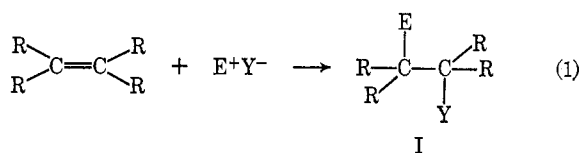# Electrophilic Additions to Strained Olefins

T. G. TRAYLOR
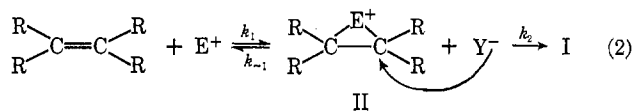
Department of Chemistry, University of California, San Diego, Revelle College, La Jolla, California

The additions of electrophilic reagents such as chlorine, bromine, sulfenyl halides, mercuric salts, and protic acids to simple cyclic and acyclic olefins usually occur with *trans* stereochemistry.[1,2]

$$(1)$$

In those cases where high stereospecificity is observed, the *trans* addition is generally attributed to the formation of a strong olefin–electrophile complex which behaves as a three-membered ring. This ring intermediate presumably opens by nucleophilic attack with inversion of configuration (SN2) at the carbon where positive charge would be most stabilized (Markovnikov addition). The examples in reactions 3 and 4

$$(2)$$

exemplify some of the results which characterize electrophilic additions.

$$(3)^3$$

$$(4)^4$$
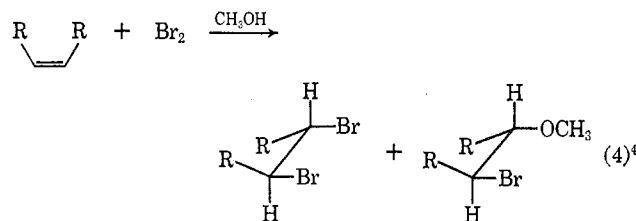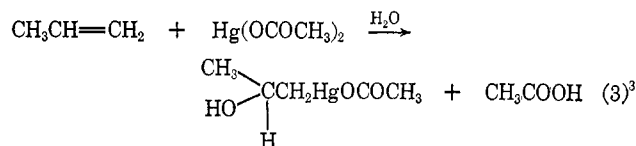
If the olefin–electrophile complex is rapidly and reversibly formed, as is often assumed, then the transition state for the addition has structure III. While there is general agreement that the *trans*-coplanar transition state, III, for electrophilic addition is lower in energy than the corresponding *cis* transition state, IV, there is no such agreement that III is always pre-

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(1) Electrophilic additions to olefins and acetylenes have been reviewed recently.[2] The reader is referred to ref 2a for discussions of various mechanisms of addition.

(2) (a) R. C. Fahey in "Topics in Stereochemistry," N. Allinger and E. L. Eliel, Ed., John Wiley & Sons, Inc., New York, N. Y., in press; (b) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier Publishing Co., New York, N. Y., 1966.
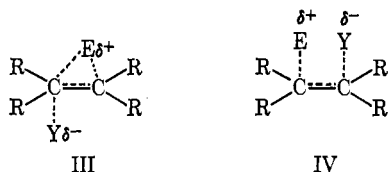
(3) (a) F. C. Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co., Reinhold Publishing Corp., New York, N. Y., 1921; (b) W. Kitching, *Organometal. Rev.*, **3**, 61 (1968); (c) N. S. Zefirov, *Russ. Chem. Rev.*, **34**, 527 (1965).

(4) Reference 2a, pp 286–288.

III   IV

ceded by ions such as II.[5,6] Practically all concerted ionic processes (E2 elimination, fragmentation, etc.)[7] appear to prefer a *trans*-coplanar arrangement of the two entering or leaving groups and the two carbons.

The addition of hypochlorous acid,[8] bromine,[9] acidified hydrogen peroxide,[10] and sulfenyl halides[9b] to the strained bicyclic olefin, norbornene, conformed to the two-step mechanism outlined above. It is well
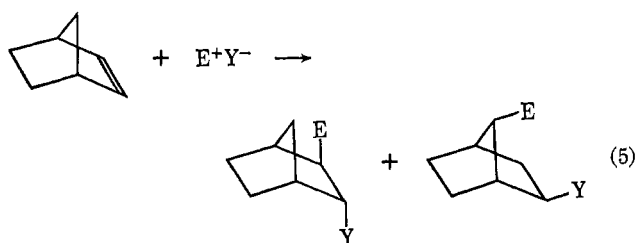
known that the bicycloheptyl ring system is unusually prone to rearrangement when positive charge is generated at C-2. Therefore, rearrrangement during addition of strong electrophiles to norbornene is a natural result of the rearrangement proclivity in this system.
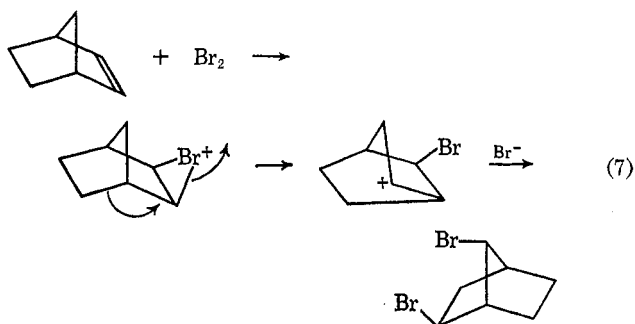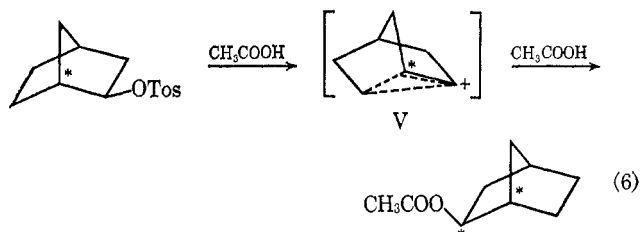
Presumably internal strain makes carbon participation competitive with bromine participation. A mixture of *trans* addition and rearrangement is easily explicable from previously known chemical behavior.

(5) G. S. Hammond and T. D. Nevitt, *J. Am. Chem. Soc.*, **76**, 4121 (1954).

(6) (a) R. C. Fahey and M. W. Monahan, *Chem. Commun.*, 936 (1967); (b) see also ref 2a for a discussion of this problem.

(7) E. M. Kosower, "Introduction to Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1968, pp 95, 105.

(8) W. Woods, R. A. Carboni, and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 5653 (1956).

(9) (a) H. Kwart and L. Kaplan, *ibid.*, **76**, 4072 (1954); (b) H. Kwart and R. K. Miller, *ibid.*, **78**, 5678 (1956); (c) H. Kaplan, H. Kwart, and P. R. Schleyer, *ibid.*, **82**, 2341 (1960).

(10) H. M. Walborsky and R. D. Loncrine, *ibid.*, **76**, 5397 (1954).

cis Addition

The discovery that norbornene reacted with mercuric salts to give neither rearrangement nor the usual *trans* addition, but exclusive *cis* addition,[11] requires a different electrophilic addition mechanism.[12] Because oxymercuration of simple unstrained olefins behaves like bromination of these olefins, there is no good explanation for *trans* bromination and *cis* oxymercuration of norbornene within the ordinary two-step mechanism. A simple carbonium ion is even less likely during mercuration than during bromination for reasons presented later.
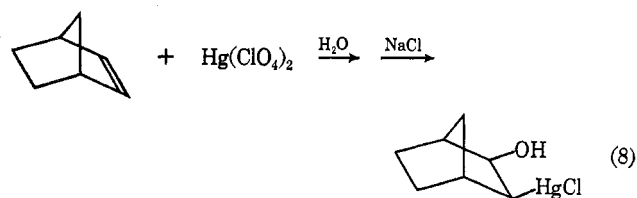
Subsequently norbornene reactions with certain protic acids,[14,15] other metal salts,[16] and nitrosyl chloride[17] were found to take this stereochemistry, and the generality of these *cis* electrophilic additions to a wide variety of bicycloheptene structures was established.[14c]
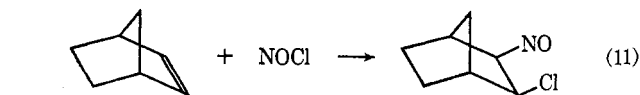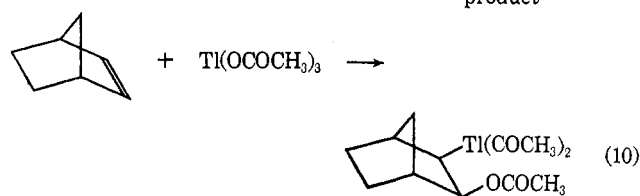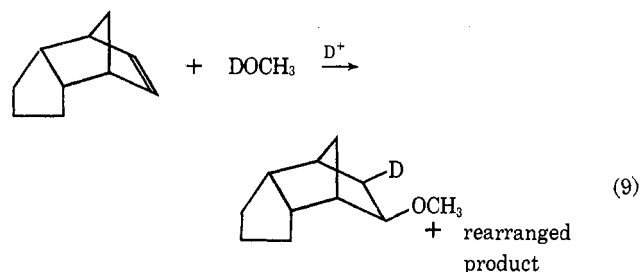
(11) T. G. Traylor and A. W. Baker, *Tetrahedron Letters*, **No. 19**, 14 (1959).

(12) Oxymercuration of norbornene cannot involve the formation of a carbonium ion pair such as that which results in *cis* hydrochlorination of phenylpropenes.[13] We shall see that acid additions to strained olefins also do not occur entirely by carbonium ion pathways.

(13) M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **85**, 3645 (1963).

(14) (a) S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Jurale, *ibid.*, **84**, 3918 (1962); (b) S. J. Cristol, L. K. Gaston, and D. W. Johnson, *Tetrahedron Letters*, 185 (1963); (c) S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Org. Chem.*, **31**, 2719 (1966).

(15) H. Vogelfanger, Ph.D. Thesis, University of California at Los Angeles, 1963.

(16) K. C. Pande and S. Winstein, *Tetrahedron Letters*, 3393 (1964).

(17) J. Meinwald, Y. C. Meinwald, and T. N. Baker, *J. Am. Chem. Soc.*, **85**, 2513 (1963).

Postulated Mechanisms

Several explanations have been proffered for the observation of *cis,exo* additions to norbornenes.

I. Bridged Carbonium Ion Formulation. Because *cis* electrophilic addition to alkenes was first discovered with norbornene and because most studies have involved bicyclo[2.2.1]heptenes,[2a] there is a tendency to relate these *cis* additions to carbonium ion reactions in the bicyclo[2.2.1]heptyl system.
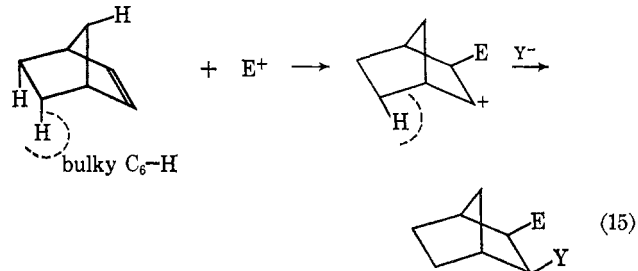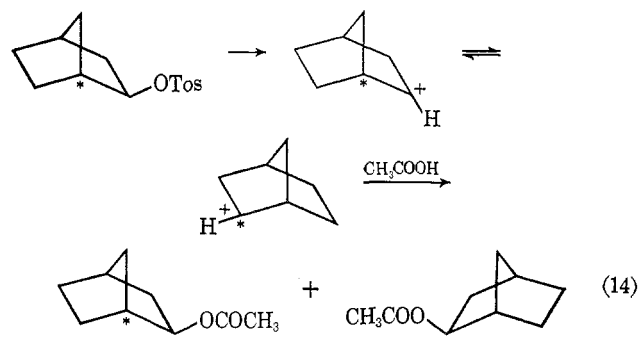
Acetolysis of 2-norbornyl tosylate gives exclusively *exo*-acetate with complete racemization and scrambling of carbons 1 and 2. A plethora of evidence indicates that C-6 participates to form the bridged ion indicated.[18-20]


(12)
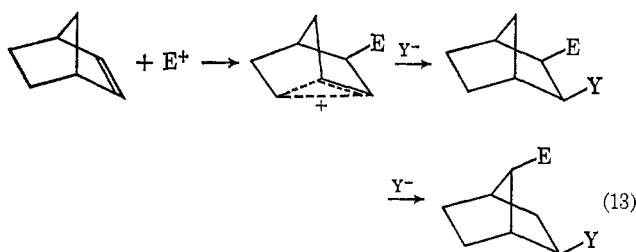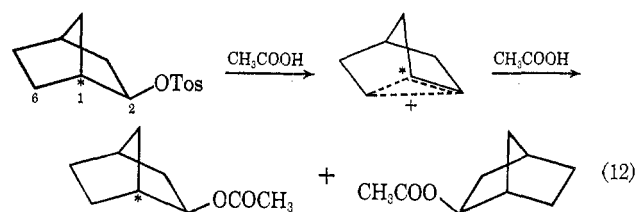
The addition of an electrophile, *e.g.*, H^+, Hg^{2+}, to norbornene might produce a similar ion (13). If the first step traverses a transition state resembling the bridged ion, then *exo* attack will be preferred. The second step results in *exo* addition of Y^- for reasons mentioned above. Thus, according to this mechanism, *cis* addition results from the usual *exo* nucleophilic attack on norbornyl cation.[21] We shall see several reasons why this cannot be the case.

II. Open Carbonium Ions and Steric Control. For reasons too complex to be reviewed here an alternative scheme for solvolysis of norbornyl tosylate (and related reactions) has been offered[23] (14). The rapidly equilibrating simple ions would cause racemization, and the *exo* product is assumed to result from steric hindrance to attack on the *endo* side. Applied to acid or metal salt additions, this mechanism assumes that both steps are sterically controlled (15). As in the bridged ion formulation, *cis* addition results from the requirement for *exo* attack.

(18) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965.

(19) G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966).
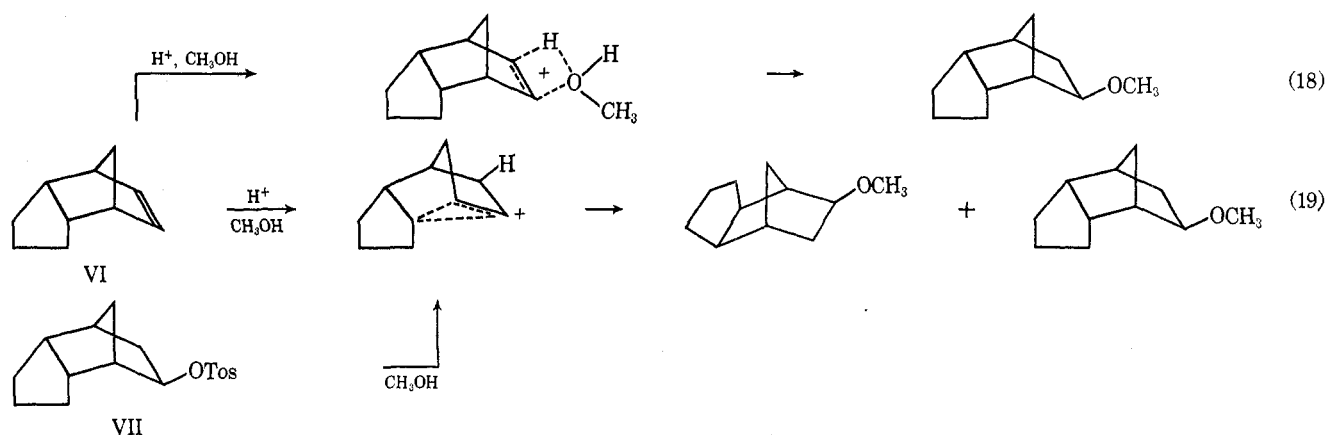
(20) Reference 7, p 137.

(21) This idea has been attributed to Winstein.[22] However, neither Winstein nor Cristol[13] has suggested that *cis,exo* acid additions result from bridged ion formation. Both have suggested molecular addition.

(22) (a) H. C. Brown and K. T. Liu, *J. Am. Chem. Soc.*, **89**, 3900 (1967); (b) *ibid.*, **89**, 3898 (1967); (c) H. C. Brown, J. H. Kawakami, and S. Ikegami, *ibid.*, **89**, 1525 (1967).

(23) H. C. Brown, *Chem. Brit.*, 199 (1966).

(14)

(15)

III. Torsional Effects. A third explanation which relates *cis* additions to the requirement for *exo* attack derives from the special geometry around the C_1-C_2 bonds in bicyclo[2.2.1]heptene or 2-norbornyl cations[24] (16, 17). *endo* attack upon norbornene by an

(16)

(17)
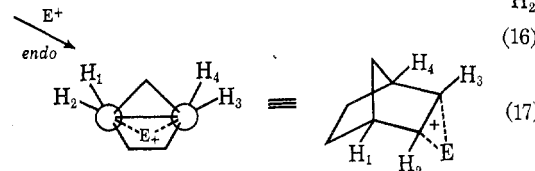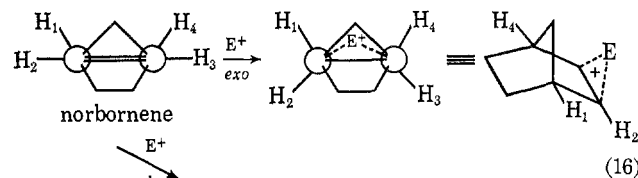
electrophile would cause the C_1-H_1 bond to eclipse the C_2-H_2 bond and the C_4-H_4 bond to eclipse the C_3-H_3 bond. *exo* attack produces a staggered configuration with no eclipsing. If this factor were important it would cause E^+ to attack *exo* and molecular additions would also proceed *exo*, the latter with possibly greater stereospecificity.

IV. Molecular Electrophilic Addition. Because methanolysis of VII and addition of protons to VI in methanol did not produce the same ratio of rearranged and unrearranged products, Cristol and coworkers[14] suggested that acids could be added to this norbornene by two mechanisms: a bridged carbonium ion mechanism and a molecular addition.

cis molecular additions of acids are conceivable since they may be viewed as the microscopic reverse of acetate pyrolyses and similar reactions.[25] However, there remains to explain the appearance of such *cis* additions only in norbornenes and other strained olefins.

(24) P. R. Schleyer, *J. Am. Chem. Soc.*, **89**, 701 (1967).

(25) S. W. Benson and A. W. Bose, *J. Chem. Phys.*, **39**, 3463 (1963). The analogy to acetate pyrolysis, a six-center process, is not a very good one.

$$\text{VI} \xrightarrow[\text{CH}_3\text{OH}]{\text{H}^+} \quad\longrightarrow\quad + \quad\longrightarrow \tag{18}$$

$$\text{VII} \quad \text{OTos} \qquad \text{CH}_3\text{OH} \tag{19}$$

V. The Twist-Strain Theory.

There is one observation in other reactions of bicyclic systems which offers a possible explanation for the finding that *cis* additions occur only to rigid olefins. Cristol and coworkers[26] have observed that base-catalyzed dehydrohalogenation in bicyclo[2.2.1]heptyl and bicyclo[2.2.2]octyl systems occurs preferentially *syn*, whereas in simple cyclic or acyclic olefins *anti* eliminations are strongly preferred.

$$\xrightarrow[.k_B \cong 100 k_A]{\text{NaOR}} \tag{20}$$
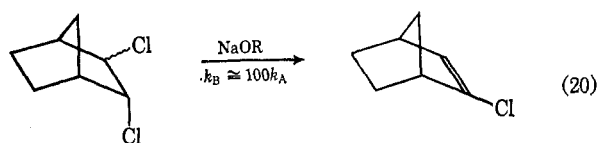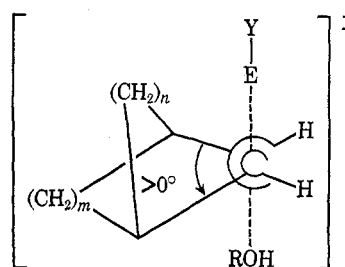
cis,endo (A) or *trans* (B)

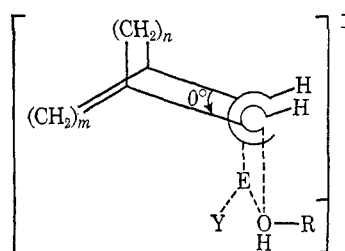The *anti* coplanar transition state for E2 reaction of A is highly strained (C). Application of this idea

C
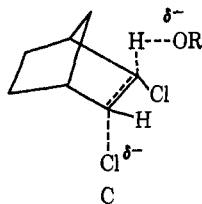
(in its microscopic reverse form) to electrophilic addition[11,27] of bicyclic olefins may be seen in the comparison of planar *syn* and *anti* transition states shown below.

Notice that the *cis* addition brings about eclipsing of two sets of bonds in the transition state, whereas these two sets are ideally staggered during *trans* addition. Thus if no constraint is placed on these conformations by the rest of the molecule, then *trans* (staggered) addition will be preferred. *trans* addition is observed with simple cyclic or acyclic systems.

On the other hand, when n and m have the values 1 and/or 2, the two bridgehead bonds are held in an eclipsed configuration and rotation away from this eclipsed state requires severe strain of the bicyclic structure. In such cases *cis* addition may be preferred. As

(26) (a) S. J. Cristol and E. F. Hoegger, *J. Am. Chem. Soc.*, **79**, 3438 (1957); (b) S. J. Cristol and R. P. Arganbright, *ibid.*, **79**, 3441 (1957).

(27) (a) T. G. Traylor and A. W. Baker, *ibid.*, **85**, 2746 (1963); (b) T. G. Traylor, *ibid.*, **86**, 244 (1964); (c) T. T. Tidwell and T. G. Traylor, *J. Org. Chem.*, **33**, 2614 (1968), (d) A. Factor and T. G. Traylor, *ibid.*, **33**, 2607 (1968); (e) A. Factor, unpublished results.

anti transition state
(for *trans* addition)

syn transition state
(for *cis* addition)

n becomes larger this preference becomes smaller, and with $n,m = 3,3$ the addition should be *trans*.

Unlike the other explanations of *cis* additions, this theory is not necessarily related to the *exo* preference in norbornenes.[14,27b]

Structural Effects on Stereochemistry and Rates

I. Olefin Structure and Stereochemistry of Addition. The stereochemistry of oxymercuration has been established for a wide variety of olefins. The few acid additions (CH_3COOH, HCl, etc.) to strained olefins behave very much like oxymercurations except that rearrangement is much more common during acid addition than during oxymercurations. It will be assumed that the oxymercuration results discussed below may be used to predict the stereochemistries of acid additions where the latter are not known.

A. Cyclic Olefins. According to the twist-strain theory the only cyclic olefin which should add HX or MX *cis* is cyclopropene. Unfortunately all attempts to oxymercurate cyclopropenes have resulted in ring opening.[27e] It is probably because of ring opening that acid additions to cyclopropene have not been reported.

Cyclobutane is bent and, although cyclobutene would tend to be flat, the transition state for electrophilic addition should approach the conformation of cyclobutane resulting in a twist which favors *trans* addition. Cyclobutene, like other cyclic olefins from


(21)

(22)

$n = 1-5$

(23)
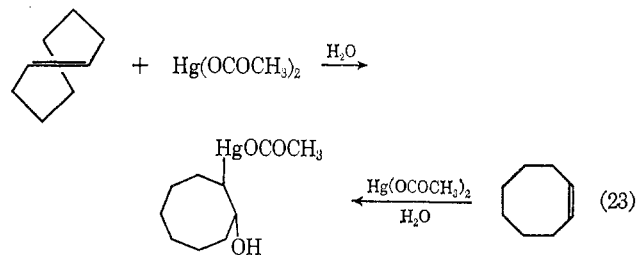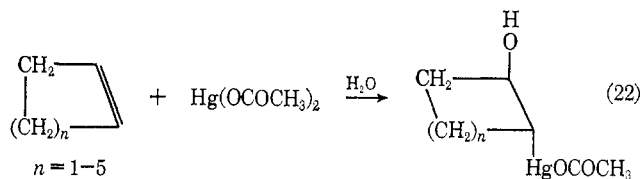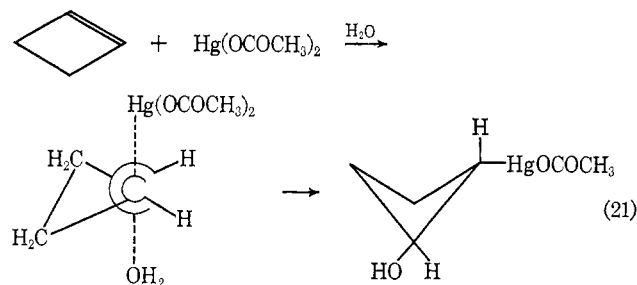
C_4 to C_8, oxymercurates *trans*[27e,28] The exception to this series is *trans*-cyclooctene which oxymercurates *cis*.[27e,29a] Inspection of molecular models of *trans*-cyclooctene reveals complete shielding of one side of the double bond by the ring. Therefore, *trans* addition is impossible, and this highly strained olefin adds *cis* for steric reasons. Additions of acids and other electrophilic reagents to cyclohexenes and cyclopentenes appear to give products derived from *trans* addition (perhaps termolecular)[2a] and carbonium ion formation.

B. Bicyclic Olefins. Except for bicyclo[2.2.1]heptenes, very few bicyclic structures have been subjected to acid additions. More is known about oxymercuration. The twist-strain theory suggests that, as the rigidity of the bicyclic structures is reduced, the stereochemistry of addition should change from *cis* to *trans*. The series of olefins in Table I represents an excellent test of this idea, particularly with inclusion of the extensive study of Bond.[30]

The results with cyclohexene and norbornene are compatible with any of the proposals discussed above. However, both bicyclo[2.2.2]octene and bicyclo[2.1.1]hexene are symmetrical about the double bond. There-

fore an open carbonium ion would have no reason to give stereospecificity (24). Similarly torsional effects[24]

(24)

(not observed)
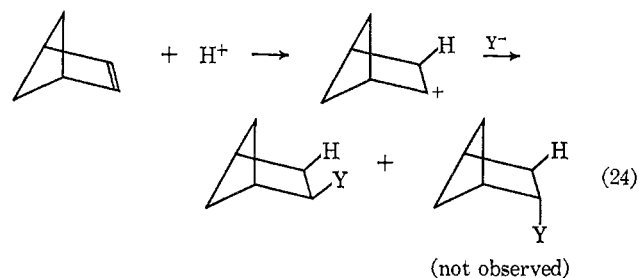
for *cis* or *trans* addition to this olefin (or to bicyclooctene) would be identical, and torsional effects therefore do not contribute to these two *cis* additions (25, 26).

(25)

(26)
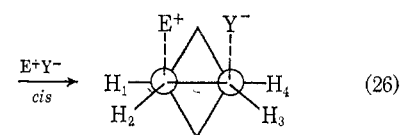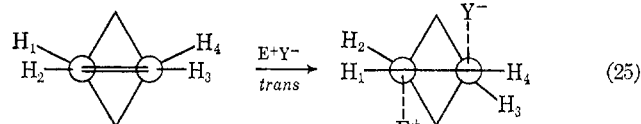
Torsional or steric effects in open carbonium ions are even less acceptable in explaining the *cis* additions to bicyclo[3.1.0]hexene observed by Freeman[31] (27).

(27)
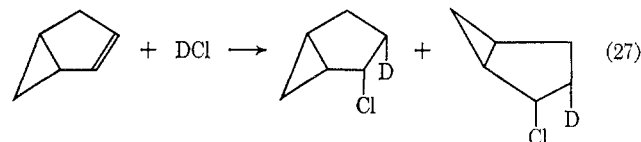
If one of these *cis* additions is due to torsional effects, then the other one is inexplicable. Examination of molecular models indicates that *trans* addition to this olefin results in some twist strain. The authors suggest a molecular addition.

If bridged ions were to be involved in DCl or CH₃-COOH additions to bicyclohexenes, then rearrangement would have been observed. No rearrangement occurred in these additions.[30]

It is clear that *cis* addition is not necessarily related to *exo* attack in the bicycloheptyl system but is a more general behavior of strained olefins. *exo* nucleophilic attack can occur without *cis* addition, and *cis* addition can occur where *exo* positions do not exist.

II. Steric Effects. There is general agreement that steric crowding of the *endo* positions by H-5 and H-6 in bicyclo[2.2.1]heptenes results in preferential *exo* attack upon trigonal C-2, *i.e.*, ketone, olefin, enolate, or carbonium ion.[32] This effect is generally thought to result in *exo* attack being 5–30 times faster than *endo* attack, although some set this figure much higher for certain reactions.[28] If this steric effect were responsible

(28) W. A. Waters, private communication.
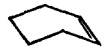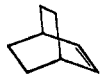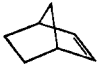
(29) (a) V. I. Sokolov, L. L. Troitskaya, and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, **166**, 136 (1966); (b) V. I. Sokolov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **6**, 1285 (1968).

(30) F. T. Bond, *J. Am. Chem. Soc.*, **90**, 5326 (1968).

(31) P. K. Freeman, F. A. Raymond, and M. F. Grostic, *J. Org. Chem.*, **32**, 24 (1967).

(32) J. A. Berson, "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 130–133.

Table I

Stereochemistry of Electrophilic Additions to Selected Olefins[b]

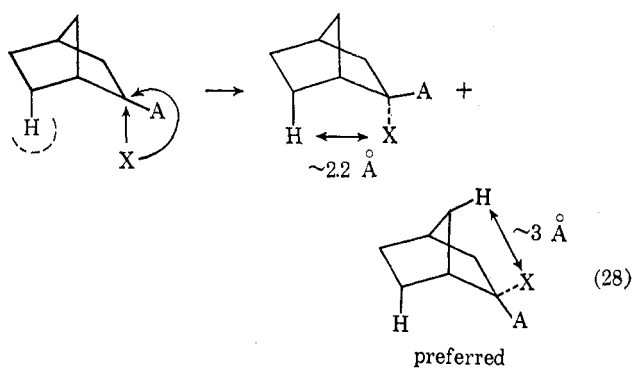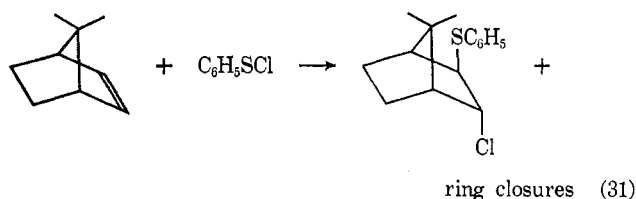|			
	-27.1^a	-28.3^a	-33^a	
Oxymercuration[c]	trans (3b)	cis (27b)	cis (27a)	cis (30)
Oxymercuration[d]	trans[h,i]	cis and trans (27b)[g]	cis (27a)	cis (30)
DCl addition	mostly trans (6a)		cis and rearrangement[i]	cis (30)
CH₃COOD addition			cis and rearrangement (15c)[c]	cis (30)
ArSCl	trans[k]	trans (35)[e,f]	trans (9b)	trans (30)

[a] ΔH_{hyd} (R. B. Turner, "Theoretical Organic Chemistry," The Kekulé Symposium, Butterworth & Co. (Publishers), Ltd., London, 1959, pp 76–77). [b] References in parentheses. [c] Hg(OCOCH₃)₂ in CH₃COOH. [d] Hg(OCOCH₃)₂ in H₂O. [e] Norbornadiene. [f] Dibenzobicyclooctatriene. [g] Similar results have been obtained with dibenzobicyclooctatriene.[22b] [h] M. M. Anderson and P. M. Henry, Chem. Ind. (London), 2053 (1961). [i] S. Wolfe and P. G. Campbell, Can. J. Chem., 43, 1184 (1965). [j] J. K. Stille, F. M. Sonnenberg, and T. H. Kinstle, J. Am. Chem. Soc., 88, 4922 (1966). [k] S. J. Cristol, R. P. Arganbright, G. D. Brindell, and R. M. Heitz, ibid., 79, 6035 (1957).


(28)

preferred

for *cis,exo* addition to norbornenes, then a large group in the *syn*-7 position should bring about predominantly *endo* attack. Tidwell[27c,33] tested this hypothesis by adding mercuric acetate to 1,4,7,7-tetramethylnorbornene and *syn*-7-bromonorbornene. The result was highly stereospecific *cis,exo* addition (29, 30). Brown

(29)

(100% by nmr and kinetics)

(30)

(100% by nmr)
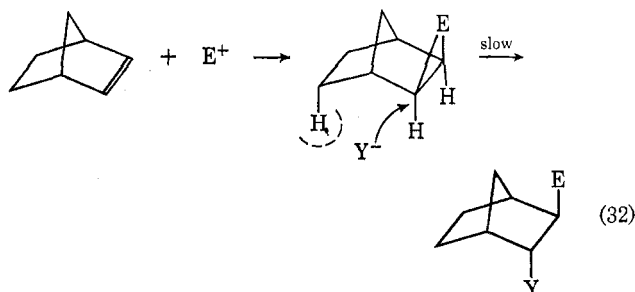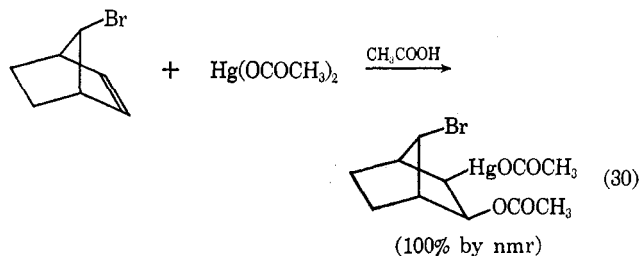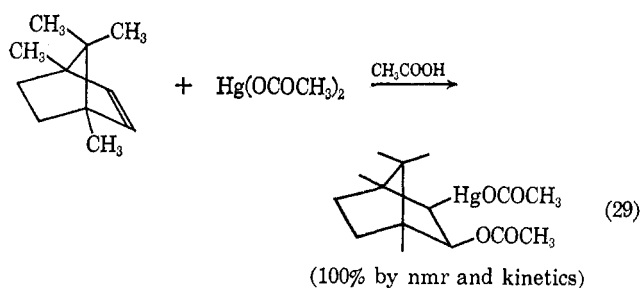
and coworkers[22c] have confirmed this finding (using 7,7-dimethylnorbornene) and have also shown that DCl adds *cis,exo* to 7,7-dimethylnorbornene.[22a] Even

(33) As quoted in ref 22c and 24. The work itself was published almost 2 years after it was submitted.

benzenesulfenyl chloride adds to this olefin with exclusive *exo* RS⁺ attack.[34]

ring closures   (31)

Clearly the stereochemistry of electrophilic additions to norbornenes is not governed by the same steric effects as are hydroboration,[22a] ketone reduction,[32] or classical carbonium ion reactions[18,19,35,36] in this ring structure, for in the latter reactions attack is predominantly *endo* when 7,7-dimethyl substitutents are present. The exclusive *cis,exo* oxymercurations of norbornadiene[17b] and benznorbornadiene[27c] having no *endo*-6 hydrogens are difficult to explain by steric effects, as are the additions to bicyclo[2.2.2]octene[27b] and bicyclo[2.1.1]hexene.[30]

One special steric feature of bicyclic systems might lead to *cis* additions for two-step processes. If, in the first step, the electrophile forms a complex having the geometry of a three-membered ring, a nucleophile would encounter neopentyl-type hindrance to backside opening (32). Because the three-membered ring is tilted away from the methylene bridge, attack from the *endo* side to open this ring must be made from the

(32)

(34) W. H. Mueller and P. E. Butler, J. Am. Chem. Soc., 90, 2075 (1968).
(35) C. L. Perrin and T. G. Traylor, ibid., 88, 4934 (1966).
(36) C. F. Wilcox, Jr., and R. G. Ilsaitis, Chem. Commun., 1046 (1967).

$$(33)$$
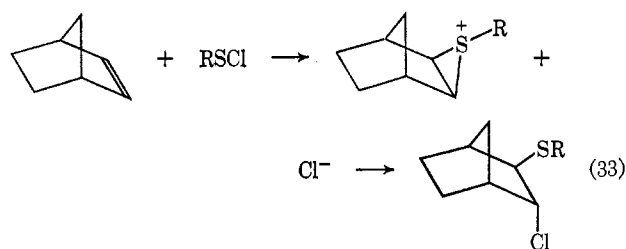
approximate direction of the C_6 endo hydrogen. This type of hindrance will be encountered in all the bicyclic systems discussed here. Yet several reagents (RSCl, Br_2) add to norbornene in just this way (33). Therefore such endo attack is not prohibited by steric effects. In fact, steric hindrance in reaction 33 should be no worse for endo RS^+ and exo Cl^- attack.

Although steric effects exist in these reactions, they seem to be much less important than electronic effects or other geometric effects.[37]

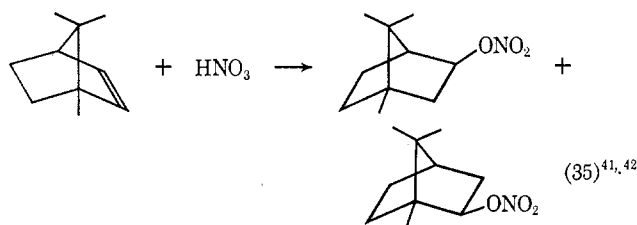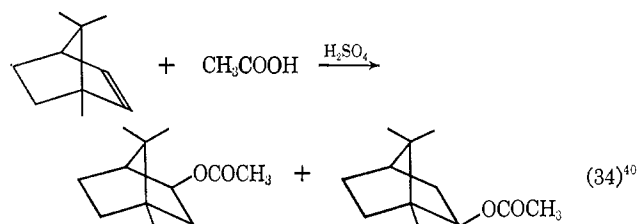**III. Electronic Effects.** Substitution of electronegative groups on norbornene or norbornadiene severely decreases the rate of addition. For example, exo-5-cyanonorbornene is oxymercurated with mercuric acetate at 1/300th the rate of norbornene in methanol.[17d] 2,3-Dicarbomethoxynorbornadiene is oxymercurated much more slowly than is norbornene (or norbornadiene),[38a] and 1,2,3,4,7,7-hexachloronorbornadiene is not oxymercurated by mercuric acetate in acetic acid.[38a] The presence of such electronegative groups in the 5 and/or 6 positions precludes any contribution from carbon bridging. Yet even such unreactive norbornenes as 7-oxa-5,6-dicarbomethoxynorbornene,[39] 5,6-dicarbomethoxynorbornadiene,[38] 5-cyanonorbornene (cis or trans), or 5-carbomethoxynorbornene[27d] oxymercurate cis,exo.

As for the effect of electron-donating groups, addition of acids to bornylene gives about equal amounts of the two isomeric products (34, 35). Since 1-methyl-2-

$$(34)^{40}$$

$$(35)^{41,42}$$

exo-norbornyl tosylate solvolyzes about 50 times faster than 2-exo-norbornyl tosylate, the above results suggest that at least a portion of these additions did not have the same charge distribution in the transition state as that obtained in tosylate solvolyses.[44]

IV. Neighboring Group Effects. Although highly strained and rigid olefins invariably add acids and metal salts cis, the same structures revert to trans addition is an internal nucleophile is present.[27d,4,45]

VIIIa, $X = H_2$
VIIIb, $X = O$

VI (E = D, $HgOCOCH_3$, I, etc.)

$$(36)$$
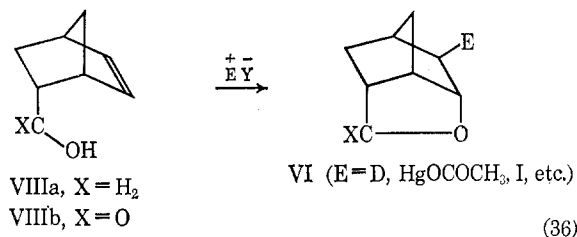
These ring closures take precedence over both cis addition and rearrangement and set rather low limits ($\sim 10^3$) upon the facility for the latter processes. Even endo electrophilic attack may be brought about by neighboring groups.

$$(37)^{27d,46a,b}$$
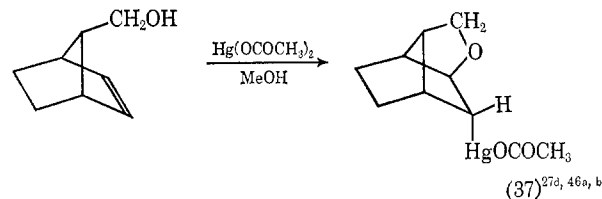
Mercuric acetate in methanol reacts at least 10^4 times faster with VIIIa than with norbornene.[38a] This acceleration is comparable to that obtained in the open-chain system where both reactions are trans.[46]

$$(38)^{47}$$

Based on limits of detectability of trans isomers, it has been estimated that cis additions (HX, HgX_2) to norbornenes predominate over trans by at least 100:1. The effects of neighboring groups suggest that this ratio is probably not more than about 10^4:1.

V. Nature of the Electrophilic Addend. Table II lists the stereochemical outcome of additions of various electrophilic reagents to norbornene. It is unfortunate that we do not have such an extensive table for bicyclo-[2.2.2]octene and bicyclo[2.1.1]hexene. All three pos-

(37) Extensive work of Winstein and coworkers reviewed in ref 18 and 19 has made this rather clear.

(38) (a) T. G. Traylor, unpublished data; (b) this result was obtained in acetic acid.

(39) Y. K. Yurev, N. S. Zefirov, and L. P. Prikazchikova, *Zh. Obshch. Khim.*, **32**, 2744 (1962).

(40) A. K. Shavrygin and N. S. Prostakov, *J. Gen. Chem. USSR*, **18**, 495 (1948).
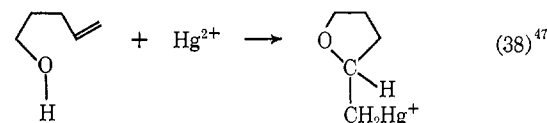
(41) L. Kuczynski and H. Kuczynski, *Roczniki Chem.*, **25**, 432 (1951).

(42) Recently this lack of discrimination has also been observed with hydrochloric[22a] and formic acids[43] and mercuric salts.[22c]

(43) P. R. Schleyer, *J. Am. Chem. Soc.*, **89**, 3901 (1967).

(44) Brown's alternate proposal that this reaction proceeds through a classical carbonium ion pair which sometimes collapses before rearrangement is discussed in the mechanism section.

(45) H. B. Henbest and B. Nicholls, *J. Chem. Soc.*, 227 (1959).

(46) (a) R. K. Bly and R. S. Bly, *J. Org. Chem.*, **28**, 3175 (1963); (b) R. S. Bly, R. K. Bly, A. O. Bedenbaugh, and O. R. Vail, *J. Am. Chem. Soc.*, **89**, 881 (1967). Both exo and endo acetoxymercuri groups were obtained when syn-7-(2-hydroxyethyl)bicyclo[2.2.1]heptene was oxymercurated.

(47) J. Halpern and H. B. Tinker, *ibid.*, **89**, 6427 (1967).

Table II
Stereochemistry of Electrophilic Additions to Norbornene

| Reagent | Percentage of isolated product | | | |
	cis,exo	trans	Rearranged	Ref
CH_3COOD^a	95	0	5	14c
DCl	60 (40)^b	0	40 (60)^{b,c}	22d
DBr (D_2O)	48	0	52	
$Hg(OCOCH_3)_2$	100	0	0	27a
$Tl(OCOCH_3)_3$	100	0	0	16
NOCl	100	0	0	17
RSCl	0	100	0	9b
Br_2	0	16	57	9a
Cl_2	3.5	6	25.5	d
H_2O_2 (H^+)	0	0	100	9c

^{a} The substrate was norbornadiene. ^{b} These two results were obtained under different conditions. ^{c} See Table I, footnote j. ^{d} M. C. Poutsma, *J. Am. Chem. Soc.*, **87**, 4293 (1965).

sibilities, *cis* and *trans* addition and rearrangement, have been found.

There seems to be a pattern for the kinds of reagents which bring about rearrangement. The fraction of rearrangement decreases in the order H_2O_2, H^+ > Cl^+ > Br^+ > H^+ > RS^+, XHg^+. This order relates to electronegativities or possibly to the tendency for the mentioned groups to stabilize a neighboring carbonium ion. Cl–, Br–, RS– may do this by neighboring group participation, *e.g.*
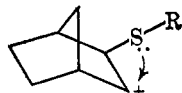
the XHg group has been shown to do this principally by hyperconjugation.[48,49]
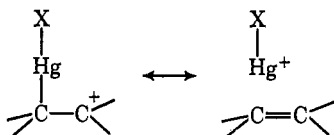
Since the XHg group is more stabilizing by several kilocalories per mole than even an RS neighboring group, it is easy to understand why rearrangements never occur in kinetically controlled oxymercurations.

If we correct for rearrangements, then the two classes of reagents for addition to rigid olefins are: *cis* addition, HX, HgX_2, TlX_3, NOCl; *trans* addition, Cl_2(?), Br_2, RSCl.

Mechanisms

Most of the *cis* additions to strained olefins are explicable in terms of two factors. (1) Certain electrophilic reagents have a tendency toward *cis* molecular addition to all olefins as a result of the tendency of the electrophile to simultaneously bind an olefin and

(48) W. Hanstein and T. G. Traylor, *Tetrahedron Letters*, 4451 (1967).
(49) If there is a positively charged intermediate in oxymercuration, then the "bridged" or "hyperconjugation" formulations are not significantly different. However, the strong hyperconjugation of HgX groups suggests that oxymercurations and deoxymercurations may be concerted termolecular processes like the hydrochloric acid additions reported by Fahey and Monahan.[6a]
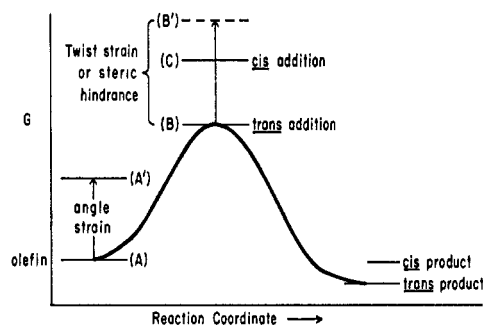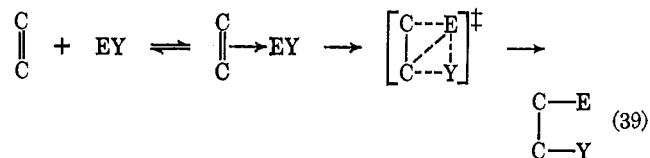

Figure 1. Energy-reaction coordinate diagram for electrophilic additions to strained olefins.

$$C \parallel C + EY \rightleftharpoons C \parallel C \rightarrow EY \rightarrow \left[\begin{matrix} C\text{---}E \\ | \nearrow \\ C\text{---}Y \end{matrix} \right]^{\ddagger} \rightarrow$$

$$\begin{matrix} C\text{---}E \\ | \\ C\text{---}Y \end{matrix} \quad (39)$$

another nucleophile[25] (39). The π complex is a weak molecular complex[2a] and is not pictured as resembling the bromonium ion. Similar complexes might be expected with mercuric or thallium salts. (2) Geometrical restrictions in the olefin may retard the rate of *trans* addition without greatly affecting the rate of *cis* addition. These geometrical restrictions are apparently imposed in two ways. The olefin may be held in a rigid, eclipsed conformation which prevents *trans* addition (this appears to be very common in additions to strained bicyclic olefins), or the olefin may be completely blocked on one side so that all reagents must approach the olefin from the same side. Thus far only the *cis* oxymercuration of *trans*-cyclooctene is attributable to this rather special steric effect.
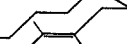
The operation of these geometrical effects may be seen in the reaction coordinate diagram in Figure 1. Both *cis* and *trans* additions are accelerated by angle strain which raises the energy of the starting olefin (A → A'). However, such strain is usually accompanied by general rigidity which introduces twist strain into the transition state for *trans* addition (A' → B' → *trans*). This twist strain may more than cancel the driving force provided by angle strain. For example, norbornene is oxymercurated >99.8% *cis* at a rate 1000 times faster than that of cyclohexene, indicating that *trans* oxymercuration of norbornene is slower than *trans* oxymercuration of cyclohexene. Therefore, I conclude that twist strain raises the transition state for *trans* addition by more than 4 kcal/mol.

On the other hand, blocked olefins may be either strained or unstrained and produce *cis* addition ($\Delta H^{\ddagger}_{A \to C}$ < $\Delta H^{\ddagger}_{A \to B'}$ and $\Delta H^{\ddagger}_{A' \to C}$ < $\Delta H^{\ddagger}_{A' \to B'}$). *cis* additions due to blocking may therefore occur rapidly or slowly, but those due to twist strain are usually fast. Examples of each class are shown in Table III.

The "polarized molecular addition" of eq 39 is preferred by Cristol and coworkers,[15] by Winstein,[50] by Freeman and coworkers,[31] and by Fahey.[2a] However,

(50) See footnotes 8 and 9 in ref 14.

Table III

Rates and Stereochemictries of Electrophilic Additions to Olefins[a]

	Un-strained, unblocked	Strained, unblocked	Strained, rigid	Strained, blocked	Un-strained, blocked
	⬡	▢	(bicyclic)	(bicyclic)	(cyclohexyl)
Rate	slow (1)	fast	very fast (10⁵)	fast	(very slow[b])
Stereo-chem	*trans*	*trans*	*cis*	*cis*	(*cis*[b])

[a] Most of these conclusions come from oxymercuration studies but are applicable to other additions. See text. [b] This is a predicted result. Such olefins have not been studied, and they would probably produce carbonium ions when allowed to react with electrophiles such as H^+ or Cl^+. Actually no slow *cis* additions to hydrocarbon olefins have been observed, a situation which, I believe, will change.

Brown and Liu[22b] and Schleyer[30] have explained the acid additions to norbornenes in terms of classical norbornyl cations.[51] Their carbonium ion mechansism might explain the *cis* additions if we assume that an ion pair is formed which can collapse before rearrangement can occur (40, 41). Such a rapid collapse (k_c) seems to be


$$\left[\quad \right]^{\ddagger} \xrightarrow[\text{fast}]{k_c} \qquad \qquad (40)$$

$$\downarrow \text{slow}$$

$$\left[\quad \right] \qquad \qquad (41)$$
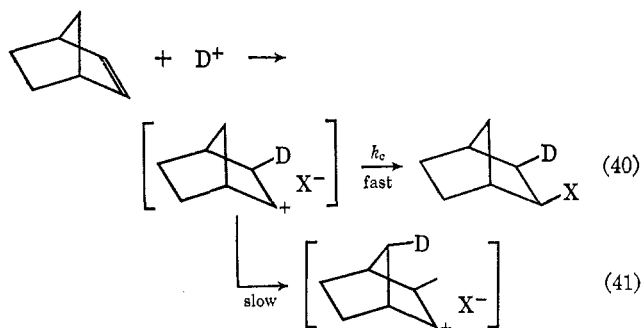
required in the additions of DX, HgX_2, and TlX_3 which are accompanied by only limited raarrangement. However, Winstein[52] has pointed out that trapping of an ion pair in this "unsymmetrical state" requires that k_c be in the order of 10^{13} (equivalent to C–C–C bending rates). Furthermore, this postulated classical ion must be trapped in this state in solvents ranging from heptane[15c] through acetic[50] and formic acids[48] to water,[27a,43] which solvents evoke considerably different probabilities of ion-pair collapse. We therefore conclude that such

(51) Both Brown[22] and Schleyer[43] have argued that HCl addition to 1-methylnorbornene should have resulted in predominant proton attack at C-3 (rather than the 55% observed) if bridged ions were transversed. A 1-methyl substituent increases rates of solvolysis of *exo*-2-norbornyl tosylate. However, as Cristol has pointed out, the transition states for acid additions attain less positive charge on carbon than do those for solvolysis.

(52) S. Winstein, *J. Am. Chem. Soc.*, **87**, 381 (1965).

Scheme I
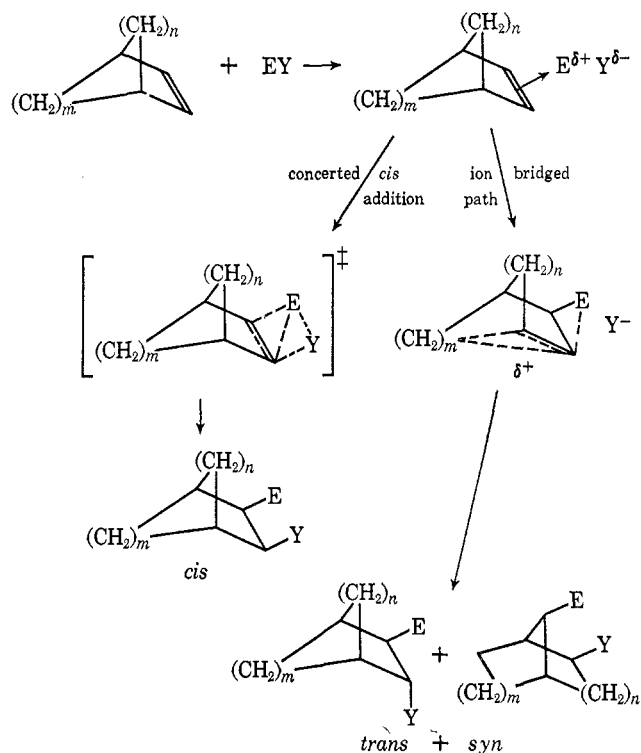
"classical" carbonium ion pairs are not intermediates in electrophilic *cis* additions to strained olefins.

Conclusion

I believe that Scheme I for strained olefins would be preferred by most workers in this field.

Whether rearrangements (and thus cations) occur depends upon the electrophile. In cases where cations occur, they should be the same as those derived from solvolysis. Thus, in the bicyclo[2.1.1]hexyl, bicyclo[2.2.1]heptyl, and bicyclo[2.2.2]octyl systems, metal salts use the concerted path, acids use the concerted plus bridged ion paths, and bromine, chlorine, etc., use bridged ion and halonium ion pathways. Because the additions to strained, rigid olefins are stereospecific, the open carbonium ion pathway probably is not used in addition to these olefins.

According to these postulates unstrained olefins will add electrophiles by carbonium ion pathways, cationic complexes (*e.g.*, brominium ion), or termolecular additions.[2a] Strained, rigid olefins will add electrophiles through molecular *cis* additions or through the kinds of carbonium ions normally encountered in the system under study. Such ions will usually involve some strain-induced delocalization leading to rearrangement.

Additions and Corrections

Volume 2, 1969

T. G. Traylor: Electrophilic Additions to Strained Olefins.

Page 154. The superscript 22 should be deleted from footnote 21 and inserted beside superscript 23 on line 30 (offered[22,23]).