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Oxymercuration of Strained Olefins. The Effect of Neighboring Groups[1]

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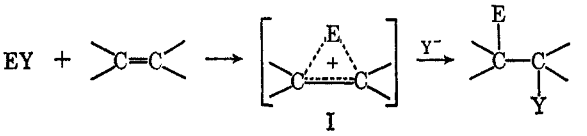
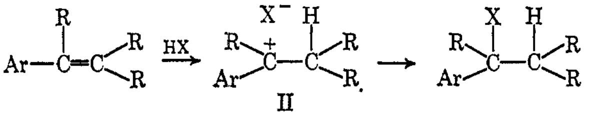
Additions of acids or mercury salts to norbornenes usually give *cis-exo* products. We have studied the effect of neighboring groups such as *endo*-5-methylol, *endo*-5-carboxylate, *endo*-5-carbomethoxy, *endo*-5-cyano, and *syn*-7-methylol upon the stereochemistry of oxymercuration of norbornene. Neighboring groups such as $-COOH$ or $-CH_2OH$ bring about *trans* addition. The *endo*-5-CN or *endo*-5-COOMe groups participate in the addition only in the presence of water. Treatment of *endo*-5-carboxynorbornene with aqueous deuteriosulfuric acid brings about *trans* addition to give the 3-*exo*-deuteriolactone (VIID) in agreement with the oxymercuration reaction. These results do not reveal the cause of the highly stereospecific *cis-exo* additions of mercuric salts and acids to norbornene, but suggest that the demand for *cis* addition is too small to compete with neighboring-group participation in such additions. The results are consistent with either two-step oxymercuration or concerted addition.

Most electrophilic additions to olefins are considered to proceed through an intermediate three-membered ring (π complex) which opens with inversion to give *trans* addition of EY.[3]



(1)

Several instances of *cis* addition of such reagents have also been reported recently.[4-9] These *cis* additions fall into two substrate categories. (1) Addition of electrophilic reagents to aryl-substituted olefins sometimes gives *cis* addition. Evidence has been presented for the occurrence of carbonium ion pairs (II) in such systems.[9] (2) Although strained olefins such as bicycloheptene or bicyclooctene usually add electrophiles with rearrangement,[5b] or with *trans* stereochemistry,[5b] several reagents add in a *cis* fashion as indicated in eq 3-6 below.



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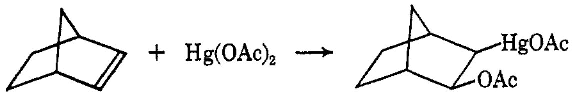
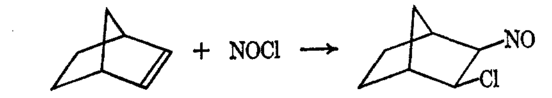


(3)[4a]



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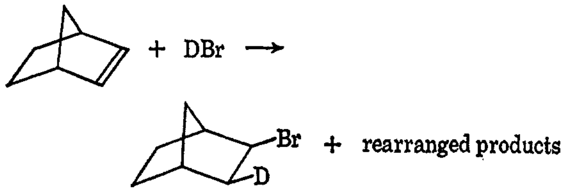

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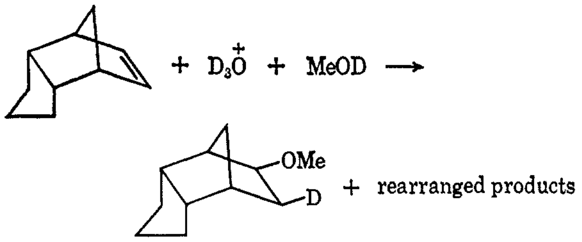

(6)[8]

The stereochemistry of oxymercuration has been investigated in a wide variety of cyclic and bicyclic olefins. *cis* addition has been observed only when the olefin is strained and bicyclic.[4b] Thus oxymercuration

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[1] Presented at the 147th National Meeting of The American Chemical Society, Philadelphia, Pa., April 1964. Although the abstract contains errors in configurations, the data and interpretations presented at that meeting were those recorded here.

[2] National Institutes of Health Postdoctoral Fellow, 1963–1964.

[3] (a) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1962, p 214; (b) J. Chatt, *Chem. Rev.*, **48**, 7 (1951).

[4] (a) T. G. Traylor and A. W. Baker, *Tetrahedron Lett.*, No. 19, 15 (1959); (b) *J. Amer. Chem. Soc.*, **85**, 2746 (1963); (c) T. G. Traylor, *ibid.*, **86**, 244 (1964); (d) A. Factor, unpublished results.

[5] (a) H. Kwart and J. L. Nyce, *J. Amer. Chem. Soc.*, **86**, 2601 (1964); (b) H. Kwart and R. K. Miller, *ibid.*, **78**, 5678 (1956).

[6] K. C. Pande and S. Winstein, *Tetrahedron Lett.*, No. 46, 3393 (1964).

[7] J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *J. Amer. Chem. Soc.*, **86**, 4074 (1964).

[8] (a) S. J. Cristol, W. K. Leifert, D. W. Johnson, and J. B. Jurale, *ibid.*, **84**, 3918 (1962); (b) S. J. Cristol, L. K. Gaston, and D. W. Johnson, *Tetrahedron Lett.*, No. 4, 185 (1963); (c) S. J. Cristol, N. L. Hause, and J. S. Meek, *J. Amer. Chem. Soc.*, **73**, 674 (1951).

[9] M. J. Dewar and R. C. Fahey, *ibid.*, **84**, 2012 (1962).

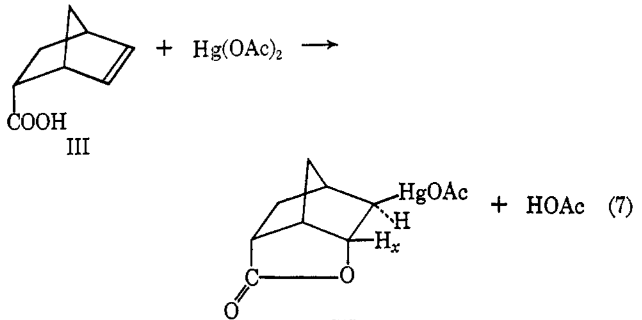
occurs in a *cis* manner with norbornenes,[4b,6,10–12] both *cis* and *trans* with bicyclo[2.2.2]octene,[4c] and *trans* with cyclohexene[4b,12] or other simple cyclic olefins.[4d] The limited data available indicate similar behavior for acid additions.[5a,7,8a,b]

We have previously suggested[4b,c] that these *cis* additions to strained olefins probably occur by a two-step path similar to that in eq 1. They are proposed to differ from the *trans* additions only in the second step in which frontside S$_N$2 opening of the π complex becomes favorable for reasons of strain or steric hindrance.

This paper reports the effects of neighboring groups on rates and stereochemistry of products from additions of acids or mercuric salts to norbornenes.

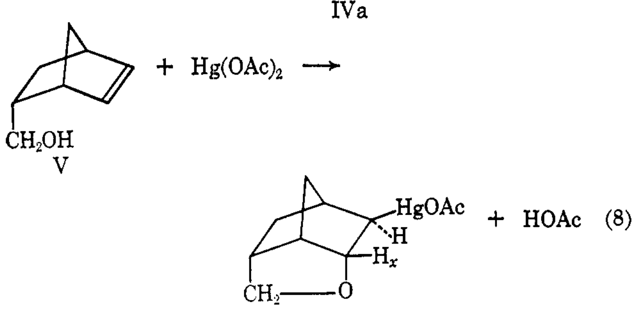
Results

Two of the oxymercurations were reported previously.[13,14] The configuration of the acetomercuri group was not proved. Furthermore, the usual assumption that electrophiles attack norbornene from the *exo* side is not justified in these cases. There is evidence[13] that hydroxy or carboxy groups complex with mercuric ions to lead the mercury into the olefins from the same side as the polar group. Therefore an unequivocal structure proof is needed.



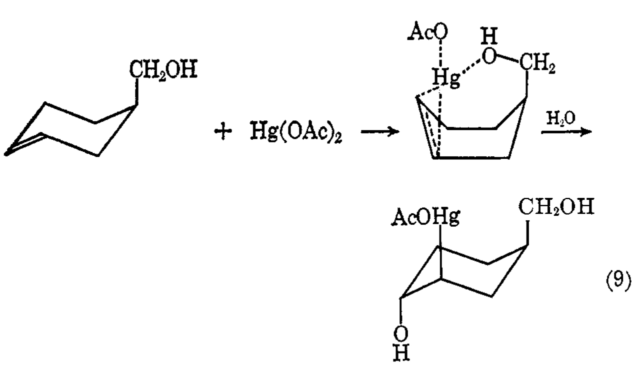
III

IVa



V

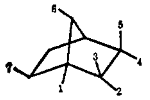
VIa



We have used the nmr spectroscopy technique developed by Anderson and Henry[12] and others to indicate the stereochemistry of the reactions studied.

I. Stereochemistry of Ring Closure in 5-*endo*-Substituted Norbornenes.—To determine the stereochemistry of IV and VI, the products of oxymercuration of bicyclo[2.2.1]hept-2-ene-5-*endo*-carboxylic acid (III) and bicyclo[2.2.1]hept-2-en-5-*endo*-ylmethanol (V) were isolated[13,14a] and their nmr spectra obtained. In both IV and VI proton 2 appeared as a simple doublet centered at τ 4.71 and 4.88, respectively, with a splitting constant (J) of 5.0 Hz. The J values in the norbornyl system are well established and are tabulated in Table I.[15–17]

Table I



H positions	J_{HH}, Hz	Ref
1, 2	0	15
1, 3	3–4	15
1, 3	5	16
2, 4	7.7	15
2, 5	2.2–2.3	15, 17a,b
2, 6	0	12, 17a
	3–4	7
3, 5	7–8	17a
	8–9	15
3, 7	0–1.4	15

Note that J between *cis* protons is quite large (8 or 9 Hz) compared with the ~2 Hz found for the *trans* protons. Also, although the bridgehead proton (1) couples with the *exo* proton (3) with a J of 3–4 Hz, it fails to couple with the *endo* proton (2). The coupling constants between vicinal protons in the norbornyl system have been found to agree quite well with those calculated using the Karplus–Conroy relationship[18a,b] between dihedral angle, ϕ, of vicinal protons and their coupling constant. Equation 10 is as implified version of this relationship[18c] (neglecting electronegativity and C–C–H bond angle and assuming sp^3 hybridization and a C–C bond length of 1.543 Å).

$$J = 4.22 + 4.5 \cos 2\phi - 0.5 \cos \phi \qquad (10)$$

Since the coupling constant found in IV and VI, 5.0 Hz, was intermediate between that for *cis* and *trans* protons, we suspected that some anomalous effect of the chloromercuri group might be operating. However, reduction with sodium–amalgam in D_2O, which has been shown[4b] to go with complete retention of configuration, gave compounds containing one deuterium in whose nmr spectra proton 2 again appeared as a doublet with a splitting constant of ~5.0 Hz.

Synthesis of these deuterated compounds by deuteriosulfuric acid treatment of the appropriate 5-*endo*-

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(10) J. K. Stille and S. C. Stinson, *Tetrahedron*, **20**, 1387 (1964).

(11) (a) N. S. Zefirov, L. P. Prikazchikova, and Yu. K. Yurev, *Dokl. Akad. Nauk. SSSR*, **152**, 869 (1963); (b) *ibid.*, *Zh. Obsch. Khim.*, **35**, 822 (1965); (c) *ibid.*, **32**, 2744 (1962).

(12) M. M. Anderson and P. M. Henry, *Chem. Ind.* (London), 2053 (1961).

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

(14) (a) M. Malaiyandi and G. F Wright, *Can. J. Chem.*, **41**, 1493 (1963); (b) A. M. Bircks and G. F Wright, *J. Amer. Chem. Soc.*, **62**, 2412 (1940).

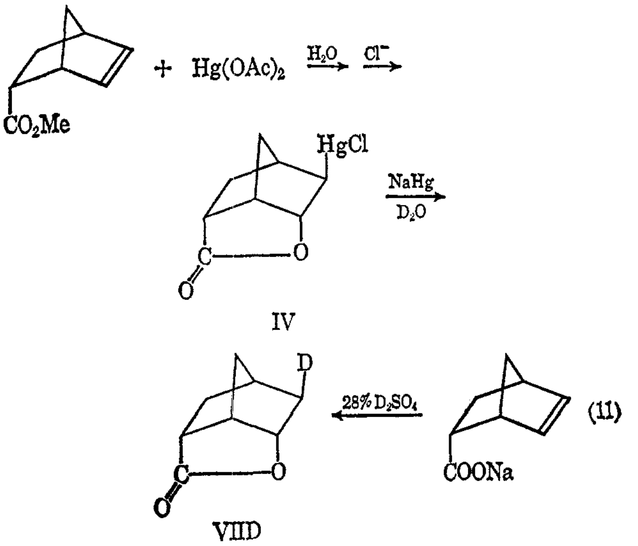
(15) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

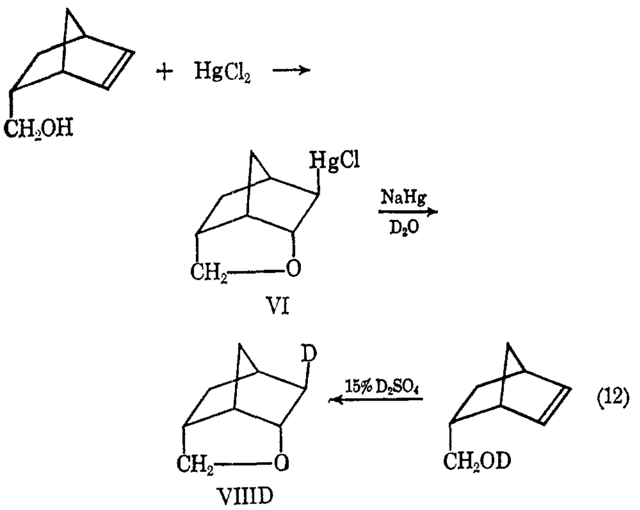
(16) W. D. Kumer, J. N. Schoolery, and F. V. Brutcher, Jr., *J. Amer. Chem. Soc.*, **80**, 2533 (1958).

(17) (a) P. Laszlo and P. R. Schleyer, *ibid.*, **85**, 2709 (1963); (b) *ibid.*, **86**, 1171 (1964).

(18) (a) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); (b) H. Conroy, "Advances in Organic Chemistry," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1960, p 265; (c) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

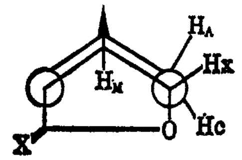
substituted 2-norbornenes gave products identical with those from the reduction of the mercurials. This indicates that the oxymercuration and the proton addition reactions proceeded with the same stereochemistry.





The recent investigations of Cristol[8] and Kwart[5a] have shown that protons, like all other electrophiles,[5b] add to norbornene from the *exo* side. Thus, on this basis, it would appear that, in the above deuteriosulfuric acid cases, the proton added *exo* and that the overall stereochemistry of addition to the double bond was *trans*.

This same conclusion was reached by a study of the nmr spectra of undeuterated compounds (Figure 1). In the spectra of both the lactone and cyclic ether, proton X appeared as a quartet. The exact same quartet was found in the spectra of these compounds run at 100 Mc on a Varian HR-100 spectrometer,[19] showing that the quartet was due to spin-spin splitting. Interpreting this as the X part of an AMX system, it can be concluded that the separation of the outer lines is equal to the sum of J_{AX} and J_{MX}. Since this was 12 Hz and it was found that replacing a proton with mercury or deuterium left a doublet of 5 Hz, it was concluded that the other coupling involved was 7 Hz.



	Dihedral angle, deg	Calcd J(Hz)[18c]
H_A–H_X	~20	7
H_M–H_X	~35	5.5
H_C–H_X	~100	0

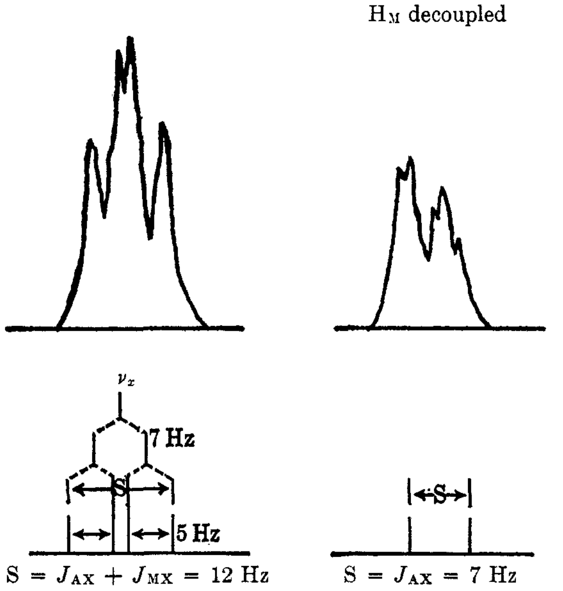


Figure 1.—Nuclear magnetic resonance spectra of cyclized norbornanes VII and VIII.

From a study of Dreiding models of these cyclized norbornanes, it is possible to estimate the dihedral angles between protons A, M, C, and X and to calculate[18] the expected coupling constants. As shown in Figure 1, these calculations indicate that the observed coupling of 5.0 Hz in the mercurials and deuterated compounds is due to coupling between the bridgehead and *exo* protons. This interpretation was substantiated by decoupling the bridgehead proton. Upon irradiation of proton H_M the original quartet collapsed to a doublet whose splitting constant was 7 Hz. These results indicate that both the chloromercuri and deuterium groups occupied the *exo* position and that both protonation and oxymercuration proceeded by an electrophilic attack on the *exo* side of these norbornenes.[20,21] The vicinial Hg^{199}–H coupling constants in these compounds agree with this assignment.[22]

II. The Stereochemistry of Ring Closure with *syn*-7-Hydroxymethyl-2-norbornene.—Recently, Bly and Bly[23a] have shown that the oxymercuration of *syn*-7-hydroxymethyl-2-norbornene occurs with ring closure. Professor Bly very kindly sent us a sample of the mercurial for nmr analysis.

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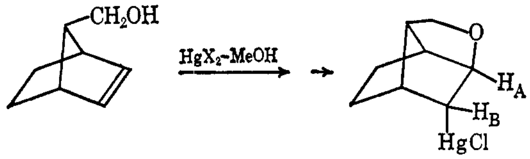
[19] We are indebted to Mr. Leroy Johnson, Varian Associates, Palo Alto, Calif., for this spectrum.

[20] K. C. Ramey, D. C. Lini, R. M. Moriarty, H. Gopal, and H. G. Walsh [*J. Amer. Chem. Soc.*, **89**, 2401 (1967)] have studied the nmr of VII in greater detail and have also assigned the 5-Hz coupling to H_1H_2.

[21] F. R. Jensen and J. J. Miller [*Tetrahedron Lett.*, No. 40, 4861 (1966)] have recently assigned the same structure to IV on the basis of a comparison of the nmr spectra of IV and its C-3 epimer. However, see ref 20 for proton assignments.

[22] M. M. Kreevoy and J. F. Schaefer, *J. Organometal. Chem.*, **6**, 589 (1966).

[23] (a) R. K. Bly and R. S. Bly, *J. Org. Chem.*, **28**, 3165 (1963); (b) R. S. Bly, R. K. Bly, A. O. Bedenbaugh, and O. R. Vail [*J. Amer. Chem. Soc.*, **89**, 881 (1967)] have more recently documented this *endo* mercury attack by obtaining both *cis-exo* and *trans* cyclic mercurials from the oxymercuration of *syn*-7-(2-hydroxyethyl)norbornene.



(13)

IX

nmr
H_A, τ 5.25
(doublet, $J = 2.3$ Hz)
H_B, τ 7.0
(multiplet, $J = 2$ Hz)

The signal from proton A appears as a doublet with $J = 2.3$ Hz. If proton B were in the *cis-endo* position, we would expect an AB coupling of 6 or 7 Hz (Table I). The splitting found, 2.3 Hz, indicates that proton B is in the *exo* position and that protons A and B are in a *trans* orientation. The *exo* assignment for proton B is further substantiated by the complexity of its nmr signal, due to bridgehead *exo* proton coupling. Another interpretation of the nmr spectrum of IX is that H_A and the 7-*anti* proton are coupled ($J = 2.3$ Hz) and that $J_{AB} = 0$ Hz. This would not be unreasonable because the dihedral angle between protons A and B would again be ~100° (see Figure 1). Nevertheless, this interpretation again indicates protons A and B to be in a *trans* orientation. Thus, we believe that the chloromercuri group must be *endo* in this mercurial and that the initial mercuric ion attack was in an unprecedented manner from the *endo* side.[23b]

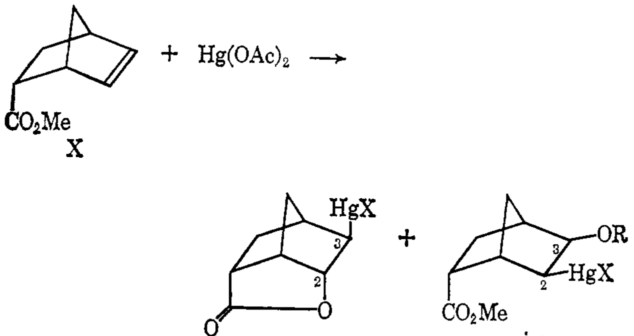
III. The Effect of Neighboring Groups on the Oxymercuration of Norbornenes Not Leading Entirely to Ring Closure.—To see if neighboring groups, which did not lead to ring closure, affected the oxymercuration of norbornene, a study was made of the oxymercuration of *endo*-5-cyano- and *endo*-5-carbomethoxy-2-norbornenes.

In Scheme I are summarized the results for the oxymercuration of *endo*-5-carbomethoxy-2-norbornene (X). Henbest[13] has reported that the oxymercuration of this ester in methanol gave exclusively lactone IV; so it was not surprising to find the lactone as the exclusive product when 25% acetone–water was used. However, when carefully dried methanol was used, no lactone was found. The nmr spectrum of the product, a clear liquid, indicated that the signal from proton 3 overlapped with that from an O–Me group. A careful examination indicated that the downfield Hg^{199}–H side band consisted of a doublet with $J \simeq 7$ Hz. Thus it is reasonable that the main peak was a doublet with $J \simeq 7$ Hz and that the major product is likely the *cis-exo*-3-methyl ether (XII). Henbest and Nichols[13] possibly used wet methanol.

Using acetic acid as solvent, oxymercuration of X also afforded no lactone but gave an 80% yield of sharp melting solid the elemental analysis and ir spectrum of which agreed with the 3-acetoxy structure XI (R = Ac). In the nmr spectrum of this compound proton 3 appeared as a doublet with $J = 6.9$ Hz indicating that the product had a *cis-exo* configuration. Thus it is seen that in the oxymercuration of this ester either *cis* or *trans* addition can be obtained by making small changes in the solvent.

SCHEME I

EFFECT OF REACTION CONDITIONS ON THE OXYMERCURATION OF *endo*-5-CARBOMETHOXY-2-NORBORNENE[a] (X)



X

IV

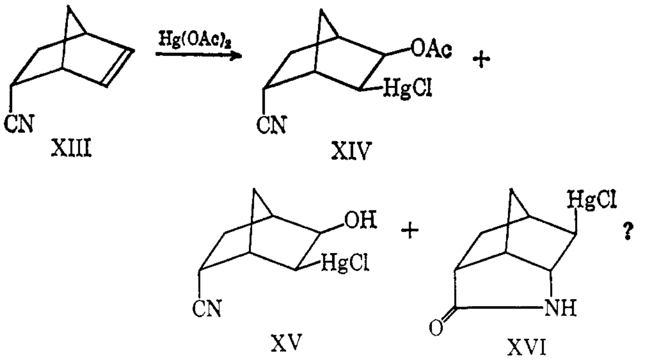
cis-exo
XI, R = Ac
XII, R = Me

		IV	XI, XII
X	$\xrightarrow{\text{25\% acetone–H}_2\text{O}}$	90%	0%
X	$\xrightarrow{\text{HOAc}}$	0%	80% white solid Mp 150.5–151.0° Nmr $J_{2,3} = 6.9$ Hz
X	$\xrightarrow{\text{anhydrous MeOH}}$	0%	100% oil, Nmr (Hg^{199}–H side band) $J_{2,3} \cong 7$ Hz

[a] X = Cl. In all cases the product was treated with sodium chloride to obtain the more stable RHgCl.

SCHEME II

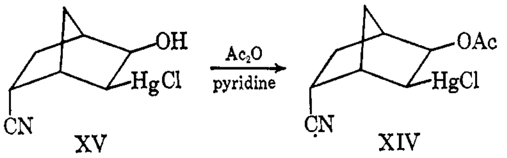
OXYMERCURATION OF *endo*-5-CYANO-2-NORBORNENE



XIII XIV XV XVI

	XIV	XV	XVI
Mp, °C	171.5	154–155	Liquid?
Ir spectrum, μ	5.78	2.75	5.85
Nmr spectrum, ppm, doublet	5.07 ($J_{2,3}$ = 7.0 Hz)	3.94 ($J_{2,3}$ = 6.9 Hz)	4.13 ($J_{1,2}$ = 5.0 Hz)

In the mercuric acetate treatment of *endo*-5-cyanonorbornene (XIII), three separate products could be isolated: two sharp-melting crystalline solids and a liquid residue. The properties of these products are summarized in Scheme II. Based on their nmr spectra the solids were assigned the *cis-exo* configurations shown. Also, acetylation of the alcohol (XV) gave the acetate (XIV). The oil showed a strong absorbtion at 5.85 μ in the infrared and showed a doublet at τ 5.87 ($J_{2,3} = 5.0$ Hz) in its nmr spectrum. This constituent was thought to be the *trans* lactam shown. That it was not an acetate was obvious from the fact that this product was also obtained with $Hg(NO_3)_2$. However, efforts to purify this component by inducing crystallization or by chromatography on deactivated

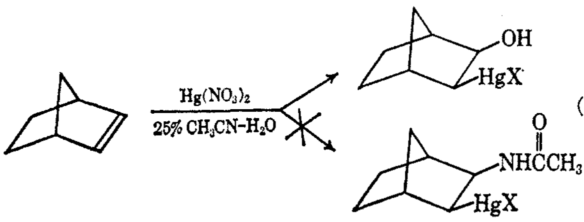


XV XIV

(14)

alumina (2% water) have failed, and no sample has been prepared pure enough for elemental analysis.

Experiments have shown that $Hg(NO_3)_2$ fails to react with aqueous acetonitrile at room temperature. Also, the oxymercuration of norbornene in 25% acetonitrile yielded only the *exo-cis*-2-chloromercuri-3-norborneol, and no (<1%) amide could be detected by infrared spectroscopy.



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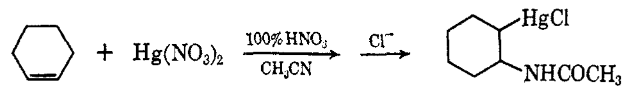
Wright[24a] has recently reported the formation of such amides when anhydrous nitric acid was present in acetonitrile solvent. These conditions are similar



(16)

to those used for the Ritter reaction.[24b] The fact that the cyclic lactam (XVI) is formed rapidly at room temperature under very mild conditions indicates that it is important that the nitrile group be in close proximity to the double bond.

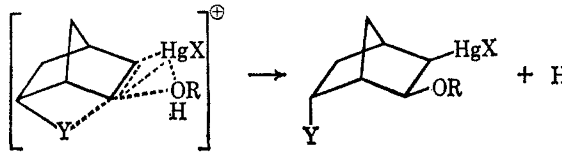
Since each of these products shown in Scheme II gave rise to an nmr doublet in a different position, an nmr spectrum of a mixture could be used as a simple means of analysis. Utilizing this, the effect of reaction conditions on product yields was studied, and the results are summarized in Scheme III. Since the acetate and the alcohol had a tendency to crystallize during the nmr analysis, the yields of these compounds represent a minimum figure, while that of the lactam is a maximum. Based on reproducibility and comparison with the values obtained by direct isolation, it is estimated that the maximum error is on the order of 5%. The product ratios shifted drastically with changing reaction conditions. Thus it was found that the addition of an equimolar amount of sodium acetate changed the yield of acetate and alcohol from 9 and 79% to 60 and 28%. Such changes in product composition were observed with norbornene[4a,b,24c] and bicyclo[2.2.2]octene.[4c]

SCHEME III

EFFECT OF REACTION CONDITIONS ON THE OXYMERCURATION OF *endo*-5-CYANO-2-NORBORNENE

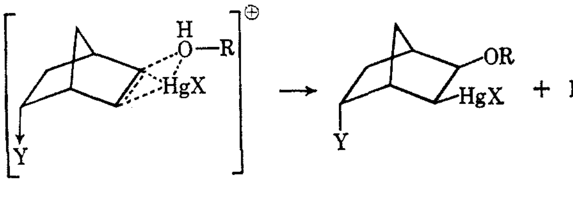
		XIV	XV	XVI
1.	XIII + $Hg(OAc)_2$ $\xrightarrow{\text{HOAc}}$	100%	...	...
2.	XIII + $Hg(OAc)_2$ $\xrightarrow{\text{25\% acetone–}H_2O}$	9.4%	78.6%	12.0%
3.	XIII + $Hg(OAc)_2$ 0.1 *M* $\xrightarrow[\text{0.1 } M \text{ NaOAc}]{\text{25\% acetone–}H_2O}$	59.7%	27.5%	12.8%
4.	XIII + $Hg(NO_3)_2$ $\xrightarrow{\text{25\% acetone–}H_2O}$	...	86%	14%
5.	XIII + $HgCl_2$ $\xrightarrow{\text{25\% acetone–}H_2O}$	...	97%	3%

Since XI, XIV, and XV are sharp melting, have sharp nmr doublets for proton 3, and are obtained in high yield, it is felt that only one of the two possible isomers is formed. Because there seems to be no evidence for rate acceleration from a neighboring group in the formation of these *cis* products (see Experimental Section), we can probably rule out a transition state in which the mercury is unsymmetrically displaced toward position 3. It is more likely that the inductive or field



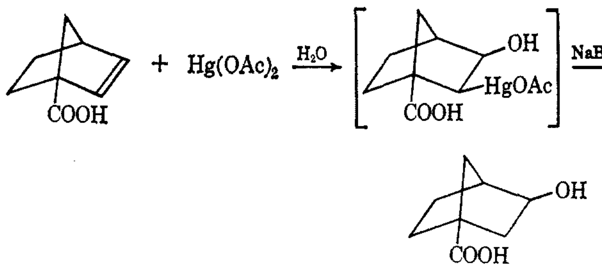
(17)

effect exerted by the cyano and ester groups makes the unsymmetric transition state having less positive charge near the substituted position the one of lowest energy,[25a]



(18)

The oxymercuration of 1-carboxynorbornene[25b] gives the product which is predicted by this hypothesis.



(19)

XVII

The hydroxy acid (XVII) differs from the known 2-*exo*-hydroxynorbornane-1-carboxylic acid.[26] Therefore, it is felt that these products have the chloromercuri group in position 2, although our evidence is equivocal on this point.

Discussion

It is now clear that *cis* additions to norbornenes and other strained olefins can be changed to *trans* additions by changes in either the rigidity of the olefin or in the availability of nucleophilic groups for *trans* attack. Whereas either acids or mercuric salts add to norbornenes *cis-exo* in the absence of neighboring groups (eq 3 and 5), the presence of neighboring groups causes both reactions to occur *trans* (eq 11 and 12). Indeed, eq 13 indicates that neighboring-group participation causes *trans* oxymercuration which places the mercury

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[24] (a) D. Chow, J. H. Robson, and G. F Wright, *Can. J. Chem.*, **37**, 1328 (1965); (b) J. J. Ritter, *J. Amer. Chem. Soc.*, **70**, 4045, 4048 (1948); (c) M. J. Abercrombie, A. Rodgman, K. R. Bharucha, and G. F Wright, *Can. J. Chem.*, **37**, 1328 (1959).

[25] (a) We have recently observed that mercuric acetate in methanol reacts with norbornene 300 times faster than with 5-cyanonorbornene. (b) We are grateful to Dr. Richard Alden who prepared and oxymercurated this olefin for another project.

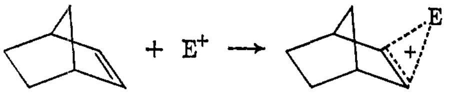
[26] W. R. Vaughan, R. Caple, J. Csapilla, and P. Scheiner, *J. Amer. Chem. Soc.*, **87**, 2204 (1965).

in the very unfavorable *endo* position.[23b] These results make it clear that those features which bring about either *cis* addition or rearrangements during electrophilic addition to norbornenes are not so strongly directing as is a neighboring hydroxyl or carboxyl function.[27] Since hydroxyl and carboxyl are not very good neighboring groups,[28] these findings set a rather low limit on the size of the much discussed steric and electronic effects in the norbornyl system.[29]

Oxymercuration is generally described as a two-step process.[30] Our finding (Scheme III, reactions 3 and 4) that approximately the same ratio of lactam to *cis-exo* product is formed under widely differing conditions agrees with this postulate. Alternatively, one-step concerted *trans* addition accompanied by one-step molecular *cis* addition would account for these results, but this would require that these two processes respond to changes in the electrophile [*e.g.*, $Hg(OAc)_2$ *vs.* $Hg(OAc)(OH)$] in the same way.

In the absence of definitive evidence for concerted addition we will consider this addition as a two-step process and ask the following questions. 1. What determines the direction of the electrophilic attack on norbornene? 2. What determines the position of the nucleophilic attack on the intermediate? Evidence will be presented concerning the first question in the following paper.

It is well known that there is a great preference for *exo* electrophilic attack on norbornenes. The attack of

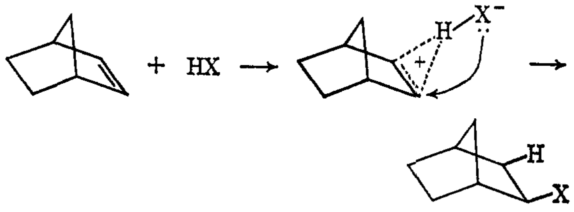


(20)

XVIII

a nucleophile on XVIII may be influenced by several things: steric hindrance by the *endo* C-6 hydrogen, carbon bridging (considered important in solvolyses[28,31]), torsional effects around C-1–C-2,[29] and torsional effects around C-2–C-3.[4] Unfortunately none of these effects can presently be shown to be dominant to the exclusion of the others. Our results in this and previous papers[4] are consistent with a mechanism in which the mercuric salt forms an *exo* complex (XVIII). *endo* attack on this complex by solvent or acetate ion can be retarded by steric hindrance by the *endo* C-6 hydrogen as well as by some nonclassical bridging[31] of C-6. In addition to these, the requirement that the norbornane skeleton be twisted in the transition state for *trans* opening of the complex must also retard *endo* attack.[4b,c] It is not possible to evaluate the relative importance of these effects from the data available.

cis additions, even to norbornene, are not general. Neither halogens nor sulfenyl halides add *cis*. The three effects just mentioned, which are common to all electrophilic additions to norbornene, should lead to some *cis* additions in all cases. We have suggested[4b] that frontside opening of complex XVIII is especially favorable to HX and $Hg(OAc)_2$ additions because the nucleophile is attached to the electrophile.



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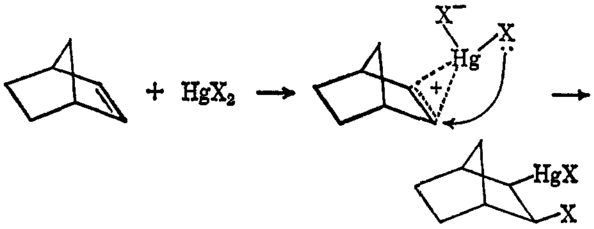
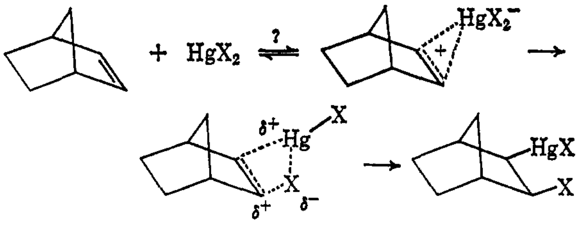


(22)

If the second step is rate limiting, as it probably is in many cases (eq 8), then the mechanisms 21 and 22 could also be described as somewhat polarized molecular or four-centered additions. In spite of many attempts



(23)

to demonstrate the existence of the mercurinium ion,[33,34] it is not possible at present to say whether it exists or, if it does exist, whether it lies so near the starting state as to be stereochemically unimportant.

We conclude that *cis-exo* additions to norbornenes result from a combination of the steric and electronic effects in the norbornene skeleton and the ability of the attacking electrophile to bind both the olefin and a nucleophile which can migrate to carbon. The combination of all these effects does not constitute a driving force sufficient to compete with the *trans* addition of a properly placed internal nucleophile.

Experimental Section

General Remarks.—Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were taken on a Perkin-Elmer Infracord 137B. Nmr spectra were measured with Varian Associates nuclear magnetic resonance spectrometers (Models HR-60, HR-100, and A-60). Chemical shifts are given in parts per million downfield from tetramethylsilane (δ) or as $\tau = 10 - \delta$. Vapor phase chromatograms were made with an Aereograph Autoprep gas chromatograph model A-700. Deuterium analyses were carried out by Josef Nemeth, Urkana, Ill.

Materials.—All solvents and reagents were commercial reagent grade. In many cases solvents were further purified by use

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[27] S. Winstein and E. Grunwald, *J. Amer. Chem. Soc.*, **70**, 828 (1948).

[28] P. D. Bartlett, "Nonclassical Ions," Benjamin Publishing Co., New York, N. Y., 1965.

[29] P. R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 701 (1967).

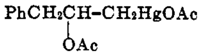
[30] M. M. Kreevoy and M. A. Turner, *J. Org. Chem.*, **30**, 373 (1965).

[31] The failure of 1-methyl group to influence direction of addition in the oxymercuration of norbornene suggests that nonclassical bridging is unimportant in oxymercuration.[32]

[32] H. C. Brown, J. W. Kawakami, and S. Ikegami, *J. Amer. Chem. Soc.*, **89**, 1525 (1967).

[33] J. Halpern and H. B. Tinker, *ibid.*, **89**, 6427 (1967).

[34] S. Wolfe, P. G. G. Campbell, and G. E. Palmer [*Tetrahedron Lett.*, 4203 (1966)] have reported evidence for mercurinium ion. Thus the compound



$$PhCH_2\underset{\displaystyle OAc}{\underset{|}{C}}H{-}CH_2HgOAc$$

pound shown is reported to exchange carbon-bound acetate more rapidly than it exchanges mercury-bound acetate in tetradeuterioacetic acid. However, we observe that mercuric acetate exchanges acetates much faster than it adds to norbornene in this solvent.

of a suitable desiccant followed by distillation.[35] Norbornene, Aldrich Chemical Co., was used without further purification. *endo*-(III) and *exo*-bicyclo[2.2.1]hept-2-ene-5-carboxylic acid, Aldrich Chemical Co., found to be 60% *endo* and 40% *exo*, were used without further purification. *endo*- (V) and *exo*-5-hydroxymethyl-2-norbornene, cyclol, kindly donated by the Interchemical Corp., were reported to be a 80:20 mixture of *endo* and *exo* isomers which was used without further purification. *endo*-5-Cyano-2-norbornene (XIII) was separated from a mixture of the *endo* and *exo* isomers (Aldrich Chemical Co.) by preparative vpc on a 20 ft × 0.375 in. aluminum column packed with 30% phenyldiethanolamine succinate (PDEAS) on Chromosorb P. Reinjection of the *endo* sample gave only one peak. The nmr spectrum (neat) corresponded exactly with that reported.[17a] The *exo* isomer was also isolated and shown to be pure by its vpc. *endo*-5-Carbomethoxy-2-norbornene (X) was obtained by the diazomethane treatment of *endo*-2-norbornene-5-carboxylic acid prepared by the method of Wright[14a] from the *endo-exo* mixture. Vapor phase chromatography with PDEAS column produced only one peak while that of an *endo-exo* mixture gave two. The nmr (neat) spectrum corresponded exactly with that reported.[17a]

Addition to *endo*-2-Norbornene-5-carboxylic Acid (III).—The reaction solution from 40:60 *exo*- and *endo*-2-norbornene-5-carboxylic acid (28.0 g, 0.2 mol), mercuric acetate (64.0 g, 0.2 mol), and 600 ml of 20% acetone–water solution was neutralized with 29.3 g of sodium chloride and 42 g of sodium bicarbonate in 600 ml of water. The resulting precipitate was separated by filtration and slurried with a solution of 15 g of sodium chloride and 15 g of sodium bicarbonate in 300 ml of water and again filtered to yield 68.2 g of a white solid (IV), mp 195–200°. This was recrystallized from 1500 ml of dioxane to yield 21.58 g of a white microcrystalline solid (IV), mp 222–223° (lit. mp 222–224°[13,14a]). The ir spectrum of this solid in a mineral oil mull had a double carbonyl band at 5.61 and 5.67 μ. The nmr spectrum (DMSO-d_6) contained a doublet at 5.29 ppm (J = 5.0 Hz).

This mercurial IV (1.2117 g, 3.24 mmol) was reduced by shaking it with mercury amalgam [4 ml of Hg and 1.03 g of sodium (0.045 g-atom)] in 3 ml of deuterium oxide for 34 hr. This product was neutralized with 2 M hydrochloric acid and extracted with ether to yield 0.3738 g of a white solid (VIID), mp 140–148°. Recrystallization from pentane raised the melting point to 154–155° (lit.[20] mp 154.2–155.2°) for *endo*-5-hydroxybicyclo[2.2.1]heptane-*endo*-2-carboxylic lactone). The ir spectrum had a carbonyl band at 5.59 μ (CCl_4). The nmr spectrum (CCl_4) contained a doublet at 4.65 ppm (J = 5.5 Hz) (*Anal.* Calcd % excess deuterium: 10.00 atom %. Found: 9.9 atom %).

This deuterated lactone (same melting point, ir and nmr spectrum) was also prepared by treating the sodium salt of acid III with 28% D_2SO_4 (*Anal.* Calcd % excess deuterium: 10.00 atom %. Found: 8.89 atom %). It was found that, if this reaction was carried out at reflux overnight, complete proton scrambling occurs. In a reaction solution in which deuterium (D_2SO_4 + norbornenyl acid) comprised 75.4% of the hydrogen, deuterium analysis indicated 65–75% deuterium in the lactone produced.

The sulfuric acid treatment of the bicyclic acid (III) or 5-cyano-2-norbornene (XIII) produced the nondeuterated lactone (VII) (78% yield), mp 154–155°. Its nmr spectrum (CCl_4) had a quartet at 4.69 ppm (see Figure 1).

Addition to *endo*-5-Hydroxymethyl-2-norbornene, Cyclol (V).—The reaction solution from cyclol (12.4 g, 0.1 mol) and mercuric chloride (19.0 g, 0.07 mol) in 300 ml of 50% acetone–water was filtered and the filtrate washed with 300 ml of hot water and dried at 65° to yield 24.9 g (0.07 mol)[36] of a white solid (VI), mp 227–228° (lit.[13] 228–229°). The nmr spectrum (DMSO-d_6) had a doublet at 5.12 ppm (J = 5.0 Hz).

This mercurial (6.76 g, 18.8 mmol) was reduced by shaking it with mercury amalgum [24 ml of Hg and 5.4 g of sodium (0.220 g-atom)] in 20 ml of deuterium oxide overnight to yield 2.150 g of a light yellow oil. Its nmr spectrum indicates that it was mainly (80+%) cyclol and ~10% the desired cyclic ether (VIIID). Also the presence of a tricyclic compound was indicated by the presence of two quartets (J = 2 Hz) at 0.37 and 0.54 ppm. This product was treated with mercuric chloride (4.95 g, 18 mmol) in 25 ml of methanol and made basic (pH 9) with 2 M sodium hydroxide. The resulting mixture was steam distilled and the distillate extracted with methylene chloride to yield, upon evaporation, 0.3049 g (2.5 mmol) of a waxen solid. This was purified by sublimation 35° (20 mm) to give solid melting 108–116° (lit.[13] mp 103–106°) (*Anal.* Calcd % excess deuterium: 9.17 atom %. Found: 7.85 atom %). The nmr spectrum (CCl_4) of the deuterated cyclic ether had a doublet, J = 4.8 Hz, at 4.20 ppm.

The same deuterated cyclic ether (identical ir and nmr spectra) was prepared by refluxing cyclol with 15% deuteriosulfuric acid for 1 hr to give a 10% yield of the cyclic ether, mp 87–90° (*Anal.* Calcd % excess deuterium: 9.17 atom %. Found: 10.50 atom %).

The cyclic ether produced from a similar treatment of cyclol with sulfuric acid, mp 83–94°, had a quartet in its nmr spectrum (CCl_4) at 4.20 ppm (see Figure 1).

Addition to Norbornenes in Acetic Acid.—It was found that 2 mmol of unsaturated compound and 2 mmol of mercuric acetate could be combined in 1 ml of acetic acid to obtain a homogeneous solution. The nmr spectra of these solutions of mercury adducts could be used to determine their configurations. Table II lists the results for several norbornenes. The acetoxymercurials were isolated by precipitation with 25 ml of saturated sodium chloride solution.

TABLE II

Compound	δ, ppm[a,b]	$J_{2,3}$ Hz	Configuration
Norbornene	5.00	7.0	*cis-exo*
exo-5-Cyanonorbornene	5.06	6.8	*cis-exo*
endo-5-Cyanonorbornene	5.07	7.0	*cis-exo*
endo-5-Carbomethoxynorbornene	5.17	6.9	*cis-exo*

[a] External tetramethylsilane standard. [b] Chemical shift of the proton on the acetoxy-substituted carbon.

The product from norbornene, 0.6274 g (1.66 mmol, 83%) of a white solid mp 125.5–126°, gave on recrystallization from acetone–*n*-heptane white microneedles, mp 130.0–130.4° (lit.[24c] mp 130.8–131.8°).

The product from *exo*-5-cyano-2-norbornene, 0.7105 g (1.73 mmol, 86%) of a white solid, mp 146.8–147.2°, gave on recrystallization from chloroform–*n*-heptane a white crystalline solid, mp 150.0–151.0°.

Anal. Calcd for $C_{10}H_{12}O_2NHgCl$: C, 28.99; H, 2.92. Found: C, 28.82; H, 2.90.

The product from *endo*-5-cyano-2-norbornene, 0.6387 g (1.54 mmol, 77%) of a white solid, mp 170–171°, gave on recrystallization from chloroform–*n*-heptane a white crystalline solid, mp 171.5°.

Anal. Calcd for $C_{10}H_{12}O_2NHgCl$: C, 28.99; H, 2.92; Cl, 8.56. Found: C, 29.21; H, 2.68; Cl, 8.44.

The product from *endo*-5-carbomethoxy-2-norbornene, 0.7101 g (1.59 mmol, 80%) of a white solid, mp 145–149°, gave on recrystallization from chloroform–*n*-heptane a white crystalline solid, mp 150.5–151.0°.

Anal. Calcd for $C_{11}H_{15}O_4HgCl$: C, 29.54; H, 3.38. Found: C, 29.71; H, 3.21.

Addition to *endo*-5-Carbomethoxy-2-norbornene (X).—The reaction mixture of the unsaturated compound (0.3818 g, 2.5 mmol), mercuric acetate (0.7973 g, 2.5 mmol), and 20 ml of 25% acetone–water gave, after treatment with a solution of 0.5 g of sodium chloride and 0.5 g of sodium bicarbonate in 5 ml of water, 0.8456 g of a white solid, mp 203°. The ir and nmr spectra of this product were identical with those of *exo*-5-chloromercuri-*endo*-6-hydroxybicyclo[2.2.1]heptane-*endo*-2-carboxylic lactone (IV).

The reaction mixture of the *endo*-5-carbomethoxy-2-norbornene (0.3801 g, 2.5 mmol), mercuric acetate (0.7947 g, 2.5 mmol), and 20 ml of dry methanol (0.0074% water by Karl Fischer titration) gave, on work-up with 0.5 g of sodium chloride and 0.5 g of sodium bicarbonate, 1.1300 g of a clear viscous liquid. Its ir spectrum ($CHCl_3$) indicated the presence of an acetate group by the band at 5.79 μ. Its nmr spectrum ($CDCl_3$) indicates that the product consists of a mixture of acetate (XI) and methyl ether (XII) in approximately a 1:5 ratio. Although the doublet due to the acetate can be seen at 4.8 ppm (J = 7.0

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(35) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1964.

(36) Since a quantitative yield of cyclic ether was obtained in the presence of 20% *exo*-5-hydroxymethyl-2-norobornene, the *endo* compound must react much faster (>100 times) than its *exo* isomer. Competition reactions with norbornene confirm this finding. Similar rate enhancement by neighboring-group participation was observed in the oxymercuration of 1-penten-5-ol.[33]

Hz), that due to the ether at ~4.5 ppm is obscured by the CH_3O—$C(=O)$- and CH_3—O- peaks. However, one can see its vicinal $Hg^{199}H$ side band 50 cps downfield which appeared as a doublet $J \cong 7.0$ Hz.

Addition to *endo*-5-Cyano-2-norbornene (XIII).—The reaction mixture of unsaturated compound (1.1908 g, 10.0 mmol) and mercuric acetate (3.1838 g, 10.0 mmol) in 100 ml of 25% acetone was worked up with a solution of 10 g of sodium chloride and 10 g of sodium bicarbonate in 200 ml of water. This mixture was continuously extracted with chloroform for 40 hr to yield 3.8236 g of a viscous orange oil. This product gave a precipitate with 2% ethanolic silver nitrate solution and a gray precipitate with ethanolic sodium borohydride. Its ir spectrum ($CHCl_3$) had bands at 2.79 and 5.79 μ (broad). Its nmr spectrum ($CHCl_3$) had doublets at 4.13 ($J = 5.0$ Hz), 3.98 ($J = 6.8$ Hz), and 5.0 ppm ($J = 7$ Hz). These were assigned to XVI, XV, and XIV, respectively. On standing in chloroform 3.1182 g of this product gave 1.7979 g of a white crystalline solid, mp 149.5–151.5°. Recrystallization from chloroform–*n*-heptane raised the melting point to 154–155°. Its ir spectrum (Nujol mull) had a band at 2.75 μ and showed no evidence of a carbonyl band. Its nmr spectrum (acetone-d_6) had a doublet at 3.94 ppm ($J = 6.9$ Hz), and therefore it was assigned structure XV.

Treatment of 0.3014 g of this product with 2 ml of acetic anhydride and 0.5 ml of dry pyridine yielded 0.2776 g of acetate (XIV), mp 170–170.2°, which was shown, by the method of mixture melting points and by exact correspondence of ir spectra, to be the same acetate obtained previously from the acetic acid-$Hg(OAc)_2$ treatment of *endo*-5-cyano-2-norbornene.

The reaction mixture from *endo*-5-cyano-2-norbornene (0.5979 g, 5.0 mmol), mercuric nitrate (1.7096 g, 5.0 mmol), and 50 ml of 20% acetone, after work-up with a solution of 1 g of sodium chloride and 1 g of sodium bicarbonate and extraction with chloroform, gave 2.1828 g of a gummy white solid. Slow crystallization from chloroform yielded 1.2679 g of alcohol XV, as indicated by the melting point (154–155°), mixture melting point, and ir and nmr spectra of the sample of alcohol previously obtained. The ir spectrum ($CHCl_3$) of the mother liquor had a carbonyl band at 5.83 μ. Its nmr spectrum showed a doublet at 4.12 ppm ($J = 5.0$ cps) and a multiplet at 7.65 ppm (olefin?). On the basis of this spectral evidence the lactam structure (XVI) was assigned to this residue (λ_{max} of γ-lactams, 5.88 μ). Further attempts to isolate this lactam by inducing crystallization or by chromatography on alumina (2% H_2O) failed to give a sample suitable for analysis.

Addition to Norbornene in Presence of Acetonitrile.—The reaction mixture of norbornene (0.3681 g, 4.0 mmol), mercuric nitrate (1.3516 g, 4.0 mmol), and 40 ml of 25% acetonitrile–water gave, after work-up with 1.2 g of sodium chloride and 1.2 g of sodium bicarbonate in 15 ml of water, 0.9517 g (69.4%) of 2-chloromercurinorborneol, mp 120–125° (lit.[24c] mp 131–131.5°). Chloroform extraction of the aqueous filtrate gave 0.3144 g (23%) more solid. The ir spectrum (Nujol mull) of this and the above product gave only a negligibly small carbonyl band, indicating less than 1% carbonyl-containing product present.

Registry No.—IV, 16487-00-6; VI, 16487-01-7; VII, 5257-51-2; VIII, 16487-03-9; IX, 16487-23-3; XI, 16487-24-4; XII, 16487-25-5; XIV, 16487-26-6; XV, 16487-27-7; XVI, 16487-28-8; product from *exo*-5-cyano-2-norbornene, 16487-04-0.

Acknowledgment.—The authors wish to thank the National Institutes of Health for a Postdoctoral Fellowship (A. F.), Varian Associates for several spectra, and the National Science Foundation for a grant (GP-242).

Oxymercuration of Strained Olefins.[1] The Effect of *syn*-7 Substituents

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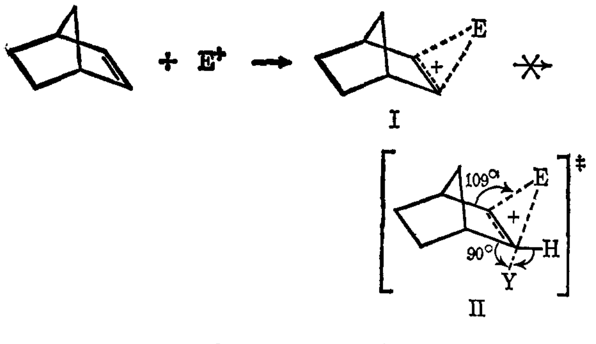
Received July 11, 1967

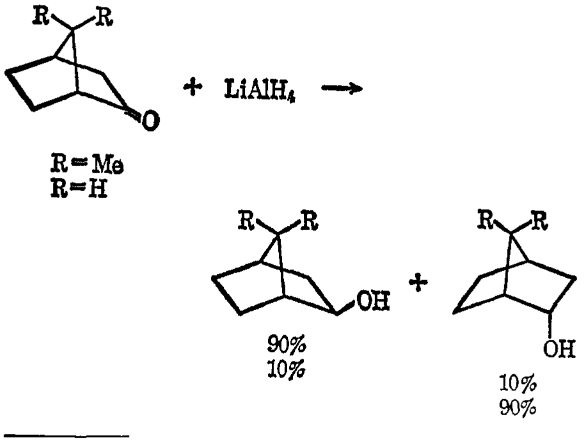
Oxymercuration of 1,4,7,7-tetramethylnorbornene produces 100% *cis-exo* product. Furthermore, *syn*-7-bromonorbornene oxymercurates completely *cis-exo*. These results are a strong indication that *cis-exo* electrophilic additions to norbornenes do not result from steric hindrance toward *endo* attack. Since the highly predominant *exo* attack on norbornenes by electrophiles is not of steric origin, it is concluded that it is an electronic effect.

The *cis* electrophilic additions to strained bicyclic olefins has been attributed to a twist strain introduced in the second step of the usual two-step *trans* addition.[3]



(1)

This postulate does not explain the highly selective *exo* attack by the electrophile to give I, and this selectivity is generally attributed to steric effects.[4] If this is true, then the addition to *syn*-7-substituted norbornene should occur *cis-endo*. Such substitution changes th stereochemistry of other reactions in the bicyclohepty system[4b] (eq 2 and 3).



(2)[5]

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[1] Supported in part by the National Science Foundation, Grant GP-2829.

[2] National Institutes of Health Postdoctoral Fellow, 1964–1965.

[3] T. G. Traylor and A. W. Baker, *J. Amer. Chem. Soc.*, **85**, 2746 (1963).

[4] (a) See, *e.g.*, J. A. Berson, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, p 166; (b) p 129; (c) H. C. Brown, *Chem. Brit.*, **2**, 199 (1966).

[5] R. Howe, E. C. Friedrich, and S. Winstein, *J. Amer. Soc.*, **87**, 379 (1965).