which may be classified as [1,2] sigmatropic shifts. Sigmatropic rearrangements of higher order as well as electrocyclic reactions have been excluded[607]. The 1,2 shifts of vinylic cations have also been omitted[320,608–611]. Those aspects of mechanism have been exphasized which are relevant to stereochemistry. The approach has been empirical, with only occasional reference to the molecular orbital theory of carbocations[612–614]. Although quantum mechanical methods have provided a wealth of otherwise inaccessible structural information, most of the results refer to the gas phase. Only recently have solvent effects on carbocations been studied theorectically[615]. A brief discussion of the ethyl cation, one of the simplest systems, will illustrate the present status of molecular orbital calculations.

Much effort has been expanded on studies of the relative stabilities of the open and bridged forms of the ethyl cation[613]. *Ab initio* investigations with the 4–31 G basis set predict the classical ion to be more stable by 7.3 kcal/mol[616]. When d functions are added to the basis set and p-type polarization functions on hydrogen are included (6–31 G**), the bridged ion becomes more stable than the open structure by 6.3 kcal/mol[613,617]. When correlation corrections are also considered, the bridged structure is favored by 9 kcal/mol[618]. MINDO/3 predicts a similar energy difference (8.5 kcal/mol)[619]. The relative energies of the most stable structures of the ethyl cation in the presence of one or two molecules of hydrogen chloride have been explored as models for solvation, using MINDO/3 and perturbation theory calculations[615]. In both cases classical structures are now preferred to the lowest energy bridged ones by roughly 14 kcal/mol. This result is in accord with qualitative expectation: solvation should stabilize a localized charge more effectively than a delocalized one.

Even smaller energy differences between open and bridged ions have been calculated for more complex cations in the gas phase. In the particular case of the 1-propyl cation for example the energy difference between the extended-chain and methyl-bridged formulations is computed to be 0.7 kcal/mol (4–31 G level)[620]. Recent extensive studies on the 2-norbornyl system indicate that the energy difference for the classical and nonclassical formulations is <0.2 kcal/mol[57b]. If solvation stabilizes the classical ions to the same extent as was reported for the ethyl cation, all bridged structures in solution may be dismissed on theoretical grounds.

This conclusion stands in stark contrast to the view emerging from experimental studies. Although external factors, such as ion pairing or micellar aggregation, influence the stereochemistry of carbocation rearrangements, they are insufficient to explain the majority of the stereochemical data. At present, bridged ions are indispensable to account for inversion at the origin of 1,2 shifts. Simple resonance theory is remarkably successful in predicting the intervention of bridged ions: the open resonance structures must be comparably rich in energy. Stabilization by alkyl groups may be offset by ring strain. If the concept of σ delocalization should ever be abandoned, some type of 1,3-nonbonded carbon-carbon interaction[621] must take its place.

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