Long-Range Interactions of Cyclopropyl Groups with Carbonium Ion Centers

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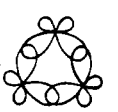
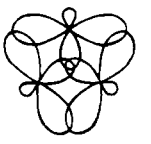
I. Introduction

The last 10–15 years have seen tremendous advances in our understanding of small ring compounds. At the center of this activity have been numerous studies of the chemical, physical, and spectroscopic properties of the smallest carbocycle, cyclopropane, and its derivatives. It has been known for some time that cyclopropanes resemble olefins much more closely than they do their higher cycloalkane homologs. This fact is difficult to explain in terms of classical bonding ideas but has been rationalized, with the support of theoretical studies, by assuming that the C–C bonds of the cyclopropyl ring have a much higher p character than do normal C–C single bonds. A consequence of this rehybridization is the widely accepted idea that the C–C bonds of cyclopropane rings are bent into so-called "banana bonds" (the Coulson–Moffitt model, **1a**), the maximum electron density of which are in the annular plane about 0.3 Å outward from the center of the line joining the two bonded atoms.[1] An alternative description (the Walsh model, **1b**), shown to be equivalent to **1a**,[1] predicts electron density in the center of the ring. The bonding in cyclopropanes and the analogies between them and double bonds have been reviewed.[1-3] More recent theoretical work has also appeared.[4]



1a



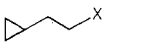
1b

One of the classic properties of double bonds is their interaction with adjacent carbonium ion centers observed in the ionization of allyl derivatives to form resonance-stabilized allylic cations.[5] It was later found that the stabilization afforded a carbonium ion by a double bond is not restricted to adjacent centers; thus long-range stabilizing interactions can occur with the formation of homoallylic cations.[6] More recently it was found that cyclopropylcarbinyl derivatives ionize to form cyclopropylcarbinyl cations which are stabilized by incorporation of the "banana bonds" of the three-membered ring into the resonance hybrid.[7] Considering the above-cited similarities between cyclopropyl compounds and olefins, it was a natural development to examine the possibility of long-range interaction between cyclopropyl groups and distant carbonium ion centers.

One can envisage such interactions occurring in two distinct phases along a reaction pathway. In the first instance, the three-membered ring can act as a neighboring group and participate in the formation of the carbonium ion. Such participation (anchimeric assistance) is usually characterized by an enhanced rate of ionization. Alternatively, a cyclopropyl group can interact with a carbonium ion which has already been formed; however, such interaction does not affect the rate of ionization but may, as in the case of cyclopropyl participation, lead to rearranged products. Neighboring group participation has been discussed in more detail elsewhere.[6b,8]

Although there are numerous pertinent reviews which discuss topics of vital interest to the present article, this review is the first devoted entirely to this subject. It covers the literature to the end of 1972 and also includes many of the important papers which were published in 1973. It attempts to correlate the numerous reports that have appeared, to discuss the somewhat divergent results that have been obtained, and to stimulate further research into this fascinating area of physical organic chemistry. In order to avoid as much as possible overlap with other reviews,[9] the present article will not stress carbonium ion structure but will instead examine a variety of systems for cyclopropyl interactions and examine the various factors which are responsible for the presence or absence of interactions. It will also briefly explore the cognate areas of interactions between carbonium ions and other small

TABLE I. Relative First-Order Rates for the Formolysis of a Series of Sulfonate Esters

Ester	Relative rate: Obsd[a]	Obsd[b]	Calcd[c]	Calcd[d]	Ref
C_2H_5X	1.00	1.00[e]			12, 15, 23
n-C_3H_7X		0.67[f]			22, 24
n-C_4H_9X		0.55			25
$(CH_3)_2CHCH_2CH_2X$	0.85				13
$CH_2{=}CHCH_2CH_2X$		2.03			25
	0.93				12, 15
	3.24		(3.24)	(3.24)	15
	1.33		(1.33)	(1.33)	15
	3.64		5.55	11.2	15
	2.56		1.73	1.90	15
	3.12		3.64	4.63	12, 15

[a] Data on brosylates in buffered formic acid at 75.0°. [b] Data on tosylates in unbuffered formic acid at 50.3°. [c] Assuming an additive relationship for increasing methyl substitution. [d] Assuming a multiplicative relationship. [e] Extrapolated from data obtained at higher temperatures. [f] Relative rate obtained in buffered formic acid at 75.0°.

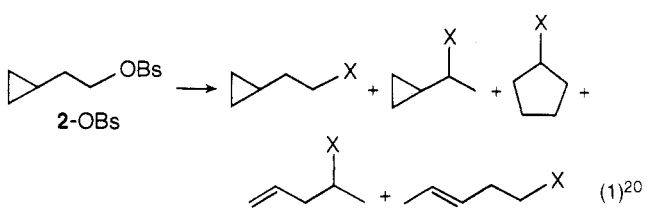
rings and interactions between cyclopropane rings and other electron-deficient centers.

II. Studies on Specific Systems

A. Conformationally Mobile Molecules

1. 2-Cyclopropylethyl and Related Systems

Despite the simplicity of the 2-cyclopropylethyl system, long-range interactions in this series have been the subject of surprisingly few investigations.[10-17] The earlier work on the parent system showed that extensive rearrangement occurs during carbonium ion reactions (eq 1);[10,11] more recent kinetic studies[12-14] demonstrated that the cyclopropyl group provides little more acceleration to ionization than that provided by simple alkyl groups (Tables I and II),[18] an observation that was unexpected in view of the spectacular kinetic accelerations by cyclopropyl groups in the solvolysis of some rigid polycyclic derivatives (*vide infra*) and the theoretical studies[19] which predict a large delocalization energy for homocyclopropylcarbinyl cations.



2-OBs (1)[20]

In contrast to the formolysis behavior of simple alkyl brosylates,[21-25] methyl substitution in the three-membered ring of **2** enhances the ionization rate by a small but significant amount (Table I). Based on this fact and supported by the extensive formation of rearranged products, Dewar and Harris[12,15] concluded that the cyclopropyl group of **2**-OBs, and of its methyl substituted analogs, does indeed participate in the ionization step. Since primary carbonium ions are relatively unstable, any ionization which is not assisted intramolecularly should occur with SN2 solvent assistance and lead to unrearranged products. From an analysis of their rate data according to the method of Schleyer and Van Dine,[26] Dewar and Harris concluded that the transition state of the ionization reaction is best represented as the π-complex **3** rather than **4**. The data given in Table I, however, show no

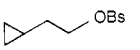
3 **4**

clear-cut distinction between an "additive" and a "multiplicative" effect of increased methyl substitution, so it would appear that this conclusion was premature. Dewar and Harris tried unconvincingly to rationalize this inconsistency in terms of concomitant SN2 processes with similar rates for the relevant substituted esters.

On the other hand, Rhodes and Takino[13] concluded that cyclopropyl participation is absent in the ionization of **2**-OBs since this ester and its open-chain analog, 3-methyl-1-butyl brosylate, demonstrate parallel kinetic behavior upon changing solvent (acetic acid, 95% ethanol, and formic acid), indicating similar transition states for the ionization of both molecules. They proposed that this transition state involves a high degree of solvent assistance and little intramolecular assistance, citing the formation of large amounts (>75%) of unrearranged, kinetically controlled product in the formolysis of **2**-OBs to support their argument.

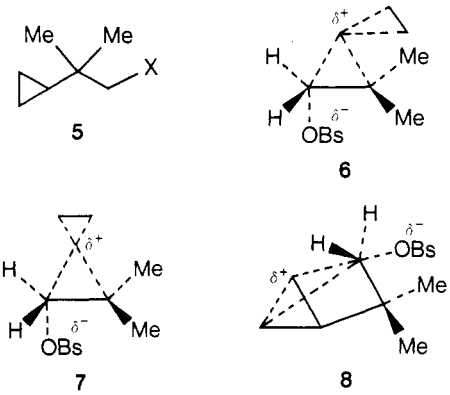
There are numerous solvolytic pathways open to 2-cyclopropylethyl derivatives (*e.g.*, cyclopropyl participation

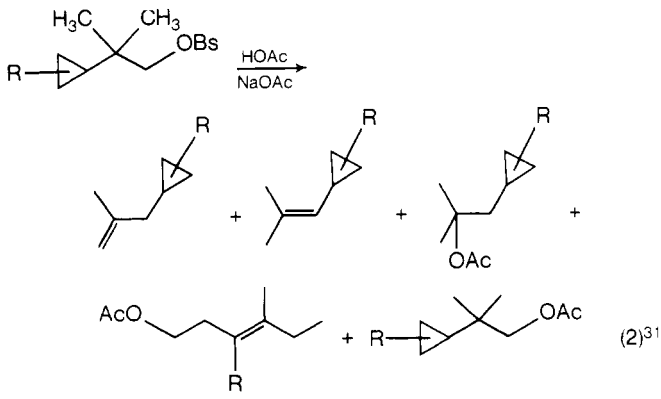
TABLE II. Relative Acetolysis Rates for a Series of Sterically Hindered Brosylates of the General Formula $RC(CH_3)_2CH_2CH_2OBs$ at 80°

R	Relative rate: Obsd	Calcd[a]	Calcd[b]	Notes
CH_3	0.03			c, d
C_2H_5	0.05			c, d
i-C_3H_7	0.13			c, d
$CH_2{=}CH-$	4.6			c, e
C_6H_5	4.8			c, f
	1.0			g
	5.7	(5.7)	(5.7)	g
	3.2	(3.2)	(3.2)	g
	0.41			g
	10.7	5.4	10.2	g
	19.1	7.9	18.2	g
	0.12			c, h

[a] Assuming an additive relationship for increasing methyl substitution. [b] Assuming a multiplicative relationship. [c] Extrapolated. [d] E. N. McElrath, R. M. Fritz, C. Brown, C. Y. LeGall, and R. B. Duke, *J. Org. Chem.*, **25**, 2195 (1960). [e] R. S. Bly and R. T. Swindell, *ibid.*, **30**, 10 (1965). [f] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2763 (1956). [g] Reference 17. [h] Reference 13.

through various transition states, migration, and participation by solvent) which may compete effectively with each other and thus render a simple kinetic analysis impossible. Solvent assistance has been greatly reduced, if not totally eliminated, by the introduction of two methyl groups at C-2 to give the neopentyl system **5** which ionizes at a much enhanced rate with distinct participation by the cyclopropyl group (Table II).[14,17] Methyl substitution on the cyclopropane ring of **5** results in rate increases which clearly follow a multiplicative relationship requiring a symmetrical transition state involving bridging to both remote carbon atoms of the three-membered ring. Three such states, **6**, **7**, and **8**, have been considered.[17] Solvolysis of the methyl derivatives of **5** (eq 2) gives varying amounts of elimination and substitution products, both rearranged and unrearranged. No definitive experimental test has yet been applied to distinguish between **6**, **7**, and **8**, but **8** seems less likely than the other two both on steric grounds[17] and because it is difficult to explain the formation of cyclopropyl migration products (eq 2) through such a transition state and the most likely cation resulting from it.[17] The higher migratory aptitude of the cyclopropyl group relative to a methyl group in **5** has analogy in numerous other studies of anionotropic cyclopropyl migration.[16,27-30]





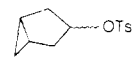
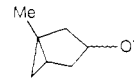
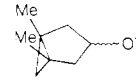
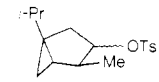
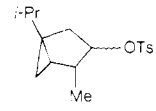
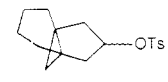
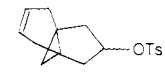
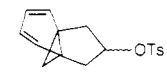
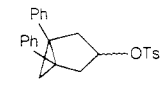
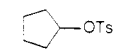
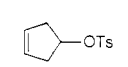
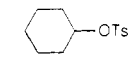
(2)[31]

2. *Bicyclo[3.1.0]hex-3-yl and Related Systems*

Historically, the bicyclo[3.1.0]hex-3-yl system was the first in which remote cyclopropyl participation in carbonium ion formation was studied, and it remains to date the most thoroughly investigated one. It has been included in several review articles.[6a,9b,32]

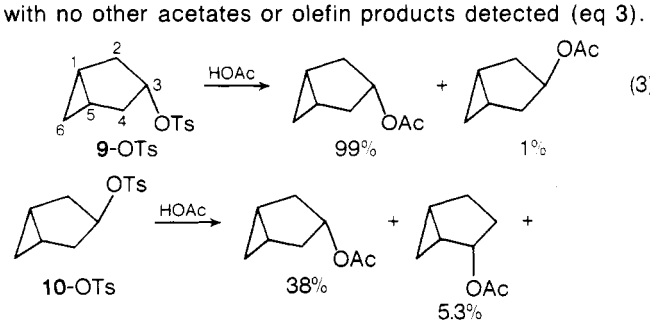
Upon acetolysis, formolysis, or hydrolysis, *cis*-bicyclo[3.1.0]hex-3-yl tosylate (**9**-OTs) ionizes faster than either its trans epimer (**10**-OTs) or suitable model compounds such as cyclopentyl, cyclopenten-4-yl, or cyclohexyl tosylates (Table III).[32-34] The ionization of **9**-OTs is characterized by a less negative activation volume than that of

TABLE III. Relative Acetolysis Rates for Some Bicyclo[3.1.0]hex-3-yl and Related Tolylates[a]

Tosylate	Relative rate[b] Cis	Trans	Cis/trans	Notes
	15	1	15	*c, d*
	78	0.87	90	*c, d*
	105	0.88	120	*c*
	96	0.30	325	*c*
	142	0.15	920	*c*
	575			*c*
	106			*c*
	595			*c*
	3.21	0.50	6.4	*e*
	16.9			*f*
	2.1			*g*
	0.46			*h*

[a] Buffered acetic acid at 25°. [b] Calculated from observed titrimetric rate constants. [c] Calculated from data in ref 39. [d] When the rate constants are adjusted to account for internal return, a somewhat higher value of cis/trans is obtained; see ref 32. Such an adjustment is necessary only with the cis tosylates. [e] Calculated from data given in ref 45. [f] Calculated from data given in ref 33. [g] Calculated from a comparison with cyclopentyl tosylate at 50° given in ref 33. [h] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2780 (1956).

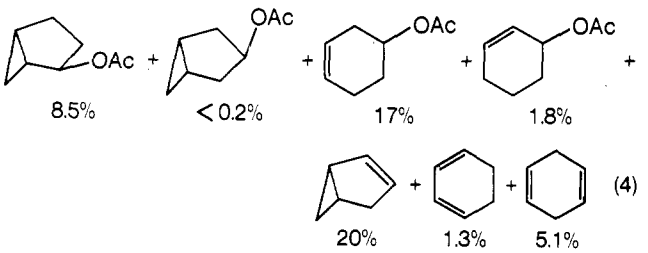
10-OTs,[35] is accompanied by a special salt effect,[36] and gives rise to recovered starting material with a deuterium label initially on C-6 equilibrated equally to positions 2, 4, and 6.[32] The acetolysis products from **9**-OTs consist of virtually pure **9**-OAc contaminated by about 1% **10**-OAc with no other acetates or olefin products detected (eq 3).



(3)

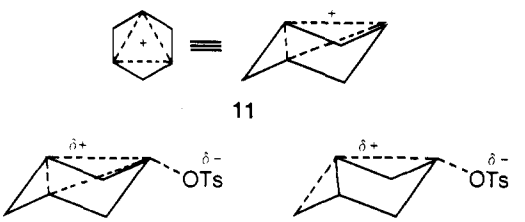
A deuterium label initially on C-1 or on C-6 is completely scrambled over positions 1, 3, and 5 or 2, 4, and 6, re-

spectively, in the acetate product. In contrast, the trans tosylate **10**-OTs shows no special salt effect and no deuterium scrambling in either recovered starting material or acetate product. The product mixture from acetolysis of **10**-OTs is very complex with **9**-OAc the major component but with at least five other acetates and three olefins also formed (eq 4).[32]



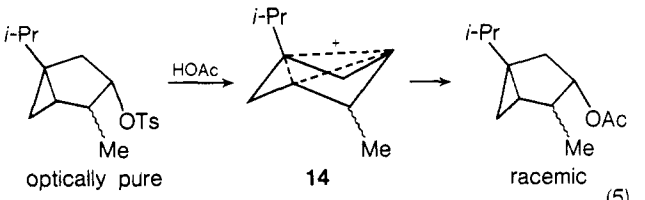
(4)

These observations can be interpreted only in terms of the cis isomer (**9**) ionizing with participation by the three-membered ring to form the relatively stable[37] symmetrical, nonclassical trishomocyclopropenyl cation **11** (ref 6a, 9a,b, 32, 34, 38). The transition state for ionization presumably resembles **12** rather than **13.** The trans tosylate **10**-OTs reacts without cyclopropyl participation to give classical ion intermediates and/or by SN2 attack by solvent;[9b,32-34] leakage to **11** apparently does not occur.

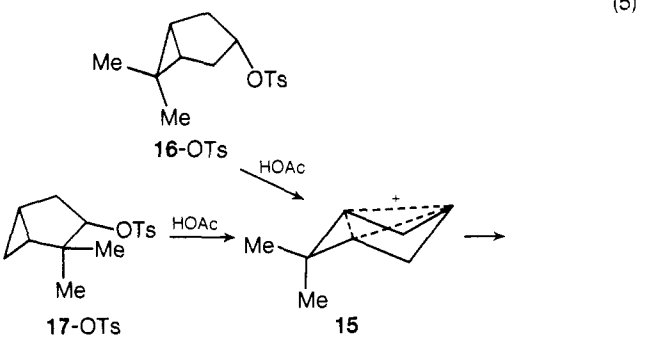


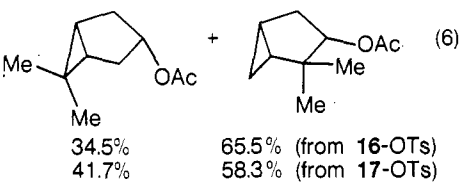
The available data on the solvolysis of alkyl substituted bicyclo[3.1.0]hex-3-yl derivatives[9b,39-44] generally corroborate the conclusions reached for the ionization of the more simple parents. The kinetic data (Table III) show not only that the cis isomers are more reactive than the trans, but also that alkyl substitution in the cyclopropane ring has a much greater accelerating effect on the ionization of the cis epimers, indicative of a stabilizing cyclopropane interaction in the transition state of the ionization step for only the cis derivatives. An analysis of these data using Schleyer and Van Dine's method[26] is complicated by the effects of the substituents on conformational free energy.[39] The products from solvolysis of the cis epimers are predominantly those resulting from attack by solvent in varying proportions at the three available cis sites of the intermediate(s) (*e.g.*, eq 5[40] and 6[41]). Other products are formed in minor amounts; acetic acid gives more complex mixtures than aqueous acetone.[39] The most widely accepted interpretation of these results is ionization of the cis isomers with cyclopropyl participation to form substituted trishomocyclopropenyl cations which then react stereospecifically with solvent to give the products shown; some leakage of these cations to other, possibly classical, cations is evident from the acetolysis products cited above. This scheme is not without difficulty, however; the failure of solvent to attack ions **14** at the tertiary center[40,42] (this is the overwhelming position of attack in the simple methyl-substituted cases[39]) and the dependence of the product ratio from **15** on starting material[41,43] have yet to be explained.

The reaction of some *cis*-bicyclo[3.1.0]hex-3-yl tosylates with azide ion has provided an alternative source of cations **14** and **15.**[42,43]



(5)

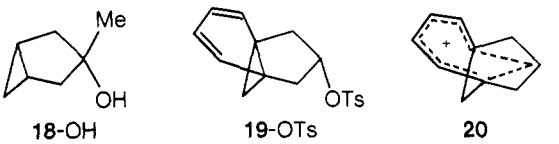




(6)

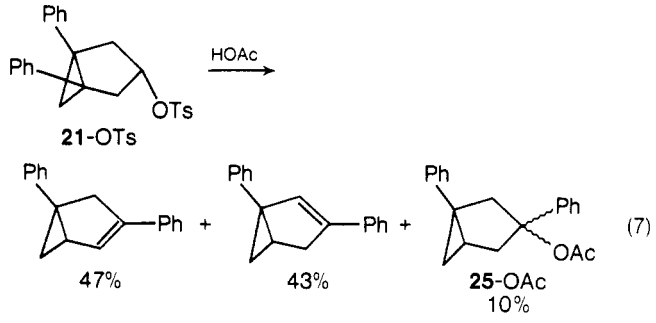
An exception to this general behavior is the trichloroacetate of **18**-OH which ionizes, apparently without cyclopropyl participation, to give products quite unlike its 1-methyl isomer.[39]

Delocalization of charge in the ion derived from **19**-OTs is presumably more extensive than in a simple trishomocyclopropenyl cation since the rate retardation due to a single double bond in this ring system is absent (Table III). The intermediate is presumably the bishomotropylium ion **20.**[39]



The trans epimers, like their unsubstituted parent, react quite differently from the cis isomers.[9b,39-44] Upon acetolysis complex mixtures of products including rearranged acetates and olefins are formed by ionization without cyclopropyl participation to give classical ion intermediates which rearrange, eliminate, or react with solvent more rapidly than leakage to nonclassical trishomocyclopropenyl cations can occur. Treatment of the trans tosylates with azide ion gives complete inversion[42,43] probably by SN2 displacement although classical cations have also been proposed for this reaction.[43] The trans epimer of **17**-OTs does not react with azide[43] presumably for steric reasons.

Corey and Uda[45] felt that phenyl substitution at C-1 and C-5 should stabilize a trishomocyclopropenyl cation relative to either the starting tosylate **21**-OTs or, more pertinently, the classical 1,5-diphenylbicyclo[3.1.0]hex-3-yl cation by analogy to the resonance stabilization afforded by the phenyl groups in diphenylcyclopropenyl cation.[46] On the basis of this expectation, one would predict an enhanced ionization rate for **21**-OTs; however, as is seen from the data in Table III, Corey and Uda observed that the ionization of **21**-OTs proceeds at a slower rate than does its unsubstituted parent and leads to a complex product mixture (eq 7) quite unlike that obtained from the alkyl-substituted cis esters. Corey and Uda concluded that a trishomocyclopropenyl cation is not



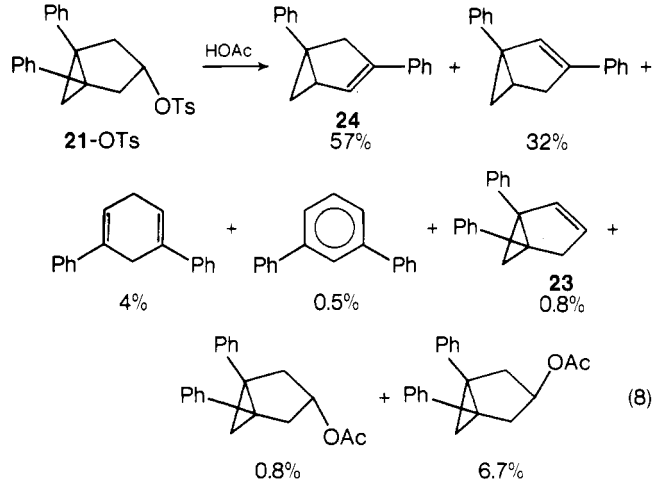
(7)

formed in this ionization, and, by inference, in other similar reactions, and proposed instead a rapidly equilibrating set of "almost nonclassical" classical ions (**22**) in which the positive center interacts weakly with the cyclopropane ring.

22

Corey and Uda's proposal has come under heavy criticism. Winstein, *et al.*,[32] felt that the phenyl group is a treacherous probe for detecting positive charge development at a carbon atom because of the complex blend of steric, inductive, and conjugative effects associated with it. Indeed theoretical considerations of the trishomocyclopropenyl cation[39,47] predict that the saturated nature of the atoms of **11** preclude resonance interactions with substituents, and, since the phenyl group is known to be inductively electron withdrawing,[48] one might expect a net deceleration in the ionization rate of **21**-OTs by as much as a factor of 100[49] although a smaller value may be more appropriate.[45] On the basis of extended Hückel calculations, ion **11** is predicted[37,39] to be more stable than either the ions **22** or a classical bicyclo[3.1.0]hex-3-yl cation.

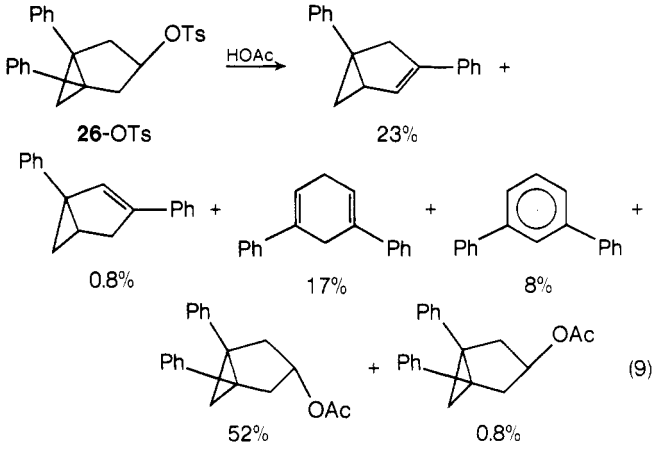
Lin[39] found that the ionization rate of **10**-OTs is much less retarded by phenyl substitution than is **9**-OTs but that a moderate cis/trans ratio still exists (Table III). Because the inductive effect of a remote phenyl group should be about the same for a cis or trans ester, this result is in accord with cyclopropyl participation in the ionization step. In his study of **21**-OTs, Lin observed a product mixture (eq 8) similar to that observed by Corey and



(8)

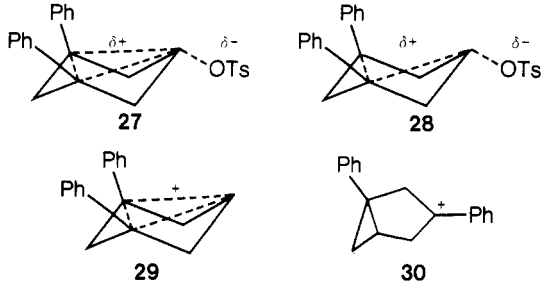
Uda. Pertinently, he observed minor amounts of hydrocarbons not reported by the previous workers, one of which, **23**, rearranges efficiently to **24** under the reaction conditions.[39,45] He also observed minor amounts of **21**-OAc but could not find the tertiary acetate **25**-OAc reported, but possibly incorrectly identified,[39] by Corey and Uda.

In contrast to the behavior of **21**-OTs, the trans epimer **26**-OTs acetolyzes to give a much higher proportion of acetate product primarily of inverted stereochemistry, presumably by SN2 displacement, and quite different proportions of the hydrocarbon products.

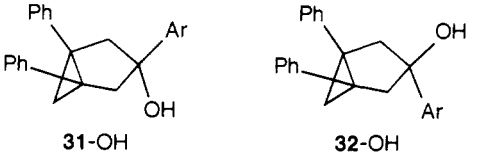


(9)

It is thus evident that **21**-OTs and **26**-OTs do not solvolyze through common intermediates. Because the stereochemistry of **21** is correct for cyclopropyl participation, because of the small amounts of isolated products with retained ring structure, and from the kinetic behavior relative to **26**-OTs, Lin felt that cyclopropyl participation is a feature of **21**-OTs ionization. Whether the ionization proceeds through a symmetrical transition state (**27**) or an unsymmetrical one (**28**) to give ions **29** or **30**, respectively, is not yet clear. No support for Corey and Uda's proposal was found.



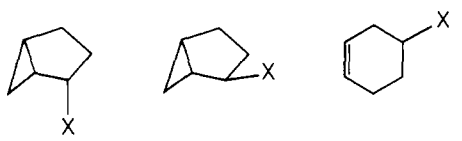
In a related study, Broser and Rahn[50] treated **31**-OH with acids and generated relatively long-lived cations whose ir, visible, and nmr spectra are in full accord with trishomocyclopropenyl structures and from which the starting alcohol could be regenerated. The generation of these cations was very solvent dependent, failing in relatively nonpolar solvents but quite successful in polar media. According to these workers the stabilizing effect of the aryl substituents on the trishomocyclopropenyl cations allows their formation from either **31**-OH or its epimer **32**-OH and is in sharp contrast to the solvolytic work discussed above (particularly on **21**-OTs) and to Corey and Uda's[45] failure to detect stable cations when they



Ar = C_6H_5, *p*-MeC_6H_4, *p*-$C_6H_5C_6H_4$, β-$C_{10}H_7$, *p*-$MeOC_6H_4$, *p*-$Me_2NC_6H_4$

treated **31**-OH with acids in a variety of polar and nonpolar solvents.

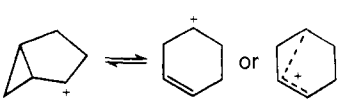
Corey and Dawson[51] deaminated the *cis*- and *trans*-bicyclo[3.1.0]hex-3-yl amines, **9**-NH_2 and **10**-NH_2, and obtained from both epimers mixtures of derivatives of **9, 10, 33,** and **34** in which a deuterium label originally on C-3 was not scrambled to C-1 or C-5. These products are very similar to the solvolytic products from **10**-OTs and are best interpreted as dissociation of both **9**-N_2^+ and **10**-N_2^+ to give classical carbonium ions.[32,51] Rearrangement and solvolytic capture of these classical ions are much more efficient than leakage to the nonclassical **11.** The absence of cyclopropyl participation in this case is not unexpected in view of the information available on deaminations.[52]



33 **34** **35**

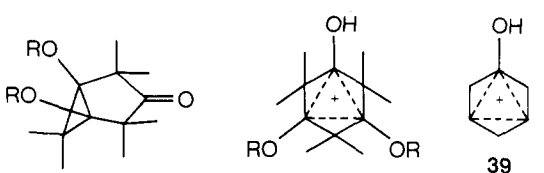
The epimeric bicyclo[3.1.0]hex-3-yl carboxylic acids (**9**-COOH and **10**-COOH) have been found[53] to undergo electrolytic oxidative decarboxylation to give predominantly the rearranged alcohols **33**-OH and **34**-OH along with minor amounts of **9**-OH and **10**-OH and the two corresponding ketones. It is evident from these data and from the fact that a deuterium atom at C-6 is unscrambled in the reaction that an ion like **11** is not an intermediate in this reaction and that cyclopropyl participation is therefore absent; however, electrode reactions are not well understood.

Similar conclusions were reached from electrophilic additions to bicyclo[3.1.0]hex-2-enes. Acid-catalyzed addition[54] of methanol, acetic acid, or hydrogen chloride to the parent olefin results in the exclusive formation of derivatives of **33, 34,** and **35.** Similar results were obtained by Banthorpe and Davies[44,55] in the treatment of 1-isopropyl-4-methylbicyclo[3.1.0]hex-3-ene with aqueous or ethereal acids. These results are not surprising in view of the reactions discussed above and related solvolytic data[56] that indicate clearly that the bicyclo[3.1.0]hex-2-yl cation, **36,** of the cyclopropylcarbinyl type is much more stable than the trishomocyclopropenyl cation, **11,** of the homocyclopropylcarbinyl type and will form in preference to it despite the aromatic stabilization afforded the symmetrical ion **11** (ref 6a, 9b, 32–34, 37, 38). It is equally clear that leakage between the classical and nonclassical ions is relatively inefficient.



36

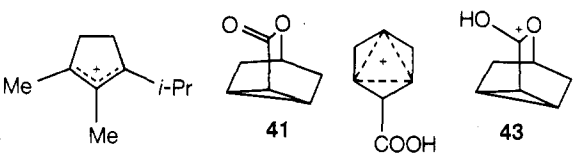
Priddy and Reusch[57] and Curphey and McCartney[58] both studied the reversible protonation of derivatives of **37** with a view to forming **38;** however, even at −60° in "superacid" medium no evidence for this nonclassical ion was found in the nmr spectrum. Protonated bicyclo[3.1.0]hexan-3-one similarly gives no evidence[39] for delocalization of the positive charge on the carbonyl group into the three-membered ring to form **39.**



37 **38** **39**

Treatment of 1,4-cyclohexadiene with a mixture of proton and Lewis acids or reaction of **35**-Br with silver salts produces a cation of formula $C_6H_9^+$ whose nmr spectrum shows only two peaks in the ratio of 1:2.[59] It was originally thought[59a] that the intermediate was **11,** but further considerations[39,59b] discredit this view. The structure of $C_6H_9^+$ remains obscure.

In a later study Olah and Lukas[60] attempted to generate **11** by abstraction of hydride from bicyclo[3.1.0]hexane by treatment with a "superacid." They were unsuccessful in their attempt, observing instead formation of the tertiary 1-methylcyclopentyl cation by protonation and cleavage of the three-membered ring. An analogous process was observed by Lin[39] upon dissolution of **9**-OH, **9**-OTs, or their methyl-substituted derivatives in "superacid" and also by Forsen and Norin;[61] dissolution of the four isomeric thujyl tosylates in 96% sulfuric acid led in each case to ion **40.**



40 **41** **42** **43**

Sauers[62] obtained an ion upon dissolution of lactone **41** in sulfuric acid to which he assigned the nonclassical structure **42.** Deno[9c] and Lin,[39] on the other hand, felt that the nmr spectrum of this ion is more consistent with the delocalized structure **43.**

It is thus evident that, although there is irrefutable evidence for trishomocyclopropenyl cations in solvolysis of some bicyclo[3.1.0]hexyl derivatives, these ions have low-energy pathways open to them which preclude their direct observation. Indeed, in some cases[53,60] such intermediates appear to be bypassed completely.

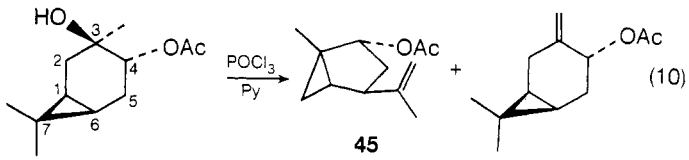
Cyclopropyl participation in bicyclo[4.1.0]hept-3-yl derivatives[62a] has been studied much less frequently despite the widespread occurrence of the carane skeleton. From the dehydration products of **44** and similar compounds, Kropp[63] concluded that only in the isomer **44,** in which the cyclopropyl group and OH substituents are cis to each other, does cyclopropyl participation occur. The formation of **45** in this reaction (eq 10) was the first example of the rearrangement of a carane skeleton into another bicyclic one and was postulated to occur *via* ionization with participation by the trans acetoxyl substituent to give conformers **46** and **47** which then collapse with cyclopropyl involvement to give **48.** Direct participation by the three-membered ring was ruled out because in the absence of the acetoxyl group no product corresponding to **45** was formed. Cyclopropyl participation in **49** and **50** was similarly absent, but unfortunately the interesting hydroxy acetate **51** was not studied. The absence of **52** and **53** in the dehydration products of **44** is pertinent since both olefins are readily formed from isomeric compounds, *e.g.,* **50.** Apparently ion **48** does not leak to a cyclopropylcarbinyl cation; equally notable is the delocalization of the C-1–C-7 bond of the three-membered ring rather than the C-1–C-6 bond. In this regard the behavior of the bicyclo[4.1.0]heptyl and bicyclo[3.1.0]hexyl ring systems are in complete contrast despite the potential homoaromatic properties of ion **54.**

Similar results were obtained when **55** and **56** were treated with acids.[63] Only in the trans epoxide **55** (corresponding to **46** and **47**) was participation leading ulti-

TABLE IV. Relative Solvolysis Rates for a Series of Steroid Derivatives[a]

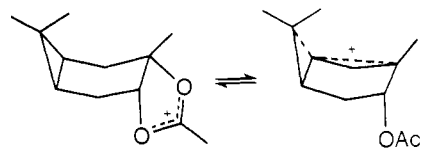
Compd	Rel rate	Compd	Rel rate
59	115	**61**	126
60	414	**62**	1

[a] Data taken from ref 64. Solvolyses were run in aqueous dioxane at 56.1°.

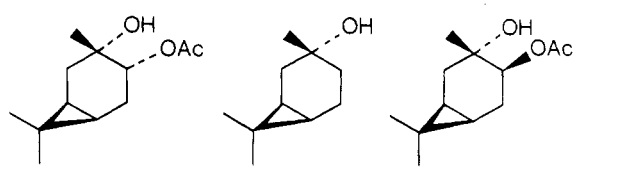


44 **45**

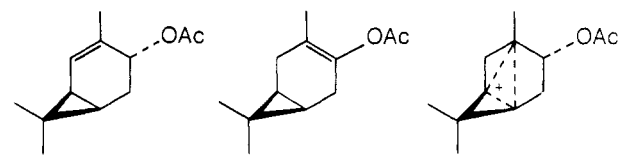
46



47 **48**

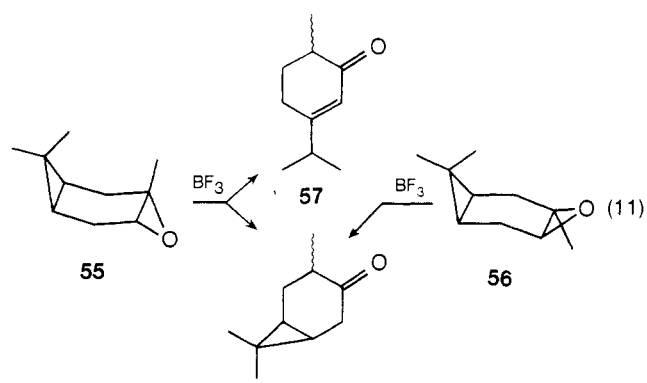


49 **50** **51**



52 **53** **54**

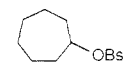
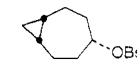
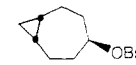
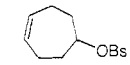
mately to **57** observed (eq 11); the cis epoxide **56** gave only traces of **57**, the major product being **58**.



55 **57** **56** **58**

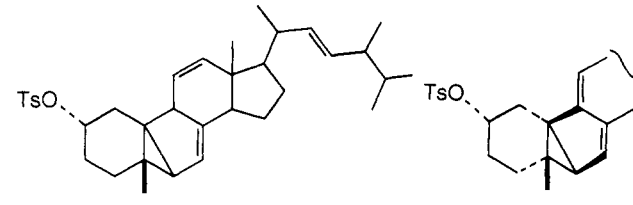
Barton, Bernasconi, and Klein[64] observed a rate acceleration for the steroids **59** and **60** relative to suitable models (**61** and **62**) (Table IV) from which it is clear that cyclopropane ring participation in the ionization step in such a system is possible. The efficiency of such participation is most readily seen from a comparison with **61** in

TABLE V. Relative Acetolysis Rates of Various Seven-Membered Ring Brosylates[a]

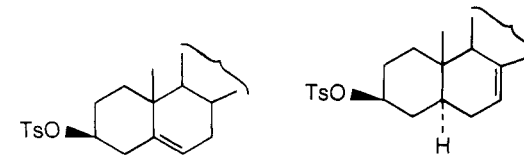
Brosylate	Rel rate	Brosylate	Rel rate
	1.0		0.12
	0.08		0.04

[a] Data taken from ref 66 at 60°.

which double bond participation is well documented and of considerable historical interest.[6,9]

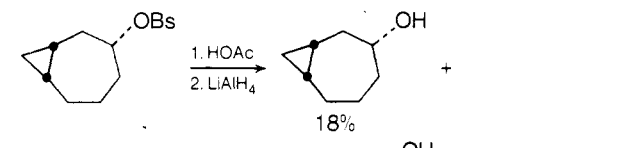


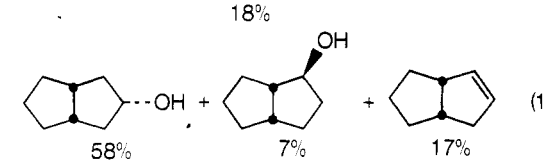
59 **60**

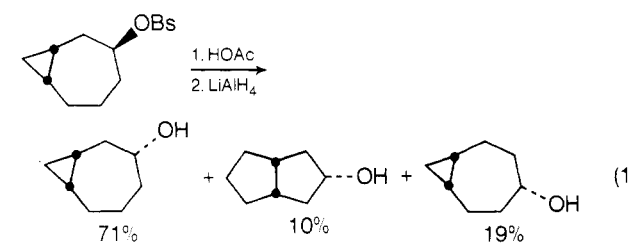


61 **62**

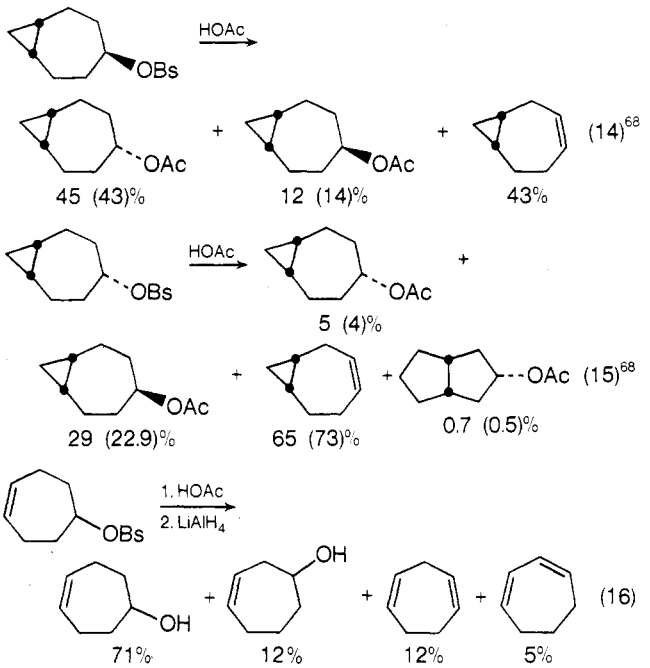
Both epimers of bicyclo[5.1.0]oct-3-yl brosylate acetolyze to give mixtures of several products (eq 12 and 13).[65] From the nature of these products it is clear that the cyclopropyl group in both isomers interacts with the positive charge; it is not clear if this interaction is in the rate-controlling ionization or in subsequent steps, however, since kinetic data are lacking. Equally obscure is the structure of the intermediates since the products can be explained by various mixtures of classical and nonclassical ion intermediates or by concerted reactions.



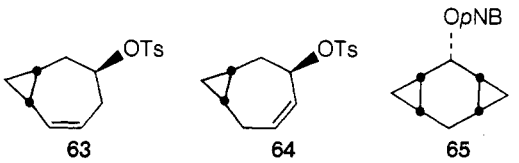




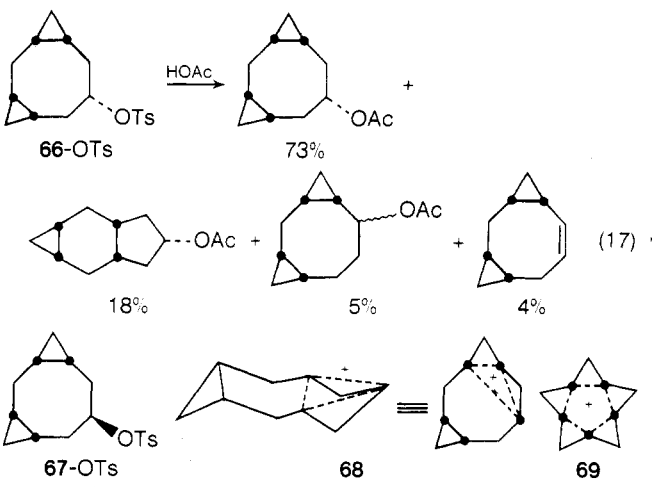
The bicyclo[5.1.0]oct-4-yl brosylates ionize at about the same rate as cyclohepten-5-yl brosylate and considerably slower than cycloheptyl brosylate (Table V), clearly indicating that in this ring system assistance by both the double bond and the cyclopropyl group is absent. The reaction products further reveal that interaction is absent even in later steps since only a minor amount of the product is of rearranged structure (eq 14, 15, and 16).[65-67]



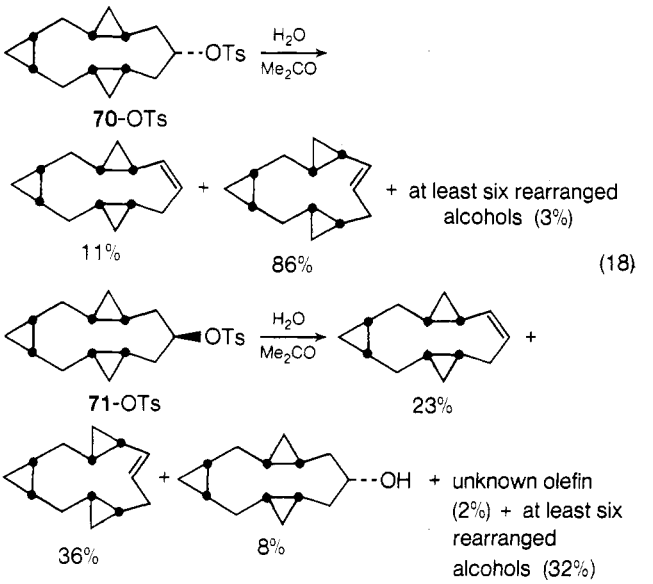
Lambert, *et al.*,[69] have investigated competition between a cyclopropyl group and a double bond in the acetolysis of **63.** This ester is more reactive than cycloheptyl tosylate (factor of 22^{70}), indicating participation in the ionization step. By an analysis of the solvolysis products and those from the closely related esters **64** and **65,** Lambert's group concluded that 80% of the ionization occurred with participation by the double bond, 20% with participation by the three-membered ring.



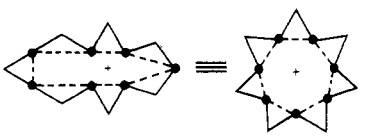
Ionization of **66**-OTs provides an opportunity to observe participation by either one or two cyclopropyl groups. This all cis tosylate ionizes more slowly than does cyclooctyl tosylate (factor of 60^{72}) but much more rapidly than its trans epimer **67**-OTs (factor of 52).[19a] Although the kinetic data do not demand cyclopropyl participation in the ionization of **66**-OTs, the reaction products can be interpreted only with an interaction by one of the three-membered rings (eq 17). A deuterium label in both cyclopropane rings gives a product distribution consistent only with interaction by only one of the two equivalent cyclopropyl groups, presumably with the formation of the trishomocyclopropenyl cation **68** as the intermediate. Capture of this ion by solvent competes with a hydride shift to give a cyclopropylcarbinyl cation and with elimination. Complete delocalization to **69** is not expected because this ion should be antihomoaromatic.[9a,b]



Extension of **66** by an additional cyclopropyl group giving **70**-OTs provides a potential precursor of the heptahomotropylium ion **72** which is anticipated to be homoaromatic.[9a,b] Acetolysis of both **70**-OTs and **71**-OTs gives large amounts of elimination and SN2 products with no equilibration of a deuterium label on the three cyclopropane rings (eq 18 and 19).[73] It is thus clear that, even



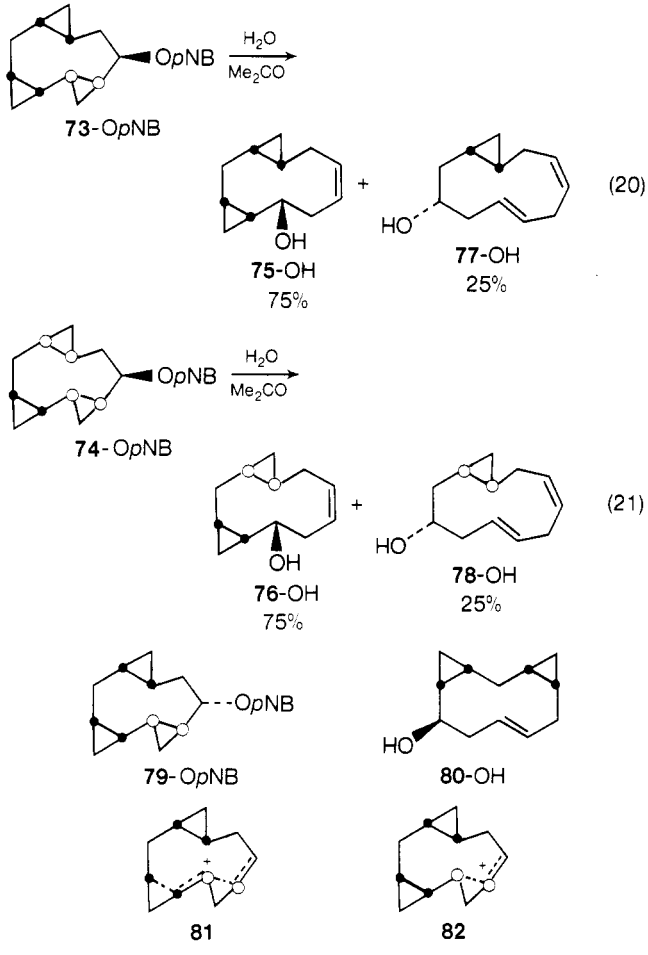
though **70**-OTs ionizes about 15 times as fast as **71**-OTs, cyclopropyl participation is not a factor in these reactions. It has been postulated[73] that these results are due to the very favorable geometry for elimination in these molecules and their less favorable geometry for cyclopropyl participation (compared to other systems). Investigation of cyclopropyl participation in the ionization of other stereoisomers of **70** and **71** has yet to be reported although the required compounds are known.[74]



72

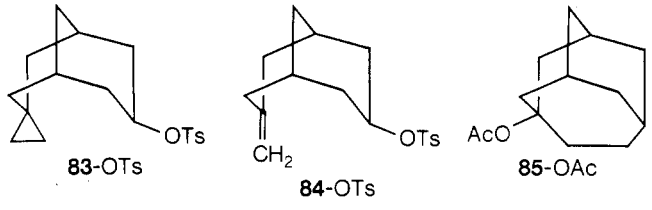
During the synthesis of derivatives of **70** and **71**, two additional examples of long-range cyclopropyl participation were uncovered.[75] Ionization of **73**-OpNB and **74**-OpNB gave mixtures of products (eq 20 and 21) containing the expected homoallylic alcohols **75**-OH and **76**-OH from the usual cyclopropylcarbinyl–homoallyl rearrangement in addition to the unexpected dienols **77**-OH and **78**-OH from opening of one additional cyclopropyl group. Such dienols can be formed by (a) opening of **75**-OH and **76**-OH, (b) rearrangement of an initially formed homoallylic ion into a second one, or (c) direct intervention of the remote three-membered ring in the ionization of the starting esters. Whalen, *et al.*,[75] concluded that pathways a and b compete with each other but that c also needs to be considered. The failure of **79**-OpNB to give similar products[75] and the relative inertness of **80**-OH under the reaction conditions[75] may be cited in support of pathway

c. Interaction either in the ionization step to give **81** or with homoallylic ion **82** is possible.

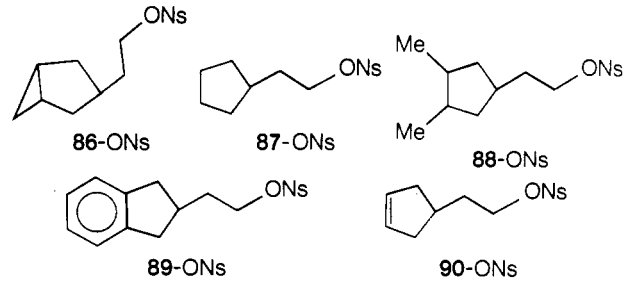


3. *Miscellaneous Conformationally Mobile Systems*

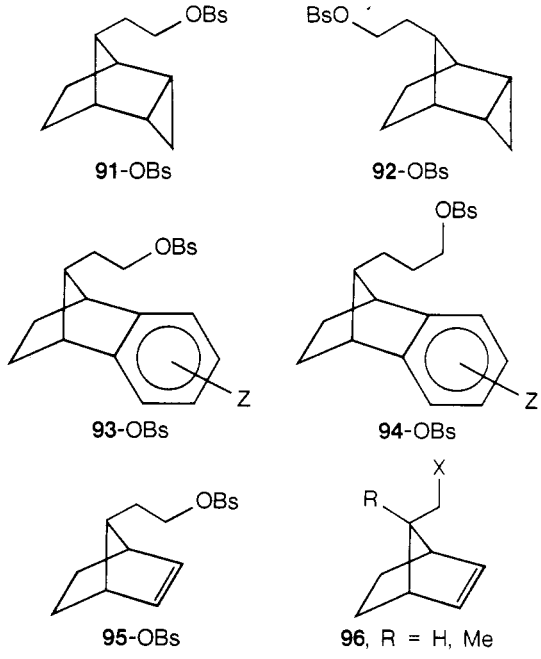
The rate enhancement exhibited in the acetolysis of **83**-OTs (factor of 3 compared to **84**-OTs) and the formation of **85**-OAc as the only product (**84**-OTs forms only 1-adamantyl acetate) demonstrate the cyclopropyl participation in this ionization.[76] Unfortunately no kinetic comparison with a saturated system has yet been reported.



Because a primary carbonium ion is much less stable than simple secondary or tertiary carbonium ions, it might be anticipated that neighboring group participation would be maximized in primary systems. Large rate enhancements are not observed in the ionization of 2-cyclopropylethyl derivatives (*vide supra*), however, nor in **86**-ONs[77] which acetolyzes[78] at about the same rate as the saturated **87**-ONs and **88**-ONs[79,80] to give unrearranged **86**-OAc as the sole product, perhaps by SN2 displacement by solvent. Participation by the benzene ring of **89**-ONs also appears to be absent,[80] but double bond participation in ionization of **90**-ONs is clearly present; thus **90**-ONs ionizes *ca.* 87 times faster than **86**-ONs–**89**-ONs,[79,80] gives only 2-norbornyl derivatives as products, and is further accelerated by methyl substitution on the double bond providing compelling evidence for olefin anchimeric acceleration.[26]



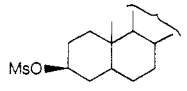
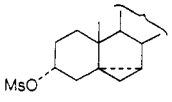
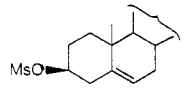
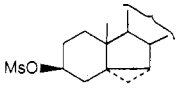
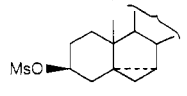
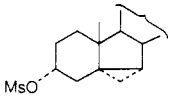
Cyclopropane participation was similarly sought in the ionization of **91**-OBs.[81] Solvolysis of this ester proceeds only slightly faster than ionization of its epimer **92**-OBs and at about the same rate as other primary brosylates, but the increase in the rate ratio (**91**/**92**) as the solvent is changed from acetic acid to the much less nucleophilic 2,2,2-trifluoroethanol indicates weak cyclopropyl participation in the ionization of **91**-OBs. Additional evidence for cyclopropyl interaction is found in the extensively rearranged acetolysis and 2,2,2-trifluoroethanolysis products; only unrearranged products are formed upon hydrolysis in aqueous dioxane.[81] A more precise study of the reaction intermediates awaits product identification.[81a] In closely related studies, benzene ring participation was noted in acetolysis of **93**-OBs but not in its anti epimer nor, surprisingly, in **94**-OBs;[82] double bond participation was observed in the acetolysis of **95**-OBs[83] but only very weakly for derivatives of **96** or its anti epimer.[84] Solvolytic studies on these olefinic derivatives have been reviewed.[6a] Obviously the presence or absence of participation is very critically dependent on geometrical factors.



Participation by the cyclopropyl groups in ionization of the four sterol derivatives shown below is apparently of relatively minor importance as demonstrated by their solvolysis rates (Table VI), but involvement in subsequent steps is noted from the extensively rearranged products that are formed (eq 22–25).[85] The origin of the alcohol products from some isomers is unclear.

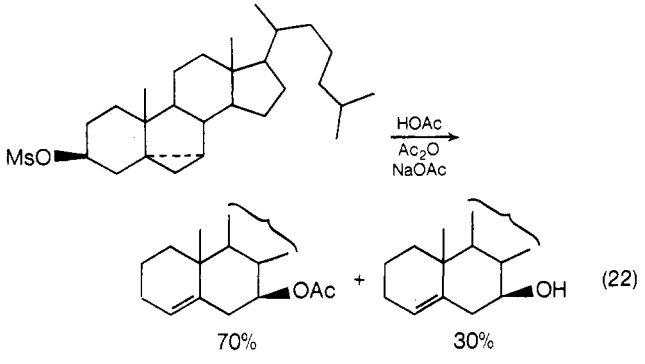
The two systems **97** and **98** are considered to be fixed in the conformation shown.[86] **97**-OAc ionizes 240 times faster than **98**-OAc but only twice as fast as **99**-OAc and 175 times slower than **100**-OAc. The complex nature of the conformational, steric, and substituent effects in these systems, the fact that acyl–oxygen cleavage com-

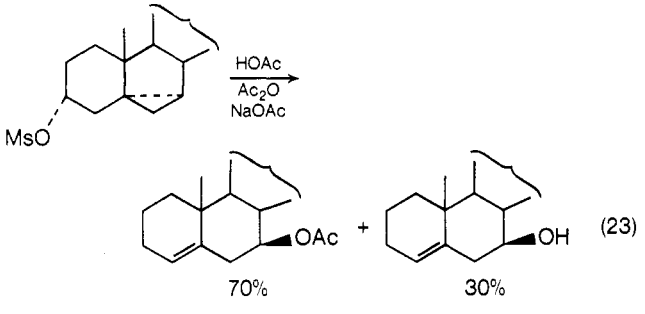
TABLE VI. Relative Acetolysis Rates of Some Cyclosteroid Mesylates[a]

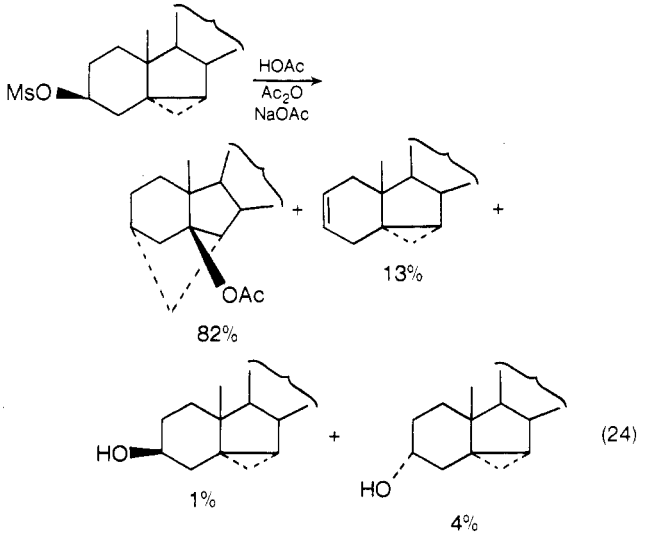
Ester	Rel rate	Ester	Rel rate
	1.0		1.0
	62		1.4
	0.7		5.9

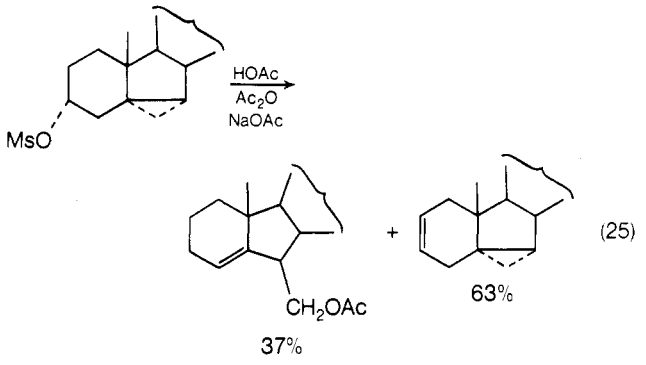
[a] Data at 80° taken from ref 85.

petes with carbonium ion formation, and the possibility of conjugation between the cyclopropane ring and the cation center through the benzene rings cloud the meaning of these data. It was felt that ion **101** is an intermediate in the solvolysis of both **97**-OAc and **98**-OAc.[86,87a]

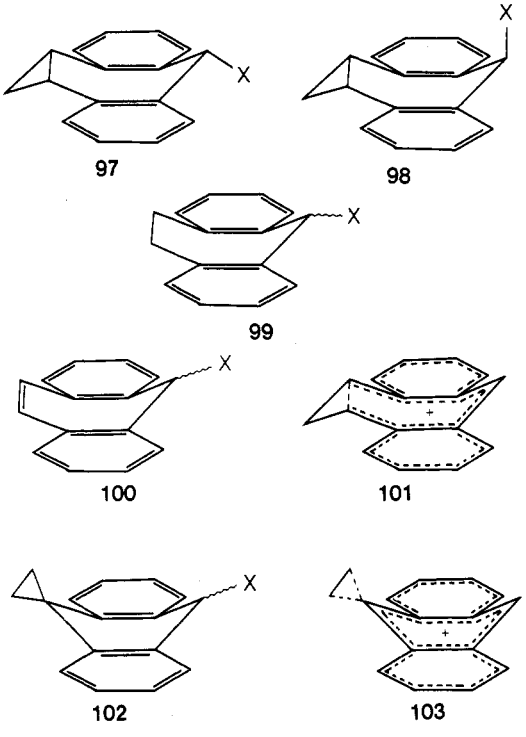








Similar problems exist for the spiro derivative **102**, the acetate of which ionizes, presumably to **103**, *ca.* 1000 times faster than its dihydro, dimethyl, or methylene analogs.[87]



B. Conformationally Rigid Systems

1. *The Tricyclo[3.2.1.0^{2,4}]octan-6-yl, Tricyclo[3.2.1.0^{2,7}]octan-4-yl, Nortricyclyl-3-carbinyl, and Related Systems*

The four isomers of the tricyclo[3.2.1.0^{2,4}]octan-6-yl system, **104–107**, were among the first rigid systems to be examined in a search for long-range cyclopropyl–carbonium ion interactions.[88,89] Cyclopropyl participation in the ionization of the two exo esters **104**-OBs and **106**-

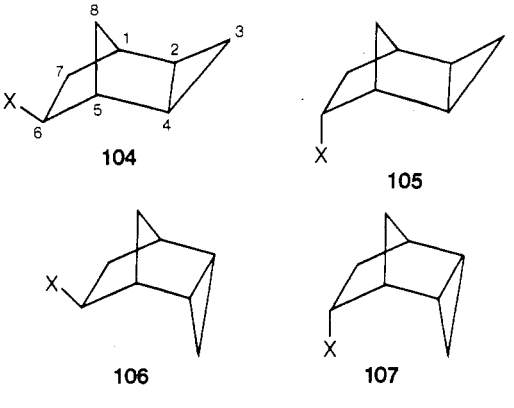
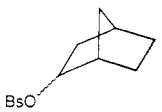
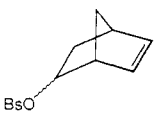
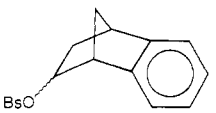
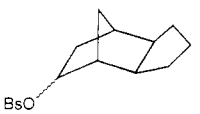
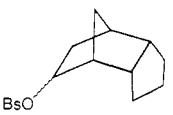
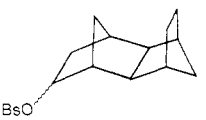
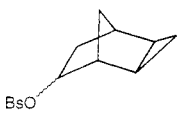
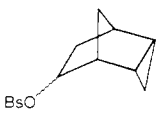
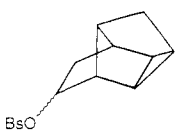


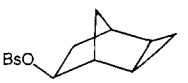
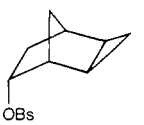
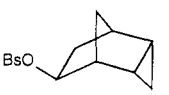
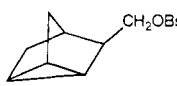
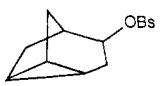
TABLE VII. First-Order Acetolysis Rate Constants for Several 2-Norbornyl Brosylates at 25°

Compound	Acetolysis rate constants ($\times 10^8$)[a] Exo	Endo	k_{exo}/k_{endo}	Notes
	8,820	25.2	350	b, c
	4,500	0.57	7,900	d
	747	0.051	14,600	e
	47	4.3	11	f
	162	1.1	150	f
	83.6	3.76	22	g
	1,360 1,690	1.21 1.2	1,130 1,410	b, h i
	680	1.77	385	b, h
	27,900	474	60	b, j

[a] Value extrapolated from data obtained at higher temperature. [b] Acetic acid buffered with sodium or potassium acetate. [c] S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *J. Amer. Chem. Soc.*, **74,** 1127 (1952). [d] S. Winstein and M. Shatavsky, *ibid.*, **78,** 592 (1956). [e] H. C. Brown and G. L. Tritle, *ibid.*, **90,** 2689 (1968). [f] Calculated from data given in ref 90. [g] L. de Vries and S. Winstein, *J. Amer. Chem. Soc.*, **82,** 5363 (1960); P. Carter and S. Winstein, *ibid.*, **94,** 2171 (1972). [h] Reference 88. [i] Reference 89. [j] Reference 103.

OBs has been demonstrated kinetically. Although the cyclopropane ring reduces the ionization rate of these two derivatives (compared to *exo*-norbornyl brosylate), the effect is even greater for the two endo esters, **105**-OBs and **107**-OBs, in which direct cyclopropyl participation is sterically precluded. This effect gives rise to an enhanced exo/endo rate ratio for **104**–**107** (Table VII) in contrast to the decrease usually observed for alkyl substitution at C-6.[90] Introduction of a double bond or benzene ring also decreases the ionization rate but greatly enhances the exo/endo rate ratio, presumably by participation in the ionization of only the exo isomer.[91] From the enhanced exo/endo ratio for the pairs **104**-OBs, **105**-OBs and **106**-OBs, **107**-OBs, one concludes that cyclopropyl participation is indeed a factor in the ionization of the exo esters.

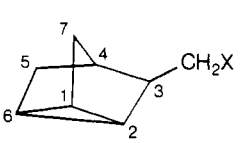
TABLE VIII. Products of Buffered Acetolysis of Several Brosylates[a]

Starting brosylate	Product acetates, %— **104**-OAc	**108**-OAc	**109**-OAc	**110**-OAc	Notes
	67.5 51	7.2 6	25.4 26	0 15	b, c d, e
	67.5	7.2	25.4	0	b, c
	68.5	6.5	25.0	0	b, c
	58.2 47 37	9.1 22 9	32.7 23 39	0 8 15	b, c f, g d, e
	0	0	65[e]	35	d, e, h, i

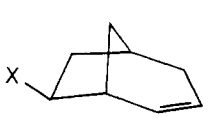
[a] Different product ratios were obtained under different solvolysis conditions. [b] Temperature unspecified. [c] Reference 88. [d] References 92 and 93. [e] At 100°. [f] Reference 94. [g] At 110°. [h] References 97 and 98. [i] At 50° about 30% **111**-OAc is formed with a reduction in the proportion of **109**-OAc; references 97 and 98.

The products of acetolysis of **107**-OBs have not yet been published, but the three esters **104**-OBs–**106**-OBs gave virtually identical mixtures of three acetate products, **104**-OAc, **108**-OAc, and **109**-OAc (Table VIII).[88] In a later study of **104**-OBs acetolysis, Berson, *et al.*,[92,93] reported the formation of a fourth acetate, **110**-OAc, not found by Wiberg and Wenzinger; neither group observed **111**-OAc. The closely related nortricyclyl-3-carbinyl brosylate (**108**-OBs) has been reported by several groups[88,92-95] to give the same products. Tricyclo[3.2.1.$0^{2,7}$]octan-4-yl brosylate (**110**-OBs) gives only **109**-OAc and **110**-OAc and under milder conditions, **111**-OAc.[92,93,96-98] The product composition is very dependent on the leaving group, solvent, and temperature; examples can be found in Table VIII and in the original reports.[88,92-98]

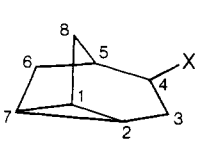
Optically active samples of **104**-OBs and **108**-OBs solvolyze to **104**-OAc and **108**-OAc with almost complete retention of optical purity, to **110**-OAc with about 30% retention, and to **109**-OAc with complete racemization.[92,93] In contrast, the solvolysis of optically active **110**-OBs is accompanied by internal return and gives racemic acetate products.



108



109

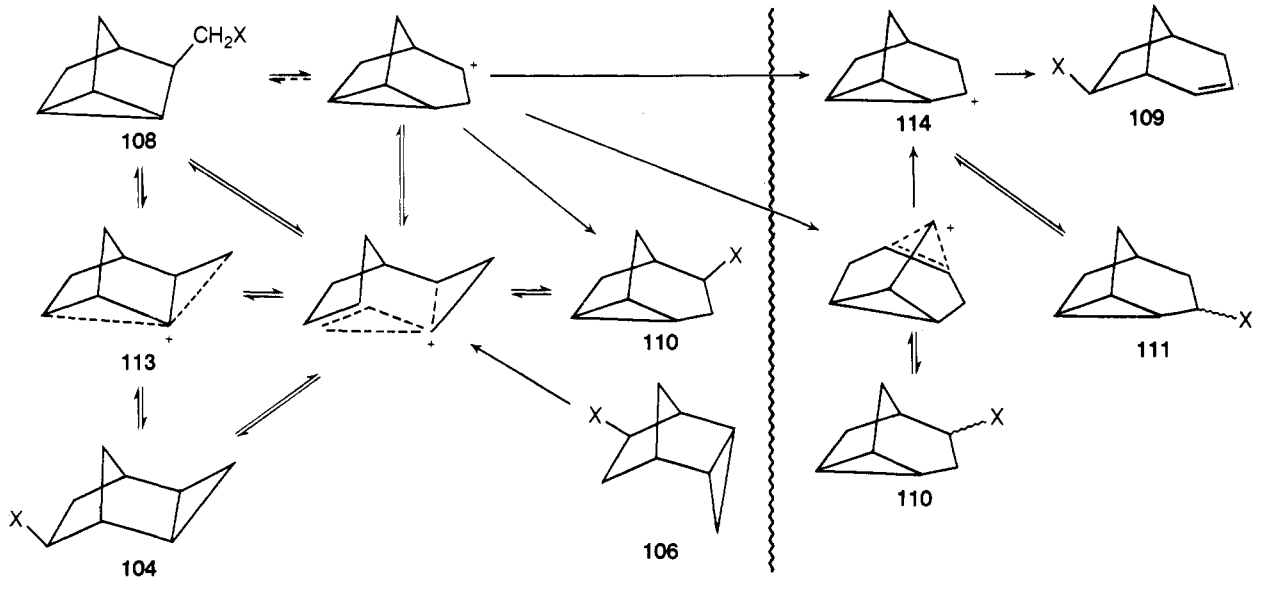


110

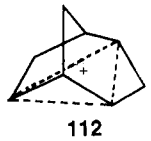
111

It is apparent from the data summarized above that the systems **104**–**108** probably give rise to common interme-

SCHEME I. Mechanistic Scheme for Ionization of Some Tricyclic Derivatives



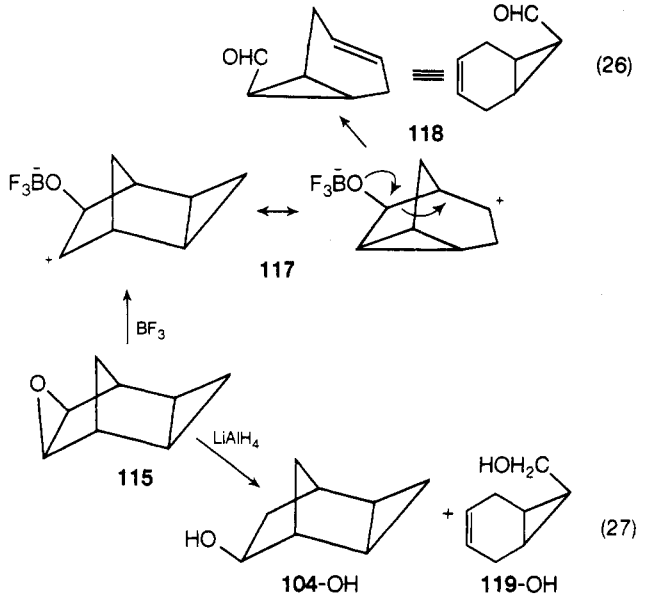
diates which are different from those arising from derivatives of **110.** The former systems must give intermediates which are stereochemically pure sources of **104**-OAc and **108**-OAc but from which **109**-OAc and **110**-OAc are formed with complete and partial racemization, respectively. Scheme I, proposed by Berson, *et al.*,[93] is in full accord with both the stereospecificity of product formation and the participation afforded by the cyclopropyl rings in **104**-OBs and **106**-OBs. Regarding this participation, Berson, *et al.*,[93] felt that symmetrical, cross-ring delocalization to give **112** does not occur although this process would be analogous to that found widely in tricyclo[3.2.1.$0^{2,4}$]octan-8-yl derivatives (*vide infra*). It is also interesting that participation is proposed for **108** but not for **110** in which no long-range interaction is envisaged even following the rate-controlling step.[93] **108**-OBs apparently does not ionize directly to **114** despite the favorable bisected geometry of this cyclopropylcarbinyl cation because overlap of the cyclopropyl ring orbitals with the adjacent developing p orbital in the transition state is particularly unfavorable.[93,95]



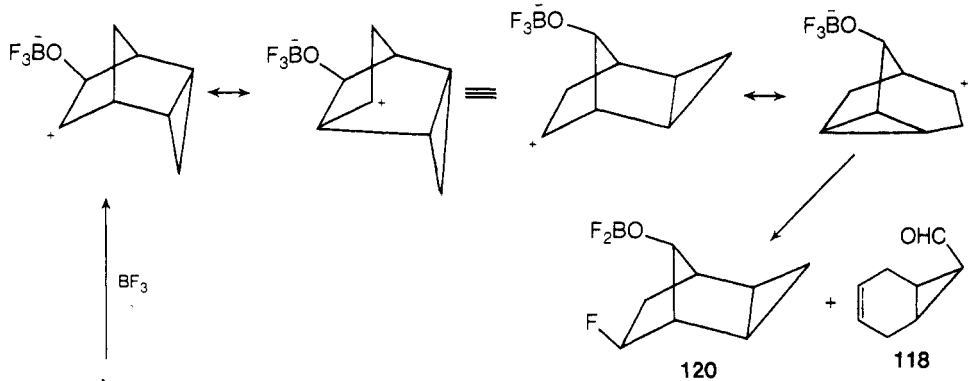
112

The two epoxides **115** and **116** are sources of carbonium ions similar to those discussed above. The two epoxides undergo reactions which demonstrate the participation of the cyclopropyl groups with carbonium ion centers. Treatment of **115** with acid catalysts in aprotic medium gives smooth rearrangement to the aldehyde **118** presumably through the carbonium ions **117** (eq 26).[99] A similar rearrangement is observed upon lithium aluminum hydride reduction, unrearranged **104**-OH and rearranged **119**-OH being formed in approximately equal amounts (eq 27).[100] No rearrangement is observed in the lithium–ammonia reduction of **115** or of **116.**[100-102]

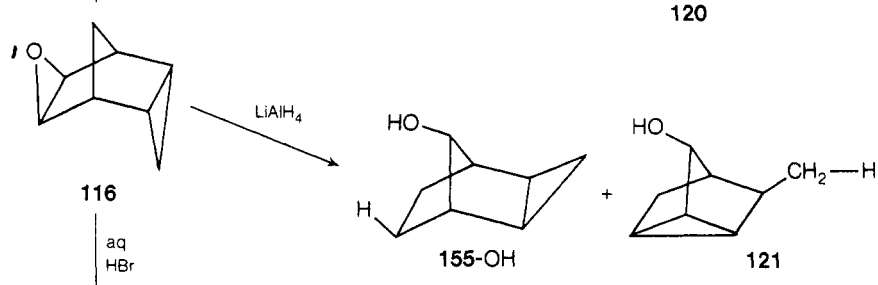
The boron trifluoride catalyzed rearrangement of **116** to **118** is much less facile and competes with intramolecular capture giving **120** (eq 28), although similar intermediates are involved.[99] Lithium aluminum hydride reduction and treatment with aqueous acid transform **116**[101,102] into precisely the same types of products observed in the acetolysis of **106**-OBs.[88] Thus the lithium aluminum hydride reduction gives **155**-OH and **121** (eq 29); aqueous hydrobromic acid gives **122, 123,** and **124** (eq 30).



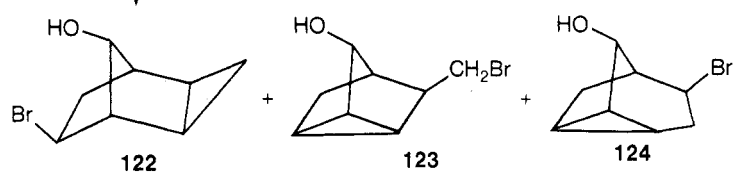
Unlike the rather complex situation found in the ionization of **104**-OBs, **115,** and similar systems discussed above, the ionization of derivatives of the deltacyclyl system, **125**-OBs and **126**-OBs, is relatively straightforward and provides compelling evidence for the involvement of the C-3–C-4 rather than the C-2–C-3 bond with the carbonium ion center. A variety of derivatives (brosylates, chlorides, amines) of both stereoisomers gave **125**-OAc as the sole product of acetolysis or of deamination in acetic acid.[103,104] Solvolysis of the exo isomer (**125**-OBs) is characterized by a rate enhancement (Table VII), complete scrambling of a deuterium label initially on C-8 (or C-9) between C-8 and C-4 (or C-9 and C-5),[104] a relatively low secondary deuterium isotope effect for an exo deuterium atom on C-9,[105] and complete retention of optical activity in the product formed from acetolysis of an active sample of **125**-OBs.[104] These results, and the nmr spectrum of the cation formed by dissolving either **125**-OH or **126**-OH in FSO_3H–SO_2 below $-10°$,[103,104] are in full accord with the direct formation of the symmetrical intermediate **127** (analogous to **113**) and rule out formation of alternative structures such as **128** or **129** or ions formed by rapid Wagner–Meerwein shifts. The rearrange-



(28)

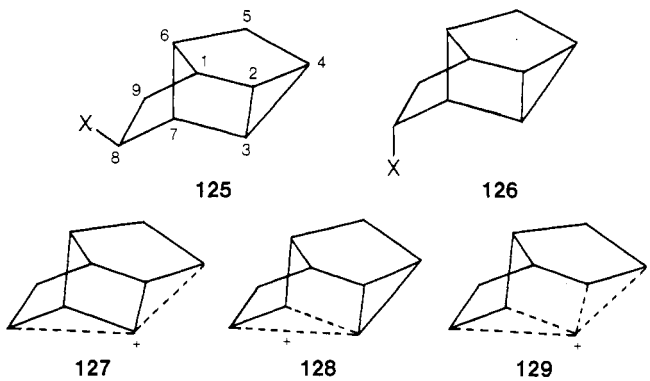


(29)



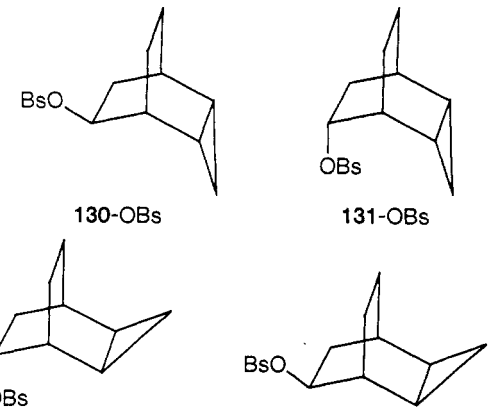
(30)

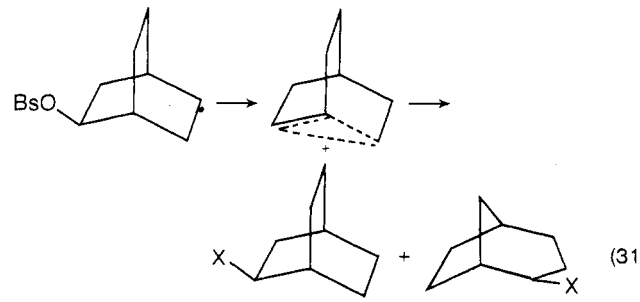
ments found in the ionization of **104**-OBs do not occur with **125**-OBs because of the steric restrictions imposed by the additional methylene group.



The endo brosylate **126**-OBs displays similar behavior with some important exceptions. A deuterium label initially on C-8 is not completely scrambled with C-4 (*ca.* 80% scrambling),[104] optical activity is partially lost in the acetolysis of active **126**-OBs (*ca.* 40% retention),[104] and the secondary isotope effect of an exo deuterium atom on C-9 is larger than for **125**-OBs.[105] These data have been interpreted[103-105] in terms of a classical ionization of **126**-OBs to form an ion which can react with acetic acid, undergo rearrangement by alkyl shifts to an ion of inverted configuration, or leak to **127**.

A preliminary report of the solvolysis of **130**-OBs–**133**-OBs has very recently appeared.[106] Three of these molecules apparently ionize in a fashion similar to that found for other bicyclo[2.2.2]octyl derivatives,[107] *i.e.*, with C–C participation (eq 31) to give either cyclopropyl migration in the case of **130**-OBs or cyclopropylcarbinyl cations in the cases of **131**-OBs and **132**-OBs. Only in the isomer **133**-OBs is direct long-range cyclopropyl participation proposed. Unfortunately the structures of the transition state and intermediate(s) in the solvolysis of **133**-OBs have not yet been reported.

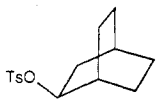
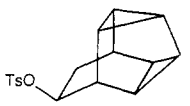
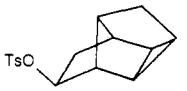




(31)

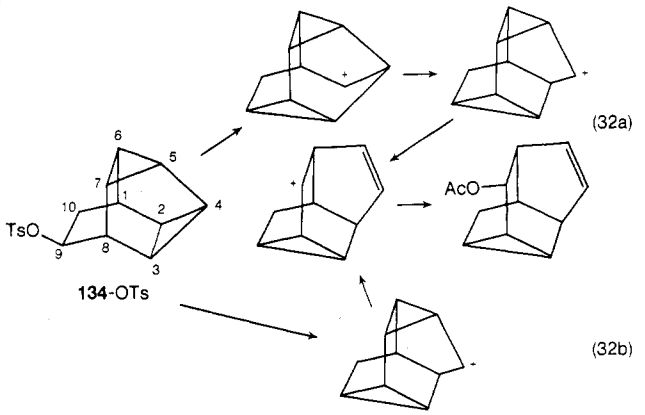
Another bridged system also closely related to **104**, **125**, and **133** is **134**-OTs[108] whose enhanced rate of acetolysis (Table IX) and clean rearrangement (eq 32) clearly demonstrate cyclopropyl interaction. Dauben and Schallhorn envisage classical ion intermediates in this solvolysis, but nonclassical ions could also be employed; there appears to be no good evidence to distinguish between these two possibilities. Dauben and Schallhorn

TABLE IX. Relative Acetolysis Rates for Some Polycyclic Tosylates at 25°

Tosylate	Rel rate	Notes
	1	*a, b*
	20	*a*
	27	*c*

[a] Reference 108. [b] The ionization of this ester is considered to be assisted; see ref 107. [c] Calculated from data on the corresponding brosylate given in ref 103.

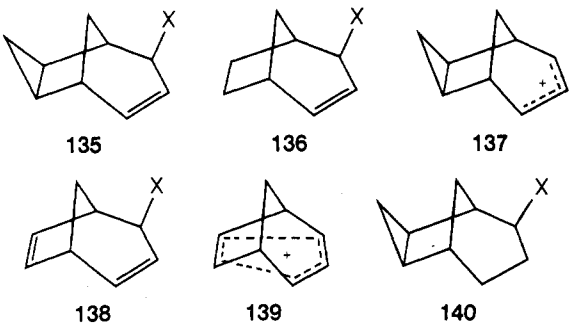
proposed participation by the C-2–C-3 bond of **134**-OTs (eq 32a) in a fashion analogous to that found for the ionization of **104**-OBs discussed above. Participation by the C-3–C-8 bond, typical of ionizations of other bicyclo[2.2.2]octyl derivatives,[107] does not appear to occur in this solvolysis. The authors do not present any evidence for their proposed mechanism, however, and do not consider a possible attractive alternative, participation by the C-3–C-4 bond amply demonstrated in the ionization of **125**-OBs. The observed product could indeed by formed very efficiently by this route (eq 32b).



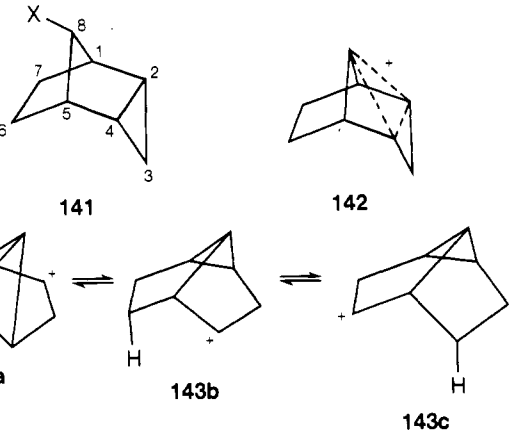
Cyclopropyl interaction was not found in the solvolysis of **135**-O*p*NB which ionized 3.1 times more slowly than **136**-O*p*NB and gave unrearranged **135**-OH as the major product (96%).[109] The allylic ion **137** was identified by nmr.[109] The dienyl ester **138**-O*p*NB exhibited a large rate deceleration (factor of 235) presumably due to the antihomoaromatic nature[9b] of **139**.[109,110] Unfortunately ionization of derivatives of **140** has not yet been reported.

2. *The Tricyclo[3.2.1.0^{2,4}]oct-8-yl and Related Systems*

This group of compounds, which all incorporate a rigid, bridged bicyclo[3.1.0]hex-3-yl moiety, provides the most dramatic examples of long-range cyclopropyl–carbonium ion interactions. It is evident from the data in Table X that, of the four stereoisomers of the title ring system, only the endo–anti one, **141**, exhibits a tremendously large rate enhancement due to direct cyclopropyl participation in the ionization step;[111-115] indeed the enhancement provided by the cyclopropyl group in **141**-O*p*NB is even greater than that due to the anti double bonds in *anti*-7-norbornenyl and 7-norbornadienyl derivatives or the



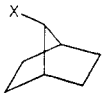
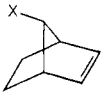
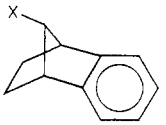
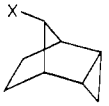
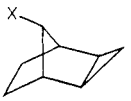
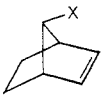
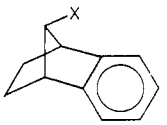
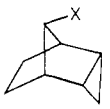
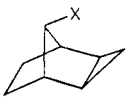
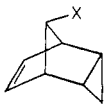
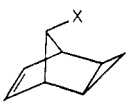
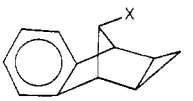
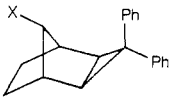
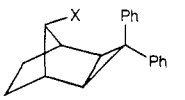
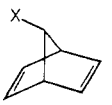
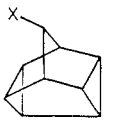
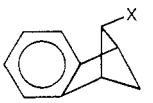
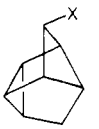
anti benzene ring in *anti*-9-benzonorbornenyl esters. In these simpler molecules the large ionization rate enhancements observed have been used as an important part of the impressive body of evidence[6a,9b,114] which supports a nonclassical structure for the intermediate in each case. Although the trishomocyclopropenyl cation **142**, derived from **141**-O*p*NB, is predicted[37] to be relatively stable, thus imparting a large rate enhancement to **141**-O*p*NB ionization, it can be argued rather convincingly that relief of steric strain[116] upon ionization, with rearrangement to classical ions **143**, accounts for the observed rate enhancement. It should be noted that a similar rearrangement in the ionization of *anti*-7-norbornenyl derivatives leads to a system with greater strain energy than the starting norbornene derivative.



Solvolysis of **141**-O*p*NB gives a simple mixture of only three products (eq 33)[111-115] formed from nucleophilic attack exclusively from the anti direction at C-8 and from the endo direction at C-2. It is quite clear, and of considerable mechanistic importance, that neither **144**-OH nor **145**-OH or their *p*-nitrobenzoates are formed (<0.02%) in the product mixture; however, in a closely related reaction a derivative of **144** is formed,[117] but this case is complicated by competition between carbene and carbonium ion processes and by the fact that a diazonium ion precursor, which is a poor model for solvolytic work,[52] was postulated. Carbene insertion into the solvent (methanol) or reaction of a "hot" carbonium ion could have produced the **144**-OMe observed.

Ketone **146**, which, because it has an sp^2-hybridized carbon atom at C-8, is considered to be a good steric model for classical ion **147**, is attacked by lithium aluminum hydride from both syn and anti directions to give a mixture of **141**-OH and **144**-OH in the ratio of 1:2;[111-114] other nucleophiles attack **146** much more predominantly from the anti direction, however.[118,119] Ketone **148**, a suitable model for **143**, is attacked by several complex metal hydrides predominantly from the less hindered exo direction to give the thermodynamically less stable alcohol **149**-OH.[113,114]

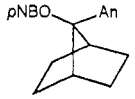
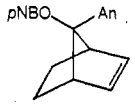
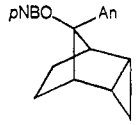
TABLE X. Relative Solvolysis Rates for Some Tricyclo[3.2.1.0^{2,4}]oct-8-yl and Related Derivatives[a]

Ring system	Relative rate, X = OBs[b]	OpNB[c]	Cl[d]	OMAc[b,e]	Notes
	1				*f, g*
	10^9	10^9	10^9		*f–l*
	10^4				*m*
		10^{12}	10^{12}		*i–k, n*
	1.7				*o*
	10^3				*f, p*
	40				*q*
	37				*i, k*
	10^4				*k*
		10^9			*r*
		10^{12}			*s,t*
	10^7				*f*
	10^3				*f, u*
	10^3				*f, u*
		10^{11}	10^{12}	10^{11}	*j, l, s, v, w*
		10^{10}			*w*
	10^3				*f, x*
				10^{11}	*v*
	10^6				*f, y*
		10^{11}			*z*
	10^7				*f, aa*

[a] Relative rates at 100° unless otherwise stated. These values are only approximate since different solvents were used in some cases and extrapolations over large temperature ranges were employed. The relative rates were arrived at after extrapolation by assuming that the rate ratio for any pair of compounds is independent of the leaving group. [b] Solvolysis in buffered acetic acid. [c] Solvolysis in 70% aqueous dioxane unless otherwise stated. [d] Solvolysis in 80% aqueous acetone; rates compared to that of anti-7-norbornenyl chloride at 25°. [e] OMAc = methoxyacetate, CH_3OCH_2COO–. [f] Calculated as three times the rate of the corresponding tosylate. [g] Calculated from data given in S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, **77,** 4183 (1955). [h] Relative rates of brosylate, tosylate, *p*-nitrobenzoate, chloride, and methoxyacetate are assumed to be the same. [i] Reference 111. [j] Reference 112. [k] Reference 113. [l] Calculated from data given in S. Winstein and C. Ordronneau, *J. Amer. Chem. Soc.*, **82,** 2084 (1960). [m] Calculated from data given in ref 128. [n] Calculated from data given in ref 115 at 25°. [o] Calculated from data given in ref 124. [p] Reference 126. [q] Calculated from data given in ref 127. [r] Calculated from data given in ref 118; at 170° this ester hydrolyzes *ca.* 10 times faster than *anti*-7-norbornenyl *p*-nitrobenzoate. [s] From a comparison at *ca.* 90° with **141**-OpNB in 70% aqueous acetone. [t] Calculated from data given in ref 125. [u] Calculated from data given in ref 130. [v] Calculated from data given in ref 139. [w] At 125° in 65% aqueous acetone, ref 121. [x] Calculated from data given in ref 137. [y] Calculated from data given in ref 148. [z] Compared to **141**-OpNB in 60% aqueous dioxane at 25°, ref 135. [aa] Calculated from data given in ref 143.

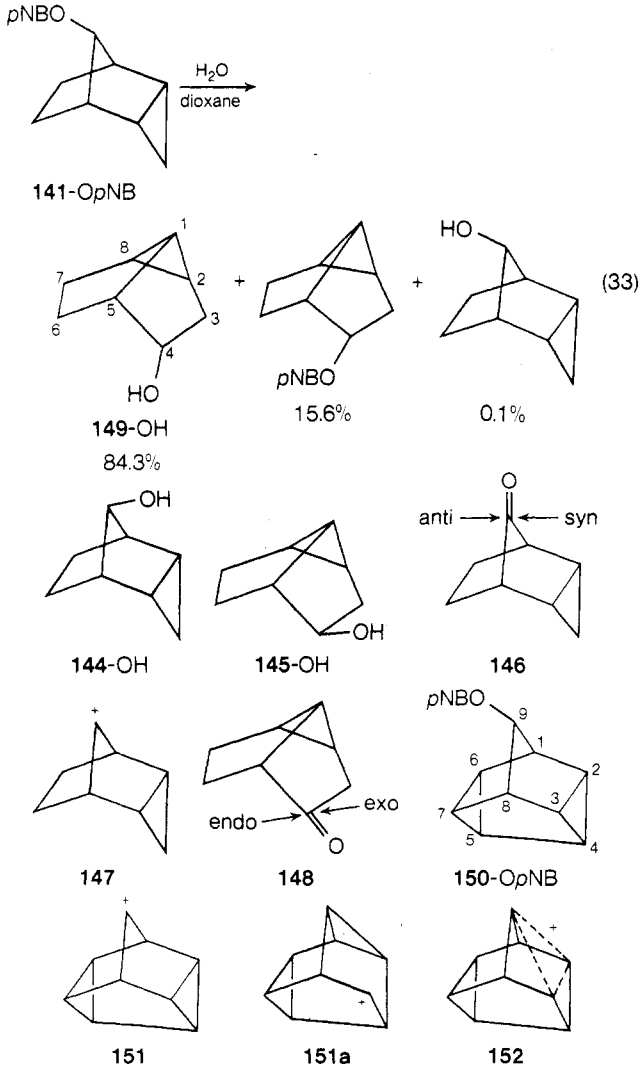
It would thus appear that the stereospecificity of the nucleophilic attack on the intermediate(s) derived from **141**-*Op*NB at *only* the anti and hindered endo sites is incompatible with a set of equilibrating classical cations, **143** and **147**, but is quite consistent with the stereoelectronic requirements of the trishomocyclopropenyl cation **142** which precludes attack from the exo and syn sites. Nonclassical ions such as **11** (*vide supra*) and those derived from *anti*-7-norbornenyl, 7-norbornadienyl, and *anti*-9-benzonorbornenyl derivatives, whose structures are more firmly established,[6a,9b,87a,114] are similarly characterized by simple product mixtures and the formation of

TABLE XI. Relative Hydrolysis Rates for Some Polycyclic *p*-Nitrobenzoates at 25°

Ester	Rel rate
	1
	3.3[a]
	3800[b]

[a] Data from ref 123 in 70:30 dioxane-water. [b] Data from ref 119 in 90:10 acetone-water.

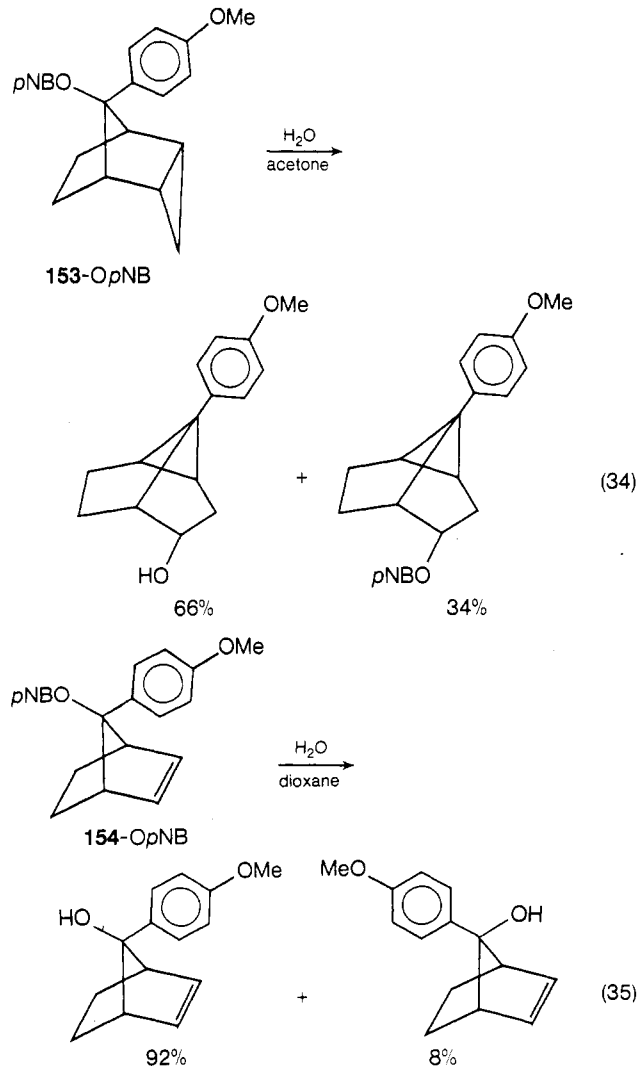
thermodynamically unstable products resulting from stereoelectronic control by the delocalized electrons. Unfortunately, attempts to observe directly by nmr the cation(s) formed from **141** have been unfruitful because the potential precursors (**141**-OH, **146** and its dimethyl ketal) are unstable in the "superacid" media employed.[120]



Although it seems unlikely, if ionization of **141**-O*p*NB is accelerated by relief of strain in going to **143**, **150**-O*p*NB should ionize without acceleration since the analogously rearranged cation, **151a**, is identical with **151** and ring strain cannot therefore be relieved. If, on the other hand, the formation of **142** accelerates the ionization of **141**-O*p*NB, ionization of **150**-O*p*NB should be similarly assisted with the formation of the trishomocyclopropenyl cation **152**.

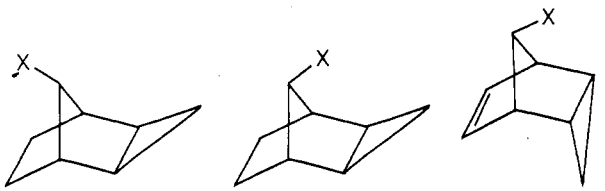
Solvolysis of **150**-O*p*NB occurs with a rate enhancement almost as large as that observed for **141**-O*p*NB and gives **150**-OH as the only product.[121] There is statistical scrambling of the deuterium atoms of **150**-O*p*NB-9-*d* and **150**-O*p*NB-*anti*-4-*d* between *only three positions:* C-9, C-2, and C-3 and C-*anti*-4, C-1 and C-8, respectively, in the recovered solvolysis product. It is clear from these labeling experiments that only one cyclopropyl ring, specifically the anti one, is involved in positive charge delocalization in this reaction. If both rings were involved, complete scrambling of the label over all positions would be expected.[122] On the basis of the kinetic and product analysis studies of **141**-O*p*NB and **150**-O*p*NB, we are almost compelled to assign structures **142** and **152** to the respective intermediate cations.

So powerful is the participation by the cyclopropyl group in the ionization of *endo-anti*-tricyclo[3.2.1.$0^{2,4}$]oct-8-yl derivatives that it even overwhelms the carbonium ion stabilization afforded by a *p*-anisyl group. Thus **153**-O*p*NB demonstrates a large anchimeric acceleration (10^3),[119] whereas the accelerating effect of the double bond in *anti*-7-norbornenyl derivatives is completely overcome by the *p*-anisyl group of **154**-O*p*NB (Table XI).[123] It thus appears that a *p*-anisyl group (and probably other aryl groups) has an upper limit to the sta-



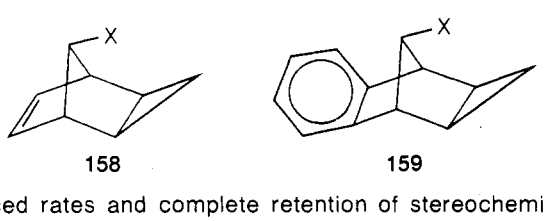
bilizing effect it can provide a carbonium ion at the benzylic position.[119] The solvolysis products from **153**-*Op*NB are completely rearranged (eq 34) whereas those from **154**-*Op*NB are partially rearranged (eq 35). These kinetic and stereochemical results are in full accord with the idea that double bond participation in **154**-*Op*NB is absent but that cyclopropyl participation in **153**-*Op*NB still remains. By analogy with the olefinic derivatives,[123] it is expected that cyclopropyl participation in **153**-*Op*NB might be overcome by the *p*-*N*,*N*-dimethylamino group.

In contrast to the derivatives of **141**, the derivatives of the other stereoisomers of the tricyclo[3.2.1.$0^{2,4}$]oct-8-yl system, **144**, **155**, and **156**, ionize without extensive cyclopropyl participation (Table X) and give rise to numerous rearranged products. The exo-anti isomer **155**-OBs is particularly revealing since its inertness to ionization rules out face participation by the cyclopropane ring.[124]

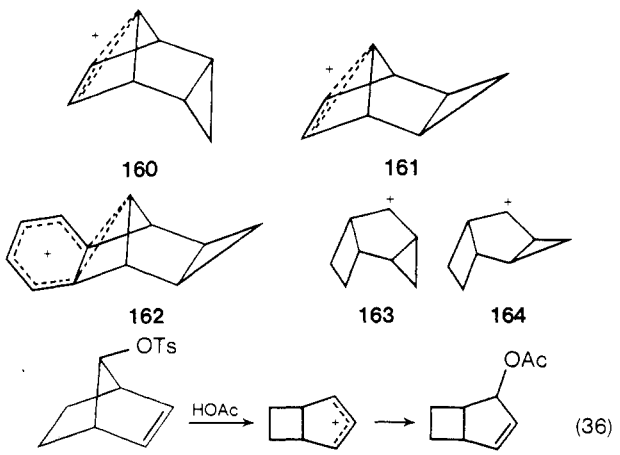


155 **156** **157**

The factors responsible for the rate enhancement observed in the solvolysis of the two syn isomers **144**-OBs and **156**-OBs (Table X) have recently been clarified by studies on the related unsaturated esters **157**-*Op*NB,[118] **158**-*Op*NB,[125] and **159**-OBs[125] which solvolyze with enhanced rates and complete retention of stereochemistry, presumably *via* the bishomocyclopropenyl cations **160**, **161**, and **162** in accord with other *anti*-7-norbornenyl and *anti*-9-benzonorbornenyl derivatives.[6a,9b] By analogy with *syn*-7-norbornenyl[126] and *syn*-9-benzonorbornenyl[127] derivatives which ionize with C–C participation to give an allylic ion and ultimately bicyclo[3.2.0]hept-2-en-3-yl products (*e.g.*, eq 36), it was suggested[113] that formation of cyclopropylcarbinyl cations **163** and **164** might accelerate the ionization of **144**-OBs and **156**-OBs, respectively; **164** was expected to be formed more readily than **163** because of the anticipated better overlap between the developing cation orbital and the exo cyclopropyl ring. It was also suggested[113] that ionization of **156**-OBs might be accelerated by steric factors.



158 **159**

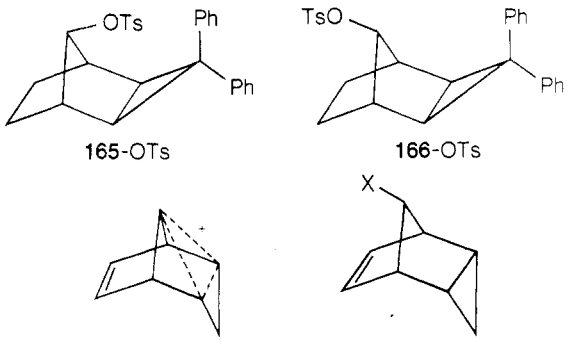


160 **161** **162** **163** **164**

(36)

From the data in Table X it is clear that the cyclopropyl groups of **157**-*Op*NB, **158**-*Op*NB, and **159**-OBs cause a rate enhancement of about the same magnitude as in **144**-OBs and **156**-OBs despite the very low probability of a C–C migration analogous to that shown in eq 36. It would thus appear that the acceleration by syn cyclopropyl groups operates independently of any other acceleration, *i.e.*, by an anti double bond, and is not electronic in origin, a conclusion corroborated by the observation that the effect of substituents in the benzene ring of *anti*-9-benzonorbornenyl brosylate[114,128] is unaltered by the cyclopropane ring of **159**-OBs.[125] Battiste, *et al.*,[125] have proposed steric acceleration, *i.e.*, relief of strain between the ester group and the cyclopropane ring methylene upon ionization, to account for the accelerating effect of an exo-syn cyclopropyl group. Their alternative explanation, a distortion of the molecule such that the bridge is bent toward the double bond or benzene ring in **158** and **159**, respectively,[129] also of steric origin, is considered to be unlikely because of the constancy of the effect even in **156** in which double bond participation cannot occur.

Surprisingly, the accelerating effect of an exo-syn cyclopropyl group is no larger in the diphenyl derivative **165**-OTs which ionizes at about the same rate as **156**-OBs and the *syn*-7-norbornenyl ester.[130] The anti derivative, **166**-OTs, is postulated to ionize with phenyl participation in addition to a concomitant or subsequent disrotatory rupture of the three-membered ring so that the rate enhancement noted for **156** relative to **155** (*ca.* 10^4) is no longer present (k(**165**)/k(**166**) = *ca.* 1.5). Such a pathway is not available to **165**-OTs.



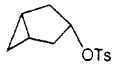
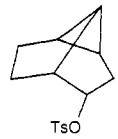
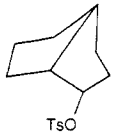
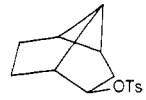
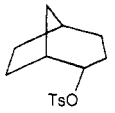
165-OTs **166**-OTs **167** **168**

An additional feature of note concerning **160** is the possibility of a "bridge flip" to **167**; apparently such a process does not occur[118] despite the expected[37] greater stability of **167**. In this regard **160** behaves like the ion derived from 7-norbornadienyl derivatives[6a,9b,131] and **152**.[121] Presumably reaction with solvent is a more efficient process than bridge flipping. Study of derivatives of the epimeric system (**168**) is clearly indicated to test more fully the theoretical predictions.[37]

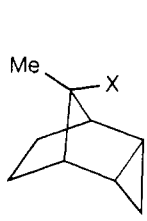
Although it is clear that **144**-OBs does not lead in high yield to **142** upon acetolysis,[113] substituted *endo*-*syn*-tricyclo[3.2.1.$0^{2,4}$]oct-8-yl derivatives give the products expected for a substituted **142** intermediate. Thus solvolysis of derivatives of **169**[132] and treatment of **170**-OH with acids[119] lead to **171** and **172**-OH, respectively. Similar acid-catalyzed rearrangements have been noted for the anti alcohols **141**-OH[111-114] and **153**-OH.[119] These results are most likely due to the increased stability of a tertiary classical ion **173** toward capture by solvent and the increased probability that a longer lived cation of this type will leak to the more stable nonclassical cation **174**.[132a]

Carbonium ions from several tricyclo[3.2.1.$0^{2,4}$]octane derivatives have been studied[133] by mass spectrometry, but the large differences found between the stereoiso-

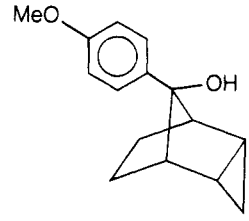
TABLE XII. Relative Solvolytic Rates for Tricyclo[3.3.0.0^{2,8}]oct-4-yl and Related Tosylates at 75°[a]

Tosylate	Rel rate	Tosylate	Rel rate
	5		270
	1		20
	1		

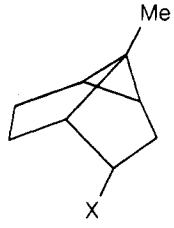
[a] Reference 114 from which these data were taken did not specify solvent.



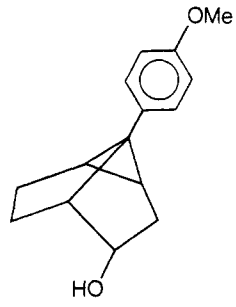
169



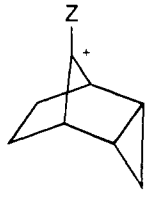
170-OH



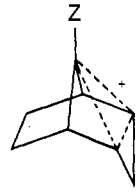
171



172-OH



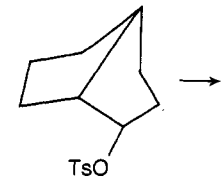
173



174

mers of this ring system in solvolytic reactions are not observed under electron bombardment.

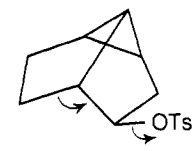
Tanida's studies[114] on the solvolysis of **149**-OTs and **145**-OTs have provided additional examples of cyclopropyl participation and corroborative evidence for ion **142**. Hydrolysis of **149**-OTs results in the formation of **141**-OH and **149**-OH as the only products in the same ratio (1:999) as that found in the hydrolysis of **141**-O*p*NB (eq 33). Optical activity in **149**-OTs is lost 3.2 times faster than the rate of product formation, thereby confirming ion-pair return. The possibility that the racemization involved a 1,3-hydride shift to give **143c** was ruled out by studies on a specifically deuterated sample of **149**-OTs. Although derivatives of **149** are considerably less reactive than those of **141**, cyclopropyl participation in the ionization of **149**-OTs was demonstrated by its enhanced reactivity compared to suitable model compounds (Table XII). From the product composition it would appear that **141**-O*p*NB and **149**-OTs ionize to the same intermediate, presumably **142**, which is quite different from the one derived from **175**-OTs which gives products of elimination, inversion, and hydride migration totally absent in the solvolyses of **141** and **149** derivatives (eq 37).



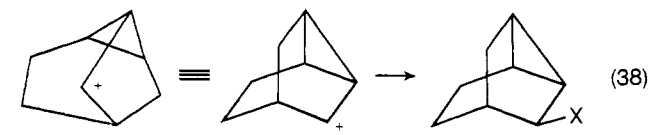
175-OTs

51% 1.7% 47% (37)

In contrast, the exo tosylate **145**-OTs solvolyzed more slowly than **149**-OTs, but this rate difference is relatively meaningless as a quantitative probe for cyclopropyl participation in **149**-OTs since **145**-OTs ionization is probably also assisted by C–C participation[107] (eq 38).[114]

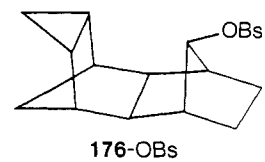


145-OTs

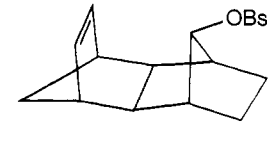


(38)

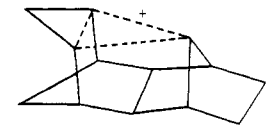
The effectiveness of even longer range cyclopropyl participation has been investigated[134] in a study of **176**-OBs which ionizes with a great amount of acceleration (Table XIII) but, unlike **141**-O*p*NB, less rapidly than the corresponding olefin **177**-OBs. This anomaly (compare **141**-O*p*NB and *anti*-7-norbornenyl *p*-nitrobenzoate, Table X) has been rationalized in terms of a more favorable geometry for participation in **141** and **177** than in 7-norbornenyl and **176**, respectively. There may be other contributing factors, however, including reduced strain in the *exo*-tricyclo[3.2.1.0^{2,4}]octane skeleton (**176**) compared to the endo stereoisomer (**141**)[134] and a possible ground-state deformation of **176** compared to **177** due to H–H repulsion resulting in the carbonium ion center and cyclopropyl group being farther apart. It is tempting to use the large rate enhancement observed for **176**-OBs ionization as proof of formation of the nonclassical ion **178**; however, the product mixture from this ester is very complex and completely rearranged unlike the products obtained



176-OBs



177-OBs



178

from other nonclassical ions. If **178** is formed, it must rearrange to other cations more rapidly than it reacts with solvent; the existence of this ion does not yet rest on firm ground.

Derivatives of **179** provide an opportunity to examine the effects of a slightly different geometry on cyclopropyl participation. As can be seen from the data in Table X, the endo-anti cyclopropyl group of **179-***Op*NB provides[135] a rate enhancement similar in magnitude to that observed in **141-***Op*NB but not significantly different from that afforded by the double bond in derivatives of **180.**[136,139] The greater acceleration observed in the ionization of **141-***Op*NB (factor of *ca.* 10) was not expected because the bridge angle in norbornanes is greater than in bicyclo[2.1.1]hexanes but could possibly result from a tilting of the substituent-bearing bridge toward the cyclopropyl ring in a fashion analogous to that found in **179-***Op*BB.[135,140] Unfortunately, structural studies on a derivative of **141** have not yet been reported; in **155-**OBs[141] and, more pertinently, in *anti*-7-norbornenyl *p*-bromobenzoate,[142] however, the bridge is tilted *away* from the cyclopropane ring and double bond, respectively.

The bridged tricyclo[3.1.1.$0^{2,4}$]hept-6-yl derivative, **181-**OTs, ionizes with much less acceleration than does **179-***Op*NB.[143] The additional bridge in this molecule is expected to alter sufficiently the geometry, rigidity, and strain energy so that a decreased anchimeric assistance is not surprising; in particular, the three-membered ring is "pulled back" so that the carbonium ion center is farther from its plane. The importance of this effect will be discussed elsewhere in this article.

By analogy to derivatives of **141,** which ionize with tremendous assistance to give derivatives of **142,** one expects **179-***Op*NB and **181-**OTs to ionize to **182** and **183,** respectively. Both the rate enhancements and observed products of these reactions are in full accord with this expectation; hydrolysis of **179-***Op*NB (eq 39) gives only **184-**OH and the internal return product **184-***Op*NB.[135] These products are only of the endo stereochemistry despite the propensity for the corresponding ketone to undergo attack from the exo direction.[135] A similar argument was used to support ion **142** (*vide supra*). No unrearranged product was reported in this reaction; however, acetolysis of **181-**OTs does lead to only partial rearrangement (eq 40).[143] These products are in full accord with ion **183.**

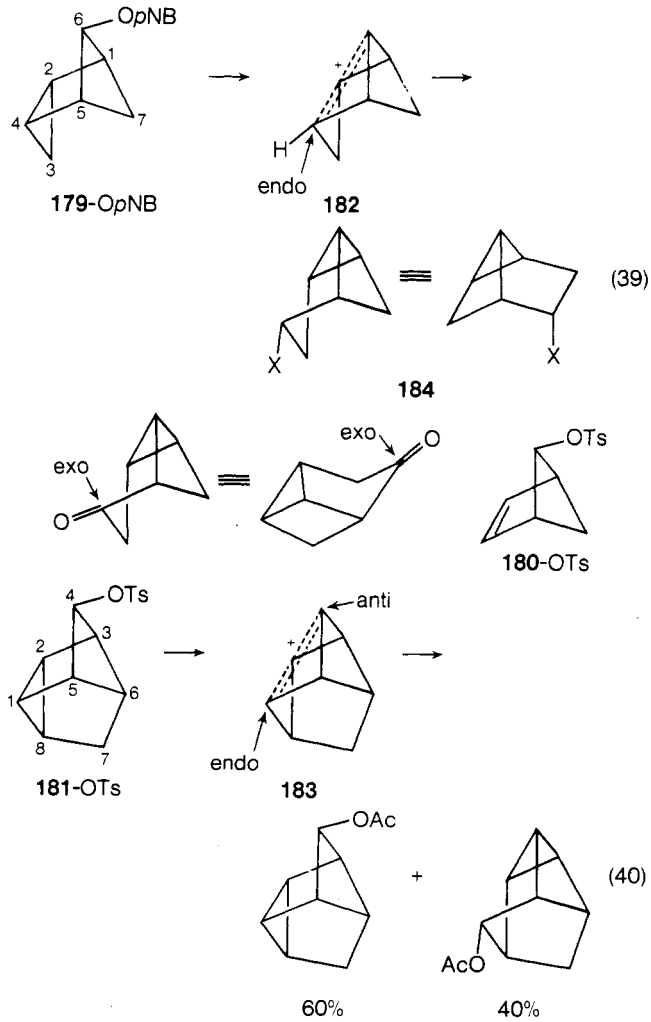
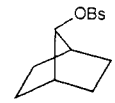
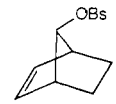
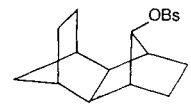
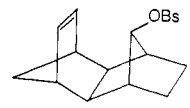
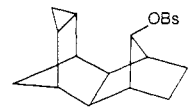
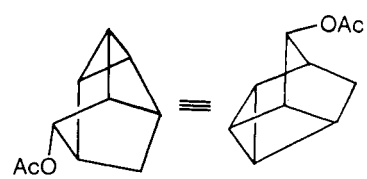


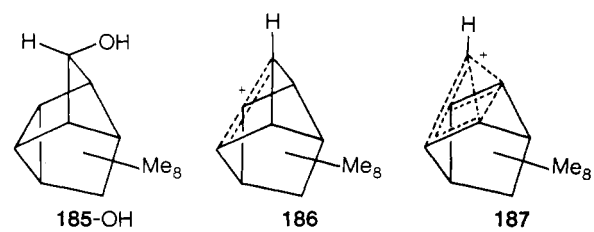
TABLE XIII. Relative Acetolysis Rates for Some Polycyclic Brosylates at 25°

Brosylate	Rel rate	Notes
	1	*a*
	$10^{11.1}$	*a*
	$10^{3.6}$	*b*
	$10^{10.6}$	*c*
	$10^{8.2}$	*d*

[a] Calculated from data given in S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.,* **77,** 4183 (1955); S. Winstein and M. Shatavsky, *ibid.,* **78,** 592 (1956). [b] S. Winstein and R. L. Hansen, *ibid.,* **82,** 6206 (1960). [c] S. Winstein and R. L. Hansen, *Tetrahedron Lett.,* **No. 25,** 4 (1960). [d] Reference 134.



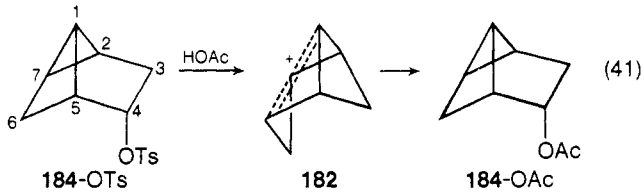
The general occurrence of ions like **182** and **183** has been cast in doubt by Hart and Kuzuya's[144] recent results. Carbonium ion reactions of the polymethylated **185-**OH lead to recovered unrearranged derivatives of **185** in which isotopic label distribution indicates an interaction by the cyclopropyl group to give an ionic intermediate of higher symmetry than **186** for which the structure **187** has been proposed. This type of ion has been predicted[145] to be relatively stable. The nmr spectrum of the



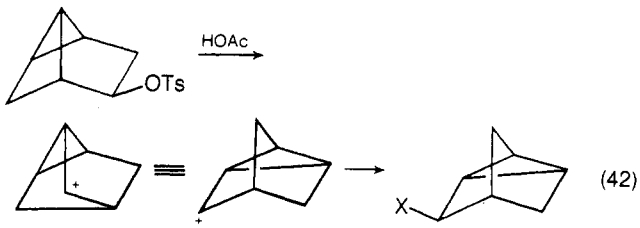
intermediate is consistent with **187** but not with **186.**[144] In view of this report, a reexamination of **181**-OTs ionization is in order.

Ion **182** has also been proposed[146] as the intermediate formed in the acetolysis of **184**-OTs. This ester ionizes with a modest acceleration by the cyclopropyl group (Table XIV) and gives **184**-OAc almost exclusively (97%) (eq 41). Although a deuterium label originally on C-4 is distributed equally between C-2 and C-4 in the isolated product, these two positions account for only half the original label, and the two methylene groups are scrambled equally. It thus appears that carbons 2, 4, 5 and 7 are scrambled in the cation derived from **184**-OTs. Such scrambling might well occur through an ion analogous to **187,** through a "bridge flip" of **182,** or through classical cations. The different products obtained from "**182**" by Masamune, *et al.*,[135] and by Lustgarten[146] and the intriguing possibilities raised by Lustgarten's labeling studies indicate an obvious need for more work on this ion and its precursors.

The exo isomer of **184**-OTs ionizes with C–C participation to give the nortricyclyl cation and ultimately nortricyclyl derivatives (eq 42).



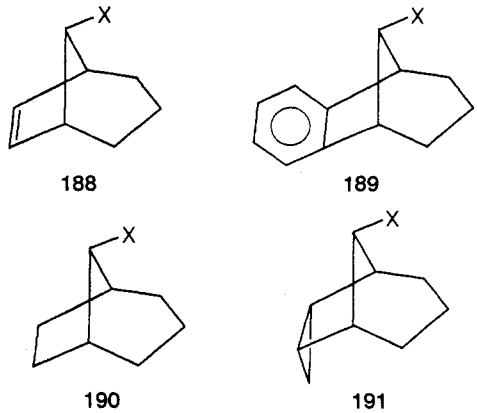
184-OTs **182** **184**-OAc (41)



(42)

X = OAc, OTs

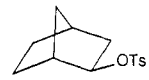
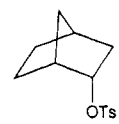
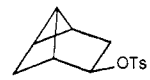
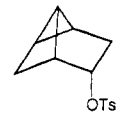
Double bond and benzene ring participation have been examined in derivatives of **188**[147] and **189**[148] and, in accord with the idea that increased internal bond angle at a carbonium ion site will reduce anchimeric assistance,[149] **188**-OTs and **189**-OTs ionize less rapidly than the corresponding norbornenyl derivatives (both by factors of *ca.* 10^3 at 25°) but still faster than the saturated **190**-OTs[150] (by factors of *ca.* 10^5 and 10, respectively). Remote cyclopropyl participation in this system, *i.e.*, in **191,** has not



188 **189** **190** **191**

yet been reported, but the recent synthesis[151] of a useful derivative, **191**-O-*t*-Bu, will undoubtedly be followed by solvolysis studies.

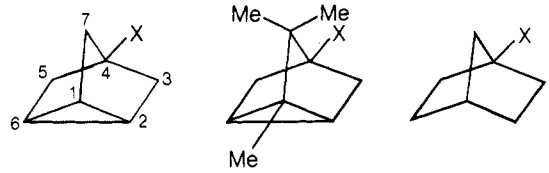
TABLE XIV. Relative Acetolysis Rates of Some Polycyclic Tosylates at 25°[a]

Tosylate	Rel rate	Tosylate	Rel rate
	280		1
	7600		13

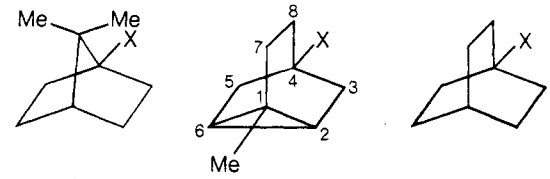
[a] Data taken from ref 146.

3. 4-Nortricyclyl Derivatives

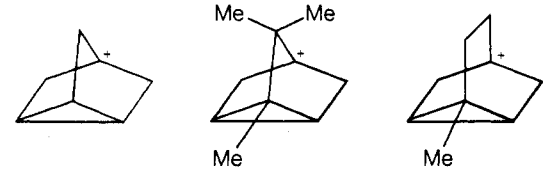
The symmetrical 4-nortricyclyl system (**192**) and its 1,7,7-trimethyl analog (**193**) have the ionization center rigidly fixed at about 2.1 Å directly above the face of the cyclopropane ring.[152] Both **192**-OTf[153] and **193**-OTf solvolyze to give only products of retained structure much more slowly than the related bridgehead derivatives **194**-OTf and **195**-OTf whose ionization is also severely retarded compared to other tertiary derivatives (Table XV).[154] In fact, **192** and **193** are among the least reactive systems known in carbonium ion formation.[155-158] Expansion of the ring system by one carbon atom to **196** increases the ionization rate, but compared to **197** the rate is still retarded.



192 **193** **194**



195 **196** **197**

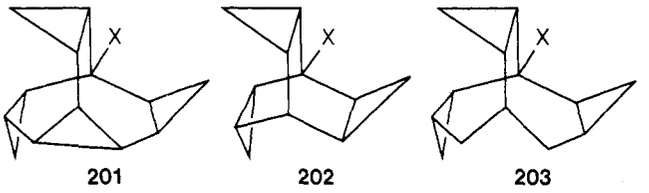


198 **199** **200**

Obviously the cyclopropane rings in ions **198–200** provide no stabilization to the positive charge; it might even by argued that the ions are electronically destabilized by the three-membered rings. However, the observed retardation in ionization rate of derivatives of **192, 193,** and **196** can be completely accounted for by the increased strain energy of these systems relative to their bicyclic analogs, and therefore no inductive deceleration is required.[155-157]

In another system, **201,** the ionization rate would not appear to be retarded by the remote cyclopropane ring. Derivatives of this system ionize more rapidly than those of **197** (factor of 10^{11}) and of **202** (factor of 10^2).[159] The significance of these results is clouded by the presence of the three adjacent cyclopropane rings, which are expected to enhance the ionization rate,[7] and by the great-

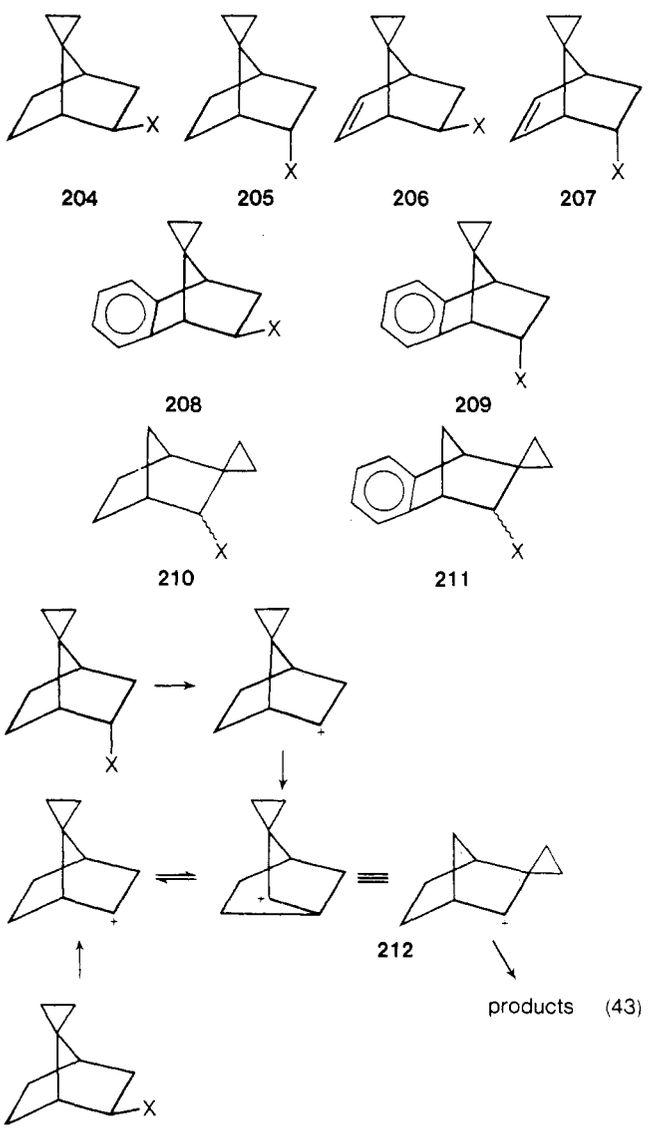
er flexibility of **201** compared to its smaller analog **202.** A comparison with **203** would be more meaningful.



201 **202** **203**

4. *Spiro[cyclopropane-1,7'-norbornan]-2'-yl Derivatives*

Derivatives of the three endo systems **205, 207,** and **209** are possible candidates for cyclopropyl participation, which, if present, would be expected to be manifested in a decreased exo/endo rate ratio for the appropriate pairs of compounds. The data in Table XVI clearly illustrate the ineffectiveness of the cyclopropane ring as a neighboring group in these molecules. The ionization rate of each endo isomer is decreased from that of the most appropriate endo model, whereas the ionization rates of the corresponding exo isomers are slightly increased resulting in an enhanced exo/endo ratio.[160,161] Derivatives of **204, 205, 208,** and **209** all rearrange on solvolysis to give mixtures of exo and endo spiro[cyclopropane-1,3'-norbornan]-2'-yl derivatives **210** and **211; 206** and **207** give only *derivatives of* **206.**[160,161] *In both aspects* (ionization rates and product composition), all six systems are very much like their respective unsubstituted norbornyl parents. A scheme (eq 43) which accounts for these results is shown below employing classical cations only for convenience.



204 **205** **206** **207**

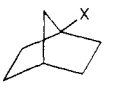
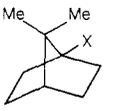
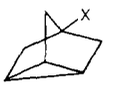
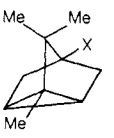
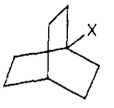
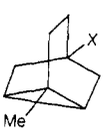
208 **209**

210 **211**

212

products (43)

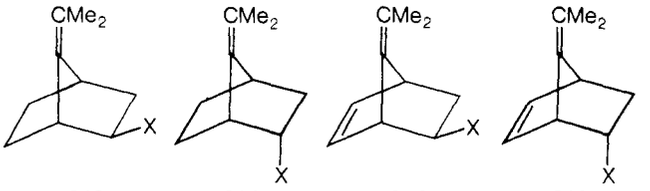
TABLE XV. Relative Solvolysis Rates of Some Bridgehead Derivatives[a]

Ring system	Rel rate	Notes
$Me_3C—X$	1	*b*
	10^{-12}	*c*
	10^{-12}	*d*
	10^{-17}	*c*
	10^{-17}	*d*
	10^{-7}	*b*
	10^{-9}	*d*

[a] Data at 25° from ref 157 unless otherwise noted. [b] Based on reactivity of the bromide in 80% aqueous ethanol. [c] Reactivity of the triflates at 100° in 50% aqueous ethanol as given in ref 156. [d] Reactivity of the triflates in 60% aqueous ethanol.

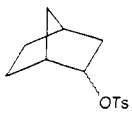
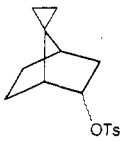
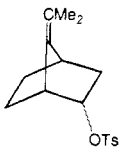
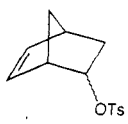
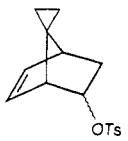
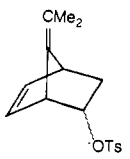
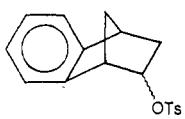
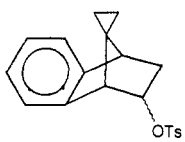
The small rate enhancement observed for derivatives of **204, 206,** and **208** is probably due to the stabilization afforded the cyclopropylcarbinyl cation **212** (or alternatively the corresponding nonclassical ion). Solvolysis of derivatives of **210** and **211,** which are predicted[160] to exhibit greater cyclopropyl participation than **205,** show the controlling influence of the cyclopropyl group by virtue of a large rate enhancement and a swamping of the usual exo/endo ratio, thus demonstrating the effectiveness of the stabilization afforded **212.**[160,161] The corresponding olefins, *e.g.,* **213,** behave similarly.[162]

The ineffectiveness of the cyclopropyl groups in **205** and **207** as neighboring groups is in complete contrast to the behavior of the corresponding olefinic derivatives **213–216.**[163] Both the kinetic data (Table XVI) and product composition demonstrate beyond doubt that the 7-isopropylidene groups in **214-OTs** and **216-OTs** participate in the ionization of these esters. The exo isomers solvolyze in the same manner as other *exo*-norbornyl and *exo*-norbornenyl derivatives.



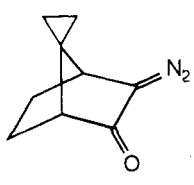
213 **214** **215** **216**

TABLE XVI. Solvolysis Rate Constants for Some 2-Norbornyl Tosylates[a]

Tosylate	Solvolysis rate constants ($\times 10^5$) Exo	Endo	k_{exo}/k_{endo}	Notes
	2,330	8.28	280	b
	7,880	4.40	1,800	c
	10,200	2260	4.5	d, e
	1,500	0.19	7,900	f
	4,050	0.175	23,000	c
	3,200	370	8.6	d, e
	671,000	120	5,400	g, h
	1,130,000	99.5	11,350	g, h

[a] Acetolysis at 25° unless otherwise stated. [b] P. v. R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Amer. Chem. Soc.*, **87**, 375 (1965). [c] Reference 160. [d] Based on the reported rate ratio at 30°. [e] Reference 163. [f] S. Winstein and M. Shatavsky, *J. Amer. Chem. Soc.*, **78**, 592 (1956). [g] Solvolysis in 80% acetone at 100°. [h] Reference 161.

In contrast, the diazo ketone **217** reacts[164] with acids to give a mixture of products including **218** which results from interaction of the cyclopropyl group with the cation center. It has been proposed[164] that **217** and **205** differ because the ketone group destabilizes an adjacent positive charge so that stabilization in the transition state is required and simple ionization to **219** cannot occur.



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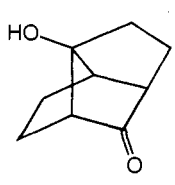

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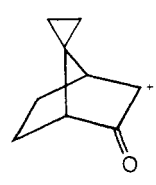
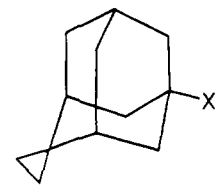


219

5. *Miscellaneous Rigid Systems*

Chloride **220** solvolyzes at about the same rate as the dimethyl analog **221** and about half as fast as 1-adamantyl chloride.[165] All three halides solvolyze without rearrangement. It is thus clear that the cyclopropyl ring in **220**-Cl does not interact with the remote positive charge, but this is not surprising considering the distance between these centers (measured from Dreiding stereomodels to be at least 3 Å).



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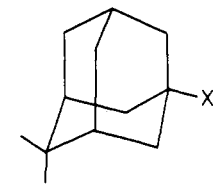
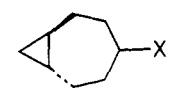


221

222-OBs acetolyzes to give **222**-OAc and olefin **223** at about the same rate as for the unassisted ionization of its two cis stereoisomers (Table V).[66] The absence of cyclopropyl interaction in **222**-OBs ionization is at first glance puzzling since the molecule is rigid and therefore does not have to become oriented in a specific conformation for interaction as do its cis isomers, and because the electron-donating bent bond of the cyclopropane ring is pointed directly at the ionization center which is about 2.4 Å from it—almost the same geometrical features found in **141**-*Op*NB, the ionization of which is tremendously accelerated.[111-115] In **141**, however, the developing p orbital is pointed directly into the sphere of influence of the cyclopropane ring (**224**), whereas in **222** it points orthogonally to this "preferred" direction into a region of space devoid of appreciable cyclopropane ring electron density (**225**). The nearest approach of the cyclopropane ring in **225** to the developing p orbital is at the carbon atom, a nodal position in the orbital, whereas in **224** the cyclopropane ring orbital approaches a developing lobe of the p orbital. The possibility that one cyclopropane ring might overlap with both lobes of the p orbital in **225** can be ruled out on grounds of symmetry.[66]



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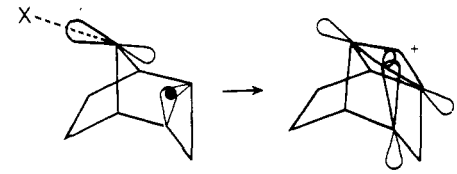

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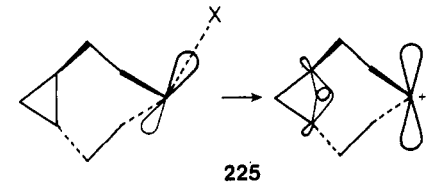
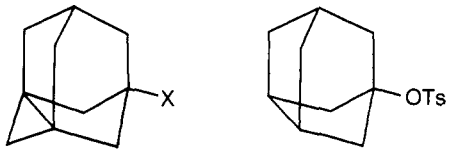


225

The exceptionally high reactivity of the bridgehead substituted system **226** has recently been noted and ascribed to cyclopropyl participation.[166] It should be noted that this system also incorporates a *cis*-bicyclo[3.1.0]hex-3-yl system locked in a favorable chair conformation. The anchimeric assistance by the cyclopropyl group of **226** might well prove to be even greater than that observed in **141** since the ionization rate of the cor-

responding saturated ester **227**-OTs is only *ca.* 10^3–10^4 greater than that of 7-norbornyl tosylate at 100°.[167]



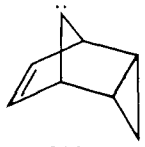
226 **227**-OTs

III. Interaction of Cyclopropane Rings with Other Electron-Deficient Centers

A. Carbene Centers

Theoretical studies[168] have predicted that the carbene **228** should be most stable in a distorted geometry in which the carbene center is tilted toward the cyclopropyl group so as to increase its interaction with the edge of the cyclopropane ring. This stabilization is afforded to only the singlet state of the carbene and is analogous to, but of less importance than, the situation in the corresponding carbonium ions **160** and **167**.[37]

The epimeric tosylhydrazones **229** and **230** decompose to give quite different mixtures of products.[117] The exo isomer gives a low yield of three isomeric bicyclo[3.3.0]octadienes as the only identified volatile products presumably by the mechanism shown in eq 44. The



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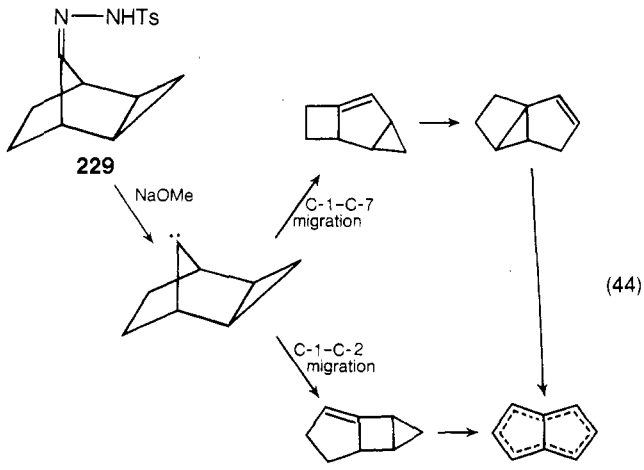
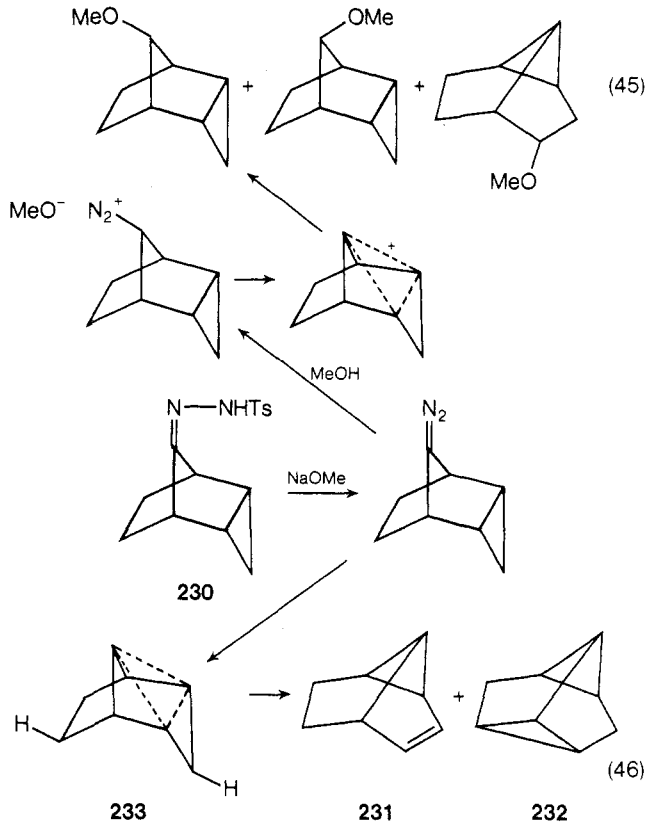


(44)

endo isomer gives a much higher yield of a mixture of **141**-OMe, **144**-OMe, **149**-OMe, **231**, and **232**; the ratio of ether to hydrocarbon products is dependent on reaction conditions. The ether products are believed to arise through the relatively stable trishomocyclopropenyl cation **142** (eq 45). The absence of bicyclo[3.3.0]octadienes in the hydrocarbon product demonstrates the interaction between the carbene center and the edge of the endo cyclopropyl group (eq 46) rather than by the adjacent C–C bonds as is found in the decomposition of **229**. Although it is clear that a long-range cyclopropyl–carbene interaction occurs, the nature of the intermediate formulated as **233** is not certain.

In contrast, bicyclo[3.1.0]hex-3-yl tosylhydrazone gives no indication[169] of cyclopropyl interaction with the incipient carbene center. The only product formed is bicyclo[3.1.0]hex-2-ene; presumably carbene insertion into the C–H bond of the adjacent carbon atom to give this olefin



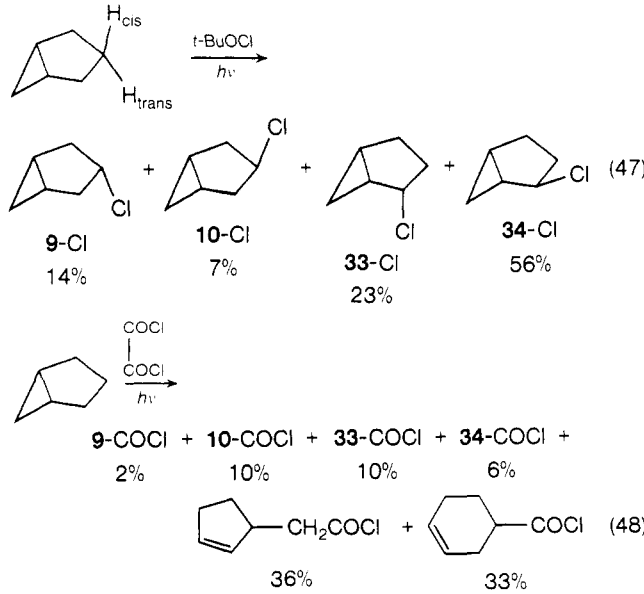
(45)

(46)

is a much more energetically favorable process and one that is not available to **233**.

B. Radical Centers

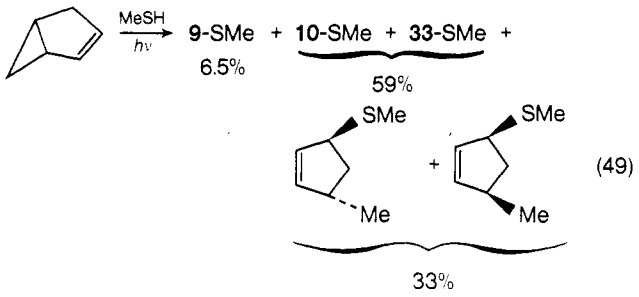
Free radical chlorination of bicyclo[3.1.0]hexane gives a mixture of the four chlorobicyclo[3.1.0]hexanes arising from abstraction of hydrogen atoms from C-2 and less predominantly from C-3 (eq 47).[170] Abstraction from C-1 or C-6 was not detected. Chloroformylation gives a more complex mixture; the major products are rearranged, bicyclo[3.1.0]hexyl derivatives comprising only a minor amount (*ca.* 30%) of the product (eq 48). The predominance of abstraction from C-2 is thought to be a result of greater cyclopropyl stabilization of the adjacent radical paralleling the stability order found in the respective carbonium ions. The only indication that some stabilizing de-



(47)

(48)

localized character might be present for **234** is the 2:1 ratio of **9**-Cl:**10**-Cl obtained in the chlorination experiment despite the expected steric hindrance to abstraction of H-3_{trans} from the predominant boat conformer[32,39,57,171-174] of the hydrocarbon. In contrast the **9**-COCl:**10**-COCl ratio obtained in the chloroformylation is about 1:5. In a similar fashion free radical addition of methanethiol to bicyclo[3.1.0]hex-2-ene[175] gives products (eq 49) which can be explained solely on the basis of

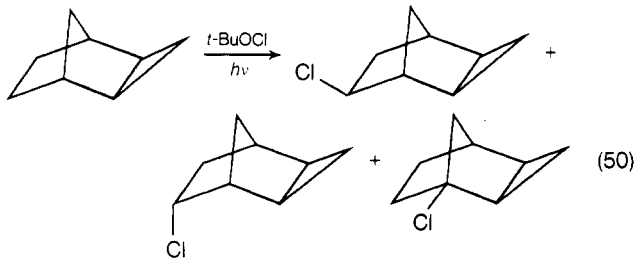


(49)

classical radical intermediates; in fact, a methylthio derivative of **235** was ruled out as the sole product-determining intermediate. These results provide no strong support for a trishomocyclopropenyl radical, **236,** as a particularly stable intermediate but do not conclusively prove its absence

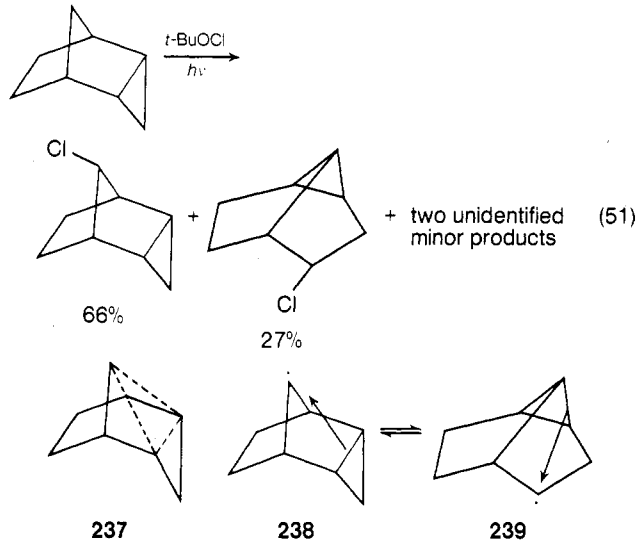
234 **235** **236**

A more distinct example of long-range interaction between a cyclopropyl group and a free radical center has recently been described.[115] Abstraction of hydrogen from *exo*-tricyclo[3.2.1.$0^{2,4}$]octane occurs only at C-1 and C-6 (eq 50) and, except for the C-1 abstraction which has not yet been explained, is very similar to the behavior of other norbornanes.[176] In this reaction no evidence of cyclopropyl interaction with radical intermediates was detected.



(50)

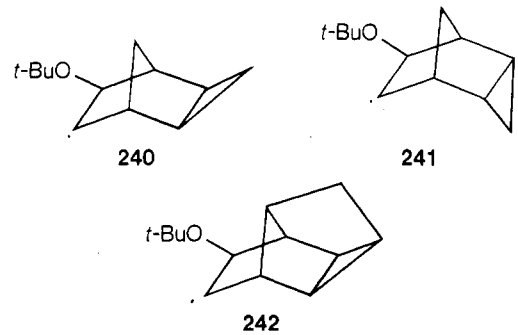
The endo isomer provides at least 93% C-8 abstraction, however, to give **141**-Cl and **149**-Cl as the only identified products (eq 51). Two minor components, 5 and 2%, were not characterized. The high regiospecificity of abstraction at C-8 and stereospecificity of radical recombination at both C-4 and C-8 can conveniently be explained in terms of edge interaction by the cyclopropane ring, but approach at either site might also be affected by steric factors. Whether the fully delocalized intermediate **237** or a rapidly equilibrating mixture of essentially classical radicals with a weak transannular interaction by the three-membered ring (**238** and **239**) is present is not yet clear, but, based on the sensitivity of product composition to *tert*-butyl hypochlorite concentration, **237** can be ruled out as the sole product-determining intermediate. It should be noted that the 7-norbornenyl radical is generally thought to be nonclassical.[177]



(51)

237 **238** **239**

In contrast, the two olefins, *exo*- and *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene, and also deltacyclene give only the products of simple cis and trans addition to the double bonds.[178] No hydrogen abstraction was detected despite the above-noted ability of the endo cyclopropyl group to interact with radical centers at C-8. It is equally evident that the cyclopropyl groups in the presumed intermediates, **240, 241** and **242,** do not interact with the radical centers. This behavior is in complete contrast to that found in the corresponding carbonium ions and reviewed elsewhere in this article.



240 **241** **242**

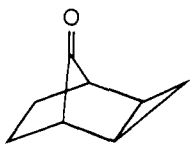
C. Other Centers

Cyclopropane rings have long been known[2,3,179] for their ability to extend[180-194] and perhaps even to transmit[195-198] conjugation from the studies of their interactions with adjacent carbonyl groups,[180-187] double bonds,[188-190] and aromatic rings[191-194] in both the ground (ref 179, 181, 183–188, 190, 191, 195–197) and excited (ref 180, 182, 189, 192–194, 198) states. Some of these studies have been summarized[199] and have recently been supported by theoretical considerations.[200] Some groups have concluded that optimum interaction is not dependent on geometry,[188,192] other groups that geometry is an important optimizing factor,[180-186,189,191] and still others that the geometrical relationship between the interacting groups becomes more important as the interacting substituent on the three-membered ring becomes more electron demanding.[193,200b]

Interactions between cyclopropyl groups and more distant unsaturated centers have been less widely studied but have proven to be very sensitive to geometrical changes. The uv spectrum of the exo ketone **243** is almost identical with that of 7-norbornanone.[201a] The spectrum of the endo ketone **146** is different, however;[201a] a hypsochromic shift of *ca.* 15 nm for the n $\rightarrow$ π^* transi-

tion and a bathochromic shift for the $\pi \rightarrow \pi^*$ (or n $\rightarrow$ σ^*[202]) transition is noted for this molecule relative to 7-norbornanone. In both respects **146** displays the same behavior as 7-norbornenone for which the spectral parameters are fully accounted by theoretical calculations involving a σ-type interaction between the π bonds of the carbonyl and olefinic groups,[37,203,204] despite the fact that most β,γ-unsaturated ketones display shifts in the opposite direction for the n $\rightarrow$ π^* transition.[205] A similar interaction has been invoked to explain the uv spectrum of **146** and has found recent theoretical support.[204] The bent cyclopropane ring bonds of **243** are directed away from the carbonyl group precluding any direct interaction.

A similar pattern has been observed[201b] for the three ketones **244–246.** The spectrum of **244** is very similar to those of **243** and 7-norbornanone, but those of **245** and **246** more closely resemble the spectra of **146** and 7-norbornenone indicating the interaction between the carbonyl group and the double bond and cyclopropane ring, respectively. Uv spectroscopy has also led to the conclusion that a cyclopropyl–carbonyl interaction occurs in the two isomeric *cis*- and *trans*-bicyclo[6.1.0]nonan-3-ones[206] but not in the bicyclo[6.1.0]nonan-4-ones[206] nor in bicyclo[3.1.0]hexan-3-one[33] in which the preferred shallow-boat conformation of the bicyclo[3.1.0]hexane ring[32,39,57,171-174] presumably precludes any interaction.



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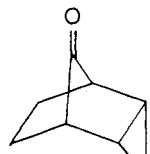

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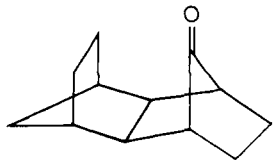

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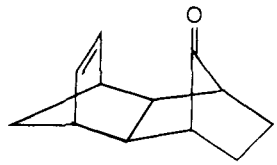

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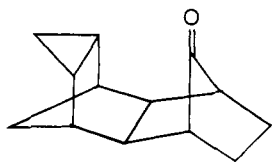
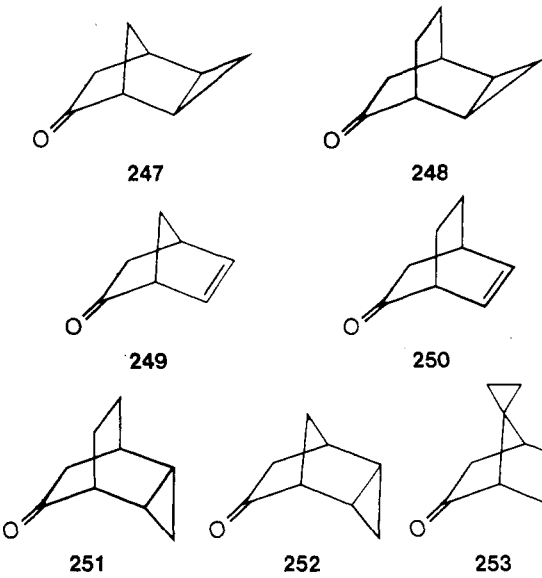


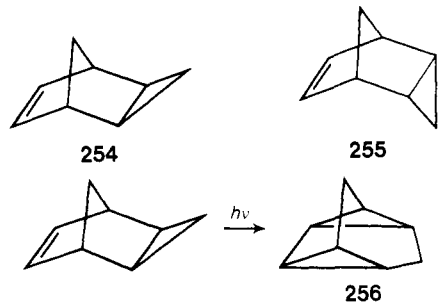
246

Optically active samples of **247** and **248** give CD spectra which are similar to those of the corresponding olefins, **249** and **250,** and much more intense than those of 2-norbornanone and **251.**[207] This behavior is characteristic of β,γ-unsaturated ketones with interacting chromophores[208] and demonstrates the stereospecificity of the interaction (compare **248** and **251**). Unfortunately the spectrum of **252** has not yet been reported,[207] but that of **253**[207] demonstrates no interaction.

The interaction of cyclopropyl groups with distant double bonds has also been demonstrated recently[209] in the photoelectron spectra of **254, 255,** and related molecules. As expected only **254** shows an interaction between the two groups. This interaction is predominantly of the through-space type rather than through the σ bonds. Despite the conclusions of the photoelectron spectroscopic investigations, the uv spectra of **254, 255,** and norbornene give no indication of any special character for **254.**[210] On the other hand, **254, 255,** and related compounds readily isomerize (*e.g.*, eq 52) upon photolysis,[121,210,211] demonstrating that this process requires no special orientation of the cyclopropyl group.



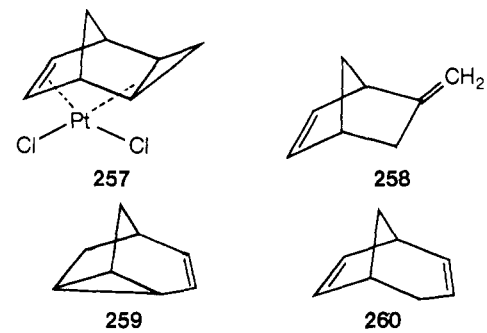
247 **248** **249** **250** **251** **252** **253**



254 **255** **256**

(52)

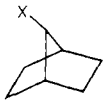
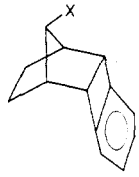
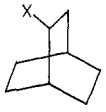
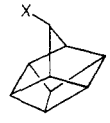
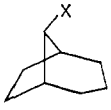
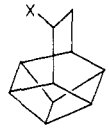
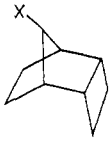
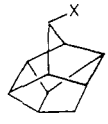
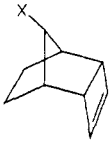
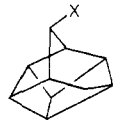
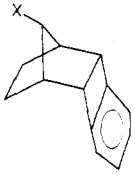
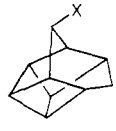
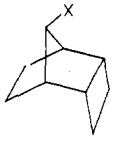
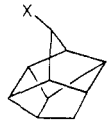
Hydrocarbons **254** and **255** are also of some interest because of their potential for forming bidentate complexes with metal atoms by involvement of both the double bond and the cyclopropyl group.[212] Reaction of **254** with either $[(C_2H_4)_2PtCl_2]_2$ or $K[(C_2H_4)_2PtCl_3]$ gives the stable complex **257,**[213a] reaction with $IrCl(CO)(Ph_3P)_2$ gives **258,**[213a] reaction with $Rh_2(CO)_4Cl_2$ gives **256,**[213b] and reaction with $(Ph_3P)_3RhCl$ gives a mixture of **256, 259,** and **260;**[214] presumably cyclopropane–metal complexes or insertion compounds are intermediates in the formation of **256, 258, 259,** and **260.**[213,214]



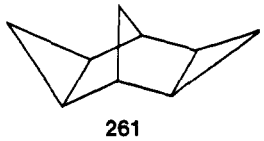
257 **258** **259** **260**

The endo olefin **255** fails to react with any of the above reagents. In accord with the idea that the metal atom will complex preferentially with the edge of the cyclopropane ring, the exo,exo dicyclopropyl compound **261** also reacts with $IrCl(CO)(Ph_3P)_2$ (to give **262**)[213a] and with either $[(C_2H_4)_2PtCl_2]_2$ or $K[(C_2H_4)_2PtCl_3]$ (to give **263**),[213a] whereas the exo,endo epimer **264** is unreactive. The failure of the cyclopropyl group in **262** to open has been explained on the basis that this olefin cannot complex to the metal as a bidentate ligand for steric reasons.[213a] It

TABLE XVII. Relative Acetolysis Rates of Some Cyclobutyl Derivatives at 25°[a,b]

Compound	Rel rate	Notes	Compound	Rel rate	Notes
	1	c		1.1	g, h
	10^9	d		10^6	i
	10^8	e		10^{12}	j, k
	2×10^4	f		5×10^5	l
	6×10^5	f		2×10^8	j, k
	7×10^4	g, h		10^7	j, k
	1.2	f		2×10^6	l

[a] In acetic acid buffered with sodium acetate. [b] Rate comparison made on tosylates unless otherwise stated. [c] S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, **77**, 4183 (1955). [d] H. L. Goering and M. F. Sloan, *ibid.*, **83**, 1992 (1961). [e] Reference 150. [f] Reference 218. [g] Comparison made on brosylates. [h] Reference 219. [i] Reference 220. [j] Comparison made on mesylates. [k] Reference 221. [l] Reference 222.



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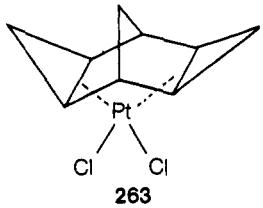
262



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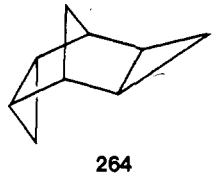


264

should be noted, however, that $Mo(CO)_6$, $W(CO)_6$, Cu_2Cl_2, $RhCl(CO)(Ph_3P)_2$, $(PhCN)_2PdCl_2$, $IrHCl_2(Ph_3P)_3$, and $Rh_2(nor\text{-}C_7H_8)_2Cl_2$ fail to react with **254, 255,** or **261.**[213a] $AgNO_3$ will form complexes with **254** and **255,** but it was felt that no interaction between the three-membered ring and the Ag atom occurs; **261** forms no $AgNO_3$ complex.[215]

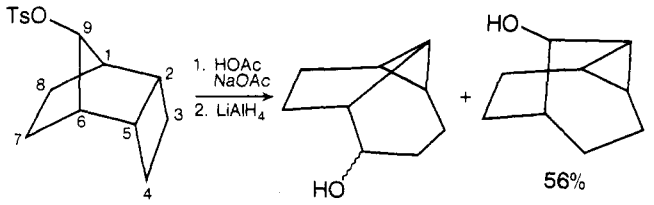
A final example of long-range interactions with cyclopropane rings comes from the recently reported examples of hydrogen bonding between O–H groups and cyclopropane rings.[173,216] The three-membered ring is less able to act as an acceptor site for hydrogen bonds than is a double bond or an aromatic ring and is quite stereospecific in this type of interaction. The preferred interaction is with the bent bond edge of the cyclopropyl group in a symmetrical manner, in complete analogy to the stabilization of remote carbonium ion centers by three-membered rings.

IV. Interaction by Cyclobutane Rings

By analogy to its smaller homolog, the cyclobutane ring is also predicted[217] to have bent C–C bonds with an abnormally high p character and is therefore expected to act as a neighboring group in a similar fashion. A relatively small number of studies have been reported.

Acetolysis of **265**-OTs proceeds with a large anchimeric acceleration[218] (Table XVII) which is made even more efficient by unsaturation in the four-membered ring (**266**-OTs[218] and **267**-OBs[219]). In contrast, the syn epimers **268**-OTs[218] and **269**-OBs[219] ionize without significant acceleration.

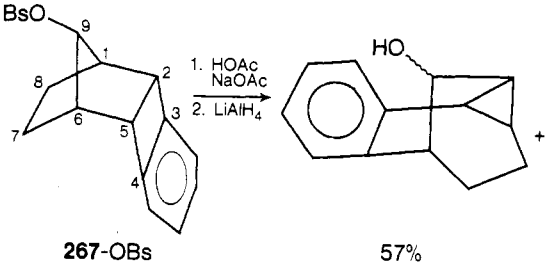
The product mixtures from **265**-OTs and **267**-OBs are much more complex than that from derivatives of **141,** indicating a flatter energy surface for the derived cations. The observed rate enhancements suggest formation of



265-OTs

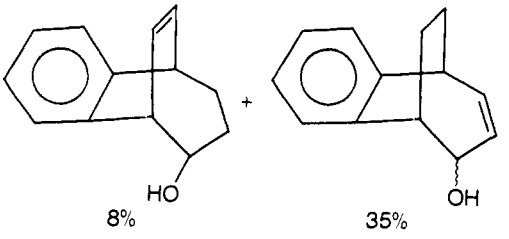
273
44%

(53)



267-OBs

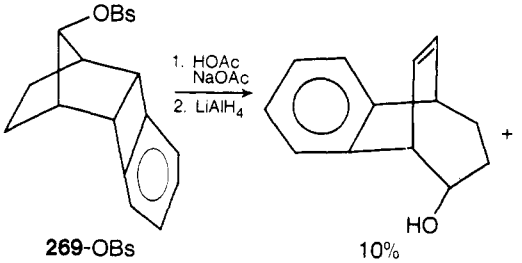
57%



8%

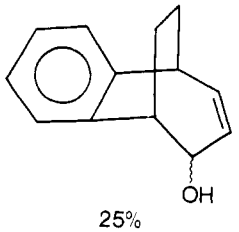
35%

(54)



269-OBs

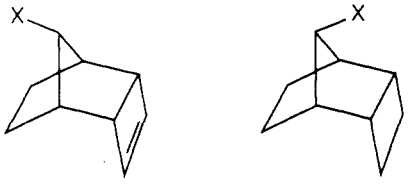
10%



25%

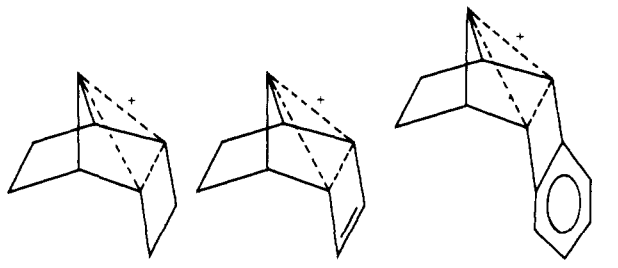
+ at least 17 unidentified components (65%)

(55)

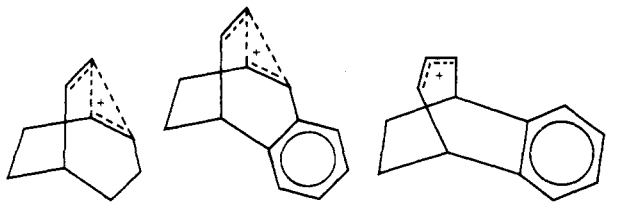


266 268

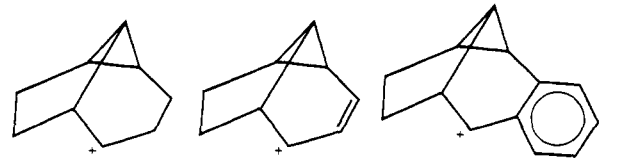
the nonclassical ions **270, 271,** and **272** by cyclobutane edge participation, but there is no other evidence for these ions. The stereochemistry of **273**-OH derived from **265**-OTs (eq 53) is crucial to the argument but has not yet been determined. If **270** and **272** are formed, it is clear that they readily rearrange, presumably to **274, 275,** and **276.** Ion **272** is particularly interesting since, if it is present, its enhanced rate of formation indicates stabilization of a trishomocyclopropenyl cation by phenyl substitution sought, but not observed, by previous workers.[45] The direct formation of classical cations **276, 277,** and **278** is an alternative interpretation of the observed anchimeric acceleration particularly attractive for **266**-OTs and **267**-OTs. The elucidation of the intermediates in these reactions remains to be finalized but is made more difficult by the large numbers of and relative instability of some of the products.



270 271 272

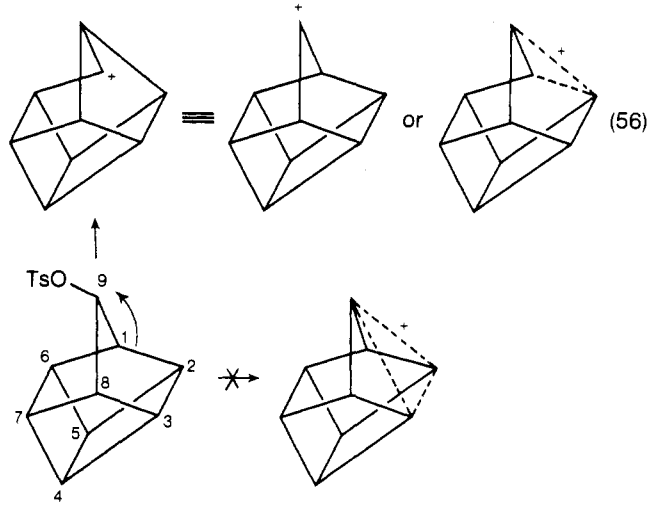


273 274 275



276 277 278

The pertinent homocubyl and bishomocubyl derivatives shown in Table XVII also ionize with large rate enhancements but apparently do so without long-range cyclobutane edge participation.[220-222] Labeling studies and product analysis demonstrate that the ionizations occur with 1,2-migration of a bond of an adjacent, rather than a remote, cyclobutane ring to give in some cases ions with multiple degeneracy as illustrated in eq 56 for homocubyl tosylate. These studies have recently been reviewed.[122]

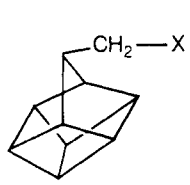


(56)

279-OTs

Remote cyclobutane ring participation in the ionization of these homocubane derivatives is not observed because participation by a bond of the adjacent cyclobutane ring is a more efficient process; participation in cyclobutylcarbinyl derivatives has been noted.[223] The efficiency of the remote cyclobutane interaction present in **265** is presumably decreased in **279** because the additional bridging alters the geometry so that the cation center is far removed from the plane of the remote four-membered ring, and overlap between the bent-bond edge

of this ring and the carbonium ion orbital is reduced. Surprisingly **280**-OTs, in which this factor should be at least partially overcome, gives no indication of C-2–C-3 bond participation but rather of participation by the C-1–C-2 bond.[224] In this regard the acetolysis of **281**-OTs, which is very similar to **150**, should prove informative; **281**-OTs has not yet been reported although the corresponding ketone is known.[225]



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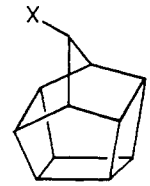
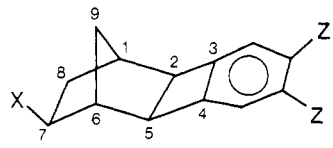


281

Remote cyclobutane ring participation is apparently absent in **282**-OTs–**285**-OTs which are characterized by low exo/endo rate ratios and relatively small ρ values upon ionization in acetic and formic acids.[226] Weak C-5–C-6 participation is proposed for these ionizations.



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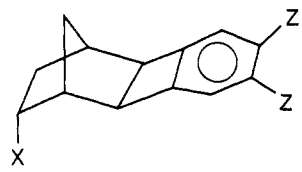

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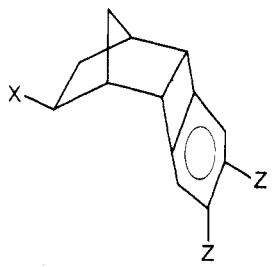

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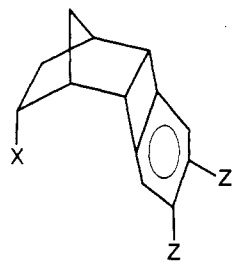


285

Z = H, NO_2, OMe

V. Geometrical Factors Which Influence Interactions

The concepts of homoconjugation and homoaromaticity developed by Winstein and others[6a,9b] have now gained wide acceptance. These ideas predict stabilization of ions or molecules by through-space delocalization of electrons, thereby bypassing the formal bonding framework and negating the normal insulating effect of saturated atoms. Of immediate interest to this review are the homocyclopropylcarbinyl, homocyclopropenyl, and, to a lesser extent, homotropylium cations which are formed from many of the systems discussed in this article and which are predicted to be relatively stable if the correct geometry is adopted. The remainder of this section will be devoted to a discussion of the geometrical features which determine the extent of cyclopropyl interaction with remote carbonium ion and other electron-deficient centers.

A. Orientation of the Cyclopropyl Group

The cyclopropane ring stabilizes a carbonium ion presumably by overlap of its bent C–C bonds, which are high in p character, with the vacant p orbital of the cation. Of the infinite number of directions from which an electrophile may approach a cyclopropane ring, edge (**286**), face (**287**), and corner (**288**) approaches may be readily identi-

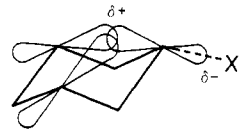
286 **287** **288**

fied. From the extensive studies on the addition of electrophiles, particularly protons, to three-membered rings, it appears that edge approach is the preferred mode.[227] The studies herein reviewed have much in common with the studies on electrophilic attack and generally support their conclusions.

The molecules discussed in this article which are sterically arranged for interaction between only the face of the cyclopropane ring and the developing positive charge, *e.g.*, **155**-OBs, **192**-OTf, **193**-OTf, and **196**-OTf, give no evidence to indicate that such an interaction (**287**) occurs despite the Walsh picture (**1b**) which predicts appreciable electron density in the center of the ring.

On the other hand, molecules such as **9**-OTs, **141**-O*p*NB, **176**-OBs, **179**-O*p*NB, **184**-OTs, and **226** are geometrically ideal for a symmetric σ overlap between the bent-bond edge of the cyclopropane ring and the developing carbonium ion orbital, *e.g.*, **289**. The large rate enhancements observed for the ionization of at least some of these molecules leave no doubt concerning the effectiveness of this stabilizing interaction, but the values of the observed enhancements and those of the respective olefinic and benzo analogs emphasize the sensitivity of this edge interaction to other factors.

It is clear, however, that interaction with the corner of a three-membered ring is also effective. Molecules such as **104**-OBs and **125**-OTs display this type of interaction giving homocyclopropylcarbinyl cations, *e.g.*, **127** *via* **290**; they do not interact with the edge of the three-membered ring to form ions like **112**, presumably because the distortion required to form this trishomocyclopropenyl cation offsets the anticipated aromatic stabilization.



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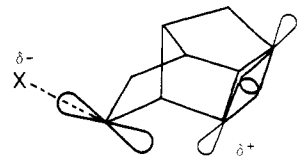

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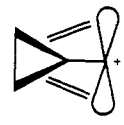
The relatively stable bisected conformation of cyclopropylcarbinyl cations (**291**)[7,228] in which the cation orbital interacts simultaneously with both flanking cyclopropane ring bonds has no well-established analog in homocyclopropylcarbinyl cations (*e.g.*, **292**) although the possibility has been explored.[13,14,17] No rigid system with the correct geometry for formation of only **292** has yet been reported, and in conformationally mobile molecules the necessary conformational constraints require too much energy. Calculations on related systems[19b] predict that such a π-type interaction will decrease much more rapidly as the centers are moved farther apart than will the σ-type interaction observed for **9** and its bridged derivatives. At distances >*ca.* 2 Å, the σ-type interaction is predicted to be more important than the π-type.



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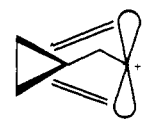
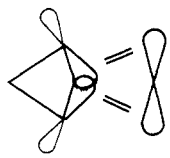


292

The possibility that the edge of a cyclopropane ring might interact with a distant p orbital lying parallel to it has been explored.[66] No such interaction (**293**) was

noted; however, this was anticipated because the maximum density of the cyclopropane ring bond lies adjacent to a node in the p orbital, and because a stabilizing interaction at one end of the p orbital should be balanced by a destabilizing interaction at the other end (**294**).



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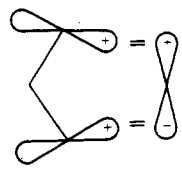
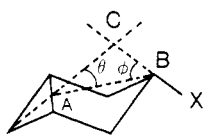


294

B. Interatomic Distances and Angles

It is obvious that the ability of a neighboring group to interact through space with a carbonium ion will be greatly affected by the potential overlap of the appropriate orbitals. This overlap in turn is determined by the interatomic distances and valency angles within the molecule. In conformationally mobile systems these factors are very difficult to assess, but they are more readily analyzed in rigid molecules.

The most dramatic examples of long-range cyclopropylcarbonium ion interactions all (except **176**) involve the *cis*-bicyclo[3.1.0]hex-3-yl skeleton locked in a chair conformation which approaches the most stable geometry calculated[37,39] for the nonclassical bicyclo[3.1.0]hexyl cation **11.** Unfortunately very few of these systems have been the subject of accurate structural determinations so that the critical distances and angles (AB, θ, and ϕ in **295**) are, in the main, unknown. Quantitative estimation of these geometric parameters from the structures of related molecules or from molecular models is hazardous because of the proclivity of some of these skeleta to be asymmetric, *i.e.*, $\alpha \neq \beta$ in **296.** This distortion is particularly well known for substituted norbornanes (ref 141, 142, 148, 229, 230) and has been recently demonstrated for the tricyclo[3.1.1.$0^{2,4}$]heptan-6-yl system (**179**)[135] as well.



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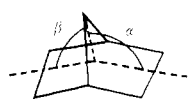


296

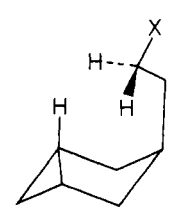
The overlap between the cyclopropane ring bond and the developing p orbital will be enhanced by factors which reduce the angles θ and ϕ. Other factors which distort the p orbital from the ABC plane, such as the asymmetric bridging in **149** and **184,** will decrease the overlap. The overlap will also depend on the AB distance, the optimum value of which is calculated[37,39] to be *ca.* 1.8 Å. Qualitative interpretation of the relative efficacy of cyclopropyl groups and double bonds in ionization rate acceleration in some molecules (**141**-O*p*NB and *anti*-7-norbornenyl *p*-nitrobenzoate) has been made[113] in terms of the relative magnitudes of the angles corresponding to θ and ϕ. In **176**-OBs, however, an increased AB distance resulting from distortions caused by steric hindrance may be an additional complicating factor.[134] It is interesting that in the very labile **226** AB is relatively short[231] (*ca.* 2.2 Å compared to *ca.* 2.4 Å in **141** as measured from Dreiding models), whereas the participating cyclopropyl ring bond is very long (1.64 Å).[231] Additional structural and theoretical studies are obviously required before a quantitative discussion is possible. It may, of course, be impossible to discuss cyclopropyl participation in quantitative terms since one can presently only speculate on the required accurate geometries for transition states, and indeed for many intermediates.

A very recent report[232] proposes that the relative symmetries of a carbonium ion p orbital and the orbitals of a distant neighboring group (specifically a double bond) may be affected by the symmetry of the intervening σ bonds. An important aspect of this proposal is that in molecules with an odd number of bonds separating the neighboring group and the carbonium ion center, overlap of the appropriate p orbitals is predicted to be destabilizing on grounds of symmetry. The ineffectiveness of the double bond in cyclohepten-5-yl derivatives as a neighboring group (Table V) is thus anticipated. This prediction is, as yet, difficult to assess in cyclopropyl cases because of the unavailability of rigid model compounds. Our group, and undoubtedly others, are currently studying suitable systems.

C. Conformational Mobility

One of the particularly striking features of the kinetic data reviewed in this article is the complete absence of large rate enhancements in the ionization of conformationally mobile molecules, even in cases in which there is compelling evidence for cyclopropyl participation. Especially poignant is the *cis*-bicyclo[3.1.0]hex-3-yl system (**9**) which undoubtedly ionizes with cyclopropyl participation to **11** but at only a moderately enhanced rate. Introduction of bridging groups of the correct configuration can result in dramatic increases in anchimeric assistance. Such bridging, as in **141, 150, 179,** and **184,** is accompanied by three clearly definable but as yet inseparable features, each of which is expected to enhance the participating effect of the three-membered ring: (a) an increase in the rigidity and ring strain of the molecule, (b) a decrease in the internal angle and flexibility at the cation center, and (c) locking of the bicyclo[3.1.0]hexane ring in a chair conformation. Feature c is important since it is generally agreed (ref 32, 39, 57, 171–174) that the most stable conformation of a bicyclo[3.1.0]hexane ring is a shallow boat. Not only are *cis*-bicyclo[3.1.0]hex-3-yl derivatives less strained than their bridged analogs, but in order to exhibit cyclopropyl participation they must adopt an unstable chair conformation which reduces the possible stabilizing effect of the assisted ionization. Substituent effects in bicyclo[3.1.0]hex-3-yl derivatives have been discussed[39] in terms of changes in the boat–chair equilibrium constant.

A similar conformational argument has been used[78] to explain the absence of an interaction in the ionization of **86**-ONs. In order to become oriented in a conformation (**297**) suitable for edge interaction by the cyclopropyl group, this molecule must overcome three destabilizing factors: (i) formation of a bicyclo[3.1.0]hexane chair, (ii) gauche interactions involving the axial alkyl group, and (iii) additional nonbonded interactions associated with the correct orientation of the side chain. Presumably the stabilizing effect of charge delocalization



297

is insufficient to overcome these destabilizing effects despite the fact that **86**-ONs is a primary derivative. In the corresponding olefin, **90**-ONs, factors ii and iii are greatly reduced and moderate double bond participation is observed.[79,80] In **91**-OBs factors i and ii are removed and weak cyclopropyl participation is noted.[81]

Conformational arguments can also be used to explain the ionization rates observed for other conformationally mobile molecules discussed elsewhere in this review.

D. Steric Strain

The tremendous rate acceleration observed for the ionization of **141**-O*p*NB, **179**-O*p*NB, and related esters might be partially accounted for by relief of ring strain;[233] unfortunately a quantitative treatment is not yet possible because of the paucity of strain energy data. From kinetic and product data, Tanida[114] has calculated a value of *ca.* 12 kcal/mol[234] for the free energy difference between **141** and **149** which could be used in support of a scheme by which **141**-O*p*NB ionized with cyclopropyl participation to give the classical ion **143** of the much less strained ring structure. It is quite clear from the stereochemistry of the products derived from **141**-O*p*NB (and **149**-OTs) and from the solvolytic behavior of **150**-O*p*NB, however, that this mechanism does not pertain and that relief of strain upon classical ionization to **143** does not provide the large driving force observed in this solvolysis. Even ionization of **141**-O*p*NB to **142** may reduce the strain of the system somewhat, since it is expected[37,39] that the C-2–C-4 bond will be longer in **142** than in **141**, but this factor may be at least partially offset by distortions which reduce the C-2–C-8 distance.[235] However, Masamune, *et al.*,[135] have suggested that the C-2–C-8 distance in **141** may be shorter than that measured from molecular models.

It is thus quite evident that factors other than relief of strain are important in rate acceleration. The most vivid example is that of **226** which ionizes at an exceptionally rapid, although as yet unmeasured, rate, perhaps even greater than the ionization rate of **141**, despite the fact that its strain energy is slightly less than that of **9**[166,233] whose ionization is relatively unaccelerated. These results suggest that strain relief may be a relatively unimportant accelerating factor.

E. Internal Angle at the Carbonium Ion Center

About two decades ago Brown and his coworkers[236] proposed the concept of *I* strain which they defined as the change in internal strain which results from a change in hybridization of a ring atom involved in a chemical reaction. This concept explains, at least in part, the extreme sluggishness to ionization of molecules with relatively fixed, compressed internal bond angles at the ionization center and conversely the high reactivity of the corresponding ketones in, for example, cyanohydrin formation or borohydride reduction. Internal strain also affects carbonyl stretching frequency.[237] The two phenomena, solvolytic reactivity and carbonyl stretching frequency, have been correlated.[238]

Because carbonium ions in compressed, rigid systems are destabilized by strain (the basis of the *I* strain concept), any factors which will stabilize the ion and the transition state of the ionization reaction, such as participation by a neighboring group, will exhibit their maximum effect in this group of compounds. This expectation is borne out dramatically in the 7-norbornyl and related systems. The bridge angle (C-1–C-7–C-4 in norbornane) in all norbornanes, norbornenes, norbornadienes, benzonorbornenes, and *exo*-tricyclo[3.2.1.$0^{2,4}$]octanes that have been studied[141,142,148,229] is in the range of 92–98° with no apparent trend within this range despite the expectation of some groups[237a,239] that introduction of unsaturation into norbornanes should increase the bridge angle. Infrared data[238] suggest that the bridge angle in the corresponding ketones is decreased in the unsaturated molecules. Structural studies on *endo*-tricyclo[3.2.1.$0^{2,4}$]octanes have not yet been reported, but there is nothing to suggest that their bridge angles do not also fall within the above range. The accelerating effect of anti double bonds, benzene rings, and endo cyclopropyl groups on the ionization of 7-norbornyl derivatives is thus not a result of decreased *I* strain but due to some other factor, presumably anchimeric assistance by the appropriate bonding electrons of each group. A possible additional accelerating factor in **141**-O*p*NB is the expected increase in the bridge angle as ionization to **142** is accomplished.

It is now well documented that rate enhancements due to neighboring olefinic[139,147] and benzo[148,149] groups are a function of bridge angle and much greater when the internal angle at the cation center is more compressed. However, insufficient data are yet available to discern a similar trend regarding cyclopropyl participation; indeed the acceleration noted in **179**-O*p*NB (Table X) is somewhat less than expected based on the bridge angle in bicyclo[2.1.1]hexanes of 82–89°.[135,148,240]

I strain is thus an important factor in determining the amount of anchimeric assistance afforded by a neighboring cyclopropyl group. Its absence is partially responsible for the relatively small accelerations noted for conformationally mobile molecules.

VI. Summary

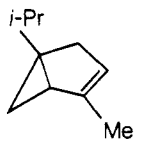
We have attempted to comprehensively review the numerous studies that have been reported in which long-range interactions between a carbonium ion center and a cyclopropyl group seem feasible. We have less thoroughly explored interactions involving other electron-deficient species and also those involving cyclobutane rings. It is clear that interactions by cyclopropyl groups are of two distinct types. In some molecules, *e.g.*, those incorporating a *cis*-bicyclo[3.1.0]hex-3-yl skeleton, the interaction is with the edge of the three-membered ring to form, in many cases, a nonclassical trishomocyclopropenyl cation. Participation by the cyclopropyl group in the formation of such intermediates may result in tremendous rate accelerations. In other molecules interaction with the corner of the cyclopropane ring to form homocyclopropylcarbinyl cations is observed. Enormous ionization rate enhancements are not generally observed for these molecules, but the evidence for cyclopropyl participation is compelling. No evidence has been found for an interaction with the face of the cyclopropane ring.

The magnitude, and indeed even the presence, of cyclopropyl participation is very dependent on geometrical factors, but it is obvious that no simple relationship exists. A qualitative discussion of some geometrical features has been presented. A more quantitative treatment will be possible when the results of new structural and theoretical studies become known. Additional studies designed to isolate the various pertinent geometrical parameters will undoubtedly be reported in the future.

VII. Addendum

Since the original version of this manuscript was submitted, a number of pertinent reports have appeared. Friedrich, Saleh, and Winstein[241] have further studied the solvolysis of derivatives of **10** and have postulated a mechanism which accounts for the numerous products

formed (eq 4). Cooper, *et al.*,[242] and Norin and Smedman[243] have reported the acid-catalyzed hydration of **298** and **299**. Both olefins give similar mixtures of diene and alcohol products; it was proposed that a common cyclopropylcarbinyl cation was involved. No evidence for a trishomocyclopropenyl cation was found. The hydration of these two olefins thus parallels the earlier work[44,54,55] on electrophilic additions to bicyclo[3.1.0]hexenes.



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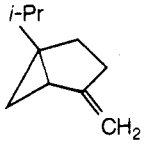

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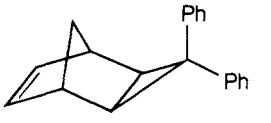
A more detailed report of the solvolysis of **63**-OTs has appeared.[244] The authors concluded that participation by the double bond is more important than by the cyclopropyl group by a factor of 4 and that each form of participation occurs from a distinct conformational isomer of **63**-OTs to give noninterconverting sets of ions. These conformers are in rapid equilibrium.

Wilt and Malloy's earlier work[130] has been extended[245] to include a study of olefin **300** and the two esters **301**-OTs and **302**-OTs. Addition of bromine to **300** occurred with cyclopropane rupture to give **303**. The hydrolysis of **301**-OTs gave only one product, **304**-OH. Similarly **302**-OTs hydrolyzed to give only one compound, **305**; however, this hydrocarbon did not arise from dehydration of **304**-OH but rather from an ion precursor. Both **301**-OTs and **302**-OTs ionize at slower rates than the corresponding exo and endo norbornyl esters (by factors of *ca.* 5 and 585, respectively). This is typical of tricyclo[3.2.1.$0^{2,4}$]oct-6-yl derivatives (see Table VII). The relatively large exo/endo rate ratio (*ca.* 4180) and the nature of the reaction products are indicative of a cyclopropane ring interaction. Wilt and Malloy propose mechanisms similar to those found in the ionization of other tricyclo[3.2.1.$0^{2,4}$]oct-6-yl derivatives (*vide supra*) with the dramatically simpler products a result of the stabilization of charge associated with the benzhydryl position.



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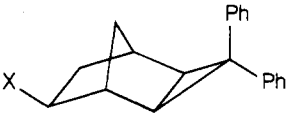

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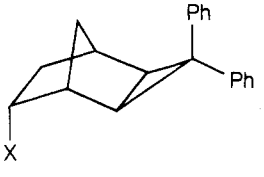

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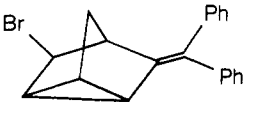

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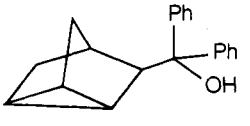
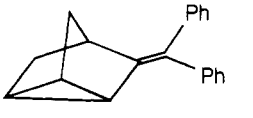


304-OH



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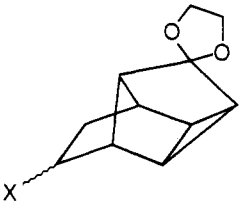
A study of the effect of electronegative C-5 substituents on the solvolysis of derivatives of **125** and **126** has been reported.[246] As anticipated, the substituents (keto, ketal, thioketal) reduce the solvolysis rates both of the endo and, more dramatically, of the exo isomers. The rate reductions correlate well with σ^* values. Substitution also influences the solvolysis product. Acetolysis of both *exo*- and *endo*-**306**-OBs gave only *exo*-**306**-OAc but *exo*- and *endo*-**307**-OBs gave mixtures of *exo*-**307**-OAc and *endo*-**307**-OAc in the ratio of *ca.* 88:12. The thioketals *exo*- and *endo*-**308**-OBs gave *exo*-**308**-OAc in addition to **309** in differing amounts. It was postulated that **309** was formed after the rate-controlling step by attack by sulfur at C-4. Both the kinetic and product data are in accord with the mechanistic scheme originally proposed[104] for the solvolysis of **125**-OBs and **126**-OBs.



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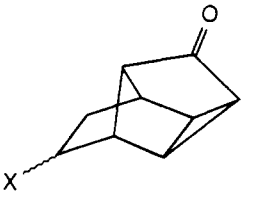

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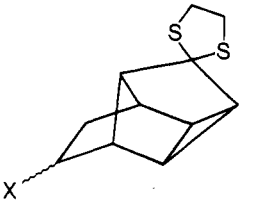

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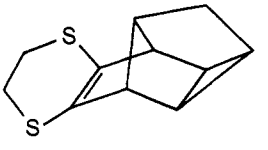
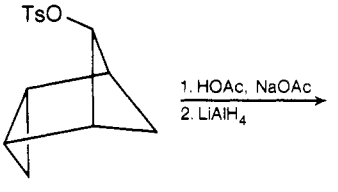


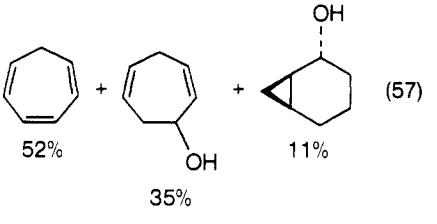
309

Gassman and Creary[247] have confirmed the earlier report[135] that derivatives of **179** ionize with great acceleration to give only rearranged products of structure **184** (eq 39) presumably *via* **182**. As might be expected the epimer **310** ionized apparently in a cyclobutyl–cyclopropylcarbinyl rearrangement to give the compounds shown (eq 57).



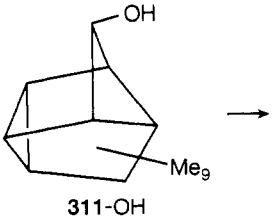
310-OTs

1. HOAc, NaOAc
2. $LiAlH_4$

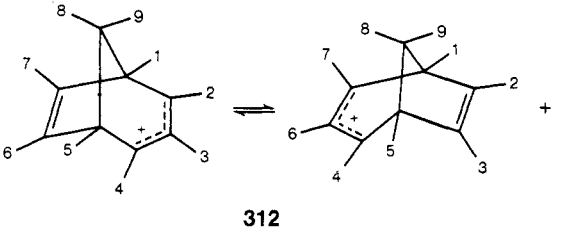


(57)

Hart and Kuzuya[248] have reported further interesting results concerning ions related to **182**, **183**, **186**, and



311-OH



312

other or alternative ions

187. Unlike **185**-OH which dissolves in a mixture of fluorosulfonic acid and fluorosulfonyl chloride to give **187**,[144] the permethylated **311**-OH forms **312.** It is thus clear that these and similar ions are very sensitive to substitution effects.

The thermal rearrangement of **187** has been reported[249] as well as the crystal structure of a derivative of the ketone corresponding to **181.**[250] The midpoint of the C-1–C-2 bond is unusually close to C-4 (2.145 Å) and the C-3–C-6 distance exceptionally long (1.60 Å). Both dimensions facilitate the previously observed[135,143,144,247,248] cyclopropane and cyclobutane participation modes.

A reexamination[251] of the solvolyses of derivatives of **179** and **184** has shown that both systems ionize to the same cation(s) whose ^1H and ^{13}C spectra are in accord with either a rapidly bridge-flipping **182,** or, preferably, a more delocalized structure similar to **187.** Deuterium labeling studies support this assignment. The ion rearranges to the 3-nortricyclyl cation above −80°. In accord with earlier studies,[144,145] Masamune, *et al.,* concluded that little charge resides on the pentagonal apical carbon atom. An additional report of the ionization of **310**-OTs to the *cis-syn-cis*-tricyclo[4.1.0.$0^{2,4}$]hept-5-yl cation has also appeared.[252]

Hydrolysis of iii (ref 132a) has been reported[253] to give rearranged 1,7-disubstituted tetracyclo[4.3.0.$0^{3,5}$.$0^{2,9}$]-nonanes as the major products. This rearrangement is fully expected (*cf.* **141**-O*p*NB), but it is somewhat surprising in view of the earlier reports[111-113,124] of successful ketone synthesis *via* ketal hydrolysis in similar ring systems. Lamaty, *et al.,*[132a] apparently did not analyze their products. Remote cyclopropyl participation appears to occur in the acid cleavage of a bridged derivative of **191**-O*t*Bu to a trishomocyclopropenyl cation.[254]

The *in vacuo* pyrolyses of the sodium salts of **229** and **230**[255] give rather different products from those observed in the methoxide ion decompositions[117] of the two tosylhydrazones. The Japanese workers also conclude, however, that carbene delocalization occurs only in the endo isomer (**233**). In a related system no evidence was found for cyclopropane stabilization in the carbene generated from the tosylhydrazone of 7,7-dimethoxy-*exo*-tricyclo-[3.2.1.$0^{2,4}$]octan-6-one.[256]

Theoretical studies on the geometry[257] and stability[258] of the 7-norbornyl and related cations have predicted abnormal destabilization of the saturated ion, providing an explanation of the unusually slow ionization rates for 7-norbornyl derivatives. Another important theoretical study claims evidence for nonplanar secondary carbonium ions.[259] This work may provide an alternative explanation of the observed predominant solvent attack from the more hindered side in ions derived from **141, 179,** and related systems.

The thermal isomerization of **254** and **255**[260] provides chemical evidence for the previously noted[209] interaction between the double bond and exo cyclopropane ring of **254.**

The epimeric cyclobutylcarbinyl derivatives, the tricyclo[4.2.1.$0^{1,6}$]nonane-7-methanol tosylates,[261] provide additional examples of long-range cyclopropane interactions. Both isomers ionize very specifically, one to give a cyclopropylcarbinyl cation, the other, surprisingly more rapidly (ref 6a, 9b, 32–34, 37, 38), to give a bridged trishomocyclopropenyl cation.

Epoxide participation was found to be absent in the ionization of the isomeric 6-oxabicyclo[3.1.0]hexan-3-yl tosylates.[262] Further evidence that the most stable conformation of the bicyclo[3.1.0]hexane ring is a shallow boat has been obtained from a lanthanide shift study of some thujanols and sabinols.[263]

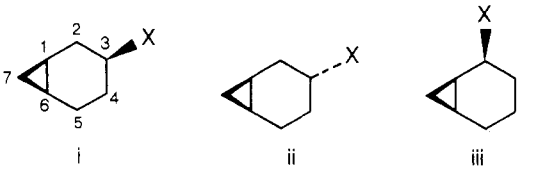
Theoretical studies concerning the approach of protons to strained hydrocarbons,[264] the torsional barriers of vinylcyclopropanes,[265] and the relative effectiveness of the cyclopropane ring as a neighboring group and a transmitter of electrical effects[266] have been presented. The σ^* value for cyclopropyl has been measured to be +0.011.[267] The energetics of neighboring group participation have been reviewed.[268]

Acknowledgment. The generous financial support of the National Research Council of Canada is gratefully acknowledged. The author thanks Dr. P. K. Freeman and Dr. P. G. Gassman for their helpful comments.

VIII. References and Notes

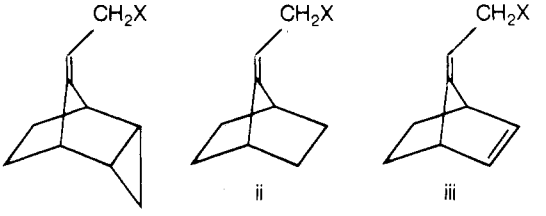
(1) Calculated from data given in W. A. Bernett, *J. Chem. Educ.*, **44,** 17 (1967).
(2) M. Yu. Lukina, *Russ. Chem. Rev.*, **31,** 419 (1962).
(3) M. Charton in "The Chemistry of Alkenes," Vol. 2, J. Zabicky, Ed., Wiley-Interscience, New York, N. Y., 1970, Chapter 10.
(4) R. D. Brown and V. G. Krishna, *J. Chem. Phys.*, **45,** 1482 (1966); M. J. S. Dewar and G. Klopman, *J. Amer. Chem. Soc.*, **89,** 3089 (1967); H. Preuss and G. Diercksen, *Int. J. Quantum Chem.*, **1,** 361 (1967); D. T. Clark, *Theor. Chim. Acta*, **10,** 111 (1968); R. J. Buenker and S. D. Peyerimhoff, *J. Phys. Chem.*, **73,** 1299 (1969); H. Marsmann, J.-B. Robert, and J. R. Van Wazer, *Tetrahedron*, **27,** 4377 (1971); R. M. Stevens, E. Switkes, E. A. Laws, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **93,** 2603 (1971); B. Bak and J. J. Led, *J. Mol. Struct.*, **3,** 379 (1969); R. Bonaccorsi, E. Scrocco, and J. Tomasi, *J. Chem. Phys.*, **52,** 5270 (1970).
(5) (a) R. H. De Wolfe and W. G. Young in "The Chemistry of Alkenes," Vol. 1, S. Patai, Ed., Wiley-Interscience, New York, N. Y., 1964, pp 681–710; (b) N. C. Deno in "Carbonium Ions," Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, Chapter 18; (c) H. G. Richey in ref 3, pp 56–67.
(6) (a) P. R. Story and B. C. Clark in "Carbonium Ions," Vol. 3, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1972, Chapter 23; (b) H. G. Richey in ref 3, pp 77–101.
(7) H. G. Richey in ref 6a, Chapter 25; K. B. Wiberg, B. A. Hess, and A. J. Ashe, *ibid.*, Chapter 26; M. Hanack and H.-J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **6,** 666 (1967); M. Hanack and H.-J. Schneider, *Fortschr. Chem. Forsch.*, **8,** 554 (1967).
(8) B. Capon, *Quart. Rev., Chem. Soc.*, **18,** 45 (1964); E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, pp 84–147; A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962.
(9) (a) G. D. Sargent, *Quart. Rev., Chem. Soc.*, **20,** 301 (1966); (b) S. Winstein, *ibid.*, **23,** 141 (1969); *Chem. Soc., Spec. Publ.*, **No. 21,** 5 (1967); (c) N. C. Deno, *Progr. Phys. Org. Chem.*, **2,** 129 (1964); (d) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," C. Eaborn, Ed., Elsevier, Amsterdam, 1966; D. Bethell and V. Gold, "Carbonium Ions, An Introduction," Academic Press, New York, N. Y., 1967; P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, New York, N. Y., 1965; "Carbonium Ions," Vol. 1–4, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1968, 1970, 1972, 1973.
(10) G. E. Cartier and S. C. Bunce, *J. Amer. Chem. Soc.*, **85,** 932 (1963).
(11) R. R. Sauers and R. W. Ubersax, *J. Org. Chem.*, **31,** 495 (1966).
(12) M. J. S. Dewar and J. M. Harris, *J. Amer. Chem. Soc.*, **90,** 4468 (1968).
(13) Y. E. Rhodes and T. Takino, *J. Amer. Chem. Soc.*, **90,** 4469 (1968).
(14) Y. E. Rhodes and T. Takino, *J. Amer. Chem. Soc.*, **92,** 5270 (1970).
(15) M. J. S. Dewar and J. M. Harris, *J. Amer. Chem. Soc.*, **92,** 6557 (1970).
(16) M. Hanack and H. M. Ensslin, *Tetrahedron Lett.*, 4445 (1965); *Justus Liebigs Ann. Chem.*, **713,** 49 (1968).
(17) M. A. Becker and Y. E. Rhodes, Abstracts, 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 1972, No. ORGN-124; M. A. Becker, Ph.D. Thesis, New York University, 1972; *Diss. Abstr.*, **33,** 2522-B (1972).
(18) It should be noted that a cyclopropyl group is expected to inductively retard cation formation; see ref 14 and 15.
(19) (a) S. Winstein, P. Bruck, P. Radlick, and R. Baker, *J. Amer. Chem. Soc.*, **86,** 1867 (1964); (b) M. Simonetta and S. Winstein, *ibid.*, **76,** 18 (1954).
(20) The product ratios are quite dependent on reaction conditions.
(21) The insensitivity of solvolysis rate to alkyl substitution is a feature of formolysis and, to a lesser extent, acetolysis which is not necessarily shared by other solvents, for example, trifluoroacetic acid.[22]
(22) I. L. Reich, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, **91,** 5635 (1969); A. Diaz, I. L. Reich, and S. Winstein, *ibid.*, **91,** 5637 (1969).
(23) S. Winstein and H. Marshall, *J. Amer. Chem. Soc.*, **74,** 1120 (1952).

(24) H. M. R. Hoffmann, *J. Chem. Soc.*, 6762 (1965).
(25) K. L. Servis and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 3773 (1964).
(26) P. v. R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, **88**, 2321 (1966).
(27) T. Shono, K. Fujita, S. Kumai, T. Watanabe, and I. Nishiguchi, *Tetrahedron Lett.*, 3249 (1972).
(28) M. Hanack and H. M. Ensslin, *Justus Liebigs Ann. Chem.*, **697**, 100 (1966).
(29) W. D. Burrows and R. H. Eastman, *J. Amer. Chem. Soc.*, **79**, 3756 (1957).
(30) S. C. Bunce and J. B. Cloke, *J. Amer. Chem. Soc.*, **76**, 2244 (1954).
(31) The relative proportions of the products vary as R is changed. Some of the acetates are not formed from some isomers.
(32) S. Winstein, E. C. Friedrich, R. Baker, and Y. Lin, *Tetrahedron, Suppl.*, **8** (II), 621 (1966).
(33) S. Winstein, J. Sonnenberg, and L. de Vries, *J. Amer. Chem. Soc.*, **81**, 6523 (1959); S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3235 (1961).
(34) S. Winstein and J. Sonnenberg, *J. Amer. Chem. Soc.*, **83**, 3244 (1961).
(35) W. J. le Noble, B. L. Yates, and A. W. Scaplehorn, *J. Amer. Chem. Soc.*, **89**, 3751 (1967).
(36) For a discussion of special salt effects, see S. Winstein and G. C. Robinson, *J. Amer. Chem. Soc.*, **80**, 169 (1958), and other papers in this series.
(37) R. J. Piccolini and S. Winstein, *Tetrahedron Suppl.*, **2**, 423 (1963); R. Hoffmann, *Tetrahedron Lett.*, 3819 (1965); see also, however, T. F. W. McKillop and B. C. Webster, *Tetrahedron*, **26**, 1879 (1970).
(38) S. Winstein, *J. Amer. Chem. Soc.*, **81**, 6524 (1959).
(39) Y. Lin, Ph.D. Thesis, University of California—Los Angeles, 1967; *Diss. Abstr.*, **28**, 3651-B (1968).
(40) T. Norin, *Tetrahedron Lett.*, 37 (1964).
(41) H. Kuczyński, M. Walkowicz, and C. Walkowicz, *Rocz. Chem.*, **42**, 1277 (1968).
(42) E. H. Massey, H. E. Smith, and A. W. Gordon, *J. Org. Chem.*, **31**, 684 (1966).
(43) H. Kuczyński and C. Walkowicz, *Rocz. Chem.*, **43**, 229 (1969); H. Kuczyński, C. Walkowicz, and M. Walkowicz, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **19**, 537 (1971).
(44) For a recent review of thujane derivatives including some carbonium ion work, see D. Whittaker and D. V. Banthorpe, *Chem. Rev.*, **72**, 305 (1972).
(45) E. J. Corey and H. Uda, *J. Amer. Chem. Soc.*, **85**, 1788 (1963).
(46) R. Breslow, J. Lockhart, and H. W. Chang, *J. Amer. Chem. Soc.*, **83**, 2375 (1961).
(47) M. J. S. Dewar and A. P. Marchand, *Annu. Rev. Phys. Chem.*, **16**, 321 (1965).
(48) For recent summaries, see C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 323 (1964); C. Laurence and B. Wojtkowiak, *Ann. Chim. (Paris)*, **5**, 163 (1970).
(49) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Amer. Chem. Soc.*, **74**, 1113 (1952).
(50) W. Broser and D. Rahn, *Chem. Ber.*, **100**, 3472 (1967).
(51) E. J. Corey and R. L. Dawson, *J. Amer. Chem. Soc.*, **85**, 1782 (1963).
(52) See, for example, L. Friedman in ref 5b, Chapter 16; C. J. Collins and B. M. Benjamin, *J. Org. Chem.*, **37**, 4358 (1972).
(53) P. G. Gassman and F. V. Zalar, *J. Amer. Chem. Soc.*, **88**, 2252 (1966).
(54) P. K. Freeman, M. F. Grostic, and F. A. Raymond, *J. Org. Chem.*, **30**, 771 (1965); P. K. Freeman, F. A. Raymond, and M. F. Grostic, *ibid.*, **32**, 24 (1967).
(55) D. V. Banthorpe and H. F. S. Davies, *J. Chem. Soc. B*, 1339 (1968).
(56) See, for example, E. C. Friedrich and M. A. Saleh, *Tetrahedron Lett.*, 1373 (1971); J. J. Tufariello and D. W. Rowe, *J. Chem. Soc., Chem. Commun.*, 1066 (1972); E. C. Friedrich and M. A. Saleh, *J. Amer. Chem. Soc.*, **95**, 2617 (1973); and references cited in these articles.
(57) D. B. Priddy and W. Reusch, *Tetrahedron Lett.*, 5291 (1969).
(58) T. J. Curphey and R. L. McCartney, *Tetrahedron Lett.*, 5295 (1969).
(59) (a) G. A. Olah and W. S. Tolgyesi, Abstracts of Papers, 18th International Congress of Pure and Applied Chemistry, Montreal, Canada, Aug 1961, p 57; (b) G. A. Olah and W. S. Tolgyesi, *J. Amer. Chem. Soc.*, **83**, 5031 (1961).
(60) G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **90**, 933 (1968).
(61) S. Forsen and T. Norin, *Tetrahedron Lett.*, 4183 (1966).
(62) R. R. Sauers, *Tetrahedron Lett.*, 1015 (1962).
(62a) Solvolysis of the parent bicyclo[4.1.0]hept-3-yl tosylates, i-OTs and ii-OTs, has also been reported (M. Hanack and P.-C. Krause, *Justus Liebigs Ann. Chem.*, **760**, 17 (1972)). Although both isomers acetolyze at enhanced rates (at 50° the following relative rates were observed: i-OTs, 37; ii-OTs, 53; cyclohexen-4-yl tosylate, 2.4;[62b] cyclohexyl tosylate, 1[33]), the kinetic data cannot be used in support of cyclopropyl participation because the cyclopropane rings of i-OTs and ii-OTs readily open in the acid media employed to give the observed products of ring rupture and elimination. In 50% aqueous acetone, both i-OTs and ii-OTs hydrolyzed nonstereospecifically to give different mixtures of i-OH, ii-OH, and iii-OH in which a deuterium label originally on C-3 is not scrambled. Similar products were formed in the deamination (dilute $HClO_4$, pH 4) of i-NH_2. The nonstereospecific nature of these reactions and the labeling studies contrast sharply with the behavior of **9**-OTs and rule out an interaction by the three-membered ring.

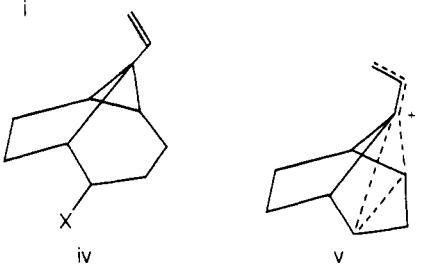


i ii iii

(62b) M. Hanack and W. Keberle, *Chem. Ber.*, **96**, 2937 (1963).
(63) P. J. Kropp, *J. Amer. Chem. Soc.*, **88**, 4926 (1966).
(64) D. H. R. Barton, R. Bernasconi, and J. Klein, *J. Chem. Soc.*, 511 (1960).
(65) A. C. Cope, S. Moon, and C. H. Park, *J. Amer. Chem. Soc.*, **84**, 4850 (1962).
(66) P. G. Gassman, J. Seter, and F. J. Williams, *J. Amer. Chem. Soc.*, **93**, 1673 (1971).
(67) A. C. Cope, C. H. Park, and P. Scheiner, *J. Amer. Chem. Soc.*, **84**, 4862 (1962).
(68) Data in parentheses are those from a second run.
(69) J. B. Lambert, J. W. Hamersma, A. P. Jovanovich, F. R. Koeng, S. A. Sweet, and P. J. Kucinski, *J. Amer. Chem. Soc.*, **92**, 6372 (1970).
(70) Calculated from data given in ref 66, 69, and 71.
(71) H. C. Brown and G. Ham, *J. Amer. Chem. Soc.*, **78**, 2735 (1956).
(72) Calculated from data given in ref 19a and 71.
(73) R. W. Thies, M. Sakai, D. Whalen, and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2270 (1972).
(74) R. W. Thies, M. Gasic, D. Whalen, J. B. Grutzner, M. Sakai, B. Johnson, and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2262 (1972).
(75) D. Whalen, M. Gašić, B. Johnson, H. Jones, and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 6384 (1967).
(76) M. A. Eakin, J. Martin, and W. Parker, *Chem. Commun.*, 955 (1967).
(77) –ONs = *p*-nitrobenzenesulfonate (nosylate).
(78) G. D. Sargent, R. L. Taylor, and W. H. Demisch, *Tetrahedron Lett.*, 2275 (1968).
(79) P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, *J. Amer. Chem. Soc.*, **87**, 1288 (1965).
(80) P. D. Bartlett and G. D. Sargent, *J. Amer. Chem. Soc.*, **87**, 1297 (1965).
(81) R. Muneyuki, T. Yano, and H. Tanida, *J. Amer. Chem. Soc.*, **91**, 2408 (1969).
(81a) Significant participation by a cyclopropane ring is noted when unsaturation is introduced into the side chain of **91** and **92** (G. D. Sargent and M. A. Herkenham, *J. Amer. Chem. Soc.*, **94**, 2892 (1972)). At 100° i-ODNB hydrolyzes 622 times faster than ii-ODNB and 24 times faster than the corresponding diene, iii-ODNB. Also indicative of the cyclopropyl participation is the formation of iv-OH and its dinitrobenzoate as the only products of hydrolysis of i-ODNB. The delocalized cation v was proposed as the intermediate. It is interesting that the greater accelerating effect of an endo cyclopropyl group in tricyclo[3.2.1.$0^{2,4}$]oct-8-yl derivatives (*vide infra*) compared to a double bond is also found in i and iii.



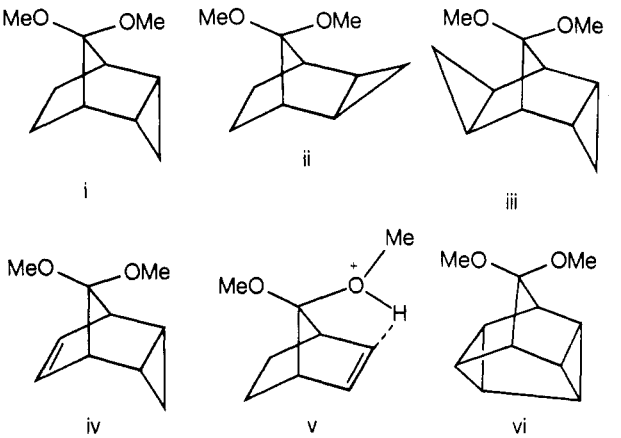
i ii iii



iv v

(82) R. Muneyuki and H. Tanida, *J. Amer. Chem. Soc.*, **90**, 656 (1968).
(83) R. S. Bly, R. K. Bly, A. O. Bedenbaugh, and O. R. Vail, *J. Amer. Chem. Soc.*, **89**, 880 (1967).
(84) R. K. Bly and R. S. Bly, *J. Org. Chem.*, **31**, 1577 (1966); J. A. Berson, J. J. Gajewski, and D. S. Donald, *J. Amer. Chem. Soc.*, **91**, 5550 (1969); J. A. Berson, D. S. Donald, and W. J. Libbey, *ibid.*, **91**, 5580 (1969).
(85) J. Fajkoš, J. Joska, and F. Sôrm, *Collect. Czech. Chem. Commun.*, **33**, 3324 (1968).

(86) R. F. Childs and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 6348 (1967); R. F. Childs, M. A. Brown, F. A. L. Anet, and S. Winstein, *ibid.*, **94**, 2175 (1972).
(87) (a) M. Brookhart, G. C. Levy, and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 1735 (1967); (b) R. Leute and S. Winstein, *Tetrahedron Lett.*, 2475 (1967).
(88) K. B. Wiberg and G. R. Wenzinger, *J. Org. Chem.*, **30**, 2278 (1965).
(89) A. K. Colter and R. C. Musso, *J. Org. Chem.*, **30**, 2462 (1965).
(90) For a review see G. D. Sargent in ref 6a, Chapter 24.
(91) For a review of norborn-5-en-2-yl and benzonorbornen-2-yl solvolyses see ref 6a, pp 1016–1019 and 1065–1071, respectively.
(92) J. A. Berson, R. G. Bergman, G. M. Clarke, and D. Wege, *J. Amer. Chem. Soc.*, **90**, 3236 (1968).
(93) J. A. Berson, R. G. Bergman, G. M. Clarke, and D. Wege, *J. Amer. Chem. Soc.*, **91**, 5601 (1969).
(94) R. R. Sauers and J. A. Beisler, *Tetrahedron Lett.*, 2181 (1964); R. R. Sauers, J. A. Beisler, and H. Feilich, *J. Org. Chem.*, **32**, 569 (1967).
(95) J. A. Berson, D. Wege, G. M. Clarke, and R. G. Bergman, *J. Amer. Chem. Soc.*, **90**, 3240 (1968).
(96) G. N. Fickes, *J. Org. Chem.*, **34**, 1513 (1969).
(97) J. A. Berson, G. M. Clarke, D. Wege, and R. G. Bergman, *J. Amer. Chem. Soc.*, **90**, 3238 (1968).
(98) J. A. Berson, D. Wege, G. M. Clarke, and R. G. Bergman, *J. Amer. Chem. Soc.*, **91**, 5594 (1969).
(99) G. D. Sargent, M. J. Harrison, and G. Khoury, *J. Amer. Chem. Soc.*, **91**, 4937 (1969).
(100) D. W. Rome and B. L. Johnson, *Tetrahedron*, **27**, 2271 (1971).
(101) B. C. Henshaw, D. W. Rome, and B. L. Johnson, *Tetrahedron Lett.*, 6049 (1968).
(102) B. C. Henshaw, D. W. Rome, and B. L. Johnson, *Tetrahedron*, **27**, 2255 (1971).
(103) P. K. Freeman and D. M. Balls, *Tetrahedron Lett.*, 437 (1967).
(104) P. K. Freeman, D. M. Balls, and J. N. Blazevich, *J. Amer. Chem. Soc.*, **92**, 2051 (1970).
(105) P. K. Freeman and J. N. Blazevich, *Chem. Commun.*, 1357 (1969).
(106) P. E. Schueler and Y. E. Rhodes, Abstracts, 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 1972, No. ORGN-129.
(107) See, for example, H. L. Goering and G. N. Fickes, *J. Amer. Chem. Soc.*, **90**, 2848, 2856, 2862 (1968); L. A. Spurlock and R. J. Schultz, *ibid.*, **92**, 6302 (1970); and references cited in these articles.
(108) W. G. Dauben and C. H. Schallhorn, *J. Amer. Chem. Soc.*, **93**, 2254 (1971).
(109) A. F. Diaz, D. L. Harris, M. Sakai, and S. Winstein, *Tetrahedron Lett.*, 303 (1971).
(110) A. F. Diaz, M. Sakai, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 7477 (1970).
(111) H. Tanida, T. Tsuji, and T. Irie, *J. Amer. Chem. Soc.*, **89**, 1953 (1967).
(112) M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *J. Amer. Chem. Soc.*, **89**, 1954 (1967).
(113) J. S. Haywood-Farmer and R. E. Pincock, *J. Amer. Chem. Soc.*, **91**, 3020 (1969).
(114) H. Tanida, *Accounts Chem. Res.*, **1**, 239 (1968).
(115) P. K. Freeman, R. S. Raghavan, and G. L. Fenwick, *J. Amer. Chem. Soc.*, **94**, 5101 (1972).
(116) The tricyclo[3.3.0.$0^{4,6}$]octyl ring system has been estimated[114] to be *ca.* 12 kcal/mol less strained than the tricyclo[3.2.1.$0^{2,4}$]octyl system.
(117) P. K. Freeman, R. S. Raghavan, and D. G. Kuper, *J. Amer. Chem. Soc.*, **93**, 5288 (1971).
(118) A. P. Jovanovich and J. B. Lambert, *J. Chem. Soc. B*, 1129 (1971).
(119) P. G. Gassman and A. F. Fentiman, *J. Amer. Chem. Soc.*, **92**, 2551 (1970).
(120) M. Brookhart, private communication.
(121) R. M. Coates and J. L. Kirkpatrick, *J. Amer. Chem. Soc.*, **90**, 4162 (1968); **92**, 4883 (1970).
(122) For reviews of degenerate carbonium ions, see (a) R. E. Leone and P. v. R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, **9**, 860 (1970); (b) R. E. Leone, J. C. Barborak, and P. v. R. Schleyer in "Carbonium Ions," Vol. 4, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1973, Chapter 33.
(123) P. G. Gassman, J. Zeller, and J. T. Lumb, *Chem. Commun.*, 69 (1968); P. G. Gassman and A. F. Fentiman, *J. Amer. Chem. Soc.*, **91**, 1545 (1969); **92**, 2549 (1970).
(124) J. Haywood-Farmer, R. E. Pincock, and J. I. Wells, *Tetrahedron*, **22**, 2007 (1966).
(125) M. A. Battiste, P. F. Ranken, and R. Edelman, *J. Amer. Chem. Soc.*, **93**, 6276 (1971).
(126) S. Winstein and E. T. Stafford, *J. Amer. Chem. Soc.*, **79**, 505 (1957).
(127) H. Tanida, Y. Hata, S. Ikegami, and H. Ishitobi, *J. Amer. Chem. Soc.*, **89**, 2928 (1967).
(128) H. Tanida, T. Tsuji, and H. Ishitobi, *J. Amer. Chem. Soc.*, **86**, 4904 (1964).
(129) R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964); *J. Amer. Chem. Soc.*, **86**, 1259 (1964); H. Konishi, H. Kato, and T. Yonezawa, *Bull. Chem. Soc. Jap.*, **43**, 1676 (1970); and references cited in these articles.
(130) J. W. Wilt and T. P. Malloy, *J. Amer. Chem. Soc.*, **92**, 4747 (1970).
(131) R. K. Lustgarten, M. Brookhart, and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2347 (1972), and references cited therein.
(132) M. S. Baird and C. B. Reese, *J. Chem. Soc., Chem. Commun.*, 523 (1972).
(132a) An additional example of long-range cyclopropane ring participation in *endo*-tricyclo[3.2.1.$0^{2,4}$]octanes has recently been reported; G. Lamaty, A. Malaval, J.-P. Rogue, and P. Geneste, *Bull. Soc. Chim. Fr.*, 4563 (1972). At 25° ketal i hydrolyzes more rapidly (k_{rel} = 120) than 7,7-dimethoxynorbornane (k_{rel} = 1) and 7,7-dimethoxynorbornene (k_{rel} = 2.3). Ketals ii, iii, and iv



also hydrolyze at enhanced rates (k_{rel} = 18, 143, and 320, respectively). It was proposed that each of the ketals studied in this work first protonates and then undergoes a rate-determining dissociation to a carbonium ion which eventually hydrolyzes to the ketone. In accord with the solvolysis studies discussed above, the endo cyclopropyl group of i is more effective at enhancing the ionization rate than is a double bond. The significance of this observation is obscured by the possibility that 7,7-dimethoxynorbornene protonates preferentially on the syn methoxyl group to form the hydrogen-bonded structure v. The double bond cannot participate effectively in the dissociation of this intermediate. Preferential protonation of i on the syn side is less likely because the cyclopropyl group is a less effective electron donor in hydrogen bonding than is a double bond[173,216] and because the exo hydrogen atoms on C-2 and C-4 of i provide steric hindrance to such hydrogen bonding. In agreement with their kinetic results Lamaty, *et al.*, proposed that participation by the endo cyclopropyl group in i, iii, and iv is weak. The formation of unrearranged **146** from i is indicative of oxonium rather than trishomocyclopropenyl character for the intermediate. Additional studies on 7,7-dimethoxynorbornadiene and on vi should be instructive.

In a related study, G. Lamaty, A. Malaval, J.-P. Rogue, and P. Geneste (*Bull. Soc. Chim. Fr.*, 4567 (1972)) measured the rates of addition of nucleophiles BH_4^- and CN^- to 7-norbornanone, 7-norbornenone, and **146**. In this case a double bond or an endo cyclopropyl group generally retards the reaction indicating a stabilization of the initial state (sp^2) relative to the transition state (sp^3). It is difficult to make a quantitive comparison because of complicating steric factors, but the effect of the cyclopropyl group is observed to be larger than that of the double bond. Addition of SO_3^{2-} to the ketones is unlike that of the other nucleophiles. Lamaty, *et al.*, proposed an sp^2-like transition state to account for this difference.

(133) C. E. Brion, J. Haywood-Farmer, R. E. Pincock, and W. B. Stewart, *Org. Mass Spectrom.*, **4**, 587 (1970).
(134) M. A. Battiste, J. Haywood-Farmer, H. Malkus, P. Seidl, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 2144 (1970).
(135) S. Masamune, R. Vukov, M. J. Bennett, and J. Purdham, *J. Amer. Chem. Soc.*, **94**, 8239 (1972).
(136) The 7-norbornyl system is probably a better model for measuring anchimeric assistance than is the bicyclo[2.1.1]hex-5-yl system because ionization of the latter system is probably also assisted.[137,138]
(137) *Cf.* K. B. Wiberg and R. Fenoglio, *Tetrahedron Lett.*, 1273 (1963); K. B. Wiberg, R. A. Fenoglio, V. Z. Williams, and R. W. Ubersax, *J. Amer. Chem. Soc.*, **92**, 568 (1970).
(138) It should be noted that the ionization of 7-norbornyl derivatives may also be assisted; *cf.* P. G. Gassman and J. M. Hornback, *J. Amer. Chem. Soc.*, **89**, 2487 (1967); F. B. Miles, *ibid.*, **89**, 2488 (1967); **90**, 1265 (1968); P. G. Gassman, J. M. Hornback, and J. L. Marshall, *ibid.*, **90**, 6238 (1968); J. E. Williams, R. Sustmann, L. C. Allen, and P. v. R. Schleyer, *ibid.*, **91**, 1037 (1969); B. Funke and S. Winstein, *Tetrahedron Lett.*, 1477 (1971).
(139) S. Masamune, S. Takada, N. Nakatsuka, R. Vukov, and E. N. Cain, *J. Amer. Chem. Soc.*, **91**, 4322 (1969).
(140) -*Op*BB = *p*-bromobenzoate.
(141) A. C. Macdonald and J. Trotter, *Acta Crystallogr.*, **18**, 243 (1965).
(142) A. C. Macdonald and J. Trotter, *Acta Crystallogr.*, **19**, 456 (1965).
(143) R. M. Coates and K. Yano, *Tetrahedron Lett.*, 2289 (1972).
(144) H. Hart and M. Kuzuya, *J. Amer. Chem. Soc.*, **94**, 8958 (1972).

(145) W.-D. Stohrer and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 1661 (1972).
(146) R. K. Lustgarten, *J. Amer. Chem. Soc.*, **94**, 7602 (1972).
(147) B. A. Hess, *J. Amer. Chem. Soc.*, **91**, 5657 (1969); **93**, 1000 (1971).
(148) Y. Hata and H. Tanida, *J. Amer. Chem. Soc.*, **91**, 1170 (1969).
(149) H. Tanida and T. Irie, *J. Org. Chem.*, **36**, 2777 (1971).
(150) C. S. Foote and R. B. Woodward, *Tetrahedron*, **20**, 687 (1964).
(151) G. W. Klumpp, G. Ellen, J. Japenga, and G. M. de Hoog, *Tetrahedron Lett.*, 1741 (1972).
(152) J. F. Chiang, C. F. Wilcox, and S. H. Bauer, *Tetrahedron*, **25**, 369 (1969).
(153) OTf = trifluoromethanesulfonate (triflate).
(154) For reviews of bridgehead reactivity, see R. C. Fort and P. v. R. Schleyer, *Advan. Alicyclic Chem.*, **1**, 283 (1966); R. C. Fort in ref 122b, Chapter 32.
(155) S. A. Sherrod, R. G. Bergman, G. J. Gleicher, and D. G. Morris, *J. Amer. Chem. Soc.*, **92**, 3469 (1970).
(156) R. C. Bingham, W. F. Sliwinski, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 3471 (1970).
(157) S. A. Sherrod, R. G. Bergman, G. J. Gleicher, and D. G. Morris, *J. Amer. Chem. Soc.*, **94**, 4615 (1972).
(158) Labeling experiments have shown that exclusive C–O rather than S–O bond cleavage occurs in the solvolysis of **172**-OTf.[157]
(159) A. de Meijere, O. Schallner, and C. Weitemeyer, *Angew. Chem., Int. Ed. Engl.*, **11**, 56 (1972).
(160) C. F. Wilcox and R. G. Jesaitis, *Tetrahedron Lett.*, 2567 (1967).
(161) D. Lenoir, P. v. R. Schleyer, and J. Ipaktschi, *Justus Liebigs Ann. Chem.*, **750**, 28 (1971).
(162) C. F. Wilcox and R. G. Jesaitis, *Chem. Commun.*, 1046 (1967).
(163) C. H. DePuy, I. A. Ogawa, and J. C. McDaniel, *J. Amer. Chem. Soc.*, **83**, 1668 (1961).
(164) P. Yates and J. D. Fenwick, *J. Amer. Chem. Soc.*, **93**, 4618 (1971).
(165) P. v. R. Schleyer and V. Buss, *J. Amer. Chem. Soc.*, **91**, 5880 (1969).
(166) W. B. Scott and R. E. Pincock, *J. Amer. Chem. Soc.*, **95**, 2040 (1973). The author is indebted to Dr. Pincock for a copy of this article prior to its publication.
(167) J. S. Wishnok, P. v. R. Schleyer, E. Funke, G. D. Pandit, R. O. Williams, and A. Nickon, *J. Org. Chem.*, **38**, 539 (1973).
(168) R. Gleiter and R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 5457 (1968).
(169) P. K. Freeman and D. G. Kuper, *J. Org. Chem.*, **30**, 1047 (1965).
(170) P. K. Freeman, F. A. Raymond, J. C. Sutton, and W. R. Kindley, *J. Org. Chem.*, **33**, 1448 (1968).
(171) M. S. Bergqvist and T. Norin, *Ark. Kemi*, **22**, 137 (1964); K. Tori, *Chem. Pharm. Bull.*, **12**, 1439 (1964); A. Dieffenbacher and W. von Philipsborn, *Helv. Chim. Acta*, **49**, 897 (1966); H. E. Smith, J. C. D. Brand, E. H. Massey, and L. J. Durham, *J. Org. Chem.*, **31**, 690 (1966).
(172) A. F. Cameron, G. Ferguson, and J. M. Robertson, *J. Chem. Soc. B*, 692 (1969); M. F. Grostic, D. J. Duchamp, and C. G. Chidester, *J. Org. Chem.*, **36**, 2929 (1971).
(173) M. Ōki, H. Iwamura, T. Murayama, and I. Oka, *Bull. Chem. Soc. Jap.*, **42**, 1986 (1969).
(174) See, however, V. Hach, R. F. Raimondo, D. M. Cartlidge, and E. C. McDonald, *Tetrahedron Lett.*, 3175 (1970).
(175) P. K. Freeman, M. F. Grostic, and F. A. Raymond, *J. Org. Chem.*, **36**, 905 (1971).
(176) E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958); V. R. Koch and G. J. Gleicher, *J. Amer. Chem. Soc.*, **93**, 1657 (1971); P. D. Bartlett, G. N. Fickes, F. C. Haupt, and R. Helgeson, *Accounts Chem. Res.*, **3**, 177 (1970).
(177) See, for example, J. Warkentin and E. Sanford, *J. Amer. Chem. Soc.*, **90**, 1667 (1968); H. O. Ohorodnyk and D. P. Santry, *ibid.*, **91**, 4711 (1969); *Chem. Commun.*, 510 (1969); P. Bakuzis, J. K. Kochi, and P. J. Krusic, *J. Amer. Chem. Soc.*, **92**, 1434 (1970); J. K. Kochi, P. Bakuzis, and P. J. Krusic, *ibid.*, **95**, 1516 (1973). See also, however, G. A. Russell and G. W. Holland, *ibid.*, **91**, 3968 (1969); S. J. Cristol and A. L. Noreen, *ibid.*, **91**, 3969 (1969).
(178) P. K. Freeman and R. S. Raghavan, *J. Org. Chem.*, **37**, 3670 (1972).
(179) J.-P. Pete, *Bull. Soc. Chim. Fr.*, 357 (1967).
(180) W. G. Dauben and G. H. Berezin, *J. Amer. Chem. Soc.*, **89**, 3449 (1967).
(181) S. A. Monti, *J. Org. Chem.*, **35**, 380 (1970).
(182) Z. Yoshida and H. Ogoshi, *Tetrahedron*, **26**, 4691 (1970).
(183) L. S. Bartell, J. P. Guillory, and A. T. Parks, *J. Phys. Chem.*, **69**, 3043 (1965).
(184) L. S. Bartell and J. P. Guillory, *J. Chem. Phys.*, **43**, 647 (1965).
(185) J. E. Katon, W. R. Feairheller, and J. T. Miller, *J. Chem. Phys.*, **49**, 823 (1968).
(186) W. G. Dauben and R. E. Wolf, *J. Org. Chem.*, **35**, 374 (1970).
(187) J.-L. Pierre, R. Bariet, and P. Arnaud, *Spectrochim. Acta, Part A*, **23**, 2297 (1967).
(188) C. H. Heathcock and S. R. Poulter, *J. Amer. Chem. Soc.*, **90**, 3766 (1968).
(189) M. J. Jorgenson and T. Leung, *J. Amer. Chem. Soc.*, **90**, 3769 (1968).
(190) M. M. Baizer, J. L. Chruma, and P. A. Berger, *J. Org. Chem.*, **35**, 3569 (1970).
(191) G. L. Closs and H. B. Klinger, *J. Amer. Chem. Soc.*, **87**, 3265 (1965).
(192) A. L. Goodman and R. H. Eastman, *J. Amer. Chem. Soc.*, **86**, 908 (1964).
(193) R. C. Hahn, P. H. Howard, S.-M. Kong, G. A. Lorenzo, and N. L. Miller, *J. Amer. Chem. Soc.*, **91**, 3558 (1969).
(194) R. S. Becker, L. Edwards, R. Bost, M. Elam, and G. Griffin, *J. Amer. Chem. Soc.*, **94**, 6584 (1972).
(195) E. N. Trachtenberg and G. Odian, *J. Amer. Chem. Soc.*, **80**, 4018 (1958).
(196) J. M. Stewart and G. K. Pagenkopf, *J. Org. Chem.*, **34**, 7 (1969).
(197) R. G. Pews and N. D. Ojha, *J. Amer. Chem. Soc.*, **91**, 5769 (1969).
(198) G. Montaudo and C. G. Overberger, *J. Org. Chem.*, **38**, 804 (1973).
(199) G. J. Karabatsos and D. J. Fenoglio, *Top. Stereochem.*, **5**, 167 (1970).
(200) (a) L. D. Kispert, C. Engelman, C. Dyas, and C. U. Pittman, *J. Amer. Chem. Soc.*, **93**, 6948 (1971); M. Pelissier, A. Serafini, J. Devanneaux, J.-F. Labarre, and J.-F. Tocanne, *Tetrahedron*, **27**, 3271 (1971); (b) W. J. Hehre, *J. Amer. Chem. Soc.*, **94**, 6592 (1972); F. A. Van-Catledge, *ibid.*, **95**, 1173 (1973).
(201) (a) R. E. Pincock and J. Haywood-Farmer, *Tetrahedron Lett.*, 4759 (1967); J. Haywood-Farmer, Ph.D. Thesis, University of British Columbia, Vancouver, British Columbia, 1967; *Diss. Abstr.*, **30**, 561-B (1969); (b) J. Haywood-Farmer and M. A. Battiste, unpublished results.
(202) S. Feinleib and F. A. Bovey, *Chem. Commun.*, 978 (1968).
(203) E. I. Snyder and B. Franzus, *J. Amer. Chem. Soc.*, **86**, 1166 (1964).
(204) I. J. Miller, *Aust. J. Chem.*, **24**, 2013 (1971).
(205) *Cf.* L. N. Ferguson and J. C. Nnadi, *J. Chem. Educ.*, **42**, 529 (1965); H. Labhart and G. Wagnière, *Helv. Chim. Acta*, **42**, 2219 (1959).
(206) K. B. Wiberg and A. deMeijere, *Tetrahedron Lett.*, 59 (1969).
(207) D. A. Lightner and W. A. Beavers, *J. Amer. Chem. Soc.*, **93**, 2677 (1971).
(208) *Cf.* K. Mislow in "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," G. Snatzke, Ed., Heyden and Son, London, 1967, pp 162–172; G. Snatzke, *ibid.*, pp 221–223.
(209) P. Bischof, E. Heilbronner, H. Prinzbach, and H. D. Martin, *Helv. Chim. Acta*, **54**, 1072 (1971).
(210) P. K. Freeman, D. G. Kuper, and V. N. M. Rao, *Tetrahedron Lett.*, 3301 (1965).
(211) H. Prinzbach and W. Eberbach, *Chem. Ber.*, **101**, 4083 (1968); H. Prinzbach, W. Eberbach, M. Klaus, and G. v. Veh, *ibid.*, **101**, 4066 (1968); H. Prinzbach, M. Klaus, and W. Mayer, *Angew. Chem., Int. Ed. Engl.*, **8**, 883 (1969).
(212) Complexes between cyclopropane rings and metal atoms are now well known. See, for example, N. A. Bailey, R. D. Gillard, M. Keeton, R. Mason, and D. R. Russell, *Chem. Commun.*, 396 (1966); W. J. Irwin and F. J. McQuillin, *Tetrahedron Lett.*, 1937 (1968); D. M. Roundhill, D. N. Lawson, and G. Wilkinson, *J. Chem. Soc. A*, 845 (1968); R. M. Moriarty, C.-L. Yeh, K.-N. Chen, and R. Srinivasan, *Tetrahedron Lett.*, 5325 (1972); M. R. Churchill and R. Mason, *Advan. Organometal. Chem.*, **5**, 93 (1967); and references cited in these articles. Cyclopropane–metal complexes are presumably formed in the catalytic hydrogenolysis of cyclopropanes. See, for example, J. Newham, *Chem. Rev.*, **63**, 123 (1963); E. J. Klabunovskii, *Russ. Chem. Rev.*, **35**, 546 (1966).
(213) (a) H. C. Volger, H. Hogeveen, and M. M. P. Gaasbeek, *J. Amer. Chem. Soc.*, **91**, 2137 (1969); (b) H. C. Volger, H. Hogeveen, and M. M. P. Gaasbeek, *ibid.*, **91**, 218 (1969).
(214) T. J. Katz and S. A. Cerefice, *J. Amer. Chem. Soc.*, **91**, 2405, 6519 (1969); **93**, 1049 (1971).
(215) B. C. Menon and R. E. Pincock, *Can. J. Chem.*, **47**, 3327 (1969).
(216) J. Joris, P. v. R. Schleyer, and R. Gleiter, *J. Amer. Chem. Soc.*, **90**, 327 (1968); Z. Yoshida, N. Ishibe, and H. Kusumoto, *ibid.*, **91**, 2279 (1969).
(217) For a recent survey, see R. Hoffmann and R. B. Davidson, *J. Amer. Chem. Soc.*, **93**, 5699 (1971).
(218) M. Sakai, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 4452 (1970).
(219) M. A. Battiste and J. W. Nebzydoski, *J. Amer. Chem. Soc.*, **92**, 4450 (1970).
(220) P. v. R. Schleyer, J. J. Harper, G. L. Dunn, V. J. DiPasquo, and J. R. E. Hoover, *J. Amer. Chem. Soc.*, **89**, 689 (1967).
(221) W. G. Dauben and D. L. Whalen, *J. Amer. Chem. Soc.*, **93**, 7244 (1971).
(222) W. L. Dilling, C. E. Reineke, and R. A. Plepys, *J. Org. Chem.*, **34**, 2605 (1969); W. L. Dilling, R. A. Plepys, and R. D. Kroening, *J. Amer. Chem. Soc.*, **94**, 8133 (1972).
(223) K. B. Wiberg and B. A. Hess, *J. Amer. Chem. Soc.*, **88**, 4433 (1966); J. J. Gajewski, R. L. Lyle, and R. P. Gajewski, *Tetrahedron Lett.*, 1189 (1970); W. G. Dauben and J. L. Chitwood, *J. Amer. Chem. Soc.*, **92**, 1624 (1970).
(224) W. G. Dauben and D. L. Whalen, *J. Amer. Chem. Soc.*, **88**, 4739 (1966).
(225) J. S. Ward and R. Pettit, *J. Amer. Chem. Soc.*, **93**, 262 (1971).
(226) R. Baker and T. J. Mason, *J. Chem. Soc., Perkin Trans. 2*, 18 (1972); *J. Chem. Soc. B*, 1144 (1971); and earlier papers in this series.
(227) C. J. Collins, *Chem. Rev.*, **69**, 543 (1969); C. C. Lee, *Progr. Phys. Org. Chem.*, **7**, 129 (1970); G. E. Schenck and F. A. L. Anet, *Tetrahedron Lett.*, 2779 (1971); L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 311 (1972); N. Bodor, M. J. S. Dewar, and D. H. Lo, *ibid.*, **94**, 5303 (1972); C. C. Lee, S. Vassie, and E. C. F. Ko, *ibid.*, **94**, 8931 (1972); and references cited in these articles.

(228) Y. E. Rhodes and V. G. DiFate, *J. Amer. Chem. Soc.*, **94**, 7582 (1972).
(229) See, for example, A. Yokozeki and K. Kuchitsu, *Bull. Chem. Soc. Jap.*, **44**, 2356 (1971); G. Dallinga and L. H. Toneman, *Recl. Trav. Chim. Pays-Bas.* **87**, 795, 805 (1968); R. Destro, C. M. Gramaccioli, and M. Simonetta, *Chem. Commun.*, 568 (1968); R. Destro, G. Filippini, C. M. Gramaccioli, and M. Simonetta, *Tetrahedron Lett.*, 5955 (1968); 3223 (1969); I. R. Bellobono, R. Destro, C. M. Gramaccioli, and M. Simonetta, *J. Chem. Soc. B.* 710 (1969); H. Koyama and K. Okada, *ibid.*, 940 (1969); T. Sato, M. Shiro, and H. Koyama, *ibid.*, 935 (1968); J. F. Chiang, C. F. Wilcox, and S. H. Bauer, *J. Amer. Chem. Soc.*, **90**, 3149 (1968); T. P. DeLacy and C. H. L. Kennard, *J. Chem. Soc., Perkin Trans. 2.* 2153 (1972); G. Filippini, C. M. Gramaccioli, C. Rovere, and M. Simonetta, *Acta Crystallogr., Sect. B*, **28**, 2869 (1972); and references cited in these articles.
(230) J. R. Edman and H. E. Simmons, *J. Org. Chem.*, **33**, 3808 (1968).
(231) C. S. Gibbons and J. Trotter, *Can. J. Chem.*, **51**, 87 (1973).
(232) T. D. Goldman, *Tetrahedron*, **28**, 3175 (1972).
(233) See L. N. Ferguson, *J. Chem. Educ.*, **47**, 46 (1970); P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Amer. Chem. Soc.*, **92**, 2377 (1970).
(234) Using the usual additive technique,[233] a somewhat lower value (4–9 kcal/mol) is obtained for this strain energy difference.
(235) Hoffmann[37] has calculated the most stable conformation of **167** to be one in which the bridge is tilted toward the cyclopropyl group.
(236) For reviews see H. C. Brown, *J. Chem. Soc.*, 1248 (1956); Ya. L. Gol'dfarb and L. I. Belen'kii, *Russ. Chem. Rev.*, **29**, 214 (1960).
(237 (a) R. Zbinden and H. K. Hall, *J. Amer. Chem. Soc.*, **82**, 1215 (1960); (b) D. Cook, *Can. J. Chem.*, **39**, 31 (1961); J. O. Halford, *J. Chem. Phys.*, **24**, 830 (1956).
(238) P. v. R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, **83**, 182 (1961); C. S. Foote, *ibid.*, **86**, 1853 (1964); P. v. R. Schleyer, *ibid.*, **86**, 1854, 1856 (1964).
(239) P. D. Bartlett and W. P. Giddings, *J. Amer. Chem. Soc.*, **82**, 1240 (1960).
(240) J. F. Chiang, *J. Amer. Chem. Soc.*, **93**, 5044 (1971); Y. Tsukuda, T. Sato, M. Shiro, and H. Koyama, *J. Chem. Soc. B*, 1166 (1969); G. Dallinga and L. H. Toneman, *Recl. Trav. Chim. Pays-Bas.* **86**, 171 (1967).
(241) E. C. Friedrich, M. A. Saleh, and S. Winstein, *J. Org. Chem.*, **38**, 860 (1973).
(242) M. A. Cooper, C. M. Holden, P. Loftus, and D. Whittaker, *J. Chem. Soc., Perkin Trans. 2.* 665 (1973).
(243) T. Norin and L.-Å Smedman, *Acta Chem. Scand.*, **25**, 2010 (1971).
(244) J. B. Lambert, A. P. Jovanovich, J. W. Hamersma, F. R. Koeng, and S. S. Oliver, *J. Amer. Chem. Soc.*, **95**, 1570 (1973).
(245) J. W. Wilt and T. P. Malloy, *J. Org. Chem.*, **38**, 277 (1973).
(246) P. K. Freeman and B. K. Stevenson, *J. Amer. Chem. Soc.*, **95**, 2890 (1973).
(247) P. G. Gassman and X. Creary, *J. Amer. Chem. Soc.*, **95**, 2729 (1973).
(248) H. Hart and M. Kuzuya, *J. Amer. Chem. Soc.*, **95**, 4096 (1973).
(249) H. Hart and M. Kuzuya, *Tetrahedron Lett.*, 4123 (1973).
(250) C. G. Biefeld, H. A. Eick, and H. Hart, *Tetrahedron Lett.*, 4507 (1973).
(251) S. Masamune, M. Sakai, A. V. Kemp-Jones, H. Ona, A. Venot, and T. Nakashima, *Angew. Chem., Int. Ed. Engl.*, **12**, 769 (1973).
(252) P. G. Gassman and X. Creary, *J. Amer. Chem. Soc.*, **95**, 6852 (1973).
(253) R. Bicker, H. Kessler, and A. Steigel, *Tetrahedron Lett.*, 2371 (1973).
(254) G. Ellen and G. W. Klumpp, *Tetrahedron Lett.*, 4171 (1972).
(255) S.-I. Murahashi, K. Okumura, T. Kubota, and I. Moritani, *Tetrahedron Lett.*, 4197 (1973).
(256) P. G. Gassman and X. Creary, *Tetrahedron Lett.*, 4407 (1972).
(257) M. J. S. Dewar and W. W. Schoeller, *Tetrahedron*, **27**, 4401 (1971).
(258) R. Hoffmann, P. D. Mollère, and E. Heilbronner, *J. Amer. Chem. soc.*, **95**, 4860 (1973).
(259) R. D. Bach, J. H. Siefert, M. T. Tribble, R. A. Greengard, and N. A. LeBel, *J. Amer. Chem. Soc.*, **95**, 8182 (1973).
(260) R. B. Kinnel and P. K. Freeman, *Tetrahedron Lett.*, 4803 (1973).
(261) P. G. Gassman and E. A. Armour, *J. Amer. Chem. Soc.*, **95**, 6129 (1973).
(262) J. M. Hornback, *J. Org. Chem.*, **38**, 4122 (1973).
(263) T. Norin, S. Strömberg, and M. Weber, *Acta Chem. Scand.*, **27**, 1579 (1973).
(264) J.-M. Lehn and G. Wipff, *J. Chem. Soc., Chem. Commun.*, 747 (1973).
(265) G. R. de Maré, S. Lapaille, L. D. Kispert, and C. U. Pittman, *J. Mol. Struct.*, **17**, 417 (1973).
(266) C. F. Wilcox, L. M. Loew, and R. Hoffmann, *J. Amer. Chem. Soc.*, **95**, 8192 (1973).
(267) Y. E. Rhodes and L. Vargas, *J. Org. Chem.*, **38**, 4077 (1973).
(268) M. I. Page, *Chem. Soc. Rev.*, **2**, 295 (1973).